A facile hydrothermal synthesis and properties of TiO$_2$ nanosheet array films

Liuyuan Lai$^1$, E Lei$^{1,2,3}$, Chaoyang Hu$^1$, Dan Zhao$^{1,2}$, Wei Zhao$^1$*, Zhengang Guo$^{1,2}$* and Dedong Huang$^1$

$^1$ School of Materials Science and Engineering, Tianjin Chengjian University, Tianjin, 300384, People’s Republic of China
$^2$ Tianjin Key Laboratory of Building Green Functional Materials, Tianjin Chengjian University, Tianjin, 300384, People’s Republic of China
$^3$ Author to whom any correspondence should be addressed.

E-mail: 846670784@qq.com, early@tcu.edu.cn, 2863052257@qq.com, zhaodan@tcu.edu.cn, zhaowei2004@tsinghua.org.cn, zhenggangguo@126.com and 1738626477@qq.com

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Abstract

A facile hydrothermal procedure was adopted to prepare TiO$_2$ nanosheet array film on Ti foil, with NaCl as a morphology control agent. SEM, EDS, XPS and XRD showed that the TiO$_2$ nanosheets with uniform morphology were vertically grown on the surface of Ti foil, and the nanosheets were interlaced with each other. When the hydrothermal reaction was controlled at 140 °C for 6 h, TiO$_2$ nanosheet array film with superhydrophilicity (water contact angle of 3°) was obtained. In addition, excellent flexibility of Ti foil with TiO$_2$ nanosheet array films could be a promising material for flexible application.

1. Introduction

TiO$_2$ films are widely used in an agent for environment cleaning or solar cell, due to the advantages of long-time corrosion resistance, stable performance, and excellent photocatalytic activity. A discovery about the superhydrophilic phenomena (water contact angle < 5°) of TiO$_2$ films was reported by Wang et al in 1997 [1]. Then, TiO$_2$ films began to receive considerable attention for the application in the field of superhydrophilicity. The well-known mechanism of superhydrophilicity is that photogenerated holes react with lattice oxygens to form surface oxygen vacancies when TiO$_2$ films are exposed to UV-light illumination [2--5].

TiO$_2$ array films, such as nanorod and nanotube array, have large specific surface area and high-density active sites to promote photochemical reactions. Meanwhile, such special structure is beneficial to accelerate the transfer rate of photo-carriers and hinder the recombination of photogenerated holes and electrons [6, 7]. So, such nanoarray morphology is favorable to transport channels that photoelectrons can directly reach to the conductive substrate, result in boosting the transfer rate of photo-carriers. Among the TiO$_2$ array films, vertically aligned TiO$_2$ nanosheet array films have been considered as an excellent material of superhydrophilicity due to the unique morphology and superior performance, which can be applied in the field of self-cleaning and solar energy conversion [8, 9].

Nowadays, some methods have been employed to prepare TiO$_2$ array films, such as chemical vapor deposition, anodic oxidation and hydrothermal method. Compared with other methods, hydrothermal synthesis of TiO$_2$ films has been considered to be beneficial to environmental friendliness, good uniform, controllable shape and size, firmness between film and substrate, low temperature process. In recent years, some research on TiO$_2$ nanosheet array films prepared by hydrothermal method have been reported. Wang et al prepared TiO$_2$ nanosheet array films on glass substrates, which exhibited good transparency due to the air pocket existing inside of the thin film between nanosheets [8]. Zhang et al fabricated TiO$_2$ nanosheet array layer, and the results showed that a remarkable increase of efficiency was achieved for a DSSC based on double-layered TiO$_2$ nanosheet arrays [10]. In this work, a facile hydrothermal procedure was developed to prepare TiO$_2$ nanosheet array films, which TiO$_2$ nanosheets were vertically grown on the surface of Ti foil. Herein, the Ti foil was chosen as substrate for the following reasons: (1) Ti foil can serve as a titanium source; (2) Ti foil can be used...
as substrate on which TiO$_2$ nanosheet array film grown; (3) the transport barrier of the photo-carriers between the TiO$_2$ nanosheet array film and the Ti substrate becomes smaller because Ti is a good conductor; (4) Ti foil has good flexibility and better application. In addition, the effects of hydrothermal temperature and time on the morphology of TiO$_2$ nanosheet array films were studied, and the influence of morphology on the hydrophilicity and photoelectric performance were further investigated.

2. Experimental

2.1. Material preparation

A typical preparation process, Ti foils were firstly ultrasonically cleaned with mixed solution of acetone, ethanol and deionized water (DW) for 10 min to make the surface clean. After cleaning, the Ti foils were submerged in a mixed solution consisting of HF (55 wt%), HNO$_3$ (65 wt%), and DW (volume ratio = 1:1:2) for 15 s to remove the surface oxide layer. Then the fresh Ti foils were placed in Teflon-lined stainless steel autoclaves filled with 5.844 g NaCl, 10 mL H$_2$O$_2$ (37 wt%) and 50 mL DW. The autoclaves were heated to different temperatures (120, 140 or 160 °C) for appropriate time (2, 4 or 6 h). After the hydrothermal synthesis, the autoclaves were cooled down naturally to room temperature. Finally, the samples were annealed at 450 °C for 4 h in air atmosphere.

