Photoelectrochemical degradation of methyl orange by TiO$_2$ nanopore arrays electrode and its comparison with TiO$_2$ nanotube arrays electrode

Yanbiao Liu, Xiaojie Gan, Baoxue Zhou, Jinhua Li, Jialing Zhang, Yimin Chen, Jing Bai, Qing Zheng, Bingchuan Liu and Weimin Cai

ABSTRACT

Highly ordered TiO$_2$ nanopore arrays (TNPs) electrode was applied as an electrode material for photoelectrochemical (PEC) degradation of methylic orange (MO). As a comparison, the self-organized TiO$_2$ nanotube arrays (TNAs) electrode about 500 nm in length was fabricated by Ti anodization in 0.5 wt% HF-H$_2$O solution. The COD removal rate and color removal rate for PEC degradation of MO using the TNPs electrode was found to be 9 and 7%, respectively, as high as that obtained for TNAs electrode when biased at 0.5 V. The results indicate that the fast electron separation and transport properties of TNPs electrode makes it possesses enhanced PEC performance for the degradation of MO. In addition, the color removal rate of MO by TNPs PEC process increased with increasing bias potential and electrolyte concentration, but decreased with the increasing pH value and initial concentration of the reaction solution.

Key words | methyl orange, photoelectrochemical, TiO$_2$ nanopore arrays, TiO$_2$ nanotube arrays

INTRODUCTION

For several decades, the treatment of poorly degradable chemical wastewater from such industrial sources as the pharmaceutical, printing and dyeing industries, has become a stubborn problem for environmental workers, and has attracted a great deal of concern (Ellis 2006; Liu et al. 2008). Among them, the widespread disposal of wastewater from the dye industry, which amounts to more than one million tons annually, combined with its slow degradation, high toxicity and potential carcinogenic risk, categorizes it as one of the most environmentally hazardous pollutants (Kuo 2009). Today, more than half of the dyes used are azo dyes, which are extensively applicable as additives in the textile, plastic, leather, and paper industries (Troupis et al. 2009). For the degradation of azo dye from wastewater, the traditionally used methods involve removal of the organics via biological degradation or physical adsorption (Mezohegyi et al. 2008; Chiang et al. 2009). Although less costly than other procedures, biological treatment is not efficient due to the high solubility of these synthetic organic pollutants and their resistance to aerobic degradation. Moreover, adsorption of these soluble organic compounds onto activated carbon essentially only transfers the organics from the liquid to the solid phase, resulting in secondary environmental pollution.

TiO$_2$-based photoelectrochemical (PEC) oxidation has been proven to be an efficient technique for degrading recalcitrant organic compounds in aqueous solution (Zhang et al. 2007; Kumar et al. 2008). Previous studies (Hidaka et al. 1997; Jiang et al. 2005) reported the use of TiO$_2$ nanoparticle film electrodes, fabricated by screen printing
or coating TiO₂ nanoparticles onto a conductive substrate, as photoanodes. However, such TiO₂ films suffer from structural disorders and vast grain boundaries, which bring obstacles to the electron transport and affect the charge separation efficiency. Moreover, the high rate of recombination and weak reactivity of the coated TiO₂ films limited their wide application (Liu et al. 2008). In response to these deficiencies, most attempts at synthesizing new TiO₂ structures (e.g. TiO₂ nanowires, nanorods, nanobelts, nanorings, nanotubes, etc.) (Wang et al. 2008) or modifying TiO₂ (e.g. by depositing a noble metal on its surface (Nam & Han 2007), sensitizing it with dyes (O’Regan & Gratzel 1991), doping it with transition metals or non-metal elements (Beranek & Kisch 2007) and complexes with matching semiconductors (Sun et al. 2008), have met with certain success.

In recent years, self-organized TiO₂ nanotube arrays (TNAs) prepared by electrochemical anodization used as an electrode in the PEC reaction have attracted much research interest due to its large specific surface area, special microstructure, high photochemical reactivity and fast electron separation and transport properties (Gong et al. 2001; Vitiello et al. 2006). Some reports (Zhuang et al. 2007; Zheng et al. 2008) have concerned the potential application of titania nanotubes with different morphologies applied as an electrode material for PEC degradation of organic pollutants. However, the weak tube-to-tube binding, as well as weak adhesion to the underlying layer of the nanotubes will inevitably influence their mechanical stability as well as the performance for the separation and transport of photo-generated electron/hole pair (Yoriya et al. 2007). We have previously reported on the fabrication and characterization of a novel kind of TiO₂ nanopore arrays (TNPs) electrode material with fast separation and transport of photo-generated electron/hole pair (Liu et al. 2009). This material was designed mainly for its enhanced capability for photochemical water splitting and degradation of organic compound in aqueous solution. In this paper, we report on a detailed investigation of the PEC degradation of MO, as given in Figure 1, using a TNPs electrode, and compare the PEC degradation results obtained by a TNAs electrode. Since MO is one of important commercial azo dye, due in part to its very short excited-state lifetime and its stability toward visible and near UV light.

