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Phase transition and thermodynamic properties of the Hard-Core-Potts model

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ABSTRACT We investigate translation-invariant Gibbs measures of the Hard-Core–Potts (HC–Potts) model on the Cayley tree. The model combines Potts-type ferromagnetic interactions with a hard-core exclusion rule, leading to a nontrivial interplay between magnetic ordering and occupancy constraints. For the hinge-type fertile graph, we analyze the cases $k = 2$ and $k = 3$, and determine explicit critical values of θ that mark the transition from uniqueness to multiplicity of Gibbs measures. The model exhibits up to five translation-invariant phases depending on the interaction strength. Thermodynamic quantities such as magnetization and quadrupolar moment are computed, revealing ordered phases at low temperatures and a paramagnetic phase at high temperatures.

KEYWORDS Gibbs distribution, Potts model, Hard-Core model, phase transition, Cayley tree

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1. Introduction

Recent progress in nanoscience and nanotechnology has increased interest in studying phase transitions and ordering phenomena in finite systems, where thermodynamic behavior differs from bulk materials. The theory of Gibbs measures provides a rigorous framework for describing ordered and disordered phases and their coexistence in lattice models. Studying Gibbs measures on Cayley trees is therefore crucial for understanding phase transition mechanisms and the stability of nanoscale systems (see, e.g., [1–3]).

Exactly solvable models play a vital role in statistical mechanics, particularly in elucidating the nature of phase transitions and collective phenomena (see, e.g., [4–10]). Among these, the Potts model serves as one of the fundamental frameworks for describing magnetic ordering, while the Hard-Core (HC) model captures systems with exclusion constraints, such as lattice gases and independent sets on graphs.

The q -state Potts model is a generalization of the Ising model and has been widely used to investigate the long-term behavior of many complex systems. It enables the study of how the internal components of a system interact based on their intrinsic properties [9, 11]. In contrast to the Ising model, the Potts model allows each spin to take any of $q > 2$ possible values. A four-component version of this model was first studied by Ashkin and Teller around 1943 [12]. The model was later named after Renfrey B. Potts, who developed its theoretical foundations in his 1952 doctoral thesis [13], following a suggestion by his advisor, C. Domb. A similar problem was independently considered by Kihara et al. two years later [14].

The Potts model on the Cayley tree (also known as the Bethe lattice) was first studied by N. Ganikhodjaev [15, 16]. Since then, many works have investigated limiting Gibbs measures of finite-state Potts models on Cayley trees (see [17–21]).

In contrast, the HC model imposes strict exclusion constraints on spin values and has found applications in combinatorics, statistical mechanics, and queueing theory. HC models are particularly relevant for studying random independent sets on graphs [22, 23] and gas molecules on lattices [4]. In [24], A. Mazel and Yu. Suhov introduced the HC model on the d -dimensional lattice $\mathbb{Z}^d$. Many studies have since analyzed the limiting Gibbs measures of finite-state HC models (see [8, 25–29]).

The combination of these two models, known as the Hard-Core-Potts (HC-Potts) model, provides a unified framework for describing both magnetic and structural ordering. This hybrid model enables the investigation of the interplay between spin alignment and particle exclusion, an important aspect of complex systems exhibiting competing interactions.

Hybrid lattice models combining different interaction types have attracted considerable attention in recent years. One important example is the Potts-SOS model, where each spin interacts through both Potts-type ferromagnetic coupling and a solid-on-solid (SOS) height constraint (see, e.g., [30]). A related extension is the mixed-type Potts-SOS model, which incorporates different coupling mechanisms at different layers or spin components, leading to complex dynamical behavior and multiple competing phases (see [31–34]).

The present work differs fundamentally from these SOS-based hybrid systems. Unlike the height-dependent SOS constraint, the HC-Potts model couples classical Potts ferromagnetism with a hard-core exclusion rule that restricts admissible configurations through local occupancy constraints. As a result, while Potts-SOS models describe a competition between magnetic order and surface fluctuations, the HC-Potts model captures the interplay between magnetic alignment and particle exclusion. This leads to a qualitatively different structure of admissible states and produces distinct critical phenomena, particularly in the presence of fertile graphs such as the hinge-type graph considered here.

Cayley trees provide a convenient mathematical framework for analyzing such models, since their recursive structure allows exact characterization of Gibbs measures and critical phenomena. In this work, we focus on translation-invariant Gibbs measures for the HC-Potts model defined on Cayley trees of order $k \geq 2$.

2. Definitions and known facts

The Cayley tree $\mathfrak{S}^k$ of order $k \geq 1$ is an infinite tree, i.e., a cycle-free graph such that from each vertex of which issues exactly $k + 1$ edges. We denote by V the set of the vertices of tree and by L the set of edges. The distance on the Cayley tree, denoted by $d(x, y)$, is defined as the number of nearest neighbor pairs of the shortest path between the vertices x and y (where a path is a collection of nearest neighbor pairs, two consecutive pairs sharing at least a given vertex)

For a fixed $x^0 \in V$, called the root, let

$$W_n = \{x \in V \mid d(x, x^0) = n\}, \quad V_n = \bigcup_{m=0}^n W_m$$

be respectively the ball and the sphere of radius n with center at x^0 . For $x \in W_n$ let

$$S(x) = \{y_i \in W_{n+1} \mid d(x, y_i) = 1, i = 1, 2, \dots, k\},$$

be the set of direct successors of x . Note that in $\mathfrak{S}^k$ any vertex $x \neq x^0$ has k direct successors, and root x^0 has $k + 1$ direct successors.

We consider Hard-Core-Potts (HC-Potts) model on a Cayley tree, where the spin takes values in the set $\Phi := \{0, 1, 2, \dots, q\}$, and is assigned to the vertices of the tree. A configuration σ on V is then defined as a function $x \in V \mapsto \sigma(x) \in \Phi$; the set of all configurations is Φ^V .

To describe the hard-core interactions between neighboring spins, let $G = (\Phi, K)$ be a graph with vertex set Φ , and edge set K . A configuration σ is called G -admissible on a Cayley tree if $\{\sigma(x), \sigma(y)\} \in K$ is an edge of G for any pair of nearest neighbors $\langle x, y \rangle \in L$. The set of all G -admissible configurations is denoted by Ω^G . For a subset $A \subset V$, σ_A denotes the restriction of σ to A , and Ω_A^G denotes the set of all G -admissible configurations on A . We also introduce a matrix of activities λ on the edges of G ,

$$\lambda: \{i, j\} \in K \rightarrow \lambda_{i,j} \in \mathbb{R}_+,$$

where $\lambda_{i,j}$ is called the activity of the pair $\{i, j\}$.

For each pair $\langle x, y \rangle \in L$, the spins interact through two mechanisms:

- **Potts ferromagnetic interaction.** The term

$$-J \delta_{\sigma(x), \sigma(y)}$$

contributes energy J if the spins coincide, and 0 otherwise. For $J > 0$, this term favors alignment.

- **Hard-Core (activity) interaction.** Each pair $i, j \in \Phi$ has a nonnegative activity weight $\lambda_{i,j}$.
 - If $\lambda_{i,j} = 0$, the pair $\{i, j\}$ is forbidden.
 - If $\lambda_{i,j} > 0$, the pair is allowed and contributes a term $-\frac{1}{\beta} \log \lambda_{i,j}$ to the energy.

Combining both interactions, the Hamiltonian of the HC-Potts model is

$$H(\sigma) = -J \sum_{\langle x, y \rangle \in L} \delta_{\sigma(x), \sigma(y)} - \frac{1}{\beta} \sum_{\langle x, y \rangle \in L} \log \lambda_{\sigma(x), \sigma(y)}. \quad (1)$$

The first term promotes magnetic ordering; the second encodes exclusion constraints and activity effects. Special cases include:

- (i) Pure Potts model: $\lambda_{i,j} = 1$,
- (ii) Pure Hard-Core model: $J = 0$.

The finite-volume Gibbs distribution on V_n defined as

$$\mu_n(\sigma_n) = Z_n^{-1} \exp \left\{ -\beta H_n(\sigma_n) + \sum_{x \in W_n} h_{\sigma(x), x} \right\}, \quad (2)$$

where $\beta = 1/T$, $T > 0$ is temperature, Z_n^{-1} is the normalizing factor and $\{h_x = (h_{0,x}, h_{1,x}, \dots, h_{q,x}) \in R^{q+1}, x \in V\}$ is a collection of vectors and

$$H_n(\sigma_n) = -J \sum_{\langle x, y \rangle \in L_n} \delta_{\sigma(x)\sigma(y)} - \frac{1}{\beta} \sum_{\langle x, y \rangle \in L_n} \log \lambda_{\sigma(x), \sigma(y)}.$$

We say that the probability distributions (2) are compatible if for all $n \geq 1$ and $\sigma_{n-1} \in \Phi^{V_{n-1}}$:

$$\sum_{\omega_n \in \Phi^{W_n}} \mu_n(\sigma_{n-1} \vee \omega_n) = \mu_{n-1}(\sigma_{n-1}). \quad (3)$$

Here $\sigma_{n-1} \vee \omega_n$ is the concatenation of the configurations. In this case, there exists a unique measure μ on Φ^V such that, for all n and $\sigma_n \in \Phi^{V_n}$

$$\mu(\{\sigma_{V_n} = \sigma_n\}) = \mu_n(\sigma_n).$$

Such a measure is called a splitting Gibbs measure corresponding to the Hamiltonian (1) and vector-valued function $h_x, x \in V$.

The following statement specifies the conditions on h_x that guarantee the compatibility of the distributions.

Theorem 1. Probability distributions $\mu_n(\sigma_n)$, $n \in \mathbb{N}$ in (2) are compatible if for any $x \in V$ the following equation holds:

$$h_x = \sum_{y \in S(x)} F(h_y, \theta), \quad (4)$$

where $F : h = (h_1, \dots, h_q) \in R^q \rightarrow F(h, \theta) = (F_1, \dots, F_q) \in R^q$ is defined as

$$F_i = \ln \left(\frac{\lambda_{i,i}(\theta - 1)e^{h_i} + \sum_{j=1}^q \lambda_{i,j}e^{h_j} + \lambda_{i0}}{\lambda_{0,0}\theta + \sum_{j=1}^q \lambda_{0,j}e^{h_j}} \right),$$

and $\theta = \exp(J\beta)$, $S(x)$ is the set of direct successors of x .

Proof. Necessity. Suppose that (3) holds, we want to prove (4). Substituting (2) into (3), obtain that for any configurations σ_{n-1} : $x \in V_{n-1} \mapsto \sigma_{n-1}(x) \in \{0, 1, \dots, q\}$:

$$\begin{aligned} \frac{Z_{n-1}}{Z_n} \sum_{\omega_n \in \Omega_{W_n}} \exp \left(\sum_{x \in W_{n-1}} \sum_{y \in S(x)} (J\beta \delta_{\sigma_{n-1}(x)\omega_n(y)} + \log \lambda_{\sigma_{n-1}(x), \omega_n(y)} + h_{\omega_n(y), y}) \right) = \\ = \exp \left(\sum_{x \in W_{n-1}} h_{\sigma_{n-1}(x), x} \right), \end{aligned} \quad (5)$$

where $\omega_n: x \in W_n \mapsto \omega_n(x)$.

From (5) we get:

$$\begin{aligned} \frac{Z_{n-1}}{Z_n} \sum_{\omega_n \in \Omega_{W_n}} \prod_{x \in W_{n-1}} \prod_{y \in S(x)} \lambda_{\sigma_{n-1}(x), \omega_n(y)} \exp(J\beta \delta_{\sigma_{n-1}(x)\omega_n(y)} + h_{\omega_n(y), y}) = \\ = \prod_{x \in W_{n-1}} \exp(h_{\sigma_{n-1}(x), x}). \end{aligned}$$

Fix $x \in W_{n-1}$ and rewrite the last equality for $\sigma_{n-1}(x) = i$, $i = 1, \dots, q$ and $\sigma_{n-1}(x) = 0$, then dividing each of them to the last one we get

$$\prod_{y \in S(x)} \frac{\sum_{u=0}^q \lambda_{i,u} \exp(J\beta \delta_{iu} + h_{u,y})}{\sum_{u=0}^q \lambda_{0,u} \exp(J\beta \delta_{0u} + h_{u,y})} = \exp(h_{i,x} - h_{0,x}), \quad i = 1, \dots, q-1. \quad (6)$$

Now we change the variables as follows

$$h_{i,x} - h_{0,x} \rightarrow h_{i,x}, \quad i = 2, \dots, q-1.$$

Then (6) implies (4).

Sufficiency. Suppose that (4) holds. It is equivalent to the representations

$$\prod_{y \in S(x)} \sum_{u=0}^q \lambda_{i,u} \exp(J\beta \delta_{iu} + h_{u,y}) = a(x) \exp(h_{i,x}), \quad i = 1, \dots, q. \quad (7)$$

for some function $a(x) > 0, x \in V$. We have

$$\text{LHS of (3)} = \frac{1}{Z_n} \exp(-\beta H(\sigma_{n-1})) \prod_{x \in W_{n-1}} \prod_{y \in S(x)} \sum_{u=1}^q \lambda_{\sigma_{n-1}(x), u} \exp(J\beta \delta_{\sigma_{n-1}(x), u} + h_{u, y}). \quad (8)$$

Substituting (7) into (8) and denoting $A_n(x) = \prod_{x \in W_{n-1}} a(x)$, we get

$$\text{RHS of (3)} = \frac{A_{n-1}}{Z_n} \exp(-\beta H(\sigma_{n-1})) \prod_{x \in W_{n-1}} \exp(h_{\sigma_{n-1}(x), x}). \quad (9)$$

Since $\mu^{(n)}, n \geq 1$ is a probability, we should have

$$\sum_{\sigma_{n-1} \in \Omega_{V_{n-1}}} \sum_{\omega_n \in \Omega_{W_n}} \mu^{(n)}(\sigma_{n-1}, \omega_n) = 1.$$

Hence from (9), we get $Z_{n-1} A_{n-1} = Z_n$, and (3) holds. $\square$

Hence, Theorem 1 follows: for any collection $h = h_x, x \in V$ satisfying the functional equation above there exists a unique splitting Gibbs measure μ , and conversely every splitting Gibbs measure corresponds to such a solution.

3. Translation-invariant Gibbs measures

In this section, we consider Gibbs measures which are translation-invariant, i.e., we assume $h_x = h = (h_1, \dots, h_q) \in R^q$ for all $x \in V$. Then from equation (4) we get $h = kF(h, \theta)$, i.e.,

$$h_i = k \ln \left(\frac{\lambda_{i,i}(\theta - 1)e^{h_i} + \sum_{j=1}^q \lambda_{i,j}e^{h_j} + \lambda_{i,0}}{\lambda_{0,0}\theta + \sum_{j=1}^q \lambda_{0,j}e^{h_j}} \right), \quad i = 1, \dots, q. \quad (10)$$

Denoting $z_i = \exp(h_i), i = 1, \dots, q - 1$, we get from (10)

$$z_i = \left(\frac{\lambda_{i,i}(\theta - 1)z_i + \sum_{j=1}^q \lambda_{i,j}z_j + \lambda_{i,0}}{\lambda_{0,0}\theta + \sum_{j=1}^q \lambda_{0,j}z_j} \right)^k, \quad i = 1, \dots, q. \quad (11)$$

Remark 1. Note that

- If in the (11) we set $\lambda = 1$, then we obtain the q -state Potts model;
- If $\theta = 1$, the Hard-Core model is obtained.

It is important to note that if the system (11) admits more than one positive solution, then each solution corresponds to a distinct translation-invariant limiting Gibbs measure (TILGM). We say that a phase transition occurs for the model (1), if the system (11) has more than one positive solution.

Definition 1. The graph is called fertile if there is an activity set λ such that the corresponding Hamiltonian has at least two TILGMs (see [25]).

Let $q = 2$. Here, we consider four types of fertile graphs [25] with three vertices 0, 1, 2 (the set of values of $\sigma(x)$), which have the forms

wand : $\{0, 0\}, \{0, 1\}, \{1, 2\}, \{2, 2\}$;

hinge : $\{0, 0\}, \{0, 1\}, \{1, 1\}, \{1, 2\}, \{2, 2\}$;

wrench : $\{0, 0\}, \{0, 1\}, \{1, 1\}, \{1, 2\}$;

pipe : $\{0, 0\}, \{0, 1\}, \{1, 2\}$.

In this paper we consider hinge-type graphs. More precisely, we consider the activity $\lambda = (\lambda_{i,j})_{\{i,j\} \in K}$ defined as (see Fig. 1)

$$\lambda_{i,j} = \begin{cases} 1, & \text{if } i = j \text{ or } |i - j| = 1; \\ 0, & \text{otherwise.} \end{cases}$$

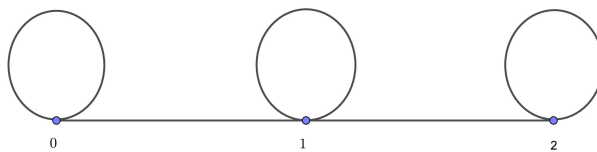


FIG. 1. The hinge-type graph with three vertices.

3.1. The case “Hinge”

In the following we restrict our attention to the case where $q = 2$. In this case, denoting $x = \sqrt[k]{z_1}$ and $y = \sqrt[k]{z_2}$, from (11), we get

$$x = \frac{\theta x^k + y^k + 1}{\theta + x^k} \quad \text{and} \quad y = \frac{\theta y^k + x^k}{\theta + x^k}. \quad (12)$$

In particular, considering only the second equation of this system, we find the solutions $y = 1$ and

$$x^k = \theta (y^{k-1} + y^{k-2} + \dots + y). \quad (13)$$

We begin by analyzing the case $y = 1$.

3.2. Case $y = 1$

In this case, from the first equation in (12), we get that

$$\theta x^{k+1} - \theta x^k + \theta x - 2 = 0 \quad (14)$$

and hence, the following statement follows.

Lemma 1. For all $k \geq 2$, there exist a unique positive root for (14).

Proof. To do this, it is sufficient to show $f'(x) > 0$ for any $x > 0$. Indeed,

$$f'(x) = (k+1)x^k - kx^{k-1} + 1.$$

It is easy to see that, if $x \geq 1$ then $f'(x) > 0$.

Let $0 < x < 1$. Then

$$f'(t) = t^k - kt + k + 1,$$

where $t = 1/x$ ($t > 1$). Due to Bernoulli's inequality we get

$$t^k + k + 1 = (1 + t - 1)^k + k + 1 \geq 1 + k(t - 1) + k + 1 = 2 + kt.$$

From here

$$f'(t) = t^k - kt + k + 1 > 0.$$

□

3.3. Case $y \neq 1$

Let us consider the second situation as presented in (12).

3.3.1. *Case $k = 2$.* In this case, using (13) and the first equation in (12), we get

$$y^4 - (\theta^3 - 2\theta^2)y^3 + (\theta^4 - 2\theta^3 + 2)y^2 - (\theta^3 - 2\theta^2)y + 1 = 0, \quad (15)$$

which is a polynomial with symmetric coefficients and hence, denoting $\xi = y + 1/y$, (15) can be rewritten as

$$\xi^2 - \theta^2(\theta - 2)\xi + \theta^4 - 2\theta^3 = 0. \quad (16)$$

If $0 < \theta < 2$ or $\theta > 1 + \sqrt{5}$, this equation has two solutions

$$\xi_{1,2} = \frac{\theta^2}{2} \left(\theta - 2 \pm \sqrt{\theta(\theta - 2)(\theta^2 - 2\theta - 4)} \right).$$

Note that $\xi > 2$ for $\theta > 1 + \sqrt{5}$ and $\xi_{1,2}(1 + \sqrt{5}) = 2 + 2\sqrt{5}$.

We find y_i , $i = 1, 2, 3, 4$ the following equation

$$y^2 - \xi_1 y + 1 = 0, \text{ and } y^2 - \xi_2 y + 1 = 0.$$

Summarizing, we obtain the following result.

Theorem 2. For the HC-Potts model with $k = 2$, there exists a critical value $\theta_1 = 1 + \sqrt{5}$ such that

1. If $\theta < \theta_1$, then there is a unique TILGM, i.e., phase transition does not occur;
2. If $\theta = \theta_1$, then there are three TILGMs, i.e., the phase transition occurs;
3. If $\theta > \theta_1$, then there are five TILGMs, i.e., the phase transition occurs;

Remark 2. Our results differ from classical Hard Core model and classical Potts model, i.e.,

- The existence of three TILGMs for the Hard Core model in the case “Hinge” and $\lambda > \frac{9}{4}$ was proved in [27].
- In [22], it is shown that for the Potts model, when $\theta > 1 + 2\sqrt{2}$, there exist five TILGMs.

3.3.2. *Case $k = 3$.* In this case, our main result is

Theorem 3. For the HC-Potts model with $k = 3$, there exist critical value $\theta_2 \approx 2.078$ such that

1. If $\theta < \theta_2$, then there is a unique TILGM, i.e., the phase transition does not occur;
2. If $\theta = \theta_2$, then there are three TILGMs, i.e., the phase transition occurs;
3. If $\theta > \theta_2$, then there are five TILGMs, i.e., the phase transition occurs.

Proof. For $k = 3$, by (13) and the first equation in (12) we obtain

$$y^8 - (\theta^4 - 3\theta^2 + 1)y^7 + y^6 + (\theta^6 - 3\theta^4 + 2)y^5 + (2\theta^6 - 7\theta^4 + 6\theta^2 - 2)y^4 + (\theta^6 - 3\theta^4 + 2)y^3 + y^2 - (\theta^4 - 3\theta^2 + 1)y + 1 = 0, \quad (17)$$

which is a polynomial with symmetric coefficients and hence, denoting $\xi = y + 1/y$, (17) can be rewritten as

$$\xi^4 - (\theta^4 - 3\theta^2 + 1)\xi^3 - 3\xi^2 + (\theta^6 - 9\theta^2 + 5)\xi + 2\theta^6 - 7\theta^4 + 6\theta^2 - 2 = 0. \quad (18)$$

(18) has solutions of the form:

$$\begin{aligned} \xi_1(\theta) &= \frac{\theta^4 - 3\theta^2 + 1 - 2\sqrt{2k(\theta)} + 2\sqrt{d_1}}{4}, & \xi_2(\theta) &= \frac{\theta^4 - 3\theta^2 + 1 - 2\sqrt{2k(\theta)} - 2\sqrt{d_1}}{4}, \\ \xi_3(\theta) &= \frac{\theta^4 - 3\theta^2 + 1 - 2\sqrt{2k(\theta)} + 2\sqrt{d_2}}{4}, & \xi_4(\theta) &= \frac{\theta^4 - 3\theta^2 + 1 - 2\sqrt{2k(\theta)} - 2\sqrt{d_2}}{4}, \end{aligned}$$

where $d_1(\theta) = -2p(\theta) - 2k(\theta) + \sqrt{\frac{2}{k(\theta)}} \cdot q(\theta)$, $d_2(\theta) = -2p(\theta) - 2k(\theta) - \sqrt{\frac{2}{k(\theta)}} \cdot q(\theta)$,

$$q(\theta) = -\frac{1}{8}(\theta^4 - 5\theta^2 + 3)(\theta^8 - 4\theta^6 + 7\theta^4 - 6\theta^2 - 9), \quad p(\theta) := -\frac{1}{8}(3\theta^8 - 18\theta^6 + 33\theta^4 - 18\theta^2 + 27),$$

$$k(\theta) = \frac{\theta(\theta^2 - 2)\alpha}{12} + \frac{\theta^3(\theta^2 + 1)(\theta^2 - 2)}{\alpha} + \frac{1}{8}(\theta^8 - 6\theta^6 + 11\theta^4 - 6\theta^2 + 9),$$

$$\alpha = \sqrt[3]{108\theta(2\theta^4 - 6\theta^2 + 9) + 12\theta\sqrt{-12\theta^{10} + 288\theta^8 - 1980\theta^6 + 5820\theta^4 - 8748\theta^2 + 6561}}.$$

A graphical analysis reveals that $\xi_1(\theta) < 0$ and $\xi_2(\theta) < 0$ for any $\theta > 0$. $\xi_3(\theta) > 2$ and $\xi_4(\theta) > 2$ for any $\theta > \theta_2 \approx 2.078$ (see Fig. 2). Note that $\xi_3(\theta_2) = \xi_4(\theta_2)$.

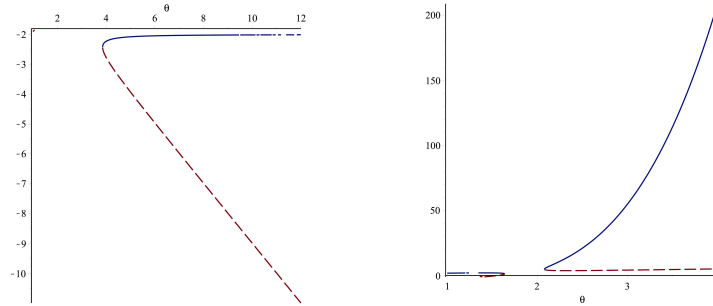


FIG. 2. On the left, the graphs of the functions $\xi_1(\theta)$ (solid line) and $\xi_2(\theta)$ (dashed line) and on the right the graphs of the functions $\xi_3(\theta)$ (solid line) and $\xi_4(\theta)$ (dashed line).

We find y_i , $i = 1, 2, 3, 4$ the following equation

$$y^2 - \xi_3 y + 1 = 0, \text{ and } y^2 - \xi_4 y + 1 = 0.$$

□

3.4. Construction of the finite-volume Gibbs measures for the case “Hinge”

Let $\theta = e^{\beta J}$ and denote

$$z_0 := 1, \quad z_1 := e^{h_1}, \quad z_2 := e^{h_2}.$$

For $q = 2$ the local sums entering Theorem 1 are

$$S_0 = \theta + z_1, \quad S_1 = \theta z_1 + 1 + z_2, \quad S_2 = \theta z_2 + z_1.$$

For translation-invariant boundary fields the fixed-point system reads

$$z_i = \left(\frac{S_i}{S_0} \right)^k, \quad i = 1, 2,$$

equivalently

$$S_i^k = S_0^k z_i, \quad i = 0, 1, 2. \quad (19)$$

For $n \geq 1$ the finite-volume Gibbs distribution on V_n with boundary field h is

$$\mu_n(\sigma_{V_n}) = \frac{1}{Z_n(h)} \exp\left(\beta J \sum_{\langle x,y \rangle \subset V_n} \delta_{\sigma(x), \sigma(y)}\right) \prod_{\langle x,y \rangle \subset V_n} \lambda_{\sigma(x), \sigma(y)} \exp\left(\sum_{x \in W_n} h_{\sigma(x)}\right). \quad (20)$$

Fix a configuration $\sigma_{V_{n-1}}$ on V_{n-1} . Summing (20) over all boundary configurations $\omega \in \Phi^{W_n}$ and using the tree factorization, one obtains

$$\sum_{\omega \in \Phi^{W_n}} \mu_n(\sigma_{V_{n-1}} \vee \omega) = \frac{1}{Z_n(h)} \exp(\beta J H_{V_{n-1}}(\sigma_{V_{n-1}})) \prod_{x \in W_{n-1}} \left(\sum_{u=0}^2 \lambda_{\sigma(x), u} e^{\beta J \delta_{\sigma(x), u}} z_u \right)^k. \quad (21)$$

Observe that the inner sums equal $S_{\sigma(x)}$, hence,

$$\sum_{\omega} \mu_n(\sigma_{V_{n-1}} \vee \omega) = \frac{1}{Z_n(h)} \exp(\beta J H_{V_{n-1}}(\sigma_{V_{n-1}})) \prod_{x \in W_{n-1}} S_{\sigma(x)}^k. \quad (22)$$

Now apply (19). Since $S_{\sigma(x)}^k = S_0^k z_{\sigma(x)}$ for every $\sigma(x) \in \{0, 1, 2\}$, we get

$$\sum_{\omega} \mu_n(\sigma_{V_{n-1}} \vee \omega) = \frac{S_0^{k|W_{n-1}|}}{Z_n(h)} \exp(\beta J H_{V_{n-1}}(\sigma_{V_{n-1}})) \prod_{x \in W_{n-1}} z_{\sigma(x)}. \quad (23)$$

To recover $\mu_{n-1}(\sigma_{V_{n-1}})$ on the right-hand side, the normalizing constants must satisfy the recursion

$$Z_n(h) = S_0^{k|W_{n-1}|} Z_{n-1}(h). \quad (24)$$

Indeed, substituting (24) into (23) yields exactly

$$\sum_{\omega} \mu_n(\sigma_{V_{n-1}} \vee \omega) = \mu_{n-1}(\sigma_{V_{n-1}}),$$

which is the Kolmogorov compatibility condition.

For the Cayley tree of order k one has

$$|W_m| = (k+1)k^{m-1}, \quad m \geq 1,$$

so that

$$\sum_{m=1}^{n-1} |W_m| = (k+1) \sum_{m=1}^{n-1} k^{m-1} = \frac{k+1}{k-1} (k^{n-1} - 1).$$

Iterating (24) from $Z_1(h)$ gives one

$$Z_n(h) = S_0^{k \sum_{m=1}^{n-1} |W_m|} Z_1(h) = S_0^{\frac{k(k+1)}{k-1} (k^{n-1} - 1)} \left(\sum_{i=0}^2 z_i S_i^{k+1} \right),$$

where $Z_1(h) = \sum_{i=0}^2 z_i S_i^{k+1}$.

Let

$$N_1 = \sum_{x \in W_n} \mathbf{1}_{\{\sigma(x)=1\}}, \quad N_2 = \sum_{x \in W_n} \mathbf{1}_{\{\sigma(x)=2\}}.$$

Then

$$\prod_{x \in W_n} z_{\sigma(x)} = z_1^{\sum_{x \in W_n} \mathbf{1}_{\{\sigma(x)=1\}}} z_2^{\sum_{x \in W_n} \mathbf{1}_{\{\sigma(x)=2\}}} = z_1^{N_1} z_2^{N_2}.$$

Using the expression for $Z_n(h)$ above, from (20), we obtain

$$\mu_n(\sigma_{V_n}) = \frac{\exp(\beta J H_{V_n}(\sigma_{V_n}))}{S_0^{\frac{k(k+1)}{k-1} (k^{n-1} - 1)} \sum_{i=0}^2 z_i S_i^{k+1}} z_1^{N_1} z_2^{N_2}.$$

This proves that for any translation-invariant fixed point z the family $\{\mu_n\}$ is Kolmogorov-consistent and hence extends to a splitting Gibbs measure on the infinite tree.

4. Thermodynamic properties of the solutions for $k = 2$.

Now we study the five resulting quantities from the thermodynamic point of view. For this purpose, we use the partition function.

Let Λ be a finite subset of V . We will denote by $\sigma(\Lambda)$ the restriction of σ to Λ . Let $\bar{\sigma}(V \setminus \Lambda)$ be a fixed boundary configuration. The total energy of $\sigma(\Lambda)$ under condition $\bar{\sigma}(V \setminus \Lambda)$ is defined as

$$H(\sigma(\Lambda) \mid \bar{\sigma}(V \setminus \Lambda)) = -J \sum_{\langle x, y \rangle: x, y \in \Lambda} \delta_{\sigma(x)\sigma(y)} - \beta^{-1} \sum_{\langle x, y \rangle: x, y \in \Lambda} \log \lambda_{\sigma(x), \sigma(y)} - \\ - J \sum_{\langle x, y \rangle: x \in \Lambda, y \notin \Lambda} \delta_{\sigma(x)\sigma(y)} - \beta^{-1} \sum_{\langle x, y \rangle: x \in \Lambda, y \notin \Lambda} \log \lambda_{\sigma(x), \sigma(y)}.$$

Then partition function $Z_\Lambda(\bar{\sigma}(V \setminus \Lambda))$ in volume Λ with boundary condition $\bar{\sigma}(V \setminus \Lambda)$ is defined as

$$Z_\Lambda(\bar{\sigma}(V \setminus \Lambda)) = \sum_{\sigma(\Lambda) \in \Omega(\Lambda)} \exp(-\beta H_\Lambda(\sigma(\Lambda) \mid \bar{\sigma}(V \setminus \Lambda))),$$

where $\Omega(\Lambda)$ is the set of all configurations in volume Λ and $\beta = \frac{1}{T}$ is the inverse temperature. Then the conditional Gibbs measure μ_Λ of a configuration $\sigma(\Lambda)$ is defined as

$$\mu_\Lambda(\sigma(\Lambda) \mid \bar{\sigma}(V \setminus \Lambda)) = \frac{\exp(-\beta H(\sigma(\Lambda) \mid \bar{\sigma}(V \setminus \Lambda)))}{Z_\Lambda(\bar{\sigma}(V \setminus \Lambda))}.$$

We consider the configuration $\sigma(V_n)$, the partition functions Z_{V_n} and the conditional Gibbs measure $\mu_\Lambda(\sigma(\Lambda) \mid \bar{\sigma}(V \setminus \Lambda))$ in volume V_n and simplicity, we denote them by σ_n , $Z^{(n)}$ and μ_n , respectively. For $q = 2$, the partition function $Z^{(n)}$ can be decomposed into the following components:

$$Z^{(n)} = Z_0^{(n)} + Z_1^{(n)} + Z_2^{(n)},$$

where

$$Z_i^{(n)} = \sum_{\sigma_n \in \Omega: \sigma(x^0) = i} \exp(-\beta H_{V_n}(\sigma \mid \bar{\sigma}(V \setminus V_n))), \quad i = 0, 1, 2.$$

Introducing notation $\theta = \exp(J\beta)$ and we get

$$Z_0^{(n)} = \left(\theta Z_0^{(n-1)} + Z_1^{(n-1)} \right)^2; \\ Z_1^{(n)} = \left(Z_0^{(n-1)} + \theta Z_1^{(n-1)} + Z_2^{(n-1)} \right)^2; \\ Z_2^{(n)} = \left(Z_1^{(n-1)} + \theta Z_2^{(n-1)} \right)^2.$$

Introducing the following notations

$$u_n(x^0) = \frac{Z_1^{(n)}(x^0)}{Z_0^{(n)}(x^0)}, \quad v_n(x^0) = \frac{Z_2^{(n)}(x^0)}{Z_0^{(n)}(x^0)}, \quad (25)$$

we obtain the following system of recurrent equations:

$$\begin{cases} u_n = \left(\frac{1 + \theta u_{n-1} + v_{n-1}}{\theta + u_{n-1}} \right)^2; \\ v_n = \left(\frac{u_{n-1} + \theta v_{n-1}}{\theta + u_{n-1}} \right)^2. \end{cases}$$

If $u = \lim u_n$ and $v = \lim v_n$ then

$$\begin{cases} u = \left(\frac{1 + \theta u + v}{\theta + u} \right)^2; \\ v = \left(\frac{u + \theta v}{\theta + u} \right)^2. \end{cases} \quad (26)$$

Remark 3. Note that, if we introduce the substitution $\sqrt{u} = x$ and $\sqrt{v} = y$ into a system of (26) equations, it coincides with a system of (12) equations. That is, the fixed points of the system of (12) equations will also be the fixed points of the system of (26).

4.1. Spontaneous Magnetization

If the spin values are given as $\sigma \in \{0, 1, 2\}$, the magnetization is defined by

$$\langle \sigma \rangle = \frac{\sum_{\sigma \in \Phi} \sigma Z_{\sigma}^{(n)}}{\sum_{\sigma \in \Phi} Z_{\sigma}^{(n)}} = \frac{Z_1^{(n)} + 2Z_2^{(n)}}{Z_0^{(n)} + Z_1^{(n)} + Z_2^{(n)}}.$$

This is not the physical magnetization yet, but only the mean value in $\{0, 1, 2\}$. From the physical point of view, spins are usually considered to take the symmetric values $\{-1, 0, +1\}$. This can be achieved by a simple linear transformation $\tilde{\sigma} = \sigma - 1$, which yields the true physical magnetization.

In this representation the definition of the magnetization becomes symmetric:

$$\langle \tilde{\sigma} \rangle = \frac{\sum_{\sigma \in \Phi} (\sigma - 1) Z_{\sigma}^{(n)}}{\sum_{\sigma \in \Phi} Z_{\sigma}^{(n)}} = \frac{Z_2^{(n)} - Z_0^{(n)}}{Z_0^{(n)} + Z_1^{(n)} + Z_2^{(n)}}.$$

Using the representation of the recursion relations given in Eqs. (25), the spontaneous magnetization per site is obtained as

$$M = \frac{v - 1}{1 + u + v},$$

where $(u; v)$ is a solution of the fixed point equations (26) or (12).

We denote by M_i the magnetization corresponding to the fixed point $(u_i; v_i)$, $i = \overline{0, 4}$, i.e.,

$$M_i = \frac{v_i - 1}{1 + u_i + v_i}.$$

Note that for $i = 0$, we have $y = 1$, and it follows that $M_0 = 0$.

In Fig. 3, plots of magnetizations M_i , $i = \overline{1, 4}$ for the HC-Potts model on the Cayley tree. Here $M_0 = 0$ corresponds to the non-magnetized (paramagnetic) phase. At low temperatures ($T < T_c$), the system exhibits four magnetized (ferromagnetic) phases, which appear as symmetric pairs with positive and negative magnetizations. As the temperature increases, these magnetized phases gradually approach $M_0 = 0$ and merge at the critical temperature T_{cr} . This behavior indicates a phase transition from the ferromagnetic to the paramagnetic phase, showing that the model possesses ordered phases at low temperatures and a disordered phase at high temperatures.

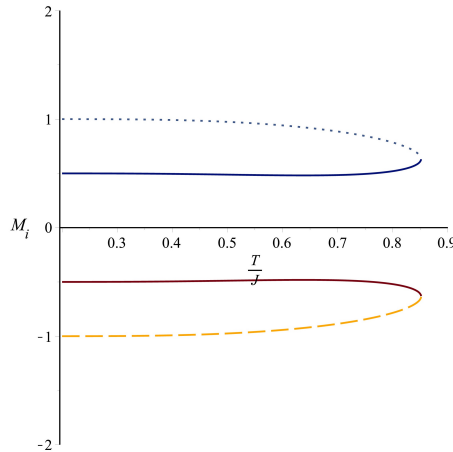


FIG. 3. Plots of spontaneous magnetizations M_i for $i = \overline{1, 4}$ for the case “Hinge”.

4.2. Quadrupolar Moment

In the three-state HC-Potts model, the quadrupolar moment is introduced to characterize the fraction of “active” spin states in the system. If the spin variables take values $\sigma \in \{0, 1, 2\}$, the quadrupolar moment is defined as

$$\langle \sigma^2 \rangle = \frac{\sum_{\sigma \in \Phi} \sigma^2 Z_{\sigma}^{(n)}}{\sum_{\sigma \in \Phi} Z_{\sigma}^{(n)}} = \frac{Z_1^{(n)} + 4Z_2^{(n)}}{Z_0^{(n)} + Z_1^{(n)} + Z_2^{(n)}}.$$

From the physical point of view, it is often more convenient to describe the system in terms of symmetric spin values $\{-1, 0, +1\}$. In the symmetric parametrization, the quadrupolar moment has a clearer interpretation. This can be obtained by applying a simple linear transformation $\tilde{\sigma} = \sigma - 1$.

Hence, the quadrupolar moment becomes as follows

$$\langle \tilde{\sigma}^2 \rangle = \frac{Z_0^{(n)} + Z_2^{(n)}}{Z_0^{(n)} + Z_1^{(n)} + Z_2^{(n)}}.$$

Using the same recursive framework, the quadrupolar moment is given by

$$Q = \frac{1 + v}{1 + u + v}$$

where $(u; v)$ is a solution of the fixed point equations (9) and (13).

Let Q_i denote the quadrupolar moment corresponding to $(u_i; v_i)$, $i = \overline{0, 4}$, i.e.,

$$Q_i = \frac{1 + v_i}{1 + u_i + v_i}.$$

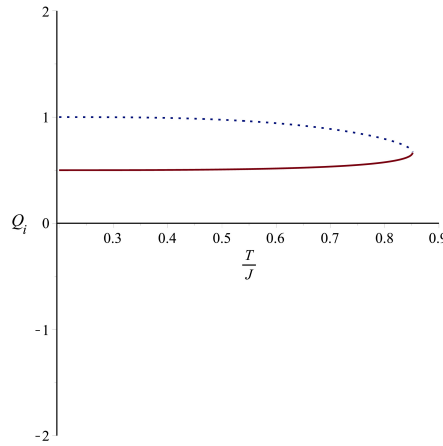


FIG. 4. Plots of Quadrupolar moments Q_i for $i = \overline{1, 4}$ for the cases “Hinge”. Here $Q_1 = Q_2$ (dashed line) and $Q_3 = Q_4$ (solid line).

In Fig. 4, the plots of the quadrupolar moments Q_i for $i = \overline{1, 4}$ are presented. The curves $Q_1 = Q_2$ and $Q_3 = Q_4$ correspond to the symmetric magnetized phases shown in Fig. 4. At low temperatures, the system exhibits an ordered (nematic-like) phase, while all Q_i values merge at the critical temperature T_c , indicating a transition to the paramagnetic (disordered) phase. Both magnetic and quadrupolar orders vanish simultaneously at this point.

5. Conclusion

In this paper, Gibbs measures for the Hard-Core–Potts model on Cayley trees were investigated. For the hinge-type graph and the cases $k = 2$ and $k = 3$, critical values of the parameter θ were found, determining the transition from a unique to multiple translation-invariant Gibbs measures. Thermodynamic analysis showed that the model exhibits ordered phases at low temperatures and a disordered phase at high temperatures, revealing the interplay between magnetic ordering and hard-core exclusion effects.

The thermodynamic analysis of the HC-Potts model on the Cayley tree reveals several important physical features arising from the interplay between ferromagnetic interactions and hard-core exclusion constraints.

The fixed-point solutions of the recursive relations show that at low temperatures (equivalently, for large values of $\theta = e^{\beta J}$), the system admits four distinct magnetized phases in addition to the paramagnetic one. These phases appear in symmetric pairs with positive and negative magnetizations, reflecting the underlying ± 1 symmetry of the transformed spin states. The presence of four magnetized phases is a direct consequence of the hard-core constraints, which restrict admissible local configurations and thereby enrich the phase structure compared to the classical three-state Potts model. As the temperature increases, thermal fluctuations dominate the ferromagnetic ordering, causing the magnetized phases to move continuously toward the paramagnetic fixed point. At the critical temperature T_c , all nonzero magnetizations collapse to zero, marking a transition from an ordered ferromagnetic regime to a disordered paramagnetic phase. This behavior illustrates the spontaneous breaking of symmetry at low temperatures and its restoration at high temperatures.

The quadrupolar order parameter provides additional insight into the distribution of active spin states. For the three-state system, it measures the relative weight of the spin values ± 1 compared to the inactive state. Our analysis shows

that each magnetized phase is accompanied by a distinct quadrupolar value, indicating that both magnetic and structural ordering are simultaneously present in the low-temperature regime. As the temperature increases, the quadrupolar moments associated with all phases converge to a common value at the same critical temperature T_c . This demonstrates that the disappearance of magnetic ordering is accompanied by the loss of structural (nematic-like) order. Consequently, the HC-Potts model undergoes a single combined phase transition at which both magnetization and quadrupolar order vanish.

Overall, these results show that the hard-core exclusion mechanism significantly modifies the thermodynamic behavior of the Potts model, producing additional magnetized phases and enforcing a coupled disappearance of magnetic and quadrupolar orders at the critical point.

References

- [1] Esfarjani K., Mansoori G.A. Statistical mechanical modeling and its application to nanosystems. *Handbook of Theoretical and Computational Nanotechnology*, 2006, **2**(14), P. 1–45.
- [2] Hill T.L. *Thermodynamics of Small Systems*. W.A. Benjamin, New York, 1963.
- [3] Hill T.L. A Different Approach to Nanothermodynamics. *Nano Letters*, 2001, **1**, P. 273–275.
- [4] Baxter R.J. *Exactly solved models in statistical mechanics*. Academic, London, 1982.
- [5] Friedli S., Velenik Y. *Statistical mechanics of lattice systems. A concrete mathematical introduction*. Cambridge University Press, Cambridge, 2018.
- [6] Georgii H.-O. *Gibbs Measures and Phase Transitions* (de Gruyter Stud. Math., Vol.9), Walter de Gruyter, Berlin, 1988.
- [7] Preston C. *Gibbs States on Countable Sets*. Cambridge University Press, London, 1974.
- [8] Rozikov U.A. *Gibbs measures on Cayley trees*, World Scientific, 2013.
- [9] Rozikov U.A. *Gibbs Measures in Biology and Physics. The Potts Model*, World Scientific, 2023.
- [10] Sinai Ya.G. *Theory of Phase Transitions: Rigorous Results* [in Russian], Nauka, Moscow, 1980; English trans. (Int. Ser. Nat. Philos., Vol. 108, Pergamon, Oxford, 1982).
- [11] Rozikov U.A. Gibbs measures of Potts model on Cayley trees: A survey and applications. *Rev. Math. Phys.*, 2021, **33**, 2130007, 58 p.
- [12] Ashkin J., Teller E. Statistics of two-dimensional lattices with four components. *Phys. Rev.*, 1943, **64**, P. 178–184, 5–6.
- [13] Potts R.B. Some generalized order-disorder transformations. *Mathematical Proceedings of the Cambridge Philosophical Society*, 1952, **48**, P. 106–109.
- [14] Kihara T., Midzuno Y., Shizume T. Virial coefficients and intermolecular potential of helium. *Journal of the Physical Society of Japan*, 1955, **10**, P. 249–255.
- [15] Ganikhodzhaev N.N. Pure phases of the ferromagnetic Potts model with three states on a second-order Bethe lattice. *Theor. Math. Phys.*, 1990, **85**, P. 1125–1134.
- [16] Ganikhodzhaev N.N. On pure phases of the ferromagnetic Potts model on the Bethe lattice [in Russian]. *Dokl. Akad. Nauk Resp. Uzb.*, 1992, **6-7**, P. 4–7.
- [17] Ganikhodzhaev N.N., Rozikov U.A. Description of periodic extreme Gibbs measures of some lattice models on a Cayley tree. *Theor. Math. Phys.*, 1997, **111**(1), P. 480–486.
- [18] Ganikhodzhaev N.N., Rozikov U.A. The Potts model with countable set of spin values on a Cayley tree. *Lett. Math. Phys.*, 2006, **75**(2), P. 99–109.
- [19] Makhammaliev M.T. Pure phases of the ferromagnetic Potts model with q states on the Cayley tree of order three. *Vestn. Udmurtsk. Univ. Mat. Mekh. Komp. Nauki*, 2024, **34**(4), P. 499–517.
- [20] Makhammaliev M.T. Extremality of the translation-invariant Gibbs measures for the Potts model with four states on the Cayley tree of order $k = 3$. *Uzbek Math. Journal*, 2022, **66**(1), P. 117–132.
- [21] Makhammaliev M.T. Periodic Gibbs measures for the antiferromagnetic Potts model on a Cayley tree of order k . *Uzbek Math. Journal*, 2021, **65**(1), P. 110–117.
- [22] Galvin D., Kahn J. On phase transition in the hard-core model on $\mathbb{Z}^d$. *Comb. Prob. Comp.*, 2004, **13**(2), P. 137–164.
- [23] Brightwell G.R., Winkler P. Hard constraints and the Bethe lattice: adventures at the interface of combinatorics and statistical physics. In: *Proceedings of the ICM 2002*, vol. III, P. 605–624. Higher Education Press, Beijing, 2002.
- [24] Mazel A.E., Suhov Yu. M. Random surfaces with two-sided constraints: an application of the theory of dominant ground states. *J. Statist. Phys.*, 1991, **64**, P. 111–134.
- [25] Brightwell G.R., Winkler P. Graph homomorphisms and phase transitions. *J. Combin. Theory Ser. B*, 1999, **77**(2), P. 221–262.
- [26] Khakimov R., Makhammaliev M., Haydarov F. New class of Gibbs measures for two-state hard-core model on a Cayley tree. *Infin. Dimens. Anal. Quantum Probab. Relat. Top.*, 2023, **26**(4), P. 2350024.
- [27] Khakimov R., Makhammaliev M., Umirzakova K. Alternative Gibbs measure for fertile three-state Hard-Core models on a Cayley tree. *Phase Transitions*, 2024, **97**(9), P. 536–556.
- [28] Martinelli F., Sinclair A., Weitz D. Fast mixing for independent sets, coloring and other models on trees. *Random Structures and Algorithms*, 2007, **31**, P. 134–172.
- [29] Rozikov U.A., Khakimov R.M., Makhammaliev M.T. Gibbs periodic measures for a two-state HC-Model on a Cayley tree. *Jour. Math. Sci.*, 2024, **278**(4), P. 647–660.
- [30] Akin H., Phase transition analysis of the Potts-SOS model on the Cayley tree. *Physica Scripta*, 2024, **99**(12), P. 125204.
- [31] Akin H., Qualitative properties of the 1D mixed-type Potts-SOS model with 1-spin and its dynamical behavior. *Physica Scripta*, 2023, **99**(5), P. 055231.
- [32] Akin H., Mukhamedov F. 3-state hybrid Potts-SOS model with different coupling constants and its phase transition phenomenon. *Physica Scripta*, 2025, **100**(8), P. 10–21.
- [33] Al Aali A., Mukhamedov F. Mixed quantum Ising-XY model on a Cayley tree of order two. *Eur. Phys. Jour. B*, 2025, **98**(4), P. 1–8.
- [34] Jahnel B., Rozikov U. Gibbs measures for hardcore-solid-on-solid models on Cayley trees. *Jour. of Stat. Mech.: Theory and Exp.*, 2024, P. 073202.

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The uniqueness of perfect star packings and the existence of pseudo-matchings in (2,6)-fullerene graphs

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ABSTRACT A perfect star packing can be described as a spanning subgraph whose connected components are isomorphic to the star graph $K_{1,3}$. A perfect pseudo-matching is a spanning subgraph in which every component is isomorphic to either K_2 or $K_{1,3}$. The study of packing problems on fullerene graphs is of particular interest due to their potential relevance in describing local bonding arrangements in carbon nanostructures. In this paper, we study the uniqueness of perfect star packing, and the existence of pseudo-matchings in (2,6)-fullerene graphs. Moreover, we show that the perfect star packing in these graphs is unique. Furthermore, we introduced some perfect pseudo-matchings in (2,6)-fullerene graphs.

KEYWORDS (2,6)-fullerene graphs; perfect star packing; perfect pseudo-matching.

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1. Introduction

Fullerenes are carbon atom-based polyhedral molecules. They come in various sizes and forms. Fullerene graphs serve as a crucial mathematical structure for modeling carbon-based nanosystems, with vertices depicting carbon atoms and edges representing covalent bonds [1]. The study of structural properties of fullerene graphs has long been motivated by their close relationship with real carbon cages and nanotube-related nanostructures [2]. Also, theoretical research on fullerenes in graph theory, in parallel with experimental experiments, has led to the identification of structural properties of stable fullerenes at macroscopic quantities. These theoretical researches have led to the investigation and prediction of the potential stability of these molecules.

One of the most interesting patterns in fullerenes is the one that allows for a resonance structure. But such patterns should not overlap, so they are modeled by packings in the corresponding graphs. A $(k,6)$ -fullerene graph is defined as a planar cubic graph in which every face is bounded by either k -cycles or 6-cycles. Došlić [3] established that such graphs exist only for $k=2,3,4$ and 5. Applying Euler's formula, one can deduce that the number of k -length faces in $(k,6)$ -fullerenes graphs for $k=2,3,4$ and 5 equals 3, 4, 6 and 12, respectively. For a graph G , a matching M is defined as a set of edges of G in which no two edges share a common vertex M . A matching is perfect if every vertex of G is incident to exactly one edge from M . In addition to mathematics, perfect matchings have also received much attention in chemistry and are known as the Kekulé structures. The number of Kekulé structures in a benzenoid hydrocarbon is intricately connected to the compound's stability. In a graph G , a perfect star packing can be described as a spanning subgraph whose connected components are isomorphic to the star graph $K_{1,3}$. Similarly, a perfect pseudo-matching is a spanning subgraph where each component is isomorphic to either K_2 or $K_{1,3}$. When all components are edges K_2 the structure forms a perfect matching, and, when all are stars $K_{1,3}$ it becomes a perfect star packing. While a pseudo-matching matching containing both types of components is called mixed pseudo-matching. Researching packing problems in fullerene graphs is intriguing because of their possible significance to local bonding configurations in nanoscale carbon structures [4,5].

Specifically, the aim of this research is to investigate the conditions under which the addition of bulky groups leads to maximum efficiency and how many bulky groups (i.e., addition to one atom prohibits addition to other atoms) can be added so that the remaining part of the molecule still has a resonance structure. The concept of packing is very useful for modeling such a situation. Understanding the uniqueness and existence of perfect star packings and pseudo-matchings in (2,6)-fullerene graphs provides insight into the structural rigidity, stability, and possible functional patterns of such nanoscale systems. Motivated by these connections, the present paper investigates the uniqueness of perfect star packings and the existence of perfect pseudo-matchings in (2,6)-fullerene graphs, highlighting their potential importance for nanoscale structural modeling.

Extensive research has been conducted on fullerene graphs for $k = 3, 4$, and 5 . However, comparatively fewer studies have focused on $(2, 6)$ -fullerene graphs. In [4, 6, 7], the authors have obtained results about perfect star packings of $(k, 6)$ -fullerene graphs for $k = 3, 4$ and 5 . Taheri-Dehkordi and Fath-Tabar [8], examined nice pairs of pentagons in chamfered fullerenes. Some properties of these graphs have been examined in [9–14]. Reference [15] provides the computation of the number of perfect star packings and pseudo-matchings in some types of fullerene graphs. Yang et al. [16], investigated the structure of $(2, 6)$ -fullerene graphs. In a recent paper [17], the existence of perfect star packing in $(2, 6)$ -fullerene graphs was investigated. In this paper, we determine the number of perfect star packings and mixed pseudo-matchings in $(2, 6)$ -fullerene graphs by considering their structural properties and the arrangements perfect star packing of these graphs.

2. Definitions and auxiliary results

This section states the important and used definitions and preliminary results. A $(2, 6)$ -fullerene graph can be characterized as a cubic planar graph in which all faces lengths are either 2 or 6. By Euler's formula, these graphs contain exactly three 2-length faces. The structure of some $(2, 6)$ -fullerene graphs is stated in [16]. The authors proved that there are $(2, 6)$ -fullerene graphs with f_G hexagonal faces, so that f_G depends on a parameter such as s . In a $(2, 6)$ -fullerene graph G , a **fragment** H refers to a subgraph that consists of a cycle and the region inside it, such that all faces contained in this interior are also faces of G [16]. In this study, four types of $(2, 6)$ -fullerene graphs with the following structure were introduced.

$(2, 6)$ -Fullerene graphs of type 1: These graphs consist of a fragment G_s as shown in Fig. 1, which consists of s hexagonal layers.

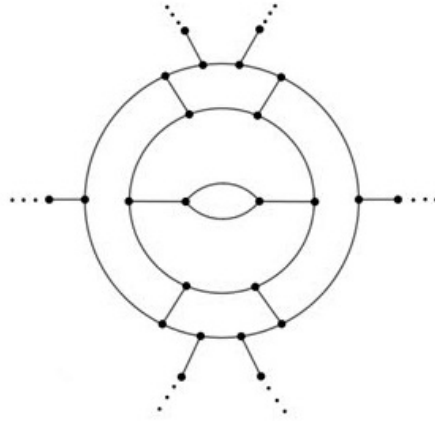


FIG. 1. The fragment G_s in $(2, 6)$ -Fullerene graphs of type 1

$(2, 6)$ -Fullerene graphs of type 2: These graphs consist of a fragment C_s as shown in Fig. 2, which consists of s hexagonal layers.

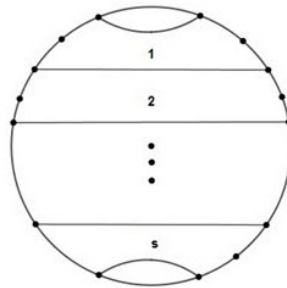


FIG. 2. The fragment C_s in $(2, 6)$ -Fullerene graphs of type 2

$(2, 6)$ -Fullerene graphs of type 3: These graphs consist of an initial fragment as shown in Fig. 3.

$(2, 6)$ -Fullerene graphs of type 4: These graphs consist of a fragment F_6 as shown in Fig. 4.

In [17], based on this structure, the existence of perfect star packing in these graphs is investigated. We summarize these results below.

Proposition 2.1 ([17]). *If G be a $(2, 6)$ -fullerene graphs of type 1 with s hexagonal layers. Then,*

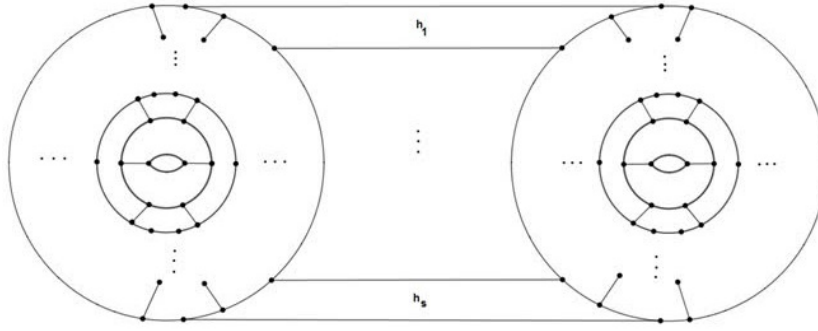
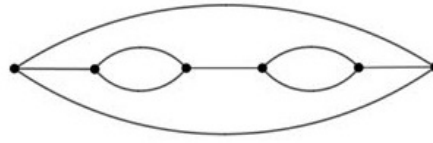


FIG. 3. The initial fragment in (2,6)-fullerene graph of type 3


 FIG. 4. The fragment F_6 in (2,6)-fullerene graph of type 4

- (1) If s is odd, then G has a perfect star packing.
- (2) If s is even, then G does not admit a perfect star packing.

Proposition 2.2 ([17]). *If G be a (2,6)-fullerene graphs of type 2 with s hexagonal faces in the first layer. Then,*

- (1) If s is odd, then G has a perfect star packing.
- (2) If s is even, then G does not admit a perfect star packing.

Proposition 2.3 ([17]). *Let G be a (2,6)-fullerene graphs of type 3 with s hexagonal layers in their fragments. Then,*

- (1) If s is odd, then G admit a perfect star packing.
- (2) If s is even, then G does not admit a perfect star packing.

Proposition 2.4 ([17]). *Let G be a (2,6)-fullerene graphs of type 4. Then, G does not have a perfect star packing.*

3. Number of perfect star packing in (2,6)-fullerene graphs

In this section, according to the structure of perfect star packings of (2,6)-fullerene graphs, introduced in [17], we calculate the number of these packings and mixed perfect pseudo-matchings in four types of these graphs. Following the notation introduced in [15], $PSP(G)$ denotes the number of perfect star packings in the graph G .

In [17], a method for the perfect star packing in (2,6)-fullerene graphs of type 1 was presented. This packing configuration is denoted by, P_1 . We show that in this type of fullerene graphs, there is no other method for packing, and also, only one packing configuration can be considered in this method. In other words, this packing is unique.

Theorem 3.1. *Let G be a (2,6)-fullerene of type 1. Then, $PSP(G) = 0$ if s is even and, $PSP(G) = 1$ if s is odd.*

Proof. According to Proposition 2.1, if s is even, G does not admit a perfect star packing and therefore, $PSP(G) = 0$. Assume that s is odd. First, we consider the innermost layer. For packing this layer, vertices v_0 and v_0' designated as the central vertices of the star structure (see Fig. 5). Also, in the last layer to cover vertices w_1, w_2, w_3 , and w_4 , vertices w_1', w_2', w_3' , and w_4' must be the central vertex of the star, respectively.

In the second layer, to cover the vertex u_0 , either u_0 itself must be the star's central vertex or u_0' , (Fig. 6). If u_0 is the star's central vertex, then we obtain the same packing as P_1 . So, Assume that u_0' is the central vertex of the star.

To cover u_1 , the vertex u_1' must necessarily be the central vertex of the star. To cover the vertex u_2 , we consider the following two cases.

- (1) u_2' is a central vertex. In this case, to cover vertex u_3 , vertex u_3' must be the central vertex of the star. Also, to cover vertex u_4 , vertex u_4' must be the central vertex of the star. Under these conditions, u_5 is not covered.
- (2) u_3 is a central vertex. In this case, to cover vertex u_5 , vertex u_5' must be the central vertex of the star. Likewise, to cover u_6 , vertex u_7 must be the central vertex, and to cover u_8 , vertex u_8' must be the central vertex of the star (Fig. 7). In this case, u_4' is not covered.

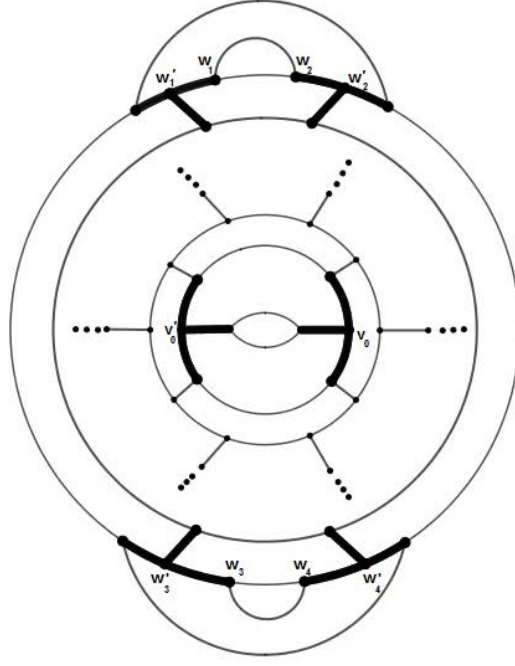


FIG. 5. Packaging in the first and last layers

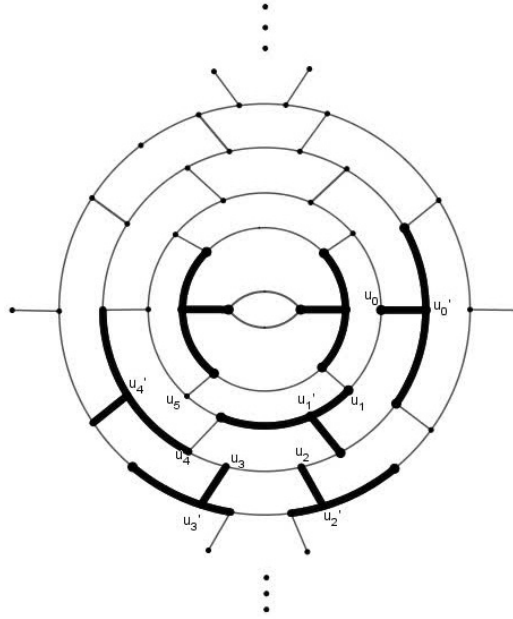


FIG. 6. Packaging in the second layer

Hence, it is impossible to obtain a perfect star packing in either case, implying that u_0' cannot be the central vertex and u_0 must be a central vertex of the star.

From the above discussion, conclude that we should have the same P_1 packing method in the second and third layers. On the other hand, subsequent layers must also be packing in pairs. Therefore, P_1 is the only packing method. Now, we need to check if there is another way to packing with this method. As mentioned, there is only one state in the first layer. An even number of layers remain, which are packed in pairs. The only way to increase the number of packing states in a pair of layers, is to rotate the stars. We consider the k -th and $(k+1)$ -th arbitrary layers, where k is an even number. There are $4k+2$ and $4k+6$ vertices in these two layers, respectively, and there are $2k+2$ star graphs in these two layers. The packing of these two layers is shown in Fig. 8.

In the neighborhood of each of the stars S_1, S_2, S_3 and S_4 , there must be a star with a central vertex in the k -th layer. (stars S_1', S_2', S_3' and S_4' in Fig. 9).

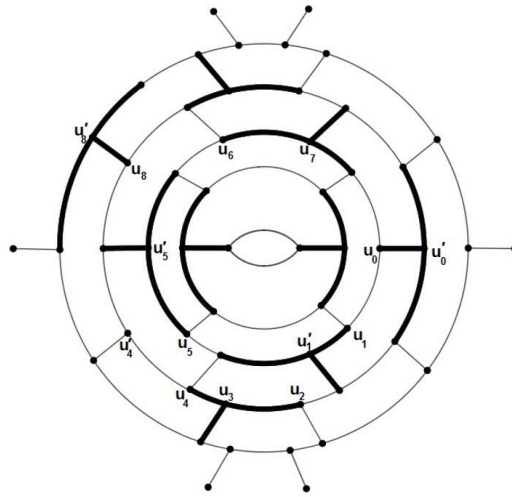


FIG. 7. Covering the vertex u_2

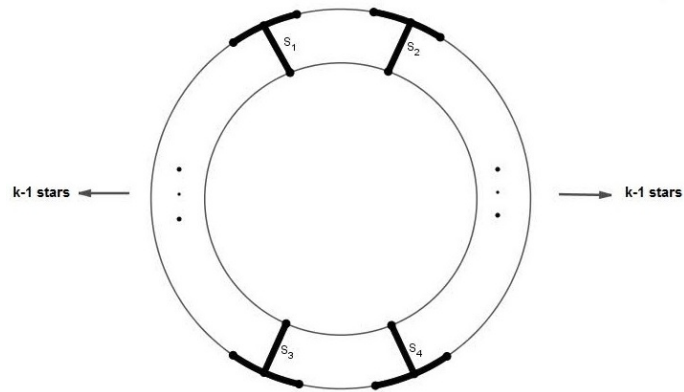


FIG. 8. Packing in two arbitrary layers

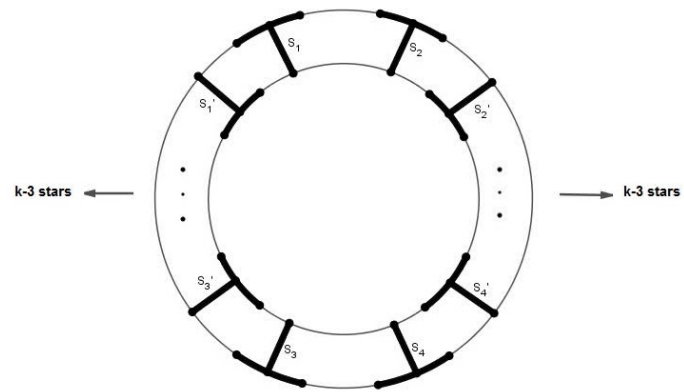


FIG. 9. Packing in two arbitrary layers

Also, adjacent to each of these star graphs, there must be a star graph with a central vertex in the $k + 1$ -th layer. Continuing this process, we will again arrive at the packing P_1 . $\square$

In [17], one technique to obtain a perfect star packing in (2,6)-fullerene graphs of type 2 and type 3 was presented. We call these packings P_2 and P_3 , respectively. In the following theorems, we show that in these types of fullerene graphs, there is no other method for packing, and also, only one packing configuration can be considered in two methods. In other words, these packings are unique.

Theorem 3.2. *Let G be a (2, 6)-fullerene of type 2. Then, $PSP(G) = 0$ if s is even, and $PSP(G) = 1$ if s is odd.*

Proof. According to Proposition 2.2, if s is even, G does not have a perfect star packing and therefore, $PSP(G) = 0$. Now, assume that s is odd. If we want to have a packing other than P_2 , the edges e_1, e_2, e_3 and e_4 should be considered as star edges (see Fig. 10).

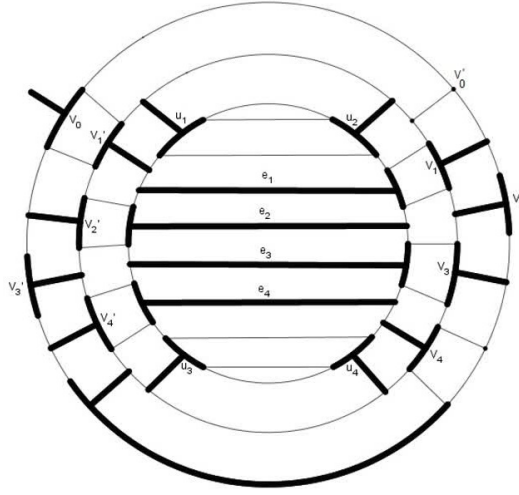


FIG. 10. A packing in G

It is necessary that u_1, u_2, u_3 and u_4 be the central vertex of the star. Also, vertices $v_1, v_2, v_3, v_4, v_1', v_2', v_3'$ and v_4' are also the central vertices of the star. To cover the vertex v_0 , this vertex itself must be the central vertex, and in this case, vertex v_0' is not covered. Therefore, the only packing method in this type of graph is the P_2 packing. Now, we prove that there is only one state for this type of packing, and we conclude that $PSP(G) = 1$. In the first two layers, due to the structure of 2-length cycles, there is only one state for packing. Now, we consider the third and fourth layers. In the packing P_2 , the vertex v_1 is the star's central vertex (Fig. 11), and the vertex v_1 is also covered.

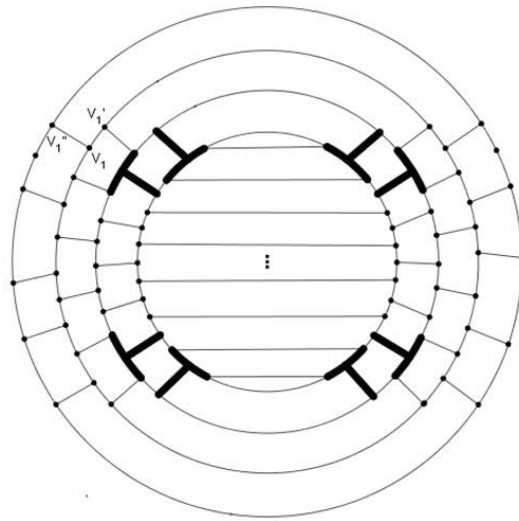


FIG. 11. Packing of vertices

If we want to consider vertex v_1'' as the central vertex of the star, then v_1' is not covered in any other way, so changing the packing in this layer is also not possible. In other layers, similar to what was stated in Theorem 3.1, the rotation of stars is not possible, and therefore, the statement is proven. $\square$

Theorem 3.3. *Let G be a $(2,6)$ -fullerene of type 3. Then, $PSP(G) = 0$ if s is even and, $PSP(G) = 1$ if s is odd.*

Proof. According to Proposition 2.3, if s is even, G does not admit a perfect star packing and therefore, $PSP(G) = 0$. Now, assume that s is odd. In $(2,6)$ -fullerene graphs of type 3, the packing of the initial fragment is done according to the packing of $(2,6)$ -fullerene graphs of type 1. Therefore, this type of packing is unique. In the last layer, we also have a unique packing. What remains are the remaining layers, the number of which is even. In these layers, as in the proof of Theorem 3.1, rotation of stars is not possible, and therefore, $PSP(G) = 1$. $\square$

It is proved in [17] that $(2,6)$ -fullerenes of type 4 do not admit a perfect star packing. Considering this, the following theorem can thus be deduced.

Theorem 3.4. *Let G be a $(2,6)$ -fullerene of type 4. Then, $PSP(G) = 0$.*

4. Perfect pseudo-matchings in $(2,6)$ -fullerene graphs

In the present section, we examine the mixed perfect packings, commonly referred to as pseudo-matchings. In a graph G , a perfect pseudo-matching is a spanning subgraph whose connected component is either a K_2 or a $K_{1,3}$.

Theorem 4.1. *Every $(2,6)$ -fullerene of type 1 with an odd number of hexagonal layers has a perfect matching.*

Proof. According to Theorem 3.1, $(2,6)$ -fullerene graphs with an odd number of layers admits a unique perfect star packing consisting of $\frac{n}{4}$ star graphs $K_{1,3}$. (n is the number of vertices of graph). Using this packing, we construct a matching M for this type of graphs. Let G be a $(2,6)$ -fullerene of type 1 with an odd number of hexagonal layers. In the first layer, we consider the matching edges as shown in Fig. 12 (dashed lines).

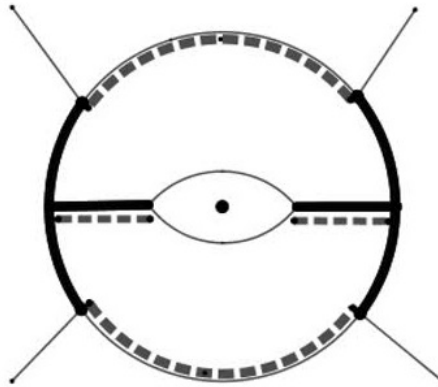


FIG. 12. Matching in the first layer

In other layers, at one pole, for two pairs of layers G , we consider the edges of M as shown in Fig. 13(a) (dashed lines). At the other pole, the edges of M are considered as shown in Fig.13(b).

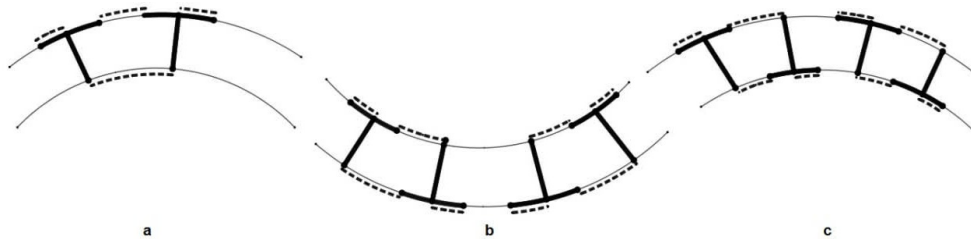


FIG. 13. Matching at two poles and two pairs of layers

In other parts, we consider the edges of M in each pair of layers as shown in Fig. 13(c) (dashed lines). Therefore, all vertices are covered by K_2 components, and thus, a perfect matching for G is obtained. $\square$

Theorem 4.2. *Let G be a $(2,6)$ -fullerene of type 1 with an odd number of hexagonal layers. Then, G contains a mixed perfect pseudo-matching comprising at least two star components.*

Proof. It is established that G admits a perfect star packing. To prove the claim, it is necessary to demonstrate that G contains two copies of $K_{1,3}$ whose union forms a nice subgraph of G . For this purpose, we consider the process of forming the graph matching in Theorem 4.1. In this matching, we consider each pair of $K_{1,3}$ star graphs. Suppose that k_1 and k_2 are two adjacent star graphs. For other star graphs in the perfect star packing, we follow the process of constructing the matching. By doing this, $G - \{k_1, k_2\}$ has a perfect matching and therefore, $k_1 \cup k_2$ is a nice subgraph of G . $\square$

By performing the method mentioned in the proof of Theorem 4.2 for each pair of stars, the following corollary can be obtained.

