



Role of the reduction site in the fluorinated or sulfated TiO₂ photocatalytic process

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Abstract

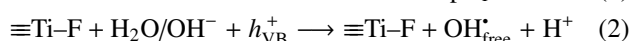
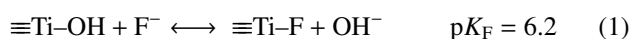
In this article, the effects of TiO₂ surface fluorination and sulfation, on the active oxygen species formed at the reduction site in the photocatalytic process, namely O₂^{•-} and H₂O₂, were investigated from a new perspective. The superoxide radical, (O₂^{•-}), was determined by colorimetry of nitroblue tetrazolium, a prominent O₂^{•-} scavenger. Hydrogen peroxide (H₂O₂) was estimated by using the iodide-starch method. In the naked TiO₂ photocatalysis, O₂^{•-}, though less reactive, was a very important intermediate. When the TiO₂ surface was fluorinated, more O₂^{•-} and H₂O₂ were produced, which indicated that the surface modification could greatly reduce the recombination of photogenerated electrons and holes, thus enhancing the photocatalytic rate. In the sulfated system, photocatalysis proceeded with a more complicated mechanism. These results added support to the view of fluoride-induced enhancement and sulfide's nonappreciable inhibition effect.

Key words: TiO₂ photocatalysis; superoxide radicals; surface modification; initial mechanism

Introduction

Photoinduced redox reactions in TiO₂ aqueous suspensions have aroused wide interest because of their promising application to environmental problems (Fox and Dulay, 1993; Hoffmann *et al.*, 1995; Fujishima *et al.*, 2000). Despite various efforts, the mechanistic details of the photocatalytic reaction remain unclear (Hufschmidt *et al.*, 2004).

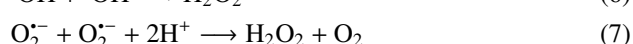
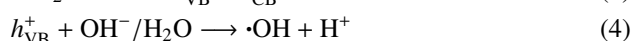
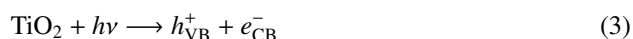
Recently, surface fluorinated TiO₂ (F-TiO₂) was used as a new diagnostic tool to explore the detailed photocatalytic mechanism (Minero *et al.*, 2000a, b; Calza and Pelizzetti, 2001; Vohra *et al.*, 2003; Chen *et al.*, 2005; Yang *et al.*, 2006a, b, 2007; Park and Choi, 2004a, b). F-TiO₂ could be formed by a simple ligand exchange between the surface hydroxyl groups on TiO₂ and the fluoride anions in water, as shown in Eq. (1).



It was reported that because of this modification there was a great promotion of degradation rate in photocatalytic phenol (Minero *et al.*, 2000a, b; Calza and Pelizzetti, 2001), tetramethylammonium (Vohra *et al.*, 2003), Orange I, Orange II, and Orange G (Chen *et al.*, 2005; Yang *et al.*, 2006a, b), and Methylene Blue (Yang *et al.*, 2007),

which was ascribed to the enhanced generation of mobile free hydroxyl radicals (OH_{free}[•]), as shown in Eq. (2). The initial process could shift from a hole-mediated surface reaction to a homogeneous •OH reaction in bulk solution (Chen *et al.*, 2005; Yang *et al.*, 2006a, b, 2007). The surface fluorination seemed to facilitate desorption of •OH from the surface to become air-borne oxidants and thus enhanced remote photocatalysis (Park and Choi, 2004a).

As is well known, several active oxygen species are involved in the photocatalytic reaction, such as, (1) hydroxyl radical (•OH), which is produced from either hydroxyl groups or from adsorbed water on the TiO₂ surface, by trapping a hole (Eq. (4)); (2) superoxide radical (O₂^{•-}), which is formed from an adsorbed oxygen molecule, by combining with an excited electron (Eq. (5)); and (3) hydroxyl peroxide (H₂O₂), which is generated at either the oxidation (Eq. (6)) or the reduction (Eq. (7)) site.



The effect of fluoride on photocatalytic reactions can be related to the whole chemical process. Most of the research interest mentioned earlier has been focused on the

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oxidation process. However, chemical reactions occurring at the reduction site of TiO₂ particles are as important as those occurring at the oxidation site. Few reported results mention the reduction process of the photocatalytic reaction in the F-TiO₂ system.

