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Photochemistry of semiconductor particles
3. Effects of surface charge on reduction rate of methyl orange photosensitized by ZnS sols

Ling Zang, Chun-Yan Liu, Xin-Min Ren*

Institute of Photographic Chemistry, Academia Sinica, Beijing 100101, China

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Abstract

The photoreduction of methyl orange sensitized by ZnS sols was studied. The reaction is diffusion controlled under the experimental conditions without stirring. A steady state equation is proposed which successfully describes the kinetic process. It can be deduced from the kinetic analysis that the reduction rate is first order with respect to the concentration of methyl orange if the diffusion effect is eliminated. The effects of the surface charge of the ZnS particles on the reaction kinetics were investigated. A positive surface charge formed by adsorbed cations, such as methylviologen (MV^{2+}), Cd^{2+} and Cu^{2+}, favours photoreduction, whereas a negative surface charge formed by adsorbed anions (e.g. S^{2-}) decreases the reaction rate. This is due to the influence of the surface charge on the electron transfer from the ZnS particle to the methyl orange molecule. In addition, the pH dependence of the reaction rate was studied. The optimum pH for the photoreduction is pH 4.0.

Keywords: Semiconductor particles; Methyl orange; Photoreduction

1. Introduction

In recent years, much attention has been paid to photocatalytic redox reactions occurring at the semiconductor–liquid interface from the viewpoint of solar energy conversion [1–3]. Although many studies have been reported on the use of time-resolved techniques to investigate photocatalytic processes [4–8], details of the steady state kinetics of reductions photosensitized by semiconductor particles remain obscure. Recently, a few research groups have focused their attention on the photoreduction of methyl orange (MO) sensitized by particulate TiO_2 [8c,d] or CdS [9,10]. Some reaction mechanisms have been proposed to fit the reduction kinetics by assuming the formation of a steady state concentration of photogenerated holes and electrons.

MO ($\lambda_{max} = 463$ nm) is an aromatic azo dye, which, in general, has a very short excited state lifetime due to rapid trans–cis photoisomerization [11]. This dye is stable to visible and near-UV light, but can be photoreduced to a hydrazine derivative in the presence of semiconductor sensitizers such as TiO_2 or CdS

$$(CH_3)_2NC_6H_4N{=}NC_6H_4SO_3^- + 2H^+ + 2e^- \longrightarrow (CH_3)_2NC_6H_4NHNHC_6H_4SO_3^- \quad (1)$$

The hydrazine derivative is colourless with an absorption maximum at $\lambda_{max} = 247$ nm. The photoreduction of MO can thus be followed by the decrease in absorbance at $\lambda_{max} = 463$ nm. There is no absorbing interference at this wavelength.

In the previous papers of this series [12], it has been shown that the fluorescence intensity of ZnS sols depends strongly on the surface condition of the ZnS particles. This dependence can be attributed to the different quenching mechanisms for various adsorbed ions. In the present work, the surface effects on the transfer of photogenerated charge carriers from ZnS particles to adsorbates were studied with MO as a probe compound. One advantage of ZnS as a photosensitizer is its large negative conduction band potential (-1.4 V vs. a saturated calomel electrode (SCE)). The large difference between the conduction band and the reduction potential of MO ($E^0(MO/MOH_2) = -(0.058\ pH)$ V vs. SCE) [13] acts as the strong driving force for the heterogeneous electron transfer at ZnS particles and is expected to cause a rapid photosensitized reduction of MO. The kinetics

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*Corresponding author.

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of the photoreduction process were analysed on the basis of the experimental results.

2. Experimental details

2.1. Materials

MO, ethylenediaminetetraacetic acid (EDTA), methylviologen (MV^{2+}), $Cd(NO_3)_2$, $Cu(NO_3)_2$, $Zn(NO_3)_2$, Na_2S, HCl and NaOH were of laboratory reagent grade and were used without further purification. Doubly distilled water was used throughout this study.