Corollary 4.3. *Every $(2, 6)$ -fullerene of type 1 with an odd number of hexagonal layers contains a mixed perfect pseudo-matching with at least two star components.*

Table 1 presents the number of K_2 and $K_{1,3}$ components in a mixed perfect pseudo-matching in $(2, 6)$ -fullerenes of type 1 with an odd number of hexagonal layers.

TABLE 1. Number of components in mixed perfect pseudo-matching

Number of $K_{1,3}$ components	Number of K_2 components
$\frac{n}{4}-2$	4
$\frac{n}{4}-4$	8
$\frac{n}{4}-6$	12
$\frac{n}{4}-8$	16
$\dots$	$\dots$

Considering the process of defining perfect star packing in $(2, 6)$ -fullerene graphs of types 2 and 3 and, similar to what was stated in the proof of Theorems 4.1 and 4.2, the following Theorems can be stated.

Theorem 4.4. *Let G be a $(2, 6)$ -fullerene of type 2 or 3 with an odd number of hexagonal layers. Then, G has a perfect matching.*

Theorem 4.5. *Let G be a $(2, 6)$ -fullerene of type 2 or 3 with an odd number of hexagonal layers. Then, G contains a perfect pseudo-matching with at least two star components.*

5. Conclusion

In this study, our results demonstrated that for types 1, 2, and 3, perfect star packings are unique. Moreover, we established the existence of perfect pseudo-matchings containing both star and matching components for the same classes of graphs. These findings contribute to a deeper understanding of the combinatorial and structural properties of fullerene graphs and may serve as a foundation for further investigations into their packing and matching configurations. The results obtained from a nano-systems science point of view describe local structural motives in carbon nanostructures based on the $(2, 6)$ -fullerenes. The uniqueness of perfect star packings shows that there is only one predominant type of local coordination - something that could be interpreted as an indication of structural stability and a reduced configurational ambiguity at the nanoscale. Therefore, the outcome of the present work can be of benefit to a wider understanding of structure-property relationships in nanoscale systems, where graph theory plays a very important role in connecting mathematics with chemistry.

References

- [1] Taylor P.F. In *Kirk-Othmer Encyclopedia of Chemical Technology*, John Wiley & Sons, Inc (Ed.), 2002.
- [2] Postnov V.N., Scaletckaya A.Ya., Krokhina O.A., Keskinov V.A., Charykov N.A., Semenov K.N. Sorption and liquid chromatographic separation of light fullerenes C_{60} and C_{70} with multiwall carbon nanotubes, *Nanosystems: Physics, Chemistry, Mathematics*, 2013, **4**(5), P. 706–715.
- [3] Došlić T. Cyclical edge-connectivity of fullerene graphs and $(k, 6)$ -cages, *J. Math. Chem.*, 2003, **33**, P. 103–112.
- [4] Došlić T., Taheri-Dehkordi M., Fath-Tabar G.H. Packing stars in fullerenes, *J. Math. Chem.*, 2020, **58**, P. 2223–2244.
- [5] Schwerdtfeger P., Wirz L.N., Avery J. The topology of fullerenes, *WIREs Comput. Mol. Sci.*, 2015, **5**, P. 96–145.
- [6] Došlić T., Taheri-Dehkordi M., Fath-Tabar G.H. Shortest perfect pseudomatchings in fullerene graphs, *Appl. Math. Comput.*, 2022, **424**, P. 127026.
- [7] Lingjuan Sh. The fullerene graphs with a perfect star packing, *Ars Mathematica Contemporanea*, 2023.
- [8] Taheri-Dehkordi M., Fath-Tabar G.H. Nice Pairs of Pentagons in Chamfered Fullerenes, *MATCH Commun. Math. Comput. Chem.*, 2022, **87**, P. 621–628.
- [9] Došlić T. On some structural properties of fullerene graphs, *J. Math. Chem.*, 2002, **31**, P. 187–195.
- [10] Fowler P.W., Cremona J.E., Steer J.I. Systematics of bonding in non-icosahedral carbon clusters, *Theor. Chim. Acta.*, 1988, **73**, P. 1–26.
- [11] Fowler P.W., Manolopoulos D.E. *An Atlas of Fullerenes*. International Series of Monographs on Chemistry, 30 (Clarendon Press, Oxford, 1995).
- [12] Shiu W.C., Zhang H. A complete characterization for k -resonant Klein-bottle polyhexes, *J. Math. Chem.*, 2008, **43**(1), P. 45–59.

- [13] Taheri-Dehkordi M. Introducing Two Transformations in Fullerene Graphs, Star and Semi-Star, *Iranian J. Math. Chem.*, 2023, **14**, P. 135–143.
- [14] Zhang F., Wang L. k -Resonance of open-ended carbon nanotubes, *J. Math. Chem.*, 2004, **35**(2), P. 87–103.
- [15] Taheri-Dehkordi M., Fath-Tabar G.H. On the Number of Perfect Star Packing and Perfect Pseudo Matching in Some Fullerene Graphs, *Iranian J. Math. Chem.*, 2023, **14**, P. 7–18.
- [16] Yang R., Yuan M. The Structural Properties of (2, 6)-Fullerenes, *Symmetry*, 2023, **15** (11), P. 2078.
- [17] Taheri-Dehkordi M. Perfect star packings in (2,6)-fullerene graphs, *Math. Interdisc. Res.*, In press, 10.22052/mir.2025.257713.1546, 2025.

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Theoretical analysis of chirped pulse effects on plasma formation in water liquid jet

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ABSTRACT We present a theoretical study of how linear chirp controls plasma density in a water jet using a two-stage framework. Stage I solves carrier-population and current equations at a single point, driven by a chirped super-Gaussian pulse. By fixing bandwidth and normalizing for intensity, we isolate a chirp-only response of plasma density, which exceeds unity and shows a consistent advantage for negative over positive chirp. Stage II propagates the field in water via the angular-spectrum method and applies the same equations across space. Normal dispersion reverses the trend: the chirp-only plasma density decreases as chirp grows, negative chirp remains less detrimental, and suppression is strongest for longer FTL pulses (e.g., 80 fs) due to dispersion-induced temporal spreading and spatio-temporal desynchronization. This study separates spectral-phase effects from bandwidth and intensity, yields testable predictions for water jets, and provides a foundation for future experiments and self-consistent propagation models.

KEYWORDS plasma density, chirped pulse.

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1. Introduction

Plasma–liquid systems have emerged as a powerful platform for nanotechnology, offering unique physicochemical environments for the synthesis, functionalization, and assembly of nanomaterials [1–3]. When high-energy laser pulses interact with liquids, dense plasmas rich in reactive oxygen and nitrogen species (RONS) are generated [4–6], initiating reduction, nucleation, and growth processes for metallic and semiconductor nanoparticles. Unlike conventional chemical synthesis, plasma–liquid techniques operate without toxic reducing agents, allowing environmentally friendly and highly controllable nanomaterial production [7, 8]. Such plasmas also enable post-synthesis surface modification, grafting functional groups onto nanostructures to enhance dispersion, catalytic activity, and biocompatibility. Applications span from catalytic nanomaterials and quantum dots for optoelectronics, to plasma-activated liquids for targeted biomedical therapies. For instance, dielectric barrier discharge plasma has been employed to functionalize graphene and carbon nanotubes, improving their dispersion in aqueous systems and enhancing their performance in energy storage and gas hydrate formation [9]. Plasma-assisted nanotechnology also provides a versatile route for producing hybrid nanostructures [10], where nanoparticles can be synthesized and simultaneously functionalized in situ, enabling direct integration into biomedical, catalytic, and sensing applications.

Within this field, laser-induced plasmas in liquids offer distinctive advantages for nanoparticle fabrication and clustering [11, 12]. The high pressure, rapid quenching rates, and strong confinement at the plasma–liquid interface promote the formation of metastable phases, fine particle size control, and narrow distributions. Additionally, by tuning laser parameters such as pulse duration, beam spot size, wavelength, and focusing conditions, researchers can tailor plasma density, temperature, and lifetime, thus influencing nucleation kinetics and particle morphology [13–16].

A particularly promising approach for controlling plasma characteristics is the use of chirped laser pulses. Chirping as a temporal variation of the instantaneous frequency within an ultrashort pulse, directly modifies the rate and dynamics of energy deposition into the liquid medium [17]. Positive and negative chirps have been shown to influence ionization rates, electron heating, and plasma density, thereby enabling fine control over plasma lifetime and expansion dynamics [17, 18]. While most studies on chirped pulse–plasma interactions have been conducted in gaseous or solid targets, liquid environments present unique opportunities due to their high nonlinear response, efficient ionization, and high damage thresholds compared to solids [15]. In water [17], experiments and simulations show that tuning the input quadratic chirp strongly reshapes nonlinear energy deposition and the plasma distribution near focus: under normal group velocity dispersion, negative pre-chirp drives the pulse closer to transform-limited at the nonlinear focus, increases deposited energy, and

can maximize plasma length and electron density depending on the input duration. These studies used envelope propagation with Kerr and Drude terms and matched experiments by adjusting ionization and collision parameters. In argon clusters [18], nanoplasma modeling indicates a strong chirp sensitivity, ionization ignites earlier for negatively chirped pulses than for unchirped or positively chirped pulses, yet the highest peak electron density occurs for a positively chirped pulse; calculations also report $\approx 20\%$ higher electron energy and larger cluster radius for negative chirp. In gas-phase wakefield acceleration [19], experiments combined with PIC simulations found a positive-chirp preference: a smoother bubble, earlier rear-bubble wavebreaking, and higher electron energies/charge than with transform-limited or negative chirp; differences appear as changes in bubble density distribution, not necessarily higher absolute plasma density for negative chirp.

Because prior liquid-phase studies typically allow peak intensity to co-vary with chirp via duration changes without normalizing it away, causally attributing changes in plasma density to chirp alone remains difficult; in our study we focus explicitly on plasma density and close this gap by (i) enforcing constant spectral width across chirp and (ii) normalizing out intensity, within a two-stage water-jet framework, single-point dynamics and water-only propagation, to quantify the intrinsic chirp effect on plasma density. All metrics, normalizations, and comparisons are defined in terms of electron-density estimates obtained from the Drude relation applied to the simulated current, evaluated across the water jet located at the focal region of focusing lens. The use of liquid jet provides a continuously renewed surface for interaction, eliminates thermal effects, and by tuning chirp parameters, it becomes possible to modulate electron density, plasma frequency, and other plasma properties. Such control can, in turn, influence nanoparticle size distribution, promote selective clustering, and enhance reproducibility in plasma-liquid synthesis processes.

2. Theoretical Background

Theoretical modeling in this work is based on the density matrix formalism [20–23], a well-established analytical framework originally developed in the foundational work [20] for describing the interaction of intense ultrashort, linearly polarized optical pulses with transparent isotropic dielectric media. It is derived under standard assumptions of non-resonant interaction in the transparency window, dominance of the linear polarization over higher-order terms, and a reduced few-state (two- and three-level) density-matrix model that accounts for Kerr, population-induced, and plasma nonlinearities [20]. The model comprises three coupled equations governing the electric field E , plasma current density j , and excited-state population ρ .

$$\begin{cases} \frac{\partial E}{\partial z} - a \frac{\partial^3 E}{\partial \tau^3} + g \frac{\partial E^3}{\partial \tau} + \frac{2\pi}{cn_0} j = 0, \\ \frac{\partial j}{\partial \tau} + \frac{j}{\tau_c} = \beta \rho E^3, \\ \frac{\partial \rho}{\partial \tau} + \frac{\rho}{\tau_p} = \alpha E^2. \end{cases} \quad (1)$$

Here, n_0 and a describe normal dispersion, while g represents the medium's cubic nonlinearity, related to the nonlinear index n_2 via $g = 2n_2/c$. α and β are coefficients quantify respectively the population efficiency of highly excited electronic states and free carrier generation in the medium. τ_c and τ_p are the relaxation times for collisions and excited states. The simulation is performed in a reduced time defined by $\tau = t - zn_0/c$, where z is the propagation axis. In its complete form, the first equation governs the temporal evolution of the radiation field, including the effects of plasma nonlinearities, and full field–plasma feedback. The second equation describes the dynamics of the quasi-free electron current density under the influence of the electric field, while the third governs the population of highly excited electronic states.

In the present work, we omit the first equation (field-propagation equation) from the Eq. system (1) and retain only the carrier–population and current equations because the laser waveform is prescribed as a chirped super-Gaussian (see Eq. (2)). Under this assumption the electric field acts as an external driver rather than a self-consistently evolving variable, allowing to isolate the influence of chirp parameter on electron excitation and current generation without introducing the computational complexity associated with full field–plasma coupling. This driver-only reduction is standard in breakdown modeling of liquids and dielectrics, where plasma dynamics are advanced from a known pulse profile to isolate how waveform parameters (here, chirp) control excitation and current, without the computational overhead and additional confounders of full field–plasma coupling. Representative precedents include rate-equation treatments of water breakdown driven by the laser irradiance [24], first-order multiphoton/avalanche models for ocular/aqueous media [25], and multiple-rate-equation frameworks that evolve carrier populations using a given ultrafast pulse [26], while ultrafast pulse-shaping tutorials justify imposing chirp as a predefined spectral phase.

This work employs a two-stage modeling strategy. Stage I isolates the temporal physics at a single point in space using reduced rate/current equations driven by a prescribed chirped field. Stage II constructs the spatiotemporal field $E(\tau, r, z)$ by linear focusing and dispersive propagation (angular-spectrum method), then applies the same local medium equations point-wise across (r, z) to obtain $\rho(\tau, r, z)$ and $j(\tau, r, z)$. This staged approach cleanly separates the role of chirp in the temporal dynamics from beam-propagation effects before moving to fully self-consistent (envelope/UPPE)

models. The input field is taken as a super-Gaussian order $m = 8$ and a linear frequency chirp implemented via a quadratic temporal phase.

$$E(\tau) = E_0 \exp\left(-\frac{2^{2m-1}}{t_p^{2m}}\tau^{2m}\right) \sin\left(\omega_0\left(\tau + \frac{A}{t_p}\tau^2\right)\right). \quad (2)$$

Where t_p is the pulse duration, ω_0 the carrier frequency, and A dimensionless chirp parameter. Differentiating the phase shows an instantaneous angular frequency $\omega_{inst}(\tau) = \omega_0(1 + 2(A/t_p)\tau)$ a linear chirp with rate $C = 2\omega_0(A/t_p)$. A negative chirp ($A < 0$) places higher frequencies at the leading edge of the pulse and lower frequencies at the trailing edge, whereas a positive chirp ($A > 0$) reverses this order. We use a super-Gaussian envelope to deliberately keep the spectrum balanced, with equal energy on both sides of the pulse. In this way, chirp modifies only spectral phase without altering the energy distribution between the spectral wings as much as possible. The super-Gaussian profile also reduces long-tail artifacts and spectral sidelobes, enabling fair and reproducible comparisons between positive and negative chirp. This approach is standard practice in pulse-shaping studies aimed at isolating phase effects [27, 28].

Implementing chirp inherently alters the spectral width of the pulse. In our model, to ensure a constant bandwidth across different chirp values, the duration of the Fourier-transform-limited (FTL) pulse is adjusted accordingly. However, modifying the pulse duration at fixed pulse energy inevitably changes the peak intensity. To distinguish the intrinsic influence of chirp from the secondary effects caused by intensity variation, the plasma density results were normalized by the corresponding normalized intensity values. This procedure isolates the “chirp-only” contribution to the plasma response.

2.1. Stage I – Single-point, chirp-driven carrier dynamics

To capture the essential plasma build-up without solving the full wave equation, we advance the density ρ of highly excited electrons and the quasi-free electron current density j under the driving field $E(\tau)$ via

$$\frac{\partial \rho}{\partial \tau} = \alpha E^2 - \frac{\rho}{\tau_p}, \quad \frac{\partial j}{\partial \tau} = \beta \rho E^3 - \frac{j}{\tau_c}. \quad (3)$$

Within the Drude picture, the macroscopic current density j is related to the free electron density n_e and the drift velocity $\mathbf{v}_d$ via Eq. (4) [29]:

$$\mathbf{J}(\tau) = -en_e(\tau)\mathbf{v}_d(\tau) = \sigma\mathbf{E}(\tau), \quad \mu = \frac{e\tau_c}{m_e}, \quad \mathbf{v}_d = \mu\mathbf{E}, \quad (4)$$

where e is the elementary charge, σ the conductivity of the medium with μ being the electron mobility and m_e is the electron mass. Combining these expressions yields an instantaneous estimate for the free electron density as:

$$n_e(\tau) = \frac{|J(\tau)|}{e|\mu E(\tau)|}, \quad (5)$$

which directly links the simulated current density from the model to the plasma density through the Drude model and Boltzmann transport framework. Because the rates scale as E^2 and E^3 , the quadratic phase shifts the timing between the envelope peak and carrier phase, which modifies how ρ builds before momentum relaxes on τ_c . The single-point model thus isolates purely temporal chirp effects on excitation and current without beam propagation.

3. Stage II – Adding space and propagation in water

To obtain the spatiotemporal driving $E(\tau, r, z)$, we apply Fourier-optical propagation. A thin lens imposes the familiar quadratic phase $\exp[i\omega r^2/(2cF)]$ of frequency-dependent curvature. We consider a liquid water jet of $150 \mu\text{m}$ thickness, positioned at the focal plane of a 20 cm focusing lens. Since plasma formation is confined to the focal region, thus, only the jet itself is included in the numerical simulation, while the air path before and after the jet is treated analytically. Specifically, the spot size, wavefront curvature, and temporal intensity profile of the pulse at the entrance surface of the water jet are obtained from the standard Gaussian beam propagation formulas [30]. These parameters define the initial input field for the propagation inside the liquid. In this way, the simulation focuses on the medium where plasma dynamics occur, while the surrounding air regions are reduced to their optical boundary conditions. This ensures both computational efficiency and physical accuracy in describing plasma evolution within the water jet. To study plasma formation across the jet thickness, propagation over a distance $\Delta z = 150 \mu\text{m}$ is carried out in the spatio-temporal frequency domain by multiplying every (k_r, ω) component by the angular-spectrum propagator:

$$H(k_r, \omega) = \exp[-ik_z(\omega, k_r)\Delta z], \quad k_z = \sqrt{\left(n(\omega)\frac{\omega}{c}\right)^2 - k_r^2}, \quad (6)$$

where $n(\omega)$ reverse to the refractive index of the medium k_r is the radial spatial frequency, and c is the speed of light. Evanescent components (when $k_r > n\omega/c$) are naturally attenuated by the propagator. This formulation is standard in Computational Fourier Optics. At each propagation step z , the computed field $E(\tau, r; z)$ drives the same local ODEs (1) at each radius r , yielding $\rho(\tau, r; z)$ and $j(\tau, r; z)$. Then maps current to plasma density by the Drude relation mentioned before. Chirp is still introduced only via the quadratic temporal phase of the input field. Within propagation, that phase

translates into a different temporal ordering of frequencies along z , thereby altering the instantaneous plasma intensity and its overlap with the relaxation dynamics governed by τ_c and τ_p across the beam.

The present model does not feed the evolving ρ, j back into the field E through a refractive index change at each step; it prescribes $E(\tau, r; z)$ from linear optics and then advances the medium locally. This deliberate simplification allows us to isolate the role of chirp before introducing self-consistent propagation models such as the unidirectional pulse propagation equation (UPPE). Nonlinear contributions, including Kerr self-focusing, plasma defocusing, and the magnetic term in the Drude response, are neglected because their effect on plasma density is minimal under the studied conditions [29, 31]. For example, at $I \sim 10^{13}$ W/cm² and $\lambda = 800$ nm, the electron quiver velocity give $v_d/c = 2 \times 10^{-3}$, confirming that magnetic forces are less than one percent of the electric force [32]. Similarly, Kerr and plasma nonlinearities primarily shorten the effective focal position through self-focusing or refocusing, while ponderomotive forces only redistribute already-generated electrons. Since plasma formation within the 150 μ m water jet is governed almost entirely by ionization at the local intensity, neglecting these effects does not alter the calculated electron density, aside from a small focal shift.

4. Results

The equation system is integrated with an explicit Runge–Kutta–Fehlberg method (ode45) on a femtosecond grid, adequate for the non-stiff dynamics here. The complete set of physical constants and pump parameters employed in the simulations is listed in Table 1.

TABLE 1. The complete set of physical constants and pump parameters used in the simulation

Pump parameters	
Laser wavelength, λ	80 nm
Pulse energy, E_{pulse}	300 μ J
Focal length of the focusing lens, F	20 cm
Beam spot diameter before the focusing lens	2 mm
Beam spot diameter at the focusing position r	$\sim 102 \mu$ m
Physical parameters	
τ_c (fs)	~ 1 [22]
τ_p (fs)	150 [22]
α (SI)	7.1687e+19 [20,22]
β (SI)	2.8879e+12 [20,22]

Introducing a linear frequency chirp to a FTL pulse modifies its spectral width, even if the temporal envelope shape is preserved. To perform chirp-dependent comparisons at constant bandwidth, we empirically adjusted the chirped pulse duration for each chirp rate until the resulting chirped pulse spectral width reproduced the one of the FTL pulse. The adjustment was carried out by comparing numerically computed spectra (via FFT) of the FTL and chirped pulses and iteratively modifying the chirped pulse duration until the full width at half maximum (FWHM) bandwidths matched within the numerical resolution. This direct spectral matching accounts for discretization, windowing, and the super-Gaussian envelope used in our model, which can cause small deviations from ideal analytic time–bandwidth scaling. Thus, we used chirp magnitudes from $|A| = 5 \times 10^{-4}$ to 2×10^{-2} , for FTL pulse widths of 20, 40, 60, and 80 fs. After bandwidth matching, the corresponding chirped FWHM durations at the largest $|A| = 0.02$ were 20.19 fs (from 20 fs), 40.95 fs (from 40 fs), 63.45 fs (from 60 fs), and 89.49 fs (from 80 fs). This procedure ensures that, in the single-point case, any change in plasma formation reflects only the imposed chirp and the deliberately adjusted pulse duration, and, in the propagation case, the same effects with material dispersion, rather than to inadvertent differences in spectral width.

Since changing pulse duration affects the peak intensity (for fixed beam area, $I_{peak} \propto E_{pulse}/t_p$), in our simulation, we adjust the pulse duration at fixed pulse energy and isolate the chirp-only contribution to plasma density as Eq. (7) represents, by dividing the normalized plasma density by the normalized pump intensity at each chirp value

$$N_{only \text{ chirp}} = \frac{N/N_0}{I/I_0}. \quad (7)$$

4.1. Results of Stage I – Single-point, chirp-driven carrier dynamics

Fig. 1 illustrates how the plasma electron density depends on chirp rate for different time durations of FTL pulses. In Fig. 1a, the overall trend of the normalized plasma density is decreasing as the chirp magnitude increases, independent of

whether the chirp is positive or negative. This reduction originates from the temporal stretching of the pulse: introducing chirp redistributes the spectral content of the pulse over a longer duration, lowering the peak intensity available to drive ionization.

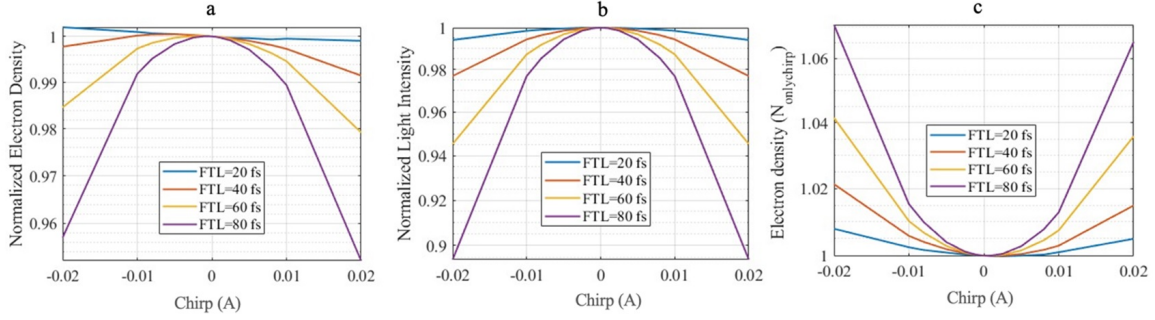


FIG. 1. a) Normalized plasma electron density of different FTL pulse durations at different chirp rates, b) light intensity of different FTL pulses, considering the chirped FWHM durations for different chirp rates, c) the isolated effect of introducing chirp on plasma electron density.

The corresponding normalized light intensities, adjusted to maintain a fixed spectral bandwidth, are shown in Fig. 1b. To separate the intrinsic effect of chirp from this intensity reduction, Fig. 1c presents the ratio of plasma density to normalized intensity $N_{\text{only chirp}}$, effectively isolating the “chirp-only” contribution. This analysis reveals that chirp has two competing influences on plasma generation. On one hand, pulse stretching lowers the peak intensity and thus reduces ionization efficiency. On the other hand, chirp alters the temporal frequency distribution within the pulse. For negative chirp, higher frequency components arrive earlier in time and coincide with higher instantaneous intensities on the leading edge of the pulse. This condition seeds ionization earlier and promotes stronger avalanche growth of free electrons. By contrast, positive chirp delays the arrival of higher frequency components until the trailing edge, where much of the available intensity has already been depleted, resulting in weaker plasma formation. The outcome is an overall asymmetry: negative chirp produces higher electron densities than positive chirp of the same magnitude. To highlight this effect, Fig. 2 provides a magnified view of the negative chirp region from Fig. 1a. At small negative chirp values, the normalized plasma density slightly exceeds unity, meaning that plasma formation is actually enhanced compared to the transform-limited case. This indicates that in this regime, the chirp-induced temporal ordering of frequencies enhances ionization more strongly than the intensity reduction suppresses it. Our finding matches water experiments and simulations that chirp sign matters, and suitable negative chirp reduces transmission and increases plasma density and deposited energy [17,33]. At larger chirp values, however, pulse stretching dominates and the plasma density falls below the baseline. As a result, chirp modifies plasma formation through a balance of pulse stretching (which suppresses ionization) and temporal frequency ordering (which can enhance it). Negative chirp is particularly effective because it aligns the high frequencies followed with the highest intensities at the leading part of the pulse.

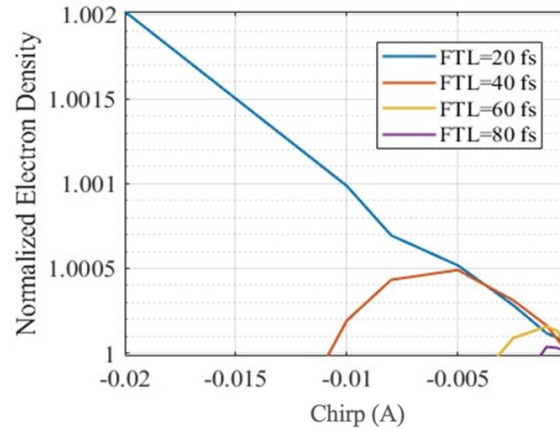


FIG. 2. Magnified view of the negative chirp region from Fig. 1a, showing normalized plasma electron density for different FTL pulses at various chirp rates.

4.2. Results of Stage II – Adding space and propagation in water

Using the same normalization procedure in Stage I (Fig. 1c), Fig. 3a. reports the chirp-only plasma response $N_{only\ chirp}$ resulting from the propagated field $E(\tau, r; z)$ in water. The curves in Fig. 3a. show chirp-only contribution for four FTL durations (20, 40, 60, 80 fs). It can be seen that all curves peak at chirp $A = 0$ and decrease as $|A|$ grows, for a given $|A|$ negative chirp exceeds positive chirp where left branch lies above right and the 80 fs FTL curve falls off most steeply the suppression is progressively weaker for 60 fs, 40 fs, then 20 fs.

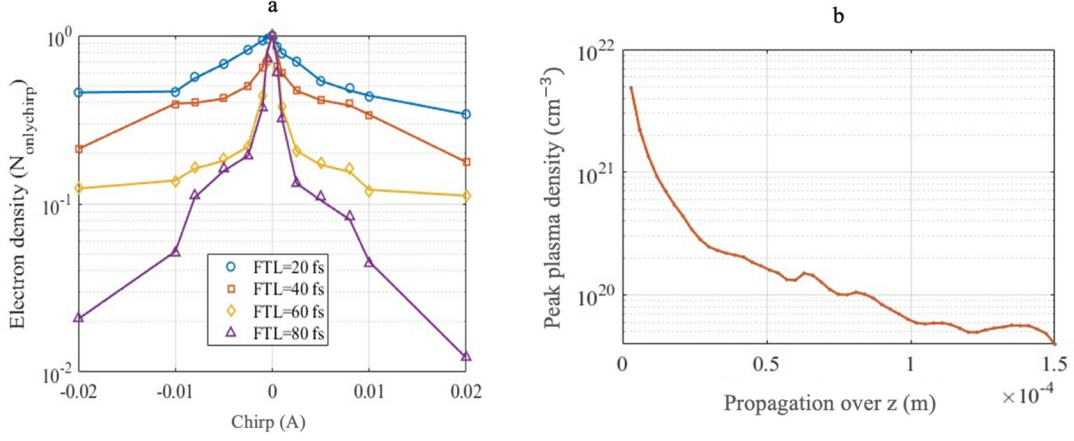


FIG. 3. a) Plasma electron density under the isolated effect of chirp for several FTL durations in case of propagated field $E(\tau, r, z)$ in water. b) Calculated peak plasma density per slice from the propagated field $E(\tau, r, z)$ in water as a function of propagation distance z , FTL duration of 20 fs with no chirp applied.

Unlike single point results in stage I, $N_{only\ chirp}$ values in Fig. 3a. fall below unity because of several factors. First our intensity normalization equalizes input bandwidth and peak power but does not fully account for the additional pulse stretching that occurs during propagation in water, where the group-velocity dispersion at 800 nm is positive and measured as $\beta_2 \approx 24.8\text{--}25.7 \text{ fs}^2 \text{ mm}^{-1}$ [34], adding a group delay dispersion of $\Phi_2 = \beta_2 z \approx 3.7\text{--}3.9 \text{ fs}^2$, the corresponding dimensionless chirp is $C_{disp} = 4 \ln(2\Phi_2)/t_d^2$ hence the chirp added by propagation over z is $A_{disp} = C_{disp} t_p / 2\omega_0$ which gives $A_{disp} \approx 0.1104(20 \text{ fs})$, $0.0552(40 \text{ fs})$, $0.0368(60 \text{ fs})$ and $0.0276(80 \text{ fs})$. These values exceed the largest applied $|A|$ in our simulation (± 0.02). Thus, a pulse that initially carries negative chirp becomes unchirped after a compensation distance z and then acquires positive chirp for the rest of its propagation. In contrast, a pulse that begins with positive chirp gains a further increasing chirp during propagation. The associated pulse duration broadening lowers the local peak intensity across the focal region. Beyond this amplitude mechanism, dispersion also alters temporal ordering of the field while propagation, so the overlap of the medium's response (ρ and the ρE^3 drive that builds plasma) drops faster than an E^2 based intensity measure, further reducing the normalized plasma yield [35]. This effect can be seen in Fig. 3b which represents peak plasma density over the propagation distance on z with no chirp applied. The resent factors pushes $N_{only\ chirp} < 1$ even before phase-timing effects are considered [34]. Moreover, angular-spectrum propagation couples space and time since $k_z(k_r, \omega)$ varies with both frequency and transverse spatial frequency, as a result, different spectral and radial components accrue different delays and diffraction, desynchronizing on-axis and off-axis contributions [36]. Consistent with prior water studies, negative chirp still performs better than positive at equal $|A|$, but once propagation-induced dispersion and these overlap effects are included then the net chirp-only whether negative or positive response is suppressive.

5. Conclusion

We presented a two-stage, spectral bandwidth-controlled and intensity-normalized analysis of how linear chirp governs plasma generation in a water jet. In Stage I (single-point), intensity-normalized analysis revealed a genuine chirp-only enhancement of plasma yield, with a persistent advantage for negative over positive chirp. In Stage II (propagation in water), the trend reverses once dispersion is included: normal GVD in water at 800 nm adds positive quadratic phase that stretches the pulse and degrades the timing between the field and the medium's response, so the plasma-per-intensity ratio drops below unity, yet negative chirp remains less detrimental than positive, and the suppression is strongest for longer FTL pulses. Our simulation further shows that the dispersion-induced chirp exceeds the largest applied chirp, so a pulse starting with negative chirp is quickly compensated, becomes unchirped, and then turns positive, this observation is important for experimental conditions, since commonly used media exhibit positive dispersion, and even a small thickness of $150 \mu\text{m}$ is sufficient to cancel an initially negative chirp during the propagation. This study directly addresses common limitations in prior liquid-phase studies by holding bandwidth fixed across chirp scans and explicitly normalizing

out intensity, thereby exposing the genuine effect of chirp on plasma density, independent of bandwidth and intensity. Looking ahead, the approach provides specific, testable predictions and a clean baseline for experiments, as well as a natural springboard to self-consistent propagation models to quantify chirp–dispersion balance under realistic focusing conditions. The findings provide new insight into the active control of plasma–liquid interactions and their implications for tailored nanoparticle synthesis and clustering in advanced nanotechnology applications.

References

- [1] Horikoshi S., Serpone N. In-liquid plasma: a novel tool in the fabrication of nanomaterials and in the treatment of wastewaters. *RSC Adv.*, 2017, **7**(75), P. 47196–47218.
- [2] Patel J. A Commentary on the Plasma-Liquid Interactions. *Russian Journal of Physical Chemistry B.*, 2024, **18**(5), P. 1301–8.
- [3] Mariotti D., Patel J., Švrček V., Maguire P. Plasma-liquid interactions at atmospheric pressure for nanomaterials synthesis and surface engineering. *Plasma Processes and Polymers.*, 2012, **9**(11–12), P. 1074–85.
- [4] Nie L., Yang Y., Duan J., Sun F., Lu X., He G. Effect of tissue thickness and liquid composition on the penetration of long-lifetime reactive oxygen and nitrogen species (RONS) generated by a plasma jet. *J. Phys. D: Appl. Phys.*, 2018, **51**(34), P. 345204.
- [5] Khlyustova A., Labay C., Machala Z., Ginebra M.P., Canal C. Important parameters in plasma jets for the production of RONS in liquids for plasma medicine: A brief review. *Front. Chem. Sci. Eng.*, 2019, **13**(2), P. 238–252.
- [6] Chauvin J., Judée F., Yousfi M., Vicendo P., Merbahi N. Analysis of reactive oxygen and nitrogen species generated in three liquid media by low temperature helium plasma jet. *Sci. Rep.*, 2017, **7**(1), P. 4562.
- [7] Skiba M., Khrokal L., Linyuchev A., Vorobyova V. State of the art on plasma-liquid route synthesis monometallic Au, bimetallic Au/Ag core-shell and alloy nanoparticles: Toxicological, analytical, antimicrobial activity for environmental control. *J. Mol. Struct.*, 2024, **1318**, P. 139293.
- [8] Shah K., Patel J., Kumar S., Pandey R., Maity G., Dubey S. Perspectives on sustainable and efficient routes of nanoparticle synthesis: an exhaustive review on conventional and microplasma-assisted techniques. *Nanoscale*, 2024, **16**(44), P. 20374–20404.
- [9] Khodadadi A.A., Mortazavi Y. and Vesali-Naseh M. Fast and clean dielectric barrier discharge plasma functionalization of carbon nanotubes decorated by electrodeposited nickel oxide: Application to glucose biosensors. *Scientia Iranica*, 2019, **26**(6), P. 3896–3904.
- [10] Cvelbar U., Santhosh N.M. (Invited) Plasma-Assisted Synthesis of Advanced Carbon Nanostructures for Batteries and Supercapacitors. *ECS Meet. Abstr.*, 2022, MA2022-01(7), P. 621.
- [11] Novotný K., Kreml I., Afonin I., Prokeš L., Vaňhara P., Havel J. Laser-induced plasma spectroscopy in pulsed laser ablation synthesis of nanoparticles in liquid. *Talanta*, 2025, **290**, P. 127767.
- [12] Burakov V.S., Butsen A.V., Tarasenko N.V. Laser-induced plasmas in liquids for nanoparticle synthesis. *J. Appl. Spectrosc.*, 2010, **77**(3), P. 386–393.
- [13] Ponomareva E.A., Ismagilov A.O., Putilin S.E., Tsyarkin A.N., Kozlov S.A., Zhang X.-C. Varying pre-plasma properties to boost terahertz wave generation in liquids. *Commun. Phys.*, 2021, **4**(1), P. 4.
- [14] Hilal S., Ismagilov A., Tsyarkin A., Melnik M. Insights from Keldysh theory to plasma electron density in liquid water under excitation wavelength scaling. *J. Sci. Tech. Inf. Technol. Mech. Opt.*, 2024, **155**(3), P. 399.
- [15] Hilal S., Melnik M., Ismagilov A., Tsyarkin A., Kozlov S. Determination of plasma properties in liquid jets through time-resolved experiments on third harmonic reflection dynamics. *Opt. Lett.*, 2024, **49**(11), P. 2990–2993.
- [16] Ponomareva E., Ismagilov A., Putilin S., Tsyarkin A. N. Plasma reflectivity behavior under strong subpicosecond excitation of liquids. *APL Photonics*, 2021, **6**(12), P. 126101.
- [17] Milián C., Jarnac A., Brelet Y., Jukna V., Houard A., Mysyrowicz A., et al. Effect of input pulse chirp on nonlinear energy deposition and plasma excitation in water. *JOSA B*, 2014, **31**(11), P. 2829–2837.
- [18] Ghaforyan H., Sadighi-Bonabi R. and Irani E. The effect of chirped intense femtosecond laser pulses on the Argon cluster. *Advances in High Energy Physics*, 2016, **2016**(1), P. 2609160.
- [19] Grigoriadis A., Andrianaki G., Tazes I., Dimitriou V., Tatarakis M., Benis E.P. and Papadogiannis N.A. Efficient plasma electron accelerator driven by linearly chirped multi-10-TW laser pulses. *Scientific Reports*, 2023, **13**(1), P. 2918.
- [20] Stumpf S.A., Korolev A.A., Kozlov S.A. Few-cycle strong light field dynamics in dielectric media. *Proceedings of SPIE*, 2007, **6614**, P. 59–70.
- [21] Ponomareva E.A., Ismagilov A.O., Putilin S.E., Tsyarkin A.N., Kozlov S.A., Zhang X.-C. Varying pre-plasma properties to boost terahertz wave generation in liquids. *Commun. Phys.*, 2021, **4**(1), P. 4.
- [22] Stumpf S., Ponomareva E., Tsyarkin A., Putilin S., Korolev A., Kozlov S. Temporal field and frequency spectrum of intense femtosecond radiation dynamics in the process of plasma formation in a dielectric medium. *Laser Phys.*, 2019, **29**(12), P. 124014.
- [23] Ponomareva E.A., Tsyarkin A.N., Putilin S.E., Stumpf S., Korolev A.A., Kozlov S.A. Double-pump technique – one step closer towards efficient liquid-based THz sources. *Opt. Express*, 2019, **27**(22), P. 32855–32862.
- [24] Noack J., Vogel A. Laser-induced plasma formation in water at nanosecond to femtosecond time scales: calculation of thresholds, absorption coefficients, and energy density. *IEEE J. Quantum Electron.*, 1999, **35**(8), P. 1156–1167.
- [25] Kennedy P.K., Boppart S.A., Hammer D.X., Rockwell B.A., Noojin G.D., Roach W.P. First-order model for computation of laser-induced breakdown thresholds in condensed media. *Proceedings of SPIE 2391*, 1995, P. 48–59.
- [26] Rethfeld B. Free-electron generation in laser-irradiated dielectrics. *Phys. Rev. B*, 2006, **73**(3), P. 035101.
- [27] Fallah R., Khorashadizadeh S. M. Influence of Gaussian, Super-Gaussian, and Cosine-Gaussian Pulse Properties on the Electron Acceleration in a Homogeneous Plasma. *IEEE Trans. Plasma Sci.*, 2018, **46**(6), P. 2085–2090.
- [28] Gong J., Liu B., Kim Y. L., Liu Y., Li X., Backman V. Optimal spectral reshaping for resolution improvement in optical coherence tomography. *Opt. Express*, 2006, **14**(13), P. 5909–5915.
- [29] Liu J., Brio M., Zeng Y., Zakharian A. R., Hoyer W., Koch S. W., et al. Generalization of the FDTD algorithm for simulations of hydrodynamic nonlinear Drude model. *J. Comput. Phys.*, 2010, **229**(17), P. 5921–5932.
- [30] Laues P. Geometrical Approach to Gaussian Beam Propagation. *Appl. Opt.*, 1967, **6**(4), P. 747–755.
- [31] Couairon A., Mysyrowicz A. Femtosecond filamentation in transparent media. *Phys. Rep.*, 2007, **441**(2), P. 47–189.
- [32] Lahiri S., Bhore T., Das K., Agarwal A. Nonlinear magnetoresistivity in two-dimensional systems induced by Berry curvature. *Phys. Rev. B*, 2022, **105**(4), P. 045421.
- [33] Stumpf S., Ponomareva E., Tsyarkin A., Putilin S., Korolev A., Kozlov S. Temporal field and frequency spectrum of intense femtosecond radiation dynamics in the process of plasma formation in a dielectric medium. *Laser Phys.*, 2019, **29**(12), P. 124014.

- [34] Stumpf S.A., Korolev A.A., Kozlov S.A. Few-cycle strong light field dynamics in dielectric media. *Laser Optics 2006: Superintense Light Fields and Ultrafast Processes. SPIE*, 2007, P. 59–70.
- [35] Chen S., Cong X., Chen J., Zang H., Li H., Xu H. Sensing Trace-Level Metal Elements in Water Using Chirped Femtosecond Laser Pulses in the Filamentation Regime. *Sensors*, 2022, **22**(22), P. 8775.
- [36] Coello Y., Xu B., Miller T.L., Lozovoy V.V., Dantus M. Group-velocity dispersion measurements of water, seawater, and ocular components using multiphoton intrapulse interference phase scan. *Appl. Opt.*, 2007, **46**(35), P. 8394–8401.
- [37] Weiner A.M. Ultrafast optical pulse shaping: A tutorial review. *Opt. Commun.*, 2011, **284**(15), P. 3669–3692.
- [38] Akturk S., Gu X., Bowlan P., Trebino R. Spatio-temporal couplings in ultrashort laser pulses. *J. Opt.*, 2010, **12**(9), P. 093001.

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Spin wave propagation in a cross-shaped microwave guides made of yttrium iron garnet film with magnetic cylinders

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ABSTRACT This study explores the application of spin waves for developing functional components for information processing, transmission, and storage within the microwave and terahertz frequency regimes. The platform is based on yttrium iron garnet thin films, with spin wave manipulation achieved via two-dimensional arrays of magnetite cylinders. A numerical micromagnetic analysis of a cross-shaped waveguide was conducted by solving the Landau-Lifshitz-Gilbert equation, examining the dependence of wave properties on the orientation of the external magnetic field. The findings indicate a viable pathway toward the realization of compact and energy-efficient magnonic devices.

KEYWORDS numerical micromagnetic modeling, yttrium iron garnet, magnetic cylinders, spin wave.

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1. Introduction

Magnonics [1] is a rapidly evolving field of modern physics and nanotechnology that studies the transfer of magnetic moment or electron spin as an alternative to conventional charge transfer. This discipline opens new possibilities for creating information processing, transmission, and storage devices in the microwave and terahertz ranges [2, 3]. In such devices, the information signal is encoded in the phase or amplitude of a spin wave (SW), and logical operations are implemented based on the principles of spin-wave interference [2]. Spin waves represent collective oscillations of magnetic moment orientations in magnetically ordered materials, which can be used to encode information through phase modulation.

One of the key materials for creating magnetic waveguiding structures is yttrium iron garnet (YIG), which exhibits record-low spin wave damping even at nanoscale thicknesses [1].

Control of spin waves is one of the key challenges in magnonics. One approach to solving it involves the use of two-dimensional arrays of magnetic nanostructures, particularly magnetite cylinders, which are responsible for the modification of SW dispersion characteristics and the control of their propagation. In our previous studies, we investigated rectangular YIG waveguides functionalized with magnetite of varying geometry [4–6]. These works demonstrated effective manipulation of spin-wave transmission, but were limited to single-channel geometries with only one output port, thereby restricting the ability to control the spatial distribution of the signal.

This work presents a numerical micromagnetic simulation of a cross-shaped YIG waveguide with a two-dimensional array of magnetite cylinders, featuring three output ports ($P_{out,1,2,3}$). We demonstrate that changing the direction of the external magnetic field along or opposite to the OY axis not only modulates the amplitude of the transmitted signal but also redistributes the spin-wave energy among the output channels. This directional control, enabled by the inhomogeneous internal magnetic field induced by the magnetite array, opens new pathways toward the realization of compact, multiport, and energy-efficient magnonic devices capable of spatial signal routing.

2. Method

The considered structure is a cross-shaped waveguide with an array of cylinders on its surface (see Fig. 1). The microwave waveguide is made from a YIG film ($Y_3Fe_5O_{12}$) with a length of $L = 4$ mm, a width of $W = 500$ μm , and a thickness of 10 μm . The cylinders were made of magnetite (Fe_3O_4), each with a diameter and height of 10 μm . The array of cylinders was positioned in a 500 $\mu m \times 500$ μm area located at the center of the structure. The distance between the centers of the cylinders, both vertically and horizontally, was $d = 10$ μm . This area contained an array of 25×25 cylinders (number along OX $\times$ OY). The ends of the structure feature exciting and receiving antennas, labeled P_{in} and $P_{out,1}$, $P_{out,2}$, $P_{out,3}$, respectively. The antennas have dimensions of 30 $\mu m \times 500$ μm .

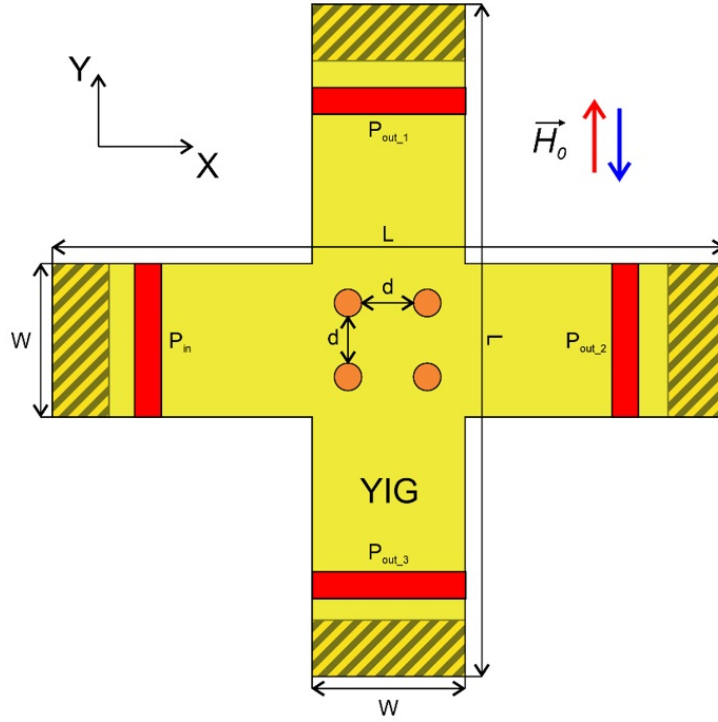


FIG. 1. Schematic illustration of the cross-shaped structure with an array of magnetite cylinders

Using micromagnetic modeling based on solving the Landau-Lifshitz-Gilbert (LLG) equation [7], a study of spin wave propagation modes in the structure (see Fig. 1) was conducted. The LLG equation can be represented as:

$$\frac{\partial \mathbf{M}}{\partial t} = \gamma [\mathbf{H}_{eff} \times \mathbf{M}] + \frac{\alpha}{M_0} \left[\mathbf{M} \times \frac{\partial \mathbf{M}}{\partial t} \right]. \quad (1)$$

Here $\mathbf{M}$ is the magnetization vector, α is the damping parameter, $\mathbf{H}_{eff} = \mathbf{H}_0 + \mathbf{H}_{demag} + \mathbf{H}_{ex}$ is the effective magnetic field, $\mathbf{H}_0$ is the external magnetic field, $\mathbf{H}_{demag}$ is the demagnetization field, $\mathbf{H}_{ex}$ is the exchange field, and $\gamma = 2.8 \text{ MHz/Oe}$ is the gyromagnetic ratio.

The damping parameters for the YIG film and magnetite are 5×10^{-4} and 2×10^{-2} , respectively. The exchange constant in the YIG film is $A_{ex1} = 3.612 \text{ pJ/m}$, and in magnetite, it is $A_{ex2} = 1.210 \text{ pJ/m}$. The saturation magnetizations of YIG and magnetite are $4\pi M_{YIG} = 1750 \text{ G}$ and $4\pi M_{Mag} = 6000 \text{ G}$, respectively. The structure was placed in a uniform static magnetic field of $H_0 = 1200 \text{ Oe}$. Cases involving the excitation of surface magnetostatic waves (SMW) were considered. In these cases, the external magnetic field $\mathbf{H}_0$ was applied along and opposite direction of the OY axis.

In the numerical simulation impulse excitation were used. For impulse excitation of SWs, a magnetic field $h_z(t) = h_0 \sin c(2\pi f_m t)$ was applied to the YIG film in the region of the input antenna P_{in} , where the central frequency $f_m = 6 \text{ GHz}$, $h_0 = 0.001 \text{ Oe}$. The value of the dynamic magnetization $M_z(x, y, t)$ was recorded in the regions of the receiving antennas $P_{out,1}$, $P_{out,2}$, $P_{out,3}$ with a time step of $\Delta t = 20 \text{ ps}$ over a period of $T = 300 \text{ ns}$, which is sufficient to reach a steady state. The mesh cell size was $2 \times 2 \times 2 \text{ } \mu\text{m}^3$. The values of $m_z(x, y, t)$ were calculated for all cells using the formula $m_z(x, y, t) = M_z(x, y, t) - M_z(x, y, 0)$, where $M_z(x, y, 0)$ corresponds to the ferromagnetic state. To reduce spin wave reflections from the boundaries of the computational domain, absorbing layers with a geometrically increasing damping coefficient α were introduced (hatched areas in Fig. 1) [8, 9]. This approach was used to create time dependencies of the magnetization $m_z(x, y, t)$, which were then analyzed using the Fast Fourier Transform [10] to obtain amplitude-frequency characteristics (AFC).

3. Results and discussion

The internal demagnetization fields in the structure were calculated for different directions of $\mathbf{H}_0$. Fig. 2 shows the distribution of the internal field in the YIG film with magnetite. It can be observed that the magnetite introduces inhomogeneity into the internal field of the YIG film.

To obtain information about what happened to the wave after interacting with the magnetite array, the spectral power density of the spin wave signal was calculated. Fig. 3 shows the AFC for the structure when varying the direction of the external magnetic field. The blue/red line corresponds to the external magnetic field directed along/opposite OY direction. The dark blue/brown line corresponds to the AFC for the YIG film without magnetite with $\mathbf{H}_0$ oriented along/opposite OY direction. The dark blue and brown curves in the passband region are qualitatively the same, which is why the dark

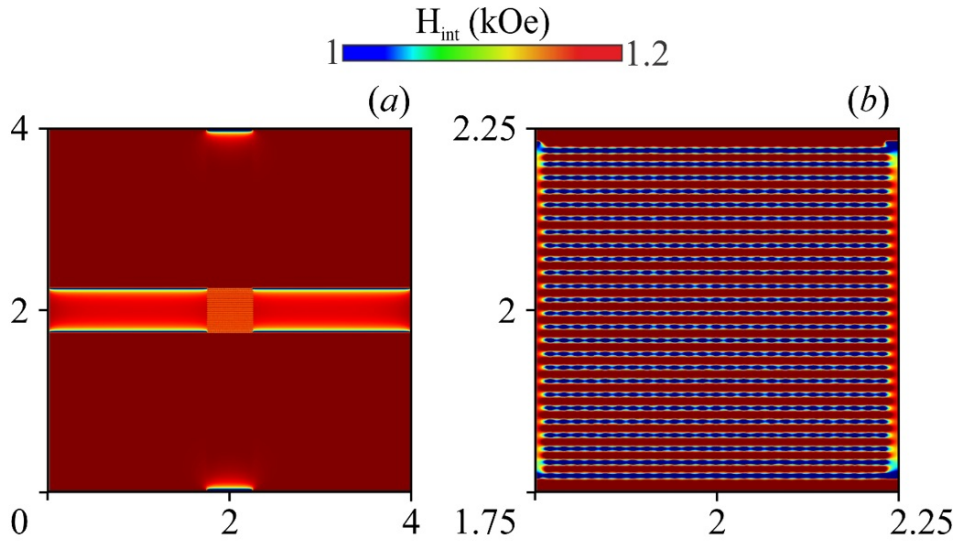


FIG. 2. A map of the internal magnetic field (H_{int}) distribution in the cross-shaped structure with an array of magnetite cylinders (a). A map of the H_{int} distribution, taken in the region where the array of magnetite cylinders is located (b)

blue curve is not visible in the AFC. Fig. 3a is plotted from data from antenna $P_{out,1}$, Fig. 3b from antenna $P_{out,2}$, and Fig. 3c from antenna $P_{out,3}$.

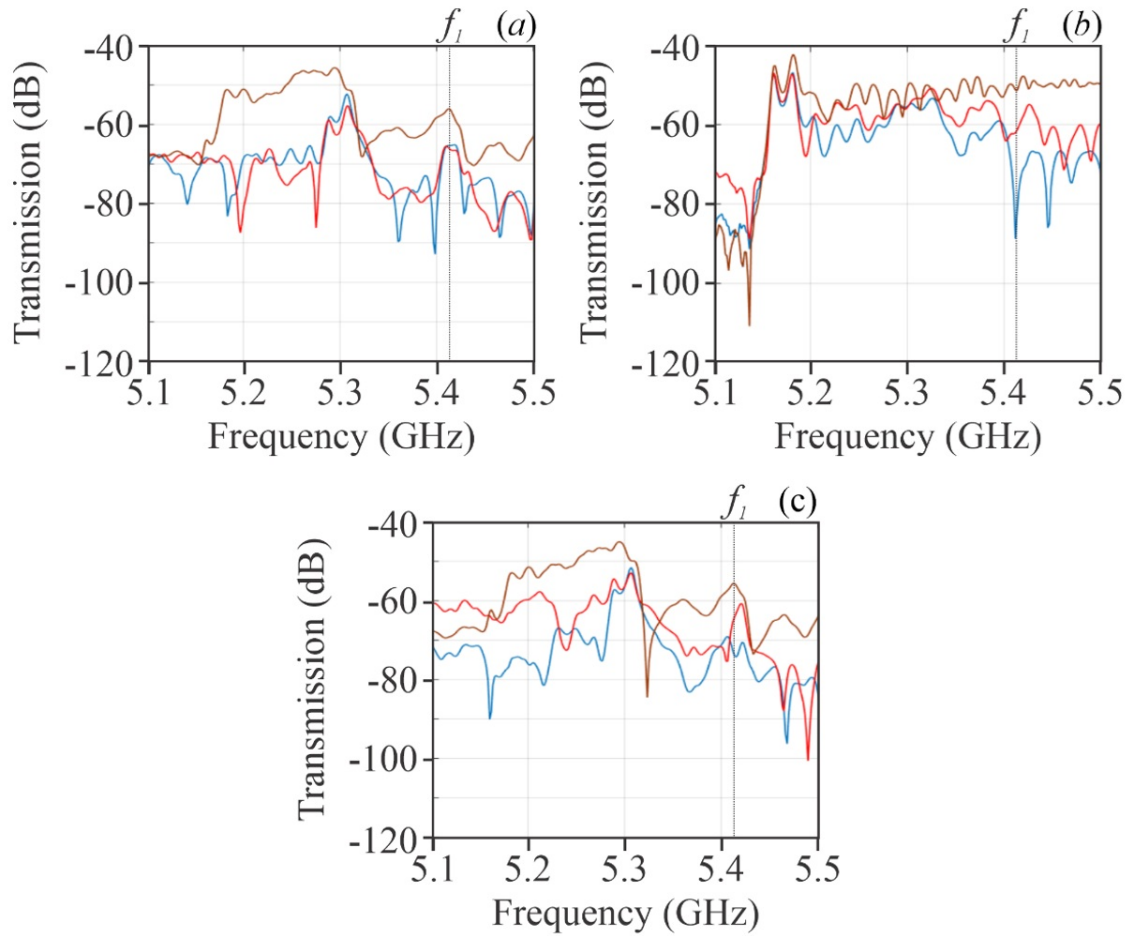


FIG. 3. Amplitude-frequency characteristics obtained for the output ports $P_{out,1}$ (a), $P_{out,2}$ (b), and port $P_{out,3}$ (c)

The AFCs show that depositing magnetite onto the YIG film results in signal degradation regardless of whether the external magnetic field $\mathbf{H}_0$ is applied along or opposite to the OY axis. When changing the direction of $\mathbf{H}_0$, a specific frequency $f_1 = 5.415$ GHz can be identified (see Fig. 3b). The AFCs show that depositing magnetite onto the YIG film results in signal degradation regardless of whether the external magnetic field H_0 is applied along or opposite to the OY axis. When changing the direction of $\mathbf{H}_0$, a specific frequency $f_1 = 5.415$ GHz can be identified (see Fig. 3b). At this frequency, the transmission characteristics differ significantly depending on the field orientation. For an external field direction opposite to the OY axis (blue curve), a deep dip is observed at port $P_{out.2}$ with a minimum transmission value of approximately -93 dB. For an external field direction along the OY axis (red curve), a significantly weaker dip is observed at the same port, with a minimum transmission value of approximately -62 dB. This means that the difference in signal amplitude between the two states at port $P_{out.2}$ is approximately 31 dB, which corresponds to a power ratio of roughly 1.3×10^3 .

Furthermore, this directional dependence is not limited to the main output port ($P_{out.2}$). At the same frequency f_1 in the upper port $P_{out.1}$ (see Fig. 3a), the minimum transmission values are approximately -65 dB for $\mathbf{H}_0$ opposite to OY and -67 dB for $\mathbf{H}_0$ along OY, indicating a smaller but still observable difference (~ 2 dB). In the lower port $P_{out.3}$ (see Fig. 3c), the minimum transmission values are approximately -65 dB for $\mathbf{H}_0$ opposite to OY and -74 dB for $\mathbf{H}_0$ along OY, showing a more pronounced difference of ~ 9 dB.

This spatially non-uniform response across the three output ports demonstrates that the reversal of the external magnetic field does not merely attenuate the signal, but actively redirects and redistributes the energy flow of the spin wave within the cross-shaped structure. The strongest control effect is observed along the primary axis of propagation (port $P_{out.2}$), while the transverse ports ($P_{out.1}$ and $P_{out.3}$) exhibit a more complex, asymmetric response, likely due to interference and mode conversion effects induced by the magnetite array's inhomogeneous demagnetizing field. The observed effects are caused by the emergence of local inhomogeneities in the internal magnetic field within the YIG film, induced by the presence of the magnetite. The magnetite creates a spatially non-uniform demagnetizing field, which disrupts the magnetization uniformity in the structure and leads to the overall signal degradation.

4. Conclusion

This article investigates the control of spin wave propagation in a cross-shaped YIG microwave waveguide with a two-dimensional array of magnetite cylinders on its surface. Numerical micromagnetic modeling demonstrated the possibility of altering spin wave characteristics by varying the orientation of the external magnetic field. It was established that the direction of the external magnetic field influences the amplitude-frequency characteristics.

The results show that changing external conditions allows for the control of spin wave parameters, opening new possibilities for creating highly efficient magnonic devices. An important aspect of this research is the technical feasibility of such structures, enabled by modern micro- and nanolithography methods. Furthermore, magnetite, used as the material for the cylinders, possesses unique magnetic properties and a broad range of applications in biomedicine [11–14] and sensor technologies [15, 16]. Its biocompatibility [17] and capacity for functionalization [12] make this material promising for developing sensors and devices used in the diagnosis and treatment of biological systems.

Thus, the presented results could find applications not only in the field of magnonics but also in related areas such as biomedical engineering and sensor technology, expanding the potential uses of spin waves and magnetic nanostructures.

References

- [1] Gurevich A. *Magnetic Resonance in Ferrites and Antiferromagnets*. Nauka Publ., Moscow, 1973, 220 p.
- [2] Stancil D.D., Prabhakar A. *Spin Waves: Theory and Applications*. Springer Publ., Berlin, 2009, 348 p.
- [3] Wang Q., Kewenig M., Schneider M., Verba R., Kohl F., Heinz B., Geilen M., Mohseni M., Lagel B., Ciubotaru F., Adelmann C., Dubs C., Cotofana S.D., Dobrovolskiy O.V., Bracher T., Pirro P., Chumak A.V. A magnonic directional coupler for integrated magnonic half-adders. *Nat. Electron.*, 2020, **3**, P. 765.
- [4] Garanin F.E., Khutueva A.B., Lomova M.V., Sadovnikov A.V. Control of spin wave properties in bioactive systems based on YIG metasurfaces/ordered polymer films with magnetic microreservoirs. *Fizika Tverdogo Tela*, 2024, **66**(9), P. 1527–1534.
- [5] Khutueva A.B., Sadovnikov A.V., Garanin F.E. [et al.] Spin wave propagation in YIG waveguides with magnetic microvolcanoes: Experiment and simulation. *Applied Physics Letters*, 2025, **126**(6), P. 062402.
- [6] Garanin F.E., Khutueva A.B., Lomova M.V., Sadovnikov A.V. Upravlennie rasprostraneniem spinovykh voln v mikrovolnovode s dvumernym massivom magnitnykh mikrochastits razlichnoy geometrii. *Izvestiya Saratovskogo universiteta*. Novayaseriya Seriya: Fizika, 2025, **25**(1), P. 4–11. [In Russian]
- [7] Vansteenkiste A., Leliaert J., Dvornik M., Helsen M., Garcia-Sanchez F., Waeyenberge B. The design and verification of MuMax3. *AIP Adv.*, 2014, **4**, P. 107133.
- [8] Venkat G., Fangohr H., Prabhakar A. Absorbing boundary layers for spin wave micromagnetics. *J. Magn. Magn. Mater.*, 2018, **450**, P. 34.
- [9] Dvornik M., Kuchko A.N., Kruglyak V.V. Micromagnetic method of s-parameter characterization of magnonic devices. *J. Appl. Phys.*, 2011, **109**, P. 07D350.
- [10] Hu J., Jia F., Liu W. Application of Fast Fourier Transform. *HSET*, 2023, **38**, P. 590.
- [11] Bustamante-Torres M., Romero-Fierro D., Estrella-Nuez J., Arcentales-Vera B., Chichande-Proao E., Bucio E. Polymeric Composite of Magnetite Iron Oxide Nanoparticles and Their Application in Biomedicine: A Review. *Polymers*, 2022, **14**, P. 752.
- [12] Ganapathie L.S., Mohamed Yunus R., Berhanuddin D. D. Magnetite (Fe_3O_4) Nanoparticles in Biomedical Application: From Synthesis to Surface Functionalisation. *Magnetochemistry*, 2020, **6**, P. 68.

- [13] Włodarczyk A., Gorgoń S., Radoń A., Bajdak-Rusinek K. Magnetite Nanoparticles in Magnetic Hyperthermia and Cancer Therapies: Challenges and Perspectives. *Nanomaterials*, 2022, **12**, P. 1807.
 - [14] Petrov K.D., Chubarov A.S. Magnetite Nanoparticles for Biomedical Applications. *Encyclopedia*, 2022, **2**, P. 1811.
 - [15] Bilgic A., Cimen A. Two Novel BODIPY-Functional Magnetite Fluorescent Nano-Sensors for Detecting of Cr(VI) Ions in Aqueous Solutions. *J. Fluoresc.*, 2020, **30**, P. 867.
 - [16] Bilgic A., Cimen A. A highly sensitive and selective ON-OFF fluorescent sensor based on functionalized magnetite nanoparticles for detection of Cr(VI) metal ions in the aqueous medium. *J. Mol. Liq.*, 2020, **312**, P. 113398.
 - [17] Mbeh D.A., França R., Merhi Y., Zhang X.F., Veres T., Sacher E., Yahia L. In vitro biocompatibility assessment of functionalized magnetite nanoparticles: Biological and cytotoxicological effects. *J. Biomed. Mater. Res. Part A*, 2012, 100A, P. 1637.
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Pulsed phase modulation with harmonic electric control signal for quantum key distribution implementations

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ABSTRACT In this work, we investigate an alternative approach to phase modulation for information encoding and decoding in quantum key distribution systems. Specifically, we propose pulsed phase modulation, i.e. it has an envelope in addition to previously considered only harmonic temporal behavior of modulation index (depth), as a replacement for the conventional use of both intensity and phase modulators, which enables a more compact and cost-effective optical design. We further analyze how the principal parameters of this scheme affect the interference observed at the receiver and, consequently, their contribution to the quantum bit error rate in a subcarrier-wave quantum key distribution implementation.

KEYWORDS Phase modulation, quantum key distribution, subcarrier wave quantum key distribution.

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1. Introduction

With the ongoing transition of quantum key distribution (QKD) [1] from the laboratory [2–11] to commercial deployment [12–18], research emphasis has shifted from foundational aspects toward applied implementations, including network applications [19–24]. The reliable preparation and measurement of quantum states lies at the core of any QKD protocol. In practice, the majority of QKD schemes employ weak coherent states (it can be phase-randomized [25]), where information encoding and decoding are realized using phase and intensity modulators. Commercial deployment of QKD places emphasis not only on performance but also on cost, and modulators constitute one of the most expensive elements in the transmitter (Alice) setup. It becomes even more crucial in terms of quantum networks and quantum Internet of Things. In this work, we focus on the subcarrier wave (SCW) QKD protocol [26–31], whose distinguishing feature is that information is encoded in the frequency spectrum rather than in the phase difference between spatial modes, as in conventional phase-coding schemes. In this protocol, intensity modulators are commonly used to align the prepared quantum states with the temporal gating of the detectors. Nevertheless, the phase-encoding structure of SCW QKD allows one to dispense with intensity modulation altogether. A natural solution is to replace the continuous-wave laser with a pulsed source. Yet, in practice, the implementation of such a source is nontrivial, as it requires meeting stringent conditions on both spectral width and pulse repetition rate.

To address this issue, we propose an alternative approach to phase encoding, referred to as pulsed phase modulation. We analyze the general framework of this modulation scheme and examine how its key parameters influence the resulting interference observed at the receiver and, as a consequence, contribution of their non-ideal alignments to quantum bit error rate (QBER, Q) of a SCW QKD setup.

The article is organized as follows. In Section 2 preliminaries of phase modulation with harmonic electric control signal is considered. Section 3 is dedicated to the description of the proposed idea that modulation index can be time-dependent. In Section 4, two cases of rectangular and Gaussian shapes of modulation index envelopes are thoroughly examined. Section 5 concludes the article.

2. Preliminaries

Coherent state after a phase-modulation with an applied harmonic electric control signal, proportional to $m_A \sin(\Omega t + \phi_A)$, is as follows [27, 32]:

$$|\alpha_0\rangle_{\omega_0} \rightarrow |\psi(\phi_A)\rangle = \bigotimes_{n=-S}^S |\alpha_0 d_{0n}^S(\beta_A) e^{in\phi_A}\rangle_{\omega_n}, \quad (1)$$

where α_0 denotes the amplitude of initial coherent state at frequency ω_0 , $d_{nk}^S(\beta)$ is the Wigner d-function, $2S + 1$ is a number of interacted frequency-modes, $\beta_A \approx \frac{m_A}{S}$ can be considered as an efficient modulation index proportional to the amplitude of an electric control signal m_A , Ω and ϕ_A is the frequency and the phase of the electric control signal respectively, $\omega_n = \omega_0 + n\Omega$ is the resulting optical frequency. After the second modulation, where the electric signal is proportional to $m_B \sin(\Omega t + \phi_B)$, a kind of interference may be observed in the following structure of the resulting state:

$$|\psi(\phi_A, \phi_B)\rangle = \bigotimes_{n=-S}^S |\alpha_0 d_{0n}^S(\beta') e^{in\phi'}\rangle_{\omega_n}, \quad (2)$$

$$\cos(\beta') = \cos(\beta_A) \cos(\beta_B) - \sin(\beta_A) \sin(\beta_B) \cos(\phi_A - \phi_B), \quad (3)$$

and ϕ' is a phase that we are not interested in.

3. Time-dependent modulation

Further, we explore how slow changes of modulation index, namely $m(t_i)$, would affect the described interference-like structure of double-modulated state. Note, we assume slowly varying envelope approximation, so that there is almost no significant change of modulation index during the time necessary for a light to travel through a modulator (T_{int}). In other words, we divide time interval in some discrete intervals, characterized by their mean values t_i , that are comparable to the interaction time T_{int} , see Fig. 1. Thus, we treat modulation index during time interval t_i as a constant. This is necessary to assure that the model from [32] can be applied, where adiabatic process is assumed.

Other assumptions are as follows. We also consider a case of standard modulators, namely, a number of interacting modes is indefinitely large, $S \rightarrow \infty$. The latter implies the following approximations applied to the Eq. (3):

$$\beta(t_i) \approx \frac{m(t_i)}{S} \rightarrow 0, \quad (4)$$

$$\cos(\beta'(t_i)) \approx 1 - \frac{(\beta'(t_i))^2}{2}, \quad (5)$$

$$\cos(\beta_A(t_i)) \cos(\beta_B(t_i)) \approx 1 - \frac{\beta_A^2(t_i) + \beta_B^2(t_i)}{2}, \quad (6)$$

$$\sin(\beta_A(t_i)) \sin(\beta_B(t_i)) \approx \beta_A(t_i) \beta_B(t_i), \quad (7)$$

resulting in

$$(\beta'(t_i))^2 = \beta_A^2(t_i) + 2\beta_A(t_i)\beta_B(t_i) \cos(\phi_A - \phi_B) + \beta_B^2(t_i). \quad (8)$$

Detection of the obtained signal involves filtering out the central (initial) frequency ω_0 since the latter does not contain any phase related to the first modulation, and it only provides energy for sidebands to flow in. In turn, detection rate is proportional to the mean number of photons at sidebands μ , that can be expressed as follows:

$$\mu = \mu_0 (1 - |d_{00}^S(\beta'(t_i))|^2), \quad \mu_0 = |\alpha_0|^2. \quad (9)$$

A relation with the classical case (see Appendix A) immediately follows from the following observation and proportionality of β and m :

$$\lim_{S \rightarrow \infty} d_{nk}^S(\beta) = J_{n-k}(m), \quad (10)$$

where $J_n(m)$ is the Bessel function of the first kind. Thus,

$$\mu = \mu_0 (1 - J_0^2(m'(t_i))), \quad (11)$$

$$m'(t_i) = \sqrt{m_A^2(t_i) + 2m_A(t_i)m_B(t_i) \cos(\phi_A - \phi_B) + m_B^2(t_i)}. \quad (12)$$

Also, if $\max_{t_i} m(t_i) \ll 1$, that is a common value for an SCW QKD system, then the following approximation of Bessel function takes place:

$$\mu \approx \mu_0 \frac{(m'(t_i))^2}{2}. \quad (13)$$

In addition, further we consider energetic characteristics of an optical signal depending on a phase difference $\phi_A - \phi_B$ proportional to the following form:

$$E(\phi_A - \phi_B) \sim \sum_{i=-\infty}^{\infty} (m'(t_i))^2. \quad (14)$$

For the sake of simplicity, it is more convenient to consider dependencies on continuous time (assuming interaction time T_{int} rather small). Hereinafter, we assume the following substitution, see Fig. 1:

$$E(\phi_A - \phi_B) \sim \sum_{i=-\infty}^{\infty} (m'(t_i))^2 \rightarrow \int_{-\infty}^{\infty} (m'(t))^2 dt. \quad (15)$$

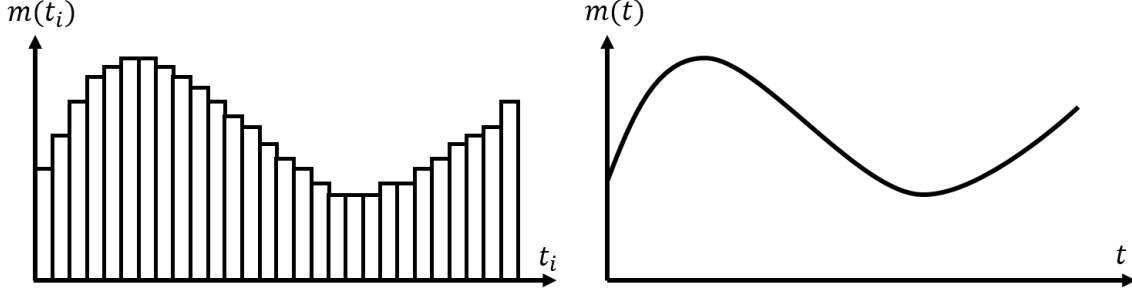


FIG. 1. **Left:** visualization of slow change of modulation index $m(t_i)$ with respect to chosen time-intervals t_i , $t_{i+1} - t_i \approx T_{int}$, where the latter is the time necessary for a light to travel through a modulator; we assume small amount of change of modulation index during T_{int} . **Right:** for the sake of simplicity, it is more convenient to consider dependence of modulation index $m(t)$ on continuous time, assuming interaction time T_{int} rather small, and allowing approximation as in Eq. (15)

4. Special cases

Further, in the section, several special cases of specific time-dependent $m(t)$ will be considered. In particular, pulse-shaped modulation is relevant in SCW QKD. It can be viewed as an alternative to pulse generation provided by an amplitude modulator, so the latter is no longer necessary. At this point, influence of relative shape difference for modulation-pulses on QBER, namely

$$Q = \frac{E(\pi)}{E(0) + E(\pi)}, \quad (16)$$

where $E(\phi_A - \phi_B)$ is the total energy of detected optical signal dependent on the phase difference between two modulation signals, should be investigated. Without loss of generality, shapes of pulses can be estimated without absolute values but with relative scaling as well as $E(\phi_A - \phi_B)$ can be estimated up to a common factor due to Q is a ratio.

