Branched TiO₂ nanorod arrays owning the surface anatase/rutile junctions for dye sensitized solar cells

Jiao Liu,^{a,b} Jicun Huo,^{a,b} Min Zhang,^{a,*} and Xiandui Dong^{a,*}

^a State Key Laboratory of Electroanalytical Chemistry, Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, Changchun, 130022, China. E-mail: min.zhang@ciac.ac.cn or dxd@ciac.ac.cn. Phone (Fax): +86-431-85262952

^b University of Chinese Academy of Sciences, Beijing 100049, China.

ABSTRACT

Branched TiO₂ nanorod arrays (TiO₂ BNRs) owning the surface anatase/rutile junctions on FTO substrates were synthesized and applied in dye-sensitized solar cells (DSCs) comparing with the TiO₂ nanorod arrays (TiO₂ NRs) owning one single crystalline phase and the TiO₂ nanoparticles (TiO₂ NPs) owning irregular surface morphology. The branched morphology owning the surface anatase/rutile junctions was revealed by field emission scanning and transmission electron microscopy, Raman, and X-ray diffraction. The power conversion efficiency (PCE) of DSCs fabricated using TiO₂ BNRs is improved to 6.5% with both enhancement of photovoltages and photocurrent densities, better than DSCs fabricated using the corresponding TiO₂ NRs and DSCs fabricated using the TiO₂ NPs.

Key words: Surface-phase junctions; Branched TiO₂ nanorods; Dye-sensitized solar cells

1 Introduction

Dye-sensitized solar cells have been widely studied because of a lot of advantages, such as low costs, convenient preparations, and so on [1-4]. However, the PCE has been increased slowly in recent years. Device engineering and development of new dye materials are the two main ways to improve the PCE of DSCs [5-6], after the early work carried out in 1991 [7]. Obviously, the photoanode material is also the crucial component to the photovoltaic performances of DSCs as dyes and electrolytes.

A variety of metal oxides as photoanode have been researched, such as tin oxide, zinc oxide and titanium dioxide [8-10]. The TiO_2 NPs were most selected as substrate materials to adsorb dyes in DSCs [11-13], however, the irregular surface morphology of TiO_2 NPs has perplexed the interface of TiO_2 layer and the working mechanism of DSCs. Also nanotubes, nanowires and nanorods were widely studied expecting their clear transportation pathway to accelerate charge transport, further to improve the properties of DSCs [14-23]. Nonetheless, low active surface area of these one-dimensional nanostructures limited the enhancement of the properties of DSCs. Generally the morphology and structure of photoanode play a vital role in the performance of DSCs [25-26]. The vertically aligned onedimensional nanostructure photoanodes are considered to be ideal to promote charge transport due to their direct transport pathway for photoinjected electrons. However, the low specific surface area of the above photoanodes results in limited low PCE due to insufficient dye loading and thus low current density [17,29]. One of the approaches to increase the surface area to improve cell performance is to enhance the surface area of photoanode, such as combining the rutile nanorod with rutile nanoparticle or rutile hierarchical nanostructures. The cell performance had increased to some extent and there was no change of the phase of photoanode [27-28]. The anatase/rutile junction we induced here has not only enhanced the surface area, but also explore the effects of combining the anatase/rutile phase on DSCs, benefiting from the advantages of the anatase TiO_2 which is favourable to photovoltaic performance and the rutile TiO_2 which can grow easily on fluorine doped tin oxide and has good electron transport properties at the same time.

In this context, TiO_2 BNRs owning the surface anatase/rutile junctions on FTO substrates were prepared by a two steps method under low temperature. The morphology and hierarchical structure were characterized by scanning electron microscopy, transmission electron microscopy and X-ray diffraction and Raman analysis. Comparing with that of TiO_2 NRs and TiO_2 NPs, the DSCs fabricated with the TiO_2 BNRs show the best performance and their PCE arrived 6.5% accompanied by both enhancement of photovoltages and photocurrent densities.