The ZnS sol (10^{-3} M) was prepared as follows. $Zn(NO_3)_2$ solution (10^{-2} M) (5 ml) was added to 44.5 ml of a 2×10^{-4} M solution of polyphosphate ($Na_5P_3O_{10}$). This was followed by the rapid addition of 0.5 ml of a 0.1 M Na_2S solution with vigorous stirring. ZnS sols thus prepared were stable for a few months. They were aged at about 10 °C in a refrigerator for about 5 h prior to use in the photoreactions. The average particle size was determined by transmission electron microscopy (TEM) to be approximately 3 nm.

2.2. Procedure

All experiments were carried out using a 1 cm quartz cell fitted with a tap to prevent the reaction solution from contacting with air. No stirring was employed during the experiments. In typical experiments, about 2 ml of 10^{-3} M ZnS sol containing an appropriate amount of MO was used as the reaction mixture, which was deaerated by bubbling with nitrogen gas for about 30 min prior to illumination. During a run, the reaction solution was subjected to absorption measurements at given time intervals. In the experiments for studying the surface effects, various ions, such as MV^{2+}, Cd^{2+}, Cu^{2+} and S^{2-}, were added to the ZnS sol to alter the surface charge of the ZnS particles. The pH of the reaction solution was adjusted by adding NaOH or HCl.

The illumination was performed with a 500 W high-pressure Hg lamp (distance about 3 cm, with a 290 nm cut-off filter).

2.3. Measurement

Absorption spectra were recorded on a diode array 8451A spectrophotometer (Hewlett-Packard Co.). The decrease in concentration of MO during the course of photoreduction was followed by measuring the absorbance at 463 nm with a Shimadzu UV-120-02 spectrophotometer. The molar adsorption coefficient for unprotonated MO ($pK_a=3.5$) at $\lambda_{max}=463$ nm was taken as 2.68×10^{-4} M^{-1} cm^{-1} [14]. The concentration of Cu^{2+} ions was measured with a Cu^{2+} ion selective electrode.

3. Results and discussion

3.1. Kinetic analysis

On irradiation, the photoreduction of MO commences in the ZnS sol. It can be seen from the absorption spectra of the reaction solutions that, as the irradiation progresses, the absorption band at 463 nm (λ_{max} of the unprotonated form of MO) disappears steadily accompanied by the appearance of a new absorption maximum at 247 nm (λ_{max} of the reduction product). Control experiments show that the presence of both ZnS and irradiation is necessary to photoreduce MO. In the absence of either, no photoreduction is observed. Fig. 1 illustrates the photoreduction of MO at various initial concentrations as a function of the irradiation time. No linear dependence of the MO concentration on the irradiation time is found, i.e. the reduction rate is not zero order with respect to [MO] as in the case of CdS sols [9b,10]. Further analysis shows that the reduction rate cannot be expressed as a single function of the concentration of MO only. Some other factors should be considered. Following the assumption that the rate-

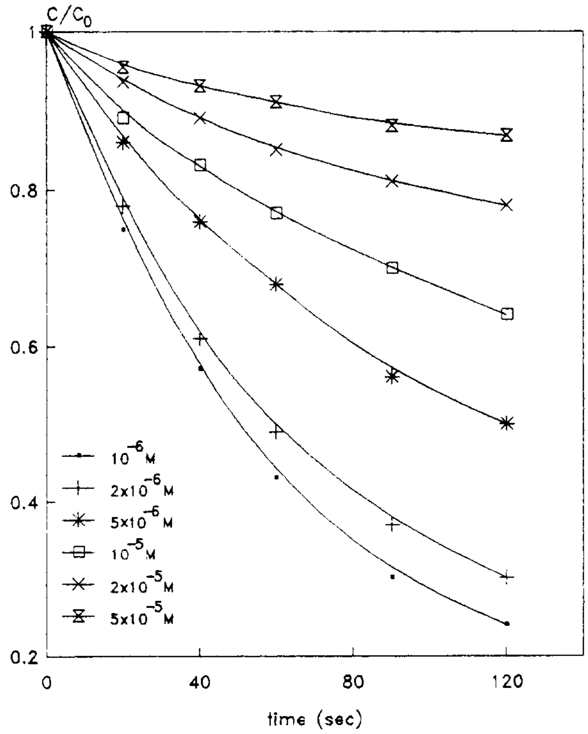

Fig. 1. Photoreduction of MO at various initial concentrations (indicated in figure) as a function of the irradiation time. The initial concentrations of MO are normalized at time zero. Experimental conditions: 10^{-3} M ZnS sol containing 2×10^{-4} M polyphosphate used as photosensitizer; pH 7.0; temperature, 15±2 °C.

