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On the spillover effect of the solid H_2 intercalation into GNF's

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1. Introduction

As is known, the hydrogen spillover effect can be characterized by three major steps, the first being where molecular hydrogen is split via dissociative chemisorption into its constituent atoms on a transition metal catalyst surface, followed by migration from the catalyst to the substrate, culminating in their diffusion throughout the substrate surfaces and/or in the bulk materials.The mechanism behind the hydrogen spillover effect has been long disputed, up to currently.

As is noted, for instance in [1-10], the hydrogen spillover effect manifestation in carbon-based nanomaterials has been not studied thoroughly, which is particularly relevant for solving the current problems of on-board hydrogen storage efficiency and safety.

2. Experimental/methodology

A thermodynamic analysis approach [11,12] for the related experimental data (including Figs. 1 – 4 from [12]) has been used.

3. Results and discussion

3.1. The physics for the intercalation of high density H_2 gaseous nanophase into graphene nanoblisters in HOPG and epitaxial graphenes (under atomic hydrogen treatment)

Figure 1 shows the two steps ((a) and (b)) of hydrogenation (at 300 K and the atomic hydrogen pressure $P_{(Hgas)} \approx 1 \cdot 10^{-4}$ Pa, without any catalyst) of surface graphene layers of a highly oriented pyrolytic graphite (HOPG) resulted in intercalation of a high density H_2 gaseous nanophase into surface graphene nanoblisters.

If we assume that the nanoblister approximates a semi-elliptical form, we obtain a blister area of $S_b \approx 2.0 \cdot 10^{-11}$ cm^2 and a volume of $V_b \approx 8.4 \cdot 10^{-19}$ cm^3. The amount of retained hydrogen in this sample becomes $Q \approx 2.8 \cdot 10^{14}$ H_2/cm^2 and the number of hydrogen molecules captured inside the blister becomes $n \approx (QS_b) \approx 5.5 \cdot 10^3$. Thus, within the ideal gas approximation, and accuracy of one order of the magnitude, the internal pressure of molecular hydrogen in a single nanoblister at near-room temperature ($T \approx 300$ K) becomes $P_{H2} \approx \{k_B(QS_b)T/V_b\} \approx 1 \cdot 10^8$ Pa. The hydrogen molecular gas density in the blisters (at $T \approx 300$ K and $P_{H2} \approx 1 \cdot 10^8$ Pa) can be estimated as $\rho_{H2} \approx \{(QM_{H2}S_b)/V_b\} \approx 0.045$ g/cm^3, where M_{H2} is hydrogen's molecular mass.

