

Effect of Transition Metal Ions on the TiO₂-Assisted Photodegradation of Dyes under Visible Irradiation: A Probe for the Interfacial Electron Transfer Process and Reaction Mechanism

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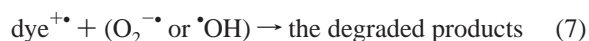
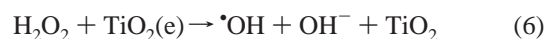
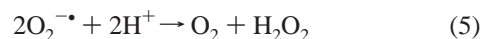
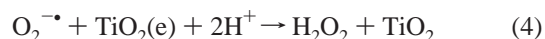
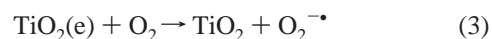
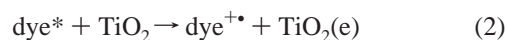
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The effect of metal ions (Cu²⁺, Fe³⁺, Zn²⁺, Al³⁺, and Cd²⁺) on the photodegradation of several dyes: sulforhodamine B (SRB), alizarin red (AR), and malachite green (MG) has been investigated in aqueous TiO₂ dispersions under visible irradiation ($\lambda > 420$ nm). Trace quantities of transition metal ions such as Cu²⁺ and Fe³⁺ having suitable redox potentials alter the electron-transfer pathway involving the dye, O₂ and TiO₂ particles, and markedly depress the photodegradation of all three dyes under visible irradiation. Other metal ions, such as Zn²⁺, Cd²⁺, and Al³⁺, have only a slight influence on the photoreaction by altering the adsorption of dyes. Photogeneration of H₂O₂ and reactive radicals, and the changes in fluorescence emission of SRB in TiO₂ aqueous dispersions were examined to elucidate the role of the metal ions. Addition of Cu²⁺ or Fe³⁺ decreases the reduction of O₂ by the conduction electrons, subsequently blocks the formation of reactive oxygen species (O^{•−}, •OH), and depresses the degradation of dyes under visible irradiation. We deduce that the reduction of O₂ is essential for the photodegradation of dyes under visible irradiation.

Introduction

Numerous studies have been reported in the past decades on the photodegradation of organic compounds using semiconductor particles as photocatalysts. To utilize more effectively the inexpensive and inexhaustible energy of solar radiation that reaches the surface of the earth, in which only less than 5% of the energy ($\lambda < 385$ nm) can excite TiO₂ particles, the photosensitization degradation of dye pollutants under visible light irradiation is an attractive approach to treat of the dye-containing wastewaters. In recent years, we have reported that various types of dyes can be photodegraded effectively in the TiO₂ dispersions under visible irradiation. The discoloration and mineralization of dyes, formation of intermediates, and photo-reaction mechanisms have also been studied in some detail.^{1–3} The major initial steps in the mechanism under visible irradiation are summarized by eqs 1–7. The pathway differs from that inferred from results obtained under UV radiation as described previously,¹ except that the fate of the injected electrons under visible irradiation is no different from that of those conduction band electrons photogenerated under UV illumination.



Clearly, the fate of the injected electron depends on the interfacial charge transfer processes, which play an important role under both UV and visible irradiation. These processes greatly depend on the surface characteristics of TiO₂ particles, and on the charge carrier mobilities and lifetimes.⁴ Consequently, the surface modification of TiO₂, such as by the adsorption of cations or anions,⁵ through addition of chelating groups⁶ or by doping noble metals,⁷ can drastically influence the processes noted above.

Although some studies examined the effect of transition metal ions on the photocatalytic degradation of organic compounds

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under UV irradiation,⁵ less attention has been expended on the effect that transition metal or posttransition metal ions have on the photosensitized degradation of dyes under visible irradiation. The occurrence of dissolved metal ions is rather common in natural waters and industrial wastewaters. For example, such transition or posttransition metal ions as Cu²⁺, Zn²⁺, Al³⁺, and Fe³⁺ are often contained in the wastewaters of textile factories. They can significantly influence the photocatalytic reactions for removal of the pollutants. A study on the effects of metal ions will therefore be greatly useful in our quest for a better understanding of the mechanism of the photosensitized degradations of dyes in TiO₂ dispersions under visible irradiation.

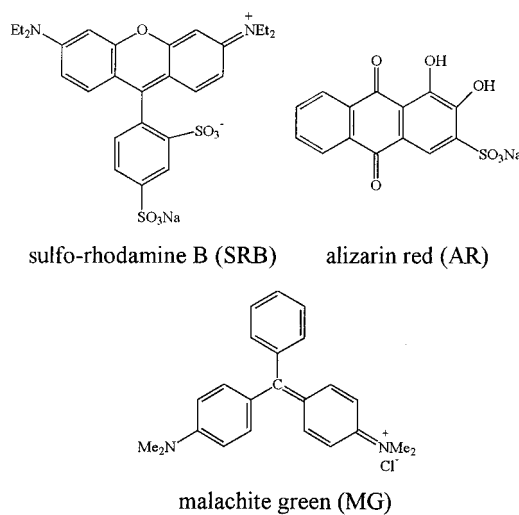
In this paper, we examined the effect of several types of metal ions (Cu²⁺, Zn²⁺, Fe³⁺, Al³⁺, and Cd²⁺) on the photodegradation of dyes in TiO₂ aqueous dispersions under visible light illumination. Three different types of dyes (see the structures below) were selected to examine the effect of metal ions: (1) sulfo-rhodamine B (SRB), an anionic dye that forms complexes neither with the metal ions nor with the TiO₂ particle surface ions, but adsorbs easily on the surface of TiO₂ by the electrostatic interaction between the negative sulfonic group of the dye molecule and the positively charged TiO₂ surface; (2) alizarin red (AR), also an anionic dye that forms strong complexes with both the metal ions and the TiO₂ particle surface; (3) malachite green (MG), a cationic dye for which the interaction with both the metal ions and the surface of the photocatalysts is considerably weaker.

