

Article ID: 1000-7032(2013)01-0061-05

Photoelectrical Properties of TiO₂ Nanorods with An Array-cluster Double-layered Structure

SUN Qiong¹, SUN Xian-miao¹, LI Yang¹, DONG Li-feng^{1,2*}

(1. College of Materials Science and Engineering, Qingdao University of Science and Technology, Qingdao 266042, China;

2. Department of Physics, Astronomy, and Materials Science, Missouri State University, Springfield, Missouri 65897, USA)

* Corresponding Author, E-mail: donglifeng@qust.edu.cn

Abstract: Titanium oxysulfate (TiOSO₄) was used as an inorganic titanium precursor to synthesize TiO₂ nanorods on a transparent, conductive fluorine-doped tin oxide (FTO) substrate by a facile hydrothermal process. The TiO₂ nanorod film was rutile phase and exhibited an array-cluster double-layered structure. Under the illumination of a solar simulator, the short-circuit photocurrent density of TiO₂ nanorods maximized at 0.17 mA/cm², which was over twice that of samples originating from organic titanium isopropoxide [Ti(iPro)₄] under the same conditions. Multi-dimensional structure and the participation of inorganic oxysulfate (OSO₄⁴⁻) anion contribute to the enhanced photocurrent response of TiO₂ nanorod films.

Key words: TiO₂ nanorod; hydrothermal method; morphology; photoelectrical property

CLC number: O484.4

Document code: A

DOI: 10.3788/fgxb20133401.0061

具有阵列-簇双层结构的 TiO₂ 纳米棒的光电性能

孙 琼¹, 孙先淼¹, 李 阳¹, 董立峰^{1,2*}

(1. 青岛科技大学 材料科学与工程学院, 山东 青岛 266042;

2. 美国密苏里州立大学 物理、天文与材料科学系, 密苏里州 斯普林菲尔德 65897)

摘要: 选择硫酸氧钛 (TiOSO₄) 作为无机钛源前驱体, 通过温和的水热法在掺氟氧化锡导电玻璃基底 (FTO) 上直接合成单晶金红石相 TiO₂ 纳米棒薄膜, 呈现阵列-簇双层结构。在模拟太阳光照射下, 该纳米棒薄膜的短路电流可达到 0.17 mA/cm², 是相同条件下由四异丙醇钛 [Ti(iPro)₄] 为有机钛源而制备的 TiO₂ 纳米棒薄膜的 2 倍多。实验结果表明, 多维层状结构和无机硫酸氧根离子 (OSO₄⁴⁻) 的存在对 TiO₂ 纳米棒薄膜的光电响应有促进作用。

关键词: TiO₂ 纳米棒; 水热法; 形貌; 光电性能

收稿日期: 2012-11-20; 修订日期: 2012-12-08

基金项目: 国家国际科技合作专项资助 (S2013ZR0296); 国家自然科学基金 (51172113); 中国博士后科学基金面上项目 (2012M521297); 山东省自然科学基金杰出青年基金 (JQ201118); 山东省博士后创新项目专项资金 (201203028); 山东省泰山学者建设工程; 青岛市国际科技合作计划 (12-1-4-136-hz); 美国密苏里州立大学科研基金资助项目

作者简介: 孙琼 (1983 -), 女, 山东青岛人, 主要从事太阳能电池材料制备、表征及组装的研究。

E-mail: sunqiong2006@yahoo.cn, Tel: (0532)84022869

1 Introduction

Titania (TiO_2) is known to have several natural polymorphs: anatase, rutile, brookite, and $\text{TiO}_2\text{-B}$, among which anatase and rutile are the most common ones encountered in photocatalytical and photoelectrical research^[1-3]. Although anatase-type TiO_2 is widely used as a catalyst for solar energy conversion because of its high photoactivity, it is metastable at high temperatures, while rutile is thermodynamically stable^[4]. Therefore, it is critically important to develop synthetic technology to obtain TiO_2 in anatase phase with high thermal stability or rutile phase with high photoactivity.

