Specific features of luminescence of Q-CdS colloids with different sizes

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The specific features of luminescence of colloidal solutions of Q-CdS with particles of different size and the regularities of luminescence quenching by quenchers of various nature were studied. The luminescence spectra of Q-CdS consist of several bands, which are shifted to the long-wave region as the particle size increases. The dependence of the integral quantum yield of luminescence on the particle size has a sharp maximum at a particle diameter of ~23Å. A Stern—Volmer-type equation including the adsorption isotherm of the quencher molecules on the surface of the Q-CdS colloidal particles was used to describe the regularities of luminescence quenching of Q-CdS colloidal solutions. The CdS particle size was found to affect the efficiency of luminescence quenching. The regularities of luminescence quenching depend both on the rate constant of electron transfer to the quencher molecules and on the ability of the quencher molecules to be adsorbed on the surface of the CdS colloidal particle.

Key words: luminescence, Q-CdS colloidal solutions.

The study of the luminescence of CdS colloids makes it possible to obtain valuable data about the energy level and nature of centers of the charge carrier recombination in colloidal particles. The regularities of quenching of the photoluminescence of colloids carry information on the dynamics of electrons and holes in semiconductor particles and on the kinetics of interphase electron transfer. Of special interest are studies on the luminescence of colloid solutions of so-called Q-semiconductors, whose properties depend on the semiconductor particle size due to quantum-dimensional effects.[1,2]

It is well known that the absorption spectra of CdS, ZnS, PbS, and ZnO colloids change when the degree of dispersion of particles is varied in the size range smaller than the characteristic exciton size for semiconductors.[3] Such dependences can be used as calibrating curves for the determination of the mean particle size.

In the present work, we studied the photoluminescence of Q-CdS colloids in the size range of $2R$ = 20—100 Å and the regularities of the quenching of Q-CdS luminescence by various quenchers on varying the particle size of the colloid.

Experimental

Cadmium chloride ($CdCl_2 \cdot 2.5H_2O$), pyridine (Py), and phosphotungstic acid $H_3PW_{12}O_{40}$ (PW_{12}) of analytical grade, sodium sulfide ($Na_2S \cdot 9H_2O$), sodium hydroxide, tetraethylammonium chloride, methylviologen dichloride ($MVCl_2$), and cyclobutylviologen dibromide ($BVBr_2$) of reagent grade (Reakhim), and thioglycerole (TG) (Fluka) were used without preliminary purification. Potassium hexathiocyanochromite was prepared by mixing concentrated solutions of $Cr(NO_3)_3$ (analytical grade) and KSCN (reagent grade) followed by fractional crystallization of the complex salt.

Absorption spectra were recorded at 20°C in quartz cells (l= 1cm) on a Shimadzu UV-300 spectrophotometer. Luminescence spectra were recorded at 20°C in mirror quartz cells (l= 1cm) on a SFL-2 spectrophotometer. The excitation and emission luminescence spectra were corrected automatically for the spectral heterogeneity of the source by dividing the output signal of the photomultiplier which measured the luminescence intensity (measuring photomultiplier) by the signal of the photomultiplier which measured the intensity of the exciting light (reference photomultiplier). The luminescence spectra were not corrected for the spectral sensitivity of the photomultiplier, since the spectral sensitivity of the measuring photomultiplier is constant to within ~10% in the wavelength range studied (350—700 nm).

The size of colloidal particles was determined according to the well-known dependence[3] between the particle size and the position of the absorption band edge in the optical spectrum.

Determination of the quantum yield of luminescence. The differential quantum yield of luminescence Φ_{sm} (hereinafter, the quantum yield of luminescence) was calculated on the basis of the quantum yield of a standard ($3 \cdot 10^{-8}$ M fluorescein with $10^{-2}M$ NaOH) according to the formula[4]

$$\Phi_{sm} = \frac{J_{em,sm}(\lambda_{sm})}{J_{em,st}(\lambda_{st})} \cdot \frac{2.3D_{st}(\lambda_{st})}{\left(1-10^{-D_{sm}(\lambda_{sm})}\right)} \cdot \Phi_{st},$$

where $J_{em,sm}(\lambda_{sm})$ and $J_{em,st}(\lambda_{st})$ are the instrument readings (ratio of the signal of the measuring photomultiplier to that of the reference photomultiplier) in the emission spectrum of the

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sample and in the spectrum of the standard expressed in dimensionless units; $D_{sm}(\lambda_{sm})$ and $D_{st}(\lambda_{st})$ are the optical densities of the sample and fluorescein at the excitation wavelength (D_{fl}(320 nm) = 0.002); Φ_{st} = 85% is the quantum yield of luminescence of the standard. The values of $J_{em,st}$ were measured at the maximum intensity, *i.e.*, at 520 nm. The luminescence emission spectrum of the standard at λ_{exc} = 320 nm was recorded after each measurement of the luminescence spectrum of the sample.

Preparation of CdS colloids. A 10^{-3} *M* solution of $CdCl_2$ (10 mL) containing a varied amount of thioglycerol was prepared in a 100 mL beaker. Then a $2 \cdot 10^{-3}$ *M* solution of Na_2S containing 10^{-3} *M* NaOH was added with vigorous stirring and ice cooling. The resulting colloidal CdS solution is yellow to almost colorless, depending on the thioglycerol concentration. After that, the concentration of thioglycerol was adjusted to $5 \cdot 10^{-2}$ mol L^{-1} to establish the same chemical composition, as the luminescence of colloidal CdS depends on solution composition. The alkali was added during the synthesis to increase the quantum yield of luminescence.

