

Preparation of TiO₂/ITO film by liquid phase deposition and its photoelectrocatalytic activity for degradation of 4-aminoantipyrine

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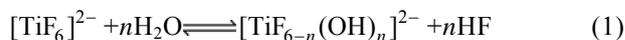
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Abstract: A thin layer of TiO₂ film was deposited on ITO surface via the liquid phase deposition (LPD) process. The photocurrent and electrochemical impedance spectroscopy (EIS) measurements indicated that the as-prepared LPD TiO₂/ITO film had an excellent photoelectrochemical performance, which showed a sensitive and rapid response to the UV irradiation. The photogenerated electron-hole pairs could be effectively separated by applying an external bias to the TiO₂ film electrode. The LPD TiO₂/ITO film was employed to study the photoelectrocatalytic (PEC) degradation of 4-aminoantipyrine. Compared with other techniques, the PEC technique based on such a LPD film electrode had a synergetic effect for 4-aminoantipyrine degradation. When the applied bias potential was +0.8 V and the supporting electrolyte concentration of Na₂SO₄ was 0.1 mol/L, the highest degradation efficiency within 120 min could reach 95% for 0.1 mmol/L 4-aminoantipyrine solution at pH 2.0.

Key words: liquid phase deposition; TiO₂ film electrode; photoelectrocatalysis; 4-aminoantipyrine

1 Introduction

As one of the most important advanced oxidation techniques for degrading non-biodegradable pollutants, photoelectrocatalysis (PEC) has been the active research field in environmental science. In PEC, TiO₂ film electrodes have been extensively utilized [1], due to the high photocatalytic activity and excellent stability of TiO₂ catalyst. There have been many methods for the preparation of TiO₂ films, such as sol-gel [2,3], microplasma oxidation [4], plasma surface alloying technique [5], magnetron sputtering [6,7], atomic layer deposition [8], metal-organic chemical vapor deposition [9] and electrochemical anodic oxidation [10]. DEKI et al [11] developed a new wet-chemical method, namely, liquid phase deposition (LPD), for the preparation of TiO₂ film. In this method, substrate is immersed in aqueous solution of (NH₄)₂TiF₆, followed by adding H₃BO₃ solution. After a period of reaction time, a layer of TiO₂ film can be deposited on the substrate surface according to the following reactions.



Compared with the traditional methods for the preparation of TiO₂ film, such a LPD technique has many advantages, such as simplicity, flexibility, low cost and no requirement of special device or substrate. Thus, LPD technique has been widely studied and utilized [12]. In the PEC degradation of pollutant, HOU et al [13] prepared TiO₂ film on active carbon fiber by the LPD process, which has been successfully applied to the removal of acid orange II. DING et al [14] prepared LPD TiO₂ film on glassy carbon electrode surface for the PEC degradation of benzotriazole.

Pharmaceuticals and personal care products (PPCPs) have been recently detected in environmental system and recognized as emerging contaminants. Because many PPCPs have the properties of good water solubility, high biological activity, high polarity, optical rotation and non-volatility, which threaten the safety of environmental eco-system and the health of human beings, the environmental problems of PPCPs have received

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considerable attention [15]. How to dispose such emerging contaminants has been an important content of environmental research [16]. 4-aminoantipyrine is a derivative of antipyrine. It is also the metabolic intermediate of dipyrrone, one of the most widely used analgesic and antipyretic medicine. Because 4-aminoantipyrine is not completely removed by the traditional biochemical process in the wastewater treatment plants, it appeared in water environment as one of the most frequently detected PPCPs [17]. The recent report has demonstrated that the technique of UV/H₂O₂ could provide high degradation efficiency for 4-aminoantipyrine [18]. However, in the UV/H₂O₂ process, large amount of H₂O₂ is consumed. It is necessary to add H₂O₂ every some period of treatment time to maintain the high degradation efficiency. In the present work, we utilized optically transparent ITO electrode as substrate to deposit TiO₂ film by the LPD process. The photoelectrochemical measurements indicated that the obtained TiO₂/ITO film electrode had high PEC activity. Considering that TiO₂/ITO film electrodes were useful to eliminate organic contaminants in wastewater [19,20], the as-prepared LPD TiO₂/ITO film electrode was employed to systematically study the PEC degradation of 4-aminoantipyrine. The results showed that such a LPD TiO₂/ITO film electrode could provide high PEC degradation efficiency for 4-aminoantipyrine under optimized conditions.