4.1. Rectangular pulses

Consider rectangular modulation pulse:

$$m_A(t) = \text{rect}(t) = \Theta\left(t + \frac{1}{2}\right) - \Theta\left(t - \frac{1}{2}\right), \quad (17)$$

$$m_B(t) = x \text{rect}\left(\frac{t - \Delta t}{y}\right) = x(\Theta(t - \Delta t + \frac{y}{2}) - \Theta(t - \Delta t - \frac{y}{2})), \quad (18)$$

where $\Theta(t)$ is the Heaviside function, $0 \leq x \leq 1$ denotes mismatch of modulation amplitude, $y \geq 0$ denotes pulse-width mismatch, and $\Delta t \geq 0$ is time-shift. Considering Eq. (13) as the mean photon number per time, total amount of energy at sidebands in pulse is proportional to the following integral, where Eq. (12) is used:

$$E(\phi_A - \phi_B) \sim \int_{-\infty}^{\infty} (m'(t))^2 dt = 1 + x^2 y + 2x f(\Delta t, y) \cos(\phi_A - \phi_B), \quad (19)$$

where

$$f(\Delta t, y) = \begin{cases} 0, & \Delta t \geq \frac{y+1}{2} \\ y, & \Delta t \leq \frac{|y-1|}{2} \text{ and } y \leq 1 \\ 1, & \Delta t \leq \frac{|y-1|}{2} \text{ and } y \geq 1 \\ \frac{1}{2} + \frac{y}{2} - \Delta t, & \frac{|y-1|}{2} \leq \Delta t \leq \frac{y+1}{2} \end{cases}. \quad (20)$$

Finally, QBER can be estimated as follows:

$$Q = \frac{1}{2} - \frac{x f(\Delta t, y)}{1 + x^2 y}. \quad (21)$$

Further, we will consider several special cases in order to determine influence of each parameter mismatch on Q .

- (1) Mismatch of only modulation amplitude of the envelope implies that $y = 1$ and $\Delta t = 0$. Then,

$$Q(x) = \frac{(1-x)^2}{2(1+x^2)}, \quad (22)$$

which is well agreed with the known case, where $m_A \neq m_B$ and both are constants. The latter dependence is shown in Fig. 2(a). Observe, that

$$Q\left(\frac{1}{x}\right) = Q(x). \quad (23)$$

Also, for a small modulation depth mismatch, i.e. $|x - 1| \ll 1$, the following approximation takes place:

$$Q(x) \approx \frac{(1-x)^2}{4}; \quad (24)$$

- (2) Mismatch of only pulse-width, $x = 1$ and $\Delta t = 0$, yields as follows:

$$Q(y) = \left| \frac{y-1}{2(1+y)} \right| = Q\left(\frac{1}{y}\right), \quad (25)$$

and it is shown in Fig. 2(b);

- (3) Displacement in time with $x = 1$ and $y = 1$ results in the following expression:

$$Q(\Delta t) = \begin{cases} \frac{\Delta t}{2}, & \Delta t \leq 1 \\ \frac{1}{2}, & \Delta t \geq 1 \end{cases}. \quad (26)$$

The obtained dependence is shown in Fig. 2(c).

4.2. Gaussian pulses

Consider Gaussian-shaped modulation pulse:

$$m_A(t) = \frac{1}{\sqrt{2\pi}} e^{-\frac{t^2}{2}}, \quad (27)$$

$$m_B(t) = \frac{x}{\sqrt{2\pi y}} e^{-\frac{(t-\Delta t)^2}{2y^2}}, \quad (28)$$

where $x \geq 0$ denotes mismatch of modulation amplitude, $y \geq 0$ denotes pulse-width mismatch, and Δt is time-shift. In this case, the total amount of energy in the pulse is as follows:

$$E(\phi_A - \phi_B) \sim \int_{-\infty}^{\infty} (m'(t))^2 dt \sim 1 + \frac{x^2}{y} + \frac{x\sqrt{2}e^{\frac{-(\Delta t)^2}{2(1+y^2)}}}{\sqrt{y^2+1}} \cos(\phi_A - \phi_B), \quad (29)$$

where we are not interested in common factors to be neglected. Thus,

$$Q = \frac{1}{2} - \frac{xy\sqrt{2}e^{\frac{-(\Delta t)^2}{2(1+y^2)}}}{(y+x^2)\sqrt{y^2+1}}. \quad (30)$$

Dependencies of Q on each misalignment are as follows:

- (1) Mismatch of modulation depth x with $y = 1$ and $\Delta t = 0$ dictates the same dependence as in the previous case of rectangular pulse, that is shown in Fig. 2(a);
- (2) Pulse-width mismatch (with $x = 1$ and $\Delta t = 0$) results in the following dependence:

$$Q(y) = \frac{1}{2} - \frac{y\sqrt{2}}{(y+1)\sqrt{y^2+1}} = Q\left(\frac{1}{y}\right). \quad (31)$$

It is shown in Fig. 2(d) and can be approximated as follows in case of small deviations, i.e. $|y - 1| \ll 1$,

$$Q(y) \approx \frac{3}{16}(y-1)^2; \quad (32)$$

- (3) Time-shift of one Gaussian relative to another, assuming $y = 1$ and $x = 1$, contributes to Q as follows:

$$Q(\Delta t) = \frac{1 - e^{-\frac{(\Delta t)^2}{4}}}{2}. \quad (33)$$

The latter is shown in Fig. 2(e); in case of small time-shift $|\Delta t| \ll 1$, it has the following approximation:

$$Q(\Delta t) \approx \frac{(\Delta t)^2}{8}. \quad (34)$$

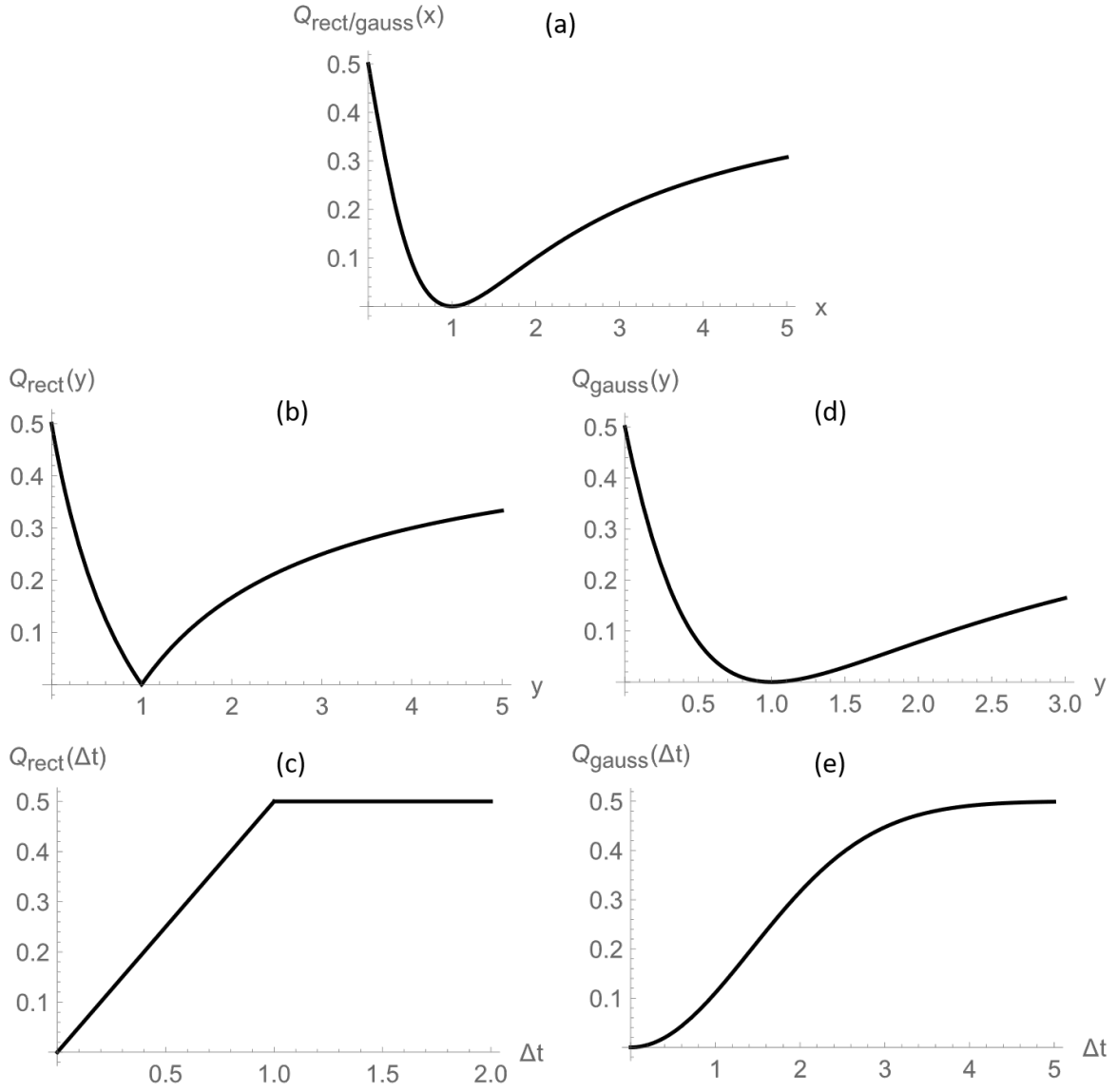


FIG. 2. Graphical representation of estimated QBER value Q dependent on various parameters of modulation-pulse shape: (a) according to Eq. (22) for both Gaussian and rectangular pulse shapes, (b) according to Eq. (25) for rectangular pulse shape, (c) according to Eq. (26) for rectangular pulse shape, (d) according to Eq. (31) for Gaussian pulse shape, (e) according to Eq. (33) for Gaussian pulse shape

5. Discussion and conclusion

In the article, utilization of time-dependent (pulsed) modulation index in a phase modulation with harmonic electric control signal is proposed, especially for implementation in SCW QKD systems. Due to the latter, necessity of an additional intensity modulation is absent. It is required that both sender's and receiver's pulses should be equal, that is not always true for a practical implementation. In the paper, we have examined how misalignment of these pulses (modulation depth scaling x , relative width y , and relative time-shift Δt) affect the QBER value, one of the most crucial characteristics for a QKD device. Obtained dependencies may be used in order to retrospectively estimate admissible bounds for misalignment parameters in case of a given QBER threshold.

Two types of pulse shapes were considered: rectangular and Gaussian, as the most simple examples. Despite the real pulse may have slightly more peculiar envelope, obtained dependencies, shown in Fig. 2, for a given examples share general features. Nonetheless, results, provided in Eqs. (11) and (12), are of a general form suited for any temporal envelope shapes of modulation index. However, during the derivation of the resulting expressions we employ several assumptions in regard of adiabatic dynamical regime, that should be met. In particular, a too rapid change of modulation index may break the mentioned assumptions and, as a result, this scenario should be considered properly. We believe, that described rapid changes may result in temporal delay between controlling electrical signal and actual change of refraction

index that causes modulation. Namely, change of refraction index do not catch up with applied electric field. Rigorous study of this problem requires thorough examination of the quasi-energy operator's eigenvalues behavior that is far beyond of the article's scope, leaning towards practical implementation.

In addition, the obtained results can be viewed as a transition of optical transformations, e.g. action of intensity modulator, to the domain of electrical ones, e.g. manipulation of modulation index envelope. From the perspective, various families of these manipulations with applied to the crystal electric field can be considered further. In particular, what kind of modulation is required in order to simulate the action of an optical filter? Or is it possible to concentrate energy in spectrum closer to the central frequency? The problem of several harmonics multiplexing is also of interest. Provided expressions (11) and (12) are the first step forward in solving these problems that may result in significant simplifications of QKD optical schemes and vastly improving their performance in various ways.

A. Appendix: Classical phase modulation with harmonic electric control signal

Classical approach for phase modulation with harmonic electric control signal is rather straightforward and well known. Consider the optical signal as a plane-wave, i.e. $Ae^{i\omega t}$, that traverses a crystal with changing refraction index due to applied external electric field. Namely, plane-wave obtains phase-shift (proportional to) $m \sin(\Omega t + \phi_1)$. Using the Jacobi-Anger expansion formula,

$$e^{iz \cos(\theta)} = \sum_{n=-\infty}^{\infty} J_n(m) e^{in\theta}, \quad (35)$$

the expression for the modulated light is as follows:

$$Ae^{i\omega t} e^{im \sin(\Omega t + \phi_1)} = \sum_{n=-\infty}^{\infty} (AJ_n(m) e^{in\phi_1}) e^{i(\omega + n\Omega)t}, \quad (36)$$

where $AJ_n(m)$ and $n\phi_1$ can be considered as amplitude and phase, respectively, of a plane-wave with frequency $\omega + n\Omega$. If one utilizes a second modulator with modulation index $m \sin(\Omega t + \phi_2)$, that differs only in phase, then the total energy (or power) of all sidebands ($n \neq 0$) is proportional to

$$\begin{aligned} \sum_{n \neq 0} |(AJ_n(m_0) e^{in\phi_0}) e^{i(\omega + n\Omega)t}|^2 &= \\ &= |A|^2 (1 - J_0^2(2m \cos(\frac{\phi_1 - \phi_2}{2}))) = \\ &= |A|^2 (1 - J_0^2(m \sqrt{2(1 + \cos(\phi_1 - \phi_2))})), \end{aligned} \quad (37)$$

where we have used identities given by

$$\begin{aligned} |Ae^{i\omega t} e^{im \sin(\Omega t + \phi_1)} e^{im \sin(\Omega t + \phi_2)}|^2 &= \\ &= |Ae^{i\omega t} e^{i(2m \cos(\frac{\phi_1 - \phi_2}{2}) \sin(\Omega t + \frac{\phi_1 + \phi_2}{2}))}|^2 = \\ &= \left[m_0 \equiv 2m \cos(\frac{\phi_1 - \phi_2}{2}), \quad \phi_0 \equiv \frac{\phi_1 + \phi_2}{2} \right] \\ &= |Ae^{i\omega t} e^{i(m_0 \sin(\Omega t + \phi_0))}|^2. \end{aligned} \quad (38)$$

Expression (37) is fully agreed with Eq. (11) and (12) in this simple example, where modulation index m is constant.

References

- [1] Pirandola S., Andersen U.L., Banchi et al. Advances in quantum cryptography. *Advances in optics and photonics*, 2020, **12**(4), P. 1012–1236.
- [2] Bennett C.H., Bessette F., Brassard G., Salvail L., Smolin J. Experimental quantum cryptography. *Journal of cryptography*, 1992, **5**(1), P. 3–28.
- [3] Townsend P.D. Experimental investigation of the performance limits for first telecommunications-window quantum cryptography systems. *IEEE Photonics Technology Letters*, 2002, **10**(7), P. 1048–1050.
- [4] Gui Y.Z., Han Z.F., Mo X.F., Guo G.C. Experimental quantum key distribution over 14.8 km in a special optical fibre. *Chin. Phys. Lett.*, 2003, **20**(5), P. 608–610.
- [5] Marand C., Townsend P. D. Quantum key distribution over distances as long as 30 km. *Optics Letters*, 1995, **20**(16), P. 1695–1697.
- [6] Hughes R.J., Morgan G.L., Peterson C.G. Quantum key distribution over a 48 km optical fibre network. *Journal of Modern Optics*, 2000, **47**(2-3), P. 533–547.
- [7] Weier H. Experimental quantum cryptography. *Diploma Dissertation, Technical University of Munich*, 2003.
- [8] Tittel W., Zbinden H., Gisin N. Experimental demonstration of quantum secret sharing. *Physical Review A*, 2001, **63**(4), P. 042301.
- [9] Stucki D., Gisin N., Guinnard O., Ribordy G., Zbinden H. Quantum key distribution over 67 km with a plug&playsystem. *New Journal of Physics*, 2002, **4**(1), P. 41.
- [10] Buttler W.T., Hughes R.J., Lamoreaux S.K., Morgan G.L., Nordholt J.E., Peterson C.G. Daylight quantum key distribution over 1.6 km. *Physical Review Letters*, 2000, **84**(24), P. 5652.
- [11] Buttler W.T., Hughes R.J., Kwiat P.G., Lamoreaux S.K., Luther G.G., Morgan G.L., et al. Practical free-space quantum key distribution over 1 km. *Physical Review Letters*, 1998, **81**(15), P. 3283.

- [12] Pljonkin A., Singh P.K. The review of the commercial quantum key distribution system. *Fifth International Conference on Parallel, Distributed and Grid Computing (PDGC) by IEEE*, 2018, P. 795–799.
- [13] Oesterling L., Hayford D., Friend G. Comparison of commercial and next generation quantum key distribution: Technologies for secure communication of information. *Conference on Technologies for Homeland Security (HST) by IEEE*, 2012, P. 156–161.
- [14] Makarov V., Abrikosov A., Chaiwongkhot P., Fedorov A.K., Huang A., Kiktenko E., et al. Preparing a commercial quantum key distribution system for certification against implementation loopholes. *Physical Review Applied*, 2024, **22**(4), P. 044076.
- [15] Al Natsheh A., Gbadegeshin S.A., Rimpiläinen A., Imamovic-Tokalic I., Zambrano, A. Identifying the challenges in commercializing high technology: A case study of quantum key distribution technology. *Technology Innovation Management Review*, 2015, **5**(1).
- [16] Cavaliere F., Prati E., Poti L., Muhammad I., Catuogno T. Secure quantum communication technologies and systems: From labs to markets. *Quantum Reports*, 2020, **2**(1), P. 80–106.
- [17] Sasaki M., Fujiwara M., Ishizuka H., Klaus W., Wakui K., Takeoka M., et al. Field test of quantum key distribution in the Tokyo QKD Network. *Optics express*, 2011, **19**(11), P. 10387–10409.
- [18] Chaiwongkhot P., Sajeed S., Lydersen L., Makarov, V. Finite-key-size effect in a commercial plug-and-play QKD system. *Quantum Science and Technology*, 2017, **2**(4), P. 044003.
- [19] Cao Y., Zhao Y., Wang Q., Zhang J., Ng S.X., Hanzo L. The evolution of quantum key distribution networks: On the road to the qinternet. *IEEE Communications Surveys & Tutorials*, 2022, **24**(2), P. 839–894.
- [20] Mehic M., Niemiec M., Rass S., Ma J., Peev M., Aguado A., et al. Quantum key distribution: a networking perspective. *ACM Computing Surveys (CSUR)*, 2020, **53**(5), P. 1–41.
- [21] Sharma P., Agrawal A., Bhatia V., Prakash S., Mishra A.K. Quantum key distribution secured optical networks: A survey. *IEEE Open Journal of the Communications Society*, 2021, **2**, P. 2049–2083.
- [22] Peev M., Pacher C., Alléaume R., Barreiro, C., Bouda J., Boxleitner W., et al. The SECOQC quantum key distribution network in Vienna. *New journal of physics*, 2009, **11**(7), P. 075001.
- [23] Dianati M., Alléaume R., Gagnaire M., Shen X. Architecture and protocols of the future European quantum key distribution network. *Security and Communication Networks*, 2008, **1**(1), P. 57–74.
- [24] Dervisevic E., Tankovic A., Fazel E., Kompella R., Fazio P., Voznak M., Mehic M. Quantum Key Distribution Networks-Key Management: A Survey. *ACM Computing Surveys*, 2025, **57**(10), P. 1–36.
- [25] Guselnikov M.S., Gaidash A.A., Miroshnichenko G.P., Kozubov A.V. Properties of multi-moded phase-randomized coherent states. *Nanosystems: Physics, Chemistry, Mathematics*, 2025, **16**(3), P. 311–316.
- [26] Gaidash A., Miroshnichenko G., and Kozubov A. Subcarrier wave quantum key distribution with leaky and flawed devices. *Journal of the Optical Society of America B*, 2022, **39**(2), P. 577–585.
- [27] Miroshnichenko G., Kozubov A., Gaidash A., Gleim A.V., and Horoshko D.V. Security of subcarrier wave quantum key distribution against the collective beam-splitting attack. *Optics express*, 2018, **26**(9), P. 11292–11308.
- [28] Sajeed Sh., Chaiwongkhot P., Huang A., Qin H., Egorov V., Kozubov A., Gaidash A., Chistiakov V., Vasiliev V., Gleim A., et al. An approach for security evaluation and certification of a complete quantum communication system. *Scientific Reports*, 2021, **11**(1), P. 1–16.
- [29] Chistiakov V., Kozubov A., Gaidash A., Gleim A., and Miroshnichenko G. Feasibility of twin-field quantum key distribution based on multi-mode coherent phase-coded states. *Optics express*, 2019, **27** (25), P. 36551–36561.
- [30] Samsonov E., Goncharov R., Gaidash A., Kozubov A., Egorov V., and Gleim A. Subcarrier wave continuous variable quantum key distribution with discrete modulation: mathematical model and finite-key analysis. *Scientific Reports*, 2020, **10** (1), P. 1–9.
- [31] Latypov I.Z., Chistyakov V.V., Fadeev M.A., Sulimov D.V., Khalturinsky A.K., Kynev S.M., Egorov V.I. Hybrid quantum communication protocol for fiber and atmosphere channel. *Nanosystems: Physics, Chemistry, Mathematics*, 2024, **15**(5), P. 654–657.
- [32] Miroshnichenko G., Kiselev A., Trifanov A., Gleim A. Algebraic approach to electro-optic modulation of light: exactly solvable multimode quantum model. *Journal of the optical society of America B*, 2017, **34**(6), P. 1177–1190.

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Umbilic surfaces as a robust topological probe of 3D solitons in cholesteric liquid crystals

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ABSTRACT The method based on umbilics that expose line-like organization of complex director fields is used to introduce umbilic surfaces as a numerically robust probe of three-dimensional (3D) topological solitons in frustrated cholesteric liquid crystals. We present a coordinate-free analytical formulation of the umbilic-line approach that ensures reliable detection of umbilics on discrete simulation grids and thus avoids the problems caused by instabilities and sensitivity to coordinate choices. By using our method we introduce the laboratory-referenced phase field giving a natural tool for intuitive surface colorization. In addition, we employ this field to define the two fundamental integer invariants of umbilic loops: the transverse index (the strength) and the longitudinal winding (the profile twist). These invariants directly link the umbilic geometry to the topological characteristics of textures, thus enabling soliton identification and a comparison of solitons by topological content. We apply the technique to the three canonical solitons obtained by the free-energy minimization: the toron and the looped cholesteric fingers of the first and second types with the Hopf indices equal to zero and unity, respectively. It is found that the umbilic-surface representation clearly exposes defect structures, discriminates between visually similar but topologically distinct textures and provides a tool for quantifying and visualizing 3D solitons from director field data.

KEYWORDS topological structures; umbilic lines; chiral liquid crystals; soliton; toron.

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1. Introduction

Topological defects in orientationally ordered systems such as liquid crystals (LCs) are universal in occurrence. The defects are of crucial importance for both understanding the fundamental properties of such systems and practical applications [1]. Typically, spatial and temporal stability of the defects in confined liquid crystals requires geometrical frustration imposed by bounding surfaces so as to inhibit the relaxation processes caused by the high cost of the elastic energy.

It is known that, in chiral nematic liquid crystals also known as the cholesteric liquid crystals (CLCs), the interplay between chirality, elasticity and surface interactions can produce topologically nontrivial localized structures (textures) [2, 3]. Specifically, in the so-called frustrated CLCs where CLC is confined between parallel plates (substrates), matching the homeotropic (perpendicular) anchoring conditions at substrates of CLC cells and the ground-state helicoidal structure cannot be done without distortion. In addition to the well-known cholesteric fingers [4], this incompatibility is known to produce a rich variety of topological soliton structures such as skyrmions, antiskyrmions, torons, bobbars, hopfions, heliknotons, and twistions [5–10]. These chirality-enabled localized structures are used as elements of singular optics [11–13] and components of diffraction gratings [14]. Note that, in magnets, chiral skyrmions [15], hopfions [16] and Bloch points in the domain walls of stressed cylindrical wires [17, 18] are well known and are often described as magnetic vortices.

Mathematically, the liquid crystal textures can be described as spatial distributions of the LC director represented by a unit vector, $\hat{n}(\mathbf{r})$, specifying the locally averaged direction of orientation of LC molecules. The geometric characterization and corresponding accurate visualization of LC textures is a challenging task that is fundamental to understanding the

geometry and topology of LC structures. For arbitrary three-dimensional topological structures, a general theory for recognizing localized linear structures in liquid crystals, magnetic materials, or other orientationally ordered systems has yet to be developed.

In addition to characterizing geometry of LC orientational configurations in terms of preimages determined by the set of all points in the LC material where the LC molecules are aligned along a fixed direction $\hat{n}$, a widely used visualization method for presenting complex director fields and identifying topology comes from the Pontryagin–Thom construction as applied to liquid crystals in [2]. In this method, the texture is depicted by showing the surface in space where the director field is normal to a fixed direction, say, $\hat{n} \perp \hat{e}_z$, where $\hat{e}_z$ is perpendicular to the substrates of a LC cell. The surface is then colored according to the values of the azimuthal angle specifying horizontal orientation of the director on it. Note that the preimages of every orientation with a fixed z component $\hat{n}_z$ fill the surface of a torus.

Alternatively, in the umbilic-lines approach developed by Machon and Alexander [19], a general analysis of the liquid crystal director can be performed through a geometric decomposition of the gradient tensor of the director field. This method allows to identify geometrically distinguished directions and relates the defects in these directions to the topology of the texture. Selinger [20] has applied this approach to give fresh perspectives on a number of known liquid crystal structures.

In this paper, the umbilic-lines approach will be our primary concern. We propose a numerically robust and coordinate free modification of the umbilic-lines method. Based on this method, we introduce two topological indices (strength and longitudinal winding) and suggest an original coloring method for visualizing umbilic lines. The umbilic topological indices are related to the well known topological charges such as the Hopf index [3, 21, 22] and the skyrmion number [5, 23].

For illustration purposes, we apply our method to the three numerically simulated and analytically designed soliton structures: (a) the toron; (b) the cholesteric finger (CF) loop of the first type (CF1-loop); and (c) the cholesteric finger loop of the second type (CF2-loop). The toron is a metastable topological structure with a double-twist toroidal core and two hyperbolic point defects above and below the torus plane [5, 24, 25]. The loop of the first type cholesteric finger possesses two pairs of nonsingular disclination circles [25–27]. The CF2-loop carries Hopf index $Q_H = 1$ (see [3]); we therefore use the term “hopfion” interchangeably with “CF2-loop”. The hopfion is a topological soliton with a knotted topological structure. Isolines of the hopfion director field are closed loops which are linked together [3, 21, 22]. We show how the umbilic-lines approach clarifies the defect structure and topological content of these textures.

The paper is organized as follows. In Sec. 2 we briefly discuss numerical modeling employed for simulation of the director field distributions using the lattice model derived as a discretization of the LC free energy functional. The umbilic-lines approach and its numerical implementation are described in Sec. 3. In Sec. 4, we introduce two independent integer invariants of umbilic loops and propose the method of umbilic-lines visualization. In Sec. 5 we describe the analytical modeling procedure that uses suitably designed director field ansatzes starting from the CF1-loop configuration. The results for the topological solitons are presented in Sec. 6. Finally, we draw the results together in Sec. 7 and make concluding remarks in Sec. 8.

2. Model

The topological solitons in CLCs are 3D orientational structures determined by the CLC director field $\hat{n}(\mathbf{r})$. From here on, a hat indicates unit vectors. Although the physical director is a line field $\hat{n} \sim -\hat{n}$, throughout this work we restrict to textures (and to the specific domains/surfaces used in our constructions) where $\hat{n}$ can be chosen continuously, i.e. a global sign convention exists. All subsequent notions that use an oriented director field (in particular, the integer windings) are understood in this sense. In the presence of sign frustration (when such a continuous choice is impossible), the phase-based constructions would require a separate treatment, which is outside the scope of the present work.

In this section, we introduce numerical procedure for finding director field $\hat{n}(\mathbf{r})$ of the topological solitons (such as torons, CF1-loop and CF2-loop (hopfion)) in the frustrated CLC.

We consider a CLC with the volume V confined in the slab geometry where the CLC is sandwiched between two parallel bounding plates (substrates): $z = -L/2$ and $z = L/2$. In this geometry, L is the thickness of the CLC cell and the z axis is normal to the substrates. Both lateral sizes of the CLC cell are equal to L_W , $L_W \gg L$, $V = LL_W^2$.

For the frustrated CLC we consider homeotropic orientation on the bounding plates: $\hat{n}|_{z=\pm L/2} = \hat{e}_z \equiv (0, 0, 1)$. The anchoring conditions are considered to be strong for both the bounding plates and the lateral surfaces of the sample. This confinement frustrates the intrinsic cholesteric twist and allows metastable localized structures to appear as local minima of the elastic free energy.

We model the director configurations of a cholesteric liquid crystal by minimizing the Frank–Oseen free-energy functional in a three-dimensional domain V . The free energy is (see, e.g., [28])

$$F[\hat{n}] = \int_V \left[\frac{K_1}{2} (\nabla \cdot \hat{n})^2 + \frac{K_2}{2} (\hat{n} \cdot \nabla \times \hat{n} + q_0)^2 + \frac{K_3}{2} (\hat{n} \times \nabla \times \hat{n})^2 \right] d\mathbf{r}, \quad (1)$$

K_1 , K_2 , K_3 are the splay, twist and bend Frank elastic constants, respectively; $q_0 = 2\pi/P_0$ is the twisting wave number; and P_0 is the equilibrium CLC pitch. In order to find the director distributions representing metastable CLC structures, the elastic free energy (1) has to be minimized.

Assuming the simplified model of CLC director dynamics where the coupling between the director and the fluid flow can be neglected, relaxation of the director field is governed by the following dynamic equation:

$$\frac{d\hat{n}}{dt} = -\eta \frac{\delta F[\hat{n}]}{\delta \hat{n}}, \quad (2)$$

where η is the rotational viscosity and the functional derivative $\frac{\delta F}{\delta \hat{n}}$ is of the following form [10]

$$\begin{aligned} \frac{\delta F[\hat{n}]}{\delta \hat{n}} = & -K_1 \nabla(\nabla \cdot \hat{n}) - K_3 [\Delta \hat{n} - \nabla(\nabla \cdot \hat{n})] \\ & + (K_2 - K_3) [2(\hat{n} \cdot \nabla \times \hat{n})(\nabla \times \hat{n}) - \hat{n} \times \nabla(\hat{n} \cdot \nabla \times \hat{n})] + 2K_2 q_0 \nabla \times \hat{n}. \end{aligned} \quad (3)$$

Steady states of Eq. (2) correspond to stationary points of the functional (1); in particular, metastable solitons correspond to local minima.

Here, we limit ourselves to considering the free energy and the relaxation equations for the director field. A more accurate but computationally expensive method is based on considering the tensor order parameter rather than the director field [28, 29].

To solve the problem numerically, we discretize the free energy (1) on a simple cubic lattice inside the rectangular cell and apply the finite difference method to Eq. (2). In this lattice model, directors are localized at the points of a simple cubic lattice inside the rectangular cell and we fix the unit length of the directors. The numerical procedures are implemented in the software package LCSim [30] that was extensively used in our simulations. As an initial approximation for the director field, we use the analytical ansatzes constructed in Sec. 5, which are designed to lie in the attraction basins of the target metastable solitons. In our simulations we choose the Frank constants and rotational viscosity corresponding to the nematic liquid crystal E7. In order to get the topological structures of interests as steady states, the equilibrium CLC pitch should be of the order of the thickness of the LC sample, $P_0 \sim L$.

3. Numerical extraction of umbilic lines

The umbilic-lines approach is proposed by Machon and Alexander for analysis and visualization of three-dimensional structures [19]. The starting point of this approach is the geometric decomposition of the gradient tensor of the director field $\hat{n}$ given by (see, e.g., [20] for a simple derivation of the decomposition formula)

$$\nabla_i \hat{n}_j = \hat{n}_i (\hat{n} \cdot \nabla) \hat{n}_j + \frac{1}{2} (\nabla \cdot \hat{n}) (\delta_{ij} - \hat{n}_i \hat{n}_j) + \frac{1}{2} (\hat{n} \cdot \nabla \times \hat{n}) \varepsilon_{ijk} \hat{n}_k + \Delta_{ij}, \quad (4)$$

where δ_{ij} and ε_{ijk} are the Kronecker delta and the Levi-Civita symbol, respectively. The first three terms represent the derivative along the director, an isotropic transverse dilation (splay contribution), and an isotropic transverse rotation (twist contribution). The last term Δ_{ij} gives the components of the traceless symmetric tensor describing the anisotropic part of orthogonal gradients of $\hat{n}$.

By using the well-known relation for the norm of the gradient tensor

$$\sum_{i,j} (\nabla_i \hat{n}_j)^2 = (\nabla \cdot \hat{n})^2 + ((\hat{n} \cdot \nabla) \hat{n})^2 + (\hat{n} \cdot \nabla \times \hat{n})^2 - \nabla \cdot [\hat{n}(\nabla \cdot \hat{n}) - (\hat{n} \cdot \nabla) \hat{n}] \quad (5)$$

and orthogonality of the modes in the decomposition (4), it is not difficult to obtain the explicit expression for the norm of Δ in the form given by Machon and Alexander [19]

$$\|\Delta\|^2 \equiv \frac{1}{2} \sum_{i,j} \Delta_{ij}^2 = \frac{1}{4} (\nabla \cdot \hat{n})^2 + \frac{1}{4} (\hat{n} \cdot \nabla \times \hat{n})^2 - \frac{1}{2} \nabla \cdot [\hat{n}(\nabla \cdot \hat{n}) - (\hat{n} \cdot \nabla) \hat{n}]. \quad (6)$$

The points, where Δ vanishes and $\|\Delta\|^2 = 0$, are called umbilics of the orientational order. These points correspond to the regions, where the orthogonal gradients of $\hat{n}$ are isotropic. Except for degenerate cases, these points form one-dimensional lines. In numerical computations, however, the condition $\|\Delta\|^2 = 0$ is rarely achieved exactly due to discretization and round-off errors, so it is more robust to consider isosurfaces of small $\|\Delta\|^2$; for sufficiently small isovalues these surfaces form thin tubes enclosing the umbilic lines. Note that uniform director configuration gives $\|\Delta\|^2 = 0$, hence, solitons embedded into a uniform phase always have an umbilic at infinity.

A closely related viewpoint is obtained by restricting the gradient of $\hat{n}$ to the transverse plane. According to [19], the decomposition formula (4) implies that the orthogonal gradient of $\hat{n}$ can be written in the form:

$$\nabla_{\perp} \hat{n} = \frac{\nabla \cdot \hat{n}}{2} I + \frac{\hat{n} \cdot (\nabla \times \hat{n})}{2} J + \Delta, \quad (7)$$

where I is the identity in the plane $\hat{\mathbf{n}}^\perp$ normal to $\hat{\mathbf{n}}$, J is the corresponding orthogonal complex structure, and Δ is a traceless symmetric (spin-2) tensor field. In a local orthonormal frame $\{\hat{\mathbf{d}}_1, \hat{\mathbf{d}}_2\}$ of $\hat{\mathbf{n}}^\perp$ the tensor Δ can be expressed in the matrix form:

$$\Delta = \begin{pmatrix} \Delta_1 & \Delta_2 \\ \Delta_2 & -\Delta_1 \end{pmatrix}, \quad \|\Delta\|^2 = \Delta_1^2 + \Delta_2^2, \quad (8)$$

and umbilics are precisely the zeros of Δ .

From the numerical standpoint, two practical difficulties arise if one attempts to use these continuum formulas directly. First, on a grid the director $\hat{\mathbf{n}}$ is known only at lattice sites; derivatives must be approximated, and higher-order derivatives are typically much noisier than lower-order ones. Second, the scalar $\|\Delta\|^2$ is nonnegative, and its vanishing generally results from cancellations between terms of comparable size; this makes direct localization of zeros from sampled data fragile, especially near the umbilic cores. Finally, the components Δ_k depend on a locally chosen transverse basis, and constructing a globally consistent family of such bases in three dimensions is challenging.

Now our task is to present a numerically robust method for detecting umbilic lines in three-dimensional CLC textures. The construction is fully tensorial, requires only first derivatives of the director field, and yields both the umbilic set and a natural phase field whose windings encode the two topological charges identified by Machon and Alexander [19]. This approach avoids the numerically ill-conditioned analytic expression (6) for $\|\Delta\|^2$, while, in the continuum limit, remaining exactly equivalent to those developed in [19].

To this end, we consider a smooth director field $\hat{\mathbf{n}}(\mathbf{r}) : \Omega \subset \mathbb{R}^3 \rightarrow S^2$ with $|\hat{\mathbf{n}}| = 1$ and assume that discrete derivatives in a cubic grid of spacing δ are implemented using centered finite differences (the notation suppresses δ since it introduces only an overall multiplicative constant in the quantities of interest). Let $\partial_l \hat{\mathbf{n}}_i$ denote the discrete approximation to the spatial derivatives of the director and define the orthogonal projector onto the plane perpendicular to $\hat{\mathbf{n}}$,

$$\Pi_{ij}(\mathbf{r}) = \delta_{ij} - \hat{n}_i(\mathbf{r}) \hat{n}_j(\mathbf{r}). \quad (9)$$

The projected gradient of the director is then given by the rank-2 tensor

$$N_{ij} = (\Pi \partial \hat{\mathbf{n}} \Pi)_{ij} = \Pi_{ik} (\partial_l \hat{n}_k) \Pi_{lj}. \quad (10)$$

This removes the gauge freedom of the director and discards all components of $\partial_l \hat{\mathbf{n}}$ parallel to $\hat{\mathbf{n}}$ or generated by changes of parametrization along $\hat{\mathbf{n}}$.

The symmetric part of N given by the relation

$$X_{ij} = \frac{1}{2} (N_{ij} + N_{ji}) \quad (11)$$

is a (3×3) symmetric tensor satisfying $X_{ij} \hat{n}_j = 0$. Thus X has one vanishing eigenvalue (along $\hat{\mathbf{n}}$) and a real two-dimensional spectrum in the orthogonal plane. These two nonzero eigenvalues encode the local curvature of the director field transverse to $\hat{\mathbf{n}}$ and correspond to the “principal curvatures” used in the geometric description of umbilics.

Let $\lambda_1(\mathbf{r})$ and $\lambda_2(\mathbf{r})$ stand for the eigenvalues of X restricted to the orthogonal plane and define the following two spectral invariants

$$T_1 = \text{Tr } X = \lambda_1 + \lambda_2, \quad T_2 = \text{Tr } (X^2) = \lambda_1^2 + \lambda_2^2. \quad (12)$$

The traceless symmetric (spin-2) part of X , $X_0 = X - \frac{1}{2} T_1 \Pi$, is nonzero precisely when $\lambda_1 \neq \lambda_2$. This can be clearly seen from the scalar umbilic field defined as follows

$$\Phi(\mathbf{r}) = 2\text{Tr } (X_0^2) = 2T_2 - T_1^2 = 2(\lambda_1^2 + \lambda_2^2) - (\lambda_1 + \lambda_2)^2 = (\lambda_1 - \lambda_2)^2. \quad (13)$$

This relation introduces the umbilic field Φ that vanishes if and only if the two principal curvatures coincide, i.e., exactly on the umbilic set. Since the director field is noisy at the grid level, we will visualize umbilics using the isosurfaces of small Φ , typically by plotting

$$\varepsilon = \log_{10} \Phi \quad (14)$$

for dynamic-range compression. Importantly, the quantity (13) is rotationally invariant and uses only first derivatives of the director field. To analyze individual umbilic lines, ε should be chosen as small as possible so that each line is enclosed by its own level surface. For sufficiently small ε the level surface is tubular; increasing the value of ε may cause isosurfaces associated with different umbilic lines to merge, create handles, and undergo other topological changes.

The traceless symmetric (spin-2) part of X , $X_0 = X - \frac{1}{2} T_1 \Pi$, is nonzero precisely when $\lambda_1 \neq \lambda_2$. Since, according to Eq. (6), $\|\Delta\|^2 = \frac{1}{2} \text{Tr } (X_0^2)$, formula (13) implies that the umbilic field differs from $\|\Delta\|^2$ only by an irrelevant factor:

$$\Phi = (\lambda_1 - \lambda_2)^2 = 4\|\Delta\|^2. \quad (15)$$

So the zeros of Φ coincide precisely with the umbilic lines defined in the continuum theory. Therefore, our formulation provides a coordinate-free numerical realization of the Machon–Alexander spin-2 invariant.

Though the analytic expression (6) for $\|\Delta\|^2$ is elegant, it is numerically ill-conditioned for the three following reasons:

- (1) It contains a divergence of a quantity already containing derivatives of $\hat{\mathbf{n}}$, hence requires accurate second derivatives on a discrete grid.
- (2) The first two (positive) terms and the divergence term are often of similar magnitude, producing small values of $\|\Delta\|^2$ only by cancellation of large numbers. This magnifies discretization noise precisely near umbilics.
- (3) The divergence is sensitive to boundary conditions, while the tensorial projection method depends only on first derivatives and is well-behaved under periodic or finite difference schemes.

For these reasons, the direct analytic evaluation of (6) is numerically unstable, whereas the projected-symmetric-tensor method provides a robust and gauge-independent alternative.

4. Index of umbilic lines and colorization of umbilic surfaces

A key advantage of the Machon–Alexander framework is that umbilics are not only a geometric diagnostic of three-dimensional textures, but also carry natural *integer-valued* topological data [19]. In their formulation, umbilics are defined as the zeros of the transverse spin-2 tensor Δ , the traceless symmetric part of $\nabla_\perp \hat{\mathbf{n}}$. In a local oriented orthonormal basis $\{\hat{\mathbf{d}}_1, \hat{\mathbf{d}}_2\}$ of the plane $\hat{\mathbf{n}}^\perp$, one may represent

$$\Delta = \begin{pmatrix} \Delta_1 & \Delta_2 \\ \Delta_2 & -\Delta_1 \end{pmatrix} = \|\Delta\| \begin{pmatrix} \cos \theta & \sin \theta \\ \sin \theta & -\cos \theta \end{pmatrix}, \quad \Delta_1 + i\Delta_2 = \|\Delta\| e^{i\theta}, \quad (16)$$

which introduces an angle field θ (defined modulo 2π) away from the umbilic core (Machon–Alexander Eq. (9)). The umbilic index (strength) of a line U through an oriented transverse surface Σ is then the winding of θ around a small loop $C \subset \Sigma$ linking U once:

$$\text{index}_\Sigma(U) = \frac{1}{2\pi} \oint_C d\theta \in \mathbb{Z} \quad (\text{Machon–Alexander Eq. (20)}). \quad (17)$$

In our construction, the symmetric projected gradient X is supported on $\hat{\mathbf{n}}^\perp$, and its traceless part coincides with the Machon–Alexander spin-2 field Δ (up to an overall factor). Consequently, any phase extracted from a complex representative of the traceless part of X yields the same integer index. In particular, in any transverse basis one has

$$a + ib = 2(\Delta_1 + i\Delta_2), \quad \arg(a + ib) = \theta, \quad (18)$$

so counting hue windings around a sufficiently small tubular level surface enclosing the umbilic core reproduces exactly the Machon–Alexander index.

The phase θ is usually introduced by expressing the spin-2 tensor Δ in an oriented orthonormal frame $\{\hat{\mathbf{d}}_1, \hat{\mathbf{d}}_2\}$ of the transverse plane $\hat{\mathbf{n}}^\perp$. To avoid constructing such a frame numerically, we exploit the canonical complex structure on $\hat{\mathbf{n}}^\perp$,

$$J\mathbf{v} := \hat{\mathbf{n}} \times \mathbf{v}, \quad J^2 = -\Pi, \quad (19)$$

and build a *chiral* (spin-1) complex vector directly from a fixed real laboratory vector $\mathbf{t}$. Define

$$\mathbf{m}(\mathbf{r}) := \Pi\mathbf{t} - i\hat{\mathbf{n}} \times (\Pi\mathbf{t}) \in \hat{\mathbf{n}}^\perp \otimes \mathbb{C}. \quad (20)$$

A direct check gives $J\mathbf{m} = i\mathbf{m}$, i.e. $\mathbf{m}$ is a $+i$ eigenvector of J . Therefore, in any local oriented orthonormal frame $\{\hat{\mathbf{d}}_1, \hat{\mathbf{d}}_2\}$ one has

$$\mathbf{m} = \rho e^{i\alpha} (\hat{\mathbf{d}}_1 + i\hat{\mathbf{d}}_2), \quad \rho > 0, \quad (21)$$

for some real angle field α . This simply means that the $+i$ eigenspace of J is one-dimensional over $\mathbb{C}$. We require $\Pi\mathbf{t} \neq 0$, i.e. $\mathbf{t} \nparallel \hat{\mathbf{n}}$ on the region of interest; in practice one may switch between two or three choices of $\mathbf{t}$.

Let $S = c\Pi$ be any isotropic transverse tensor. Then

$$\mathbf{m}^\top S \mathbf{m} = c \mathbf{m}^\top \mathbf{m}. \quad (22)$$

However, $\mathbf{m}$ is a complex null vector:

$$\mathbf{m}^\top \mathbf{m} = (\Pi\mathbf{t}) \cdot (\Pi\mathbf{t}) - (\hat{\mathbf{n}} \times \Pi\mathbf{t}) \cdot (\hat{\mathbf{n}} \times \Pi\mathbf{t}) - 2i(\Pi\mathbf{t}) \cdot (\hat{\mathbf{n}} \times \Pi\mathbf{t}) = 0, \quad (23)$$

since $|\hat{\mathbf{n}} \times (\Pi\mathbf{t})| = |\Pi\mathbf{t}|$ and $(\Pi\mathbf{t}) \perp (\hat{\mathbf{n}} \times \Pi\mathbf{t})$. Therefore, contraction with $\mathbf{m}$ automatically eliminates the isotropic part, so that only the traceless-symmetric (spin-2) component contributes.

We can now define a complex scalar field that encodes the transverse anisotropy together with a phase:

$$\zeta(\mathbf{r}) := \mathbf{m}(\mathbf{r})^\top X(\mathbf{r}) \mathbf{m}(\mathbf{r}). \quad (24)$$

On the transverse plane one has $X = (T_1/2)\Pi + (\text{antisymmetric}) + \Delta$, and the first two terms do not contribute to (24). The isotropic term vanishes by the null property above, while the antisymmetric term vanishes by symmetry of the contraction. Consequently,

$$\zeta = \mathbf{m}^\top \Delta \mathbf{m} = 2\rho^2 (\Delta_1 + i\Delta_2) e^{2i\alpha} = 2\rho^2 \|\Delta\| e^{i(\theta+2\alpha)}. \quad (25)$$

Thus $\arg \zeta = \theta + 2\alpha$. On a small loop linking an umbilic line (if $\Pi t \neq 0$ on the spanning disk) the angle field α is smooth and single-valued, so $\oint d\alpha = 0$ and the winding of $\arg \zeta$ equals the Machon–Alexander index.

For numerical colorization it is convenient to avoid constructing the chiral vector (20) and instead extract a phase from a fixed laboratory projection of X . We introduce two fixed traceless symmetric matrices

$$A_{ij} = \delta_{i1}\delta_{j1} - \delta_{i2}\delta_{j2}, \quad B_{ij} = \delta_{i1}\delta_{j2} + \delta_{i2}\delta_{j1} \quad (26)$$

and define the complex scalar

$$\zeta_{\text{lab}}(\mathbf{r}) := \langle A, X(\mathbf{r}) \rangle + i \langle B, X(\mathbf{r}) \rangle, \quad \langle Y, Z \rangle := \text{Tr}(Y^\top Z). \quad (27)$$

In Cartesian components, this is simply

$$a = X_{11} - X_{22}, \quad b = X_{12} + X_{21}, \quad \zeta_{\text{lab}} = a + ib, \quad (28)$$

and we set

$$\theta_{\text{lab}}(\mathbf{r}) := \arg \zeta_{\text{lab}}(\mathbf{r}). \quad (29)$$

The reason is that, at each point $\mathbf{r}$, the spin-2 field $\Delta(\mathbf{r})$ lives in a two-dimensional real vector space $S(\hat{\mathbf{n}}(\mathbf{r}))$ (traceless symmetric bilinear forms on $\hat{\mathbf{n}}^\perp$). The laboratory map $L(M) := (\langle A, M \rangle, \langle B, M \rangle)$ restricts to a linear map $L|_{S(\hat{\mathbf{n}})} : S(\hat{\mathbf{n}}) \rightarrow \mathbb{R}^2$. A direct calculation shows that this restriction is invertible if and only if $n_z \neq 0$; more precisely,

$$\det(L|_{S(\hat{\mathbf{n}})}) \propto n_z (n_x^2 + n_y^2 + 2n_z^2), \quad (30)$$

so the only degeneracy locus on the unit sphere is the circle $n_z = 0$. Equivalently, if $n_z \neq 0$ then $a = b = 0$ implies $\Delta = 0$.

Therefore, in any region where $n_z \neq 0$, the two numbers (a, b) uniquely specify the local spin-2 tensor (up to an overall scale) and thus define the same phase as (Δ_1, Δ_2) , differing only by a smooth, nonsingular linear mixing. Consequently, for any small loop C linking an umbilic line U and lying in a region where $n_z \neq 0$, the winding of θ_{lab} is equal to the Machon–Alexander umbilic index:

$$\frac{1}{2\pi} \oint_C d\theta_{\text{lab}} = \frac{1}{2\pi} \oint_C d\theta = \text{index}_\Sigma(U), \quad (31)$$

provided $\zeta \neq 0$ on the chosen tubular isosurface (so that θ_{lab} is continuous there). In practice, this condition is enforced by choosing the isosurface away from the degeneracy set $n_z = 0$ and monitoring that $|\zeta_{\text{lab}}|$ does not approach zero on the rendered surface.

If $|\zeta_{\text{lab}}|$ becomes (numerically) small on the rendered tubular surface, so that $\theta = \arg \zeta_{\text{lab}}$ is ill-conditioned, we switch to an alternative laboratory chart obtained by a cyclic permutation of axes. Concretely, we recompute (a, b) using another coordinate pair in the plane orthogonal to $\hat{\mathbf{n}}$:

$$(a_x, b_x) := (X_{22} - X_{33}, X_{23} + X_{32}) \quad (n_x \neq 0), \quad (32)$$

$$(a_y, b_y) := (X_{33} - X_{11}, X_{31} + X_{13}) \quad (n_y \neq 0), \quad (33)$$

and set $\theta := \arg(a + ib)$ using the chart for which $|a + ib|$ stays safely away from zero on the surface. On overlaps where two charts are valid, they are related by a smooth nonsingular linear mixing of the spin-2 components, so the winding index is unchanged provided the integration contour avoids points where $a = b = 0$.

In Sec. 3 we have introduced umbilic level surfaces $\Phi = \text{const}$, which form thin tubes around umbilic lines. These surfaces are more convenient for numerical analysis than the lines themselves; accordingly, they are used in a number of works, including [19, 31] and related studies. Once a phase θ is available in the laboratory frame, we can color the isosurface in a way that makes its topological content immediately visible by mapping θ to the hue of the HSL color scheme,

$$\text{hue}(\mathbf{r}) = \frac{\theta(\mathbf{r})}{2\pi}. \quad (34)$$

This colorization highlights both local structure (winding around individual umbilic cores) and global organization (phase variation along closed umbilic loops) encoded by the umbilic set.

There are two independent integer-valued topological indices introduced in correspondence with ones defined by Machon and Alexander [19] and naturally associated with umbilic lines.

(i) *Transverse index (strength)*. Let $U \subset \Omega$ be an umbilic line and choose a sufficiently small tubular neighbourhood $N_\varepsilon(U)$. Pick a point $p \in U$ and let $D_p \subset N_\varepsilon(U)$ be a small oriented *normal disk* transverse to U at p . Its positively oriented boundary $\gamma := \partial D_p$ is a *meridian* linking U once.

We will use the signed intersection number $\text{Int}(U, \Sigma) \in \mathbb{Z}$ between an oriented curve U and an oriented surface Σ (assumed transverse), defined by

$$\text{Int}(U, \Sigma) := \sum_{x \in U \cap \Sigma} \text{sign}_x(U, \Sigma), \quad (35)$$

where $\text{sign}_x(U, \Sigma) = \pm 1$ is fixed by the orientations of U and Σ as follows: $\text{sign}_x(U, \Sigma) = +1$ if the positively oriented tangent to U at x , together with a positively oriented tangent basis of Σ at x , gives the positive (right-handed) orientation of the ambient domain Ω , and $\text{sign}_x(U, \Sigma) = -1$ otherwise.

Assume that the chosen phase construction (in particular, the laboratory chart used to define θ) is nondegenerate on the meridian γ , so that $d\theta$ is well-defined along γ . We define the *transverse index* of U with respect to the disk D_p by

$$\text{index}_{D_p} U := \frac{1}{2\pi} \oint_{\gamma} d\theta \in \mathbb{Z}, \quad (36)$$

and its *strength* by $s := |\text{index}_{D_p} U| \in \mathbb{N}$. Equivalently, $\text{index}_{D_p} U = s \text{Int}(U, D_p)$. For generic umbilics one finds $s = 1$, whereas higher strengths may occur in axisymmetric textures.

By construction, U intersects the disk fiber D_p once and transversely. To fix orientations, we first consider an oriented tangent $\mathbf{t}$ at p . The meridian $\gamma = \partial D_p$ is then oriented by the following geometric rule: when looking along $\mathbf{t}$ (with $\mathbf{t}$ pointing towards the observer), the positively oriented traversal of γ goes counterclockwise. The orientation of the umbilic line U is then fixed by the condition $\text{index}_{D_p} U > 0$.

The strength s requires only that the laboratory phase construction be nondegenerate in a small neighbourhood of the chosen meridian γ around each intersection point. If such a degeneracy is encountered, one must either switch to an alternative chart or deform the meridian within $N_\varepsilon(U)$ so that $d\theta$ remains well defined.

To connect transverse umbilic indices with the skyrmion number, we now consider an arbitrary oriented surface $\Sigma \subset \Omega$ that is transverse to all umbilic components U_i and such that $\hat{\mathbf{n}}$ is smooth on Σ . Machon and Alexander [19] show that the total transverse winding of umbilics through Σ reproduces the skyrmion number Q of $\hat{\mathbf{n}}$ on Σ , with an additional contribution associated with $\partial\Sigma$ when $\partial\Sigma \neq \emptyset$. In the simplest case when $\partial\Sigma = \emptyset$ (or, more generally, when the boundary contribution vanishes), the relation reduces to

$$\sum_i s_i \text{Int}(U_i, \Sigma) = 4Q. \quad (37)$$

In our setting Σ is typically a planar section whose boundary lies on the boundary of the computational box. Even under homogeneous (Dirichlet) anchoring, the boundary contribution is not generically zero; rather, it can be reinterpreted after compactification. Indeed, if $\hat{\mathbf{n}}$ is fixed on $\partial\Omega$, one may identify all boundary points in order-parameter space and attach a “cap” closing Σ to a topological sphere. The additional intersection required for (37) is then naturally attributed to an *umbilic at infinity*: a contribution supported on (or arbitrarily close to) the boundary and induced by the homogeneous far-field/anchoring condition.

In practice we access this “umbilic at infinity” through umbilic level surfaces (isosurfaces of Δ or Φ), which typically approach the boundary over large areas. The same phase-winding measurement used for interior umbilics can then be performed on these boundary-adjacent portions, providing a direct numerical estimate for the compactification contribution.

(ii) *Longitudinal profile winding.* Let U be a closed umbilic loop and let N_U be a sufficiently small tubular neighbourhood of U (a solid torus) such that the phase field θ is well-defined on $N_U \setminus U$. To quantify how the transverse umbilic profile twists as one goes once around the loop, we integrate the globally defined 1-form $d\theta$ along a *preferred longitude* on the boundary torus ∂N_U .

Choose a simple closed curve $\lambda_0 \subset \partial N_U$ with linking $\text{Lk}(\lambda_0, U) = 0$ that is fixed by a framing of U . For instance, one may take

$$\lambda_0 := \Sigma_U \cap \partial N_U, \quad (38)$$

where Σ_U is an oriented Seifert surface with $\partial\Sigma_U = U$. The orientation of λ_0 is chosen so that λ_0 runs along U in the same direction as the oriented tangent of U , where the orientation of U was fixed in the definition of the transverse index. We then define the *longitudinal profile winding* by

$$k := \frac{1}{2\pi} \oint_{\lambda_0} d\theta \in \mathbb{Z}. \quad (39)$$

The integer k measures how the transverse umbilic profile twists as one goes once around the loop. The choice of λ_0 (equivalently, the framing) matters: replacing λ_0 by $\lambda_0 + m\mu$, where μ is a meridian defined above, changes k by $ms\text{Int}(U, D_p)$, where s is the transverse winding. With the preferred longitude fixed as above, k is a well-defined invariant of the umbilic loop.

In particular, k is related to the self-linking of U once a canonical push-off of U is specified by the transverse profile (i.e. by a choice of framing). It also contributes to the Hopf index of the director field through the usual linking interpretation of the Hopf charge.

Thus, the same phase field θ encodes both transverse and longitudinal invariants, and the hue colorization of umbilic isosurfaces provides a direct visual readout of these windings.

5. Analytical design and soliton relaxation

To access metastable localized states in a frustrated cholesteric cell, it is advantageous to complement direct numerical relaxation with *analytical design* of initial director configurations. In this section we construct analytical director-field configurations (ansatzes) that (i) provide physically interpretable templates for common soliton textures in homeotropic CLC cells and (ii) serve as initial conditions for the energy-minimization procedure described in Sec. 2. This combination is standard in the soliton literature: a well-designed ansatz places the system in the basin of attraction of the desired local minimum, while subsequent relaxation removes any artifacts of the analytical construction and yields a numerically equilibrated texture.

Following [32,33], we begin with simple CLC structures and use these results to construct the ansatzes for cholesteric fingers of different types, as well as the CF1-loop, the toron and the CF2-loop (hopfion). The ansatz parameters used below are chosen to match the representative soliton geometries considered in our simulations and to provide reliable convergence under energy minimization.

We use the following parameters for the toron and CF1-loop ansatzes [32]. For the looped helix as a core part of the toron, the pitch and the tilt angle are $P = 15 \mu\text{m}$ and $\tan \theta = 0.7$. The radius of the toron is $R_1 = 7 \mu\text{m}$. The surface-mask parameters are $d = 1.1 \mu\text{m}$, $p = 2$, and $\kappa = 0.7$. For CF1-loop we take $P = 12 \mu\text{m}$ and $\tan \theta = 0.7$, with inner and outer radii $R_0 = 5 \mu\text{m}$ and $R_1 = 23 \mu\text{m}$; the parameters d , p , and κ are the same as for toron.

For the energy-minimization procedure we use the following parameters [32]: the Frank constants are $K_1 = 10.5 \text{ pN}$, $K_2 = 6.2 \text{ pN}$, and $K_3 = 18.7 \text{ pN}$, the rotational viscosity is $\eta = 203.6 \text{ mPa}\cdot\text{s}$. In the lattice model, the numbers of grid points along the normal and along each lateral direction are 40 and 240, respectively. The cell thickness is $L = 10 \mu\text{m}$, and both lateral sizes of the CLC cell are $L_W = 60 \mu\text{m}$. For the toron the helix pitch is $P_0 = 10.0 \mu\text{m}$, and for CF1-loop it is $P_0 = 9.0 \mu\text{m}$.

We model the CF2-loop following [33]. For the configuration considered here the linked-preimage construction yields Hopf index $Q_H = 1$. We use the following parameters for the hopfion ansatz. The radius R of the finger loop is $50 \mu\text{m}$, and the ansatz parameters are $\alpha_w = 0.2$ and $A = -0.9\pi$. To find a local minimum of the energy (1) for the hopfion we use the following parameters [34,35]: the Frank constants are $K_1 = 10.3 \text{ pN}$, $K_2 = 7.4 \text{ pN}$, and $K_3 = 16.5 \text{ pN}$, the rotational viscosity is $\eta = 203.6 \text{ mPa}\cdot\text{s}$. The helix pitch is $P_0 = 36 \mu\text{m}$. In the lattice model, the numbers of grid points along the normal and along each lateral direction are 50 and 250, respectively. The cell thickness is $L = 33 \mu\text{m}$, and both lateral sizes of the CLC cell are $L_W = 165 \mu\text{m}$.

6. Visualization of topological solitons by the umbilic-lines approach

We now apply the umbilic-lines framework to representative localized structures in homeotropic cholesteric cells. We compare the relaxed configuration obtained by energy minimization and the corresponding analytical ansatz, and then interpret the umbilic set in terms of the transverse strength s and the longitudinal winding k introduced in Sec. 4. This provides a compact description of the soliton topology that complements more traditional visualizations based on director cross-sections and isolines.

Fig. 1 shows the director field (panels a and c) and the corresponding umbilic structures visualized as isosurfaces of ε (panels b and d) for the toron. Panels a and b correspond to the relaxed configuration obtained by energy minimization, whereas panels c and d show the analytical ansatz. The toron ansatz reproduces the main characteristics of the relaxed toron well. In particular, the texture contains two hyperbolic point defects and a $+1$ disclination ring. The dotted lines indicate the regions associated with the disclination ring. In panels b and d, the umbilic set consists of a fusiform tube connecting the point defects in the center and a closed loop corresponding to the disclination ring. The strength of the fusiform tube is $s = 2$, since each hue appears twice on a cross-section of the tube. For the loop, the strength is $s = 1$ and the longitudinal winding number is $k = 2$. The loop has a very small extent in the z direction, on the order of one or two lattice constants; therefore, determining its transverse index s is challenging at the given numerical resolution.

Consider a toron embedded in a uniform far field, and a planar section $\Sigma = \{y = y_0\}$ chosen such that it contains no singular points where the director is ill-defined. Since $\hat{n}|_\Sigma$ approaches a constant (the far-field direction) at large in-plane distances, the section can be compactified by a point at infinity and defines a map $\Sigma \simeq S^2 \rightarrow S^2$ (after a continuous choice of the $\hat{n} \sim -\hat{n}$ lifting on the section, when needed). The skyrmion number

$$Q = \frac{1}{4\pi} \int_\Sigma \hat{n} \cdot (\partial_x \hat{n} \times \partial_z \hat{n}) dx dz \quad (40)$$

is therefore well defined and integer-valued on such sections. Moreover, Q cannot change under a continuous translation of the section parameter y_0 unless the section crosses a genuine singularity (e.g., a point defect core) or the far-field boundary condition changes. Hence Q is constant for all admissible sections and, in particular, equals the value on a plane placed far from the soliton, where the director is uniform; therefore $Q = 0$ for any section Σ not intersecting singular cores.

The same conclusion follows from the Machon–Alexander relation between skyrmion number and umbilic intersections. For a compactified section Σ on which the spin-2 field is well defined away from umbilics, the weighted intersection sum satisfies (37). In the toron geometry the closed ring umbilic intersects Σ in two points with opposite intersection signs,

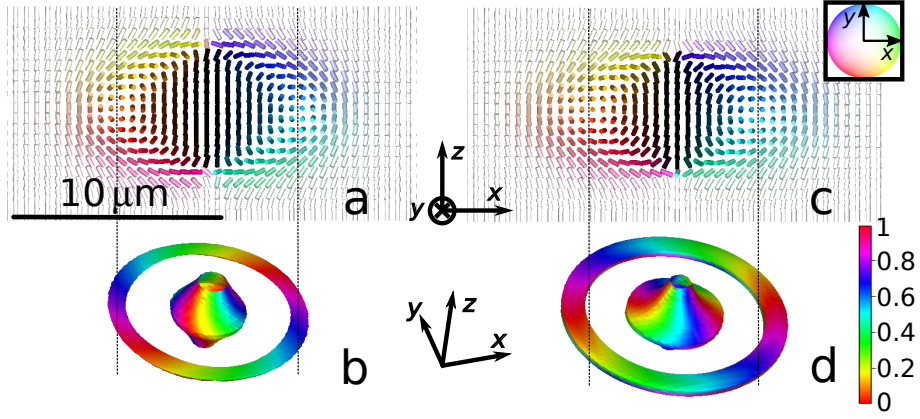


FIG. 1. Umbilic surfaces in torons. Director fields (a and c) and isosurfaces for ε (b and d) for the toron structure: a and c – director field distributions in the xz plane (the middle cross-section of the cell at $y = 0$). The color palette in the inset describes the x and y projections of the director used in a and c. This color wheel represents the northern hemisphere of director orientations where n_z is non-negative. In the southern hemisphere, the colors become darker as n_z decreases approaching the southern pole with $n_z = -1$. a – the structure obtained by the energy minimization, c – ansatz for toron. b – umbilic surfaces (isosurfaces for ε), $\varepsilon = -2.64$, d – umbilic surfaces for ansatz, $\varepsilon = -3.4$. The color bar shows the coloring method according to Eq. (34).

so its net contribution to the sum vanishes. In addition, there exists an umbilic line that closes through the far field (equivalently, through the compactification point at infinity); for any generic section Σ it also intersects the plane in two points with opposite signs, and therefore contributes zero net intersection number. Consequently, the total weighted intersection sum vanishes and the Machon–Alexander formula again yields $Q = 0$, consistent with the homotopy argument above.

Fig. 2 shows the results for the simulated CF1-loop structure obtained from the lattice model. This texture contains only smooth director deformations. The simulated CF1-loop configuration is characterized by continuous isolines forming closed loops. These isolines are not linked, indicating a trivial Hopf index $Q_H = 0$. The skyrmion number is also zero, $Q = 0$.

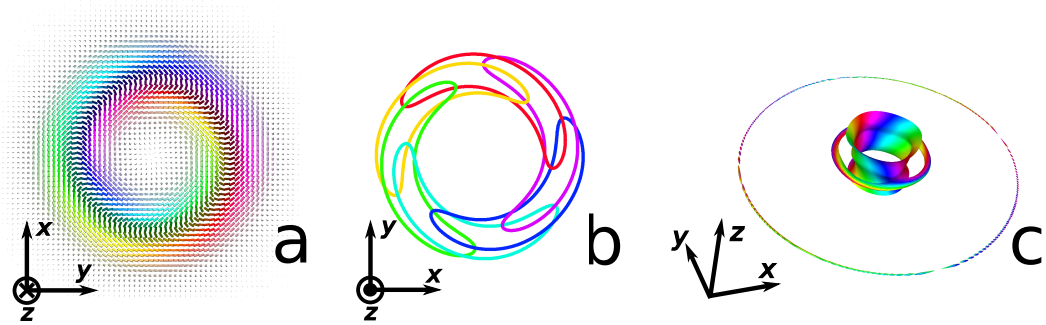


FIG. 2. Umbilic surfaces in the CF1-loop structure. a – director distribution in the xy plane (the middle cross-section of the cell at $z = 0$). b – isolines for the z projection of the director in the xy plane. c – umbilic surfaces for $\varepsilon = -4.2$. The color wheel and the color bar are the same as in Fig. 1.

The umbilic set consists of a broad central tube and two additional loops. The presence of the central tube indicates that the director field in the core region of CF1-loop is nearly homogeneous. In contrast to the toron, the tube here is wide, suggesting an extended region of quasi-uniform director field. The strength of the tube is $s = 2$, since each hue appears twice on a cross-section of the tube. Each of the two loops has strength $s = 1$ and longitudinal winding number $k = 2$. For the CF1-loop structure, there is no point defects. If we again pull the boundary to a point, the central tube transforms to a closed loop without any defects. It means that for the cross-section by the plane $\Sigma = \{z = z_0\}$ the closed loop formed by the central tube intersects the plane Σ twice. In each intersection the strength $s = 2$, but due to the orientation of this umbilic surface the transverse indices $\text{index}_{D_p} U$ in intersections have opposite signs. So the closed to infinity central tube gives zero input to the left hand side of Eq. (37). It means that $Q = 0$ for this cross-section of the CF1-loop. Note, that we should not consider here the cross section Σ with $z = 0$ as in this plane the Machon–Alexander formula (37) is not applicable.

This example highlights the importance of accounting for “infinitely remote” umbilics (or, in a finite simulation box, umbilic sets supported near the domain boundary) when using umbilic-intersection formulas to compute the skyrmion index. If one were to keep only the “central” tubular component while ignoring the boundary-supported continuation required by the uniform far field, the weighted intersection sum would generally produce a spurious nonzero value for Q , in contradiction with the homotopy argument and with the direct evaluation of Eq. (37). In a finite computational domain, the “umbilic at infinity” is represented by an extended, smeared umbilic surface (or tube) distributed along the boundary region where the spin-2 field becomes ill-conditioned, and its intersections are essential for the cancellation of the total signed intersection number.

Fig. 3 illustrates how the umbilic set evolves as the isovalue is varied. At low ε the umbilic structure appears as two thin tubes, while at higher ε it becomes two loops. The petal-like features at the edges of panel e are artifacts caused by the finite sample boundary and can be ignored. In panel f, each loop has longitudinal winding number $k = 2$ and the strength $s = 1$. As ε is increased further, the isosurfaces begin to merge and the associated topological features can no longer be cleanly assigned to individual components. This behavior is typical in practical visualization: sufficiently small ε isolates individual umbilic cores, while larger ε probes a coarser, more “global” organization of the texture.

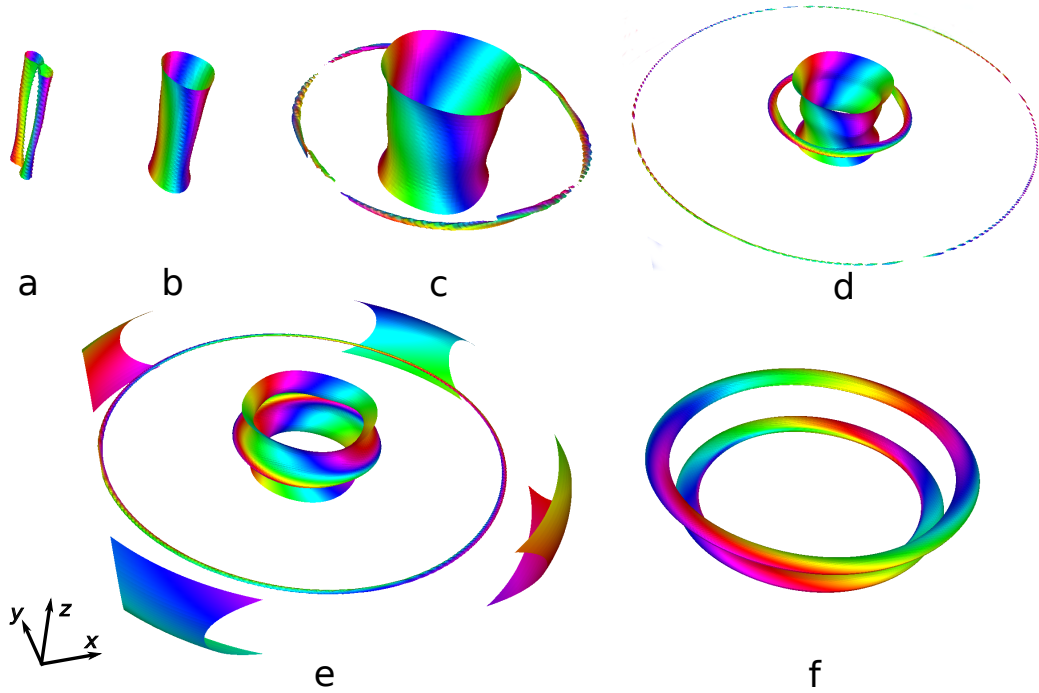


FIG. 3. Umbilic surfaces in the CF1-loop structure. Isosurfaces for different values of ε : a, b, c, d, e, f are umbilic surfaces at $\varepsilon = -7.5$, $\varepsilon = -6.5$, $\varepsilon = -4.85$, $\varepsilon = -4.2$, $\varepsilon = -3.6$, $\varepsilon = -0.65$. The scale in panels a, b and c is doubled. The color bar is the same as in Fig. 1.

Using Fig. 4 we analyze the topological features of the CF2-loop obtained by energy minimization. The relaxed configuration is characterized by looped and linked isolines (Fig. 4b, c). Depending on the director-field structure, the isolines can be linked with different handedness; in our case $Q_H = 1$. The hopfion also contains two disclination lines.

The umbilic set resembles that of CF1-loop: we again observe a wide central tube and two loops. The central tube for the CF2-loop is similar to one for the CF1-loop. However, the associated indices for two loops are different from the same loops in the CF1-loop. On Fig. 4d–f one can see that the hues progress of the inner and outer umbilic loops are different. It means that both umbilic loops for any plane Σ has the strength $s = 1$, but due to different orientation the transverse indices $\text{index}_{D_p} U$ in intersections have opposite signs. Different orientation of the inner and outer umbilic loops gives the different direction of traversal in Eq. (39) when calculating the indices k . It gives $k = 2$ for the inner umbilic loop and $k = -2$ for the outer umbilic loop.

In the case of CF2-loop, we can see that two topological indices are related because the orientation of the umbilic line introduced for transverse index determines the direction of traversal for longitudinal winding. If one aims to resolve or compare different topological structures, the umbilic-surface representation provides additional discriminating information, since it exposes not only the presence of closed umbilic loops but also their transverse indices and longitudinal windings.

