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Synthesis of CdSTe nanoparticles by laser ablation

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ABSTRACT Synthesis of CdSTe nanoparticles using $CdCl_2$, $Na_2S_2O_3$ and TeO_2 solutions under the action of laser radiation was experimentally studied. The radiation source was a pulsed Nd:YAG laser with built-in generators of the 2nd and 3rd harmonics, designed to generate radiation with a wavelength of 1064, 532, and 335 nm. The laser pulse duration was 10 ns with an energy of 135 mJ per pulse. In a colloidal solution, the formation of nanoparticles with a diameter of 10 to 50 nm was observed. X-ray diffraction analysis established that the crystal structure of the nanoparticles is the same as that of the bulk material (hexagonal). It is shown that the photoluminescence emission of the obtained nanoparticles has a green color (∼560 nm) and is associated with the radiative recombination of free excitons.

KEYWORDS CdSTe nanoparticles, laser ablation, photoluminescence.

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1. Introduction

Among the most common semiconductor nanoparticles of groups II–VI, CdSTe nanocrystals are of great interest for applications in optoelectronics, solar cells, LEDs, and biology [1–5]. Due to the developed surface (in a 1 nm particle, almost all atoms are surface atoms) and the manifestation of the quantum confinement effect [6], nanosized semiconductors have unique optical, electronic, catalytic, and other properties that are attractive to researchers. For example, solar cells based on nanosized cadmium telluride demonstrate a record efficiency of solar energy conversion and are currently considered more promising for mass application compared to traditional silicon batteries [7,8]. To obtain nanoclusters and nanostructured materials, various methods are used: gas-dynamic, chemical, plasma, beam [9–18]. CdSTe nanocrystals in solution are most often obtained by chemical synthesis using organometallic "precursors". These methods provide nearly monodisperse nanocrystals that exhibit narrow photoluminescence emission (up to ∼30 nm) as well as high quantum yields. However, in general they require the use of expensive, pyrophoric, hazardous chemical precursors, as well as high temperatures and long reaction times.

One of the most promising methods for the synthesis of clusters is pulsed laser ablation (PLA) [1, 4]. Its main advantage is the ability to exclude the presence of foreign impurities in synthesized nanostructures, which is especially important for applications (one foreign atom in a 2 nm particle corresponds to a defect concentration of $\sim 10^{21}$ cm^{-3} and can significantly change its properties). The advantages of the PLA method also include its flexibility and the ability to control the process of cluster growth. The formation of nanoclusters during PLA can occur according to two different scenarios: aggregation of the initial ablation products (atoms, molecules) in an expanding laser plasma and direct emission from the irradiated surface. Recently, significant progress has been made in the PLA synthesis of single-component semiconductor nanoclusters with controlled size, shape, and optical properties [19, 20], as well as in the understanding and quantitative description of the cluster formation process [21–23]. Laser ablation of nanoparticles in a liquid has attracted great interest due to its simplicity, the absence of the need for surfactants, and good control of the size and shape of synthesized nanoparticles [24,25]. In this method, many parameters, such as laser radiation flux density, laser radiation wavelength, pulse duration, and type of colloidal solution, can affect the characteristics of synthesized nanoparticles.

It should be noted that in all the above works devoted to laser ablation, bulk CdSTe crystals grown by the Bridgman method were used as target materials. Laser ablation was carried out either in a vacuum or by immersing the target in various liquids, using ultrashort nano and femtosecond laser pulses. Indeed, the synthesis of CdSTe nanoparticles by laser ablation, as noted, has great advantages over other methods. However, it should be taken into account that this method requires the growth of undoped CdSTe crystals, which is by no means a simple technological problem. In this work, we propose a new method for obtaining nanoparticles, direct interaction of laser radiation with solutions that make up the components of CdSTe nanoparticles. As shown by our experimental studies, the structural characteristics and optical properties of CdSTe nanoparticles are significantly superior to those of nanoparticles obtained using a solid target.