2.2. Characterization

The morphology was characterized by scanning electron microscopy (SEM, JSM-7800F, Japan) equipped with X-ray energy dispersive spectroscopy (EDS, X-Max$^\text{N}$, Britain). The crystal structure was determined by X-ray diffraction (XRD, D/MAX-Ultima IV, Japan) with high-intensity Cu K$_\alpha$ radiation (λ = 1.5406 Å). The surface composition and surface binding states were determined by X-ray photoelectron spectroscopy (XPS, ESCALAB 250Xi, America) with a resolution of 0.3–0.5 eV. The contact angle measurements were obtained by drop contact angle analysis machine (JC2000D4, China). The photoelectric performance was tested in a standard three-electrode system using a 0.5 mol L$^{-1}$ Na$_2$SO$_4$ solution. The test procedure was carried out by an electrochemical workstation (CHI 760E, America), in which Pt electrode was the counter electrode, TiO$_2$ nanosheet array film electrode was the working electrode, and Ag/AgCl electrode was the reference electrode.

3. Results and discussion

SEM images of TiO$_2$ nanosheet array films were shown in figures 1(a)–(d). At 120 °C, the sample I displayed a three-dimensional network with the bore diameter in range of 30–70 nm (figure 1(a)). When the hydrothermal temperature was increased to 140 °C, the morphology of the sample II changed extremely, and the surface of the film was uniformly composed of nanosheets with a thickness of approximately 20 nm (figure 1(b)). With further increase of the hydrothermal temperature to 160 °C, the nanosheets thickness of the sample III was reduced slightly to 13 nm (figure 1(c)). However, there were some agglomerations appearing on the surface of the sample. When the hydrothermal temperature kept at 140 °C and hydrothermal time extended to 6 h, more regular polygonal nanosheets about 100 nm in length and 10 nm in thickness were formed on the surface of the sample IV (figure 1(d)). Compared with the sample II, the nanosheets in the sample IV were regular polygons with thinner thickness and higher growth intensity. The thickness of the array film was observed to be 11.4 μm (figure 1(h)). The EDS mapping pictures of the components on the surface of TiO$_2$ nanosheets were shown in figures 1(e) and (f), Ti and O elements were present along with the atomic ratio of Ti:O = 1:2 which indicated the formation of TiO$_2$ on the surface of Ti foil [11]. It was suspected that NaCl played an important part in the formation process of TiO$_2$ nanosheet array films. As a comparison, a reaction medium without NaCl was applied. The preparation process was as follows: Ti foil was placed in autoclave filled with 10 mL H$_2$O$_2$ and 50 mL DW, then the autoclave was heated at 140 °C for 6 h. Compared with the sample IV, the morphology of the sample V was like luffa cylindrical sponge (figure 1(i)). Therefore, it can be proved that NaCl has an effect on the morphology of TiO$_2$ nanosheet array films, which means the formation of TiO$_2$ nanosheet may depend on the synergic effect between Cl$^-$ and Na$^+$. There are two reasons: on the one hand, addition of NaCl greatly increases the ionic strength of the growth solution; on the other hand, the role of Cl$^-$ is to change composition or coordination structure of the growing unit and influence the morphology through adsorption of Cl$^-$ onto the (110) plane of TiO$_2$ [12, 13].

The growth process of TiO$_2$ nanosheet array film was described in figure 2. In the initial stage, Ti foil reacted with H$_2$O$_2$ in the aqueous solution (figure 2(a)) to produce a number of TiO$_2$ nuclei (Ti + 2H$_2$O$_2$ → TiO$_2$ + 2H$_2$O, figure 2(b)), which transformed into nanocrystals. Then the nanocrystals continued to grow and form nanosheets under the action of NaCl (figure 2(c)). As a result, nanosheets started to grow vertically on the Ti substrate by the dissolution-crystallization process (figure 2(d)).
Figure 1. SEM images of TiO$_2$ films on Ti foil. (a) The sample I prepared at 120 °C, 4 h; (b) the sample II prepared at 140 °C, 4 h; (c) the sample III prepared at 160 °C, 4 h; (d) the sample IV prepared at 140 °C, 6 h; (e) and (f) EDS elemental mappings corresponding to Ti and O; (g) the atomic ratio of Ti and O elements; (h) fractography of sample IV; (i) the sample V prepared at 140 °C, 6 h.