2 Experimental details

2.1 Synthesis of TiO₂ materials

Three kinds of TiO₂ electrodes were prepared, such as TiO₂ BNRs, TiO₂ NRs, and TiO₂ NPs. For the first two, to begin with, Fluorine-doped SnO₂ (FTO) conducting glasses were ultrasonically cleaned in distilled water, ethyl alcohol and propyl alcohol in turn for 3 times. The prepared FTO glasses were immersed into a TiCl₄ aqueous solution for half an hour and followed drying under 60 °C to form a seed layer. The FTO conducting glasses with a seed layer were put in a solution containing 15 ml deionized water, 2.5 ml NaCl saturated aqueous solution, 15 ml HCl aqueous solution (36–38%) and 0.4 ml titanium isopropoxide in a Teflon-lined stainless steel autoclave (50 mL) at 170 °C for 15 h for hydrothermal synthesis of TiO₂ NRs and the autoclave was cooled to room temperature naturally. The obtained TiO₂ NRs samples were washed with deionized water and dried at 80 °C in air [29-30]. Next, part of this TiO₂ NRs samples were further put into an aqueous solution containing ammonium hexafluoro-titanate ([NH₄]₂TiF₆) and boric acid (H₃BO₃) for 40 h at room temperature to form TiO₂ BNRs [30-31].

For TiO₂ NPs electrodes, transparent films of 20-nm-sized TiO₂ particles were printed on FTO treated with 50 mM TiCl₄ aqueous solution at 70 °C for 40 min, the films were gradually heated to 500 °C under oxygen and subsequently hold for 15 minutes for sintering and then cooled to room temperature naturally, this transparent layer was prepared based on the previous study [30]. TiO₂ NPs films whose thickness are equivalent to that of NRs or BNRs are too thin to load enough dyes, therefore 4 µm-thick TiO₂ NPs films electrodes were selected for DSCs fabrication.

2.2 Fabrication of DSCs

DSCs were fabricated following same procedure. The as-prepared TiO₂ film electrodes (TiO₂ BNRs, TiO₂ NRs, and TiO₂ NPs) were annealed under 450 °C and then cooled naturally, and then were immersed into a 150 µM dye solution (chloroform/ethanol, v/v, 1/9, with no co-absorber) for 12 hours at 25°C for dye-loading. A dye C218 we synthesised was used [33]. The Pt-coated FTO as a counter electrode was prepared by dropping H₂PtCl₆ (5 mM) solution on the FTO glass followed by heating at 400°C for 15 min in air. A

25- μm -thick Surlyn circular mask that heated at 130 $^{\circ}\text{C}$ was used to adhere the negative electrode and a platinum coated FTO electrode. The recipe of the electrolyte infiltrated in the internal space of solar cells is: DMII/I₂/LiI/TBP/GNCS: 1M/20Mm/50Mm/1M/0.1M in acetonitrile [34].

2.3 Instrumentation of characterizations

Scanning electron microscope (SEM) images were obtained by the scanning electron microscope (Zeiss supra 55) manufactured from German Carl Zeiss. The thickness of the samples was measured by a step profiler. TEM images were obtained using a JEOL JEM-2100F transmission electron microscope at an acceleration voltage of 200 kV. The absorption spectra were obtained from a UV-Vis spectrophotometer (UNICO, UV-2802PC). The X-ray diffraction analysis was performed on a D/max 2500 Rigaku X-ray diffractometer. Raman spectra of samples were received by 380 nm exciting light on a Renishaw Raman system model 1000 spectrometer.

2.4 Instrumentation of photovoltaic performance

The system of EQEs measurement is consisted of a 500 W Xenon Light Source (CHF-XM500, Trusttech), an automatic grating monochromator (Omni- λ 300, Zolix), a standard monocrystalline silicon solar cell (S1337-1010BQ, Hamamatsu), and a sourcemeter (Keithley 2400). The data were acquired using LabVIEW 8.0 software. A solar simulator (LS1000-4S-AM1.5G-1000W, Solar Light Com. Inc.) was used for J - V measurement. The irradiation intensity was corrected by a solar radiation intensity meter (PMA2144) and a radiation meter (PMA 2100). A filter ultraviolet antireflective film ($\lambda < 380$ nm, ARKTOP, ASAHI Glass) was attached on the top of DSCs to reduce light reflection loss and to protect dyes from degradation by the UV light. A mask with an inner hole area 0.158 cm^2 was used to determine the incident light area and a suit of neutral metal meshes were employed to adjust the incident light intensity. Electrochemical impedance spectra (EIS) were measured by IM6ex electrochemical workstation (ZAHNER, Germany) and analysed with Z-View software.

