

Review Article

One-Dimensional TiO₂ Nanostructures as Photoanodes for Dye-Sensitized Solar Cells

Jie Qu¹ and Chao Lai²

¹ Center for Low-Dimensional Materials, Micro-Nano Devices and System and Jiangsu Key Laboratory for Solar Cell Materials and Technology, Changzhou University, Changzhou 213164, China

² School of Chemistry and Chemical Engineering, Jiangsu Normal University, Xuzhou, Jiangsu 221116, China

Correspondence should be addressed to Chao Lai; laichao@jsnu.edu.cn

Received 22 December 2012; Accepted 2 February 2013

Academic Editor: Xijin Xu

Copyright © 2013 J. Qu and C. Lai. This is an open access article distributed under the Creative Commons Attribution License, which permits unrestricted use, distribution, and reproduction in any medium, provided the original work is properly cited.

Titanium dioxide (TiO₂) is star materials due to its remarkable optical and electronic properties, resulting in various applications, especially in the fields of dye-sensitized solar cells (DSSCs). Photoanode is the most important part of the DSSCs, which help to adsorb dye molecules and transport the injected electrons. The size, structure, and morphology of TiO₂ photoanode have been found to show significant influence on the photovoltaic performance of DSSCs. In this paper, we briefly summarize the synthesis and properties of one-dimensional (1D) TiO₂ nanomaterials (bare 1D TiO₂ nanomaterial and 1D hierarchical TiO₂) and their photovoltaic performance in DSSCs.

1. Introduction

Titanium dioxide (TiO₂) is one of the most extensively studied oxides because of its remarkable optical and electronic properties. Due to its unique physical and chemical properties, TiO₂ has been extensively used for various applications, such as dye-sensitized solar cells (DSSCs), lithium ion batteries (LIBs), photocatalysis, water treatment, and gas sensors [1–21].

A typical DSSC consists of a dye-sensitized semiconductor electrode, redox electrolyte, and counter electrode [23, 24]. Once dye molecules absorb light, the excited dye injects electrons to the semiconductor. At the same time, the oxidized dye cation is reduced by the redox electrolyte, which competes with the recombination of injected electrons. Electrons are collected at the semiconductor electrode, pass through the external circuit, and then reenter the cell at the counter electrode to reduce the oxidized electrolyte [25]. A closed circuit is thereby established to continuously convert the solar light to electricity. Nanostructure-based DSSCs show advantages of low cost, high efficiency, and simple in preparation, which is promising as a renewable energy resource for sustainable development of the future [2, 23, 26, 27]. A breakthrough in DSSCs was achieved in

1991, O'Regan and Grätzel firstly introduced wide bandgap semiconductor nanocrystal (TiO₂ nanoparticle) into DSSCs as the transporting medium of photo-induced electrons, and conversion efficiency was reached to 7% [2]. Recently the efficiency of DSSCs has been increased to 12.3% [28].

Dye-sensitized semiconductor electrode is usually the efficiency determining component of DSSCs due to the competition between electron separation and recombination accompanying with many electron transfer processes [5, 29, 30]. In brief, semiconductor oxides receive the injected electrons from the excited state of sensitizer dye, and the electrons could be competitively trapped by oxidized dye cation, I₃⁻ anion in electrolyte, and surface state in TiO₂ (e.g., oxygen vacancy) that is known as recombination, before they are transported to an external circuit. The described electron transfer processes in the semiconductor electrode affect essentially conversion efficiency of DSSCs, which depends on the nature and morphology of nanocrystalline semiconductor oxides [31–34].

Wide bandgap semiconductor nanoparticles were the first material used as an efficient photoanode. Due to the small size of the nanoparticles, it can provide a large surface area and a relatively high porosity [2], possible to adsorb enough dye for efficient light harvesting and a relative high

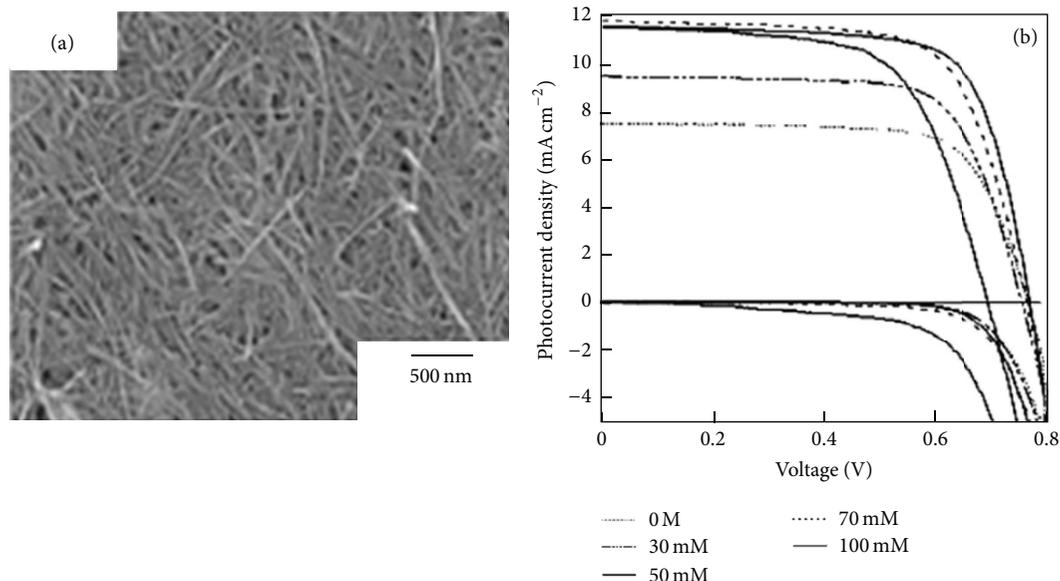


FIGURE 1: (a) SEM images of mesoporous electrodes sintered at 500°C made of TNTs paste B. (b) Photocurrent-voltage curves obtained from the cells with TNTs electrodes at various Li^+ concentrations [22].

conversion efficiency. However, TiO_2 nanoparticles used in DSSCs are usually as a random network of crystallographically misaligned crystallites, and lattice mismatches at the grain boundaries could influence electron scattering and act as electron trap [31, 34, 35]. This could limit electron transport and reduce electron lifetime. Further improvement of DSSC-based nanoparticle is hindered by the previous drawbacks. One-dimensional TiO_2 nanostructures [36–48] have a relatively small amount of grain boundaries and can act as single crystal, which is able to reduce the grain boundary effect and provide fast electron transport. It shows great potential in achieving high performance DSSCs. The recombination rate in TiO_2 nanotubes has been found to be 10 times slower than that in nanoparticles [37]. However, it is more difficult for the liquid electrolyte to penetrate into one-dimensional titania than into nanoparticles network, because the one-dimensional titania has usually relatively low surface area, large size, and inefficient intact surface compared with nanoparticles. This usually leads to a large interface charge-transfer resistance for one-dimensional nanostructured materials-based photoanode.

To resolve the drawbacks of the nanoparticles and 1D nanostructures, 1D hierarchically structured materials were designed by combining nanoparticles and nanorods or nanowires. They have been used to take advantage of both the large surface area of nanoparticles and efficient charge transport of 1D nanostructures [50]. The interpenetration of electrolyte in the 1D hierarchical structure could be improved, and the interfacial area could be increased which might leads to more electron separation and fast transport [31, 34, 35, 51–57]. Compared with the nanoparticles and 1D nanostructures, the photovoltaic properties of 1D hierarchical structure are superior. This indicate a potential approach to overcome the limitations of nanoparticles and one-dimensional nanostructures as photoanode materials, though the increase of

the grain boundary effect is inevitable in a hybrid structure matrix due to the formation of grain boundaries between nanoparticles and nanorods or nanowires.

