

## Research Article

# Photoelectrocatalytic Degradation of Organic Pollutants in Aqueous Solution Using a Pt-TiO<sub>2</sub> Film

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A series of Pt-TiO<sub>2</sub> films with nanocrystalline structure was prepared by a procedure of photodeposition and subsequent dip-coating. The Pt-TiO<sub>2</sub> films were characterized by X-ray diffraction, scanning electronic microscope, electrochemical characterization to examine the surface structure, chemical composition, and the photoelectrochemical properties. The photocatalytic activity of the Pt-TiO<sub>2</sub> films was evaluated in the photocatalytic (PC) and photoelectrocatalytic (PEC) degradation of formic acid in aqueous solution. Compared with a TiO<sub>2</sub> film, the efficiency of formic acid degradation using the Pt-TiO<sub>2</sub> films was significantly higher in both the PC and PEC processes. The enhancement is attributed to the action of Pt deposits on the TiO<sub>2</sub> surface, which play a key role by attracting conduction band photoelectrons. In the PEC process, the anodic bias externally applied on the illuminated Pt-TiO<sub>2</sub> films can further drive away the accumulated photoelectrons from the metal deposits and promote a process of interfacial charge transfer.

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## 1. Introduction

The widespread pollution of drinking water or effluents from industries and household with hazards and biorecalcitrant organic compounds demands an increasing effort towards the development of technologies for the cleanup of such wastewater [1, 2]. In past decades heterogeneous photocatalysis using TiO<sub>2</sub> has been attracted much attention in the field of environmental research for the degradation of undesirable organics in aqueous solution [3, 4]. The appeal of this technology is the prospect of complete mineralization of the pollutants into harmless compounds to environment in addition to the abundance, relatively low cost, chemical stability, and nontoxic nature of the catalyst. However, the PC efficiency is limited by the high degree of electron-hole recombination [5, 6].

Recently many studies have been devoted to improving PC activity by modifying TiO<sub>2</sub> using the deposition of noble metals [7–10]. In these cases, a Schottky barrier between the metal and TiO<sub>2</sub> is formed, while both metal and TiO<sub>2</sub>

Fermi levels equilibrate. Upon irradiation, the conduction band electrons flow from TiO<sub>2</sub> to the deposited metal that can act as a sink for the photogenerated electrons. This migration of the generated electrons to metal particles, on the one hand, can increase the lifetime of holes and suppress the electron-hole recombination, thus favoring PC oxidation of organic pollutants [7, 8, 10]; on the other hand, the migration can also enhance the PC reductive activity of TiO<sub>2</sub> [11, 12]. The reduction of organic pollutant is a process of increasing COD, generally unbeneficial to environmental protect. Moreover, the positive-charged holes, negative-charged metal particles, and organic pollutants are in a same reaction system; as a result, the system possibly suffers from a disadvantage that the intermediates of oxidized organic pollutants are re-reduced, leading to the formation of short-circuit similar to the mechanism of TiO<sub>2</sub> deactivation by chlorine ions [13] because any species with a reduction potential more positive than the flat band potential of TiO<sub>2</sub> (~ -0.7 V versus SCE, at pH 7), in theory, can be reduced [14]. In fact, recently many authors have demonstrated

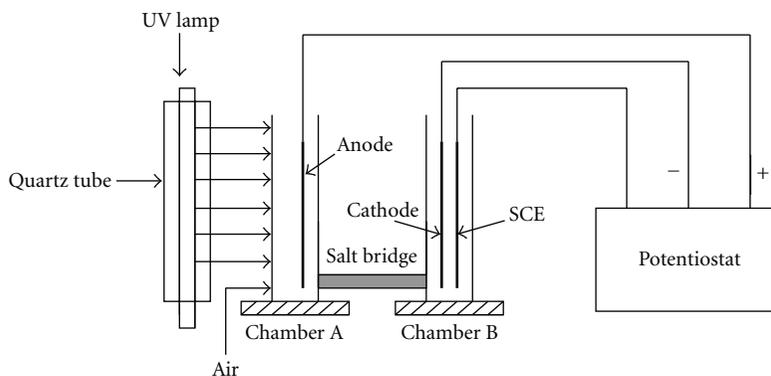


FIGURE 1: Schematic diagram of PC and PEC photoreactor systems.

that the PC oxidation activity of the metallized  $\text{TiO}_2$  is comparable to, and what is more, less than that of native  $\text{TiO}_2$  [15–17].

Based on the above considerations, it is significant for the oxidation of organic pollutants to further transfer the migrated electrons on the metal particles out of the reaction system by the alternatively externally applied anodic bias; the process is addressed as PEC one [18]. The externally anodic bias potential on the illuminated metal-loaded  $\text{TiO}_2$  film cannot only spatially separate the capture of conduction band electrons from the oxidation process but also drive away the accumulated photogenerated electrons on metal particles to another compartment of cell. Although many efforts have been directed to the PEC degradation of organic pollutants on  $\text{TiO}_2$  film [19–23], to date, rare information is available on the PEC oxidation of organic pollutants on metal-loaded  $\text{TiO}_2$  film except our recent reported examples [24, 25]. The above-mentioned situation aroused us to make attempts to prepare a novel platinum-deposited titanium dioxide film, Pt- $\text{TiO}_2$  film, and to investigate photoelectrochemical performance of Pt- $\text{TiO}_2$  film electrode and PEC activity towards the oxidation of organic pollutants on Pt- $\text{TiO}_2$  film electrode.

