

DYNAMICS OF THE RADIATIVE RECOMBINATION OF CHARGE CARRIERS IN CdS NANOPARTICLES STABILIZED WITH POLYETHYLENEIMINE

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The dynamics of the radiative recombination of charge carriers in CdS nanoparticles stabilized in aqueous solutions of polyethyleneimine was studied. It was shown that decay of the photoluminescence of the nanoparticles is characterized by a set of time constants in the range of 10^{-1} - 10^2 ns, while its rate depends on the energy of the radiation quanta. This relationship is interpreted as the result of competition between the processes of radiative recombination and vibrational dissipation of the excitation energy.

Key words: CdS nanoparticles, polyethyleneimine, radiative recombination, photoluminescence kinetics, flash photolysis.

The colloidal nanoparticles (NP) of cadmium sulfide formed in aqueous solutions of polyethyleneimine (PEI) have a series of unique characteristics [1] differing greatly from the characteristics of CdS nanoparticles formed in aqueous solutions in the presence of traditional polymeric stabilizers – polyvinyl alcohol, gelatin, sodium polyphosphate, etc. [2-4]. Among such characteristics it is necessary to mention the ultrasmall size of CdS-PEI nanoparticles ($d = 1.8$ nm), the narrow particle size distribution of the nanoparticles (~10%), and the fairly high quantum yield of photoluminescence (PL), amounting to 10%. These characteristics in conjunction with the broad spectral range of the radiation of the CdS-PEI nanoparticles (400-600 nm) determine the prospects for the use of such colloids for the creation of devices that emit “white” light and luminescent markers [5, 6].

It is clear that the development of methods for increasing the effectiveness and variation of the spectral parameters in the luminescence of CdS-PEI nanoparticles requires a detailed study of the mechanisms and dynamics of the photophysical and primary photochemical processes occurring in them. In this connection in the present work the dynamics of the consumption of

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the charge carriers photogenerated in CdS-PEI nanoparticles was studied with the use of kinetic luminescence spectroscopy and laser flash photolysis.

EXPERIMENTAL

Polyethyleneimine ($M_n = 50000$ g/mol), $\text{Na}_2\text{S}\cdot 9\text{H}_2\text{O}$, and CdSO_4 supplied by Aldrich (reagent grade) were used, and extra-pure anthracene (Acros Organics) was used for the fluorescence investigations. The CdS colloids were produced in the reaction of CdSO_4 and Na_2S in a 0.25% solution of PEI at 18-20 °C [1].

The absorption spectra were recorded on an HP Agilent 8453 spectrophotometer. The stationary photoluminescence spectra were recorded on a Perkin-Elmer LS55 luminescence spectrometer at room temperature and 77 K. The kinetic curves for the disappearance of the photoluminescence were recorded by the photon count method using an FLS920 spectrofluorimeter (Edinburgh Instruments). A semiconductor laser with wavelength 375 nm and pulse length 60 ps was used for excitation of the samples. The PL quantum yield ϕ was determined with solid anthracene ($\phi = 100\%$) as luminescence standard [7] at CdS concentrations securing full light absorption. Low-temperature measurements of ϕ were carried out with a standard Perkin-Elmer adapter fitted with a reservoir for liquid nitrogen and a cold lead connecting the reservoir to the quartz capillary in which the investigated sample was placed. The experiments on laser pulse photolysis were conducted on an automated instrument equipped with a pulse neodymium laser (third harmonic $\lambda = 355$ nm) with a pulse duration of 5 ns and energy of 1-10 mJ. The energy of the laser pulses was measured by means of a Gentec-EO system (Canada) (SOLO-2 monitor and pyroelectric head QE25SP-H-MB).

