

## Photoelectrocatalytic Degradation of Methylene Blue Dye on Titania Nanotube Array Film

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TiO<sub>2</sub> nanotube array was fabricated via anodization, and the resulting film was investigated by XRD and SEM. The degradation of Methylene Blue (MB) dye demonstrated its superior photoelectrochemical activity. By comparison of photocatalysis (PC) and photoelectroncatalysis (PEC), it was found that PEC oxidation was a convenient and effective process to mineralize the organic matters. In addition, the excellent capability of adsorption derived from nanoporous configuration on such electrode also plays an important role in accelerating the degradation process.

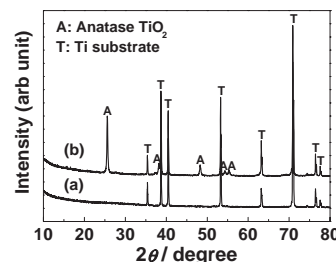
The process of heterogeneous photocatalysis, especially with the use of TiO<sub>2</sub> as a catalyst, has been extensively studied in the purification of wastewater<sup>1–3</sup> and other areas. The development of photoelectrocatalytic (PEC) oxidation process with an externally applied anodic bias has also been receiving attention in recent years,<sup>4–6</sup> when a bias potential was introduced into the photocatalytic process, which is referred to photoelectrocatalysis, the recombination of electron–hole pairs was reduced. Furthermore, TiO<sub>2</sub>-based nanotubes began to attract wide attention because of the large surface area. From the viewpoint of photocatalytic kinetics, when supported TiO<sub>2</sub> nanotubes were used as working electrode in a PEC system, the oxidation efficiency would be further improved. Many efforts have been incorporated on the modification and application of TiO<sub>2</sub> nanotube structures since Grimes' group first reported on the successful fabrication of TiO<sub>2</sub> nanotube arrays by anodization method.<sup>7,8</sup> However, few works have been reported on the degradation of organic pollutants via PEC process using TiO<sub>2</sub> nanotube arrays.

In the present study, the photocatalytic activity of the TiO<sub>2</sub> nanotube array films was evaluated in the PC and PEC processes by measuring the degradation of Methylene Blue (MB) dye. The main purpose of this study is to investigate the efficiency of photoelectrocatalysis using TiO<sub>2</sub> nanotube array film for the removal of organic compounds.

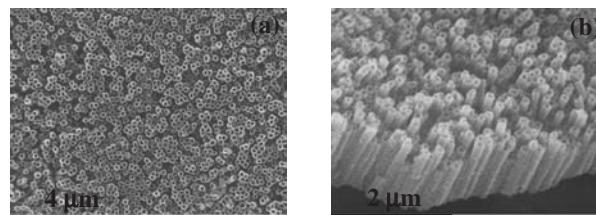
TiO<sub>2</sub> nanotube arrays were prepared by anodization of Ti foil in an electrolyte containing 1.0 M NH<sub>4</sub>H<sub>2</sub>PO<sub>4</sub> and 0.5 wt % NH<sub>4</sub>HF<sub>2</sub>, the Ti foil is used as an anode and graphite was chosen as a cathode. The anodization voltage and time were fixed at 20 V and 2 h, respectively. All experiments were conducted at room temperature with magnetic agitation. The as-anodized TiO<sub>2</sub> nanotube films were annealed at 450 °C for 1 h with the heating rate of 10 °C/min.

Each electrochemical experiment was performed on IM6e workstation connected with a three-electrode system which was established in a quartz beaker. A saturated calomel electrode (SCE) and a platinum foil served as the reference electrode and counter electrode, respectively.

The PEC degradation of MB was performed with a potentiostat and simulated solar light (250-W metal halogen lamp) with



**Figure 1.** XRD patterns of TiO<sub>2</sub> nanotube array before (a) and after (b) annealing in air at 450 °C.



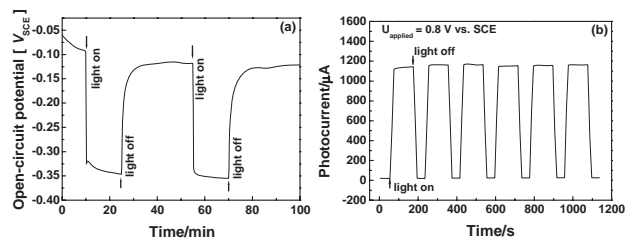
**Figure 2.** SEM morphologies of TiO<sub>2</sub> nanotube array films annealed at 450 °C. (a) top view and (b) cross section.

intensity of 100 mW·cm<sup>-2</sup>. 100 mL of solution containing MB (10 mg/L) and NaCl (0.1 M) was added into the quartz reactor without pH control. The TiO<sub>2</sub> nanotube electrode (area: 4 cm<sup>2</sup>), a SCE and a Pt foil were placed in the reactor and connected with the potentiostat.

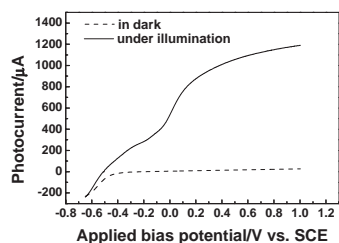
XRD diffraction patterns of nanotube films before and after being annealed at 450 °C are shown in Figure 1. It is clear that the as-anodized nanotubes were amorphous, while it transformed into anatase after heat treatment at 450 °C. Figure 2 shows the SEM morphologies of the nanotubes. It can be seen that the thin films were composed of compact and well-aligned nanotubes. The average diameter, tube length and tube wall thickness of these nanotubes were about 130 nm, 2.0 μm, and 30 nm, respectively.