determining step for the reduction of MO is electron transfer from the semiconductor particles to the adsorbed MO molecules [8d,9a], the reduction rate will decrease with decreasing initial concentration of MO. It should be noted that H_2O or H^+ ions [2] and occluded oxygen [9b] can compete effectively with MO for the photogenerated electrons at low MO concentration. The dependence of the reduction rate on the initial concentration of MO in Fig. 1 implies that the reduction process may be controlled by the diffusion of MO molecules in the reaction solution. This is reasonable in view of the fact that no stirring was employed in the experiments.

Since the intensity of the irradiating light decreases exponentially in the optical path due to absorption by ZnS particles and MO molecules, and since the photoreduction rate of MO is proportional to the irradiation intensity [9], the reduction of MO on the two sides of the reaction cell must occur at different rates. As a result, a concentration gradient of MO will appear in the reaction solution. In such conditions, the reaction course should be controlled by the diffusion of MO. It is very difficult to deduce a reduction rate of MO directly from the real experimental conditions, because the change in MO concentration is very complicated during the photoreduction process. In this regard, we assume two extreme situations in describing the initial reaction process: (1) the majority of reduction occurs in the region (termed 'reaction zone') near the irradiated side, since the irradiation intensity in this region is much higher than that at the other side; (2) the reduction in the 'reaction zone' is so rapid that, during the photoreduction, the concentration of MO in this region is maintained at zero and there is no change at sufficiently large distances from the zone. We can see that these two situations are very similar to the case of an electrode reaction in which the current is governed by the diffusion rate of the electroactive material [15]. Using the same mathematical treatment as in Ref. [15], the photoreduction rate of MO can be derived

$$\frac{\mathrm{d}c}{\mathrm{d}t} = -kct^{-1/2} \tag{2}$$

where t is the irradiation time, c is the concentration of MO and k is a constant. Considering the discrepancy between the assumption above and the actual experimental conditions, Eq. (2) should be revised as

$$\frac{\mathrm{d}c}{\mathrm{d}t} = -kct^{-n} \tag{3}$$

where n is a parameter used to evaluate the effect of the degree of diffusion on the reaction kinetics. The more significant the diffusion effect, the higher the value of n. For the diffusion-controlled reaction n approaches its maximum value of one-half as shown in Eq. (2). The value of n in Eq. (3) must be lower than one-half, because there are two facts which contrast with the two extreme situations given above: (1) there is always some reduction taking place far from the 'reaction zone' due to the weak irradiation which reaches there; (2) the real reduction rate of MO in the 'reaction zone' is not as fast as is supposed in the extreme situation. Thus the concentration gradient of MO formed in the reaction solution is not so large as that assumed.

The integrated form of Eq. (3) is

$$\ln\left(\frac{c_0}{c}\right) = \frac{k}{1-n}\,t^{1-n} \tag{4}$$

where c_0 is the initial concentration of MO. Taking the natural logarithm of Eq. (4) gives

$$\ln\left[\ln\left(\frac{c_0}{c}\right)\right] = \ln\left(\frac{k}{1-n}\right) + (1-n)\ln t \tag{5}$$

Obviously, a plot of $\ln[\ln(c_0/c)]$ vs. $\ln t$ should be a straight line with a slope of $(1-n)$. This is confirmed by the results shown in Fig. 2, in which all plots of $\ln[\ln(c_0/c)]$ vs. $\ln t$ show good linearity as predicted by Eq. (5) (correlation coefficients, greater than 0.99). With decreasing initial concentration of MO (c_0), the slope of the plot increases and tends to unity as summarized in Table 1. Simultaneously, the value of n decreases monotonically to zero at quite low concentrations. In such conditions, Eq. (3) can be simplified to