On the other hand, the fluoride-induced enhancement and the sulfide's nonappreciable inhibition effect, as discussed in the previous articles (Chen *et al.*, 2005; Yang *et al.*, 2006a, b, 2007), may perform different mechanisms. Fluoride is very stable against oxidation, even by TiO₂ valence holes, because the redox potential of the couple F[•]/F⁻ is about 3.6 V. Sulfide, however, can react with the positive hole, as shown in Eq. (8) (Hu *et al.*, 2003).



The purpose of this article is to investigate the effects of TiO₂ surface fluorination and sulfation on the active oxygen species formed at the reduction site, namely O₂^{•-} and H₂O₂.

1 Experimental

1.1 Materials

TiO₂ (P-25, ca. 80% anatase, 20% rutile; BET area, ca. 50 m²/g; mean particle size, ca. 30 nm) was supplied by the Degussa Co., and 4-(2-hydroxy-1-naphthylazo) benzene-sulfonic acid (Orange II, OII) and nitroblue tetrazolium (NBT) were obtained from the Sigma Chemical Co., and were directly used without further purification. Other chemicals were of analytical reagent grade quality. All experiments were carried out using deionized and double distilled water.

1.2 Photocatalytic arrangement

The concentration of TiO₂ was fixed at 1.0 mg/ml. The electron donor in the photocatalytic degradation experiments was OII (5.71×10^{-5} mol/L), or isopropanol (4%, 4.0 ml isopropanol was diluted to 100 ml with 10^{-2} mol/L HClO₄). NaF (10^{-2} mol/L) or Na₂SO₄ (10^{-2} mol/L) was added in the indicated cases only.

Photocatalytic reactions were carried out in a Pyrex glass reactor (10.0 ml). Two 6 W UV lamps ($\lambda_{\text{max}} = 365$ nm) were used as the UV light source, and the distance between the light window (4.0 cm × 6.0 cm) and reactor was 4.0 cm. Substrates were added to an aqueous TiO₂ suspension in the reactor and equilibrated for 15.0 min, prior to illumination. Air (about 50 m/min) was continuously bubbled through the suspension. The photoirradiation time was 30 min. After irradiation, the suspension was centrifuged and then filtered through a Millipore filter (pore size 0.22 μm) to remove the TiO₂ particles. All comparisons were made within the same reactor and all experiments were duplicated.

1.3 Analysis

The reaction filtrates were analyzed for UV-Vis absorbance (200–800 nm) in a 1-cm quartz cell with a Shimadzu UV1206 spectrophotometer. The absorption

spectra of OII in water were characterized by four bands. Two bands in the visible region, with a major absorption band at 484 nm and a shoulder band at 430 nm, were seen because of the hydrazone form and azo form of OII, respectively (Bauer *et al.*, 2001). Two bands in the ultraviolet region located at 230 nm and 310 nm were attributed to the benzene and naphthalene rings of OII, respectively (Wu *et al.*, 2000). The degradation of OII was monitored by measuring its discolorment ($\lambda = 484$ nm).

NBT is a commercially available analytical reagent. The analytical method of NBT reduction assay is usually used to evaluate the superoxide dismutase activity (Vajragupta *et al.*, 2004). The reaction between O₂^{•-} and NBT, as shown in Fig.1, leads to the formation of purple formazan (Goto *et al.*, 2004). The absorption spectra of NBT in an aqueous solution are shown in Fig.2. There is a strong absorption below 400 nm and a characteristic band located at 260 nm. The authors estimated the amount of NBT by detecting the intensity of the absorbance of NBT in the ultraviolet region.

Starch (1.0 g) was ground with 10 ml cold water and then slowly added into 200 ml hot water. The suspension was boiled till it was translucent and then cooled to room temperature. The supernatant fraction of the starch solution was used in the experiments. The produced H₂O₂ was determined by the addition of 1.0 ml starch solution as the

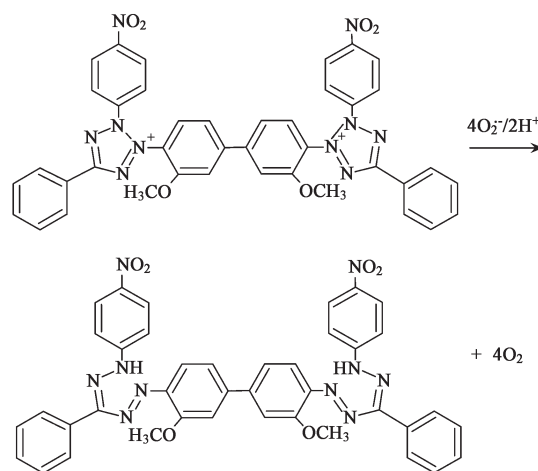


Fig. 1 Reaction between NBT and superoxides.

