

## EFFECT OF TEMPERATURE ON THE OPTICAL PROPERTIES OF POLYETHYLENIMINE-STABILIZED CdS NANOPARTICLES

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*An unusually pronounced temperature dependence was found for photoluminescence intensity and energy of size quantization levels of polyethylenimine-stabilized CdS nanoparticles with diameter ~1.8 nm in the range 280-353 K. Evidence was given to support the hypothesis that these changes result from the reversible dissociation of a complex of the polymer amino groups with coordinatively unsaturated Cd(II) ions on the nanoparticle surface and the completion of the coordination sphere of these ions by water molecules participating in the non-radiative dissipation of the electronic excitation energy of CdS nanoparticles. Promise for the use of such nanoparticles is found in the development of sensor systems for monitoring the temperature of microvolumes and the diagnosis of heat exchange phenomena.*

**Key words:** cadmium chalcogenides, CdS nanoparticles, quantum dots, photoluminescence, polyethylenimine, temperature dependence.

Luminescent cadmium chalcogenide nanoparticles (NP) hold broad promise of practical application as luminophors in various sensor devices, in particular, in luminescent biodiagnostic systems [1, 2]. The attractiveness of such nanoluminophors is related to their photostability, which is greater than for organic fluorophors, and the possibility of varying the emission spectral parameters in a broad range by changing the size of the NP. In many cases, cadmium chalcogenide NP display rather strong temperature dependence of the emission parameters at close-to-room temperatures, which offers the prospect of developing nanosensors for studying heat exchange in living organisms [3-5]. We might expect that the use of individual CdSe/ZnS NP as thermal sensors would permit overcoming the threshold for spatial resolution of thermocouples (~100  $\mu\text{m}$ ) and heat-sensitive dyes (~1  $\mu\text{m}$ ) and reach submicron resolution [5]. On the other hand, presently available luminescent systems derived from cadmium chalcogenide NP sensitive to change in temperature have a several serious disadvantages, in particular, low sensitivity and irreversibility of thermal changes, which hinder their competition with other types of nanoluminophors such as NP dopes with rare earth ions [2, 6].

In the present work, we showed that ultrasmall cadmium sulfide NP stabilized in aqueous solution and polyethylenimine films display unusually high temperature dependence for luminescence efficiency and the energy of size quantization levels, which are reversible in nature and may find use in luminescent sensor systems.

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## EXPERIMENTAL

In this work, we used cadmium chloride, Na<sub>2</sub>S·9H<sub>2</sub>O, 50 mass % polyethylenimine (weight average molecular mass  $M_w = 50,000$  g/mol), and glass plates for deposition of a conducting layer of mixed indium–tin oxide (ITO) with resistance  $70 \Omega/\text{cm}^2$  (from Sigma Aldrich).

Colloidal CdS nanoparticles stabilized by polyethylenimine (CdS-PEI) were obtained by our previous method [7, 8]. Typical concentrations of cadmium sulfide and PEI were  $1 \cdot 10^{-2}$  mol/L and 0.5 mass %, respectively, the CdS-PEI films on ITO were obtained by drying aliquots of the colloidal solution deposited on the surface of the conducting plates with natural air circulation and heating to 323-333 K. A polyethylene dielectric film was placed between the CdS-PEI layer and ITO plate surface in individual experiments.

Specord 220 and HP Agilent 8453 spectrophotometers were used to record the optical absorption spectra of the colloidal solutions and films. The photoluminescence (PL) spectra were taken using Perkin-Elmer LS55 and Edinburgh Instruments FLS920 spectrofluorimeters. The PL kinetics was recorded in a photon counting regime using the FLS920 instrument with sample excitation by 60-ps pulses from an EPL-375 picosecond diode laser at 375 nm. The kinetic curves were approximated by a linear combination of four exponential functions:

$$I(t) = \sum_i A_i e^{-t/\tau_i}$$

where  $I$  was the PL intensity and  $i$  varied from 1 to 4; amplitudes  $A_i$  and exponential times  $\tau_i$  were fitting parameters. The mean luminescence lifetime  $\langle \tau \rangle$  was determined by the following formula [9]:

$$\langle \tau \rangle = \frac{\sum_i A_i \tau_i^2}{\sum_j A_j \tau_j}$$

The temperature dependence of the absorption and PL spectra of the colloidal CdS-PEI solutions was studied in thermostatted 10-mm-thick quartz cells. The CdS-PEI films were heated on the ITO surface by applying a voltage of 3-26 V on the conducting plate.