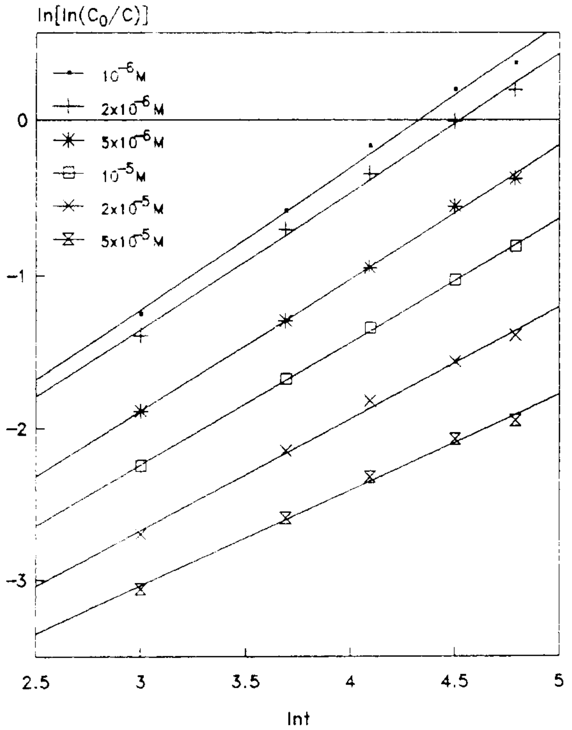

Fig. 2. Plots of $\ln[\ln(c_0/c)]$ vs. $\ln t$. Data from Fig. 1.

Table 1
Values of $(1-n)$ and n for the plots in Fig. 2

	5×10^{-5} M	2×10^{-5} M	10^{-5} M	5×10^{-6} M	2×10^{-6} M	10^{-6} M
$1-n$	0.62	0.74	0.82	0.87	0.89	0.92
n	0.38	0.26	0.18	0.13	0.11	0.08

$$\frac{dc}{dt} = -kc \qquad (6)$$

First-order kinetics with respect to MO concentration are obtained for the photoreduction. Evidence for this argument is provided by the experimental results in which the reduction of MO with an initial concentration of less than 10^{-6} M obeys approximate first-order kinetics. This indicates that, in sufficiently dilute solution, the diffusion effect is negligible and the photoreduction rate depends only on the concentration of MO. The more pronounced changes in n at c_0 higher than 10^{-5} M implies that at higher concentrations the diffusion effect becomes more significant.

It is well known that stirring eliminates or lessens the effects of diffusion on the reaction kinetics. If stirring is used in the experiments, the photoreduction of MO is not controlled by diffusion and follows apparent first-order kinetics as presented by Eq. (6). Fig. 3 illustrates a comparison between the reduction of 10^{-5} M MO with and without stirring. First-order reaction kinetics are observed with stirring by continuous bubbling of N_2 (200 ml min^{-1}) during the reduction. Control experiments indicate that a bubbling rate of about 150 ml min^{-1} is sufficient to eliminate the diffusion effect. Above this rate, the kinetics of photoreduction are little affected by a further increase in bubbling rate.

