Colloidal CdS Fluorescence Quenching by MV^{2+} Under Continuous Irradiation

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This paper describes the photochemical behavior of the colloidal $CdS/MV^{2+}/COP$ system in excess of Na_2S. We determined the rate constants for all the reactions which take place in solution under continuos irradiation and put into evidence the following intermediates: the monomer radical $MV^{\bullet+}$ which dimerizes in $(MV^{\bullet+})_2$ radical and the double reduced form MV^0 of methylviologen. By this continuos irradiation technique we showed that the same reactions which take place on CdS particle surface with ultra fast rates can undergo also in bulk, but with a much slower rates.

INTRODUCTION

Interfacial photochemistry has undergone a vigorous expansion in the last. While colloidal crystallites of ≥ 10 nm diameter behave as a bulk semiconductor, crystallite ≤ 10 nm has only incomplete band structure development and excited electronic states [1–3]. In this limit the apparent crystallite (i.e. cluster) band gap and the electron and hole redox potentials, are size dependent. An excited state consists of a hole in the homo and an electron in the lumo. This excited state "exciton" can luminesce, undergo nonradiative recombination through surface states or undergo redox reactions with surface adsorbed molecules having energies inside the crystallite's gap.

The study of semiconductor particles is very attractive because of possible applications especially for the direct conversion of solar energy into the chemical one [4]. Therefore it seems important to investigate processes such as interfacial electron transfer and electron-hole recombination occurring in illuminated semiconductor colloidal particles. Many authors have investigated this system from different points of views. Serpone *et al.* [5] reported picosecond absorption spectra of reduced methylviologen $MV^{\bullet+}$ and claimed that the photoinduced electron transfer from CdS to MV^{2+} adsorbed on the particle occurred at the rate of 10^9 s^{-1}. Rossetti and Brus [6] reported that the life time of the $MV^{\bullet+}$ radical is between 5 ns and 20 ps from a picosecond resonance Raman scattering study, when the colloidal CdS was stabilized with polyacrylic acid (PAA). By adopting the data for the stabilizer styrene-maleic anhydride copolymer (COP) this rise life time is five time longer.

From all these studies it may be concluded that the dynamic mechanism of the photoinduced reduction of MV^{2+} on the colloidal CdS surface is the following: conduction band electrons induced by irradiation are trapped within 3 ps at some site on the surface which is like a sulphur vacancy or a surface Cd^{2+} ion. Then the trapped electron transfers to the adsorbed MV^{2+} ion in the time range between 20 ps and 0.1 ns. What happens with these species after this period is the subject of our investigations in the present paper.

EXPERIMENTAL

Colloidal CdS (8.73×10^{-4} M) was synthetized in laboratory from $Cd(SO_4)_2$ (Merck) using

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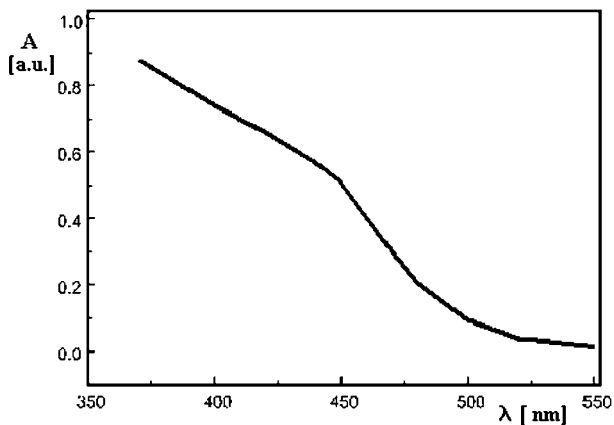[3] To whom correspondence should be addressed.

Fig. 1. Absorption spectra of synthetized CdS/COP.

Fig. 3. Spectral evolution of colloidal CdS/MV^{2+}/COP system at different irradiation times.

