

Research Article

Photoelectrocatalytic Degradation of Organic Pollutants in Aqueous Solution Using a Pt-TiO₂ Film

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A series of Pt-TiO₂ films with nanocrystalline structure was prepared by a procedure of photodeposition and subsequent dip-coating. The Pt-TiO₂ 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-TiO₂ films was evaluated in the photocatalytic (PC) and photoelectrocatalytic (PEC) degradation of formic acid in aqueous solution. Compared with a TiO₂ film, the efficiency of formic acid degradation using the Pt-TiO₂ films was significantly higher in both the PC and PEC processes. The enhancement is attributed to the action of Pt deposits on the TiO₂ surface, which play a key role by attracting conduction band photoelectrons. In the PEC process, the anodic bias externally applied on the illuminated Pt-TiO₂ 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 TiO₂ 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 TiO₂ using the deposition of noble metals [7–10]. In these cases, a Schottky barrier between the metal and TiO₂ is formed, while both metal and TiO₂

Fermi levels equilibrate. Upon irradiation, the conduction band electrons flow from TiO₂ 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 TiO₂ [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 TiO₂ deactivation by chlorine ions [13] because any species with a reduction potential more positive than the flat band potential of TiO₂ (~ -0.7 V versus SCE, at pH 7), in theory, can be reduced [14]. In fact, recently many authors have demonstrated

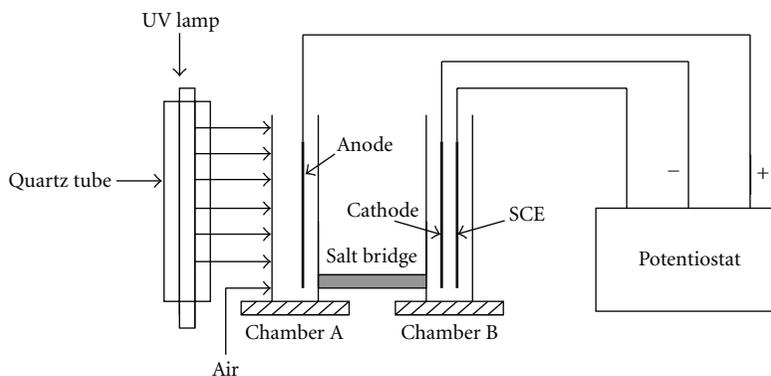


FIGURE 1: Schematic diagram of PC and PEC photoreactor systems.

that the PC oxidation activity of the metallized TiO_2 is comparable to, and what is more, less than that of native 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 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 TiO_2 film [19–23], to date, rare information is available on the PEC oxidation of organic pollutants on metal-loaded 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- TiO_2 film, and to investigate photoelectrochemical performance of Pt- TiO_2 film electrode and PEC activity towards the oxidation of organic pollutants on Pt- TiO_2 film electrode.

2. Experimental

2.1. Materials. Photocatalyst was TiO_2 (Degussa P25). Formic acid solution was 15 mmol^{-1} (COD: 239 mg l^{-1}). ITO (indium-tin oxide) conductive glass plates were used as a support of platinised TiO_2 film to conveniently perform photoelectrochemical measurements.

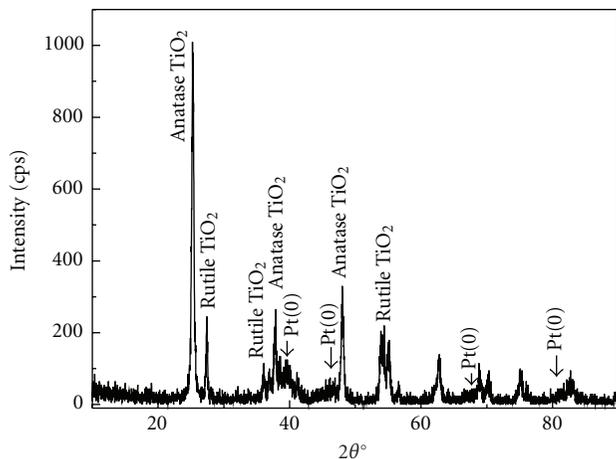
2.2. Preparation of TiO_2 and Pt- TiO_2 Film. A TiO_2 /ITO film was first prepared according to the procedure described in literature [23], in which, 40 g of TiO_2 powder was added into 500 mL of distilled water. The TiO_2 slurry was sonicated for 30 minutes to break the loosely-attached aggregates up and then vigorously agitated to form fine TiO_2 suspension. Then the 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 TiO_2 -coated ITO film was dried for 15 minutes on a hot plate at 100°C and subsequently