Results and Discussion

Luminescence spectra of Q-CdS colloids. Figure 1 shows the luminescence spectra of Q-CdS colloids whose particle size was in the range ($2R$ = 19—50 Å) in which the strongest changes in the optical absorption spectra of CdS are observed.[2] One can distinguish the long-wave and the short-wave bands, whose intensity ratio depends on the particle size of colloidal CdS. As the particle size is increased, the intensity of the short-wave band decreases in comparison with that of the long-wave band, *i.e.*, the absorption spectrum is shifted to the long-wave region.

The dependence of the integral quantum yield of luminescence on the particle size (Fig. 2) has a sharp maximum around ~23 Å. The increase in luminescence intensity at particle size from 48 to 23 Å can be explained by the increase in probability of recombination of electrons and holes that are trapped on centers located at ever smaller distances from each other, whereas the sharp decrease in luminescence intensity at $2R <$ 23 Å has not yet been given an experimentally confirmed explanation. It can be assumed that at $2R <$ 23 Å, both the nature of recombination centers and the chemical structure of the particles start changing. It is also possible that in this size range, the rate of some of the reactions of interphase electron transfer changes due to the increase in the contribution of "hot" electrons. However, all of these assumptions require additional experimental verification.

Figure 3 displays the dependence of the mean irradiation energy (E) of colloidal Q-CdS on the particle size:

$$E = \left(\int_0^{\infty} EI(E)\mathrm{d}E\right) \Big/ I_{\mathrm{i}},$$

where $I(E)$ is the intensity of irradiation with a quantum energy of E in relative units and I_{i} is the integral intensity of luminescence. This dependence is analogous to the dependence of the forbidden band width of CdS on the particle size and is probably caused by the same quantum-dimensional effects.[1—3]

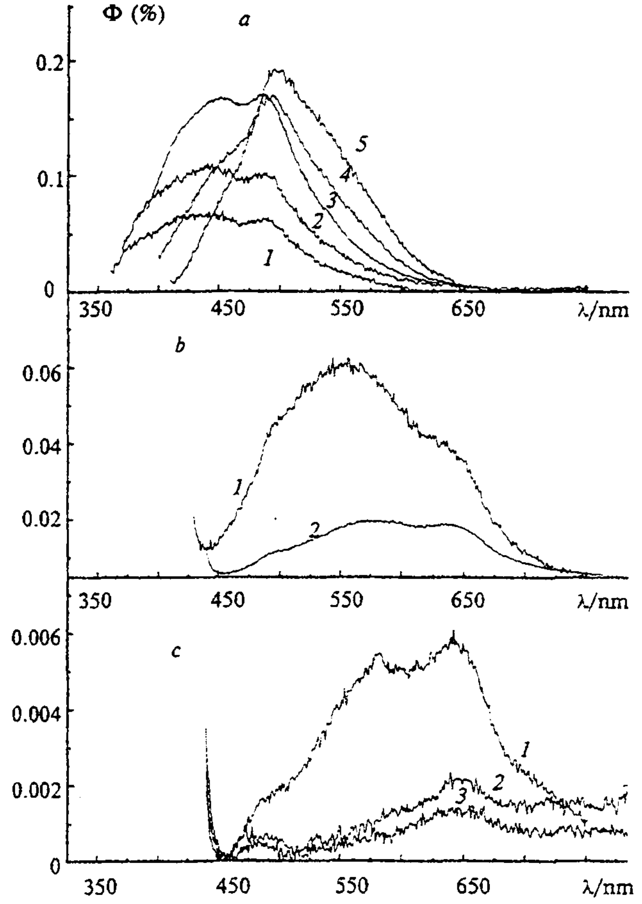

Fig. 1. Luminescence spectra of aqueous Q-CdS colloids with various particle size. *a*: *1* — $2R \approx$ 19.2 Å, λ_{exc} = 330 nm, *2* — $2R \approx$ 19.8 Å, λ_{exc} = 340 nm, *3* — $2R \approx$ 20.5 Å, λ_{exc} = 360 nm, *4* — $2R \approx$ 22.5 Å, λ_{exc} = 370 nm, *5* — $2R \approx$ 23 Å, λ_{exc} = 380 nm; *b*: *1* — $2R \approx$ 26 Å, λ_{exc} = 400 nm, *2* — $2R \approx$ 30.5 Å, λ_{exc} = 410 nm; *c*: *1* — $2R \approx$ 35 Å, λ_{exc} = 410 nm, *2* — $2R \approx$ 43.5 Å, λ_{exc} = 410 nm, *3* — $2R \approx$ 48 Å, λ_{exc} = 410 nm. Concentration of CdS $5 \cdot 10^{-4}$ mol L^{-1}, T = 23 °C.

Quenching of luminescence of colloidal CdS. For the most part, the quenching of luminescence of CdS colloids is caused by reactions of interphase electron transfer involving either an electron or a hole. Therefore, the irradiation produced by this process makes it possible to determine the regularities of the key steps of redox photocatalytic reactions on the surface of CdS particles. In addition, the use of various luminescence quenchers (anions, cations, neutral molecules) allows one to reveal the nature of electron-trapping centers on the CdS surface.