2 Experimental

2.1 Preparation of TiO₂/ITO film

The TiO₂ films were prepared on ITO (In₂O₃:Sn) conducting glass (10–15 Ω/□, 2 mm thick, 2 cm×2 cm) by the LPD process. Before deposition, ITO was cleaned by sonication in ethanol and water for 10 min. After being dried with a stream of high purity nitrogen gas, the ITO substrate was soaked vertically into the mixed aqueous solution of 0.1 mol/L (NH₄)₂TiF₆ and 0.3 mol/L H₃BO₃ at 50 °C for 10 h. After being cleaned with water and dried with nitrogen, the film was calcinated under 350 °C for 1 h.

2.2 PEC degradation of 4-aminoantipyrine

The PEC degradation of 4-aminoantipyrine was performed in a cylindrical reactor containing 150 mL 4-aminoantipyrine solution. A 15W low pressure UV lamp with a major emission wavelength of 254 nm was used as the illumination resource, which was protected in a quartz tube and then inserted into the center of the degradation solution. The PEC degradation experiments were controlled with a CHI660A electrochemical workstation (Shanghai Chenhua Instrument Co., China) using conventional three-electrode system. A TiO₂/ITO

film electrode, a platinum plate and a saturated calomel electrode (SCE) were inserted into the reactor to be employed as the working, counter and reference electrodes, respectively. The distance between the UV lamp and TiO₂/ITO film was about 2 cm. During the degradation experiments, air was purged into the solution using an air pump with the flow rate of 3.0 L/min.

2.3 Characterization and analytical methods

The surface morphology of the TiO₂ film was characterized with a field emission scanning electron microscopic (SEM) instrument (JSM-7400F, JEOL, Japan). The X-ray diffraction (XRD) analysis was carried out in an X'Pert PRO diffractometer (PANalytical B.V., Netherlands) using Cu K_α radiation. The concentration of 4-aminoantipyrine was analyzed at the maximum absorption wavelength of 4-aminoantipyrine at 243 nm (Fig. 1) with a UV-visible spectrometer (WFZ UV-2000, Unico Instruments Co., Ltd., Shanghai, China).

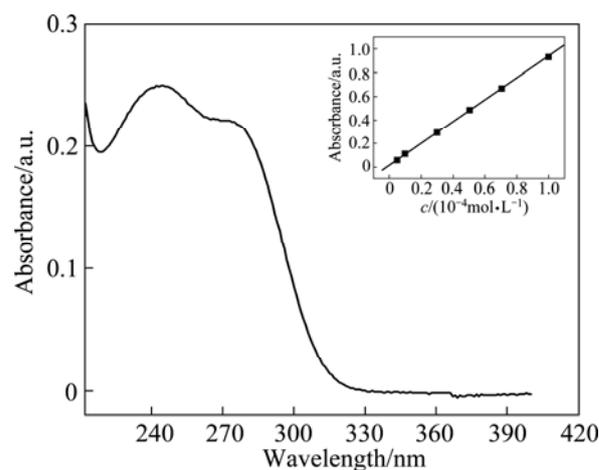


Fig. 1 UV-visible spectrum of 1.0×10^{-4} mol/L 4-aminoantipyrine (Inset: Linear relationship between absorbance at 243 nm and concentration of 4-aminoantipyrine)

3 Results and discussion

3.1 Surface characterization of LPD TiO₂ film

To characterize the TiO₂ film deposited on the ITO surface by the LPD process, the obtained film was observed by SEM. From Fig. 2, it is clearly observed that a layer of compact film is formed on the surface of ITO, which is similar to the LPD film prepared on the glassy carbon surface [14]. However, there appear many cracks in the film due to the internal stress of film during the drying process. The thickness of the deposited TiO₂ film is ca. 400 nm, measured at cross-section of the film by SEM (Fig. 2(b)). The XRD analysis (Fig. 3) for calcinated film confirms that the LPD film is composed of TiO₂ (anatase) particles [14].