Figure 2. Schematic diagram of the fabrication of TiO$_2$ nanosheet array film on Ti foil by hydrothermal reaction.
To further investigate the crystal structure and phase of TiO₂ nanosheet array films, XRD patterns of the sample IV and Ti foil were carried out (Figure 3(a)). However, no characteristic peaks of TiO₂ could be found and only diffraction peaks of Ti existed, which was from the Ti foil substrate (JCPDS No. 44–1294). Thus XPS was employed to determine the surface composition and surface binding states, as shown in figures 3(b)–(d). The survey scan spectrum showed Ti, O and C elements existing on the surface of the sample (figure 3(b)). The peak of C was mainly attributed to exogenous carbon as a calibration reference. Ti 2p spectra with two peaks were Ti 2p₃/2 at 458.4 eV and Ti 2p₁/2 at 464.1 eV (figure 3(c)). The area ratio of the two peaks was about 0.5 and the binding energy difference was 5.7 eV, which was typical XPS spectra of Ti⁴⁺ in TiO₂ [14–17]. Meanwhile, Ti³⁺ at 457.6 eV or Ti²⁺ at 456.4 eV was not found in the spectra. O 1 s spectra was fitted by two Gaussian components at 530.0 eV and 531.8 eV (figure 3(d)), which belonged to oxygen vacancies and Ti-OH group existing in TiO₂ and hydrophilic surface [18–21].

It is usually considered that the wettability of solid surfaces depends on the chemical properties and geometrical shapes [4, 22, 23]. Moreover, the hydrophilicity of TiO₂ nanosheet array films is affected by the crystal structure, morphology, surface hydroxyl content and specific surface area. The schematic illustration of superhydrophilicity on TiO₂ nanosheet array film before and after UV-light illumination was shown in figure 4. Before the UV-light illumination, the water droplet will fill the gap between the nanosheets, which results in reducing water contact angle. Under the UV-light illumination, the photogenerated electrons will be trapped by O₂ adsorbed on the surface to form ·O₂⁻. Meanwhile, photogenerated holes react with lattice oxygens to form surface oxygen vacancies. Then water molecules may coordinate into the oxygen vacancies, resulting in dissociation and adsorption of water molecules on the surface. This process can reduce water contact angle of TiO₂ nanosheet array film to 0° [2].

Figure 3. XRD pattern of the sample IV and Ti foil, and XPS spectra of the sample IV. (a) XRD pattern of the sample IV and Ti foil; (b) XPS survey spectrum; (c) and (d) the high-resolution spectrum of Ti 2p and O 1 s.

Figure 4. Schematic illustration of superhydrophilicity on TiO₂ nanosheet array films before and after UV-light illumination.
The images of water contact angles on TiO$_2$ nanosheet array films before and after UV-light illumination were shown in figure 5. Before UV-light illumination, the initial contact angles increased with the increase of hydrothermal temperature and time. After 0.5 h UV-light illumination, the change law of contact angles with hydrothermal temperature and time were consistent with that before UV-light illumination. Contact angles were 4° and 3° after UV-light illumination for 1 h (figures 5(c) and 5(l)), thence, both sample I and IV became superhydrophilic.

There was a reversible hydrophilic/superhydrophilicity transition of the sample IV by alternating UV-light illumination and storage in the dark. Before UV-light illumination, the initial contact angle of TiO$_2$ nanosheet array film was 65° in figure 6(a); the contact angle of the sample was 3° after 1 h UV-light irradiation in figure 6(b); the contact angle of the sample stored in the dark for 0.5 h was 52° in figure 6(c). The change of contact angles indicated that the sample had the reversible transition between hydrophilic and superhydrophilic state when light on or off.

The superhydrophilic of TiO$_2$ mainly depended on photo-carriers generation, electron-hole pairs separation and electron transfer efficiency on the surface of the semiconductor catalyst. Therefore, the response photocurrent intensity can reflect the overall photoelectron conversion efficiency [24]. The photocurrent-time curve results under the condition of on/off illumination with the solar simulator light source (AM 1.5 G,
and a bias voltage of 0.6 V were shown in figure 7. It can be seen that the rise and fall reflect the fast response of photocurrent when the light was turned on or off. After applying the light illumination, the photocurrent value of the sample I was 21.7 μA/cm², which was higher than the sample II (18 μA/cm²), sample III (8 μA/cm²) and sample IV (12 μA/cm²).

Combined the results of contact angles and photocurrent, it can be concluded that the superhydrophilicity of the sample I was contributed to the three-dimensional network and excellent photoelectric performance. As to the sample IV, the uniformity of TiO₂ nanosheet array played an important role in the superhydrophilic. The sample IV had lots of interspace in which the water droplet could fill along the nanosheets, meanwhile, water molecules entered into the oxygen vacancies from that photogenerated holes reacted with lattice oxygens.

4. Conclusion

TiO₂ nanosheet array films can be synthesized on Ti foil by one-step hydrothermal method in a mix aqueous solution of H₂O₂ and NaCl, with Ti foil as both substrate and precursor. TiO₂ nanosheet array film prepared at 140 °C for 6 h possesses the optimum morphology with regular polygonal nanosheets about 100 nm in length and 10 nm in thickness. After UV-light illumination for 1 h, the TiO₂ nanosheet array film behaved superhydrophilicity with the contact angle of 3°.

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ORCID iDs

E Lei  https://orcid.org/0000-0002-0488-2077

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