Formation of reactive oxygen species, such as [•]OH or O₂^{•-}, during the visible light irradiation was examined in the absence and presence of various metal ions. The fluorescence characteristics were also explored to obtain more details on the photoreaction mechanism in combination with results from measurements of reactive oxygen species by ESR technique. Experimental results strongly suggest that the adsorption of Cu²⁺ on the TiO₂ surface alters the electron-transfer pathway between the dyes, molecular oxygen, and TiO₂ particles. Owing to trapping of the conduction band electrons by the adsorbed Cu²⁺, reduction of O₂ molecules by the photoelectron becomes rather difficult, and formation of reactive oxygen species (O₂^{•-}/[•]OOH, [•]OH) is suppressed. Accordingly, this leads to a decrease of the photodegradation rate of dyes under visible irradiation.

Experimental Section

Materials. TiO₂ particles (P25, ca. 80% anatase, 20% rutile; BET area, ca. 50 m² g⁻¹) were kindly supplied by Degussa Corp. Horseradish peroxidase (POD) was purchased from Huamei Biologic Engineering Co. (China), and the *N,N*-diethyl-*p*-phenylenediamine (DPD) reagent was from Merck (p.a.). The reagent 5,5-dimethyl-1-pyrroline-*N*-oxide (DMPO), used as a spin trap, was purchased from Sigma Chemical Co. The dye SRB was laser grade. The dyes Alizarin Red (AR) and Malachite Green (MG) were analytical reagent grade. The sodium diethyldithiocarbamate (DDTC), Cu(NO₃)₂, Fe(NO₃)₃, Zn(NO₃)₂, Al(NO₃)₃, Cd(NO₃)₂, and other chemicals were all analytical grade and used without further purification. All the metal ions were introduced into the dispersions by their nitrate salts, since adsorption of the nitrate anions onto the surface of TiO₂ is weak; this decreases the effect of the competitive adsorption between the dyes and the anions. Deionized and doubly distilled water was used throughout. The pH of the solutions was adjusted using diluted aqueous solutions of either NaOH or HClO₄.

Photoreactor and Light Source. A 500-W halogen lamp (Institute of Electric Light Source, Beijing) was positioned inside a cylindrical Pyrex vessel surrounded by a circulating water



jacket (Pyrex) to cool the lamp. A cutoff filter was placed outside the Pyrex jacket to completely remove any radiation below 420 nm and to ensure illumination by visible light only.

Procedure and Analyses. The TiO₂ aqueous dispersions were prepared by addition of a given weight of TiO₂ to 60 mL aqueous solutions containing the dyes and metal ions. Prior to irradiation, the suspensions were magnetically stirred in the dark for ca. 30 min to ensure the establishment of adsorption/desorption equilibrium of dyes and metal ions on the surface of TiO₂. The dispersions were kept under constant air-equilibrated conditions before and during the irradiation. At given time intervals, 3 mL aliquots were sampled, centrifuged, and then filtered through a Millipore filter (pore size 0.22 μm) to remove the TiO₂ particles. The filtrates were analyzed by recording variations of the absorption band maximum (564 nm for SRB, 423 nm for AR, and 617 nm for MG) in the UV–vis spectra of the dyes using a Lambda Bio-20 spectrophotometer (Perkin-Elmer Co.). The extent of adsorption of dyes on TiO₂ was determined by the difference in the concentration of dyes between the original solution and the filtrate of the dye/TiO₂ dispersions before irradiation. The concentration of total peroxides (including organoperoxides and H₂O₂) formed during the irradiation was determined immediately by the spectrophotometric DPD method⁸ after irradiation and removal of the TiO₂ particles by centrifugation and filtration.

Electron spin resonance (ESR) signals of radicals spin-trapped by DMPO were recorded at ambient temperature on a Bruker ESP 300E spectrometer: the irradiation source was a Quanta-Ray Nd:YAG pulsed laser system (λ = 532 nm, 10 Hz). The settings for the ESR spectrometer were: center field, 3486.70 G; sweep width, 100 G; microwave frequency, 9.82 GHz; modulation frequency, 100 kHz; and power, 5.05 mW.

