Int. J. Electrochem. Sci., 6 **(2011)** 1871 - 1879

International Journal of
ELECTROCHEMICAL
SCIENCE
www.electrochemsci.org

Solvothermal Growth of Well-Aligned TiO_2 Nanowire Arrays for Dye-Sensitized Solar Cell: Dependence of Morphology and Vertical Orientation Upon Substrate Pretreatment

Zhen Wei, Yu Yao, Tao Huang, Aishui Yu[*]

Department of Chemistry, Shanghai Key Laboratory of Molecular Catalysis and Innovative Materials,
Institute of New Energy, Fudan University, Shanghai 200438, China
[*]E-mail: asyu@fudan.edu.cn

Received: 19 March 2011 / *Accepted:* 15 may 2011 / *Published:* 1 June 2011

Self-assembled and well-aligned rutile TiO_2 nanowire arrays (TNAs) are synthesized on pretreated transparent conducting substrate by solvothermal route. X-ray diffraction (XRD) and field-emission scanning electron microscopy (FE-SEM) are used to characterize the as-prepared TNAs. The results show that the TiO_2 array surface morphology and vertical orientation are highly dependent upon substrate pretreatment before solvothermal synthesis. For a typical pretreated substrate of being immersed in 0.05 M $TiCl_4$ aqueous solution at 25℃for 12 h, the as-prepared TNAs are comprised of nanowires with excellent vertical orientation perpendicular to the substrate, along the (002) crystal plane direction. The corresponding dye-sensitized solar cell (DSSC) assembled with the as prepared TNA as photoanode achieves an overall photoelectric conversion efficiency of 1.81%.

Keywords: Titania nanowire array, solvothermal crystal growth, substrate pretreatment, dye-sensitized solar cells, photoanode

1. INTRODUCTION

DSSCs have been received considerable attention lately because they are cost-effective and environmentally friendly, with overall light-to-electricity conversion efficiency of over 10.6% [1, 2]. The electron-collecting layer in a DSSC is typically a 10-15 μm thick nanocrystalline film comprised of a three dimensional network of interconnected 15–20 nm sized nanoparticles [3]. However electron transport is a limiting factor in the performance of these nanoporous/nanocrystalline electrodes, hindering progress in achieving higher efficiency. Compared with TiO_2 nanoparticles, TiO_2 nanorod/wire/tube arrays constrain the movement of electrons and photons in one direction, which increases the electron transport rate, and thus improves the performance of the device. Thereby, TiO_2-based materials with one-dimensional structures have been intensively investigated [4-7].

Recently, various synthesis techniques have been used to form oriented TiO_2 nanorod/wire/tube arrays including template-assisted method, electrochemical anodic oxidation method, chemical vapor deposition (CVD) and hydrothermal method [8-11]. Among these methods, hydrothermal/solvothermal synthesis of TNAs is a promising approach due to its simple process, fast reaction velocity and low cost. In solvothermal crystal growth, nucleation sites have huge impact on the morphology and orientation of the TNAs, so it is of great importance to investigate the relationship between them.

This report presents various modifications of FTO glass substrate by coating titania particles as crystal seeds. It reveals how these seeds affect the surface morphology and vertical orientation of as-prepared TNAs, and also photoelectric conversion efficiency of corresponding solar cells. The modification methods include spin-coating of nanoparticles, hydrolysis of titanium tetrachloride in organic solution and in aqueous solution. Our purpose is to evaluate the vertical orientation and photoelectric performances of the TNAs at various modification conditions.

2. EXPERIMENTAL PROCEDURE

2.1. Preparation of TiO_2 nanowire arrays

Fluorine-doped tin dioxide (FTO) (14 $\Omega\cdot cm^{-2}$) conducting glass and 25 nm titania particles were purchased from Wuhan Geao Instruments Science & Technology Co., Ltd. The 6 nm titania particles were purchased from Tomorrow Nano Science and Technology Co., Ltd. and the other chemicals were purchased from Shanghai Chemical Co., Ltd. All chemicals were used as received without any further purification.

In a typical synthesis, FTO conducting glass was initially cleaned by being immersed in isopropanol saturated with potassium hydroxide for 24 h, and subsequently cleaned by ultrasonication in ethanol and deionised water for 30 min, respectively.

