Role of oxygen active species in the photocatalytic degradation of phenol using polymer sensitized TiO$_2$ under visible light irradiation

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ABSTRACT

The role of dissolved oxygen, and of active species generated by photo-induced reactions with oxygen, in the photocatalytic degradation of phenol was investigated using polymer [poly-(fluorene-co-thiophene) with thiophene content of 30%, so-called PFT30] sensitized TiO$_2$ (PFT30/TiO$_2$) under visible light irradiation. The photoluminescent (PL) quantum yield of PFT30/TiO$_2$ was about 30% of that of PFT30/Al$_2$O$_3$, proving that electron transfer took place between the polymer and TiO$_2$. The result that photocatalytic degradation of phenol was almost stopped when the solution was saturated with N$_2$ proved the importance of O$_2$. Addition of NaN$_3$, an effective quencher of singlet oxygen (^{1}O$_2$), caused about a 40% decrease in the phenol degradation ratio. Addition of alcohols caused about a 60% decrease in the phenol photodegradation ratio, indicating that the hydroxyl radicals (OH$^\bullet$), whose presence was confirmed by electron spin resonance (ESR) spectroscopy, was the predominant active species in aqueous solution. In anhydrous solution, singlet oxygen (^{1}O$_2$) was the predominant species. These results indicate that oxygen plays a very important role in the photocatalytic degradation of phenol.

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1. Introduction

Over the last 20 years, the use of heterogeneous photocatalysis as a method for eliminating organic pollutants during water treatment has been a subject of great interest. Photocatalytic degradation of pollutants using TiO$_2$ has attracted considerable attention for its potential application to environmental problems, and the mechanism of this reaction has been intensively studied [1–3]. Despite this research, which has focused mainly on the role of active species leading to the initial photoreaction process, details of the mechanisms of photocatalytic oxidation processes at the TiO$_2$ surface remain elusive [4]. The major uncertainty concerns the reaction pathway, with some researchers suggesting that oxidation proceeds via direct electron transfer between substrate and positive holes, while others have suggested a hydroxyl radical-mediated pathway.

An active area of this research is the role played by O$_2$, both in the scavenging of conduction band electrons (e$^-_{cb}$) to effectively prevent their recombination with valence band holes (h$^+_{vb}$) and in the formation of active oxygen radicals [5–10]. In the well-known process of excitation of a semiconductor, absorption of a photon with suitable energy is followed by the promotion of an electron from the valence band to the conduction band, leaving behind a positive charge vacancy, i.e., a hole. In order for a photochemical change to proceed, the charge-transfer reaction must compete efficiently with the recombination process, which takes place on the nanosecond time scale. For this rigorous requirement to be satisfied, the preadsorption of charge-trapping species (usually oxygen molecules) is assumed to lead to efficient chemical reactions to generate active oxygen species such as singlet oxygen (^{1}O$_2$), hydroxyl radicals (OH$^\bullet$) and superoxide radicals (O$_2^{\bullet-}$).

The copolymer poly-(fluorene-co-thiophene) (PFT) is capable of being a sensitizer of TiO$_2$. It has been proved that the photocatalytic degradation of phenol can be carried out under visible light using PFT sensitized TiO$_2$, whose diffuse reflectance spectra was red-shifted toward the visible light region [11,12]. In this paper, the copolymer with a thiophene content of 30% (so-called PFT30) was used. The oxidation potential of PFT30 is 1.30 [13], therefore it is more stable during the reaction process compared with other organic photosensitizers. Our objective was to identify the active oxygen species generated in a visible light/PFT30/TiO$_2$ system, and to determine the roles of the main active species in the photodegradation of phenol under visible light irradiation.