Samples used for the fluorescence quenching were prepared as follows: 0.6 mL solutions containing SRB (1.2 × 10⁻⁵ M SRB) and various amounts of Cu²⁺ were added to 200 mg TiO₂. These samples were sonicated for 30 min to ensure the establishment of adsorption/desorption equilibrium in the dark. Subsequently, the fluorescence spectra were recorded using a Hitachi F-4500 spectrofluorimeter.

The concentration of Cu²⁺ in the filtrate after removal of the TiO₂ particles was determined by the spectrophotometric DDTC method: A 2-mL sample, 1 mL of DDTC (0.1M), and 2 mL of the acetic buffer solution (0.1M) were added together; then the formed Cu²⁺-DDTC complex was extracted using 5 mL of chloroform. The absorbance was measured at λ_{max} = 436 nm (ε = 1.4 × 10⁴ M⁻¹ cm⁻¹).

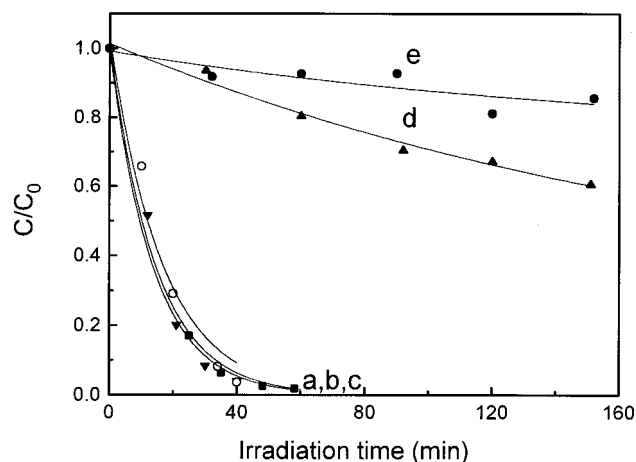


Figure 1. The effect of various metal ions on the degradation rate of SRB under visible light illumination. (a) blank, (b) Zn^{2+} , (c) Cd^{2+} , (d) Cu^{2+} , and (e) Fe^{3+} . Initial concentration of metal ions, $100 \mu\text{M}$; TiO_2 loading, 2 g L^{-1} ; concentration of dye (SRB), $20 \mu\text{M}$; $\text{pH} = 2.5$.

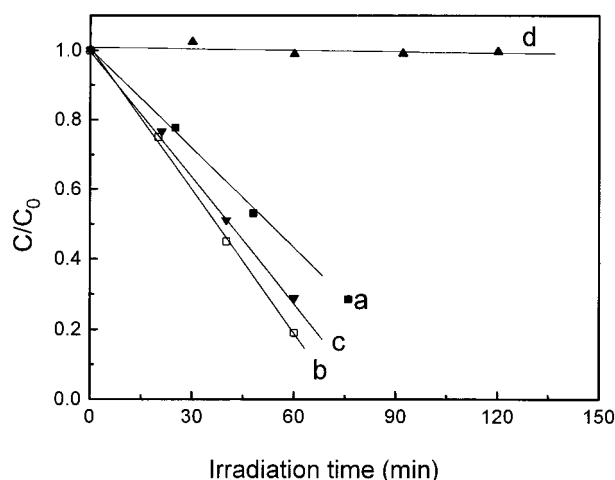


Figure 2. The effect of various metal ions on the degradation rate of AR under visible light illumination. (a) blank, (b) Al^{3+} , (c) Zn^{2+} , and (d) Cu^{2+} . Initial concentration of metal ions, $100 \mu\text{M}$; TiO_2 loading, 1 g L^{-1} ; concentration of dye (AR), $100 \mu\text{M}$; $\text{pH} = 4.0$.

Results and Discussion

Effects of Metal Ions on the Photodegradation Rates of Dyes. The photodegradation of the three dyes (SRB, AR, and MG) in TiO_2 aqueous dispersions in the presence and absence of various metal ions is illustrated in Figures 1, 2, and 3, respectively.

The concentration of SRB decreases exponentially with irradiation time via a pseudo-first-order process ($k \sim 0.0034 \text{ min}^{-1}$; Figure 1a–c) in the presence of Zn^{2+} , Al^{3+} , or in the metal ion-free dispersions (blank). In the presence of Cu^{2+} or Fe^{3+} , the slow degradation of SRB follows a pseudo-zero-order kinetics, $k \sim 0.043 \mu\text{M min}^{-1}$ and $0.025 \mu\text{M min}^{-1}$, respectively (Figure 1d,e). For both AR (Figure 2) and MG (Figure 3), the changes in the concentrations of the dyes as a function of the irradiation time appear linear, taking place by a pseudo-zero-order process in both the absence and presence of various metal ions.