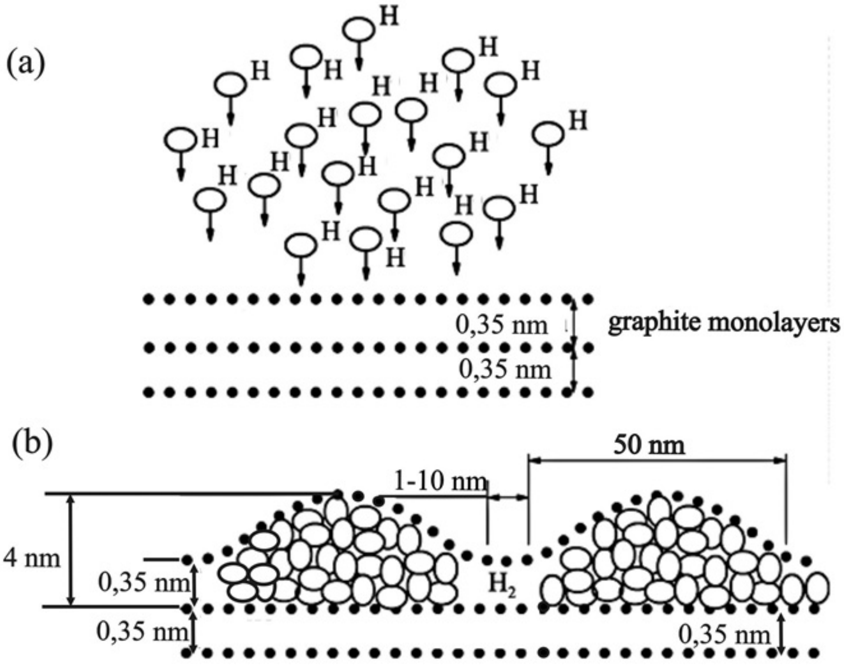

FIG. 1. Model {from STM and AFM data} showing the hydrogen accumulation (intercalation) in HOPG, with the formation of blister-like surface nanostructures; hydrogenation was done at 300 K and the atomic hydrogen pressure $P_{(Hgas)} \approx 1 \cdot 10^{-4}$ Pa, without any catalyst. (a) Pre-atomic hydrogen penetration (intercalation) step. (b) Molecular gaseous hydrogen, "captured" inside the surface graphene nanoblisters (at $P_{(H2gas)} \approx 1 \cdot 10^8$ Pa), after the intercalation step. Sizes are not drawn exactly in scale. The hydrogen compression effect is of 12 orders (from $P_{(Hgas)} \approx 1 \cdot 10^{-4}$ Pa to $P_{(H2gas)} \approx 1 \cdot 10^8$ Pa). According to analysis [11,12], it occurs at the expense of the energy of association of hydrogen atoms to the "captured" molecules, Eqs. (1), (2)

These data (Fig. 1) can be quantitatively described, with an accuracy of one order of magnitude, and interpreted within the thermodynamic approach [11,12], by using the conditions of thermo-elastic equilibrium for the reaction of ($2\mathrm{H}_{(gas)} \rightarrow \mathrm{H}_{2(gas\_in\_blisters)}$), as follows:

$$(P_{H2}/P^0_{H2}) = (P_H/P^0_H)^2 \exp\{[\Delta H_{dis} - P^*_{H2}\Delta V]/k_BT\}, \tag{1}$$

where $P*_{H2}$ is related to the blister "wall" back pressure (caused by P_{H2}) – the so called surface pressure ($P*_{H2} \approx P_{H2} \approx 1 \cdot 10^8$ Pa), P_H is the atomic hydrogen pressure corresponding to the atomic hydrogen flux ($P_H \approx 1 \cdot 10^{-4}$ Pa), $P^0_{H2} = P^0_H = 1$ Pa is the standard pressure, $\Delta H_{dis} = 4.6$ eV is the dissociation energy (enthalpy) of one molecule of gaseous hydrogen (at room temperature), $\Delta S_{dis} = 11.8k_B$ is the dissociation entropy, $\Delta V \approx (S_b r_b/n)$ is the apparent volume change, r_b is the radius of curvature of nanoblisters at the nanoblister edge ($r_b \approx 30$ nm, Fig. 1), N_A is Avogadro's number, and T is the temperature ($T \approx 300$ K). The quantity of

$(P^{*}_{H2}\Delta V)$ is related to the work of the nanoblister surface increasing with an intercalation of 1 molecule of hydrogen.

The value of the tensile stresses σ_b (caused by P^{*}_{H2}) in the graphene nanoblister "walls" with a thickness of d_b and a radius of curvature r_b can be evaluated from another condition (equation) of the thermo-elastic equilibrium for the system in question, which is related to Eq. (1), as follows:

$$\sigma_b \approx P^{*}_{H2}(r_b/2d_b) \approx (\varepsilon_b E_b), \tag{2}$$

where ε_b is a degree of elastic deformation of the graphene nanoblister walls, and E_b is the Young's modulus for the graphene nanoblister walls.

Substituting in the first part of Eq. (2) the quantities of $P^{*}_{H2} \approx 1 \cdot 10^{8}$ Pa, $r_b \approx 30$ nm and $d_b \approx 0.15$ nm results in the value of $\sigma_b \approx 1 \cdot 10^{10}$ Pa.

The degree of elastic deformation for the graphene nanoblister walls, apparently reaches $\varepsilon_b \approx 0.1$ (Fig. 1). Hence, with Hooke's law of approximation, using the second part of Eq. (2), one can estimate, with the accuracy of one order of the magnitude, the value of the Young's modulus for the graphene nanoblister walls: $E_b \approx (\sigma_b/\varepsilon_b) \approx 0.1$ TPa. It is close (within reasonable error) to the experimental value [13, 14] for the Young's modulus of perfect (that is, without defects) graphene ($E_{graphene} \approx 1.0$ TPa).

Similar STM, AFM and other data from different researchers for epitaxial graphenes (for instance, Fig. 2) can be analyzed and interpreted in a similar manner [11, 12], within the same physical concept (Eqs. 1, 2).

In this connection, it is expedient to note that a number of researchers (for instance, [15, 16]) have not sufficiently considered the "thermodynamic forces" and/or energetics of formation (under the atomic hydrogen treatment) for graphene nanoblisters in the surface HOPG layers and epitaxial graphenes.

