Reaction site and mechanism in the UV or visible light induced TiO₂ photodegradation of Orange G

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Abstract: For TiO₂ heterogeneous reaction, the reaction site and the detailed mechanism are interesting and controversy topics. In this paper, effects of surface fluorination of TiO₂ on the photocatalytic degradation of an azo dye, Orange G(OG) under UV or visible light irradiation were investigated, and the possible reaction site and mechanism were elucidated. The adsorption of OG on TiO₂ was nearly inhibited by fluoride but its UV light induced photodegradation rate was greatly increased by a factor of about 2.7, which was due to the more generated free hydroxyl radicals. It supported the views that fluoride could desorb the oxidant species from surface and that the reaction sites could move to the bulk solution. In TiO₂/Vis system, the observed inhibition effects of fluorination could be interpreted by the competitive adsorption, which provided additional evidences that the visible light sensitized photodegradation of dye pollutants on the catalyst surface.

Keywords: photocatalytic degradation; mechanism; adsorption; fluorination; dye pollutants

Introduction

Heterogeneous photocatalysis is attracting considerable attentions as an emerging destructive technology leading to the total mineralization of most of organic pollutants(Fox and Dulay, 1993; Hoffmann *et al.*, 1995; Fujishima *et al.*, 2000). Surface characteristics and surface species of TiO₂ nanoparticles are essential factors for the photocatalytic degradation of organic substrates. It has been confirmed that the degradation relates tightly to the surface chemistry at the TiO₂-water interface. It is often been inferred that degradation occurs on the particle surface, not in the bulk (Fox and Dulay, 1993). The oxidants involved in photocatalysis remain on the surface and react with substrates that are preadsorbed or diffusing onto the surface.

The evidence for the reason is confusing till now (Hufschmidt *et al.*, 2004). There are findings as to whether the photocatalytic reaction takes place on the surface or in solution bulk (Yang and Davis, 2000). Although the fact that the initial rates of photodegradation follow the Langmuir-Hinshelwood kinetic model for solid-liquid interfaces seems responsible for the surface oxidation, it cannot be taken as a solid proof that the reaction occurs at the surface(Hoffmann *et al.*, 1995).

We have focused our attention on the effect of TiO₂ surface fluorination on the UV-light induced photodegradation of an azo dye, Acid Orange 7(Chen, 2005). It was found that the degradation was mostly initiated by direct electron transfer reaction, and when the surface was fluorinated, the initial process could shift from surface reaction to homogeneous radical reaction in bulk solution. To get a better understanding of this issue, more proofs are still required.

In this study, we used TiO₂ surface fluorination as a diagnostic tool, to investigate the UV light induced photocatalytic mechanism of another azo dye, Orange G (OG), and experiments were also conducted to examine the influence of surface fluorination on the visible light sensitized photocatalytic process.

1 Materials and methods

1.1 Chemicals

Orange G (OG) as shown in Fig.1 is obtained from Sigma Chemical Co. TiO₂(P25, ca. 80% anatase, 20% rutile; BET area, ca. 50 m²/g; mean particle size, ca. 30 nm) was supplied by Degussa Co.
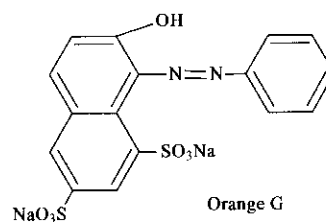

Fig.1   Structure of Orange G molecule.

1.2 Photocatalytic experiments

A detailed description of the experimental arrangement was reported previously(Wang *et al.*, 2004). In brief, two 6-W UV lamps(λ_{max}= 365 nm)

were used as a UV light source. And a 175-W metal halide lamp(Philips) was used as a visible light source. $NaNO_2$(2 mol/L) solution was circulated through the jacket to filter out the UV emission of the lamp below 400 nm (Lettmann *et al.*, 2001). The initial concentration of OG and TiO_2 were fixed at 40 mg/L and 1.0 g/L, respectively. Prior to irradiation, the dispersions were magnetically stirred in the dark for 0.5 h to achieve the adsorption and desorption equilibrium among the TiO_2, dye and dissolved oxygen.

1.3 Analysis methods

The degradation of OG was monitored by measuring the absorbance of 478 nm with a Shimadzu UV1206 spectrophotometer as a function of irradiation time. The photodegradation rates were well described by pseudo-first-order model as presented in Table 1.

