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Photoelectrochemical performance of Ag–TiO_2/ITO film and photoelectrocatalytic activity towards the oxidation of organic pollutants

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Abstract

Ag–TiO_2 composite film was supported on indium–tin oxide glass (ITO) by a dip-coating and subsequent photodeposition procedure. The composite film was characterised by UV-Vis diffuse reflectance spectra, X-ray reflection diffraction (XRD) spectra, scanning electron microscope (SEM) and photoelectrochemical measurement. It was used as a photoanode in a two-compartment photoelectrochemical cell to investigate the feasibility of a hybrid technology of Ag deposition combined with the application of an external electric field. The experimental results show that the combination has an apparent additive effect with respect to suppressing the recombination between the photogenerated charge carriers and enhancing the photoelectrocatalytic (PEC) oxidation of formic acid. A primary approach to a pulse PEC technology presents the possibility that the Ag–TiO_2/ITO film electrode is performed at an anodic bias over the oxidation potential of the deposited Ag.

Keywords: Photoelectrochemistry; Photocatalysis; Ag deposition; TiO_2; Formic acid

1. Introduction

The widespread pollution of effluents from industries with biorecalcitrant organic pollutants demands an increase in effort towards the development of technologies for the cleanup of such wastewater [1]. In this field, heterogeneous photocatalytic (PC) process particularly with TiO_2 as photocatalyst has attracted considerable attention over last more than 10 years [2,3]. The appeal of this technology is the prospect of complete mineralisation of the pollutants into harmless compounds to environment in addition to the abundance and relatively low cost, chemical stability and non-toxic nature of the catalyst. However, the practical application of this technology has been limited due to its low PC efficiency [4,5].

The high degree of recombination between photogenerated electrons and holes is a major limiting factor controlling the PC efficiency [6]. In this regard, various attempts have been performed to improve the PC activity of TiO_2. One of them is associated with noble metal deposition. In this case, the deposited metal on the surface of TiO_2 can act as a sink for photoinduced charge carrier, promoting interfacial charge-transfer process. 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, beneficial to the PC oxidation of organic pollutants [6–9]; on the other hand, some photogenerated positive holes will be attracted by negative-charged metal particles, if the accumulated negative charges are not consumed or not further transferred out of the metal particles, becoming recombination centres [8]:

$$h^+ + e^-(\text{metal}) \rightarrow \text{N} + \text{energy} \qquad (1)$$

where N represents a neutral center. In fact, it has been reported that Pt/TiO_2 is less active than neat TiO_2 for the PC oxidation of liquid cyclohexane [10] and 4-chlorophenol [11]. Furthermore, the positive-charged holes, negative-charged metal particles and organic pollutants are in the same reaction system, as a result, it is possible that the pollutants and degraded intermediates are oxidised by the hole or reduced on the metal particles. For example, the reduction potential of methylene blue (MB), E^0_{red} is 0.011 V (NHE) [12], while the energy level of the conduction band for TiO_2 is $E_{\text{cb(e)}} = -0.5$ V (NHE) [13]. On this basis, MB is possibly photoreduced in the presence of TiO_2. Actually, recently Wang et al. [12] have observed the photoreduction of MB in the Au/TiO_2 system. This reduction

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is a process of increasing chemical oxygen demand (COD) in water, not beneficial to environmental protect.

In a single-crystal semiconductor-based photoelectrochemical cell, the problem of charge recombination can be overcome by applying a positive bias, as was first demonstrated by Fujishima and Honda [14]. Recently, it has been reported that the semiconductor films immobilised on conductive substrate provide also alternative way of manipulating the PC reaction by electrochemical methods. If one applies an external anodic bias to metal-loaded TiO_2 film, expectedly, the externally anodic bias potential on the illuminated metal-loaded TiO_2 film not only can drive away the accumulated photogenerated electrons on metal particles to another compartment of cell, reducing the electron–hole recombination and separating oxidation and reduction sites, but also can spatially separate the capture of conduction band electrons from the oxidation process [15]. Although the photoelectrocatalytic (PEC) degradation of organic pollutants has been carried out with a TiO_2 film [16–20], the PEC oxidation of organic pollutants on metal-loaded TiO_2 film has been rarely reported still to date. The above situation arouses our interests in investigating a hybrid technology associated with the combination of noble metal deposition with the application of external electric field in order to improve the efficiency of PC degradation of organic pollutants.

As a preliminary work, the present paper is mainly devoted to approaching photoelectrochemical performance of Ag–TiO_2 film immobilised on indium–tin oxide (ITO) glass, Ag–TiO_2/ITO, and its PEC activity towards the oxidation of organic pollutant, particularly, to the enhancement effect of external electric field on PC degradation of organic pollutant with Ag-loaded TiO_2 film. HCOOH was employed as a target chemical because it can be oxidised to CO_2 without forming any intermediates and no homogeneous reaction occurs in the range of UV light employed in these studies (300–400 nm) [21]. Furthermore, formic acid also exists in some actual industrial wastewater such as effluents from tanners, dye workshops, and printed fabrics mills [22].