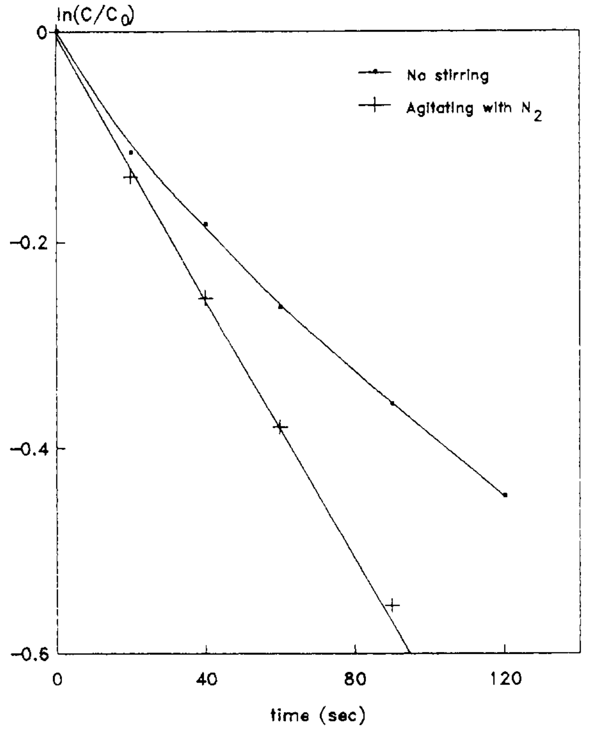

Fig. 3. Effect of stirring on the reaction kinetics of photoreduction of MO (10^{-5} M). Experimental conditions: 10^{-3} M ZnS sol containing 2×10^{-4} M polyphosphate used as photosensitizer; pH 7.0; temperature, 15±2 °C; bubbling rate of N_2, 200 ml min^{-1}.

3.2. Effects of surface charge

In the previous work of Mills and coworkers [9], EDTA was used as an electron donor for the photoreduction of MO sensitized by CdS and was found to be effective in promoting the reaction by scavenging the photogenerated holes. In our experiments, the same compound was used and was expected to be able to act as a hole scavenger. Unfortunately, however, the photoreduction rate of MO is markedly decreased with the addition of 5×10^{-4} M EDTA to the reaction solution (Fig. 4). This indicates that EDTA has an inhibiting effect in the reduction process rather than hole scavenging. It is plausible to envisage that the

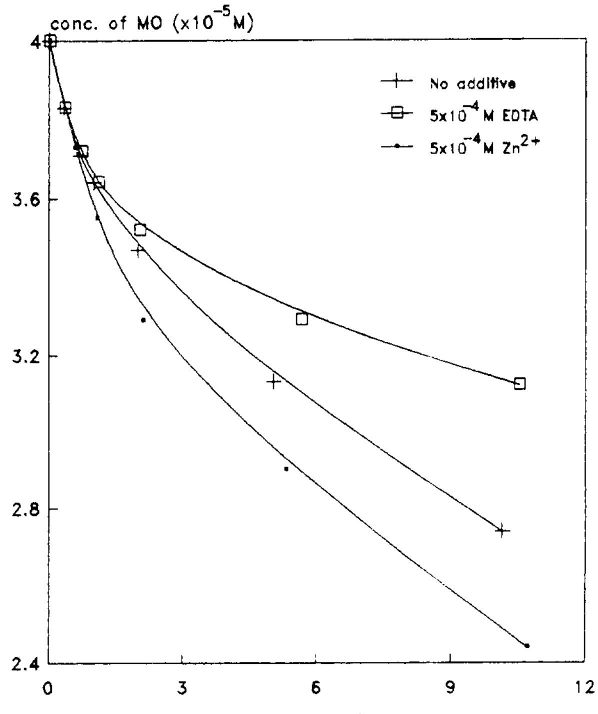

Fig. 4. Effect of addition of 5×10^{-4} M EDTA or Zn^{2+} on the photoreduction of MO (same experimental conditions as in Fig. 1).

adsorbed EDTA ions form a negative electrostatic field around the ZnS particle. Such an electrostatic field will hinder the transfer of photogenerated electrons from the ZnS particles to the MO molecules. On the other hand, adsorption of cations would be favourable for the transfer of electrons at the ZnS–electrolyte interface. Fig. 4 also illustrates the effects of Zn^{2+} ions (5×10^{-4} M) on the photoreduction of MO. A higher reaction rate is obtained. This is in contrast with the observation made by Peral and Mills [10]. They found that the reduction rate of MO decreased with the addition of Cd^{2+} ions to the CdS sol which was used as a photosensitizer. The difference may be due to the weak ability of Zn^{2+} to capture photogenerated electrons [12].

