

# Synthesis of CdSe Colloidal Quantum Dots and Quantum Transitions under Action of Low Power Optical Excitation

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**Abstract** — CdSe colloidal quantum dots were synthesized at low temperature (80-85 °C) on the basis of chemical reactions in colloidal solutions using trioctylphosphine (TOP), pure Se, oleic acid and cadmium acetate Cd(CH<sub>3</sub>COO)<sub>2</sub>. The average size of the synthesized nanocrystals is 2.04 nm, that is less than exciton Bohr radius in the bulk material, which is equal to 5.6 nm. Therefore in such QDs the electron with spin 1/2 and the hole with total angular momentum 3/2 are in localized or slightly delocalized states. In absorption spectra in the UV-VIS range the lines corresponding to quantum transitions between hole state 1S<sub>3/2</sub>(h), 2S<sub>3/2</sub>(h), 1P<sub>3/2</sub>(h) and electron state 1S<sub>1/2</sub>(e), 1P<sub>1/2</sub> (1S<sub>3/2</sub>(h) → 1S<sub>1/2</sub>(e), 2S<sub>3/2</sub>(h) → 1S<sub>1/2</sub>(e) and 1P<sub>3/2</sub>(h) → 1P<sub>1/2</sub>(e)) are detected.

The location of photoluminescence maxima of QDs in hexane and in powder state coincide in the limits of experimental errors (570 and 568 nm, respectively). In photoluminescence spectra of powder QDs a broad long-wavelength band of low intensity with maximum at 570 nm was detected.

**Index Terms** — CdSe nanoparticles, colloidal synthesis, photoluminescence, absorption, quantum dots.

## I INTRODUCTION

The unique properties of semiconductor quantum dots (QDs) are due, in particular, to their atomic-like density of states. The atomic-like state density behaviour leads to the relative ease of generating single excitations, single spins per dot, and the long lifetime and coherence time of these excitations [1-5]. Unlike “real” atoms or molecules, a unique feature of solid state QDs is the formation of Wannier-Mott excitations giving experimental access to both the Coulomb and the electron-hole exchange interaction in three-dimensionally confined solid state systems. Therefore, QDs have recently attracted much interest both experimentally and theoretically.

In contrast to quantum well, the colloidal QDs are frequently suspended in a solvent or matrix. Even rather large colloidal structures of up to 10 nm significant fraction of the atoms is located on the surface [6]. Charging effects resulting from dangling bonds or strain in the nanocrystals are therefore profoundly affecting the photophysics of such systems [7-9].

The excitons in QDs differs from excitons in bulk materials and represent a distinct class of excitons that differs from bulk-type excitons or molecular excitations. The new aspect of the excitations that is prevalent in nanoscience is that the physical size and the shape of the material strongly influence the nature and dynamics of the electronic excitation. Therefore, a deciding property of excitons in nanoscale systems is that the exciton size is dictated not by electron-hole Coulomb interaction, but by physical dimensions of the material or the arrangement of distinct building blocks. Interesting spectroscopic properties of excitons, which are often miniscule in the

bulk materials, are greatly accentuated in nanometer-sized materials and molecules. For example, the electron-hole exchange interaction is of the order of millielectron volts in bulk semiconductor materials, but is increased 1,000 fold in QDs [10-16]. Nanoscale excitons can be described starting from the point of view of either a delocalized or localized excitation. In a delocalized representation of the problem, nanoscale excitons are subject to quantum confinement and their spectroscopy become richer.

In this paper, the results concerning synthesis of CdSe colloidal QDs at relatively low temperatures (80-85 °C) are presented. On the basis of the powder XRD data their structural parameters were determined. The optical absorption in the UV-VIS range was studied. The photoluminescence spectra at optical excitation by two low power (10 mW) light emitters with 392 nm wavelength were investigated too. The photoluminescence spectra were studied using a setup built on the basis of monochromator MДP-23.

## II. METHODS

**Chemicals.** Tri-*n*-octylphosphine (Aldrich, 90%), selenium shot (Aldrich, 99.999%), diphenyl ether (DPE) (Fluka, 98%), cadmium acetate dihydrate (Aldrich, 99.999%), and oleic acid (cis-9-octadecenoic acid, Aldrich, 90%) were used as purchased without further purification.

Anhydrous, hexane, chloroform, acetone, were purchased from different companies and used without further purification. Trioctylphosphineselenide, 1M, (TOP-Se) was prepared by the complete dissolving of the necessary amount of selenium in 50 ml of TOP at 60–70°C under moderate stirring. The TOP-Se solution

described above was prepared and stored in a argon glove box.