## 2. Experimental

**2.1. Materials.** Photocatalyst was  $\text{TiO}_2$  (Degussa P25). Formic acid solution was  $15 \text{ mmol}^{-1}$  (COD:  $239 \text{ mg l}^{-1}$ ). ITO (indium-tin oxide) conductive glass plates were used as a support of platinised  $\text{TiO}_2$  film to conveniently perform photoelectrochemical measurements.

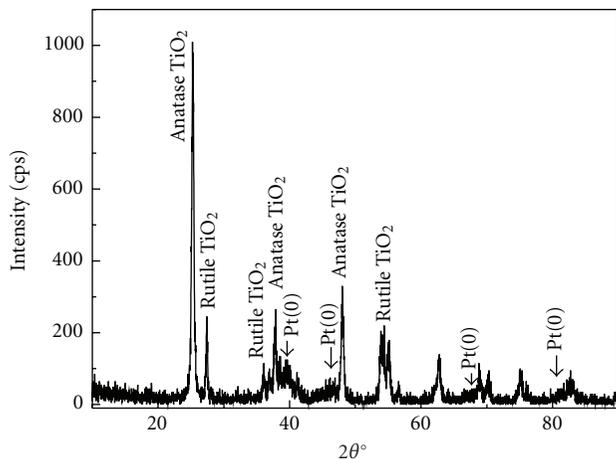
**2.2. Preparation of  $\text{TiO}_2$  and Pt- $\text{TiO}_2$  Film.** A  $\text{TiO}_2$ /ITO film was first prepared according to the procedure described in literature [23], in which, 40 g of  $\text{TiO}_2$  powder was added into 500 mL of distilled water. The  $\text{TiO}_2$  slurry was sonicated for 30 minutes to break the loosely-attached aggregates up and then vigorously agitated to form fine  $\text{TiO}_2$  suspension. Then the  $\text{TiO}_2$  in the suspension was loaded on the ITO glass plate ( $1.0 \text{ cm} \times 5.0 \text{ cm}$ ) by a procedure of dip-coating, drying, and sintering. The  $\text{TiO}_2$ -coated ITO film was dried for 15 minutes on a hot plate at  $100^\circ\text{C}$  and subsequently

sintered in a muffle furnace at  $400^\circ\text{C}$  for 2 hours to obtain the  $\text{TiO}_2$ /ITO film. The quantity of  $\text{TiO}_2$  loading was about  $1.07\text{--}1.10 \text{ mg cm}^{-2}$ .

Pt- $\text{TiO}_2$  film was prepared using a dip-coating procedure followed by Pt photodeposition. An aqueous suspension of  $\text{TiO}_2$  ( $80.0 \text{ g l}^{-1}$ ) was sonicated 30 minutes before coating. The suspension was loaded on an ITO glass ( $12 \text{ cm} \times 4.8 \text{ cm}$ ), dried 15 minutes on a hot plate at  $100^\circ\text{C}$  and then sintered 2 hours at  $400^\circ\text{C}$ . The loading, drying, and sintering was repeated three times. The quantity of  $\text{TiO}_2$  was about  $0.94\text{--}1.00 \text{ mg cm}^{-2}$  by weighing. The resulting  $\text{TiO}_2$  plate was immersed in a 40-mL aqueous solution containing  $\text{H}_2\text{PtCl}_6$  ( $2.2 \text{ mmol}^{-1}$ ) and  $\text{HCOOH}$  ( $1 \text{ mol}^{-1}$ ) and then subjected to photodeposition of Pt. The deposited Pt content was controlled under the different illumination time of 0.5, 1.0, 5.0, 10.0, and 20.0 minutes. An EDS analysis was carried out to confirm the amount of Pt content in the  $\text{TiO}_2$  films, which were 0.7%, 1.8%, 2.7%, 3.5%, and 4.2% (Wt. Pt/ Wt.  $\text{TiO}_2$ ), respectively.

**2.3. Characterization of  $\text{TiO}_2$ /ITO and Metal-Deposited  $\text{TiO}_2$  Films.** X-ray reflection diffraction (XRD) was performed using D/Max-III A Diffractometer (Rigaku Corporation, Japan) with Radiation of Cu target ( $K\alpha_1, \lambda = 1.54056 \text{ nm}$ ). Scanning electron microscope (SEM) images were obtained on a JSM-6330F-mode Field Emission Scanning Electron Microscope (JEOL, Japan). A UV-PC3101PC spectrophotometer (SHIMASZU, Japan) was used for recording the UV absorption spectra of solution. Photoelectrochemical measurement was performed with a Model CH650 Potentiostat.

**2.4. Experiments of PC and PEC Oxidation.** Formic acid chemical with analytical grade was supplied by Guangzhou Chemical Co. and used as a model chemical in this study. 15 mM formic acid solution was first prepared with an initial COD concentration of  $239 \text{ mg L}^{-1}$  and pH 2.73. About 35.0 mL of the 15 mM formic acid solution was used in both the PC and PEC reactions. Both of PC and PEC oxidation reactions were carried out in a photoreactor system as shown in Figure 1, consisting of two chambers (A and B,  $2.0 \text{ cm} \times 1.1 \text{ cm} \times 8.0 \text{ cm}$ ) connected via a salt bridge. When the PC reaction was conducted using the chamber

FIGURE 2: XRD spectra of Pt-TiO<sub>2</sub>.