Regularities of fluorescence quenching of colloidal CdS by methylviologen dication. Analysis of the dependence of luminescence spectra of colloidal CdS particles (with

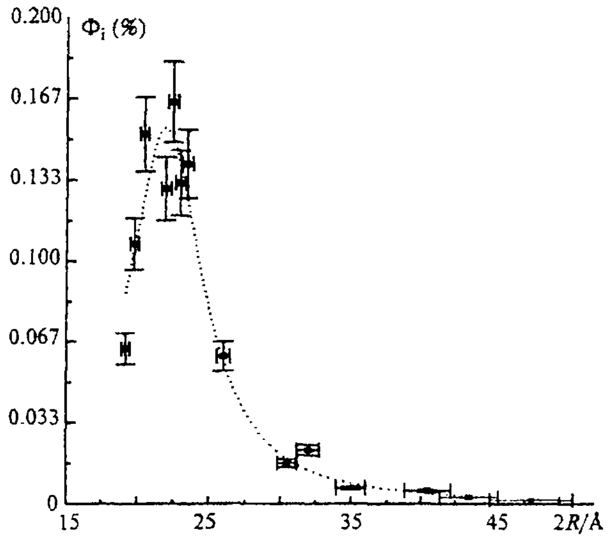

Fig. 2. Dependence of the integral quantum yield of luminescence (Φ_i) of Q-CdS colloidal solutions on the particle size (2R). T = 23 °C.

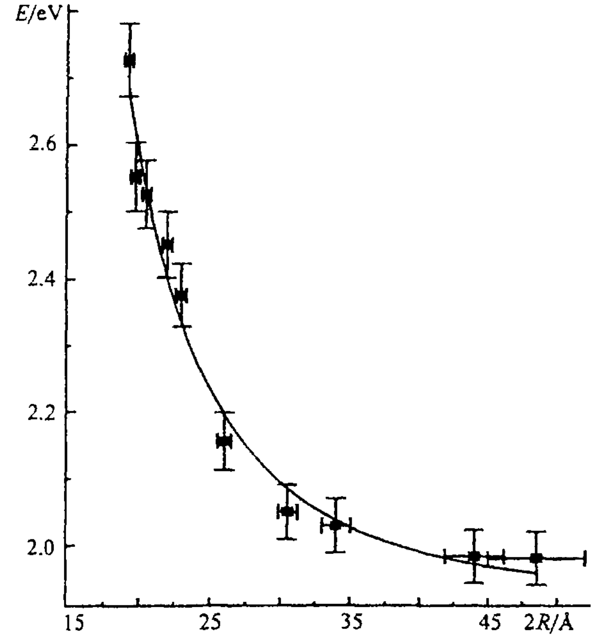

Fig. 3. Dependence of the mean emission energy of luminescence (E) of Q-CdS on the colloidal particle size (2R). T = 23 °C.

particle sizes from 20 to 44 Å) on the concentration of methylviologen (Fig. 4) makes it possible to conclude that the efficiency of luminescence quenching increases with an increase in wavelength and particle size.

In order to interpret quantitatively the results obtained, let us analyze processes involving an excited electron that can occur in a colloidal semiconductor particle exposed to steady-state irradiation. First, these include bulk recombination (radiative and nonradiative) of nonequilibrium charge carriers. Since luminescence is totally quenched in our experiments, it may be assumed that the fraction of radiative recombination in the particle bulk is negligible. Let us also assume that the recombination rate is described by a linear law in the concentration of charge carriers, as is the case at low generation of minority carriers, when the recombination rate is limited by the rate of trapping of a nonequilibrium carrier by a recombination center.[5] In this case, the rate of nonradiative recombination in the bulk is $k_{b,n}Ve$, where $k_{b,n}$ is the rate constant of nonradiative recombination in the bulk; V is the volume of the colloidal particle; and e is the steady-state concentration of electrons in the colloidal particle. It should also be noted that, according to earlier studies,[6] for a particle with a size of several hundred Angström exposed to steady-state irradiation, the concentration of electrons and holes within the particle along its radius is constant.

Another pathway for the disappearance of nonequilibrium charge carriers involves their recombination at the particle surface (radiative with rate constant $k_{s,r}$ and nonradiative with rate constant $k_{s,n}$). It is of critical importance to find out whether the centers of surface recombination are the same as the adsorption centers of the quencher, *i.e.*, whether the adsorption of an electron acceptor can make the surface recombination centers disappear. If the answer is positive (case *1*), the rate of surface recombination is $(k_{s,r} + k_{s,n})S(1 - \Theta_a)e$, where S is the surface area of the particle and Θ_a is the fraction of the surface occupied by the quencher. Otherwise (case *2*), the $(1 - \Theta_a)$ multiplier should be excluded. Below, we analyze both variants, compare them with experimental data, and select the one which better describes the observed phenomena.

The third pathway for the disappearance of nonequilibrium electrons is by their transfer to the quencher molecules. The expression for the quenching rate has the form $k_{Q,Red}S\Theta_a e$, where $k_{Q,Red}$ is the heterogeneous rate constant of electron transfer to the acceptor.

Under steady-state irradiation conditions, the rate of generation of nonequilibrium charge carriers equals the rate of their disappearance. Therefore, the following equations can be written for cases *1* and *2*, respectively:

$$k_{b,n}eR/3 + (k_{sr,r} + k_{sr,n})(1 - \Theta_a)e + k_{Q,Red}\Theta_a e = \alpha I_0 R/3, \quad (1)$$

$$k_{b,n}eR/3 + (k_{sr,r} + k_{sr,n})e + k_{Q,Red}\Theta_a e = \alpha I_0 R/3. \quad (2)$$

Here R is the particle radius, I_0 is the intensity of incident irradiation, and α is the coefficient of light absorption by the CdS particle.