It is also expedient to note that very recent experimental data [17] show that a hydrogen atom can not pass through a perfect graphene network. Conversely, the analysis [11, 12] of a number of experimental data (including Fig. 1, 2) shows that a hydrogen atom can pass through permeable defects in graphene, for instance, through triple junctions of grain boundaries. In Fig. 2 a and b, one can imagine some grain boundary network substituted (obviously, in some nano-regions at grain boundaries) by some nano-protrusions.

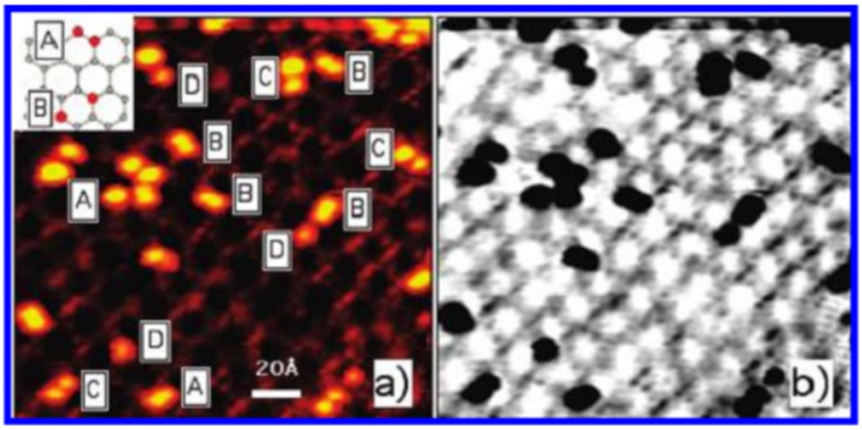

FIG. 2. (a) STM image of hydrogenated graphene/SiC. (b) Same image as in (a) with inverted color scheme, giving emphasis to preferential hydrogen adsorption on the SiC surface. Hydrogen dose at $T_{(beam)} = 1600$ K, $t = 5$ s, $F = 10^{12} - 10^{13}$ atoms/cm$^{2}\cdot$ s ($P_{(Hgas)} \approx 1 \cdot 10^{-4}$ Pa [11, 12])

3.2. The physics of intercalation of the solid H_2 nanophase into hydrogenated graphite nanofibers (with metallic catalysts)

The physics for the intercalation of high density solid molecular hydrogen ($\rho_{H2} \approx 0.5$ g/cm^3, Fig. 3) into closed (in the definite sense) nanoregions in hydrogenated GNFs (Fig. 4) is related to the same concept, Eqs. of type (1), (2) [11, 12].

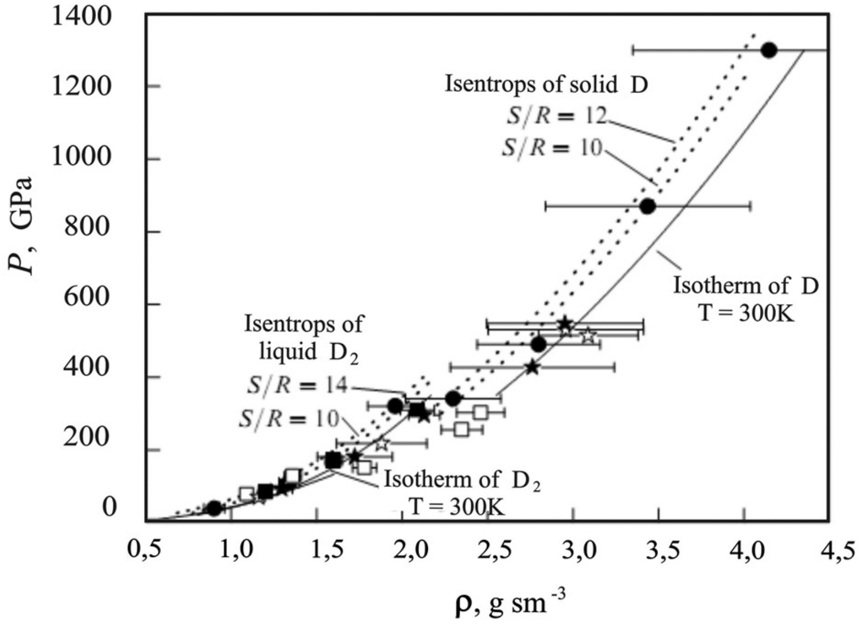

FIG. 3. Data on isentropes (S/R) and isotherms for deuterium and protium. The density (ρ) of protium (H_2, H) is increased by a factor of two (for the scale reasons). The experimental and theoretical isotherms show that at $T = 300$ K and the external compression pressure of $P = 50$ GPa hydrogen exists in a high density solid molecular state $\rho_{H2} \approx 0.5$ g/cm^3 [12]

Obviously, it is a manifestation of the spillover effect, relevant to providing the necessary partial pressure of atomic gaseous hydrogen (with material hydrogenation at an initial molecular hydrogen pressure $P_{H2} = 8$ MPa).

