

Sizes and Fluorescence of Cadmium Sulfide Quantum Dots

S. V. Rempel^{a, b, *}, A. A. Razvodov^b, M. S. Nebogatikov^b,
E. V. Shishkina^b, V. Ya. Shur^b, and A. A. Rempel^{a, b}

^a *Institute of Solid State Chemistry, Ural Branch of the Russian Academy of Sciences,
ul. Pervomaiskaya 91, Yekaterinburg, 620990 Russia*

* *e-mail: svetlana_rempel@ihim.uran.ru*

^b *Ural Federal University named after the First President of Russia B.N. Yeltsin,
ul. Mira 19, Yekaterinburg, 620002 Russia*

Received August 1, 2012

Abstract—Cadmium sulfide quantum dots have been synthesized by wet chemical deposition from an aqueous solution. The sizes of the quantum dots determined by dynamic light scattering directly in the colloidal solution and by intermittent-contact atomic force microscopy in the dry sediment agree with each other. It has been found that splitting of the fluorescence peaks of the quantum dots can be affected by the disorder of the atomic structure of cadmium sulfide quantum dots.

DOI: 10.1134/S1063783413030244

1. INTRODUCTION

New materials, whose physical, optical, and other properties are related to their linear size, are increasingly used nowadays. In particular, quantum dots (II–IV and II–VI semiconductor nanoparticles) are actively used in optics, biology, and medicine as optically stable markers instead of traditional dyes. Special interest in quantum dots is due to a considerable difference between the discrete exciton spectrum of the quantum dots and the spectrum of a bulk crystal of the same chemical composition. This difference leads to a change in the optical properties of quantum dots as compared to the bulk material. In particular, the emission band of the quantum dots can be located, depending on their size, in any part of the spectrum from the ultraviolet to infrared range [1, 2]. This makes it possible to produce markers of various color for optical coding [3] and to use quantum dots in optoelectronics [4] and for studying the structure of biological cells and influence of various factors on the cells [5, 6].

It is difficult to observe the lines associated with the excitonic states in the luminescence spectra of bulk chalcogenide semiconductors at room temperature. The quantum yield from these states is low owing to the large effective radius of the exciton. In addition, the excitons intensively decay due to the thermal motion. The binding energy and oscillation strength of the exciton increase under its confinement at least in one direction to a size comparable with the exciton radius. This makes possible creation of new materials and devices, whose operation is based on the physical properties determined by the excitonic states. The motion of an exciton in a quantum dot is confined in all three directions. Placing a zero-dimensional semi-

conductor into a dielectric matrix can give rise to an additional enhancement of the electron–hole Coulomb interaction. In particular, coating a quantum dot by a semiconductor shell with a wider band gap (e.g., CdSe/ZnS quantum dot) leads to an increase in the quantum yield.

Cadmium sulfide-based quantum dots are promising materials for optics, optoelectronics, biology, and medicine [4–7]. Cadmium sulfide quantum dots were initially grown and studied in a dielectric matrix, e.g., in a glass [7]. Quantum dots in colloidal solutions are of considerable fundamental and applied interest. Quantum dots in liquid-phase nanomaterials can be used to control biomedical parameters [5, 6]. The techniques of synthesizing semiconductor quantum dots in organic solvents are being successfully developed [8]. Such quantum dots have unique optical characteristics and are widely applied. However, they are generally synthesized with the use of two-stage high-temperature techniques. The use of toxic solvents limits the biological and medical applications of quantum dots. Whereas the properties of quantum dots produced in organic solvents have been studied pretty well [8], the data on quantum dots in aqueous solutions are quite poor [6].