Before the solvothermal experiment, five methods of substrate modification were processed as follows: (1) unpretreated, (2) spin-coated by 6 nm sized particles, (3) spin-coated by 25 nm sized particles, (4) pretreated by a drop of 0.05 M $TiCl_4$ isopropanol solution, (5) immersed in 0.05 M $TiCl_4$ aqueous solution at 25 ℃ for 12 h. The spin-coating of modifications (2) and (3) are operated at 2000 rpm for 40 s with a suspension concentration of 0.05 M. Then the modified substrates were heated in air at 500 ℃ for 30 min [5] for better adhesion.

For solvothermal synthesis, modified FTO glass substrate was placed into a sealed Teflon autoclave (50 mL) and subsequently 10 mL of toluene, 1 mL of hydrochloric acid (37 wt %), 1 mL of tetrabutyl titanate and 1 mL of titanium tetrachloride (1 M in toluene) were added into the autoclave. The reaction temperature and duration are fixed at 200 ℃ and 2 h, respectively. After the solvothermal experiment, the resulting sample was rinsed with ethanol, and then dried in air.

Prior to dye adsorption, the as-prepared sample was placed in 0.05 M $TiCl_4$ aqueous solution at 70 ℃ for 0.5 h. Then the $TiCl_4$-treated sample was annealed in air at 450 °C for 30 min inside a furnace. The sensitizer used here was cis-bis(isothiocyanato)bis(2,2'-bipyrridyl-4-4'-dicarboxylato)-ruthenium(II) bis-tetrabutylammonium dye (N-719 as received from Solaronix). The dye was adsorbed to titania film by soaking for 24 h in 0.3 mM ethanolic solution of N719.

2.2. Measurement of dye loading in the TiO_2 photoelectrodes

The N719 dye-sensitized TiO_2 photoelectrodes were dipped into 5mL of 0.01M aqueous ethanolic (1:1) alkaline solution of NaOH for 1h, for complete desorption of the N719 dye. The alkali solution containing the fully desorbed dye was carefully measured by UV–visible spectroscopy at 515 nm. The adsorbed dye was calculated according to the Beer–Lambert law.

$$A = \varepsilon l c \qquad (1)$$

where A is absorbance of the UV–visible spectra at a wavelength of 515 nm, the molar extinction coefficient of the dye at 515 nm is $\varepsilon = 14100\ M^{-1}\ cm^{-1}$, l is the path length of the light beam and c is the concentration of the dye [12].

2.3. Fabrication of DSSCs

The dye-adsorbed TiO_2 nanowire film on FTO glass was used as the photoanode of dye-sensitized solar cell. A platinum-coated FTO substrate spaced from the TiO_2 nanorod photoanode with 25 µm thick Teflon strips (Pike Technologies) was used as the counter electrode. A thin layer of electrolyte was introduced into the interelectrode space. The electrolyte contains 0.1 M LiI, 0.05 M I_2, 0.6 M 1,2-dimethyl-3-n-propylimidazolium iodide (Tomiyama Pure Chemical Industries Ltd.) and 0.5 M 4-tertbutylpyridine (TBP) in dehydrated acetonitrile.

2.4. Characterization

The crystal structure of the sample was identified by X-ray diffraction (XRD) analysis on a Bruker D8 Advance X-ray diffractometer using Cu Kα radiation. The morphology was characterized using field emission scanning electron microscopy (FE-SEM) with a Hitachi S-4800 microscope. The UV–visible spectrum was measured by UV-3150 Shimadz. The current density-voltage curve was measured with a calibrated solar simulator, using air mass 1.5 global (AM 1.5 G) illumination with an intensity of 100 mW cm^{-2}.

