Two competitive primary processes in the photodegradation of cationic triarylmethane dyes under visible irradiation in TiO_2 dispersions

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The photocatalytic degradation of two cationic triarylmethane dyes, crystal violet (CV) and fuchsin basic (FB), was examined in aqueous TiO_2 suspensions under visible light irradiation. The techniques of ^{1}HNMR, UV-Vis and EPR have been used to identify the photodecomposed products and intermediates and to demonstrate the photocatalytic mechanism of the dye on the semiconductor surface. The degradation undergoes a competitive primary process between demethylation and decomposition of the whole conjugated structure.

In recent years, considerable interest has been shown in investigating TiO_2 photocatalyzed degradation of organic pollutants under UV-light irradiation in aqueous dispersions.[1–3] It was found that this approach is possible and effective for the treatment of most organic pollutants,[4–6] even those that are difficult to degrade by conventional methods. However, UV-light sources are relatively expensive, while the amount of UV light in sunlight is very little in comparison with visible light; these considerations limit the application of semiconductor photocatalysis.

Recently, we[7,8] reported the photocatalytic degradation of dyes under visible irradiation in aqueous TiO_2 dispersions and found that organic dyes are not only photodegraded but also mineralized to CO_2 to some extent. The photocatalytic mechanism under visible irradiation[9,10] is different from that under UV irradiation: in the former the dyes (as a photosensitizer), rather than TiO_2 nanoparticulates, are excited by visible light to appropriate singlet or triplet states; the excited dye then injects an electron into the conduction band of TiO_2 semiconductor *via* electron transfer to generate a conduction electron that is scavenged by the adsorbed O_2 on the TiO_2 particulate to form $O_2^{-\bullet}$ or more active radicals such as $^{\bullet}OH$ or $^{\bullet}OOH$.[9,10] These active oxygen species attack the cationic dye radical ($Dye^{+\bullet}$) or the dye molecule, leading to degradation and mineralization *via* several intermediates. Once the dispersion discolors completely, the degradation is terminated as visible light is no longer absorbed.

In an aqueous system, TiO_2 is amphoteric[11] (pI = 6.8).

$$>\!Ti{-}O^- \xleftarrow{OH^-} >\!Ti{-}OH \xrightarrow{H^+} >\!Ti{-}OH_2^+ \qquad (1)$$

Thus, the electrical property of the TiO_2 surface varies with the pH of the dispersion. The surfaces of TiO_2 would be charged negatively and adsorb easily cationic species under pH > pI conditions; in the reverse condition it would adsorb anionic ones. However, adsorption of the substrate on the TiO_2 surface directly affects the occurrence of electron transfer between the excited dye and TiO_2 and further influences the degradation rate.

In previous studies,[7,8,10] we reported some work on the photocatalytic degradation of dyes containing carboxyl ($-COO^-$) or sulfonic ($-SO_3^-$) groups, which are, in general, easy to adsorb on the TiO_2 surface. In this work we studied a pure cationic dye of crystal violet (CV, a kind of triarylmethane dye) as the target compound and further reveal the photodegradation mechanism and adsorption model; in particular, the competitive processes of *N*-demethylation and decomposition of the conjugated structure in the photodegradation of CV are demonstrated. We also examined the degradation of fuchsin basic (FB) as a model compound for the degradation intermediate (of triarylmethane dyes such as CV). UV-Vis, EPR and ^{1}HNMR techniques were utilized to identify the intermediate products and elucidate the reaction mechanism.

Experimental section

Materials

Titanium dioxide photocatalyst (P25, 80% anatase, 20% rutile, specific surface area of 50 $m^2\ g^{-1}$) was kindly supplied by Degussa Co. Crystal violet (CV), fuchsin basic (FB) and sodium dodecylbenzenesulfonate (DBS) were of laboratory reagent grade used without further purification. Horseradish peroxidase (POD) was purchased from Huamei Biologic Engineering Co. (China), *N*,*N*-diethyl-*p*-phenylenediamine (DPD) from Merck (p.a), and 5,5-dimethyl-1-pyrroline (DMPO) from Sigma. Deionized and doubly distilled water was used throughout.

