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Studies on the kinetics of interfacial electron transfer sensitized by colloidal CdS

D.V. Bavykin *, E.N. Savinov, V.N. Parmon

Boreskov Institute of Catalysis, Lavrentieva 5, Novosibirsk, Russia

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Abstract

Flash photolysis was used to study photobleaching of colloidal CdS particles with the controlled size. The rate constant of the photobleaching relaxation was found to depend on the size of the colloidal particles, an increase of the particle size resulting in a decrease of the rate constant. The influence of various electron acceptors on the photobleaching relaxation kinetics was investigated too. The addition of well adsorbing acceptor molecules decreases the initial amplitude of photobleaching and practically does not change the rate constant of the photobleaching relaxation. The photobleaching decay kinetics remains unchanged compared to the photobleaching relaxation kinetics of pure CdS. The addition of acceptor molecules with the small adsorption constant results in an increase of photobleaching relaxation rate constant, while the initial amplitude of photobleaching remains unchanged. Moreover, in the last case the photobleaching decay kinetics became exponential. ©2000 Published by Elsevier Science S.A. All rights reserved.

Keywords: Electron transfer; Photobleaching; CdS; Kinetic; Colloids

1. Introduction

Over the last decade, interfacial charge transfer as well as the dynamics of photoexcited state relaxation in nanosized semiconductors were under intensive investigations. It was stimulated by application of these materials as photocatalysts and also by their unusual physical and chemical properties. Numerous attempts have been made to characterize the kinetics of the photoexcited charge transfer by various methods in a wide range of time scales, down to femtoseconds [1,2]. The powerful light pulses generate usually a photoinduced blue shifts, or photobleaching of nanosized semiconductors, which is related to an excess of the conduction band electrons (the Burstein–Moss [3,4] effect). The decay of photobleaching in semiconductors reflects directly the kinetics of interfacial transfer of the excess conduction band electrons.

We used the semiconductor photobleaching to study the peculiarities of the interfacial photoexcited electron transfer from nanosized CdS of a various sizes to the surrounding media. Due to heterogeneity of the colloidal systems, one should take into account the surface effects and adsorption properties of CdS particles to describe peculiarities of the electron transfer. In order to demonstrate an importance of adsorption in CdS colloids, we studied the influence of added electron acceptors of different nature of the kinetics of the CdS photobleaching decay. The adsorption properties of CdS nanoparticles were controlled during their preparation. The excess of Cd^{2+} or S^{2-} ions are shown below to determine the possibility of electron acceptor ions to adsorb on the surface of CdS particles.

2. Experimental section

2.1. Materials

Cadmium chloride ($CdCl_2{\cdot}2.5H_2O$), tungstophosphoric heteropolyacid sodium salt ($NaH_2PW_{12}O_{40}$ denoted as PW_{12}^{3-}), sodium dodecyl sulfate (SDS), methylviologen chloride ($MVCl_2$ denoted as MV^{2+}) (high-purity grade, Reachim), sodium sulfide ($Na_2S{\cdot}9H_2O$), thioglycerol (Thio) (Fluka) were used without further purification.

2.2. Methods of the colloid preparation

Aqueous solutions of CdS nanoparticles with a definite particles size were prepared according to the previously developed procedure [5] with the thioglycerol used as a size adjusting and stabilizing agent.

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* Corresponding author.
E-mail address: bav@catalysis.nsk.su (D.V. Bavykin)

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2.3. Cds colloids with Cd^{2+} ions excess (denoted as CdS/Cd)

10 ml of solution with 2×10^{-3} M $CdCl_2$, 2×10^{-2} M SDS and the *required* amount (in range of 0–10^{-2} M) of thioglycerol were mixed with 10 ml of 10^{-3} M Na_2S solution in a 100 ml vessel under vigorous stirring. The color of the produced transparent solution depended on the amount of thioglycerol and varied from colorless to yellow. Five minutes after the preparation, in all samples an extra amount of thioglycerol was added (up to 5×10^{-2} M) in order to make the chemical composition of the colloids same.