In this paper, we review the recent developments in using of one-dimensional (1D) nanostructures as photoanodes for efficient DSSCs. Various randomly oriented and vertically aligned 1D nanostructures, and their composites with nanoparticles used in DSSCs are discussed, for which the order is randomly oriented 1D nanotubes and nanorods, vertically aligned 1D nanotubes and nanorods, randomly oriented 1D hierarchical TiO_2 and vertically aligned 1D hierarchical TiO_2 .

2. Applications in DSSC Photoanode

The photoanode shows significant effects on the photocurrent and photovoltage of a DSSC. As a key material in photoanode, fast electron transfer kinetics of TiO_2 are necessary to avoid photoelectron recombination, which usually depends strongly on the micromorphology and crystallographic structure of TiO_2 . Therefore, it is very important to synthesize controllably titania nanomaterials with specific structures and big surface area with optimized electron transfer kinetics.

2.1. Randomly Oriented 1D TiO_2

2.1.1. Randomly Oriented 1D TiO_2 Nanotube. To overcome the electron transport limit of nanoparticles, TiO_2 nanotubes were the first reported 1D nanomaterial for use as a bifunctional photoanode material, which exhibiting both efficient generation of photon-generated electrons and good light-scattering property. Uchida et al. [58] have developed a facile one-step hydrothermal method to synthesize TiO_2 nanotube [59]. The nanotube is 100 nm long with an outer diameter of

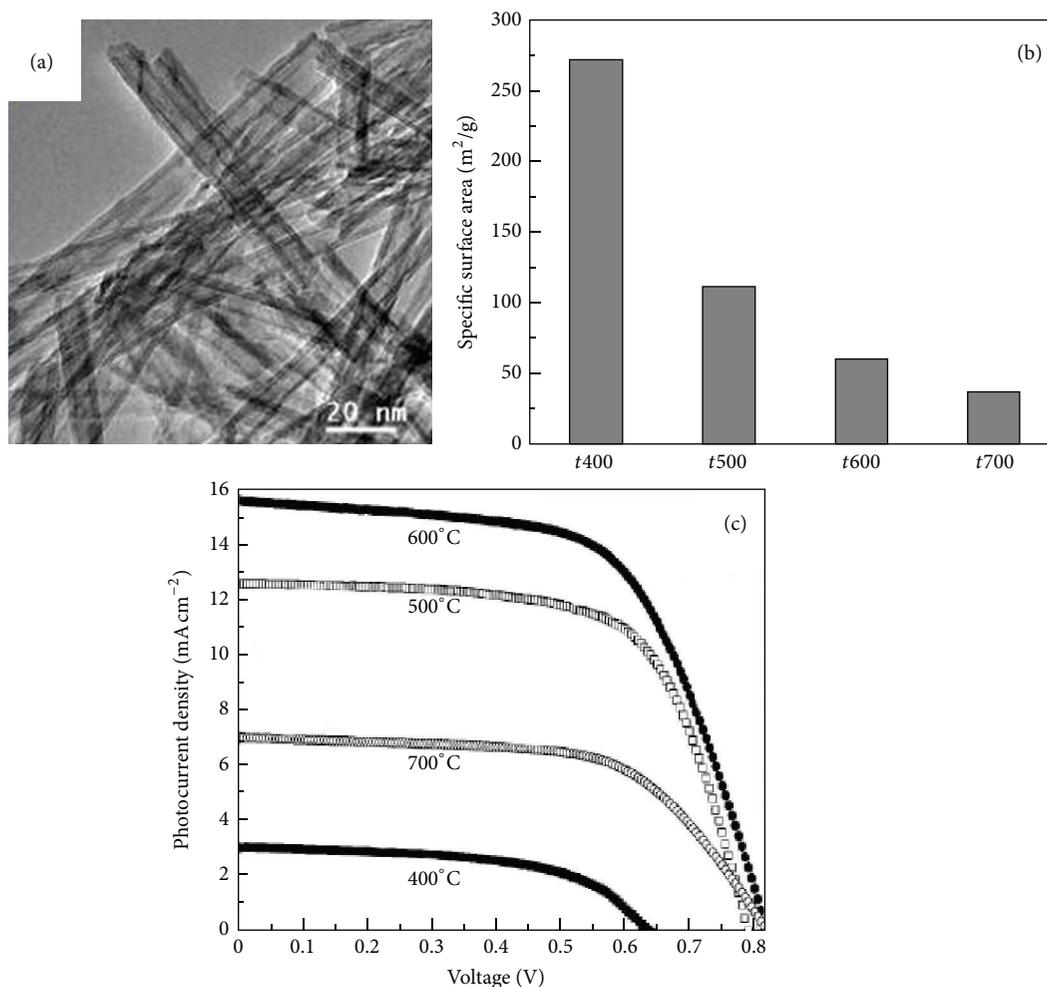


FIGURE 2: (a) TEM micrographs of titanate nanotubes calcined at 400°C. (b) Specific surface area of samples calcined at different temperatures. (c) *I*-*V* curves for titanate nanotubes calcined at different temperatures. Illumination intensity of 100 mW cm⁻² with global AM 1.5 and an active area of 0.25 cm² were applied [16].

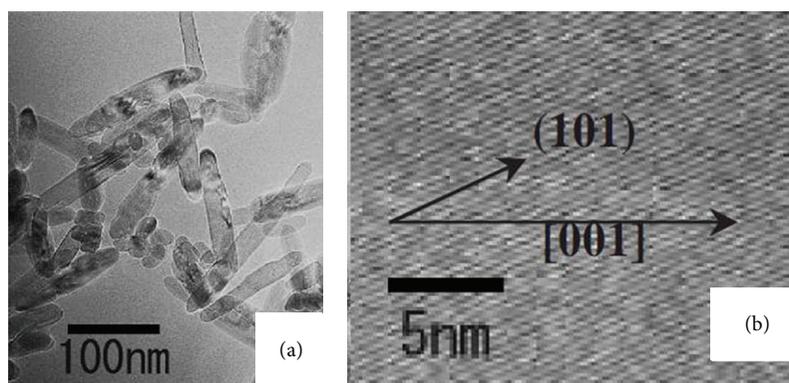


FIGURE 3: (a) TEM image of nanorods prepared with F127. (b) HRTEM image of (a) [49].

8 nm. The specific surface area can reach to 270 m²/g. DSSC with such nanotube showed a 2.9% conversion efficiency, which was not better than that of nanoparticles. The main reason for the previous result may due to the aggregate of the TiO₂ nanotube, which could reduce electricity contact and

increase impedance between TiO₂ nanotube and conductive glass. And the nanotube wall here could also block the diffusion of the I⁻/I₃⁻.