2. Experimental details

2.1. Material

The photocatalyst is titanium dioxide (Degussa P25) with a surface area of 50 $m^2 g^{-1}$. Formic acid was prepared with deionised water to 10 mmol l^{-1} (COD: 157 ppm). ITO glass plates (1.3 mm thick, 30.4 cm × 40.4 cm, 2 Ω cm^{-2}) were obtained from Shenzhen Nanya Technology Co. Ltd., PR China.

2.2. Preparation of ITO glass-supported TiO_2 film electrode

The TiO_2/ITO film was prepared using a procedure similar to that reported in [23]. An aqueous suspension of TiO_2 (80.0 g l^{-1}) was agitated and sonicated 30 min before coating ITO glass pieces. The titania suspension was loaded on one side of the ITO glass pieces (12 cm × 4.8 cm), dried 15 min on a hot plate at 100 °C and then sintered 2 h in an oven at 400 °C. Loading, drying and sintering was repeated three times. The quantity of TiO_2 was about 0.94–1.00 mg cm^{-2}. The thickness of TiO_2 film was estimated from scanning electron microscope (SEM) image to be about 2–3 μm.

2.3. Preparation of Ag-deposited TiO_2/ITO film

A method of photochemical deposition was employed to prepare Ag–TiO_2/ITO film electrode. The glass plate with TiO_2/ITO film was immersed in a 40 ml solution containing formic acid (10 mmol l^{-1}) and $AgNO_3$ (2 mmol l^{-1}) and subjected to an illumination of UV light for certain time, resulting in an Ag-loaded TiO_2/ITO film.

2.4. Apparatus

A UV-PC3101PC spectrophotometer (SHIMAZU, Japan) with an integrating sphere (Specular Reflectance ATT.5DEG) was used to directly record the diffuse reflectance spectra of the ITO glass with TiO_2 film. The base line correction was done using a calibrated sample of barium sulphate. The same spectrophotometer was used for recording the UV absorption spectra of solution. SEM images were obtained on a JSM-6330F-mode Field Emission Scanning Electron Microscope (JEOL, Japan). X-ray reflection diffraction (XRD) was performed using D/Max-IIIA Diffractometer (Rigaku Corporation, Japan) with Radiation of Cu target ($K \propto 1$, $\lambda = 1.54056$ nm). ICP analysis was performed on IRIS Advantage (HR).

2.5. Analysis

COD was measured with potassium dichromate after the sample was digested with a WMX COD microwave digestion system [24]. Ag^+ determination was carried out by ICP technology. Photoelectrochemical measurement was performed with a Model CH 650 potentiostat.

2.6. PC set-up

The schematic diagram of the PC apparatus is presented in Fig. 1. The apparatus consists of four parts, a 500 W high-pressure mercury lamp, a double-welled quartz glass cooling tube with a 5.0 mm-thick cooling water, a batch quartz glass reactor (5.8 cm × 0.8 cm × 13 cm) open to air and the Ag–TiO_2/ITO glass plate. The UV lamp was suspended vertically in the cooling tube with a cooling water flow (650 ml min^{-1}) to maintain reaction isothermality. The circulating water also ensured infrared filtering of the incident ray. The Ag–TiO_2/ITO glass plate was immersed in the reactor, located 2.0 cm in front of the UV lamp.

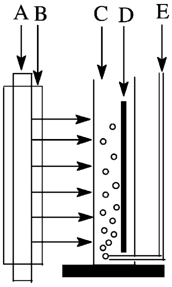

Fig. 1. Schematic diagram of PC set-up. (A) 500 W high-pressure mercury lamp; (B) double-welled quartz glass cooling tube with a 5.0 mm-thick cooling water; (C) batch quartz glass reactor (5.8 cm × 0.8 cm × 13 cm); (D) ITO glass plate with Ag–TiO_2 film; (E) inlet of compressed air.

PEC experiment was conducted in a two-compartment (anodic and cathodic compartment) reactor connected via a salt bridge. The above PC apparatus was used as the photoanodic compartment of the PEC reactor while the cathodic compartment is a plastic container whose size and shape is identical to the anodic compartment. A Pt electrode and saturated calomel electrode (SCE) were used as a counter and reference one, respectively.

2.7. *Experimental procedure*

2.7.1. *PC process*

Prior to starting PC reaction, a 35 ml solution of 10 mmol l^{-1} formic acid was fed into the photoreactor, and then Ag–TiO_2/ITO plate was immersed in the solution. The reactor was timed starting when illumination and compressed air supply were switched on. Except as indicated, general treating conditions were 50 l h^{-1} airflow and 60 min for a batch run. The resulting solution was remained for optical absorption and COD analysis.

2.7.2. *PEC process*

The experiment detail is similar to that of the above photocatalysis but an anodic bias was applied to the TiO_2 film electrode in the two-compartment PEC reactor.