2.4. CdS colloids with an excess of S^{2-} ions (denoted as CdS/S)

10 ml of solution with 10^{-3} M $CdCl_2$ and various amount (in range of 0–10^{-2} M) of thioglycerol were mixed with 10 ml of 2×10^{-3} M Na_2S solution in a 100 ml vessel under vigorous stirring. The color of the produced transparent solution depended on the amount of thioglycerol. Five minutes after the preparation, an extra amount of thioglycerol was added (up to 5×10^{2} M) to all the samples in order to make the chemical composition of the colloids same.

2.5. Flash photolysis experiments

The kinetics of the photobleaching decay for the colloidal CdS was measured by a flash photolysis set-up. Its characteristics were the following. The excitation light source was a flash mercury lamp (pulse time 5 μs, INP2-7/120). The probing light source was a 150 W Xenon high pressure arc lamp (DKsSH- 150). The probing light passed at right angle to the excitation light through the sample cell (length 10 cm, volume 10 ml), then through a monochromator and fell on a photomultiplier with 1024 registration channels connected to a computer. In order to prevent errors from scattered light, the photomultiplier was 2.5 m distant from the sample cell. To adjust the wavelength of the excitation and the probe light, conventional glass cut-off filters were used. A dose of radiated light was measured by using well-known ferrioxalate actinometry [6]. In all experiments the dose of adsorbed excitation light in sample cell was approximately 10^{-6} Einstein per one flash.

3. Results and discussion

Fig. 1 shows the kinetic decay curves and spectra of photobleaching for the CdS/Cd colloids of four different sizes. The photobleaching spectrum are reconstructed from the kinetic curves as the magnitudes of the photobleaching at the time right away the flash of lamp. The maximum of photobleaching spectrum is congruent with a high precision to the absorption threshold of the semiconductor. According to the quantum size effect, the maximum of the photobleaching in the spectra shifts to the longer wavelength region at an increase of the CdS/Cd particles size.

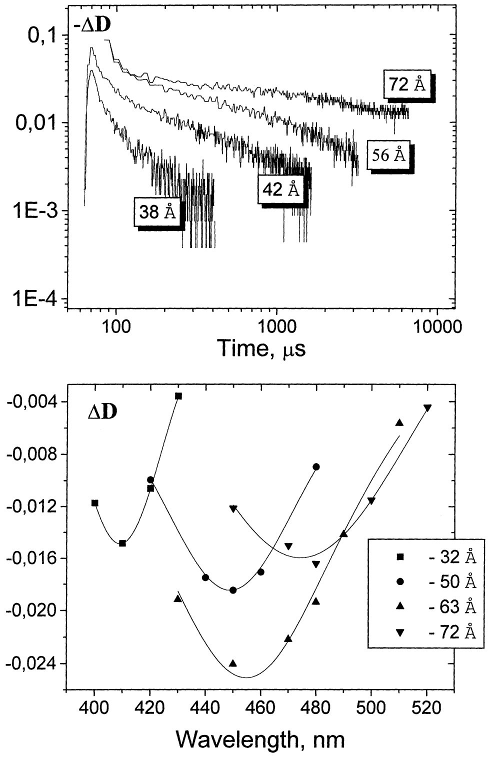

Fig. 1. The kinetic curves of photobleaching decay and spectra of photobleaching of different sized CdS/Cd nanocolloids. ΔD *is a difference between optical density before and after the flash*. Photoexcitation at $\lambda < 360$ nm. The kinetic curves of photobleaching decay were measured at a maximum of photobleaching. [CdS] = 10^4 M, [SDS] = $2\times l0^3$ M, [Thio] = 5×10^3 M, 1 = 10 cm, $T = 20°C$.

The kinetic curves of the photobleaching relaxation in Fig. 1 are nonmonoexponential, and they could be described by the logarithmic equation

$$\Delta D(t) = \Delta D_0 + A\ \ln(1 + B(t - t_0)) \tag{1}$$

where ΔD is a change of optical density, t_0 is a parameter of time shift at the zero time point, ΔD_0 is a parameter which corresponds to the photobleaching magnitude at the zero time point, A and B are the fitted parameters characterizing the rate constant of the photobleaching decay.