To synthesize TiO₂ nanotube with high dispersion and crystallization could improve the photoelectrochemical

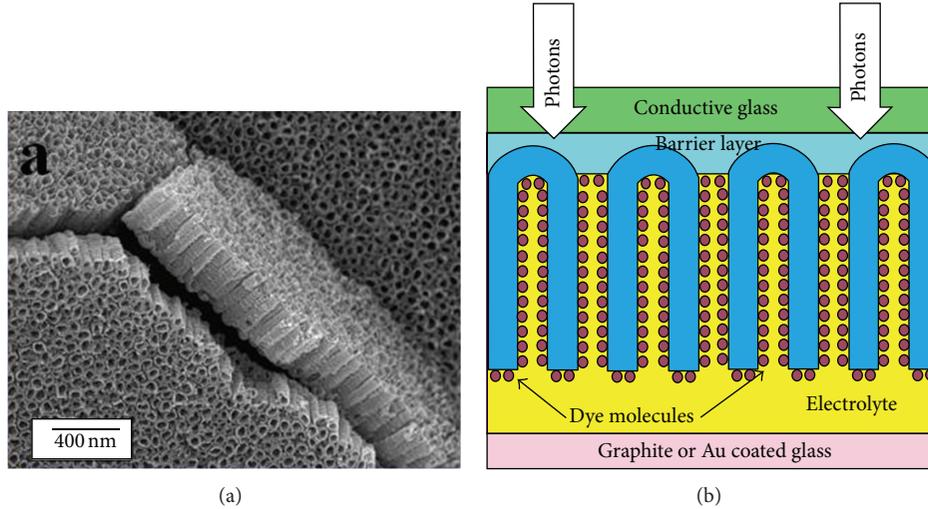


FIGURE 4: (a) Lateral view FESEM images of titanium nanotubes grown from a 500 nm thick Ti thin film (sputtered onto $\text{SnO}_2:\text{F}$ coated glass at 500°C) anodized using a 0.5% HF electrolyte concentration at a potential of 12 V. (b) Integration of transparent nanotube array architecture into dye solar cell structure [38].

TABLE 1: Detailed IMPS/IMVS parameters of the DSSC with titanate nanotubes calcined at different temperatures [16].

Calcination temperature	τ_d (ms) ^a	τ_n (ms) ^a	D_n (cm^2/s) ^a	L_n (μm) ^a
400°C	1.83	14.2	3.5×10^{-4}	22.3
500°C	1.18	53	5.4×10^{-4}	53.6
600°C	0.94	106	6.8×10^{-4}	85
700°C	1.47	17.7	4.4×10^{-4}	27.8

properties. Adachi et al. [60] and Ohsaki et al. [22] have reported such TiO_2 nanotubes (TNTs) with large aspect ratio and large specific surface area. The conversion efficiency could reach to 6.4% (Figure 1). After treating with the TiCl_4 , the conversion efficiency could increase to 7.1%. Single crystal of TiO_2 facilitates the fast transport of electron. And large aspect ratio of TiO_2 nanotubes could help to reduce the grain boundary effect. The research also indicated that the increased electron density and electron lifetime in the photoanode could be beneficial for the improved photoelectrochemical properties.

Our group [16] also reported the protonated TiO_2 nanotube prepared from one-step hydrothermal method with anatase TiO_2 and 10 M NaOH solution as the starting materials [15, 61]. After being calcined at 400°C , single crystal of $\text{TiO}_2(\text{B})$ nanotube was obtained (Figure 2). Although nanotubes have the advantage in morphology and surface area for enhancing photoelectrochemical performance, $\text{TiO}_2(\text{B})$ nanotubes in this work showed relatively poor photovoltaic properties with the η value of only 1.05%. The poor performance here was mainly related to the serious recombination in numerous surface defects and a relatively open tunnel structure of $\text{TiO}_2(\text{B})$ [15]. Higher temperature calcination would reduce the surface defects, but the tube morphology could not exist.

2.1.2. Randomly Oriented 1D TiO_2 Nanorod. One-dimensional TiO_2 nanorods have a relatively small amount of grain boundaries and can act as single crystal, which is able to reduce the grain boundary effect and provide fast electron transport [51–53]. And the rod could keep the rod morphology with higher temperature calcination. Many researches were focused on TiO_2 nanorods.

Jiu et al. [49, 62] have reported single crystalline anatase TiO_2 nanorods synthesized by surfactant-assisted hydrothermal method. Short rods with the diameter 20–30 nm and length 100–150 nm have been obtained (Figure 3). The clear lattice strips indicated that the nanorods with high crystallinity and fewer defects have been obtained, which is beneficial for the transfer of electrons in the rods. A high light-to-electricity conversion yield of 7.06% was achieved by applying the TiO_2 nanorods as thin film of dye-sensitized solar cells. The nanorod shows the same advantages as nanotubes: the fast electron transport, the reduced recombination, and the long lifetime.

We also fabricated such small size nanorods with a special method different from the tradition. The nanorods were obtained by calcination of protonated TiO_2 nanotube at 600°C for 2 h [16]. It is much thicker and shorter with a diameter of 15–30 nm and a length of about 100 nm. The interference fringe spacing of the nanorods is about 0.35 nm, corresponding to the interplanar distance of the (101) plane in the anatase phase. And the conversion efficiency could reach to 7.71%. IMPS and IMVS were used to investigate further the electron transport and recombination processes, as shown in Table 1. Compared with nanotube calcined at 400°C , nanorods calcined at 600°C show a longer lifetime, which is over 10-fold longer than that for $\text{TiO}_2(\text{B})$ nanotube and a shorter electron transport time only half of the $\text{TiO}_2(\text{B})$ nanotube. This indicates that anatase nanorods with a good crystallinity are beneficial to a faster electron transport and a longer electron lifetime. In fact, it is considered that the

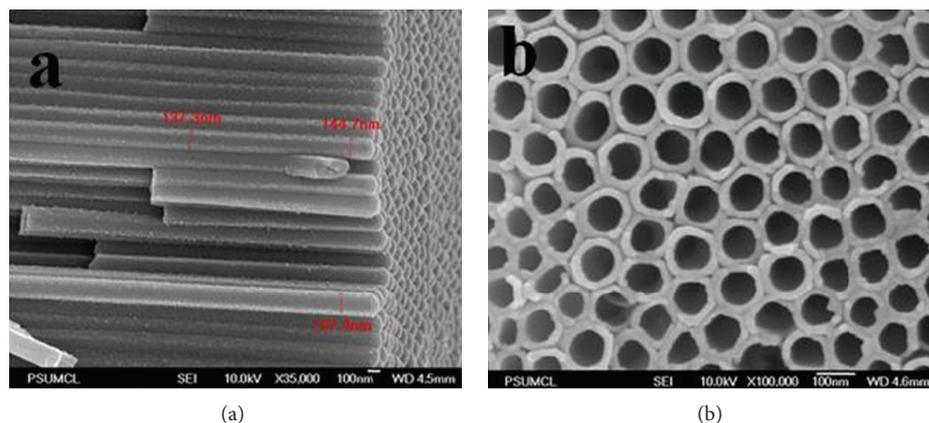


FIGURE 5: Illustrative FESEM cross-sectional (a) and top images (b) of a nanotube-array sample grown at 60 V in an ethylene glycol electrolyte containing 0.25 wt% NH_4F [63].

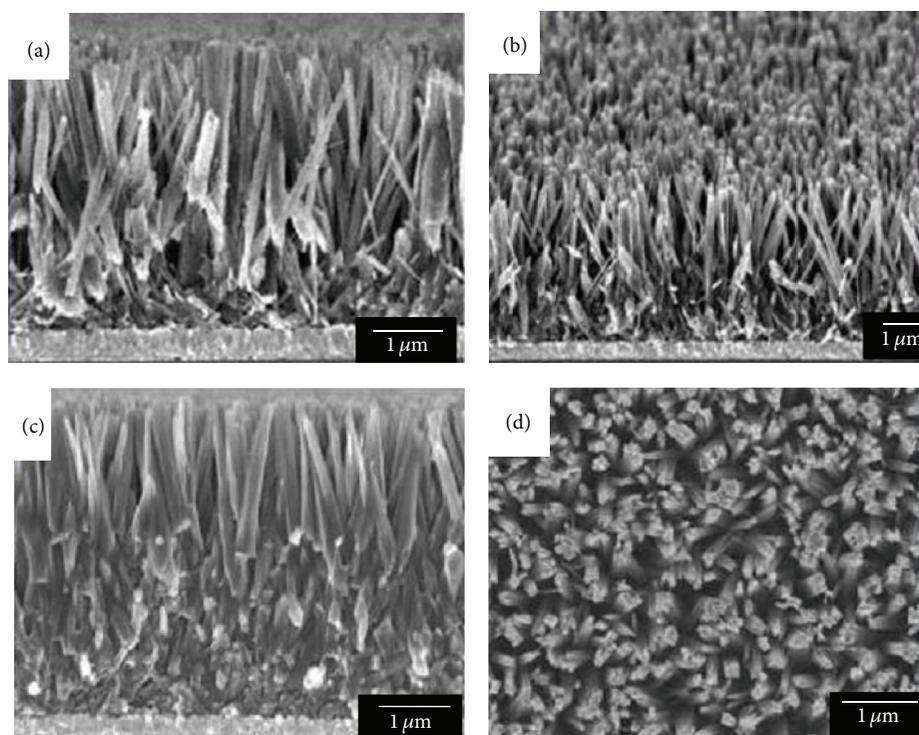


FIGURE 6: FESEM images of oriented rutile TiO_2 nanorod films grown from a two-step hydrothermal reaction; (a, b) and (c, d) with and without addition of saturated aqueous NaCl solution [44].