The initial degradation rates and the extent of adsorption of three dyes on the TiO_2 surface in the absence and presence of various metal ions are summarized in Table 1. We found no correlation between the adsorption amounts of SRB and the photodegradation rates upon the presence of different metal ions. However, in the dispersions containing Cu^{2+} ions, the initial

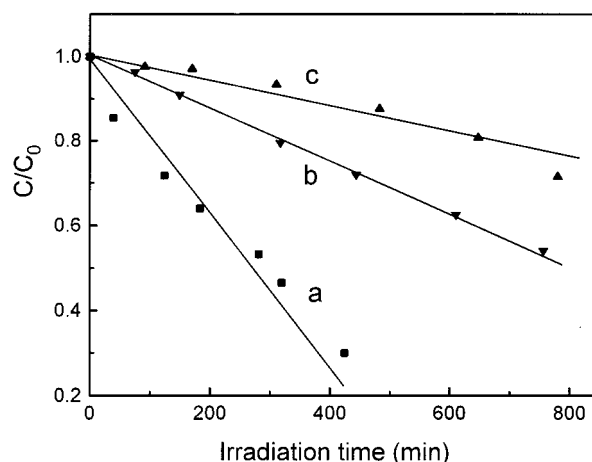


Figure 3. The effect of various metal ions on the degradation rate of MG under visible light illumination. (a) blank, (b) Zn^{2+} , and (c) Cu^{2+} . Initial concentration of metal ions, $100 \mu\text{M}$; TiO_2 loading, 1 g L^{-1} ; concentration of dye (MG), $10 \mu\text{M}$; $\text{pH} = 6.0$.

TABLE 1: Initial Degradation Rates r_{in} and Extent of Adsorption (ads) of Dyes*

dye		blank	Zn^{2+}	Cd^{2+}	Cu^{2+}	Al^{3+}
SRB	$r_{\text{in}} (\mu\text{M min}^{-1})$	0.066	0.069	0.061	0.0043	/
	ads ($\mu\text{mol g}^{-1} \text{TiO}_2$)	0.088	0.069	0.086	0.089	/
AR	$r_{\text{in}} (\mu\text{M min}^{-1})$	0.937	1.223	/	0.0070	1.51
	ads ($\mu\text{mol g}^{-1} \text{TiO}_2$)	1.69	2.83	/	3.74	3.34
MG	$r_{\text{in}} (\mu\text{M min}^{-1})$	0.012	0.0041	/	0.0029	/
	ads ($\mu\text{mol g}^{-1} \text{TiO}_2$)	0.114	0.090	/	0.074	/

*Experimental conditions are the same as those described in Figures 1–3.

rate was much slower than that witnessed in other systems. During the degradation of SRB in acidic media ($\text{pH} = 2.5$), the surface of TiO_2 particles is positively charged (the pH of zero charge point of P25 TiO_2 is $\text{pH} 6.25$),⁹ so that the extent of adsorption of cationic metal ions is relatively insignificant.¹⁰ Consequently, any effect that the metal ions may have on the adsorption of SRB on the TiO_2 particles should be relatively small, if not negligible. The data in Table 1 supports this notion; the metal ions Zn^{2+} and Cd^{2+} have little effect on both the initial rates of degradation and extent of adsorption, except for Cu^{2+} ions which, while not affecting the extent of adsorption, the initial rate is decreased by nearly an order of magnitude.

Metal ions also enhance the adsorption of AR (anionic dye) on the surface of TiO_2 . The initial rates increase concomitantly with the adsorption of dye caused by the addition of metal ions (Figures 2a–c), except for Cu^{2+} , which increases the adsorption of AR but decreases the degradation rate (Figure 2d) by nearly 2 orders of magnitude smaller relative to the blank. For the AR system ($\text{pH} = 4.0$), the higher pH permits more metal ions to adsorb on the TiO_2 particle surface.¹⁰ Accordingly, both the extent of adsorption and the initial degradation rate of this anionic dye are enhanced by addition of Al^{3+} or Zn^{2+} ions to the dye/ TiO_2 dispersions. Yet again, the presence of Cu^{2+} ions shows the strongest effect on the rate, but not so significant on the extent of adsorption of AR (Table 1).

Metal ions tend to weaken the adsorption of cationic dye MG. The photodegradation rate of this dye is decreased upon addition of both Cu^{2+} and Zn^{2+} ions relative to the control blank. The detrimental effect of Cu^{2+} , however, is more evident than the effect of Zn^{2+} (Figure 3). The photodegradation of MG was carried out in a dispersion at a higher pH ($\text{pH} = 6.0$) because of its instability and weak adsorption ability on the TiO_2 surface in the acidic solution. Under these conditions, adsorption of

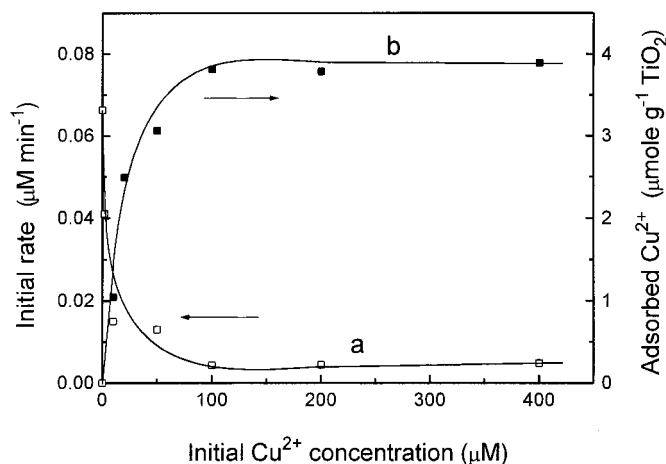


Figure 4. Relationship between the degradation rate of (a) SRB and the adsorption of (b) Cu²⁺ under visible light irradiation. TiO₂ loading, 2 g L⁻¹; initial concentration of SRB, 20 μM; pH = 2.5.