2 Results and discussion

Table 1　Photocatalytic kinetic rate constants of the UV or visible light induced photodegradation of Orange G

	OG/UV		OG+NaF/UV		OG/Vis	OG+NaF/Vis
	−	√	−	√		
k, h^{-1}	0.55	0.37	1.47	0.09	0.07	0.01
R^2	1.00	0.99	0.99	0.99	0.99	0.98

Notes: -. without isopropanol; √. with isopropanol; k. rate constants (h^{-1})

2.1 UV light system

Fig.2 shows the influence of fluoride on the adsorption of OG and on the photodegradation of dye under UV light irradiation in aqueous TiO_2 suspensions and suspensions with added isopropanol.

The preadsorption measurement showed that about 60% of OG was adsorbed on naked TiO_2 surface because of the electrostatic attraction. The presence of 0.1 mol/L isopropanol had no influence on the adsorption. And the rate constant did not decrease significantly from 0.55 h^{-1} to 0.37 h^{-1}, which suggested that the photodegradation of OG performed a hole-dominated surface reaction mechanism since alcohols have commonly been used as diagnostic tools for suppressing the hydroxyl radical-mediated process (Sun and Pignatello, 1995; Richard *et al.*, 1997; El-Morsi *et al.*, 2000). On naked TiO_2 system, OG molecule was firstly adsorbed onto the surface and subsequently captured by the photogenerated reactive species, i.e. mainly by holes and partly by adsorbed hydroxyl radicals, as Reaction 1.

$$OG_{ads} + hole/OH_{ads} \longrightarrow products \qquad (1)$$
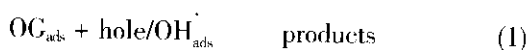
Fluoride shows very strong adsorption on TiO_2. Surface fluorination TiO_2 (F-TiO_2) can be prepared by a simple ligand exchange between surface hydroxyl
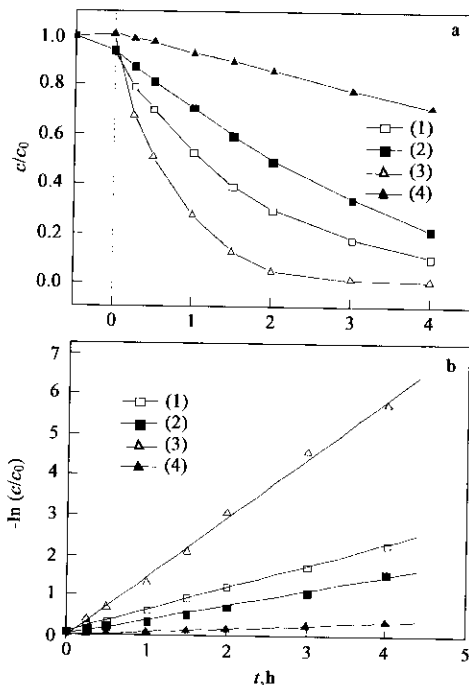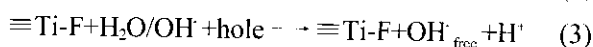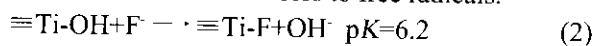

Fig.2　Effect of fluorination on the UV light induced photodegradation of Orange G in aqueous TiO_2 suspensions and suspensions with added isopropanol (a); the variation of $\ln(c/c_0)$ with irradiation time(b) (1) dye only; (2) dye + 0.10 mol/L isopropanol; (3) dye + 0.01 mol/L NaF; (4) dye + 0.01 mol/L NaF + 0.10 mol/L isopropanol

groups on TiO_2 and fluoride anions as Rreaction 2. In the presence of 0.01 mol/L fluoride, the adsorption of OG was nearly inhibited, but its photodegradation rate was greatly increased by a factor of about 2.7. Then, what oxidant species is responsible for this enhancement is an interesting issue. OG molecules have no chance to be oxidized directly by photogenerated hole because of the surface occupation by fluoride. The formation of adsorbed hydroxyl radicals was also mainly restrained. Fluoride is very stable against oxidation, even by TiO_2 valence band holes. So the generation of mobile free hydroxyl radicals was accordingly promoted as Reaction 3 (Minero *et al.*, 2000). As a result, OG was easily oxidized by the more generated homogeneous hydroxyl radicals. Therefore, isopropanol, good hydroxyl radical scavenger, nearly quenched the OG degradation in F-TiO_2 system, as shown in Fig.2. The results proved again the fact that the reaction sites could move from the surface to the solution bulk, and the major oxidants seem alter from holes to free radicals.

