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Interaction of human serum albumin with CdTe quantum dots probed by optical spectroscopy methods

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ABSTRACT

In this work, colloidal CdTe nanoparticles were synthesized by using thioglycolic acid (TGA) as passivator. In the absorption spectra of the colloidal CdTe nanoparticles exciton band was found to be shifted to higher photon energy as compared with bulk crystals due to quantum confinement effect. It was shown that addition of human serum albumin (HSA) to colloidal CdTe nanoparticles led to a gradual decrease of absorption and broadening of exciton structure. However, energy position of the exciton band in this case remains not shifted. In photoluminescence spectra of solution CdTe quantum dots and HSA so-called quenching effect has been observed. The quenching of HSA fluorescence intensity by semiconductor nanoparticles was analysed in framework of the formation of quantum dots-HSA protein complex.

Keywords: CdTe, semiconductor nanoparticles, human serum albumin (HSA), optical density, photoluminescence.

1. INTRODUCTION

Over the past few decades, semiconductor nanoparticles (quantum dots) have attracted great interest because of their unique properties and various potential applications in different branches of science and technology. The tunable optical and electronic properties of the nanoparticles owing to quantum size confinement effect make them excellent objects in nanoscale photonic, photovoltaic and light-emitting diode devices. From point of view of biomedical applications II-VI semiconductor based nanoparticles are the most studied. Since their introduction as labels in cellular imaging in 1998 [1, 2], numerous reports have shown advantages of this kind of semiconductor nanoparticles before organic fluorophores. These advantages include broad absorption spectra, narrow photoluminescence spectra, size-tunable spectra and superior resistance to photobleaching, photostability, signal multiplexing and high sensitivity. In addition, II-VI semiconductor compounds have another functionality as a basic matrix for diluted magnetic semiconductors (DMSs), where a fraction of semiconductor cations are replaced by transition metals (3d or 4f elements). Among DMSs Mn-doped II-VI semiconductor based nanoparticles are the most promising because of their chemical stability and strong fluorescence in visible region. The main feature of bulk DMSs is the strong sp-d spin exchange interaction between the band carriers and the magnetic ions which results in a large Zeeman splitting of the valence and conduction band states, a giant Faraday rotation and the formation of magnetic polarons.

Due to the tremendous focus on applying the nanoparticles to biological and biomedical applications, there has been increasing interest in estimating the toxicity of II-VI undoped and doped semiconductor based nanoparticles.

It is well known that the human serum albumin (HSA) is the most abundant protein in blood plasma and involved in the transport of a variety of endogenous and exogenous ligands. Transportation, distribution, physiological and toxicological actions of the ligands in vivo are closely related to their binding with proteins. So, it is very significant to investigate the interaction between the nanoparticles and the major carrier protein like HSA. Several reports have been devoted to study such kind of interaction between II-VI semiconductor based nanoparticles and bovin serum albumin (BSA) and HSA. Xiao et al. [3] systematically investigated the interaction between charge-capped CdSe/ZnS quantum dots and BSA by