**Synthesis.** As a basis for the synthesis was taken the method describing the procedure of preparing cadmium selenide nanoparticles. [17, 21, 22].

A standard synthesis of CdSe nanoparticles was performed in a round-bottom three-neck flask equipped with a magnetic stirrer, a thermocouple, and a temperature control unit. Cadmium oleate was prepared by heating a mixture of 2 mmol cadmium acetate, 4 mmol of oleic acid, and 20 mmol 20 ml of diphenyl ether. Oleic acid was employed both for group II precursor formation and nanoparticle stabilization during the synthesis intended for nucleation and reaction rate control. The subsequent synthesis of cadmium selenide QDs was carried out by rapid injection of trioctylphosphine selenide (TOP-Se) solution maintained at room-temperature into a vigorously stirred mixture containing cadmium oleate heated from 80 to 85°C under Ar atmosphere. The reaction mixture was maintained at a fixed temperature for 6 hours and then promptly cooled to room temperature using an ice-water bath. The solution quickly turned dark citric during the synthesis due to the formation of CdSe colloidal solution.

A solvent containing two parts of hexane, one part of anhydrous ethanol, and five parts of acetone was prepared to purify the nanoparticles from unreacted precursor, excess surfactant, and high-boiling point solvents. A size-selective precipitation was carried out by centrifugation, using a polar/nonpolar solvent combination, consisting of acetone and either hexane. After precipitation, the CdSe nanoparticles were isolated and re-suspended in chloroform and hexane, and followed by ultrasonic treatment to form stable colloidal solutions used for further preparation and characterization. The chemical analysis and atomic absorption spectroscopy confirmed the CdSe composition of the nanomaterial deposited after multiple purifying and re-suspension of the original solution.

**Nanocrystalline sample characterization.** The powder XRD data were recorded with Fe K<sub>α</sub> radiation (λ = 1.93728 Å) using DPOH-YM 1 with Mn filter operating in the Bragg–Brentano geometry. Samples for the XRD measurements were prepared by the deposition of concentrated CdSe colloidal solutions in chloroform or trichloroethylene onto a glass substrate. The 2θ range scanned from 20° to 80°, TOPSe/cadmium oleate molar ratio *r* = 2.0. Diphenyl ether was used as the high-boiling heat-transfer agent. As mentioned above, the samples were prepared for X-ray powder diffraction by depositing the colloidal solution onto a glass substrate drop wise.

### III. RESULTS AND DISCUSSION

The typical powder diffraction patterns of resulting CdSe nanocrystals are shown in Fig. 1.

XRD revealed three broad peaks positioned at 2θ = 31°, 52.50° and 64° with corresponding interplanar spacings of 3.510, 2.149 and 1.833Å, respectively (Table 1). These peaks are uniquely assigned to the (111), (220) and (112) planes of sphalerite structure of CdSe implies a reduction in particle size.

In Table.1 θ, d, β, D and *a* are the diffraction angles, the interplanar distance, the width of the XRD line at half maximum, which were determined at different diffraction angles, size of QDs and the crystalline cell parameter,

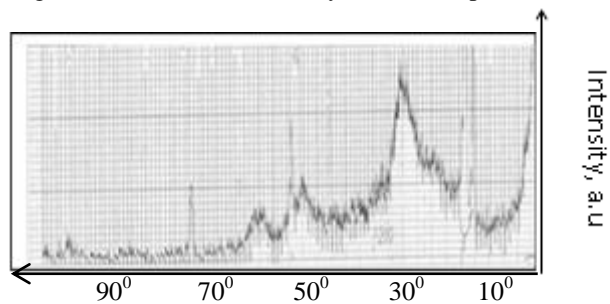


Fig.1. The powder diffraction patterns of CdSe QDs synthesized at the relatively low temperatures (80°-85°C).

respectively.

An average size of 2.04 nm for the CdSe nanocrystals was estimated from X-ray powder diffraction data using Debye-Scherrer equation

$$d = k\lambda/\beta\cos\theta, \quad (1)$$

where k=0.9 (the QDs are considered spherical shape). In (1) λ means the wavelength of the centre of gravity of the X-Ray doublet (K<sub>α1</sub>,K<sub>α2</sub>) of K-01series:

$$\lambda_{K\alpha} = \frac{2\lambda_{K\alpha_1} + \lambda_{K\alpha_2}}{3}, \quad (2)$$

where λ<sub>Kα<sub>1</sub></sub> = 1.93597Å and λ<sub>Kα<sub>2</sub></sub> = 1.93991 Å.

Table1. X-Ray diffraction data for CdSe QDs.