## RESULTS AND DISCUSSION

In previous work [7, 8], we showed that the interaction between cadmium chloride and sodium sulfide in aqueous solutions of PEI leads to the formation of ultrasmall colloidal CdS particles (diameter  $\sim 1.8$  nm) with a narrow size distribution ( $\sim 10\%$ ). The absorption spectra of aqueous CdS-PEI colloids show a series of maxima, the first of which appears at 355 nm ( $E_1 = 3.50$  eV, Fig. 1a, curve 1). Broad PL bands in the visible spectral region are seen at 400-600 nm (Fig. 1a, curves 2-10). The PL quantum yields are 3-5% in the solutions and 25-30% in the CdS-PEI films obtained by evaporation of the solvent at room temperature.

### Temperature Dependence of the PL Intensity of Aqueous Colloidal CdS-PEI Solutions

A strong dependence of the PL intensity on temperature is found for aqueous CdS-PEI solutions (Fig. 1a,b). An increase in temperature from 281 to 343 K is accompanied by a decrease in PL intensity by more than an order of magnitude with retention of the shape and position of the bands. The spectral changes are reversible in nature; cooling of the colloid is accompanied by restoration of the initial PL intensity (Fig. 1b). These changes are reproduced upon multiple cyclic repetition of the heating and cooling procedure.

The increment in the temperature required to reduce the initial PL intensity by a factor of 2 ( $\Delta T_{1/2}$ ) was taken as a quantitative parameter characterizing the temperature dependence of the PL intensity. For the aqueous CdS-PEI colloids