2. Experimental technique

CdSTe nanoparticles were synthesized in solution using the reactive laser ablation method. Highly pure $CdCl_2$ (99.9 % pure from Sigma Aldrich), $Na_2S_2O_3$ (99.95 % pure from Sigma Aldrich) and TeO_2 (99.99 % pure from Sigma Aldrich) powders mixed with distilled water were used as initial raw materials. The reaction proceeded according to the following formula:

$$2CdCl_2 + 2TeO_2 + Na_2S_2O_3 + H_2 = 2CdSTe + 2NaCl + 2HCl + 4O_2 \quad (1)$$

Immediately after irradiation with a laser pulse, CdSTe nanoparticles were formed. The ablation process was performed by laser radiation with a wavelength of $\lambda = 1064$ nm, with a pulse energy of 135 mJ and an ablation time of ~ 10 min. The radiation source was pulsed Nd:YAG laser with built-in generators of the 2nd and 3rd harmonics, designed to generate radiation with a wavelength of 1064, 532, and 335 nm. The laser pulse duration was 10 ns with a maximum power of ~ 12 MW/cm^2. The radiation intensity was varied using calibrated neutral light filters. The optical absorption and luminescence spectra of CdSTe nanoparticles were studied using an automatic M833 double dispersion monochromator (spectral resolution ~ 0.024 nm at a wavelength of 600 nm), with computer control and a detector that records radiation in the wavelength range of 350–2000 nm. The scheme of the experimental setup for ablation of CdSTe nanoparticles is shown in Fig. 1.

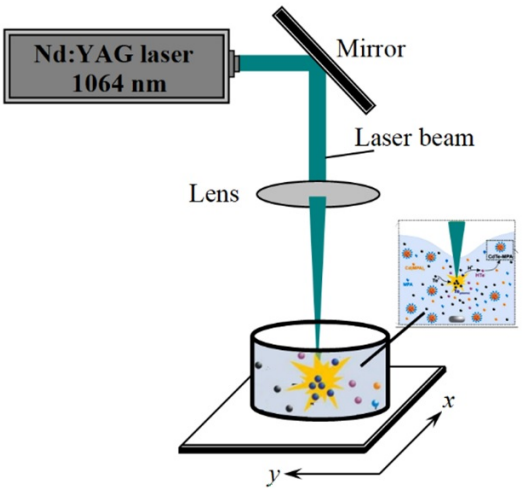

FIG. 1. Scheme of the experimental setup

Fig. 2 shows the diffraction pattern (XRD) of nanoparticles from drops of a colloidal solution of CdSTe dried on a clean glass substrate. CuKα, λ=1.544178 Å SSFOM: F17-610.0.5.10.60 were used as the radiation source. It is shown that the diffraction planes (111), (200), (220), (311), (222), (400), (331), (422), and (511) at 2θ diffraction angles 23.620, 27.890, 38.970, 45.280, 49.340, 56.750, 63.600, 73.220, and 76.840, respectively, correspond to the cubic (zinc blende) structure of the bulk CdSTe crystal [24], which confirms the crystal structure of the synthesized nanoparticles, which is the same as that of the bulk material. Based on the X-ray diffraction patterns, using the Debye–Scherer formula [21], the sizes of the obtained nanoparticles were calculated:

$$D = \frac{k\lambda}{\beta \cos\theta} \quad (2)$$

where D is the sizes of nanoparticles, $k = 0.9$ is the line shape factor (shape factor), $\beta = 0.035$ Å is the intensity maximum half-width (FWHM- Full Width at Half Maximum), λ is the X-ray wavelength, $\lambda = 1.54$ Å, θ-Bragg angle, $\cos\theta = 0.727$.

Estimates show that the average size of CdSTe crystallites is 27.434 nm (see Table 1).

Morphologists. The surfaces of the synthesized CdSTe nanoparticles were studied using AFM analysis. Fig. 3 shows a 3D AFM image of CdSTe nanoparticles on a glass substrate. As can be seen from the figure, a homogeneous distribution of particles in the presented figure is not observed.

The histogram of particle size distribution is shown in Fig. 4. The average particle size estimated using the software was about 40–50 nm. The particle size value is higher than calculated by X-ray diffraction analysis. This is due to the fact that XRD depends on the free volume of dimensional defects, while AFM directly visualizes the grain without taking into account the degree of defectiveness of the crystal.