Photoreactor and light source

A 500 W halogen lamp (made by Institute of Electric Light Source of Beijing) as the visible light source was placed in a cylindrical glass vessel with a glass thimble filled with circulating water to avoid overheating. A cutoff filter was utilized to remove wavelengths below 470 nm and guarantee only visible irradiation.

Procedures and analyses

For the UV-Vis spectroscopy studies, an aqueous TiO_2 suspension was prepared by adding 100 mg TiO_2 nanoparticulates to a 50 ml solution containing crystal violet (2×10^{-5} mol l^{-1}), which was stirred in the dark for 30 min under constant air-equilibrated conditions to reach an adsorption-desorption equilibrium. At given irradiation intervals, 4 ml of suspension was taken out and centrifuged. TiO_2 was separated from the suspension by filtration and the filtrates were analyzed with a Lambda Bio 20 spectrometer.

For the ^{1}HNMR and EPR studies the samples were prepared from 100 ml suspensions containing 5×10^{-5} mol l^{-1} CV and 100 mg TiO_2, which were irradiated for different times. The filtrate, from which TiO_2 particles were removed by centrifuging and filtering, was dried by reduced pressure distillation (below 50 °C) and the remaining residue was dissolved in DMSO-d_6 for recording the NMR spectra with a Varian 300 spectrometer. Electron paramagnetic resonance (EPR) signals of radicals trapped by DMPO (0.16 mol l^{-1}) were detected with a Brucker EPR 300 E spectrometer. The irradiation source for EPR measurements was an *in situ* Quanta Ray Nd : YAG pulsed laser system ($\lambda = 532$ nm, 10 pulses s^{-1}).

The concentration of H_2O_2 generated after the irradiation f a 50 ml suspension containing dye (5×10^{-5} mol l^{-1}) and TiO_2 (100 mg) at various time intervals was determined immediately by the DPD method[12] (a photometric method) in which the DPD reagent is oxidized by H_2O_2 based on the peroxidase catalyzed reaction[12] ($\lambda_{max} = 531$ nm, $\varepsilon = 21\,000$ M^{-1} cm^{-1}).

Results and discussion

Degradation of cationic crystal violet dye

It was found that under acidic conditions the cationic dye CV was difficult to adsorb on the TiO_2 surface and hence the photodegradation of CV was very slow. CV dye can adsorb on the TiO_2 surface to some extent in alkaline media, but if the pH value is too high (pH > 9.5), CV molecules change to a leuco compound. So all experiments were carried out at pH = 9. Scheme 1 shows a proposed adsorption model in which the TiO_2 surface is negatively charged and the CV adsorbs onto the TiO_2 surface through the positive ammonium groups.

The spectral changes taking place during the TiO_2-assisted photodegradation of CV under visible irradiation are displayed in Fig. 1. Spectra 1 and 2 show respectively absorption of CV in the absence and presence of TiO_2 particles before irradiation. The characteristic absorption of CV at 590 nm ($\lambda_{max} = 590$ nm, $\varepsilon = 88\,000$ M^{-1} cm^{-1}) decreased by *ca.* 10% after addition of TiO_2, reflecting the adsorption extent of CV on the TiO_2 surface in the dark. The absorption peak of CV decreased, and a hypsochromic shift occurred simultaneously with increasing irradiation time. Not only did the maximum absorption wavelength shift from 590 to 540 nm, but also the color of the solution changed from violet to pink, which coincides well with the maximum absorption wavelength and the color of fuchsin basic ($\lambda_{max} = 540$ nm, $\varepsilon = 60\,000$ M^{-1} cm^{-1}). The hypsochromic shift process is a *N*-demethylation process (see Scheme 1). Comparing spectrum 5 with spectrum 2, approximately 45.1% of CV formed fuchsin basic after being fully demethylated and the rest was degraded through destruction of the conjugated structure. With further irradiation, FB was also further degraded as shown in Fig. 1 (spectra 5–8). From comparison with blank experiments (TiO_2-free) shown in Fig. 2, it was found that the TiO_2-assisted photodecomposition of CV was much faster and more complete than that in the absence of TiO_2 for both the *N*-demethylation (wavelength shift) and the destruction of the conjugated structure (change of absorbance). Fig. 3 shows the photodegradation of FB under visible irradiation in the presence of TiO_2 and its degradation process is similar to the degradation of CV after full demethylation. From Fig. 1–3 we conclude that the TiO_2-assisted photocatalytic degradation of CV occurs *via* two competitive processes: *N*-demethylation and the destruction of the conjugated structure.