metal ions on the particle surface is expected to be somewhat greater than for the SRB (pH = 2.5) and AR (pH = 4.0) cases.¹⁰ Addition of metal ions to the dispersion inhibits somewhat the adsorption of cationic MG on the TiO₂ surface. As a result, the degradation of MG is slowed considerably by both Zn²⁺ and Cu²⁺ ions (Table 1).

Common to all three dyes, addition of Cu²⁺ ions suppresses greatly the photodegradation. It is evident from Table 1 that the depressing effect of Cu²⁺ on the kinetics of photodegradation cannot be attributed solely to any effect this ion may have on the extent of adsorption of the dyes, although the preadsorption of dyes is a prerequisite for the photodegradation of dyes. Considering the similarity between Cu²⁺ ions and Fe³⁺ ions, the Cu²⁺ ions are chosen for further experiments because they can keep the ionic form at a wider pH range than Fe³⁺ ions.

Figure 4 illustrates the dependence of the initial rate of photodegradation of the SRB dye, and the extent of adsorption of Cu²⁺ ions on the surface of TiO₂ particles, on the concentration of added Cu²⁺ ions. As the concentration of Cu²⁺ increases from 0 to 100 μM, the initial rate decreases dramatically from about 0.066 to 0.0043 μM min⁻¹ (Figure 4a), although the effect of Cu²⁺ addition on the adsorption of SRB was negligible. At concentration of Cu²⁺ greater than 100 μM, the initial rate is no longer [Cu²⁺]-dependent and reaches a minimal value around 0.004 μM min⁻¹. By contrast, the related Zn²⁺ ions has no effect whatsoever on the photodegradation of SRB even at concentrations of Zn²⁺ as high as 1000 μM.

Earlier reports^{5d,11,12} demonstrated that, under UV irradiation, some transition metal ions at appropriate concentrations can accelerate the decomposition of organic pollutants, but can suppress the photooxidation at very high concentrations of metal ions. In the photodegradation of SRB under visible irradiation, addition of Cu²⁺ at any concentration always hindered the degradation of this dye. The maximum adsorption amount of Cu²⁺ under the present experimental conditions (pH = 2.5) is ca. 3.8 μmol g⁻¹ TiO₂. The adsorption isotherm of Cu²⁺ correlates with the degradation rate of SRB, indicating that adsorption of metal ions on the TiO₂ surface is an essential factor influencing the degradation rate of dyes, i.e., only the Cu²⁺ ions adsorbed on the particle surface can suppress the degradation of dyes.

Generation of Hydrogen Peroxide. Formation of H₂O₂ during the photodegradation of SRB in aqueous TiO₂ dispersions under visible irradiation in the absence and presence of metal ions is illustrated in Figure 5. In accord with earlier studies,^{1b}

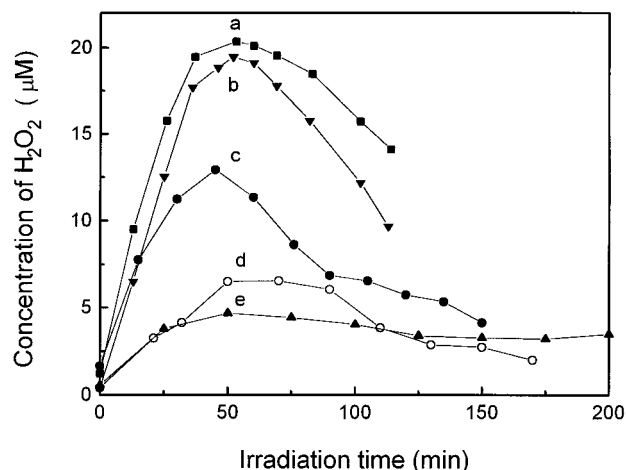


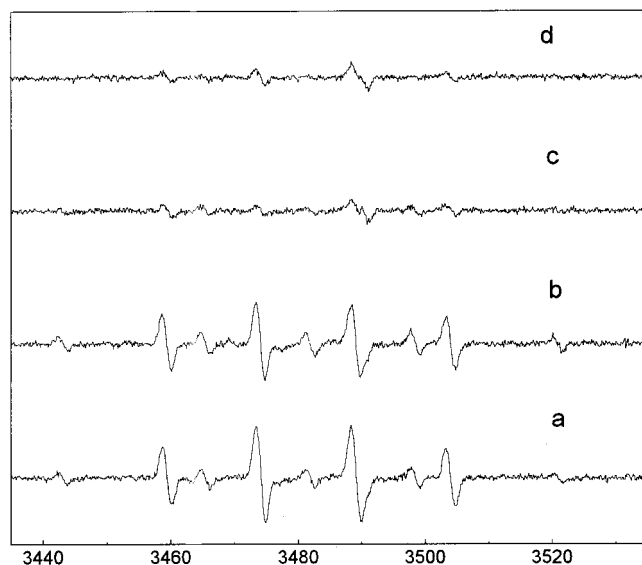
Figure 5. The formation of hydrogen peroxide during the photodegradation of SRB under visible irradiation. (a) blank, (b) 100 μM Zn²⁺, (c) 1 μM Cu²⁺, (d) 5 μM Cu²⁺, and (e) 20 μM Cu²⁺. Initial conditions same as those in Figure 1.

