Front. Optoelectron. 2016, 9(1): 53–59
DOI 10.1007/s12200-016-0565-8

RESEARCH ARTICLE

Micro-scale hierarchical photoanode for quantum-dot-sensitized solar cells based on TiO_2 nanowires

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Abstract This paper proposed a new architecture design for nanowire-based quantum-dot-sensitized solar cells to improve the photovoltaic performance. Microstructured rough substrate was used to increase the surface area of the photoanode without influence on charge carrier transport in the system. Compared to conventional devices, the short circuit current density and power conversion efficiency were enhanced by 50%. And the technology can be widely used in the photoelectrochemical (PEC) field, and it can be combined with other hierarchical nanostructures.

Keywords quantum-dot-sensitized solar cell (QDSSC), hierarchical structure, TiO_2 nanowires

1 Introduction

Metal oxide nanowire arrays based on wide bandgap semiconductors, such as TiO_2 and ZnO, are widely used in photoelectrochemical (PEC) devices, such as dye-sensitized solar cell (DSSC) [1], quantum dot sensitized solar cell (QDSSC) [2], hydrogen generation [3], etc. Compared to conventional PEC devices using mesoporous photoanodes that consist in nanocrystals, the ones formed by nanowires have much longer majority carrier diffusion length along the crystal axis, because grain boundaries and traps on the electron transmission path are in lower density [4]. However, most of the PEC devices based on nanowire arrays have lower power conversion efficiency (PCE) than those based on nanoparticle layers, resulting from smaller surface area to load light absorbers [5]. To enhance the surface area of nanowire arrays, various hierarchical nanostructures which we collectively call structure engineering are applied to PEC devices [6]. One strategy is to increase the nanowire length and nanowire count per unit area, according to the calculation that surface area is proportional to them [7]. And another strategy is to generate fine branches on existing nanowires, and the dendriform nanostructures are typically synthesized by chemical etching [8] or multi-step hydrothermal methods [9]. Here, we introduce a strategy to replace conventional smooth transparent conducting substrates with microstructured ones, and this is not conflict with the former strategies. The photoanode with rough substrate covered by nanowire arrays has a much larger surface area than smooth one, and the gain factor depends on the roughness of the substrate. The two critical size parameters related to the performance of PEC devices are the distance between photoanode and cathode ($L_{\text{electrolyte}}$), and the thickness of light absorption layer, i.e. length of nanowires (L_{nanowire}). Usually, $L_{\text{electrolyte}}$ is in magnitude of $100-1000$ μm in consideration of the ion transport in electrolyte, and L_{nanowire} depends on the electrical properties of the metal oxide materials, which is $1-10$ μm for TiO_2 nanowires in rutile phase and $10-100$ μm for ZnO nanowires [10,11]. On account of chemical stability, ZnO seems not an ideal choice in practice, although electron concentration and mobility of ZnO are higher than those of TiO_2. Thus we only focus on rutile-nanowires-based QDSSC in this work.

The permissible roughness of substrate ($R_{\text{substrate}}$) is limited by $L_{\text{electrolyte}}$ and L_{nanowire}: if $R_{\text{substrate}}$ is larger than $L_{\text{electrolyte}}$, the active material around depressions of substrate has little chance to be reduced; if $R_{\text{substeate}}$ is smaller than L_{nanowire}, the enhancement of surface area is not significant enough to improve the performance of devices. Therefore, former researchers only tried to develop structure engineering in the scale under L_{nanowire}, and we turn to the scale between L_{nanowire} and $L_{\text{electrolyte}}$. And our approach can be combined with other methods for synthesis of hierarchical nanostructures to fully cover the

Received November 23, 2015; accepted December 14, 2015

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range from 1 nm to 100 μm, so that the performance of devices can be fully optimized, in theory.