good crystallinity and the cylindrical geometry could allow the nanorods to support radial electric fields, which could keep the electrons away from the nanorods surface, thereby reducing surface electron densities and recombination.

2.2. Vertically Aligned 1D TiO_2 . Randomly oriented 1D TiO_2 nanomaterial undoubtedly plays as the “electron speedways;” however, these nanotubes and nanorods are disordered and random. It has not realized the direct electron transport. So, it is significant to design and study the vertically aligned 1D TiO_2 nanomaterials would be much more significant.

2.2.1. Vertically Aligned 1D TiO_2 Nanotube. Vertically aligned TiO_2 nanotubes provide a vertical pathway for electron transport along the tube and thus minimize electron loss during diffusion process, and the vertically ordered tubular structure will facilitate the filling of new sensitizer or electrolyte for a further increase in efficiency. As such, self-aligned TiO_2 nanotube arrays have been widely studied for applications as photoanodes in DSSCs [65–74].

Mor et al. [38] have reported a highly ordered 360 nm long TiO_2 nanotube arrays, made by anodization of thick-film titanium foil (Figure 4). After treating with TiCl_4 and

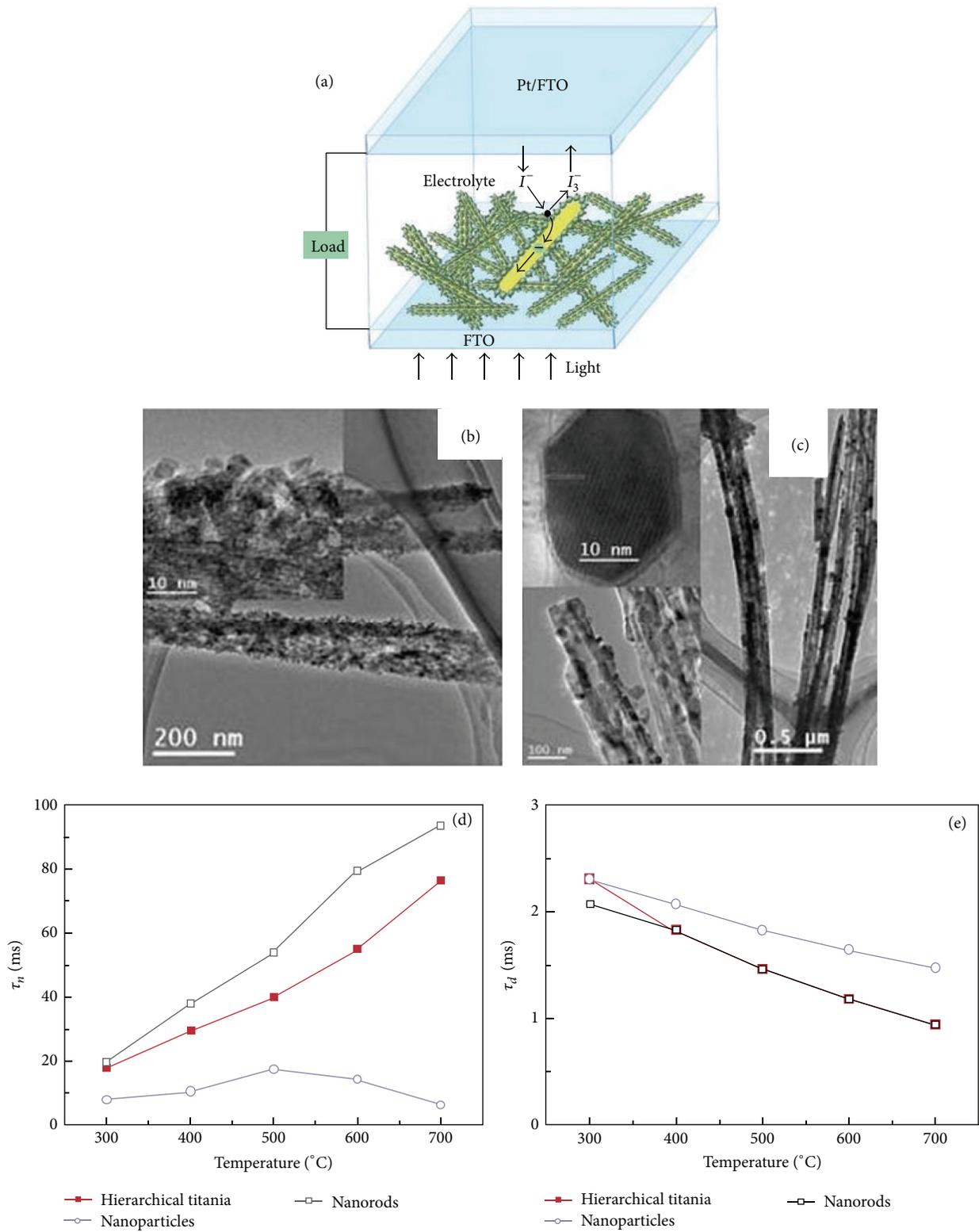


FIGURE 7: (a) Schematic diagram of the dye-sensitized solar cell with the one-dimensional hierarchical titania as photoanode on FTO, showing the processes involved in current generation. (b, c) TEM images of the one-dimensional titania with hierarchical structures after calcination at 300°C (b) and 700°C (c). (d, e) The electron lifetime (τ_n) (d) and electron transport time (τ_d) (e) for DSSCs of titania with hierarchical structures, nanorods, and nanoparticles [50].

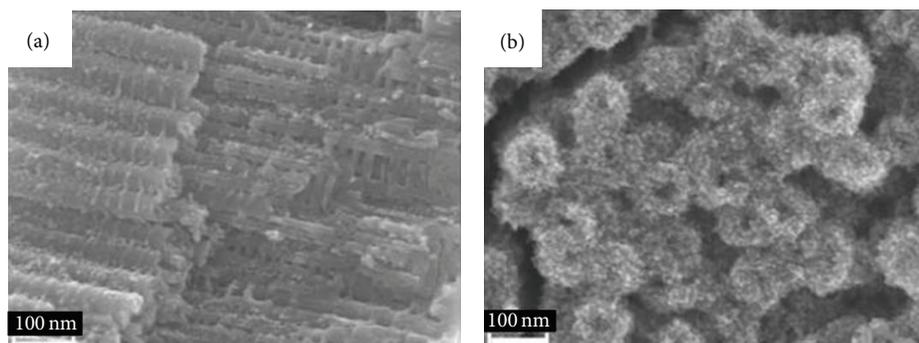


FIGURE 8: (a) SEM images of one-cycle infiltration: inside view of the split NTs. (b) NT and NP mixed structure after two-cycle infiltration [64].