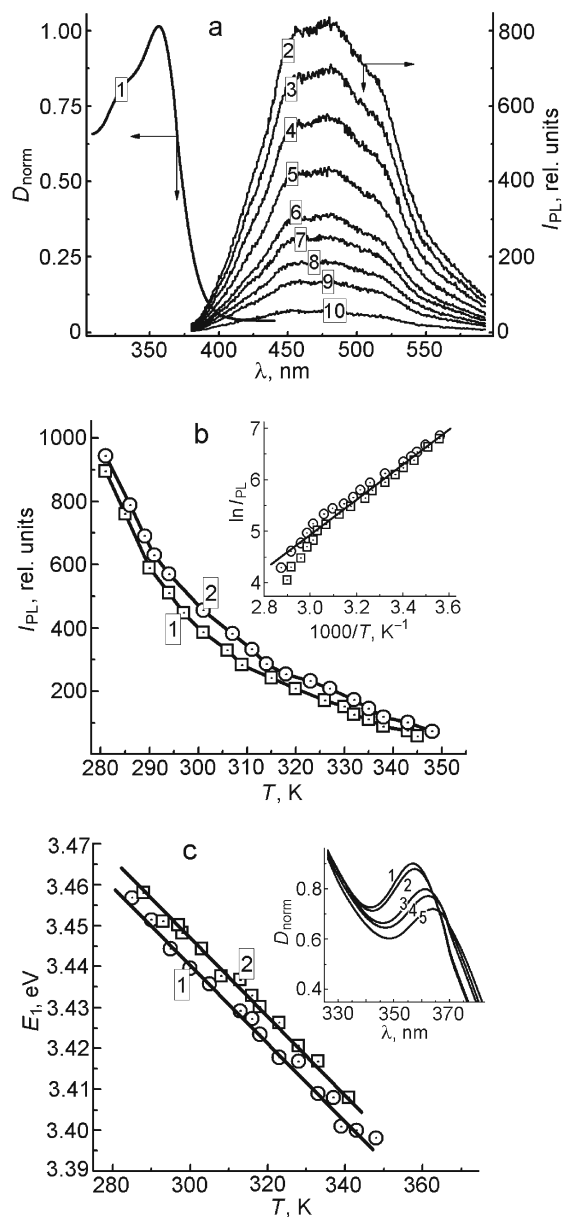


Fig. 1. a) Optical absorption spectrum (1) and photoluminescence spectra (2-10) of the CdS-PEI colloid in water taken at 281 (2), 285 (3), 290 (4), 297 (5), 306 (6), 315 (7), 326 (8), 333 (9), and 343 K (10) (the PL excitation wavelength was 350 nm); b) change in the integral photoluminescence intensity  $I_{\text{PL}}$  of the CdS-PEI colloid in water upon increasing the solution temperature from 281 to 343 K (1) and its subsequent decrease from 345 to 281 K (2) (the insert gives spectra 1 and 2 in a plot for  $\ln I_{\text{PL}}$  vs.  $1000/T$ ); c) change in the position of the first maximum  $E_1$  in the absorption spectrum of the CdS-PEI colloid in water with increasing temperature from 285 to 353 K (1) and subsequent cooling from 343 to 287 K (2) (the insert gives the normalized absorption spectrum of the CdS-PEI colloid in water at 288 (1), 298 (2), 328 (3), 338 (4), and 348 K (5)).

studied,  $\Delta T_{1/2} = 20$  K. Similar values ( $\Delta T_{1/2} = 15-40$  K) were obtained for CdSe/ZnS NP in the work of Liu et al. [10], which depend on the thickness of the passivating ZnS layer. However, the photoluminescence changes observed by Liu et al. [10] were irreversible due to oxidative corrosion of the NP. Similar increment values ( $\Delta T_{1/2} = 35$  K) were obtained for colloidal CdSe particles with diameter 2-5 nm aggregated in clusters with diameter 27-30 nm [5]. On the other hand, the temperature dependence of the PL parameters (intensity and position of the maximum) in this case is more likely a collective property of the cluster than of the individual component CdSe NP and is only partially reversible. For colloidal CdSe/ZnS NP with diameter of about 5 nm, which were proposed by Walker et al. [4] for use as luminescent temperature probes,  $\Delta T_{1/2} \approx 80-90$  K.

The temperature dependence of the PL intensity of semiconductor nanoparticles ( $I_{PL}$ ), as a rule, is described by an empirical expression  $I_{PL}(T) = B(A \exp(-\varepsilon/k_B T) + 1)^{-1}$  [11], where  $B$  and  $A$  are empirical constants,  $\varepsilon$  is the activation energy,  $k_B$  is the Boltzmann constant. Typical activation energies for cadmium chalcogenide NP are on the order of the phonon energy and vary in the range 20-80 meV or 2-8 kJ/mol [11, 12]. The insert in Fig. 1b shows that the curve for  $I_{PL}(T)$  in the case of colloidal CdS-PEI in a plot for  $\ln(I_{PL})$  vs.  $T^{-1}$  is linear over virtually the entire temperature range studied. In comparison with the data of Santhi [11] and Bagaev [12], the function  $I_{PL}(T)$  for CdS-PEI NP is characterized by a much higher activation energy ( $\varepsilon = 0.30-0.31$  eV or 29-30 kJ/mol), which corresponds in order of magnitude to the energies of the coordination and van der Waals bonds. Hence, the temperature dependence of PL quenching in the CdS-PEI system may proceed through a mechanism different from the mechanism usually proposed for cadmium chalcogenide NP stabilized by ligands covalently bonded to the NP surface or, on the other hand, encapsulated in solid matrices such as a glass [11].

In our previous work [8], we established that the quenching of the PL of CdS-PEI nanoparticles by water is a consequence of the competition between the PEI amino groups and water molecules for incompletely coordinated Cd(II) ions on the NP surface. Taking into account that water molecules have a large number of vibrational degrees of freedom and may be activated in the initial photochemical processes involving photogenerated charges, we may assume that the dissociation of surface complexes of the Cd(II) ion with the PEI amino groups and formation of complexes with water should accelerate non-radiative dissipation of the electron excitation energy of CdS NP. Evidence for this hypothesis is found in the multifold increase in the PL intensity of colloidal CdS NP stabilized in water by sodium polyphosphate upon the introduction of PEI into the solution.