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2. Experimental

2.1. Materials

TiO_2 (P-25, 80% anatase, 20% rutile; BET area, ca. 50 m^2 g^{-1}, mean particle size, ca. 30 nm) was supplied by Degussa Co. and dried at 120 °C for 12 h before use. The polymer PFT30 was synthesized according to Hou et al. [14]; its chemical structure and the sensitization of TiO_2 by PFT30 was according to Song et al. [12]. Isopropanol (*i*-PrOH), methanol (MeOH) and acetonitrile were dehydrated by anhydrous Na_2SO_4 before use. The spin trap reagent 5,5-dimethyl-1-pyrroline-*N*-oxide (DMPO) was purchased from Sigma. All other chemicals were analytical grade and used without further purification. Purified water was obtained from a Millipore filtration system (Millipore ZLXS50020).

2.2. Measurements and procedures

The concentration of phenol was measured by UV-2450 UV-Visible spectrophotometer (SHIMADZU, Japan) at a wavelength of 510 nm through 4-aminoantipyrine method. Photoluminescent (PL) quantum yield was determined in an integrating sphere IS080 (Labsphere, USA) equipped with a UDT370 digital photometer with 325 nm excitation of a He–Cd laser (Mells Griod). Light intensity was measured by a UV-A Ultraviolet Meter (Photoelectric Instrument Factory of Beijing Normal University) equipped with two probes with wavelength of 420 and 365 mm, respectively.

Electron spin resonance (ESR) signals of spin-trapped paramagnetic species with DMPO were recorded with a Brucker ESP 300E spectrometer to examine the formation of active radical species. The settings for ESR spectrometer were center field 3480.0 G, sweep width 100.0 G, microwave frequency 9.78 Hz, modulation frequency 100 kHz, and power 5.05 mW.

The photodegradation experiment was carried out in a column glass reactor. Three 1 W LED (light-emitting diode, Shenzhen Lanbaoli Photo-electricity Technology Co. Ltd., China, light intensity: $E_{420} \approx 2 \times 10^3$ μW/cm, $E_{365} = 0$) lights with a radiant wavelength of 450–475 nm were used as the visible light source. The lights were placed tightly against the reactor, and were spaced 120° from each other. The reactor was open to air to ensure enough oxygen in the reaction solution. Prior to photoreaction, the 50 mL solution containing photocatalyst (1 g L^{-1}) and phenol (10 mg L^{-1}) was magnetically stirred in darkness for 30 min to establish adsorption–desorption equilibrium. Before and after 2 h irradiation time, a 5-mL aliquot of the reaction mixture was removed to be centrifuged and filtered, and the change in the concentration of phenol was monitored spectrophotometrically. We found that the removing of 5 mL aliquot of the reaction mixture did not significantly affect the concentration of phenol in the remaining solution. The reaction mixture was stirred throughout the reaction to keep the mixture in suspension.

A series of blank experiments revealed that little phenol was decomposed with or without TiO_2 under visible light. No appreciable degradation of phenol was observed with photocatalyst in the dark [12].

In the N_2-saturated experiment, the reaction solution was saturated by highly purified N_2 gas (99.99%) for 30–60 min, and

transferred to an anaerobic chamber (BACTRON 1.5, SHELLAB, USA) quickly. Then the solution and photocatalyst were added to a 50 mL crimp neck headspace-vial in the chamber. Finally the vial was sealed and put into the photocatalytic reactor.

3. Results and discussion

3.1. The process of electron transfer

The generation of electron-hole pairs by excited semiconducting materials is a typical photo-physical process in photocatalytic reactions. In a dye sensitized TiO_2 system, excited dye molecules generate electron-hole pairs by electron transfer, after which the electrons return from the excited state to the ground state, recombining with holes within an extremely short time and causing photoluminescence. If electrons are transferred into the conduction band of TiO_2, they will return to ground state from the conduction band, a process in which the probability of recombination of electrons and holes is much smaller, resulting in lower PL quantum yield [15].

