



## Enhanced photocatalytic activity of TiO<sub>2</sub> by surface fluorination in degradation of organic cationic compound

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### Abstract

Experiments were carried out to investigate the influence of TiO<sub>2</sub> surface fluorination on the photodegradation of a representative organic cationic compound, Methylene Blue (MB). The electropositive MB shows poor adsorption on TiO<sub>2</sub> surface; its degradation performs a HO· radical-mediated mechanism. In the F-modified system, the kinetic reaction rate enlarged more than 2.5 fold that was attributed mainly to the accumulating adsorption of MB and the increased photogenerated hole available on the F-modified TiO<sub>2</sub> surface.

**Key words:** photocatalysis; mechanism; adsorption; surface fluorination; photogenerated hole; Methylene Blue(MB)

### Introduction

TiO<sub>2</sub> is a very important material that possesses self-cleaning, anti-fogging and air-cleaning functions, etc. Heterogeneous photocatalysis, using TiO<sub>2</sub> as the photocatalyst, is a useful technique for the degradation of many contaminants in air, in water or on solid surfaces (Fox and Dulay, 1993; Hoffmann *et al.*, 1995; Fujishima *et al.*, 2000). Photocatalytic reactions take place when the semiconductor particle absorbs a photon of light which is more energetic than its bandgap. Thus an electron is excited from the valence band to the conduction band, leaving a hole at the valence band. In aqueous solutions the hole may be trapped by H<sub>2</sub>O or OH<sup>-</sup> adsorbed at the surface, thus forming the highly reactive hydroxyl radical, which can promote the oxidation of organic compounds.

The mechanism of these reactions has been intensively studied. However, the behavior of active species, especially in the initial steps, has not been fully understood, and the underlying details remain unclear (Hufschmidt *et al.*, 2004).

Surface modifications of semiconductor photocatalysts may have a marked influence on the photocatalytic processes occurring at the water-semiconductor interface. Recently, surface fluorinated TiO<sub>2</sub> (F-TiO<sub>2</sub>) has been used as a new diagnostic tool to explore the detailed photocatalytic mechanism (Minero *et al.*, 2000a, b; Park and Choi, 2004a, b). F-TiO<sub>2</sub> can be formed by a simple ligand exchange between surface hydroxyl groups on TiO<sub>2</sub> and fluoride ions in water as Eq.(1).



We have focused our attention on the effect of TiO<sub>2</sub> surface fluorination on the photodegradation of organic anionic compounds under UV or Visible light illumination (Chen *et al.*, 2005; Yang *et al.*, 2005; 2006a, b).

It is well documented that the degradation relates tightly to the properties of substrates and the surface chemistry at the TiO<sub>2</sub>-water interface. Organic cationic compounds may behave differently from organic anionic compounds in the adsorption process on the surface of TiO<sub>2</sub> and in the UV light induced degradation process.

In this paper, experiments were conducted to examine the effects of TiO<sub>2</sub> surface fluorination on the photocatalytic degradation of Methylene Blue (MB), a representative organic cationic compound, under UV light irradiation. And the mechanism was also discussed in detail.

## 1 Materials and methods

### 1.1 Chemicals

Methylene Blue (MB) was obtained from Sigma Chemical Co. TiO<sub>2</sub> (P25, ca. 80% anatase, 20% rutile; BET area, ca. 50 m<sup>2</sup>/g; mean particle size, ca. 30 nm) was supplied by Degussa Co. The concentration of TiO<sub>2</sub> was fixed at 1.0 mg/ml. Other chemicals were of analytical reagent grade quality. The concentration of isopropanol and NaF were 0.10 and 0.01 mol/L respectively. All the experiments were carried out using deionized and double distilled water.

Starch (1.0 g) was ground with 10 ml cold water and then was slowly added to 200 ml hot water. The suspension

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was boiled to be translucent and then cooled to room temperature. The supernatant fraction of the starch solution was used in the experiments.