sintered in a muffle furnace at 400°C for 2 hours to obtain the TiO_2 /ITO film. The quantity of TiO_2 loading was about $1.07\text{--}1.10 \text{ mg cm}^{-2}$.

Pt- TiO_2 film was prepared using a dip-coating procedure followed by Pt photodeposition. An aqueous suspension of TiO_2 (80.0 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°C and then sintered 2 hours at 400°C . The loading, drying, and sintering was repeated three times. The quantity of TiO_2 was about $0.94\text{--}1.00 \text{ mg cm}^{-2}$ by weighing. The resulting TiO_2 plate was immersed in a 40-mL aqueous solution containing H_2PtCl_6 (2.2 mmol^{-1}) and HCOOH (1 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 TiO_2 films, which were 0.7%, 1.8%, 2.7%, 3.5%, and 4.2% (Wt. Pt/ Wt. TiO_2), respectively.

2.3. Characterization of TiO_2 /ITO and Metal-Deposited 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 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-TiO₂.

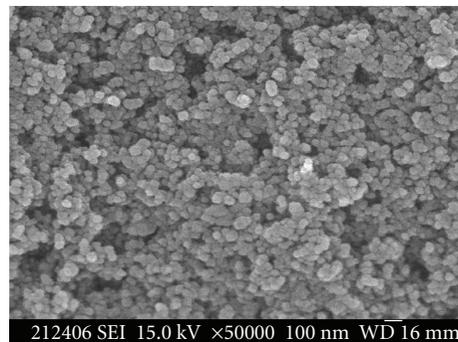
A only, the PEC reaction was performed using both the chambers. In the meantime, a 500-W UV lamp with main emission at 365 nm was used as a UV source, and air bubbling was continuously provided during reaction. Either the TiO₂ or Pt-TiO₂ plate was placed in the chamber A and used as an anodic electrode, 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].

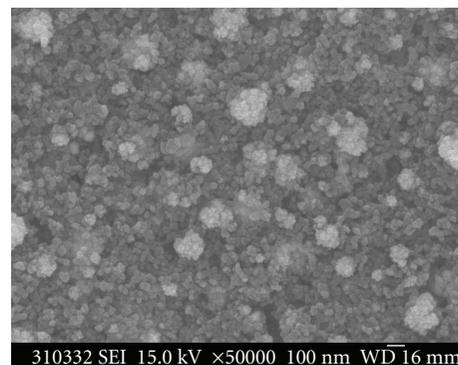
3. Results and Discussion

3.1. Preparation and Characterization of Pt-TiO₂ Film. In our previous work, nano-Ag and Cu were successfully deposited on TiO₂ film by photoreduction [24, 25]. Herein, we also try to directly deposit Pt on the film surface by the same method, using H₂PtCl₆ as a Pt precursor and HCOOH as a hole scavenger, in order to prepare Pt-TiO₂ film. Upon illuminating TiO₂ film inserted in the H₂PtCl₆-HCOOH solution, a layer of black deposits on the surface of TiO₂ film was observed. The XRD pattern of the black deposits mixed with TiO₂ 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.

