

Synergic effect of simultaneous fluorination and platinization of TiO₂ surface on anoxic photocatalytic degradation of organic compounds†

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Simultaneously surface fluorinated and platinized TiO₂ (F-TiO₂/Pt) exhibits a novel photocatalytic activity for the anoxic degradation of organic compounds, which is attributed to the unique synergic effect of surface fluorination and platinization on the photo-induced charge transfer process.

The application of TiO₂ for the remediation of polluted water and air has been extensively studied and demonstrated to be a technically viable process.¹ TiO₂ photocatalysis is based on the photoinduced interfacial charge transfer reactions of valence band holes and conduction band electrons. A TiO₂ nanoparticle is a photoelectrochemical nano-reactor on which both the hole transfer and electron transfer take place concurrently with harnessing photoenergy to drive various chemical reactions. Most TiO₂ photocatalytic reactions for environmental cleanup are the hole-driven oxidation of organics coupled with the dioxygen reduction. Therefore, dioxygen is an essential reagent of TiO₂ photocatalysis and the overall photocatalysis does not proceed in the anoxic condition.^{2–4} Here we demonstrate that the *anoxic photocatalytic degradation of organic compounds* can be made possible by using TiO₂ modified with simultaneous surface fluorination and platinization (F-TiO₂/Pt).

Pt deposition on the surface of TiO₂ (Degussa P25) was done by the photocatalytic reduction of chloroplatinic acid (Pt content = 3.7 wt%) in the presence of methanol as an electron donor.⁵ For the fluorination of the TiO₂ surface, 10 mM NaF was added into the aqueous suspension of Pt/TiO₂ and then pH was adjusted to 3.0 to maximize the fluoride adsorption.^{6,7} The coexistence of Pt and F on the surface of TiO₂ powder that was prepared by the above procedure was confirmed by X-ray photoelectron spectroscopy (Fig. S1†). A 300 W Xe-arc lamp was used as the light source for the photocatalytic activity test and photodegradation of 4-CP (4-chlorophenol), BPA (bisphenol A), and 2,4-D (2,4-dichlorophenoxyacetic acid) was compared using bare TiO₂, F-TiO₂, Pt/TiO₂, and F-TiO₂/Pt in the illuminated suspension. Light passed through a 10 cm IR filter and a cutoff filter ($\lambda > 300$ nm), and then the filtered light was focused onto a 30 mL reactor. To remove dissolved oxygen, N₂ was purged for 30 min prior to irradiation and then continuously during irradiation.

Fig. 1 compares the time profiles of 4-CP and BPA degradation in the illuminated anoxic suspension of bare TiO₂, F-TiO₂,

Pt/TiO₂, and F-TiO₂/Pt. Note that the anoxic degradation of both 4-CP and BPA was greatly enhanced with F-TiO₂/Pt while other photocatalysts show only limited or negligible activity. The complete dechlorination of 4-CP could be achieved with F-TiO₂/Pt in the anoxic condition. However, the mineralization could not be achieved at all: the total organic carbon (TOC) content in the catalyst suspension remained unchanged throughout the irradiation for all cases shown in Fig. 1 (Fig. S2†). That is, the aromatic organics could be rapidly transformed into intermediates in the anoxic suspension of F-TiO₂/Pt, but not to CO₂ at all. The following intermediates were identified by HPLC analysis from the anoxic degradation of 4-CP on F-TiO₂/Pt: 4-chlorocatechol, 4-chlororesorcinol, benzoquinone, hydroquinone, hydroxyhydroquinone. In Fig. 2, the anoxic photocatalytic degradation of 2,4-D is compared. F-TiO₂ was inactive while Pt/TiO₂ and F-TiO₂/Pt removed 2,4-D successfully even in the absence of O₂. Although both Pt/TiO₂ and F-TiO₂/Pt can degrade 2,4-D anoxically, Pt/TiO₂ could attain only a limited level of dechlorination along with a significant production of a toxic intermediate, 2,4-DCP (2,4-dichlorophenol). However, F-TiO₂/Pt was able to achieve both