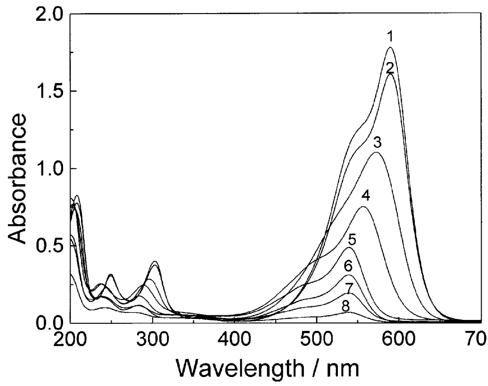


Fig. 1 Changes in absorption spectra during the photodegradation of CV (2×10^{-5} mol l^{-1}) in an aqueous TiO_2 suspension (2 g l^{-1}). Spectrum 1 is before addition of TiO_2 and spectra 2, 3, 4, 5, 6, 7 and 8 are after visible irradiation for 0, 0.5, 1.5, 6, 11.5, 13.5 and 19 h in the presence of TiO_2 respectively.

Probing the reaction process by ^{1}HNMR

We utilized the ^{1}HNMR technique to verify the intermediates as shown in Fig. 4. Spectrum *a* is the proton NMR signal of

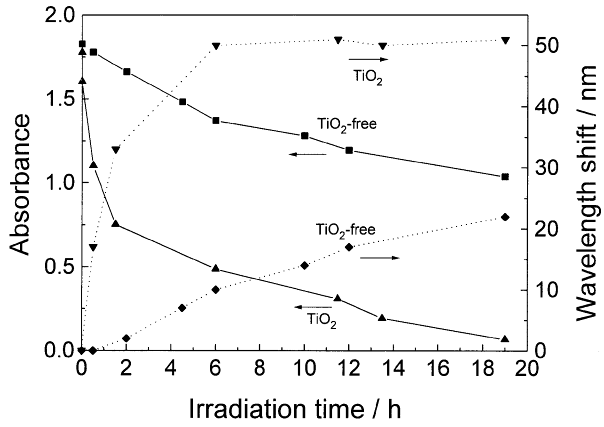
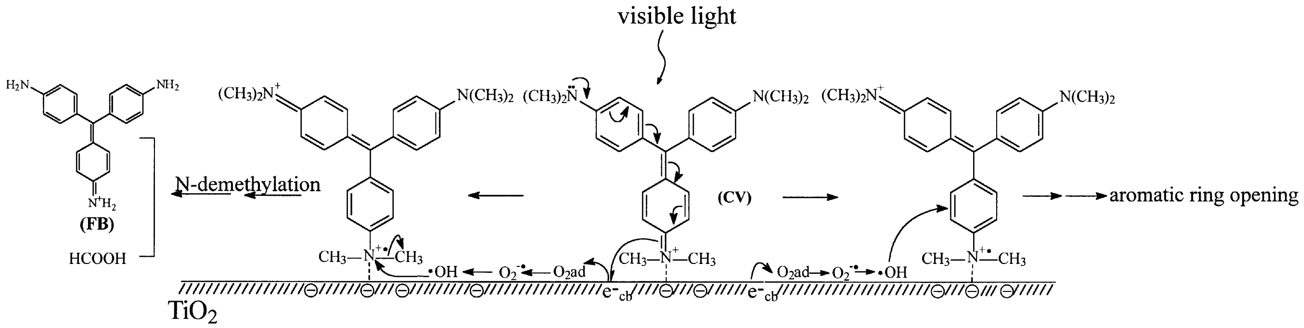