3. Results and discussion

3.1. *Ag photodeposition on TiO_2/ITO film*

The photodeposition of silver under an oxygen atmosphere has been carried out by several authors and the resulting samples with various colours have been reported [8,25–27]. In our experiment, the colour of TiO_2/ITO film changed from white to brown during illumination. The XRD pattern of the brown material mixed TiO_2 is shown in Fig. 2. The characterization of the XRD identifies that the brown material is metallic silver. This process of Ag photodeposition on TiO_2/ITO film was monitored using UV diffuse reflectance spectra. As shown in Fig. 3, the diffuse reflectance peak of the TiO_2 film at 406.5 nm rapidly decreases with the progress of PC reaction. After a 0.5 min reaction, its hypochromicity rate reaches 69%. Simultaneously, two new peaks appear in the range of visible (608.6 nm) and UV (349.0 nm) light, respectively, and a well-defined *iso*-isosbestic point is observed at 325.3 nm with the proceeding of reaction. These new peaks can be attributed to the diffuse reflectance spectra of deposited Ag on the surface of TiO_2 film. After 5 min, the diffuse reflectance peak of the TiO_2 film completely disappeared and whole spectrum fully characterised the diffuse reflectance of deposited Ag. SEM image (Fig. 4) of the film seems to indicate that the considerable surface of TiO_2 film is uncovered by these Ag particles (about 100–200 nm) even after 20 min deposition. However, it cannot be ruled out that some Ag particles are too small to be observed at the resolution of the used microscope.

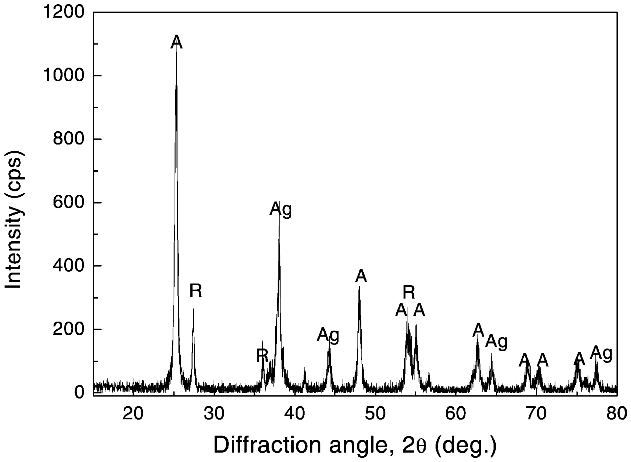

Fig. 2. XRD spectrum of the sample from Ag-deposited TiO_2 film (A: anatase, R: rutile).

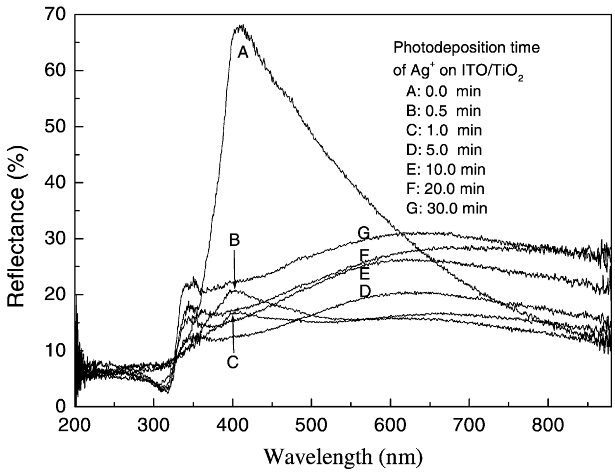

Fig. 3. Change of diffuse reflectance of TiO_2 film with time of Ag deposition.

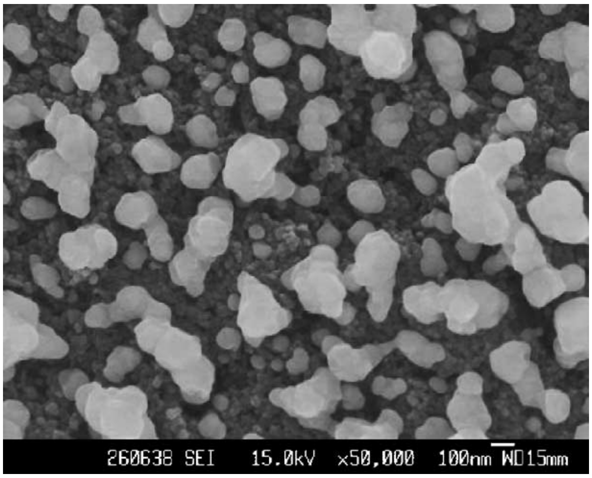

Fig. 4. SEM image of the surface of Ag-deposited TiO_2 film by a 20 min photodeposition.

3.2. Open circuit photovoltage

Although the photoelectrochemical performances of metal-loaded TiO_2/ITO film, such as Pt– and Au–TiO_2/ITO films, etc. have been investigated by several groups, very few studies concerned the Ag-loaded TiO_2/ITO films [8,28]. As a sequence, the Ag–TiO_2/ITO film is photoelectrochemically characterised in this context, prior to probing its catalytic activity towards photoelectro-oxidation of organic pollutants.