N <sub>o</sub>	θ	d, Å	β,rad	Miller indexes	D,Å	a, Å
1	15.5°	3.510	0.1047	(111)	16.99	6.0794
2	26.25°	2.149	0.0872	(220)	21.86	6.0782
3	32°	1.833	0.0872	(311)	23.42	6.0793

From small angles in the Fig.1 two intensive bands are shown corresponding to unsolved X-ray doublet Fe K<sub>α</sub> and single emission line Fe K<sub>β</sub>, the intensity of which is far above CdSe QDs XRD lines intensities.

At 2θ = 57° and 78.5° on the Fig.1 are manifested two intense lines, one more line of low intensity in this series is observed at large diffraction angles 2θ = 104.5°. These three lines correspond to third, fourth and fifth order reflections from atomic planes (300), (400) and (500). Their occurrence is due to the fact that, during the measurements, the samples were not prepared using adhesives. The nanocrystalline samples were slightly pinched on the substrate, whereupon the resulting mechanical stress could lead to texturing samples – formation of a system of parallel planes (200), (300), (400). However, this effect requires a more detailed research.

To study the photoluminescence of colloidal CdSe QDs

two low power (10 mW) light emitters with 392 nm wavelength were used.

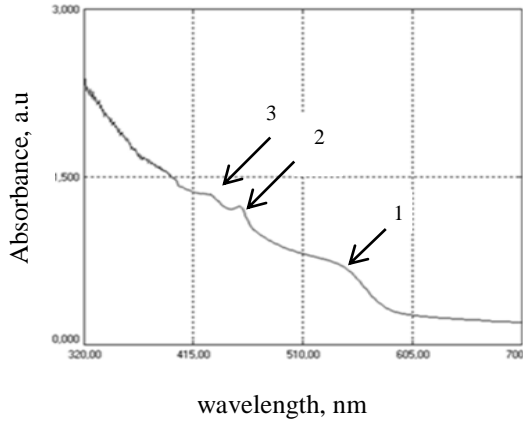


Fig.2. The absorption spectrum of CdSe QDs in hexane.

Quantum transitions on the Fig.2 : 1 -  $1S_{3/2}(h) \rightarrow 1S_{1/2}(e)$ ,  
 2 -  $2S_{3/2}(h) \rightarrow 1S_{1/2}(e)$ ,  
 3 -  $1P_{3/2}(h) \rightarrow 1P_{1/2}(e)$ .

In the Fig. 2 the absorbance spectrum of the CdSe QDs in hexane at low concentration of the solution is shown. The solution itself has an orange color.

In the Fig. 3 the photoluminescence spectrum is presented of the same solution, containing QDs, the optical absorption spectrum of which was shown in the Fig. 2.

In the Fig. 4 the photoluminescence spectrum of the same CdSe QDs in solid state is shown.

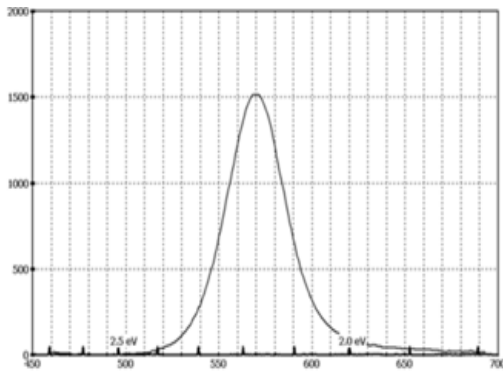


Fig. 3. The photoluminescence spectrum of CdSe QDs in hexane.

The peculiarities of the optical absorbance of CdSe QDs are well corresponding to the theory. Let us to consider the case when the dimensions of QDs are less than the exciton Bohr radius in bulk samples. Exactly this case is being observed for CdSe QDs with dimensions of several nanometers while the exciton Bohr radius in the bulk CdSe is  $a_{ex}^{bulk} = 5,6 \text{ nm}$  [18]. This case corresponds to almost full localization or slightly delocalization of the electron and hole and the energy spectrum of QDs is a set of discrete slightly broadened levels of electrons and holes.

The discrete structure of the energy spectra for CdSe QDs is being demonstrated, first of all, by optical absorbance

spectra. Due to the narrow distribution by size of QDs, on these spectra are readily evident the particularities corresponding to interband optical transitions, related to different electron and hole quantum states. These properties

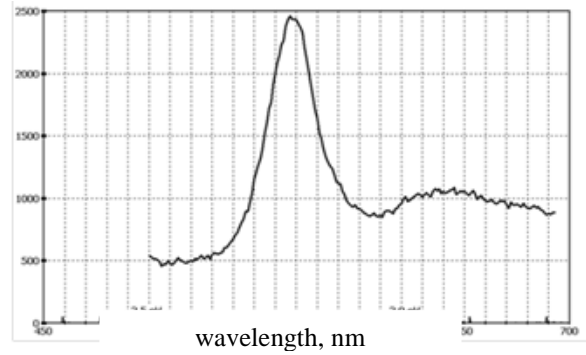


Fig. 4 . The photoluminescence spectrum of powder CdSe QDs.

may be described within the framework of effective mass model, if it is taken into account the splitting of valence band into three valence subbands due to quantum restrictions.