In light of the lack of literature data on the stability constants and activation energy for the dissociation of the complex of the Cd(II) ion with PEI, we examined the system consisting of the complex of Cd(II) with ethylenediamine with similar structure, for which the stability constant has been reported ( $\log \beta = 5.45$  [13]). Neglecting, in a first approximation, the entropy component in the expression for the free energy of dissociation of the Cd—N bond in the Cd(en)<sub>2</sub> complex  $\Delta G_{Cd-N}$  and taking  $\Delta G \approx -RT \ln \beta$ , we may show that  $\Delta G_{Cd-N}$  in the temperature interval studied varies in the range 29.5-36.8 kJ/mol, which corresponds to the activation energy for the thermal quenching of photoluminescence (29-30 kJ/mol) determined above in analyzing the function  $I_{PL}(T)$ . Thus, we may propose that the reason for the anomalously strong temperature dependence of the photoluminescence intensity of colloidal CdS-PEI NP in the temperature range 280-353 K is dissociation of the complex of PEI with coordinatively unsaturated Cd(II) ions on the nanoparticle surface and formation of complexes with water, which can act as sites for the non-radiative recombination of photogenerated charge carriers. In concluding this examination of the temperature dependence of the PL intensity, we note that a change in temperature on the order of 1 K in the range 280-353 K may be quite reliably detected.

### **Temperature Dependence of the Energy of the Size Quantization Levels of Colloidal CdS-PEI Nanoparticles**

An increase in the temperature of CdS-PEI colloids in the range 290-353 K is accompanied by a decrease in the energy of the first maximum ( $E_1$ ) in the absorption spectrum of the colloid from  $\sim 3.46$  to  $\sim 3.40$  eV (Fig. 1c, curve 1). Upon cooling of the solution,  $E_1$  again increases up to the initial value (Fig. 1c, curve 2). The reversibility of the spectral shift of the position of the maximum in the absorption spectrum corresponding to the electron transition between size quantization levels in the valence band and conduction band of CdS-PEI particles indicates that this effect is not a consequence of an increase in nanoparticle size but rather a change in the electronic properties of the NP without an increase in size.

The temperature dependence of energy  $E_1$  of the CdS-PEI nanoparticles is linear and typical for semiconductor NP at temperatures far from 0 K [14]. Thus, the coefficient  $\alpha$ , corresponding to the change in  $E_1$  upon increasing the temperature by

1 K, was taken as a quantitative index of the curve  $E_1(T)$ . We found  $\alpha = 0.95\text{-}1.00$  meV/K for the colloidal CdS-PEI NP examined in this work in the temperature range 290-353 K. We should note that much lower values of  $\alpha$  are observed, as a rule, for cadmium chalcogenide NP. Thus, according to Vossmeier et al. [15], the value of  $\alpha$  for thioglycerin-stabilized CdS colloids varies from 0.40 meV/K for CdS NP with diameter  $\sim 10$  nm to 0.55 meV/K for ultrasmall CdS particles with diameter 1.2-1.3 nm. For CdS NP incorporated in a glass [11] and colloidal trioxylphosphine-stabilized CdSe NP [16],  $\alpha \approx 0.4\text{-}0.5$  meV/K. *Ab initio* calculations carried for the  $(\text{CdSe})_{33}$  cluster with diameter about 1.7 nm [17] gave  $\alpha = 0.73$  meV/K, which is greater than experimental values found for CdSe NP (0.3-0.5 meV/K [17]) but less than the values of  $\alpha$  determined in the present work for colloidal CdS-PEI NP.