The dependence of open circuit voltages on deposited amount of Ag in N_2- and O_2-saturated solution containing 10 mmol l^{-1} HCOOH and 0.1 mol l^{-1} Na_2SO_4 are presented in Fig. 5. Generally, the magnitude of V_{oc} represents the energy difference between the Fermi level of semiconductor film and the reduction potential of the redox couple in the solution. In dark, the Fermi level of a semiconductor film equilibrates with the redox couple in solution; upon illumination of the film with bandgap excitation, the photogenerated electrons accumulate in the film, leading to a shifting of Fermi level to more negative potential. As a result, any accumulation of electrons in the film will present a greater shift in V_{oc}. The scenario was observed in our experiments. For the N_2-saturated solution, a small increase in V_{oc} is observed when Ag nanoparticle deposition increases up to about 0.36 wt.% (Ag/TiO_2). After then, V_{oc} decreases apparently, leading a highest V_{oc} of 0.52 V. The increase is consistent with the fact that Ag nanoparticles is highly electronegative as the Fermi level can be shifted to negative potentials with chemical modification or charging effect [29], while the decrease can be attributed to the absorption or/and block of incident light by Ag nanoparticles on the surface of the film, as shown in Fig. 3. The highest V_{oc} represents a balance result of above two effects. In other words, the amount of the deposited Ag, 0.36%, corresponding to the highest V_{oc}, can be optimal, simultaneously considering the roles of deposited Ag and the exposed surface of TiO_2. For the O_2-saturated solution, the V_{oc} is much lower than that for N_2-saturated solution and decreases rapidly with increasing the Ag-deposited amount, as shown in Fig. 5. This result is associated with O_2 scavenging the photogenerated electrons followed by decreasing accumulated electron on the Ag–TiO_2/ITO film, in addition to the block of incident light by Ag particles. This aspect was shown more clearly in Fig. 6. The open circuit voltage decays rapidly with time in O_2-saturated solution, after light is turned off, while it decreases rather slowly in the absence of O_2.

According to Chandrasekharan and Kamat's view [30], the difference between the two open circuit voltages in N_2- and O_2-saturated solutions, $[V_{oc}(N_2) - V_{oc}(O_2)]$, is directly proportional to the fraction of electrons that can be scavenged by O_2 in the system. It is seen from the curve A of Fig. 7 that the difference was increased by two times following increasing Ag deposition from 0.0 to 4.6% on the TiO_2 film. Thus, we can derive from the figure that the deposition of Ag has positive effect on the scavenging of the

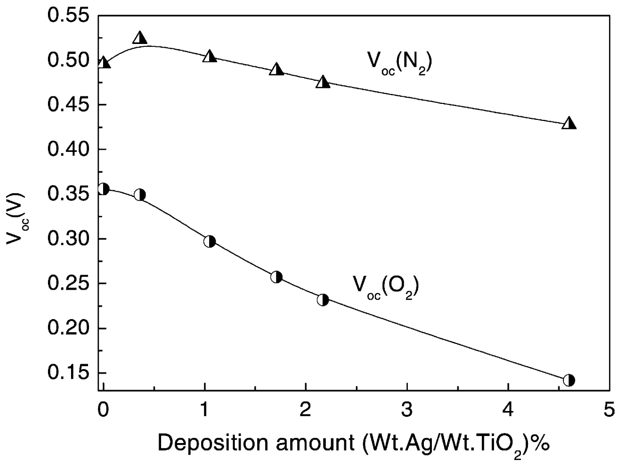

Fig. 5. Change of open circuit voltage (V_{oc}) of Ag–TiO_2/ITO with deposited Ag amount ($V_{oc}(N_2)$: for N_2-saturated solution; $V_{oc}(O_2)$: for air-saturated solution).

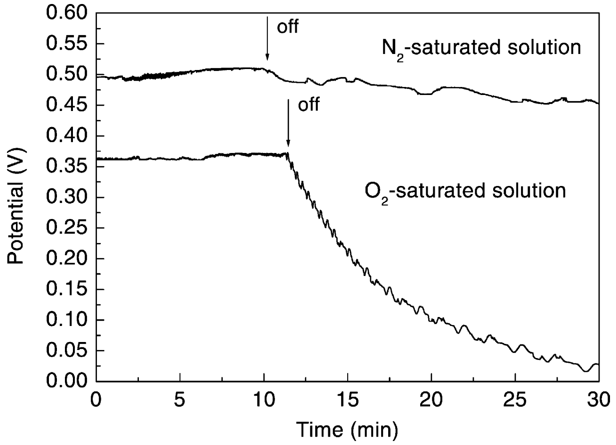

Fig. 6. Decay curves of open circuit voltage after light is turned off.

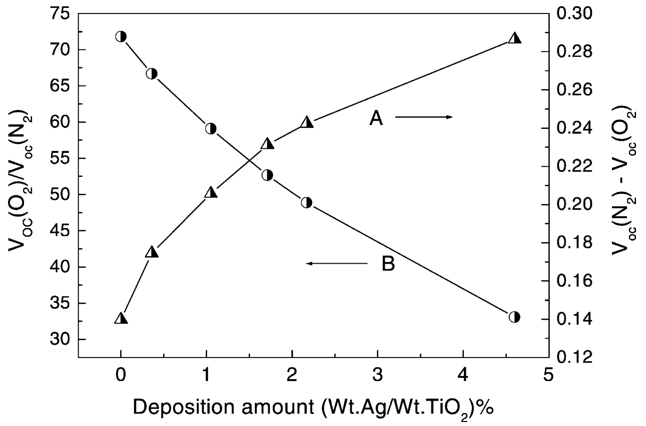

Fig. 7. Dependence of $[V_{oc}(O_2)/V_{oc}(N_2)]$ or $[V_{oc}(N_2) - V_{oc}(O_2)]$ on deposited Ag amount (A: $[V_{oc}(N_2) - V_{oc}(O_2)]$; B: $[V_{oc}(O_2)/V_{oc}(N_2)]$).