calcining at 450°C , a highly ordered photoanode was obtained. The DSSC exhibited a J_{sc} of 7.87 mA/cm^2 , a V_{oc} of 0.75 V , and an overall conversion efficiency of 2.9% . This result was no better than nanoparticles. A low surface area with a length of only 360 nm could be responsible for the result of insufficient dye-loading and low light-harvesting efficiency. However, highly ordered arrays showed a long lifetime and excellent electron transport path compared to nanoparticles. To resolve the problem of the low surface area, many efforts were done. Nanotubes with lengths up to $100\text{ }\mu\text{m}$ have been produced to increase the surface area for dye-loading [63, 75]. Shankar et al. [63] even obtained ultralong TiO_2 nanotubes with length over $200\text{ }\mu\text{m}$ (Figure 5), which delivered significantly improved DSSC efficiency of 6.89% . However, synthesis of these ultralong nanotubes costs much time (more than 10 h) and electricity for anodization process, and the reported efficiencies of TiO_2 -nanotube-array-based DSSCs are still lower than DSSCs based on mesoporous TiO_2 films due to the relative low internal surface area for dye-loading of nanotube arrays [44, 76, 77].

2.2.2. Vertically Aligned 1D TiO_2 Nanorod. Different from 1D nanotube array, DSSCs based on 1D TiO_2 nanorods array remain a challenge [43, 78–86], which is mainly owing to the low dye-loading ability resulting from the insufficient specific surface area. Liu and Aydil [44] reported a facile, hydrothermal method for the first time to grow oriented, single-crystalline rutile TiO_2 nanorod films on transparent conductive fluorine-doped tin oxide (FTO) substrates (Figure 6). The growth parameters, such as growth time, growth temperature, initial reactant concentration, acidity, and types additives, could effectively influence the diameter, length, and density of the nanorods. A small lattice mismatch between the FTO substrate and rutile TiO_2 is key in driving the nucleation and growth of the rutile TiO_2 nanorods on FTO. $4\text{ }\mu\text{m}$ long TiO_2 nanorod films were obtained through the previous method. After treating with TiCl_4 , a light-to-electricity conversion efficiency of 3% was achieved.

Many efforts have done to modify the oriented rutile TiO_2 nanorod to improve the photoelectrochemistry properties. Lv et al. [87] have reported a densely aligned TiO_2 nanorod arrays (NRAs) with high surface area. These densely aligned

TiO_2 NRAs with tunable thickness were grown directly on transparent conductive fluorine-doped tin oxide (FTO) substrates by hydrothermal method. Dilute hydrochloric acid was used as chemical etching liquid to further increase the specific surface area of the TiO_2 NRAs. TiO_2 nanorods were split into secondary nanorods with a reduced diameter during the etching treatment. And the inner surface area of the TiO_2 NRAs was markedly enlarged. Finally, a conversion efficiency of 5.94% was achieved by using such NRAs. It is so far the best reported results for the 1D rutile TiO_2 NRA films.

2.3. 1D Hierarchical TiO_2 Nanomaterial. TiO_2 nanoparticles used in DSSCs have its limitations, such as influencing the electron scattering and acting as an electron trap. 1D nanostructured TiO_2 could reduce the grain boundary effect and provide fast electron transport. However, it is more difficult for the liquid electrolyte to penetrate into one-dimensional titania than into nanoparticles network. And the small surface area would block the improving of the photoelectrochemistry properties. In general, fast reaction kinetics (fast electron transport, long electron lifetime, and less recombination) together with large specific surface area are the essential properties of the superior photoanode materials with excellent photoelectrochemical properties.

2.3.1. Randomly Oriented 1D Hierarchical TiO_2 . To achieve highly efficient DSSCs, one-dimensional hierarchical composites were designed as show in Figure 7 [50], which combine the high electron transport from 1D nanostructures and large surface area to attach enough dyes from nanoparticles. A proposed electron transfer model is shown in the following; the injected electrons in the nanoparticles standing on nanorods are subject to transfer into the nanorods and then are rapidly transported to FTO substrate due to the single-crystal feature of the nanorods. The results indicate that one-dimensional hierarchical titania cannot only provide a matrix similar to the hybrid structure matrix but also avoid forming a large amount of grain boundaries with optimized fast reaction kinetics: low charge-transfer resistance, fast electron transport, and long electron lifetime. And the existed nanoparticles greatly improve the surface area of the nanorods. The conversion efficiency of one-dimensional

hierarchical titania can reach to 4.46%, which is about 5 times higher than that of their corresponding nanorods.

2.3.2. Vertically Aligned 1D hierarchical TiO₂. Pan et al. [64] have reported vertically aligned 1D hierarchical TiO₂. 10 nm size of TiO₂ NPs were uniformly coated on the side walls of NTs through infiltration with TiCl₄ solution and hydrothermal synthesis (Figure 8). Compared with the bare NT structure, dye-loading of mixed NT and NP structure was two times doubled. The larger surface area resulted in more recombination which slightly reduced the electron lifetime. However, the diffusion length was still longer than the tube length used. This means most electrons are collected.

3. Summary

In this paper, we have summarized the using of 1D TiO₂ nanostructures as electrode materials for DSSC photoanode.

Randomly oriented 1D TiO₂ (nanotubes and nanorods) with cylindrical geometry could support radial electric fields that could keep the electrons away from the nanorods surface, thereby reducing surface electron densities and recombination. And large aspect ratio of TiO₂ would help to reduce the grain boundary effect. The electron lifetime would also increase. All these advantages could be beneficial for the improved photoelectrochemical properties. However, randomly oriented 1D TiO₂ nanomaterial are disordered and random. It has not realized the direct electron transport. Vertically aligned TiO₂ nanotubes provide a vertical pathway for electron transport along the tube and thus minimize electron loss during diffusion process, and the vertically ordered tubular structure will facilitate the filling of new sensitizer and electrolyte for a further increase in efficiency. However, the small surface area made the photoelectrochemistry properties worse than the randomly oriented 1D TiO₂ nanomaterial. In general, fast reaction kinetics (fast electron transport, long electron lifetime, and less recombination) together with large specific surface area are the essential properties of the superior photoanode materials with excellent photoelectrochemical properties. To achieve highly efficient DSSCs, 1D hierarchical TiO₂ were designed. Both randomly oriented and vertically aligned 1D nanostructures have been used as the photoanode materials. Detailed study showed that this 1D hierarchical TiO₂ could combine the high electron transport from 1D nanostructures and large surface area to attach enough dyes from nanoparticles. Furthermore, the bigger pores inside the hierarchically structured films are also beneficial for the permeation and diffusion of electrolyte in the photoanode, forming good ohmic contact. The results provide a potential approach to obtain highly effective solar conversion materials.

Acknowledgments

This work has been supported by the Chinese National Science Funds (no. 51202094); the Priority Academic Program Development of Jiangsu Higher Education Institutions;

the Natural Science Foundation (no. 12KJB150010 and no. 12KJB430001) of Jiangsu Education Committee of China.