The structure engineering technology of microstructured substrate can be widely used in PEC devices as mentioned above, and we applied it to QDSSCs for demonstration to verify the effect. QDSSC is deemed as an analog of DSSC, and the quantum dot sensitizers are typically CdS, CdSe, PbS, PbSe, and InP [12–16]. The light absorption coefficient of quantum dots is higher than most dyes, and their absorption spectrum can be tailored by size confinement. But the PCE of QDSSC is lower than that of DSSC with same device structure due to the charge separation and recombination processes at interfaces [17]. Although our work cannot solve the problem of photo-generated carrier transport, the efficiency of QDSSCs increased 50% by using microstructured substrate, consistent with the estimation of surface area increment.

2 Experimental

2.1 Synthesis of rutile nanowires

The commercial 3 mm thick white glass was processed into rough glass by Beijing Yaxingwanbo Glass Co. LTD. During the etching process, the glass was covered by plastic mask, and 4 mm × 4 mm patterns were exposed in etchant. The fluorine-doped tin oxide (FTO) coating process was accomplished by magnetron sputtering from Wuhan Geao Co. LTD. Before photoanode fabrication, the rough FTO glass was ultrasonic cleaned in ethanol for 15 min and flushed by deionized water. The rough FTO glass was covered by Teflon tape leaving the active area exposed. The precursor solution was prepared by 15 mL deionized water and 15 mL concentrated HCl with 0.66 mL isopropyl titanate. The FTO glass was dipped in the solution heated at 150°C for 12 h in hydrothermal synthesis reactor. The substrate was flushed by deionized water again, and annealed at 450°C for 30 min.

2.2 Quantum dots deposition

The quantum dots deposition process was finished under 10°C water bath. The substrate with rutile nanowires was dipped in the solution of 20 mM[1)] $CdCl_2$, 66 mM NH_4Cl, 140 mM thiocarbamide, and 230 mM ammonia, for 1 h, followed by water flushing. The substrate was transferred to the solution with 26 mM $CdSO_4$, 40 mM N $(CH_2COONa)_3$, and 26 mM Na_2SeSO_3. After 5 h, the substrate was immersed in the solution with 0.1 M Zn $(CH_3COO_2)_2$ and Na_2S for 1 min, and this could be repeated for 2 times. The prepared samples were annealed at 100°C for 10 min in inert ambient.

2.3 Preparation of QDSSCs

The cathode was cleaned brass sheet, and the electrolyte was the solution with 1 M Na_2S and 1 M S. The whole device was sandwiched by photoanode and cathode, and the electrolyte was injected in the gap.

2.4 Characterizations

The surface morphology of FTO glass was characterized by stylus profiler (DEKTAK XT). The morphology of TiO_2 nanowires was characterized by scanning electron microscopy (Nova nanoSEM 430, FEI company). The *J-V* measurement was obtained using an Agilent B2900 Series precision source/measure unit, and the cell was illuminated by a solar simulator (Solar IV-150A, Zolix) under AM1.5 irradiation (100 mW/cm^2).

3 Results and discussion

Figures 1(a)–1(d) depict the schematic diagrams of the four classes of QDSSCs: the one with TiO_2 nanowires on smooth FTO glass, with TiO_2 nanowires on rough FTO glass, with TiO_2 nanoparticles on smooth FTO glass, and with TiO_2 nanoparticles on rough FTO glass, respectively. Rutile nanowire array was synthesized on the substrate directly by the hydrolysis of Ti^{4+} in acid condition by using hydrothermal method [18]. And the TiO_2 nanowire in rutile phase was several micrometers in length and hundreds nanometers in diameter. Conventional QDSSC with mesoporous TiO_2 nanoparticle layer was used as control group. Commercial TiO_2 nanoparticles in anatase phase were deposited on substrate by doctor blading