An important characteristic of each material is the Bohr radius of the exciton. For CdS it is 3.2 nm. The CdS particles with a size from 2 to 10 nm correspond to the regime of moderate or strong confinement. According to the calculations [9], the binding energy of the exciton in a 2.5- to 5-nm CdS quantum dots should be several times greater than in a single crystal. This prevents the decay of the exciton at room temperature, allows one to consider nanosystems of CdS quantum dots as active media of semiconductor lasers,

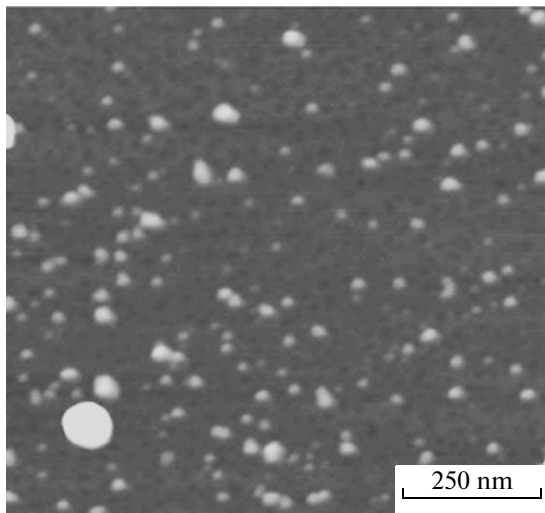


Fig. 1. Cadmium sulfide quantum dots deposited from a colloidal solution onto the mica surface. Intermittent-contact atomic force microscopy image of the surface profile.

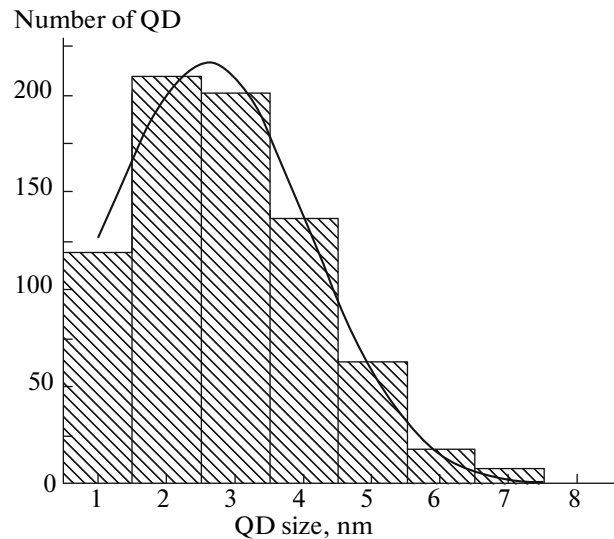


Fig. 2. Histogram of the size distribution of CdS quantum dots according to the analysis of the ICAFM image of the particles deposited onto the mica surface. The experimental data are fitted to the normal distribution.

and significantly extends other fields of their possible application. In many cases, it is necessary to produce quantum dots in aqueous solutions. However, there are still many open questions regarding the tendencies of growth and fluorescence of CdS quantum dots in aqueous solutions. As a rule, it is required to produce quantum dots of strictly specified size. Even a very small dispersion in the size of the quantum dots can lead to a significant change in their optical properties.

Measurement of the sizes of quantum dots is a complicated experimental problem. Different physical methods often yield different results for the same quantum dots. The most adequate size measurement technique seems to be the direct visualization of quantum dots, which allows one to estimate not only the sizes but also their dispersion and the degree of agglomeration. The reliability of the results obtained by this method can be confirmed by using it in combination with indirect measurement techniques.

2. SAMPLES, EXPERIMENTAL TECHNIQUE, AND EXPERIMENTAL RESULTS

In this work, we studied CdS quantum dots produced by wet chemical deposition according to the technique described elsewhere [10]. This method provides stable colloidal aqueous solution of quantum dots without the use of toxic organic solvents and gives the opportunity to avoid additional laborious operations associated with the solubilization process.

The size of the quantum dots was determined by different methods both in a solution and in a powder. The size of the quantum dots was measured directly in the solution by the dynamic light scattering on a Zetasizer Nano-ZS dispersion analyzer. The size of the

dried quantum dots was measured by intermittent-contact atomic force microscopy (ICAFM) with the use of an NTEGRA Spectra nanolaboratory.

To measure the size of the quantum dots a 2- μ L droplet of the colloidal solution of CdS nanoparticles was dispensed to the surface of a fresh mica chip. Slow evaporation of the dispersion medium can knowingly lead to the formation of ordered structures owing to capillary effects. To avoid coarsening of the colloidal particles during evaporation of water, the microdroplet was dried by blowing clean air for 30 s.