References

- [1] A. Fujishima and K. Honda, "Electrochemical photolysis of water at a semiconductor electrode," *Nature*, vol. 238, no. 5358, pp. 37–38, 1972.
- [2] B. O'Regan and M. Grätzel, "A low-cost, high-efficiency solar cell based on dye-sensitized colloidal TiO₂ films," *Nature*, vol. 353, pp. 737–740, 1991.
- [3] M. R. Hoffmann, S. T. Martin, W. Choi, and D. W. Bahnemann, "Environmental applications of semiconductor photocatalysis," *Chemical Reviews*, vol. 95, no. 1, pp. 69–96, 1995.
- [4] R. Wang, K. Hashimoto, A. Fujishima et al., "Light-induced amphiphilic surfaces," *Nature*, vol. 388, no. 6641, pp. 431–432, 1997.
- [5] M. Grätzel, "Photoelectrochemical cells," *Nature*, vol. 414, no. 6861, pp. 338–344, 2001.
- [6] S. U. M. Khan, M. Al-Shahry, and W. B. Ingler, "Efficient photochemical water splitting by a chemically modified n-TiO₂," *Science*, vol. 297, no. 5590, pp. 2243–2245, 2002.
- [7] P. V. Kamat, "Meeting the clean energy demand: nanostructure architectures for solar energy conversion," *Journal of Physical Chemistry C*, vol. 111, no. 7, pp. 2834–2860, 2007.
- [8] E. Maciak and Z. Opilski, "Transition metal oxides covered Pd film for optical H₂ gas detection," *Thin Solid Films*, vol. 515, no. 23, pp. 8351–8355, 2007.
- [9] M. G. Manera, J. Spadavecchia, D. Buso et al., "Optical gas sensing of TiO₂ and TiO₂/Au nanocomposite thin films," *Sensors and Actuators B*, vol. 132, no. 1, pp. 107–115, 2008.
- [10] F. Campus, P. Bonhôte, M. Grätzel, S. Heinen, and L. Walder, "Electrochromic devices based on surface-modified nanocrystalline TiO₂ thin-film electrodes," *Solar Energy Materials and Solar Cells*, vol. 56, no. 3–4, pp. 281–297, 1999.
- [11] D. P. Partlow and T. W. O'Keeffe, "Thirty-seven layer optical filter from polymerized sol-gel solutions," *Applied Optics*, vol. 29, no. 10, pp. 1526–1529, 1990.
- [12] A. Brudnik, H. Czernastek, K. Zakrzewska, and M. Jachimowski, "Plasma-emission-controlled d.c. magnetron sputtering of TiO_{2-x} thin films," *Thin Solid Films*, vol. 199, no. 1, pp. 45–58, 1991.
- [13] L. Yang, S. S. Saavedra, N. R. Armstrong, and J. Hayes, "Fabrication and characterization of low-loss, sol-gel planar waveguides," *Analytical Chemistry*, vol. 66, no. 8, pp. 1254–1263, 1994.
- [14] L. Xiao-e, A. N. M. Green, S. A. Haque, A. Mills, and J. R. Durrant, "Light-driven oxygen scavenging by titania/polymer nanocomposite films," *Journal of Photochemistry and Photobiology A*, vol. 162, no. 2–3, pp. 253–259, 2004.
- [15] H. Zhang, G. R. Li, L. P. An, T. Y. Yan, X. P. Gao, and H. Y. Zhu, "Electrochemical lithium storage of titanate and titania nanotubes and nanorods," *Journal of Physical Chemistry C*, vol. 111, no. 16, pp. 6143–6148, 2007.
- [16] J. Qu, Q. D. Wu, Y. R. Ren, Z. Su, C. Lai, and J. N. Ding, "Enhanced high-rate performance of double-walled TiO₂-B nanotubes as anodes in lithium-ion batteries," *Chemistry*, vol. 7, no. 11, pp. 2516–2518, 2012.
- [17] P. G. Bruce, B. Scrosati, and J. M. Tarascon, "Nanomaterials for rechargeable lithium batteries," *Angewandte Chemie—International Edition*, vol. 47, no. 16, pp. 2930–2946, 2008.

