

Optical properties of CdS and PbS nanocrystals adsorbed on silica nanoparticles

*Yu.V.Yermolayeva, N.A.Matveevskaya,
V.P.Semynozhenko, A.V.Tolmachev*

STC "Institute for Single Crystals", Institute for Single Crystals, National Academy of Sciences of Ukraine, 60 Lenin Ave., 61001 Kharkiv, Ukraine

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The adsorption mechanism of CdS and PbS semiconductor nanocrystals on the surface of spherical silica particles has been investigated. The presence of quantum size effects in the "core-shell" heteronanostructures with dielectric SiO₂ core and semiconductor shell consisting of nanocrystals has been established. Influence of the core size and a degree of its covering with CdS, PbS nanocrystals on optical properties of heteronanostructures has been shown.

Изучен механизм адсорбции полупроводниковых нанокристаллов CdS и PbS на поверхности сферических наночастиц диоксида кремния. Установлено наличие квантовых размерных эффектов в гетеронаноструктурах типа "ядро-оболочка" с диэлектрическим ядром SiO₂ и нанокристаллической полупроводниковой оболочкой. Показано влияние размера ядра и степени его заполнения нанокристаллами CdS, PbS на оптические свойства гетеронаноструктур.

In last decades, the interest of researchers is seen to be turned sharply to the field of nanodimensional structures. The most perspective is investigation of optical properties of semiconductor nanoparticles of a size comparable to the Bohr exciton radius, where the quantum size effects appear because of changes in the electron structure of semiconductor crystal [1, 2]. These changes result mainly in a band gap broadening of the semiconductor ("blue" shift of the fundamental absorption edge), quantization and reduction of electronic state density at edges of the conduction and valence bands [3]. Thus, it is possible to change the energy spectrum of the system by varying the semiconductor crystal size (quantum confinement value) that promotes the optimization of the known semiconductor devices and the development of new ones.

Methods for preparation and investigation of semiconductor nanoparticles are widely presented in literature, the most studied are nanoparticle of cadmium, lead,

zinc chalcogenides [2, 4–7]. However, development of ordered structurization methods is necessary to provide materials on the basis of semiconductor nanocrystals with preservation of quantum size effects. Two ways to nanostructured materials have been defined in the last decade. The first is volumetric structurization of nanocrystals in the matrix voids, e.g., in long polymeric molecules; the second consists in formation of nanoparticles on a nanoparticle surface (SiO₂, Al₂O₃, polymeric nanoparticles) [8–11]. Nanomaterials of the surface type are more chemically active than materials with nanoimpurities in bulk, that is why they are more perspective for making various luminous diodes, the sensor controls, new effective catalytic agents [12, 13].

Heteronanostructures with dielectric silica core and an external shell consisting of metal particles (Au, Ag) [14] and semiconductors particles (CdS, CdSe, ZnS) have been obtained before [8–10]. However, the question of an opportunity to manage the

optical parameters of semiconducting heteronanostructures is still open. In this connection, the purpose of our research was to study the directional surface adsorption process of semiconductor nanocrystals (CdS, PbS) on silica particles of various diameter, to investigate the manifestations of quantum size effects of CdS, PbS nanocrystals in optical absorption spectra and influence of semiconductor shell composition and the core size on light absorption by SiO₂/CdS, SiO₂/PbS heteronanostructures.