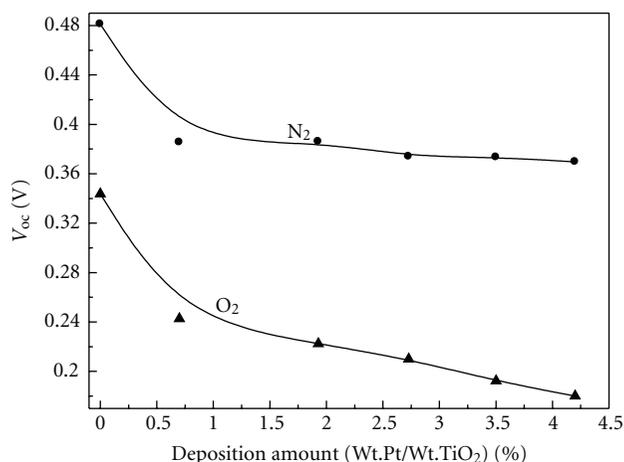
Figure 3 represents the SEM micrographs of the TiO₂ and platinised films. The morphologies are noticeably dependent on the composition of films. TiO₂ film was of highly porous and particulate surface (Figure 3(a)). The particulate size is estimated to be approximate 50 nm, greater than that of the original P25 TiO₂ powder (30 nm). The fact indicates that



(a)



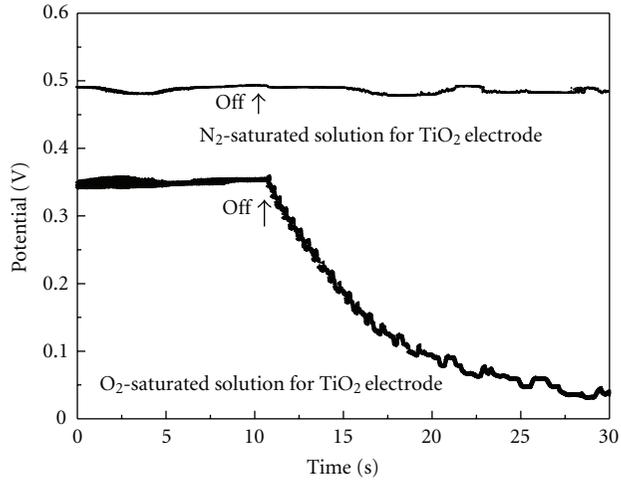
(b)

FIGURE 3: SEM images of TiO₂ and Pt-TiO₂ films (a) TiO₂ film and (b) Pt-TiO₂ with 1.8 wt.% Pt.FIGURE 4: Change of V_{oc} of Pt-TiO₂ with deposited Pt amount (V_{oc} (N₂) for N₂-saturated solution and V_{oc} (O₂) for O₂-saturated solution).

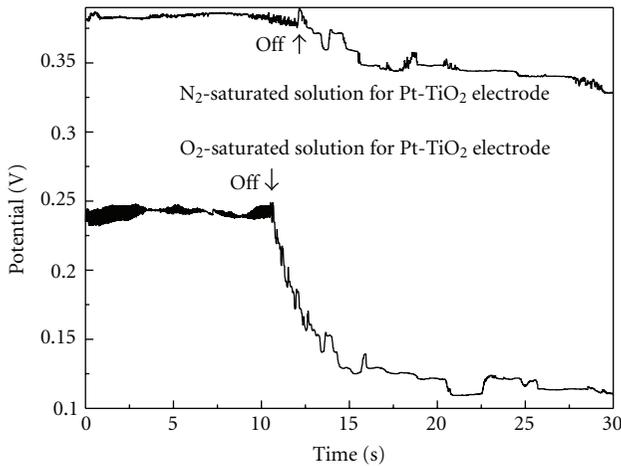
the TiO₂ particles were slightly aggregated during sintering. The surface of Pt-TiO₂ film is similar to that of TiO₂ film (Figure 3(b)). It characterized a porous and particulate appearance, but the particulate size was smoother than that of the particulates on TiO₂ film according to the resolution used; therefore, it means that the supported film contains smaller grains in the Pt-TiO₂ than in pure TiO₂.