3 Results and discussion

3.1 Morphology and structure of TiO₂ NRs and TiO₂ BNRs

The SEM measurement gives the most visualized information of morphology TiO_2 materials on the FTO substrate. From the SEM images of synthesized TiO_2 films (shown in Fig. 1), it's easy to discover that the surface of TiO_2 NRs is smooth, the diameter of most nanorods are 30~100 nm. Besides, there are a lot of interspaces between the nanorods. The low surface area is the restriction of such TiO_2 NRs with one-dimensional structure. Utilizing these gaps to an extreme will enhance the specific surface area of TiO_2 NRs which will further bring in benefits such as enhancement of light harvesting and charge collection. TiO_2 BNRs were prepared from part of TiO_2 NRs samples of same batch whose morphology are shown in Figs. 1b, 1c and 1d with different scales and also confirmed by cross-section SEM images. It's worth noting that the newer about 30~50 nm thickness TiO_2 branches grown uniformly to form pineapple-shape and covered original nanorods thoroughly. And that almost the same thickness 741~745 nm were acquired for TiO_2 BNRs films and the TiO_2 NRs films. These results reveal the hierarchical nano-architecture of TiO_2 BNRs films and the high consistency and comparability between TiO_2 BNRs films with TiO_2 NRs films. The TiO_2 BNRs owning oriented arrangement enhanced the device performance further proved by the dye-loading amounts listed in Table 1 below.

The observation of the TEM will provide more information on the morphology and crystal structure of the TiO_2 nanostructures. To identify the phase junctions of the TiO_2 BNRs, TEM images were taken from interfacial region of TiO_2 branches and nanorods (as shown the Fig. 1(e) and Fig. 1(f)). The results confirm that the branch is single anatase phase which could be indicated by the lattice fringes with (101) interplanar spacing 0.35 nm. Meanwhile, the (110), (001) and (100) faces of tetragonal rutile phase were observed only in nanorod region by the Lattice fringes with interplanar spacing 0.32 nm, 0.29 nm and 0.23 nm. These facts give the direct structure evidence for the surface anatase/rutile junctions formed between the branches and nanorods.

Also the prepared TiO_2 films on FTO substrates were characterized by XRD spectrum, as shown in Fig. 2(a). The XRD pattern of TiO_2 NRs contains 8 peaks, four of which arise from the FTO substrate. The other characteristic peaks are 26.6°, 36.1°, 38.8° and 63.0° assigned to the (110), (101), (200) and (002) planes of rutile phase of TiO_2 (JCPDS

No.21-1276). For that of TiO₂ BNRs films, expect for the diffraction peaks that assigned to rutile phase of TiO₂ and FTO, there are two new peaks at 48.1° and 53.9° which can be indexed to (200) and (105) planes of anatase of TiO₂ (JCPDS No.89-4921). The coexistence of anatase and rutile phases observed from XRD spectra further confirms the evidence for the surface anatase/rutile junctions existed on the TiO₂ BNRs.

Raman spectrum was also used to characterize the prepared samples on FTO substrates, as shown in Fig. 2(b). The TiO₂ NRs showed Raman peaks at 245 cm⁻¹, 442 cm⁻¹ and 609 cm⁻¹, which is typical feature of rutile phase. Raman peak of anatase phase at 161 cm⁻¹ were observed on the TiO₂ BNRs films only. The results of Raman spectra demonstrated that the TiO₂ BNRs had the heterogeneous structures of rutile and anatase phases. The XRD and Raman spectra, along with TEM images all proved that TiO₂ BNRs owning the surface anatase/rutile junctions on FTO substrates were synthesized. The structure of TiO₂ BNRs is hierarchical nano-architecture consisted with two phases TiO₂, one is rod-shape rutile core with 30~100 nm, one is pineapple-shape anatase shell with 30~50 nm thickness covered on core. In addition, the TiO₂ NPs that we used in this context have been proved to own bicrystalline anatase and rutile phases as usual.