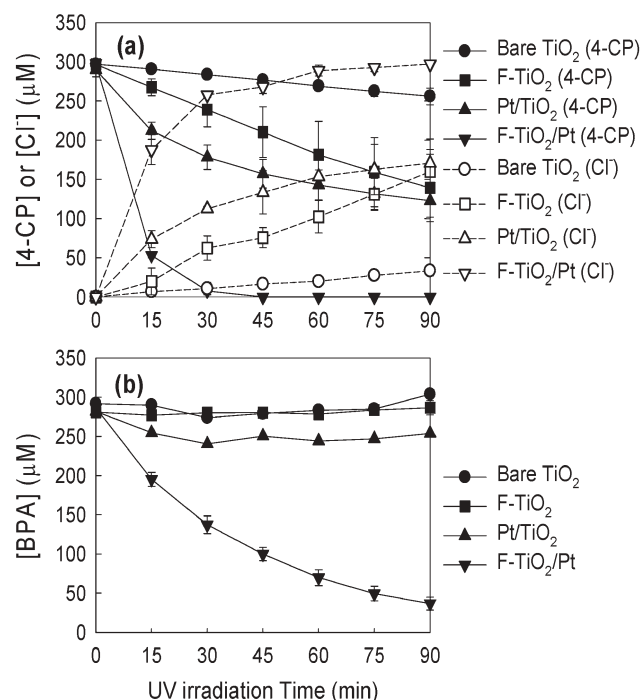


Fig. 1 (a) Anoxic photocatalytic degradation of 4-CP and the accompanying production of chloride. (b) Anoxic degradation of BPA in aqueous suspensions of bare TiO₂, F-TiO₂, Pt/TiO₂, and F-TiO₂/Pt.

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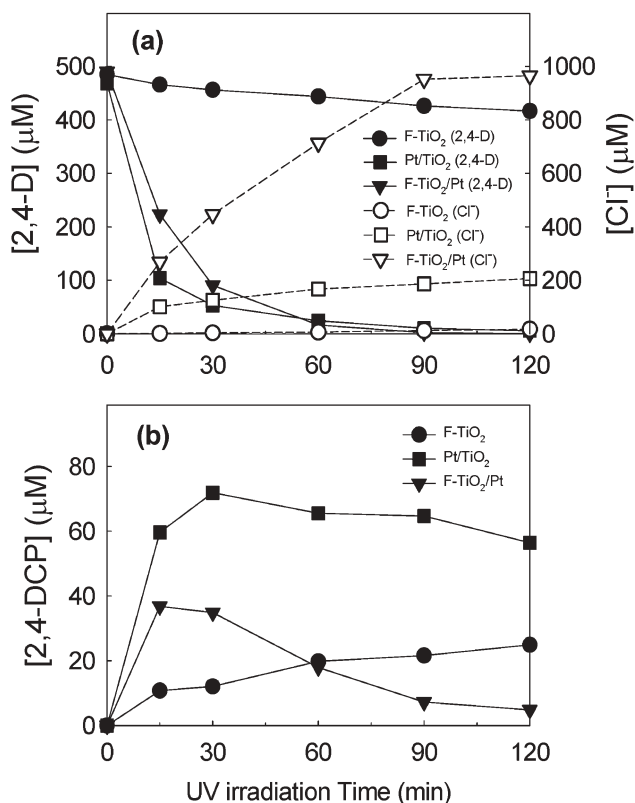


Fig. 2 (a) Anoxic photocatalytic degradation of 2,4-D and the accompanying production of chloride. (b) The concurrent generation of 2,4-DCP as an intermediate from the degradation of 2,4-D under the anoxic condition.

complete removal and dechlorination simultaneously with a minimized production of 2,4-DCP. This synergic effect of surface fluorination and platinization was observed not only in the anoxic but also in the aerated condition (Fig. S3[†]). Fig. 1 and 2 clearly show that the photocatalytic reactions occurring on F-TiO₂/Pt are synergically influenced by the two surface modification methods and proceed through a different mechanistic path.