According to the Fig. 1 an increase of the colloidal particle size results in a decrease of the photobleaching decay rate. In other words the smaller the particle size the greater the rate of interfacial electron transfer. This means that decreasing particle size could improve the efficiency of photogenerated charge separation. This phenomena was predicted by Gerischer [7].

The application of Eq. (1) can be proved by the following physical-chemical reasons. It is well known that the presence of photoexcited electrons in a colloidal semiconductor particle results in a shift of the flat band potential. In general electrochemistry, the rate of the interfacial electron transfer is known to depend on the overvoltage η:

$$\frac{\mathrm{d}n}{\mathrm{d}t} = -k\mathrm{e}^{((1-\alpha)F\eta)RT} = -k\mathrm{e}^{\gamma n} \qquad (2)$$

where k is an interfacial electron transfer rate constant, n is the concentration of photogenerated electrons in the colloidal particle, F is a Faraday number, R and T are the universal gas constant and the temperature, γ is a parameter which characterizes what overvoltage would be generated by n electrons at the surface of the colloidal particle. Integrating Eq. (2) and taking into account that ΔD could be proportional [8] to n ($\Delta D = Cn$, where C is a proportionality factor), one can deduce Eq. (1), where $A = -1/\gamma$, $B = \gamma k\ \exp(\gamma n_0)$. A detailed discussion of these assumptions was published elsewhere [9].

There is also another explanation of the observed nonexponentiality of the photobleaching decay. According to Fig. 1, the rate constant of the photobleaching decay depends on the size of the CdS colloidal particles. The particles in the real colloids have a size distribution. In principle, existence of such size distribution should distort the exponentiality of the decay of photobleaching.

Unfortunately, Eq. (1) depends weakly on the parameter B. Therefore it is difficult to estimate the exact value of the interfacial electron transfer rate constant k with the high precision.

Since the relaxation of photobleaching in colloids of a semiconductor reflects the interfacial electron transfer, it is of interest to investigate the influence the addition of electron acceptors on the kinetics of the photobleaching decay. It was found that electron acceptors can affect the kinetic curves of photobleaching decay in different ways.

Fig. 2 shows the kinetic curves of the CdS/Cd photobleaching decay after addition of MV^{2+} and PW_{12}^{3-} It is evident that the positively charged CdS/Cd particles possess a high ability to adsorb the negatively charged PW_{12}^{3-} anions and only a low ability to adsorb positively charged MV^{2+} cations. Thus, the addition of the PW_{12}^{3-} anions to the CdS/Cd colloids results in a decrease of initial photobleaching amplitude (ΔD_0) and in an increase of the interfacial electron transfer rate constant k (B) due to the photoexcited electron transfer to the adsorbed PW_{12}^{3-} anions (Fig. 2b). Unfortunately, it was difficult to determine quantitatively the dependence of these parameters on the PW_{12}^{3-} concentration because of the difficulties described above. The shape of the kinetic curves remains nonexponential. The addition of the MV^{2+} cations to the CdS/Cd colloids results in a change of the kinetic curves shape. The kinetic curves of the photobleaching decay become exponential and the rate constant of the interfacial electron transfer increases linearly with respect to an increase of the MV^{2+} concentration (Fig. 3). Such behavior of the photobleaching relaxation seems to originate from the fact that MV^{2+} cations could not adsorb on the surface of the positively charged CdS/Cd particles. Hence, the rate of the photoexcited electron transfer is lim-