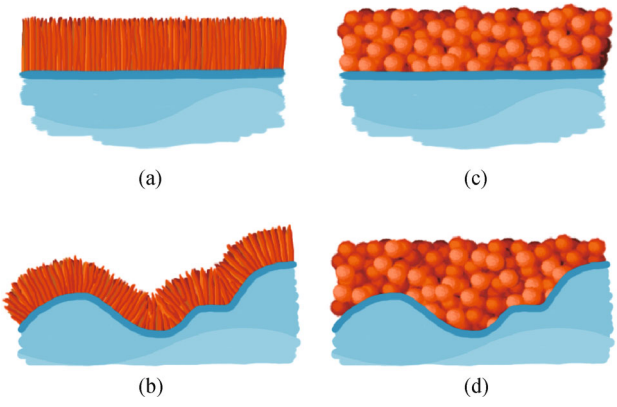


Fig. 1 Schematic diagrams of QDSSC photoanodes with rutile nanowires on smooth FTO glass (a), rutile nanowires on rough FTO glass (b), anatase nanoparticles on smooth FTO glass (c), and anatase nanoparticle on rough FTO glass (d). The size of nanoparticles is exaggerated for easy reading

1) 1 mM = 1 mmoL/L

process, and the diameter of nanoparticle was 20 nm. Either of them could form uniform films on common FTO glass, respectively. On the other hand, we processed glass with chemical etching followed by magnetron sputtering of FTO to fabricate microstructured substrate (more details are shown in Methods Section 2.1). TiO_2 nanowires or nanoparticles (control group) were deposited on it to prepare QDSSCs. Due to the epitaxial growth, TiO_2 nanowires covered the surface of substrate uniformly. In details, each nanowire stands vertically to its root facet, and the density of nanowires remains unchanged. However, in case of TiO_2 nanoparticles, a flat film was formed on the substrate, and the thickness was not uniform because of the morphology of substrate.

The morphology of rough FTO glass was characterized by profiler study as shown in Fig. 2(a). The scan area is 499.2 μm × 632.8 μm (3.159×10^5 μm^2). The roughness is 8.989 μm (standard deviation of height), and the maximum height difference is 36.12 μm. Compared with the projected area, namely scan area, the actual surface area proved to be 4.773×10^5 μm^2 – a 51.09% increase. Figure 2(b) shows the optical microscopic image of microstructured FTO glass. The surface was composed by blocks of pyramids ranging from 10 to 100 μm, corresponding to the profiler results. Transmission spectra demonstrate a ~70% transmission for rough FTO glass (Fig. 2(c)).

Figure 3 shows the scanning electron microscopic (SEM) images of the micro-scale hierarchical photoanodes. After TiO_2 deposition and quantum dot sensitizing, the surface of rough FTO glass was covered by TiO_2 nanowire arrays uniformly (Fig. 3(a)). Every TiO_2 nanowire is coated by a layer of CdSe quantum dots (Fig. 3(b)). TiO_2 nanowires grow epitaxially no matter the surface is rough or smooth as shown in cross-sectional SEM images (Figs. 3(c)–3(d)). And the morphologies of nanowires on rough FTO glass and smooth FTO glass are exactly the same (length: ~ 5.0 μm, diameter: ~ 200 nm, density: ~ 15/μm^2). So the surface area of the TiO_2 nanowire arrays (A_{arr}) was in direct proportion to the surface area of the substrate (A_{sub}):