The ICAFM image of the surface profile is shown in Fig. 1. As is seen, there are mainly small rounded nanoparticles (quantum dots) on the atomically flat surface of mica; among these small nanoparticles one can find individual relatively coarse particles. The ICAFM measurements of the surface profile revealed the presence of two types of objects, 1) quantum dots with a size of less than 10 nm and a density of about 100 particles per μm^2 and 2) coarse particles with a size from 30 to 45 nm and a density of about one particle per μm^2 .

The size of nanoparticles was determined according to the height of the surface relief. Having measured 750 small particles we found their average size (2.9 nm) and the root-mean-square deviation (1.3 nm). The nanoparticle size distribution histogram (Fig. 2) was fitted to the normal distribution with a maximum at 2.6 nm.

To find the fraction of coarse particles, the system was centrifuged on a Sawates SM 180-Hp250HDMS instrument with speeds of 1000 and 3000 rpm immediately after the deposition of a colloidal solution microdroplet on the substrate. The ICAFM study of

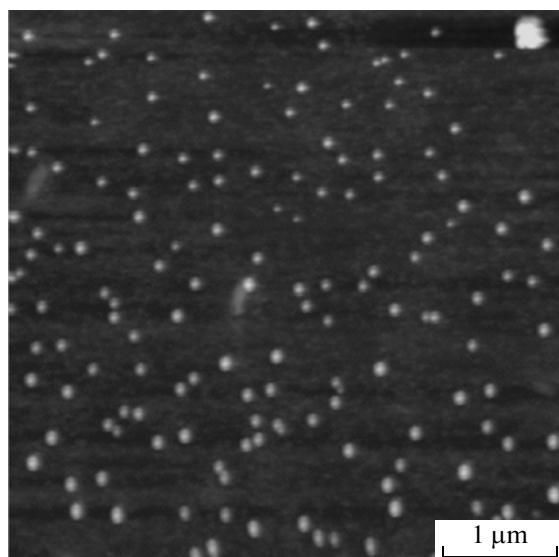


Fig. 3. Cadmium sulfide quantum dots on the mica surface after centrifugation with a speed of 3000 rpm. The ICAFM image of the surface profile.

the produced samples again revealed the presence of nanoparticles with different sizes (Fig. 3).

The size of quantum dots directly in the aqueous suspension was measured by the dynamic light scattering. The suspension with the particles was placed into a cell with a volume of 3 cm³ and irradiated by a helium–neon laser with a wavelength of 633 nm. The detector of the scattered light was situated at an angle of 173°. The distribution function of the scattering centers versus their size indicated that the majority of particles have a size of 15.2 nm (Fig. 4).

The fluorescence spectrum of CdS quantum dots was measured by scanning confocal laser microscopy. The wavelength of the excitation light was 472.8 nm. The spectrum included a pretty narrow fluorescence peak with the maximum at about 557 nm and a broad long-wave peak (Fig. 5). The detailed investigation of the spectra in the vicinity of the fluorescence maximum by means of a 1800-lines per mm diffraction grating with a spectral resolution of 0.027 nm resolved two close peaks (Fig. 6). The observed luminescence lines are strongly broadened due the dispersion of the quantum dot size. Therefore, the accurate determination of their position is problematic. Fitting of the spectrum to two Lorentzians yields the positions of the peaks to be 557 and 563 nm. The distance between the lines in the luminescence spectrum corresponds to 0.02 eV.

3. DISCUSSION OF THE RESULTS

The sizes of the CdS quantum dots measured by different techniques are somewhat different. According to the ICAFM measurements, the majority of nanoparticles have a size of 2 to 3 nm. The dynamic

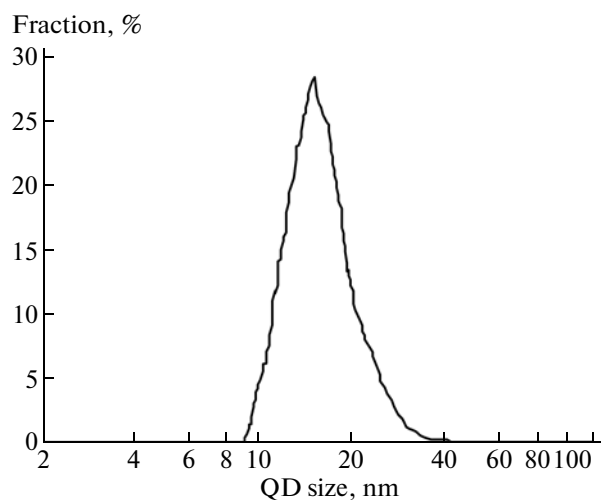


Fig. 4. Size distribution of the quantum dots determined by dynamic light scattering.