RESULTS AND DISCUSSION

Colloidal CdS-PEI nanoparticles are characterized by an absorption band in the near UV region (Fig. 1a, curve 1) with clear exciton maxima at 360 (E_1) and 330 nm (E_2). As shown by our assessments [1], such an absorption spectrum is typical for CdS nanoparticles with sizes in the order of 1.8 nm, existing in a regime of strong spatial limitation of the exciton. The aqueous CdS-PEI colloids are characterized by fairly intense photoluminescence in a wide range of $\lambda = 400$ -600 nm (Fig. 1a, curve 2), the quantum yield of which amounts to 10%.

Kinetics of Disappearance of the Photoluminescence

Typical PL kinetic curves, recorded in a time window of 0...50 ns with excitation of the CdS-PEI nanoparticles by light with $\lambda = 375$ nm, are shown in Fig. 1b. It is seen that the kinetic curves have the complex character typical for semiconductor nanoparticles characterized by broad energy distribution in the emitting states [5, 8]. The kinetic curves can be approximated by the sum of four exponential functions $I(t) = \sum A_i \exp(-t/\tau_i)$ [8], where $i = 1, \dots, 4$, and the amplitudes A_i and times τ_i are adjustment parameters. Typical time parameters of PL decay are $\tau_1 = 0.20 \pm 0.01$ ns, $\tau_2 = 0.90 \pm 0.02$ ns, $\tau_3 = 6.30 \pm 0.2$ ns, and $\tau_4 = 38.0 \pm 0.5$ ns (recorded at $\lambda = 500$ nm). All four components of the PL decay curves reveal a dependence on the recording wavelength λ_{rec} , increasing by 2-5 times with increase of λ_{rec} from 400 to 580 nm (Fig. 1c).

Several models have been proposed to interpret the dependence of the PL decay rate on the emission quantum energy [5, 8, 9]. They include resonance transfer of energy between the nanoparticles, the presence of particle size distribution in the nanoparticles and size dependence of the PL decay rate, and also in the case of PL involving charges captured by local surface states (traps), their distribution with respect to energy (the depth in the forbidden band of the nanoparticle). The first of these mechanisms presupposes overlap of the absorption and emission spectra of the nanoparticles and clearly cannot be realized in the investigated system on account of the significant Stokes shift (0.6-0.8 eV) between the absorbing and emitting levels. The size dispersion of the CdS-PEI nanoparticles is small, ~10%, but this factor can clearly make a definite contribution to the