we detected no other organoperoxides except H₂O₂ during the irradiation. In the absence of metal ions (curve a) and in the presence of Zn²⁺ (curve b), the concentration of H₂O₂ generated increases at the beginning of irradiation, reaches a maximum (20 and 19 μM, respectively) after about 60 min, and then decreases gradually at longer irradiation times. However, with increasing quantities of Cu²⁺ ions, the maximal concentration of photogenerated H₂O₂ is sharply reduced. At concentrations greater than 100 μM, formation of H₂O₂ is not observed.

Isotopic labeling experiments¹³ with ¹⁸O have demonstrated that all the oxygen in the hydrogen peroxide arises from molecular oxygen as a result of the reduction of dioxygen by the conduction band electrons of carboxylic acids/TiO₂ dispersions under UV irradiation. The notion that the fate of the electrons injected into the conduction band by excited dyes under visible irradiation should be no different from the fate of those electrons generated under UV irradiation leads us to suppose that the oxygen in H₂O₂ formed under visible irradiation also originates from molecular oxygen.

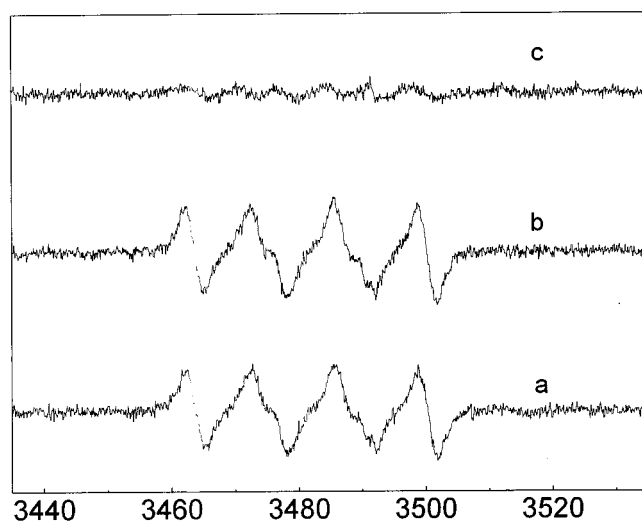
Spin-Trap ESR Detection of •OH and O₂^{-•} Radicals during in Situ Visible Irradiation. The DMPO spin-trap ESR spectroscopic method, a useful technique to monitor intermediate radicals, was employed to detect the reactive oxygen species generated during the visible irradiation of the SRB/TiO₂ system in the absence and presence of Cu²⁺ ions. Figure 6a displays the spin-trap ESR spectrum in the blank experiment; it is the typical signature of DMPO•OH adducts. Addition of Cu²⁺ and Fe³⁺ (Figure 6, parts c and d, respectively) leads to a marked decrease of the signal intensity of these DMPO•OH adducts, whereas addition of Zn²⁺ (Figure 6b) has relatively no influence on the •OH radical formation. Although the formation of superoxide radical anion was expected owing to the scavenging of the electrons by O₂ (eq 3), the spin-adduct DMPO•OOH was not detected in the aqueous system. It is probably because the facile disproportionation reaction of superoxide in water¹⁴ precludes the slow reactions between O₂^{-•} or •OOH and DMPO (*k* = 10 and 6.6 × 10³ M⁻¹ s⁻¹, respectively).¹⁵

In the SRB/TiO₂/ethanol system (Figure 7), the O₂^{-•}/•OOH radicals, which originate from oxygen, are more stable owing to the absence of water; consequently, generation of •OH radicals is less probable (equations 3–6). Figure 7a illustrates the spin-trap ESR pattern in the metal ion-free ethanol dispersions; this is a typical signature of DMPO•OOH adducts. No DMPO•OH signature is observed. After addition of Cu²⁺ ions (Figure



Magnetic field (G)

Figure 6. ESR spectra of radical adducts with DMPO in SRB/TiO₂ aqueous system after 1 min irradiation by a Nd:YAG pulsed laser ($\lambda = 532$ nm, 10 Hz). (a) blank, (b) Zn²⁺, (c) Cu²⁺, and (d) Fe³⁺. Concentration of metal ions, 100 μ M; TiO₂ loading, 2 g L⁻¹; SRB concentration, 100 μ M; pH = 2.5.



Magnetic field (G)

Figure 7. ESR spectra of radical adducts with DMPO in SRB/ethanol/TiO₂ dispersions after 1 min of irradiation by a Nd:YAG pulsed laser ($\lambda = 532$ nm, 10 Hz). (a) blank, (b) Zn²⁺, and (c) Cu²⁺. Concentration of metal ions, 100 μ M; TiO₂ loading, 2 g L⁻¹; SRB concentration, 100 μ M.