Due to their efficient charge separation and transport properties, thin films of oriented TiO_2 nanorods or nanowires have shown great potential applications in novel photovoltaic devices, especially dye sensitized solar cells (DSSCs) and quantum dot sensitized solar cells (QDSCs)^[5]. Since Liu^[6] introduced a direct hydrothermal method to grow oriented, single-crystalline rutile TiO_2 nanorod films on fluorine-doped tin oxide (FTO) conductive substrates, many studies of DSSCs and QDSCs have been carried out with TiO_2 nanorod films through this in-situ growth process^[7-8]. Except for the facile synthesis procedure, the obtained rutile TiO_2 nanorods were comparable to anatase TiO_2 in DSSCs, with additional advantages including better chemical stability and higher refractive index. In a typical synthesis, organic titanium precursor is chosen as the reactant, although only few reports utilize inorganic titanium precursors (*e. g.* TiCl_4)^[9].

As a titanium precursor, TiOSO_4 is often employed to synthesize anatase TiO_2 with high phase stability and photoactivity^[10-11]. In this work, to the best of our knowledge, TiOSO_4 is used for the first time as the precursor for the growth of TiO_2 nanorods on FTO substrates, and surface morphology, crystalline phase, and photoelectrical activity of the TiO_2 nanorods were also investigated.

2 Experiments

2.1 Materials

Deionized water was used throughout this study,

and the chemicals were used as received without further purification.

2.2 Hydrothermal Synthesis of TiO_2 Nanorod Arrays

Deionized water (13 mL) was mixed with 5 mL of hydrochloric acid (36.5%) and 2 mL of hexadecyltrimethylammonium bromide (CTAB) surfactant aqueous solution (1.0 g/L) in a Teflon-lined stainless steel autoclave (30 mL). The employment of CTAB ensured reactant dispersal and avoided the aggregation of the products throughout the hydrothermal process. The mixture was stirred for 5 min, followed by adding 0.4 mL of 2.88 mol/L TiOSO_4 aqueous solution and stirring for another 5 min. A piece of FTO substrate was placed at an angle against the wall of the Teflon-liner with the conducting side facing up, and subsequently, the hydrothermal reaction was executed at 155 °C for 4 h. After being cooled to room temperature under dripping water for 30 min, FTO substrates were removed from the autoclave and washed with deionized water to remove the residual reactants and CTAB, then dried in ambient air and stored in dark conditions.

2.3 Morphology and Crystallinity Characterizations

Surface morphologies of TiO_2 nanorods were investigated by field emission scanning electron microscopy (FESEM, JEOL JSM-6700F). Energy-dispersive X-ray spectroscopy (EDS, OXFORD INCA) was employed to examine the elemental constituents and their concentrations. Crystal compositions of the products were examined on an X-ray diffractometer (XRD, Rigaku D/MAX-2500/PC) using $\text{Cu K}\alpha$ as the X-ray source (40 kV; 100 mA). The fine structure of TiO_2 nanorods was examined on a high resolution transmission electron microscope (TEM/HRTEM, FEI Tecnai G20).

2.4 Photovoltaic Measurements

Short-circuit photocurrent response was recorded on a CHI 660D electrochemical station under 100 mW/cm² irradiation from a full spectrum solar simulator (Newport 96000) with air mass 1.5 global filter (AM 1.5G, Newport 81094). A saturated calomel electrode (SCE) was used as a reference

electrode, a platinum wire as a counter electrode, and the round TiO₂/FTO film with an exposed area of 0.5 cm² as a working electrode. During the test, the working electrode was vertically faced to incident light, and the illumination was changed between on and off every 10 s.

3 Results and Discussion

3.1 Morphology and Crystallinity Characterizations of TiO₂ Nanorods

Typical FESEM images and EDS spectrum of TiO₂ nanorods with a double-layer structure grown on an FTO substrate are shown in Fig. 1(a) ~ (e). At the same time, the TiO₂ nanorod films were synthesized using organic titanium precursor [titanium isopropoxide, Ti(*i*Pro)₄] under the same reaction conditions for comparison, and a representative FESEM image is shown in Fig. 1(f). Obviously, the length of the nanorods from TiOSO₄ (~ 1.3 μm) is much shorter than that obtained from Ti(*i*Pro)₄ (~ 1.9 μm). According to the Ref. [6], the driving force of the nanorod growth on FTO substrates was due to the small lattice mismatch between the tetragonal FTO ($a = b = 0.4687$ nm) and rutile TiO₂ ($a = b = 0.4594$ nm), which may promote the epitaxial nucleation and growth of rutile TiO₂ nanorods on FTO. Therefore, in this study, the formation of the double-layer structures has two steps: initially, the arrays of TiO₂ nanorods grow vertically on the conductive surface of the FTO substrate. After the entire surface is uniformly covered with TiO₂ nanorods, the nanorods begin to assemble into flower-shaped clusters on the top of the arrays. Both the arrays and clusters are, in fact, bundles of minute nanorods with a diameter of 300 nm and a length of 1.2 μm. From the EDS analysis [Fig. 1(e)], the atom percents of Ti and O are 37% and 60%, namely, the ratio of Ti to O is approximately 1:2. Moreover, minimal S (1.99%) and Cl (0.56%) from the reactants remained, and no characteristic elements of CTAB (*e. g.* N, Br, *etc.*) were detected, thus demonstrating that the CTAB had been removed completely and did not react with other reactants.