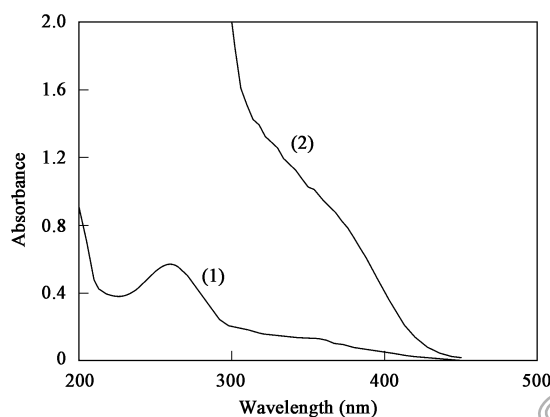


Fig. 2 Absorbance of NBT in aqueous. (1) 10^{-5} mol/L; (2) 10^{-4} mol/L.

indicator, after the addition of 1.0 ml of 10⁻² mol/L KI to 3.0 ml particle-removed reaction filtrates. Isopropanol was used instead of OII, as the electron donor, to suppress the •OH-mediated oxidation process.

2 Results and discussion

2.1 Superoxide radical

2.1.1 In the naked TiO₂ system

Direct photolysis of NBT did not occur under the experimental conditions. Furthermore, no decrease of NBT was observed in the TiO₂-assisted photocatalysis, when the experiments were conducted in the absence of an electron donor. That is to say, NBT cannot be directly oxidized by a photogenerated hole or a hydroxyl radical.

Orange II (OII), a commercial textile azo dye, is very stable (Bauer *et al.*, 2001; Styliidi *et al.*, 2004). Fig. 3 shows the UV-light induced photocatalytic reaction of OII in the absence and presence of 10⁻⁵ mol/L NBT. Without NBT, the characteristic color adsorption band ($\lambda = 484$ nm) of OII is decreased by about 50% after photoirradiation for 30 min in TiO₂ aqueous suspension. When decolorization occurs, the intensities of the band at 230 nm and 310 nm continue to decrease simultaneously, indicating that the azo linkage, benzene, and naphthalene ring of OII are all destroyed. After the reaction, the TiO₂ particles show a white color when well washed.

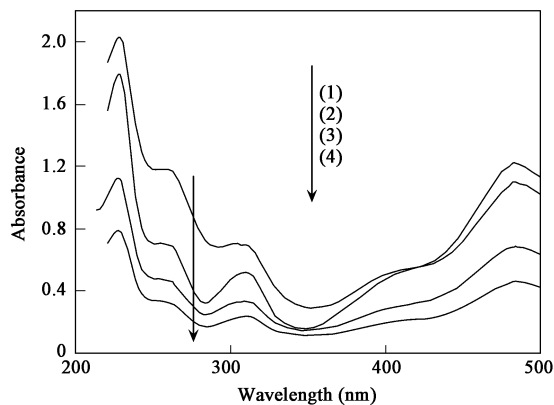


Fig. 3 Effects of 10⁻⁵ mol/L NBT on the photocatalytic reaction. Changes in the absorption spectra of (1) OII + NBT, before photoirradiation; (2) OII, before photoirradiation; (3) OII; (4) OII + NBT.

The degradation of OII was promoted in the presence of NBT. After photoirradiation for 30 min the intensities of all wavelengths from 200 nm to 500 nm decreased more rapidly than in the case without NBT. Meanwhile, the absorption of $\lambda = 260$ nm was even weaker than that of only 10⁻⁵ mol/L NBT, indicating the decrease in the amount of NBT in the solution.