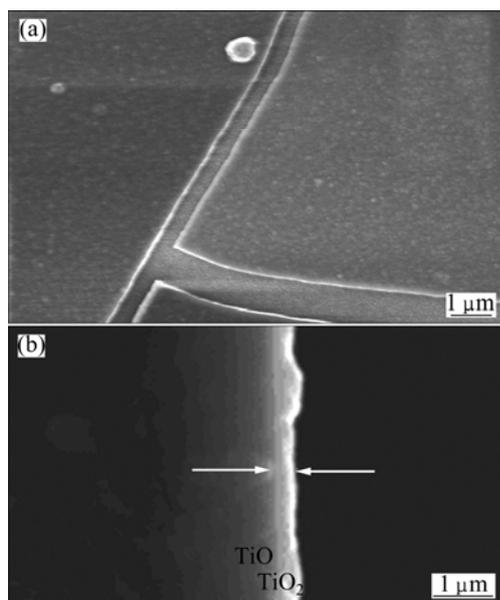


Fig. 2 Surface (a) and cross-section (b) SEM images of LPD TiO₂/ITO film

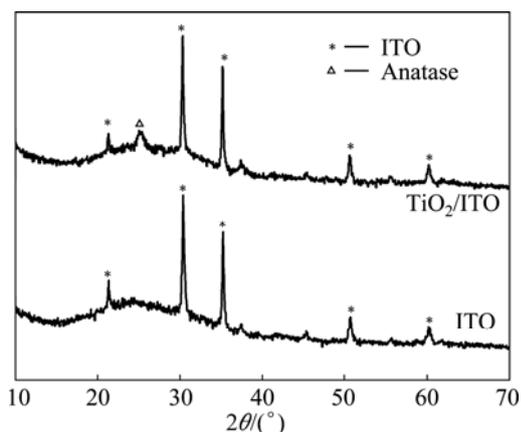


Fig. 3 XRD patterns of TiO₂/ITO film and ITO substrate

3.2 Photoelectrochemical property of TiO₂/ITO film

Figure 4 shows the photocurrent response of TiO₂/ITO film electrode at 0.8 V under UV irradiation. As can be seen, the LPD TiO₂ film electrode shows a fast and sensitive photochemical response to the UV light irradiation. The dark current without UV irradiation is only 8×10^{-8} A; whereas under UV irradiation, the photocurrent is quickly improved to 1.3×10^{-4} A. The large photocurrent is attributed to the photogenerated electrons on the TiO₂ film driven to the counter electrode by the applied bias potential, demonstrating the excellent photoelectrochemical property of LPD TiO₂/ITO film.

At the same time, in order to further investigate the photoelectrochemical property of such a LPD TiO₂/ITO film electrode, electrochemical impedance spectroscopic (EIS) measurements were carried out before and after UV irradiation, as shown in Fig. 5. From Fig. 5, the

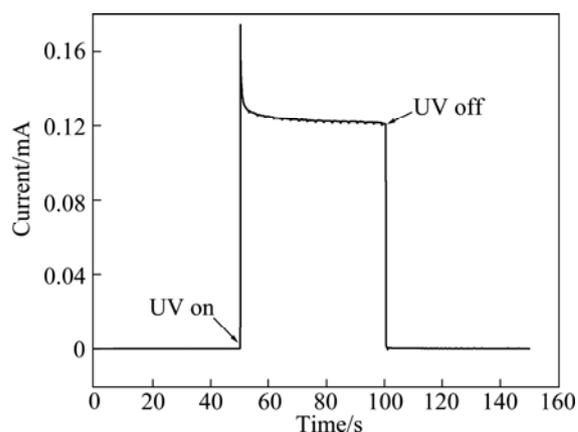


Fig. 4 Photocurrent response curve of LPD TiO₂/ITO film electrode under UV irradiation