Kalyanasundaram's method [7] by replacing (NH$_4$)$_2$S with Na$_2$S (Fluka) in an excess of 2×10^{-4} M, bubbling Argon during the synthesis. A styrene-maleic anhydride (1:1) copolymer prepared also in laboratory was used as stabilizer. To record absorbtion and emission spectra we used an Unicam α Helyos spectrophotometer and an Aminco–Bowman spectrofluorimeter, respectively. As a quencher we used methylviologen (Sigma).

RESULTS AND DISCUSSIONS

We characterized our colloidal CdS by their absorption (Fig. 1) and emission spectra (Fig. 2).

Using the method of "fluorescence quenching" with methylviologen, MV^{2+}, we calculated an average particle size of about 60 Å what recommended them as nanoparticles.

We observed that if we use MV^{2+} concentration between 10^{-9}–10^{-7} M the quenching method works, but if we increase MV^{2+} concentration from 10^{-6} to 10^{-4} M
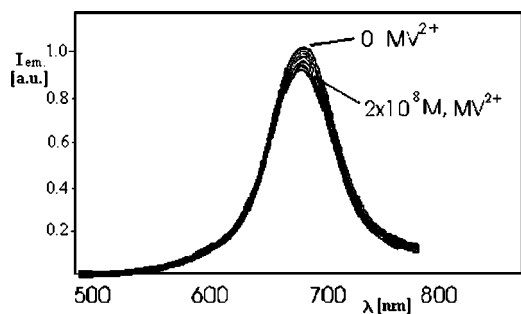
the fluorescence emission height begin to increase proportionaly as well as the fluorescence maximum is shifted to longer wavelength. We ascribe this behavior to the formation of a new complex CdS/MV^{2+}/COP and study their photochemical behavior under continous irradiation using a home made apparatus. The continous irradiation of the sample containing 7.56×10^{-4} M CdS and 1×10^{-4} M MV^{2+} in 2×10^{-4} M Na$_2$S excess stabilized with COP, bubbled with Ar, showed after different irradiation times the spectral behavior in Fig. 3.

For each irradiation time was used a new sample with the same content.

The spectrophotometric measurements were carried out versus a reference cell containing the same composition of the solution but with out methylviologen.

One observes that immediately after illumination in the first 30 s the initial yellow colloidal CdS solution becomes bluish due to MV$^{\bullet+}$ radical formation from MV^{2+} reduction, therefore the absorbance of the solution increases in both maxima of the MV$^{\bullet+}$ absorption spectrum at 603 nm as well as at 398 nm.

$$MV^{2+} + e^- \rightarrow MV^{\bullet+} \tag{1}$$

We calculated the rate constants for MV$^{\bullet+}$ formation, which obey a first order kinetics, and that is $k_\mathrm{I} = 7 \times 10^{-3}$ s^{-1} for $\lambda = 603$ nm and $k_\mathrm{I} = 6.92 \times 10^{-3}$ s^{-1} for $\lambda = 398$ nm (Fig. 4).