The nanocrystals were obtained by colloid synthesis in aqueous solutions in presence of poly(acrylic) acid as a stabilizer. As precursors, cadmium and lead nitrates and sodium sulfide were used. The monodispersed spherical shape silica nanoparticles have been prepared by tetraethyl orthosilicate hydrolysis using the modified Stober method [15]. The size of obtained silica nanoparticles (40–350 nm) was controlled by varying the reaction time, ratio of reagents, and temperature. To prepare heteronanostructures, the surface of silica nanoparticles has been modified using bifunctional organic compound, 3-aminopropyl triethoxysilane, which forms covalent chemical bond with silanol groups of the core and provides connection of a semiconductor shell to the core due to the amino group. Synthesis of core-shell heteronanostructures with dielectric silica core and semiconductor shell was carried out varying the core diameter (40 nm, 100 nm, 350 nm) and the density of its covering with semiconductor nanoparticles. The colloid solution of synthesized nanocrystals with the specified concentration was mixed with aqueous suspension of SiO₂ particles. The synthesis was carried out at low concentrations of semiconductor solutions ([CdS] = 2·10⁻⁴ mol/l, [PbS] = 2·10⁻⁵ mol/l) to prevent formation of conglomerates on the silica surface. The precipitate of obtained heteronanostructures was separated and dispersed by ultrasound in a small amount of water. To get a thicker coating, the procedure was repeated. Such stage-by-stage shell formation provides uniform distribution of semiconductor nanocrystals on the silica surface.

The photometer method was used to determine the concentration of adsorbed PbS nanocrystals on the silica surface. It was calculated that at each stage of the shell formation, an average of 5·10² PbS nanocrystals are adsorbed on a core. Transmission electron microscopy of synthesized

nanostructures was performed using a EM-125 microscope at the accelerating voltage 100 kV. The samples were prepared using a standard procedure by placing a drop of aqueous solution of nanoparticles onto carbon film deposited on a copper grid. Optical absorption spectra of the colloid solutions of nanostructures were measured in the wavelength range 200 to 900 nm using Specord M-40 spectrophotometer in a quartz cell of 1 cm thickness. The phase composition of CdS and PbS nanoparticle samples was examined by X-ray diffraction using DRON-2.0 (Fe_α radiation, λ = 1.93728 Å, the scanning field 2θ = 20 to 110°). The samples were prepared by precipitation of nanocrystals from the concentrated colloid solution using an OPN-3 centrifuge and drying of obtained precipitate.

The colloid synthesis method is technologically simple, does not demand special equipment and allows to obtain CdS, PbS nanocrystals of a specified size and narrow size distribution (<15 %) and at the same time to structure them on silica particle surface. An advantage of this method is that semiconductor nanocrystals are anchored on a surface of spherical silica particles, while being available for "external" actions, e.g., for interaction with light quanta. The obtained solutions of SiO₂/CdS, SiO₂/PbS heteronanostructures show stability against aggregation during several weeks at the core sizes less than 100 nm. Obtaining of photon crystals as close packing opal structures with adjustable properties is also possible at greater core sizes by natural sedimentation.

The size and morphology of synthesized nanostructures were examined by means of transmission electron microscopy (Fig. 1). It has been shown that CdS and PbS semiconductor nanocrystals are of 2 and 3 nm size, respectively, do not coagulate in solution, and are uniformly dispersed on the silica particle surface forming a monolayer of CdS or PbS nanocrystals. The monolayer thickness is defined by the nanocrystal size. The synthesized silica nanoparticles are of spherical shape and the preset size (40 nm, 100 nm, 350 nm) at a narrow size distribution (<10 %).

The phase composition of the obtained semiconductor PbS and CdS nanoparticles has been investigated by X-ray diffraction. X-ray diffraction spectra of the semiconductor nanocrystals CdS and PbS are presented in Fig. 2. The system of diffraction peaks indicates the cubic structure of CdS