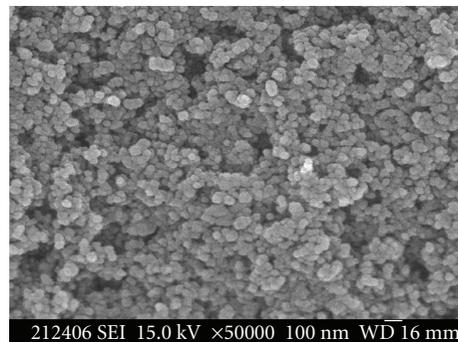
A only, the PEC reaction was performed using both the chambers. In the meantime, a 500-W UV lamp with main emission at 365 nm was used as a UV source, and air bubbling was continuously provided during reaction. Either the TiO<sub>2</sub> or Pt-TiO<sub>2</sub> plate was placed in the chamber A and used as an anodic electrode, while a Pt electrode and a saturated calomel electrode (SCE) were positioned in the chamber B and used as counter and reference electrodes, respectively. The photoelectrochemical measurement was performed with a potentiostat (Model CH 650, Shanghai).

**2.5. Analysis.** Chemical oxygen demand (COD) was measured with potassium dichromate after the sample was digested with a WMX COD microwave digestion system [26].

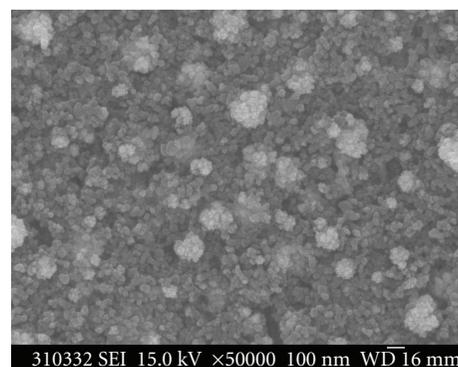
### 3. Results and Discussion

**3.1. Preparation and Characterization of Pt-TiO<sub>2</sub> Film.** In our previous work, nano-Ag and Cu were successfully deposited on TiO<sub>2</sub> film by photoreduction [24, 25]. Herein, we also try to directly deposit Pt on the film surface by the same method, using H<sub>2</sub>PtCl<sub>6</sub> as a Pt precursor and HCOOH as a hole scavenger, in order to prepare Pt-TiO<sub>2</sub> film. Upon illuminating TiO<sub>2</sub> film inserted in the H<sub>2</sub>PtCl<sub>6</sub>-HCOOH solution, a layer of black deposits on the surface of TiO<sub>2</sub> film was observed. The XRD pattern of the black deposits mixed with TiO<sub>2</sub> was shown in Figure 2. Four weak and broad XRD peaks were observed at 2θ angles of 39.74, 46.16, 67.56, and 80.98. The 2θ angles are corresponding to that of metallic Pt, and the breadth of these peaks is characteristic of Pt nanocrystals [9, 27]. Their average crystal size was calculated as 8 nm by using the Scherrer equation.

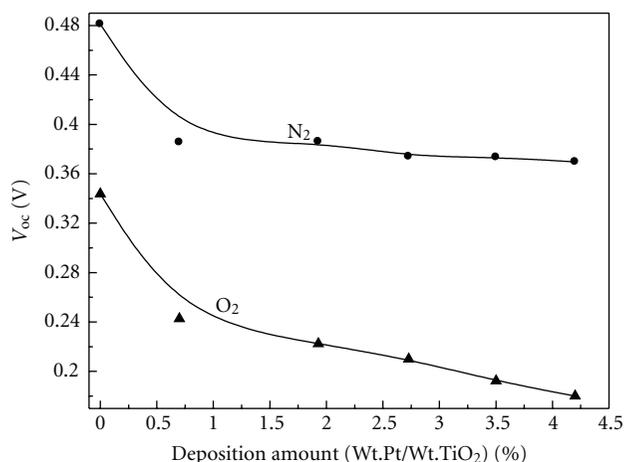
Figure 3 represents the SEM micrographs of the TiO<sub>2</sub> and platinumised films. The morphologies are noticeably dependent on the composition of films. TiO<sub>2</sub> film was of highly porous and particulate surface (Figure 3(a)). The particulate size is estimated to be approximate 50 nm, greater than that of the original P25 TiO<sub>2</sub> powder (30 nm). The fact indicates that



(a)