**EXPERIMENTAL**

**Preparation of TNPs**

The detailed methodology of preparation highly ordered titania nanopores have been published elsewhere (Liu et al. 2009). Hence only key points of the fabrication processes were summarized here. The titanium sheets (0.25 mm thick, 99.9% purity, Kurumi Works, Japan) were cut into samples of size 2 × 5 cm². All anodization experiments were carried out with vigorous magnetic agitation at 5°C in a two-electrode system (4 cm separation). The anodization voltage was set at 40 V and the electrolyte was dimethyl sulfoxide (DMSO, ≥99.8%) containing 5% HF solution (≥40 wt%). The TNPs can be fabricated by a two-step process: after anodization for 70 h, the sample was post-sonicated for 10 min to remove the uppermost film completely. The obtained TNPs, which are initially amorphous, are crystallized by annealing in an air atmosphere for 8 h at 450°C with heating and cooling rates of 1°C/min. The morphologies of the TNPs were studied using a field emission scanning electron microscope (PHILIPS, Netherlands, Sirion200). The pore depth of the TNPs sample was measured using an atomic force microscope (BioScope) from Veeco Instruments Inc. (USA).

**Photoelectrochemical experiment**

The PEC experiments were carried out in a rectangular shaped quartz reactor (20 × 40 × 50 mm) using a three-electrode system with a platinum foil counter
electrode, a saturated Ag/AgCl reference electrode and a TiO₂ working electrode. The supply bias and work current were controlled using a CHI electrochemical analyzer (CHI 660C, CH Instruments, Inc., USA). A 4 W UV lamp (GE, Japan G4T5) with a central wavelength of 254 nm was chosen as the UV light source. The PEC degradation of MO was performed under the following conditions: UV irradiation (1.0 mW cm⁻² light intensity), vigorous stirring, 0.5 V (vs. Ag/AgCl) of electric bias, pH 5.5, 0.01 M sodium sulphate as electrolyte, and no airflow. The initial concentration of the MO solution was 0.06 mM and the reaction solution during the experiment was 25 ml. At different time intervals, the reaction solution was analyzed using a UV–Vis spectrophotometer (UV2102 PCS, UNICO, Shanghai) at a wavelength of 462 nm. The COD determination of the reaction solutions were carried out according to reference (Zheng et al. 2008; Zhang et al. 2009).

RESULTS AND DISCUSSION

Characterization of TNPs electrode

Figure 2(a) shows the field emission scanning electron microscopy (FE-SEM) image of the as-annealed TNPs sample anodized in 5 wt% HF-DMSO electrolyte solution at 40 V for 70 h using methods similar to those employed in our previous work (Liu et al. 2009). Compared with unannealed TNPs sample, the as-annealed nanopores still kept highly ordered morphologies and the average pore diameter is around 200 nm. Figure 2(b) gives the atomic force microscopy (AFM) image of the same TNPs sample and presents a dense and uniform 2D image. The cross-section image (Figure 1(c)) taken along the line given in image 2b demonstrates that the average pore depth for the sample is ~50 nm.

PEC degradation of MO

In order to compare the PEC activity of the TNPs electrode with that of a titania nanotubes electrode, the TNAs electrode was prepared by Ti anodization in 0.5 wt% HF aqueous at 20 V for 0.5 h (Gong et al. 2001; Bai et al. 2008). These nanotubes have a length of ~500 nm and a diameter of ~100 nm. As can be seen from Figure 3, Within 3 h, the COD removal rate of 87% can be achieved by TNPs electrode. This value compares favourably with a COD removal efficiency of 78% for TNAs electrode under the same conditions. The inset in Figure 3 indicates that the color removal of MO by the PEC process of TNPs electrode and TNAs electrode. It is evident that the COD removal rate and color removal rate of MO solution reveals similar changing trend on the two electrode materials. The color removal rate of MO reached 92% for TNPs electrode after 3 h PEC reaction, which is higher than that attained (85%) for TNAs electrode under the same
conditions. That means the PEC oxidation process not only can destroy the azo chromophoric groups, but also can mineralize the organic compound to CO₂ and H₂O. The results indicate that the fast electron separation and transport properties of TNPs electrode (Liu et al. 2009) makes it possesses enhanced PEC performance for the degradation of MO solution. Within TNPs, the porous structure was directly connected with Ti substrate. Hence, the TNPs combine with the Ti substrate more directly and compactly, resulting in a lower transport resistance for photo-generated electrons.

**Parameters influencing PEC degradation of MO**

**Effect of applied potential**

PEC technology is an enhanced photochemical technology. In this case, the photo-generated electrons can be transported to the outer circuit by applying a bias potential across the immobilized TiO₂ film electrode, which results in a highly efficient separation of the photo-generated electron/hole pair (Zhang et al. 2007). Hence, the bias potential is a key factor that influences the PEC efficiency of the electrode material. Four levels of bias potential, 0.0, 0.1, 0.2, 0.5 V were studied in the present work. As given in Figure 4(a), the color removal rate of MO increased as the applied bias potential increased from 0.0 to 0.5 V. As such, 92% MO was removed at a bias of 0.5 V over a period of 3 h, which is much higher than 3.8% MO removal rate obtained without a bias potential. As given in Figure 4(b), the corresponding reaction rate constants are ranked as: 0.5 V (k = 0.795 h⁻¹) > 0.2 V (k = 0.407 h⁻¹) > 0.1 V (k = 0.319 h⁻¹) > 0.0 V (k = 0.012 h⁻¹).