The probabilities of the optical transitions at band edges in QDs are governed by the matrix element of the operator  $e\mathbf{p}$  between the states at the valence band top and the bottom of the conduction band, where  $\mathbf{p}$  is the momentum operator and  $\mathbf{e}$  is the polarization vector of the emitted or absorbed photon. The electron wave function,  $1S_e$ , at the bottom of the conduction band can be written as [19]

$$\Psi_e(\mathbf{r}) = j_0(k_1^0 r) Y_{00}(\theta, \varphi) |S_\alpha\rangle \quad (3)$$

where  $|S_\alpha\rangle$  is the Bloch function of the conduction band,  $\alpha$  is the projection of the electron spin,  $Y_{00}$  is the spherical harmonics and  $j_0(k_1^0 r)$  is the spherical Bessel function.

Optical transitions from the electron state (3) are possible only to the hole states in the valence bands which have the S-state as a component because

$$\int Y_{Lm} Y_{00} d\Omega = \delta_{L,0} \delta_{m,0}.$$

The optical transition probability from the bottom of the conduction band to a hole state in the value band is given by [19]

$$P_{\alpha\beta} = \left| \int dr r^2 j_0(k_1^0 r) (cR_0(r)) \right|^2 \left| \langle u_\mu \beta | e\mathbf{p} | S_\alpha \rangle \right|^2,$$

where  $c$  is the component of the S-state  $R_0(r)$  in the hole wave function,  $\beta$  is the spin projection of the removal electron in the hole state and  $u_\mu$  are Bloch wave functions of the hole states:  $u_\pm = |1, \pm 1\rangle$ ,  $u_0 = |1, 0\rangle$ .  $P_{\alpha\beta}$  is zero if  $\alpha \neq \beta$ .

Optical transitions from the bottom of the conduction band to the top of the valence band are not possible in the following cases:

- 1) if the hole state does not have a component of the S-state (i.e. if  $c = 0$ );
- 2) if the spin projections of the removal electron in the hole state and the electron in the conduction band are not equal,  $\alpha \neq \beta$ . Since the spin projection of the hole state is obtained by flipping the spin projection of the electron removed, it follows that the optical transitions are

not possible if the spins of the electron and the hole are parallel. Thus, if the top of the valence band is a P-state, or the electron at bottom of the conduction band and the hole at the top of the valence bande are in a triplet state , a dark exciton is formed [20].

The first two bands, from left to right, in the absorption spectrum plotted in the Fig.2 correspond to the wavelengths 544 nm and 456 nm and are related with transitions between the lowest level of the electron (1S) and two different hole energy states (1S<sub>3/2</sub> and 2S<sub>3/2</sub>). Electron and hole are the more localized if the inequality  $R < a_{ex}^{bulk}$  is better satisfied (R is the quantum dot radius). The third absorption band located at 393 nm is due to quantum transitions between 1P<sub>3/2</sub> hole state and 1P<sub>1/2</sub> electron state.

#### IV. CONCLUSIONS

1. At relatively low temperature synthesis, the high quality nanocrystals CdSe with average size 2.04 nm. were obtained.
2. In the absorption spectrum of CdSe QDs in the UV-VIS range the quantum transitions 1S<sub>3/2</sub>(h)→1S<sub>1/2</sub>(e), 2S<sub>3/2</sub>(h)→1S<sub>1/2</sub>(e) and 1P<sub>3/2</sub>(h)→1P<sub>1/2</sub>(e) were identified.
3. From CdSe QDs XRD data the texturing of QDs along the direction perpendicular to the planes of the type (h00) due to the slight mechanical stress was found.
4. The photoluminescence spectra at optical excitation of nanocrystals by means of two low power (10mW) light emitting diodes at wavelength  $\lambda = 396$  nm were detected and investigated.
5. It is shown that positions of photoluminescence maxima for powder QDs and dissolved in hexane QDs coincide to within the accuracy of measurement ( $\pm 1$  nm). However their full width at half maximum are different ( $\Delta\lambda_1 = 30$  nm,  $\Delta\lambda_2 = 30$  nm, respectively).

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