To check the stability of F-TiO₂/Pt catalyst, the anoxic photocatalytic degradation of 4-CP was repeated up to four cycles in the same batch of the catalyst reactor with injecting 300 μM 4-CP every 30 min. As shown in Fig. 3, the anoxic activity is

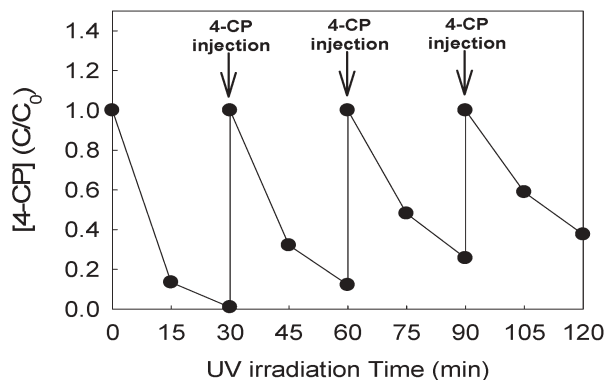


Fig. 3 Repeated runs of the degradation of 4-CP in F-TiO₂/Pt suspension under anoxic condition.

largely maintained although the activity is slightly reduced with repeated uses. The gradual loss of activity seems to be due to both the loss of the catalyst from sampling and the accumulation of intermediates, not to the deactivation of F-TiO₂/Pt catalyst. This indicates that the surface fluoride species are not significantly depleted during the anoxic photocatalytic reaction. The dark control test showed that the removal of 4-CP by adsorption on F-TiO₂/Pt in the anoxic catalyst suspension was negligible in the experiment of Fig. 3.

The surface platinization^{5,8,9} and surface fluorination^{6,7} of TiO₂ have been studied independently and each modification method influences the photocatalytic activity in very different ways. The Pt nanoparticles deposited on the surface of TiO₂ are known to serve as an electron sink (Schottky-barrier electron trapping) retarding the charge recombination.^{8,9} As a result, the interfacial charge transfer and the photocatalytic reaction are enhanced. On the other hand, surface fluorinated TiO₂ seems to increase the photocatalytic oxidation and enhances the generation of mobile (unbound) OH radicals that are stronger oxidants than the surface adsorbed OH radicals.^{6,7,10}

To investigate further how the surface platinization and fluorination interact synergically in the photoinduced electron transfer process on TiO₂, photocurrents collected from the aqueous catalyst suspension were monitored before and after the addition of 4-CP as illustrated in Fig. 4. The redox couple of Fe³⁺/Fe²⁺ serves as an electron shuttle that transfers electrons from TiO₂ to a Pt collector electrode in the illuminated catalyst suspension.¹¹ Note that the current increase, ΔI_{ph} , is directly related to the oxidation of 4-CP. When 4-CP is present as an electron donor (hole scavenger), more electrons can be transferred to the collector electrode. In accordance with the anoxic photocatalytic degradation of 4-CP shown in Fig. 1(a), ΔI_{ph} was also markedly enhanced with F-TiO₂/Pt whereas ΔI_{ph} with F-TiO₂ or Pt/TiO₂ was only slightly higher than that obtained with bare TiO₂.

The evidence presented above (both photocatalytic and photoelectrochemical) clearly indicate that the anoxic photocatalytic oxidation of aromatic organics is surely enhanced on F-TiO₂/Pt. This highly synergic effect of surface fluorination and platinization might be related to the substrate-surface interaction and the charge transfer/recombination characteristics that should depend on the surface property of TiO₂. The unique anoxic photocatalytic activity of F-TiO₂/Pt implies that the charge

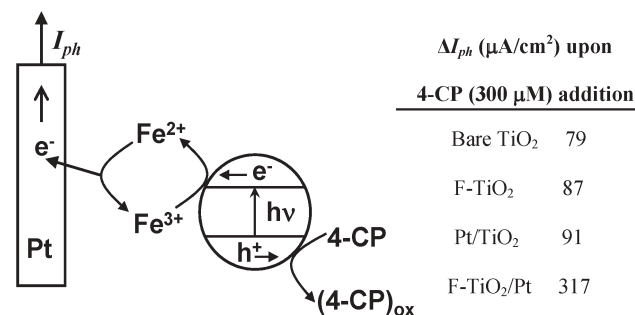
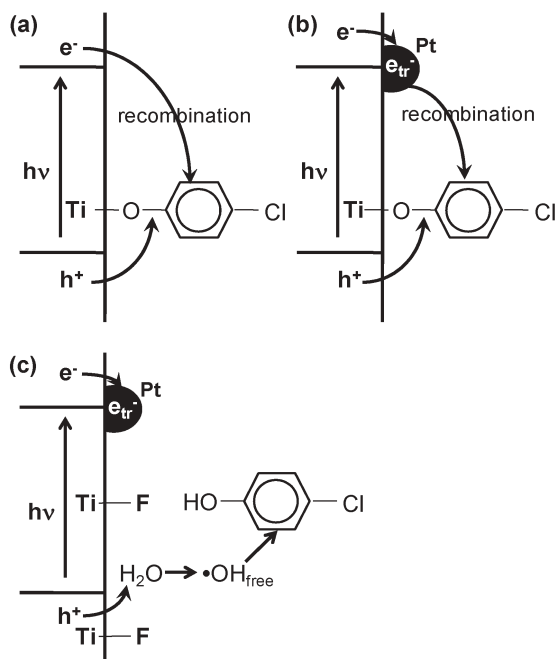


