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Letter

Synthesis of carbon-modified TiO_2 nanotube arrays for enhancing the photocatalytic activity under the visible light

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ABSTRACT

TiO_2 nanotube arrays modified with carbon were prepared by anodization of Ti foil followed by a hydrothermal treatment in glucose aqueous solution. The morphologies, crystalline structures were characterized by a scanning electron microscope, an energy-dispersive X-ray spectrometer and an X-ray diffraction spectrometer. The optical and photoelectric properties were studied using a UV–vis spectrophotometer and an electrochemical workstation. The photocatalytic activities of the samples were evaluated with the degradation of methylene blue under the visible light irradiation. The results revealed that the carbon-modified TiO_2 nanotube arrays exhibit a considerable enhancement of the photocatalytic activity comparing with the pure TiO_2 nanotube arrays under the visible light.

1. Introduction

In recent years, metaloxide semiconductor photocatalyst has attracted many attentions in the application in photocatalytic degradation of organic compounds for the treatment of wastewater and air pollution [1,2]. Among various oxide photocatalysts, TiO_2 is indicated to be an excellent and high efficient photocatalyst [3]. However, it still remains many challenges before TiO_2 becomes an economically feasible photocatalyst. For example, the enhancement of solar energy utilization ratio and the suppression of the recombination of photogenerated electron–hole pairs. A variety of methods have been developed to increase the photocatalytic efficiency of TiO_2, such as doping TiO_2 with metallic ions [4,5] or nonmetallic ions [6,7] to increase the visible light absorbance; modifying or coating TiO_2 with noble metal [8], semiconductor [9], carbon [10–12] or graphite [13] for improving the transport of photocarriers during photocatalysis.

Enlarging the specific surface area of TiO_2 can also improve the photocatalytic efficiency [3], and many efforts have been made to obtain nanostructured TiO_2-based materials with a large specific surface area [14]. TiO_2 nanotubes are of larger specific surface area comparing with regular TiO_2 nano-particles and nano-rods, and have shown a potential application in photocatalysis [15]. Variant processes have been used for producing TiO_2 nanotubes in the past few years, such as template-assistant deposition [16], hydrothermal processes [17] and anodization [18]. Among these fabrication methods, anodization is indicated to be a simple and precisely controllable method for synthesizing highly ordered TiO_2 nanotube arrays in fluoride-based baths [18–21].

Modifying TiO_2 with carbon can improve the photocatalytic activity by improving the transport of photocarriers during photocatalysis through the formation of electronic interactions between TiO_2 and carbon, and many approaches [10–12] have been published in recent years. To the best of our knowledge, few efforts have been made for the carbon-modified TiO_2 nanotube arrays. In the present work, TiO_2 nanotube arrays prepared by anodization were modified with carbon from a simple method and exhibited a considerable enhancement of photocatalytic activity comparing with the pure TiO_2 nanotube arrays under the visible light. The mechanism of the enhancement of photocatalytic activity was investigated systematically.

2. Experimental

The synthesis of carbon-modified TiO_2 nanotube arrays (C-TNT) consisted of three steps: (1) anodization of Ti foils to form the pristine TiO_2 nanotube arrays and annealing the pristine TiO_2 nanotube arrays in ambient air at 450 °C for 3 h to produce crystallized TiO_2 nanotube arrays (TNT), (2) hydrothermal treatment of the pristine TiO_2 nanotube arrays in a glucose aqueous solution at 180 °C for 4 h, and (3) annealing the treated TiO_2 nanotube arrays in argon (Ar) at 450 °C for 3 h.

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In the anodization experiments, Ti foils (1 cm × 1 cm in size, 0.25 mm thick, 99.5% purity) were degreased by sonicating in acetone, ethanol and deionized (DI) water followed by drying in ambient air. Glycerol/water/ammonium fluoride electrolyte consisted of a mixture of DI water and glycerol prepared in volumetric ratio of 1:1 with 0.27 M NH_4F, and all chemicals were of analytical grade. A two-electrode system involving a graphite plate as cathode electrode and a direct current power supply was used for the electrochemical anodization. The electrochemical anodization consisted of a voltage ramp from the open-circuit potential (OCP) to 15 V, followed by holding this constant voltage during the anodization process. The anodization process lasted for 3 h, and was carried out at room temperature.