Solving these equations for electron concentration e for cases *1* and *2*, respectively, one obtains

$$e = \alpha I_0(R/3)[k_{b,n}R/3 + (k_{sr,r} + k_{sr,n})(1 - \Theta_a) + k_{Q,Red}\Theta_a]^{-1},$$

$$e = \alpha I_0(R/3)[k_{b,n}R/3 + (k_{sr,r} + k_{sr,n}) + k_{Q,Red}\Theta_a]^{-1}.$$

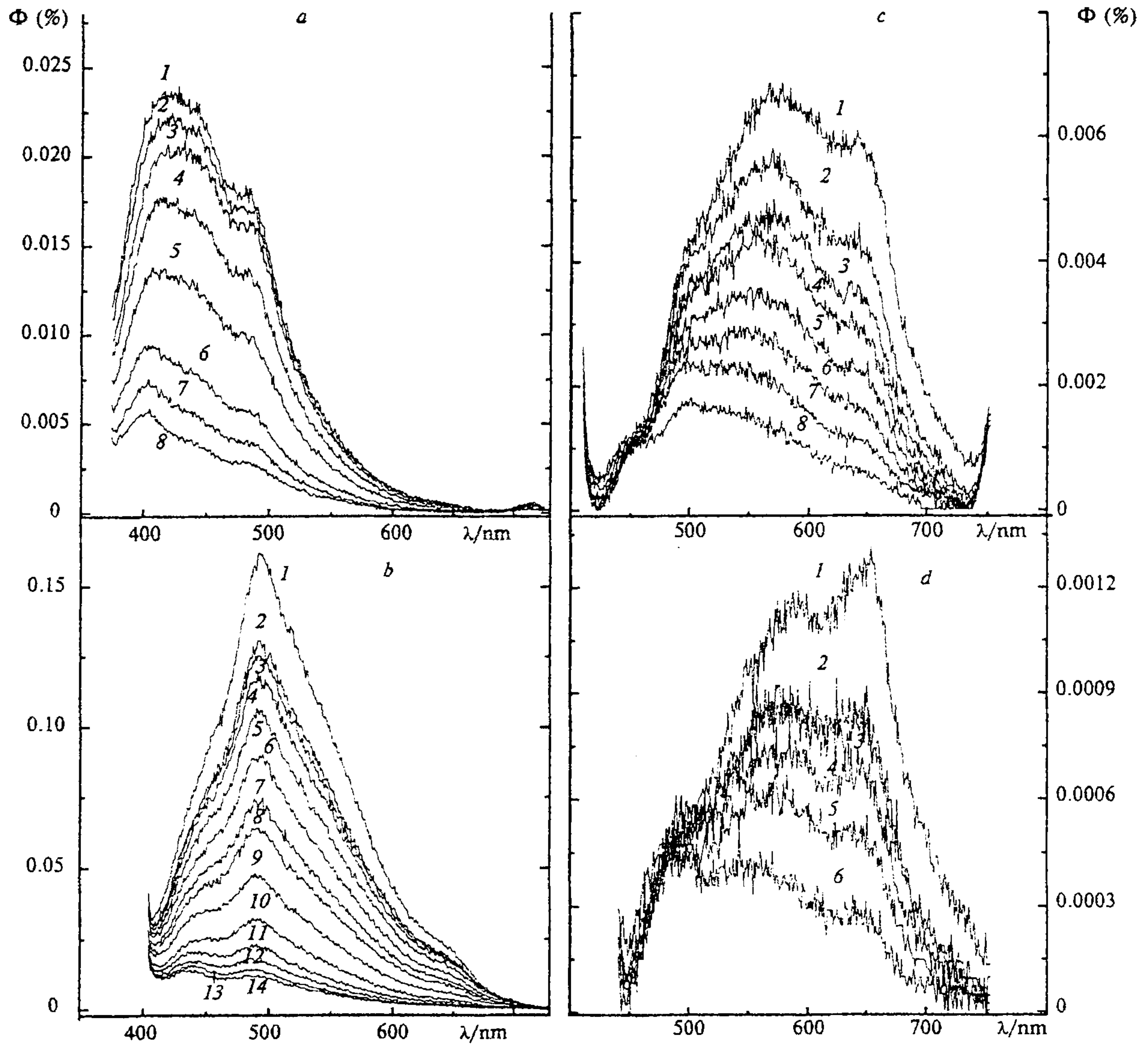

Fig. 4. Changes in luminescence spectra of Q-CdS colloidal solutions with $2R \approx 20$ Å, $\lambda_{exc} = 345$ nm (*a*), $2R \approx 23$ Å, $\lambda_{exc} = 375$ nm (*b*), $2R \approx 34$ Å, $\lambda_{exc} = 380$ nm (*c*), $2R \approx 44$ Å, $\lambda_{exc} = 400$ nm (*d*) on addition of methylviologen. The concentration of $MVCl_2$ added was: *a*) 0 (*1*), 10^{-5} (*2*), $5 \cdot 10^{-5}$ (*3*), 10^{-4} (*4*), $2 \cdot 10^{-4}$ (*5*), $5 \cdot 10^{-4}$ (*6*), 10^{-3} (*7*), $2 \cdot 10^{-3}$ (*8*) mol L^{-1}; *b*) 0 (*1*), 10^{-7} (*2*), $5 \cdot 10^{-7}$ (*3*), 10^{-6} (*4*), $2 \cdot 10^{-6}$ (*5*), $5 \cdot 10^{-6}$ (*6*), 10^{-5} (*7*), $2 \cdot 10^{-5}$ (*8*), $4 \cdot 10^{-5}$ (*9*), $8 \cdot 10^{-5}$ (*10*), $1.5 \cdot 10^{-4}$ (*11*), $2 \cdot 10^{-4}$ (*12*), $3 \cdot 10^{-4}$ (*13*), $4 \cdot 10^{-4}$ (*14*) mol L^{-1}; c) 0 (*1*), 10^{-7} (*2*), $2 \cdot 10^{-7}$ (*3*), $5 \cdot 10^{-7}$ (*4*), 10^{-6} (*5*), $2 \cdot 10^{-6}$ (*6*), $5 \cdot 10^{-6}$ (*7*), 10^{-5} (*8*) mol L^{-1}; *d*) 0 (*1*), 10^{-7} (*2*), $2 \cdot 10^{-7}$ (*3*), $5 \cdot 10^{-7}$ (*4*), 10^{-6} (*5*), $5 \cdot 10^{-6}$ (*6*) mol L^{-1}. The concentration of CdS was $5 \cdot 10^{-4}$ mol L^{-1}, $T = 23$ °C.