light scattering indicates that the majority of particles have a size of 15 nm. This can be explained by the fact that the dynamic light scattering determines the size of scattering centers rather than the quantum dots themselves. Cadmium sulfide nanoparticles in an aqueous solution are situated in micelles, which include stabilizer molecules and polarized solvent molecules [10]. These particular formations, each consisting of a CdS nanoparticle, a stabilizing layer and a solvation sphere of the molecules of the dispersion medium, are the scattering centers. This implies that the size of the majority of particles is less than 10 nm. In addition, both techniques revealed the presence of coarse particles.

Centrifugation failed to produce a particle size-homogeneous fraction. Roldugin [11] mentioned that,

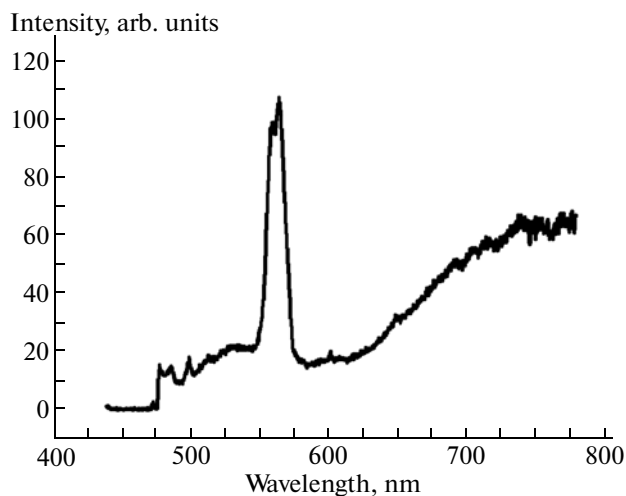


Fig. 5. Fluorescence spectrum of CdS nanoparticles. The wavelength of the excitation light is 472.8 nm.

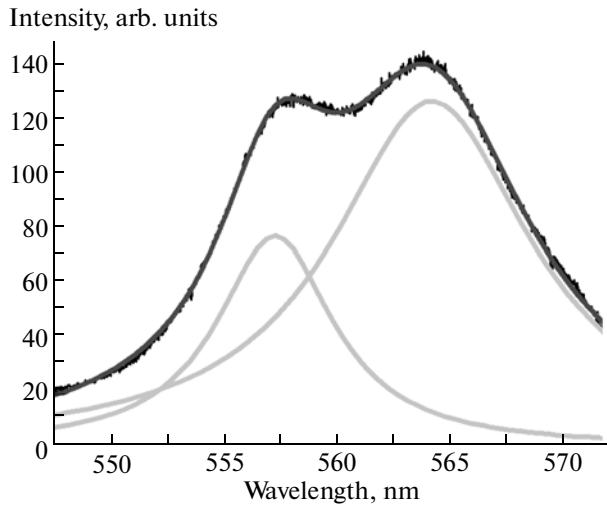


Fig. 6. Fluorescence spectrum of CdS nanoparticles and its fit to the sum of two Lorentzians.

owing to a tendency of nanoparticles to self-organization, new self-organized nanoparticle objects can be observed after centrifugation. However, no self-organization of nanoparticles after centrifugation was detected in this work.

The measurement of the zeta potential indicated that the state of nanoparticles corresponds to the boundary of the stability region, so that their coagulation cannot be excluded. Consequently, coarse particles detected in all our experiments could be agglomerations of CdS nanoparticles (Fig. 7).

Most interesting are the short-wave peaks in the fluorescence spectra. According to [12], the luminescence spectra of nanocrystals with the size $a \leq 3.5$ nm are largely due to band–impurity and impurity–impurity transitions. As is known, the spectral position of all luminescence lines is blue-shifted with a decrease in the size of nanocrystals. This fact in combination with the bimodal size distribution of the nanoparticles suggests that the presence of two close peaks at 557 and 563 nm can be explained by the size effect. However, the spectra of the colloidal solutions with nanoparticles larger than 30 nm feature the same peaks.