4. Conclusions

The "thermodynamic forces" and energetics of forming of graphene nanoblisters (under atomic hydrogen treatment, without catalysts) in the surface HOPG layers (Fig. 1) and epitaxial graphenes (Fig. 2) are quantitatively described, particularly, two conditions of the thermal-elastic thermodynamic equilibrium – Eqs. (1),(2) – are considered.

The physics for the intercalation of a high density gaseous H_2 nanophase ($\rho_{H2} \approx 0.045$ g/cm^3) into graphene nanoblisters (Figs. 1, 2) is considered – Eqs (1), (2). The hydrogen compression effect of 12 orders of magnitude (from $P_{(Hgas)} \approx 1 \cdot 10^{-4}$ Pa to $P_{(H2gas)} \approx 1 \cdot 10^{8}$ Pa), at the expense of the energy of association of hydrogen atoms to the "captured" molecules, is shown.

The physics for the intercalation of the high density solid H_2 nanophase ($\rho_{H2} \approx 0.5$ g/cm^3, [18]) into hydrogenated graphite nanofibers with Pd-catalyst (Figs. 3, 4) is considered.

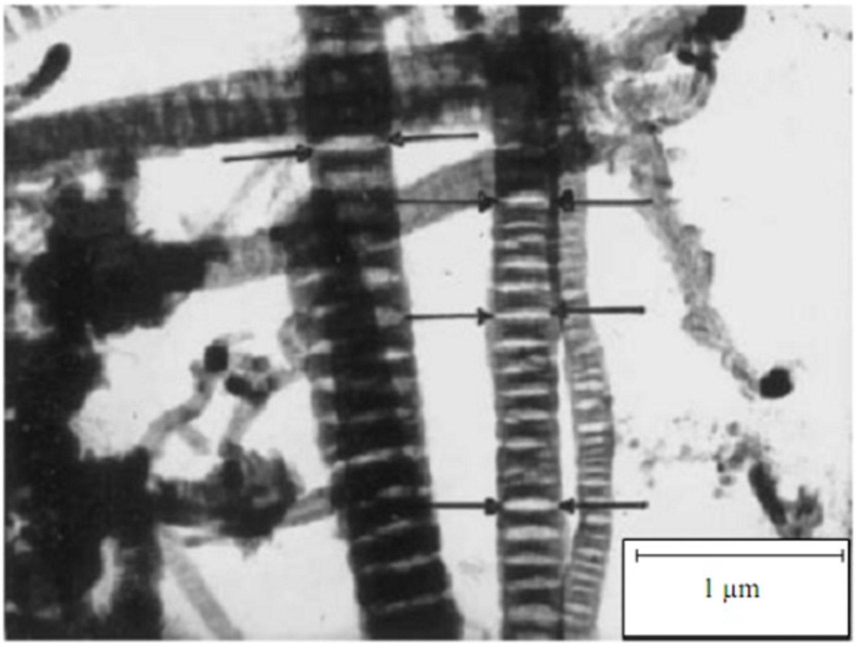

FIG. 4. Micrograph of hydrogenated graphite nanofibers (GNFs), with Pd-catalyst (hydrogenated at 300 K and an initial pressure of $P_{(H2gas)} \approx 8$ MPa), after release from them, at 300 K, for 10 min, of the intercalated solid H_2 nanophase (17 wt%) of a high density of $\rho_{H2} \approx 0.5$ g/cm^3 (analysis [11, 12]). The arrows in the picture indicate some of the slit-like closed nanopores of the lens shape, where the solid H_2 intercalated nanophase (under pressure of $\sim$50 GPa, according to data on Fig. 3) was localized. Such a pressure level can be also evaluated by the consideration of the material deformation and the necessary stresses for forming the lens shape closed nanopores (at the expense of the energy of association of hydrogen atoms to molecules "captured" inside the nanopores, Eqs. of type (1), (2)

In the light of analysis [11,12], the spillover effect is obviously manifested in the extraordinary data [19].

This effect can be used for solving of the current problem of the efficient and safe hydrogen on-board storage [20].

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