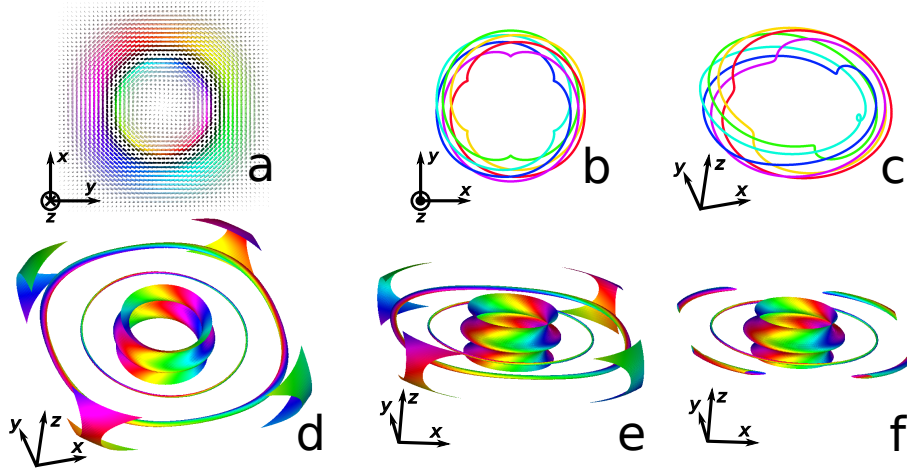


FIG. 4. Umbilic surfaces in the CF2-loop. a – director distribution in the xy plane (the middle cross-section of the cell at $z = 0$). b and c – isolines for the z projection of the director in the xy plane and from another viewpoint. d, e, and f – umbilic-surface representation with $\varepsilon = -3.4$. Panel f shows a cross-section of the isosurfaces from panel e. The color wheel and the color bar are the same as in Fig. 1.

7. Discussion

The overall motivation for using umbilics is that they offer a compressed representation of a three-dimensional director field. The proposed characterization of umbilics in terms of longitudinal and transverse charges makes it possible to avoid a detailed inspection of the full three-dimensional director field while still extracting topological information about the texture and its cross-sections. In particular, the transverse winding of the phase captures the local strength of each umbilic line, while the longitudinal winding along a closed umbilic loop captures a distinct invariant linked to the three-dimensional soliton topology. Taken together, these two integers provide a compact descriptor that connects directly to familiar global charges such as the skyrmion number.

The practical limitation in analyzing topological features is set by lattice resolution. The proposed color scheme is defined on the discrete grid: effectively, only one hue is assigned per lattice spacing. If the number of lattice points is insufficient—for instance, near highly localized structures or near singular regions—reliable extraction of the winding becomes difficult. In such cases the resolution must be increased. This is straightforward when working with analytical ansatzes, whereas in full numerical minimization increasing the number of nodes inevitably makes the search for equilibrium configurations more computationally expensive. In practice, this motivates using umbilic surfaces both as a visualization tool and as a diagnostic of whether the chosen discretization is adequate for robust topological readout.

We have considered, following Machon and Alexander [19], umbilic lines and their topological indices using the director field. However, a more accurate description of topological structures can be obtained by considering the tensor order parameter. It is of interest to generalize the Machon and Alexander umbilic lines analysis starting from the tensor order parameter.

Note that umbilics and disclination lines represent different types of line objects. A disclination line is associated with a breakdown of orientational order, typically via a singularity or a vanishing order parameter. In contrast, an umbilic is a region in which the transverse gradients of the director are isotropic: it is defined by a degeneracy of the transverse “principal curvatures” rather than by a loss of order. In some cases these objects can coincide. For example, for a λ disclination line (e.g., $\lambda^{1/2}$), sufficiently close to the line the orientational structure becomes independent of direction and depends only on the distance to the line, which is precisely the umbilic condition. This coincidence of λ -type disclination lines with umbilics follows from the symmetry structure of the elastic energy (1). Conversely, the presence of an umbilic does not imply a defect or a loss of order. In the degenerate case of a completely homogeneous director configuration, the entire region is umbilic, yet no disclination lines are present. In this sense, an umbilic can be viewed as a generalized disclination concept that also admits a zero charge.

Accurate localization of umbilics is challenging because it amounts to finding the zeros of a scalar field with high precision. Instead, one can vary the parameter ε in Eq. (14) and construct isosurfaces for successive values of ε , effectively foliating the domain by a family of level sets. The topological charges can then be evaluated on each surface. If a surface encloses an umbilic line, it must carry the same charges as that line. For sufficiently large ε , distinct isosurfaces begin to merge; the charges of the merged components combine accordingly, both longitudinally and transversely. Analyzing the charges of isosurfaces at larger ε may therefore provide additional information about soliton structure and can simplify the computation of topological charges for specific textures. More broadly, viewing umbilics through the evolution of

ε -level sets provides a convenient multiscale perspective: small ε isolates individual umbilic cores, while larger ε probes how these cores assemble into the global geometry of a three-dimensional soliton.

8. Conclusion

In this paper, we have developed the numerically robust modification of the umbilic-lines approach that provides a useful framework for analyzing three-dimensional topological structures in liquid crystals, magnets, and other anisotropic media supporting topological solitons. Our method yields a stable numerical realization of the Machon-Alexander umbilic invariant that is tailored to high-resolution three-dimensional simulations. It is based on the projector-symmetrization construction that defines the umbilic scalar field (13) whose near-vanishing identifies umbilic cores. The associated complex structure (18) is found to produce a natural phase field whose windings recover the two fundamental integer charges. The modified method requires only first derivatives, involves no gauge choice, and is, therefore, ideally suited for high-resolution three-dimensional computations of umbilic geometry in realistic simulated textures. We have demonstrated the efficiency of the method by using it to visualize the three topologically nontrivial structures: the toron, the cholesteric finger loop of the first type, and the cholesteric finger loop of the second type.

References

- [1] Kleman M., Lavrentovich O.D. *Soft matter physics: an introduction*. Springer, New York, 2003.
- [2] Chen B.G.G., Ackerman P.J., Alexander G.P., Kamien R.D., Smalyukh I.I. Generating the Hopf fibration experimentally in nematic liquid crystals. *Phys. Rev. Lett.*, 2013, **110**, P. 237801.
- [3] Ackerman P.J., Smalyukh I.I. Diversity of knot solitons in liquid crystals manifested by linking of preimages in torons and hopfions. *Phys. Rev. X*, 2017, **7**, P. 011006.
- [4] Oswald P., Baudry J., Pirkel S. Static and properties of cholesteric fingers in electric field. *Physics Reports*, 2000, **337**, P. 67.
- [5] Ackerman P.J., Trivedi R. P., Senyuk B., van de Lagemaat J., Smalyukh I.I. Two-dimensional skyrmions and other soliton structures in confinement-frustrated chiral nematics. *Phys. Rev. E*, 2014, **90**, P. 012505.
- [6] Afghah S., Selinger J.V. Theory of helicoids and skyrmions in confined cholesteric liquid crystals. *Phys. Rev. E*, 2017, **96**, P. 012708.
- [7] Durey G., Sohn H.R.O., Ackerman P.J., Brasselet E., Smalyukh I.I., Lopez-Leon T. Topological solitons, cholesteric fingers and singular defect lines in Janus liquid crystal shells. *Soft Matter*, 2020, **16**(11), P. 2669–2682.
- [8] Smalyukh I.I. Knots and other new topological effects in liquid crystals and colloids, *Rep. Prog. Phys.*, 2020, **83**, P. 106601.
- [9] Wu J.-S., Smalyukh I.I. Hopfions, heliknotons, skyrmions, torons and both abelian and nonabelian vortices in chiral liquid crystals. *Liquid Crystals Reviews*, 2022, **10**(1-2), P. 34.
- [10] Tambovtsev I.M., Leonov A.O., Lobanov I.S., Kiselev A.D., Uzdin V.M. Topological structures in chiral media: effects of confined geometry. *Phys. Rev. E*, 2022, **105**, P. 034701.
- [11] Hamdi R., Petriashvili G., Lombardo G., De Santo M.P., Barberi R. Liquid crystal bubbles forming a tunable micro-lenses array. *J. Appl. Phys.*, 2011, **110**, P. 074902.
- [12] Yang B., Brasselet E. Arbitrary vortex arrays realized from optical winding of frustrated chiral liquid crystals. *J. Opt.*, 2013, **15**, P. 044021.
- [13] Hess A.J., Poy G., Tai J.S.B., Žumer S., Smalyukh I.I. Control of light by topological solitons in soft chiral birefringent media. *Phys. Rev. X*, 2020, **10**, P. 031042.
- [14] Ackerman P.J., Qi Z., Smalyukh I.I. Optical generation of crystalline, quasicrystalline, and arbitrary arrays of torons in confined cholesteric liquid crystals for patterning of optical vortices in laser beams. *Phys. Rev. E*, 2012, **86**, P. 021703.
- [15] Nagaosa N., Tokura Y., Topological properties and dynamics of magnetic skyrmions. *Nat. Nanotechnol.*, 2013, **8**, P. 899–911.
- [16] Lobanov I.S., Uzdin V.M. Lifetime, collapse, and escape paths for hopfions in bulk magnets with competing exchange interactions. *Phys. Rev. B*, 2023, **107**, P. 104405.
- [17] Chichay K.A., Lobanov I.S., Uzdin V.M. The structure of magnetic domain walls in cylindrical nano- and microwires with inhomogeneous anisotropy. *Nanosystems: Phys. Chem. Math.*, 2024, **15**(1), P. 55–59.
- [18] Chichay K.A., Lobanov I.S., Uzdin V.M. Magnetic structure of domain walls in stressed cylindrical wires. *Nanosystems: Phys. Chem. Math.*, 2025, **16**(3), P. 325–332.
- [19] Machon T., Alexander G.P. Umbilic lines in orientational order. *Phys. Rev. X*, 2016, **6**(1), P. 011033.
- [20] Selinger J.V. Interpretation of saddle-splay and the Oseen-Frank free energy in liquid crystals. *Liquid Crystals Reviews*, 2018, **6**(2), P. 129.
- [21] Tai J.-S.B., Ackerman P.J., Smalyukh I.I. Topological transformations of Hopf solitons in chiral ferromagnets and liquid crystals. *Proc. Natl. Acad. Sci.*, 2018, **115**(5), P. 921–926.
- [22] Tai J.-S.B., Wu J.-S., Smalyukh I.I. Geometric transformation and three-dimensional hopping of Hopf solitons. *Nat. Commun.*, 2022, **13**(1), P. 2986.
- [23] Foster D., Kind C., Ackerman P.J., Tai J.-S.B., Dennis M.R., Smalyukh I.I. Two-dimensional skyrmion bags in liquid crystals and ferromagnets. *Nat. Phys.*, 2019, **15** (7), P. 655–659.
- [24] Varanytsia A., Posnjak G., Mur U., Joshi V., Darrah K., Mušević I., Čopar S., Chien L.-C. Topology-commanded optical properties of bistable electric-field-induced torons in cholesteric bubble domains. *Sci. Rep.*, 2017, **7**(1), P. 16149.
- [25] Pirkel S., Ribière P., Oswald P. Forming process and stability of bubble domains in dielectrically positive cholesteric liquid crystals. *Liq. Cryst.*, 1993, **13** (3), P. 413–425.
- [26] Trivedi R.P., Lee T., Bertness K.A., Smalyukh I.I. Three dimensional optical manipulation and structural imaging of soft materials by use of laser tweezers and multimodal nonlinear microscopy. *Opt. Express*, 2010, **18**, P. 27658–27669.
- [27] Shen Y., Dierking I. Electrically driven formation and dynamics of skyrmionic solitons in chiral nematics. *Phys. Rev. Appl.*, 2021, **15**, P. 054023.
- [28] de Gennes P.G., Prost J. *The Physics of Liquid Crystals*. Clarendon Press, Oxford, 1993.
- [29] Ravník M., Žumer S. Landau-de Gennes modelling of nematic liquid crystal colloids. *Liq. Cryst.*, 2009, **36**, P. 1201–1214.
- [30] LCSim, 2021–2026, <https://gitlab.com/alepoydes/lcsim>.
- [31] Pollard J., Posnjak G., Čopar S., Mušević I. and Alexander G.P. Point defects, topological chirality, and singularity theory in cholesteric liquid-crystal droplets. *Phys. Rev. X*, 2019, **9**, P. 021004.

- [32] Lobanov I., Aksenova E., Orlova T., Darmoroz D., Uzdin V., Kiselev A.D. Optical imaging and analytical design of localized topological structures in chiral liquid crystals. *Symmetry*, 2022, **14**(12), P. 2476.
- [33] Shvetsov S.A., Darmoroz D.D., Vasil'ev A., Orlova T., Lobanov I.S., Rafayelyan M. Light-induced isotropic pen for generation of topological solitons and hopfion–toron transition in frustrated chiral nematic films. *Chaos, Solitons & Fractals*, 2025, **199**(3), P. 116905.
- [34] Strömer J.F., Raynes E.P. Study of elastic constant ratios in nematic liquid crystals. *Appl. Phys. Lett.*, 2006, **88**, P. 051915.
- [35] Bennett T., Proctor M., Kaczmarek M., D'Alessandro G. Lifting degeneracy in nematic liquid crystal viscosities with a single optical measurement. *J. Colloid Interface Sci.*, 2017, **497**, P. 201–206.

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The first example of synthesis Au-nanoparticles with amidine derivatives of *closo*-decaborate anion as stabilizing ligand

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ABSTRACT In this work, we report the one-pot aqueous synthesis of AuNPs using novel amidine derivatives of the *closo*-decaborate anion, functionalized with pendant thiol groups, as combined reducing and stabilizing agents. A comprehensive characterization using transmission electron microscopy (TEM) revealed the formation of nanoparticles with a distinctive and unusual hollow-core/dense-shell architecture, where a gold-rich shell encapsulates a low-Z element core. This unique morphology accounts for the observed absence of a characteristic surface plasmon resonance (SPR) band in the UV-Vis spectra, distinguishing these materials from classical solid-core AuNPs. X-ray photoelectron spectroscopy (XPS) confirmed the covalent attachment of the ligands via Au-S bonds and the integrity of the boron cage on the nanoparticle surface. The synthesis was optimized, establishing a 1:6 (Au:Ligand) molar ratio as ideal for achieving a narrow particle size distribution.

KEYWORDS boron cluster anion, *closo*-decaborate, amidine, cysteamine, gold nanoparticles

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1. Introduction

Gold nanoparticles (AuNPs) have garnered significant attention across diverse fields of modern research due to their unique physicochemical properties. Their biocompatibility, tunable optical characteristics, and ease of surface functionalization open vast possibilities for applications in medicine, biotechnology, and materials science. AuNPs are increasingly utilized for the detection and imaging of biomolecules, proteins, and nucleic acids at cellular and molecular levels [1], as well as for drug delivery [2] and as antioxidants [3].

The synthesis method critically determines the size, shape, and subsequently, the unique properties of the obtained nanomaterials [4, 5]. For instance, AuNPs smaller than 2 nm exhibit significant cytotoxicity due to nuclear penetration, whereas particles ranging from 15 to 30 nm are capable of permeating capillaries and tumor tissues [6]. Particle shape also dictates functionality; for example, gold nanospheres are preferred in diagnostics and drug delivery due to their structural consistency [7].

A particularly promising area of research involves the creation of conjugates between gold nanoparticles and boron clusters [8]. Boron cluster anions $[B_nH_n]^{2-}$ ($n = 10, 12$) possess essential properties such as high thermal stability, low toxicity, and a robust polyhedral framework, making them attractive for bio-applications, including biosensors and energy storage devices [9, 10]. A key application is Boron Neutron Capture Therapy (BNCT), a binary radiotherapeutic modality for treating locally aggressive tumors like gliomas and chordomas [11–14]. The efficacy of BNCT relies heavily on the selective accumulation of the non-radioactive boron-10 isotope in tumor cells. Consequently, the development of delivery agents that ensure high tumor-to-normal tissue ratios is of paramount importance.

Currently, the electrophile-induced nucleophilic substitution (EINS) of the $[B_{10}H_{10}]^{2-}$ anion is a well-established method for obtaining derivatives with a wide spectrum of functional groups [15, 16]. These derivatives can serve as stabilizing ligands for AuNPs, forming a monolayer with a specific chemical composition on the gold surface [17]. For example, recent studies reported AuNPs functionalized with polyethylene glycol thiols and inorganic cobalt bis(dicarbollide) derivatives, which showed high *in vivo* stability but limited tumor selectivity [18].

In this work, we report the synthesis of gold nanoparticles stabilized by novel amidine derivatives of the *closo*-decaborate anion containing pendant thiol groups. We investigate the synthesis of the ligand systems via nucleophilic addition of cysteamine to nitrilium derivatives of $[B_{10}H_{10}]^{2-}$ and explore the formation of AuNPs. A notable feature of the obtained nanoparticles is the absence of a characteristic surface plasmon resonance (SPR) band, which distinguishes them from classical citrate- or thiol-stabilized gold colloids. The structural features, morphology, and chemical composition of the hybrid nanomaterials are discussed in detail.

2. Experimental

2.1. Methods

2.1.1. IR spectra were recorded on an FT-08 Infracum infrared spectrometer in the range of $4000 - 600\text{ cm}^{-1}$ with a resolution of 1 cm^{-1} . Samples were prepared as KBr pellets.

2.1.2. 1H , $^{13}C\{^1H\}$, $^{11}B\{^1H\}$ NMR spectra of solutions in CD_3CN were recorded on a q-ONE AS400 Quantum I Plus spectrometer at frequencies of 399.879, 161.874, 128.297 MHz, respectively, with internal deuterium stabilization. TMS and $BF_3 \cdot OEt_2$ were used as external standards, respectively.

2.1.3. High-resolution mass spectra were recorded on a LCMS-9030 device (Shimadzu, Japan) by electrospray ionization mass spectrometry (ESI-MS). Measurements were carried out in negative and positive ion mode; samples were dissolved in acetonitrile and injected into the mass-spectrometer chamber from an HPLC system LC-40 Nexera (Shimadzu, Japan). The following parameters were used: capillary voltage -3.0 kV (4 kV for positive ions); mass scanning range: $m/z\ 50 - 1000$; external calibration with solution NaI in $MeOH/H_2O$; drying and heating gases (nitrogen) (each 10 L/min); nebulizing gas (nitrogen) (3 L/min); interface temperature: $250\text{ }^\circ\text{C}$; flow rate 100% acetonitrile or $(50:50\text{ (v/v)})$ acetonitrile/water 0.4 mL/min . Molecular ions in the spectra were analyzed and matched with the appropriately calculated m/z and isotopic profiles in the LabSolutions v.5.114 program.

2.1.4. Dynamic light scattering (DLS) and ζ -potential measurements were carried out at $20\text{ }^\circ\text{C}$, using a Photocor Compact-Z analyser (Photocor, Moscow, Russia) equipped with a 636.65 nm laser. The correlation function for each sample was obtained by averaging ten curves, each being acquired for 20 s . The hydrodynamic diameter of aggregates was determined using DynaLS software (Moscow, Russia).

2.1.5. Scanning electron microscopy (SEM) and scanning transmission electron microscopy (STEM) images were taken using a Tescan Amber GMH scanning electron microscope. STEM images were acquired using a R-STEM detector at magnifications of $\times 200,000 - 900,000$ with an accelerating voltage of 30 kV . To obtain STEM images, sols were dropped on a copper grid coated with formvar and dried at room temperature overnight. SEM images were obtained using an Everhart-Thornley detector at an accelerating voltage of 1 kV . To obtain SEM images, sols were dropped on the carbon tape and dried at room temperature overnight.

2.1.6. The XPS measurements were performed using a "PREVAC EA15" electron spectrometer. In the current work, $AlK\alpha$ ($h\nu = 1486.6\text{ eV}$, 150 W) were used as a primary radiation source. The pressure in analytical chamber did not exceed $5 \cdot 10^{-9}\text{ mbar}$ during spectra acquisition. The binding energy (BE) scale was pre-calibrated using the positions of $Ag3d5/2$ (368.3 eV) from silver foils. Samples in the form of a suspension of colloidal particles after dialysis were supported to the holder. To take into account the effect of surface charging, the C1s at ($E_b = 284.8\text{ eV}$) from the carbon was used as an internal standard.

2.2. Synthetic protocols

2-Aminoethanethiol (ABCR, 98%), $H[AuCl_4] \cdot (H_2O)_n$ (Acros Organic), $Na[BPh_4]$ (ABCR, 98%) were used without additional purification. All solvents were purified according to the literature method [19]. Nitrilium derivatives of *closo*-decaborate anion ($Bu_4N[2-B_{10}H_9NCR]$ ($R = Et$ [20], nPr [20], iPr [20])) were synthesized by known procedures.

2.2.1. General procedure for the synthesis of amidine derivatives ($Bu_4N[2-B_{10}H_9NH=C(NHC_2H_4SH)R]$ ($R = Et$ (4), nPr (5), iPr (6)). A mixture of the corresponding nitrilium derivative 1–3 (1.0 mmol) and cysteamine (304 mg , 2.0 mmol) was dissolved in methanol (10 mL). The reaction mixture was stirred under a dry argon atmosphere for 30 min and then concentrated on a rotary evaporator. The residue was dissolved in CH_2Cl_2 (5 mL) and washed successively with aqueous hydrazine hydrate solution and distilled water until neutral pH. The organic phase was dried over anhydrous Na_2SO_4 , filtered, and concentrated to dryness.

2.2.2. $(\text{Bu}_4\text{N})[2\text{-B}_{10}\text{H}_9\text{NH}=\text{C}(\text{Et})\text{NHC}_2\text{H}_4\text{SH}]$ (4). IR (KBr, cm^{-1}): 3425, 3296, 3233 ν (N–H), 2475 ν (B–H), 1636 ν (C=N). $^{11}\text{B}\{^1\text{H}\}$ -NMR (CD_3CN) δ (ppm): 1.6 (s, 1B, B(10)), –5.9 (s, 1B, B(1)), –16.5 (s, 1B, B(2)), –25.2 (s, 4B, B(3,5,6,7)), –28.2 (s, 3B, B(4,8,9)). ^1H NMR (CD_3CN) δ (ppm): 8.43 (br.s., 1H, NH–C), 6.37 (br.s., 1H, NH=C), 3.68 (m, 2H, N–CH₂CH₂SH), 3.31 (8H, Bu₄N), 3.00 (t, 2H, N–CH₂CH₂SH, 7 Hz), 2.41 (q, 2H, CH₂CH₃, 8 Hz), 1.70 (8H, Bu₄N), 1.33 (8H, Bu₄N), 1.01 (t, 3H, CH₂CH₃, 8 Hz), 0.87 (12H, Bu₄N). ^{13}C NMR (CD_3CN) δ (ppm): 169.8 (NH=C–CH₂CH₃), 58.6 (Bu₄N), 41.8 (NCH₂CH₂SH), 37.5 (NCH₂CH₂SH), 24.9 (NH=C–CH₂CH₃), 23.9 (Bu₄N), 19.7 (Bu₄N), 13.2 (Bu₄N), 10.3 (NH=C–CH₂CH₃). HRMS(ESI) m/z : 248.2336 (found for $[(\text{B}_{10}\text{H}_9\text{NHC}(\text{C}_2\text{H}_5)\text{NH}_2\text{C}_2\text{H}_4\text{S})_2]^{2-}$, calculated for $[\text{A}]^{2-}$ 248.2351).

2.2.3. $(\text{Bu}_4\text{N})[2\text{-B}_{10}\text{H}_9\text{NH}=\text{C}(\textit{i}Pr)\text{NHC}_2\text{H}_4\text{SH}]$ (5). IR (KBr, cm^{-1}): 3415, 3296, 3233 ν (N–H), 2478 ν (B–H), 1632 ν (C=N). $^{11}\text{B}\{^1\text{H}\}$ NMR (CD_3CN) δ (ppm): 1.1 (s, 1B, B(10)), –6.1 (s, 1B, B(1)), –17.0 (s, 1B, B(2)), –25.7 (s, 4B, B(3,5,6,7)), –28.7 (s, 3B, B(4,8,9)). ^1H NMR (CD_3CN) δ (ppm): 8.43 (br.s., 1H, NH–C), 6.13 (br.s., 1H, NH=C), 3.67 (m, 2H, N–CH₂CH₂SH), 3.08 + 3.01 (m, 10H, Bu₄N + N–CH₂CH₂SH), 2.28 (q, 2H, CH₂CH₂CH₃, 8 Hz), 1.59 (8H, Bu₄N), 1.48 (m, 2H, CH₂CH₂CH₃), 1.36 (8H, Bu₄N), 0.96 (12H, Bu₄N), 0.89 (t, 3H, CH₂CH₂CH₃, 8 Hz). ^{13}C NMR (CD_3CN) δ (ppm): 167.8 (NH=C–CH₃), 59.2 (Bu₄N), 42.6 (NCH₂CH₂SH), 40.1 (NCH₂CH₂SH), 25.5 (NH=C–CH₂CH₂CH₃), 24.2 (Bu₄N), 20.7 (NH=C–CH₂CH₂CH₃), 20.1 (Bu₄N), 13.7 (Bu₄N), 13.5 (NH=C–CH₂CH₂CH₃). HRMS(ESI) m/z : 262.2523 (found for $[(\text{B}_{10}\text{H}_9\text{NHC}(\text{C}_3\text{H}_7)\text{NH}_2\text{C}_2\text{H}_4\text{S})_2]^{2-}$, calculated for $[\text{A}]^{2-}$ 262.2507); 264.2546 (found for $[\text{B}_{10}\text{H}_9\text{NHC}(\text{C}_3\text{H}_7)\text{NH}_2\text{C}_2\text{H}_4\text{SH}]^{1-}$, calculated for $[\text{A}]^{1-}$ 264.2549).

2.2.4. $(\text{Bu}_4\text{N})[2\text{-B}_{10}\text{H}_9\text{NH}=\text{C}(\textit{i}Pr)\text{NHC}_2\text{H}_4\text{SH}]$ (6). IR (KBr, cm^{-1}): 3420, 3292, 3235 ν (N–H), 2501 ν (B–H), 1640 ν (C=N). $^{11}\text{B}\{^1\text{H}\}$ NMR (CD_3CN) δ (ppm): 1.1 (s, 1B, B(10)), –6.1 (s, 1B, B(1)), –16.4 (s, 1B, B(2)), –25.5 (s, 4B, B(3,5,6,7)), –28.6 (s, 3B, B(4,8,9)). ^1H NMR (CD_3CN) δ (ppm): 8.48 (br.s., 1H, NH–C), 5.72 (br.s., 1H, NH=C), 3.74 (m, 2H, N–CH₂CH₂SH), 3.09 + 3.03 (m, 10H, Bu₄N + N–CH₂CH₂SH), 2.89 (m, 1H, CH(CH₃)₂), 1.60 (8H, Bu₄N), 1.35 (8H, Bu₄N), 1.04 (d, 6H, CH(CH₃)₂, 7 Hz), 0.96 (12H, Bu₄N). ^{13}C NMR (CD_3CN) δ (ppm): 173.0 (NH=C–CH₃), 59.2 (Bu₄N), 42.0 (NCH₂CH₂SH), 38.4 (NCH₂CH₂SH), 29.2 (NH=C–CH(CH₃)₂), 24.2 (Bu₄N), 20.2 (Bu₄N), 19.2 (NH=C–CH(CH₃)₂), 13.8 (Bu₄N). HRMS(ESI) m/z : 262.2520 (found for $[(\text{B}_{10}\text{H}_9\text{NHC}(\text{C}_3\text{H}_7)\text{NH}_2\text{C}_2\text{H}_4\text{S})_2]^{2-}$, calculated for $[\text{A}]^{2-}$ 262.2507).

2.2.5. *Preparation of sodium salts.* The corresponding tetrabutylammonium salt 4–6 (0.5 mmol) was dissolved in ethanol (10 mL) and treated with an aqueous solution of sodium tetraphenylborate (155 mg, 0.45 mmol) under stirring for 30 min. The formation of a fine white precipitate $(\text{Bu}_4\text{N})[\text{BPh}_4]$ was observed. The mixture was filtered, and the filtrate was concentrated on a rotary evaporator. The residue was recrystallized from an acetonitrile / diethyl ether mixture to yield the sodium salts $\text{Na}[2\text{-B}_{10}\text{H}_9\text{NH}=\text{C}(\text{NHC}_2\text{H}_4\text{SH})\text{R}]$.

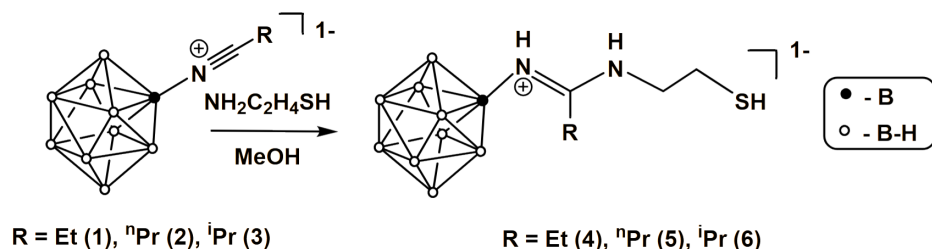
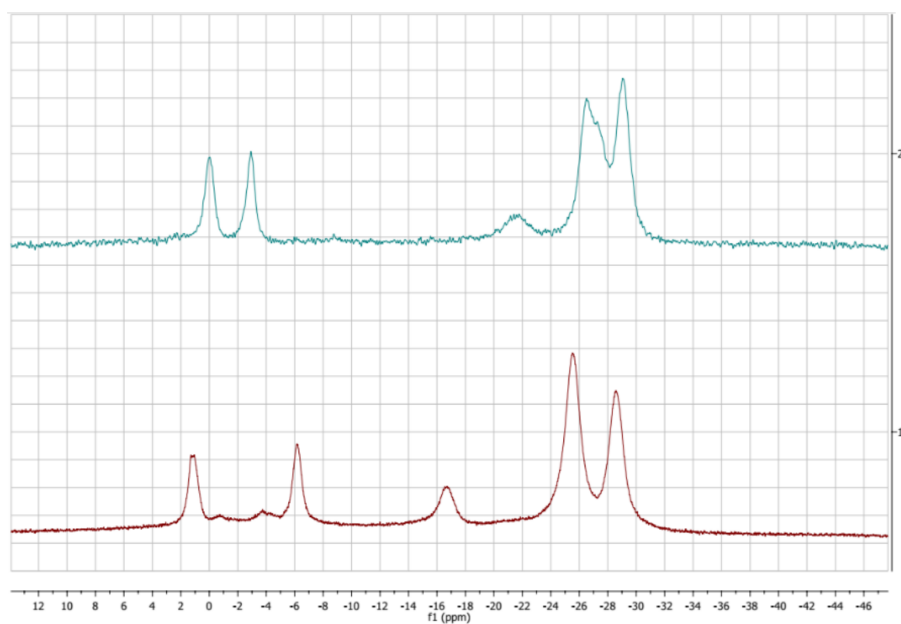
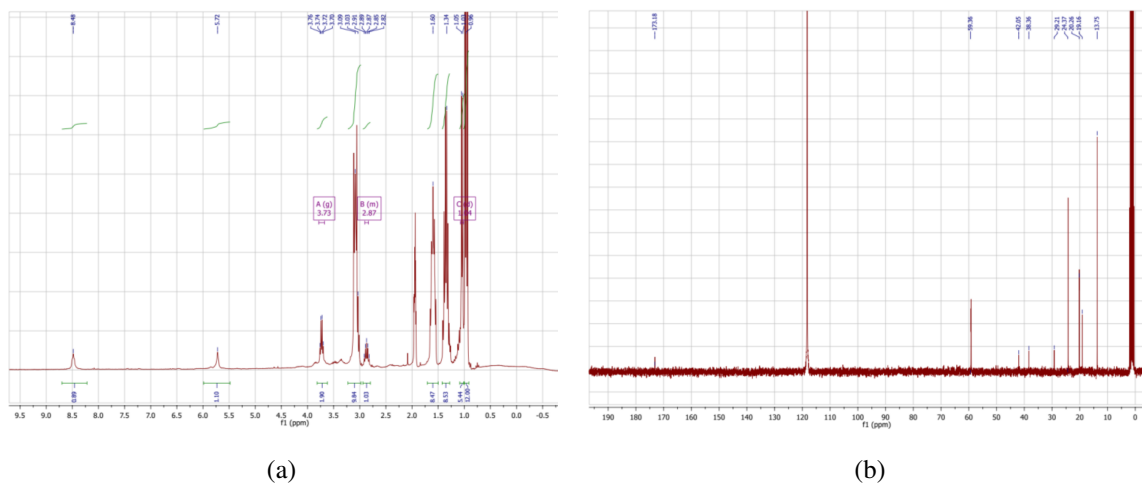
2.2.6. *Synthesis of gold nanoparticles (AuNPs).* Gold nanoparticles were synthesized via the direct reaction of hydrogen tetrachloroaurate $\text{H}[\text{AuCl}_4]$ with the sodium salts of the amidine-functionalized closo-decaborates. In a typical procedure, an aqueous solution of $\text{H}[\text{AuCl}_4]$ (0.025 M) was mixed with an aqueous solution of the ligand **Na(4–6)** at molar ratios ranging from 1:1 to 1:12 (Au:Ligand). The mixture was stirred for 30 min at room temperature, during which the solution turned a reddish-brown color. The resulting sol was centrifuged to remove bulk by-products (borates), and the supernatant was filtered through a 200 nm PTFE filter.

3. Results and discussions

3.1. Synthesis and characterization of amidine ligands

Novel amidine derivatives of the closo-decaborate anion were synthesized via the nucleophilic addition of cysteamine to the triple bond of nitrilium derivatives $[2\text{-B}_{10}\text{H}_9\text{NCR}]^{1-}$ ($\text{R}=\text{Et}$, ^nPr , ^iPr) in methanol (Fig. 1). The reaction progress was monitored by ^{11}B NMR spectroscopy (Fig. 4). The formation of the amidine functionality is evidenced by characteristic changes in the chemical shifts of the boron cage atoms. Specifically, the signal of the substituted boron atom B(2) shifts downfield to the range of –15.5 to –17.0 ppm compared to the initial nitrilium derivative. Concurrently, the signal of the antipodal apical atom B(10) appears in the region of 1.0 – 1.6 ppm, while the signal of the proximal apical atom B(1) undergoes a significant upfield shift to the range of –4.8 to –6.3 ppm (Fig. 2).

The structure of the obtained compounds was further confirmed by ^1H and ^{13}C NMR spectroscopy and high-resolution ESI-MS. For instance, the ^1H NMR spectrum of compound **5** (Fig. 3a) displays distinct signals corresponding to the iso-propyl group of the amidine fragment and the ethylene linker of the cysteamine moiety. The ESI-HRMS data are in good agreement with the calculated isotopic profiles for the dianionic species $[(\text{B}_{10}\text{H}_9\text{NHC}(\text{R})\text{NH}_2\text{C}_2\text{H}_4\text{S})_2]^{2-}$ (disulfide form) and monoanionic species (thiol form), confirming the integrity of the boron cage and the ligand attachment. To facilitate water solubility for subsequent AuNP synthesis, the derivatives were converted into their sodium salts via metathesis with sodium tetraphenylborate.

FIG. 1. General scheme of synthesis of *closo*-borate amidine **4-6**FIG. 2. $^{11}\text{B}\{^1\text{H}\}$ NMR spectra of $(\text{Bu}_4\text{N})[2\text{-B}_{10}\text{H}_9\text{NCC}_2\text{H}_5]$ (1) (top) and $(\text{Bu}_4\text{N})[2\text{-B}_{10}\text{H}_9(\text{NHC}(\text{C}_2\text{H}_5)\text{NHC}_2\text{H}_4\text{SH})]$ (4) (bottom)FIG. 3. ^1H NMR (a) and ^{13}C NMR (b) spectra of $(\text{Bu}_4\text{N})[2\text{-B}_{10}\text{H}_9(\text{NHC}(^i\text{C}_3\text{H}_7)\text{NHC}_2\text{H}_4\text{SH})]$ (6)

3.2. Synthesis and morphology of gold nanoparticles

Gold nanoparticles were synthesized by the direct reduction/stabilization method using sodium salts of the synthesized ligands **Na(4–6)** and $\text{H[AuCl}_4\text{]}$ in aqueous solution. This approach aimed to produce biocompatible AuNPs with a core size suitable for medical applications (≤ 100 nm). In this process, the boron cluster derivative acts as a stabilizing agent through the formation of strong Au–S bonds via the pendant thiol group.

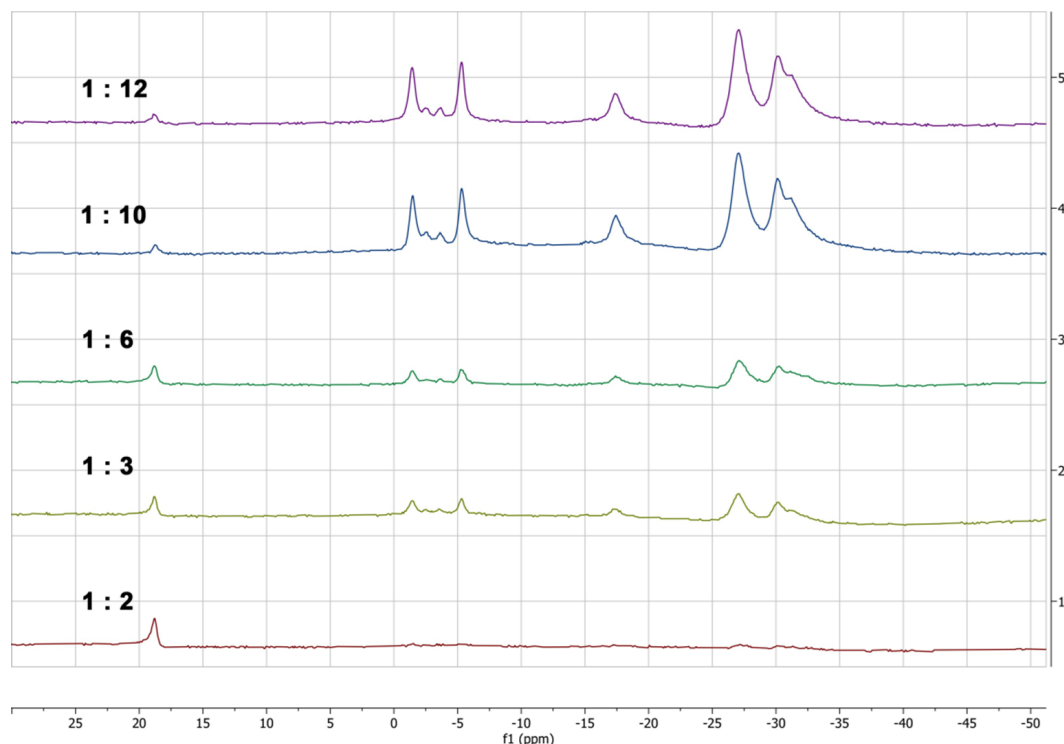


FIG. 4. $^{11}\text{B}\{^1\text{H}\}$ NMR of AuNPs@Na(6) sols obtained by varying the molar ratio $\text{Au}^{3+} : \text{Na(6)}$.

The reagent ratio ($\text{Au}^{3+} : \text{Ligand}$) was optimized by varying the molar ratio from 1:1 to 1:12. The optimization was guided by DLS measurements and $^{11}\text{B}\{^1\text{H}\}$ NMR spectroscopy of the reaction supernatants. At low ligand ratios (1:1 and 1:2), $^{11}\text{B}\{^1\text{H}\}$ NMR spectra revealed the disappearance of the cluster signals and the emergence of a signal at 19 – 20 ppm characteristic of borates (B(OH)_3), indicating the oxidative degradation of the boron cage by Au(III) species. Conversely, at ratios of 1:6 and higher, the integrity of the excess ligand was preserved (Fig. 4).

DLS analysis (Fig. 5) indicated that the optimal hydrodynamic size and polydispersity were achieved at a ratio of 1:6. For example, AuNPs stabilized by ligand **Na(6)** exhibited a hydrodynamic diameter of approximately 51 nm. Increasing the ligand excess further (1:10, 1:12) led to a slight increase in the mean diameter but maintained a narrow size distribution. It also leads to excessive consumption of the cluster ligand.

The morphology of the obtained nanoparticles was investigated by SEM and STEM (Figs. 6, 7). The sample AuNPs@Na(6) consists of aggregated spherical nanoparticles with a diameter of approximately 20 – 30 nm. The sample AuNPs@Na(5) formed larger spheres (40 – 80 nm). STEM images reveal a core-shell structure where the dense gold shell is surrounded by a lighter organic contrast, attributed to the boron-cluster ligand shell. It is important to note that the ring-like structures observed in some micrographs are actually spheres observed in a transmission (STEM) mode, as confirmed by SEM images showing solid spherical particles (Fig. 7).

Specifically, the particles appear to consist of a low-Z element core (likely composed of boron cluster aggregates or solvent-swollen organic phase) surrounded by a dense gold shell. This gold shell is, in turn, stabilized by an outer layer of the amidine-boron ligands. Such a multi-layered structure (“organic core”@“Au shell”@“ligand corona”) is distinct from classical solid gold nanoparticles. This unique morphology may also explain the absence of the typical surface plasmon resonance band in the UV-Vis spectra, as the optical response of gold nanoshells is highly sensitive to the shell thickness and core dielectric constant, often shifting the plasmon band into the near-infrared region or broadening it significantly. The formation of agglomerates inside the particles may be associated with the tendency of salts of the $[\text{B}_{10}\text{H}_{10}]^{2-}$ anion to form coordination compounds with gold with the formation of M–B bonds [21].

Having established the optimal reagent ratio (1:6), we compared the hydrodynamic size distributions of AuNPs stabilized by ligands **Na(4)**, **Na(5)**, and **Na(6)**. As shown in Fig. 7, all three ligands facilitate the formation of relatively monodisperse nanoparticles. However, the nature of the alkyl substituent in the amidine fragment influences the final particle size. AuNPs stabilized by the ethyl-substituted ligand **Na(4)** and *n*-propyl-substituted **Na(5)** exhibit slightly

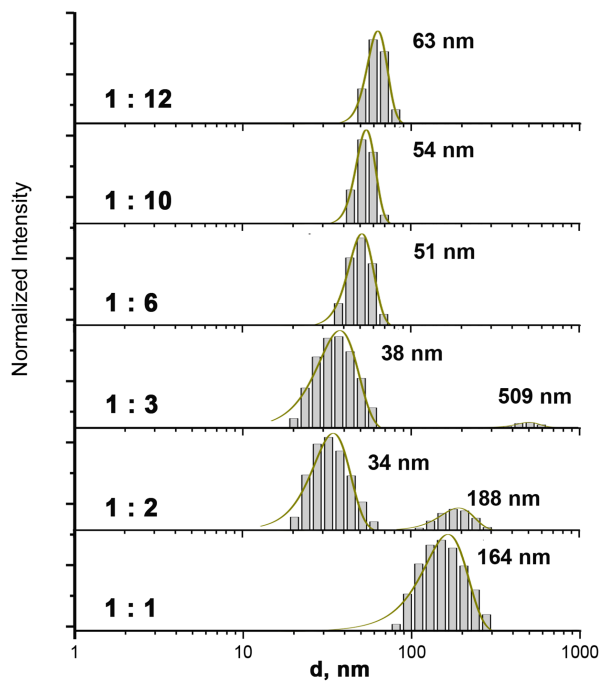


FIG. 5. DLS analysis of AuNPs@Na(6) sols obtained by varying the molar ratio $\text{Au}^{3+} : \text{Na(6)}$

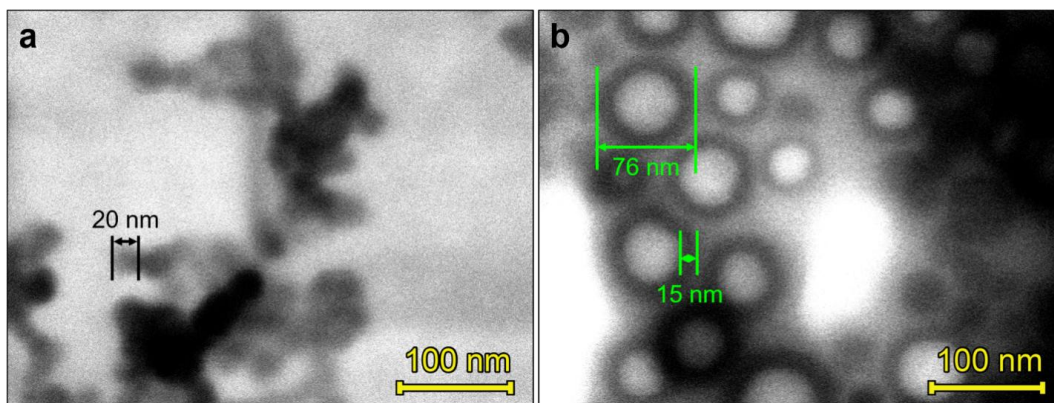


FIG. 6. STEM images of a) AuNPs@Na(6) and b) AuNPs@Na5 samples taken in a bright field mode

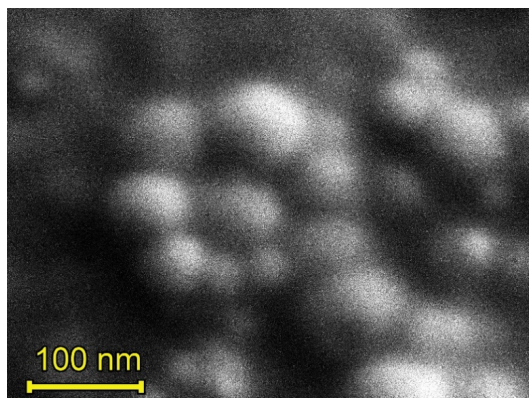


FIG. 7. SEM image of AuNPs@Na5 sample

larger hydrodynamic diameters compared to the *i*-propyl derivative **Na(6)**. This trend suggests that the steric hindrance of the branched isopropyl group in **Na(6)** may provide more effective surface screening during the nucleation and growth stages, limiting the final aggregate size more efficiently than the linear alkyl chains.

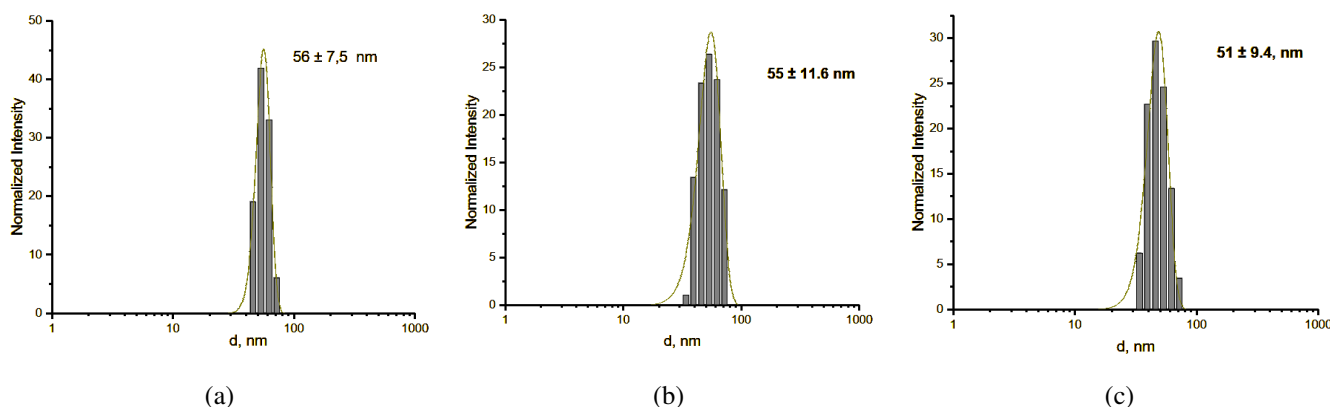


FIG. 8. DLS analysis of AuNPs@Na(4) (a), AuNPs@Na(5) (b) and AuNPs@Na(6) (c) sols obtained by the molar ratio $\text{Au}^{3+} : \text{Ligand} = 1 : 6$

3.3. Surface chemistry (XPS Analysis)

X-ray photoelectron spectroscopy (XPS) confirmed the elemental composition of the nanoparticles (Au, S, B, N, C, O) (Figs. 8–10). The $\text{Au}4f_{7/2}$ binding energy in Na(4)–Na(6) samples is ~ 84.5 eV. The value of the binding energy is higher than that of the gold foil (84.0 eV), which is due to the influence of the particle size [22, 23]. The B1s signals show the presence of two major components: B–B bonds in the cluster with binding energies at ~ 187.5 eV, and a small amount of boron (III) in B_2O_3 or $\text{B}(\text{OH})_3$ up to 15 % at ~ 192.0 eV, respectively [24, 25]. The S2p signals show the presence of two major components: Au–S bonds with binding energies at 162.7–162.8 eV ($\text{S}2p_{3/2}$) and at ~ 163.9 eV ($\text{S}2p_{1/2}$), and just 40 – 60 % of unbound thiol characterized by two components in a 2:1 ratio at ~ 163.8 eV ($\text{S}2p_{3/2}$) and 164.9 eV ($\text{S}2p_{1/2}$), respectively [22, 23].

3.4. Stability and purification

Initially, the crude colloidal solutions exhibited a tendency toward gradual agglomeration upon concentration, likely due to the high ionic strength arising from the excess reagents and by-products (sodium salts, borates). However, we found that purification of the sols via dialysis against distilled water significantly enhanced their colloidal stability. The dialyzed sols of Na(4)–Na(6) stabilized AuNPs retained their optical properties and hydrodynamic size distribution for several months when stored at 4 °C. This enhanced stability confirms that the *closo*-decaborate amidine derivatives form a robust stabilizing shell, and the removal of destabilizing electrolytes is the key step for obtaining long-term stable dispersions suitable for biological studies.

4. Conclusions

In summary, we have successfully developed a synthetic route for novel amidine derivatives of the *closo*-decaborate anion functionalized with pendant thiol groups. These compounds were used for the first time as combined reducing and stabilizing agents for the one-pot synthesis of gold nanoparticles in an aqueous medium.

A key finding of this work is the formation of nanoparticles with an unconventional low-density core/dense-shell architecture, where a gold-rich shell encapsulates a core composed of low-Z elements, likely boron cluster aggregates. This unique morphology is responsible for the observed absence of a characteristic surface plasmon resonance band, distinguishing these materials from classical solid-core AuNPs.

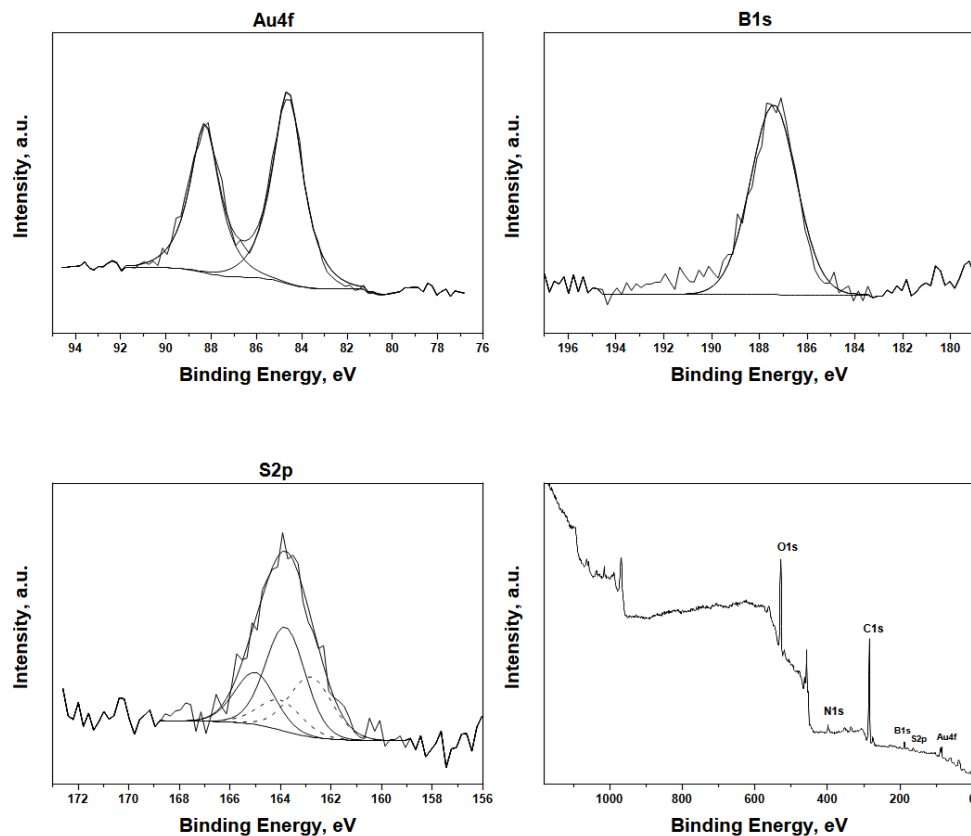


FIG. 9. XPS Au4f, B1s, S2p and survey spectra of AuNPs@Na(4)

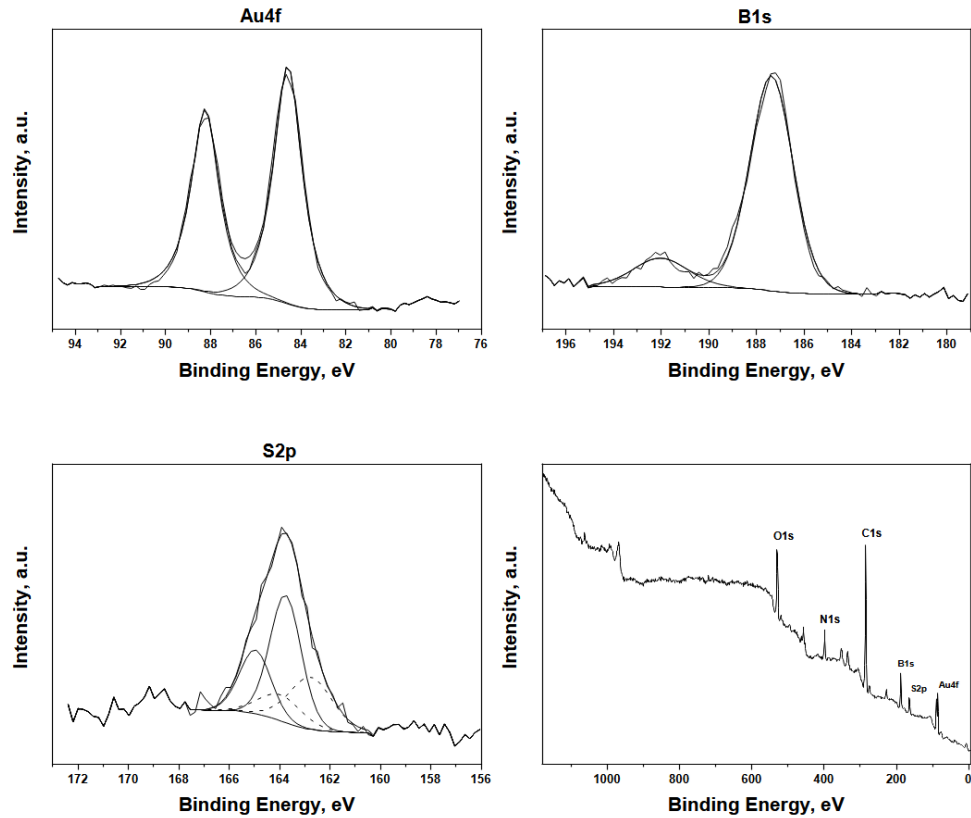


FIG. 10. XPS Au4f, B1s, S2p and survey spectra of AuNPs@Na(5).

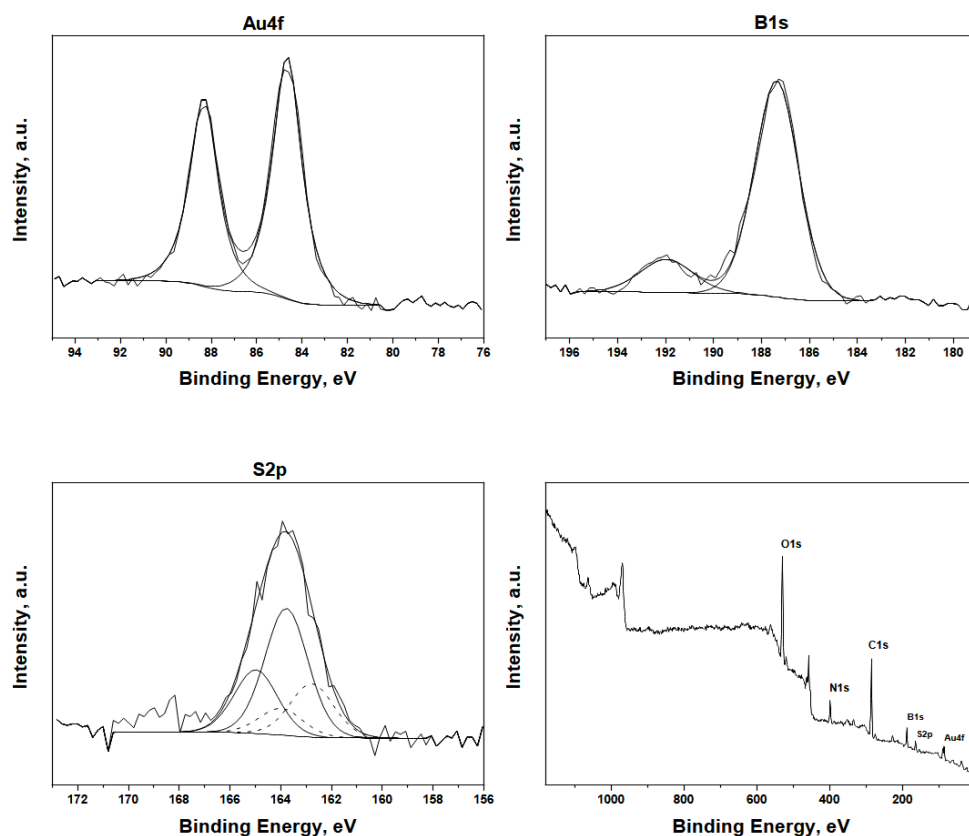


FIG. 11. XPS Au4f, B1s, S2p and survey spectra of AuNPs@Na(6)

References

- [1] Fernandes D.A. Multifunctional gold nanoparticles for cancer theranostics. *3 Biotech*, 2024, **14**, 267.
- [2] Tan D.K., Tai Y., Nguyen T.T. Gold nanoparticles for targeting of biomedical applications: A review. *Asian J. Chem.*, 2024, **36** (8), P. 1741–1746.
- [3] Asih S., Budi S., Katas H. Synthesis and application of gold nanoparticles as antioxidants. *Pharmacia*, 2024, **71**, P. 1–19.
- [4] Kattumuri V., Katti K., Bhaskaran S., et al. Gum arabic as a phytochemical construct for the stabilization of gold nanoparticles: in vivo pharmacokinetics and X-ray-contrast-imaging studies. *Small*, 2007, **3** (2), P. 333–341.
- [5] Nirmala J.G., Rachineni K., Choudhary S., et al. Triphala polyphenols-functionalized gold nanoparticles impair cancer cell survival through induction of tubulin dysfunction. *J. Drug Deliv. Sci. Technol.*, 2021, **61**, 102167.
- [6] Xia Y., Wu X., Zhao J., et al. Three dimensional plasmonic assemblies of AuNPs with an overall size of sub-200 nm for chemo-photothermal synergistic therapy of breast cancer. *Nanoscale*, 2016, **8** (44), P. 18682–18692.
- [7] Zhao R., Xiang J., Wang B., et al. Recent advances in the development of noble metal NPs for cancer therapy. *Bioinorg. Chem. Appl.*, 2022, **2022**, 2444516.
- [8] Sakore P., Gaikwad S., Aadil K.R., et al. The theranostic potential of green nanotechnology-enabled gold nanoparticles in cancer: A paradigm shift on diagnosis and treatment approaches. *Results Chem.*, 2024, **7**, 101264.
- [9] Amendola V., Pilot R., Frascioni M., et al. Surface plasmon resonance in gold nanoparticles: a review. *J. Phys.: Condens. Matter*, 2017, **29** (20), 203002.
- [10] Huang X., El-Sayed M.A. Gold nanoparticles: Optical properties and implementations in cancer diagnosis and photothermal therapy. *J. Adv. Res.*, 2010, **1** (1), P. 13–28.
- [11] Wu C.-Y., Hsieh H.-H., Chang T.-Y., et al. Development of MRI-detectable boron-containing gold nanoparticle-encapsulated biodegradable polymeric matrix for boron neutron capture therapy (BNCT). *Int. J. Mol. Sci.*, 2021, **22**, 8050.
- [12] Ready A.D., Nelson Y.A., Torres Pomares D.F., Spokoyny A.M. Redox-active boron clusters. *Acc. Chem. Res.*, 2024, **57**, P. 1310–1324.
- [13] Ohta K. Basic organic and inorganic chemistry of boron clusters and its application to drug discovery. *Yakugaku Zasshi*, 2022, **142** (8), P. 855–863.
- [14] Soriano-Ursúa M.A. Boron applications in prevention, diagnosis and therapy for high global burden diseases. *Inorganics*, 2023, **11** (9), 358.
- [15] Hirose K., Konishi T., Tanaka H., et al. Boron neutron capture therapy using cyclotron-based epithermal neutron source and borofalan (^{10}B) for recurrent or locally advanced head and neck cancer (JHN002): An open-label phase II trial. *Radiother. Oncol.*, 2021, **155**, P. 182–187.
- [16] Fujikawa Y., Kawabata S., Tsujino K. et al. Chordoma Treatment with Boron Neutron Capture Therapy (BNCT): Experimental Insights. *Proceedings*, 2024, **95** (1), 13.
- [17] Licitra L., Orlandi E., Bossi P., et al. Developing a trial design to establish BNCT as clinical application: insight for the national italian center for oncological hadrontherapy (CNAO). *Health Technol.*, 2024, **14** (5), P. 1037–1041.
- [18] Zhizhin K.Yu., Zhdanov A.P., Kuznetsov N.T. Derivatives of closo-decaborate anion $[\text{B}_{10}\text{H}_{10}]^{2-}$ with exo-polyhedral substituents. *Russ. J. Inorg. Chem.*, 2010, **55** (14), P. 2089–2127.
- [19] Williams D.B.G., Lawton M. Drying of Organic Solvents: Quantitative evaluation of the efficiency of several desiccants. *J. Org. Chem.*, 2010, **75**, P. 8351–8354.
- [20] Zhdanov A.P., Bykov A.Yu., Kubasov A.S., et al. Hydrolysis of nitrilium derivatives of the closo-decaborate anion $[\text{2-B}_{10}\text{H}_9(\text{N}\equiv\text{CR})]^-$. *Russ. J. Inorg. Chem.*, 2017, **62**, P. 468–475.

- [21] Avdeeva V.V., Malinina E.A., Kuznetsov N.T. Boron cluster anions and their derivatives in complexation reactions. *Coord. Chem. Rev.*, 2022, **469**, 214636.
- [22] Gobbo P., Biesinger M.C., Workentin M.S. Facile synthesis of gold nanoparticle (AuNP)–carbon nanotube (CNT) hybrids through an interfacial michael addition reaction. *Chem. Commun.*, 2013, **49**, 2831.
- [23] Gobbo P., Novoa S., Biesinger M.C., Workentin M.S. Interfacial strain-promoted alkyne–azide cycloaddition (I-SPAAC) for the synthesis of nanomaterial hybrids. *Chem. Commun.*, 2013, **49**, 3982.
- [24] Liu Y.-S., Ray K.G., Jørgensen M., et al. Nanoscale Mg–B via surfactant ball milling of MgB₂: morphology, composition, and improved hydrogen storage properties. *J. Phys. Chem. C*, 2020, **124**, P. 21761–21771.
- [25] Saldin V.I., Ignat'eva L.N., Nikolenko Yu.M., et al. Thermal conversions of chitosanium dodecahydro-*closo*-dodecaborate. *Russ. J. Inorg. Chem.*, 2010, **55**, P. 1221–1227.

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In situ XRD study of the crystallization process of $\text{MnO}_x\text{--ZrO}_2$ oxide

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ABSTRACT The crystallization process of $\text{MnO}_x\text{--ZrO}_2$ mixed oxide in different gas environments was studied by in situ X-ray diffraction and thermogravimetric analysis. The non-modified ZrO_2 was used as a reference. The process of crystallization in Mn-containing sample depends on the environment: the crystallization temperature in reducing and inert environment was 450 – 455 °C and in oxidizing it was 560 °C. Thus, the addition of manganese led to the shift of crystallization temperature to the higher values compared to reference sample ZrO_2 (425 °C). The resulting crystalline phase was $\text{Zr}_{1-y}\text{Mn}_y\text{O}_2$ solid solution rather than pure zirconia. Mn cations seemed to stabilize the tetragonal zirconia instead of monoclinic.

KEYWORDS in situ XRD, crystallization, manganese oxide, solid solution, zirconia

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1. Introduction

Zirconia-based materials are applied for different practical purposes: as refractory materials, pigments, piezoelectric devices, ceramic capacitors, oxygen sensors, etc. These materials are also used as catalysts and supports [1] for WGS reaction [2], reduction of CO , NO_x and volatile organic compounds (VOC) [3], alkane isomerization reactions [4, 5] etc.

Zirconia has three stable modifications: monoclinic (m- ZrO_2), tetragonal (t- ZrO_2) and cubic (c- ZrO_2). Monoclinic modification is stable at room temperature, tetragonal at temperatures of 1170 – 2370 °C and cubic above 2370 °C [6]. One of the ways to obtain solid crystalline form of zirconia phase is the calcination of amorphous precursor. During calcination, crystallization occurs with the formation of various modifications of ZrO_2 or their mixture. The crystalline phase (or phases) directly depends on the state of the original amorphous compound, thus, understanding the nature of the amorphous precursor and the process of its crystallization is important to unravel the structure and, consequently, the properties of the resulting crystalline materials.

The pathway of phase transformations during the crystallization of an amorphous precursor is directly influenced by local structure of initial compound. This is because the local structure reflects the state of the crystalline grains. Yanwei et al. [7] described a local structure of amorphous phase as monoclinic-like in xerogel and aerogel synthesized ZrO_2 samples. Crystallization took place at the temperature of 400 °C with the formation of monoclinic ZrO_2 crystallites. Tiseanu et al. [8] found crystallographic planes typical for m- ZrO_2 and t- ZrO_2 in amorphous sample synthesized by oil-in-water method. Temperature-induced crystallization has resulted in the formation of crystalline tetragonal zirconia at 450 °C.

Both the crystallization temperature and the resulting phases depend on the state of the amorphous precursor. The introduction of dopant atoms also has a significant effect on the crystallization process. For example, the authors [9, 10] showed that the introduction of vanadium into amorphous ZrO_2 leads to an increase in the crystallization temperature. Ushakov et al. [11] showed a similar effect during doping with lanthanum and yttrium. In all these works, it was shown that doping of amorphous zirconia can lead to the preferential formation of thermodynamically metastable tetragonal and/or cubic modification of zirconia instead of monoclinic.

To the best of our knowledge, there are no works that would consider the crystallization process of amorphous zirconium doped with Mn. However, the addition of manganese can have a crucial effect on the catalytic properties [12–16]. Catalytic activity in oxidation reactions of manganese oxides is associated with the variety of oxidation states of manganese and due to the ability of manganese ions to easily change their oxidation state [17]. In $\text{MnO}_x\text{--ZrO}_2$ mixed oxide catalysts, various active states can be formed depending on the synthesis conditions. For example, wet impregnation of zirconia with a manganese nitrate solution results in the formation of nanoparticles of $\alpha\text{-Mn}_2\text{O}_3$ supported on ZrO_2 . By coprecipitation of metal acetates and nitrates, $\text{Mn}_x\text{Zr}_{1-x}\text{O}_2$ solid solution is obtained [15, 18, 19]. Previously [20] we

succeeded in synthesizing the amorphous phase by coprecipitation of manganese and zirconium nitrates. This amorphous phase itself had low catalytic activity, but calcination at higher temperatures led to the formation of a highly active $\text{Mn}_x\text{Zr}_{1-x}\text{O}_2$ solid solution and in the tetragonal/cubic modification. Therefore, on the one hand, it is important to study the crystallization process as a path to the formation of a solid solution, and on the other hand, the investigation of the amorphous precursor can shed light on the influence of dopant atoms on this process. In this work we focused on determining the crystallization mechanism of amorphous $\text{MnO}_x\text{-ZrO}_2$ oxide catalyst depending on the gas atmosphere. Conventional X-ray diffraction (XRD) analysis is not suitable for studying amorphous compounds due to the lack of long-range order. Instead, better approach is to determine their local structure using pair distribution function analysis (PDF). In order to investigate temperature-induced phase transformations and structural changes in different environments in situ X-ray diffraction technique and thermogravimetric analysis (TGA) were applied. Morphology of the investigated samples was studied via transmission electron microscopy (TEM) and BET technique.

2. Experimental

2.1. Catalyst preparation

Catalysts with the ratio $\text{Mn/Zr} = 1/4$ were synthesized by co-precipitation of a joint solution of $\text{ZrO}(\text{NO}_3)_2$ and $\text{Mn}(\text{NO}_3)_2$ salts by the dropwise addition of $\text{NH}_3(\text{aq})$ and vigorous stirring until pH 10 was reached. The resulting precipitate was filtered, washed with water to pH 6–7 and dried at 120 °C, and then calcined at a given temperature for 4 h at the temperatures 400 and 700 °C. The catalysts obtained were designated as Mn-Zr-T , where T is the calcination temperature. The reference sample containing no manganese admixture was synthesized by similar precipitation of zirconium nitrate and calcined at 300 °C for 4 hours. This sample was designated as $\text{ZrO}_2\text{-300}$.

2.2. Ex situ & in situ X-ray diffraction (XRD)

The XRD patterns were obtained via diffractometer STOE STADI MP (Germany) in the 2θ range from 10 to 50° with a step of 0.015° and an accumulation time of 70 s per point. $\text{MoK}\alpha$ radiation with wavelength $\lambda = 0.7093 \text{ \AA}$ was applied. In situ XRD studies were carried out on a High Precision Diffractometry II station (The Siberian Synchrotron and Terahertz Radiation Centre, Novosibirsk, Russia). The X-ray diffractometer at the station included a monochromator, a collimation system, and an OD-3M single-coordinate position-sensitive detector [21]. The working radiation wavelength ($\lambda = 1.6467 \text{ \AA}$) was set by a single reflection from a Ge (111) crystal monochromator. The diffractometer is equipped with a high-temperature reactor XRK-900 (Anton Paar, Austria). A quadrupole mass spectrometer (SRS UGA100, USA) was used to control the gas environment. Heating was carried out at a constant rate of 10 °/min, the gas mixture feed rate was 100 ml/min. The ICDD PDF-2 powder database was used for phase analysis [22]. Quantitative phase analysis and refinement of the lattice parameters were performed by the Rietveld method using the XPert HighScore Plus software [23]. CSR were calculated via Sherrer equation [24]. Corundum was used to subtract the instrumental broadening.

In order to compare the lattice parameters of cubic and tetragonal zirconia phases, we used the normalized lattice parameter a^* in the case of tetragonal oxide:

$$a^* = \left(\frac{V_{\text{tetr}} \cdot Z_{\text{cub}}}{Z_{\text{tetr}}} \right)^{1/3},$$

where $V_{\text{tetr}} = a^2 \cdot c$ is the volume of a tetragonal cell, $Z_{\text{cub}} = 4$, $Z_{\text{tetr}} = 2$ is the number of units in the cubic and tetragonal cells, respectively.

2.3. Pair Distribution Function analysis (PDF)

The diffraction pattern for PDF analysis was recorded using a laboratory diffractometer STOE STADI MP (Germany) with $\text{MoK}\alpha$ radiation ($\lambda = 0.7093 \text{ \AA}$) in the range of 2θ from 1.5 to 126.9° with a step of 0.015° for 200 s at each point. The relationship between the distribution function of atomic pairs $G(r)$ and coherent scattering of X-rays is determined through the Fourier transform:

$$G(r) = \frac{2}{\pi} \int_0^{\infty} Q \cdot i(Q) \cdot \sin(Qr) \cdot dQ.$$

To obtain pair distribution functions from X-ray diffraction data by Fourier transform we used PDFgetX2 [25]. The obtained PDF data were then analyzed using PDFgui software [26].

2.4. Thermogravimetric analysis (TGA)

Thermogravimetric analysis of Mn-Zr-400 and ZrO_2 samples was carried out using STA 449 C Jupiter synchronous thermal analysis device from NETZSCH (Germany). A sample portion (45.14 mg) was placed in a corundum crucible. The sample was heated in an air and helium atmosphere from the room temperature to 900 °C with a heating rate of 5 °C/min and a gas feed rate of 30 ml/min. The experimental data were analyzed using the NETZSCH Proteus Thermal Analysis software package.

2.5. Transmission electron microscopy (TEM)

The morphology and microstructure of the samples were studied by transmission electron microscopy. TEM images were obtained on a ThemisZ Thermo Fisher Scientific microscope (Thermo Fisher Scientific, Eindhoven, The Netherlands) with a resolution of 0.7 Å. EDX analysis was carried out on an energy dispersive spectrometer SuperX (Thermo Fisher Scientific). Samples for research were fixed on standard copper grids using ultrasonic dispersion of the catalysts in ethanol.

The specific surface area was calculated with the Brunauer–Emmett–Teller (BET) method using nitrogen adsorption isotherms measured at liquid nitrogen temperatures on QuadraSorb SI MP Station (Micromeritics Instrument Corp., Norcross, GA, USA).