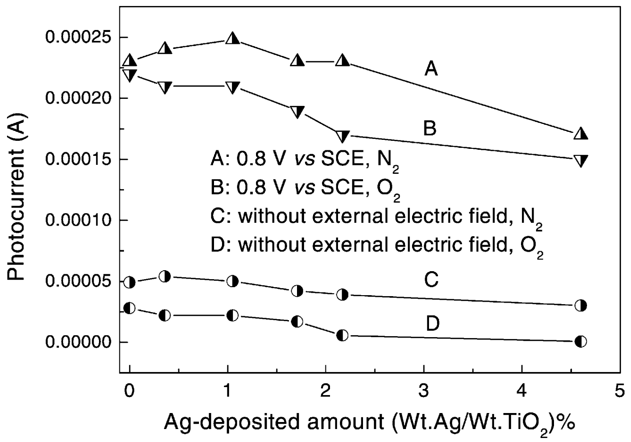

Fig. 8. Short-circuit current vs. deposited Ag amount.

photogenerated electrons by O_2. Generally, this scavenging was followed by the increase of the photogenerated holes and $O^{\bullet -}$ radicals by the following reaction:

$$O_2 + e \rightarrow O^{\bullet -} \quad (2)$$

Both the generation of the hole and $O^{\bullet -}$ radicals are beneficial to the oxidation of organic pollutants, however, we still cannot infer, according to the above observation, that the more the deposited Ag, the higher the oxidation efficiency of organic pollutants because Ag deposition has also a negative effect on PC reaction, blocking UV light, leading to the decrease in total illumined area of TiO_2 film. Noticeably, if $V_{oc}(N_2)$ represents the maximum accumulation of the electrons, $[V_{oc}(O_2)/V_{oc}(N_2)]$ is the fraction of the remained photogenerated electrons after the electrons are partly scavenged by O_2. From curve B of Fig. 7, it can be concluded that there are still rather remained electrons on Ag–TiO_2/ITO film in the experimental range although Ag deposition can promote the efficiency of O_2 scavenging the electrons. For example, for TiO_2/ITO film with 0.36% deposited Ag, the fraction of the remaining electrons is 67%. Therefore, it is reasonable to employ an anodic bias to drive away the remaining accumulation electrons in order to increase PC efficiency, as mentioned previously.

3.3. Short-circuit current

The dependence of short-circuit current on the amount of the deposited Ag is presented in Fig. 8. Basically, the photocurrent decreases with increasing Ag amount. Simultaneously, it is also seen that the application of anodic bias can considerably increase the short-circuit current. For example, for the Ag–TiO_2/ITO film with the Ag-deposited amount of 1.1% in the N_2-saturated solution, the photocurrent in the presence of an anodic bias of 0.8 V versus SCE is increased by five times compared with that in the absence of external electric field. The fact shows again that, even in the presence of deposited Ag, the anodic bias can also drive away the photogenerated charge carriers in different directions followed by a decrease in the recombination of hole and electron. On the other hand, it can be also seen from the figure that the photocurrent for the O_2-saturated solution is apparent lower than that for the N_2-saturated solution in the presence of 0.8 V versus SCE anodic bias. The difference between them is more apparent due to the Ag deposition. Obviously, the change denotes that the deposited Ag can enhance the role of O_2 scavenging the photogenerated electrons. As a result, it is expected that, even in the presence of the external anodic bias, Ag deposition will be also beneficial to the PC oxidation of organic pollutant.

3.4. Dependence of COD removal efficiency on Ag-deposited content

Fig. 9 presents the dependence of COD removal efficiencies on the amount of deposited Ag in PC and PEC processes, respectively. It can be seen from the figure that PC and PEC activities are strongly dependent on the amount of deposited silver. The lower load of Ag can increase the COD removal efficiencies for either PC or PEC processes, while

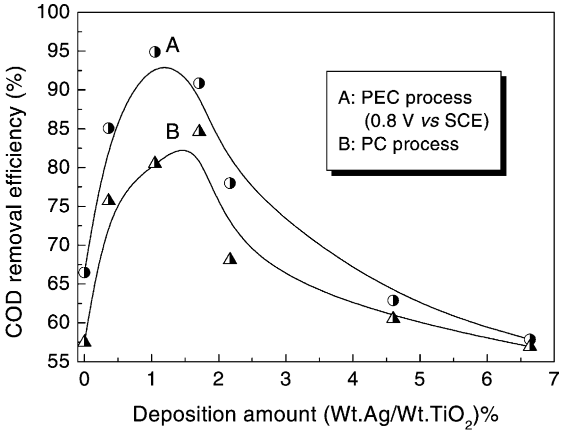

Fig. 9. Dependence of COD removal efficiency on deposited Ag amount.

higher load of Ag decreases the COD removal efficiencies of the two processes due to the blocking of UV light by the over-coated Ag grains, similar to the result reported by Kim and Anderson [21]. Although the two curves have a similar change tendency, the following two differences are also observed.