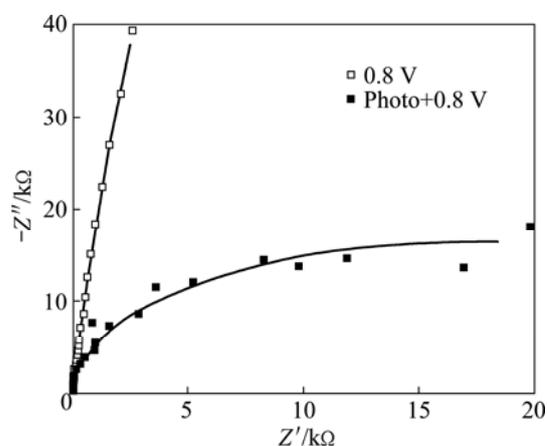


Fig. 5 Electrochemical impedance spectra (square) and corresponding fitting curves (line) of LPD TiO₂/ITO film electrode with and without UV irradiation

electron transfer resistance (R_t) was calculated by fitting the diameter of semicircle appearing at the high frequency part of EIS using Zview software. When only bias potential is applied, the R_t value is 1685 kΩ. The large R_t value is assigned to the low conductivity of the compact semiconductive film. While UV irradiation and bias potential are simultaneously applied, the R_t value is remarkably decreased to 34 kΩ, meaning the promoted electron transfer in the electrode interface. The fast electron transfer is attributed to the effective separation of photogenerated electron-hole pairs on TiO₂ by applied bias potential.

3.3 PEC degradation of 4-aminoantipyrine on TiO₂/ITO film

The LPD TiO₂/ITO film electrode was employed to study the PEC degradation of 4-aminoantipyrine. Figure 6 compares the degradation curves of 4-aminoantipyrine treated by different techniques such as electrolysis (EC), direct photolysis (DP), photocatalysis (PC) and PEC. In

all these degradation experiments, the initial concentration of 4-aminoantipyrene was 0.1 mmol/L and the supporting electrolyte was 0.1 mol/L Na₂SO₄. The EC process was carried out by applying +0.8 V anodic bias potential on the TiO₂/ITO film electrode without UV irradiation. The DP process was carried out under UV irradiation in the absence of film electrode and bias potential. The PC process was carried out under UV irradiation on the film electrode, but without applying bias potential. The PEC process was carried out under UV irradiation on the film electrode and simultaneously applying +0.8 V bias potential.

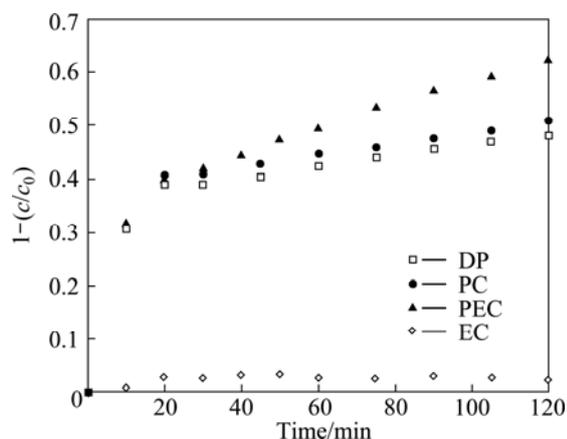


Fig. 6 4-aminoantipyrene degradation efficiency–time curves by different treatment processes

It can be seen from Fig. 6 that the degradation efficiency of EC is very low. After 120 min EC treatment, only about 3% of 4-aminoantipyrene is degraded. In comparison, DP process is more efficient and the degradation efficiency reaches 48.0% after 120 min. When 4-aminoantipyrene is treated with PC process for 120 min, the degradation efficiency is 50.8%. The higher degradation efficiency of PC than DP indicates the photocatalytic activity of TiO₂/ITO film. For PEC process, the degradation efficiency reaches 62.1% after 120 min treatment, obviously higher than the sum of degradation efficiencies of EC and PC, demonstrating the synergetic effect of photocatalysis and electrolysis. This result is attributed to the effective inhibition of anodic bias potential to the recombination of photogenerated electron-hole pairs which provides more photogenerated electrons and holes to participate the degradation reactions.