Using an approach analogous to that used to derive the Stern—Volmer equation,[7] it is easy to show that the quantum yield Φ of luminescence in the steady-state mode for cases *1* and *2*, respectively, can be expressed by the following equations:

$$\frac{\Phi^0}{\Phi} - 1 = \frac{k_{Q,Red} + k_{b,n} R/3}{k_{b,n} R/3 + (k_{sr,r} + k_{sr,n})} \cdot \frac{\Theta_a}{1 - \Theta_a}, \tag{3}$$

$$\frac{\Phi^0}{\Phi} - 1 = \frac{k_{Q,Red}}{k_{b,n} R/3 + (k_{sr,r} + k_{sr,n})} \cdot \Theta_a, \tag{4}$$

where Φ^0 is the quantum yield of luminescence with no quencher added.

The dependence of Θ_a on the quencher concentration in solution can, to a first approximation, be described by the Langmuir adsorption isotherm:

$$\Theta_a = AK_{ads}C_Q/(1 + K_{ads}C_Q), \tag{5}$$

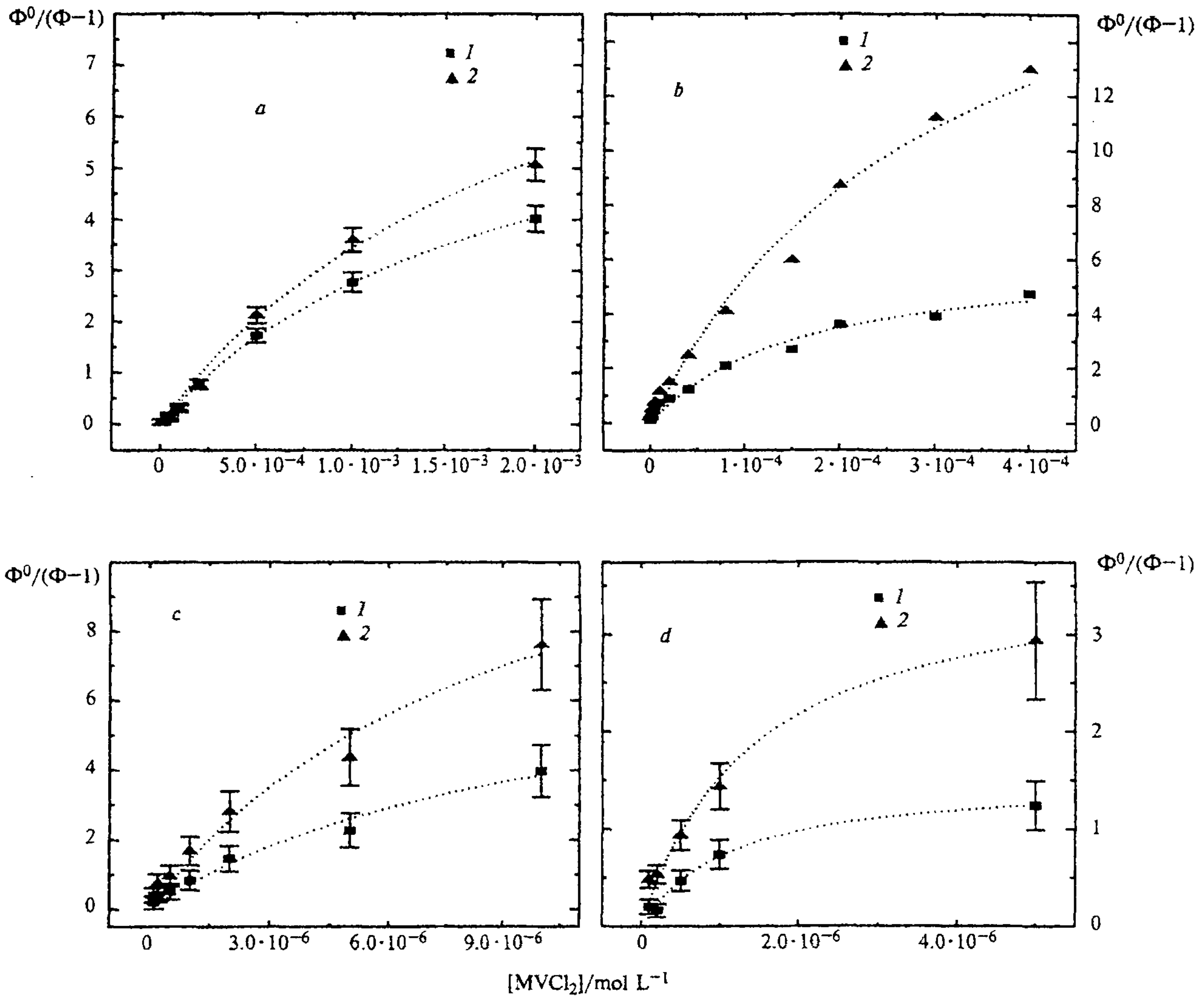

Fig. 5. Dependence of the luminescence quantum yield of colloidal CdS with particles of various sizes on the concentration of methylviologen in the Stern—Volmer equation coordinates. Particle size: *a*) $2R \approx 20$ Å, bands at 420 nm ($A = 7.4763\pm0.2848$, $K = 585.06\pm39.34$) (*1*) and 480 nm ($A = 10.186\pm1.180$, $K = 510.60\pm99.94$) (*2*); *b*) $2R \approx 23$ Å, bands at 440 nm ($A = 6.3614\pm0.6128$, $K = 6066.4\pm1345$) (*1*) and 500 nm ($A = 22.323\pm13.57$, $K = 3148.4\pm3069$) (*2*); c) $2R \approx 34$ Å, bands at 560 nm ($A = 7.4103\pm1.617$, $K = 1.084\cdot10^5\pm4.103\cdot10^4$) (*1*) and 640 nm ($A = 13.798\pm2.878$, $K = 1.144\cdot10^5\pm4.214\cdot10^4$) (*2*); *d*) $2R \approx 44$ Å, bands at 560 nm ($A = 1.5204\pm0.1130$, $K = 8.981\cdot10^5\pm1.729\cdot10^5$) (*1*) and 640 nm ($A = 3.7603\pm0.3443$, $K = 6.859\cdot10^5\pm1.551\cdot10^5$) (*2*). The concentration of CdS was $5\cdot10^{-4}$ mol L^{-1}, $T = 23$ °C.

where C_Q is the quencher concentration in the solution and K_{ads} is the equilibrium constant of quencher adsorption on the CdS surface.

Substituting Eq. (5) into Eqs. (3) and (4) gives

$$\frac{\Phi^0}{\Phi} - 1 = \frac{k_{Q,Red} + k_{b,n}R/3}{k_{b,n}R/3 + (k_{sr,r} + k_{sr,n})} \cdot K_{ads}C_Q, \qquad (6)$$

for case *1*, and

$$\frac{\Phi^0}{\Phi} - 1 = \frac{k_{Q,Red}}{k_{b,n}R/3 + (k_{sr,r} + k_{sr,n})} \cdot \frac{K_{ads}C_Q}{1 + K_{ads}C_Q} =$$

$$= \frac{AK_{ads}C_Q}{1 + K_{ads}C_Q}. \qquad (7)$$

for case *2*. It is evident that in case *1*, Φ^0/Φ depends linearly on the quencher concentration, which disagrees with the experiment (Fig. 5). Therefore, we shall henceforth treat the experimental data according to Eq. (7), which describes the case where the recombination centers are different from the adsorption centers. The variable parameters include A and K_{ads}. The physical meaning of the parameter A is the ratio of the probability of electron transfer to the quencher molecules to the overall probability of death of the electron in the recombination process.