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UV-Vis absorption, fluorescence and circular dichroism spectroscopy under the physiological conditions. This group also studied [4] the conformation changes of HSA induced by CdTe quantum dots with different sizes and the obtained results indicated that the biological activity of HSA is weaker for quantum dots with bigger sizes. Wu et al. [5] reported on the interaction between BSA and ZnS quantum dots by spectroscopic techniques and showed strong quenching of fluorescence. Recently, Hemmateenejad and Yousefinejad [6] have revealed the presence of static type of quenching mechanism in the binding of ZnS nanoparticles to HSA. Bhogale et al. [7] studied the interaction of ZnO nanoparticles with HSA and discuseed the quenching of fluorescence of phluorophores in HSA, which was attrtibuted to formation of HSA-ZnO complex in the solution. Mansur et al. [8] reported on the bioconjugation of CdS quantum dots with BSA and showed that BSA is effective on stabilizing fluorescent quantum dots in aqueous dispersions. Nithyaja et al. [9] discussed band gap tenability of CdS nanoparticles in biotemplates BSA and demonstrated that the band gap of these semiconductor nanoparticles can be controlled effectively by changing the concentration of BSA biopolymer. Poderys et al. [10] showed that interaction of water-soluble CdTe quantum dots with BSA significantly enhanced stability and photoluminescence quantum yield of the quantum dots and prevented them from agglomerating. Concerning to study of DMDs nanoparticles and their interaction with BSA. HSA model proteins we have found two such papers. Khani et al. [11] applied the UV-Vis absorption and fluorescence spectroscopic methods to compare the optical properties of pure and iron doped ZnS quantum dots upon interaction with BSA. It was revealed the fluorescence quenching of BSA by the quantum dots due to formation of quantum dots-BSA complex in solution. Liu et al. [12] have studied the interaction of chitosan coated Fe_3O_4@ZnS:Mn magnetic fluorescent nanoparticles with BSA and have got evidence for the demage of BSA molecule in the presence of the nanoparticles under UV illumination.
Herein, we report on optical studies of CdTe nanoparticles and their interaction with HSA. Main attention is paid to conventional UV-Vis absorption and fluorescence spectroscopic methods.

2. EXPERIMENTAL

Among different technological approaches for growth of CdTe nanoparticles we have chosen previously reported method of colloidal chemistry. Aqueous synthesis of nanoparticles offer many benefits for biological studies. The synthesis of particles in a solution occurs by chemical reactions resulting in the formation of nuclei and subsequent particle growth. Nanoparticles of CdTe were synthesized in aqueous solution at room temperature using procedure similar to described in [13]. Briefly, 3 mmol of $CdCl_2$ were dissolved in 225 ml of deionized water followed by adding 7.7 mmol of TGA under magnetic stirring.

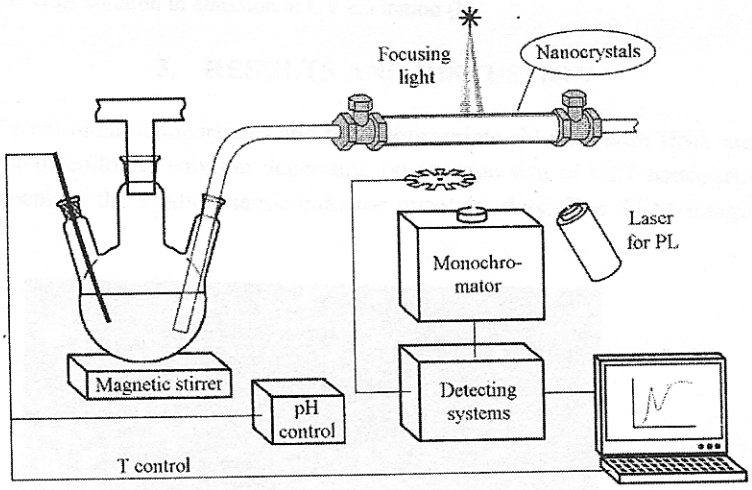
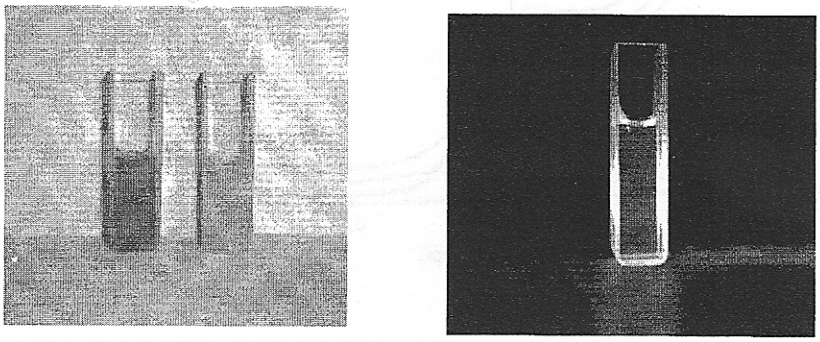


Fig. 1. Experimental setup for *in situ* measurements of optical absorption and photoluminescence spectra of colloidal semiconductor nanoparticles.