7c), the intensities of the O₂^{-•}/*OOH signals decrease relative to those observed in the absence of Cu²⁺ ions (blank), under otherwise identical conditions. By contrast, addition of Zn²⁺ shows no effect on the formation of reactive oxygen species in both aqueous and ethanolic dispersions (Figure 6b and Figure 7b, respectively).

The reaction of Cu²⁺ or Fe³⁺ with H₂O₂ (Fenton reaction) to generate *OH efficiently is well-documented.^{5d,16} Consequently, formation of *OH radicals should be enhanced upon addition of Cu²⁺ or Fe³⁺ if the same amount of H₂O₂ were produced during the photodegradation process. The fact that relatively few *OH radicals were detected in the presence of Cu²⁺ indicates

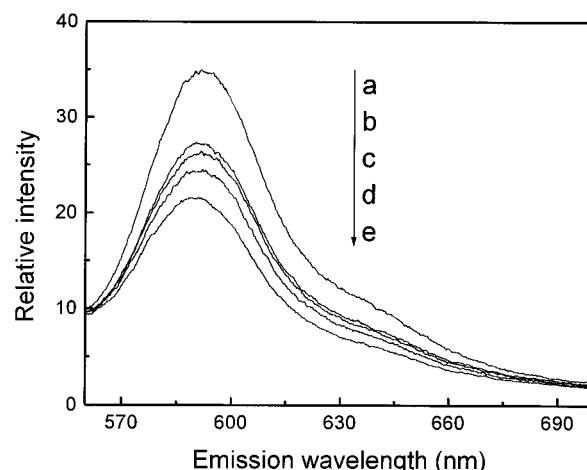
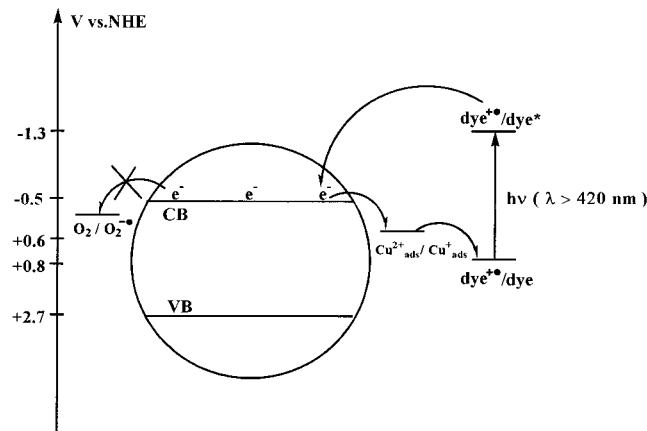


Figure 8. The reflectance fluorescence spectra of SRB/TiO₂/Cu²⁺ dispersions excited by $\lambda_{\text{ex}} = 480$ nm. Concentrations of Cu²⁺: (a) 0.8 mM, (b) 2 mM, (c) 5 mM, (d) 10 mM, (e) 20 mM. TiO₂ loading, 200 mg; SRB concentration, 1.2×10^{-5} M; sample volume, 0.6 mL; pH = 2.5.

the presence of little amount of H₂O₂ in the system. Hence, the decrease in the concentration of hydrogen peroxide after addition of Cu²⁺ cannot be attributed to the (photo-)Fenton like reaction. The most appropriate explanation is that addition of Cu²⁺ hinders the reduction of dioxygen and thereby the generation of H₂O₂.

Fluorescence Quenching of SRB in TiO₂ Aqueous Dispersions in the Presence of Cu²⁺. A study of the fluorescence from dyes can provide useful information about the interfacial electron injection process.^{17,18} In aqueous TiO₂ dispersions, the fluorescence spectra are difficult to record using the right-angle illumination method because of the opaque feature of the dispersions. Thus the front-surface illumination was employed. The fluorescence spectra of SRB ($\lambda_{\text{ex}} = 480$ nm; maximum at ca. $\lambda_{\text{max}} = 591$ nm) in aqueous TiO₂ dispersions were recorded at different Cu²⁺ concentrations (Figure 8). It indicates that increasing the concentration of Cu²⁺ leads to a decrease in the fluorescence emission intensity of SRB.