The results in Table 1 show that there was little difference in PL quantum yield between pure PFT30 (14.7%) and PFT30/Al_2O_3 (13.3%), while that of PFT30/TiO_2 was much lower (only 3.8%, or about 30% of that of PFT30/Al_2O_3). These results indicate that much more electrons transferred from the polymer to the conduction band of the semiconductor TiO_2 than those transferred to the non-semiconductor Al_2O_3. It was suggested that the PL quantum yield of PFT30 was quenched by TiO_2, which proved that electron transfer took place between PFT30 and TiO_2. Such electron transfer is a necessary precursor to subsequent photochemical processes.

3.2. The role of dissolved oxygen

The role of O_2 during photocatalytic processes has been long debated. Although its electron-scavenging character is well documented, the roles of its reduction products (e.g. $HO_2^•$) are questionable. There is evidence for and against the importance of these species. It is noteworthy that not only $O_2^{•-}$ or $HO_2^•$, but also dissolved O_2, can react with radicals formed during the degradation process [16]. In a visible light/sensitizer/TiO_2 system, almost all active species are generated following the reaction in which oxygen captures the e^-_{cb}. Oxygen is an indispensable reactant to generate active oxygen radicals including singlet oxygen ($^1O_2$), hydroxyl radical ($OH^•$), superoxide radical ($HO_2^•$ or $O_2^{•-}$), and hydrogen peroxide (H_2O_2) [2]. Therefore, oxygen is very important in photocatalytic reactions induced by visible light. It not only scavenges e_{cb}^- to effectively prevent the recombination of e_{cb}^- and $dye^{+•}$, but is also the predominant reactant to generate active species.

To test the role of dissolved O_2 in the photocatalytic degradation process of phenol, N_2 was bubbled through the suspension for 30–60 min to ensure the reaction was operated without O_2. The results are presented in Fig. 1.

The experimental results show that the photocatalytic degradation of phenol was almost stopped in the presence of N_2 but without an efficient electron scavenger, it proved the importance of electron scavenger such as O_2 in the photocatalytic reaction. The use of inorganic compounds such as Cr(VI) has been demonstrated to

Table 1
PL quantum yield of PFT30 film, PFT30/TiO_2, and PFT30/Al_2O_3

	Abs. edge (nm)	PL max (nm)	Band gap (eV)	E_{red} (V)	PL quantum yield (%)
PFT30 film	480	480, 510	2.58	−1.28	14.7
PFT30/TiO_2	490	480, 510	–	–	3.8
PFT30/Al_2O_3	490	480, 510	–	–	13.3
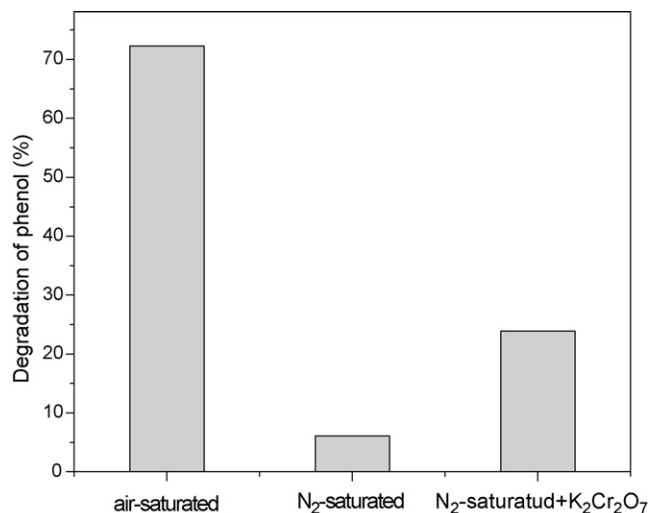
Fig. 1. The role of dissolved oxygen in the photocatalytic degradation of phenol.