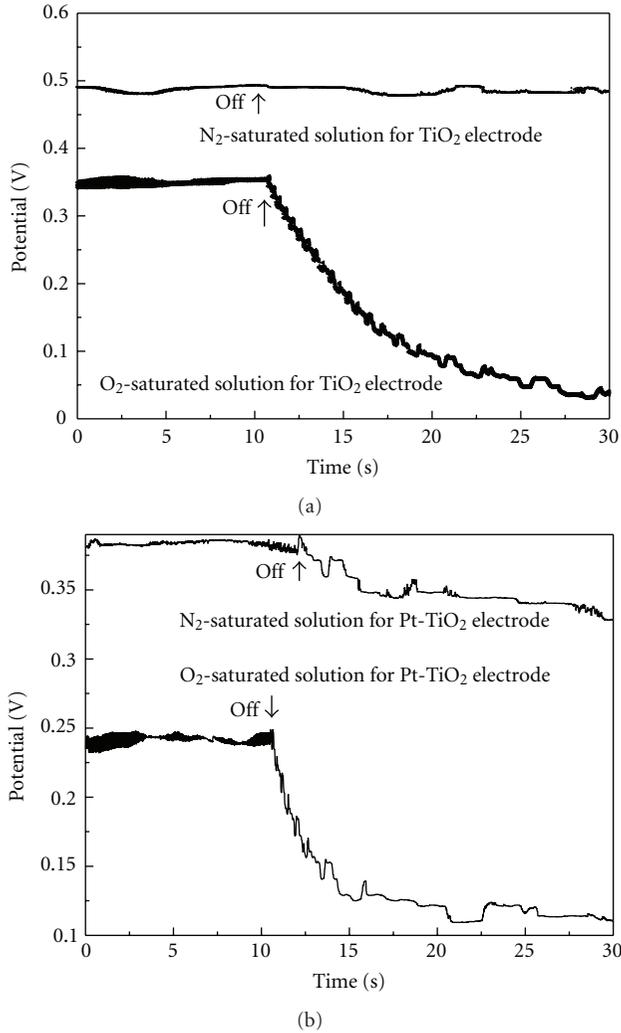
(b)

FIGURE 3: SEM images of TiO<sub>2</sub> and Pt-TiO<sub>2</sub> films (a) TiO<sub>2</sub> film and (b) Pt-TiO<sub>2</sub> with 1.8 wt.% Pt.FIGURE 4: Change of  $V_{oc}$  of Pt-TiO<sub>2</sub> with deposited Pt amount ( $V_{oc}$  (N<sub>2</sub>) for N<sub>2</sub>-saturated solution and  $V_{oc}$  (O<sub>2</sub>) for O<sub>2</sub>-saturated solution).

the TiO<sub>2</sub> particles were slightly aggregated during sintering. The surface of Pt-TiO<sub>2</sub> film is similar to that of TiO<sub>2</sub> film (Figure 3(b)). It characterized a porous and particulate appearance, but the particulate size was smoother than that of the particulates on TiO<sub>2</sub> film according to the resolution used; therefore, it means that the supported film contains smaller grains in the Pt-TiO<sub>2</sub> than in pure TiO<sub>2</sub>.

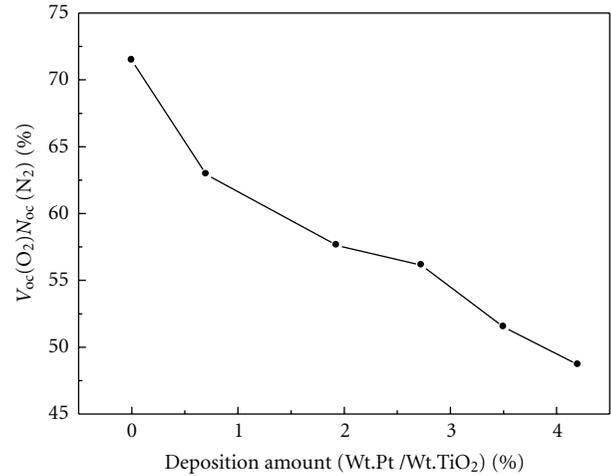
TABLE 1: The values of kinetic coefficient  $k$  in four experiments with application of the first-order kinetic model.

ID	Catalyst	Process	Rate constant ( $\text{min}^{-1}$ )	$k$ Correlation coefficient (R)
A	TiO <sub>2</sub>	PC	0.007	0.9600
B	TiO <sub>2</sub> electrode	PEC	0.011	0.9914
C	Pt-TiO <sub>2</sub>	PC	0.028	0.9901
D	Pt-TiO <sub>2</sub> electrode	PEC	0.038	0.9726

FIGURE 5: Decay curves of open circuit voltage after light was turned off (a) TiO<sub>2</sub> film and (b) Pt-TiO<sub>2</sub>.

### 3.2. Photoelectrochemical Characterization of Pt-TiO<sub>2</sub> Film.

The dependence of photovoltage of Pt-TiO<sub>2</sub> film on Pt content in N<sub>2</sub>- or O<sub>2</sub>-saturated solution is shown in Figure 4. In the dark, the Fermi level of a semiconductor film equilibrates with the redox couple in solution; upon excitation of TiO<sub>2</sub> film, the photogenerated electrons accumulate in the TiO<sub>2</sub> particulate film, leading to a rise in the photovoltage. As a result, any accumulation of electrons in the film will present a rise in  $V_{oc}$ . The observation that  $V_{oc}(O_2)$  of Pt-TiO<sub>2</sub> film in O<sub>2</sub>-saturation solution is lower than that in N<sub>2</sub>-saturated

FIGURE 6: Dependence of  $[V_{oc}(O_2)/V_{oc}(N_2)]$  on deposited Pt amount.