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

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



(a)

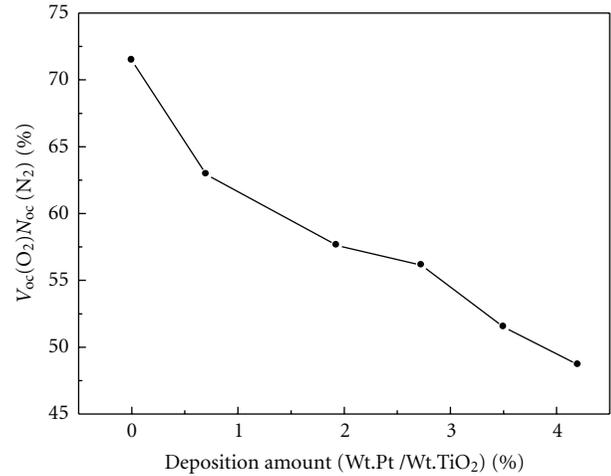


(b)

FIGURE 5: Decay curves of open circuit voltage after light was turned off (a) TiO₂ film and (b) Pt-TiO₂.

3.2. Photoelectrochemical Characterization of Pt-TiO₂ Film.

The dependence of photovoltage of Pt-TiO₂ film on Pt content in N₂- or O₂-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 TiO₂ film, the photogenerated electrons accumulate in the TiO₂ 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-TiO₂ film in O₂-saturation solution is lower than that in N₂-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 O₂ scavenging the photogenerated electrons in the O₂-saturated solution. In addition to the above evidence, it is noting that in either N₂- or O₂-saturated solution for Pt-TiO₂ film, V_{oc} decreases with increase of Pt content. Generally, TiO₂ 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, O₂ reduction (1) and H₂ evolution (2):



Figure 5 clearly shows that, after UV light turns off, the V_{oc} of Pt-TiO₂ film decreases more rapidly than that of TiO₂ film, either for N₂-saturated solution or for O₂-saturated solution, suggesting that deposited Pt can facilitate the reactions of scavenging photogenerated electrons for Pt-TiO₂ film via the reactions (1) and (2).

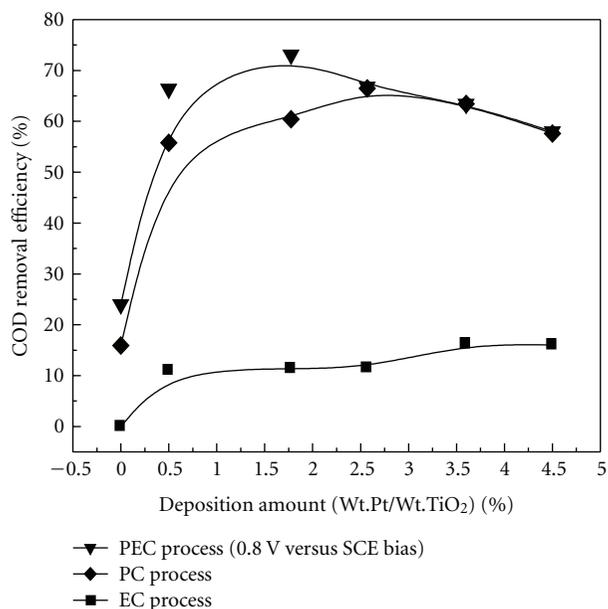


FIGURE 7: Dependence of COD removal efficiency on deposited Pt amount.

At the same time, it is also seen from Figure 5 that, compared with O₂-saturated solution, all the V_{oc} for N₂-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-TiO₂ film in the experimental range although Pt deposition can increase the efficiency of the charge separation. For example, for Pt-TiO₂ 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-TiO₂ Film. The PC and PEC oxidation activities of Pt-TiO₂ 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