The absorption curve from a colloidal solution of CdSTe nanoparticles is shown in Fig. 5a. The onset of absorption at ~ 500 nm is consistent with the absorption of an ensemble of nanoparticles whose maximum diameter is ~ 50 nm. Taking into account that CdSTe is a semiconductor with a direct band gap, from the dependence , the band gap of the

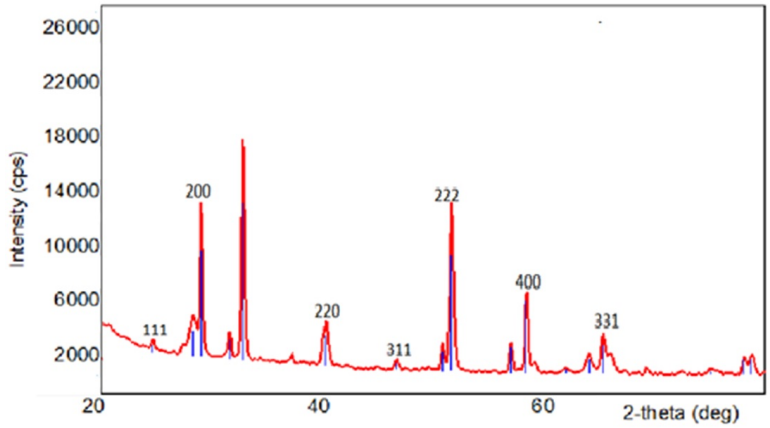

FIG. 2. Diffraction pattern (XRD) of CdSTe nanoparticles on a glass substrate

TABLE 1. Crystallite size

2 theta	**Crystallite size**
23.62(3) 111	28.27 nm
27.891(9) 200	34.91 nm
38.97(3) 220	16.31 nm
45.28(5) 311	23.66 nm
49.347(14) 222	39.72 nm
56.75(8) 400	47.17 nm
63.60(5) 331	20.78 nm
73.2(1) 422	10.87 nm
76.84(3) 511	25.22 nm
average crystallite size:	**27.434 nm**

studied samples was determined, which turned out to be equal to Eg = 2.46 eV (Fig. 5b). This value is 0.97 eV larger than the band gap of a bulk undoped CdSTe crystal, (eV (∼827 nm) [1]. It should be noted that the shift of the red absorption band of nanoparticles to the short-wavelength region of the spectrum compared to a bulk crystal is a characteristic feature of semiconductor nanoparticles, which is related to the quantum size effect.