- [18] A. R. Armstrong, G. Armstrong, J. Canales, and P. G. Bruce, "TiO₂-B nanowires," *Angewandte Chemie*, vol. 116, no. 17, pp. 2336–2338, 2004.
- [19] G. Armstrong, A. R. Armstrong, J. Canales, and P. G. Bruce, "Nanotubes with the TiO₂-B structure," *Chemical Communications*, no. 19, pp. 2454–2456, 2005.
- [20] C. Lai, H. Z. Zhang, G. R. Li, and X. P. Gao, "Mesoporous polyaniline/TiO₂ microspheres with core-shell structure as anode materials for lithium ion battery," *Journal of Power Sources*, vol. 196, no. 10, pp. 4735–4740, 2011.
- [21] C. Lai, G. R. Li, Y. Y. Dou, and X. P. Gao, "Mesoporous polyaniline or polypyrrole/anatase TiO₂ nanocomposite as anode materials for lithium-ion batteries," *Electrochimica Acta*, vol. 55, no. 15, pp. 4567–4572, 2010.
- [22] Y. Ohsaki, N. Masaki, S. Yanagida et al., "Dye-sensitized TiO₂ nanotube solar cells: fabrication and electronic characterization," *Physical Chemistry Chemical Physics*, vol. 7, no. 24, pp. 4157–4163, 2005.
- [23] A. Hagfeldt and M. Grätzel, "Molecular photovoltaics," *Accounts of Chemistry Research*, vol. 3, pp. 269–277, 2000.
- [24] J. Bisquert, D. Cahen, G. Hodes, S. Rühle, and A. Zaban, "Physical chemical principles of photovoltaic conversion with nanoparticulate, mesoporous dye-sensitized solar cells," *Journal of Physical Chemistry B*, vol. 108, no. 24, pp. 8106–8118, 2004.
- [25] Y. Tachibana, J. E. Moser, M. Grätzel, D. R. Klug, and J. R. Durrant, "Subpicosecond interfacial charge separation in dye-sensitized nanocrystalline titanium dioxide films," *Journal of Physical Chemistry*, vol. 100, no. 51, pp. 20056–20062, 1996.
- [26] M. K. Nazeeruddin, A. Kay, I. Rodicio et al., "Conversion of light to electricity by cis-X₂bis(2,2'-bipyridyl-4,4'-dicarboxylate)ruthenium(II) charge-transfer sensitizers (X = Cl⁻, Br⁻, I⁻, CN⁻, and SCN⁻) on nanocrystalline TiO₂ electrodes," *Journal of the American Chemical Society*, vol. 115, no. 14, pp. 6382–6390, 1993.
- [27] A. Hagfeldt and M. Grätzel, "Light-induced redox reactions in nanocrystalline systems," *Chemical Reviews*, vol. 95, no. 1, pp. 49–68, 1995.
- [28] A. Yella, H. W. Lee, H. N. Tsao et al., "Porphyrin-sensitized solar cells with cobalt (II/III)-based redox electrolyte exceed 12 percent efficiency," *Science*, vol. 334, no. 6056, pp. 629–634, 2011.
- [29] S. A. Haque, E. Palomares, B. M. Cho et al., "Charge separation versus recombination in dye-sensitized nanocrystalline solar cells: the minimization of kinetic redundancy," *Journal of the American Chemical Society*, vol. 127, no. 10, pp. 3456–3462, 2005.
- [30] K. Pan, Y. Dong, C. Tian et al., "TiO₂-B narrow nanobelt/TiO₂ nanoparticle composite photoelectrode for dye-sensitized solar cells," *Electrochimica Acta*, vol. 54, no. 28, pp. 7350–7356, 2009.
- [31] T. Berger, T. Lana-Villarreal, D. Monllor-Satoca, and R. Gómez, "An electrochemical study on the nature of trap states in nanocrystalline rutile thin films," *Journal of Physical Chemistry C*, vol. 111, no. 27, pp. 9936–9942, 2007.
- [32] D. H. Chen, F. Z. Huang, Y. B. Cheng, and R. A. Caruso, "Mesoporous anatase TiO₂ beads with high surface areas and controllable pore sizes: a superior candidate for high-performance dye-sensitized solar cells," *Advanced Materials*, vol. 21, no. 21, pp. 2206–2210, 2009.
- [33] J. F. Qian, P. Liu, Y. Xiao et al., "TiO₂-coated multilayered SnO₂ hollow microspheres for dye-sensitized solar cells," *Advanced Materials*, vol. 21, no. 36, pp. 3617–3667, 2009.
- [34] M. J. Bierman and S. Jin, "Potential applications of hierarchical branching nanowires in solar energy conversion," *Energy and Environmental Science*, vol. 2, no. 10, pp. 1050–1059, 2009.
- [35] L. Hu, S. Dai, J. Weng et al., "Microstructure design of nanoporous TiO₂ photoelectrodes for dye-sensitized solar cell modules," *Journal of Physical Chemistry B*, vol. 111, no. 2, pp. 358–362, 2007.
- [36] M. Law, L. E. Greene, J. C. Johnson, R. Saykally, and P. Yang, "Nanowire dye-sensitized solar cells," *Nature Materials*, vol. 4, no. 6, pp. 455–459, 2005.
- [37] K. Zhu, N. R. Neale, A. Miedaner, and A. J. Frank, "Enhanced charge-collection efficiencies and light scattering in dye-sensitized solar cells using oriented TiO₂ nanotubes arrays," *Nano Letters*, vol. 7, no. 1, pp. 69–74, 2007.
- [38] G. K. Mor, K. Shankar, M. Paulose, O. K. Varghese, and C. A. Grimes, "Use of highly-ordered TiO₂ nanotube arrays in dye-sensitized solar cells," *Nano Letters*, vol. 6, no. 2, pp. 215–218, 2006.
- [39] M. Y. Song, D. K. Kim, K. J. Ihn, S. M. Jo, and D. Y. Kim, "Electrospun TiO₂ electrodes for dye-sensitized solar cells," *Nanotechnology*, vol. 15, no. 12, pp. 1861–1865, 2004.
- [40] W. Zhang, R. Zhu, L. Ke, X. Liu, B. Liu, and S. Ramakrishna, "Anatase mesoporous TiO₂ nanofibers with high surface area for solid-state dye-sensitized solar cells," *Small*, vol. 6, no. 19, pp. 2176–2182, 2010.
- [41] Q. L. Huang, G. Zhou, L. Fang, L. Hu, and Z. S. Wang, "TiO₂ nanorod arrays grown from a mixed acid medium for efficient dye-sensitized solar cells," *Energy and Environmental Science*, vol. 4, no. 6, pp. 2145–2151, 2011.
- [42] M. Adachi, Y. Murata, J. Takao, J. Jiu, M. Sakamoto, and F. Wang, "Highly efficient dye-sensitized solar cells with a titania thin-film electrode composed of a network structure of single-crystal-like TiO₂ nanowires made by the "oriented attachment" mechanism," *Journal of the American Chemical Society*, vol. 126, no. 45, pp. 14943–14949, 2004.
- [43] X. Feng, K. Shankar, O. K. Varghese, M. Paulose, T. J. Latempa, and C. A. Grimes, "Vertically aligned single crystal TiO₂ nanowire arrays grown directly on transparent conducting oxide coated glass: synthesis details and applications," *Nano Letters*, vol. 8, no. 11, pp. 3781–3786, 2008.
- [44] B. Liu and E. S. Aydil, "Growth of oriented single-crystalline rutile TiO₂ nanorods on transparent conducting substrates for dye-sensitized solar cells," *Journal of the American Chemical Society*, vol. 131, no. 11, pp. 3985–3990, 2009.
- [45] A. Vomiero, V. Galstyan, A. Braga et al., "Flexible dye sensitized solar cells using TiO₂ nanotubes," *Energy and Environmental Science*, vol. 4, no. 9, pp. 3408–3413, 2011.
- [46] L. L. Li, Y. J. Chen, H. P. Wu, N. S. Wang, and E. W. G. Diau, "Detachment and transfer of ordered TiO₂ nanotube arrays for front-illuminated dye-sensitized solar cells," *Energy and Environmental Science*, vol. 4, no. 9, pp. 3420–3425, 2011.
- [47] L. D. Sun, S. Zhang, X. Wang, X. W. Sun, D. Y. Ong, and A. K. K. Kyaw, "A novel parallel configuration of dye-sensitized solar cells with double-sided anodic nanotube arrays," *Energy and Environmental Science*, vol. 4, no. 6, pp. 2240–2248, 2011.
- [48] J. R. Jennings, A. Ghicov, L. M. Peter, P. Schmuki, and A. B. Walker, "Dye-sensitized solar cells based on oriented TiO₂ nanotube arrays: transport, trapping, and transfer of electrons," *Journal of the American Chemical Society*, vol. 130, no. 40, pp. 13364–13372, 2008.
- [49] J. Jiu, F. Wang, S. Isoda, and M. Adachi, "Highly efficient dye-sensitized solar cells based on single crystalline TiO₂ nanorod film," *Chemistry Letters*, vol. 34, no. 11, pp. 1506–1507, 2005.