Figure 5 presents experimental data on luminescence quenching of CdS colloidal particles of various sizes in the Stern—Volmer equation coordinates. The data correspond to different luminescence bands. The same figure contains curves approximating the experimental points to the values calculated according to Eq. (7). Both the A and K_{ads} parameters can be found from these curves. As seen in Fig. 5, quenching of CdS luminescence by methylviologen is different for different bands and depends on the colloidal particle size. In particular, the adsorption constant of methylviologen increases as the CdS colloidal particle size increases. It follows from Fig. 6 that the adsorption constant K_{ads} decreases exponentially with increase in the inverse diameter of the colloidal particle. These data allow one to assume that the adsorption constant K_{ads} of methylviologen depends on the particle size of the colloidal adsorbent in the same way as the solubility product of ultradispersed particles; this is probably due to the common nature of these phenomena.[8,9]

For particles of same size, the long-wave band is characterized by higher A, which indicates a change in the rate constant of luminescence quenching, k_Q, since for one particular particle the constants of bulk ($k_{b,n}$) and surface ($k_{sr,n} + k_{sr,r}$) recombination remain unchanged. It follows from Fig. 7, which displays the dependence of the logarithm of the parameter A on the depth of the energy level of the recombination center with respect to the bottom of the conduction band, that the transfer of an electron from a recombination center to a quencher molecule passes through an inverted activation barrier,[10] *i.e.*, the so-called inverted Marcus region,[11] in which the rate constant decreases with decrease in reaction enthalpy. In fact, the deeper the energy level of the recombination center, the smaller the difference between the energies of this level and that of the quencher molecule, and hence the smaller the activation energy of such transfer. The processes in question are depicted schematically in Fig. 8.

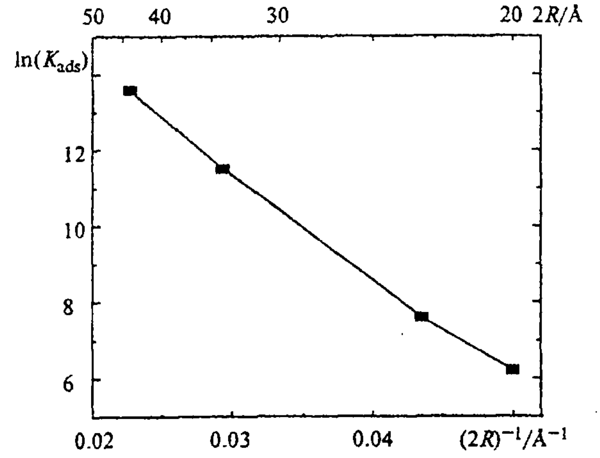

Fig. 6. Dependence of the calculated adsorption constant of methylviologen K_{ads} on CdS particles on the size of colloidal particles. The K_{ads} values were found by approximation of experimental data on luminescence quenching according to Eq. (7).

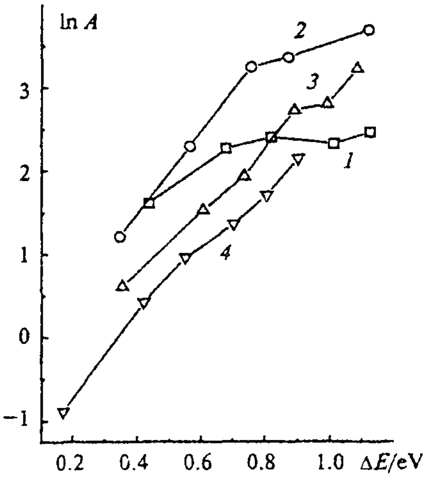

Fig. 7. Dependence of the calculated parameter A proportional to the rate constant of interphase electron transfer from CdS to quencher molecules on the position of the energy level of the recombination center for CdS particles of various sizes: $2R \approx$ 20 (*1*), 23 (*2*), 34 (*3*), 44 (*4*) Å. The energy level position (ΔE) was calculated with respect to the bottom of the conduction band.