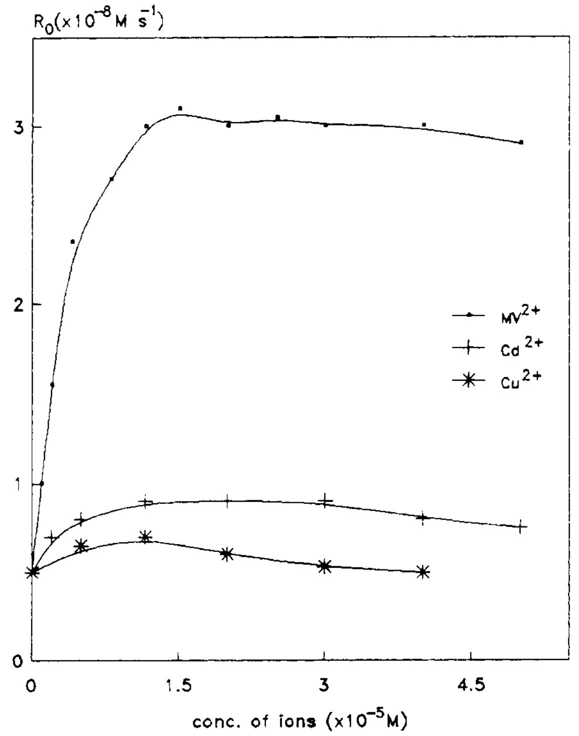

Fig. 5. Plots showing the dependence of the initial photoreduction rate (R_0) of MO (10^{-5} M) on the concentrations of various added cations (same experimental conditions as in Fig. 1).

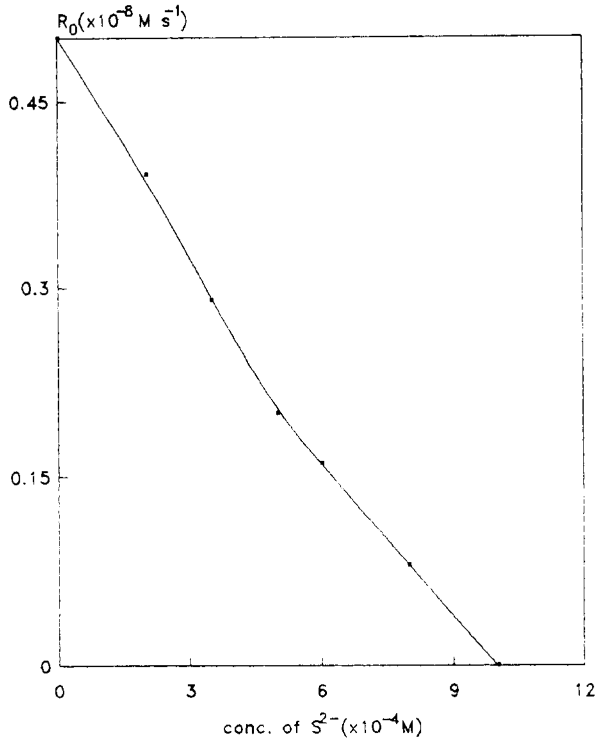

Fig. 6. Plots showing the dependence of the initial photoreduction rate (R_0) of MO (10^{-5} M) on the concentration of added S^{2-} ion (same experimental conditions as in Fig. 1, except for the different pH at various concentrations of S^{2-}).

Further information on the effects of surface charge is given in Figs. 5 and 6, which illustrate the dependence of the reaction rates on the concentration of various added ions, such as MV^{2+}, Cd^{2+}, Cu^{2+} and S^{2-}. These ions were used in previous work [12b] as fluorescence quenchers for the ZnS sols. As observed for Zn^{2+} ions, the three cations can also accelerate the photoreduction (Fig. 5). Of all the ions employed, the MV^{2+} ion appears to be most effective in increasing the reaction rate. This is due to its dynamic mechanism of quenching of photogenerated electrons, the details of which have been described in Ref. [12b]. The MV^{2+} ion, an effective electron scavenger [3], can trap a photogenerated electron giving the radical $MV^{\bullet+}$,

