Research Article

Photoelectrocatalytic Degradation of Organic Pollutants in Aqueous Solution Using a Pt-TiO$_2$ Film

Chun He, Mudar Abou Asi, Ya Xiong, Dong Shu, and Xiangzhong Li

1 School of Environmental Science and Engineering, Sun Yat-sen University, Guangzhou 510275, China
2 Key Lab of Electrochemical Technology on Energy Storage and Power Generation in Guangdong Universities, School of Chemistry and Environment, South China Normal University, Guangzhou 510006, China
3 Department of Civil and Structural Engineering, The Hong Kong Polytechnic University, Hong Kong, China

Correspondence should be addressed to Chun He, hechun@mail.sysu.edu.cn

Received 1 April 2009; Accepted 27 June 2009

A series of Pt-TiO$_2$ films with nanocrystalline structure was prepared by a procedure of photodeposition and subsequent dip-coating. The Pt-TiO$_2$ 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$_2$ films was evaluated in the photocatalytic (PC) and photoelectrocatalytic (PEC) degradation of formic acid in aqueous solution. Compared with a TiO$_2$ film, the efficiency of formic acid degradation using the Pt-TiO$_2$ films was significantly higher in both the PC and PEC processes. The enhancement is attributed to the action of Pt deposits on the TiO$_2$ 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$_2$ films can further drive away the accumulated photoelectrons from the metal deposits and promote a process of interfacial charge transfer.

Copyright © 2009 Chun He et al. This is an open access article distributed under the Creative Commons Attribution License, which permits unrestricted use, distribution, and reproduction in any medium, provided the original work is properly cited.

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$_2$ 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$_2$ using the deposition of noble metals [7–10]. In these cases, a Schottky barrier between the metal and TiO$_2$ is formed, while both metal and TiO$_2$ Fermi levels equilibrate. Upon irradiation, the conduction band electrons flow from TiO$_2$ 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$_2$ [11, 12]. The reduction of organic pollutant is a process of increasing COD, generally unfavorable 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$_2$ deactivation by chlorine ions [13] because any species with a reduction potential more positive than the flat band potential of TiO$_2$ (∼−0.7 V versus SCE, at pH 7), in theory, can be reduced [14]. In fact, recently many authors have demonstrated
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 cm $\times$ 4.8 cm), dried 15 minutes on a hot plate at 100$^\circ$C and then vigorously agitated to form fine TiO$_2$ suspension. The resulting TiO$_2$ was immersed in a 40-mL aqueous solution containing H$_2$PtCl$_6$ (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 ($K\alpha_1, \lambda = 1.54056$ nm). Scanning electron microscope (SEM) images were obtained on a JSM-6330F-mode Field Emission Scanning Electron Microscope (JEOL, Japan). A UV-PC3101PC spectrophotometer (SHIMASU, 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 cm $\times$ 1.1 cm $\times$ 8.0 cm) connected via a salt bridge. When the PC reaction was conducted using the chamber

**Figure 1:** Schematic diagram of PC and PEC photoreactor systems.
A only, the PEC reaction was performed using both the chamber. 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 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.
3.2. Photoelectrochemical Characterization of Pt-TiO$_2$ Film.

The dependence of photovoltage of Pt-TiO$_2$ film on Pt content in N$_2$- or O$_2$-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$_2$ film, the photogenerated electrons accumulate in the TiO$_2$ 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 $V_{oc}$ of Pt-TiO$_2$ film in O$_2$-saturation solution is lower than that in N$_2$-saturated solution confirms the fact, due to the surface-adsorbed O$_2$ scavenging the photogenerated electrons in the O$_2$-saturated solution. In addition to the above evidence, it is noting that in either N$_2$- or O$_2$-saturated solution for Pt-TiO$_2$ film, $V_{oc}$ decreases with increase of Pt content. Generally, TiO$_2$ 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$_2$ reduction (1) and H$_2$ evolution (2):

\[
\text{O}_2 + e^- = 2O^{2-} \quad \text{(1)}
\]

\[
2H^+ + e^- = H_2 \quad \text{(2)}
\]

Figure 5 clearly shows that, after UV light turns off, the $V_{oc}$ of Pt-TiO$_2$ film decreases more rapidly than that of TiO$_2$ film, either for N$_2$-saturated solution or for O$_2$-saturated solution, suggesting that deposited Pt can facilitate the reactions of scavenging photogenerated electrons for Pt-TiO$_2$ film via the reactions (1) and (2).
accumulated electrons on Pt-TiO₂ film in the experimental (Figure 6) suggested that there are still rather remained amount.

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_{\text{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 \( V_{\text{oc}}(\text{O}_2)/V_{\text{oc}}(\text{N}_2) \) [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 trigger 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 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.
4. Conclusion

The feasibility of improving the PC activity of TiO\textsubscript{2} 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\textsubscript{2} 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\textsubscript{2} film towards the oxidation of formic acid were considerably dependent on the amount of deposited Pt. Compared with a TiO\textsubscript{2} film, the degradation efficiency of formic acid on the Pt-TiO\textsubscript{2} films increased markedly in both the PC and PEC oxidation processes.

Acknowledgments

The authors wish to thank for the financial support to this work from the National Natural Science Foundation of China (no. 20877025), the Specialized Research Fund for the Doctoral Program of Higher Education of China Education Ministry (no. 200805611015), and the Scientific Research Foundation for the Returned Overseas Chinese Scholars, State Education Ministry.

References