3.4 Influence of experimental conditions on PEC degradation of 4-aminoantipyrene

Figure 7(a) shows the PEC degradation curves of 4-aminoantipyrene by applying different anodic bias potentials. It can be seen that when the bias potential is increased from +0.4 V to +0.8 V, the degradation

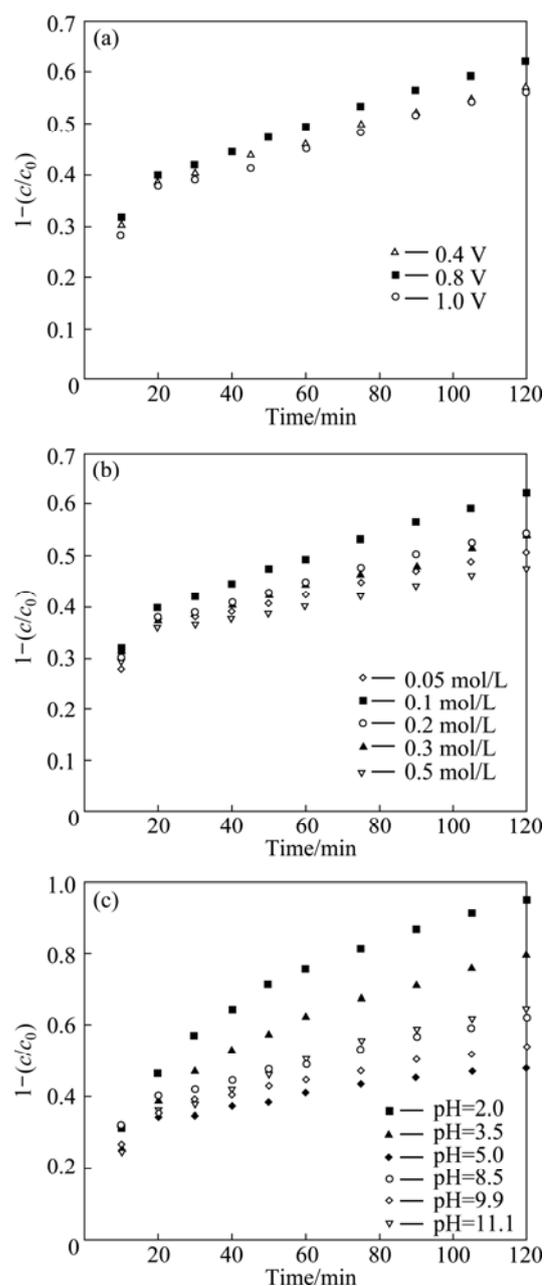


Fig. 7 Effects of bias potential (a), Na₂SO₄ concentration (b) and pH (c) on degradation efficiency of 4-aminoantipyrene on TiO₂/ITO film electrode

efficiency is obviously improved. This phenomenon can be attributed to the fact that increasing bias potential could promote the electron transfer rate which improves the inhibition efficiency to the recombination of photogenerated electron-hole pairs. However, while the bias potential is further increased from +0.8 V to +1.0 V, the degradation efficiency is decreased. It is considered that the thickness of the photoanode is finite and thus the thickness of the space charge layer can not exceed the thickness of semiconductive film. Under a fixed light intensity, the photogenerated electrons is also limited. When the bias potential is increased to a value, the photogenerated carrier is sufficiently separated and thus

foms the saturated photocurrent [21]. Even if the bias potential is further increased, the photocurrent would not increase. On the contrary, the current efficiency is decreased. Thus, +0.8 V is selected as the optimized bias potential for the PEC degradation of 4-aminoantipyrine on the LPD TiO₂/ITO film electrode.