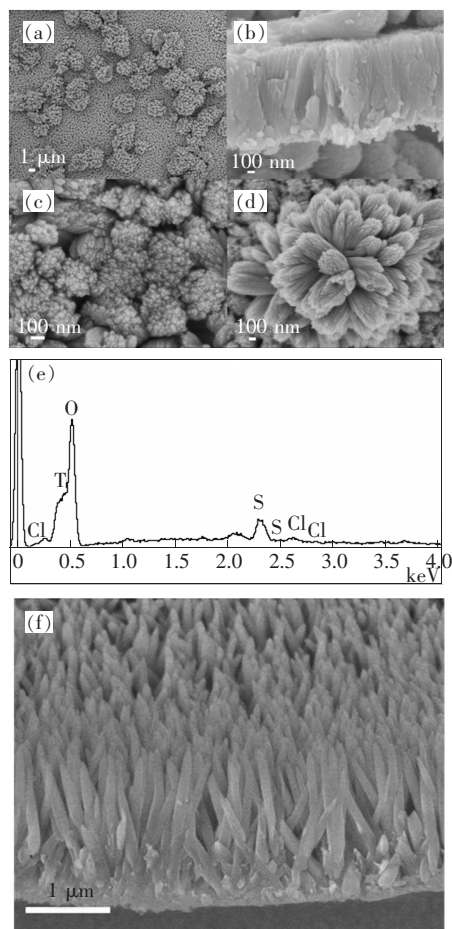


Fig. 1 FESEM images of TiO₂ nanorod films grown on FTO substrates synthesized from TiOSO₄ at 155 °C for 4 h: (a) top view, (b) cross sectional view, (c) the bottom nanorod arrays, and (d) the top nanorod clusters. The corresponding EDS spectrum is shown in Fig. 1(e). Fig. 1(f) is the FESEM image of TiO₂ nanorod film grown on FTO substrate synthesized from [Ti(*i*Pro)₄] at 155 °C for 4 h.

The crystal phase and crystallinity of TiO₂ nanorods from TiOSO₄ is shown in Fig. 2, in which all diffraction peaks that appear upon nanorod growth can be indexed as tetragonal rutile phase. In comparison to the reference peaks of polycrystalline rutile TiO₂ (PDF#21-1276), the diffraction peak with the highest intensity of TiO₂ nanorods is (002) instead of (110). The XRD pattern of TiO₂ nanorods using Ti(*i*Pro)₄ as the precursor is also listed for comparison [Fig. 2(b)]. If the vertical growth of the nanorods from these two precursors are the same, the crystal composition of the underlying nanorod film from TiOSO₄ would be the same as that

measured from $\text{Ti}(\text{iPro})_4$, and the appearance of (110) and (111) peaks would occur during the growth of the top clusters. In addition, no noticeable diffraction signals of anatase TiO_2 could be detected. These results suggest that, instead of a thermally unstable anatase phase, rutile TiO_2 nanorods can be synthesized from TiOSO_4 using a simple in-situ hydrothermal method.

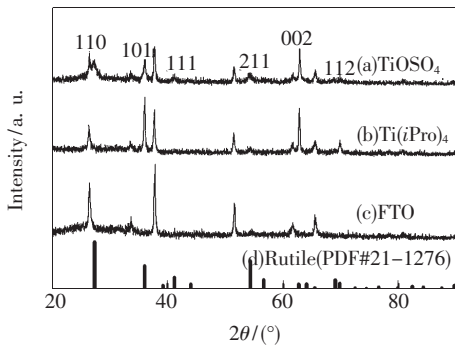


Fig. 2 XRD patterns of TiO_2 nanorods prepared from (a) TiOSO_4 and (b) $\text{Ti}(\text{iPro})_4$ at 155°C for 4 h, (c) blank FTO substrate, and (d) polycrystalline rutile TiO_2 (PDF#21-1276).

