



# Photocatalytic decompositions of gaseous HCHO and methylene blue with highly ordered TiO<sub>2</sub> nanotube arrays

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## ABSTRACT

The highly ordered TiO<sub>2</sub> nanotubes (NTs) were fabricated by the anodic oxidation method. Their morphology, structure and crystalline phase were characterized by scanning electron microscopy (SEM) and X-ray diffractometer (XRD). The effects of morphology, specific surface area, pore structures and photocatalytic activity of the TiO<sub>2</sub> NTs were investigated. UV–vis spectra analysis showed that its light absorption had been extended to the visible light range. The photocatalytic activity of the as-prepared samples was evaluated by photocatalytic oxidation of gaseous HCHO and MB aqueous solution. The samples had better adhesion strength in the dark and showed a higher photocatalytic activity than nanoparticles. Especially, with ultraviolet light pretreatment, the nanotubes exhibited more stable active for photocatalytic decomposition and the photodecomposition rate remained at high level after 3 cycles of the photocatalysis experiment. Thus, how the number of surface active group •OH increased and the mechanism for the great improvement for the photocatalytic activity are discussed.

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## 1. Introduction

Titanium dioxide remains one of the most promising materials for photocatalysis due to its high oxidation efficiency, nontoxicity, high photostability, chemical inertness, low cost and environmentally friendly nature [1,2]. Compared with TiO<sub>2</sub> nanoparticles, highly ordered TiO<sub>2</sub> nanotube arrays (TiO<sub>2</sub> NTs) with aligned porosity, higher crystallinity and oriented nature properties show higher efficiency of charge collection caused by rapid electron transport and low charge recombination [3,4]. And they have superior photoreactivity and long-term stability. They avoid three vital technical problems which the particulate suspended system encountered: (a) the need for separation or filtration steps after the photodegradation reaction, (b) the particle aggregation especially at high concentrations, and (c) the problematic use in continuous flow systems [5–7]. After a simple anodization process, the nanotubes are produced, which utilization of sunlight better and have more efficient electron transport than those of randomly oriented TiO<sub>2</sub> nanoparticles. Thus, TiO<sub>2</sub> NTs have attracted much attention.

In the past few years, Wang et al. [8] summarized the impact of several factors on the photocatalytic performance of TiO<sub>2</sub> NTs, such as wall thickness, annealing temperature. Zhuang [9] and Yu et al. [10] studied the photocatalytic effect of TiO<sub>2</sub> NTs on different

degradation agents. It is worth noting that the study on the renewable photocatalytic activity of nanostructures is rarely performed [11]. The research on degrading gaseous HCHO of the TiO<sub>2</sub> NTs is relatively less and enhancing photocatalytic activity of TiO<sub>2</sub> NTs with ultraviolet light irradiation pretreatment has not been reported.

In the present paper, the TiO<sub>2</sub> NTs prepared by anodic oxidation method has higher photocatalytic performance. To evaluate the photocatalytic activity of the TiO<sub>2</sub> NTs and TiO<sub>2</sub> nanoparticles, the samples and commercial-grade TiO<sub>2</sub> nanoparticles (P25, Degussa AG, Germany) are irradiated by ultraviolet light and visible light in the presence of formaldehyde (HCHO) and Methylene Blue (MB). It has been shown that the activity of TiO<sub>2</sub> NTs is much higher than TiO<sub>2</sub> nanoparticles. Moreover, the photocatalytic activities and reusability of the TiO<sub>2</sub> NTs before and after ultraviolet light pretreatment were comparatively investigated.

## 2. Experimental

### 2.1. Preparation

The TiO<sub>2</sub> NTs were fabricated by electrochemical anodization of 99% pure titanium plates. The titanium plates, 10 mm × 20 mm × 0.2 mm, were ground, finely polished, and then degreased in an ultrasonic bath with acetone. The materials were rinsed in absolute ethyl alcohol and distilled water, and then dried

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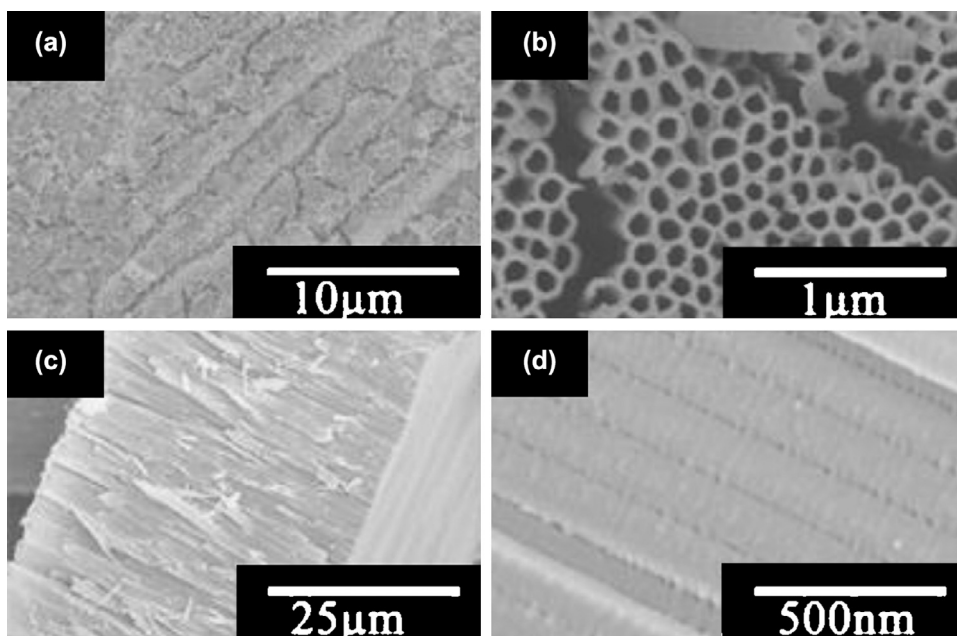