- [50] J. Qu, G. R. Li, and X. P. Gao, "One-dimensional hierarchical titania for fast reaction kinetics of photoanode materials of dye-sensitized solar cells," *Energy and Environmental Science*, vol. 3, no. 12, pp. 2003–2009, 2010.
- [51] E. Enache-Pommer, J. E. Boercker, and E. S. Aydil, "Electron transport and recombination in polycrystalline TiO₂ nanowire dye-sensitized solar cells," *Applied Physics Letters*, vol. 91, no. 12, Article ID 123116, 3 pages, 2007.
- [52] M. Kläui, H. Ehrke, U. Rüdiger et al., "Direct observation of domain-wall pinning at nanoscale constrictions," *Applied Physics Letters*, vol. 87, no. 10, Article ID 102509, 3 pages, 2005.
- [53] S. H. Kang, S. H. Choi, M. S. Kang et al., "Nanorod-based dye-sensitized solar cells with improved charge collection efficiency," *Advanced Materials*, vol. 20, no. 1, pp. 54–58, 2008.
- [54] B. Tan and Y. Wu, "Dye-sensitized solar cells based on anatase TiO₂ nanoparticle/nanowire composites," *Journal of Physical Chemistry B*, vol. 110, no. 32, pp. 15932–15938, 2006.
- [55] J. J. Wu, G. R. Chen, C. C. Lu, W. T. Wu, and J. S. Chen, "Performance and electron transport properties of TiO₂ nanocomposite dye-sensitized solar cells," *Nanotechnology*, vol. 19, no. 10, Article ID 105702, 2008.
- [56] M. D. Hernández-Alonso, F. Fresno, S. Suárez, and J. M. Coronado, "Development of alternative photocatalysts to TiO₂: challenges and opportunities," *Energy and Environmental Science*, vol. 2, no. 12, pp. 1231–1257, 2009.
- [57] S. Gubbala, V. Chakrapani, V. Kumar, and M. K. Sunkara, "Band-edge engineered hybrid structures for dye-sensitized solar cells based on SnO₂ nanowires," *Advanced Functional Materials*, vol. 18, no. 16, pp. 2411–2418, 2008.
- [58] S. Uchida, R. Chiba, M. Tomiha, N. Masaki, and M. Shirai, "Application of titania nanotubes to a dye-sensitized solar cell," *Electrochemistry*, vol. 70, no. 6, pp. 418–420, 2002.
- [59] T. Kasuga, M. Hiramatsu, A. Hoson, T. Sekino, and K. Niihara, "Formation of titanium oxide nanotube," *Langmuir*, vol. 14, no. 12, pp. 3160–3163, 1998.
- [60] M. Adachi, Y. Murata, I. Okada, and S. Yoshikawa, "Formation of titania nanotubes and applications for dye-sensitized solar cells," *Journal of the Electrochemical Society*, vol. 150, no. 8, pp. G488–G493, 2003.
- [61] Y. Lan, X. P. Gao, H. Y. Zhu et al., "Titanate nanotubes and nanorods prepared from rutile powder," *Advanced Functional Materials*, vol. 15, no. 8, pp. 1310–1318, 2005.
- [62] J. Jiu, S. Isoda, M. Adachi, and F. Wang, "Dye-sensitized solar cells based on a single-crystalline TiO₂ nanorod film," *Journal of Physical Chemistry B*, vol. 110, no. 5, pp. 2087–2092, 2006.
- [63] K. Shankar, G. K. Mor, H. E. Prakasam et al., "Highly-ordered TiO₂ nanotube arrays up to 220 μm in length: use in water photoelectrolysis and dye-sensitized solar cells," *Nanotechnology*, vol. 18, no. 6, Article ID 065707, 2007.
- [64] X. Pan, C. H. Chen, K. Zhu, and Z. Y. Fan, "TiO₂ nanotubes infiltrated with nanoparticles for dye sensitized solar cells," *Nanotechnology*, vol. 22, Article ID 235402, 2011.
- [65] O. K. Varghese, M. Paulose, and C. A. Grimes, "Long vertically aligned titania nanotubes on transparent conducting oxide for highly efficient solar cells," *Nature Nanotechnology*, vol. 4, no. 9, pp. 592–597, 2009.
- [66] M. D. Ye, X. K. Xin, C. J. Lin, and Z. Q. Lin, "High efficiency dye-sensitized solar cells based on hierarchically structured nanotubes," *Nano Letters*, vol. 11, no. 8, pp. 3214–3220, 2011.
- [67] M. Paulose, K. Shankar, O. K. Varghese, G. K. Mor, B. Hardin, and C. A. Grimes, "Backside illuminated dye-sensitized solar cells based on titania nanotube array electrodes," *Nanotechnology*, vol. 17, no. 5, pp. 1446–1448, 2006.
- [68] J. M. Macák, H. Tsuchiya, A. Ghicov, and P. Schmuki, "Dye-sensitized anodic TiO₂ nanotubes," *Electrochemistry Communications*, vol. 7, no. 11, pp. 1133–1137, 2005.
- [69] S. H. Kang, J. W. Lim, H. S. Kim, J. Y. Kim, Y. H. Chung, and Y. E. Sung, "Photo and electrochemical characteristics dependent on the phase ratio of nanocolumnar structured TiO₂ films by RF magnetron sputtering technique," *Chemistry of Materials*, vol. 21, no. 13, pp. 2777–2788, 2009.
- [70] G. K. Mor, K. Shankar, M. Paulose, O. K. Varghese, and C. A. Grimes, "Enhanced photocleavage of water using titania nanotube arrays," *Nano Letters*, vol. 5, no. 1, pp. 191–195, 2005.
- [71] M. Paulose, K. Shankar, S. Yoriya et al., "Anodic growth of highly ordered TiO₂ nanotube arrays to 134 μm in length," *Journal of Physical Chemistry B*, vol. 110, no. 33, pp. 16179–16184, 2006.
- [72] J. H. Park, T. W. Lee, and M. G. Kang, "Growth, detachment and transfer of highly-ordered TiO₂ nanotube arrays: use in dye-sensitized solar cells," *Chemical Communications*, no. 25, pp. 2867–2869, 2008.
- [73] S. P. Albu, A. Ghicov, J. M. Macak, R. Hahn, and P. Schmuki, "Self-organized, free-standing TiO₂ nanotube membrane for flow-through photocatalytic applications," *Nano Letters*, vol. 7, no. 5, pp. 1286–1289, 2007.
- [74] J. Wang and Z. Q. Lin, "Freestanding TiO₂ nanotube arrays with ultrahigh aspect ratio via electrochemical anodization," *Chemistry of Materials*, vol. 20, no. 4, pp. 1257–1261, 2008.
- [75] M. Paulose, K. Shankar, S. Yoriya et al., "Anodic growth of highly ordered TiO₂ nanotube arrays to 134 μm in length (Journal of Physical Chemistry B (2006) 110B)," *Journal of Physical Chemistry B*, vol. 112, no. 47, p. 15261, 2008.
- [76] J. B. Baxter and E. S. Aydil, "Nanowire-based dye-sensitized solar cells," *Applied Physics Letters*, vol. 86, no. 5, Article ID 053114, 3 pages, 2005.
- [77] C. Xu, P. H. Shin, L. Cao, J. Wu, and D. Gao, "Ordered TiO₂ nanotube arrays on transparent conductive oxide for dye-sensitized solar cells," *Chemistry of Materials*, vol. 22, no. 1, pp. 143–148, 2010.
- [78] Q. Huang, G. Zhou, L. Fang, L. Hu, and Z. S. Wang, "TiO₂ nanorod arrays grown from a mixed acid medium for efficient dye-sensitized solar cells," *Energy and Environmental Science*, vol. 4, no. 6, pp. 2145–2151, 2011.
- [79] T. Krishnamoorthy, V. Thavasi, G. M. Subodh, and S. Ramakrishna, "A first report on the fabrication of vertically aligned anatase TiO₂ nanowires by electrospinning: preferred architecture for nanostructured solar cells," *Energy and Environmental Science*, vol. 4, no. 8, pp. 2807–2812, 2011.
- [80] S. Fujihara, E. Hosono, K. Kakiuchi, and H. Imai, "Growth of submicrometer-scale rectangular parallelepiped rutile TiO₂ films in aqueous TiCl₃ solutions under hydrothermal conditions," *Journal of the American Chemical Society*, vol. 126, no. 25, pp. 7790–7791, 2004.
- [81] J. J. Wu and C. C. Yu, "Aligned TiO₂ nanorods and nanowalls," *Journal of Physical Chemistry B*, vol. 108, no. 11, pp. 3377–3379, 2004.
- [82] Q. Zhou, X. F. Yang, S. Q. Zhang et al., "Rutile nanowire arrays: tunable surface densities, wettability and photochemistry," *Journal of Materials Chemistry*, vol. 21, no. 39, pp. 15806–15812, 2011.
- [83] Y. Liu, H. Wang, Y. Wang, H. Xu, M. Li, and H. Shen, "Substrate-free, large-scale, free-standing and two-side oriented single crystal TiO₂ nanorod array films with photocatalytic

- properties," *Chemical Communications*, vol. 47, no. 13, pp. 3790–3792, 2011.
- [84] G. Wang, H. Wang, Y. Ling et al., "Hydrogen-treated TiO₂ nanowire arrays for photoelectrochemical water splitting," *Nano Letters*, vol. 11, no. 7, pp. 3026–3033, 2011.
- [85] X. Feng, J. Zhai, and L. Jiang, "The fabrication and switchable superhydrophobicity of TiO₂ nanorod films," *Angewandte Chemie—International Edition*, vol. 44, no. 32, pp. 5115–5118, 2005.
- [86] E. Barea, X. Q. Xu, V. Gonzalez-Pedro, T. Ripolles-Sanchis, F. Fabregat-Santiago, and J. Bisquert, "Origin of efficiency enhancement in Nb₂O₅ coated titanium dioxide nanorod based dye sensitized solar cells," *Energy and Environmental Science*, vol. 4, no. 9, pp. 3414–3419, 2011.
- [87] M. Q. Lv, D. J. Zheng, M. D. Ye et al., "Densely aligned rutile TiO₂ nanorod arrays with high surface area for efficient dye-sensitized solar cells," *Nanoscale*, vol. 4, no. 19, pp. 5872–5879, 2012.



Hindawi

Submit your manuscripts at
<http://www.hindawi.com>