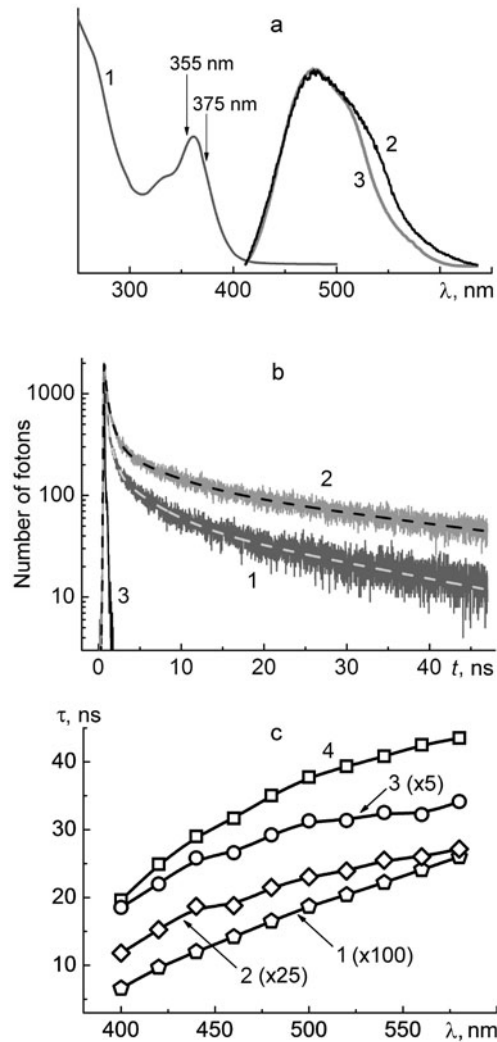


Fig. 1. a) The normalized absorption (1) and PL (2, 3) spectra of the aqueous CdS-PEI colloid at room temperature (2) and 77 K (3); the wavelengths of luminescence excitation and pulsed laser emission are indicated by the arrows. b) The kinetic curves of PL decay of the colloidal CdS-PEI nanoparticles, recorded at 460 nm (1) and 560 nm (2); 3 corresponds to the form of the exciting pulse; the dashed lines show the result of approximation of the kinetic curves by the sum of four exponential functions. c) The dependence of the parameters τ_i of the decay of the PL of the CdS-PEI nanoparticles [$i = 1$ (1), 2 (2), 3 (3), and 4 (4)] on the wavelength at which the kinetic curve is recorded.

$\tau_i(\lambda_{\text{rec}})$ relation if it assumed that the dependence of the rate of electron–hole recombination on the size of the nanoparticles increases sharply in the region of $d < 2$ nm [8].

The interpretation based on the presence of a wide energy distribution of charge carrier traps is probably the most acceptable for the investigated ultrasmall CdS nanoparticles having a large specific surface area. In its characteristics and in

particular the Stokes shift and spectral width the PL band of the CdS-PEI nanoparticles is very close to the parameters of the so-called defect luminescence bands of larger CdS nanoparticles and also of the bulk crystals of cadmium sulfide, which arise as a result of recombination involving one or both charge carriers captured by deep surface or volume traps.

However, together with this similarity, which at first glance can serve as an argument in favor of the assignment of the luminescence of CdS-PEI nanoparticles to the defect type, there are fundamental differences between the photoluminescence of these nanoparticles and the previously studied larger nanoparticles of CdS [2, 3]. For the typical cases of defect photoluminescence of CdS nanoparticles there is a substantial change (narrowing, long-wave shift) in the PL bands with decrease of temperature, due to retardation of the electronic transitions between local levels–traps of different energy. At the same time the change in the form of the PL band of the CdS-PEI nanoparticles with decrease of temperature to 77 K (Fig. 1a, curve 3) is less clearly defined than for CdS nanoparticles of size 6-7 nm [3] and is most likely due to changes in the fraction of the largest particles in the CdS-PEI nanoparticle assembly. Moreover, as a rule the defect PL is characterized by low yields since the surface states involved in radiative recombination can also be drawn into competing nonradiative processes. In the case of aqueous CdS-PEI colloids the quantum yields of emission are fairly high, ~10%, and the effectiveness of the PL is greatly increased during freezing, reaching 100%, indicating the absence of nonradiative channels for expenditure of the electronic excitation energy.

Apparently, in the case of the ultrasmall CdS nanoparticles examined here a combined version of radiative recombination is realized, where annihilation of the exciton occurs on the surface of the nanoparticles. The direct electronic transitions from the valence band to the surface states involved in the emission are clearly characterized by a small oscillator force and cannot be populated during photoexcitation. Here the bands associated with the electronic transitions in the core of the nanoparticle predominate. Certain analogies can be drawn with the phosphorescence of molecules taking place with the participation of triplet states, the probability of population of which by direct excitation from the ground singlet state of the molecule is as a rule very low.

The photogenerated charge carriers populate the surface states, dissipating the excess energy in vibrational processes. As a result of the small size of the nanoparticle the electron and the hole are characterized by substantial overlap of the wave functions, and this finds expression in the high probability of radiative recombination. It should be noted that the relaxation of the charge carriers on the surface of the nanoparticles is accompanied by significant loss of energy, calculated in hundreds of vibrational quanta of the cadmium sulfide lattice. In spite of the fact that vibrational relaxation is usually observed in the subpicosecond range [5, 8] in the investigated case it can take tens of picoseconds. It may be this factor that gives rise to the observed dependence of the time parameters of PL decay on λ_{rec} – the longer the exciton photogenerated in the nanoparticle remains in the surface-bonded state, the greater the fraction of the energy that can be dissipated in the form of phonons.