A strong effect of the ligand environment on the electronic properties of a semiconductor (spatial restriction of charge carriers) is a characteristic feature of ultrasmall cadmium chalcogenide particles with diameter  $d < 3$  nm, which distinguishes them from larger NP. Thus, the energy of the first ( $E_1$ ) and subsequent size quantization levels (maxima in the absorption spectrum) of CdS particles with diameter  $\sim 1.7$  nm depends significantly on the nucleophilicity of the stabilizer ligand [18]. Thus, for example, the value of  $E_1$  drops from 3.82 to 3.47 eV in going from mercaptopropionate ligands to more electropositive thiophenolate ligands stabilizing the NP.

Semiempirical calculations carried out by Nguyen et al. [19], the adsorption of 33 ammonia molecules on the surface of the  $(\text{CdSe})_{33}$  cluster, whose diameter (1.7 nm) is close to that of the CdS-PEI NP examined here (1.8 nm), leads to a significant increase in the spatial restriction of charge carriers in this cluster and an increase in  $E_1$  from 2.7 to 3.0 eV. Schreuder et al. [20] showed the first maximum in the absorption spectrum of ultrasmall CdSe particles ( $d < 1.7$  nm) stabilized by alkylphosphonic acids is shifted toward higher energies with increasing electronegativity of the alkyl substituents due to greater spatial restriction of the photogenerated charge carriers. Sarkar et al. [21] showed the possibility of reversible change in energy  $E_1$  of CdS nanoparticles by the adsorption/desorption of cyanide anions. The observed increment in  $E_1$  due to the absorption of  $\text{CN}^-$  anions increases with decreasing size of the CdS NP, reaching 0.25 eV for particle diameter 3.0-3.5 nm [21].

Our results indicate that the temperature dependence for PL quenching for CdS-PEI nanoparticles observed above and the decrease in the energy of the size quantization levels are both caused by reversible dissociation of the complexes of PEI with the coordinatively unsaturated Cd(II) ions on the CdS NP surface. As a result, the polymer amino groups are eliminated by water molecules, leading to decreased effective electron density in the immediate environment of the nanoparticles and weakening of the spatial restriction of the charge carriers in the CdS NP. Cooling the solution leads to the reverse elimination of water molecules by the polyethylenimine amino groups, which can affect the electron system of the ultrasmall particles due the unshared electron pairs, thereby increasing the effective spatial restriction and, thus, the energies of the size quantization levels. We should also note that in analogous colloid systems containing PEI and larger CdS particles with diameter 6-7 nm obtained in the presence of sodium polyphosphate [22], no shift of the position of the maximum or of the edge of the fundamental absorption band is observed with increasing solution temperature. This failure is probably related to the much less pronounced spatial restriction of the charge carriers and weak effect of the ligand environment on the electronic properties of the semiconductor in these nanoparticles.

### Temperature Dependence of the Spectral Properties of CdS NP in PEI Films

Passing an electric current through the conducting ITO layer, on whose surface PEI films containing CdS NP are deposited, leads to heating of the polymer film and decrease in the photoluminescence intensity (Fig. 2a, curve 1) as well as to a decrease in energy  $E_1$  (Fig. 2b) similar to the behavior observed upon increasing the temperature of the starting colloidal CdS-PEI solutions. Passing current directly across the CdS-PEI film is not a necessary condition for these changes since they are also observed when a dielectric layer is located between the ITO and PEI film and the increase in the temperature of the film occurs due to heating by the current through the ITO plate. The observed shifts in the position of  $E_1$  probably cannot be caused by the action of an external electric field since significant changes in the absorption spectra of cadmium chalcogenide NP incorporated in polymers are observed in much stronger fields on the order of  $10^5\text{-}10^6$  V/cm [23, 24]. Upon switching off the current and cooling of the film, the parameters of the absorption and PL spectra return to their initial values.