Quenching of fluorescence can take place either by interfacial charge-transfer, or by energy-transfer, or by concentration quenching (singlet-singlet annihilation) of the adsorbed dye molecules.^{17,18} As noted above (Table 1), addition of Cu²⁺ ions hardly affects adsorption of the dyes, so that the concentration quenching can be excluded. Considering that the band gap energy (3.2 eV, onset of absorption at $\lambda = 385$ nm) of TiO₂ particles is much greater than the excited singlet state energy of SRB (2.1 eV, estimated from the fluorescence emission and absorption spectra of SRB, $\lambda = 588$ nm), energy-transfer from the excited singlet states (¹SRB*) to TiO₂ is also unlikely. The redox potential of the excited singlet dye $E^0_{(\text{SRB}^+/\text{SRB}^*)} = -1.30$ V vs NHE,³ whereas the conduction band potential of TiO₂ particles is ca. -0.5 V vs NHE. These data point to an interfacial electron-transfer process between the excited dyes and TiO₂ particles. In the controlled experiments, addition of TiO₂ to a SRB solution greatly quenched fluorescence emission of the dye. Accordingly, we deduce that fluorescence quenching occurs through electron injection from the excited dye (¹SRB*) to the conduction band of TiO₂. Note that addition of Cu²⁺ to homogeneous SRB aqueous solutions (without TiO₂) resulted in no observable effect on the fluorescence emission. We also infer that the quenching of fluorescence occurs on the surface of TiO₂, in accord with the results displayed in Figure 4. Also, addition of Zn²⁺ to the TiO₂/SRB aqueous dispersions led to

SCHEME 1: Cartoon Illustrating the Electron Transfer Pathway on Addition of Cu²⁺ in TiO₂ Aqueous Dispersions under Visible Irradiation


no remarkable change in the fluorescence emission of the dispersions. This further supports the notion that inhibition of degradation is due to the high redox potential of Cu²⁺, rather than to the adsorption of dyes. Hence, it is unreasonable to attribute the hindering effect of Cu²⁺ ions on the photodegradation of SRB to a hindering effect on the electron injection process. Rather, to some extent addition of Cu²⁺ enhances the electron injection.

Proposed Pathway. On the bases of all the above evidence, the mechanism of depressing effect of Cu²⁺ ions on the TiO₂-assisted photodegradation of dyes under visible irradiation is illustrated in Scheme 1.

The redox potentials of the Cu²⁺/Cu⁺ couple {E° (Cu²⁺/Cu⁺) = 0.159 V vs. NHE} and of the Fe³⁺/Fe²⁺ couple {E° (Fe³⁺/Fe²⁺) = 0.771 V vs NHE}¹⁹ are much more positive than the potential of conduction band of TiO₂ particles {E_{cb} = -0.5 V vs NHE at pH = 1}.²⁰ Poznyak, and co-workers²¹ recently evidenced the existence of monovalent copper ions (Cu⁺) on the TiO₂ surface, associated with the partial reduction of adsorbed Cu²⁺ ions by electrons of the TiO₂ matrix. The copper-induced surface states were said to be located ca. 1.1 eV below the conduction band edge, i.e., E(Cu_{ads}²⁺/Cu_{ads}⁺) = +0.6 V vs NHE. It is also known that the Cu²⁺ ions adsorbed on the surface are difficult to reduce to copper metal, Cu⁰, even under UV light irradiation.^{11,22} The reduced metal ions species for Cu²⁺ and Fe³⁺ on the TiO₂ surface should thus be Cu⁺ and Fe²⁺, respectively, which are relatively unreactive toward the organic substrates. Considering that the potential of the copper-induced surface state (+0.6 V vs NHE) is lower than that of the ground state of dye (E°(SRB^{•+}/SRB) = +0.8 V vs NHE), the charge recombination between the copper-induced surface state and the dye radical cation is possible.

Consequently, the injected electrons can be easily trapped by the adsorbed Cu²⁺ ions, thereby diminishing considerably the reduction of preadsorbed O₂. Inasmuch as all the reactive oxygen species (O₂^{•-}/•OOH, •OH) result from the reduction of O₂ in aqueous TiO₂ dispersions in the visible-induced photodegradation of dyes,¹⁻³ the formation of these reactive oxygen species, which is essential for the degradation of dyes, is markedly suppressed upon addition of Cu²⁺ or Fe³⁺ ions (see Figures 5-7). Hence the photodegradation of dyes is depressed greatly.

It should be pointed out that in the presence of preadsorbed Cu²⁺ ions, the reduction of preadsorbed molecular dioxygen by the conduction electron is seriously hindered but by no means

eliminated. There are still opportunities for molecular O₂ to be reduced by the conduction electrons either directly or by subsequently the electrons trapped by the Cu²⁺, even if the surface of TiO₂ was saturated with Cu²⁺. The degradation of the SRB was not completely obstructed even at very high concentrations of the Cu²⁺ ion (see Figure 4).

Conclusion

Copper(II) and iron(III) ions have a strong suppressing effect on the photodegradation of all three dyes examined by altering the interfacial electron-transfer pathway under visible light irradiation. Addition of Cu²⁺ and Fe³⁺ decreases the reduction of O₂ by the conduction electrons, subsequently blocks the formation of reactive oxygen species (O₂^{•-}/•OOH, •OH), and hence suppresses the photodegradation of dyes under visible irradiation. However, the other metal ions such as Zn²⁺, Cd²⁺, and Al³⁺, affect the photoreaction only slightly through an alteration of the adsorption of dyes. It should be noted that only the Cu²⁺ ions that are adsorbed on the surface of TiO₂ can change the electron-transfer pathway and suppress the photo-assisted degradation of dyes. Molecular oxygen, O₂, is essential for the photodegradation of dyes and cannot be substituted by other electron acceptors under visible light irradiation.

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