3. Results

3.1. XRD analysis

The diffraction patterns of double oxides Mn–Zr-400, Mn–Zr-700 and reference sample ZrO_2 -300 are shown in Fig. 1. The sample Mn–Zr-700 is presented by the diffraction maxima at $2\theta = 13.9, 15.8, 16.1, 19.6, 22.6, 22.8, 26.5, 26.8, 27.9, 32.1, 32.5, 35.3, 35.5, 36.18, 40.0, 41.5$ and 42.6° , which correspond to the peaks $hkl = 011, 002, 110, 012, 112, 020, 013, 121, 022, 004, 220, 123, 031, 114, 132, 124$ and 231 of the $t\text{-ZrO}_2$ phase (s.g. $P4_2/nmc$, PDF 50-1089). The Rietveld refinement showed the lattice parameters $a = b = 3.606(1)$ Å and $c = 5.078(1)$ Å that corresponds the normalized lattice parameter $a^* = 5.090(1)$ Å. The lattice parameter for pure $c\text{-ZrO}_2$ is 5.11 Å [27], which indicates the formation of the $\text{Zr}_{1-y}\text{Mn}_y\text{O}_2$ solid solution phase due to the ionic radius of Mn ($\text{Mn}^{3+} - 0.66$ Å) being smaller than the ionic radius of Zr ($\text{Zr}^{4+} - 0.79$ Å) [28].

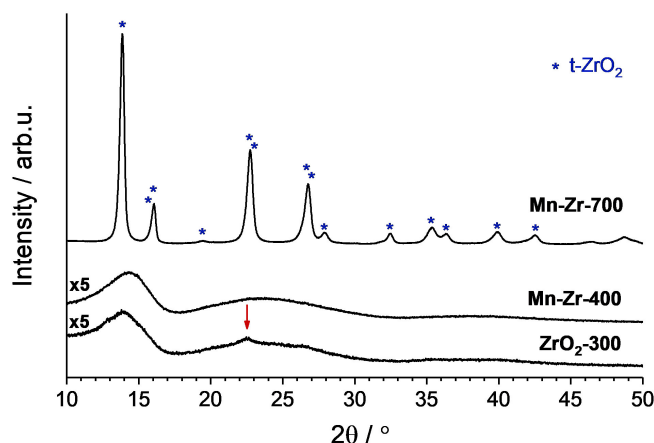


FIG. 1. XRD patterns of ZrO_2 -300, Mn–Zr-400 and Mn–Zr-700; $\lambda = 0.7093$ Å.

The diffraction patterns of Mn–Zr-400 and ZrO_2 -300 samples contain broad diffraction maxima typical for amorphous state. The XRD pattern of ZrO_2 also has a small narrow diffraction peak at $2\theta = 22.4^\circ$, which probably indicates partial formation of a crystalline phase. This peak does not belong to any specific phase, but according to the literature on zirconium modifications, the formation of $m\text{-ZrO}_2$ is most likely at this temperature [6]. However, the sample Mn–Zr-400 does not contain any narrow peaks other than broad amorphous ones. Moreover, there is a significant difference in the specific surface area (S_{BET}) which is shown in Table 1. It can be seen that S_{BET} of Mn–Zr-400 sample is $331 \text{ m}^2/\text{g}$, which is three times larger than that of ZrO_2 sample ($108 \text{ m}^2/\text{g}$). Usually, the specific surface area decreases with the increase in the calcination temperature, but we see an inverse relationship, indicating that the Mn presence in Mn–Zr-400 sample contributes to a significant increase in the specific surface area. The S_{BET} of the sample Mn–Zr-700 is only $38 \text{ m}^2/\text{g}$, which is expected given the increase in calcination temperature up to 700°C .

It is known that heating of pure amorphous ZrO_2 leads to the formation of monoclinic [7] or a mixture of monoclinic and tetragonal zirconia [8,29]. In the case of Mn doping, only the tetragonal modification is formed. This is probably due to the stabilization by introducing manganese. In addition, the presence of manganese apparently delays the crystallization process, since the Mn–Zr-400 sample does not show any narrow peaks corresponding to the crystalline phase.

3.2. TEM and EDX analysis

TEM images of Mn–Zr-400 show the presence of large amorphous aggregates of about 200 – 400 nm in size (Fig. 2a) and long cylindrical particles about 150 – 200 nm long and 10 – 30 nm wide (Fig. 2b). The large particles are an amorphous state containing no crystalline planes (Fig. 2c). According to the EDX analysis (Fig. 2d, area 1), in these regions Zr and

TABLE 1. Structural characteristics of the samples

Sample	Phase composition, wt. %	CSR, Å	Normalized lattice parameter, Å	S_{BET} , m ² /g
ZrO ₂ -300	amorphous	—	—	108
Mn-Zr-400	amorphous	—	—	331
Mn-Zr-700	t-ZrO ₂ *	100	5.090(1)	38

* $Zr_{1-y}Mn_yO_2$ solid solution

Mn atoms have a uniform distribution with a ratio $Mn/Zr = 0.22$. The cylindrical particles contain only Mn atoms which is shown by the EDX analysis (Fig. 2d, area 2), and these particles have visible crystalline planes (Fig. 2c) corresponding to the Mn_3O_4 phase (s.g. I 4₁/amd, PDF 240734).

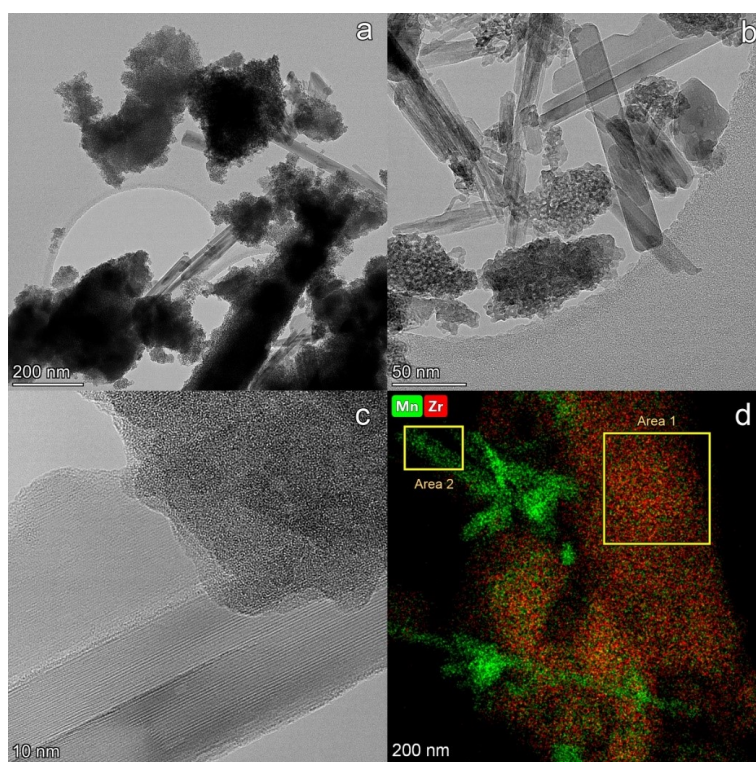


FIG. 2. TEM images (a, b, c) and EDX mapping (d) of Mn-Zr-400

In Fig. 3 TEM images of Mn-Zr-700 sample are shown. It can be seen that the sample contains crystalline particles of 20 – 30 nm in size combined together into large aggregates of about 500 nm and bigger. According to the EDX analysis (Fig. 3c, Area 1), the distribution of Zr and Mn atoms in the sample is mostly uniform. Mn/Zr atomic ratio is approximately 0.22, as in the amorphous sample Mn-Zr-400. Unlike the Mn-Zr-400 sample, the crystalline planes are detected in the particles, so the formation of crystalline $Zr_{1-y}Mn_yO_2$ solid solution is observed, that matches the XRD data. However, this sample also contains areas with higher manganese content (Fig. 3d, Area 3), which also indicates the presence of a separate manganese oxide phase.

TEM images of ZrO₂-300 are shown in Fig. 4. This sample mainly consists of amorphous particles (Fig. 4b) forming layered large aggregates (Fig. 4a). However, there are also few regions containing crystalline planes (Fig. 4b, Area 1). This result also correlates with the XRD data, which showed the presence of small peaks corresponding to crystalline zirconia unlike the sample Mn-Zr-400.

Thus, the results of TEM and EDX analysis indicate the formation of particles with uniform distribution of Mn and Zr atoms in the Mn-Zr-400 and Mn-Zr-700 samples. The atomic ratio of Mn/Zr in both remains approximately 0.22. So, we can conclude the formation of $Zr_{1-y}Mn_yO_2$ solid solution in both samples, but it is amorphous in the sample Mn-Zr-400. Also, both samples show the formation of manganese oxide phase, despite the $Mn-Zr$ atomic distribution is

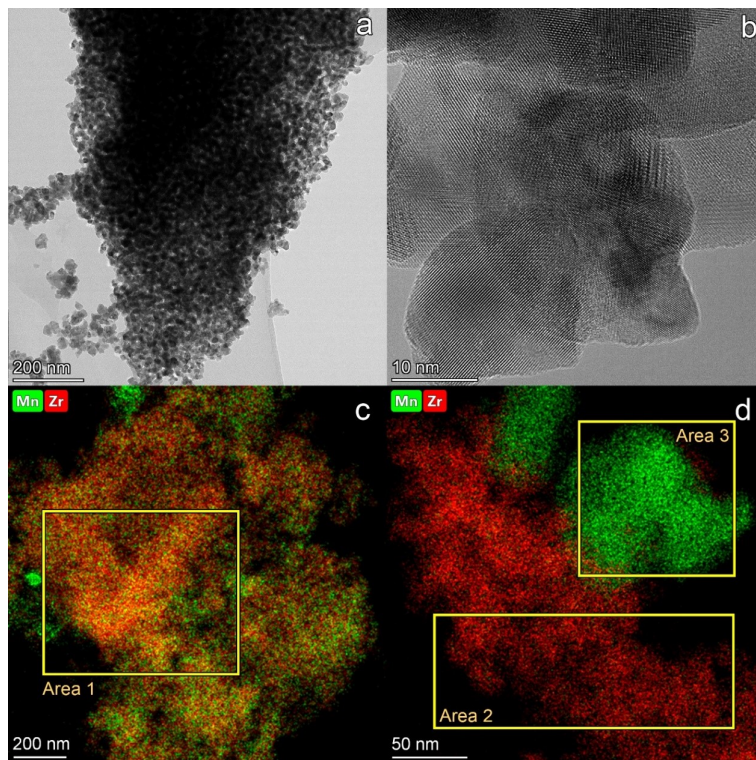
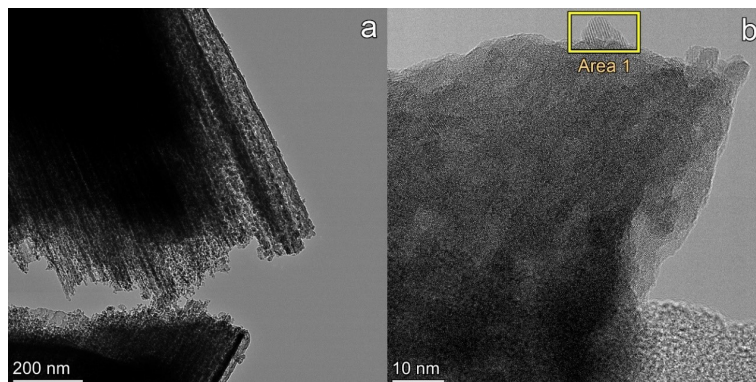


FIG. 3. TEM images (a, b) and EDX mapping (c, d) of Mn-Zr-700

FIG. 4. TEM images (a, b) of $\text{ZrO}_2\text{-300}$

mostly uniform. The detected crystalline particles of Mn_3O_4 probably cannot be detected by XRD due to their disorder, planar defects, and small amount relative to the solid solution phase.

3.3. PDF analysis

The catalysts Mn-Zr-400 and Mn-Zr-700 were investigated by the PDF analysis, and $\text{ZrO}_2\text{-300}$ was used as a reference sample. Fig. 5a shows the $G(r)$ functions for these samples. It is seen that the PDFs of low-temperature oxides Mn-Zr-400 and $\text{ZrO}_2\text{-300}$ fall off at about 10 Å, indicating the typical for amorphous state absence of long-range order. These particles can be considered as crystalline nuclei, which form the bulk crystalline phase ZrO_2 with increasing temperature [7]. On the contrary, the Mn-Zr-700 sample, has the typical PDF for a crystalline compound – the amplitude of the $G(r)$ peaks does not decrease at large r . Nevertheless, a comparison of these PDFs is possible within the first few coordination spheres.

In the case of Mn-containing oxides, the first coordination distance Zr-O is about 2.12 – 2.14 Å, whereas for the $\text{ZrO}_2\text{-300}$ sample it is about 2.20 Å. This difference is probably due to the presence of the MnO_x phase, which was detected by TEM. However, at large distances, there is more similarity between the Mn-Zr-700 and $\text{ZrO}_2\text{-300}$ samples than between Mn-Zr-700 and Mn-Zr-400. This is probably due to the fact that $\text{ZrO}_2\text{-300}$, according to the XRD data, contains some crystalline ZrO_2 phase.

To estimate the contribution of the added manganese, the $G(r)$ function of ZrO_2 -300 was subtracted from the $G(r)$ of Mn-Zr-400. The residual $G(r)$ is shown in Fig. 5b. The Mn–O distance is about 2.01 Å, that is close to the distance 2.02 Å corresponding both Mn_2O_3 (s.g. Ia-3, COD 1514107) and Mn_3O_4 (s.g. I 4₁/amd, COD 1011262). Mn–Mn distances of the nearest coordination spheres are in the r range of 2.84 – 4.22 Å, that are close to those of the oxides Mn_2O_3 (2.86 – 4.24 Å) and Mn_3O_4 (2.80 – 4.23 Å). However, according to TEM data, this phase is most likely to represent Mn_3O_4 . Thus, the residual $G(r)$ function is likely to represent manganese oxide phase in the sample Mn-Zr-400.

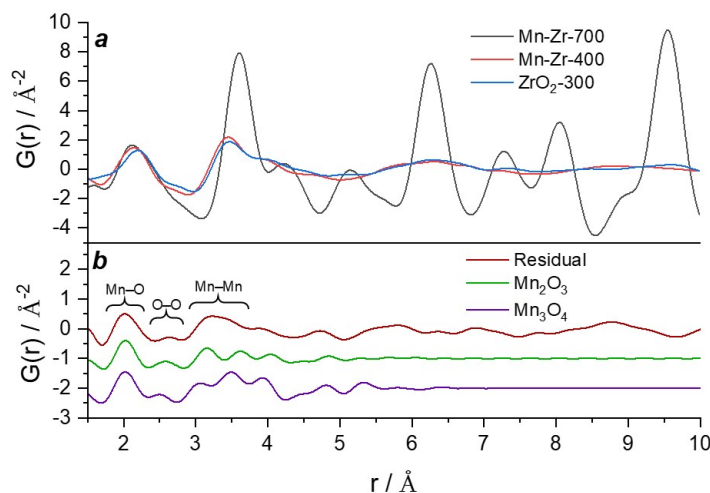


FIG. 5. Comparison of $G(r)$ functions of Mn-Zr-700, Mn-Zr-400 and ZrO_2 -300 (a); residual $G(r)$ of Mn-Zr-400 and ZrO_2 -300 (b)

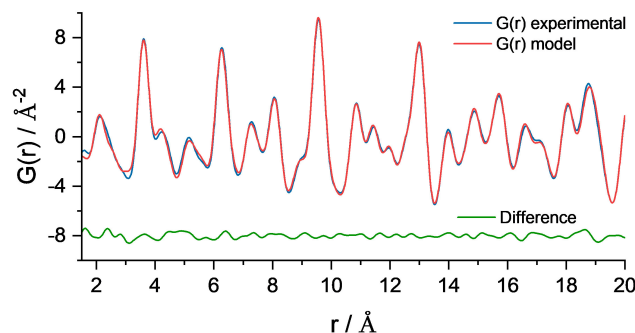


FIG. 6. Experimental and calculated ($P 4_2/nmc$, $\text{Zr}_{0.89}\text{Mn}_{0.11}\text{O}_{1.88}$) functions $G(r)$ of the sample Mn-Zr-700

Figure 6 shows the experimental and calculated functions $G(r)$ for the Mn-Zr-700 sample. All coordination peaks of this function correspond to the distances typical for the fluorite structure. According to the XRD data, calculated $G(r)$ function should contain $\text{Zr}_y\text{Mn}_{1-y}\text{O}_2$ solid solution phase based on t- ZrO_2 structure. The normalized lattice parameter a^* is 5.099(1) Å is close to Rietveld refined one. Refinement model contains the atomic ratio Mn/Zr in solid solution phase 0.11/0.89 and the oxygen occupancy 0.94. It also should be mentioned that, according to the TEM data, this sample contains the MnO_x phase. Probably, some discrepancy between the experiment and simulation is due to the contribution of this phase.

3.4. In situ XRD

To establish the peculiarities of the crystallization process depending on the temperature and gas environment, in situ XRD experiment was carried out for the sample Mn-Zr-400. The catalyst was heated to 700 °C in inert (He), reducing (H_2/He , 10/90 sccm) and oxidizing (O_2/He , 20/80 sccm) environments at a rate of 5 °C /min.

The diffraction patterns obtained by heating Mn-Zr-400 in He are shown in Fig. 7a. At room temperature, a broad halo is observed, indicating an amorphous state. The crystallization process begins at 455 °C, small peaks of the crystalline phase appear. The resulting crystalline phase is cubic ZrO_2 (s.g. Fm-3m, PDF 77-2157) which is represented by diffraction

maxima at 32.6 and $37.8^\circ 2\theta$ corresponding to reflections 111 and 200, respectively. During heating, intensity of these peaks gradually increases along with the disappearance of the amorphous phase that indicates crystallization of solid solution.

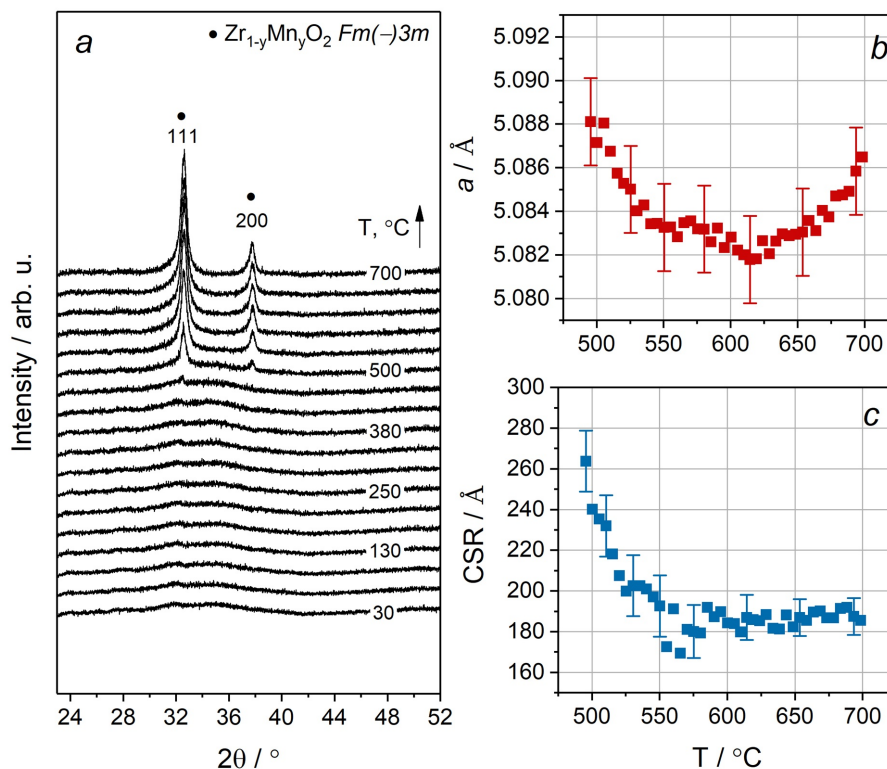


FIG. 7. XRD patterns of Mn-Zr-400 recorded upon heating from 30 to 700°C with a rate of 5°C/min in the He medium; $\lambda = 1.6467 \text{ \AA}$ (a) change in the lattice parameter (b) and CSR (c) of $\text{Zr}_{1-y}\text{Mn}_y\text{O}_2$ with temperature

The lattice parameter of the crystalline phase at 500°C is $5.088(2) \text{ \AA}$. Despite the thermal expansion of the lattice, this value is lower than for pure ZrO_2 ($5.11 \text{ \AA}$), which indicates the formation of the $\text{Zr}_{1-y}\text{Mn}_y\text{O}_2$ solid solution phase instead of pure zirconia. During further heating, the lattice parameter decreases even more (Fig. 7b), reaching a minimum value $5.082(2) \text{ \AA}$ at $600 - 650^\circ\text{C}$. The continuous nature of this process indicates that the formation of the solid solution phase is gradual. Mn cations probably migrate from the Mn_3O_4 oxide phase detected by TEM and / or from the remaining amorphous precursor and slowly substitute Zr cations. So, at the temperatures of $600 - 650^\circ\text{C}$, the highest concentration of manganese is achieved in $\text{Zr}_{1-y}\text{Mn}_y\text{O}_2$. At the same time, the CSR value of $\text{Zr}_{1-y}\text{Mn}_y\text{O}_2$ decreases from 260 to $180 \text{ \AA}$ (Fig. 7c). After reaching the minimum value at $600 - 650^\circ\text{C}$, the lattice parameter increases with temperature reaching the maximum value $5.086(2) \text{ \AA}$ at 700°C . However, CSR of phase $\text{Zr}_{1-y}\text{Mn}_y\text{O}_2$ is generally stable upon further heating. Besides thermal expansion, the parameter growth may indicate two processes: the reduction of Mn cations in the solid solution or the decomposition of the solid solution with the release of manganese. In the first case, the parameter growth is due to the fact that the ionic radius of Mn cations is inversely proportional to their oxidation state [28]. In the second case, manganese atoms are released from the solid solution lattice with formation of MnO_x oxide.

In the reducing environment (H_2/He), the crystallization process occurs similarly (Fig. A1 in Appendix). The diffraction maxima of the $\text{Zr}_{1-y}\text{Mn}_y\text{O}_2$ solid solution phase appear at 450°C indicating the beginning of the crystallization process. The lattice parameter of $\text{Zr}_{1-y}\text{Mn}_y\text{O}_2$ is about $5.088(2) \text{ \AA}$, and it gradually decreases with heating to the minimum value $5.075(2) \text{ \AA}$ at the temperature about $550 - 600^\circ\text{C}$. Simultaneously, there is a decrease in the CSR value from the initial 290 to $190 \text{ \AA}$. Further heating leads to an increase in the lattice parameter of $\text{Zr}_{1-y}\text{Mn}_y\text{O}_2$ up to $5.083(2) \text{ \AA}$ at 700°C , while CSR is stable. Therefore, we can conclude that the reducing environment has no significant effect on the crystallization process of the $\text{Zr}_{1-y}\text{Mn}_y\text{O}_2$ solid solution phase compared to an inert environment.

In the oxidizing environment (O_2/He), the XRD peaks of the crystalline phase $\text{Zr}_{1-y}\text{Mn}_y\text{O}_2$ appear at the temperature 560°C (Fig. 8a), which means that the crystallization process begins at a higher temperature than in inert and reducing environments. The lattice parameter of $\text{Zr}_{1-y}\text{Mn}_y\text{O}_2$ also decreases with increasing temperature from initial $5.086(2) \text{ \AA}$ to its minimum value $5.072(2) \text{ \AA}$ at $660 - 700^\circ\text{C}$ (Fig. 8b). The CSR value at the beginning of the crystallization process is lower than in reducing and inert environments ($200 \text{ \AA}$), but also steadily decreases to $120 \text{ \AA}$ upon heating (Fig. 8c).

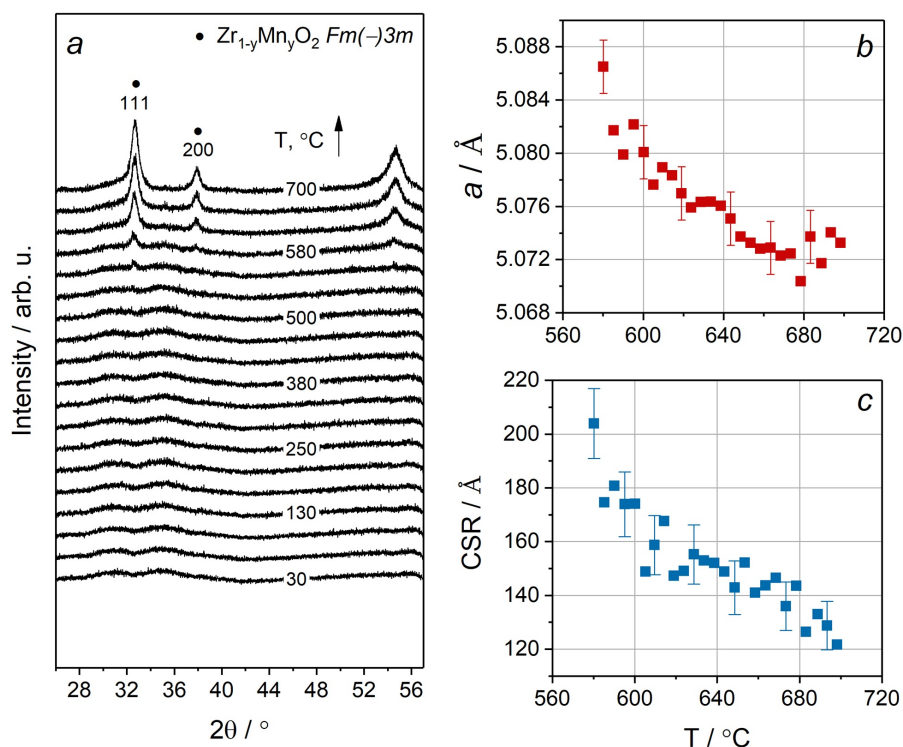


FIG. 8. XRD patterns of Mn–Zr-400 recorded upon heating from 30 to 700 °C with a rate of 5 °C/min in the O_2/He medium; $\lambda = 1.6467$ Å (a) change in the lattice parameter (b) and CSR (c) of $\text{Zr}_{1-y}\text{Mn}_y\text{O}_2$ with temperature

Table 2 shows the properties of the Mn–Zr-400 catalyst after in situ XRD experiments carried out in the corresponding environments. The $\text{Zr}_{1-y}\text{Mn}_y\text{O}_2$ solid solution phase is obviously preserved, as indicated by the lattice parameter value being in the range 5.055(1) – 5.065(1) Å. It was shown that the effect of an oxidizing environment led to the formation of a solid solution with the lowest lattice parameter (5.055(1) Å).

TABLE 2. Phase composition, CSR and lattice parameter in Mn–Zr-400 oxide after the in situ XRD experiments

Medium	Phase composition, wt. %	CSR ($\text{Zr}_{1-y}\text{Mn}_y\text{O}_2$), Å	Lattice parameter a of ZrO_2^* , Å
He	99% $\text{Zr}_{1-y}\text{Mn}_y\text{O}_2$; 1% MnO	190	5.064(1)
H_2/He	99% $\text{Zr}_{1-y}\text{Mn}_y\text{O}_2$; 1% MnO	200	5.065(1)
O_2/He	99% $\text{Zr}_{1-y}\text{Mn}_y\text{O}_2$; 1% Mn_2O_3	130	5.055(1)

In addition, in oxygen-containing atmosphere, the phase with the lowest CSR value is formed. Besides, small amount of manganese oxide (1 %) is present in all samples. In the case of inert and reducing environments, this is MnO, while in the oxidizing environment Mn_2O_3 oxide is formed. This is consistent with the TEM data, which showed the presence of a Mn_3O_4 phase in the sample Mn–Zr-400. Probably the presence of this phase became more obvious during heating, while the gas environment led to the reduction/oxidation of the precursor oxide. On the other hand, the presence of manganese oxide may indicate partial decomposition of the solid solution phase.

3.5. Thermogravimetric analysis

The TGA and DSC curves for the Mn–Zr-400 sample in He and in air are shown in Fig. 9a and Fig. 9b, respectively. The total weight loss from room temperature to 900 °C of is 9.7 and 10 %, respectively. The endothermic peak at 52 °C in He and at 65 °C in air corresponds to the removal of residual water and/or gases, which is accompanied by a weight loss of approximately 7 %. A very intense exothermic peak is observed at 645 °C in He (Fig. 9a) and 658 °C in air (Fig. 9b). In this case, this peak is likely to be due to the crystallization process [10, 30], which is also accompanied by rapid loss of a small amount of mass. In air, crystallization is shifted to the higher temperatures by approximately 13 °C, which indicates the influence of the environment on the process. Additionally, the heat release is more intense in air than in He (the maximum value is 0.27 $\mu\text{V}/\text{mg}$ and 0.19 $\mu\text{V}/\text{mg}$, respectively). This extra heat release could be caused by

the oxidation of Mn cations in the solid solution phase or the oxidation of Mn_3O_4 oxide to Mn_2O_3 , since the latter was detected by XRD analysis (Table 2). In the temperature range of approximately 700 – 900 °C, an endothermic behavior is observed, which indicates the instability of the formed phase [31]. This may be due to a further phase transformation of cubic/tetragonal zirconia to monoclinic modification which is typical for doped ZrO_2 [20,32].

For comparison, a similar experiment was also carried out for the ZrO_2 -300 sample in He (Fig. 9c) and in air (Fig. 9d). The total weight loss was approximately 12 % in both cases. At temperatures of 61 – 65 °C, a small endothermic peak is observed, which similarly to Mn-Zr-400 sample is associated with the removal of water and residual gases, which is also accompanied by a weight loss of approximately 3 – 4 %. At 425 °C, an exothermic peak is observed both in He and in air. In this case, this peak corresponds to the crystallization process with the formation of monoclinic ZrO_2 , that is stable in this temperature range. Further heating leads to exothermic behavior. Probably this part of the curve may represent further phase transformation from monoclinic to tetragonal zirconia [6], which is not completed up to 900 °C.

Thus, a comparison of the TGA and DSC data of Mn-Zr-400 and ZrO_2 -300 showed that the presence of the Mn dopant leads, firstly, to a shift in the crystallization temperature to the higher values, and, secondly, makes the crystallization process dependent on the gas environment.

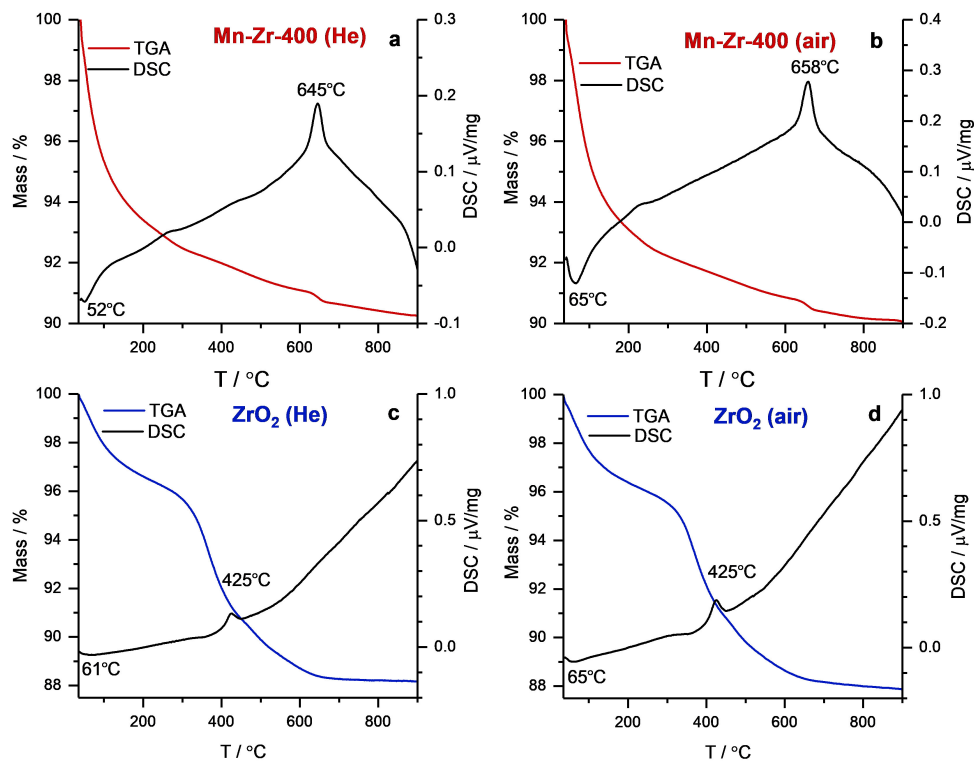


FIG. 9. TGA and DSC curves of Mn-Zr-400 sample in He (a) and in an air (b) and of ZrO_2 -300 sample in He (c) and in an air (d)

4. Discussion

As it was shown in the in situ XRD experiments (Fig. 7–8), the process of crystallization is accompanied by the decrease in CSR of zirconia phase with temperature. Typically, the crystal growth implies the increase of the particle size and, consequently, of CSR. However, it is known that Mn-Zr solid solutions are characterized by a smaller particle size than pure zirconia [27]. In this case, we observe an average picture in the diffraction patterns, so CSR calculated from these patterns is also an average value. Therefore, the reduction of CSR upon heating may be due to an increase in the content of the phase of solid solution $\text{Zr}_{1-y}\text{Mn}_y\text{O}_2$ with a higher manganese content and smaller particle size. At the same time, the amount of ZrO_2 phase with larger particle size decreases. Furthermore, it can be assumed that the process of solid solution formation delays the particle growth. Thus, we observe a decrease in CSR from 200 – 290 Å to 120 – 190 Å with heating. According to the TEM and PDF data, the manganese oxide phase is present in the Mn-Zr-400 sample, which is also preserved in the sample synthesized at 700 °C. The exact content of this phase is unknown, since the corresponding peaks are absent in the XRD patterns. However, Mn atoms uniformly distributed among Zr atoms in the amorphous precursor apparently prevented the formation of a bulk phase of pure crystalline zirconia. At the same time, this probably led to the preferable formation of a solid solution phase $\text{Zr}_{1-y}\text{Mn}_y\text{O}_2$. In situ XRD data show that the lattice parameter of the formed crystalline phase decreases with increasing temperature. Since an increase in the

parameter usually occurs during heating, we associate this behavior with structural transformations inside the sample. In this case, similar to the observed CSR dependance, we observe the gradual decrease in the lattice parameter from 5.086(1) – 5.088(1) Å to 5.072(1) – 5.082(1) Å with heating. This result is associated with the formation of the solid solution $\text{Zr}_{1-y}\text{Mn}_y\text{O}_2$ with a smaller lattice parameter and simultaneous decrease in the content of ZrO_2 with a larger lattice parameter.

In papers [9–11] doping zirconia with vanadium, lanthanum and yttrium leads to the crystallization temperature increase. The authors explain this by the presence of admixture atoms (or oxide molecules) on the surface, which prevents grain growth, that results in a higher temperature to be required to initiate the crystallization process. In our case, the shift of the crystallization process to a higher temperature region seemed to prevent the formation of monoclinic ZrO_2 crystallites. Instead, the crystalline phase formed at temperatures of 460–560 °C has a cubic (or tetragonal) structure stabilized by manganese cations (Table 1). Previously [20], we showed that at the calcination temperature 800 °C, m- ZrO_2 was formed in similar coprecipitated Mn–Zr catalyst. This can be explained by the Mn–Zr solid solution decomposition resulting in the formation of pure undoped zirconia phase, for which the monoclinic modification is stable at 800 °C.

For Mn–Zr-400 sample the presence of Mn leads to the crystallization temperature being dependent on the environment. While in an inert and reducing environments the crystallization temperature, according to in situ XRD data, is 450 – 455 °C, in an oxidizing environment it is 560 °C. Moreover, TGA of ZrO_2 -300 did not show a dependence of the crystallization temperature on the environment, unlike the manganese-containing catalyst, which is likely to be due to the redox properties of manganese. After treatment in an oxidizing environment, we also observed a smaller value of the lattice parameter of the solid solution $\text{Zr}_{1-y}\text{Mn}_y\text{O}_2$ than in the other two cases. This may indicate both a higher concentration of manganese cations in the solid solution and their partial oxidation.

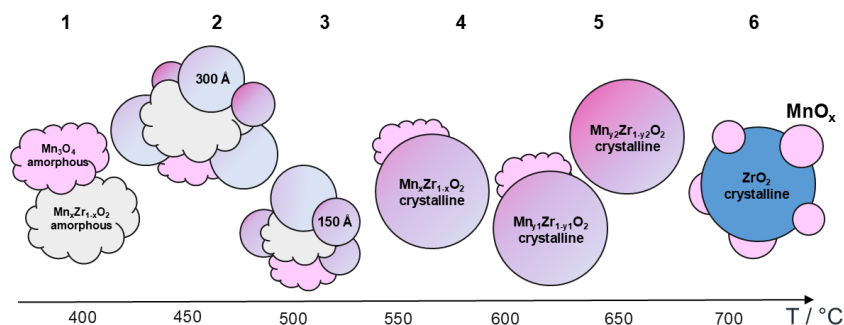


FIG. 10. Illustration of crystallization process: 1 – amorphous Mn–Zr mixed phase and oxide Mn_3O_4 ; 2 – thermally activated crystallization with the formation of large (300 Å) crystallites; 3 – formation of the solid solution phase $\text{Mn}_x\text{Zr}_{1-x}\text{O}_2$; 4, 5 – crystallization finishes; 5, 6 – decomposition of solid solution with the formation of bulk manganese oxide phase.

The possible course of this process is shown schematically in Fig. 10. At 400 °C an amorphous phase containing uniformly distributed Zr and Mn atoms is present, as well as a small amount of Mn_3O_4 (1). At 460 – 560 °C the crystallization process starts, during which crystalline ZrO_2 phase is formed (2). Further heating leads to a decrease in the content of ZrO_2 phase with a larger particle size with simultaneous increase in the content of solid solution $\text{Mn}_y\text{Zr}_{1-y}\text{O}_2$ with smaller particle size, which results in a decrease in the CSR from 200 – 290 to 120 – 190 Å (3). Crystallization is completed at 600 – 650 °C and the concentration of Mn atoms in the solid solution phase reaches its maximum (4 – 5). At 650 – 700 °C partial decomposition of the solid solution probably occurs with the formation of the bulk MnO_x phase (5 – 6).

5. Conclusion

The samples Mn–Zr-400 and Mn–Zr-700 were obtained by co-precipitation and calcination at the temperatures 400 and 700 °C, respectively. The sample ZrO_2 -300 calcined at 300 °C was used as a reference. These samples were characterized by X-ray diffraction, pair distribution function analysis, BET and transmission electron microscopy. Mn–Zr-400 is shown to be amorphous and containing uniformly distributed Mn and Zr atoms, as well as a small amount of MnO_x phase. Mn–Zr-700 contains $\text{Zr}_{1-y}\text{Mn}_y\text{O}_2$ solid solution phase based on tetragonal zirconia and also shows traces of MnO_x phase. The sample ZrO_2 -300 mainly consists of amorphous particles, but also shows the presence of crystalline zirconia phase unlike the sample Mn–Zr-400.

The process of crystallization was studied via in situ X-ray diffraction and thermogravimetric analysis. The crystallization temperature of Mn–Zr-400 in reducing and inert environments is 450 – 455 °C and in oxidizing is 560 °C. The crystallization of pure zirconia occurs at 425 °C in both oxidizing and inert environments. As the result of crystallization $\text{Zr}_{1-y}\text{Mn}_y\text{O}_2$ solid solution phase based on tetragonal modification. Further heating leads to an increase in the concentration of manganese in the solid solution (y), after which $\text{Zr}_{1-y}\text{Mn}_y\text{O}_2$ is stable up to 700 °C.

Thus, it was shown that the presence of manganese leads to the following effects:

- Shift of the crystallization onset to the higher temperatures compared to pure amorphous zirconia;
- The resulting phase of crystallization is the solid solution $\text{Zr}_{1-y}\text{Mn}_y\text{O}_2$ rather than pure ZrO_2 .

Mn cations seem to stabilize the tetragonal modification of zirconia, while in this temperature range usually monoclinic zirconia is stable. Besides, the addition of manganese allows the crystallization temperature to be controlled by varying the environment. While the reducing environment apparently has no significant effect compared to the inert one, the oxidizing environment allowed the crystallization temperature to be increased.

Appendix

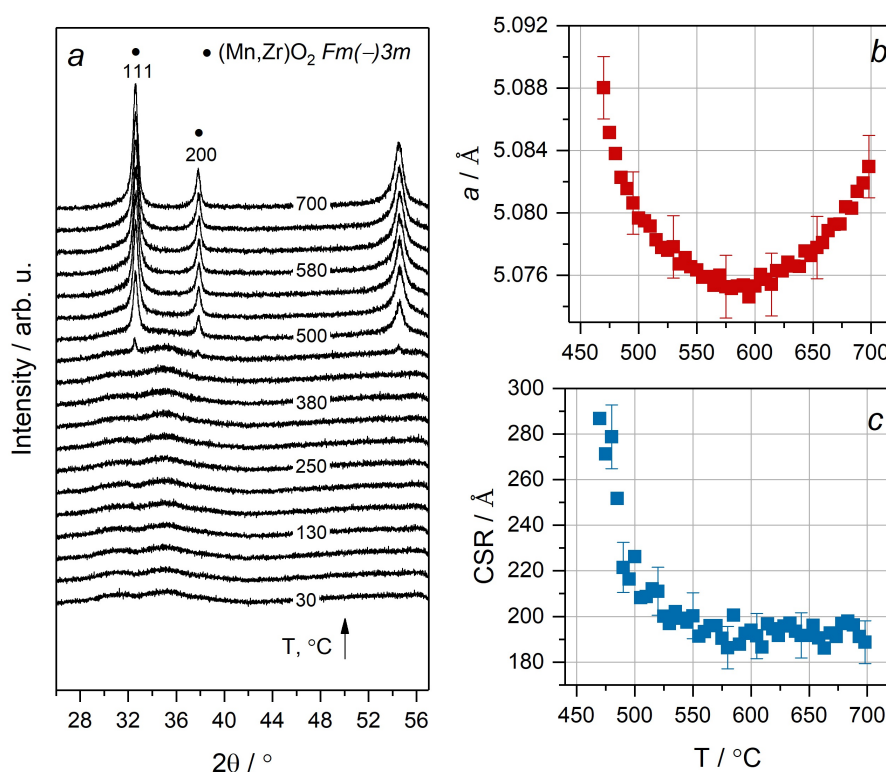


FIG. A1. XRD patterns of Mn–Zr-400 recorded upon heating from 30 to 700 °C with a rate of 5 °C/min in the H_2/He medium; $\lambda = 1.6467 \text{ \AA}$ (a) change in the lattice parameter (b) and CSR (c) of $\text{Zr}_{1-y}\text{Mn}_y\text{O}_2$ with temperature

References

- [1] Scotti N., Bossola F., Zaccheria F., Ravasio N. Copper–zirconia catalysts: Powerful multifunctional catalytic tools to approach sustainable processes. *Catalysts*, 2020, **10** (2), 168.
- [2] Goscińska J., Ziolk M., Gibson E., Daturi M. Novel mesoporous zirconia-based catalysts for WGS reaction. *Appl. Catal. B Environ.*, 2010, **97**, P. 49–56.
- [3] Liu J., Zhao Z., Xu C., Liu J. Structure, synthesis, and catalytic properties of nanosize cerium-zirconium-based solid solutions in environmental catalysis. *Chinese J. Catal.*, 2019, **40**, P. 1438–1487.
- [4] Khurshid M., Al-Daous M. A., Hattori H., Al-Khattaf S.S. Effects of hydrogen on heptane isomerization over zirconium oxide modified with tungsten oxide and platinum. *Appl. Catal. A Gen.*, 2009, **362**, P. 75–81.
- [5] Kumar A., Badoni R.P., Singhal S., Agarwal S., Tripathi A.R. Synthesis and characterization of zirconia-based catalyst for the isomerization of n-hexane. *Chem. Eng. Commun.*, 2017, **205** (1), P. 92–101.
- [6] Howard C.J., Hill R.J., Reichert B.E. Structures of ZrO_2 polymorphs at room temperature by high-resolution neutron powder diffraction. *Acta Crystallogr.*, 1988, **B44**, P. 116–120.
- [7] Yanwei Z., Fagherazzi G., Polizzi S. The local structure characterization and resulting phase-transition mechanism of amorphous ZrO_2 . *J. Mater. Sci.*, 1995, **30**, P. 2153–2158.
- [8] Tiseanu C., Parvulescu V.I., Cojocaru B., Pearnin K., Sanchez-Dominguez M., Boutonnet M. In situ Raman and time-resolved luminescence investigation of the local structure of ZrO_2 in the amorphous to crystalline phase transition. *J. Phys. Chem. C*, 2012, **116** (31), P. 16776–16783.
- [9] Svoboda R., Bulánek R., Galusek D., Hadidimasouleh R., Ganjkanlou Y. Crystal formation in vanadium-doped zirconia ceramics. *Cryst. Eng. Comm.*, 2018, **20**, P. 3105–3116.
- [10] Sohn J.R., Cho S.G., Pae Y.I., Hayashi S. Characterization of vanadium oxide-zirconia catalyst. *J. Catal.*, 1996, **159** (1), P. 170–177.
- [11] Ushakov S.V., Brown C.E., Navrotsky A. Effect of La and Y on crystallization temperatures of hafnia and zirconia. *J. Mater. Res.*, 2004, **19**, P. 693–696.

- [12] Afonasenkov T.N., Bulavchenko O.A., Gulyaeva T.I., Tsybulya S.V., Tsyurul'nikov P.G. Effect of the Calcination Temperature and Composition of the $\text{MnO}_x\text{-ZrO}_2$ System on Its Structure and Catalytic Properties in a Reaction of Carbon Monoxide Oxidation. *Kinet. Catal.*, 2018, **59**, P. 104–111.
- [13] Grabchenko M.V., Mamontov G.V., Chernykh M.V., Vodyankina O.V., Salaev M.A. Synergistic effect in ternary $\text{CeO}_2\text{-ZrO}_2\text{-MnO}_x$ catalysts for CO oxidation and soot combustion. *Chem. Eng. Sci.*, 2024, **285**, 119593.
- [14] Liberman E.Y., Kleusov B.S., Naumkin A.V. Thermal Stability and Catalytic Activity of the $\text{MnO}_x\text{-CeO}_2$ and the $\text{MnO}_x\text{-ZrO}_2\text{-CeO}_2$ Highly Dispersed Materials in the Carbon Monoxide Oxidation Reaction. *Inorg. Mater. Appl. Res.*, 2021, **12**, P. 468–476.
- [15] López E.F., Escribano V.S., Resini C., Gasllardo-Amores J.M., Busca G. A study of coprecipitated Mn-Zr oxides and their behaviour as oxidation catalysts. *Appl. Catal. B Environ.*, 2001, **29**, P. 251–261.
- [16] Qu Y., Zhu S., Zhang L. Low-temperature catalytic combustion of benzene over Zr-Mn mixed oxides synthesized by redox-precipitation method. *J. Mater. Sci.*, 2021, **56**, P. 13540–13555.
- [17] Xu H., Yan N., Qu Z., Liu W., Mei J., Huang W., Zhao S. Gaseous Heterogeneous Catalytic Reactions over Mn-Based Oxides for Environmental Applications: A Critical Review. *Environ. Sci. Technol.*, 2017, **51** (16), P. 8879–8892.
- [18] Koh D.J., Chung J.S., Kim Y.G., Lee J.S., Nam I., Moon S.H. Structure of MnZr mixed oxide catalysts and their catalytic properties in the CO hydrogenation reaction. *Journal of Catalysis*, 1992, **138**, P. 630–639.
- [19] Choudhary V.R., Uphade B.S., Pataskar S.G. Low temperature complete combustion of dilute methane over Mn-doped ZrO_2 catalysts: Factors influencing the reactivity of lattice oxygen and methane combustion activity of the catalyst. *Appl. Catal. A Gen.*, 2002, **227** (1–2), P. 29–41.
- [20] Bulavchenko O.A., Konovalova V.P., Saraev A.A., Kremneva A.M., Rogov V.A., Gerasimov E.Y., Afonasenkov T.N. The Catalytic Performance of CO Oxidation over $\text{MnO}_x\text{-ZrO}_2$ Catalysts: The Role of Synthetic Routes. *Catalysts*, 2023, **13**, 57.
- [21] Aulchenko V.M., Evdokov O.V., Kutovenko V.D., Pirogov B.Ya., Sharafutdinov M.R. One-coordinate X-ray detector OD-3M. *Nucl. Instruments Methods Phys. Res. Sect. A Accel. Spectrometers, Detect. Assoc. Equip.*, 2009, **603**, P. 76–79.
- [22] Kabekkodu S.N., Dosen A., Blanton T.N. PDF-5+: A comprehensive powder diffraction file™ for materials characterization. *Powder Diffr.*, 2024, **39**, P. 47–59.
- [23] Degen T., Sadki M., Bron E., König U., Nénert G. The high score suite. *Powder Diffraction*, 2014, **29**, S13–S18.
- [24] Patterson A.L. The Scherrer Formula for X-ray Particle Size Determination. *Phys. Rev.*, 1939, **56**, 978.
- [25] Qiu X., Thompson J.W., Billinge S.J.L. PDFgetX2: A GUI-driven program to obtain the Pair Distribution Function from X-ray Powder Diffraction Data. *J. Appl. Cryst.*, 2004, **37**, 678.
- [26] Farrow C.L., Juhas P., Liu J.W., Bryndin D., Božin E.S. PDFfit2 and PDFgui: computer programs for studying nanostructure in crystals. *J. Phys. Condens. Matter*, 2007, **19**, 33.
- [27] Bulavchenko O.A., Vinokurov Z.S., Afonasenkov T.N., Tsyurul'nikov P.G. Reduction of mixed Mn-Zr oxides: in situ XPS and XRD studies. *Dalt. Trans.*, 2015, **44**, P. 15499–15507.
- [28] Shannon R.D. Revised effective ionic radii and systematic studies of interatomic distances in halides and chalcogenides. *Acta Crystallogr.*, 1976, **A32**, P. 751–767.
- [29] Vanderbilt D., Zhao X., Ceresoli D. Structural and dielectric properties of crystalline and amorphous ZrO_2 . *Thin Solid Films*, 2005, **486**, P. 125–128.
- [30] Aguilar D.H., Torres-Gonzalez L.C., Torres-Martinez L.M., Lopez T., Quintana P. A study of the crystallization of ZrO_2 in the sol-gel system: $\text{ZrO}_2\text{-SiO}_2$. *J. Solid State Chem.*, 2001, **158**, P. 349–357.
- [31] Prasad K., Pinjari D.V., Pandit A.B., Mhaske S.T. Synthesis of zirconium dioxide by ultrasound assisted precipitation: Effect of calcination temperature. *Ultrason. Sonochem.*, 2011, **18**, P. 1128–1137.
- [32] Afonasenkov T.N., Glyzdova D.V., Yurpalov V.L., Konovalova V.P., Rogov V.A., Gerasimov E.Y., Bulavchenko O.A. The Study of Thermal Stability of Mn-Zr-Ce, Mn-Ce and Mn-Zr Oxide Catalysts for CO Oxidation. *Materials*, 2022, **15** (21), 7553.

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Ni(OH)₂ and Co(OH)₂ modified g-C₃N₄ for photocatalytic CO₂ reduction

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ABSTRACT This study presents the synthesis and characterization of composite photocatalysts based on g-C₃N₄ modified with Ni(OH)₂ and Co(OH)₂ for CO₂ reduction under visible light ($\lambda = 410$ nm). XRD, UV-Vis spectroscopy, and high-resolution TEM analyses revealed that the deposition of hydroxides did not disrupt the g-C₃N₄ structure but caused a slight increase in the interlayer spacing and band gap; Ni(OH)₂ formed nanoparticles of ~ 7 nm, whereas Co(OH)₂ crystallized as larger particles of ~ 24 nm. TEM showed that after the photocatalytic CO₂ reduction, partial agglomeration of Ni(OH)₂/NiO occurs. The catalyst containing 0.1 wt.% Ni(OH)₂ exhibited the highest activity – $7.04 \mu\text{mol}\cdot\text{g}^{-1}\cdot\text{h}^{-1}$, achieving a CO₂ reduction rate 1.9 times higher than that of pristine g-C₃N₄. The 0.5 wt.% Co(OH)₂/g-C₃N₄ photocatalyst was achieved a 1.3-fold increase in activity compared to pristine g-C₃N₄. This enhancement is attributed to the formation of a II type heterojunction between g-C₃N₄ and Ni(OH)₂, which facilitates charge transfer and suppresses recombination.

KEYWORDS g-C₃N₄, photocatalysis, Ni(OH)₂, Co(OH)₂, CO₂ reduction

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1. Introduction

In today’s world, the intensification of the greenhouse effect and climate change are global problems that the entire international scientific community is interested in solving [1–3]. The concentration of carbon dioxide (CO₂) in the atmosphere continues to increase due to the use of fossil fuels in modern energy production [4–7]. Therefore, it seems reasonable not only to capture CO₂ but also to convert it into valuable products in order to achieve a balance between energy demands and environmental sustainability [8, 9]. Converting CO₂ into valuable chemicals not only decreases its atmospheric concentration, but also helps to store solar energy in the form of stable chemical bonds [10–12]. This is important because CO₂ is available in huge volumes and can serve as a raw material for various materials. Among various CO₂ conversion approaches, photocatalysis is particularly attractive as it utilizes solar energy to transform CO₂ into CO, CH₄, CH₃OH, and other products and is carried out at room temperature and atmospheric pressure [13, 14], unlike industrial processes [15].

Efficient CO₂ conversion into chemical compounds requires catalytic systems with high activity and selectivity for the target products, and resistance to photodegradation. Current challenges in this area include selecting efficient and durable materials, reducing the energy required for CO₂ activation, increasing the proportion of target products, and minimizing side reactions such as H₂ evolution and H₂O splitting. Photocatalytic systems based on semiconductors, in particular graphitic carbon nitride (g-C₃N₄), doped with metals or metal oxides are of particular interest [16–18]; g-C₃N₄ has a favorable band gap, the ability to absorb visible light, and great potential as a photocatalyst [19–21]. However, pristine g-C₃N₄ has limitations: a relatively small surface area, rapid recombination of photogenerated charge carriers, and low selectivity in CO₂ reduction reactions [20, 22, 23]. To overcome these limitations, g-C₃N₄ modification through doping, heterostructure formation, and active phase deposition is widely used [20, 24, 25]. In this regard, transition metal hydroxides such as Ni(OH)₂ and Co(OH)₂ act as effective cocatalysts. Introducing them into the g-C₃N₄ system improves the separation of photogenerated charge carriers, more effectively adsorbs CO₂ molecules on the material surface, and reduces side reactions, thereby paving the way for increased activity and selectivity [26–28].

This study aims to compare the effect of $\text{Ni}(\text{OH})_2$ and $\text{Co}(\text{OH})_2$ supported on $\text{g-C}_3\text{N}_4$ on the photocatalytic activity and selectivity in CO_2 reduction. The results will provide recommendations for the optimal ratio of $\text{Ni}(\text{OH})_2$ and $\text{Co}(\text{OH})_2$ phases deposited onto $\text{g-C}_3\text{N}_4$, which will increase the yield of target products.

2. Experimental

2.1. Photocatalyst synthesis

2.1.1. $\text{g-C}_3\text{N}_4$ synthesis. A suspension was prepared from a mixture of melamine, cyanuric acid and distilled water (300 ml) and heated with constant stirring for 12 h at 90 °C [29]. The resulting supramolecular complex of melamine-cyanuric acid was washed with water, dried in vacuum, and calcined in air at 550 °C for 1 h at a heating rate of 1 °C/min.

2.1.2. $\text{Ni}(\text{OH})_2$ and $\text{Co}(\text{OH})_2$ deposition. A suspension was prepared by dispersing 500 mg of $\text{g-C}_3\text{N}_4$ in 20 ml of acetone. The required amount of nickel or cobalt nitrate ($\text{M}(\text{NO}_3)_2$) was then added to the suspension. The mixture was sonicated for 1 min, after which acetone was removed using a rotary evaporator. To convert the metal species into the hydroxide form on the $\text{g-C}_3\text{N}_4$ surface, small portions of the dried $\text{M}(\text{NO}_3)_2/\text{g-C}_3\text{N}_4$ samples were added to a 0.5 M NaOH solution with intensive stirring. After 10 min, the samples were filtered through a PTFE membrane, washed twice with water and dried under vacuum at 40 °C for 10 hours.

2.2. Photocatalyst characterization

The synthesized catalysts were studied using a set of physicochemical analysis methods: X-ray diffraction (XRD), diffuse reflectance spectroscopy (DRS), and high-resolution transmission electron microscopy (HRTEM). The phase composition and particle size were determined by XRD. XRD patterns were recorded on a Bruker D8 Advance diffractometer in the 2θ range from 10° to 65° using Cu $K\alpha$ radiation. DRS in the UV- and visible spectral regions were obtained on a Shimadzu UV-2501 PC spectrophotometer with an ISR-240A diffuse reflectance attachment in the 200 – 800 nm wavelength range. The optical band gap was calculated from a linear fit to the Tauc plot for indirect allowed transitions. Surface morphology was studied using HR TEM on a ThemisZ microscope (Thermo Fisher Scientific) with an accelerating voltage of 200 kV. To prepare for analysis, samples were dispersed in an ultrasonic bath and applied to perforated carbon substrates.

2.3. Photocatalytic CO_2 reduction experiment

The photocatalytic CO_2 reduction was performed in a static glass reactor ($V = 170$ ml) with a quartz window (16 cm^2) (Fig. 1a). Typically, 30 mg of photocatalyst dispersed in 500 μl of ultrapure water (NuZar Q water purification system), after that this suspension was applied to a glass support (8 cm^2). The photocatalyst was then dried and illuminated with LED-410 nm for 30 min to remove organic contaminants from the photocatalyst surface. The glass support with the deposited photocatalyst was then placed in a reactor containing 1 ml of ultrapure water. The reactor was purged with Ar for 20 min to remove O_2 , followed by CO_2 (99.995 %) purging also for 20 min, and then irradiated with 410-nm LED (Fig. 1b). The gas phase was analyzed by Chromos GKh-1000 gas chromatograph equipped with a flame ionization detector with methanator and a thermal conductivity detector. Samples were collected every hour, and the photocatalytic experiment lasted 4 hours. The production rates (CO , CH_4) were calculated by linear approximation of the kinetics curves. The total electron absorption rates were calculated by the following formula:

$$W_{e-}(\text{CO}_2\text{RR}) = 2 \times W(\text{CO}) + 8 \times W(\text{CH}_4), \quad (1)$$

where 2 and 8 are coefficients for electron balance, and $W(\text{CO})$ and $W(\text{CH}_4)$ are the production rates of CO and CH_4 , respectively.

3. Results and discussion

The photocatalysts $\text{g-C}_3\text{N}_4$, 2.5 % $\text{Ni}(\text{OH})_2/\text{g-C}_3\text{N}_4$, and 2.5 % $\text{Co}(\text{OH})_2/\text{g-C}_3\text{N}_4$ were analyzed by XRD. Fig. 2 shows the XRD patterns of these photocatalysts. The diffraction peaks at 13.6° and 27.7° correspond to the (210) and (002) reflections, respectively [29]. In addition to the two characteristic peaks of the $\text{g-C}_3\text{N}_4$ structure, several weaker peaks are observed, including a peak near 57° related to the (004) plane. This confirms the formation of $\text{g-C}_3\text{N}_4$ with an orthorhombic structure [30, 31].

Furthermore, the impact of the supported $\text{Ni}(\text{OH})_2$ and $\text{Co}(\text{OH})_2$ on the coherent scattering region (CSR) of the intraplanar structure of $\text{g-C}_3\text{N}_4$ and the interplanar spacing is evident. The CSR of $\text{Co}(\text{OH})_2$ is significantly higher than that of $\text{Ni}(\text{OH})_2$, which indicates crystallization. The deposition of $\text{Ni}(\text{OH})_2$ and $\text{Co}(\text{OH})_2$ does not lead to the appearance of new reflections in the XRD patterns. This indicates the absence of bulk crystalline hydroxide phases and their high dispersion on the $\text{g-C}_3\text{N}_4$ surface.

However, quantitative analysis of the XRD patterns (see Table 1) revealed the influence of the modifying additives on the $\text{g-C}_3\text{N}_4$ structural parameters. Specifically, the interplanar spacing d_{002} increases from 3.217 Å for unmodified $\text{g-C}_3\text{N}_4$ to 3.244 and 3.236 Å for composites with 2.5 % $\text{Ni}(\text{OH})_2$ and $\text{Co}(\text{OH})_2$, respectively. This indicates the successful interaction between the deposited hydroxides and the $\text{g-C}_3\text{N}_4$ lattice. Calculating the CSR sizes using the Scherrer

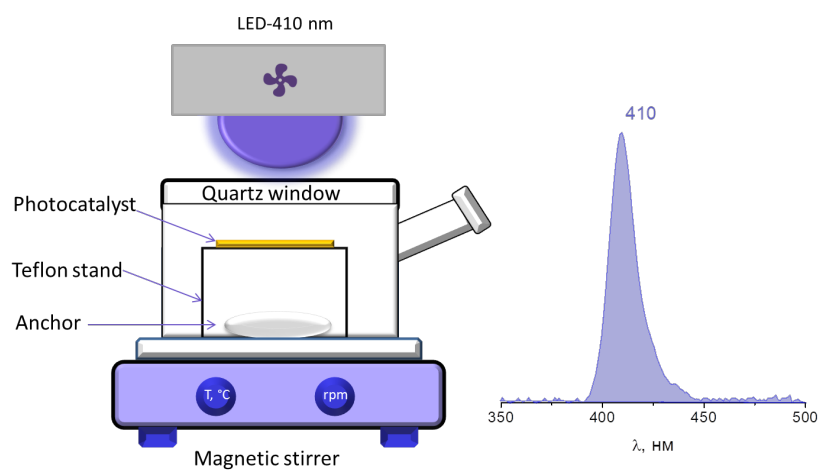


FIG. 1. Photocatalytic reactor for CO_2 reduction and the emission spectra of LED-410 nm

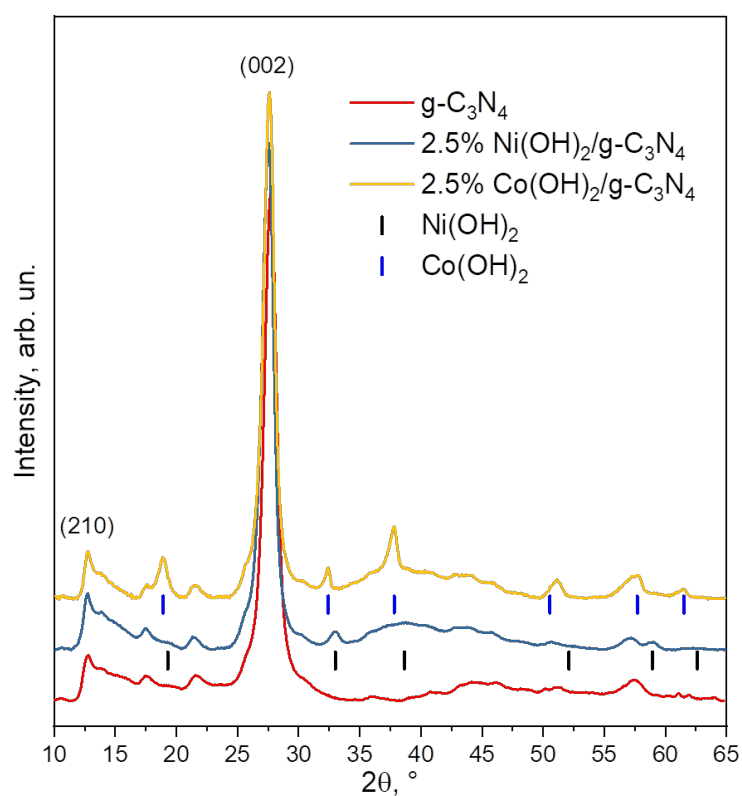


FIG. 2. XRD patterns of $\text{g-C}_3\text{N}_4$, 2.5 % $\text{Ni}(\text{OH})_2/\text{g-C}_3\text{N}_4$ and 2.5 % $\text{Co}(\text{OH})_2/\text{g-C}_3\text{N}_4$

TABLE 1. Structural characteristics of $\text{g-C}_3\text{N}_4$, 2.5 % $\text{Ni}(\text{OH})_2/\text{g-C}_3\text{N}_4$ and 2.5 % $\text{Co}(\text{OH})_2/\text{g-C}_3\text{N}_4$ photocatalysts calculated from XRD data

Photocatalyst	$d_{210}/\text{\AA}$	L_a , nm	$d_{002}/\text{\AA}$	L_c , nm	$\text{Ni}(\text{OH})_2/\text{Co}(\text{OH})_2$ CSR, nm
$\text{g-C}_3\text{N}_4$	6.95(1)	8(1)	3.217(5)	7(1)	—
2.5 % $\text{Ni}(\text{OH})_2/\text{g-C}_3\text{N}_4$	6.98(1)	11(1)	3.244(5)	8(1)	7(1)
2.5 % $\text{Co}(\text{OH})_2/\text{g-C}_3\text{N}_4$	6.94(1)	11(1)	3.236(5)	8(1)	24(1)

formula showed that Ni(OH)_2 forms nanosized particles measuring ~ 7 nm, while Co(OH)_2 crystallizes as significantly larger particles (~ 24 nm). Such difference in crystallite size may significantly affect the photocatalytic properties of the synthesized materials.

The optical properties of all synthesized photocatalysts were investigated. Fig. 3(a and c) presents the diffuse reflectance spectra, showing that all photocatalysts absorb visible light in the 400 – 800 nm range. The absorption edge is located in the 425 – 460 nm region. Fig. 3(b and d) shows the plots in Tauc coordinates for calculating the optical band gap. Upon the addition of Ni(OH)_2 and Co(OH)_2 , the optical band gap slightly increases from 2.68 to 2.87 eV. This is due to the fact that Ni(OH)_2 and Co(OH)_2 are wider-bandgap semiconductors [32, 33].

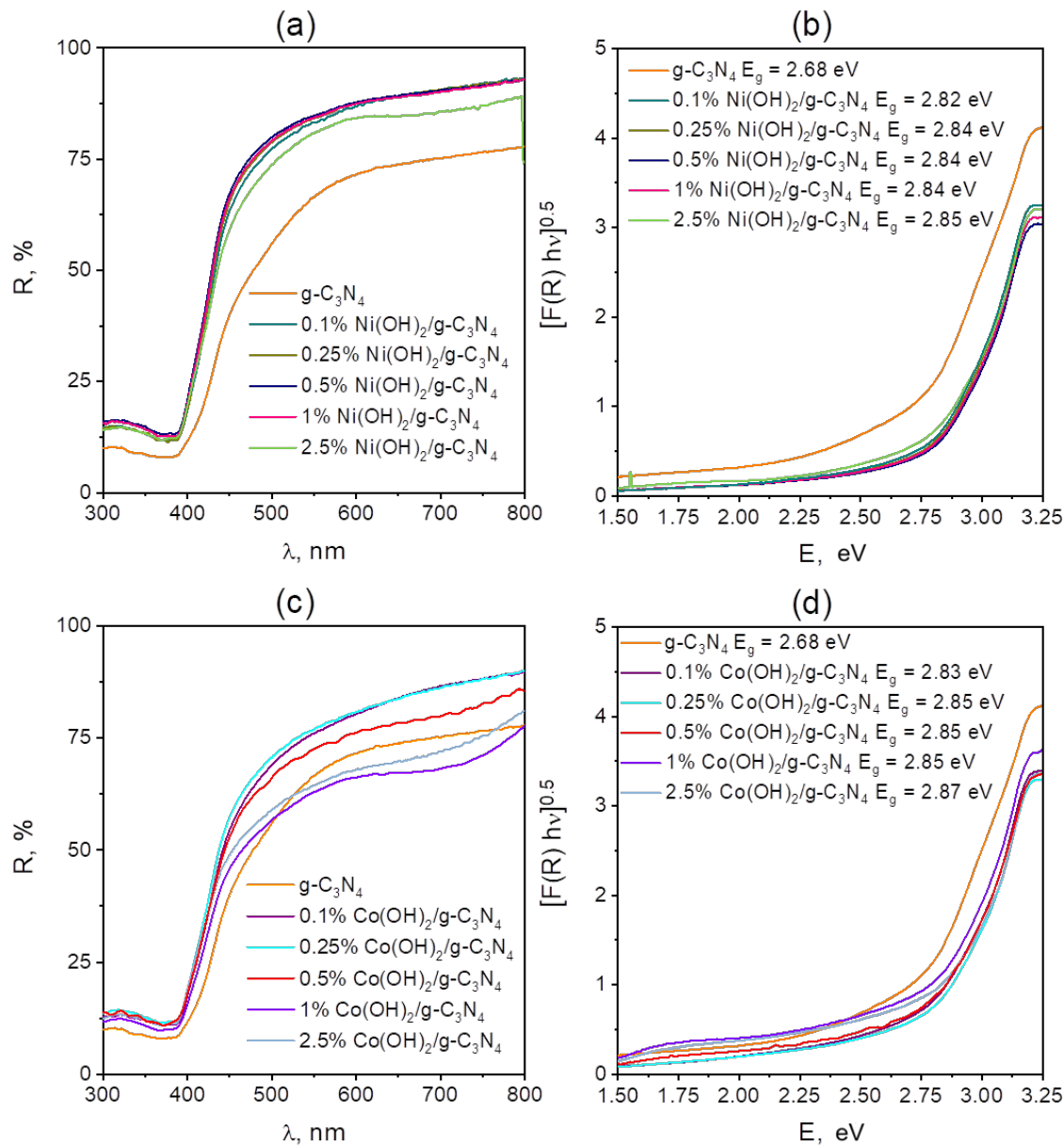


FIG. 3. (a, c) UV-Vis spectra of photocatalysts; (b, d) Tauc plots for calculating E_g of the x % $\text{Ni(OH)}_2/\text{g-C}_3\text{N}_4$ and x % $\text{Co(OH)}_2/\text{g-C}_3\text{N}_4$ ($x = 0 - 2.5$ wt.%) photocatalysts

TEM was used to study the 1 % $\text{Ni(OH)}_2/\text{g-C}_3\text{N}_4$ photocatalyst (Fig. 4(a–c)). It was shown that g-C₃N₄ is represented by rounded thin nanosheets. Following the deposition of 1 % Ni(OH)_2 , the surface became covered with uniformly distributed nanoparticles of $\sim 0.5 - 2$ nm thick, corresponding to 2 – 5 stacked Ni(OH)_2 layers, while preserving the layered structure (Fig. 4(a, b)). Ni(OH)_2 exhibits strong adhesion to the surface of g-C₃N₄. The (001) plane of Ni(OH)_2 is oriented parallel to the corresponding (002) (from XRD data (Fig. 2)) plane of g-C₃N₄ and is consistent with the observed lamellar morphology. The Ni(OH)_2 particles are in close contact with the g-C₃N₄ surface (Fig. 4(c)), ensuring effective interfacial interaction and the formation of local type II heterojunctions. This organization promotes the spatial separation of photogenerated charge carriers, reduces their recombination and directs electrons to the cocatalyst surface, where CO_2 reduction occurs.

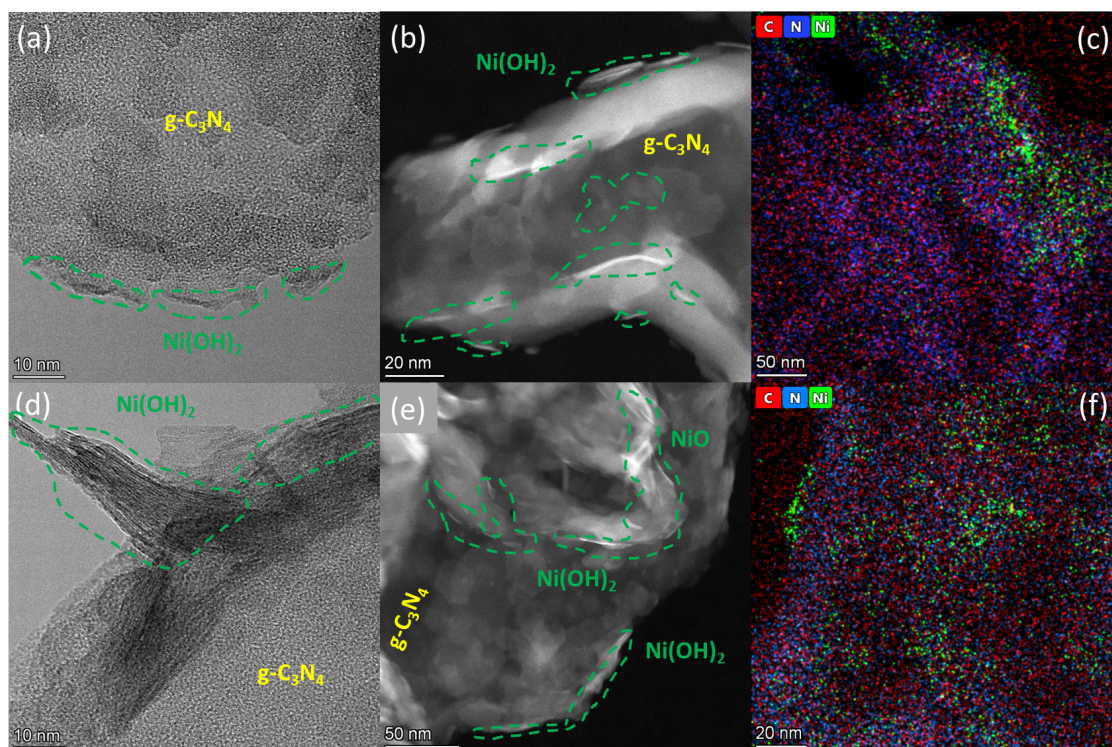


FIG. 4. (a) HR TEM, (b) HAADF STEM, (c) elemental mapping for 1 % Ni(OH)₂/g-C₃N₄ photocatalysts; (d) HR TEM, (e) HAADF STEM, (f) elemental mapping for 1 % Ni(OH)₂/g-C₃N₄ photocatalysts after CO₂ reduction

All synthesized x % Ni(OH)₂/g-C₃N₄ and x % Co(OH)₂/g-C₃N₄ photocatalysts were studied in the CO₂ reduction under 410-nm LED irradiation. Fig. 5(a) shows the rates of CO and CH₄ formation in the presence of x % Ni(OH)₂/g-C₃N₄ photocatalysts. As can be seen, the main product formed during the CO₂ reduction reaction is CO. Fig. 5(b) shows the overall rate of CO₂ reduction. The most active photocatalysts were 0.1 % and 0.25 % Ni(OH)₂/g-C₃N₄ with a CO₂ reduction rate of 7.04 and 7.08 $\mu\text{mol}\cdot\text{g}^{-1}\cdot\text{h}^{-1}$, respectively. The reaction rate of photocatalysts containing 1 and 2.5 % Ni(OH)₂ differed little from the rates of 0.1 % Ni(OH)₂/g-C₃N₄ and 0.25 % Ni(OH)₂/g-C₃N₄. Therefore, we will consider 0.1 % Ni(OH)₂ to be the most effective composition, since even a small addition of cocatalyst allows for a 1.9-fold increase in the CO₂ reduction rate.