$$A_{arr} = A_{NW} \times D_{NW} \times A_{sub}.$$

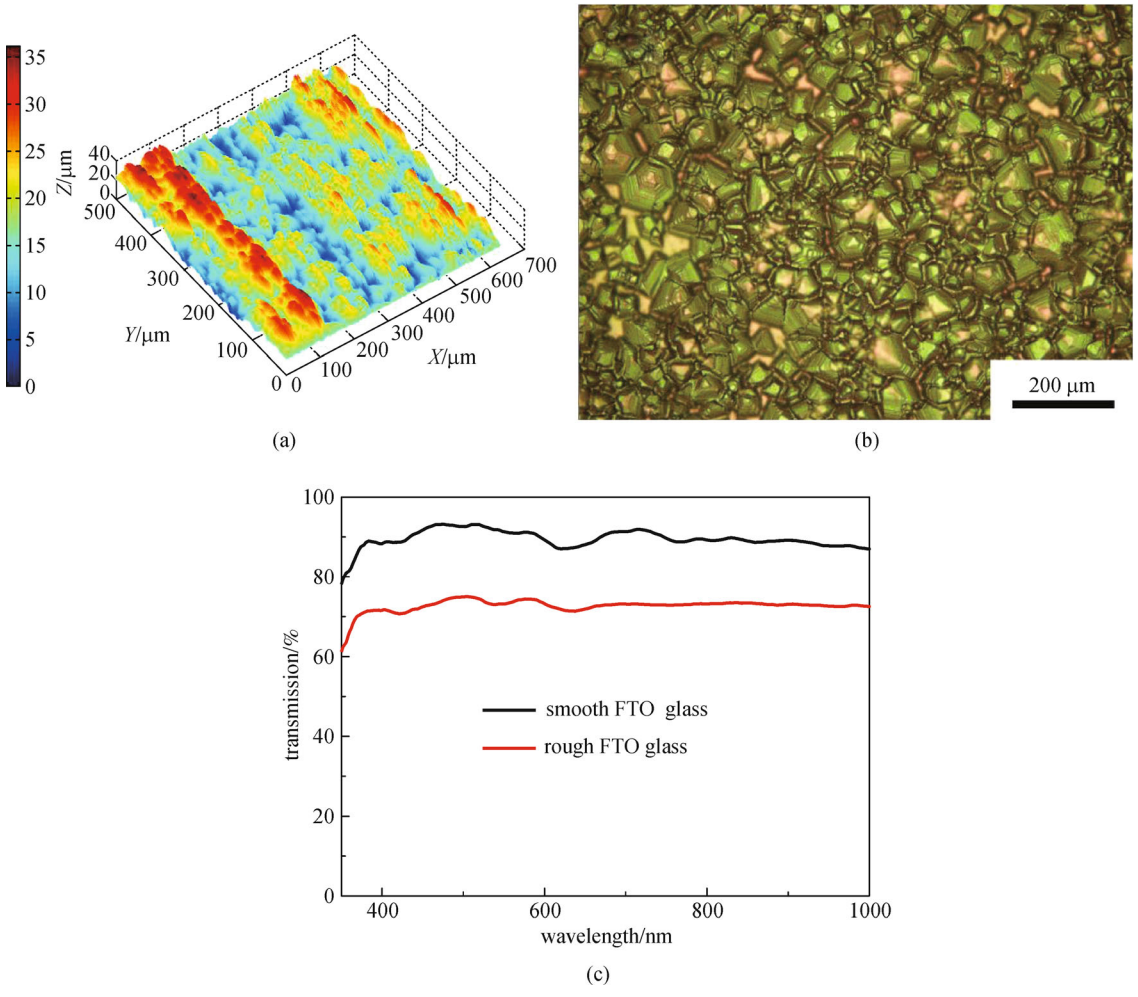


Fig. 2 (a) Profile image of rough FTO glass surface; (b) optical microscopic image of rough FTO glass surface; (c) transmission spectra of smooth FTO glass and rough FTO glass

