



Preparation of nitrogen-doped anatase TiO₂ nanoworm/nanotube hierarchical structures and its photocatalytic effect



Xian Hou^a, Cheng-Wei Wang^{a,*}, Wei-Dong Zhu^a, Xiang-Qian Wang^a, Yan Li^a, Jian Wang^a, Jian-Biao Chen^a, Tian Gan^a, Hai-Yuan Hu^b, Feng Zhou^b

^aKey Laboratory of Atomic and Molecular Physics & Functional Materials of Gansu Province, College of Physics and Electronic Engineering, Northwest Normal University, Lanzhou 730070, China

^bState Key Laboratory of Solid Lubrication, Lanzhou Institute of Chemical Physics, Chinese Academy of Science, Lanzhou 730000, China

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ABSTRACT

As-anodized amorphous TiO₂ nanotube arrays (TNAs) are immersed in hot ammonia solution (90 °C), which can both spontaneously reconstruct the amorphous TNAs to be anatase nanoworm/nanotube hierarchical structures in situ and simultaneously implant nitrogen into them. These hierarchical structures, having larger surface area, higher electrical conductivity and broader light absorption range than the original TNAs, possess dramatically enhanced photocatalytic activity for degradation of methyl orange (MO) under visible light irradiation. The optimized nitrogen doped hierarchical structures exhibit a best photodegradation rate (*K*) of 0.722 h⁻¹, which greatly exceeds the degradation rate of the original TNAs annealed in ambient air at 500 °C for 2.5 h. This simple technique would enable us conveniently to design and fabricate highly photoactive one-dimensional TNAs-based functional materials applicable to photocatalysis and solar energy conversion.

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1. Introduction

TiO₂ nanotubes arrays (TNAs) have drawn ever-increasing attention in photocatalysts due to their exceptional properties, including higher surface area, better adsorption ability, good electrical transport, chemical stability, nontoxicity and abundance etc. [1–7]. Anodization has been widely considered as one of the most prominent way to fabricate vertical TNAs with a controllable morphology [8]. However, TNAs fabricated by anodization are usually in an amorphous state and exhibit negligible photocatalytic activity. To obtain the expected crystalline phase of anatase or rutile, they ordinarily need annealing [9,10] or hydrothermal post-treatments [11–14] before being used, which unexceptionally involve additional energy consumption, complicated processes and expensive equipments. Furthermore, only 3–5% of UV in solar spectrum can absorb by pure anatase TNAs due to the wide bandgap of 3.2 eV, which restricts their photocatalytic applications to the visible light range [15,16]. This is the main drawback of TNAs

–hole is another hindrance for pure anatase or rutile TNAs, which leads to a low photocatalytic reaction and poor quantum efficiency.

In order to enhance the photocatalytic performance of TNAs, one of the endeavors is to increase their optical activity by shifting the onset of their response from UV to visible region. Many previous studies demonstrated that doping titania with nitrogen was one of the most effective ways to improve photocatalytic activity of titania in visible light region [17–19], which is not only useful for generating more electron–hole pairs under the visible light, but also effectively for preventing the photoelectron–hole pairs from recombining. For example, C. Burda et al. [17] reported that nitrogen-doped TiO₂ could improve photocatalytic activity for the decomposition of methylene blue at wavelengths up to 650 nm. Up to now, a variety of methods such as ion implantation method [20], sputtering method [21], annealing under ammonia gas [22], sol–gel method [23], electro-chemistry method [24] and hydrothermal method [25] have been extensively carried out to dope nitrogen into TNAs. However, most of the above methods also need a high temperature or complicated and expensive equipments. Therefore, it is necessary to develop a low-temperature nitrogen doping method for extending the application of the TNAs photocatalysts.

Besides the doping TNAs with nitrogen mentioned above, to enlarge their surface area is another way for improving their photocatalytic efficiency, since photodegradation is happen at their

* Corresponding author. Tel.: +86 18509311337; fax: +86 9317971503.

E-mail addresses: cwwang@nwnu.edu.cn, chengwwang@aliyun.com (C.-W. Wang).

surface and the larger surface area could facilitate the reactions between the photocatalysts and the pollutants [26,27]. Recently, Wang et al. [12] reported that inducing the anodized TNAs by water at room temperature could transform the amorphous TNAs to the crystallization state and their surface area markedly increased. Liao et al. [13] immersed the anodized TNAs in water at 92 °C, the amorphous TNAs quickly crystallized and a rough surface replaced the former smooth tube wall. Inspired by these interesting researches, we considered that if the nitrogen source exists in aqueous solution, would it be possible to make the amorphous TNAs both crystallized and nitrogen doped in liquid environment? Sure, our experimental results confirm the proposal completely doable.

In this paper, we present a simple technique that the as-anodized amorphous TNAs are immersed in hot ammonia solution (90 °C), which enables amorphous TNAs not only spontaneously to transform into nanoworm/nanotube titania hierarchical structures, but also simultaneously to dope nitrogen into them at a low temperature. These anatase hierarchical nanostructures have larger surface area, higher electrical conductivity and broader light absorption range than the original TNAs, resulting in a pronounced enhanced photocatalytic activity for degradation MO under visible light irradiation. Obviously, this strategy to make the amorphous TNAs both crystallized and nitrogen doped in liquid environment has promising potential applications in development of high performance and low cost TNAs-based photocatalysts, solar cells, and many other photoelectric devices.