Figure 3 illustrates the curve of open-circuit potential (OCP) for the TiO<sub>2</sub> film in 0.1 M NaCl solution. On illumination, the OCP of the electrode negatively shifted to around -350 mV (vs. SCE) rapidly as a result of the sudden generation of electron–hole pairs in the film. And eventually steady states were obtained with approximately unchanging OCP values, owing to the balancing rate between creation and depletion of photo-generated carriers. When the illumination cut off, the electrode potential positively shifted to ca. -120 mV in a few minutes. Similar phenomenon also appeared in the photocurrent response with intermittent illumination when constant potential was applied (Figure 3b).

The current responses of TiO<sub>2</sub> electrode in presence and



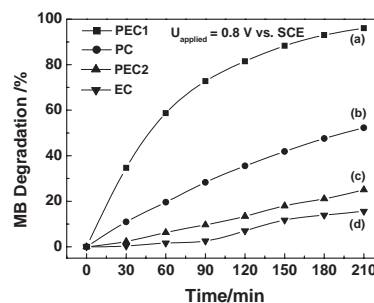
**Figure 3.** OCP changes (a) and photocurrent response (b) of TiO<sub>2</sub> nanotube array electrode (area: 4 cm<sup>2</sup>) as a function of time in 0.1 M NaCl solution.



**Figure 4.** Photocurrent response of the TiO<sub>2</sub> nanotube array film (area: 4 cm<sup>2</sup>) under dynamic applied bias potentials in 0.1 M NaCl solution.

absence of illumination with the applied bias potential swept from  $-0.65$  to  $1.0$  V vs. SCE at rate of  $10 \text{ mV} \cdot \text{s}^{-1}$  are shown in Figure 4. For the purpose of demonstrating the enhancement of photoelectrocatalysis, the dark current curve is to act as a benchmark for the measurement of practical photocurrent intensity. As depicted in Figure 4, negligible current was detected without illumination. On illumination of the TiO<sub>2</sub> electrode, a significant increase in the anodic current was observed. It is obvious that photocurrent increases with increasing the applied anodic bias potential, which implies that the photogenerated electrons and holes are effectively separated. In this case, the photogenerated holes trapped at the reactive surface site near the valence band edge oxidize Cl<sup>-</sup> or OH<sup>-</sup>, whereas the conduction band electrons are driven to the underlying Ti substrate and from there to the external circuit.

Because the anodic overpotential of Cl<sub>2</sub> is lower than that of O<sub>2</sub>, in the present weak acidic medium (pH 6.0), the preponderant adsorbing specie would be Cl<sup>-</sup>, and the PEC experiment could lead to formation of Cl<sup>·</sup>, Cl<sub>2</sub><sup>·</sup>, or active chlorine (Cl<sub>2</sub>, HClO) as powerful oxidizing species.<sup>9</sup> We suppose that there is likely existed mutual competition between the chloride ion and water for the positive photogenerated holes. Under present acidic conditions, chloride competes more advantageously and chlorine production is prevalent. Moreover, the higher specific surface area of TiO<sub>2</sub> nanotubes favors adsorbing more dye molecules to be oxidized, as shown in Figure 5, direct PC achieved rather lower removal than PEC under identical illumination intensity, in which the MB removal was 52.29 and 96.70% after 210 min of illumination, respectively. The low degradation rate



**Figure 5.** Degradation of 10 mg/L MB solution during various catalytic oxidation process. The PEC1 and PEC2 represent PEC process using nanotubular and compact film, respectively.

of compact film prepared via electrophoretic deposition (Figure 5c) further indicates that the superior adsorbility of nanotubular structure undoubtedly has its advantage in accelerating the degradation process. Besides, it should be noted that the single electrocatalysis (EC) showed the lowest efficiency in degradation experiments, which means the content of active chlorine produced by single electrolyzing NaCl at present potential is rather low. Generally, the efficiency of the photocatalytic process is determined by the competition between the recombination of hole/electron and the separation of interfacial charge transferred to the electron donor/electron acceptor species. Nevertheless, the actual rate of charge-transfer reactions is affected by the reactant adsorption on the TiO<sub>2</sub> surface.

In summary, PEC degradation of MB dye has been achieved effectively in medium containing chloride ions using TiO<sub>2</sub> nanotubes array photoanode and visible light illumination without pH control. The reasons for that may be attributed to the synergetic effect of photoelectrocatalysis and the superior adsorbility of nanoporous structure.

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## References

- 1 G. Waldner, J. Krýsa, *Electrochim. Acta* **2005**, *50*, 4498.
- 2 X. Z. Li, C. He, N. Graham, Y. Xiong, *J. Appl. Electrochem.* **2005**, *35*, 741.
- 3 H. Liu, A. Imanishi, Y. Nakato, *J. Phys. Chem. C* **2007**, *111*, 8603.
- 4 J. Li, L. Zheng, L. Li, Y. Xian, L. Jin, *J. Hazard. Mater.* **2007**, *139*, 72.
- 5 P. A. Carneiro, M. E. Osugi, J. J. Sene, M. A. Anderson, M. V. B. Zanoni, *Electrochim. Acta* **2004**, *49*, 3807.
- 6 X. Zhao, Y. Zhu, *Environ. Sci. Technol.* **2006**, *40*, 3367.
- 7 G. K. Mor, O. K. Varghese, M. Paulose, K. Shankar, C. A. Grimes, *Sol. Energy Mater. Sol. Cells* **2006**, *90*, 2011.
- 8 J. M. Macák, H. Tsuchiya, A. Ghicov, P. Schmuki, *Electrochim. Commun.* **2005**, *7*, 1133.
- 9 M. V. B. Zanoni, J. J. Sene, M. A. Anderson, *J. Photochem. Photobiol., A* **2003**, *157*, 55.