Fig. 4 Photocurrent (I_{ph}) collected (via Fe³⁺/Fe²⁺ redox couple) in the anoxic aqueous suspension of modified photocatalysts.¹³ The increase of I_{ph} upon the addition of 4-CP (ΔI_{ph} in 30 min) is compared among different photocatalysts.



Scheme 1 Photo-induced charge transfer/recombination processes occurring on (a) bare TiO_2 , (b) Pt/TiO_2 , and (c) $\text{F-TiO}_2/\text{Pt}$ in the presence of 4-CP and the absence of O_2 .

recombination can be retarded even in the absence of the dominant electron acceptor, O_2 . The plausible scenarios occurring on bare TiO_2 , Pt/TiO_2 , and $\text{F-TiO}_2/\text{Pt}$ are illustrated in Scheme 1. In the absence of O_2 , the charge recombination is dominant and the overall photocatalytic reactions hardly occur on bare TiO_2 (Scheme 1a). The surface-complexed 4-CP may serve as an external hole trap, which immediately reacts with a conduction band electron in the absence of O_2 to make a null reaction. On Pt/TiO_2 , however, the anoxic photocatalytic reactions may occur for some substrates because the Pt deposits can serve as a temporary electron reservoir,⁵ which is clearly demonstrated for the case of 2,4-D (Fig. 2a). However, the anoxic activity of Pt/TiO_2 in general is limited because the trapped electrons in Pt slowly recombine with holes in the absence of O_2 (Scheme 1b). On $\text{F-TiO}_2/\text{Pt}$ (Scheme 1c), on the other hand, the trapped electrons in the Pt phase may persist much longer because the surface complex-mediated recombination is hindered by the presence of surface fluorides. The fact that the surface complexation of 4-CP is hindered on F-TiO_2 surface has been reported.¹² Under this

condition, while the substrate is oxidized by the mobile OH radical off the surface, the electrons remain trapped in the Pt phase. The accumulated electrons on Pt eventually react with water or protons. With this scenario, the overall photocatalytic conversion taking place on $\text{F-TiO}_2/\text{Pt}$ can be highly enhanced even in the absence of O_2 that serves as a dominant electron acceptor in most photocatalytic reactions.

We have demonstrated that *anoxic photocatalytic oxidation of aromatic organics* can occur on the simultaneously fluorinated and platinized surface of TiO_2 . The synergic effect of the two modification methods was prominently demonstrated both photocatalytically and photoelectrochemically. The present $\text{F-TiO}_2/\text{Pt}$ catalyst has demonstrated the highest activity yet for *anoxic photocatalysis* to our knowledge. It is proposed that the charge recombination on $\text{F-TiO}_2/\text{Pt}$ is inhibited through the synergic action of two different surface species. However, the detailed photocatalysis mechanism taking place on $\text{F-TiO}_2/\text{Pt}$ is largely unknown at this stage and needs to be further studied.

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- Experimental conditions for the photocurrent measurement: [catalyst] = 0.5 g L^{-1} , [NaF] = 10 mM, [LiClO_4] = 0.1 M, [Fe^{3+}] = 0.1 mM, [4-CP]_{add} = 300 μM , Reactor volume = 75 mL, Applied potential = $+0.7 \text{ V}_{\text{SCE}}$, pH = 1.6, $\lambda > 300 \text{ nm}$, Continuous N_2 purged.