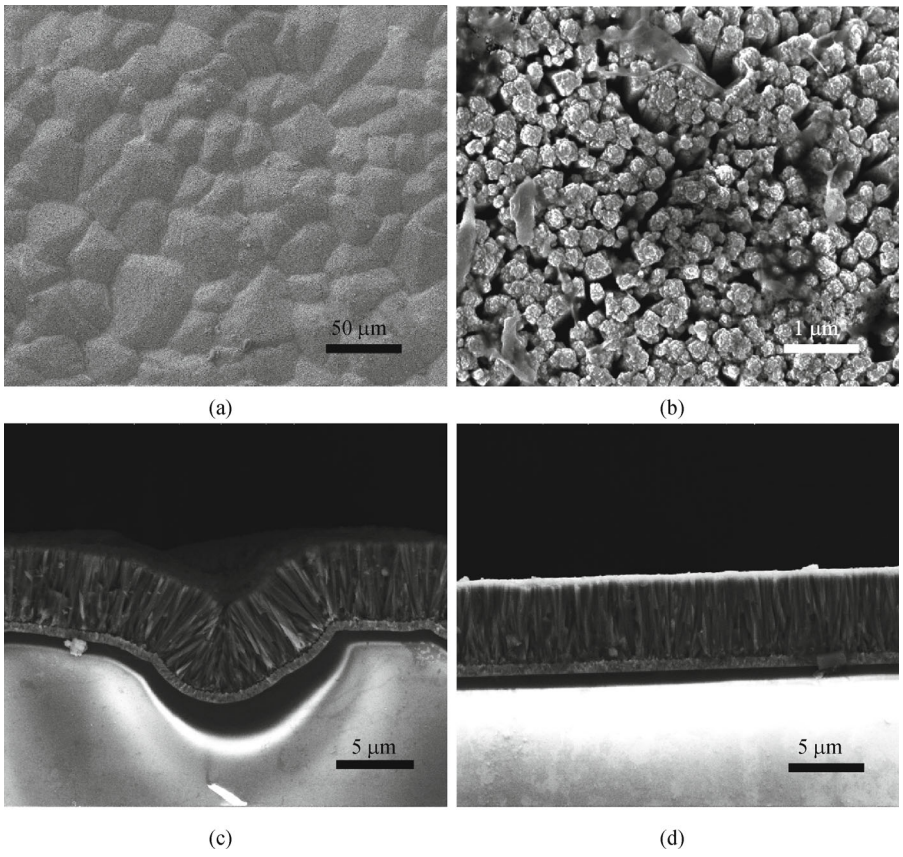


Fig. 3 (a) and (b) SEM images of QDSSC photoanodes with rutile nanowires on rough FTO glass; (c) and (d) cross-section SEM images of QDSSC photoanodes with rutile nanowires on rough FTO glass and smooth FTO glass, respectively

Here, A_{NW} stands for the surface area of one nanowire, and D_{NW} stands for the counting density of TiO_2 nanowires. The surface area of rough FTO glass was about 1.5 times that of smooth FTO glass, and so does the quantum dot load capacity, light absorption, short circuit current density (J_{sc}), and PCE, theoretically. Figure 4(a) shows the performance of a pair of QDSSCs fabricated simultaneously based on different substrate. J_{sc} increases from 4.411 to 6.750 mA/cm^2, rising 53.03%. PCE increases from 0.775% to 1.162%, rising 49.94%. The statistics of 12 pairs of QDSSCs are more convincing. The average J_{sc} increases from 3.922 to 5.283 mA/cm^2, rising 34.70%. The average PCE increases from 0.723% to 0.989%, rising 36.79% (Fig. 4(b)). The average J_{sc} and PCE both increase by about 35%, which demonstrates the enhanced surface area. Figure 4(b) shows the scatter plot of PCE vs J_{sc}, they are linearly dependent according to the equation, where *FF* is fill factor:

$$\mathrm{PCE} = FF \times V_{oc} \times J_{sc}.$$

After simple regression of PCE and J_{sc}, the slope represented the average coefficient $FF \times V_{oc}$, which decreases from 0.24 to 0.16 V. The rough FTO glass was also applied to conventional QDSSCs based on TiO_2 nanoparticles. But the performance of the devices was not improved after replacing the photoanode substrate. Figure 5(a) shows the profile curve of the rough FTO glass coated with TiO_2 nanoparticle layers in different thickness. The black line represents the cross sectional line of the microstructured FTO glass surface. The left part is smooth because it was protected during etching glass process. The right part is 12.2 μm lower than the left in average because of chemical etching. The deposition of TiO_2 nanoparticles was achieved by doctor blading, so the TiO_2 layer was flat and the microstructure of substrate was fully covered. Based on the smooth substrate, the thickness of TiO_2 layer can be controlled to about 10 and 20 μm. In the case of microstructured substrate, the depth of etching area (~10 μm) should be considered when estimating the TiO_2 thickness. The *J-V* measurements of various samples are shown in Fig. 5(b). The performance of QDSSCs depends on the thickness of TiO_2 layers, and the optimized parameter was 21.8 μm for the device with rough FTO glass, which is comparable to the one with smooth FTO glass and 20.3 μm thickness. It indicates that the performance of TiO_2-nanoparticle-based QDSSCs only relies to the average thickness of TiO_2 layer, with no