## 1.2 Photocatalysis and analysis

A detailed description of the experimental arrangement and the analysis method was reported previously (Chen *et al.*, 2005; Yang *et al.*, 2005). The samples were analyzed for UV-Vis absorbance with a Shimadzu UV1206 spectrophotometer. The degradation of MB was monitored by measuring absorbance at 664 nm as a function of irradiation time. A special experiment was conducted to examine the effect of TiO<sub>2</sub> surface fluorination and it will be described detailedly in the following text.

## 2 Results

### 2.1 Adsorption

Fig.1 shows the influence of fluoride on the adsorption of MB. Prior to irradiation, the dispersions were magnetically stirred in the dark for 0.5 h to achieve the adsorption/desorption equilibrium between TiO<sub>2</sub> and MB. The pre-adsorption measurement showed that about 12% of MB was adsorbed on naked TiO<sub>2</sub> surface. The presence of 0.1 mol/L fluoride ion could significantly improve the adsorption of MB (to 30%). However, isopropanol (0.1 mol/L) could reduce the adsorption obviously (to 6% on naked TiO<sub>2</sub> and to 22% on fluorinated TiO<sub>2</sub>).

### 2.2 Degradation of MB

Fig.1 also shows the influence of surface fluorination on the photodegradation of MB under UV light irradiation in aqueous suspensions and suspensions with added isopropanol. The corresponding initial kinetic rate constants are summarized in Table 1. The photodegradation rates are described by pseudo-first-order model. And all the calculated rate constants have excellent correlations coefficients ( $R^2$ ). It is interesting that fluoride ion showed a significant enhancement for the degradation of MB. The rate constant increased more than 2.5 fold (from  $k=1.15 \text{ h}^{-1}$  to  $2.93 \text{ h}^{-1}$ ).

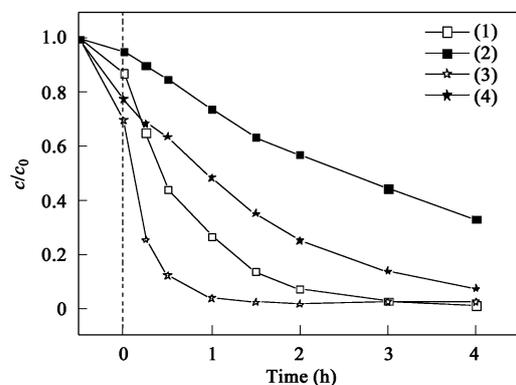


Fig. 1 Effects of fluorination on the adsorption and the degradation of MB in aqueous TiO<sub>2</sub> suspension. (1) without additive; (2) with  $C_{\text{isopropanol}}=0.10 \text{ mol/L}$ ; (3) with  $C_{\text{F}^-}=0.01 \text{ mol/L}$ , and (4) with  $C_{\text{F}^-}=0.01 \text{ mol/L}$  and  $C_{i\text{-PrOH}} = 0.10 \text{ mol/L}$ , respectively.

**Table 1 Photocatalytic kinetic rate constants( $k$ ) of the UV light induced photodegradation of MB**

	MB	MB/F	MB/isopropanol	MB/F/isopropanol
$k \text{ (h}^{-1}\text{)}$	1.146	2.929	0.263	0.598
$R^2$	0.998	0.993	0.999	0.998

But the inhibition of isopropanol is pronounced: the rate constants decreased to  $0.26 \text{ h}^{-1}$  and  $0.60 \text{ h}^{-1}$  for naked and fluorinated TiO<sub>2</sub> respectively.

## 3 Discussion

### 3.1 Adsorption

It is well known that the surface of TiO<sub>2</sub> is readily hydroxylated in aqueous solution. When H<sub>2</sub>O dissociates on a pure TiO<sub>2</sub> surface, two distinctive hydroxyl groups are formed (Turchi and Ollis, 1990). The amphoteric surface will be formed because of the acid-base equilibria as Eqs. (2) and (3) shown. Therefore, there are three kinds of surface species, TiOH<sub>2</sub><sup>+</sup>, TiOH, and TiO<sup>-</sup>, whose proportion depends on the solution pH and the  $\text{pH}_{\text{pzc}}$  of TiO<sub>2</sub> (point of zero charge, 6.8 for P25) (Jaffrezic-Renault *et al.*, 1986).