Fig. 2. The effect of NaN$_3$ addition on the degradation of phenol.

trap photogenerated electrons [17,18]. As shown in Fig. 1, the photodegradation ratio of phenol in the presence of 1×10^{-3} M Cr$_2$O$_7^{2-}$ in a N$_2$-saturated system was about one-third of the case that O$_2$ was present as electron scavenger. It should be pointed out that the homogeneous photochemical reaction between Cr$_2$O$_7^{2-}$ and phenol was negligible, because the extent of oxidation of phenol by Cr$_2$O$_7^{2-}$ was less than 4% under the same experimental conditions without the photocatalyst. Cr(VI) is apparently more capable of scavenging e$_{cb}^-$ than it is of taking electrons from phenol, thus it indirectly proves that participation of oxygen in the reaction is necessary. Liu et al. [6] used the ESR spin-trapping technique to detect active oxygen radicals and GC–MS to analyze intermediates formed during self-sensitized photodegradation with in situ visible light irradiation of alizarin red (AR)/TiO$_2$ dispersions. They concluded that oxygen played a very important role in preventing recombination of dye$^{+\bullet}$ and electrons as well as in the formation of active oxygen radicals, which lead to the photodegradation and partial mineralization of AR. Aguer and Richard [19] studied the reactive species produced on irradiation at 365 nm of humic acid; they found that no consumption of phenol was observed in deoxygenated medium, and that the rate of phenol disappearance was dependent on the oxygen concentration. This line of research has demonstrated that dissolved oxygen plays a very important role in sensitized photodegradation reactions.

3.3. The role of singlet oxygen

In the photocatalytic degradation of organic pollutants using PFT30/TiO$_2$, the polymer firstly transforms to the singlet excited state by absorbing photon energy, and then continues to the triplet excited state, finally reacts with oxygen to generate singlet oxygen (^{1}O$_2$) by energy transfer. NaN$_3$ is an effective quencher of singlet oxygen [19], so NaN$_3$ concentration with a range of 2.5, 12.5, 25, 125, and 250 mM was added to the reaction system to observe its effect on the photocatalytic degradation of phenol (Fig. 2).

The results show that the degradation ratio of phenol gradually decreased with increasing NaN$_3$ concentration, indicating that ^{1}O$_2$ was generated in the system under visible light irradiation. ^{1}O$_2$ with high energy (22.5 kcal mol^{-1}) can degrade phenol directly, so the fact that the addition of NaN$_3$ was able to decrease the phenol degradation ratio by only about 40%, compared to the control, suggests that ^{1}O$_2$ was not the predominant active species in this reaction. Similarly, in a study of the photocatalytic degradation of

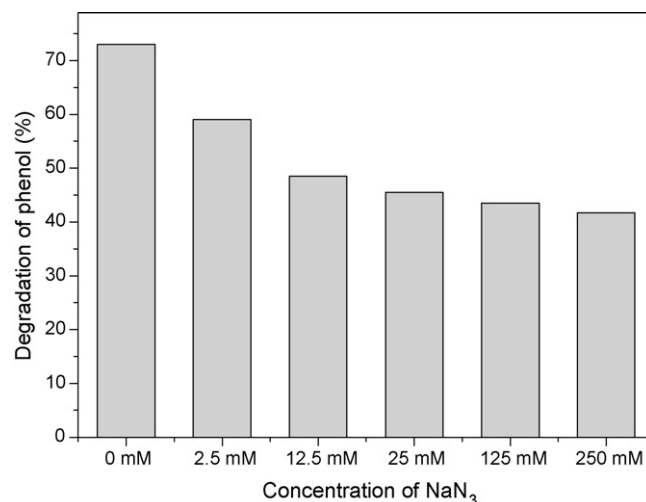2,4-dichlorophenol using xanthene dyes as photosensitizers of TiO$_2$ under visible light irradiation, Li et al. [20] found that the decomposition yield of 2,4-DCP was reduced by only about 12% by NaN$_3$.

3.4. The role of hydroxyl radical

The oxidative ability of OH$^\bullet$ is 2.05 times higher than that of Cl$_2$, 1.58 times higher than that of H$_2$O$_2$, and 1.35 times higher than that of O$_3$. Thus, hydroxyl radicals are usually considered to be the major species responsible for photocatalysis of organic pollutants in wastewater, based on evidence that includes detection of hydroxylated intermediates, distribution of the hydroxylation products, and spin trapping with subsequent ESR detection. [21,22].