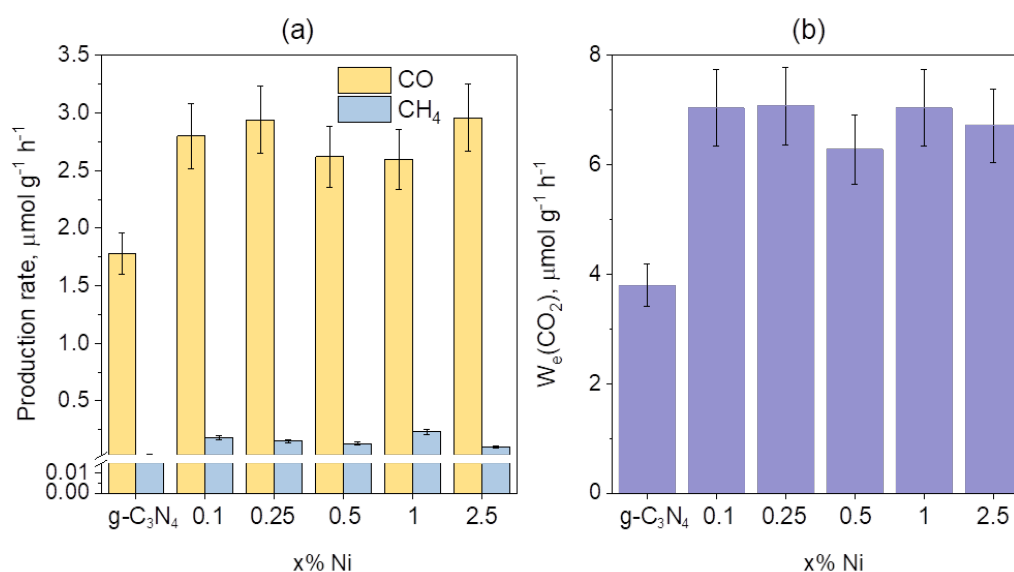


FIG. 5. (a) CO and CH₄ production rates; (b) total electron consumption rate during CO₂ reduction in the presence of x % Ni(OH)₂/g-C₃N₄ photocatalysts. Conditions: $m(\text{cat.}) = 30$ mg, $t(\text{reaction}) = 4$ h. Light source: LED with $\lambda = 410$ nm.

Figure 6(a) illustrates the CO and CH₄ formation rates in the presence of the x % Co(OH)₂/g-C₃N₄ photocatalysts. As can be seen, the main product formed during the CO₂ reduction is also CO. Fig. 6(b) shows the total rate of CO₂ reduction. The most active photocatalyst was 0.5 % Co(OH)₂/g-C₃N₄ with CO₂ reduction rate of 4.84 $\mu\text{mol}\cdot\text{g}^{-1}\cdot\text{h}^{-1}$. The rates of photocatalysts containing 1 % and 2.5 % Co(OH)₂ did not differ significantly from the rate of the 0.5 % Co(OH)₂/g-C₃N₄ photocatalyst within the measurement error. Unfortunately, only a slight increase in the photocatalytic activity is achieved for Co(OH)₂ deposition on the surface of g-C₃N₄.

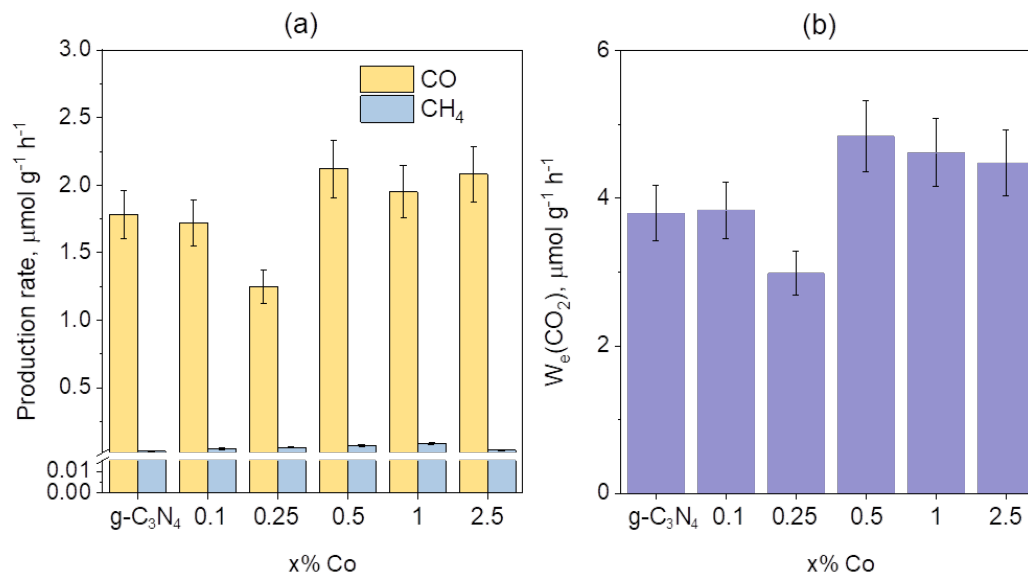


FIG. 6. (a) CO and CH₄ production rates; (b) total electron consumption rate during CO₂ reduction in the presence of x % Co(OH)₂/g-C₃N₄ photocatalysts. Conditions: $m(\text{cat.}) = 30 \text{ mg}$, $t(\text{reaction}) = 4 \text{ h}$. Light source: LED with $\lambda = 410 \text{ nm}$.

After the CO₂ reduction, the most active photocatalyst – 0.1 % Ni(OH)₂/g-C₃N₄ was studied by TEM (Fig. 4(d–f)). Some of the Ni(OH)₂ is converted into NiO, creating defects and oxygen vacancies that enhance photocatalytic activity. Adhesion is maintained, with the partial agglomeration of Ni(OH)₂/NiO particles on the g-C₃N₄ surface. A partial increase in particle size as a result of the CO₂ reduction reaction is observed in an increase in the thickness of layered particles (Fig. 4(d, e)), while the uniformity of the distribution of Ni(OH)₂ particles over the surface of g-C₃N₄ is maintained (Fig. 4(f)). After the photocatalytic CO₂ reduction, it is important to note that there are no signs of photocatalyst degradation: the layered g-C₃N₄ morphology and the Ni(OH)₂ dispersion are both preserved. This indicates the catalyst's structural stability under reaction conditions and confirms its high photocatalytic activity.

Also, the mechanism of photocatalytic CO₂ reduction on Ni(OH)₂/g-C₃N₄ (Fig. 7(a)) and Co(OH)₂/g-C₃N₄ (Fig. 7(b)) composites was proposed. Upon light irradiation, both semiconductors (g-C₃N₄ and Ni(OH)₂ or Co(OH)₂) are photoexcited. Electrons from the conduction band (CB) of g-C₃N₄ are transferred to the CB of the hydroxides, while holes from the valence band (VB) of the hydroxides migrate to the VB of g-C₃N₄, where they participate in the H₂O oxidation. This type II heterojunction scheme ensures the spatial separation of photogenerated charge carriers suppresses their recombination and directs electrons to the cocatalyst surface [34, 35], where activation and CO₂ reduction occur. The CB level of g-C₃N₄ provides sufficient potential for the two-electron reduction of CO₂ to CO, which explains why CO is the main reaction product. The comparatively low rate of CO₂ reduction in the presence of Co(OH)₂/g-C₃N₄ compared to Ni(OH)₂/g-C₃N₄ may be associated with the rather large size of cobalt hydroxide particles, three times larger than the size of nickel hydroxide particles (see Table 1).

4. Conclusion

This study presents the synthesis and characterization of composite photocatalysts based on g-C₃N₄, modified with Ni(OH)₂ and Co(OH)₂, for the photocatalytic reduction of CO₂ under visible light ($\lambda = 410 \text{ nm}$). The introduction of hydroxides did not disrupt the structure of g-C₃N₄, but rather to increase the interplanar spacing and optical band gap, indicating interaction between the phases. Note that Ni(OH)₂ forms nanoparticles with a CSR approximately 7 nm, whereas Co(OH)₂ crystallizes into larger particles of around 24 nm. TEM study showed that partial agglomeration of Ni(OH)₂/NiO particles observed after CO₂ reduction while adhesion was maintained, indicating morphological stability. The presence of cocatalysts promotes efficient charge separation and increases activity in the CO₂ reduction reaction. Catalysts containing 0.1 and 0.25 wt.% Ni(OH)₂ have comparable CO₂ reduction rates and exceed the activity of the unmodified g-C₃N₄ by 1.9 times. The 0.1 % Ni(OH)₂/g-C₃N₄ was selected as the optimal photocatalyst, as it provides

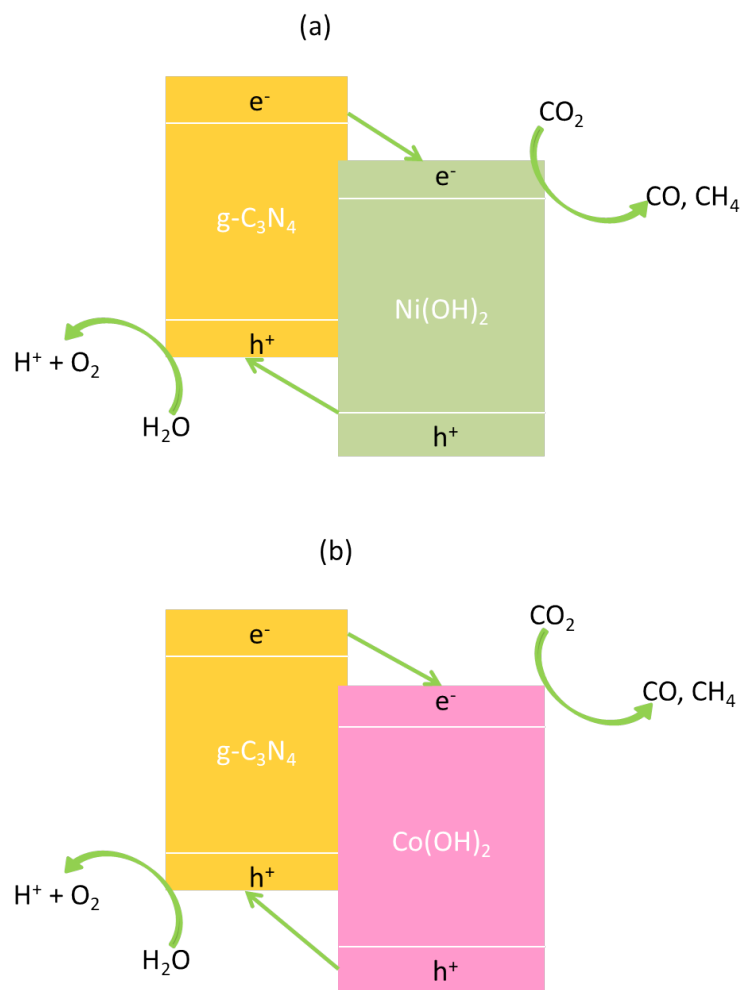


FIG. 7. Heterojunctions between (a) $\text{Ni}(\text{OH})_2$ and $\text{g-C}_3\text{N}_4$; (b) $\text{Co}(\text{OH})_2$ and $\text{g-C}_3\text{N}_4$

the same level of activity with minimal cocatalyst loading. For photocatalysts containing 0.5-2.5 % $\text{Co}(\text{OH})_2$, the CO_2 reduction rate was almost the same and exceeded the activity of the pristine $\text{g-C}_3\text{N}_4$ by ~ 1.3 times. Therefore, 0.5 % $\text{Co}(\text{OH})_2/\text{g-C}_3\text{N}_4$ was chosen as the active photocatalyst from all modified $\text{Co}(\text{OH})_2$, as it provides the maximum effect with a minimum cocatalyst loading. This increase in activity is attributed to the formation of a type II heterojunction between $\text{g-C}_3\text{N}_4$ and the transition metal hydroxides, facilitating charge transfer and suppressing charge recombination. Therefore, modifying $\text{g-C}_3\text{N}_4$ with transition metal hydroxides is an effective strategy to improve the photocatalytic activity of CO_2 reduction under visible light irradiation.

References

- [1] Filonchik M., Peterson M.P., Zhang L., Hurynovich V., He Y. Greenhouse gases emissions and global climate change: Examining the influence of CO₂, CH₄, and N₂O. *Sci. Total Environ.*, 2024, **935**, 173359.
- [2] Schneider S.H. Greenhouse Effect: Science and Policy. *Science*, 1989, **243**, P. 771–781.
- [3] Zlotin S.G., Egorova K.S., Ananikov V.P., Akulov A.A., Varaksin M.V., Chupakhin O.N., Charushin V.N., Bryliakov K.P., Averin A.D., Beletskaya I.P., Dolengovski E.L., Budnikova Y.H., Sinyashin O.G., Gafurov Z.N., Kantyukov A.O., Yakhvarov D.G., Aksenov A.V., Elinson M.N., Nenajdenko V.G., Chibiryayev A.M., Nesterov N.S., Kozlova E.A., Martyanov O.N., Balova I.A., Sorokoumov V.N., Guk D.A., Beloglazkina E.K., Lemenovskii D.A., Chukicheva I.Y., Frolova L.L., Izmet'shev E.S., Dvornikova I.A., Popov A.V., Kutchin A.V., Borisova D.M., Kalinina A.A., Muzafarov A.M., Kuchurov I.V., Maximov A.L., Zolotukhina A.V. The green chemistry paradigm in modern organic synthesis. *Russ. Chem. Rev.*, 2023, **92**, RCR5104.
- [4] Kozlova E.A., Lyulyukin M.N., Kozlov D.V., Parmon V.N. Semiconductor photocatalysts and mechanisms of carbon dioxide reduction and nitrogen fixation under UV and visible light. *Russ. Chem. Rev.*, 2021, **90**, P. 1520–1543.
- [5] Alekseev R.F., Saraev A.A., Kurenkova A.Y., Kozlova E.A. Heterostructures based on g-C₃N₄ for the photocatalytic CO₂ reduction. *Russ. Chem. Rev.*, 2024, **93**, 5124.
- [6] Karnauskas K.B. Fossil Fuel Combustion Is Driving Indoor CO₂ Toward Levels Harmful to Human Cognition. *GeoHealth*, 2020, **4**, e2019GH000237.
- [7] Nunes L.J.R. The Rising Threat of Atmospheric CO₂: A Review on the Causes, Impacts, and Mitigation Strategies. *Environments*, 2023, **10**, 66.
- [8] Eldesouki M.H., Rashed A.E., Abd A., Moneim E. A comprehensive overview of carbon dioxide, including emission sources, capture technologies, and the conversion into value-added products. *Clean Technol. Environ. Policy*, 2023, **25**, P. 3131–3148.
- [9] Garcia-Garcia G., Fernandez C., Armstrong K., Woolass S. Analytical Review of Life-Cycle Environmental Impacts of Carbon Capture and Utilization Technologies. *ChemSusChem*, 2021, **14**, P. 995–1015.
- [10] Liu Y., Sun J., Huang H., Bai L., Zhao X., Qu B., Xiong L., Bai F., Tang J. Improving CO₂ photoconversion with ionic liquid and Co single atoms. *Nat. Commun.*, 2023, **14**, 1457.
- [11] Ulmer U., Dingle T., Duchesne P.N., Morris R.H., Tavasoli A., Wood T., Ozin G.A. Fundamentals and applications of photocatalytic CO₂ methanation. *Nat. Commun.*, 2019, **10**, 3169.
- [12] Shoaib S., Shah A., Altaf M., Khan K., Hussain I., Tayyab M., Alarfaji S.S., Hassan A.M., Sohail M., Sufyan M., Najam T. Solar energy storage to chemical: Photocatalytic CO₂ reduction over pristine metal-organic frameworks with mechanistic studies. *J. Energy Storage*, 2024, **75**, 109725.
- [13] Wang Y., Chen E., Tang J. Insight on Reaction Pathways of Photocatalytic CO₂ Conversion. *ACS Catal.*, 2022, **12**, P. 7300–7316.
- [14] Qu T., Wei S., Xiong Z., Zhang J., Zhao Y. Progress and prospect of CO₂ photocatalytic reduction to methanol. *Fuel Process. Technol.*, 2023, **251**, 107933.
- [15] Arun J., Priyadharsini P., Shyam S., Subathra M., Gopinath K.P. A review on conversion of carbon dioxide (CO₂) to methanol and methane by photocatalytic reactors: a comparative analysis with algae-based CO₂ sequestration. *J. Chem. Technol. Biotechnol.*, 2025, **101**, P. 241–254.
- [16] Potapenko K., Kurenkova A., Saraev A., Aydaykov E., Mishchenko D., Gerasimov E., Zhurenok A., Lomakina V., Byambajav E., Kozlova E. Efficient hydrogen production from water solutions of plant biomass components over “core-shell” Ni(OH)₂/NiO/Ni modified g-C₃N₄ under visible light. *Int. J. Hydrogen Energy*, 2025, **185**, 151954.
- [17] Vasilchenko D., Zhurenok A., Saraev A., Gerasimov E., Cherepanova S., Kovtunova L., Tkachev S., Kozlova E. Platinum deposition onto g-C₃N₄ using a labile nitratocomplex for generation of highly active hydrogen-evolution photocatalysts. *Int. J. Hydrogen Energy*, 2022, **47**, 11326.
- [18] Zhang Y., Ligthart D.A.J.M., Quek X.Y., Gao L., Hensen E.J.M. Influence of Rh nanoparticle size and composition on the photocatalytic water-splitting performance of Rh/graphitic carbon nitride. *Int. J. Hydrogen Energy*, 2014, **39**, P. 11537–11546.
- [19] Parameters R., Design S., Methods E. Recent Advances in g-C₃N₄ Photocatalysts: A Review of Reaction Parameters, Structure Design and Exfoliation Methods. *Catalysts*, 2023, **13**, 1402.
- [20] Zhurenok A.V., Vasilchenko D.B., Kozlova E.A. Comprehensive Review on g-C₃N₄-Based Photocatalysts for the Photocatalytic Hydrogen Production under Visible Light. *Int. J. Mol. Sci.*, 2022, **24**, 346.
- [21] Bhandari D., Lakhani P., Modi C.K. Graphitic carbon nitride (g-C₃N₄) as an emerging photocatalyst for sustainable environmental applications: a comprehensive review. *RSC Sustain.*, 2024, **2**, P. 265–287.
- [22] Gao R.H., Ge Q., Jiang N., Cong H., Liu M., Zhang Y.Q. Graphitic carbon nitride (g-C₃N₄)-based photocatalytic materials for hydrogen evolution. *Front. Chem.*, 2022, **10**, 1048504.
- [23] Zhang P., Li N., Li L., Yu Y., Tuerhong R., Su X. g-C₃N₄-Based Photocatalytic Materials for Converting CO₂ Into Energy: A Review. *Chem. Phys. Chem.*, 2024, **25**, e202400075.
- [24] Wudil Y.S., Ahmad U.F., Gondal M.A., Al-osta M.A., Almohammadi A., Sa R.S., Hrahsheh F., Haruna K., Mohamed M.J.S. Tuning of graphitic carbon nitride (g-C₃N₄) for photocatalysis: A critical review. *Arabian Journal of Chemistry*, 2023, **16**, 104542.
- [25] Khan M.A., Mutahir S., Shaheen I., Qunhui Y., Bououdina M., Humayun M. Recent advances over the doped g-C₃N₄ in photocatalysis: A review. *Coord. Chem. Rev.*, 2025, **522**, 216227.
- [26] Zhang G., Zang S., Wang X. Layered Co(OH)₂ Deposited Polymeric Carbon Nitrides for Photocatalytic Water Oxidation. *ACS Catalysis*, 2015, **5**, 941.
- [27] Yu J., Wang S., Cheng B., Lin Z., Huang F. Noble metal-free Ni(OH)₂-g-C₃N₄ composite photocatalyst with enhanced visible-light photocatalytic H₂-production activity. *Catal. Sci. Technol.*, 2013, **3**, 1782.
- [28] Potapenko K.O., Kurenkova A.Y., Mishchenko D.D., Gerasimov E.Y. Synthesis of effective NiO/Ni/g-C₃N₄ photocatalysts for CO₂ reduction under visible-light irradiation. *Kinet. Catal.*, 2024, **65**, 724.
- [29] Vasilchenko D., Zhurenok A., Saraev A., Gerasimov E., Cherepanova S., Tkachev S., Plusnin P., Kozlova E. Highly efficient hydrogen production under visible light over g-C₃N₄-based photocatalysts with low platinum content. *Chem. Eng. J.*, 2022, **445**, 136721.
- [30] Fina F., Callear S.K., Carins G.M., Irvine J.T.S. Structural investigation of graphitic carbon nitride via XRD and neutron diffraction. *Chem. Mater.*, 2015, **27**, P. 2612–2618.
- [31] Alwin E., Nowicki W., Wojcieszak R., Zieliński M., Pietrowski M. Elucidating the structure of the graphitic carbon nitride nanomaterials via X-ray photoelectron spectroscopy and X-ray powder diffraction techniques. *Dalt. Trans.*, 2020, **49**, P. 12805–12813.
- [32] Soni A., Harish, Akash, Kumar V., Mishra R.K., Gwag J.S., Poddar N.K., Singhal R., Mukhopadhyay A.K., Kumar P. Optical band gap enhancements of chemically synthesized α-Ni(OH)₂ nanoparticles by a novel technique: Precipitator molarity variation. *Luminescence*, 2023, **38**, 1287.
- [33] Suksomboon M., Kongsawatvoragul K., Duangdangchote S. Reducing the Energy Band Gap of Cobalt Hydroxide Nanosheets with Silver Atoms and Enhancing Their Electrical Conductivity with Silver Nanoparticles. *ACS Omega*, 2021, **6**, 20804.

- [34] Noureldien M.S., Nassar M.Y., Ibrahim I.M., A.H. M. Tandem NiO–Ni(OH)₂/VS₂ nanosheets: a robust photocatalyst for hydrogen evolution. *Mater. Adv.*, 2024, **5**, 9107.
- [35] Xiao Z., Do H., Yusuf A., Jia H., Ma H., Jiang S. Facile synthesis of multi-layer Co(OH)₂/CeO₂-g-C₃N₄ ternary synergistic heterostructure for efficient photocatalytic oxidation of NO under visible light. *J. Hazard. Mater.*, 2024, **462**, 132744.

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Stability of solid-phase heteronanostructures based on zinc and silver sulfides to oxidation

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ABSTRACT For the first time the thermal stability of the phase composition of $(\text{ZnS})(\text{Ag}_2\text{S})_x$ sulfide heteronanostructures are studied. Solid-phase heteronanostructures $(\text{ZnS})(\text{Ag}_2\text{S})_x$ with $x = 0.002 - 0.50$ are synthesized by hydrochemical co-deposition of ZnS and Ag_2S sulfides. The ZnS nanoparticle size, estimated from the broadening of diffraction reflections, in the produced initial heteronanostructures is 2 – 4 nm. Annealing of the synthesized $(\text{ZnS})(\text{Ag}_2\text{S})_x$ heteronanostructures in air at temperature from 25 to 530 °C and above leads to a change in their phase composition due to the oxidation of cubic ZnS sulfide to hexagonal zinc oxide. Oxidation begins at a temperature of approximately 250 °C; the ZnO nanoparticle size varies in a range of 12 to 17 – 25 nm. Oxidation of solid-phase $(\text{ZnS})(\text{Ag}_2\text{S})_x$ heteronanostructures in air showed that weight loss that occurs upon heating from ~250 to ~430 – 450 °C is associated with the beginning of oxidation of the ZnS sulfide and the formation of the ZnO oxide. The most significant weight loss is observed after heating from ~450 to ~580 °C due to an increase in the ZnO content, oxidation of sulfur and its removal in the form of SO_2 .

KEYWORDS chemical co-deposition, heteronanostructure $(\text{ZnS})(\text{Ag}_2\text{S})_x$, stability of phase composition

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1. Introduction

Semiconductor sulfides ZnS and Ag_2S are widely used in various electronic devices, solar cells, light-emitting diodes, luminophores, and catalysts [1–6]. Cubic (space group $F\bar{4}3m$) zinc sulfide α -ZnS is a wide bandgap semiconductor with a band gap of $E_g = 3.50 - 3.76$ eV [4]. Silver sulfide has two main modifications: monoclinic (space group $P2_1/c$) acanthite α - Ag_2S , which exists at temperatures below 180 °C, and body-centered cubic (space group $Im\bar{3}m$) argentite β - Ag_2S , which exists in a temperature range of 180 – 585 °C. The conventional band gap of silver sulfide with α - Ag_2S acanthite structure is 0.9 – 1.1 eV [3].

An increase in the band gap of nanostructured sulfides and heteronanostructures is possible by decreasing the size of nanoparticles and by creating nanocomposites of two sulfides. The most promising is the production of semiconductor nanocomposites consisting of zinc and silver sulfide nanoparticles. In the ideal case, the change in the band gap of the sulfide heteronanostructure of ZnS and Ag_2S can cover a wide part of the spectrum from the infrared to the near ultraviolet. An increase in the Ag_2S content in $(\text{ZnS})(\text{Ag}_2\text{S})_x$ heteronanostructures leads to a decrease in the band gap E_g from ~3.6 – 3.7 to ~3.0 eV [5]. The use of $(\text{ZnS})(\text{Ag}_2\text{S})_x$ heteronanostructures extends the spectral sensitivity to the visible long-wavelength region and allows obtaining new nanomaterials for converting solar energy into electricity, for solid-state UV lasers and fast-acting resistance switches.

The thermal stability of the phase composition of $(\text{ZnS})(\text{Ag}_2\text{S})_x$ heteronanostructures is important for their possible application. During the heating of $(\text{ZnS})(\text{Ag}_2\text{S})_x$ heteronanostructures, the sulfides can be oxidized. Therefore, for the use of $(\text{ZnS})(\text{Ag}_2\text{S})_x$ heteronanostructures, it is necessary to know the stability of their phase composition. There are no published data on the thermal stability of $(\text{ZnS})(\text{Ag}_2\text{S})_x$ heteronanostructures. This work is devoted to studying the thermal stability of the composition of $(\text{ZnS})(\text{Ag}_2\text{S})_x$ sulfide heteronanostructures containing different relative amounts of silver sulfide x from 0.002 to 0.50.

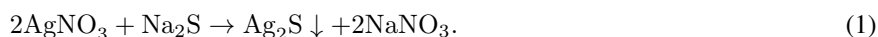
2. Experimental

Aqueous solutions of reagents for the synthesis of solid-phase heteronanostructures of zinc and silver sulfides were prepared using high-purity deionized water as a solvent.

Synthesis of solid-phase $(\text{ZnS})(\text{Ag}_2\text{S})_x$ heteronanostructures by hydrochemical two-stage co-deposition of ZnS and Ag_2S is described in detail earlier in study [5].

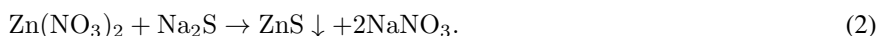
Aqueous solutions of reagents for synthesis of ZnS and Ag₂S sulfides and their heteronanostructures based on ZnS and Ag₂S sulfides were prepared with the use of high-purity deionized water as a solvent. High-purity deionized water was produced using the Milli-Q Reference (Merck, Millipore) water preparation system. The specific resistivity of water is equal 18.2 MΩ·cm at 298 K (electrical conductivity is below 5.5×10^{-6} S·m⁻¹), the total content of organic carbon did not exceed 5×10^{10} ppb (5×10^{10} mg·L⁻¹).

The solubility products K_{sp} of sulfides ZnS ($K_{sp} = 2.5 \times 10^{-22}$) and Ag₂S ($K_{sp} = 6.3 \times 10^{-50}$) differ very strongly. Therefore, heteronanostructures ZnS/Ag₂S have been synthesized in two stages. First, silver sulfide Ag₂S was synthesized by chemical deposition from aqueous solutions of silver nitrate AgNO₃ and sodium sulfide Na₂S in the presence of sodium citrate Na₃Cit. In aqueous solutions, sodium citrate can reduce Ag⁺ ions to form silver metal nanoparticles [3,4] and create a citrate shell on Ag₂S particles [3]. Therefore, to obtain colloidal solutions of silver sulfide without Ag impurities and without a citrate shell, reaction mixtures with a small relative excess of sodium sulfide Na₂S and with Na₃Cit concentration from 0.8 to 10.0 mmol·L⁻¹ were used which is lower than the concentration of Na₂S. The synthesis of a colloidal Ag₂S solution was carried out in the dark in a neutral medium at pH ≈ 7 according to the following reaction scheme



For the synthesis of (ZnS)(Ag₂S)_x heteronanostructures, solution of sodium sulfide Na₂S was added to an aqueous zinc nitrate or sulfate solutions under constant stirring and obtained ZnS solution was mixed with synthesized colloidal silver sulfide solution.

The deposition of zinc sulfide occurs by the following reaction scheme



A total of ten (ZnS)(Ag₂S)_x heteronanostructures with relative silver sulfide Ag₂S content x from 0.002 to 0.50 were synthesized. The oxidation of (ZnS)(Ag₂S)_x heteronanostructures with low ($x < 0.025$) silver sulfide content is almost indistinguishable from the oxidation of zinc sulfide. Therefore, in this work, the stability to oxidation of four (ZnS)(Ag₂S)_x heteronanostructures with maximum relative silver sulfide content x from 0.025 to 0.50 is considered in detail. The compositions of the reaction mixtures and composition x of synthesized (ZnS)(Ag₂S)_x heteronanostructures are given in Table 1.

TABLE 1. Composition of reaction mixtures (mmol·L⁻¹), composition x of synthesized (ZnS)(Ag₂S)_x heteronanostructures, and lattice constant a_{B3} of zinc sulfide in the prepared heteronanostructures

No.	Synthesis of ZnS		Synthesis of Ag ₂ S			Content x in heteronanostructures (ZnS)(Ag ₂ S) _x	a_{B3} , nm
	Zn(NO ₃) ₂	Na ₂ S	AgNO ₃	Na ₂ S	Na ₃ Cit		
1	50	50	2.5	1.25	0.8	0.025	0.5388
2	50	50	5.0	2.5	2.0	0.05	0.5385
3	50	50	10.0	5.0	4.0	0.10	0.5387
4	50	50	50.0	25.0	10.0	0.50	0.5398

*Lattice parameters of monoclinic (space group $P2_1/c$) acanthite α-Ag₂S, the diffraction reflections of which are observed in the XRD patterns of the synthesized heteronanostructures 3 and 4 are $a = 0.4220$ nm, $b = 0.621$ nm, $c = 0.9531$ nm, and $\beta = 125.43^\circ$.

The Zn(NO₃)₂ and Na₂S concentration was 50 mmol·L⁻¹ in all reaction mixtures. The synthesized solid-phase powders were washed by decantation and were dried by the sublimation method in an Alpha 1-2 LDplus freeze dryer (Martin Christ) at an ice condenser temperature of -55°C . Dried sulfide heteronanostructures stored in a Vacuum Desiccator Sanplatec MB, evacuated to a residual pressure of 13.3 Pa (0.1 mm Hg).

The deposited sulfide powders and the same powders after annealing were studied by X-ray diffraction (XRD) on a Shimadzu XRD-7000 diffractometer using CuKα_{1,2} radiation at room temperature. XRD measurements were performed in the angle interval $2\theta = 20 - 95^\circ$ with a step $\Delta(2\theta) = 0.02^\circ$ at a scanning time of 10 s per point. The determination of the crystal lattice parameters and the final refinement of the structure of the synthesized sulfide powders were carried out using the X'Pert Plus software package [7]. The diffraction reflections of all synthesized nanopowders are significantly broadened due to the small particle size. Nanoparticle size D of ZnS, Ag₂S, and ZnO was determined from the broadening of the diffraction reflections.

The microstructure of the synthesized ZnS/Ag₂S heteronanostructures was studied using a ThemisZ transmission electron microscope (Thermo Fisher, USA) in direct image and in high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) mode.

The oxidation of the synthesized heteronanostructures was studied on a Netzsch STA 449C Jupiter thermal analyzer coupled to a QMS 403C Aeolos quadrupole mass spectrometer. The measurements were performed by combined thermogravimetry (TG) and differential scanning calorimetry (DSC) in lidless alundum crucibles under conditions of continuous heating of samples to 700 °C at a rate of 10 °C·min⁻¹ in a stream (30 cm³·min⁻¹) of synthetic air (79 % N₂ + 21 % O₂). Analysis of gases formed during the heating of the samples was carried out taking into account the mass numbers 18, 44, 64 and 80 characteristic of water and CO₂, SO₂, and SO₃ oxides.

3. Results and discussion

The effect of annealing temperature on the evolution of the XRD patterns of heteronanostructures (ZnS)(Ag₂S)_{0.025}, (ZnS)(Ag₂S)_{0.10}, and (ZnS)(Ag₂S)_{0.50} (see Table 1) containing different amounts of silver sulfide is shown in Figs. 1 and 2, respectively.

Evolution of the XRD patterns of the (ZnS)(Ag₂S)_{0.025} and (ZnS)(Ag₂S)_{0.10} heteronanostructures due to annealing in air at temperatures of up to 380 °C is shown in Fig. 1. Performed quantitative analysis and comparison with the literature

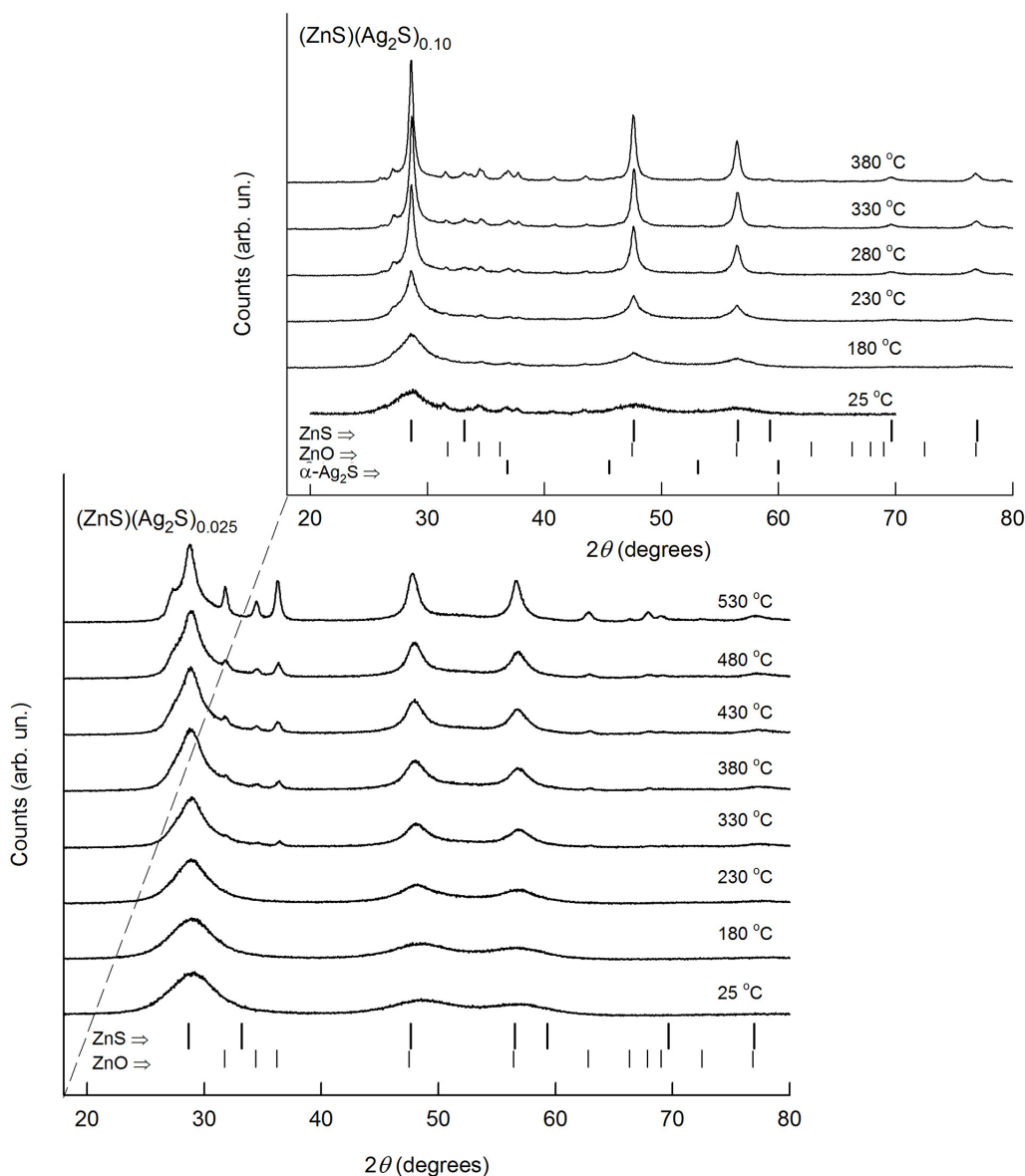


FIG. 1. Effect of an annealing temperature of 25 – 530 °C on XRD patterns of heteronanostructures (ZnS)(Ag₂S)_{0.025} and effect of annealing temperature of 25 – 380 °C on (ZnS)(Ag₂S)_{0.10}. Long and medium-length ticks show the positions of reflections of cubic (space group $F43m$) zinc sulfide ZnS and hexagonal (space group $P6_3mc$) zinc oxide ZnO, respectively. Short ticks in bottom of XRD of (ZnS)(Ag₂S)_{0.10} heteronanostructure show the positions of reflections of monoclinic (space group $P2_1/c$) acanthite α-Ag₂S

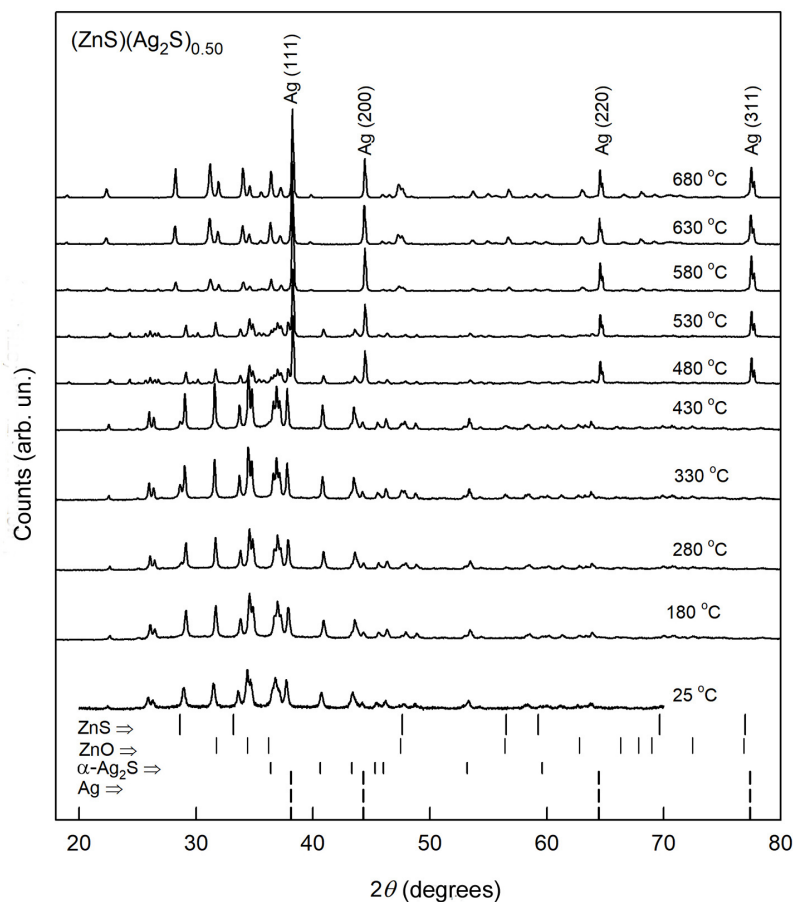


FIG. 2. Evolution of the XRD patterns of heteronanostructure $(\text{ZnS})(\text{Ag}_2\text{S})_{0.50}$ due to annealing in air at temperatures from 25 to 680 °C. Long, medium-length, and short ticks show the positions of reflections of cubic zinc sulfide ZnS, hexagonal (space group $P6_3mc$) zinc oxide ZnO, and monoclinic (space group $P2_1/c$) acanthite $\alpha\text{-Ag}_2\text{S}$, respectively. The dashed ticks in bottom show the positions of the reflections of the metallic cubic silver Ag.

data showed that the observed sets of diffraction reflections of the initial heteronanostructures at room temperature 25 °C correspond to single-phase cubic (space group $F\bar{4}3m$) sulfide ZnS with a sphalerite structure ($B3$ type). The XRD pattern of the initial heteronanostructures at 25 °C exhibits only highly broadened diffraction reflections of cubic sulfide ZnS. The ZnS nanoparticle size in initial heteronanostructure is $\sim 3 - 4$ nm. The lattice constant a_{B3} of the ZnS nanoparticles is ~ 0.5387 nm (Table 1). An increase in the annealing temperature is accompanied by the intensity growth of diffraction reflections due to size increase in the cubic ZnS sulfide particles and the appearance of reflections of hexagonal oxide ZnO. The ZnS nanoparticle size after heating this heteronanostructure in air at 330 and 380 °C is $\sim 15 - 16$ and $\sim 18 - 24$ nm, respectively. In the XRD patterns of the heteronanostructure $(\text{ZnS})(\text{Ag}_2\text{S})_{0.10}$ at temperatures up to 380 °C, diffraction reflections of monoclinic silver sulfide (acanthite) $\alpha\text{-Ag}_2\text{S}$ are also observed. The oxidation of the $(\text{ZnS})(\text{Ag}_2\text{S})_{0.025}$ and $(\text{ZnS})(\text{Ag}_2\text{S})_{0.10}$ heteronanostructures with the formation of zinc oxide ZnO begins at 280 °C. According to the data of energy-dispersive X-ray analysis, the content of zinc and sulfur in the synthesized heteronanostructures with a mean ZnS nanoparticle size of $\sim 3 - 4$ nm is 50.2 ± 0.1 and 49.9 ± 0.1 at.%, respectively, which corresponds to the stoichiometric ZnS sulfide.

The evolution of the XRD patterns of the $(\text{ZnS})(\text{Ag}_2\text{S})_{0.05}$ heteronanostructure upon heating in air is the same as for the $(\text{ZnS})(\text{Ag}_2\text{S})_{0.025}$ heteronanostructure. According to the X-ray diffraction data, oxidation of the $(\text{ZnS})(\text{Ag}_2\text{S})_{0.05}$ heteronanostructure begins at a temperature 280 °C, when diffraction reflections (100) and (101) of hexagonal zinc oxide ZnO appear.

Changes in the XRD patterns of the $(\text{ZnS})(\text{Ag}_2\text{S})_{0.50}$ heteronanostructure due to heating in air at temperatures of up to 680 °C is shown in Fig. 2. Note that XRD patterns of the samples annealed at temperatures of 180 – 680 °C were recorded at room temperature. Due to the high silver sulfide content, the initial heteronanostructure exhibits, along with diffraction reflections of cubic ZnS, diffraction reflections of monoclinic (space group $P2_1/c$) acanthite $\alpha\text{-Ag}_2\text{S}$ (at 25, 180, 280, 330, 430 °C). Diffraction reflections of body-centered cubic argentite $\beta\text{-Ag}_2\text{S}$, which is equilibrium at a temperature 330 °C and above, are not observed, because the acanthite $\leftrightarrow$ argentite transition is reversible. As a consequence, after

cooling the annealed samples, only reflections of monoclinic acanthite, which is an equilibrium low-temperature phase of silver sulfide, are detected.

As in the case of the $(\text{ZnS})(\text{Ag}_2\text{S})_{0.025}$ and $(\text{ZnS})(\text{Ag}_2\text{S})_{0.10}$ heteronanostructures, oxidation of heteronanostructure $(\text{ZnS})(\text{Ag}_2\text{S})_{0.50}$ with the formation of hexagonal (space group $P6_3mc$) zinc oxide ZnO begins at 280 °C too. The size of ZnO nanoparticles in all heteronanostructures during oxidation varies in a range of 12 to 17 – 25 nm. At a temperature of 480 °C and above, due to heating in air, silver sulfide $\beta\text{-Ag}_2\text{S}$ decomposes to release cubic metallic silver Ag with a lattice constant $a_{\text{Ag}} = 0.4086$ nm (Fig. 2). It is caused by the specific properties of silver sulfide compared with properties of other sulfides. Indeed, Ag_2S does not interact with oxygen during heating in air to a temperature of ~ 480 °C. Annealing in air at temperature > 480 °C is accompanied by the decomposition of silver sulfide with releasing metallic silver Ag and sulfur S. Sulfur is oxidized to gaseous sulfur dioxide:



As a consequence, at temperature 480 °C and above, the diffraction reflections of cubic sulfide ZnS, hexagonal oxide ZnO, and cubic silver Ag are observed in the XRD pattern of heteronanostructure $(\text{ZnS})(\text{Ag}_2\text{S})_{0.50}$. A similar spontaneous release of Ag in the form of whiskers during heating Ag_2S to 530 – 630 °C was found in [8]. The appearance of Ag whiskers on the surface of a compressed $\alpha\text{-Ag}_2\text{S}$ tablet heated in air to ~ 300 °C was observed in study [9].

Figure 3 shows the TEM image of the $(\text{ZnS})(\text{Ag}_2\text{S})_{0.50}$ heteronanostructure in the HAADF-STEM mode and the distribution of the elements Ag, Zn and S in it. The heteronanostructure is a nanocrystalline matrix of zinc sulfide particles doped with silver sulfide nanoparticles. The content of Ag, Zn and S elements in this heteronanostructure is ~ 28.5 , ~ 28.5 and ~ 42.9 at.%, respectively.

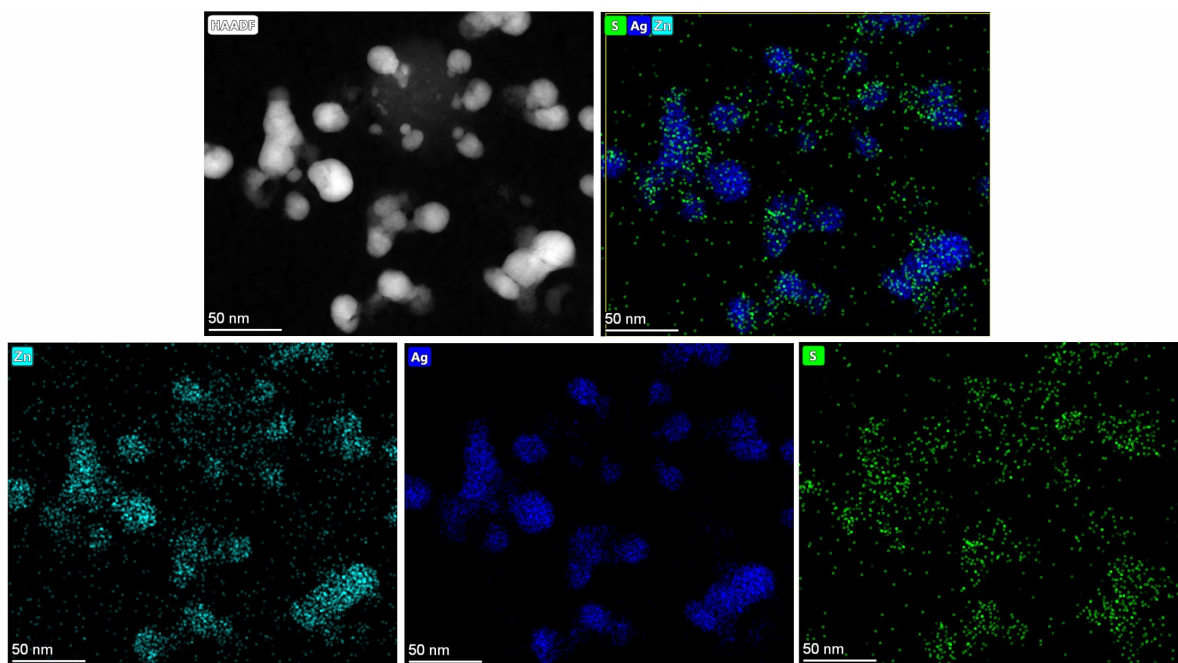


FIG. 3. HAADF image of the initial synthesized heteronanostructure $(\text{ZnS})(\text{Ag}_2\text{S})_{0.50}$, HAADF-STEM image of this heteronanostructure with an overlay of EDX distribution maps of S, Zn and Ag, and EDX distribution maps of zinc Zn, silver Ag and sulfur S in this heteronanostructure

From Fig. 3 it is seen that darker silver-containing Ag_2S nanoparticles ~ 3 nm in size are predominantly located on the surface lighter ZnS nanoparticles containing zinc. According to X-ray diffraction data, in the initial synthesized $(\text{ZnS})(\text{Ag}_2\text{S})_{0.50}$ heteronanostructure, the size of ZnS and Ag_2S nanoparticles is 6 – 7 and 3 – 4 nm, respectively.

Transformations that occur during heating in air and the oxidation of $(\text{ZnS})(\text{Ag}_2\text{S})_x$ heteronanostructures were studied by the differential thermal analysis (DTA) – differential thermogravimetry (DTG) method.

Figure 4 shows as an example typical temperature dependences of ion current I_{ion} and DTA-DTG dependences measured during the heating of the $(\text{ZnS})(\text{Ag}_2\text{S})_{0.50}$ heteronanostructure in air to 700 °C. An effect associated with the removal of 3 – 4 wt.% of adsorbed water was revealed in the DSC curve at 106 °C. The evaporation of water is confirmed by the presence of a maximum at ~ 117 °C in the temperature dependence of ion current for a mass number of 18 corresponding to H_2O [9]. When heating the $(\text{ZnS})(\text{Ag}_2\text{S})_{0.50}$ heteronanostructure, the beginning of oxidation is recorded on the DSC curve at 254 °C. It is due to a decrease in the sample mass and the appearance of a small exothermic effect that accompanied by the release of SO_2 . This can be explained not only by the partial sublimation of the formed ZnO, but also by the continuation of the ZnS oxidation, which is confirmed by the XRD data. The exothermic effect detected in the

DSC curve at 401 °C corresponds to the release of CO₂ due to the oxidation of the citrate carbon-containing radical to carbon dioxide. The presence of a citrate carbon-containing shell on the surface of heteronanostructures was confirmed earlier in [5]. This is confirmed by the maximum at 388 °C observed in the temperature dependence of ion current for a mass number 44 corresponding to CO₂ (see Fig. 4).

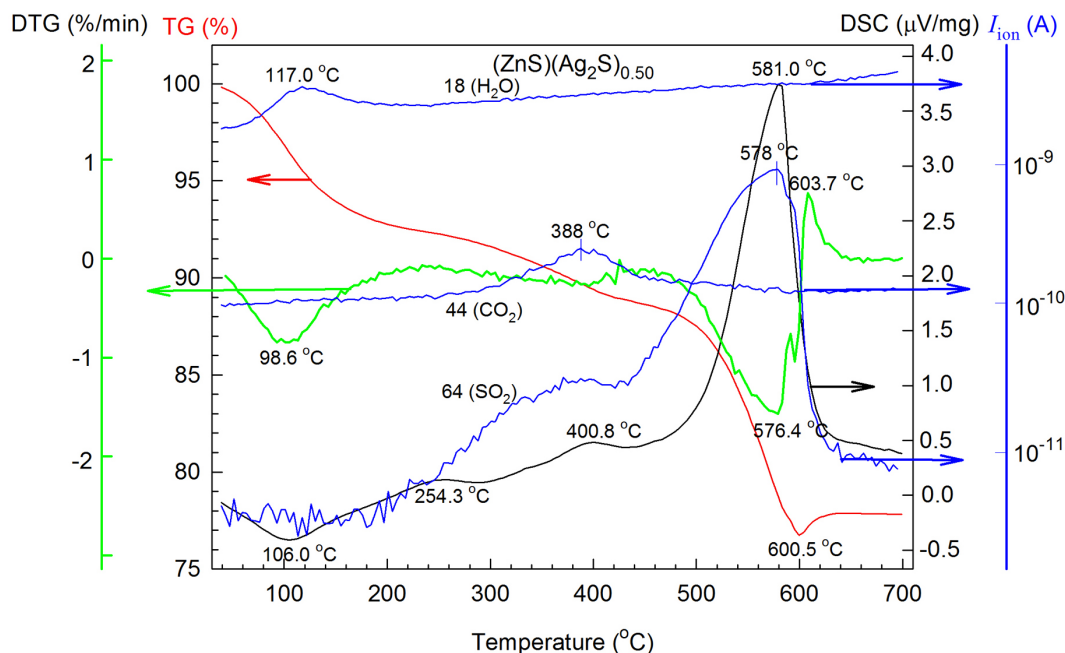


FIG. 4. Differential thermal analysis – DTG dependences measured during the heating of heteronanostructure (ZnS)(Ag₂S)_{0.50} in air and analysis of the evolved gases. Maxima observed in the temperature dependencies of ion current I_{ion} at ~117, ~388, and ~370 – 400 °C are attributed to the release of H₂O steam and CO₂ and SO₂ gases, respectively.

The mass loss occurring upon heating the sample from the beginning oxidation temperature 254 °C to ~430 – 450 °C is associated with the beginning of ZnS oxidation and the formation of ZnO oxide, which has a lower molecular weight than ZnS. The largest mass loss ~12 % is observed during heating from ~500 to ~580 °C and is due to an increase in the ZnO content and partial oxidation of sulfur, which is removed as gaseous SO₂ dioxide. The exothermic effect on the DSC curve with a maximum at 581 °C correlates with the release of SO₂ into the gas phase and continued oxidation of the heteronanostructure. The release of SO₂ is confirmed by the presence of maxima at ~400 and ~578 °C on the temperature dependence of the ion current for the mass number 64 corresponding to SO₂. The partial oxidation of sulfur and its removal in the form of SO₂ were observed earlier during the oxidation of silver sulfide [10, 11] and zinc sulfide nanopowders [12–14].

During oxidation of the (ZnS)(Ag₂S)_{0.10} heteronanostructure in air, the same DTA-DTG dependencies were observed as in the case of the (ZnS)(Ag₂S)_{0.50} heteronanostructure. The beginning of oxidation at 254 °C agrees with the X-ray diffraction data (see Fig. 1) on the oxidation of ZnS with the formation of hexagonal zinc oxide ZnO. The mass loss observed upon heating the sample to ~420 – 460 °C is due to the appearance of ZnO oxide, which has a lower molecular weight compared to ZnS. The largest mass loss about 11 % is observed after heating from ~500 to ~580 °C and is caused by an increase in the ZnO content and partial oxidation of sulfur, which is removed as gaseous dioxide SO₂. The exothermic effect on the DSC curve with a maximum at ~580 °C correlates with the removing SO₂ into the gas phase, which is confirmed by the presence of maxima at ~400 and ~578 °C on the temperature dependence of the ion current for mass number 64, corresponding to SO₂.

4. Conclusion

Heteronanostructures (ZnS)(Ag₂S)_x with different amounts of Ag₂S were synthesized by the hydrochemical co-deposition method. For the first time the thermal stability of the phase composition of (ZnS)(Ag₂S)_x sulfide heteronanostructures has been studied. The annealing of the synthesized (ZnS)(Ag₂S)_x heteronanostructures in air at 25 – 530 °C and above is accompanied by evolution of their phase composition due to the oxidation of cubic zinc sulfide to hexagonal zinc oxide and to an increase in the ZnS nanoparticles size. The oxidation of the heteronanostructures begins at a temperature of 280 – 330 °C; at an annealing temperature 530 °C, the zinc oxide content in heteronanostructures (ZnS)(Ag₂S)_{0.25} and (ZnS)(Ag₂S)_{0.50} achieves ~26 – 30 wt.%. The ZnO nanoparticle size depends on the composition of the initial

heteronanostructures. At annealing temperatures 380 and 430 °C, it varies from 12 to 17 – 24 nm and from 13 to 25 – 30 nm.

The mass loss observed upon heating to ~120 °C is caused by the removal of adsorbed water from the samples, which is confirmed by the presence of a maximum in the temperature dependence of the ion current corresponding to H₂O. Studies of the oxidation of the (ZnS)(Ag₂S)_x heteronanostructures in air by the DTA-DTG method have shown that oxidation begins at ~250 °C. The largest weight loss ~12 % is observed after heating from ~450 to ~580 °C and is caused by increase of the ZnO content, the partial oxidation of sulfur, and its removal in the form of SO₂. This is confirmed by the presence of maxima at ~400 and ~578 °C in the temperature dependence of the ion current corresponding to SO₂.

References

- [1] Fang X., Zhai T., Gautam U.K., Li L., Wu L., Bando Y., Golberg D. ZnS nanostructures: From synthesis to applications. *Progr. Mater. Sci.*, 2011, **56** (2), P. 175–287.
- [2] Wang X., Huang H., Liang B., Liu Z., Chen D., Shen G. ZnS nanostructures: Synthesis, properties, and applications. *Crit. Rev. Solid State Mater. Sci.*, 2013, **38** (1), P. 57–90.
- [3] Sadovnikov S.I., Gusev A.I. Recent progress in nanostructured silver sulfide Ag₂S: From synthesis and nonstoichiometry to properties. *J. Mater. Chem. A*, 2017, **5** (34), P. 17676–17704.
- [4] Sadovnikov S.I., Rempel A.A., Gusev A.I. Nanostructured silver sulfide: Synthesis of various forms and their applications. *Rus. Chem. Rev.*, 2018, **87** (4), P. 303–327.
- [5] Sadovnikov S.I., Ishchenko A.V., Weinstein I.A. Synthesis and optical properties of nanostructured ZnS and heteronanostructures based on zinc and silver sulfides. *J. Alloys Comp.*, 2020, **831**, 154846.
- [6] Liang C.H., Terabe K., Hasegawa T., Aono M. Resistance switching of an individual Ag₂S/Ag nanowire heterostructure. *Nanotechnology*, 2007, **18** (48), 485202.
- [7] Xu Z., Bando Y., Wang W., Bai X., Golberg D. Real-time *in situ* HRTEM-resolved resistance switching of Ag₂S nanoscale ionic conductor. *ACS Nano*, 2010, **4** (5), P. 2515–2522.
- [8] Basu M., Nazir R., Mahala C., Fageria P., Chaudhary S., Gangopadhyay S., Pande S. Ag₂S/Ag heterostructure: a promising electrocatalyst for hydrogen evolution reaction. *Langmuir*, 2017, **33** (13), P. 3178–3186.
- [9] Yang W., Zhang L., Hu Y., Zhong Y., Wu H.B., Lou X.W. Microwave-assisted synthesis of porous Ag₂S-Ag hybrid nanotubes with high visible-light photocatalytic activity. *Angew. Chem. Int. Ed.*, 2012, **51** (46), P. 11501–11504.
- [10] Kitova S., Eneva J., Panov A., Haefke H. Infrared photography based on vapor-deposited silver sulfide thin films. *J. Imaging Sci. Technol.*, 1994, **38** (5), P. 484–488.
- [11] Minami T. Recent progress in superionic conducting glasses. *J. Non-Cryst. Solids*, 1987, **95–96** (1), P. 107–118.
- [12] Hull S., Keen D.A., Sivia D.S., Madden P.A., Wilson M. The high-temperature superionic behaviour of Ag₂S. *J. Phys. Condens. Matter*, 2002, **14** (41), L9–L17.
- [13] Lim W.P., Zhang Z., Low H.Y., Chin W.S. Preparation of Ag₂S nanocrystals of predictable shape and size, *Angew. Chem. Int. Ed.*, 2004, **43** (42), P. 5685–5689.
- [14] Fang X.S., Bando Y., Golberg D. Inorganic semiconductor nanostructures and their field-emission applications. *J. Mater. Chem.*, 2008, **18** (5), P. 509–522.
- [15] Zhu Y.C., Bando Y., Xue D.F. Spontaneous growth and luminescence of zinc sulfide nanobelts. *Appl. Phys. Lett.*, 2003, **82** (11), P. 1769–1771.
- [16] Fang X.S., Ye C.H., Zhang L.D., Wang Y.H., Wu Y.C. Temperature-controlled catalysis growth of ZnS nanostructures by the evaporation of ZnS nanopowders. *Adv. Funct. Mater.*, 2005, **15** (1), P. 63–68.
- [17] X'Pert HighScore Plus. Version 2.2e (2.2.5). ©2009 PANalytical B. V. Almedo, the Netherlands.
- [18] Sadovnikov S.I. Effect of elastic properties of nanostructured Ag₂S and ZnS sulfides on interface formation. *Mater. Sci. Semicond. Proc.*, 2022, **148**, 106766.
- [19] Corish J., O'Brian C.D. Electrochemically controlled growth and dissolution of silver whiskers. *J. Mater. Sci.*, 1971, **6** (3), P. 252–259.
- [20] Živković D., Sokić M., Živković Ž., Manasijević D., Lj. Balanović L., Štrbac N., Čosović V., Boyanov B. Thermal study and mechanism of Ag₂S oxidation in air. *J. Therm. Anal. Calorim.*, 2013, **111** (2), P. 1173–1176.
- [21] Sadovnikov S.I., Gusev A.I. Thermal expansion, heat capacity and phase transformations in nanocrystalline and coarse-crystalline silver sulfide at 290–970 K. *J. Therm. Anal. Calorim.*, 2018, **131** (2), P. 1155–1164.
- [22] Fu Q.-S., Xue Y.-Q., Cui Z.-X., Wang M.-F. Study on the size-dependent oxidation reaction kinetics of nanosized zinc sulfide. *J. Nanomater. (Hindawi)*, 2014, **2014**, 856489.
- [23] Klyushnikov A.M., Pikalov S.M., Gulyaeva R.I. Kinetics of solid-state oxidation of iron, copper and zinc sulfide mixture. *Chim. Techno Acta*, 2023, **10** (2), 202310202.
- [24] Sadovnikov S.I., Sergeeva S.V. Thermal stability of nanocrystalline zinc sulfide ZnS. *Rus. J. Inorg. Chem.*, 2023, **68** (4), P. 379–385.

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Self-propagating high-temperature synthesis of Zr-based ceramics from Zr–B₄C composite powder

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ABSTRACT The ZrB₂–ZrC ceramic powders were prepared by self-propagating high-temperature synthesis (SHS) using Zr–B₄C composite powders as a precursor. Composite powders were obtained by ball milling in hexane (3–12 min). The structure, morphology, phase and fractional composition were investigated for both composite powders and SHS products. It was found that B₄C grains are intensively embedded in Zr, and their distribution in composite particles becomes uniform by 9 min of ball milling. The possible route of the SHS reaction is proposed.

KEYWORDS ultra-high temperature ceramics, ceramic powder, self-propagating high-temperature synthesis, ball milling, zirconium, boron carbide, zirconium diboride, zirconium carbide.

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1. Introduction

Transition metal diborides (MB₂, M = Zr, Hf, Ti) exhibit outstanding characteristics such as a high melting point (>3000 °C), chemical resistance, excellent mechanical properties (E = 340–560 GPa, H = 20–35 GPa [1]), electrical and thermal conductivity. These materials retain their properties even at high temperatures (> 550 °C), are resistant to thermal shock and possess moderate thermal expansion [2]. As a result, they found application in ultrahigh-temperature ceramics (UHTC) [3–5]. To obviate the limitations of single-phase UHTC, they are alloyed with various additives: carbides [6, 7], nitrides [8, 9] and silicides [10, 11] of transition metals, Mo, W, Ta and Si [12, 13], as well as SiC. In particular, the development of ZrB₂–ZrC composite ceramics allows for reducing their brittleness and increasing damage resistance [14].

Self-propagating high-temperature synthesis (SHS) is a common method for ZrB₂ synthesis. This process is faster and less energy-consuming than traditional techniques [15–18]. Its products demonstrate excellent sinterability and remarkable mechanical properties. Johnson *et al.* [19] proposed to obtain ZrB₂–ZrC ceramic composite using Zr–B₄C as a reaction system. They managed to produce a non-porous material via the directed reaction of Zr with porous B₄C at 1900 °C in an argon atmosphere. The product represented a composite, consisting of ZrC_x and residual metal matrix reinforced with ZrB₂ platelets. A more recent study by Hu *et al.* [20] compares the characteristics of products derived from Zr–B₄C and Al–Zr–B₄C systems using SHS in an argon atmosphere. In both cases, mixtures of ZrB₂ and ZrC were obtained. Along with Al, other metals, such as Ni [21] and Cu [22], which prevent particle agglomeration, are often considered. The possibility of producing ZrB₂–ZrC in air was discussed in Tsuchida and Yamamoto study [23], for the Zr/B/C powder mixture. After that, research in this area was not continued. All these investigations aim to reduce particle size and decrease the cost of synthesis. Preliminary ball milling of the initial powders may also help to achieve these

goals. However, such a synthesis route, which includes preliminary mechanical treatment and subsequent SHS, is poorly studied.

In this paper, ZrB_2 – ZrC ceramic powders were obtained using Zr – B_4C composite powders prepared by ball milling. For the first time, such ceramic powders were produced via SHS in air. The influence of preliminary ball milling on the composite powders and the SHS products is considered. These results may be of interest for developing means to reduce the cost of manufacturing UHTC ceramics. The promising directions of further exploration are also established.

2. Materials and Methods

2.1. Synthesis of ZrB_2 – ZrC ceramic powders

The composite powders were prepared using boron carbide (grade F1200, $\omega(\text{B}_4\text{C}) = 95.0$ wt. %, $D_{av} = 4.8$ mm, TS 3988-002-64050283-2013) and zirconium (grade PtZrK-1, $\omega(\text{Zr}) \geq 96.8$ wt. %, $D_{av} = 12.3$ mm, TS 48-4-234-84) powders. The vacuum-dried (50 mbar, 180°C , 8 h) initial reagents were mixed in stoichiometric ratio, i.e. 83:17 by weight.

The mechanical treatment of the initial mixture was carried out in water-cooled AGO-2U planetary ball mill using hexane (95 %) medium for $\tau = 3 \div 12$ min. The mixture load consisted of 10 g and the balls load was 120 g. Solid-to-liquid ratio was 1:1.5. The balls and vials are manufactured from steel. The resulting composite powders were separated from the balls and dried in air (1 h). The samples were pressed into tablets ($d = 1.0$ mm, $m = 1$ g, $P = 30$ MPa) and heated using a nichrome spiral in air until they self-ignited ($\sim 300^\circ\text{C}$). The ceramic cake was ground into a homogeneous powder using an agate mortar and ethanol medium.

2.2. Phase composition, structural and morphological characteristics

The structure and morphology of composite powders dispersed on a conductive adhesive tape were examined by scanning electron microscopy using JSM-6460LA (JEOL) equipped with EDX detector.

The microstructure of composite powders, as well as the morphology of SHS products, was investigated in cross-sections with a focused ion beam scanning electron microscope TESCAN AMBER. The composite powders were mixed with a bakelite conductive resin and hot-pressed. The resulting cross-sections were sanded and cleaned of abrasive particles in an ultrasonic bath.

The phase composition of the samples was determined using an Empyrean (Malvern) X-ray diffractometer with a Ni-filtered copper anode ($\lambda(\text{CuK}\alpha) = 1.5418$ Å) in angular ranges of 20 – 60° (for composite powders) and 20 – 80° (for ceramic powders). Crystalline phases were identified using ICDD PDF-2 database. Full-profile analysis of the X-ray patterns was performed utilizing the BGMN algorithm implemented in the Profex software package.

The fractional composition of the samples was examined with a Winner2308A laser particle analyzer (Jinan Winner Particle Instrument). Distilled water was used as the measurement medium for the composite powders, isopropyl alcohol – for the SHS products.

3. Results and Discussion

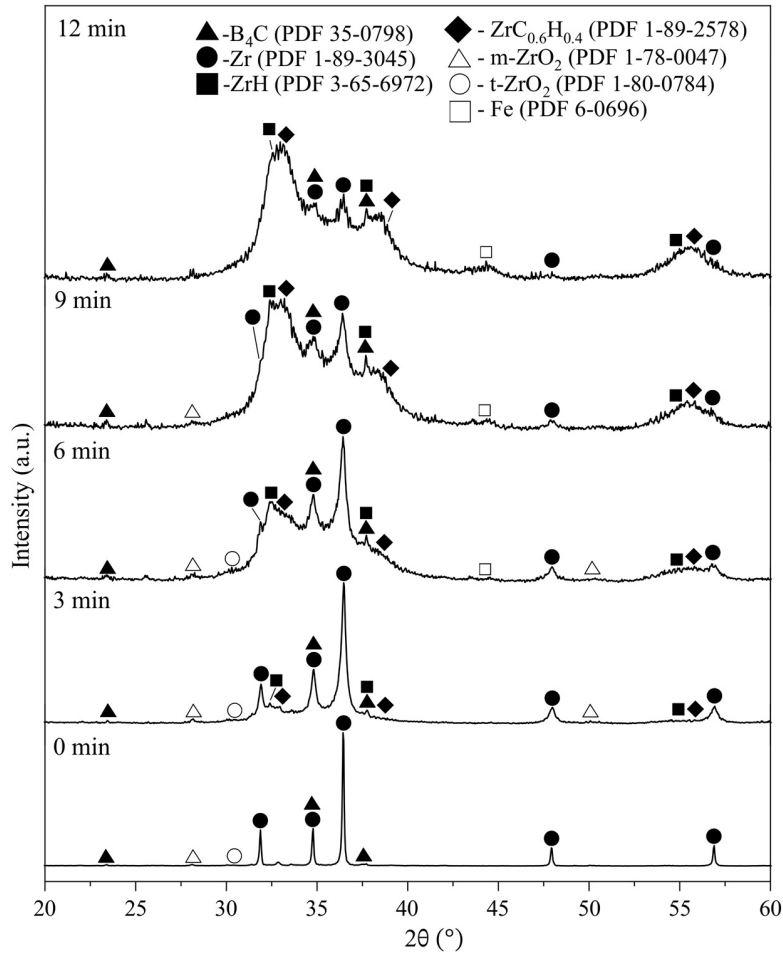
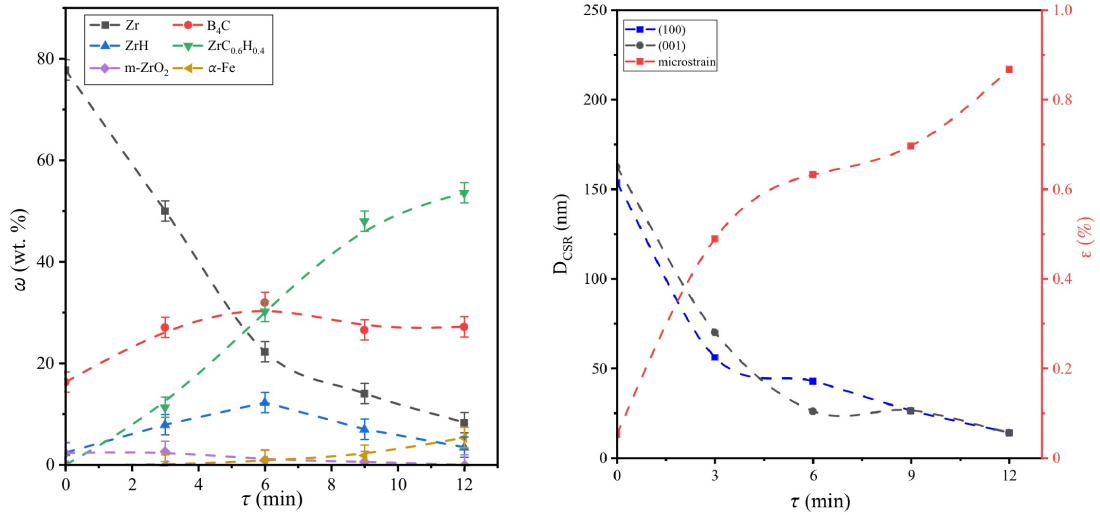
3.1. Phase composition of Zr – B_4C composite powder

The formation of composite powders involves several interrelated processes: embedding hard B_4C grains in plastic Zr particles, cold welding and crushing. According to XRD data (Fig. 1), in course of the mechanical treatment of Zr and B_4C mixture mechanosynthesis also occurs. Cubic phases containing light elements (C, H), such as Zr hydride (PDF 3-65-6972) and carbohydride (PDF 1-89-2578), are formed. The X-ray patterns also indicate the presence of α -Fe (PDF 6-0696) contamination, caused by wear of the balls and vials of planetary mill. The samples also comprise m- ZrO_2 (PDF 1-78-0047) and t- ZrO_2 (PDF 1-80-0784) present as an oxide film on the particles of initial Zr powder.

It is important to note that, due to the formation of a significant fraction of amorphous phases, full-profile analysis does not provide a satisfactory level of accuracy. Despite this fact, we can establish general patterns of mechanosynthesis and evolution in the Zr crystal structure during ball milling. The treatment duration (hereinafter – τ) increase expectedly leads to a significant rise in Zr carbohydride content from ~ 2.43 to ~ 57.1 wt. % (Fig. 2a). Alongside, the metallic Zr content decreases tenfold. Mechanosynthesis is obviously associated with the mechanical destruction of hydrocarbons adsorbed on fresh metal surfaces during mechanical treatment in hexane. Its mechanisms will be discussed in detail elsewhere.