solution confirms the fact, due to the surface-adsorbed O<sub>2</sub> scavenging the photogenerated electrons in the O<sub>2</sub>-saturated solution. In addition to the above evidence, it is noting that in either N<sub>2</sub>- or O<sub>2</sub>-saturated solution for Pt-TiO<sub>2</sub> film,  $V_{oc}$  decreases with increase of Pt content. Generally, TiO<sub>2</sub> electrode deposited metallic nanoparticles shifts the photovoltage to more positive value, ascribing to the fact that the metallic nanoparticles improve the accumulation of electrons within the particulate film by facilitating the hole transfer at the electrolyte interface [7, 24]. An alternative explanation for the above-observed decrease of  $V_{oc}$  was based on the consideration while metal nanoparticles are surrounded by electron donors, and these deposited Pt can diminish the accumulation of photogenerated electrons. We attribute decrease of  $V_{oc}$  to the two tentative factors. Firstly, the deposited Pt can facilitate the reactions of scavenging photogenerated electrons, such as, O<sub>2</sub> reduction (1) and H<sub>2</sub> evolution (2):



Figure 5 clearly shows that, after UV light turns off, the  $V_{oc}$  of Pt-TiO<sub>2</sub> film decreases more rapidly than that of TiO<sub>2</sub> film, either for N<sub>2</sub>-saturated solution or for O<sub>2</sub>-saturated solution, suggesting that deposited Pt can facilitate the reactions of scavenging photogenerated electrons for Pt-TiO<sub>2</sub> film via the reactions (1) and (2).

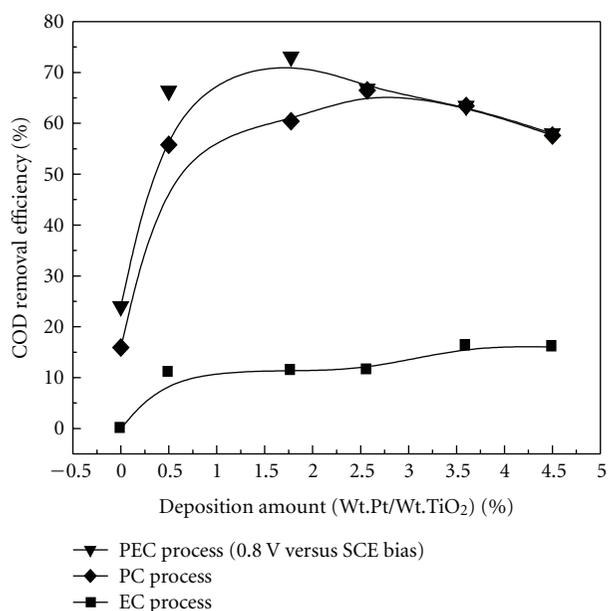


FIGURE 7: Dependence of COD removal efficiency on deposited Pt amount.

At the same time, it is also seen from Figure 5 that, compared with  $O_2$ -saturated solution, all the  $V_{oc}$  for  $N_2$ -saturated solution merely decreases slightly, indicating that the capture of electrons is mainly by the reaction (1), not (2). Therefore, the fraction of the remained photogenerated electrons on the platinised film can be approximately estimated by  $V_{oc}(O_2)/V_{oc}(N_2)$  [28]. The estimated results (Figure 6) suggested that there are still rather remained accumulated electrons on Pt-TiO<sub>2</sub> film in the experimental range although Pt deposition can increase the efficiency of the charge separation. For example, for Pt-TiO<sub>2</sub> film with 0.7% Pt content, the fraction of the remained electrons is 63%. Therefore, it is reasonable to employ an anodic bias to drive away the remained accumulation electrons in order to increase PC efficiency.

**3.3. PC and PEC Oxidation of Pt-TiO<sub>2</sub> Film.** The PC and PEC oxidation activities of Pt-TiO<sub>2</sub> films towards formic acid were evaluated in the term of COD removal efficiency in the present investigation. Presently, the influence of Pt content concentration on COD removal efficiencies is studied in a range from 0 to 4.5% not only for PC process but also for electrochemical and PEC processes. As shown in Figure 7, respectively, the COD removal efficiency is dependent on the amount of the Pt content for both PC and PEC processes, while the COD removal efficiency of electrochemical (EC) process changes slightly with Pt content. For PC processes, the COD removal efficiencies increase with the Pt content in the range of 0% ~ 2.7%. The enhancement effect further shows that Pt serves as an electron trapper and reduces the recombination of hole-electron pairs. However, over-deposited Pt resulted in a decrease in PC activity due to the reason that the cluster or aggregation of metal deposits on the surface changes the function

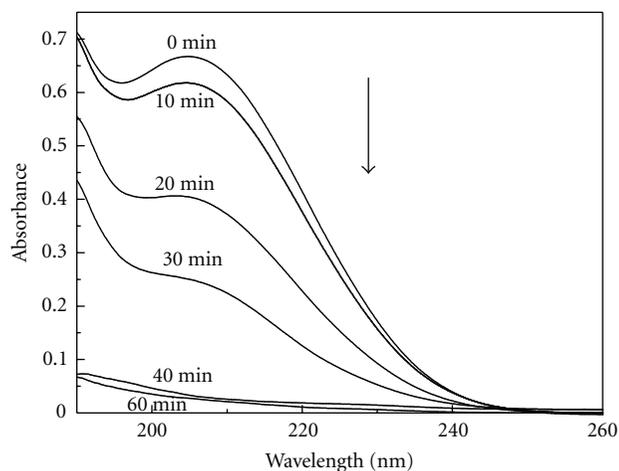


FIGURE 8: Change of UV spectra of formic acid at various reaction intervals for PEC process in the presence of 0.8 V versus SCE anodic bias.

from an electron separation center to an electron recombination center and consequently reduced the PC activity [29].