The DMPO spin-trap ESR spectroscopic method, a useful technique to monitor intermediate radicals, is commonly used to detect active radicals in photocatalytic systems [5,6,23–25]. In order to examine and confirm the active oxygen radicals formed in the visible light/PFT30/TiO$_2$ system, ESR spectra of DMPO spin-trapped adducts were recorded in situ during irradiation of PFT30/TiO$_2$ suspensions by LED lights at 450–475 nm. Fig. 3 shows the ESR spectra signals of spin-trapped DMPO–OH$^\bullet$ radicals formed in the suspensions. The characteristic peak intensity of 1:2:2:1 is the evidence that OH$^\bullet$ radicals were indeed formed in the visible light/PFT30/TiO$_2$ system. Although the formation of the superoxide radical anion was expected owing to the scavenging of electrons by
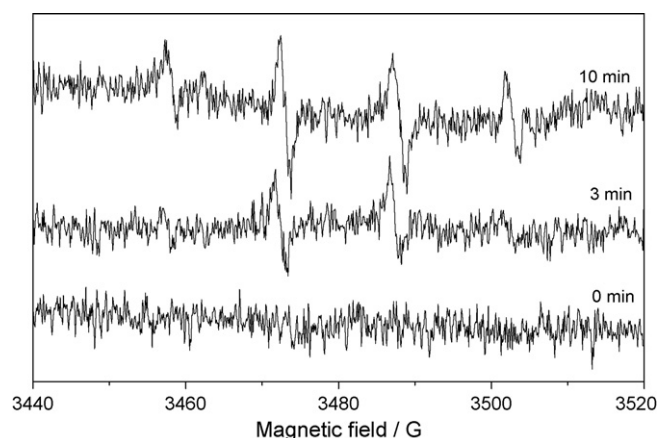

Fig. 3. ESR spectra of radical adducts with DMPO in PFT30/TiO$_2$ suspensions.
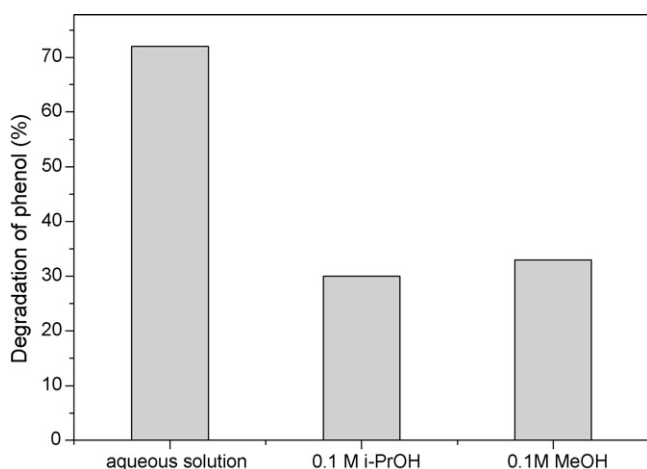
Fig. 4. Photocatalytic degradation of phenol with *i*-PrOH or MeOH addition.

O_2, the spin-adduct DMPO–OOH• was not detected in the aqueous system, probably because the facile disproportionation reaction of superoxide in water precludes the slow reactions between $O_2^{•−}$ or OOH• and DMPO ($k = 10$ and 6.6×10^3 M^{-1} s^{-1}, respectively) [24].

Alcohols such as MeOH and *i*-PrOH are commonly used as diagnostic tools for OH•-mediated mechanisms [26–29]. Though direct oxidation of short aliphatic alcohols by photogenerated holes probably happens, it is negligible because they have very weak adsorption on the TiO$_2$ surface in aqueous media. Of the two alcohols that we used, *i*-PrOH, which is considered an excellent capturer of hydroxyl radicals, is more easily oxidized by OH•. Its reaction rate constant with OH• is 1.9×10^9 M^{-1} s^{-1}, a rate of almost the diffusion limit. MeOH, whose reaction rate constant with OH• is 1.0×10^9 M^{-1} s^{-1}, a little less than that of *i*-PrOH, is also an excellent capturer of OH• [28].