2. Experimental

2.1. Preparation of nitrogen doped nanoworm/nanotube hierarchical structures

High pure titanium sheets (99.9% purity, 8 mm × 8 mm × 0.3 mm) were ultrasonically degreased in acetone, alcohol, and deionized water, in that order, and then eroded in a mixture of HF solution and hydrochloric acid ($\text{Vol}_{(\text{HF})}:\text{Vol}_{(\text{HCl})} = 1:8$) for 15 s until a mirror finish was exposed. After rinsing with deionized water and drying in a nitrogen stream, they were anodized in an ethylene glycol solution containing NH_4F (0.5 wt. %) and H_2O (3 wt. %) at 40 V at room temperature for 40 min. After that, rinsed with deionized water for several times and dried in nitrogen stream. Then, the as-anodized TNAs were immersed in deionized water and various concentrations of ammonia solution ($\text{Vol}_{(\text{Ammonia(A)})}:\text{Vol}_{(\text{Deionized water(DI)})} = 1:10, 1:5, 1:2$ and $1:1$, respectively). The concentration of original ammonia solution is 25 wt. %, sealed in high pressure autoclave and kept 8 h at 90 °C. For comparison, besides those hot solution treatments mentioned above, the as-anodized amorphous TNAs were also annealed in ambient air at 500 °C for 2.5 h.

2.2. Characterization of the nanoworm/nanotube hierarchical structures

The surface morphology of samples was examined by a field emission scanning electron microscopy (FE-SEM, JSM-6701F, operated at 5 kV). The structure of the TNAs was analyzed by X-ray diffraction (XRD) using a Rigaku D/max-2400 diffractometer (with $\text{Cu K}\alpha_1$ 0.154056 nm radiation at 40 kV and 150 mA in the 2θ range from 20° to 80°, and the scanning speed was 15°min^{-1} at a step of 0.02°), and material compositions were determined by X-ray photoelectron spectroscopy (XPS, PHI-5702) using $\text{Al-K}\alpha$ monochromatic radiation. The electrical conductivity of the samples was measured using the two-probe method on a Keithley 4200 SCS at room temperature in ambient air. The reference electrode was connected to the metallic substrate and the working electrode

was connected to the TNA film under the gold contact with a contact area of $5.0 \times 10^{-6} \text{ m}^2$. UV–vis spectra of as-prepared samples were recorded with a UV–vis spectrophotometer (Uv-2550, Shimadzu).

2.3. Evaluation of photocatalytic activities under visible light

Photocatalytic activity in the aqueous phase under visible light irradiation (The light source was a 500 W Xe lamp (CHF-XM500, Beijing Trusttech Co., Ltd) attached with cutoff filters to limit the irradiation wavelength, the light beam was cut-off wavelengths shorter than 400 nm) led to the degradation MO aqueous solution with a concentration of 0.05 mmol/L of the reaction. The distance between the sample and the lamp was fixed at 10 cm. Prior to photoreaction, the suspension was magnetically stirred in the dark for 30 min to establish an adsorption–desorption equilibrium between the photocatalyst and MO.

3. Results and discussion

3.1. Structure characterization

3.1.1. SEM analysis

The microscopic morphology of the prepared samples was examined by FE-SEM. As exhibited in Fig. 1(a), the as-anodized TNAs possess uniform porous morphology on top. The inset of Fig. 1(a) is the corresponding side-view image, revealing that the TNAs have smooth tube wall and the tube average inner diameter is about 50 nm. From Fig. 1(b), it is seen that after the TNAs was soaked in hot water over 8 h, many small particles with a particle size of 30–35 nm appear on the top surface and original smooth tube wall morphology disappears, instead of a rough surface morphology, as seen in the inset of Fig. 1(b). However, when the as-prepared TNAs were immersed in ammonia solution with various concentrations ($\text{Vol}_{(\text{A})}:\text{Vol}_{(\text{DI})} = 1:10, 1:5, 1:2$ and $1:1$, respectively), the morphology of TNAs change greatly. Fig. 1(c) shows the sample immersed in ammonia solution with the concentration $\text{Vol}_{(\text{A})}:\text{Vol}_{(\text{DI})} = 1:10$, it is seen that many small worm-like titania with a length of ~100 nm appear both on the top surface and inner wall of the TNAs. At the same time, the nanotube wall becomes thinner but the tubular structure is retained. Along with the ammonia solution concentration gradually increased to $\text{Vol}_{(\text{A})}:\text{Vol}_{(\text{DI})} = 1:1$, worm-like titania become crowded and grow up we can see from Fig. 1(d–f). These hierarchical nanostructures can markedly increase the surface area, which is conducive to enhancing the photocatalytic capacity.

3.1.2. XRD analysis

To examine whether the as-anodized TNAs immersed in hot ammonia solution are successfully crystallized by using of XRD. It is found that as-anodized TNAs are in amorphous state; however, strong characteristic peaks of anatase phase can be clearly detected after being immersed in hot ammonia solution for 8 h as exhibited in Fig. 2. This means that the amorphous TNAs can spontaneously transform into crystalline anatase through the ammonia solution treatment at 90 °C. According to Scherrer's formula from anatase (101) diffraction peak, the average crystalline sizes for samples treated by ammonia solution with the concentration $\text{Vol}_{(\text{A})}:\text{Vol}_{(\text{DI})} = 1:10, 1:1$ are 30 nm and 24.3 nm, respectively, this indicates that crystalline growth is significantly suppressed with the increase of nitrogen content in TNAs lattice, which favors the formation of smaller titania crystallites.

3.1.3. XPS analysis

XPS is an effective surface analysis technique for characterizing elemental composition and chemical states. Fig. 3 shows the

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