Firstly, the COD removal efficiency for PEC process is apparently higher than that of pure PC process on either neat TiO_2 film or Ag-loaded TiO_2 film. For example, in the absence of Ag, the COD removal efficiency of the former is 66.5% while the latter is only 57.5%. For Ag-loaded TiO_2 film with an Ag-loaded amount of 1.1 wt.% (Ag/TiO_2), the COD removal efficiency of the former is 94.9% while the latter is 80.4%. The difference of COD removal efficiencies is 14.5%, higher than that for neat TiO_2 film (9%), indicating that the enhancement effect of the external electric field in the presence of Ag is more obvious than in the absence of Ag. This more obvious enhancement effect denotes that deposited Ag can not only trap the photogenerated electrons but also assist the external electric field to migrate them from the TiO_2 film anode to counter electrode in another compartment of the cell.

Secondly, the optimal amount of loaded Ag for PEC process is deferent from that for the PC process. The former is 1.1% while the latter is 1.7%. As a result, only in view of the less Ag-deposited need, the photoelectrochemical process is more attractive for practical application. In addition, our all the following experiments were conducted using the Ag–TiO_2/ITO film with deposited Ag content of 1.1%.

3.5. Effect of applied anodic bias on COD removal efficiency

Fig. 10 presents the COD removal efficiencies of PEC processes in 60 min on TiO_2/ITO or Ag–TiO_2/ITO film electrodes at various applied anodic biases. It can be seen from the figure that the two curves exhibit a different change tendency. With respect to PEC process on TiO_2/ITO film electrode, the COD removal efficiencies increase with increasing applied anodic bias below 4.2 V, and then, reach an approximate flat. Compared with the COD removal efficiency at the condition of open circuit, the COD removal efficiency increases from 57 to 77.6%. The dependence of COD removal efficiency on applied anodic bias is similar to that reported by Kim and Anderson [31]. However, other authors have reported conflicting results that the rate of oxidation of organic pollutants on TiO_2/ITO film electrode increased with increasing anodic potential [18,32]. With respect of PEC process on Ag–TiO_2/ITO film electrode, the COD removal efficiency increases rapidly with increasing applied voltage. At 0.8 V, it reached a maximum value, 94.9%, and then, gradually decreased. In the absence of illumination, negligible electrochemical oxidation of formic acid on the two film electrodes was observed in the range of 0.0–9.1 V versus SCE. As a result, the above enhancement in COD removal efficiency can be ascribed to that the externally applied anodic bias drives away the accumulated electrons on Ag particles via the external circuit, thus promoting the oxidation of formic acid. The decrease in COD removal efficiency at higher applied voltage was supposed to be an electrochemical oxidation of Ag, dissolving from TiO_2 film. The assumption was verified by the following ICP analysis of the treated solution. For example, when an anodic bias of 9.1 V was applied for 60 min, Ag^+ ions of 10^{-7} mol l^{-1} were found in the treated solution. Regarding this fact, a suitable applied voltage should be carefully selected when one actually applies the PEC process on the Ag–TiO_2/ITO film electrode to degrade organic pollutants.

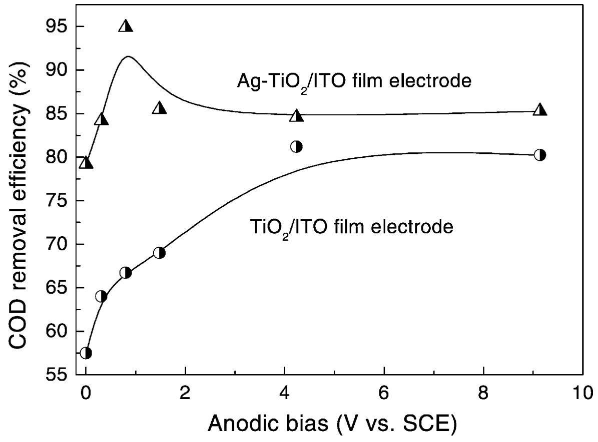

Fig. 10. Dependence of COD removal efficiency on anodic bias.

In addition, compared with the two curves in Fig. 10, it was found that COD removal efficiency of Ag–TiO_2/ITO film electrode is always higher than that of TiO_2/ITO film electrode in the whole range of the studied applied voltages, further indicating that, totally, the deposited Ag on TiO_2/ITO film is beneficial to PEC oxidation of formic acid.

Another interesting observation is that the optimal applied anodic bias of Ag–TiO_2/ITO is different from that of TiO_2/ITO film electrodes. The former is ca. 0.8 V, much less than that of the latter (ca. 4.2 V). This fact shows that a lower anodic bias for Ag–TiO_2/ITO provides enough band bending to withdraw electron to the counter electrode, implying that the existence of Ag on TiO_2/ITO improving the conductivity of the film.