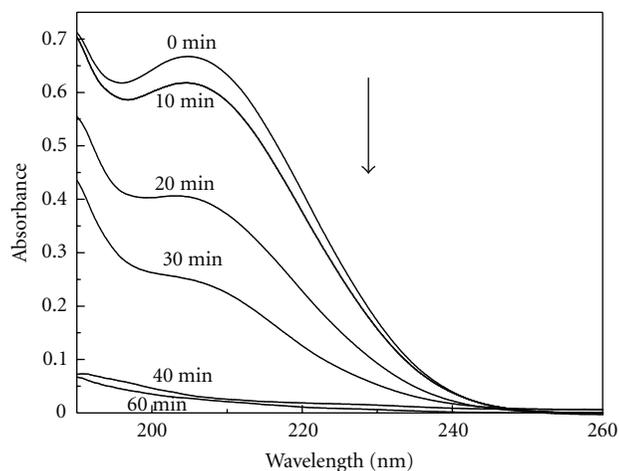


FIGURE 8: Change of UV spectra of formic acid at various reaction intervals for PEC process in the presence of 0.8 V versus SCE anodic bias.

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 TiO₂ 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-TiO₂ films with a Pt content of 1.7% is 13%, higher than that for neat TiO₂ 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 TiO₂ film to counter electrode in another compartment of the cell by improving electric conductivity of TiO₂ film as well as decrease the recombination. For either PEC or PC process, the Pt-TiO₂ 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-TiO₂ 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-TiO₂ film or PEC process on TiO₂ film as shown in Figure 9.

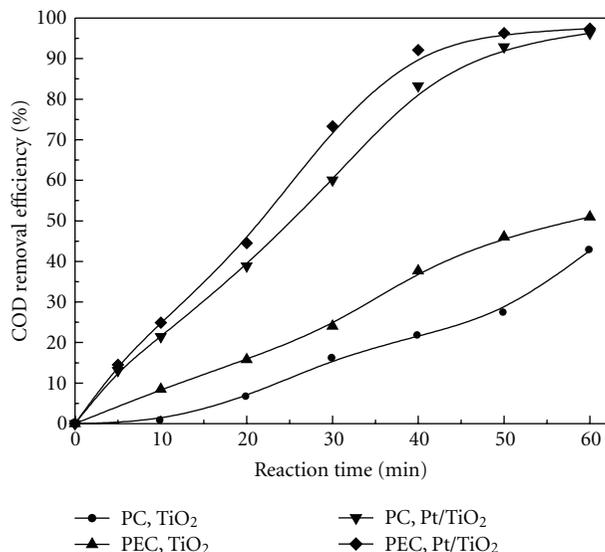


FIGURE 9: Dependence of COD removal efficiency on treatment time for various processes.

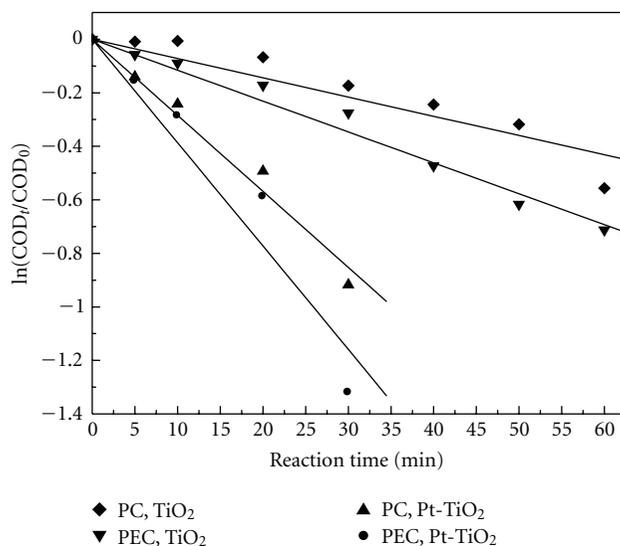


FIGURE 10: Logarithm of formic acid normalized COD concentration as a function of treatment time for the four processes.

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-TiO₂ film electrode are more than 4 times or 5.4 times of the PC oxidation on TiO₂ 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 TiO₂ 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-TiO₂ 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-TiO₂ film towards the oxidation of formic acid were considerably dependent on the amount of deposited Pt. Compared with a TiO₂ film, the degradation efficiency of formic acid on the Pt-TiO₂ films increased markedly in both the PC and PEC oxidation processes.

Acknowledgments

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