When the initial concentration of NBT increased to 10⁻⁴ mol/L, the ultraviolet region absorption of the mixed solution enhanced greatly as shown in Fig. 4. After photocatalytic reaction under the same condition, the orange color completely disappeared and the intensity of the ultraviolet region decreased too. The TiO₂ particles presented a

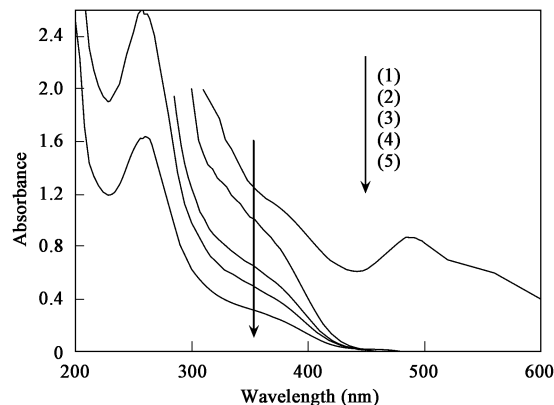


Fig. 4 Effects of fluorination and sulfation on the photocatalytic reaction in the presence of 10⁻⁴ mol/L NBT. Changes in the absorption spectra of (1) OII + NBT, before photoirradiation; (2) NBT; (3) OII + NBT; (4) OII + NBT + SO₄²⁻; (5) OII + NBT + F⁻.

deeper color because of the precipitation of formazan on their surface. That is to say, more NBT consumed more O₂^{•-} and brought about a more rapid photocatalytic rate.

The behaviors of O₂^{•-} in TiO₂ photocatalytic reactions recently provoked a great deal of interest (Hirakawa and Nosaka, 2002). O₂^{•-} is known as an oxidizing agent that promotes aromatic ring-opening phenols via addition to intermediate phenoxy radicals (Zhao *et al.*, 2000; Antunes *et al.*, 2004; Lanzalunga and Biatti, 2000; Jonsson *et al.*, 1993). O₂^{•-} was mainly responsible for As(III) photocatalysis (Ryu and Choi, 2004).

In contrast, the authors once introduced Cr(VI) as an electron scavenger (Schrank *et al.*, 2002) upon purging with nitrogen, to eliminate the generation of O₂^{•-} and it was observed that O₂^{•-} had a negligible effect on the photodegradation of OII (Chen *et al.*, 2005). The results in this study confirmed the view that O₂^{•-} itself was less reactive than other active species in the photocatalytic process, as the decrease of O₂^{•-} actually enhanced the reaction (Hong *et al.*, 1987). The pH in this study was about 6. The TiO₂ surface was weakly positive because of the predominant species TiOH²⁺ and TiOH. The electropositive NBT molecules could not easily transport to the surface. The reaction between the photogenerated electron and NBT was negligible. The amount of superoxide ion generated can be determined as a result of the photocatalytic reaction, by detecting the intensity of the absorbance of NBT in the ultraviolet region.

2.1.2 In the surface-fluorinated TiO₂ system

Fluoride shows a very strong adsorption on TiO₂ and the F-Ti ligands formed on the surface of particles could be related to the surface charge distribution, the substrate-surface interaction, the reaction mechanism, and so on. Fig. 4 shows the influence of the 10⁻² mol/L fluoride ion on the photocatalytic reaction, in the presence of 10⁻⁴ mol/L NBT. It is found that the photocatalytic rate is greatly enhanced by fluorination. OII discolors much more rapidly, and the TiO₂ particles are rendered into a very deep purple as more formazan is deposited on them.

It was found that the photocatalysis of OII was signif-

icantly increased in the presence of fluoride ions, in the authors' articles (Chen *et al.*, 2005; Yang *et al.*, 2006a). The enhanced generation of free OH, as shown in Eq. (2), must be because of more available holes. Accordingly, the recombination of photogenerated electrons and holes is reduced in the F-TiO₂ system. Therefore, more conduction band electrons are produced and need to be scavenged by the adsorptive oxygen. From this point of view, more formazan formation proves that in the F-TiO₂ system more O₂^{•-} is generated, and that the quantum efficiency of photocatalysis is enhanced.

This result adds support to the mechanism of the F-TiO₂ system proposed before (Minero *et al.*, 2000a; Vohra *et al.*, 2003; Ryu and Choi, 2004). When the surface of TiO₂ particles is fluorinated, more ·OH are produced and desorbed from the surface to the bulk solution, to oxidize the substrates. The reaction processes dominated by O₂^{•-} in photocatalysis can be theoretically improved by the fluorination on TiO₂ as well. This is the reason why the As(III) photocatalytic rate does not show a reduction on fluorinated TiO₂ though its adsorptive capacity has markedly reduced (Ryu and Choi, 2004).