Glucose aqueous solution consisted of 16 ml DI water and 0.1 g glucose was prepared, and was subsequently transferred into a 20-ml autoclave where the pristine TiO_2 nanotube arrays were placed in and hydrothermally treated at 180 °C for 4 h. After that, hydrothermally treated samples were annealed in Ar at 450 °C for 3 h.

The morphologies and chemical compositions of the TNT and the C-TNT samples were characterized by a scanning electron microscope (SEM, FEI SIRION, The Netherlands) with an energy-dispersive X-ray spectrometer (EDS). The crystalline structures were revealed by an X-ray diffraction spectrometer (XRD) (D8 Advanced XRD, Bruker AXS, Germany) with Cu Kα radiation ($\lambda = 0.15406$ nm) working at 40 mA and 40 kV.

The UV–vis diffuse reflectance spectra of the TNT and the C-TNT samples were measured by a diffuse reflectance accessory of UV–vis spectrophotometer (UV-2550, Shimadzu, Japan).

The photocatalytic activities of the TNT and the C-TNT samples were evaluated with the degradation of methyl blue (MB) under the visible light at room temperature. Each sample of the TNT and the C-TNT was placed in a quartz cuvette filled with 2 ml MB aqueous solution (1.0×10^{-5} M) and irradiated with a visible light source at a distance of 25 cm. A high pressure mercury lamp (160 W) with a cutoff filter ($\lambda > 390$ nm) to remove radiation below 390 nm was used as the visible light source. The variation of the MB concentration was evaluated by the absorbance of the solution at 665 nm, and the absorbance was measured by the UV–vis spectrophotometer (UV-2550, Shimadzu, Japan) for every 60 min.

The photocurrent response experiments were carried out under the visible light pulsed-irradiation using an electrochemical workstation (CHI600C, CH Instruments Co.) to investigate the photoelectric properties of the TNT and the C-TNT samples. The visible light source (the same as that in the MB degradation experiments) was away from the working electrode with a distance of 15 cm, all experiments were carried out at room temperature.

3. Results and discussion

Fig. 1 shows the SEM views and the EDS patterns of the TNT and the C-TNT samples. It can be seen that the highly ordered TiO_2 nanotube arrays were obtain by anodization of Ti foils in the optimized conditions, the diameter of the TiO_2 nanotubes were about 60–70 nm. Generally, the formation of the TiO_2 nanotube arrays is proposed to have the two competitive processes: (1) electrochemical oxidation, and (2) chemical dissolution [19]. The electrochemical oxidation can be formulated as Eqs. (1)–(4), and the chemical dissolution of TiO_2 is formulated as Eq. (5):

$$2H_2O \rightarrow 4H^+ + 4OH^- \tag{1}$$

$$4OH^- \rightarrow 2H_2 + O_2 + 4e^- \tag{2}$$

$$\text{Anode}: Ti^{4+} + 2O^{2-} \rightarrow TiO_2 \tag{3}$$

$$\text{Cathode}: H^+ + 4e^- \rightarrow 2H_2 \tag{4}$$

$$TiO_2 + 6F^- + 4H^+ \rightarrow [TiF_6]^{2-} + 2H_2O \tag{5}$$

The C-TNT samples were prepared according to the following process: the pristine TiO_2 nanotube arrays were hydrothermal treated in a glucose aqueous solution; and the glucose was hydrolyzed at high temperature (180 °C), therefore, a carbon layer was coated on the nanotubes. The EDS measurements indicate that a carbon peak is observed in the C-TNT sample and the atom percentage of C is 10.98%, which demonstrates that TiO_2 nanotube arrays are successfully modified with carbon, as shown in Fig. 1(d). The modified carbon was probably amorphous because the hydrothermal treatment (180 °C) and anneal (450 °C) temperature were too low to transfer amorphous carbon into graphite-like carbon.

Fig. 2 shows the high-resolution (HR) TEM images of the C-TNT sample. The images show that the TiO_2 nanotubes are surrounded by a very thin amorphous carbon layer, which is in good agreement with our other results. Because of this structure, a good electronic contact between TiO_2 and carbon is achieved.