Fig. 2 Changes in the maximum absorption band and the corresponding wavelength shifts of CV under visible irradiation in the presence (down triangle and up triangle) and absence (square and diamond) of TiO_2. The experimental conditions were the same as in Fig. 1.



Scheme 1 The adsorption model and the degradation mechanism of triarylmethane dyes on TiO_2 surfaces *via* two competitive processes: *N*-demethylation and destruction of the conjugated structure.

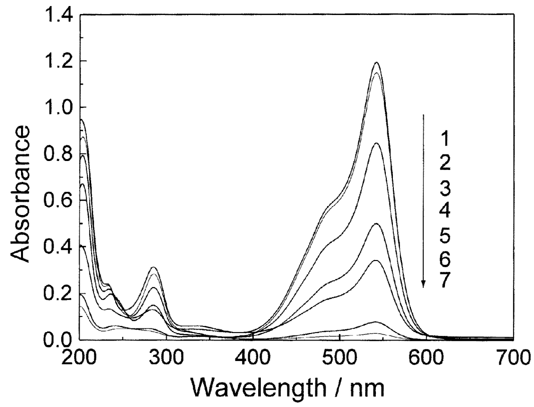


Fig. 3 Changes in absorption spectra during the photodegradation of FB (2×10^{-5} mol l^{-1}) in an aqueous TiO_2 suspension (2 g l^{-1}). Spectrum 1 is before addition of TiO_2 and spectra 2, 3, 4, 5, 6, 7 are after visible irradiation for 0, 2, 4, 6, 10 and 14 h in the presence of TiO_2, respectively.

CV before irradiation and spectra *b* and *c* are after irradiation for 15 and 30 h, respectively. With increasing irradiation time, the methyl signal ($\delta = 3.2$) of $-N(CH_3)_2$ decreased in intensity and disappeared; concomitantly, the methyl signal ($\delta = 2.9$) of $-NH(CH_3)$ appeared and subsequently disappeared. The proton signals of the aromatic rings changed radically during the irradiation process, going from two simple peaks at δ 7.0 and 7.3 to many complicated peaks at $\delta = 6.8$–7.8. Moreover, new signals were also observed at $\delta = 8.2$, 4.8 and 1.2. We attribute the signal at $\delta = 8.2$ to HCOOH, $\delta = 4.8$ to phen-NH_2 or phen-NRH, and $\delta = 1.2$ to $-CH_3$, which results from aromatic ring opening. The NMR spectra further illustrate that the photocatalytic degradation process of CV under visible irradiation is *N*-demethylation accompanied by direct degradation through destruction of the conjugated structure or opening of the aromatic ring.