The results presented in Fig. 4 show that the photodegradation ratio of phenol decreased to 30% and 33% with 0.1 M *i*-PrOH and MeOH, respectively. Compared with the reaction in aqueous solution, the degradation ratio decreased by about 60%, which indicated that *i*-PrOH and MeOH seriously inhibited the photocatalytic degradation of phenol, and also suggested that hydroxyl radicals are the predominant active species in the photocatalytic degradation of phenol.

3.5. The effect of reaction solvent

TiO$_2$ is usually surrounded by adsorbed water in aqueous suspension, so water molecules are likely oxidized to hydroxyl radicals by photogenerated holes. The use of a non-aqueous reaction medium can prevent the participation of OH• radicals in the oxidation process. Acetonitrile is an extremely stable molecule that has been used as a solvent in studies of photocatalytic oxidation reactions in which the electron-hole transfer mechanism between substrate and holes has been suggested [30,31].

Experiments were carried out in anhydrous acetonitrile suspension to minimize the formation of OH• (Fig. 5). Phenol molecules were oxidized either directly by photogenerated holes or other active oxygen species ($^1O_2$ or $O_2^{•−}$).

As anticipated, the degradation ratio that was obtained in acetonitrile solvent (70.4%) differed little from the result obtained in an aqueous system (72%). However, in the acetonitrile solvent, the addition of 25 mM NaN$_3$ had more of an effect on the degradation of phenol (decreased to 16.3%) than that occurred in aqueous suspension (decreased to 46.2%); while the addition of 0.1 M *i*-PrOH had less of an effect (decreased less than 5%) than occurred in aque-
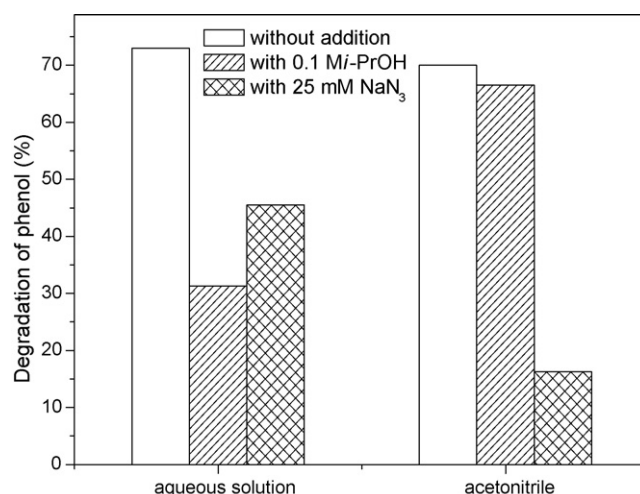

Fig. 5. The effect of reaction solvent in the absence and presence of *i*-PrOH and NaN$_3$ on the photodegradation of phenol.

ous suspension (decreased to 31.2%). These results indicate that no hydroxyl radicals were generated in the anhydrous solution and that singlet oxygen ($^1O_2$) was the predominant active species.

4. Conclusions

In the present paper, experiments were carried out to investigate electron transfer and identify the active species in the photodegradation of phenol in a polymer sensitized TiO$_2$ system, using charge-trapping species as diagnostic tools. The results showed that electron transfer took place between polymer and TiO$_2$ under visible light irradiation. The excited polymer reacted with oxygen to generate singlet oxygen ($^1O_2$), which contributed to the degradation reaction. Hydroxyl radicals (OH•) detected using the ESR method were shown to be the predominant active species in the photodegradation of phenol in aqueous suspension. Oxygen played an important role not only in scavenging conduction band electrons (e_{cb}^-) but also in the formation of active oxygen radicals. In anhydrous solution, singlet oxygen ($^1O_2$) became the predominant active species.