The pristine TiO_2 nanotube arrays typically exhibit an amorphous structure, and can be transformed into anatase phase at temperatures below 450 °C in air [20]. The XRD spectra reveals that both of the TNT and the C-TNT samples consist of pure anatase

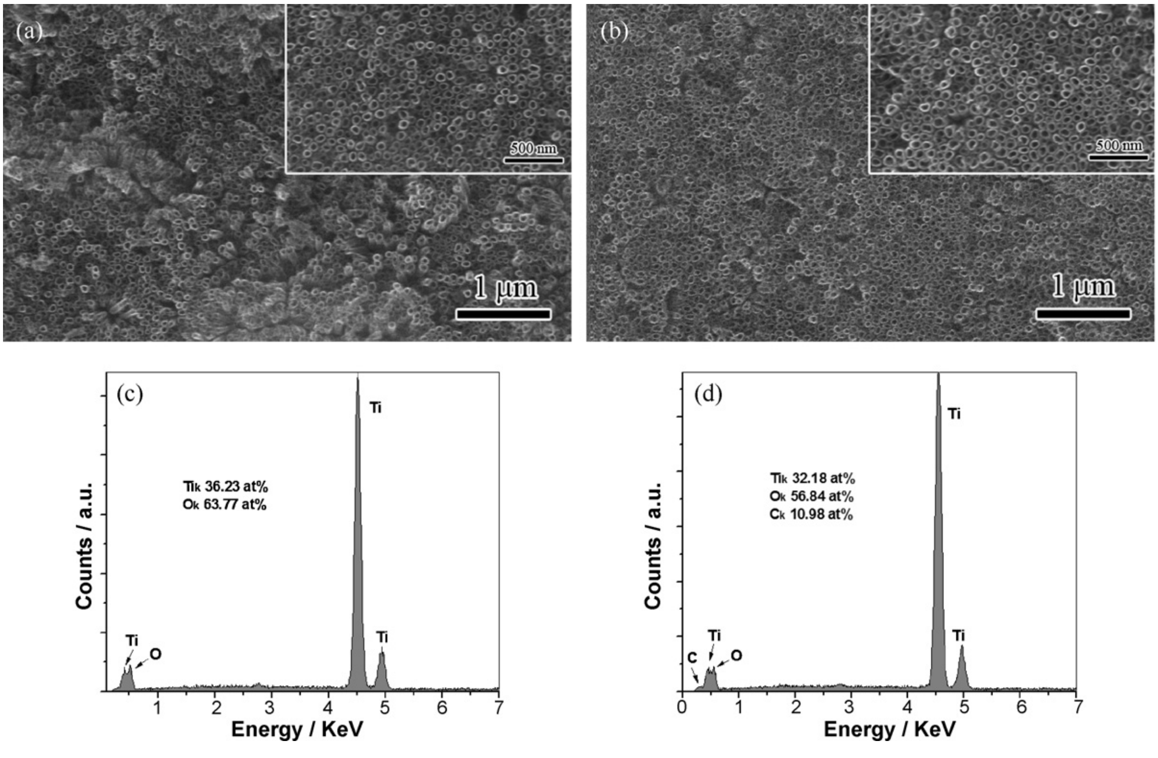

Fig. 1. SEM morphologies and EDS patterns of the (a, c) TNT and the (b, d) C-TNT samples. The insets are the high magnification views.

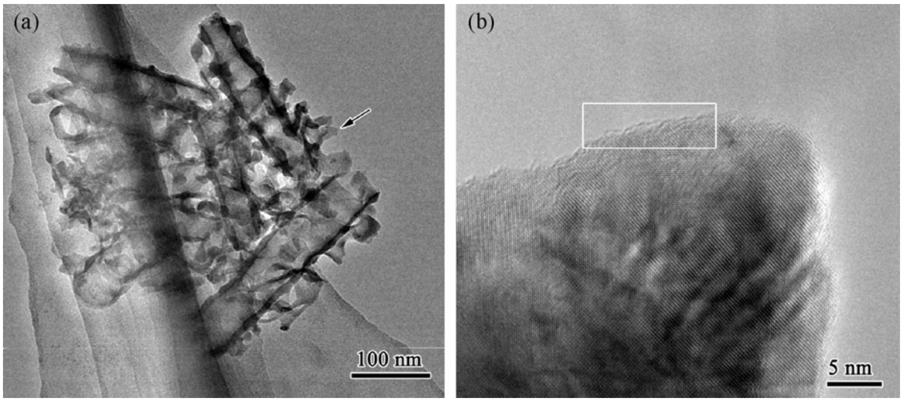

Fig. 2. High-resolution (HR)–TEM images of the C-TNT sample.

phase due to the annealing temperature (450 °C), which shows the potential for photocatalytic application, as shown in Fig. 3.