Fig. 1. SEM images of TiO<sub>2</sub> NTs with different magnifications: (a, b) top view, (c, d) profile view.

by air. The anodization was performed in a two-electrode electrochemical cell with the titanium foil as the working electrode and platinum foil as the counter electrode at room temperature (23 °C). Ethylene glycol containing 0.05 wt% NH<sub>4</sub>F and 0.05 wt% deionized water was used as the electrolyte for the anodization [12]. The titanium sheet was anodized at different voltages for 6 h in electrolyte, using a direct-current power supply. After anodization, the TiO<sub>2</sub> NTs samples were rinsed thoroughly with deionized water and isopropyl alcohol, and then dried by air. Anodized samples were annealed in furnace in dry air at 450 °C for 2 h with 1 °C/min of ramp up and cooled down to obtain TiO<sub>2</sub> NTs.

## 2.2. Morphology and structure characterization

The morphologies of the samples were studied using a scanning electron microscope (SEM, Philips XL-30). The phase purity and crystal structure of the prepared samples were examined by a X-ray diffractometer (XRD, Rigaku, D/max-2500) with a Cu K $\alpha$  radiation ( $\lambda = 0.154059$  nm) as the X-ray source. The scanning rate was 0.02° s<sup>-1</sup> in the  $2\theta$  range of 20°–70°. The UV–vis absorption spectra of the resultant samples were obtained by a spectrometer (DU-88, Shanghai, China) with a wavelength range from 300 nm to 600 nm. The contact angle was measured by a contact angle measuring instrument (DSA series, Germany).

## 2.3. Photocatalytic activity

The degradation of gaseous HCHO by TiO<sub>2</sub> NTs was conducted in a volume of 400 mL vessel at room temperature. Three pieces of TiO<sub>2</sub> NTs were placed in the reaction vessel 400 mL. Then, a measured quantity of reaction gas (0.1 mL HCHO aqueous solution whose concentration was  $8 \times 10^{-5}$  mg/L) was introduced into it. After establishing the adsorption equilibrium of gaseous HCHO on the TiO<sub>2</sub> NTs surface in the dark for 0.5 h, the reactor was placed under the ultraviolet lamp ( $\lambda = 365$  nm). The decrease in gaseous HCHO concentration was monitored using formaldehyde detector (Inters, Type 4160, USA) every 30 min. The degree of gaseous HCHO

degradation  $D_1$  was calculated by:

$$D_1 = \frac{P_0 - P}{P_0} \times 100\% \quad (1)$$

$P_0$  is the initial concentration (ppm); and  $P$  is the concentration after a period of time  $t$  (ppm).

The TiO<sub>2</sub> NTs can get rid of matters accompanying by the method of heating at 100 °C for 2 h and can be re-used. The experiment of photocatalytic degradation MB aqueous solution was carried by placing 3 pieces of TiO<sub>2</sub> NTs substrates and 10 mL MB aqueous solution in a 5 cm diameter Petri dish. The concentration of MB aqueous solution was 20 mg/L, and the catalyst area of each sample was 10 mm  $\times$  15 mm. The weight of the Petri dish was maintained constant during the measurement at different periods of time to eliminate the dye concentration change caused by water evaporation. Prior to measurement the solution was stabilized for 30 min to let the solution reach equilibrium as a result of the dye absorption on the TiO<sub>2</sub> NTs substrates. Ultraviolet lamp (365 nm) or fluorescent lamp was placed 20 cm above the Petri dish. A UV–vis spectrophotometer (Type 7320 G, Shanghai, China) was used to measure the solution adsorption intensity. The maximum light absorption intensity of MB solution aqueous at 660 nm wavelength was used to calculate the MB degradation rate  $D_2$  according to the following equation:

$$D_2 = \frac{A_0 - A}{A_0} \times 100\% \quad (2)$$

$A_0$  is the initial absorbance of reactant; and  $A$  is the absorbance of reactant after illumination time  $t$ .

## 3. Results and discussion

### 3.1. Morphology and structure

Fig. 1 shows the different views of TiO<sub>2</sub> NTs. The structure of TiO<sub>2</sub> NTs can be clearly observed from Fig. 1(b). TiO<sub>2</sub> NTs are highly ordered, without impurity at the entrance of the pores, and distribute uniformly. Although the surface of TiO<sub>2</sub> NTs is rough slightly and there are large cracks on it, the TiO<sub>2</sub> NTs are high-density, well-ordered. TiO<sub>2</sub> NTs are well aligned with an average

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