In our study, the pH was about 6. The TiO<sub>2</sub> surface was weakly positive due to predominant species TiOH<sub>2</sub><sup>+</sup> and TiOH. The electropositive MB molecules could not easily transport to the surface. The adsorption of MB on TiO<sub>2</sub> may be ascribed to the electronic reorganization during the passage of MB adsorbed to the sulfoxide form (Fig.2). This kind of adsorption is very weak. The distance between the MB molecules and the surface may be much far. Isopropanol, which has a very poor adsorption power on TiO<sub>2</sub> surface in aqueous media, even obviously inhibited the adsorption of MB.

In the presence of fluoride ions, the adsorption process of organic cationic compound is different from that of organic anionic compound. Fluoride shows a very strong adsorption on TiO<sub>2</sub>. An inner F-TiO<sub>2</sub> complex is formed by the replacement of surface hydroxyl groups. Therefore, the adsorption of the electronegative organic anionic compound is nearly suppressed (Chen *et al.*, 2005; Yang *et al.*, 2006a, b). However, the existence of fluoride ion partially

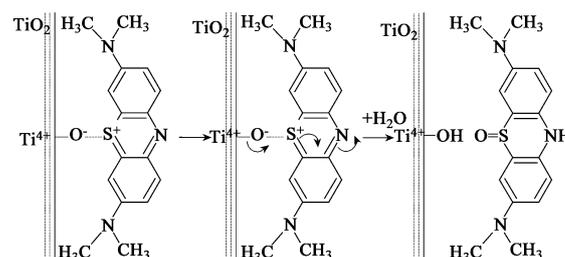


Fig. 2 Electronic reorganization during the passage of MB adsorbed to the sulfoxide form.

neutralizes the positive charge on the surface of  $\text{TiO}_2$ , MB molecules are adsorbed on the surface of  $\text{TiO}_2$  through an electrostatic interaction with fluoride ion but not the real surface of  $\text{TiO}_2$ .

### 3.2 Degradation

In the study of photocatalytic mechanism, one controversy is about the role of direct electron transfer to the hole versus hydroxyl radical oxidation of the organics (Hufschmidt *et al.*, 2004). The degradation of organic anionic compounds performed a mainly direct hole mechanism since they show great adsorption ability (Chen *et al.*, 2005; Yang *et al.*, 2006a, b). At low molecule coverage on the surface replaced by fluoride ion, the initial process could shift from surface reaction to homogeneous radical reaction in bulk solution.

In the case of photocatalytic MB, the direct electron transfer between the hole and MB molecules is nearly impossible. The photogenerated holes firstly react with surface hydroxyl groups or water molecule to form  $\text{HO}\cdot$  radicals, and the formed  $\text{HO}\cdot$  radicals subsequently oxidize MB molecules. So it is  $\text{HO}\cdot$  radical-mediated mechanism, which can be proved by the significant inhibition of 0.10 mol/L isopropanol (*i*-PrOH), since alcohols could scavenge  $\text{HO}\cdot$  radicals effectively (Sun and Pignatello 1995; Richard *et al.*, 1997; El-Morsi *et al.*, 2000).

When the surface was modified by fluoride ion, more MB molecules, unlike organic anionic compounds, moved to the surface of  $\text{TiO}_2$ . There were more chances for MB to be oxidized by the formed  $\text{HO}\cdot$  radicals, and this is an important reason why the rate of MB degradation was increased notably. However, more significant factor is the increased hole availability in the F-modified system.

### 3.3 Increased hole availability

To testify the effect of fluoride ion on the initial mechanism, iodine ion oxidation experiments by  $\text{TiO}_2$  photocatalysis with and without surface fluorination were both carried out (Fig.3). Ishibashi and Fujishima (2000) once estimated the quantum yield of photogenerated holes simply by iodide ion photocatalytic oxidation. As have been known, iodide ion could be strongly bound to the  $\text{TiO}_2$  surface. It is an excellent scavenger which reacts with the valence band holes or probably with the subsequently formed hydroxyl radicals (Ishibashi and Fujishima, 2000; El-Morsi *et al.*, 2000; Rabani *et al.*, 1998). It is also known that  $\text{I}^-$  is very easily oxidized by photoexcited  $\text{TiO}_2$  to produce  $\text{I}_2$ . Therefore, the yield of holes can be determined by observing the produced  $\text{I}_2$ .