Fig. 4 illustrates the optical properties of the TNT and the C-TNT samples probed with UV–vis diffuse reflectance spectroscopy (DRS). The TNT sample shows a spectrum with its fundamental absorption sharp edge rising at 380 nm, while the C-TNT sample shows a higher absorption in the visible light region because of the presence of carbon.

The photocatalytic activities of the TNT and the C-TNT samples were evaluated with the degradation of MB under the visible light irradiation, as shown in Fig. 5. The results indicate that (1) the blank test (without any sample) shows only a small amount of MB degradation; (2) the amount of MB degraded by the TNT sample is only 40% after 5 h; (3) the amount of MB degraded by the C-TNT sample was almost 85%. The C-TNT sample exhibits a considerable enhancement of photocatalytic activity comparing with the TNT sample under the visible light irradiation.

The photocatalytic activity of semiconductor oxide is mainly governed by surface area, crystalline structure. The TNT and C-TNT samples have the similar surface area and crystalline structure, hence, the interaction between carbon and TiO_2 nanotube arrays is considered to be an important factor for the photocatalytic activity of the C-TNT sample. Therefore, the photocurrent response experiments under the visible light were carried out to investigate the electronic interaction of carbon and TiO_2 nanotube arrays.

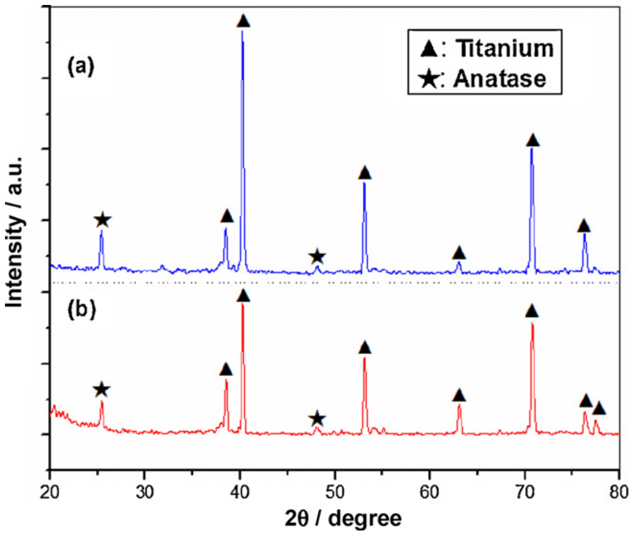

Fig. 3. XRD patterns of the (a) TNT and the (b) C-TNT samples.

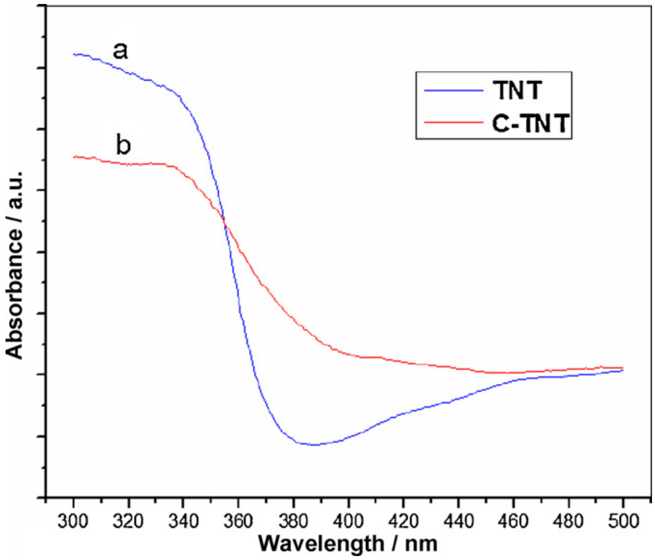

Fig. 4. UV–vis diffuse reflectance spectra (DRS) of the (a) TNT and the (b) C-TNT samples.