Zr undergoes significant mechanical deformation during ball milling, which leads to a rapid decrease in the size of coherent scattering regions (D_{CSR}) from ~ 154 to ~ 56 nm ((001) axe) within 3 min of treatment (Fig. 2b). The formation of Zr -based phases and accumulation of microstrain also influence D_{CSR} . At $\tau = 12$ min, it reaches a minimum value of ~ 14 nm.

Slight variations in the ratio of the relative intensities of B_4C reflections may indicate its partial decomposition into graphite and a boron-enriched carbide phase. However, this assumption requires additional study.

FIG. 1. X-ray diffraction patterns of Zr-B₄C composite powders obtained at $\tau = 0 \div 12$ minFIG. 2. Dependencies of the phase composition of Zr-B₄C composite powders (a), D_{CSR} and microstrain of Zr phase (b) on τ

3.2. Structural and morphological characteristics of Zr-B₄C composite powder

The initial stage of ball milling ($\tau \leq 6$ min) involves intense cold welding of Zr particles and active embedding of large hard B₄C grains into a relatively plastic metal. Consequently, the composite particle size (D_{50} , median size) increases from ~ 5.3 to ~ 6.2 μm (Fig. 3). The treatment duration increase results in the embrittlement of the material due to plastic strain accumulation and continuous embedding of B₄C. After 12 min of treatment the composite particle size decreases and reaches ~ 5 μm . At the same time, as shown by electron micrographs (Fig. 4), equiaxed particles typical of quasi-brittle fracture form both at $\tau = 6$ and 12 min.

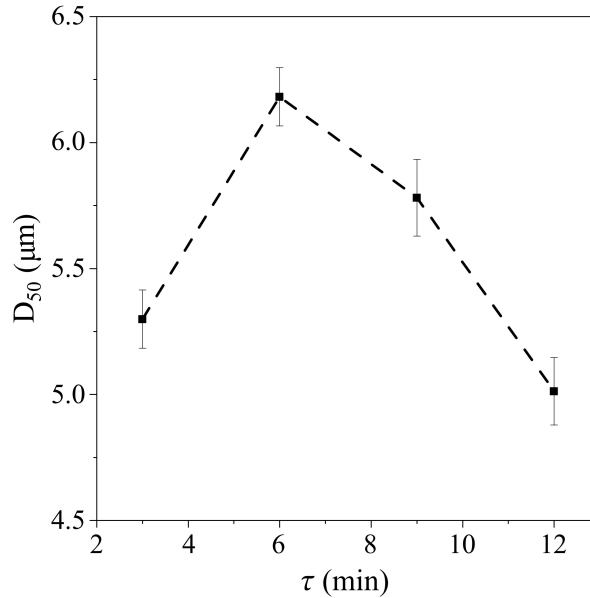


FIG. 3. Dependence of Zr-B₄C composite powder average particle size on τ

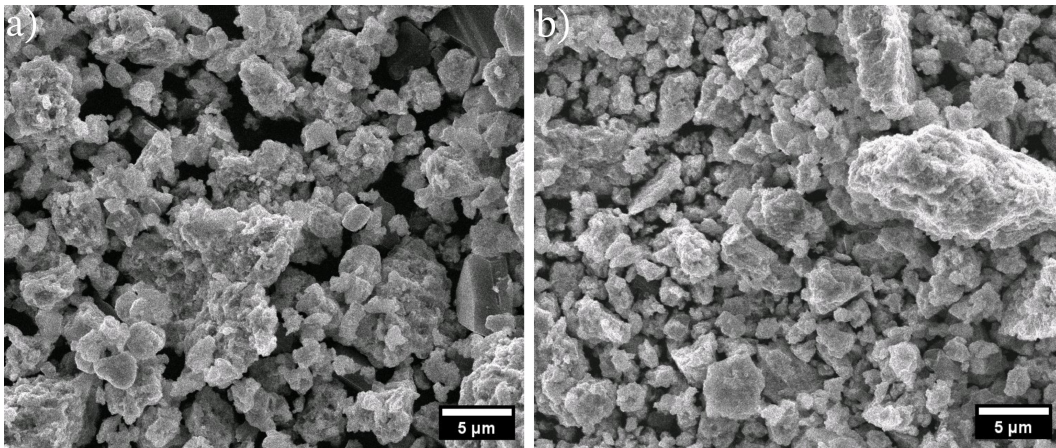


FIG. 4. SEM images of Zr-B₄C composite powder obtained at $\tau = 6$ min (a) and $\tau = 12$ min (b)

The investigation of composite powder cross-sections allowed us to obtain data on the distribution of B₄C inclusions within them in relation with treatment duration. As can be observed from the dependencies shown in Fig. 5, intense embedding of B₄C grains into the metal is followed by a decrease in their average size from ~ 230 to ~ 130 nm (Fig. 5b). Due to the aforementioned fact and as the filler (B₄C inclusions) content grows (Fig. 5a), the specific interfacial area between B₄C and Zr also increases. It is important to note that the dependence of matrix occupancy on τ shown in Fig. 5a does not consider the area of B₄C inclusions and demonstrates only their quantity in the cross-section of the composite particle. In contrast, the dependence of filler content on τ represents the ratio of B₄C inclusions area to the total particle area. Despite the tendency towards a monotonous decrease in the average size of B₄C inclusions, the dependence of their content possesses an apparent minimum at $\tau = 6$ min. The microstructure of the samples indicates that a nearly uniform distribution of B₄C inclusions over the composite particle volume can only be achieved after 9 min of treatment (Fig. 6). The corresponding fractional composition of B₄C inclusions shown in Fig. 6c implies that almost entire mass of embedded

B₄C is concentrated in submicron-sized particles. It should be marked that the fraction of embedded micrometer-sized particles (with an initial average particle size of B₄C $D_{av} = 4.8 \mu\text{m}$) is very small.

Therefore, the embedding of large B₄C grains into the surface layers of metal is a dominant process at the initial stages of ball milling ($\tau \leq 6$ min). A further increase in treatment duration leads to the predominant crushing and migration of nanoscale B₄C grains deep into the bulk metal particle.

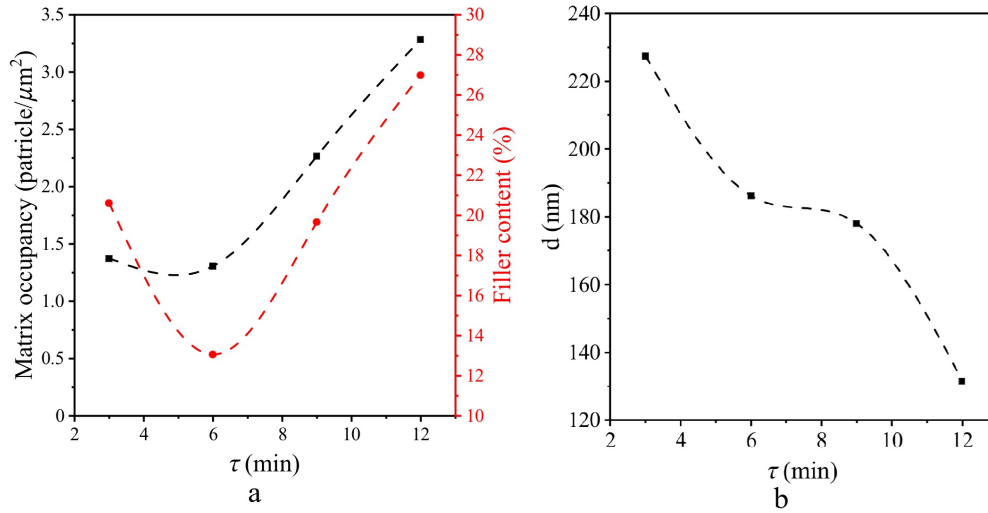


FIG. 5. Dependencies of the content of B₄C inclusions in the Zr matrix (a) and the average size of B₄C inclusions (b) on τ

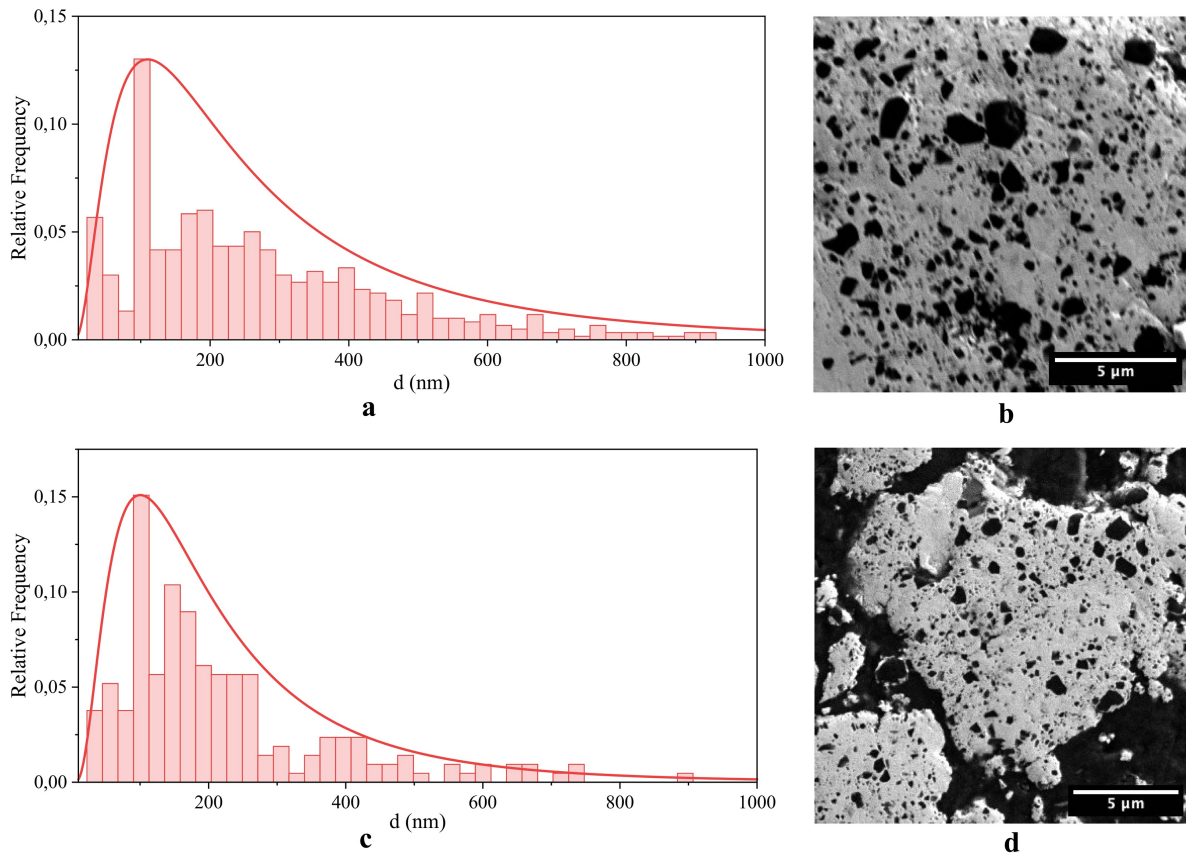


FIG. 6. Size distributions of B₄C inclusions and SEM images of Zr-B₄C composite powder cross-sections at $\tau = 3$ min (a,b) and $\tau = 9$ min (c,d), respectively

Obviously, B₄C inclusions are regarded as a barrier to dislocation motion. Therefore, the rise of their concentration should lead to embrittlement of Zr and, consequently, a decrease in the size of composite particles, which is confirmed

by a relevant data (Fig. 3). As follows from our studies the impact of mechanosynthesis and embedding of B_4C on the embrittling mechanism are comparable, at least for short treatment duration.

3.3. Properties of ZrB_2 – ZrC ceramic powder

According to XRD data (Fig. 7), the SHS products are mainly composed of ZrB_2 (PDF 1-89-3930) and ZrC (PDF 1-89-3829) phases. Quantitative phase composition of the obtained ceramic powders is shown in Fig. 8. The samples also contain the admixtures of $t\text{-}ZrO_2$ (PDF 1-80-0784) and $m\text{-}ZrO_2$ (PDF 1-78-0047). At $\tau > 6$ min, Fe (PDF 6-0969) and FeB (PDF 1-75-1065) are also revealed. Importantly, at $\tau = 0\div 6$ min, a small amount of unreacted Zr is present in the samples.

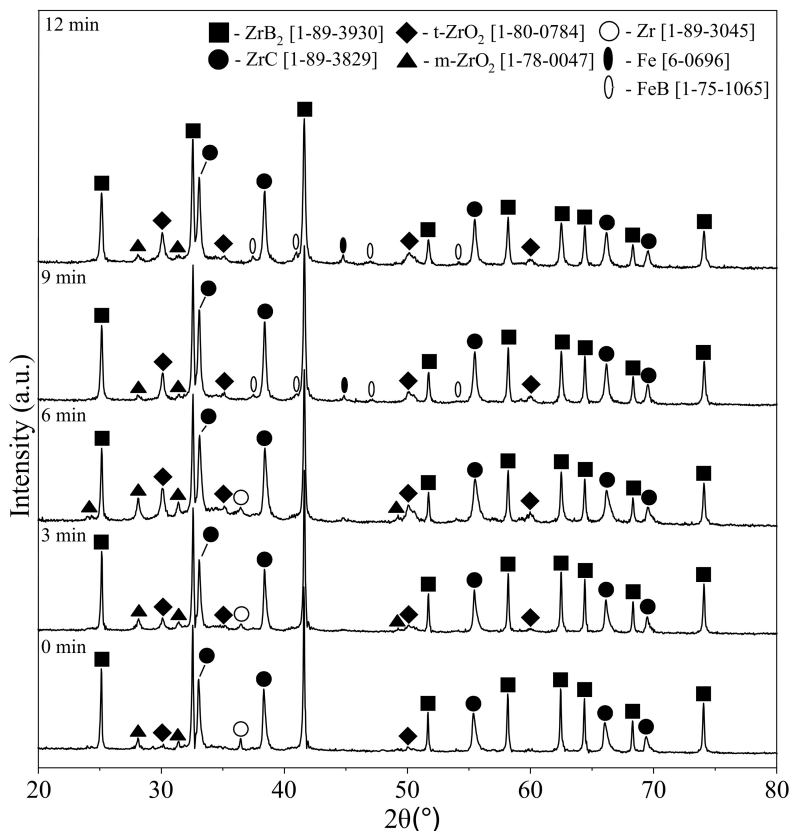


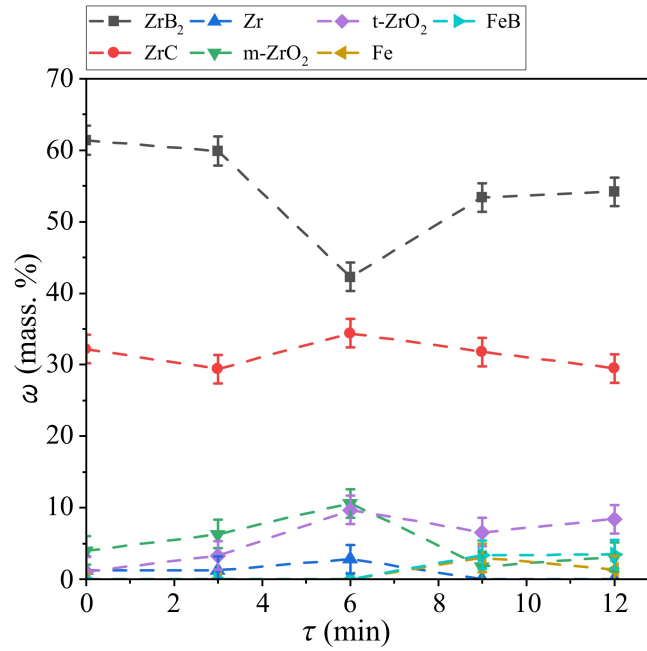
FIG. 7. X-ray diffraction patterns of SHS products obtained at $\tau = 0\div 12$ min

The dependence of the ZrB_2 content on treatment duration exhibits a minimum corresponding to 42.3 wt. % ($\tau = 6$ min). Simultaneously, the dependence of the oxide phases total content on τ has a maximum (20.3 wt. %) at the same τ . Here-with, the ZrC content remains close to a constant value of 32.0 ± 2.5 wt. %.

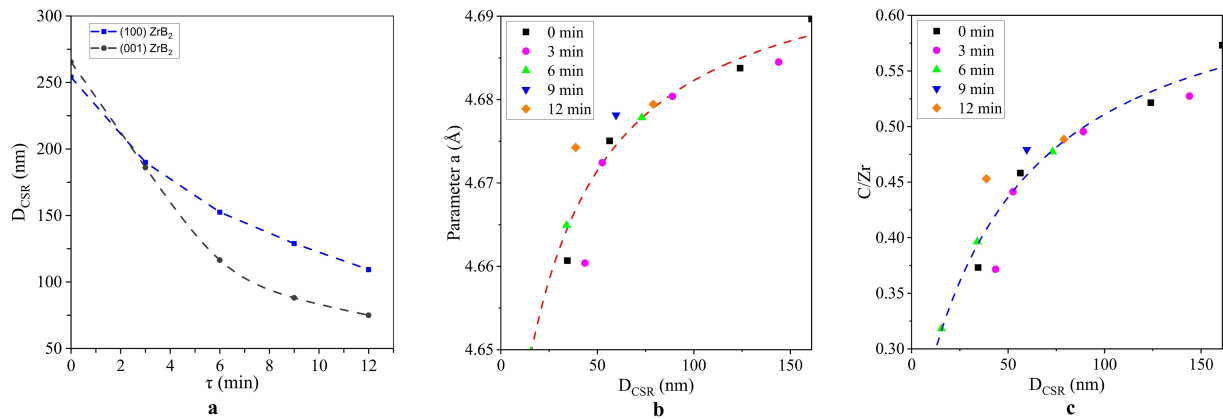
Such results can be explained by the dependence of the ceramic powder composition on the characteristics of composite powders obtained at different τ . Diffraction suggests that the presence of an amorphous Zr carbohydride phase in composite powders does not significantly impact the formation of the carbide phase during SHS. A possible reason for this is the nanoscale size of the carbohydride phase and the resulting rapid oxidation. Further, at $\tau = 6$ min, composite particles are already rather coarse and contain a substantial amount of carbohydride phases, but the volume fraction of embedded B_4C is still low.

The SHS reaction is obviously a solid-state and diffusion-controlled reaction. Thus, at $\tau \leq 6$ min the diffusion of unreacted material across the product layer is hindered. In turn, this sum of factors leads to an increase in oxide impurities and a decrease in the ZrB_2 phase contents. As the distribution of B_4C inclusions in composite powders becomes uniform ($\tau \geq 9$ min), the amount of main phases increases significantly.

As expected, the accumulation of defects in the structure of composite powders leads to a decrease in D_{CSR} of the ZrB_2 phase from ~ 265 nm to ~ 75 nm and from ~ 254 nm to ~ 110 nm along (001) and (100) axes, respectively (Fig. 9a). However, the peaks of the ZrC phase exhibit anisotropic broadening at high angles. So, we cannot describe the carbide phase by considering only anisotropy of D_{CSR} and microstrain. It may be explained by the formation of non-stoichiometric carbides with different crystal lattice parameters. In the course of full-profile analysis, the carbide phase was described as a combination of carbide phases that share similar structure but possess distinct cell parameters. Fig. 9b shows the dependence of the refined carbide cell parameter on D_{CSR} .

FIG. 8. Dependence of the phase mass content in SHS products on τ

The dependence of the ZrC cell parameter on its stoichiometry and the presence of impurities is well studied [24]. The change in the cell parameter due to the carbon content in pure ZrC can be described by the Mitrokhin *et al.* equation [25]. Calculation results for this equation based on experimental data are shown in the Fig. 9c. In accordance with these results, two notable observations can be made. Firstly, smaller crystallites possess a significantly smaller cell parameter, and consequently, a much lower apparent carbon content in the carbide phase. Secondly, with the C/Zr ratio values obtained (from 0.32 to 0.57), the ZrC phase with Fm-3m structure does not exist. It may indicate that the smallest crystallites represent either the ZrB phase (PDF 1-089-3932) or some non-stoichiometric Zr-based phase containing B, C, O, and N. The cell parameters of Zr-based cubic phases are very close, so their reliable identification is impossible. As the treatment duration increases the aforementioned broadening of the ZrC peaks becomes less distinct. Also the distribution of D_{CSR} and cell parameters of this phase becomes more uniform.

FIG. 9. Dependence of the ZrB₂ CSR size on τ (a), ZrC cell parameter a (b) and C/Zr (c)

The SHS products consist of tightly bonded aggregates of submicron spheroidal particles (Figs. 10–11), except for the sample obtained at $\tau = 0$ min. It is composed of rather dense coarse shards with an average size of $\sim 8.4 \mu\text{m}$ (Fig. 12). The dependence of the average particle size of ceramic powders on τ is similar to that for composite powders (Fig. 13). However, ceramic particles are 1–2 μm larger.

The patterns described herein allow us to propose a mechanism for the SHS reaction in composite powders. During the solid-state SHS reaction, due to high temperatures, a solid solution of Zr, B and C is formed. Then, this homogenous phase decomposes on ZrB₂ and depleted non-stoichiometric ZrC phases. The latter forms clusters which subsequently combine, saturate with C and grow. The more uniform the distribution of B₄C in the composite powder, the finer the

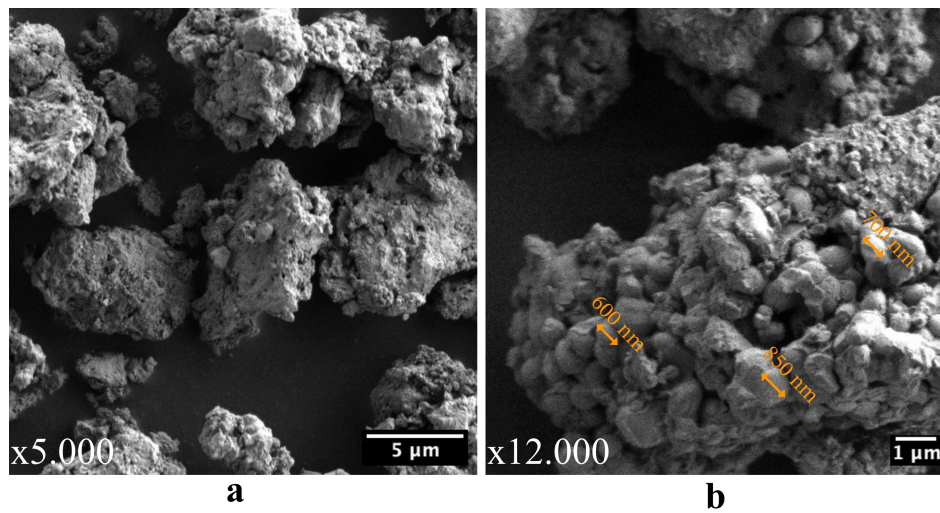


FIG. 10. SEM images of SHS product obtained at $\tau = 9$ min at different magnification: 5.000 (a) and 12.000 (b)

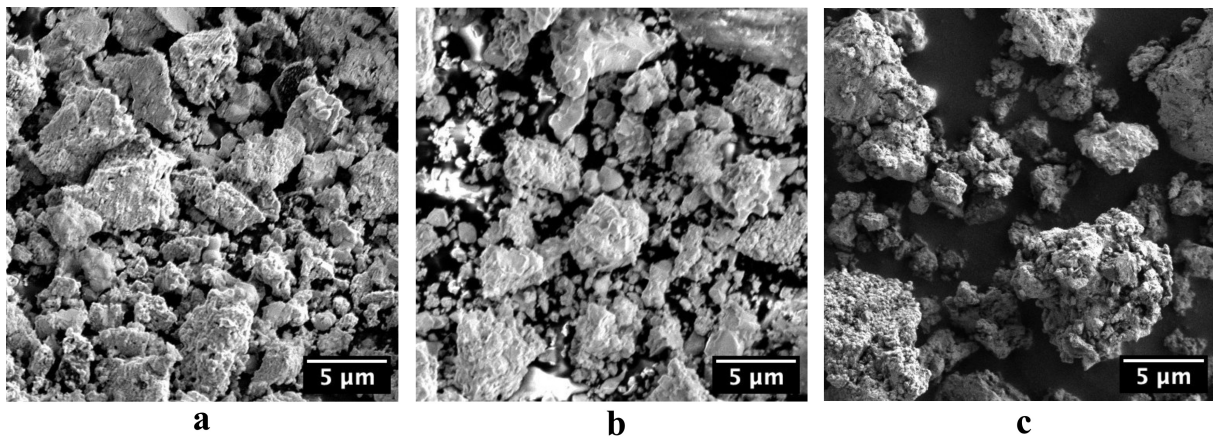
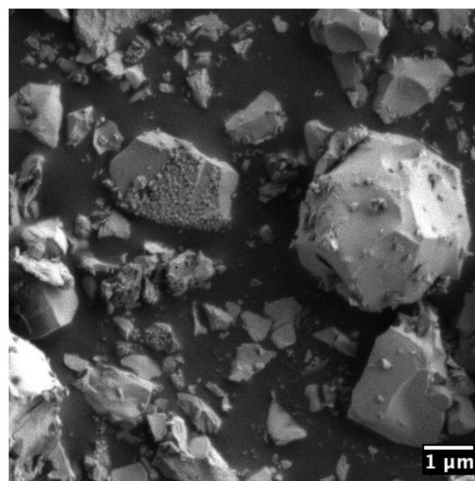


FIG. 11. SEM images of SHS product obtained at $\tau = 3$ (a), 6 (b) and 12 (c) min



$\tau = 0$ min, $D_{50} = 8.4 \mu\text{m}$

FIG. 12. SEM images of the SHS product obtained at $\tau = 0$ min

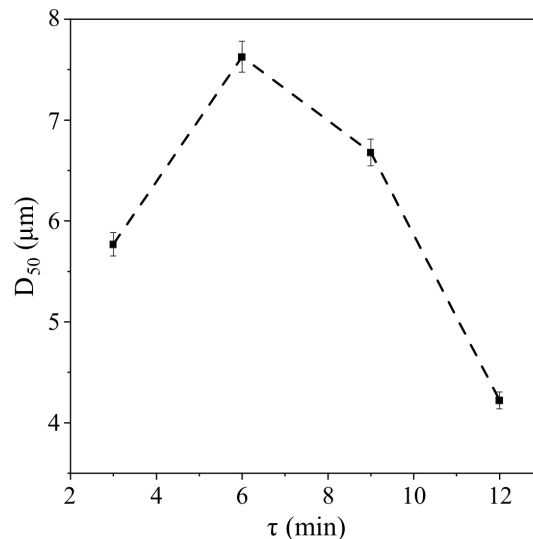


FIG. 13. The dependence of SHS product average particle size on τ

SHS products obtained. In the same way, the content of the main products should also rise. But fine product particles are easier to oxidize, so the oxide content barely decrease. Definitely, a more in-depth investigation is necessary to verify this hypothesis.

4. Conclusion

In this paper, Zr–B₄C composite powders obtained by ball milling as well as their SHS products were considered. Their structure, morphology, phase and fractional composition were investigated. Mechanochemical processes were determined to actively proceed during ball milling in hexane. As a result, Zr hydride and carbohydride phases form. The most uniform distribution of B₄C inclusions in the composite particles correspond to treatment duration of 9–12 min. During SHS in air, ZrB₂–ZrC ceramic powders with t-ZrO₂ and m-ZrO₂ admixtures are produced. They consist of tightly bonded aggregates of submicron spheroidal particles. The dependencies of the phase and fractional compositions of SHS products on the duration of treatment are obtained. The experimental results allowed us to formulate an assumption about a possible mechanism for the SHS reaction in composite powders: the formation of a solid solution and its subsequent decomposition.

References

- [1] Golla B.R., et al. Review on ultra-high temperature boride ceramics. *Progress in Materials Science*, 2020, **111**, P. 100651.
- [2] Pulci G., et al. High temperature mechanical behavior of UHTC coatings for thermal protection of re-entry vehicles. *Journal of thermal spray technology*, 2011, **20**, P. 139–144.
- [3] Wuchina E., et al. UHTCs: ultra-high temperature ceramic materials for extreme environment applications. *The Electrochemical Society Interface*, 2007, **16** (4), P. 30–36.
- [4] Pakseresht A., Mosas K.K.A. *Ceramic Coatings for High-Temperature Environments*. Engineering Materials, 2023, 491 p.
- [5] Wyatt B.C., et al. Ultra-high temperature ceramics for extreme environments. *Nature Reviews Materials*, 2024, **9**(11), P. 773–789.
- [6] Tiwari M., et al. The microstructural and mechanical behavior of in-situ synthesized ZrB₂–ZrC and ZrB₂–SiC–ZrC composites: A comparative study. *Vacuum*, 2023, **214**, P. 112199.
- [7] Xu L., et al. In situ synthesis of ZrB₂–ZrCx ceramic tool materials toughened by elongated ZrB₂ grains. *Materials & Design*, 2013, **49**, P. 226–233.
- [8] Zhao H., et al. In situ synthesis mechanism of ZrB₂–ZrN composite. *Materials Science and Engineering: A*, 2007, **452**, P. 130–134.
- [9] Cheng E.J., Katsui H., Goto T. Microstructure of ZrB₂–ZrN directionally solidified eutectic composite by arc-melting. *Journal of Asian Ceramic Societies*, 2018, **6**(1), P. 102–107.
- [10] Silvestroni L., Meriggi G., Sciti D. Oxidation behavior of ZrB₂ composites doped with various transition metal silicides. *Corrosion Science*, 2014, **83**, P. 281–291.
- [11] Sciti D., et al. Microstructure and mechanical properties of ZrB₂–MoSi₂ ceramic composites produced by different sintering techniques. *Materials Science and Engineering: A*, 2006, **434**(1–2), P. 303–309.
- [12] Hwang S.S., Vasiliev A.L., Padture N.P. Improved processing and oxidation-resistance of ZrB₂ ultra-high temperature ceramics containing SiC nanodispersoids. *Materials Science and Engineering: A*, 2007, **464**(1–2), P. 216–224.
- [13] Zhang S.C., Hilmas G.E., Fahrenholtz W.G. Mechanical properties of sintered ZrB₂–SiC ceramics. *Journal of the European Ceramic Society*, 2011, **31**(5), P. 893–901.
- [14] Rangaraj L., et al. Low-temperature processing of ZrB₂–ZrC composites by reactive hot pressing. *Metallurgical and Materials Transactions A*, 2008, **39**, P. 1496–1505.
- [15] Tsuchida T., Yamamoto S. Spark plasma sintering of ZrB₂–ZrC powder mixtures synthesized by MA-SHS in air. *Journal of Materials Science*, 2007, **42**(3), P. 772–778.
- [16] Qiu H.Y., et al. ZrB₂ powders prepared by boro/carbothermal reduction of ZrO₂: The effects of carbon source and reaction atmosphere. *Powder Technology*, 2012, **217**, P. 462–466.

- [17] Sacks M.D., et al. Carbothermal reduction synthesis of nanocrystalline zirconium carbide and hafnium carbide powders using solution-derived precursors. *Journal of Materials Science*, 2004, **39**, P. 6057–6066.
- [18] Zhang S., et al. Novel synthesis of ZrB_2 powder via molten-salt-mediated magnesiothermic reduction. *Journal of the American Ceramic Society*, 2014, **97**(6), P. 1686–1688.
- [19] Johnson W.B., Nagelberg A.S., Breval E. Kinetics of formation of a platelet-reinforced ceramic composite prepared by the directed reaction of zirconium with boron carbide. *Journal of the American Ceramic Society*, 1991, **74**(9), P. 2093–2101.
- [20] Hu Q., et al. Combustion and formation behavior of hybrid ZrB_2 and ZrC particles in $\text{Al-Zr-B}_4\text{C}$ system during self-propagation high temperature synthesis. *International Journal of Refractory Metals and Hard Materials*, 2012, **31**, P. 89–95.
- [21] Xu J., et al. Reaction behavior and formation mechanism of ZrB_2 and ZrC from the $\text{Ni-Zr-B}_4\text{C}$ system during self-propagating high-temperature synthesis. *Materials*, 2022, **16**(1), P. 354.
- [22] Zhang M., et al. The effect of B_4C particle size on the reaction process and product in the $\text{Cu-Zr-B}_4\text{C}$ system, *Journal of Asian Ceramic Societies*, 2015, **3**(1), P. 38–43.
- [23] Tsuchida T., Yamamoto S. Mechanical activation assisted self-propagating high-temperature synthesis of ZrC and ZrB_2 in air from Zr/B/C powder mixtures. *Journal of the European Ceramic Society*, 2004, **24**(1), P. 45–51.
- [24] Gasparini C., et al. On the stoichiometry of zirconium carbide. *Scientific Reports*, 2020, **10**(1), P. 6347.
- [25] Mitrokhin V.A., Lyutikov R.A., Yurkova R.S. Change in the lattice constant of zirconium carbide in the region of homogeneity. *Inorg. Mater. (USSR) (Engl. Transl.)*, 1975, **11**(6), P. 978–980.

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Assessment of the effectiveness of 2D graphene structures derived from various biopolymers as modifiers of the properties of thermally stable polyimide films

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ABSTRACT A comparative assessment of the influence of 2D graphene structures derived from lignin, starch and cellulose through the self-propagating high-temperature synthesis method on the mechanical, thermal and electrical properties of poly(4,4'-oxydiphenylene pyromellitimide) films was conducted. It was found that the incorporation of synthesized nanoparticles allows for the modification of the mechanical properties of the polyimide material without a significant decrease in volume and surface resistivity. Dependencies of the changes in properties of nanocomposite film materials on the following factors have also been established and analyzed: the type of biopolymer from which the nanofiller was obtained; the morphometric parameters of the prepared nanosized material; the concentration of the nanofiller.

KEYWORDS nanocomposites, 2D graphene structures, polyimides, biopolymers, mechanical properties, thermal properties

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1. Introduction

Many branches of modern industry increasingly require polymer materials that can maintain functionality under extreme operating conditions. Such materials include thermally stable aromatic polyimides (PIs), which combine record-high mechanical, thermal, and dielectric properties and exhibit high hydrolytic and radiation resistance [1,2]. Due to these properties, PIs find wide applications in various engineering fields as thermally and chemically resistant electrical insulation films [1,2] and protective coatings [3], as well as in structural materials with high mechanical performance [1,2]. However, despite significant advancements in the synthesis of polyimide materials, their most critical performance characteristics, such as mechanical stiffness, thermal stability, heat resistance and others, need further improvement. Modifying the polymer matrix with high dispersity fillers is the most promising approach for obtaining polymer materials with improved physicochemical and physico-mechanical properties, leading to the development of composite materials [4–8]. This trend is based on a phenomenological model that suggests that nano-dispersed particles within the polymer matrix influence not a single specific parameter (most commonly referred to as mechanical stiffness) of the polymer material but rather affect a complex set of its physicochemical parameters [6–8].

Theoretical methods, particularly all-atomistic molecular-dynamics simulations [9–11], allow for a reasonably accurate prediction of the trends regarding the influence of nanoparticles on the polymer matrix and the revealing of matrix parameters which will change most significantly depending on the nature, architecture, and dispersity of the nanoparticles. However, these methods require verifying the models used against experimental data and comparing simulation results

with experimental findings. Thus, the selection of nanoparticles as fillers to enhance a specific performance parameter or a set of parameters largely depends on the experimenter's intuition and experience. It is important to note that each case is unique, and extensive experimental testing and optimization may be required to achieve the desired results.

Among the various types of nanoparticles, 2D graphene structures (graphene oxide, reduced graphene oxide, graphene-modified in multiple ways, etc.) are of particular interest because many structures of this type possess the unique properties, such as high mechanical stiffness, electrical conductivity, and thermal conductivity [12, 13]. Research shows [14–18] that, due to the unique characteristics of graphene nanoparticles, their incorporation into a polymer matrix leads to improvements in the nanocomposite material's mechanical, thermal, anti-corrosive, and tribological properties.

However, despite the apparent advantages, the widespread use of graphene nanostructures is limited by several factors. The first is the high cost of graphene structures and the low productivity of most existing methods for their production. The second important factor is the potential environmental hazards associated with most known methods of synthesizing graphene nanostructures of industrial output, which arise from using aggressive acidic and alkaline agents to process the starting graphite. The third factor is the tendency of graphene structures to aggregate when introduced into polymer solutions and melts [19]. In this regard, there is currently active research aimed at developing more cost-effective and safer methods for the production of graphene nanostructures and optimizing the methods and conditions for surface treatment of these nanoparticles prior to their incorporation into the polymer matrix. These efforts aim to reduce nanoparticle aggregation and enhance their interaction with the polymer matrix.

One of the promising methods is a recently developed approach for the production of graphene nanostructures through the carbonization of biopolymers of plant origin (lignin, cellulose, starch, and glucose) [20], as well as plant biomass in the form of tree bark [21] and hogweed [22], under the conditions of a self-propagating high-temperature synthesis (SHS) process. The SHS method refers to the process of the propagation of a spin wave of a strongly exothermic reaction through a mixture of reagents (oxidizer and reducer), in which heat release is localized in a layer and transferred from layer to layer via heat conduction through a branched-chain ignition mechanism [23].

In contrast to thermal ignition, branching chain ignition is caused by the avalanche multiplication of active intermediate products (free atoms, radicals, and sometimes excited particles) in their rapid reactions with the initial reagents and among themselves. This mechanism ensures the realization of the reaction in a narrow zone that propagates through the material due to heat transfer following the local initiation of the response in a layer of cold reagent mixture that is not subjected to volumetric heating. Regarding performance and environmental safety, SHS fully meets the requirements imposed on modern technologies. It should be noted that our synthesis method of graphene structures refers to “bottom-up” processes. In other words, at the first stage, the initial biopolymer (precursor) is destroyed to low-molecular products due to thermo-oxidative SHS processes. Subsequently, these products form 2D graphene structures, namely particles of few-layer graphene (FLG), due to self-organization processes.

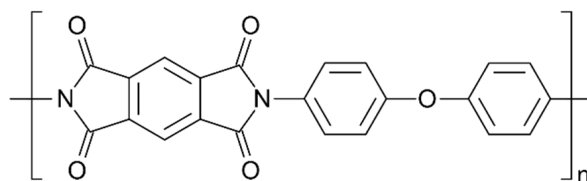
Considering this circumstance, it can be assumed that the use of “traditional” methodologies based on various mechanisms for obtaining graphene structures “top-down” (in particular, the Hummers method [24]) and “bottom-up” approaches (specifically, the SHS method proposed by us) will lead to graphene structures that differ in a range of characteristics, such as the defectiveness of graphene layers, including Stone–Wales defects [25]; the polydispersity parameters of graphene particles; and the nature and quantity of functional groups. Consequently, the differences in the morphometric parameters of graphene particles synthesized through different mechanisms and using various precursors may also influence the nature of their interaction with the polymer matrix.

Thus, although our proposed synthesis method offers advantages in terms of productivity and environmental friendliness compared to methods based on the exfoliation of graphene layers from natural graphite, its use as an alternative to “traditional” graphene production methods requires experimental validation of the quality of the obtained products. This work's objectives included the characterization of the properties of FLG nanoparticles obtained by the SHS method from various biopolymers and the investigation of the possibilities for modifying the properties of thermally stable polymer films by incorporating the synthesized nanoparticles. The matrix polymer film material selected is aromatic PI – poly(4,4'-oxydiphenylene pyromellitimide) (PMDA-ODA) [1, 2], which is widely used in various fields of engineering, primarily as heat-resistant dielectric materials with high mechanical properties.

2. Materials and methods

2.1. Materials

The structure of the matrix polymer PMDA-ODA is as follows:



The solution of polyamic acid (PAA) in N-methylpyrrolidone (concentration 15 wt %) – the polymer-precursor of PI PMDA-ODA was obtained from Sigma-Aldrich (product No. 575828). N-methylpyrrolidone (chemically pure) was obtained from Vekton (Russia). Ammonium nitrate (chemically pure) and isopropyl alcohol (chemically pure) were acquired from Lenreaktiv (Russia). As precursors for the synthesis of graphene structures, lignin, microcrystalline cellulose, and starch were selected. Lignin was extracted from the black liquor of industrial cooking processes at Mondi SLPK joint-stock company (Russia) by treating the partially evaporated black liquor with sulfuric acid (10 wt. %) at a temperature of 60 °C until a pH of 4 was reached. The precipitate was washed with distilled water until a neutral pH was achieved and then dried at a temperature of 35 – 40 °C. Removal of low-molecular-weight organic impurities was carried out by extraction with diethyl ether. The carbonized product obtained from lignin by means of SHS is designated as FLG-1. Starch and microcrystalline cellulose were obtained from Aptekhný Sklad Khimfarmprodukt Co (Russia); their carbonized products are designated as FLG-2 and FLG-3, respectively. As a reference sample, graphene supplied by Sigma-Aldrich (product cat. No. 900394, Merck, Germany) was used – FLG-0. The particle size of FLG-0 is $< 2 \mu\text{m}$ and the specific surface area is 300 m²/g.

2.2. Synthesis of FLG

The synthesis of FLG was carried out according to the methodology previously developed by the authors [20–22]. Before use, all biopolymers underwent preliminary treatment: they were dried, ground and sieved to obtain a homogeneous mass. Then, the prepared samples were mixed with the oxidizer powder in a mass ratio of biopolymer to oxidizer = 1:1. In this study, ammonium nitrate was used as the oxidizer. The resulting reaction mixture was placed in a glass flask that was immersed in an oil bath heated to 220 °C. In the course of the reaction, significant gas evolution was observed; the termination of this gas evolution indicated the completion of the SHS process. The obtained powder was washed with hot distilled water and isopropyl alcohol and then the solvent was removed under vacuum at 280 °C.

2.3. Films preparation

A two-stage synthesis method was used to prepare the control and nanocomposite films [1, 26, 27]. At the first stage of synthesis, a soluble polymer-precursor – PAA was obtained (this stage was carried out by Sigma-Aldrich). The layers of PAA solutions were cast onto flat glass plates using a template and dried in a thermostat at a temperature of 80 °C for 4 hours. Then, to obtain PIs, the PAA films were cyclized by heating on the substrate in an oven at a rate of 3 °C/min up to 360 °C, followed by a hold at this temperature for 30 minutes. The composite films were prepared using a standard solution processing technique. The calculated amount of nanoparticles were subjected to thermal treatment for 1 hour at 100 °C to remove the residual water sorbed during the storage, after which these nanoparticles were dispersed in N-methyl pyrrolidone using an ultrasonic disperser. The obtained dispersion was combined with the PAA solutions, followed by homogenization of the mixture through prolonged stirring (24 hours) using a top-driven mechanical stirrer at 1000 rpm. Nanocomposite films based on PI were produced from the homogenized mixtures using the methodology described above.

2.4. Characterization techniques

The electron micrographs of the carbonized products were obtained using a Zeiss Libra 200FE transmission electron microscope (ZEISS, Germany) at 50 kV. The morphology of the FLG-1 to FLG-3 samples, as well as the nanocomposite film materials based on them, was investigated using a SUPRA-55VP scanning electron microscope (SEM) (Carl Zeiss, Oberkochen, Germany). The samples were mounted on the microscope holders using a special adhesive. To study the morphology and assess the charge dissipation properties of the FLG particles, they were intentionally left uncoated, forgoing the standard platinum sputtering procedure. X-ray diffraction (XRD) analysis of the samples was conducted using an XRF-1800 spectrometer (Shimadzu, Japan). The measurement was performed on a pressed pellet consisting of the investigated material and polyvinyl alcohol (as a binder) on a boric acid substrate. Pressing was carried out using a Carber 3912 tool. Raman spectra were obtained using a Horiba Yobin Yvon LabRam HR 800 spectrometer (532 nm laser, 1800 lines/mm diffraction grating, microscope with x20 magnification). Infrared absorption spectra were recorded using the InfraLUM FT-08 spectrometer (Lumex, Russia). The elemental analysis of nanoparticles samples obtained by the SHS method was performed using a CHN Vario EL III elemental analyzer (Elementar Analysensysteme GmbH, Germany). The specific surface was measured using ASAP 2020 MR (Micromeritics, USA) by the BET method. Nitrogen was used as the adsorbate gas. Before the measurement, the samples were held for 2 h in vacuo at 300 °C. True density was measured using gas (helium) pycnometry on the Ultrapycnometer 1000 instrument (Quantachrome Instruments, USA).

The thermal characteristics of the FLG-1 to FLG-3 samples, as well as the nanocomposite film materials containing these nanoparticles, were investigated using simultaneous thermogravimetric (TGA) and differential thermal (DTA) analyses in a static air environment with a DTG-60 analyzer (Shimadzu, Japan). The heating rate of the samples was set at 5 °C/min. Based on the analysis results, the temperature at which the destruction process is completed ($T_{\text{full dest}}$), beyond which the sample mass remains unchanged and the coke residue (m_{fin}/m_0) were determined. Additionally, the temperatures corresponding to the onset of thermal degradation (τ_0) and the temperatures at which the sample mass decreases by 1, 5 and 10 % (τ_1 , τ_5 and τ_{10} , respectively) were calculated. Furthermore, the temperature at which the maximum rate of mass loss was recorded ($T|_{dm/dT \text{ max}}$) was determined from the first derivative of the mass loss curve (DTG). The

glass transition temperatures (T_g) of the PI-based nanocomposite film samples were determined using thermomechanical analysis (TMA) with a TMA 402 F1 Hyperion apparatus (NETZSCH, Germany). The tests were performed in a uniaxial stretching mode under a constant tensile force of 0.5 MPa while the sample was heated at a steady rate of 5 °C/min in an argon atmosphere.

The mechanical tests of the films were conducted at room temperature in a uniaxial stretching mode using a universal testing machine, Autograph AGS-X 5 kN (Shimadzu, Japan). The samples, with a working size of 20×2 mm, were tested at a stretching rate of 10 mm/min. During the tests, the following material properties were determined: Young's modulus (E), yield stress (σ_y) (in cases where it could be achieved during the sample stretching), break stress (σ_b) and ultimate deformation (ε_b). For each tested material, average values and standard deviations were calculated based on measurements taken from 6 – 9 fragments of the material. The values of the matrix and composite films' volume and surface electrical resistivity were determined using a two-electrode method on a teraohmmeter E6-A13 (Metromex, Russia). The samples were placed in a specially designed circular cell connected to the electrodes. To eliminate surface leakage current during the measurement of the samples' volume electrical resistivity, a special guard ring surrounding the measuring circular electrode was employed, this ring was grounded during the measurement. When measuring the surface electrical resistance with the given electrode configuration, the voltage is applied between the guard ring and the central electrode, the bottom electrode being grounded. The values of the volume and surface resistances of the dielectric sample were determined under a constant voltage of $U = 100$ V using the following formula.

$$R_{V(S)} = \frac{U}{I_{V(S)}}, \quad (1)$$

where $I_{V(S)}$ is the current flowing through the volume or along the surface of the sample after the charge transfer process has reached equilibrium. The volume resistivity of the material was determined using the following formula:

$$\rho_V = \frac{R_V \cdot S}{h} = \frac{U \cdot S}{I_V \cdot h}, \quad (2)$$

where I_V is the measured volume current; U is the voltage across the electrodes; S is the area of the central measuring electrode; h is the thickness of the dielectric; and R_V is the volume resistance of the sample. The surface resistivity can be calculated using the following formula:

$$\rho_S = \frac{R_S \cdot \pi \cdot (d_1 + d_2)}{d_1 - d_2}, \quad (3)$$

where R_S is the surface electrical resistance of the dielectric sample confined between the electrodes; d_1 is the inner diameter of the guard ring; and d_2 is the diameter of the central electrode.

3. Results and discussion

Earlier, we demonstrated that the carbonization of natural biopolymers under the conditions of the self-propagating high-temperature synthesis process leads to the formation of 2D graphene structures, which are promising for use as modifying additives in polymer matrices [28]. In this study, three types of biopolymers were chosen as precursors: starch, microcrystalline cellulose, and sulfonated lignin. These biopolymers significantly differ in the architecture of their macromolecular chains [29, 30]. Consequently, one could expect differences in the morphometric parameters of the final FLG.

3.1. Characterization of carbonized products

The carbonized products were studied using a combination of complementary methods, such as electron microscopy, Raman and FTIR spectroscopy, and X-ray diffraction analysis. The density and specific surface area values of these samples were also determined. The morphology of the SHS-synthesized FLG was characterized by SEM and TEM (Fig. 1). As was established in our earlier studies, the lateral dimensions of the synthesized nanoparticles reached up to 0.2 – 0.3 μm [31]. The analysis of the TEM images presented in Fig. 1(a–c) showed that the particles of powders FLG-1 to FLG-3 have a leaf-like shape with varying degrees of transparency. Since each individual monolayer particle is transparent, the presence of darker areas can be explained by multiple graphene sheets in the stack. Furthermore, the chaotic distribution of transparent and dark regions may indicate that the resulting particles have a curved surface, meaning they are “scaly” particles, characteristic of 2D carbon structures [32].

SEM analysis revealed a pronounced dependence of morphology and charge dissipation behavior on the nature of the precursor. While all synthesized samples exhibited some degree of charge accumulation, FLG derived from lignin (Fig. 1(d)) and cellulose (Fig. 1(f)) demonstrated a highly ordered platelet-like structure with relatively minimal defectivity and showed the most effective charge dissipation among them. In contrast, the analogues obtained from starch (Fig. 1(e)) exhibited a severely disrupted structure composed of defective platelets along with a significantly higher propensity for charge accumulation, indicating their inferior electrical conductivity.

The Raman scattering data presented in Fig. 2 demonstrate four peaks: 1355 – 1365 cm^{-1} (D), 1574 – 1595 cm^{-1} (G), 2730 – 2760 cm^{-1} (2D), and 2930 – 2960 cm^{-1} (D+G). The D peak corresponds to a defect in the sp^2 lattice, while the G peak is associated with sp^2 hybridized carbon. The overall shape of the resulting Raman spectra of the carbonized

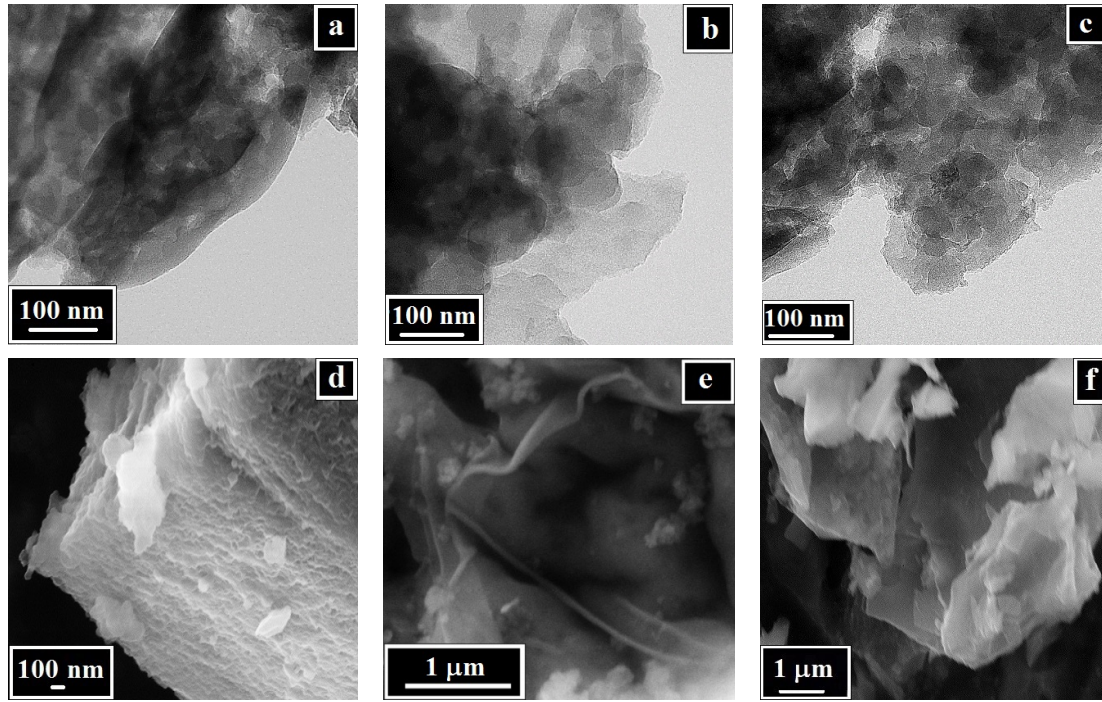


FIG. 1. TEM (a–c) and SEM (d–f) images of samples FLG-1 (a, d), FLG-2 (b, e), and FLG-3 (c, f)

products align with the spectral characteristics of 2D graphene structures [33, 34]. The defectiveness of the synthesized FLG samples can be assessed by the intensity ratio of the D and G peaks. A ratio close to 1 indicates a high level of defectiveness in the obtained samples. Comparing the Raman scattering data for the synthesized FLG samples, it can be concluded that FLG-1 ($I_D/I_G = 0.62$) is characterized by the lowest defectiveness, while FLG-2 ($I_D/I_G = 0.97$) exhibits the highest defectiveness.

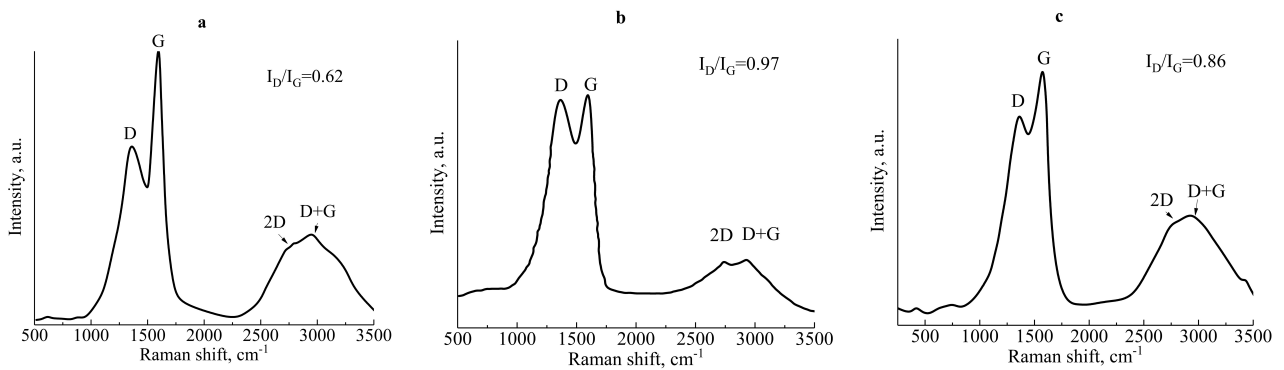


FIG. 2. Raman spectra of FLG-1 (a), FLG-2 (b), FLG-3 (c) samples

Let us note that the nature of the precursor determines not only the defectiveness of the synthesized FLG but also its specific surface area and density (Table 1).

TABLE 1. Specific surface area and density of samples FLG-1, FLG-2 and FLG-3

FLG-1	FLG-2	FLG-3
Density, g/cm ³		
2.011	1.910	1.975
Specific surface area, m ² /g		
590	436	621

The synthesized FLG particles differ somewhat in properties from commercially available graphene structures obtained through the most commonly used methods. For example, (Fig. 3), in addition to the C–H, C–OH, CO–C, and C=C bonds characteristic of graphene structures, the synthesized particles also exhibit a C–N bond, indicating the presence of nitrogen-containing groups in the FLG obtained by this method. The presence of these groups is due to the use of ammonium nitrate as an oxidizer.

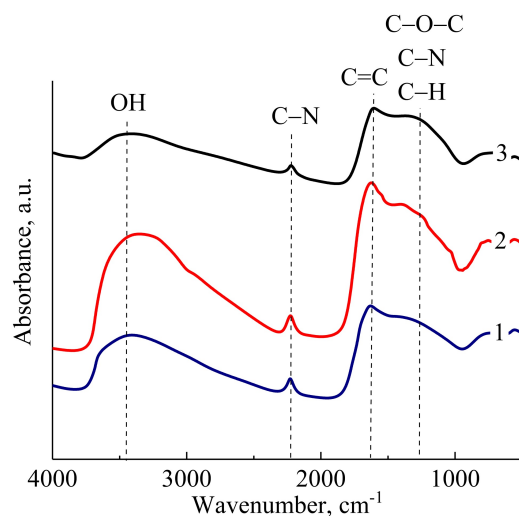


FIG. 3. IR spectra of samples FLG-1 (1), FLG-2 (2) and FLG-3 (3)

The results of the elemental analysis conducted on a CHN analyzer in this study showed that the concentration of nitrogen atoms in the synthesized FLG significantly depends on the type of precursor: in the samples FLG-1, FLG-2, and FLG-3, the nitrogen content is 7.75, 14.60, and 15.19 %, respectively. XRD was conducted to demonstrate the absence of graphite structures other than FLG, namely graphite, thermally expanded graphite, graphene oxide in the obtained materials. The X-ray diffraction pattern of the FLG-3 sample is presented in Fig. 4 as an illustration.

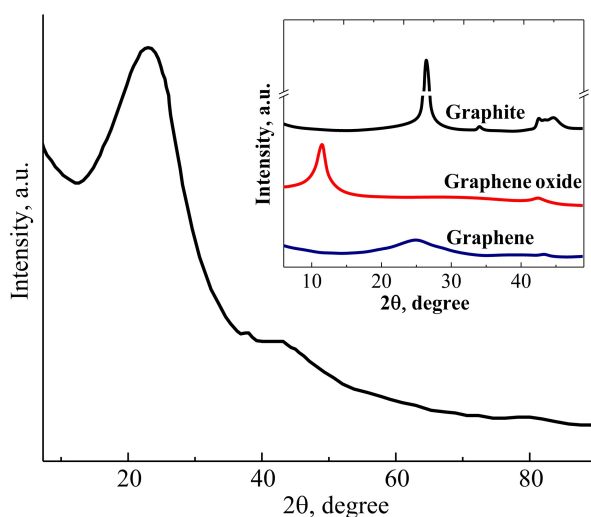


FIG. 4. X-ray diffraction pattern of the FLG-3. For comparison, the insert shows the X-ray diffraction patterns of graphite, graphene oxide, and graphene obtained in the study [35]

The presence of only two halos in the range of 10 to 35 degrees and in the area from approximately 43 to 50 degrees without any sharp diffraction peaks demonstrates the absence of any graphite regions in the material (Fig. 4), whose diffraction is characterized primarily by a narrow and intense peak at around 26 degrees, as well as a narrow peak with low intensity in the range of 54 – 55 degrees [35,36].

3.2. Thermal analysis of samples FLG-1 to FLG-3

The results of the combined thermal analysis TGA and DTA, presented in Table 2 and Fig. 5, show that upon heating samples FLG-1 to FLG-3 from room temperature to 100 – 120 °C, a significant mass loss (5 – 10 %) was observed,

accompanied by the appearance of an endothermic peak on the DTA curves, with a maximum at 65 – 70 °C. This phenomenon undoubtedly corresponds to the removal of water adsorbed on the surface and/or within the volume of the particles. This effect is likely attributed to the presence of hydrophilic oxygen-containing functional groups on the surfaces of the synthesized materials and their relatively loose and porous structure (Table 1).

After the onset of thermal degradation, the process rate increases monotonically with rising temperature, reaching a maximum value in the range of 482 – 524 °C. In the same temperature region, an exothermic thermal effect is observed on the DTA curves, with maxima at 475 – 526 °C.

TABLE 2. Thermal characteristics of samples FLG-1 to FLG-3

Sample	τ_0 , °C	τ_1 , °C	τ_5 , °C	τ_{10} , °C	$T _{dm/dT_{max}}$, °C	$T_{full\ dest}$, °C	m_{fin}/m_0 , %
FLG-1	245	281	332	364	482	580	4.47
FLG-2	205	235	281	308	524	550	1.93
FLG-3	275	316	373	403	494	595	2.24

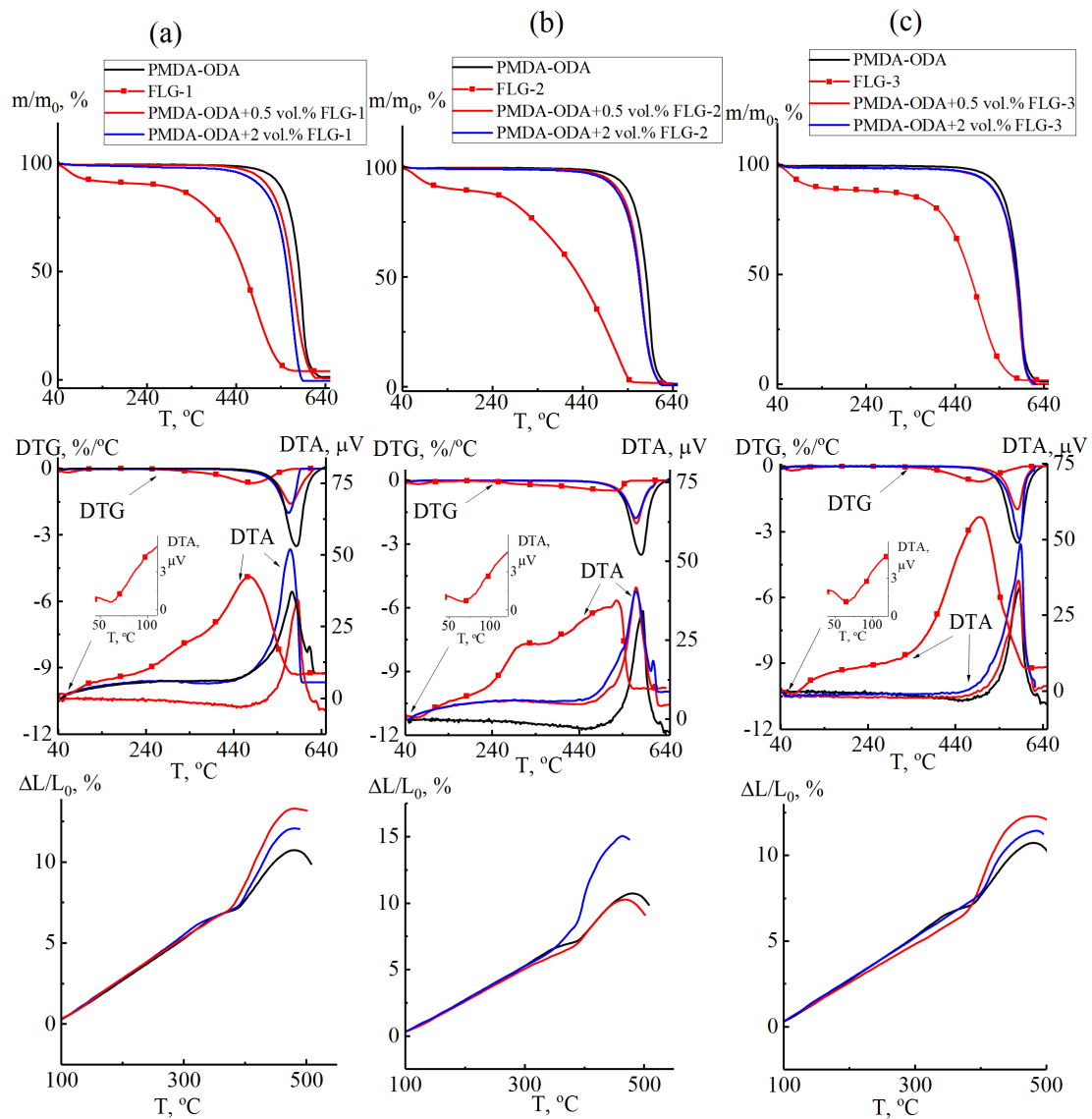


FIG. 5. TGA, DTG, DTA and TMA curves of matrix and composite films of PMDA-ODA containing 0.5 and 2 vol. % FLG-1 (a), FLG-2 (b) and FLG-3 (c). Inset: DTA curves of the samples in the temperature range of 40 – 120 °C

The depression of mass of all the FLG samples studied during the TGA process was completely stopped up to the temperatures range of 550 – 595 °C (Fig. 5). The further heating of the samples did not provoke any additional fall of their mass (in the control experiments we have tested the mass in the heating process up to 800 °C. It is well known that even heat-resistant polymer materials completely degrade in air, forming volatile compounds in a temperature range up to ~ 600 °C [37]. This is all the more true for thermo-oxidative destruction processes of biopolymers and their reprocessing products. Thus, it can be concluded that the residual mass of the sample (1.93 – 4.47 %) recorded in our experiments when heating FLG above 600 °C refers to inorganic impurities present in the samples. The experimental methods at our disposal do not allow to specify the elemental composition of these impurities, but they can reliably estimate their amount in studied FLG.

It should be noted that the thermal stability of FLG is determined by the type of biopolymer used for its synthesis. The data presented in Table 2 show that the sample FLG-3, synthesized from cellulose, demonstrates the highest thermal stability. These particles exceed FLG-1, obtained from lignin, by 39 °C in terms of τ_{10} , and FLG-2, synthesized from starch, by 95 °C. The observed differences in thermal stability are likely related to the varying content of oxygen-containing and nitrogen-containing functional groups in the synthesized materials.

It can be hypothesized that the enhanced thermal stability observed for the FLG-3 sample is largely attributable to a lower content of oxygen-containing functional groups and a higher abundance of nitrogen-containing functional groups compared to the FLG-1 and FLG-2 samples. The elemental analysis data support this hypothesis presented earlier, as well as the DTA results depicted in Fig. 5. In contrast to FLG-3, the DTA curves of FLG-1 and FLG-2 samples exhibit an additional exothermic thermal effect within the temperature range of 240 to 370 °C, with a maximum at 300 °C, which may be indicative of the removal of oxygen-containing functional groups from the graphene structure [38].

3.3. Thermal analysis of nanocomposite film samples

The results of TGA and DTA, presented in Fig. 5 and Table 3, indicated that incorporating all types of FLG particles used in the work does not qualitatively affect the thermal degradation processes of the polyimide material. For both the control film PMDA-ODA and the composite films, the thermal degradation process begins in the range of approximately 400 – 460 °C, with the maximum degradation rate occurring at around 570 – 590 °C, and this process is finished in the range of roughly 590 – 630 °C. The incorporation of nanoparticles of all types into PMDA-ODA films generally resulted in a certain reduction in thermal stability metrics. Such an effect was anticipated, as the TGA results (Fig. 5, Tables 2 and 3) indicate lower thermal stability values (up to τ_{10}) for the nanoparticles themselves compared to the thermal stability of the PI matrix.

The TMA results are presented in Fig. 5 and Table 3. The incorporation of synthesized nanoparticles into the PI matrix generally decreases the material's glass transition temperature. It is noteworthy that, in some cases, this reduction was accompanied by an increase in the films' flexibility beyond the glass transition (Fig. 5). The most likely reason for this effect is the formation of excess free volume in the polymer material due to the aggregation of the synthesized nanoparticles. However, the PMDA-ODA film sample containing 2 vol. % FLG-3 was an exception: the glass transition temperature of the nanocomposite film increased by 11 °C compared to the unfilled sample. This is likely attributed to additional interactions between the surface groups of FLG-3 and the matrix polymer. It appears that such interactions, despite the significant aggregation of these nanoparticles, may hinder the segmental mobility of the polymer chain and slightly increase the glass transition temperature of the composite material.

TABLE 3. Thermal characteristics of PMDA-ODA matrix films and PMDA-ODA-based composite materials

Sample	T_g , °C	τ_5 , °C	τ_{10} , °C	$T _{dm/dT_{max}}$, °C
PMDA-ODA	391	523	540	584
PMDA-ODA+0.5 vol. % FLG-1	382	493	516	570
PMDA-ODA+2 vol. % FLG-1	390	476	502	564
PMDA-ODA+0.5 vol. % FLG-2	387	501	524	572
PMDA-ODA+2 vol. % FLG-2	384	498	520	570
PMDA-ODA+0.5 vol. % FLG-3	385	512	532	582
PMDA-ODA+2 vol. % FLG-3	402	508	529	586

3.4. Mechanical properties

It is well known [39] that the positive influence of nanosized fillers on the mechanics of polymer film materials primarily manifests as reinforcement of the matrix material, leading to an increase in its stiffness. This results in a growth

of Young's modulus and, to a lesser extent, the material's yield stress. As for the strength characteristics, increasing the material's strength is quite rare in this context. As a rule [39], an increase in the concentration of nanoparticles increases the material's stiffness, accompanied by a significant decrease in strength and ultimate deformation. Researchers often attribute this effect to the heterogenization of the material's structure and the emergence of additional stresses at the phase boundaries of the "polymer matrix – nanoparticles". However, this decrease in break stress and ultimate deformation is not critical when considering the situation from the perspective of practical material usage. Indeed, for most polymer film materials, including the PMDA-ODA matrix, failure occurs at relatively large deformations, where these deformations are inherently irreversible. Thus, the actual magnitude of deformations permissible during the material's service life does not exceed a few percent. It is precisely within this range that the reinforcement effect manifests quite significantly, provided it can be achieved by incorporating nanoparticles.

For composite films filled with the studied nanoparticles, the realization of the aforementioned reinforcement effect within certain limits can be stated (Table 4). A slight (11 %) increase in Young's modulus was achieved by incorporating 2 vol. % of FLG-1 particles into the PMDA-ODA matrix. A less pronounced increase in the modulus (6 %) was observed with the introduction of 2 vol. % of FLG-2 into the polymer. The same increase in Young's modulus was recorded with the addition of 0.5 vol. % of FLG-3; however, further increasing the concentration of these nanoparticles caused the modulus to drop below the value characteristic of the unfilled film. Finally, as expected, introducing all the nanoparticles used in this study led to a consistent decrease in the ultimate deformation and, consequently, the break stress of the material as their concentration increased.

TABLE 4. Mechanical properties of PMDA-ODA matrix films and PMDA-ODA-based composite materials

Sample	E , GPa	E/E_0	σ_y , MPa	σ_b , MPa	ε_b , %
PMDA-ODA	2.85 ± 0.11	1.00	96 ± 3	149 ± 12	63 ± 4
PMDA-ODA+0.5 vol. % FLG-1	3.06 ± 0.09	1.07	97 ± 1	125 ± 5	30 ± 2
PMDA-ODA+2 vol. % FLG-1	3.15 ± 0.07	1.11	106 ± 3	128 ± 2	27 ± 1
PMDA-ODA+0.5 vol. % FLG-2	2.92 ± 0.06	1.02	104 ± 1	131 ± 1	41 ± 3
PMDA-ODA+2 vol. % FLG-2	3.03 ± 0.09	1.06	103 ± 3	126 ± 2	27 ± 1
PMDA-ODA+0.5 vol. % FLG-3	2.99 ± 0.06	1.05	96 ± 2	112 ± 6	25 ± 6
PMDA-ODA+2 vol. % FLG-3	2.79 ± 0.14	0.98	—	98 ± 6	17 ± 3

E_0 – Young's modulus of the PMDA-ODA matrix polymer film

Summarizing this part of the research, it can be concluded that the most effective modifier of the PI mechanical properties is the FLG-1 material. Its superiority is directly due to its optimal dispersibility within the polymer matrix and minimal tendency to agglomerate, which is confirmed by SEM analysis data (Fig. 6).

In contrast to FLG-1 (Fig. 6(a,d)), the composites with FLG-2 (Fig. 6(b,e)) and FLG-3 (Fig. 6(c,f)) form significantly larger and more numerous agglomerates. These structures act as stress concentrators, leading to a consequent deterioration in the material's strength characteristics. The greatest propensity for aggregation is observed in FLG-3 particles, which is consistent with previously published data [20] and explains the most substantial decline in mechanical properties precisely in this nanocomposite.

3.5. Dielectric properties

As is known [40] and demonstrated by the example of PMDA-ODA films containing commercially available graphene FLG-0, the introduction of carbon nanoparticles, even in small concentrations, can significantly increase the electrical conductivity of polymer materials (Table 5). Considering PI films' primary application area, this sharply narrows their practical application range. Therefore, it was imperative to evaluate how introducing synthesized nanoparticles affects the dielectric properties of PI films.

Based on the data from Table 5, it is evident that the nanocomposite films containing the synthesized nanoparticles exhibit high values of volume and surface resistivity, corresponding to these materials' low electrical conductivity. Since the electrical conductivity of such nanocomposite materials filled with carbon nanoparticles is realized through the movement of charge carriers across the filler particles, it is most likely that the observed effect is due to the presence of functional groups on the surface of the synthesized nanoparticles [41, 42]. These groups contribute to blocking electrical contacts between the conductive nanoparticles, meaning there are no continuous electrical pathways within the material, known as the percolation cluster, which directly affects the conductivity of the nanocomposite polymer material. For nanocomposites filled with control graphene particles (FLG-0), the effect of blocking contacts between nanoparticles is not observed, which suggests the absence of any non-conducting groups on their surface.