3.6. Rates of COD reduction for various processes

The curves of COD reduction for different processes are compared in Fig. 11. The rate constant for the COD reduction was determined from the pseudo-first-order kinetic analysis of the figure. As shown in Table 1, the order of the rate constants for the four catalytic processes is (d) > (c) > (b) > (a). The PEC process using Ag–TiO_2/ITO electrode can more efficiently degrade formic acid than the other processes. Its rate constant is three times more than that for the PC oxidation on TiO_2/ITO film. Obviously, the combination of the Ag deposition and the application of anodic bias has

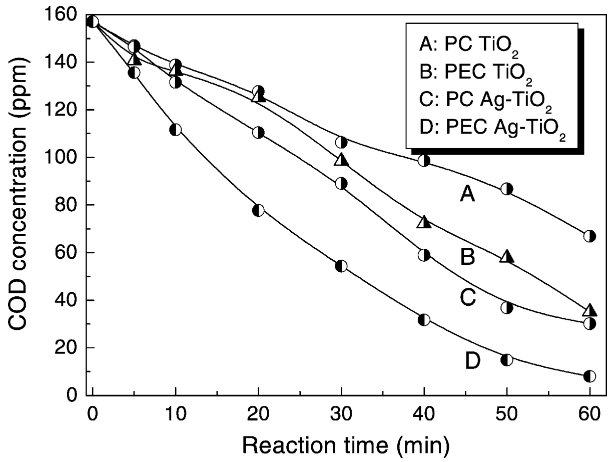

Fig. 11. Kinetic curves of COD removal for various processes.

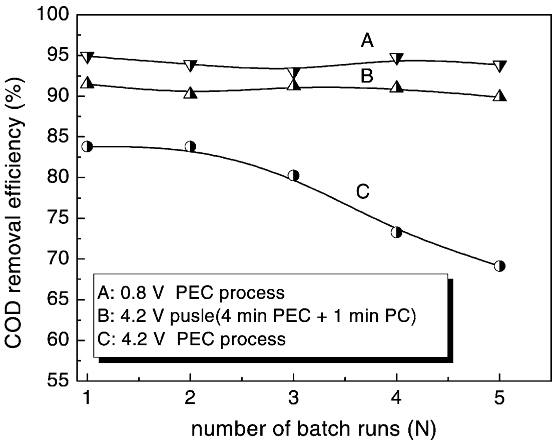

Fig. 12. Change of COD removal efficiency in the process of repeated use.

a considerably beneficial effect to enhancing the rate of the PC degradation of formic acid. Upon close examination of these values, it is found that the rate constant for the PEC process on Ag–TiO_2/ITO film electrode (0.05 min^{-1}) is basically a simple sum of rate constants for the individual PC process on Ag–TiO_2/ITO film (0.028 min^{-1}) and PEC process on TiO_2/ITO film electrode (0.023 min^{-1}). As a result, one can infer that the enhancement observed in the combined methods is an additive effect, consistent with the photoelectrochemical performance observed previously. However, the additive effect will be more important when one considers the need for degradation of some organic pollutants that are usually recalcitrant to electrochemical or heterogeneous PC treatments.

3.7. Performance of Ag–TiO_2/ITO film in the process of repeated use

The above discussions are only based on one time run for an Ag–TiO_2/ITO film. From the view of actual application, an important question to be answered is whether the repeated use of the film electrode affects the PC activity of the film or whether there is the possibility of re-oxidation and dissolving of the deposited Ag by external anodic bias. To make clear the issues, the Ag–TiO_2/ITO film electrode was repeatedly used to treat the formic acid solution.

These experimental results are presented in Fig. 12. It is seen from the figure that the COD removal efficiencies basically remains unchanged in the process of five-time batch runs when an anodic bias of 0.8 V versus SCE is applied. However, in the presence of 4.2 V versus SCE anodic bias, the COD removal efficiencies decrease apparently during successive batch run. In the resulting solution of the fifth run for the former process, no Ag^+ ion was observed with ICP analysis while Ag^+ ions of 10^{-8} mol l^{-1} was found in the resulting solution of the fifth run for the latter process. These facts suggest that the oxidation of Ag can be negligible for PEC process in the presence of 0.8 V versus SCE anodic bias while an anodic bias of 4.2 V versus SCE can oxidize the deposited Ag on TiO_2/ITO film electrode. Obviously, the above decrease of COD removal efficiency can be attributed to the electro-oxidation and dissolving of the deposited Ag under a higher anodic bias.

Table 1
Comparison of rate constants *k* value calculated based on the assumption that both PC and PEC (0.8 V) processes follow the first-order reaction

Catalytic films	Catalytic processes	Rate constants *k* (min^{-1})	Correlation coefficients (*R*)
TiO_2/ITO	(a) PC process	0.013	0.9893
	(b) PEC process	0.023	0.9674
Ag–TiO_2/ITO	(c) PC process	0.028	0.9857
	(d) PEC process	0.050	0.9885

It is well known that Ag^+ ions are easily photoreduced, and even its photoreduction activity is higher than Au^{3+} with a higher redox potential ($E^0_{Ag^+/Ag} = 0.7995$ V; $E^0_{Au^{3+}/Au} = 1.50$ V) [33]. The fact encouraged us to test a pulse PEC technology that PEC and PC processes are alternately conducted at regular intervals, in which the oxidised Ag^+ ions are expected to be re-photoreduced to Ag on the TiO_2 film in the PC process in order to tackle the problem associated with Ag re-oxidation at higher anodic bias. The curve B of Fig. 12 gives the result of the pulse PEC experiment that 4 min PEC process and 1 min PC process were alternately conducted. The COD removal efficiency is much higher than that of PEC process with a constant anodic bias (curve C), furthermore, no apparent decrease in COD removal efficiency in the repeated batch runs was observed. It is easily seen from the concerning morphology of Ag–TiO_2/ITO film (Fig. 13) why the COD removal efficiency can remain basically constant. Compared with Fig. 13a–c, it is found that there are few greater Ag particles remaining on the TiO_2/ITO film after five-time repeated runs in the presence of a constant 4.2 V versus SCE while the greater Ag particles on the Ag–TiO_2/ITO film after five-time pulsed-PEC runs were similar to that on the fresh Ag–TiO_2/ITO film.