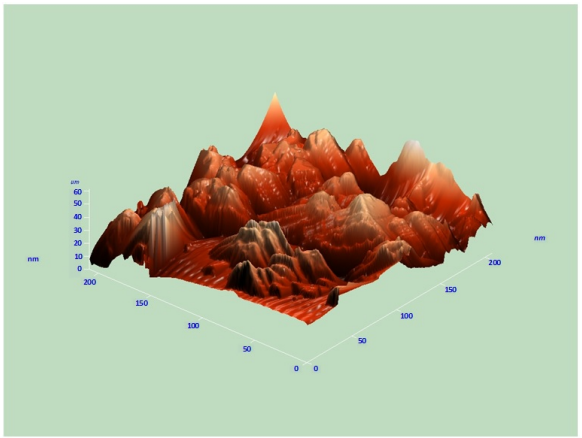

FIG. 3. AFM image of CdSTe nanoparticles on a glass substrate

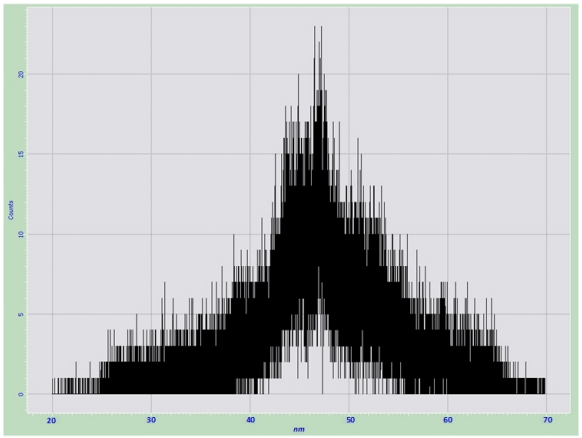

FIG. 4. Histogram of particle size distribution

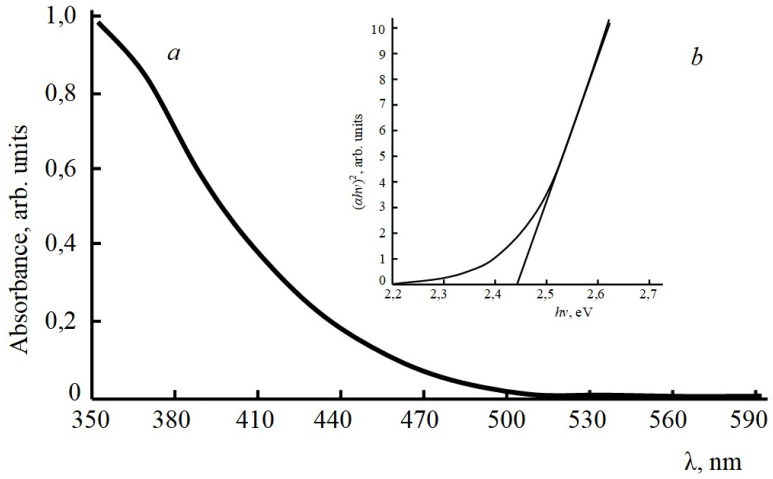

FIG. 5. Optical absorption spectrum (a) and dependence $\alpha^2 \sim f(h\nu)$ (b) of CdSTe nanoparticles obtained in a colloidal solution

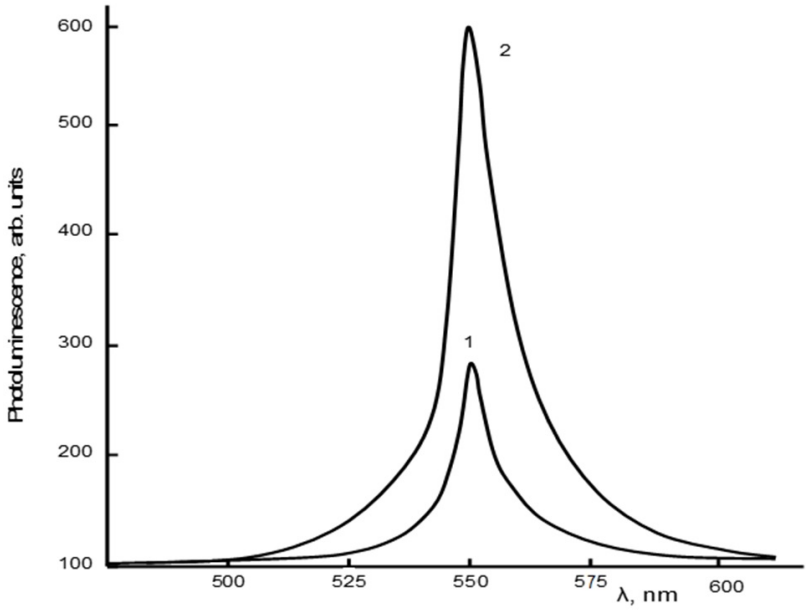

FIG. 6. Photoluminescence spectra of CdSTe nanoparticles at two different excitation powers, the second harmonic of a neodymium laser (eV): 1–1 MW/cm^2; 2–10 MW/cm^2

Fig. 6 shows the photoluminescence spectra of CdSTe nanoparticles excited by the second harmonic of the Nd:YAG laser (eV). As can be seen from the figure, the emission maximum of nanoparticles corresponds to wavelengths ~ 510 nm (2.43 eV). An increase in the laser light power by 1.2 times does not affect the position of the spectra, but leads to an increase in the radiation intensity by ~ 2.1 times. As regards the nature of the observed radiations, in our opinion they are due to the radiative recombination of free excitons.

Knowing the energy of free excitons in CdSTe (~ 29 meV), it is possible to determine the band gap of nanoparticles, which is equal to 2.46 eV, which is in satisfactory agreement with the value determined from the absorption spectrum.

3. Conclusion

A new method for synthesizing CdSTe nanoparticles by laser radiation is proposed. Highly pure $CdCl_2$, $Na_2S_2O_3$ and TeO_2 powders mixed with distilled water were used as initial raw materials. The ablation process was performed by laser radiation with a wavelength of 1064 nm, with a pulse energy of 135 mJ and an ablation time of ~ 10 min. Under these ablation conditions in a colloidal solution, the formation of nanoparticles with diameters from ~ 10 to ~ 50 nm was observed. It is shown that the synthesized nanoparticles retain the crystalline structure of the bulk material and emit photoluminescence at 560 nm associated with the radiative recombination of free excitons.

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