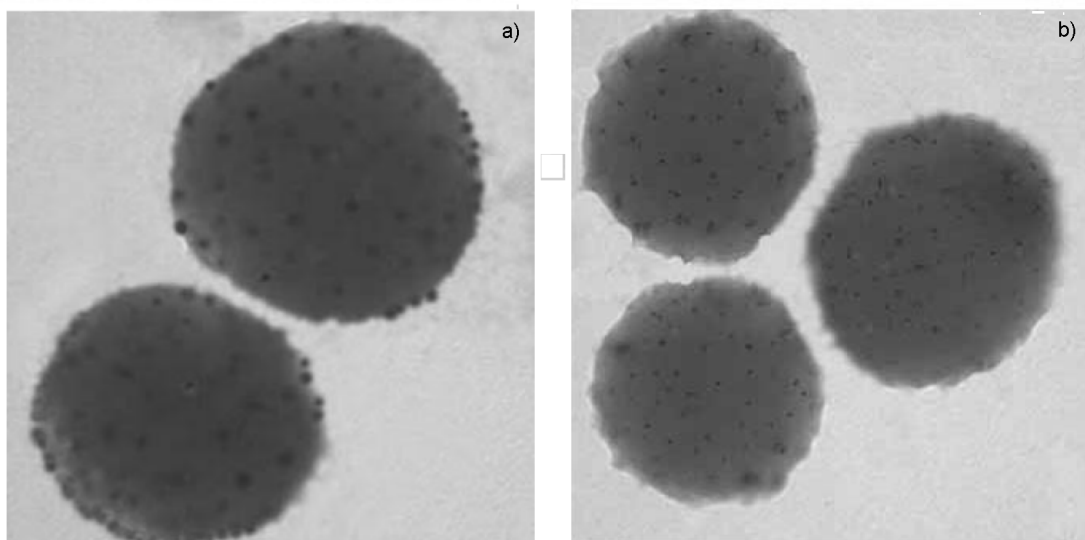


Fig. 1. Transmission electron microscopy images of heteronanoparticles SiO_2/PbS (a) and SiO_2/CdS (b). SiO_2 particle diameter 100 nm.

and PbS nanocrystals with the period 5.82 Å and 5.95 Å, respectively. The broadening of diffraction peaks is due to the finite size of the nanocrystals and indicated that the dimensions of the nanoparticles are very small. The size of semiconductor nanocrystals were estimated using the Scherrer equation [16]. The size of CdS and PbS nanocrystals (coherent dispersion field) is 2.3 nm and 8.0 nm, respectively, which is in good accordance with sizes determined by transmission electron microscopy.

The light absorption by semiconductor nanocrystals with non-degenerate energy bands depends on two factors: width of a band gap between allowed bands (the optical band gap energy E_g) and densities of the defective levels in the optical band gap energy. The first factor defines the position of the absorption edge in the long-wave area relative to the expected absorption edge for bulk material (blue-shifted absorption edge when the band gap energy increases), while the second, the shape of absorption edge and intensity of absorption in the field of $h\nu < E_g$ (where $h\nu$ is the photon energy) [1, 3].

Optical absorption spectra semiconductor nanocrystals in solutions are presented in Fig. 3. The absorption edges are characterized by sharply expressed absorption at $h\nu = E_g$ with negligible absorption at $h\nu < E_g$, thus evidencing that light absorption by CdS and PbS nanocrystals results from the allowed direct band-to-band electron transitions.