**Effect of electrolyte solution**

In a typical PEC process, the selection and concentration of the electrolyte solution was also very important. In this

study, sodium sulphate was selected as the electrolyte solution and three levels of concentration (0.0, 0.005, 0.01 M) were used to investigate the influence of electrolyte concentration, as given in Figure 5(a). The experimental result indicates that the color removal rate of MO increased with increasing electrolyte concentration from 0 to 0.01 M. The rate constant was $0.153$, $0.510$, and $0.795$ h$^{-1}$ for an electrolyte concentration of 0, 0.005 and 0.01 M, respectively (Figure 5(b)). This phenomenon can be explained by the increased conductivity of the solutions contributing positively to the photo-generated electron transport between the TiO$_2$/solution interfaces.

**Effect of pH**

The pH of the solution is one of the factors known to influence the rate of degradation of organic compounds in the PC and PEC process (Kormann *et al.* 1999). As such, pH is also an important operational parameter in wastewater treatment. Figure 6(a) demonstrates the influence of pH on the color removal of MO by TNPs electrode PEC process using three levels of pH (5.5, 7.5, and 10.5). From this figure, it is evident that the removal efficiency of MO decreased with the increase in the pH of the reaction solution. The PEC degradation of MO performed at pH values of 5.5 and 10.5 resulted in a reduction of the MO removal efficiency from 92 to 56%. When the pH was lower than the isoelectric point ($pH = 6.2$ (Wu *et al.* 2008)) of the solution system, the surface of the electrode material was positively charged, which is favorable for the degradation of negatively charged donors (dyes). However, when the pH was higher than the isoelectric point, the surface of the electrode material was negatively charged, which is unfavorable for the adsorption of dye molecules on the electrode surface, resulting in a poor MO removal rate.

![Figure 6](https://iwaponline.com/wst/article-pdf/62/12/2783/445785/2783.pdf)

**Figure 6** (a) Effect of solution pH values on the color removal rate of MO by TNPs PEC process; (b) The PEC kinetic curves of MO for TNPs electrode at different pH value of the initial MO solution.

![Figure 7](https://iwaponline.com/wst/article-pdf/62/12/2783/445785/2783.pdf)

**Figure 7** (a) Effect of initial concentration of MO on the color removal rate of MO by TNPs PEC process; (b) The PEC kinetic curves of MO for TNPs electrode in different initial concentration of MO.
(Zheng et al. 1997). The corresponding reaction rate constants are ranked as: pH5.5 (k = 0.795 h−1) > pH7.5 (k = 0.320 h−1) > pH10.5 (k = 0.275 h−1) (Figure 6(b)).

Effect of initial concentration of MO

The effect on the PEC degradation rate of different initial MO concentrations was carried out on annealed TNPs electrode. In this work, the initial concentration was chosen from 0.06 to 0.15 mM. The descriptions of different initial concentrations versus time profiles were present in Figure 7(a). It is evident that the degradation efficiency increased with decreasing initial concentration of MO. At the MO concentration of 0.06 mM, ~92% of the MO was degraded by TNPs electrode in 3 h PEC process. When the initial concentration of MO further increases to 0.15 mM, the degradation efficiency of MO sharply decreased to 42% over 3 h PEC reaction for the same electrode under similar conditions. The reaction rate constants for TNPs PEC process in 0.06, 0.09 and 0.15 mM MO solution is 0.795, 0.115 and 0.091 h−1, respectively (Figure 7(b)).

CONCLUSIONS

The PEC performance of TNPs electrode and TNAs electrode were compared by investigating MO degradation. Within TNPs electrodes, the excellent charge separation and transport properties makes it an effective electrode material. Hence, TNPs electrode reveals enhanced PEC activity for MO degradation in comparison with TNAs electrode. Furthermore, the bias potential, electrolyte concentration, pH value and initial concentration of the reaction solution were found to be important factors influencing the PEC degradation of MO using the TNPs electrode as the working electrode. The experimental results suggest that ordered nanoporous structures may serve well as catalysts and may provide an easy and efficient method to remove recalcitrant organic pollutant from wastewater.

ACKNOWLEDGEMENTS

The authors would like to acknowledge the Shanghai Basic Research Key Project (08JC1411300), the National Nature Science Foundation of China (No.20677059) and the Program of New Century Excellent Talents in University (No.NCET-04-0406) for financial support.

REFERENCES


Ellis, J. B. 2006 Pharmaceutical and personal care products (PPCPs) in urban receiving waters. Environ. Pollut. 144(1), 184–189.