$$\equiv Ti\text{-}OH + F^- \longrightarrow \equiv Ti\text{-}F + OH^- \quad pK=6.2 \qquad (2)$$

$$\equiv Ti\text{-}F + H_2O/OH^- + hole \longrightarrow \equiv Ti\text{-}F + OH^{\cdot}_{free} + H^+ \quad (3)$$

$$OG + OH^{\cdot}_{free} \longrightarrow products \qquad (4)$$

It was reported that hydroxyl generates at the surface of semiconductor and possibly leaves the surface to bulk solution to form free hydroxyl radicals

(Turchi and Ollis, 1990). Recent findings (Haick and Paz, 2001; Tatsuma *et al.*, 2002) showed that substrate could be oxidized despite of the absence of direct contact with the TiO_2 surface. They proposed that remote oxidation be carried out by photogenerated air-borne oxidants that may desorb from TiO_2 surface.

2.2 Visible light system

Fig.3 compares the visible light ($\lambda>400$ nm) sensitized degradation of OG in the naked TiO_2 and the F-TiO_2 suspensions. The degradation rates were much slower compared with that under UV light irradiation.
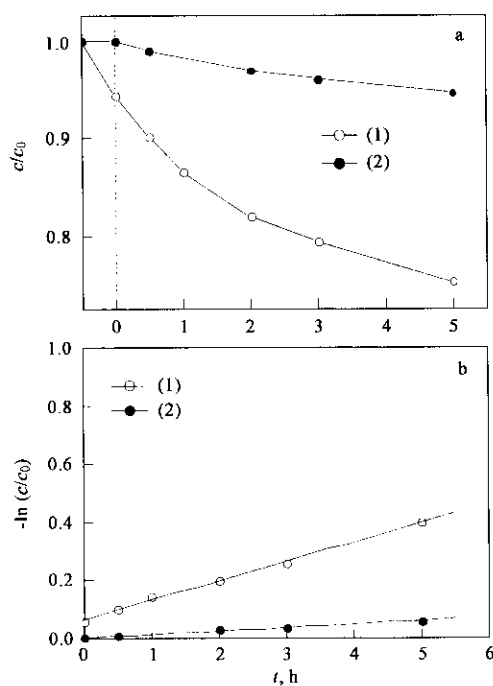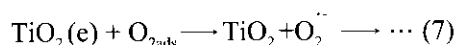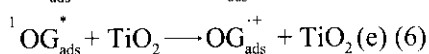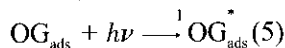

Fig.3 Effect of fluoride on the visible light sensitized photodegradation of Orange G in aqueous TiO_2 suspensions (a); the variation of $\ln(c/c_0)$ with irradiation time(b)

(1) dye only; (2) dye + 0.01 mol/L NaF

Some studies on the visible light induced photodegradation of organic dye in the presence of TiO_2 particles have been reported (Vinodgopal *et al.*, 1996; Liu *et al.*, 2000; Stylidi *et al.*, 2004). Under visible light irradiation, the exited dye molecule will inject an electron to the conduction band of TiO_2, whereas the dye is converted to cationic dye radical as Reactions 5 and 6. The injected electron can reduce surface chemisorbed oxygen molecule to form the oxidizing species that bring about photodegradation as Reaction 7. In accordance with this expectation, visible light induced degradation of dyes requires that dye molecules be in direct contact with the TiO_2 surface for an efficient electron injection.

So, the visible light sensitized degradation of OG in F-TiO_2 system was nearly stopped because OG adsorption was markedly reduced by fluoride, as

shown in Fig.3. These results provide additional evidences that the visible light sensitized photodegradation of dye pollutants occurs mainly on the catalyst surface. And the preadsorption of dyes on TiO_2 surface is a prerequisite for efficient photodegradation(Zhao *et al.*, 1998).

$$OG_{ads} + h\nu \xrightarrow{1} OG^{*}_{ads} (5)$$

$$^{1}OG^{*}_{ads} + TiO_2 \longrightarrow OG^{\cdot+}_{ads} + TiO_2(e) (6)$$

$$TiO_2(e) + O_{2ads} \longrightarrow TiO_2 + O_2^{\cdot-} \longrightarrow \cdots (7)$$

3 Conclusions

In conclusion, surface fluorination of TiO_2 could affect not only the surface characteristics but also the mechanistic process of photocatalysis and even the reaction sites. Fluoride could desorb the oxidant species from surface and the reaction sites could move from the surface to the bulk solution. The visible light sensitized photodegradation of dye pollutants occurs on the catalyst surface. These results would allow one to better interpret the UV or visible light induced photocatalytic processes.

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