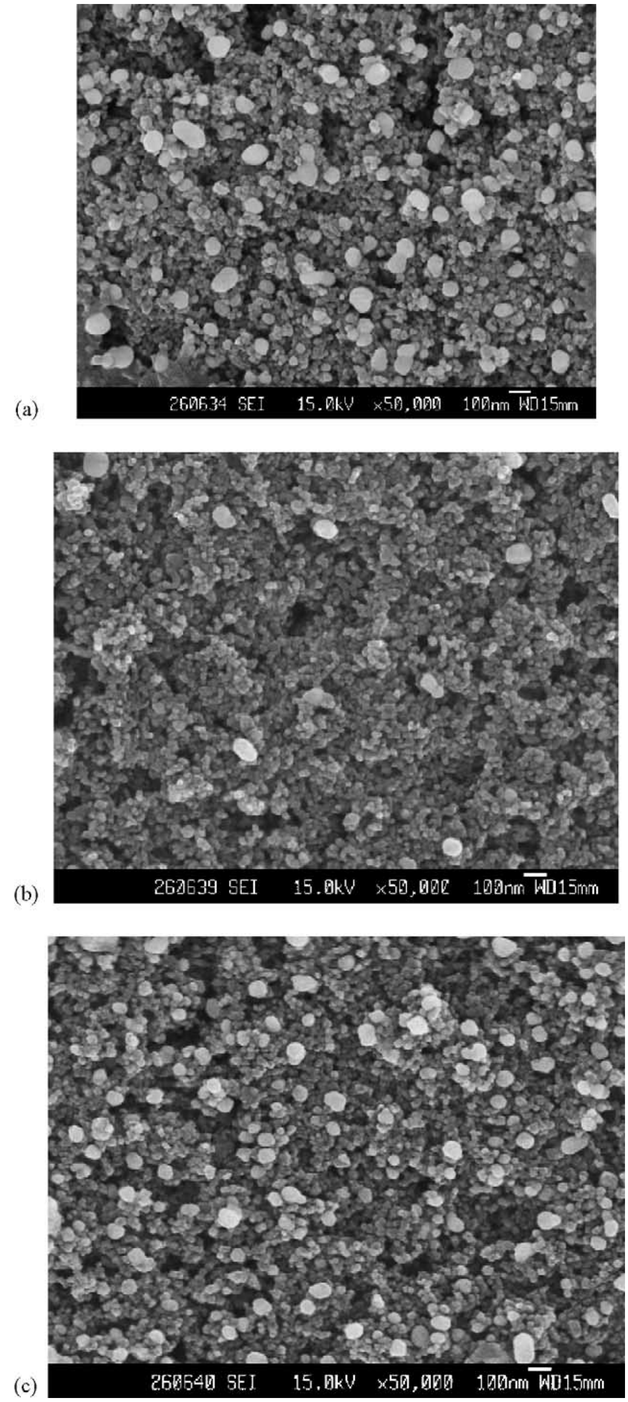

Fig. 13. SEM images of the surface of Ag–TiO_2/ITO film: (a) Ag–TiO_2/ITO film with 1.1 wt.% Ag (Ag/TiO_2); (b) after being used five times at 4.2 V vs. SCE anodic bias; (c) after being used five times by pulse PEC process.

The former can be caused by the oxidation of deposited Ag to dissolving Ag^+ ions under the higher anodic bias; the latter can be attributed to the re-photoreduction of the oxidised Ag^+, as expected. The result presents a possibility that the metal-deposited film can be repeatedly used at a higher anodic bias. However, the above results are only based on a primary investigation on this pulse PEC technology, a thorough research about the technology is proceeding.

4. Conclusions

The feasibility of a hybrid technology of Ag deposition combined with the application of an external electric field was investigated in order to improve the PC activity of TiO_2 film towards the oxidation of organic pollutant. The following conclusions were derived from the investigation.

(1) With respect to Ag–TiO_2/ITO film electrode, its photoelectrochemical performance and the PEC activity towards the oxidation of formic acid was considerably dependent on the amount of deposited Ag.
(2) There are still rather remaining accumulated electrons on Ag–TiO_2/ITO film in the experimental range although Ag deposition can increase the efficiency of O_2 scavenging the electron. As a result, it is reasonable to employ an anodic bias to drive away the remained accumulated electrons in order to increase PC efficiency.
(3) The combination of deposited Ag and applied anodic bias have an apparent additive effect with respect to suppressing the recombination between the photogenerated charge carriers or enhancing the PC oxidation of formic acid.
(4) A primary approaching to a pulse PEC technology presents the possibility that the Ag–TiO_2/ITO film electrode can be performed at an anodic bias over the oxidation potential of the deposited Ag in the process of repeated use.

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