

# Photoelectrocatalytic degradation Rhodamine B over highly ordered TiO<sub>2</sub> nanotube arrays photoelectrode



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## ABSTRACT

Different nanotube length of TiO<sub>2</sub> nanotube arrays (NTAs) electrodes was successfully prepared by anodization method with different duration time. The as-prepared electrodes were characterized by field-emission scanning electron microscopy (FE-SEM), X-ray diffraction (XRD), cyclic voltammetry (CV), electrochemical impedance spectroscopy (EIS) and Mott-Shottky measurement. The influence of bias potential, illumination and nanotube length on Rhodamine B (RhB) degradation was investigated. The results show that applied bias potential and short nanotube length are beneficial to RhB degradation due to the enhanced charge transfer. Moreover, it is found that an induction period exists in the RhB photoelectrodegradation with short nanotube length and the rate is sensitive to the carriers' concentration. This can be attributed to the increased effective holes for degradation RhB and the decreased recombination rate of electrons-holes. Nevertheless, RhB photoelectrodegradation with long nanotube length did not display the similar kinetic characteristic. The possible explanation is that long nanotube length increases the recombination rate of electrons-holes and limits the charge transfer, hence decreases the amount of effectively charge carriers. This may decrease the degradation rate and thus result in the disappearing of the second degradation constant. Moreover, we further demonstrate our deduction by the electrochemical impedance spectroscopy (EIS) and Mott-Shottky measurement.

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## 1. Introduction

Semiconductor photocatalytic technology has attracted wide attention due to its potential application in pollutant degradation [1–5], dye-sensitized cells [6–8], sensors [9–11] and water splitting for hydrogen generation [12–14]. It is well known that the surface performance including surface area and surface charge is significantly important to the photocatalytic reaction [15–17]. Many efforts have been devoted to improving the photocatalytic efficiency via modifying the photocatalyst or changing the specific photocatalytic reaction process [18–20]. However, the rapid recombination of electrons-holes pairs is still the limiting factor to the photocatalytic reaction. Highly ordered TiO<sub>2</sub> nanotube arrays (NTAs) are regarded as the most promising photocatalyst for its big surface area, excellent photostability and excellent charge transport performance [21–24]. The particular structure of TiO<sub>2</sub> NTAs provides a pathway for carriers transfer and accelerates the separation of charges [25–27]. Many architectural parameters such as nanotube length, wall thickness and pore diameter were pre-

cisely designed and controlled to increase the propagation and absorption of light [28–30]. On the basis of photocatalytic technology, a novel technique named photoelectrocatalytic technology has drawn growing interest in recent years. With the assistance of applied potential, the separation of electrons-holes pairs significantly enhanced. Nevertheless, seldom research has been conducted on the photoelectrocatalytic process. Therefore, understanding the specific photoelectrocatalytic process is considered to be crucial for enhancing the photoelectrocatalytic efficiency.

In this work, we first fabricated vertically oriented TiO<sub>2</sub> NTAs with different nanotube length via oxidation method and then studied the photoelectrochemical properties of TiO<sub>2</sub> NTAs electrodes in two supporting electrolyte. The effect of bias potential, illumination and nanotube length on RhB degradation was studied. It is expected that we can comprehend the specific photoelectrocatalytic process through these findings.

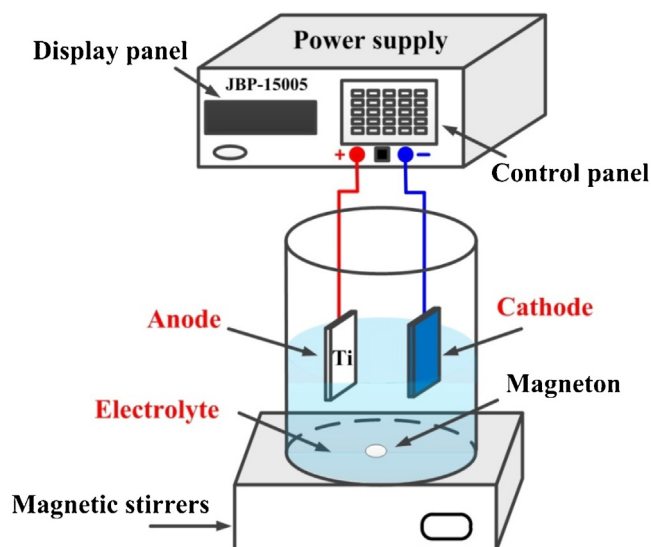
## 2. Experimental details

### 2.1. Materials

The Ti foil (>99.6% purity, BaoTi Co., Ltd., China, 0.5 mm thickness) was cut into pieces with a dimension of 2 × 4 cm. These

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**Fig. 1.** Depiction of a two-electrode electrochemical cell in which the Ti samples are anodized.

titanium foils were degreased by ultrasonating in isopropanol and ethanol, followed by cleaning with deionized water. All chemicals were of analytical grade and were used without any further purification.