The data shown in Fig. 2a,b show that the application of a voltage on the ITO/CdS-PEI structure leads to change in the same direction of the photoluminescence intensity (Fig. 2a, curve 1), mean emission lifetime  $\langle \tau \rangle$  of the excited state of the

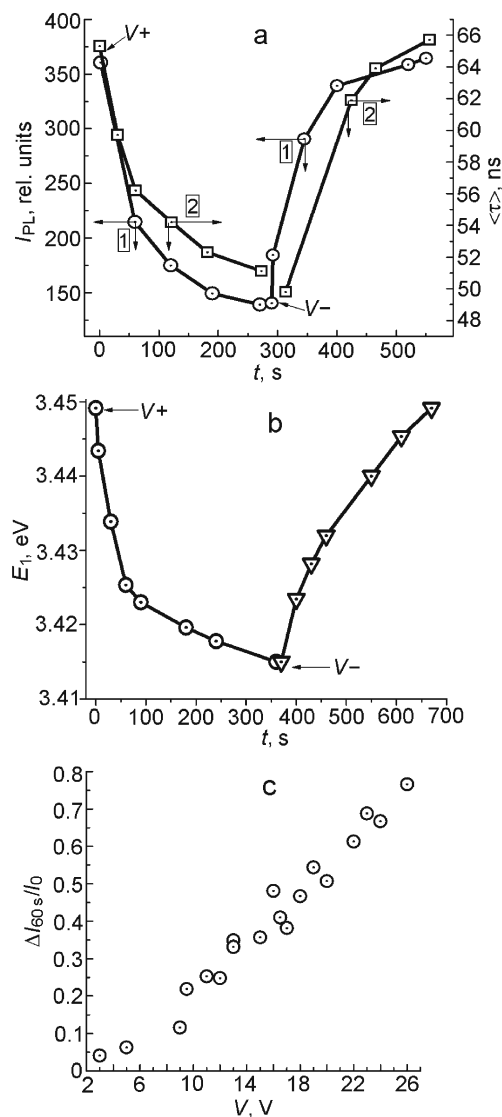


Fig. 2. a,b) Change in the integral photoluminescence intensity  $I_{PL}$  (a, 1), in the mean emission lifetime  $\langle\tau\rangle$  of the excited state of CdS nanoparticles in PEI film on ITO (a, 2), and energy of the first maximum  $E_1$  in the absorption spectrum (b) during maintenance of the film at potential difference  $V = 15$  V (the instant of applying the potential difference is indicated at  $V+$ , the instant of switching off the current is indicated as  $V-$ ), and subsequent maintenance of the film at 291 K, c) dependence between the efficiency of the temperature quenching of the luminescence of CdS nanoparticles ( $\Delta I_{60s}/I_0$ ) in a PEI film on an ITO surface on the voltage applied to the ITO  $V$ .

CdS NP (Fig. 2a, curve 2), and energy of the maximum in their electronic spectra (Fig. 2b). Heating the CdS-PEI film as the result of passing current for 250-280 s leads to a decrease in  $E_1$  from 3.450 to 3.415 eV, a drop in the photoluminescence intensity by a factor of more than 2.5, and decrease in  $\langle\tau\rangle$  from 64-65 to 49-50 ns. The decrease in  $\langle\tau\rangle$  indicates activation of the non-radiative channels for the dissipation of excitation energy. The quenching of the PL of CdS nanoparticles in a PEI film, evaluated as the ratio of the decrease in PL intensity after 60 s current passage ( $\Delta I_{60s}$ ) to the initial value  $I_0$  increases almost directly proportionally to the voltage applied to the ITO plate (Fig. 2c).

Thus, we have established unusually strong temperature dependence of the photoluminescence intensity and energy of the size quantization levels of ultrasmall polyethylenimine-stabilized CdS nanoparticles in aqueous solution and in films at 280-353 K. Our findings indicate that these changes are the result of a single factor, namely, the reversible dissociation of the complex of the polymer amino groups with the coordinatively unsaturated Cd(II) ions on the nanoparticle surface and their filling of the coordination sphere by water molecules, which participate actively in non-radiative dissipation of the electronic excitation energy of the CdS nanoparticles. These properties of polyethylenimine-stabilized CdS nanoparticles account for the interest in these materials in the development of new sensor systems for monitoring of temperature in microvolumes and the diagnosis of heat transfer processes.

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