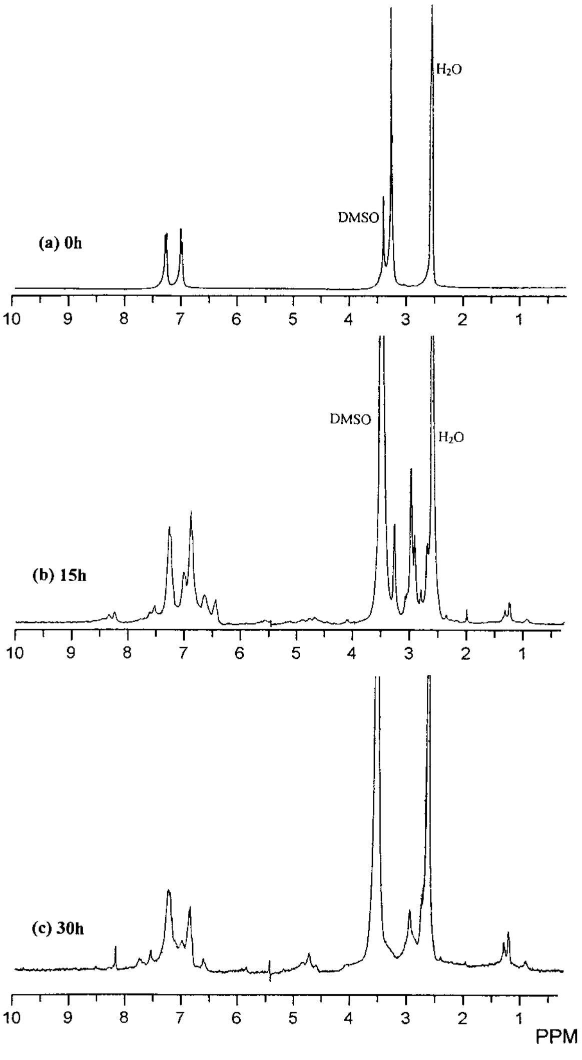


Fig. 4 ^{1}HNMR spectra of CV (5×10^{-5} mol l^{-1}) (a) before and after visible irradiation for (b) 15 and (c) 30 h in the presence of TiO_2 (2 g l^{-1}). (The strong signal at δ 2.5 is that of DMSO and the signal at δ 3.36 is attributed to H_2O.)

Formation of H_2O_2

In the photocatalytic degradation mechanism under UV light irradiation, the electron in the conduction band (e_{cb}) participates in the formation of H_2O_2 through reaction with adsorbed O_2 [eqn. (2)–(4)].

$$e_{cb} + O_{2ad} \rightarrow O_2^{-\cdot} \qquad (2)$$

$$O_2^{-\cdot} + 2H^+ + e_{cb} \rightarrow H_2O_2 \qquad (3)$$

$$2O_2^{-\cdot} + 2H^+ \rightarrow H_2O_2 + O_2 \qquad (4)$$

H_2O_2 must be yielded in the photodegradation of dyes under visible light irradiation during which e_{cb} is generated by an electron transfer process from the excited dye to the conduction band of TiO_2. The DPD method[12] was employed for detecting H_2O_2. However, for the dye/TiO_2 suspension, no H_2O_2 was detected under visible irradiation. Probably, the generation of H_2O_2 is too slow or H_2O_2 formed adsorbs on the TiO_2 surface.[3,13] In a previous report,[14] it was found that addition of the anionic surfactant DBS at an appropriate concentration near to its CMC into the rhodamine B/TiO_2 dispersion can enhance significantly the electron transfer from the excited dye to the TiO_2 and hence accelerate greatly the photodegradation of rhodamine B under visible irradiation, since the DBS molecules can adsorb strongly and co-adsorb with rhodamine B on the TiO_2 surface. To detect more easily the formation of H_2O_2, DBS (at its CMC of 1.2 mmol l^{-1}) was added into the CV/TiO_2 dispersion to not only enhance electron transfer from the excited dye to the TiO_2 but also to impede the adsorption of H_2O_2 generated under visible irradiation. After adding DBS, the photodegradation rate of CV increased significantly. Fig. 5 shows that H_2O_2 is formed and that its concentration increased with increasing visible irradiation time to attain a maximum value at 1.5 h, and then gradually decreased and finally tended to a constant value. During the irradiation period, the H_2O_2 formed was also decomposed by accepting an e_{cb}.

$$H_2O_2 + e_{cb} \rightarrow {}^{\cdot}OH + OH^- \qquad (5)$$

The quantity of H_2O_2 formed reflects the extent of the photocatalytic reaction of CV and also affects the active $^{\cdot}OH$ generation in the photocatalytic process.