2.1.3 In the surface-sulfated TiO₂ system

The effect of SO₄²⁻ on photocatalysis revealed different results (Antunes *et al.*, 2004; Hu *et al.*, 2003). It decreased the oxidation rates of salicylic acid, aniline, ethanol (Abdullah *et al.*, 1990), and dichloroethane (Chen *et al.*, 1997), because of the competitive adsorption with substrates and the trapping of holes or ·OH (Hu *et al.*, 2003). However, it showed a 100% increase for the pesticide monocrotophos (Zhu *et al.*, 1995) and a nonreduced rate for OII, although the adsorption was mostly inhibited (Chen *et al.*, 2005; Yang *et al.*, 2006a).

Sulfide is adsorbed onto the surface of TiO₂, the surface charge distributing has changed, and the photocatalytic process has been affected. The sulfate radical anion (SO₄^{•-}) formed, as shown in Eq. (8), is a very strong one-electron transfer oxidant ($E^0 = 2.6$ V (NHE)) (Goldstein *et al.*, 1994; Malato *et al.*, 1998). It is believed that SO₄^{•-} can directly participate in the degradation processes of OII in the photocatalytic process as shown in Eqs. (9) and (10) (Goldstein *et al.*, 1994), as the redox potential of OII is 0.76 V (NHE) (Bandara *et al.*, 1999). Also, it can generate ·OH as shown in Eq. (11) (Goldstein *et al.*, 1994). Owing to these equations, the presence of sulfide is expected to increase OII degradation. In addition, recombination with the photogenerated electrons or trapping O₂^{•-} or H₂O₂ may occur, which is expected to decrease OII degradation.

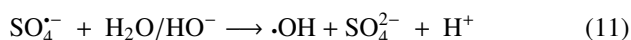
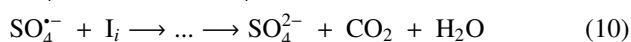
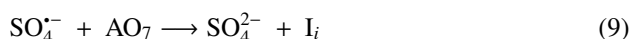


Figure 4 displays the effect of sulfate on the photocatalysis of OII in the presence of NBT. The photocatalytic rate is slightly increased, though there may exist a competition between NBT and SO₄^{•-} for O₂^{•-}. That is to say, the amount of O₂^{•-} reaction with NBT to form formazan in a sulfate modified TiO₂ system, is more than that in the

naked TiO₂ system. It is not a trivial result. After all, it can be confirmed that, for OII photocatalysis in the presence of sulfate, the recombination of photogenerated electrons and holes is also reduced to some extent. It seems that more SO₄^{•-} participates in oxidizing OII because more holes will be available. The positive effect of sulfate may prevail over its negative one under this experimental condition. The sulfate can be anchored on the surface of titania after treatment with ammonium sulfate and it acts as an electron trap leading to an enhancement of photocatalytic activity (Gomez *et al.*, 2003). It may also be used to interpret the increasing effect of sulfide on the photocatalysis of azo dyes, Procion Red MX-5B, and Cationic Blue X-GRL, in acid solutions, as the sulfide ion is adsorbed onto the TiO₂ surface (Hu *et al.*, 2003).

2.2 Hydroxyl peroxide

There is a close relationship between the photocatalytic activity and the formation of H₂O₂ (Hirakawa and Nosaka, 2002). Some suggest that it is produced at the oxidation site and others propose that it is generated at the reduction site (Shiraishi *et al.*, 2003; Cai *et al.*, 2003). Alcohols, such as, methanol, ethanol, and tert-butanol, have been used as diagnostic tools for suppressing the ·OH-mediated process (Minero *et al.*, 2000a, b; Park and Choi, 2004; Daneshvar *et al.*, 2004; Ilisz and Dombi, 1999). As it is known, isopropanol is a good ·OH scavenger, as the rate constant is 1.9×10^9 mol/(L·s), a rate of diffusion limit. Hence, if isopropanol is used as an electron donor, the ·OH can be quenched efficiently, and the H₂O₂ generated from the oxidation process as shown in Eq. (6) will be negligible. According to Eq. (7), the more H₂O₂ generated from the reduction process, the more O₂^{•-} is formed. Therefore, the formation of superoxide radicals can be revealed by the determination of the generated H₂O₂ at the reduction site.