The PEC degradation of 4-aminoantipyrine was investigated in the presence of supporting electrolyte Na₂SO₄ at the concentration of 0.05–0.5 mol/L (Fig. 7(b)). The results indicate that when the concentration of Na₂SO₄ is increased from 0.05 mol/L to 0.1 mol/L, the degradation efficiency of 4-aminoantipyrine is improved. While the concentration of Na₂SO₄ is increased to be higher than 0.1 mol/L, the degradation efficiency of 4-aminoantipyrine shows a declining tendency. It is well known that with increasing the concentration of electrolyte concentration, the conductivity of solution is enhanced, which could decrease the cell volatge and improve the applied potential efficiency. While the concentration of Na₂SO₄ is further increased, more SO₄²⁻ would compete with 4-aminoantipyrine by attracting photogenerated hole, leading to the inhibited degradation. So, 0.1 mol/L was considered the optimized concentration of supporting electrolyte.

The pH of solution had an obvious effect on the PEC degradation of 4-aminoantipyrine. Figure 7(c) shows the PEC degradation experimental results in different pH solutions. The pH of solution was adjusted by adding a small amount of H₂SO₄ or NaOH. It is observed that the highest degradation efficiency is obtained at pH 2.0 and the 120-min degradation efficiency reaches 95.0%, which is obviously higher than that obtained in other pH solutions. The possible explanation is that 4-aminoantipyrine molecule carries more negative charges at pH 2.0, which could be effectively adsorbed on the positively charged TiO₂. While the pH of solution is increased to 5.0, the degradation efficiency is reduced to a low value. Whereas the pH is varied in the alkaline range, the degradation efficiency is not changed regularly. This result implies the complex mechanism for pH effect on the PEC degradation of 4-aminoantipyrine. On one hand, pH influences the band-edge positions of valance and conduction bands of TiO₂, surface charge of TiO₂, adsorption of organic molecules on the caltalyst surface, as well as the desorption/adsorption of electron-hole pairs. On the other hand, the molecular structure of 4-aminoantipyrine may be changed significantly at high pH, leading to the varied degradation efficiency.

4 Conclusions

1) TiO₂ film was deposited on the ITO surface by

the LPD process. The obtained TiO₂/ITO film had an excellent photoelectrochemical performance.

2) Using such a TiO₂/ITO film, the degaration of 4-aminoantipyrine by PEC technique was systematically investigated. Under optimized conditions such as +0.8 V applied bias potential, 0.1 mol/L Na₂SO₄ and pH 2.0, the highest degradation efficiency could reach 95% for 0.1 mmol/L 4-aminoantipyrine after 120 min PEC treatment.

3) LPD process provides a simple wet-chemical approach to the preparation of TiO₂/ITO film. The as-prepared LPD TiO₂/ITO film electrode is promising for PEC degradation of organic pollutants.

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TiO₂/ITO 膜的液相沉积法制备及其用于 4-氨基安替比林降解的光电催化活性

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摘要: 利用液相沉积(LPD)法在 ITO 表面制备 TiO₂ 薄膜。光电流和交流阻抗 (EIS) 测试表明, 这种 TiO₂/ITO 液相沉积膜具有良好的光电性能, 对紫外光产生灵敏、快速的电流响应, 在此膜电极上通过施加一定的阳极偏压可有效分离光生电子-空穴对。将 TiO₂/ITO 膜用于 4-氨基安替比林的光电催化降解研究, 与其他方法相比, 利用此液相沉积膜电极的光电催化技术对于 4-氨基安替比林的降解具有明显的协同效果, 适合于该污染物的降解处理。当外加阳极偏压为+0.8 V, 支持电解质 Na₂SO₄ 浓度为 0.1 mol/L, 溶液 pH 为 2.0 时, 0.1 mmol/L 4-氨基安替比林 120 min 的光电催化降解效率最高可达 95%。

关键词: 液相沉积; 二氧化钛膜电极; 光电催化; 4-氨基安替比林

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