In order to minimize the irradiation time and exactly determine the concentration of  $\text{I}_2$ , a small UV spectrophotometer cell (10 ml) was used. Two 6 W UV lamps ( $\lambda_{\text{max}}=365$  nm) were used as UV light source. The distance between the light window (4.0 cm $\times$ 6.0 cm) and reactor was 4.0 cm.  $\text{TiO}_2$  was added to 0.1 mol/L KI aqueous and equilibrated for 15.0 min prior to illumination. Air (about 50 ml/min) was continuously bubbled into the suspension. The amount of  $\text{I}_2$  formed in the reaction was determined by the iodo-starch reaction. When a 3.0-ml of starch solution

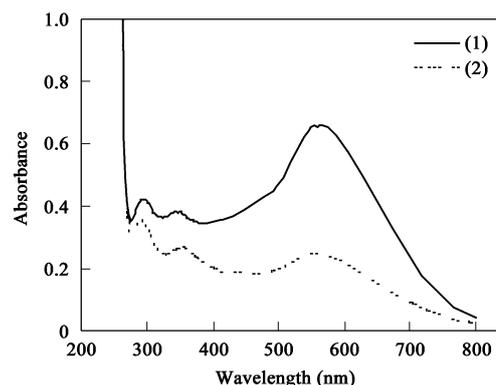


Fig. 3 Effects of  $\text{F}^-$  on the degradation of  $\text{I}^-$  in aqueous  $\text{TiO}_2$  suspension. (1) with  $C_{\text{F}}=0.01$  mol/L; (2) without additive.

was added to a 3.0-ml filtrate after UV light illumination for 30 min, the solution turned blue as the result of the iodo-starch reaction. There was a broad peak at  $\lambda = 580$  nm in the UV-Vis absorption spectra of the reaction solution, suggesting the generation of  $\text{I}_2$ .

Interestingly, from the absorbance of the spectra in Fig.3, the concentration of iodine formed in the presence of  $\text{F}^-$  was up to about 3 times of that in the absence of  $\text{F}^-$ . This result revealed that many more holes were generated when the  $\text{TiO}_2$  particles were modified by fluoride ion. That is to say, surface fluorination promotes hole availability greatly.

### 3.4 Proposed mechanism

Organic cationic compounds showed different behaviors from organic anionic compounds in the UV light induced degradation process (Fig.4). Unlike organic anionic compounds, the adsorption of MB is very weak; while hydroxyl radicals (Path D), not the holes (Path A), play a major role in its photocatalytic degradation. When the  $\text{TiO}_2$  surface was modified by fluoride ion, more holes were available and subsequently more hydroxyl radicals generated (Path B and C). Simultaneously, the adsorption amount of MB near the surface was increased. As a result, the photocatalytic rate was enhanced by surface fluorination (Fig.4).

## 4 Conclusions

This study clearly demonstrated that the surface fluorination of  $\text{TiO}_2$  enhances the photocatalytic activity greatly. The enhancement is mainly due to the more generated

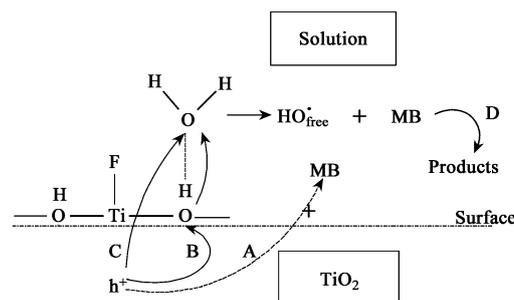


Fig. 4 Illustration of the simplified kinetic pathways of fluoride influence on MB photodegradation.

hydroxyl radicals from more available holes. For such an electropositive organics, as MB, its increased adsorption is another important reason. From a practical point of view, F-TiO<sub>2</sub> is certainly better than pure TiO<sub>2</sub> in the photocatalytic degradation of organic pollutants.

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