Absorption of a light quantum by semiconductor nanocrystals with the energy ex-

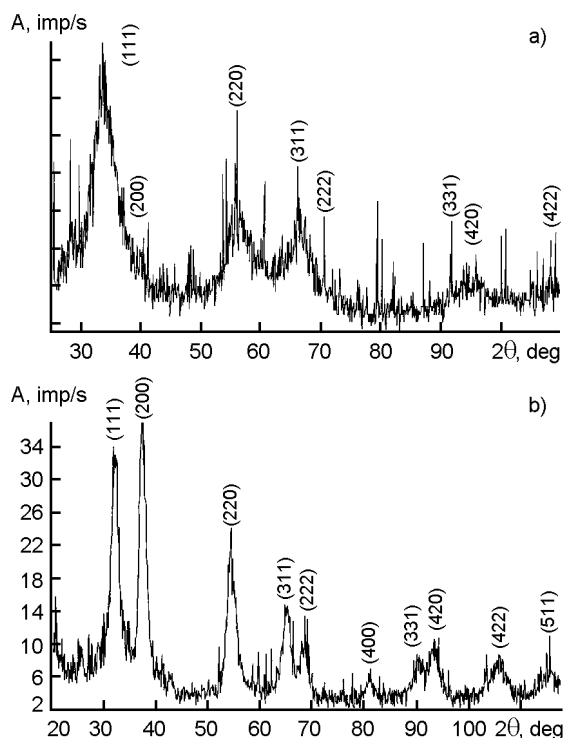


Fig. 2. X-ray diffraction of CdS (a) and PbS (b) nanocrystals.

ceeding E_g results in formation of an electron-hole pair connected together due to Coulomb interaction. The Coulomb interaction between opposite charges restricts their free motion, thus, they move as a single whole and can be considered as a quasi-particle. Excitonic states in the bulk semiconductors can be easily destroyed by a thermal motion of the lattice because of small bind-

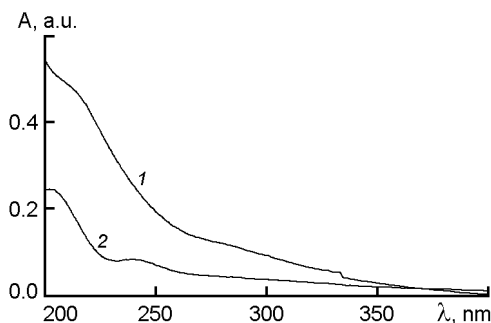


Fig. 3. Optical absorption spectra for water solutions of CdS (1) and PbS (2) nanocrystals.

ing energies and large exciton radius. In low-dimensional systems, excitonic states are stable in a much wider temperature range; that results in a series of exciton peaks at the fundamental absorption edge [3]. For CdS nanocrystals, two stable exciton maxima are observed near 220 and 340 nm. The position and intensity of peaks is maintained in absorption spectra of SiO₂/CdS heteronanostructures, that confirms conservation of quantum size effects for CdS nanocrystals adsorbed on silica surfaces. Exciton maxima for PbS nanocrystals are observed near 210 and 250 nm. Exciton maximum near 210 nm is maintained for SiO₂/PbS heteronanostructures (Fig. 4).

As the coating density of a core with semiconductor increases, the peak position is kept. Increase of the maximum intensity appears at concentration of semiconductor nanocrystals $1.5 \cdot 10^3$ per one silica particle (Fig. 4, curve 2). The further increase of semiconductor nanoparticle concentration in the solution and on the silica surface (10^4 particles and more) results in deterioration of all exciton states due to a shielding of Coulomb interactions as it occurs in bulk semiconductor samples (Fig. 4, curve 4). Exciton maxima in this case are also merged with the common spectrum edge.

The optical band gap energies and diameters of CdS and PbS particles in solution and on silica surfaces have been calculated (Table). Calculations have shown a significant increase of optical band gap energies for CdS and PbS semiconductor nanocrystals as compared to the bulk samples (ΔE makes 4.5 eV and 1.9 eV for PbS and CdS, respectively) that is manifested in absorption spectra for semiconductor nanoparticles as a blue shift of long-wavelength fundamental absorption edge. The size of nanocrystals has been calculated under effective mass approximation which is based

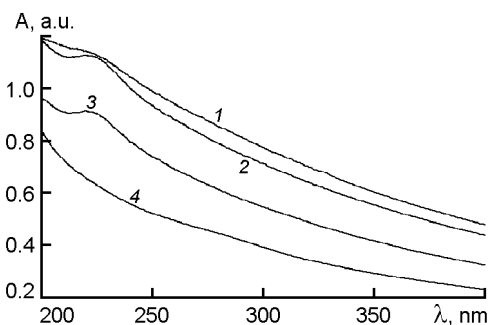


Fig. 4. Optical absorption spectra of aqueous solutions of SiO₂/PbS heteronanoparticles. Number of PbS particles per one SiO₂ particle: $5 \cdot 10^2$ (1); $1.5 \cdot 10^3$ (2); $2 \cdot 10^3$ (3); $1 \cdot 10^4$ (4). SiO₂ particle diameter 100 nm.

on the assumption of the effective mass invariance for electron and hole when passing from bulk to nanodimensional systems [16].