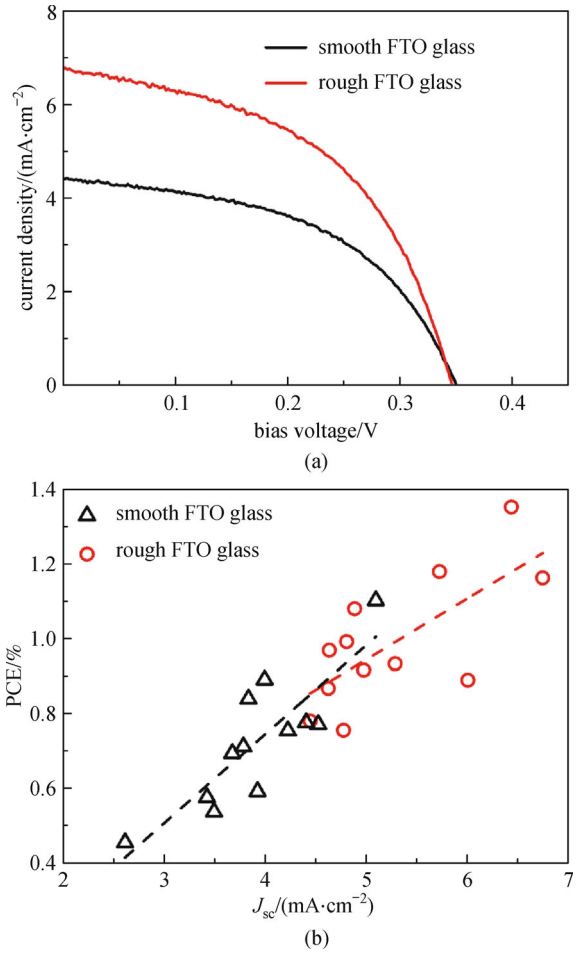


Fig. 4 (a) *J-V* curves of the QDSSCs based on smooth FTO glass and rough FTO glass; (b) PCE as a function of J_{sc} for smooth FTO glass and rough FTO glass of 24 devices