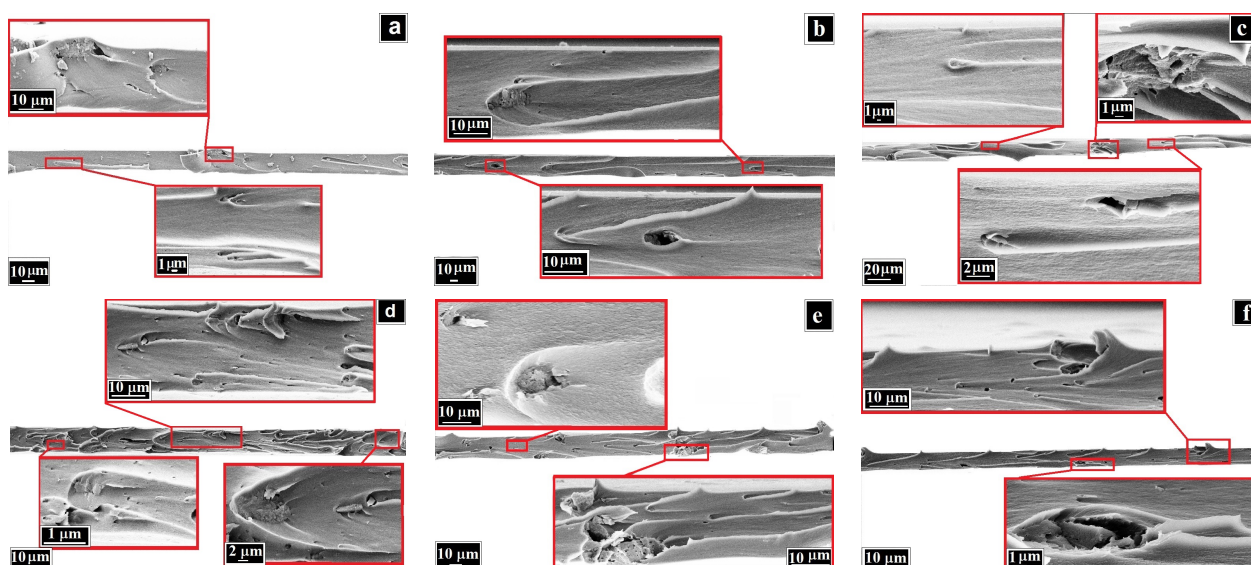


FIG. 6. SEM micrographs of the cryo-fractured surfaces of PMDA-ODA polyimide composites with different fillers and concentrations: 0.5 vol.% FLG-1 (a), 0.5 vol.% FLG-2 (b), 0.5 vol.% FLG-3 (c), 2 vol.% FLG-1 (d), 2 vol.% FLG-2 (e), 2 vol.% FLG-3 (f)

TABLE 5. Dielectric characteristics of PMDA-ODA matrix films and PMDA-ODA-based composite materials

Sample	$\rho_V, \Omega \cdot m$	ρ_s, Ω
PMDA-ODA	4.64E+13	1.03E+10
PMDA-ODA+0.5 vol. % FLG-0	1.67E+05	8.62
PMDA-ODA+2 vol. % FLG-0	3.96E+04	117
PMDA-ODA+0.5 vol. % FLG-1	2.12E+13	6.90E+09
PMDA-ODA+2 vol. % FLG-1	3.84E+12	1.21E+09
PMDA-ODA+0.5 vol. % FLG-2	2.71E+12	5.86E+08
PMDA-ODA+2 vol. % FLG-2	1.96E+12	5.86E+08
PMDA-ODA+0.5 vol. % FLG-3	3.23E+13	9.66E+09
PMDA-ODA + 2 vol. % FLG-3	5.12E+10	3.10E+07

4. Conclusions

Comprehensive studies have demonstrated the potential of introducing synthesized 2D graphene structures obtained from various biopolymers into the PMDA-ODA polymer matrix as a method for preparing new composite materials.

It was established that the most significant change in Young's modulus (by 11 %) of the film material was recorded with the introduction of 2 vol. % FLG-1, derived from lignin. Similar, albeit less pronounced, changes in the mechanical properties of PI are observed with the introduction of FLG obtained from cellulose and starch.

Incorporating synthesized nanoparticles into the PMDA-ODA PI matrix significantly affects the thermal characteristics of the film materials. Although a decrease in thermal stability was observed in all cases, the effect on the glass transition temperature was ambiguous. For instance, the introduction of 2 vol. % FLG-3, synthesized from cellulose, increased the glass transition temperature by 11 °C, while in other cases, a decrease was recorded. It is also worth noting that introducing synthesized nanoparticles into the PMDA-ODA matrix did not significantly reduce volume and surface resistivity in any of the cases considered.

Thus, the results of this study have shown that the degree of change in the properties of the polymer material significantly depends on the nature of the biopolymer from which the FLG was synthesized. This opens new opportunities for developing and optimizing polyimide film materials with specified characteristics for various engineering fields, including protective dielectric films and coatings. Further research in this area may lead to a deeper understanding of the interaction mechanisms between components and contribute to creating materials with tailored properties.

References

- [1] Bessonov M.I., Koton M.M., Kudryavtsev V.V., Laius L.A. *Polyimides – Thermally Stable Polymers*. New York: Plenum Publishing Corp., 1987, 374 p.
- [2] Ha C.-S., Mathews A.S. Polyimides and high performance organic polymers. *Advanced Functional Materials*, 2011, P. 1–36.
- [3] Sezer Hiciylmaz A., Celik Bedeloglu A. Applications of polyimide coatings: a review. *SN Applied Sciences*, 2021, **3** (3), P. 1–22.
- [4] Paul D.R., Robeson L.M. Polymer nanotechnology: nanocomposites. *Polymer*, 2008, **49** (15), P. 3187–3204.
- [5] Jabeen S., Kausar A., Muhammad B., Gul S., Farooq M. A review on polymeric nanocomposites of nanodiamond, carbon nanotube, and nanobi-filler: structure, preparation and properties. *Polymer-Plastics Technology and Engineering*, 2015, **54** (13), P. 1379–1409.
- [6] Rizvanova P.G., Magomedov G.M., Kozlov G.V., Dolbin I.V. Local and spatial structure of nanofiller in polymer matrix and its influence on the properties of nanocomposites. *Inorganic Materials: Applied Research*, 2020, **11**, P. 665–668.
- [7] Khlebtsov B.N. Functional nanoparticles: synthesis and practical applications. *Colloid Journal*, 2023, **85** (4), P. 475–478.
- [8] Gudkov M.V., Stolyarova D.Y., Shiyanova K.A., Mel'nikov V.P. Polymer composites with graphene and its derivatives as functional materials of the future. *Polymer Science, Series C*, 2022, **64** (1), P. 40–61.
- [9] Larin S.V., Glova A.D., Serebryakov E.B., Nazarychev V.M., Kenny J.M., Lyulin S.V. Influence of the carbon nanotube surface modification on the microstructure of thermoplastic binders. *RSC advances*, 2015, **5** (64), P. 51621–51630.
- [10] Lyulin S.V., Larin S.V., Nazarychev V.M., Fal'kovich S.G., Kenny J.M. Multiscale computer simulation of polymer nanocomposites based on thermoplastics. *Polymer Science, Series C*, 2016, **58**, P. 2–15.
- [11] Falkovich S.G., Nazarychev V.M., Larin S.V., Kenny J.M., Lyulin S.V. Mechanical properties of a polymer at the interface structurally ordered by graphene. *The Journal of Physical Chemistry C*, 2016, **120** (12), P. 6771–6777.
- [12] Akinwande D., Brennan C.J., Bunch J.S., Egberts P., Felts J.R., Gao H., et al. A review on mechanics and mechanical properties of 2D materials – Graphene and beyond. *Extreme Mechanics Letters. Elsevier Ltd*, 2017, **13**, P. 42–77.
- [13] Saha J.K., Dutta A. A review of graphene: material synthesis from biomass sources, waste and biomass valorization. Springer Netherlands, 2022, **13**, P. 1385–1429.
- [14] Fazil S., Bangesh M., Rehman W., Liaqat K., Saeed S., Sajid M., Waseem M., Shakeel M., Bibi I., Guo C.Y. Mechanical, thermal, and dielectric properties of functionalized graphene oxide/polyimide nanocomposite films. *Nanomaterials and Nanotechnology*, 2019, **9**, P. 1–8.
- [15] Huang T., Xin Y., Li T., Nutt S., Su C., Chen H., Liu P., Lai Z. Modified graphene/polyimide nanocomposites: reinforcing and tribological effects. *ACS applied materials & interfaces*, 2013, **5** (11), P. 4878–4891.
- [16] Li D., Yang W., Chen Y., Xiao C., Wei M. Effect of modified graphene on thermal, mechanical and tribological performance of polyimide based composites. *Materials Research Express*, 2018, **5** (6), 065304.
- [17] Ogbonna V.E., Popoola P.I., Popoola O.M., Adeosun S.O. A review on recent advances on improving polyimide matrix nanocomposites for mechanical, thermal, and tribological applications: Challenges and recommendations for future improvement. *Journal of Thermoplastic Composite Materials*, 2023, **36** (2), P. 836–865.
- [18] Liu P., Yao Z., Zhou J. Mechanical, thermal and dielectric properties of graphene oxide/polyimide resin composite. *High Performance Polymers*, 2016, **28** (9), P. 1033–1042.
- [19] Tayouri M.I., Estaji S., Mousavi S.R., Salkhi Khasraghi S., Jahanmardi R., Nouranian S., Arjmand M., Khonakdar H.A. Degradation of polymer nanocomposites filled with graphene oxide and reduced graphene oxide nanoparticles: A review of current status. *Polymer Degradation and Stability*, 2022, **206**, 110179.
- [20] Voznyakovskii A., Vozniakovskii A., Kidalov S. New way of synthesis of few-layer graphene nanosheets by the self-propagating high-temperature synthesis method from biopolymers. *Nanomaterials*, 2022, **12** (4), 657.
- [21] Neverovskaya A.Y., Voznyakovskii A.P., Krupskaya L.T., Shugalei I.V., Vozniakovskii A.A. Conifer Bark as a Precursor of 2D Graphene Structures: Synthesis and Application. *Russian Journal of General Chemistry*, 2023, **93** (13), P. 3474–3482.
- [22] Voznyakovskii A.P., Karmanov A.P., Neverovskaya A.Y., Vozniakovskii A.A., Kocheva L.S., Kidalov S.V. Biomass of Sosnowsky's hogweed as raw material for obtaining 2d carbonic nanostructures. *Russian Journal of Bioorganic Chemistry*, 2021, **47** (7), P. 1381–1388.
- [23] Merzhanov A.G. The chemistry of self-propagating high-temperature synthesis. *Journal of Materials Chemistry*, 2004, **14** (12), P. 1779–1786.
- [24] Zaaba N.I., Foo K.L., Hashim U., Tan S.J., Liu W.W., Voon C.H. Synthesis of graphene oxide using modified hummers method: solvent influence. *Procedia Engineering*, 2017, **184**, P. 469–477.
- [25] Stone A.J., Wales D.J. Theoretical studies of icosahedral C₆₀ and some related species. *Chemical Physics Letters*, 1986, **128** (5–6), P. 501–503.
- [26] Kuntsman I., Nikolaeva A., Didenko A., Vlasova E., Ivan'kova E., Gofman I., Larin S. The role of carbon nanofillers in the aging processes of polyimide composites. *Journal of Polymer Research*, 2025, **32** (6), 223.
- [27] Nikolaeva A.L., Bugrov A.N., Sokolova M.P., Ivan'kova E.M., Abalov I.V., Vlasova E. N., Gofman I.V. Metal oxide nanoparticles: an effective tool to modify the functional properties of thermally stable polyimide films. *Polymers*, 2022, **14** (13), 2580.
- [28] Voznyakovskii A.P., Neverovskaya A.Y., Gorelova E.V., Zabelina A.N. Facile synthesis of 2D carbon structures as a filler for polymer composites. *Nanosystems: Physics, Chemistry, Mathematics*, 2018, **9** (1), P. 125–128.
- [29] Richardson S., Gorton L. Characterisation of the substituent distribution in starch and cellulose derivatives. *Analytica Chimica Acta*, 2003, **497** (1–2), P. 27–65.
- [30] Li J., Li Y., Wu Y., Zheng M. A comparison of biochars from lignin, cellulose and wood as the sorbent to an aromatic pollutant. *Journal of hazardous materials*, 2014, **280** (15), P. 450–457.
- [31] Podlozhnyuk N., Vozniakovskii A., Kidalov S., Voznyakovskii A. Performance properties of epoxy resin modified with few-layer graphene obtained by the method of self-propagating high-temperature synthesis. *Polymers*, 2025, **17** (6), 812.
- [32] Huang L., Zhang D., Zhang F.H., Feng Z.H., Huang Y.D., Gan Y. High-contrast SEM imaging of supported few-layer graphene for differentiating distinct layers and resolving fine features: there is plenty of room at the bottom. *Small*, 2018, **14** (22), 1704190.
- [33] Kim J., Kim F., Huang J. Seeing graphene-based sheets. *Materials Today*, 2010, **13** (3), P. 28–38.
- [34] Scardaci V., Compagnini G. Raman spectroscopy investigation of graphene oxide reduction by laser scribing. *Journal of Carbon Research*, 2021, **7** (2), 48.
- [35] Johra F.T., Lee J.W., Jung W.G. Facile and safe graphene preparation on solution based platform. *Journal of Industrial and Engineering Chemistry*, 2014, **20** (5), P. 2883–2887.
- [36] Stobinski L., Lesiak B., Malolepszy A., Mazurkiewicz M., Mierzwa B., Zemek J., Jiricek P., Bieloshapka I. Graphene oxide and reduced graphene oxide studied by the XRD, TEM and electron spectroscopy methods. *Journal of Electron Spectroscopy and Related Phenomena*, 2014, **195**, P. 145–154.
- [37] Buhler K-U. *Spezialplaste*. Berlin: Academie. Verlag, 1978, 1015 p.

- [38] Ioni Y.V., Sapkov I.V., Chentsov S.I., Efremova E.I., Gubin S.P. New method for preparation of composite based on montmorillonite and graphene oxide. *Russian Journal of Inorganic Chemistry*, 2023, **68** (4), P. 487–495.
- [39] Gofman I.V., Abalov I.V., Yudin V.E., Tiranov V.G. Mechanical and thermal properties of nanocomposite films based on an aromatic polyimide and carbon nanocones. *Physics of the Solid State*, 2011, **53**, P. 1509–1515.
- [40] Kamalov A., Didenko A., Ivanov A., Kodolova-Chukhontseva V., Terebova N., Ivan'kova E., Popova E., Yudin, V. Effect of the rigidity of polyimide matrices on the electrical conductivity of graphene-containing composites. *Journal of Polymer Research*, 2025, **32** (1), P. 1–13.
- [41] Smirnova V.E., Gofman I.V., Ivan'kova E.M., Didenko A.L., Krestinin A.V., Zvereva G.I., Yudin V.E.. Effect of single-walled carbon nanotubes and carbon nanofibers on the structure and mechanical properties of thermoplastic polyimide matrix films. *Polymer Science Series A*, 2013, **55**, P. 268–278.
- [42] Guadagno L., De Vivo B., Di Bartolomeo A., Lamberti P., Sorrentino A., Tucci V., Vertuccio L., Vittoria V. Effect of functionalization on the thermo-mechanical and electrical behavior of multi-wall carbon nanotube/epoxy composites. *Carbon*, 2011, **49** (6), P. 1919–1930.

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Interfacial stabilization of Nafion membrane with graphene and PTFE: A path to more durable polymer electrolyte membrane water electrolyzers

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ABSTRACT Stability and durability of electrochemical energy conversion systems are significant issues. In this study, two stabilization strategies were investigated: 1) the application of few-layer graphene as a barrier layer on both sides of the Nafion membrane, and 2) the incorporation of polytetrafluoroethylene directly into the catalyst layers. Electrochemical performance was assessed in a two-electrode configuration: potentiostatic aging at 2.5 V and hydrogen crossover measurements. The characterization of materials functioning as barrier layers was conducted using scanning and transmission electron microscopy, laser correlation spectroscopy, and differential thermal analysis. It is shown that both components stabilize Nafion through interfacial interactions, resulting in a longer service life and reduced hydrogen crossover. While the reference sample showed increased crossover, the modified samples exhibited reductions of 50% and 33%. These findings underscore the potential of the studied materials in enhancing the stability of polymer electrolyte membrane water electrolyzers, contributing to the advancement of more durable and efficient systems for hydrogen energy applications.

KEYWORDS graphene; PTFE; stabilized Nafion; membrane-electrode assemblies; water electrolyzer.

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1. Introduction

The development and industrial implementation of electrochemical energy conversion devices with a proton exchange membrane is currently an intensively developing field [1]. Among these devices are water electrolyzers [2–5]. One of the important aspects that determines the competitiveness of a device in the economy is the reliability (stability and long-term operation). Problems related to the durability, stability, and safety of such systems are currently being addressed in many research facilities around the world. These issues have not yet been fully resolved. Norazahar et al. [6] noted that the reliability aspect is critical to ensure safe production of hydrogen as a fuel. Efficient hydrogen production depends on the reliability of electrolyzers. Polymer electrolyte membrane water electrolyzer (PEMWE) is one of the most promising technologies for hydrogen production. However, properties such as hydrogen solubility, diffusion coefficient, and the partial pressure differential between flow channels may influence the reliability and safety of the system. Operating conditions may also lead to safety issues within the PEMWE due to membrane degradation or thinning. The damaged membrane initiates the migration of hydrogen into the anode space and may lead to an explosion. Hydrogen crossover through even an undamaged membrane also plays a significant role in the performance of the electrolyzer, as it reduces its efficiency. Shirvanian et al. [7] highlighted that degradation is a significant issue in the use of PEMWEs. Research and development of new components are likely to result in outcomes in the long-term perspective. In the short term, it is crucial to be able to produce high-performance, cost-effective PEMWE systems with a long service life based on existing technologies. In the referenced article, the authors investigate the impact of operating conditions on the longevity of the electrolyzer. They conclude that one of the most effective approaches for ensuring extended and safe operation is to maintain “soft” operating conditions, including low temperatures and pressures, low overpotentials, and current densities. Moreover, it is noted that dispersing the Ir catalyst on stable support materials (such as carbides or nitrides of transition metals) may enhance the catalyst’s durability.

One of the key factors affecting the long-term performance of a PEMWE is the degradation of the proton exchange material (membrane and ionomer in the electrode layer) [7–9]. Papakonstantinou et al. [10] pointed out the excellent stability of the anodes in modern electrolyzers, as well as the instability of the proton exchange membrane, which constrains the device's service life. For proton exchange membrane fuel cells (PEMFCs) extensive research has been conducted, resulting in various types of hybrid composite membranes based on Nafion®, such as Nafion®/inorganic fillers, Nafion®/ionic liquid, and other modified Nafion® membranes [11]. Despite some achievements, the search for new compositions to increase the longevity and performance of membranes continues, as evidenced by the emergence of new publications on this topic.

To address ionomer degradation, the most commonly used stabilization approaches are reinforcement and filling of the membranes:

1. reinforcement refers to the creation of a coating or matrix that enhances mechanical stability [12–14];
2. filling refers to the introduction of inorganic additives that improve chemical stability [15–17].

Jaio et al. [14] used polytetrafluoroethylene (PTFE) as a reinforcing material. The PTFE-Nafion membrane features low cost, high mechanical strength, and minimal swelling.

The use of fillers to create composite (filled) membranes has proven to be an effective way to enhance water loss resistance and thermal stability [16]. Ibrahim et al. [16] presented the key approaches to modifying ion-exchange materials, primarily focusing on the creation of hybrid membranes containing nanoparticles of inorganic materials. They highlighted that the main factor contributing to the enhanced conductivity and selectivity of hybrid membranes is the change in pore and channel structures and the distribution of carrier concentrations.

When creating stabilized composites based on perfluorinated polymers with sulfonic groups (Nafion – an ionomer with long side chains in the molecule, Aquivion – an ionomer with short side chains, and related ionomers), materials containing few-layer graphene (G) as a stabilizer have proven to be effective [18–20]. As shown in these works, stabilization of the ionomer occurs due to the formation of surface compounds of the polymer on G.

Graphene and graphene-based materials are of significant interest due to their unique structure and properties. These materials possess a two-dimensional structure and can exist in various forms, differing in both the number of layers and the presence of surface functional groups, which can be precisely controlled, for instance, during electrochemical synthesis [21,22]. For example, reference [22] presents comparative results for producing graphene with tailored characteristics using various methods, including ultrasonic dispersion at different power levels and electrochemical exfoliation under various conditions. The study reports the feasibility of synthesizing few-layer (1-3 layers) graphene with a tunable oxygen content, dependent on the processing parameters. Graphene materials are unique substances with an easily tunable pseudo-2D structure and modifiable surface functional group composition. This tunability offers significant flexibility for designing composite membranes. Furthermore, graphene exhibits selective permeability: it is permeable to protons while being impermeable to most other substances, including gases, fuels, and oxidizers. Its incorporation into membranes significantly reduces reactant crossover. In [23], the effect of incorporating various forms of carbon nanomaterials as additives into Nafion membranes on the performance of direct methanol fuel cells (DMFCs) was investigated. The study demonstrated that carbon nanomaterials substantially influence the development of polymer electrolytes for DMFCs. The performance of the composite membrane electrolyte depends on the choice of carbon nanomaterial, such as two-dimensional graphene oxide (GO), one-dimensional carbon nanotubes (CNTs) or carbon nanofibers (CNFs/GNFs), and fullerenes. The structural orientation and composition of these carbon materials within the polymer matrix significantly affect the membrane's properties. Surface functionalization of these nanomaterials imparts hydrophilicity, fine-tunes the composite's conductivity, and enhances interfacial adhesion with the polymer matrices. For Nafion® membranes, GO has been identified as a particularly suitable nanofiller, especially where reducing methanol permeability is critical; the planar sheet structure of graphene-based materials is more effective than the tubular structure of CNTs in mitigating fuel crossover.

It is important to note that most published studies focus on the stability of the membranes, while little attention has been paid to the stability of the ionomer distributed in the electrode layer. To a certain extent, this can be viewed as a serious gap in addressing the issue of electrochemical system stability, since even with a stable membrane, the electrodes must also be functional.

The aim of this work was to investigate and compare the efficiency of two distinct approaches to stabilize the MEA: i) applying a barrier layer of few-layer graphene directly onto the Nafion membrane, and ii) incorporating PTFE as a stabilizer within the catalyst layers to reinforce the Nafion ionomer. The primary object of the study is the membrane-electrode assembly (MEA) as a whole, with a focus on mitigating hydrogen crossover and improving durability. A key outcome of this study is the demonstration that the graphene barrier layer provides superior mitigation of hydrogen crossover, halving it after aging, thereby offering a more promising path to durable PEM electrolyzers.

2. Experimental Section

2.1. MEA Fabrication

Platinized carbon black (Pt/C) was used as both a cathode and an anode catalyst. The selection of platinum over iridium for the anode was made to speed up the degradation process of the electrolyzer and to carry out real-time operation tests, as opposed to using accelerated stress tests (AST).

A 2% aqueous solution of Nafion, prepared by diluting a 10% stock solution of Nafion DE1021 (DuPontTM, Wilmington, DE, USA), was used. An aqueous dispersion of PTFE (OJSC “Plastpolymer”, St. Petersburg, Russia) with a spherical particle size of 250–400 nm was used. Thermally expanded graphite (TEG) was used as a precursor for G fabrication. TEG was obtained from NPO “Graphene Materials” LLC, St. Petersburg, Russia. The technology of synthesis is described in [24]. Commercial platinized carbon black (40% Pt) from E-TEK was used as the electrocatalyst. Isopropanol (99.80%, ECOS-1 JSC), and deionized water with resistivity at room temperature $\rho \geq 18 \text{ MOhm} \times \text{cm}$ were used. A solution of H_2O_2 , grade 8–4 (Lega LLC, Dzerzhinsk, Russia) was used.

To study the physicochemical properties and fabricate membrane-electrode assemblies (MEAs), component dispersions were initially prepared in an isopropanol-water medium with a 1:1 volume ratio. The samples were prepared by mixing accurately weighed components and then subjected to ultrasonic treatment for 40 hours in a Branson 3510 ultrasonic bath (Branson Ultrasonics Corporation, Danbury, CT, USA).

MEAs were prepared by depositing a homogeneous dispersion of components directly on a PEM through a stainless-steel mask. The catalyst inks for the electrodes were applied by hand brushing directly onto the membrane (or onto the graphene barrier layer for the MEA G-layer). Prior to the deposition of the electrode material, the membrane was treated in 3% H_2O_2 solution for 10 min at a temperature of 70–80°C, followed by immersion in 0.5 M sulfuric acid for 15 min at a temperature of 70–80°C, and then was washed five times with deionized water. The electrodes were prepared by depositing of prepared composite dispersions containing Pt on a PEM of Nafion 212 type, MF-4SK (OJSC “Plastpolymer”, St. Petersburg, Russia), of thickness 50 μm . The membrane was thermostated at 85°C on an Ika C-MAGPH 7 wafer (IKA-Werke GmbH & Co. KG, Staufen, Germany) with a heat controller. The amount of the deposited material was monitored gravimetrically.

Three types of MEAs were fabricated: a standard MEA (reference), a MEA with a G barrier layer, and a MEA with a PTFE barrier layer (Table 1).

TABLE 1. Composition of samples used for the study

Type of sample	Composition, wt%			MEA Cathode/Anode Pt loading, mg/cm^2	Barrier layer
	Nafion	Pt/C (40% Pt)	PTFE		
Reference MEA	20	80	–	0.23/ 0.20	–
MEA PTFE-layer	20	60	20	0.29/ 0.31	+
MEA G-layer	20	80	–	0.23/ 0.27	+

G barrier layers were first deposited on both sides of the membrane via airbrushing, with a layer thickness of ~ 0.5 – $1 \mu\text{m}$. Subsequently, the catalyst layers were applied. The barrier ink was formulated by dispersing thermally expanded graphite (TEG) in a 2% Nafion solution using an isopropanol/water (1:1 vol) medium. The total loading of the dry barrier layer was $0.01 \text{ mg}/\text{cm}^2$, corresponding to a graphene (TEG) loading of $0.008 \text{ mg}/\text{cm}^2$ and a Nafion loading of $0.002 \text{ mg}/\text{cm}^2$. The PTFE barrier layers were applied to both sides of the membrane by spreading a dispersion (Pt/C-Nafion-PTFE). Following the assembly, all MEAs underwent a final conditioning step to activate proton conductivity by boiling in 0.5 M H_2SO_4 for 1 hour, followed by thorough rinsing with deionized water.

2.2. Microscopic Studies

Target-oriented approach was utilized for the optimization of the analytic measurements [25]. Before measurements the samples were mounted on a 3 mm copper grid and fixed in a grid holder. Samples morphology was studied using Hitachi SU8000 (Hitachi High-Tech Corp., Tokyo, Japan) field-emission scanning electron microscope (SEM). Images were acquired in bright-field STEM mode at 30 kV accelerating voltage.

2.3. Energy-Dispersive X-ray Spectroscopy

EDX measurements were carried out using the FEI Quanta 200 scanning electron microscope (FEI Company, Hillsboro, OR, USA).

2.4. Study of particle size using laser correlation spectroscopy

The particle study was conducted using a Zetasizer Nano ZS analyzer (Malvern Panalytical, Malvern, United Kingdom) at a temperature of 25°C. The dispersion medium was a mixture of isopropanol and water in a 1:1 volume ratio. The following parameters of the dispersion medium and material were used:

- Refractive index of the dispersion medium: 1.359;
- Refractive index of the material (Nafion): 1.35;
- Viscosity of the dispersion medium: 2.5966 mPa·s;
- Absorption coefficient of the material (Nafion): 0.

A He–Ne laser with a wavelength of 632.8 nm was used as the light source. The Smoluchowski equation was applied to calculate the zeta potential.

2.5. Differential thermal studies

The study of thermal degradation was carried out on a derivatograph of Mettler Toledo TGA/DSC 1 type with the software STARe System (Mettler-Toledo LLC, Columbus, OH, USA) with blowing air through the derivatograph chamber at a rate of 30 cm³/min in the mode of uniform temperature rise at a rate of 10 K/min in the temperature range $T = 35\text{--}1000^\circ\text{C}$. A sample of material weighing a few mg was placed in an alund crucible, and mass and thermal curves were recorded during heating. Dispersions for the study were evaporated, poured onto a glass substrate and dried at a.c. to air-dry (~40–50% relative humidity), and then the dry residue was removed with a metal (stainless steel) spatula.

2.6. Electrochemical study

The electrochemical characteristics of the MEAs were studied in two modes: fuel cell mode and electrolyzer mode, implemented in a two-electrode configuration. The MEAs were placed in Heliocentris cells (Heliocentris Academia International GmbH, Berlin, Germany). Measurements were performed using an Elins P-40X potentiostat (Elins LLC, Chernogolovka, Russia).

Hydrogen crossover was measured by linear sweep voltammetry following a previously described method [26]. N₂/H₂ were passed through the electrodes. The working electrode was scanned at a rate of 4 mV/s from 0 V to 0.8 V. Experiments were conducted at room temperature and atmospheric pressure. Measurements were taken before and after aging.

MEA aging was carried out in electrolyzer mode applying a constant voltage of 2.5 V for 145 h. The MEA was placed in an electrolyzer cell, filled with water, and the required voltage was applied via the potentiostat. The experiments were performed at room temperature and atmospheric pressure.

3. Results and Discussion

Fig. 1 shows micrographs of the composite system: G-Nafion-Pt/C. The figure demonstrates that platinized carbon black is positioned on the surface of G sheets. The TEM image shows black dots corresponding to platinum nanoparticles distributed on the surface of carbon black (lighter spherical particles). In the TEM image, the G sheet exhibits increased transparency, which corresponds to its thin structure. The G edges are distinguishable in the images, appearing as bright stripes in the SEM image and darker stripes in the TEM image. An approximate evaluation of the thickness of the bright edges marked by yellow arrows, corresponding to the edges of graphene sheets, indicates a size of less than 10 nm. Fig. 1(d) shows a homogeneous structure, uniform over hundreds of nanometers, composed of evenly distributed spherical and semi-spherical features. No graphene sheets are present. The feature size is primarily in the ~100–300 nm range, characteristic of PTFE. Smaller features (<100 nm) are attributed to spherical platinum/carbon black particles.

3.1. Particle size analysis

Fig. 2 illustrates the particle size distributions for dispersions of different systems containing the Nafion ionomer, PTFE, and few-layer G as the dispersed phase. The PTFE-Nafion system demonstrates relatively narrow distributions with a single peak, whereas the G-Nafion sample exhibits a polydisperse nature with multiple peaks over a broad size range, which may be associated with the polydispersity of few-layer G.

In the case of pristine Nafion sample (6.7 g/L), the particle size distribution spans approximately 0.4–1.8 nm for both volume and number distributions, with maxima at 0.8 nm (v) and 0.7 nm (n). A zeta potential of -39 ± 3 mV was recorded, reflecting the good stability of the dispersion. For pristine PTFE (6.7 g/L), the particle size distribution is broader, ranging from approximately 100 to 1000 nm in both volume-based and number-based measurements, with peaks at 342 nm (v) and 106 nm (n). The zeta potential of -6.4 ± 0.5 mV was measured, which is significantly lower than 30 mV in absolute value, indicating low dispersion stability. In the case of the PTFE-Nafion sample, with a concentration of 6.7 g/L for each component, the particle size range was found to be similar to that of pristine PTFE (~100–1000 nm). The maximum for the volume distribution of the PTFE-Nafion sample coincides with the maximum for pure PTFE (342 nm). The peak of the number-based distribution is displaced towards larger sizes, with a value of 142 nm. It should be noted that particles around 1 nm, typical for pristine Nafion in the ~0.4–1.8 nm range, are not present in the PTFE-Nafion

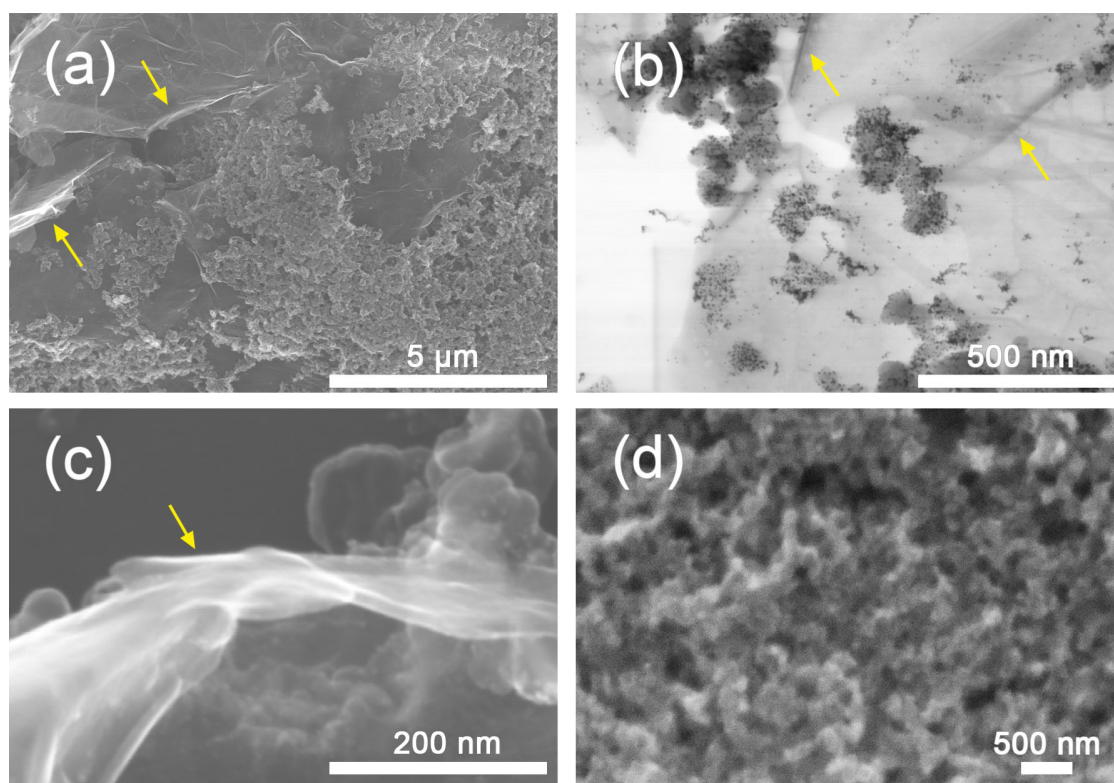


FIG. 1. Microstructure of the composite electrode materials: (a [18], c) SEM and (b) STEM images of the G-Nafion-Pt/C; (d) SEM image of the PTFE-Nafion-Pt/C

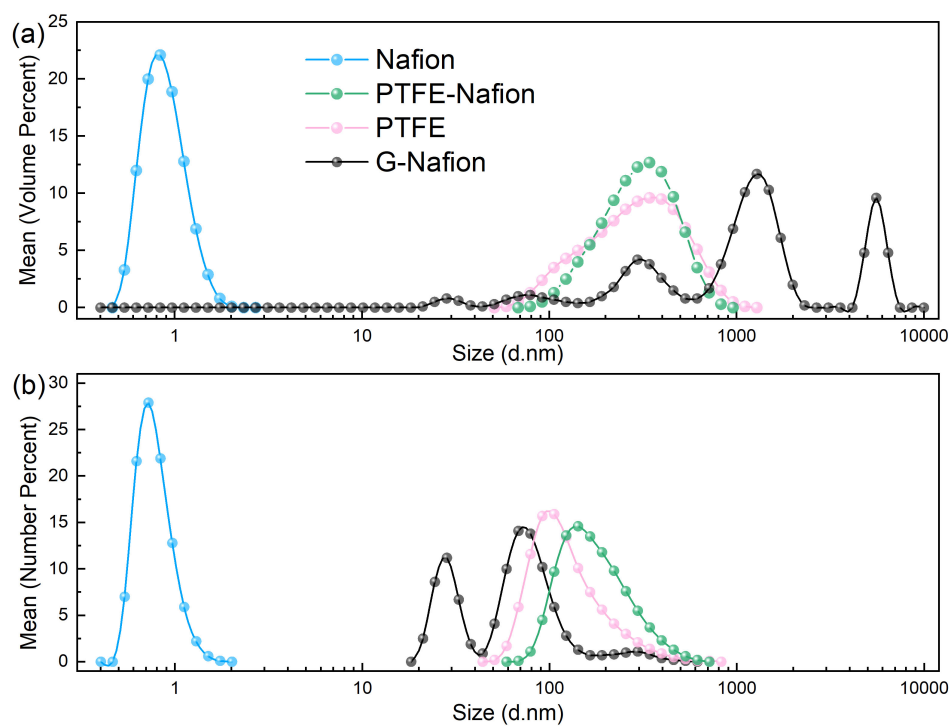


FIG. 2. Volume (a) and number (b) particle size distributions in an isopropanol-water medium with a 1:1 volume ratio for different dispersions: Nafion, PTFE, PTFE-Nafion, G-Nafion

sample. Additionally, the peak of the number-based particle size distribution shifts toward larger sizes compared to pristine PTFE. The shift in the peak of the number-based particle size distribution toward larger sizes compared to pristine PTFE, combined with the absence of ~ 1 nm Nafion particles, indicates the formation of a Nafion polymer coating on PTFE particles. For the G-Nafion dispersion with concentrations of 0.33 g/L (G) and 0.083 g/L (Nafion), multiple peaks are observed in the size ranges of approximately ~ 20 to ~ 7500 nm for the volume-based distribution and ~ 20 to ~ 600 nm for the number-based distribution. Particles in the ~ 1 nm range, which are characteristic of Nafion, are not present. It indicates that Nafion polymer adsorbs onto the G surface. The dispersion includes few-layer G particles with submicron sizes: 28, 68, and 295 nm. The volume-based distribution shows two maxima at approximately ~ 1300 and ~ 5600 nm. These larger particles are likely associated with the undispersed fraction of TEG. Nafion is located on the surface of G. The zeta potential of the particles is -76 ± 14 mV, which indicates excellent stability of the dispersion.

Thus, the particle size analysis of the binary dispersion systems revealed that Nafion is structurally associated with the second component and is located on the surface of its larger particles. The resulting dispersions exhibit a high zeta potential, greater than 30 mV, indicating their high stability.

3.2. Differential thermal studies

Fig. 3 shows a comparison of the derivatograms of the studied materials for the water electrolyzer: pristine Nafion, PTFE, and their composites. The thermal oxidative decomposition of pristine Nafion occurs in the temperature range of 260 – 504°C with several rate maxima. The lowest temperature maximum of the destruction rate associated with desulfurization of the molecule [27], is observed at 344°C . In the case of the G-Nafion composite, thermal decomposition initiates at higher temperatures, specifically within the 360 – 470°C range, with a single rate maximum occurring at 422°C . These results indicate the stabilization of the Nafion polymer and a change in its decomposition mechanism, aligning with previously reported data [18]. Higher temperature peaks in the mass loss rate are associated with G oxidation [18].

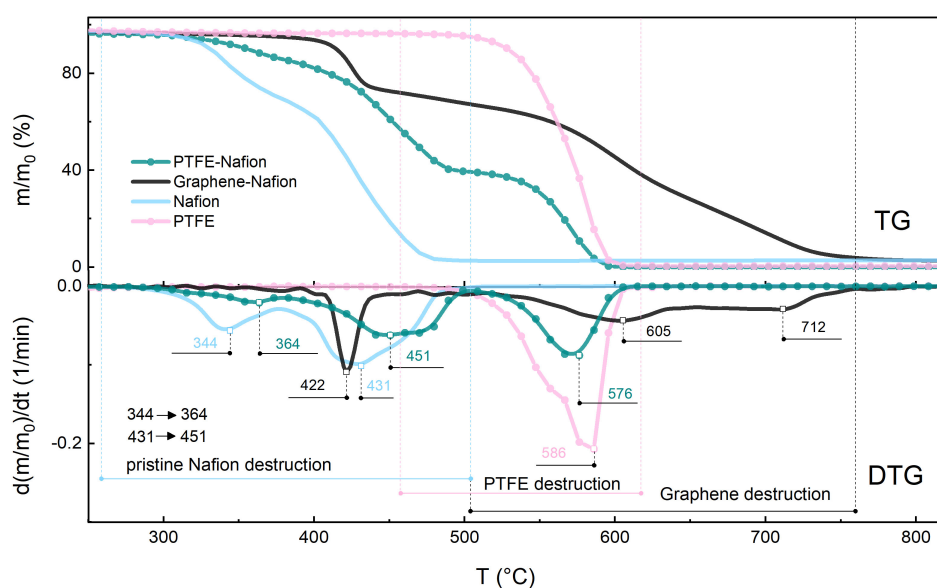


FIG. 3. Derivatograms of the electrode materials used in the electrolyzer. The heating rate is 10 K/min. TG – thermogravimetric curve, DTG – differential thermogravimetric curve

The thermal oxidative destruction of pristine PTFE occurs in a single stage within the temperature range of 457 – 617°C , with a maximum rate observed at 586°C . In the PTFE-Nafion composite, similar patterns are observed. However, Nafion in the composite undergoes decomposition differently than the pristine polymer: the onset of decomposition is shifted by 20°C toward a higher temperature region compared to pristine Nafion. The completion of Nafion decomposition coincides with the initiation of PTFE decomposition ($\sim 504^\circ\text{C}$). The maintained peak structure on the DTG curve for the PTFE-Nafion system suggests that the thermal decomposition mechanism of Nafion remains unchanged in the composite. The temperature shift toward higher values confirms the stabilization of Nafion through weak (adsorptive) interactions with the PTFE surface. These findings align with the particle size measurements.

Thus, the analysis of the derivatograms indicates that there is a strong interfacial interaction between the Nafion ionomer and G, with a weaker interaction observed between Nafion and PTFE. Nafion stabilizes on the surfaces of the materials, G and PTFE, which is consistent with the particle size analysis for these systems.

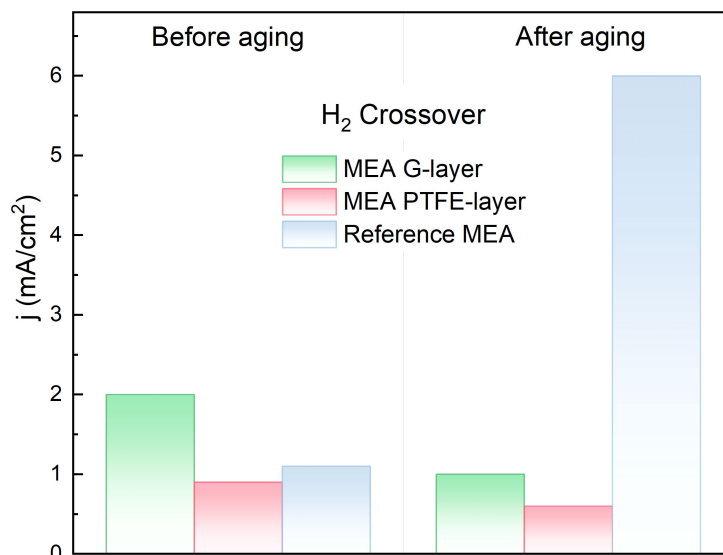


FIG. 4. H_2 crossover current density before and after aging of different samples

3.3. Investigation of Hydrogen Crossover Through the Membrane

Fig. 4 illustrates the hydrogen crossover current density before and after aging for three MEAs with varying electrode compositions: reference (Nafion-Pt/C), with PTFE as a stabilizer, and with a G barrier layer.

As shown in Fig. 4, the hydrogen crossover current density after aging was reduced by 50% (MEA G-layer) and 33% (MEA PTFE-layer) in the modified samples, indicating a substantial improvement in membrane performance. In contrast, the hydrogen crossover of the reference sample increased by approximately 5.5 times after aging.

It can be assumed that the mechanism for the reduction in hydrogen crossover during aging is related to structural changes in the near-surface layer of the membrane, which occur as a result of the aging process. This applies to both the graphene- and PTFE-modified samples, since in both cases, there is a strong interfacial interaction between Nafion and the additive. A similar effect is described in the scientific literature.

As shown in [28], the incorporation of graphene oxide (GO) into a Nafion membrane reduces acetone and hydrogen crossover in an acetone electrochemical hydrogenation cell. Impedance analysis confirmed the rearrangement of GO flakes during cell operation, reflected by a decrease in high-frequency resistance (HFR) and the interfacial resistance of the blocking interlayer after a continuous 15-hour electrochemical testing protocol. This observation is supported by transmission electron microscopy, which reveals structural changes within the GO interlayer.

Furthermore, in reference [29], rheological analysis of sulfonated graphene oxide (SGO) dispersions in a Nafion solution demonstrated a sharp increase in viscosity, peaking at an SGO content of 0.5%. The authors note that this indicates a strong interaction between the components at this specific ratio. As the SGO content increases further, particle agglomeration occurs, and the viscosity drops. The authors explain SGO's effect on crossover by two mechanisms: the steric factor of graphene particles and the formation of denser (and less permeable) ionomer structures in the presence of graphene compared to pure Nafion (see rheology data).

In our case, the reduction in hydrogen crossover during aging for MEAs with barrier layers can be explained by a structural reorganization of the membrane's near-surface layer adjacent to the graphene or PTFE. This likely involves partial penetration of the modifiers into this layer due to migration in the electric field and a resulting densification of the structure.

Thus, G and PTFE layers on Nafion membranes exhibit a barrier effect against undesirable fuel crossover, which is attributed to the interfacial interactions between the Nafion ionomer and the stabilizing materials. In the case of G, the interaction is realized through strong surface adsorption of the polymer chains, likely involving π - π stacking and van der Waals forces, leading to denser chain packing and increased thermal stability. For PTFE, the interfacial interaction is of a weaker, adsorptive nature, which nonetheless results in the formation of a polymer shell around PTFE particles, thereby reducing ionomer mobility and swelling. These interactions suppress hydrogen crossover and contribute to improved mechanical and chemical stability of the membrane-electrode assembly.

3.4. Polarization curves

Fig. 5 demonstrates the dynamics of polarization curves during the aging process. The pattern of change in the dependencies during the aging process of the reference sample differs from that of the modified MEAs. For the PTFE- and G-modified MEAs, an improvement in performance is observed at the beginning of operation, with an increase in current density. The improvement is attributed to the activation processes of the MEA, which involve the desorption of

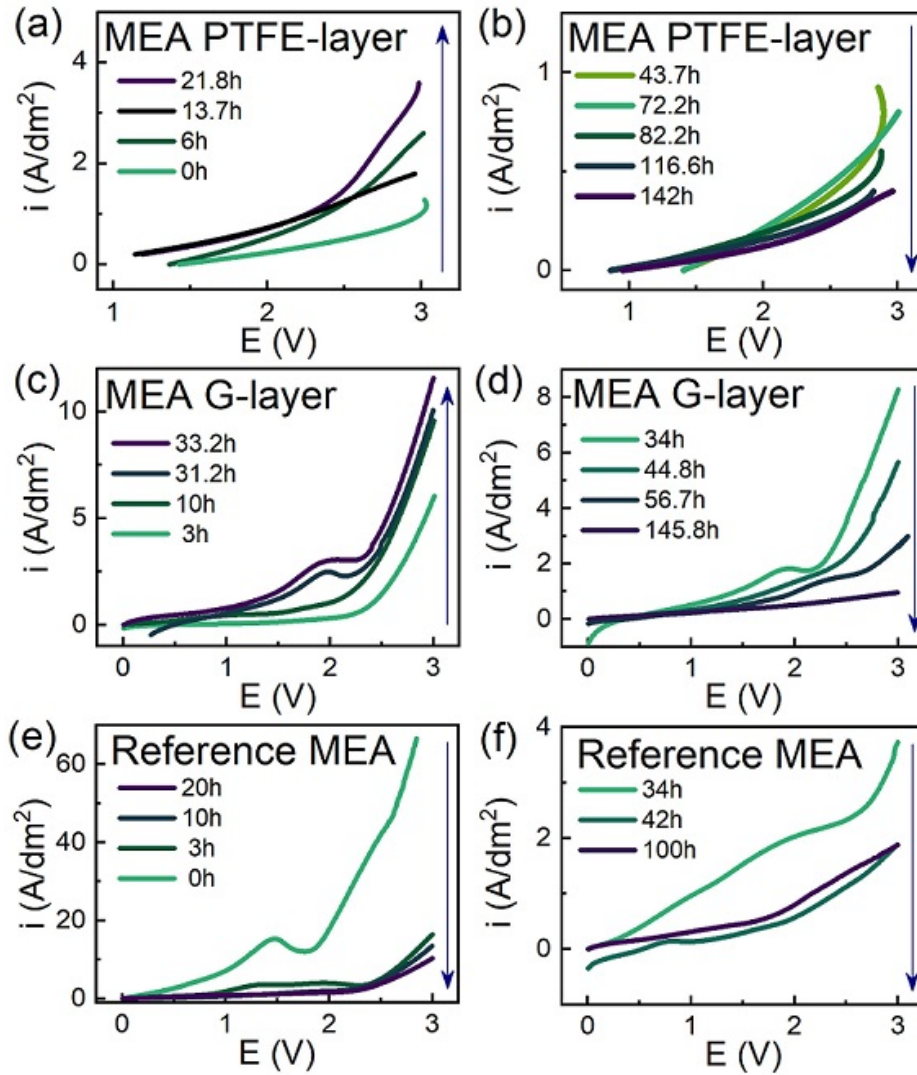


FIG. 5. Dynamics of polarization curves in electrolyzer mode during the aging of MEAs of various compositions under potentiostatic conditions at 2.5 V: PTFE-stabilized sample, performance improvement (a) and degradation (b) periods; G-stabilized sample, performance improvement (c) and degradation (d) periods; standard composition sample at the early stage of degradation (e) and at the end of operation (f); $t = 25^\circ\text{C}$, atmospheric pressure

impurities from the platinum surface, the hydration of the electrode layers and membrane, and the formation of charge and mass transfer channels [30] (Fig. 5a,c). Subsequently, deterioration of characteristics occurs (Fig. 5b,d), associated with degradation processes. In the case of the reference sample, high specific values are observed initially, followed by a sharp decline in performance (Fig. 5e), which then continues to decrease monotonically (Fig. 5f).

4. Conclusion

The stabilization of the proton-conducting polymer Nafion on the surfaces of nanostructured materials, such as few-layer G and PTFE, occurs through interfacial interactions between the G-Nafion and PTFE-Nafion components.

The G-Nafion system, achieved through ultrasonic dispersion of TEG, exhibits polydispersity, containing few-layer G particles with sizes in the submicron region (28, 68, 295 nm) and a small number of large TEG particles (around 1300 and 5600 nm) that remain undispersed. Nafion is positioned on the surface of G.

The PTFE-Nafion system is relatively monodisperse, and the Nafion polymer forms a coating on the surface of the PTFE particles.

The analysis of particle sizes in binary dispersions showed that Nafion is structurally integrated with the second component, positioning itself on the surface of the larger particles. The dispersions obtained exhibit a high zeta potential, greater than 30 mV, indicating their high stability.

Thermal analysis demonstrated the presence of interfacial interactions of different strengths between the components: a strong interaction between the Nafion ionomer and G, and a weaker one between Nafion and PTFE. Nafion stabilizes on the surfaces of these materials.

The modified MEAs show lower hydrogen crossover through the membrane in comparison with the standard sample after 145 h of aging at a constant voltage. The principal finding is that the application of a few-layer graphene barrier layer on the membrane surface is a more effective strategy than the incorporation of PTFE into the catalyst layers. This conclusion is quantitatively supported by the post-aging hydrogen crossover measurements, which showed a twofold reduction for the graphene-modified MEA compared to a 1.5-fold reduction for the PTFE-modified MEA.

References

- [1] de Sá M.H. Electrochemical Devices to Power a Sustainable Energy Transition—An Overview of Green Hydrogen Contribution. *Applied Sciences*, 2024, **14**(5), P. 2168.
- [2] Wang T., Cao X., Jiao L. PEM water electrolysis for hydrogen production: fundamentals, advances, and prospects. *Carbon Neutrality*, 2022, **1**(1), P. 21.
- [3] Shiva Kumar S., Himabindu V. Hydrogen production by PEM water electrolysis – A review. *Materials Science for Energy Technologies*, 2019, **2**(3), P. 442–454.
- [4] Thomassen M.S., Reksten A.H., Barnett A.O., Khoza T., Ayers K. PEM water electrolysis. In: *Electrochemical Power Sources: Fundamentals, Systems, and Applications*, Elsevier, 2022, P. 199–228.
- [5] Salehmin M.N.I., Husaini T., Goh J., Sulong A.B. High-pressure PEM water electrolyser: A review on challenges and mitigation strategies towards green and low-cost hydrogen production. *Energy Conversion and Management*, 2022, **268**, P. 115985.
- [6] Norazahar N., Khan F., Rahmani N., Ahmad A. Degradation modelling and reliability analysis of PEM electrolyzer. *International Journal of Hydrogen Energy*, 2024, **50**, P. 842–856.
- [7] Shirvanian P., van Berkel F. Novel components in Proton Exchange Membrane (PEM) Water Electrolyzers (PEMWE): Status, challenges and future needs. A mini review. *Electrochemistry Communications*, 2020, **114**, P. 106704.
- [8] Kuhnert E., Mayer K., Heidinger M., Rienessell C., Hacker V., Bodner M. Impact of intermittent operation on photovoltaic-PEM electrolyzer systems: A degradation study based on accelerated stress testing. *International Journal of Hydrogen Energy*, 2024, **55**, P. 683–695.
- [9] Phan T.T., Kim S.K., Islam J., Kim M.J., Lee J.H. Degradation analysis of polymer electrolyte membrane water electrolyzer with different membrane thicknesses. *International Journal of Hydrogen Energy*, 2024, **49**, P. 875–885.
- [10] Papakonstantinou G., Algara-Siller G., Teschner D., Vidaković-Koch T., Schlögl R., Sundmacher K. Degradation study of a proton exchange membrane water electrolyzer under dynamic operation conditions. *Applied Energy*, 2020, **280**, P. 115911.
- [11] Prykhodko Y., Fatyeyeva K., Hespel L., Marais S. Progress in hybrid composite Nafion®-based membranes for proton exchange fuel cell application. *Chemical Engineering Journal*, 2021, **409**, P. 127329.
- [12] Shi S., Weber A.Z., Kusoglu A. Structure/property relationship of Nafion XL composite membranes. *Journal of Membrane Science*, 2016, **516**, P. 123–134.
- [13] Shin S.H., Nur P.J., Kodir A., et al. Improving the Mechanical Durability of Short-Side-Chain Perfluorinated Polymer Electrolyte Membranes by Annealing and Physical Reinforcement. *ACS Omega*, 2019, **4**(21), P. 19153–19163.
- [14] Jao T.C., Jung G.B., Kuo S.C., Tzeng W.J., Su A. Degradation mechanism study of PTFE/Nafion membrane in MEA utilizing an accelerated degradation technique. *International Journal of Hydrogen Energy*, 2012, **37**(18), P. 13623–13630.
- [15] Agarwal T., Sievert A.C., Komini Babu S. Enhancing durability of polymer electrolyte membrane using cation size selective agents. *Journal of Power Sources*, 2023, **580**, P. 233362.
- [16] Ibrahim A., Hossain O., Chaggar J., Steinberger-Wilckens R., El-Kharouf A. GO-nafion composite membrane development for enabling intermediate temperature operation of polymer electrolyte fuel cell. *International Journal of Hydrogen Energy*, 2020, **45**(8), P. 5526–5534.
- [17] Teixeira F.C., Teixeira A.P.S., Rangel C.M. Chemical stability of new nafion membranes doped with bisphosphonic acids under Fenton oxidative conditions. *International Journal of Hydrogen Energy*, 2023, **48**(96), P. 37489–37499.
- [18] Krasnova A.O., Glebova N.V., Kastsova A.G., Rabchinskii M.K., Nechitailov A.A. Thermal Stabilization of Nafion with Nanocarbon Materials. *Polymers*, 2023, **15**(9), P. 2070.
- [19] Glebova N.V., Mazur A.S., Krasnova A.O., Pleshakov I.V., Nechitailov A.A. Investigation of stability of composite Nafion/nanocarbon material. *Nanosystems: Physics, Chemistry, Mathematics*, 2023, **14**(2), P. 202–207.
- [20] Primachenko O.N., Kulvelis Y.V., Odinkov A.S. New Generation of Compositional Aquivion®-Type Membranes with Nanodiamonds for Hydrogen Fuel Cells: Design and Performance. *Membranes*, 2022, **12**(9), P. 827.
- [21] Kastsova A.G., Krasnova A.O., Glebova N.V., Pelageikina A.O., Nechitailov A.A. Long-term durability of membrane electrode assemblies of proton exchange fuel cells: challenges and solutions. *Russian Chemical Reviews*, 2025, **94**, RCR5135.
- [22] Krasnova A.O., Glebova N.V., Nechitailov A.A., Kastsova A.G., Pelageikina A.O., Kirilenko D.A., Shvidchenko A.V., Shestakov M.S., Koroleva A.V., Khrapova E.K. Comparative Study of Graphite Exfoliation Techniques Using Nafion as a Surfactant. *C-Journal of Carbon Research*, 2025, **11**, P. 76.
- [23] Rambabu G., Bhat S.D., Figueiredo F.M.L. Carbon Nanocomposite Membrane Electrolytes for Direct Methanol Fuel Cells—A Concise Review. *Nanomaterials*, 2019, **9**, P. 1292.
- [24] Method of Producing Porous Carbon Material Based on Highly Disintegrated Graphite, Patent Patent 2014116365/05 Russia: IPC C01B 31/04, Mazin V.I., N 2581382, Bull. N 11, 2016, p. 9.
- [25] Kachala V.V., Khemchyan L.L., Kashin A.S. Target-oriented analysis of gaseous, liquid and solid chemical systems by mass spectrometry, nuclear magnetic resonance spectroscopy and electron microscopy. *Russian Chemical Reviews*, 2013, **82**(7), P. 648–685.
- [26] Tang Q., Li B., Yang D., Ming P., Zhang C., Wang Y. Review of hydrogen crossover through the polymer electrolyte membrane. *International Journal of Hydrogen Energy*, 2021, **46**, P. 22040–22061.
- [27] Lage L.G., Delgado P.G., Kawano Y. Thermal stability and decomposition of nafion® membranes with different cations. *Journal of Thermal Analysis and Calorimetry*, 2004, **75**(2), P. 521–530.
- [28] Komma M., Marth A., Maier M., Hutzler A., Böhm T., Thiele S. Applicability of Graphene Oxide Interlayers in PEMs for Reducing Crossover in Electrochemical Acetone Hydrogenation Reactors. *Journal of The Electrochemical Society*, 2024, **171**, P. 104502.
- [29] Chien H.-C., Tsai L.-D., Huang C.-P., Kang C., Lin J.-N., Chang F.-C. Sulfonated graphene oxide/Nafion composite membranes for high-performance direct methanol fuel cells. *International Journal of Hydrogen Energy*, 2013, **38**, P. 13792–13801.

- [30] Taghiabadi M.M., Zhiani M., Silva V. Effect of MEA activation method on the long-term performance of PEM fuel cell. *Applied Energy*, 2019, **242**, P. 602–611.

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Paper abstracts in Russian / Аннотации статей

Фазовый переход и термодинамические свойства модели Поттса с жестким ядром

Хакимов Р.М., Махаммадалиев М.Т., Муталлиев Н.Н.

Мы исследуем трансляционно-инвариантные меры Гиббса модели Поттса с жестким ядром (НС–Potts) на дереве Кэли. Модель сочетает ферромагнитные взаимодействия типа Поттса с правилом исключения жесткого ядра, что приводит к нетривиальному взаимодействию между магнитным упорядочением и ограничениями на заселенность. Для фертильного графа шарнирного типа мы анализируем случаи $k = 2$ и $k = 3$ и определяем явные критические значения β_c , которые отмечают переход от единственности к множественности мер Гиббса. Модель демонстрирует до пяти трансляционно-инвариантных фаз в зависимости от силы взаимодействия. Вычисляются термодинамические величины, такие как намагниченность и квадрупольный момент, выявляющие упорядоченные фазы при низких температурах и парамагнитную фазу при высоких температурах..

Ключевые слова: распределение Гиббса, модель Поттса, модель Hard-Core, фазовый переход, дерево Кэли.

Единственность идеальных звездных упаковок и существование псевдосоответствий в графах фуллеренов (2,6)

Тахери-Дехкорди М.

Идеальная звездная упаковка может быть описана как остовный подграф, связные компоненты которого изоморфны звездному графу $K_{1;3}$. Идеальное псевдосоответствие — это остовный подграф, в котором каждая компонента изоморфна либо K_2 , либо $K_{1;3}$. Изучение задач упаковки на графах фуллеренов представляет особый интерес из-за их потенциальной значимости в описании локальных связей в углеродных наноструктурах. В данной работе мы изучаем уникальность идеальной звездной упаковки и существование псевдосоответствий в графах фуллеренов (2;6). Более того, мы показываем, что идеальная звездная упаковка в этих графах уникальна. Кроме того, мы ввели некоторые идеальные псевдосоответствия в графах фуллеренов (2;6).

Ключевые слова: графы фуллеренов (2;6); идеальная звездная упаковка; идеальное псевдосоответствие

Теоретический анализ влияния чирпированных импульсов на формирование плазмы в струе воды

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В работе представлен теоретический анализ влияния линейного чирпа лазерного импульса на плотность плазмы в струе воды в рамках двухэтапной модели. На первом этапе решается система уравнений для плотности носителей и плотности тока в одной пространственной точке при воздействии чирпированного супергауссовского импульса. При фиксированной спектральной ширине и нормировке по интенсивности выделяется чисто вклад чирпа в формирование плазмы, при котором относительная плотность плазмы превышает единицу и демонстрирует устойчивое преимущество отрицательного чирпа по сравнению с положительным. На втором этапе моделируется распространение оптического поля в воде методом углового спектра с применением той же системы уравнений во всем пространстве. Учет нормальной дисперсии приводит к изменению наблюдаемой тенденции: плотность

плазмы, обусловленная исключительно чирпом, уменьшается с ростом величины чирпа, при этом отрицательный чирп демонстрирует больше значения, чем положительный. Наиболее сильное уменьшение вклада наблюдается для длинных нечирпированных импульсов (например, 80 фс), что связано с дисперсионным временным распылением и пространственно-временной рассинхронизацией поля. Полученные результаты позволяют отделить эффект влияния спектральной фазы от спектральной ширины и интенсивности, формируют проверяемые предсказания для водяных струй и создают основу для будущих экспериментальных исследований и самосогласованных моделей распространения.

Ключевые слова: плотность плазмы, чирпированный импульс.

Распространение спиновых волн в крестообразном микроволноводе из пленки железо-иттриевого граната с магнитными цилиндрами

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В данном исследовании рассматривается применение спиновых волн для разработки функциональных компонентов, обеспечивающих обработку, передачу и хранение информации в микроволновом и терагерцовом диапазонах частот. Платформа основана на тонких плёнках железо-иттриевого граната, при этом управление спиновыми волнами осуществляется с помощью двумерных массивов магнитных цилиндров из магнетита. Проведён численный микромагнитный анализ крестовидного волновода путём решения уравнения Ландау–Лифшица–Гильберта, в ходе которого изучалась зависимость характеристик волн от ориентации внешнего магнитного поля. Полученные результаты указывают на перспективность данного подхода для создания компактных и энергоэффективных магнитных устройств.

Ключевые слова: численное микромагнитное моделирование, железо-иттриевый гранат, магнитные цилиндры, спиновая волна.

Импульсная фазовая модуляция с гармоническим электрическим управляющим сигналом для реализаций квантового распределения ключей

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В данной работе мы исследуем альтернативный подход к фазовой модуляции для кодирования и декодирования информации в системах квантового распределения ключей. В частности, мы предлагаем импульсную фазовую модуляцию, то есть модуляцию с временной огибающей в дополнение к ранее рассматриваемому только гармоническому временному поведению индекса модуляции (глубины модуляции), в качестве замены традиционного использования как модуляторов интенсивности, так и фазовых модуляторов, что позволяет создать более компактную и экономичную оптическую схему. Мы также анализируем, как основные неидеальности этой схемы влияют на помехи, наблюдаемые на приемной стороне, и, следовательно, на их вклад в уровень ошибок при реализации квантового распределения ключей на основе боковых частот фазомодулированного излучения.

Ключевые слова: фазовая модуляция, квантовое распределение ключа, квантовое распределение ключа на боковых частотах фазомодулированного излучения.

Поверхности умбиликов как надежный метод топологического анализа трехмерных солитонов в холестерических жидких кристаллах

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Метод, основанный на умбиликах, которые выявляют линейную структуру сложного распределения полей директора, используется для введения поверхностей умбилика в качестве численно надежного зонда трехмерных (3D) топологических солитонов в фрустрированных холестерических жидких кристаллах. Мы представляем не зависящую от координат аналитическую формулировку подхода с использованием линий умбилика, которая обеспечивает надежное обнаружение умбиликов на дискретных сетках моделирования и, таким образом, позволяет избежать проблем, вызванных нестабильностью и чувствительностью к выбору координатной системы. В рамках используемого метода можно ввести фазовое поле с лабораторной привязкой, которое предоставляет естественный инструмент для интуитивной раскраски поверхности. Кроме того, это поле используется для определения двух фундаментальных целочисленных инвариантов петель умбилика: поперечного индекса и продольного закручивания. Эти инварианты напрямую связывают геометрию умбилика со стандартными топологическими характеристиками поля директора, позволяя напрямую идентифицировать и сравнивать солитоны по их топологическому содержанию. Мы применяем эту методику к трем каноническим солитонам, полученным путем минимизации свободной энергии: торону и петлеобразным холестерическим пальцам первого и второго типов с индексами Хопфа, равными нулю и единице соответственно. Показано, что анализ поверхности умбилика четко выявляет дефектные структуры, позволяет различить визуально похожие, но топологически различные текстуры, и предоставляет удобный инструмент для количественной оценки и визуализации 3D-солитонов на основе данных о поле директора.

Ключевые слова: топологические структуры; линии умбиликов; хиральные жидкие кристаллы; солитон; торон.

Первый пример синтеза наночастиц золота с амидиновыми производными клозо-декаборатного аниона в качестве стабилизирующих лигандов

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В данной работе представлен одностадийный водный синтез золотых наночастиц (AuNPs) с использованием новых амидиновых производных клозо-декаборатного аниона, функционализированных терминальными тиольными группами, в качестве одновременно восстановителей и стабилизирующих агентов. Комплексная характеристика методом просвечивающей электронной микроскопии (ПЭМ) выявила образование наночастиц с необычной архитектурой типа «полое ядро – плотная оболочка», где оболочка, обогащённая золотом, инкапсулирует ядро из лёгких элементов. Данная уникальная морфология объясняет отсутствие характерной полосы поверхностного плазмонного резонанса (SPR) в УФ-видимых спектрах, что отличает полученные материалы от классических наночастиц золота с плотным металлическим ядром. Методом рентгенофотоелектронной спектроскопии (РФЭС) подтверждено ковалентное связывание лигандов через связи Au–S и сохранение борного кластера на поверхности наночастиц. Проведена оптимизация синтеза: установлено, что молярное соотношение 1:6 (Au:лиганд) является оптимальным для получения узкого распределения частиц по размерам.

Ключевые слова: Кластерные анионы бора, клозо-декаборат, амидин, цистеамин, наночастицы золота

In situ дифракционное исследование процесса кристаллизации $\text{MnO}_x\text{-ZrO}_2$ оксида

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Для изучения процесса кристаллизации смешанного $\text{MnO}_x\text{-ZrO}_2$ оксида в различных средах применялись методы *in situ* рентгеновской дифракции и термогравиметрического анализа. В качестве референсного образца использовался чистый ZrO_2 . Показано, что процесс кристаллизации в Mn-содержащем образце зависит от среды: температура кристаллизации в восстановительной и инертной среде составляла 450–455 °С, а в окислительной – 560 °С. Таким образом, добавление марганца привело к смещению температуры кристаллизации в сторону более высоких значений по сравнению с чистым ZrO_2 (425 °С). Полученная кристаллическая фаза представляет собой твердый раствор $\text{Zr}_{1-y}\text{Mn}_y\text{O}_2$, а не чистый ZrO_2 . Вероятно, катионы Mn позволили стабилизировать тетрагональный диоксид циркония вместо моноклинного.

Ключевые слова: *in situ* рентгеновская дифракция; кристаллизация; оксид марганца; твёрдый раствор; оксид циркония.

g- C_3N_4 , модифицированный $\text{Ni}(\text{OH})_2$ и $\text{Co}(\text{OH})_2$, для фотокаталитического восстановления CO_2

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В работе представлены синтез и характеристика композитных фотокатализаторов на основе g- C_3N_4 , модифицированного $\text{Ni}(\text{OH})_2$ и $\text{Co}(\text{OH})_2$, для восстановления CO_2 под действием видимого света ($\lambda = 410$ нм). Исследования методом РФА, УФ-вид спектроскопии и ПЭМ ВР показали, что осаждение гидроксидов не нарушает кристаллическую структуру g- C_3N_4 , однако приводит к незначительному увеличению межслоевого расстояния и ширины запрещенной зоны. $\text{Ni}(\text{OH})_2$ представлен наночастицами размером около 7 нм, тогда как $\text{Co}(\text{OH})_2$ кристаллизуется в виде более крупных частиц размером ~24 нм. По данным ПЭМ установлено, что после фотокаталитического восстановления CO_2 происходит частичная агрегация $\text{Ni}(\text{OH})_2/\text{NiO}$. Катализатор, содержащий 0,1 масс.% $\text{Ni}(\text{OH})_2$, продемонстрировал наибольшую фотокаталитическую активность – 7,04 мкмоль $\text{г}^{-1} \text{ч}^{-1}$, что в 1,9 раза выше по сравнению с исходным g- C_3N_4 . Для фотокатализатора 0,5 масс.% $\text{Co}(\text{OH})_2/\text{g-C}_3\text{N}_4$ наблюдалось увеличение активности в 1,3 раза относительно исходного g- C_3N_4 . Полученное улучшение активности обусловлено формированием гетероперехода типа II между g- C_3N_4 и $\text{Ni}(\text{OH})_2$, что способствует эффективному переносу зарядов и подавлению их рекомбинации.

Ключевые слова: g- C_3N_4 , фотокатализ, $\text{Ni}(\text{OH})_2$, $\text{Co}(\text{OH})_2$, восстановление CO_2 .

Стабильность твердофазных гетеронаноструктур сульфидов цинка и серебра к окислению на воздухе

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Впервые изучена термическая стабильность фазового состава сульфидных гетеронаноструктур сульфида $(\text{ZnS})(\text{Ag}_2\text{S})_x$. Твердофазные гетеронаноструктуры $(\text{ZnS})(\text{Ag}_2\text{S})_x$ с $x = 0.002\text{--}0.50$ синтезированы методом гидрохимического соосаждения сульфидов ZnS и Ag_2S . Размер наночастиц ZnS, оцененный по уширению дифракционных отражений, в полученных исходных гетеронаноструктурах составляет 2–4 нм. Отжиг синтезированных гетеронаноструктур $(\text{ZnS})(\text{Ag}_2\text{S})_x$ на воздухе при температуре от 25 до 530 °С и выше приводит к изменению их фазового состава за счет окисления кубического сульфида ZnS до гексагонального оксида цинка. Окисление начинается при температуре ~250 °С; размер

наночастиц ZnO варьируется в диапазоне от 12 до 17–25 нм. Окисление твердофазных гетеронаноструктур $(\text{ZnS})(\text{Ag}_2\text{S})_x$ на воздухе показало, что потеря веса, происходящая при нагревании от ~250 до ~430–450 °C, связана с началом окисления сульфида ZnS и образованием оксида ZnO. Наиболее значительная потеря веса наблюдается после нагревания от ~450 до ~580 °C из-за увеличения содержания ZnO, окисления серы и ее удаления в виде SO_2 .

Ключевые слова: химическое соосаждение; гетеронаноструктура $(\text{ZnS})(\text{Ag}_2\text{S})_x$; стабильность фазового состава.

Самораспространяющийся высокотемпературный синтез керамик на основе циркония из композиционного порошка Zr-B₄C

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В работе получены керамические порошки $\text{ZrB}_2\text{-ZrC}$ методом самораспространяющегося высокотемпературного синтеза (СВС) из композиционных порошков-прекурсоров Zr-B₄C. Композиционные порошки были получены путем механообработки смеси порошков Zr и B₄C в планетарной шаровой мельнице в течение 3–12 минут среде гексана. Изучена структура, морфология, фазовый и фракционный состав композиционных порошков-прекурсоров и керамических порошков, полученных методом СВС. Показано, что в процессе механообработки частицы B₄C интенсивно внедряются в Zr, достигая равномерного распределения спустя 9 минут обработки. Сделано предположение о возможном механизме СВС.

Ключевые слова: ультравысокотемпературная керамика, керамический порошок, самораспространяющийся высокотемпературный синтез, шаровой размол, цирконий, карбид бора, диборид циркония, карбид циркония.

Оценка эффективности 2D графеновых структур, полученных из различных биополимеров, как модификаторов свойств пленок термостойкого полиимида

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Проведена сравнительная оценка влияния 2D графеновых структур, полученных из лигнина, крахмала и целлюлозы методом самораспространяющегося высокотемпературного синтеза, на механические, термические и электрические свойства плёнок поли-4,4'-оксидифениленпиромеллитимида. Обнаружено, что введение синтезированных наночастиц позволяет модифицировать механические свойства полиимидного материала без значительного снижения удельного объёмного и поверхностного сопротивления. Также были установлены и проанализированы зависимости изменения свойств нанокомпозитных пленочных материалов от различных факторов: типа биополимера, из которого был получен нанонаполнитель; морфометрических параметров приготовленного наноразмерного материала и концентрации нанонаполнителя.

Ключевые слова: нанокомпозиты, 2D графеновые структуры, полиимиды, биополимеры, механические характеристики, термические характеристики

Межфазная стабилизация мембраны Nafion с помощью графена и ПТФЭ: путь к созданию более прочной полимерной электролитной мембраны для электролиза воды

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Стабильность и долговечность электрохимических систем преобразования энергии являются важными проблемами. В данном исследовании изучались две стратегии стабилизации: 1) нанесение барьерного слоя из многослойного графена на обе стороны мембраны Nafion и 2) введение политетрафторэтилена непосредственно в каталитические слои. Электрохимические характеристики оценивались в двухэлектродной конфигурации: путем потенциостатического старения при 2,5 В и измерения кроссовера водорода. Характеристика материалов, выполняющих функции барьерных слоев, проводилась с использованием сканирующей и просвечивающей электронной микроскопии, лазерной корреляционной спектроскопии и дифференциального термического анализа. Показано, что оба компонента стабилизируют Nafion за счет межфазных взаимодействий, что приводит к увеличению срока службы и снижению кроссовера водорода. В то время как в контрольном образце наблюдалось увеличение кроссовера, в модифицированных образцах оно снизилось на 50% и 33%. Эти результаты подчеркивают потенциал изучаемых материалов для повышения стабильности электролизеров воды с полимерной электролитной мембраной, что способствует созданию более долговечных и эффективных систем для применения в водородной энергетике.

Ключевые слова: графен; ПТФЭ; стабилизированный Nafion; мембранно-электродные блоки; электролизер.



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