For PEC process, a similar change tendency was observed. However, it was also found that the COD removal efficiency for PEC process is considerably higher than that of PC process. For example, in the absence of Pt, the COD removal efficiency of PEC process is 24.0% while that of PC process is only 15.9%. For TiO<sub>2</sub> film with a Pt content of 1.7%, the COD removal efficiency of the PEC process is 73.4% while that of PC process is 60.4%, higher than the sum the COD removal efficiency for individual PC process (60.4%) and electrochemical process (11%). The observations denote that there is a significant synergistic effect existing in the PEC process.

In addition, the difference between PEC and PC processes on Pt-TiO<sub>2</sub> films with a Pt content of 1.7% is 13%, higher than that for neat TiO<sub>2</sub> film (8%), indicating that the enhancement effect of the external electric field in the presence of Pt is more obvious than in the absence of Pt. The more obvious enhancement effect can be explained by the fact that the Pt can not only trap the photogenerated electrons but also assist the external electric field to migrate them from the TiO<sub>2</sub> film to counter electrode in another compartment of the cell by improving electric conductivity of TiO<sub>2</sub> film as well as decrease the recombination. For either PEC or PC process, the Pt-TiO<sub>2</sub> films with Pt content of 1.7% possess a relative good performance of COD removal, all the rest of our experiments was conducted using the Pt-TiO<sub>2</sub> films with Pt content of 1.7%.

**3.4. Comparison of Rate Constants for PC or PEC Processes.** The UV spectra of formic acid in the PEC process at various reaction intervals are presented in Figure 8. It can be observed from the figure that formic acid decreased dramatically. And the COD removal efficiencies, at any tested time, are much higher than that for either PC process on Pt-TiO<sub>2</sub> film or PEC process on TiO<sub>2</sub> film as shown in Figure 9.

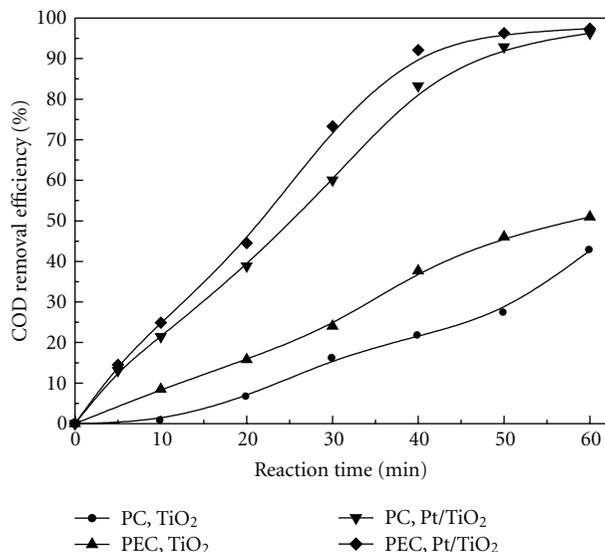


FIGURE 9: Dependence of COD removal efficiency on treatment time for various processes.

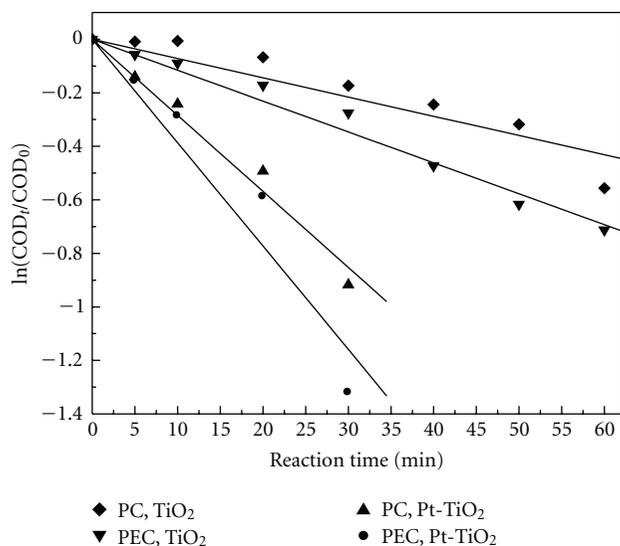


FIGURE 10: Logarithm of formic acid normalized COD concentration as a function of treatment time for the four processes.

It is also well recognized that PC degradation of organic pollutants accords with the first-order kinetics [30–32]. In this work, the first-order kinetics were also confirmed not only in the PC but also in the PEC process by the linear transforms  $\ln(\text{COD}_t/\text{COD}_0) = -kt$  of Figure 9 as shown in Figure 10. The kinetic regression equations and parameters were listed in Table 1; the rates for the PC oxidation or the PEC oxidation on Pt-TiO<sub>2</sub> film electrode are more than 4 times or 5.4 times of the PC oxidation on TiO<sub>2</sub> film, respectively. The observation further confirms that the combination of Pt deposition and the application of external electric field had a beneficial effect on enhancing the efficiency of the PC oxidation of formic acid.