After a longer irradiation, 180 s, the absorbance continues to increase at 398 nm, which shows the increase of MV$^{\bullet+}$ concentration but at 603 nm it keeps practically constant. This behavior suggests that when the MV$^{\bullet+}$ concentration takes a suitable value concomitantly with its generation its consumption also takes place with formation of the dimmer radical (MV$^{\bullet+}$)$_2$ which
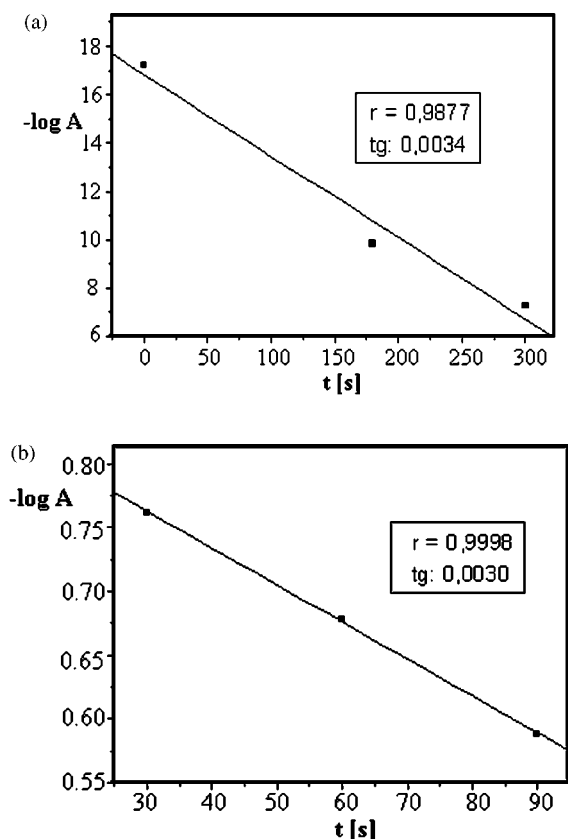

Fig. 2. Fluorescence CdS quenching with MV^{2+}.

Fig. 4. First order kinetics for MV$^{\bullet+}$ formation at: a) $\lambda = 603$ nm and b) $\lambda = 398$ nm.

absorbs partly in the same visible region as the monomer MV$^{\bullet+}$. This conclusion is supported by the increase of absorbancies below 500 nm in the absorption band of (MV$^{\bullet+}$)$_2$. We observed that the dimmer radical formation does not obey a simple second order kinetics as we see in Fig. 5.
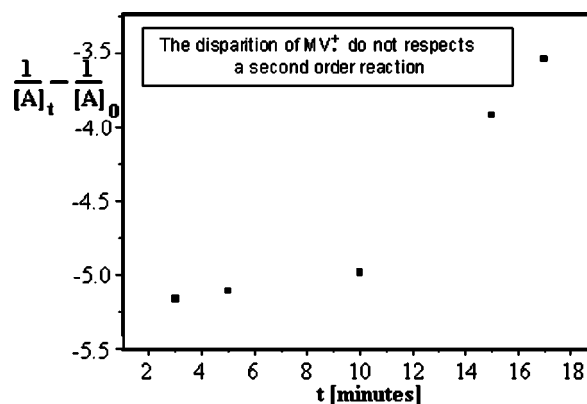

Fig. 5. Dimmer radical formation due not obey a simple second order kinetics.

As we know, for a simple second order kinetics the absorbancies must obey the relation:

$$\frac{1}{[A]_t} = \frac{kt + 1}{[A]_0} \qquad (2)$$

If the rate constant depends on temperature as Arrhenius equation indicates:

$$k = B \cdot e^{[-Ea/Rt]} \qquad (3)$$

for our homogeneous system and small temperature variation, we could consider a linear variation temperature/time: $T = f(t)$ as $T = T_0 + \alpha t$. We obtained:

$$\frac{1}{[A]_t} - \frac{1}{[A]_0} = \left\{ B \cdot e^{[-Ea/R(T_0 + \alpha t)]} \right\} \cdot t \qquad (4)$$

By fitting with a suitable function we obtain a second order reaction in which k depends on temperature. Results $B = 6.7 \times 10^{-3}$ M·s^{-1} and $E_a = 10.9$ kJ/mol = 2.61 kcal/mol. This small value of E_a demonstrates that our reaction takes place between radicals and is photochemical activated [8,9]. Our conclusion is in perfect mach with our presumption that the formation of dimmer radical takes place from two monomer radicals:

$$2MV^{\bullet+} \leftrightarrow (MV^{\bullet+})_2 \qquad (5)$$
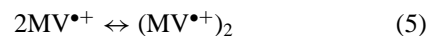
For a temperature of about 315 K, which we presume to have our irradiated solution, we obtain $k_{II} = 2.7 \times 10^{-5}$ M s^{-1} for the dimmer formation.