To study the fine structure of the spectra of a nanocrystal ensemble one has to implement size-selective luminescence techniques at low temperature. We can only make certain assumptions on the nature of the peaks because accurate identification of the fluorescence spectra of such compounds is difficult due to a number of reasons. In particular, lattice defects in II–VI semiconductor compounds can lead to the formation of deep centers, which play an important role in recombination processes. Cadmium vacancies can appear in different charge states, whereas the Jahn–Teller distortion of the crystal lattice – the displacement of an atom toward the nearest interstice – results

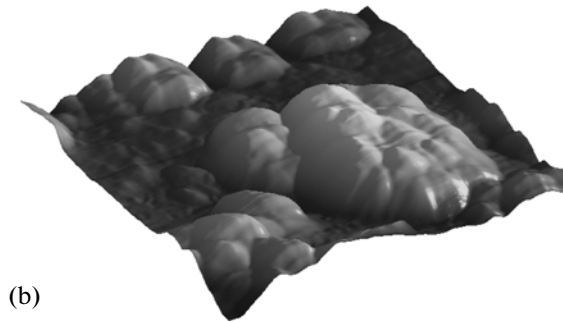
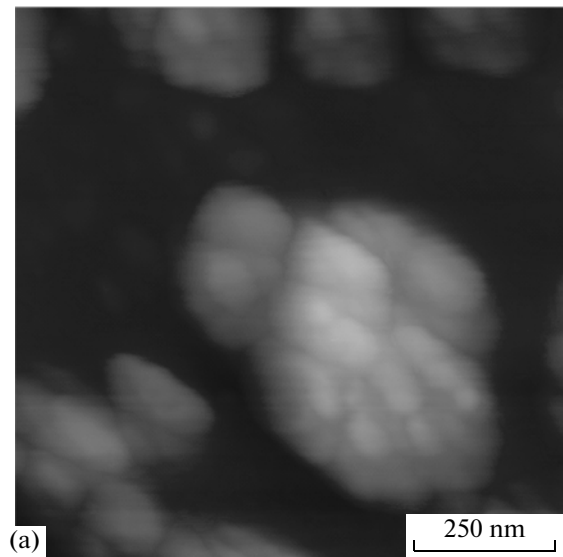


Fig. 7. (a) Two-dimensional and (b) three-dimensional intermittent-contact atomic force microscopy images of the profile of the surface covered by CdS nanoparticles.

in breaking the bond with an atom of the adjacent sublattice. These phenomena can lead to the formation of various complexes, to which excitons are bound. The relation of two possible structural modifications of CdS, wurtzite and zinc-blende ones, with the size of nanoparticles and their optical spectra was studied in [13, 14]. These investigations imply the following general conclusion. Each structural modification or their combination at a phase transition contribute to fluorescence spectra and determine the optical properties of the nanoparticles. Lozada-Morales et al. [14] studied polycrystalline CdS films on glass. The emergence of a yellow line in the fluorescence spectra of the film was attributed to the simultaneous presence of two phases and the formation of Frenkel (interstitial Cd atom–Cd vacancy) pairs at the cubic-to-hexagonal phase transition. The formation of a Frenkel pair is associated with a change in the position of a cadmium atom under structural transformation. At this point, there are two peaks separated by 0.02 eV in the fluorescence spectrum. When the hexagonal phase starts to dominate, the Frenkel pairs decay and the intensity of the yellow line decreases considerably. On the other

hand, in our previous work [15], we showed that CdS nanoparticles similar to those studied in this work have a disordered structure. Their lattice consists of alternating atomic layers typical for α or β phase of CdS. If only first three coordination spheres are taken into account, this disordered structure supports two possible surroundings of a cadmium atom. Presumably, the appearance of two peaks in the fluorescence spectrum separated by 0.02 eV is associated with the disordered nature of the structure and, consequently, with two different surroundings of a cadmium atom, which are inherent to wurtzite and zinc-blende structure.