By adding 1 M NaOH value of pH was adjusted to 10. Then, gas mixture of Ar and H_2Te was passed through the solution. The reaction time was varied to achieve different molar ratio of Cd^{2+}:Te^{2-}:TGA. Solutions of CdTe

nanoparticles with HSA were prepared by adding a small amount of concentrated HSA solution in salin. All measurements were performed immediately after preparation of solutions.
Transmission electron microscopy (TEM) was used in order to confirm the nanocrystallinity of the grown samples, estimate shape and determine the average size of nanoparticles. The electron microscope that provides maximum resolution of 0.5 nm was used. In order to estimate surface morphology of composite PVA/CdS:Mn nanoparticles films the atomic force microscopy (AFM) analysis was performed.
Optical absorption and photoluminescence measurements were carried out using a home-designed setup, which schematically is shown in Fig. 1. Main component of this setup is UV-Vis spectrometer on the base of diffraction monochromator MDR-23 (LOMO). The excitation of photoluminescence was carried out by a He-Cd laser operating at wavelength of 325 nm and power of 10 mW. All spectral measurements were performed at room temperature.



a b

Fig. 2. Photoimages of CdTe colloidal nanoparticles with different average sizes in transmission (a) and photoimage of CdTe nanoparticles with HSA solution in emission at UV excitation (b).

3. RESULTS AND DISCUSSION

The photographs of CdTe colloidal nanoparticles and their appropriate solution with HSA are shown in Fig. 2. It should be noticed different color of colloidal solution depending on average size of CdT nanoparticles. This is visible evidence for quantum confinement in the studied semiconductor quantum dots. The TEM image of colloidal CdTe nanoparticles is shown in Fig. 3.

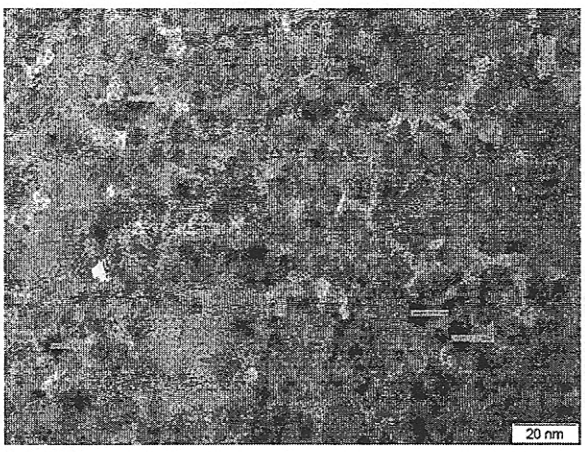


Fig. 3. TEM image of colloidal CdTe nanoparticles.

Namely this kind of analysis was used to estimate average size of CdTe nanoparticles. The 2D and 3D AFM images of the composite PVA/CdTe nanoparticles film show the regular fluctuation profile of the studied film due to the dispersed

nanoparticles. The maximum height fluctuation is about 25 nm and the root-mean-square surface roughness is about 7 nm. The nanoparticles are lens shaped and their diameter cannot be read out from the AFM images because we have to take into account the shape of the AFM probe. After appropriate correction the resulting diameters of the nanoparticles range from 2.5 nm to 5 nm, which is well correlated with results of TEM analysis.