3.2 Optical performance of the TiO₂ films

UV-vis spectra were commonly utilized to study the optical properties of TiO₂ materials. The absorption spectrum of the TiO₂ BNRs film was further investigated comparing with the TiO₂ NRs and the TiO₂ NPs on FTO, as shown in Fig. 3a. Due to the electron excitation from the valence band to the conduction band of TiO₂, there is an obvious absorption band in the ultraviolet region for the three samples. The max absorption intensity of the TiO₂ BNRs is weaker than that of the TiO₂ NRs, and the maximum absorption is located at 324 nm for the TiO₂ NRs, 300 nm for the TiO₂ BNRs and 291 nm for the TiO₂ NPs. Based on the curves of the plots of the $(ah\nu)^{1/2}$ vs the energy of absorbed light presented in Fig. 3b, the band gaps estimated for the TiO₂ NRs, TiO₂ BNRs and TiO₂ NPs, are approximately 2.68 eV, 2.78 eV and 3.12 eV respectively. The wider band gap of TiO₂ BNRs than that of the TiO₂ NRs is reasonable to understand due to the addition of the anatase phase TiO₂ branches. As the blue shift of absorption band edge (Fig. 3a), the transmittances of the

TiO₂ nano materials become larger and TiO₂ BNRs should be more suitable for absorbing dyes to fabricate DSCs than TiO₂ NRs. Nevertheless, the TiO₂ NPs owning the bluest absorption band edge maybe most appropriate for DSCs by reducing the absorption itself extremely, however, TiO₂ NPs is consisted of the disordered stacking of TiO₂ nanoparticles unfavoured electron transfer.

3.3 Photovoltaic performance for DSCs

To research the effects of the anatase phase branches and the surface anatase/rutile junctions on photovoltaic performance of devices, DSCs with dye-coated TiO₂ BNRs, TiO₂ NRs and TiO₂ NPs were fabricated with high consistency and comparability. First of all, the external quantum efficiencies (EQEs) at short-circuit were examined using monochromatic lights at the wavelength interval of 10 nm, and shown in Fig. 4a. The photocurrent action spectra manifest that DSCs using TiO₂ NRs, TiO₂ BNRs and TiO₂ NPs exhibit maxima of 60%, 79% and 73% respectively. Meanwhile, Current-voltage (*J-V*) curves measured under an irradiance of 100 mW cm⁻² simulated AM1.5G sunlight were presented in Fig. 4b and table 1. DSCs-TiO₂ BNRs behaves the largest *J*_{sc} and highest *V*_{oc}. The difference of day-Loading cannot explain enough the *J*_{sc} changes of these devices. The IPCE boosting at longwave region and the *J*_{sc} enhancement of DSCs-TiO₂ BNRs maybe imply the positive effect of the anatase-covered-rutile hierarchical nano-architecture both on structure and electronics. The *J-V* curves of these DSCs samples were further measured under different irradiances of attenuated lights with a suit of neutral metal meshes for different attenuated lights: 100 mW cm⁻², 50.94 mW cm⁻², 22.85 mW cm⁻² and 12.3 mW cm⁻². Open-circuit photovoltages plotted against short-circuit photocurrent densities and the linear fitting lines are presented in Fig. 4c, the similar *V*_{oc}~*J*_{sc} feature of top two lines suggests TiO₂ BNRs and TiO₂ NPs might well have similar mechanism for electron transfer. *J-V* curves of DSCs made with TiO₂ BNRs films tested under different irradiances of attenuated lights were shown in Fig. 4d and table 2. DSCs using the TiO₂ BNRs films show a prominent enhancement on PCE, both of open-circuit photovoltages and short-circuit photocurrent densities are increased obviously, comparing with that of the TiO₂ NRs and the TiO₂ NPs. Especially, the enhanced open-circuit photovoltages

indicate that the DSCs using the two-phases TiO_2 BNRs fabricated in this work have reduced the recombination of the electrons in TiO_2 conduction band comparing with previous researches about other TiO_2 BNRs [35-37].