$$MV^{2+} + e^- \longrightarrow MV^{\bullet+} \tag{7}$$

This is followed by a rapid reaction with MO to produce MV^{2+} again

$$MV^{\bullet+} + MO + H^+ \longrightarrow MV^{2+} + MOH^\bullet \tag{8}$$

The semi-reduced radical $MOH^\bullet$ can then obtain another electron from $MV^{\bullet+}$ to yield the completely reduced form MOH_2

$$MV^{\bullet+} + MOH^\bullet + H^+ \longrightarrow MV^{2+} + MOH_2 \tag{9}$$

The role of MV^{2+} in such a process can be considered as an electron transfer relay which helps the process kinetics.

The reaction rate is only slightly increased by Cd^{2+} ions at low concentrations. This is somewhat surprising since the quenching efficiency of Cd^{2+} for the fluorescence of ZnS sols was found to be comparable with that of MV^{2+} [12b]. The different quenching mechanism of Cd^{2+} ions seems to be responsible for the appearance of this surprising phenomenon. It has been found that the capture of photogenerated electrons by Cd^{2+} is a static process. The electrons trapped at the adsorbed Cd^{2+} (in the form of Cd^+) cannot be transferred to the MO molecule so rapidly as in the case of MV^{2+} ions. The increase in reaction rate at the beginning can be assigned to the effect of the positive electrostatic field around the ZnS particle formed by the adsorbed

Cd^{2+} ions. Similar results are obtained for Cu^{2+} ions as shown in Fig. 5.

At higher concentrations, the reduction of the cation itself competes with MO reduction for the capture of photogenerated electrons. The reduction rate of MO decreases with increasing concentration of the cation. In a control experiment, irradiation of a ZnS sol (10^{-3} M) containing 10^{-5} M MO and 5×10^{-5} M Cu^{2+} under an N_2 atmosphere resulted in a decrease in the concentration of Cu^{2+} ions, whereas in the case of 5×10^{-6} M Cu^{2+} little reduction of Cu^{2+} was observed.

The results shown in Fig. 6 offer further support for the argument that the essence of the dependence of the photoreduction of MO on the surface charge is the influence of the surface electrostatic field on the transfer of photogenerated electrons from ZnS particles to MO molecules. The S^{2-} ion, which can trap the photogenerated hole at the ZnS particle surface [12b], is expected to favour the photoreduction of MO sensitized by ZnS sols. The unexpected results shown in Fig. 6 indicate that the dominant role of S^{2-} ions in the reaction is as an inhibitor of interfacial electron transfer rather than a scavenger of positive holes. This is in agreement with the fact that strongly adsorbed S^{2-} ions form a negative electrostatic field around the ZnS particles.

3.3. *Influence of pH*

The influence of pH on the photoreduction rate of MO has been studied extensively by previous workers [8d,9a,10]. Various experimental results and interpretations have been reported in the literature. In this work, we tried to obtain more information on the effects of pH on the photoreduction of MO. Fig. 7 shows the initial rate of photoreduction of MO as a function of pH. The rate increases with decreasing pH from 9 to 4, but then passes through a maximum at pH 4.0, and decreases sharply with a further decrease in pH. This is in contrast with the results obtained by Mills and coworkers [9a,10] using CdS as photosensitizer. They found that the photoreduction rate of MO increased monotonically with decreasing pH. The increase in the reaction rate at pH 4–9 can be explained by two effects: (1) an increase in H^+ concentration always favours reaction (1) in a dynamic sense; (2) on hydration, the surface of the ZnS particle is positively charged at pH <PZC (point of zero charge). This is favourable for the adsorption of deprotonated MO ($pK_a=3.5$). As reported by Moignard et al. [16], the PZC of ZnS is about 6.7. This is in agreement with the result of Fig. 7. The initial reaction rate starts to increase at pH 6.7.