From the XRD patterns, the enhanced (002) diffraction peak indicates that TiO_2 nanorods are highly oriented on the FTO substrate, and the growth direction of TiO_2 nanorods is along the [001] direction perpendicular to the substrate surface^[12], which could also be supported by HRTEM characterization. Examinations of individual nanorods with TEM and HRTEM demonstrate that they consist of vast nanowire bundles [Fig. 3 (a)] and are completely crystalline along their length [Fig. 3 (b)]. The lattice fringe with interplanar spacing $d_{110} = (0.32 \pm 0.01)$ nm is clearly imaged and consistent with the rutile phase. The [110] axis is perpendicular to the

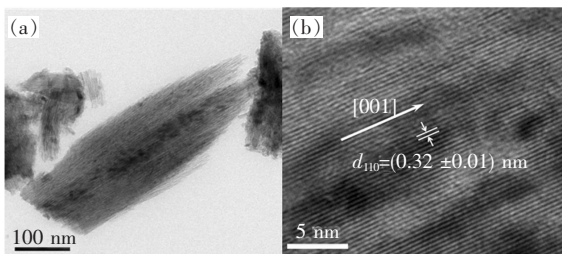


Fig. 3 (a) TEM and (b) HRTEM images of a single TiO_2 nanorod synthesized from TiOSO_4 at 155°C for 4 h

nanorod side walls, and the nanorods grow along the [001] direction, consistent with the XRD data.

3.2 Photoelectrical Characteristics of TiO_2 Nanorods

When employed as a photoanode in a photoelectrochemical cell, TiO_2 nanorods can generate anodic photocurrent. The magnitude of the photocurrent represents the charge collection efficiency of the electrode surface. Herein we use short-circuit photocurrent of TiO_2 nanorod films under the irradiation of a solar simulator to detect their photoelectrical properties, as shown in Fig. 4. At the same time, the photocurrent of TiO_2 nanorod films synthesized from [$\text{Ti}(\text{iPro})_4$] is also measured for comparison.

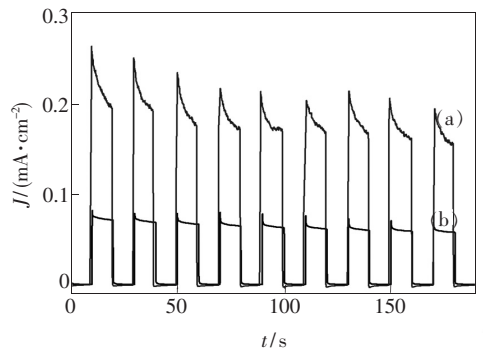


Fig. 4 Photocurrent density *vs.* time curves of TiO_2 nanorods synthesized at 155°C for 4 h using TiOSO_4 (a) and $\text{Ti}(\text{iPro})_4$ (b) as the titanium precursor, respectively.

The photocurrent density of TiO_2 nanorods obtained from TiOSO_4 (a) and $\text{Ti}(\text{iPro})_4$ (b) is about $0.17 \text{ mA}/\text{cm}^2$ and $0.06 \text{ mA}/\text{cm}^2$, respectively, and the photostability of these two samples was considerable during a 90 s irradiation. It is obvious that the photocurrent response of sample (a) is much stronger than that of sample (b), indicating that the TiO_2 nanorods prepared from TiOSO_4 possess higher charge collection ability. Considering the morphologies of these two samples, the TiO_2 nanorods grown on FTO substrates from $\text{Ti}(\text{iPro})_4$ existed in a monolayer form of oriented rutile TiO_2 array, while the TiO_2 nanorods from TiOSO_4 consist of a double-layered structure containing the bottom arrays and top clusters. When TiOSO_4 was used as the precursor, the enhanced photocurrent response of TiO_2 nanorod films may result from the multi-dimensional

structure of TiO₂ nanorods with various diameters and lengths as well as the participation of inorganic oxysulfate (OSO₄⁴⁻) anion. Detailed experiments are underway currently to investigate possible mechanisms.