Current-voltage curves and electronic impedance spectra (EIS) under dark conditions were measured to explore the electrochemical features of the DSCs samples. In the first place, as shown in Fig. 5a, comparing under same potential, the DSCs based on the TiO_2 BNRs show smallest dark currents, which indicated that recombination would be blocked more. In the second place, the electronic impedance spectra of the corresponding DSCs in the dark condition under a bias of 0.8 V were further carried out to understand the effect of the TiO_2 BNRs (Fig. 5b). The resistance R_s represents the series resistance component of circuit. C_μ is constant phase element resulting from the capacitor components represented interfaces in DSCs. The resistance R_{ct1} represents the charge transfer process between the counter electrode and the electrolyte interface. The resistance R_{ct2} is related to charge transfer processes at $\text{TiO}_2/\text{dye}/\text{electrolyte}$ interfaces which used to qualify the recombination [38-39]. As shown in Fig. 5 (b), the R_s and R_{ct1} have almost no differences which verified that the substrate of TiO_2 materials and the counter electrode/electrolyte interface are the same. Here we focused on the comparison of R_{ct2} since the others are almost the same. The fitting values of R_{ct2} of the TiO_2 215.7 Ω for TiO_2 NRs, 313.4 Ω for TiO_2 BNRs, 254.4 Ω for TiO_2 NPs, respectively. DSCs based on the TiO_2 BNRs had shown a biggest recombination resistance than that based on TiO_2 NRs and TiO_2 NPs [39-40]. It implies that the DSCs based on the TiO_2 BNRs own longest electron lifetime which was beneficial for the more effective charge collect and charge transfer process at the $\text{TiO}_2/\text{dye}/\text{electrolyte}$ interfaces. These experiments implied that branched anatase NRs bring effective pathway for charge transfer to improve the photovoltaic performance for DSCs.

On the one hand, due to the addition of the anatase phase TiO_2 branches, the photovoltaic performance of the DSCs fabricated using TiO_2 BNRs is superior to the other DSCs justified by the experiments data listed in Table 1. Dye-loading amounts were obtained by measuring the difference of ultraviolet absorption of dye solution before and

after dye adsorption on the TiO_2 materials [37, 41]. Look back the Fig. 3, comparing to the TiO_2 NRs, low absorption of the TiO_2 BNRs at blue-violet region, which mostly avoiding competing with dyes to absorb lights is beneficial for dyes on its surface to absorb more lights by the improved transmittances. In addition, longer electron lifetime shown by the DSCs based on the TiO_2 BNRs contributed also improves the photovoltaic performance. So it is reasonable to understand the superior photovoltaic performance of the DSCs fabricated using TiO_2 BNRs due to the addition of the anatase phase TiO_2 branches.

On the other hand, the phase junctions facilitate the electron transfer from the anatase surface to the rutile which further improves the charge-separation efficiency and the TiO_2 BNRs own clear information on its morphology and phases which could be tuned by controlling the reaction conditions. Anatase-rutile TiO_2 junctions are often encountered in photocatalytical researches, but the underlying reasons are still under exploring. For example, Tetsuro Kawahara et al. put forward that the remarkable coexistent effect of rutile and anatase would arise from the increase in the charge separation efficiency due to photo-induced interfacial electron transfer from anatase to rutile through measuring the photocatalytic activity [42]. Photogenerated electron transfer to the rutile nanorods, then the energy barrier restrains electron transfer back due to the higher conduction band energy of anatase branched, further efficiently increased the lifetimes of carriers [30]. But Jing Zhang et al. proposed that the phase junctions may facilitate transfer of the photogenerated electron from the conduction band of the rutile phase to the trapping sites on the anatase surface [43]. In 2013, a study on XPS/modeling suggested that the band energy alignment in the anatase-rutile heterojunction should result in electron transfer to anatase and hole transfer to rutile [44]. However, just recently, Durrant et al. found that holes transferred to anatase, not to rutile with transient absorption spectroscopy studies [45]. It can be deduced that, under high charge carrier concentration, the properties of anatase/rutile junctions probably are dependent on the dynamic pathway of electron transfer, and not simply dependent on the band bending on the interface which induced by the doping, structure, crystalline size and/or preparation method, et.al. Comprehensively, in our instance, the photovoltaic performance of the

DSCs fabricated using TiO₂ BNRs owning the surface anatase/rutile junctions makes a progress comparing with the DSCs fabricated using TiO₂ NRs and TiO₂ NPs.