The rate decrease at pH <4 may be due to acid corrosion of the ZnS particles

$$ZnS+2H^+ \longrightarrow Zn^{2+}+H_2S \qquad (10)$$

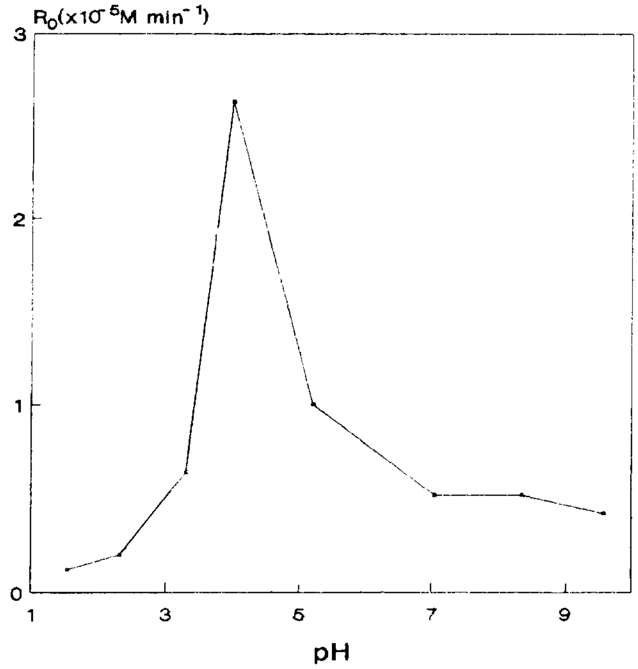

Fig. 7. Initial rate (R_0) of photoreduction of MO (4×10^{-5} M) as a function of pH. Experimental conditions: 10^{-3} M ZnS sol containing 2×10^{-4} M polyphosphate used as photosensitizer; temperature, 15±2 °C.

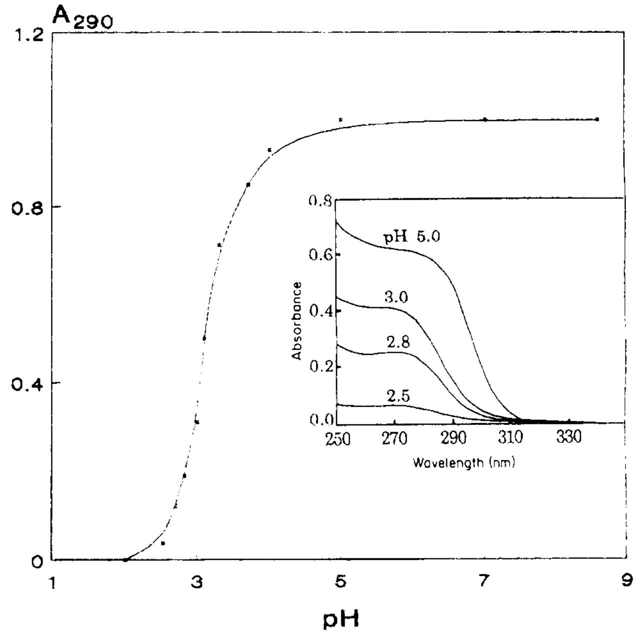

Fig. 8. Absorbance at 290 nm of ZnS sols (4×10^{-4} M) as a function of pH. The absorbance was normalized at pH 7.0. Inset: pH dependence of the absorption spectra of ZnS sols. At pH >5.0, the spectral shape was almost the same.

This is confirmed by experiments in which the stability of ZnS sols in acid media was studied. It was found, from the marked decrease in absorbance of the ZnS sol, that the dissolution of ZnS colloids occurs at low pH (inset of Fig. 8). In Fig. 8, the absorbance at 290 nm of a ZnS sol is plotted as a function of pH. At pH >5, the ZnS sol is very stable, whereas it undergoes decomposition at pH <5 according to Eq. (10).

Since the conduction band potential of ZnS (−1.4 V vs. SCE) is much more negative than that of MO (−(0.058 pH) V vs. SCE), the decrease in the rate in acid conditions cannot be caused by the anodic shift of the conduction band as proposed by Brown and Darwent [8d]. The anodic shift is not large enough to bring about such a dramatic change.

Acknowledgments

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