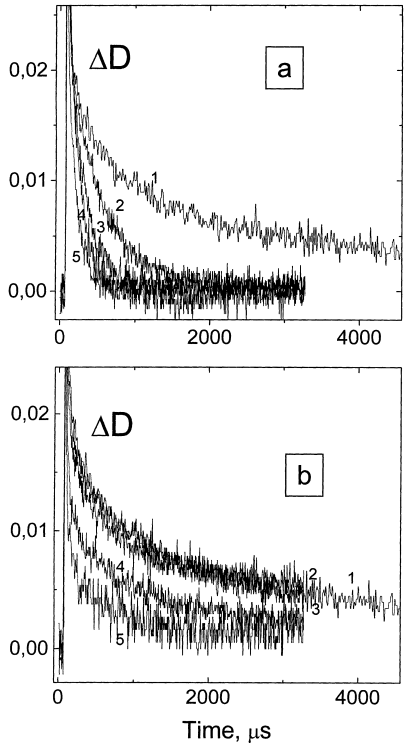

Fig. 2. The kinetic curves of CdS/Cd nanocolloids ($2R \sim 4$ nm) photobleaching relaxation after addition of MV^{2+} and PW_{12}^{3-} Photoexcitation at $\lambda < 360$ nm. The kinetic curves were measured at $\lambda = 470$ nm. [CdS] = 10^{-4} M, [SDS] = 2×10^{-3} M, [Thio] = 5×10^{-3} M, 1 = 10 cm, $T = 20°C$ (a) concentration of added MV^{2+} is **1**: 0 M, **2**: 2×10^{-8} M, **3**: 5×10^{-8} M, **4**: 8×10^{-4} M, **5**: 10^{-7} M; (b) concentration of added PW_{12}^{3-} is **1**: 0 M, **2**: 4×10^{-8} M, **3**: 8×10^{-8} M, **4**: 10^{-7} M, **5**: 3×10^{-7} M.

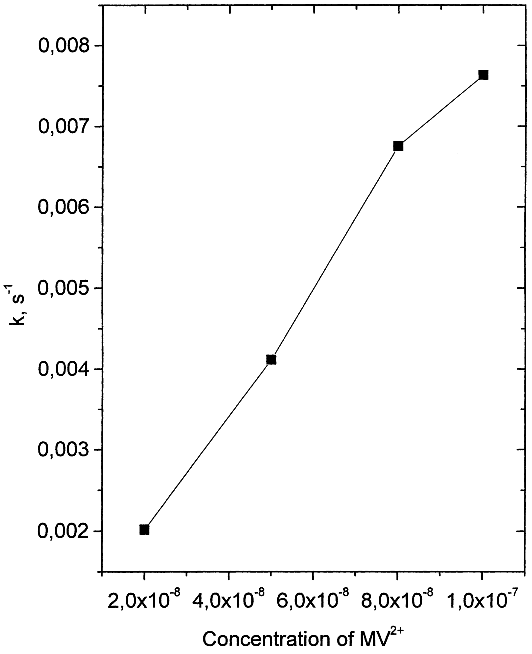

Fig. 3. The rate constant of the interfacial electron transfer from photoexcited colloidal CdS/Cd ($2R \sim 4$ nm) to MV^{2+} in solution as a function of MV^{2+} concentration. [CdS] = 10^{-4} M, [SDS] = 2×10^{-3} M, [Thio] = 5×10^{-3} M, $T = 20°C$.