4 Conclusions

The two-phase TiO₂ BNRs were synthesized by a two steps method under low temperature and successfully optimized the PCE of DSCs with enhancing on both of open-circuit photovoltages and short-circuit photocurrent densities comparing to the TiO₂ NRs and TiO₂ NPs, because the surface anatase/rutile junctions have blocked recombination and improved electron transfer. This work provides an evidence of effects of the surface anatase/rutile junctions on DSCs. Using surface junctions to improve DSCs performance would be an approach worth exploring.

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Fig. 1. SEM images of the TiO₂ NRs (a) and the TiO₂ BNRs (b), (c), (d) with different scales. TEM images of the TiO₂ branch (e) and the TiO₂ nanorod (f) covered by branches. In addition, for lattice fringes and interplanar spacing, there is no difference between the TiO₂ NRs and the trunks inside TiO₂ BNRs. The insert images at (a) and (b) are the cross-section SEM images corresponded.

Fig. 2. XRD patterns (a) and Raman spectra (b) for TiO₂ NRs (black) and TiO₂ BNRs (red) films.

Fig. 3 (a) Absorption spectra of a dummy cell possessing the TiO₂ NRs, the TiO₂ BNRs and TiO₂ NPs films. (b) Plots of the transformed Kubelka–Munk function versus the energy of light over the TiO₂ NRs, the TiO₂ BNRs and TiO₂ NPs films.

Table 1

Photovoltaic parameters of DSCs fabricated with dye-coated TiO₂ NRs, the TiO₂ BNRs and TiO₂ NPs films under the simulated AM1.5G sunlight (100 mW cm^{-2}), the data were measured with at least 4 cells of same batch for each kind to ensure consistency and comparability.

Samples	J_{SC}^{EQE} [mA cm^{-2}]	J_{SC} [mA cm^{-2}]	V_{OC} [mV]	FF [%]	PCE [%]	c_m [$\text{mol cm}^{-2} \mu\text{m}^{-1}$]
DSCs-TiO ₂ NRs	8.48 ± 0.12	8.34 ± 0.12	754 ± 3	71.4 ± 0.2	4.5 ± 0.1	1.78×10^{-8}
DSCs-TiO ₂ BNRs	12.41 ± 0.13	12.22 ± 0.13	811 ± 3	65.6 ± 0.1	6.5 ± 0.1	2.02×10^{-8}
DSCs-TiO ₂ NPs	9.91 ± 0.11	9.91 ± 0.12	801 ± 3	71.7 ± 0.1	5.7 ± 0.1	1.97×10^{-8}

Fig. 4 (a) Plots of external quantum efficiencies (EQEs) as a function of wavelengths (λ) for DSCs fabricated with dye-coated TiO_2 NRs (black), dye-coated TiO_2 BNRs (red) films and dye-coated TiO_2 NPs (blue). (b) Current–voltage (J – V) curves measured under an irradiance of 100 mW cm^{-2} simulated AM1.5G sunlight. On top of a DSC was laminated with an antireflection film. The aperture area of our metal mask was 0.160 cm^2 . (c) Drawing of open-circuit photovoltages (V_{oc}) plotted against short-circuit photocurrent densities (J_{sc}) by testing J – V curves under different irradiances of attenuated lights with a suit of neutral metal meshes for different hydrothermal of attenuated lights: 100W (black), 50.94 W (red), 22.85 W (blue), 12.3 W (green). The solid linear fittings were also included. (d) J – V curves of DSCs made with dye-coated TiO_2 BNRs tested under different irradiances of attenuated lights.

Table 2

J – V parameters of DSCs fabricated with dye-coated TiO_2 BNRs films tested under different attenuated lights, the data were measured with at least 4 cells.

Attenuated lights [mW cm^{-2}]	J_{sc} [mA cm^{-2}]	V_{oc} [mV]	FF [%]	PCE [%]
100	12.22 ± 0.13	811 ± 3	65.6 ± 0.1	6.5 ± 0.1
50.94	6.26 ± 0.11	777 ± 2	66.0 ± 0.1	6.6 ± 0.1
22.85	2.84 ± 0.12	756 ± 3	67.7 ± 0.1	6.7 ± 0.1
12.3	1.51 ± 0.11	741 ± 3	68.3 ± 0.2	6.5 ± 0.1

Fig. 5 (a) dark current-voltage measurements and (b) EIS's Nyquist plots of DSCs based on the TiO_2 NRs, the TiO_2 BNRs and TiO_2 NPs.