Figure 5 illustrates the H₂O₂ generation at the reduction site in photocatalysis of isopropanol on naked and fluorinated or sulfated TiO₂. There was a broad absorption around $\lambda = 580$ nm after solutions of KI and starch were added to the reaction filtrates in turn. As anticipated, the intensity of the absorbance in the F-TiO₂ system was about 2.5 folds greater than that in the naked TiO₂

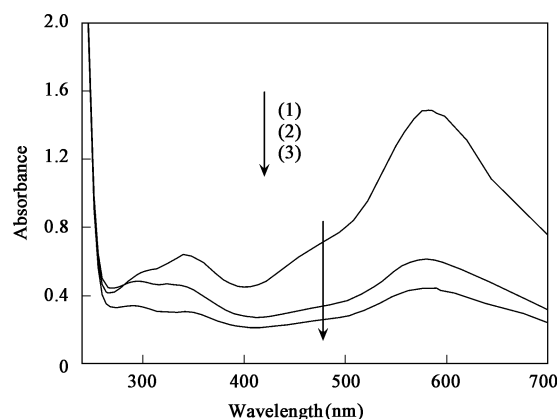
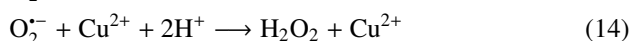


Fig. 5 UV-Vis absorption spectra of the reaction filtrates after addition of KI and starch. (1) isopropanol + F⁻; (2) isopropanol + SO₄²⁻; (3) isopropanol.

system, indicating that more H₂O₂ was formed. This result again confirmed that fluorination could greatly reduce the recombination of photogenerated electrons and holes, thus enhancing the photocatalytic rate. SO₄^{•-} seemed to have a potential to consume H₂O₂; a smaller quantity of H₂O₂ was detected. In a word, the reaction mechanism in the SO₄²⁻-TiO₂ system is much more complicated than that in the F-TiO₂ system.

2.3 Proposed mechanism

Generally speaking, in the TiO₂ photocatalytic process, electron-hole recombination is extremely efficient (Hoffmann *et al.*, 1995), which represents a major energy wasting and limits it to achieve a high quantum yield. It is well known that the rate-determining step is the mass transfer of oxygen and the electron capture by adsorbed O₂ because of the limited O₂ adsorption capacity of TiO₂ (Gomez *et al.*, 2003). However, the generation of O₂^{•-}, from an adsorbed oxygen molecule, combined with an excited electron, seems efficient, though it is followed by interfacial recombination as shown in Eq. (12) (Cornu *et al.*, 2001). O₂^{•-} has a long decay time of about 140 s (Cornu *et al.*, 2001). There seems to be a traffic jam of electron current at the step of O₂^{•-} transformation. If O₂^{•-} has a chance to be captured by NBT, the recombination can be reduced, and more OII is oxidized in the oxidation process. Recently Cai *et al.* (2003), tapped the latent potentialities of O₂^{•-} by the addition of a small amount of copper ions as shown in Eqs. (13) and (14), and H₂O₂ was increased dramatically up to 20 times. In the surface modified TiO₂ system, fluoride facilitates the formation of O₂^{•-} at the reduction site and •OH at the oxidation site. Although the detailed mechanism of the sulfated-system is unsure, the e_{CB}^-/h_{VB}^+ recombination also seems to be reduced.



3 Conclusions

In this article, roles of the superoxide radical (O₂^{•-}) and hydrogen peroxide (H₂O₂) formed on naked, fluorinated, and sulfated TiO₂ at the reduction site were investigated from a new perspective.

The fluoride-enhanced effect in the TiO₂-assisted photocatalytic processes was confirmed by the determination of active oxygen species generated at the reduction site. TiO₂ surface fluorination results showed not only more free •OH at the oxidation site, but also more O₂^{•-} and H₂O₂ at the reduction site, indicating that the quantum efficiency of photocatalysis was enhanced.

From a practical point of view, surface-fluorinated TiO₂ is certainly better than naked TiO₂. The sulfation effect on photocatalysis is much more complicated. The inhibition may be limited by the ability of the sulfate radical itself to oxidize organics or may further slow down recombination

of the electron and hole pair.

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