Flash Photolysis of CdS-PEI Nanoparticles

The exposure of aqueous CdS-PEI colloids to laser pulses with $\lambda = 355$ nm leads to a reversible short-wave shift of the edge of the absorption band of the CdS nanoparticles, which in the differential absorption spectrum takes the form of a negative nonstationary signal – a decolorization band (Fig. 2a). This shift, known as the Burstein–Moss effect [10-12], is due to an increase in the energy of the electronic transitions as a result of population of part of the electronically excited states of the CdS nanoparticles by the action of the laser pulse. As the excess charge is used up in reactions with electron acceptors present in the system or recombination processes the intensity of the decolorization band decreases, and its maximum is shifted toward the long-wave region (Fig. 2a, curve 2). The last circumstance is evidently due to the fact that the rate of interphase transfer of the electron to the acceptor decreases with increase in the size of the CdS nanoparticles, as a result of which in the closing stage of relaxation nanoparticles with size greater than the average, which absorb in a more long-wave region in relation to E_1 , make a contribution to the nonstationary signal.

Figure 2b shows the kinetic curves for the relaxation of the nonstationary signal for aqueous cadmium sulfide colloids stabilized with PEI (curve 1) and, for comparison, sodium polyphosphate, SPP (curve 2). In colloids of the latter type, previously investigated in detail [3, 4, 13], there is a fairly wide particle size distribution (~20-30%) with a maximum at 6-7 nm. The kinetic curves were recorded at the maxima of the nonstationary decolorization bands of the CdS colloids, stabilized with PEI and SPP, at 375 and 470 nm respectively. As seen from the presented data, the effectiveness of the photoinduced

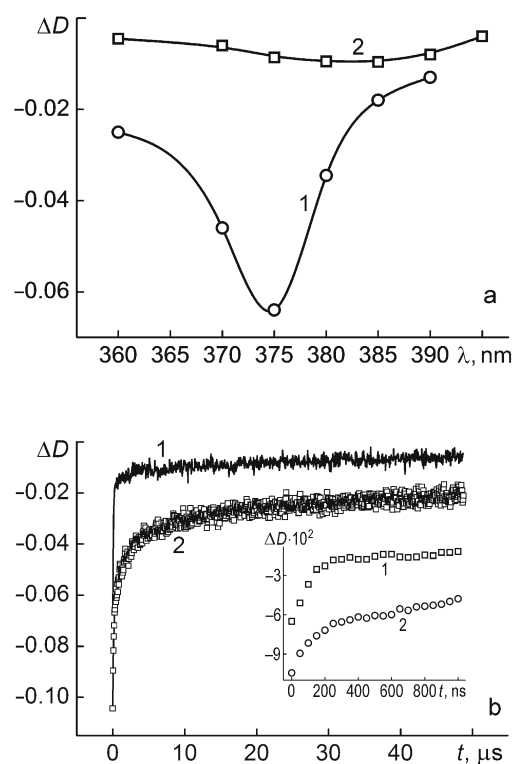


Fig. 2. a) The nonstationary decolorization spectrum of the aqueous CdS-PEI colloid during excitation by laser pulses with $\lambda = 355$ nm at the moment corresponding to total decay of the pulse $t = 0$ (1) and after the passage of 200 ns (2); $[\text{CdS}] = 1 \cdot 10^{-3}$ M, 0.25% PEI. b) The kinetic curves for relaxation of the signals of the nonstationary decolorization of CdS-PEI (1) and CdS-SPP (2) colloids, recorded at 375 and 470 nm respectively. Inset: 1 and 2 corresponding to a time window of 0...1000 ns.

charging of the CdS-PEI nanoparticles, which can be assessed from the amplitude of the nonstationary signal in the initial period of recording, is several times lower than in the case of CdS-SPP nanoparticles, while the subsequent discharge takes place significantly more quickly due, evidently, to the high probability of radiative electron-hole recombination. As seen from Fig. 2b (inset), in the case of the CdS-PEI nanoparticles the bulk of the excess charge is consumed over the first 200 ns, corresponding to the time interval of photoluminescence decay. From this it is possible to conclude that the main path for the consumption of the excess electrons is their radiative recombination with the holes, in contrast to the CdS-SPP nanoparticles, in which the relaxation of the nonstationary signal lasts hundreds of nanoseconds-microseconds and corresponds to interaction of the electrons with the acceptors – water and dissolved oxygen [4, 12].