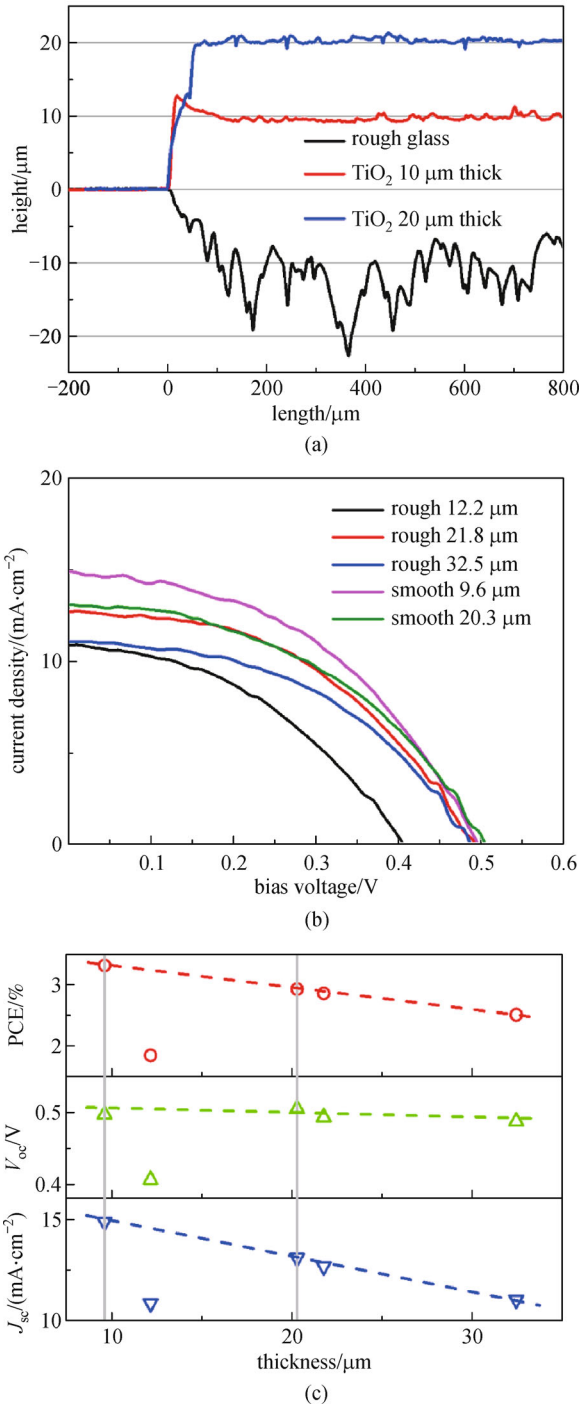


Fig. 5 Profile images (a) and *J-V* curves (b) of QDSSCs with various average photoanode thickness. The photoanode is based on TiO_2 nanoparticles. (c) Photovoltaic properties (PCE, V_{oc}, and J_{sc}) of the QDSSCs as a function of average photoanode thickness. The photoanode is based on TiO_2 nanoparticles

relation to the morphology of substrate, under normal conditions. However, if the TiO_2 coverage is too thin with average thickness of 12.2 μm, V_{oc} of the device would be 0.1 V lower, demonstrating the short circuit risk. The relation between PCE (V_{oc}, J_{sc}) and TiO_2 thickness is plotted in Fig. 5(c), and the outliers represent the device with thin active layer on rough substrate.

4 Conclusions

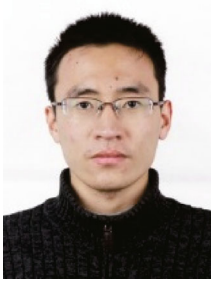
The device design of QDSSCs based on microstructured substrate and rutile nanowires is proved to be effective, and the PCE and J_{sc} of devices can be increased by 50% compared to conventional ones with smooth substrate. The charge transport space in the device is fully utilized, in scale of 10 to 100 μm, which has never been noticed before. The microstructure would not impact the charge collection efficiency in the device, but increase the surface area of photoanode significantly. Although the technology does not work in the case of TiO_2 nanoparticles, the microstructure design can be combined with the reported hierarchical nanostructures to further improve the performance of QDSSCs. Furthermore, we will apply the hierarchical design to other PEC devices, such as

photocatalysis or water splitting. It leads a way to low-cost high efficient light energy utilizations.

Acknowledgements This work was supported by the National Key Basic Research Program of China (973 Program) (Nos. 2013CB932602 and 2011CB707601), the National Natural Science Foundation of China (Grant Nos. 51272007 and 11234001). Q.Z acknowledges Beijing Nova Program (No. XX2013003) and the Program for New Century Excellent Talents in University of China.