## 4. Conclusion

The feasibility of improving the PC activity of TiO<sub>2</sub> film towards the oxidation of organic pollutant by combining the modification of Pt nanoparticles with the application of anodic bias was investigated. In this experiment Pt-TiO<sub>2</sub> films were used as photoanodes in a two-compartment photoelectrochemical cell to investigate its photoelectrochemical performance and the PEC activity towards the oxidation of formic acid. The experimental results showed that the deposited Pt has an apparent enhancement effect with respect to suppressing the recombination between the photogenerated charge carriers and enhancing the PC oxidation of formic acid, and the PC and PEC activities of Pt-TiO<sub>2</sub> film towards the oxidation of formic acid were considerably dependent on the amount of deposited Pt. Compared with a TiO<sub>2</sub> film, the degradation efficiency of formic acid on the Pt-TiO<sub>2</sub> films increased markedly in both the PC and PEC oxidation processes.

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## References

- [1] G. Ceñti, P. Ciambelli, S. Perathoner, and P. Russo, "Preface: outlooks for environmental catalysis," *Catalysis Today*, vol. 75, no. 1–4, pp. 1–2, 2002.
- [2] D. Simonsson, "Electrochemistry for a cleaner environment," *Chemical Society Reviews*, vol. 26, no. 3, pp. 181–189, 1997.
- [3] A. Fujishima, T. N. Rao, and D. A. Tryk, "TiO<sub>2</sub> photocatalysts and diamond electrodes," *Electrochimica Acta*, vol. 45, no. 28, pp. 4683–4690, 2000.
- [4] D. A. Tryk, A. Fujishima, and K. Honda, "Recent topics in photoelectrochemistry: achievements and future prospects," *Electrochimica Acta*, vol. 45, no. 15–16, pp. 2363–2376, 2000.
- [5] J. C. Yu, J. Lin, and R. W. M. Kwok, "Enhanced photocatalytic activity of Ti<sub>1-x</sub>V<sub>x</sub>O<sub>2</sub> solid solution on the degradation of acetone," *Journal of Photochemistry and Photobiology A*, vol. 111, no. 1–3, pp. 199–203, 1997.
- [6] S. Li, G. Ye, and G. Chen, "Low-temperature preparation and characterization of nanocrystalline anatase TiO<sub>2</sub>," *Journal of Physical Chemistry C*, vol. 113, no. 10, pp. 4031–4037, 2009.
- [7] V. Subramanian, E. Wolf, and P. V. Kamat, "Semiconductor-metal composite nanostructures. To what extent do metal nanoparticles improve the photocatalytic activity of TiO<sub>2</sub> films?" *Journal of Physical Chemistry B*, vol. 105, no. 46, pp. 11439–11446, 2001.
- [8] D. Hufschmidt, D. Bahnemann, J. J. Testa, C. A. Emilio, and M. I. Litter, "Enhancement of the photocatalytic activity of various TiO<sub>2</sub> materials by platinumisation," *Journal of Photochemistry and Photobiology A*, vol. 148, no. 1–3, pp. 223–231, 2002.
- [9] Z. Luo, K. Katayama-Hirayama, K. Hirayama, T. Akitsu, and H. Kaneko, "Photocatalytic degradation of pyrene in