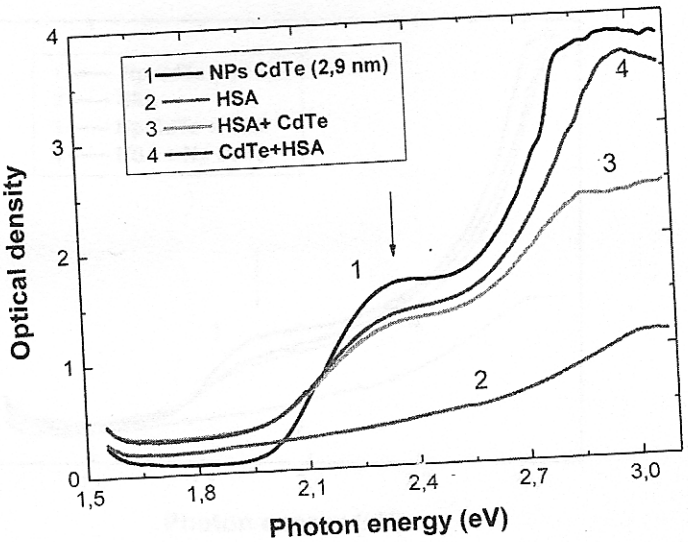


Fig. 4. Optical density as function of photon energy for solution of colloidal CdTe nanoparticles with average size of 2.9 nm and HSA (curve 1 corresponds to CdTe nanoparticles only, 2 corresponds to HSA solution only, 3 cirresponds to HSA +1,5 x 10^{-3} mmol/L np CdTe, 4 corresponds to 1,5 x 10 -3 mmol/L np CdTe + HSA).

To study optical spectra it was chosen two colloidal solutions with average diameter of CdTe nanoparticles about 2.8 and 2.9 nm. Fig. 4 shows optical density as a function of photon energy for four solution samples contained in the same quartz container with inner thickness of 10 mm which correspond to different materials. Curve 1 corresponds to the sample of CdTe nanoparticles with average diameter of 2.9 nm and curve 2 corresponds to HSA solution. Curves 3 and 4 correspond to mixed solutions of CdTe nanoparticles and HSA. In optical absorption spectrum of CdTe nanoparticles one can see clear exciton band with maximum at 2.32 eV indicated by arrow. Its maximum is blue shifted as compared with bulk CdTe crystals. A blue shift with respect to the absorption peak for bulk crystals is due to the confinement effect. The energy difference ΔE due to the confinement effect within a simple effective mass approximation [14] is given by expression

$$\Delta E = E_{gNano} - E_{gBulk} = \frac{\hbar^2 \pi^2}{2R^2}\left[\frac{1}{m_e} + \frac{1}{m_h}\right] - \frac{1.8e^2}{\varepsilon R} + P \quad , \qquad (1)$$

where m_e, m_h, ε and P are effective mass of electron, hole, dielectric constant and polarization term, respectively. By neglecting small polarization term P and using values of m_e, m_h, ε for bulk CdTe, the experimental value of ΔE=0.83 eV an average radius of the studied CdTe nanoparticles was estimated as R ≈ 1.4 nm.

As shown in Fig. 4 (curves 3 and 4) addition of HSA to colloidal CdTe nanoparticles leads to a gradual decrease of optical density and broadening of exciton structure. However, energy position of the exciton band in this case remains not shifted.

Similar picture we can see also for the other sample of colloidal CdTe nanoparticles with an average size of 2.8 nm (Fig. 5). Probably, the above results indicate that the binding process between quantum dots and protein molecules may change the conformation of HSA.