Zhao et al. [16] considered the energy level diagrams of CdS–glass composites and colloidal solutions of CdS. They mentioned that it is more difficult to observe the emission of free excitons in the colloidal solutions owing to the presence of a large number of V_S , V_{Cd} , I_S , etc., defects and surface states. These defects behave as traps for free excitons. Colloidal solutions inhere the appearance of deep levels in the bad gap associated with interstitial sulfur, sulfur vacancies and surface Cd atoms. According to this scheme, the above lines in the fluorescence spectrum can be contributed to by the recombination of conduction-band or I_S electrons with V_{Cd} holes.

According to Zhao et al. [16], the width of the band gap of colloidal solutions of CdS is 2.62 eV, somewhat lower than for composites. This value nearly coincides with the width 2.66 eV of the band gap previously found from the absorption spectra of the colloidal solutions studied in this work.

4. CONCLUSIONS

Thus, quantum dots produced by wet chemical deposition in an aqueous solution have been investigated by various physical methods. It has been shown that the majority of nanoparticles are smaller than 10 nm. According to atomic force and confocal microscopy, the average nanoparticle size is 3 nm. In addition to these particles, the samples include small number of larger ones with a size of about 40 nm. Fluorescence spectra of CdS quantum dots exhibit intense peaks at 557 and 563 nm and a broad long-range peak. The presence of a double peak at 557 nm can be due to the disordered atomic structure of the nanoparticles.

ACKNOWLEDGMENTS

We are grateful to N.S. Kozhevnikova for the synthesis of the CdS quantum dots and to K.D. Kuznetsov for his assistance in performing the measurements.

This study was supported by the Russian Foundation for Basic Research (project no. 11-03-00257) and the Ural Branch of the Russian Academy of Sciences (project no. 12-P-234-2003).

REFERENCES

1. A.P. Alivisatos, *Semicond. Clusters Sci.* **271** (5251), 933 (1996).
2. M. A. Hines, and P. Guyot-Sionnest, *J. Phys. Chem.* **100** (2), 468 (1996).
3. N. Jumaa, M. Lansalot, A. Thretts, A. Elaissari, A. Sukhanova, M. Artemyev, I. Nabiev, and J. N. M. Cohen, *Langmuir* **22** (4), 1810 (2006).
4. A. A. Rempel', *Usp. Khim.* **76** (5), 474 (2007).
5. S. V. Rempel, N. S. Kozhevnikova, N. N. Aleksandrova, and A. A. Rempel, *Inorg. Mater.* **47** (3), 223 (2011).
6. S. V. Rempel', N. S. Kozhevnikova, N. N. Aleksandrova, and A. A. Rempel', *Dokl. Chem.* **440** (Part 1), 241 (2011).
7. H. Yukselici, P. D. Persans, and T. M. Hayes, *Phys. Rev. B: Condens. Matter* **52** (16), 11763 (1995).
8. P. B. Kocherginskaya, A. V. Romanova, I. A. Prokhorenko, D. M. Itkis, V. A. Korshun, E. A. Gudilin, and Yu. D. Tret'yakov, *Usp. Khim.* **80** (12), 1263 (2011).
9. S. I. Pokutnii, *Semiconductors* **44** (4), 448 (2010).
10. N. S. Kozhevnikova, A. S. Vorokh, and A. A. Rempel', *Russ. J. Gen. Chem.* **80** (3), 391 (2010).
11. V. I. Roldugin, *Usp. Khim.* **73** (2), 124 (2004).
12. A. I. Ekimov, I. A. Kudryavtsev, M. G. Ivanov, and Al. L. Efros, *Sov. Phys. Solid State* **31** (8), 1385 (1989).
13. N. G. Piven, L. G. Shcherbak, P. I. Feichuk, S. M. Kalitichuk, S. G. Krylyuk, and D. V. Korbutyag, *Kondensirovannyye Sredy Mezhfaznye Granitsy* **8** (4), 315 (2006).
14. R. Lozada-Morales, O. Zelaya-Angel, and G. Torres-Delgado, *Appl. Phys.* **73**, 61 (2001).
15. A. Rempel and A. Magerl, *Acta Crystallogr., Sect. A: Found. Crystallogr.* **66**, 479 (2010).
16. X. S. Zhao, J. Schroeder, P. D. Persans, and T. G. Bilo-deau, *Phys. Rev. B: Condens. Matter* **43** (15), 12580 (1991).

Translated by A. Safonov