References

1. Grätzel M. Dye-sensitized solar cells. Journal of Photochemistry and Photobiology C, Photochemistry Reviews, 2003, 4(2): 145–153
2. Rühle S, Shalom M, Zaban A. Quantum-dot-sensitized solar cells. ChemPhysChem, 2010, 11(11): 2290–2304
3. Walter M G, Warren E L, McKone J R, Boettcher S W, Mi Q, Santori E A, Lewis N S. Solar water splitting cells. Chemical Reviews, 2010, 110(11): 6446–6473
4. Wu J, Chen G, Yang H, Ku C, Lai J. Effects of dye adsorption on the electron transport properties in ZnO nanowire dye-sensitized solar cells. Applied Physics Letters, 2007, 90(21): 213109
5. Baxter J, Aydil E. Nanowire-based dye-sensitized solar cells. Applied Physics Letters, 2005, 86(5): 053114
6. Bierman M J, Jin S. Potential applications of hierarchical branching nanowires in solar energy conversion. Energy & Environmental Science, 2009, 2(10): 1050–1059
7. Xu C, Wu J, Desai U V, Gao D. High-efficiency solid-state dye-sensitized solar cells based on TiO_2-coated ZnO nanowire arrays. Nano Letters, 2012, 12(5): 2420–2424
8. Wu X J, Zhu F, Mu C, Liang Y, Xu L, Chen Q, Chen R, Xu D. Electrochemical synthesis and applications of oriented and hierarchically quansi-1D semiconducting nanostructures. Coordination Chemistry Reviews, 2010, 254(9-10): 1135–1150
9. Ko S H, Lee D, Kang H W, Nam K H, Yeo J Y, Hong S J, Grigoropoulos C P, Sung H J. Nanoforest of hydrothermally grown hierarchical ZnO nanowires for a high efficiency dye-sensitized solar cell. Nano Letters, 2011, 11(2): 666–671
10. Sauvage F, Di Fonzo F, Li Bassi A, Casari C S, Russo V, Divitini G, Ducati C, Bottani C E, Comte P, Grätzel M. Hierarchical TiO_2 photoanode for dye-sensitized solar cells. Nano Letters, 2010, 10(7): 2562–2567
11. Law M, Greene L E, Radenovic A, Kuykendall T, Liphardt J, Yang P. ZnO-Al_2O_3 and ZnO-TiO_2 core-shell nanowire dye-sensitized solar cells. Journal of Physical Chemistry B, 2006, 110(45): 22652–22663
12. Lee Y, Chang C. Efficient polysulfide electrolyte for CdS quantum dot-sensitized solar cells. Journal of Power Sources, 2008, 185(1): 584–588
13. Yu X Y, Liao J Y, Qiu K Q, Kuang D B, Su C Y. Dynamic study of highly efficient CdS/CdSe quantum dot-sensitized solar cells fabricated by electrodeposition. ACS Nano, 2011, 5(12): 9494–9500
14. Zhao N, Osedach T P, Chang L Y, Geyer S M, Wanger D, Binda M T, Arango A C, Bawendi M G, Bulovic V. Colloidal PbS quantum dot solar cells with high fill factor. ACS Nano, 2010, 4(7): 3743–3752
15. Zhang J, Gao J, Church C P, Miller E M, Luther J M, Klimov V I, Beard M C. PbSe quantum dot solar cells with more than 6% efficiency fabricated in ambient atmosphere. Nano Letters, 2014, 14 (10): 6010–6015
16. Zaban A, Micic O I, Gregg B A, Nozik A J. Photosensitization of nanoporous TiO_2 electrodes with InP quantum dots. Langmuir, 1998, 14(12): 3153–3156
17. Law M, Greene L E, Johnson J C, Saykally R, Yang P. Nanowire dye-sensitized solar cells. Nature Materials, 2005, 4(6): 455–459
18. Liu B, Aydil E S. Growth of oriented single-crystalline rutile TiO_2 nanorods on transparent conducting substrates for dye-sensitized solar cells. Journal of American Chemical Society, 2009, 131(11): 3985–3990



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Qing Zhao got her Ph.D. degree in physics from School of Physics, Peking University. Then she spent three years in University of Washington as a postdoc. She joined School of Physics, Peking University in 2009. Her research area is energy materials and devices in low dimensional, including perovskite solar cells and supercapacitors. The present work proposed a new architecture design for nanowire-based quantum-dot-sensitized solar cells to improve the photovoltaic performance. Microstructured rough substrate was used to increase the surface area of the photoanode without influence on charge carrier transport in the system.