## 2.2. Fabrication of TiO<sub>2</sub> NTAs electrode

Highly ordered TiO<sub>2</sub> NTAs electrodes were synthesized by anodization method. Anodization experiments were carried out in a two-electrode configuration with the Ti sheet as both anode and cathode, as shown in Fig. 1. The distance between the two electrodes was kept at 2.5 cm. Anodization was carried out for different time (1 h/2 h/3 h) at a constant applied voltage of 50 V in the electrolyte containing 97 vol% ethylene glycol (EG) and 3 vol% deionized water with 0.3 wt% ammonium fluoride (NH<sub>4</sub>F). The experiment temperature maintains constant by the thermostatic water bath. After anodization, the as-synthesized TiO<sub>2</sub> NTAs samples were rinsed with deionized water and then subjected to ultrasonication to remove the sediment. Finally, these obtained samples were annealed in air at 500 °C for 2 h to induce crystallization (the heating and cooling rate were both 1 °C/min).

## 2.3. Characterization

The surface morphology of the as-synthesized samples was characterized by a field-emission scanning electron microscopy (FE-SEM, JEOL, JSM-6700F). X-ray diffraction (XRD) patterns were obtained by using an X'pert PRO MRD diffractometer with a scanning angle (2θ) range of 10–80°. Total organic carbon (TOC) measurement was performed on the ET1020A TOC Analyzer. Chemical oxygen demand (COD) was measured by the ET99722 Lovibond Water Testing.

The photoelectrochemical performance of these electrodes was performed on a CHI 660D electrochemical workstation (Chenhua, Shanghai) using a conventional three-electrode system with the as-prepared electrodes as the working electrode, Pt foil as the counter electrode, and Ag/AgCl electrode as the reference electrode. The cyclic voltammetry (CV) measurements were conducted in 0.1 M Na<sub>2</sub>SO<sub>4</sub> aqueous solutions between –1.2 V and 1.0 V at a scan rate of 50 mV/s. Electrochemical impedance spectroscopy (EIS) measurements were also carried out to understand the charge transport properties of the electrodes in dark and under illumination. The

frequency range used is 100 kHz–100 mHz and the amplitude of sinusoidal wave is 10 mV. The CV and EIS in 0.1 M Na<sub>2</sub>SO<sub>4</sub> aqueous solution with the presence of RhB were also measured to investigate the properties of electrochemical characterization before degradation experiment. Moreover, Mott-Shottky measurement was also conducted to investigate the donor concentration on the electrode surface. The test was performed at single frequency of 3 Hz. The potential range is –0.6 V to 0.4 V with the potential amplification 0.02 V.

## 2.4. Degradation of RhB

The degradation process was carried out in the photoelectrochemical cell (PEC) with a 375 nm LED as the simulated excitation light source. The TiO<sub>2</sub> NTAs electrode, Pt sheet and Ag/AgCl electrode were employed as the working electrode, counter electrode and reference electrode, respectively. The 2 × 2 cm [2] of photocatalyst was exposed to 40 mL supporting electrolyte with 10 ppm RhB and 0.1 M Na<sub>2</sub>SO<sub>4</sub> aqueous solutions. The solutions were continuously stirred for 30 min in dark to ensure the establishment of an adsorption-desorption equilibrium between the RhB and photocatalyst before experiment. Then RhB degradation on different condition was carried out to investigate the influence of bias potential, light and nanotube length. The dark adsorption and photocatalytic degradation were performed on the PEC under the open circuit. Other experiments were conducted on the certain bias potential. In addition, the solutions were shined with a 375 nm LED monochromatic source placed outside the PEC during illumination. The samples were taken out from the PEC every 10 min for UV–vis measurement (UV2600, LongNiKe Co., Ltd., China). The maximum adsorption wavelength of RhB is 554 nm.

## 3. Results and discussion

### 3.1. The morphology and structure of TiO<sub>2</sub> NTAs electrodes

The morphologies of the TiO<sub>2</sub> NTAs electrodes obtained at different oxidation time were characterized by FE-SEM, as shown in Fig. 2a–f. It is found that the nanotube length increases with the oxidation time. The corresponding average nanotube length of the TiO<sub>2</sub> NTAs electrodes obtained at different oxidation time is 8.64 μm (t = 1 h), 15.55 μm (t = 2 h) and 24.67 μm (t = 3 h), respectively. From the top view of the TiO<sub>2</sub> NTAs electrodes we observe that the duration time did not change the tube diameter. The TiO<sub>2</sub> NTAs electrodes obtained at different oxidation time all have an average inner tube diameter of approximately 119 nm. As is known to all, the growth of the nanotube is dependent on the field-assisted oxidation, field-assisted migration, field-assisted dissolution and chemical dissolution. The nanotube length increases until the rate of oxide growth at Ti/TiO<sub>2</sub> interface ultimately equals the rate of oxide dissolution at the pore-bottom/electrolyte interface. As for a given electrolyte concentration and anodization potential, the nanotube length will be independent of the anodization duration after this point is reached [31–33]. In this work, the relationship between duration time and nanotube length is shown in Fig. 2g. It is observed that the nanotube length increases linearly with the duration time, and the growth rate is 8.125 μm/h.

The XRD technique was employed to identify the composition, phase structure, and crystalline of the as-synthesized samples. Fig. 3 shows the XRD patterns of the as-prepared TiO<sub>2</sub> NTAs electrodes. We can observe that the TiO<sub>2</sub> NTAs exhibits the reflections of anatase TiO<sub>2</sub> with sharp diffraction peaks appearing at 2θ = 25.3°, 37.8°, 48.1°, 53.9°, 62.7°, 68.8°, 75.0°, which are assigned to the (101), (004), (200), (105), (204), (116) and (215) planes of TiO<sub>2</sub> (JCPDS#21-1272), respectively. Researchers have reported

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