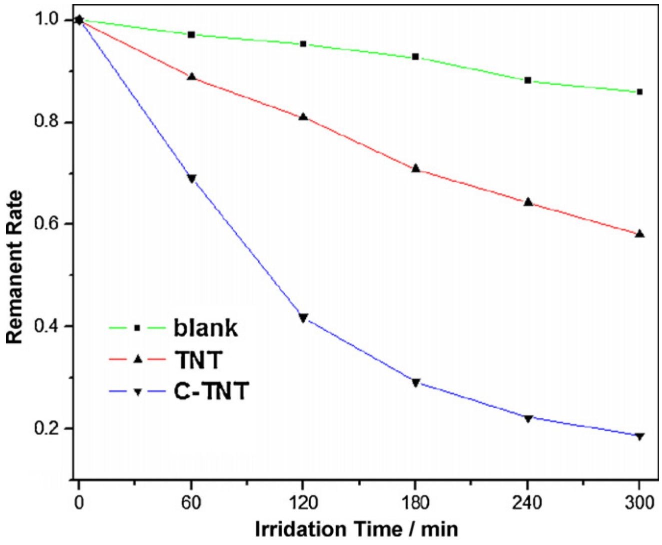

Fig. 5. The concentration change of methyl blue as a function of irradiation time under the visible light for the TNT and the C-TNT samples.

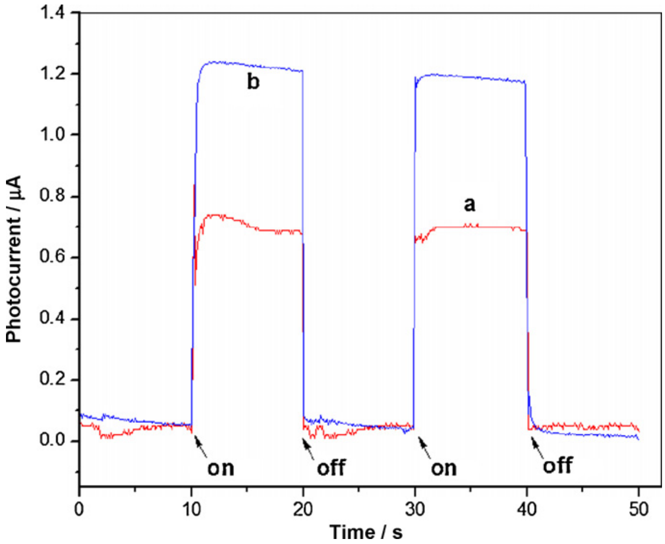

Fig. 6. Photocurrent response of the (a) TNT and the (b) C-TNT samples under the visible light.

A standard three-electrode configuration with a platinum foil as counter electrode and a saturated calomel electrode (SCE) as reference electrode was used, the electrolyte consisted of 0.5 M Na_2SO_4 aqueous solution, and the potential of working electrode versus Pt counter electrode was set to be 0 V. The photocurrent response curves were shown in Fig. 6, and the photocurrent of the C-TNT electrode was nearly two times as high as that of the TNT electrode, which indicated that the separation of photoinduced electrons and holes were improved through the electronic interaction between carbon and TiO_2 nanotube arrays [10].

The result is in agreement with that of the DRS and the MB degradation experiments, therefore, the mechanism of the enhancement of photocatalytic activity under the visible light is supposed to be that: carbon absorbs visible light and the excited state electrons are subsequently transferred to the TiO_2 due to the electronic interaction [10], then the excited electrons react with oxygen to form superoxide radicals for photocatalysis. Modifying TiO_2 nanotube arrays with carbon enhances the absorption of visible light and improves the separation of photoinduced electron–hole pairs during irradiation. Therefore, the C-TNT sample exhibits a considerable enhancement of photocatalytic activity comparing with the TNT sample under the visible light irradiation.

4. Conclusions

In summary, highly ordered TiO_2 nanotube arrays were prepared by anodization of Ti foils in the glycerol/water/ammonium fluoride electrolyte and then hydrothermal treated in glucose aqueous solution for modifying with carbon. MB degradation experiments revealed that the carbon-modified TiO_2 nanotube arrays exhibited a considerable enhancement of the photocatalytic activity comparing with the pure TiO_2 nanotube arrays under the visible light irradiation. Photocurrent experiments indicated that modifying TiO_2 nanotube arrays with carbon improved the separation of photoinduced electrons and holes through the electronic interaction between carbon and TiO_2 nanotube arrays, therefore, enhanced the photocatalytic activity under the visible light irradiation.

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