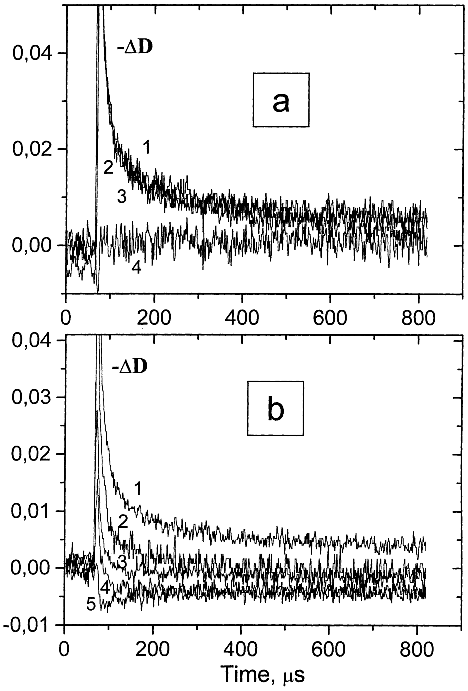

Fig. 4. The kinetic curves of CdS/S nanocolloids ($2R \sim 6.9$ nm) photobleaching relaxation after addition of MV^{2+} and PW_{12}^{3-}. Photoexcitation at $\lambda < 360$ nm. The kinetic curves were measured at $\lambda = 490$ nm. $[CdS] = 10^{-4}$ M, $[PAA] = 2 \times 10^{-3}$ M, $[Thio] = 5 \times 10^{-3}$ M, $1 = 10$ cm, $T = 20°C$ (a) concentration of added PW_{12}^{3-} is **1**: 0 M, **2**: 10^{-6} M, **3**: 10^{-5} M, **4**: 10^{-4} M; (b) concentration of added MV^{2+} is **1**: 0 M, **2**: 10^{-9} M, **3**: 2×10^{-9} M, **4**: 8×10^{-9} M, **5**: 1.2×10^{-8} M.

ited by the diffusion of the MV^{2+} cations to the surface of the colloidal particles. Therefore, the kinetic curves of the photobleaching decay appear to be exponential and the rate constant of the photobleaching decay depends on the MV^{2+} concentration in a linear manner. Thus, it is obvious that the electrostatic charge of the colloidal particle surface and the charge on the electron acceptors ions affect significantly the character of the photobleaching relaxation.

It was interesting to check the above consideration by adding PW_{12}^{3-} and MV^{2+} to the negatively charged CdS/S colloidal particles. The kinetic curves of the CdS/S photobleaching relaxation after addition of PW_{12}^{3-} and MV^{2+} are presented in Fig. 4. One can see that after addition of PW_{12}^{3-} in the concentration up to 10^{-4} M there is no visible change in the kinetic curves. However, when the concentration of PW_{12}^{3-} exceeds 10^{-4} M, the photobleaching of the CdS/S colloids disappears suddenly. This can be explained by recharging of the CdS/S surface during the consecutive addition of the tungstophosphoric heteropolyacid. Indeed, H_2S is rather weak acid. Therefore addition of strong acids should result in adsorption of H^+ ions on the surface of CdS/S and its recharging from negative to positive. After this recharging, effective adsorption of PW_{12}^{3-} occurs resulting in disappearance of CdS/S photobleaching because of the fast (faster then time resolution of flash photolysis set-up) photoexcited electron transfer to adsorbed PW_{12}^{3-}. Recently [10] the same behavior of the CdS/S colloids was observed in experiments for colloidal CdS/S luminescence quenching by PW_{12}^{3-}. The CdS/S colloids luminescence was found to be quenched rapidly after addition of a certain quantity of PW_{12}^{3-}.

The addition of the positively charged MV^{2+} to the CdS/S colloids results in a decrease of the initial photobleaching amplitude ΔD_0 and an increase of parameter B in the same manner as in the case of adding the PW_{12}^{3-} ions to the CdS/Cd colloids. However, it is seen from Fig. 4b, this effect is not so clear due to a masking by the photogenerated reduced form of methylviologen ($MV^{+\bullet}$) which absorbs light in the region of the photobleaching.

4. Conclusions

Colloids of CdS with an excess of either Cd^{2+} or S^{2-} ions were prepared with particles of different sizes. The peculiarities of the photoexcited electron transfer from these particles were studied by flash photolysis measurements. It was found that the rate of the CdS photobleaching relaxation increases as the particle size decreases. The kinetic curves of the photobleaching decay are nonexponential and are fairly well by a logarithmic law. The influence of the addition of electron acceptors with different electric charges on the photobleaching relaxation was studied. It was shown that the ability of electron acceptors to be adsorbed on the surface of colloidal CdS determines the character of observed changes in the photobleaching decay curves. This ability depends mainly on the signs of electric charge of the electron acceptors and colloidal particles. In case of the opposite signs, a pronounced adsorption does occur. When the acceptor molecules are well adsorbed on the surface of the CdS particles, the photobleaching relaxation is limited by the reaction of electron transfer from colloidal particle to the adsorbed acceptors. When the acceptor molecules are poorly adsorbed on the CdS surface, the photobleaching relaxation is limited by the diffusion of acceptor molecules to the surface of colloidal particles.

Acknowledgements

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