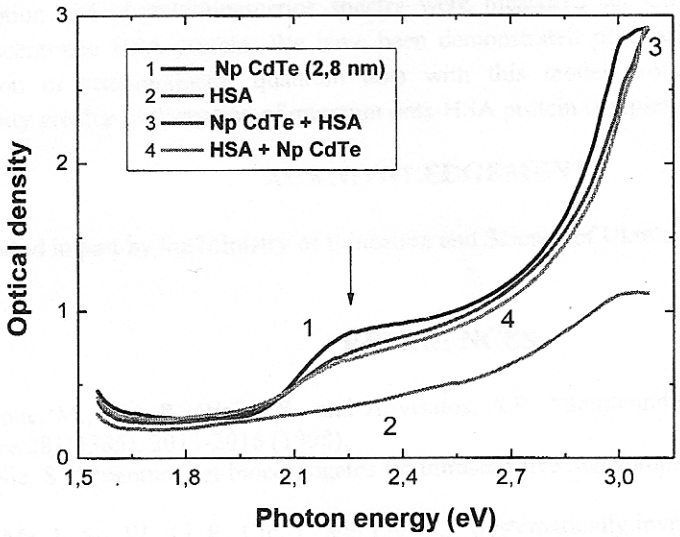


Fig. 5. Optical density as function of photon energy for solution of colloidal CdTe nanoparticles with average size of 2.8 nm and HSA (curve 1 corresponds to CdTe nanoparticles only, 2 corresponds to HSA solution only, 3 corresponds to 1,5 x 10^{-3} mmol/L np CdTe + HSA, 4 corresponds to HSA +1,5 x 10^{-3} mmol/L np CdTe).

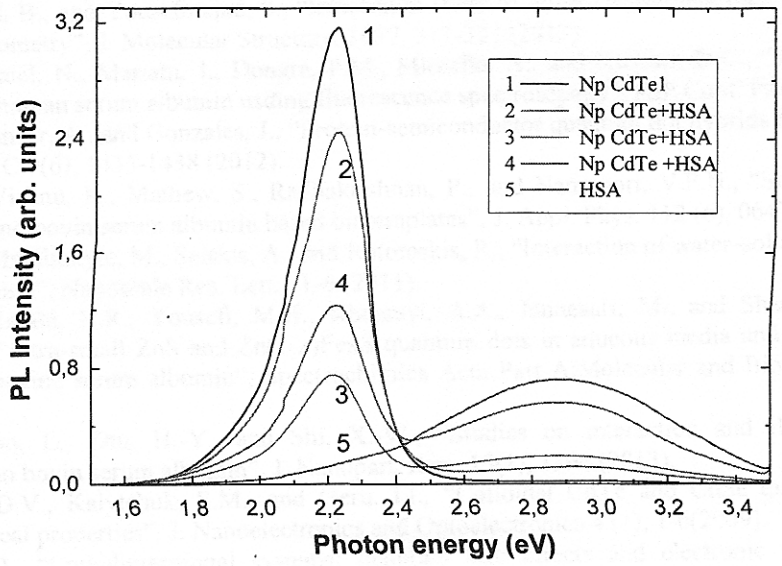


Fig. 6. Photoluminescence spectra of CdTe (2,9 nm) nanoparticles in HSA (curve 1 corresponds to CdTe, nanoparticles only, 2 corresponds to HSA + 1,5 x 10^{-3}mmol/L np CdTe, 3 corresponds to HSA + 0,9 x 10^{-3}mmol/L np CdTe, 4 corresponds to HSA + 0,6 x 10^{-3} mmol/L np CdTe, 5 corresponds to HSA solution only).

Fig. 6 shows photoluminescence spectra of colloidal CdTe nanoparticles (curve 1), HSA (curve 5) and their solutions (curves 2 - 4). Main finding from these experiments is so-called quenching effect, which was observed recently also for

CdTe quantum dots [4]. The quenching of HSA fluorescence intensity by semiconductor nanoparticles was analysed in framework of Stern-Volmer equation and its modification [15].

4. CONCLUSIONS

In conclusion, colloidal CdTe nanoparticles (quantum dots) in aqueous solution and passivated by TGA have been prepared. Optical absorption and photoluminescence spectra were measured for CdTe quantum dots with adding different amounts of concentrated HSA protein. We have been demonstrated peculiarities of spectral characteristics, which confirm interaction of semiconductor quantum dots with this model protein. The observed changes in photoluminescence intensity are due to formation of quantum dots-HSA protein complex.

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