Acknowledgements

References

[1] M.A. Fox, M.T. Dulay, Heterogeneous photocatalysis, Chem. Rev. 93 (1993) 341–357.
[2] D. Chatterjee, A. Mahata, Photoassisted detoxification of organic pollutants on the surface modified TiO$_2$ semiconductor particulate system, Catal. Commun. 2 (2001) 1–3.
[3] A. Fujishima, T.N. Rao, D.A. Tryk, Titanium dioxide photocatalysis, J. Photochem. Photobiol. C: Photochem. Rev. 1 (2000) 1–21.
[4] D. Hufschmidt, L. Liu, V. Seizer, D. Bahnemann, Photocatalytic water treatment: fundamental knowledge required for its practical application, Water Sci. Technol. 49 (2004) 135–140.
[5] G.M. Liu, J.C. Zhao, H. Hidaka, ESR spin-trapping detection of radical intermediates in the TiO$_2$-assisted photo-oxidation of sulforhodamine B under visible irradiation, J. Photochem. Photobiol. A 133 (2000) 83–88.
[6] G.M. Liu, X.Z. Li, J.C. Zhao, S. Horikoshi, H. Hidaka, Photooxidation mechanism of dye alizarin red in TiO$_2$ dispersions under visible illumination: an experimental and theoretical examination, J. Mol. Catal. A 153 (2000) 221–229.
[7] K.W. Kim, E.H. Lee, Y.J. Kim, M.H. Lee, K.H. Kim, D.W. Shin, A relation between the non-stoichiometry and hydroxyl radical generated at photocat-

alytic TiO$_2$ on 4CP decomposition, J. Photochem. Photobiol. A 159 (2003) 301–310.

[8] R. Nakamura, Y. Nakato, Primary intermediates of oxygen photoevolution reaction on TiO$_2$ (rutile) particles, revealed by in situ FTIR absorption and photoluminescence measurements, J. Am. Chem. Soc. 126 (2004) 1290–1298.

[9] Y. Cho, W. Choi, C.H. Lee, T. Hyeon, H.I. Lee, Visible light-induced degradation of carbon tetrachloride on dye-sensitized TiO$_2$, Environ. Sci. Technol. 35 (2001) 966–970.

[10] T.X. Wu, T. Lin, J.C. Zhao, H. Hidaka, N. Serpone, TiO$_2$-assisted photodegradation of dyes. 9. Photooxidation of a squarylium cyanine dye in aqueous dispersions under visible light irradiation, Environ. Sci. Technol. 33 (1999) 1379–1387.

[11] L. Song, R.L. Qiu, Y.Q. Mo, D.D. Zhang, H. Wei, Photocatalytic activities of TiO$_2$ modified by poly(fluorene-*co*-thiophene) under visible light, Acta Sci. Nat. Univ. Sunyatseni 45 (2006) 125–126.

[12] L. Song, R.L. Qiu, Y.Q. Mo, D.D. Zhang, H. Wei, Y. Xiong, Photodegradation of phenol in a polymer-modified TiO$_2$ semiconductor particulate system under the irradiation of visible light, Catal. Commun. 8 (2007) 429–433.

[13] R.L. Qiu, L. Song, D.D. Zhang, Y.Q. Mo, E. Brewer, X.F. Huang, Characterization of cojugated polymer poly(fluorene-*co*-thiophene) and its application as photo-sensitizer of TiO$_2$, Int. J. Photoenergy 1 (2008) 1–5.

[14] Q. Hou, Y.H. Niu, W. Yang, R.Q. Yang, M. Yuan, Y. Cao, Synthesis and electroluminescent properties of copolymer of fluorine and thiophene, Acta Polym. Sinica 2 (2003) 161–166.

[15] P.V. Kamat, M.A. Fox, Photosensitization of TiO$_2$ colloidals by erythrosin B in acetonitrile, Chem. Phys. Lett. 102 (1983) 379–384.