Heteronanostructures of the core diameter of 40 nm, 100 nm, 350 nm and identical core coating density with semiconductor nanocrystals have been synthesized to analyze the core size influence on light absorption by SiO₂/PbS and SiO₂/CdS heteronanostructures. It has been established that the adsorption process of nanocrystals on the silica surface runs in the same manner for all the core diameters and is quantitatively defined only by the surface area of silica particles. Absorption spectra of obtained SiO₂/PbS colloid solutions with various diameter of a core are presented in Fig. 5. The position of exciton maxima is kept at all core diameters, and their intensity depends only on the semiconductor shell density.

It is established in experiment that the shell consisting of PbS or CdS monolayer is formed in our synthesis conditions, nanocrystals do not form conglomerates on the core surface what is testified by keeping of the nanocrystal size at adsorption on the silica surface. It is possible to approve that the core in heteronanostructures acts as a

Table . Optical band gap energy and diameters of PbS and CdS nanocrystals in the solution and on the surface of silica particles

	E_g , eV	R , nm
PbS	4.90	3.0
SiO ₂ /PbS	4.85	3.1
CdS	4.28	2.2
SiO ₂ /CdS	4.25	2.4

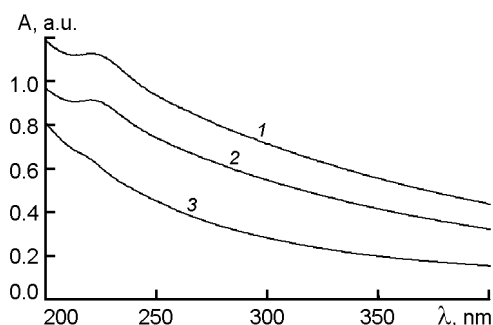


Fig. 5. Optical absorption spectra of aqueous solutions of SiO_2/PbS heteronanoparticles with of the core diameter (nm): 350 (1); 100 (2); 40 (3).

support only and does not influence essentially the optical characteristics of PbS and CdS semiconductor nanocrystals.

To conclude, the adsorption mechanism of CdS and PbS semiconductor nanocrystals on the surface of spherical silica particles has been studied. The method of stage-by-stage shell formation has been developed that provides a uniform distribution of semiconductor nanocrystals on the silica core surface. It has been calculated that at each stage of the core coating with semiconductor shell, average $5 \cdot 10^2$ semiconductor nanocrystals are absorbed per one silica particle. The presence of quantum size effects in "core-shell" heteronanostructures with the dielectric core SiO_2 and semiconductor shell has been established. It has been shown that it is obviously possible to adjust optical properties of heteronanostructures (intensity of exciton maximum) by changing the dielectric core coating density by CdS or PbS semiconductor nanocrystals, the core

size doing not influence the position and intensity of exciton maximum.

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Оптичні властивості нанокристалів CdS та PbS, адсорбованих на наночастинках діоксиду кремнію

Ю.В.Єрмолаєва, Н.А.Матвєєвська,
В.П.Семиноженко, О.В.Толмачов

Вивчено механізм адсорбції напівпровідникових нанокристалів CdS та PbS на поверхні сферичних наночастинок діоксиду кремнію. Встановлено наявність квантових розмірних ефектів у гетеронаноструктурах типу "ядро-оболонка" з діелектричним ядром SiO_2 та нанокристалічною напівпровідниковою оболонкою. Показано вплив розміру ядра й ступеня його заповнення нанокристалічними CdS та PbS на оптичні властивості гетеронаноструктур.