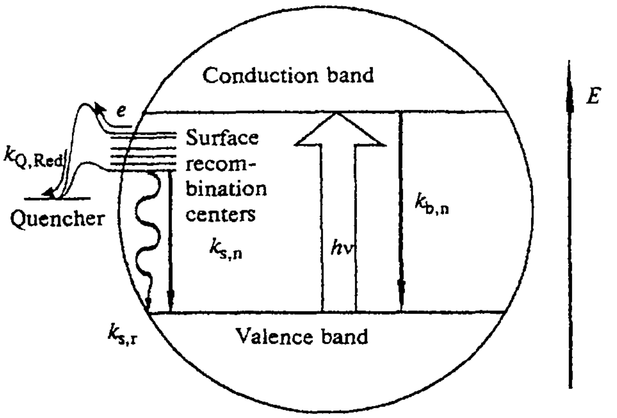

Fig. 8. Schematic representation of energy levels and ways of relaxation of photoexcited nonequilibrium charge carriers in a semiconductor particle.

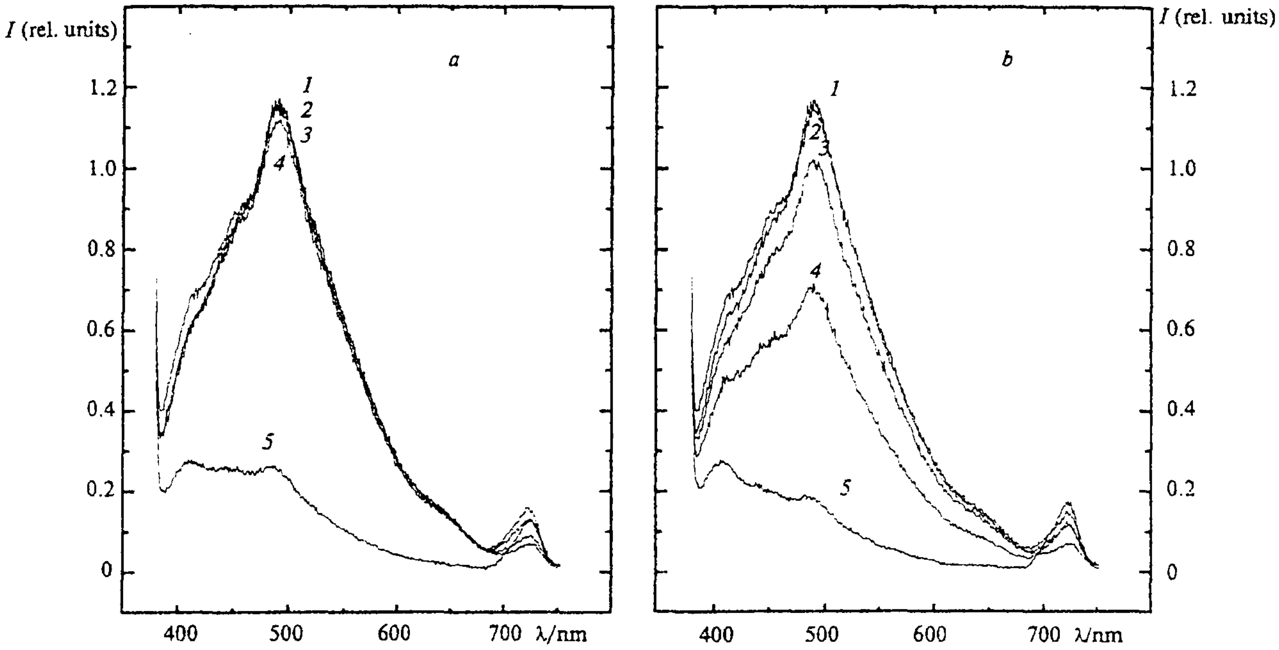

Fig. 9. Change in the luminescence spectrum of colloidal Q-CdS solutions (λ_{exc} = 350 nm) on addition of PW_{12}. *a*) *1* — original spectrum, *2—5* — gradual addition to a concentration: $2 \cdot 10^{-5}$ (*2*), 10^{-4} (*3*), $2 \cdot 10^{-4}$ (*4*), $4 \cdot 10^{-4}$ (*5*) mol L^{-1}. *b*) *1* — original spectrum, *2—5* — addition of PW_{12} ($4 \cdot 10^{-4}$ mol L^{-1}) first (*2*), then H_2SO_4 to a concentration of $2.5 \cdot 10^{-4}$ (*3*), $5 \cdot 10^{-4}$ (*4*), $7.5 \cdot 10^{-4}$ (*5*) mol L^{-1}. Concentration of CdS $5 \cdot 10^{-4}$ mol L^{-1}, T = 23 °C.

The above analysis of the dependence of parameter A on the depth of the recombination center energy level is a qualitative one. Real specimens of a colloid always have a size distribution. Both the adsorption constant of the quencher and the luminescence emission spectrum depend on the particle size. This introduces a certain error into the true value of A. The error is particularly significant for "deep" and "shallow" energy levels of the surface recombination center.

Specific features of luminescence quenching of colloidal CdS by quenchers of various nature. Methylviologen is a dication and is therefore well adsorbed on negatively charged colloidal particles. Let us analyze the regularities of luminescence quenching by other electron acceptors, *viz.*, heteropolyanions.