- porous Pt/TiO<sub>2</sub>-SiO<sub>2</sub> photocatalyst suspension under UV irradiation," *Nano*, vol. 3, no. 5, pp. 317–322, 2008.
- [10] A. Sclafani and J.-M. Herrmann, "Influence of metallic silver and of platinum-silver bimetallic deposits on the photocatalytic activity of titania (anatase and rutile) in organic and aqueous media," *Journal of Photochemistry and Photobiology A*, vol. 113, no. 2, pp. 181–188, 1998.
- [11] F. Boccuzzi, A. Chiorino, M. Manzoli, and D. Andreeva, "Gold, silver and copper catalysts supported on TiO<sub>2</sub> for pure hydrogen production," *Catalysis Today*, vol. 75, no. 1–4, pp. 169–175, 2002.
- [12] R. M. Lahtinen, D. J. Fermín, H. Jensen, K. Kontturi, and H. H. Girault, "Two-phase photocatalysis mediated by electrochemically generated Pd nanoparticles," *Electrochemistry Communications*, vol. 2, no. 4, pp. 230–234, 2000.
- [13] F. Sunada and A. Heller, "Effects of water, salt water, and silicone overcoating of the TiO<sub>2</sub> photocatalyst on the rates and products of photocatalytic oxidation of liquid 3-octanol and 3-octanone," *Environmental Science and Technology*, vol. 32, no. 2, pp. 282–286, 1998.
- [14] P. S. M. Dunlop, J. A. Byrne, N. Manga, and B. R. Eggins, "The photocatalytic removal of bacterial pollutants from drinking water," *Journal of Photochemistry and Photobiology A*, vol. 148, no. 1–3, pp. 355–363, 2002.
- [15] U. Siemon, D. Bahnemann, J. J. Testa, D. Rodríguez, M. I. Litter, and N. Bruno, "Heterogeneous photocatalytic reactions comparing TiO<sub>2</sub> and Pt/TiO<sub>2</sub>," *Journal of Photochemistry and Photobiology A*, vol. 148, no. 1–3, pp. 247–255, 2002.
- [16] J. Chen, D. F. Ollis, W. H. Rulkens, and H. Bruning, "Photocatalyzed oxidation of alcohols and organochlorides in the presence of native TiO<sub>2</sub> and metallized TiO<sub>2</sub> suspensions. Part (I): photocatalytic activity and pH influence," *Water Research*, vol. 33, no. 3, pp. 661–668, 1999.
- [17] V. Vamathavan, R. Amal, D. Beydoun, G. Low, and S. McEvoy, "Photocatalytic oxidation of organics in water using pure and silver-modified titanium dioxide particles," *Journal of Photochemistry and Photobiology A*, vol. 148, no. 1–3, pp. 233–245, 2002.
- [18] K. Vinodgopal and P. V. Kamat, "Enhanced rates of photocatalytic degradation of an azo dye using SnO<sub>2</sub>/TiO<sub>2</sub> coupled semiconductor thin films," *Environmental Science and Technology*, vol. 29, no. 3, pp. 841–845, 1995.
- [19] R. Pelegrini, P. Peralta-Zamora, A. R. De Andrade, and J. Reyes, "Electrochemically assisted photocatalytic degradation of reactive dyes," *Applied Catalysis B*, vol. 22, no. 2, pp. 83–90, 1999.
- [20] X. Z. Li, H. L. Liu, P. T. Yue, and Y. P. Sun, "Photoelectrocatalytic oxidation of rose Bengal in aqueous solution using a Ti/TiO<sub>2</sub> mesh electrode," *Environmental Science and Technology*, vol. 34, no. 20, pp. 4401–4406, 2000.
- [21] D. H. Kim and M. A. Anderson, "Solution factors affecting the photocatalytic and photoelectrocatalytic degradation of formic acid using supported TiO<sub>2</sub> thin films," *Journal of Photochemistry and Photobiology A*, vol. 94, no. 2–3, pp. 221–229, 1994.
- [22] M. V. B. Zanoni, J. J. Sene, and M. A. Anderson, "Photoelectrocatalytic degradation of Remazol Brilliant Orange 3R on titanium dioxide thin-film electrodes," *Journal of Photochemistry and Photobiology A*, vol. 157, no. 1, pp. 55–63, 2003.
- [23] J. Rodriguez, M. Gomez, S. E. Lindquist, and C. G. Granqvist, "Photo-electrocatalytic degradation of 4-chlorophenol over sputter deposited Ti oxide films," *Thin Solid Films*, vol. 360, no. 1–2, pp. 250–255, 2000.
- [24] C. He, Y. Xiong, D. Shu, and X. H. Zhu, "Enhanced photocatalytic efficiency of TiO<sub>2</sub> by combining the modification of Ag nanoparticles with the application of anodic bias," *Chinese Chemical Letters*, vol. 14, no. 5, pp. 539–542, 2003.
- [25] C. He, Y. Xiong, and X. Zhu, "Improving photocatalytic activity of Cu-loaded TiO<sub>2</sub> film using a pulse anodic bias," *Catalysis Communications*, vol. 4, no. 4, pp. 183–187, 2003.
- [26] Y. Xiong, P. J. Strunk, H. Xia, X. Zhu, and H. T. Karlsson, "Treatment of dye wastewater containing acid orange II using a cell with three-phase three-dimensional electrode," *Water Research*, vol. 35, no. 17, pp. 4226–4230, 2001.
- [27] D. K. Lee and D. S. Kim, "Catalytic wet air oxidation of carboxylic acids at atmospheric pressure," *Catalysis Today*, vol. 63, no. 2–4, pp. 249–255, 2000.
- [28] N. Chandrasekharan and P. V. Kamat, "Improving the photoelectrochemical performance of nanostructured TiO<sub>2</sub> films by adsorption of gold nanoparticles," *Journal of Physical Chemistry B*, vol. 104, no. 46, pp. 10851–10857, 2000.
- [29] A. Sclafani and J. M. Herrmann, "Influence of metallic silver and of platinum-silver bimetallic deposits on the photocatalytic activity of titania (anatase and rutile) in organic and aqueous media," *Journal of Photochemistry and Photobiology A*, vol. 113, no. 2, pp. 181–188, 1998.
- [30] J. Matos, J. Laine, and J. M. Herrmann, "Synergy effect in the photocatalytic degradation of phenol on a suspended mixture of titania and activated carbon," *Applied Catalysis B*, vol. 18, no. 3–4, pp. 281–291, 1998.
- [31] T. C. An, X. H. Zhu, and Y. Xiong, "Synergic degradation of reactive brilliant red X-3B using three dimension electrode-photocatalytic reactor," *Journal of Environmental Science and Health A*, vol. 36, no. 10, pp. 2068–2082, 2001.
- [32] T. C. An, X. H. Zhu, and Y. Xiong, "Feasibility study of photoelectrochemical degradation of methylene blue with three-dimensional electrode-photocatalytic reactor," *Chemosphere*, vol. 46, no. 6, pp. 897–903, 2002.