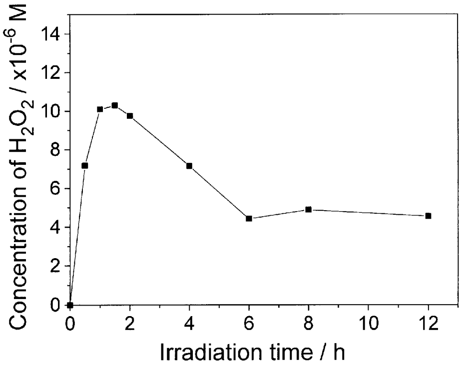


Fig. 5 Formation of H_2O_2 during the photodegradation of CV (5×10^{-5} mol l^{-1}) in the presence of DBS (1.2 mmol l^{-1}) and photocatalyst TiO_2 (2 g l^{-1}).

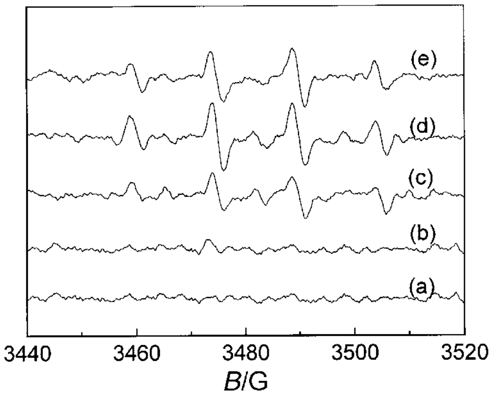


Fig. 6 EPR signals of DMPO-trapped ˙OH radicals. (*a*) CV/DBS system under visible irradiation (pulsed laser, $\lambda = 532$ nm, 10 pulse s^{-1}); (*b*) CV/DBS/TiO_2 system without irradiation; (*c*), (*d*) and (*e*) CV/DBS/TiO_2 system under visible laser irradiation for 2, 4, 6 min, respectively. (CV, 5×10^{-5} mol l^{-1}, DBS, 1.2 mmol l^{-1}, TiO_2, 2 g l^{-1}, DMPO, 0.16 mol l^{-1}).

Measurement of ˙OH radicals by EPR

According to the photocatalytic degradation mechanism, ˙OH may be generated and play an important role in the photocatalytic reaction. Since the lifetime of ˙OH is very short, it cannot be detected directly. When DMPO as a radical trapping reagent was added to the CV/TiO_2 dispersion, only very weak EPR signals appeared and then disappeared quickly, while in the CV/DBS/TiO_2 system, as shown in Fig. 6 EPR signals were observed under visible irradiation (532 nm). The four peaks with an intensity ratio of 1 : 2 : 2 : 1 are consistent with those of DMPO–˙OH, as reported in the literature.[4,15] In blank experiments, no EPR signals were detected in both the CV/DBS/TiO_2 system in the dark and the CV/DBS system in the absence of TiO_2 under visible irradiation. So the active radical ˙OH was generated in the TiO_2-assisted photodegradation of the dye under visible irradiation through an electron transfer process and the amount of ˙OH radicals generated was related closely with the adsorption of the dye on the surface of TiO_2 particles.

Conclusion

From the above results we can see that the TiO_2-assisted photodegradation of cationic triarylmethane dye CV under visible irradiation undergoes two competitive pathways: *N*-demethylation and destruction of the conjugated structure (as shown in Scheme 1). The excited dye generates $Dye^{+\bullet}$ after injecting an electron into the TiO_2 conduction band; this injected electron can be scavenged by an oxygen molecule to generate $O_2^{-\bullet}$, H_2O_2 and ˙OH species. When the N atom is attacked by ˙OH radicals, *N*-demethylation occurs and gives rise to FB and HCOOH, while attack on the conjugated structure of CV leads to decomposition of the molecular structure. The TiO_2 semiconductor particles play a pivotal role in the photocatalytic degradation of the dye.

Acknowledgements

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