[16] I. Ilisz, A. Dombi, Investigation of the photodecomposition of phenol in near-UV-irradiated aqueous TiO$_2$ suspensions. II. Effect of charge-trapping species on product distribution, Appl. Catal. A: Gen. 180 (1999) 35–45.

[17] S.G. Schrank, H.J. Jose, R.F.P.M. Moreira, Simultaneous photocatalytic Cr(VI) reduction and dye oxidation in a TiO$_2$ slurry reactor, J. Photochem. Photobiol. A 147 (2002) 71–76.

[18] S. Malato, J. Blanco, C. Richter, B. Braun, M.I. Maldonado, Enhancement of the rate of solar photocatalytic mineralization of organic pollutants by inorganic oxidizing species, Appl. Catal. B 17 (1998) 347–356.

[19] J.P. Aguer, C. Richard, Reactive species produced on irradiation at 356 nm of aqueous solutions of humic acids, J. Photochem. Photobiol. A 93 (1996) 193–198.

[20] X.Z. Li, W. Zhao, J.C. Zhao, Visible light-sensitized semiconductor photocatalytic degradation of 2,4-DCP, Sci. China (Ser. B) 45 (2002) 421–425.

[21] C.S. Turchi, D.F. Ollis, Photocatalytic degradation of organic water contaminants: mechanisms involving hydroxyl radical attack, J. Catal. 122 (1990) 178–192.

[22] R. Terzian, N. Serpon, R.B. Draper, M.A. Fox, E. Pelizzetti, Pulse radiolytic studies of the reaction of pentahalophenols with OH radicals: formation of pentahalophenoxyl, dihydroxypentahalocyclohexadiemyl, and semiquinone radicals, Langmuir 7 (1991) 3081–3089.

[23] T.X. Wu, G.M. Liu, J.C. Zhao, Photoassisted degradation of dye pollutants. V. self-photosensitized oxidative transformation of rhodamine B under visible light irradiation in aqueous TiO$_2$ dispersions, J. Phys. Chem. B 102 (1998) 5845–5851.

[24] C.C. Chen, W.H. Ma, J.C. Zhao, Effect of transition metal ions on the TiO$_2$-assisted photodegradation of dyes under visible irradiation: a probe for the interfacial electron transfer process and reaction mechanism, J. Phys. Chem. B 106 (2002) 318–324.

[25] W. Zhao, C.C. Chen, X.Z. Li, J.C. Zhao, Photodegradation of sulforhodamine-B dye in platinized titania dispersions under visible light irradiation: influence of platinum as a functional co-catalyst, J. Phys. Chem. B 106 (2002) 5022–5028.

[26] H. Park, W. Choi, Effect of TiO$_2$ surface fluorination on photocatalytic reactions and photoelectrochemical behaviors, J. Phys. Chem. B 108 (2004) 4086–4093.

[27] T.M. El-morsi, W.R. Budakowski, A.S. Abd-el-aziz, K.J. Friesen, Photocatalytic degradation of 1,10-dichlorodecane in aqueous suspensions of TiO$_2$: a reaction of adsorbed chlorinated alkane with surface hydroxyl radicals, Environ. Sci. Technol. 34 (2000) 1018–1022.

[28] P. Calza, E. Pelizzetti, Photocatalytic transformation of organic compounds in the presence of inorganic ions, Pure Appl. Chem. 73 (2001) 1839–1848.

[29] Y.X. Chen, S.Y. Yang, K. Wang, L.P. Lou, Role of primary active species and TiO$_2$ surface characteristic in UV-illuminated photodegradation of Acid Orange 7, J. Photochem. Photobiol. A 172 (2005) 47–54.

[30] O.S. Mohamed, A.M. Gaber, A.A. Abdel-Wahab, Photocatalytic oxidation of selected aryl alcohols in acetonitrile, J. Photochem. Photobiol. A 148 (2002) 205–210.

[31] S. Vijaikumar, N. Somasundaram, C. Srinivasan, Photoinduced oxidation of benzhydrol and reduction of benzyls on titanium dioxide, Appl. Catal. A 223 (2002) 129–135.