Summing up, we note that in this paper we have discussed the results from an investigation of CdS nanoparticles, stabilized with polyethyleneimine in aqueous solutions, by pico-nanosecond kinetic luminescence spectroscopy and nanosecond flash photolysis. It was shown that the decay of the photoluminescence of the CdS nanoparticles can be described by the sum of four exponential functions with a set of time constants in the range of 10^{-1} - 10^2 ns, while its rate depends on the quantum energy of the radiation. This relationship was interpreted as the consequence of the existence of an energy distribution in the traps of the photogenerated charges and also competition between the processes of radiative recombination and vibrational dissipation of the excitation energy. Under the conditions of powerful pulse photoexcitation charging of the CdS

nanoparticles occurs, and this leads to a reversible increase in the energy of the electronic transitions in the nanoparticles. Discharge of the CdS nanoparticles occurs after 200 ns on the average as a result of radiative electron–hole recombination.

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REFERENCES

1. A. E. Raevskaya, G. Ya. Grodzyuk, A. L. Stroyuk, et al., *Teor. Éksp. Khim.*, **46**, No. 4, 225-229 (2010). [*Theor. Exp. Chem.*, **46**, No. 4, 233-238 (2010) (Engl. Transl.)]
2. A. L. Stroyuk, V. N. Dzhagan, and S. Y. Kuchmii, *Teor. Éksp. Khim.*, **43**, No. 5, 275-281 (2007). [*Theor. Exp. Chem.*, **43**, No. 5, 297-305 (2007) (Engl. Transl.)]
3. V. M. Dzhagan, O. L. Stroyuk, O. Ye. Rayevska, et al., *J. Colloid Interface Sci.*, **345**, No. 2, 515-523 (2010).
4. A. L. Stroyuk, A. E. Rayevskaya, A. V. Korzhak, et al., *Teor. Éksp. Khim.*, **45**, No. 1, 8-16 (2009). [*Theor. Exp. Chem.*, **45**, No. 1, 12-22 (2009) (Engl. Transl.)]
5. A. Rogach (ed.), *Semiconductor Nanocrystal Quantum Dots. Synthesis, Assembly, Spectroscopy, and Applications*, Springer, New York (2008).
6. A. Rogach, N. Gaponik, J. M. Lupton, et al., *Angew. Chem. Int. Ed.*, **47**, No. 35, 6538-6549 (2008).
7. P. Pringsheim and M. Vogel, *Luminescence of Liquids and Solids* [in Russian], Izd. Inostr. Lit., Moscow (1948).
8. S. V. Gaponenko, *Optical Properties of Semiconductor Nanocrystals*, Univ. Press, Cambridge (1996).
9. N. Chestnoy, T. D. Harris, R. Hull, and L. E. Brus, *J. Phys. Chem.*, **90**, No. 15, 3393-3399 (1986).
10. C. Liu and A. J. Bard, *J. Phys. Chem.*, **93**, No. 8, 3232-3237 (1989).
11. P. V. Kamat, N. M. Dimitrijević, and A. J. Nozik, *J. Phys. Chem. B*, **93**, No. 8, 2873-2875 (1989).
12. E. N. Savinov, V. E. Nagorny, and V. N. Parmon, *Khim. Fiz.*, **13**, No. 1, 56-65 (1994).
13. A. E. Raevskaya, A. L. Stroyuk, and S. Ya. Kuchmii, *J. Nanoparticle Res.*, **6**, No. 1, 149-158 (2004).