By fitting with a Boltzman curve the absorbencies values for $\lambda = 603$ nm at a longer irradiation time we obtained $t = 136$ s which represents the time after irradiation beginning when the dimmer is form simultaneous in all solution volume (Fig. 6).

Because the absorbencies at $\lambda = 398$ nm and $\lambda = 603$ nm are both characteristic for MV$^{\bullet+}$ their intensities ratio must be constant.
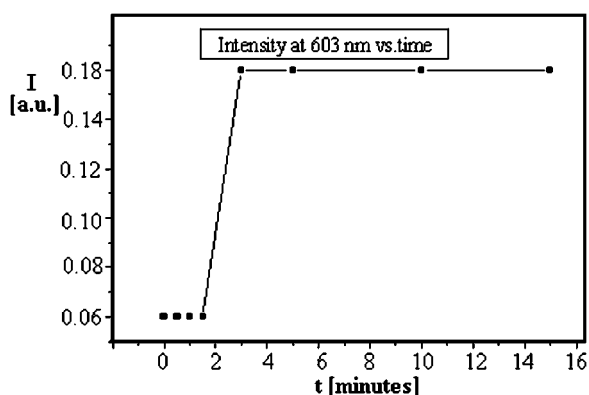

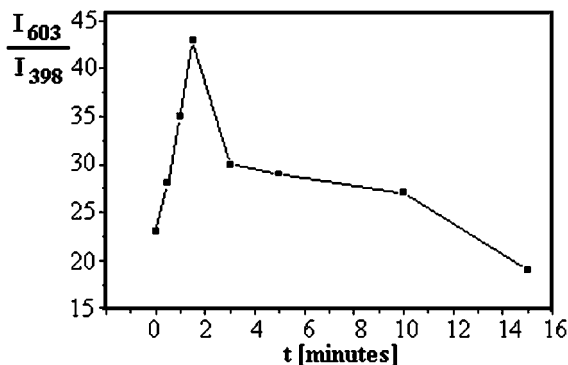**Fig. 6.** Absorbencies at $\lambda = 603$ nm vs. time.

Fig. 7. 398 nm and 603 nm absorbencies ratio, proving the formation of MV$^{\bullet+}$.

The experimental values shows a variation which probes the formation of another species, which absorbs also at about 603 nm and namely (MV$^{\bullet+}$)$_2$ (Fig. 7).

After a longer irradiation time, the absorbancies increase again in both absorption bands, $\lambda = 398$ nm and $\lambda = 603$ nm, and continue in the same manner up to 300 s irradiation. This denotes that in solution takes place the regeneration of the monomer radical resulted from the process:

$$(MV^{\bullet+})_2 + e^- \rightarrow MV^{\bullet+} + MV^0 \qquad (6)$$

with a reaction rate much slower than that on CdS particle surface.

If we calculated the ratio between the intensities for the monomer MV$^{\bullet+}$ and the double reduce form, MV^0, we observed that after a longer irradiation time, this ratio became approximatevely constant, which denotes that at a longer irradiation time one reaches an equilibrium state between this three forms of methylviologen (Fig. 8).
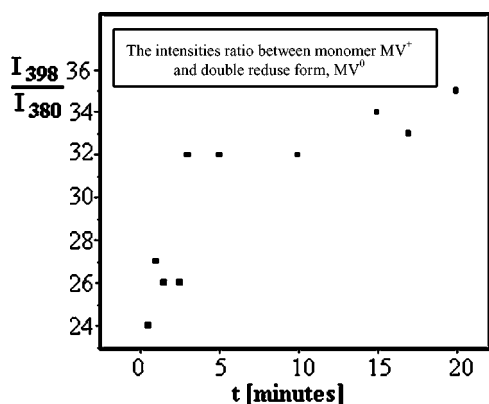

Fig. 8. The intensities ratio between monomer, MV$^{\bullet+}$ and double reduce form MV^0.