4 Conclusion

In this research, TiOSO₄ was chosen as the titanium precursor for the synthesis of TiO₂ nanorod films on FTO substrates by a facile hydrothermal method. A double-layered film, including bottom arrays and top clusters, was finally produced, and the nanorods were composed of abundant, extremely thin nanowires. On the surface of FTO substrate, the TiO₂ nanorod arrays grew oriented along the [001] direction, and flowerlike clusters of TiO₂ nanorods

then formed on the top of the arrays, both of which were in rutile phase. The photoelectrical properties of the TiO₂ nanorods were represented by the short-circuit photocurrent measurement under the irradiation of a solar simulator. Under the same synthesis conditions, the photocurrent response of TiO₂ nanorods prepared from inorganic TiOSO₄ was more than twice that obtained from nanorods prepared from organic titanium precursor [Ti(iPro)₄]. The multi-dimensional structure of the top TiO₂ nanorod clusters may improve the scattering and absorption of the incident photons, and the residual OSO₄⁴⁻ on the surface of TiO₂ may accelerate the photoinduced charge transfer. In summary, using TiOSO₄ as the titanium precursor in the synthesis of TiO₂ nanorod films offers significant potential in further applications of DSSCs and QDSCs.

References:

- [1] Chen H. Calculations of optical properties in anatase TiO₂[J]. *Chin. J. Lumin.* (发光学报), 2009, 30(5):697-701 (in Chinese).
- [2] Yang X, Qu Y, Fan Y, *et al.* Y-branched TiO₂ nanotubes prepared by electrochemical anodization [J]. *Chin. J. Lumin.* (发光学报), 2012, 33(3):269-274 (in Chinese).
- [3] Hirano M, Nakahara C, Ota K, *et al.* Direct formation of zirconia-doped titania with stable anatase-type structure by thermal hydrolysis [J]. *J. Am. Ceram. Soc.*, 2002, 85(5):1333-1335.
- [4] Peng T, Zhao D, Dai K, *et al.* Synthesis of titanium dioxide nanoparticles with mesoporous anatase wall and high photocatalytic activity [J]. *J. Phys. Chem. B*, 2005, 109(11):4947-4952.
- [5] Chu S Z, Wada K, Inoue S, *et al.* Fabrication and structural characteristics of ordered TiO₂-Ru(-RuO₂) nanorods in porous anodic alumina films on ITO/glass substrate [J]. *J. Phys. Chem. B*, 2003, 107(37):10180-10184.
- [6] Liu B, Aydil E S. Growth of oriented single-crystalline rutile TiO₂ nanorods on transparent conducting substrates for dye-sensitized solar cells [J]. *J. Am. Chem. Soc.*, 2009, 131(11):3985-3990.
- [7] Lv M, Zheng D, Ye M, *et al.* Densely aligned rutile TiO₂ nanorod arrays with high surface area for efficient dye-sensitized solar cells [J]. *Nanoscale*, 2012, 4(19):5872-5879.
- [8] Liao W P, Hsu S C, Lin W H, *et al.* Hierarchical TiO₂ nanostructured array/P3HT hybrid solar cells with interfacial modification [J]. *J. Phys. Chem. C*, 2012, 116(30):15938-15945.
- [9] Wang H, Bai Y, Zhang H, *et al.* CdS quantum dots-sensitized TiO₂ nanorod array on transparent conductive glass photoelectrodes [J]. *J. Phys. Chem. C*, 2010, 114(39):16451-16455.
- [10] Hirano M, Ota K, Iwata H. Direct formation of anatase (TiO₂)/silica (SiO₂) composite nanoparticles with high phase stability of 1 300 °C from acidic solution by hydrolysis under hydrothermal condition [J]. *Chem. Mater.*, 2004, 16(19):3725-3732.
- [11] Li W, Bai Y, Liu C, *et al.* Highly thermal stable and highly crystalline anatase TiO₂ for photocatalysis [J]. *Environ. Sci. Technol.*, 2009, 43(14):5423-5428.
- [12] Zhou Z, Fan J, Wang X, *et al.* Effect of highly ordered single-crystalline TiO₂ nanowire length on the photovoltaic performance of dye-sensitized solar cells [J]. *ACS Appl. Mater. Interf.*, 2011, 3(11):4349-4353.