When phosphotungstic acid (PW_{12}) is added to a colloidal solution of CdS, a sharp dependence of luminescence intensity on the amount of added PW_{12} is observed: up to a PW_{12} concentration of $2 \cdot 10^{-4}$ mol L^{-1}, the luminescence intensity remains almost unchanged but decreases abruptly as the concentration is increased to $4 \cdot 10^{-4}$ mol L^{-1} (Fig. 9, *a*). Simultaneously, the pH changes from 9 to 6. On the other hand, if H_2SO_4 is gradually added to a colloid already containing $2 \cdot 10^{-4}$ mol L^{-1} PW_{12} (Fig. 9, *b*), the relative intensity of luminescence also decreases as pH changes within the same range. This result can be explained by "recharging" of the colloidal particle surface upon acidifying the solution. In fact, a colloidal particle is charged negatively before the addition of PW_{12} due to the adsorption of excess sulfide ions on it; therefore, PW_{12} is poorly adsorbed on the colloid. After the solution acidity is increased, the colloidal particle surface can be "recharged" due to the adsorption of protons on it; this should increase abruptly the affinity of phosphotungstic acid molecules to the surface and hence increase the probability of electron transfer to this acceptor.

The phenomenon in question does not allow Eq. (7) to be used for the description of experimental regularities of luminescence quenching by phosphotungstic acid in the absence of a buffer in the entire range of PW_{12} concentration, as in this case K_{ads} becomes a function of C_Q. However, the latter experiment clearly demonstrates the heterogeneous character of the process studied and indicates that the adsorption of an electron acceptor affects significantly the rate of photocatalytic redox processes on semiconductor colloids.

Data on luminescence quenching of colloidal CdS by quenchers of various nature are listed below ([CdS] = $5 \cdot 10^{-4}$ mol L^{-1}, $2R \approx 23$ Å, T = 23 °C, λ_{exc} = 360 nm, λ_{rec} = 500 nm).

Quencher	K_{ads}	A
$K_3[Cr(SCN)_6]$	65±60	15±12
Et_4NCl	8200±6900	0.15±0.02
$BVBr_2$	1200±300	11±2
$MVCl_2$	2000±500	8.5±1.3
Py	23±250	0.35±3

It is evident that cations (MV^{2+}, BV^{2+}) are characterized by both high adsorption constants and high rates of luminescence quenching, whereas the $[Cr(SCN)_6]^{3-}$ anions have a small adsorption constant but a high A parameter.

The compounds which are inactive in electron transfer reactions (Et_4NCl and Py) are characterized by small A parameters.

PW_{12} has a small value of $AK_{ads} << 1$, since this compound almost does not display activity in quenching of excitated particles in the concentration range from 0 to $2 \cdot 10^{-4}$ mol L^{-1} (while surface recharging has not yet occurred). $K_3[Cr(SCN)_6]$, which at pH ≈ 8—9 exists in the colloidal CdS solution in the form of $Cr(SCN)^{3-}$, is characterized by a high value of A.

Compounds like Et_4NCl and Py, which have weak redox properties and are therefore inactive in electron transfer, are characterized by small values of A. Approximating the experimental dependences of Φ^0/Φ on C_Q by Eq. (7) gives $K_{ads} \approx 8200 \pm 6900$ L mol^{-1} for Et_4NCl, which exists in solution as the Et_4N^+ cation, and $K_{ads} \approx 23 \pm 250$ for pyridine, whose molecules at pH ≈ 8—9 are mostly uncharged. Such a difference in K_{ads} values agrees with the concept that the adsorption of various compounds on charged surfaces depends primarily on the electrical charge of the molecules of these compounds.

Equation (7) suggested above correctly reflects the changes in the properties of luminescence quenchers and, on the whole, describes the experimental data well. In addition, the data obtained make it possible to assume that the negatively charged S atoms on the surface play the role of quencher adsorption centers, where cations are adsorbed readily, while anions are adsorbed poorly. Since the CdS used in the entire series of the experiments was prepared with an excess of sulfide ions, either vacancies of the Cd atoms or interstitial S atoms are the predominating surface defects. Judging by the literature data,[12,13] both surface defects can serve as recombination centers for minority charge carriers. However, while quencher cations can potentially replace a surface Cd vacancy, they should not affect the interstitial S atoms. Based on the assumption that the quencher adsorption does not result in the disappearance of the recombination centers for minority charge carriers, the interstitial S is more probable as a recombination center.

Thus, the discovered dependence of the mean emission energy of luminescence on the particle size of the colloid is similar to the well-known dependence of the forbidden band width of Q-CdS on the particle size and is probably a manifestation of quantum-dimensional effects: it can be stated that as the forbidden band width increases on decreasing the particle size, the energy levels of recombination centers in Q-CdS are also shifted in a symbate way.

The differences in the efficiency of quenching of various luminescence bands of the same colloid, the sharp increase in the efficiency of luminescence quenching due to surface "recharging" of CdS colloidal particles, and the different efficiencies of luminescence quenching of Q-colloids of different particle size have been revealed.

As during the photoreduction of methylviologen on colloidal CdS, the photoexcited electron is transferred from the colloid particle to the methylviologen molecules adsorbed on it,[14] a Stern—Volmer-type equation for the efficiency of luminescence quenching has been suggested under the assumption of the linear dependence of the recombination rate on the concentration of nonequilibrium charge carriers in the semiconductor particle. The validity of this assumption has been confirmed by the good agreement of experimental data with the calculated values and with the results reported previously.[15]

It has been shown that the recombination and adsorption centers do not coincide, at least for the quenchers studied.

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