There are some authors [10–14] who admit the idea of an electron transfer in bulk. Our experimental results confirm this, and we consider that the stabilizer COP can play the same role as an electron relay thanks to their structure, facilitating the electron transfer to MV^{2+} and (MV$^{\bullet+}$)$_2$ species in bulk.

In the favor of this supposition we present our experiment carried out by mixing methyl viologen (8×10^{-2} M) with Na$_2$S (1.7×10^{-1} M) when suddenly a dark blue color appeared in the absence of the light absorbing CdS. The reduction of MV^{2+} takes place in this case only with the electrons offered by S^{2-} ions:

$$MV^{2+} + S^{2-} \rightarrow MV^{\bullet+} + S^- \qquad (7)$$

Then the solution becomes gradually brown because of S$^-$ ion dimerization:

$$2S^- \rightarrow S_2^{2-} \qquad (8)$$

Finally brown polysulphures chains are formed.

Let us return to the irradiated CdS/MV^{2+}/COP samples. After 20 min illumination, one observes the decrease of the absorbancies even up to negative values in the whole absorption spectrum due to the destruction of the system. Indeed on the bottom cell one observes a yellow crystalline precipitate of CdS, at the same time we also notice the appearance of an adherent colloidal S on the cell walls.

CONCLUSIONS

One studies the photochemical behavior of a complex CdS/MV^{2+}/COP under continous irradiation.

We put into evidence the MV$^{\bullet+}$ formation from MV^{2+} reduction, the appearance of the dimmer radical (MV$^{\bullet+}$)$_2$ and the regeneration of the monomer radical from the dimmer reduction with MV^0 formation.

We calculated, for the first time as we know, the rate constants and Arrhenius parameters for all this reactions which take place in solution. Our experiment results confirm the presumption that the same electron transfer reactions like on CdS particle surface, but more slowly, exist in solution, the stabilizer playing the role of an electron relay.

REFERENCES

1. J. K. Thomas (1987). *J. Phys. Chem.* **91**, 267–282.
2. R. Rosetti, S. Nakahira, and L. Brus (1983). *J. Chem. Phys.* **79**, 1086–1088.
3. L. Brus (1989). *J. Phys. Chem.* **90**, 2555–2562.
4. M. Gratzel (1981). *Acc. Chem. Rev.* **14**, 376–384.

5. N. Serpone, D. K. Sharma, M. A. Jamieson, M. Gratzel, and J. J. Ramsden (1985). *J. Chem. Phys. Lett.* **115**, 473–476.

6. R. Rosseti and L. Brus (1986). *J. Phys. Chem.* **90**, 558–560.

7. K. Kalyanasundaram, E. Borgarello, D. Dounghoug, and M. Gratzel (1981). *Angew. Chem.* **93**(11), 1012–1017.

8. A. A. Frost and G. R. Pearson (1961). *Kinetics and Mechanism*, 2nd ed., Wiley, New York, p. 104.

9. G. Calvert and J. N. Pitts (1966). *Photochemistry*, Wiley, New York, p. 271.

10. Y. Nosaka and M. A. Fox (1987). *Langmuir* **3**, 1547–1550.

11. T. Nakahira and M. Gratzel (1984). *J. Phys. Chem.* **88**, 4006–4010.

12. D. Duonhong, J. Ramsden, and M. Gratzel (1982). *J. Am. Chem. Soc.* **104**, 2977–2982.

13. A. Henglein (1981). *Mechanism of Reactions on Colloidal Microelectrodes and Size Quantization Effects*, Topics in Current Chemistry, Vol. 143, I. C., Springer-Verlag, Berlin, Heidelberg.

14. T. Rajh and J. Rabani (1991). *Langmuir* **21**, 35–40.