3. RESULTS AND DISCUSSION

Fig. 1(a) shows the XRD peaks of FTO substrate and Fig. 1(b, c, d, e, f) are XRD patterns of TiO_2 nanowire arrays fabricated on diverse modified substrates. Diffraction peaks marked as "▲" in

Fig. 1(a) are ascribed to FTO glass, which also appear in Fig. 1(b-f). All the other peaks in Fig. 1(b-f) can be indexed as tetragonal rutile TiO_2 (JCPDS No. 21-1276). For FTO glass spin-coated by 6 nm and 25 nm particles of Fig. 1(c, d), diffraction peaks of crystal planes (110), (101), (111), (211), (002), (112) occur, and (101) face shows the strongest intensity, the same with TiO_2 powder. The results illustrate that all these six planes of crystal seeds expose to the solution, so TNA can grow along any plane. For the other three curves of Fig. 1(b, e, f), crystal planes (110), (111) disappear, which indicates that no TiO_2 nanowires grow along these two directions. Meanwhile, (002) plane owns the strongest intensity. Typically, TNA grown on FTO glass immersed in 0.05 M $TiCl_4$ aqueous solution shown in Fig. 1(f) presents an extremely strong (002) peak, which illustrates the TNA is well crystallized and has an excellent orientation along (002) face.

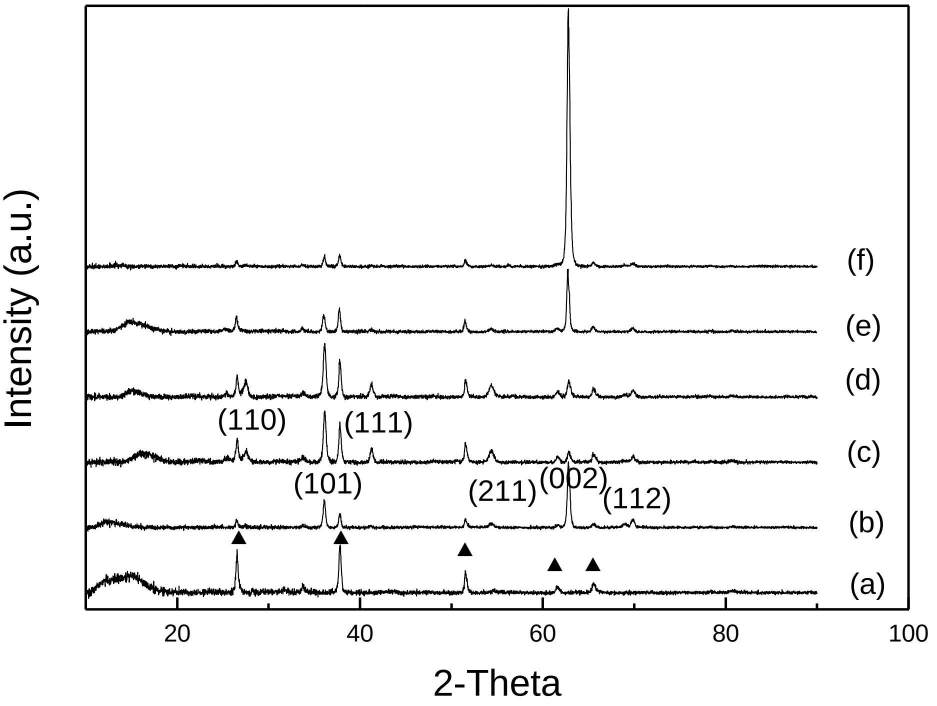

Figure 1. (a) XRD pattern of FTO glass; **Fig. 1**(b-f) XRD patterns of TiO_2 nanowire arrays fabricated at various modifications: (b) unpretreated FTO glass, (c) spin-coated by 6 nm particles, (d) spin-coated by 25 nm particles, (e) 0.05M $TiCl_4$ isopropanol solution, (f) 0.05M $TiCl_4$ aqueous solution

Fig. 2 reveals the FE-SEM images of TiO_2 nanowire arrays fabricated on various modified substrates. All the essential structure of these samples is a single nanowire, and several nanowires bundle together to form a secondary structure, that's a nanowire bundle. TNA can grow directly on unpretreated FTO glass, as shown in Fig. 2(b). That's because of small lattice mismatch between tetragonal FTO (a=b=0.4687 nm [13]) and rutile TiO_2 (a=b=0.4594 [14]), which promotes the epitaxial nucleation and growth of rutile TiO_2. But TNA grows not perpendicular to the substrate, i.e. not in very good vertical orientation.

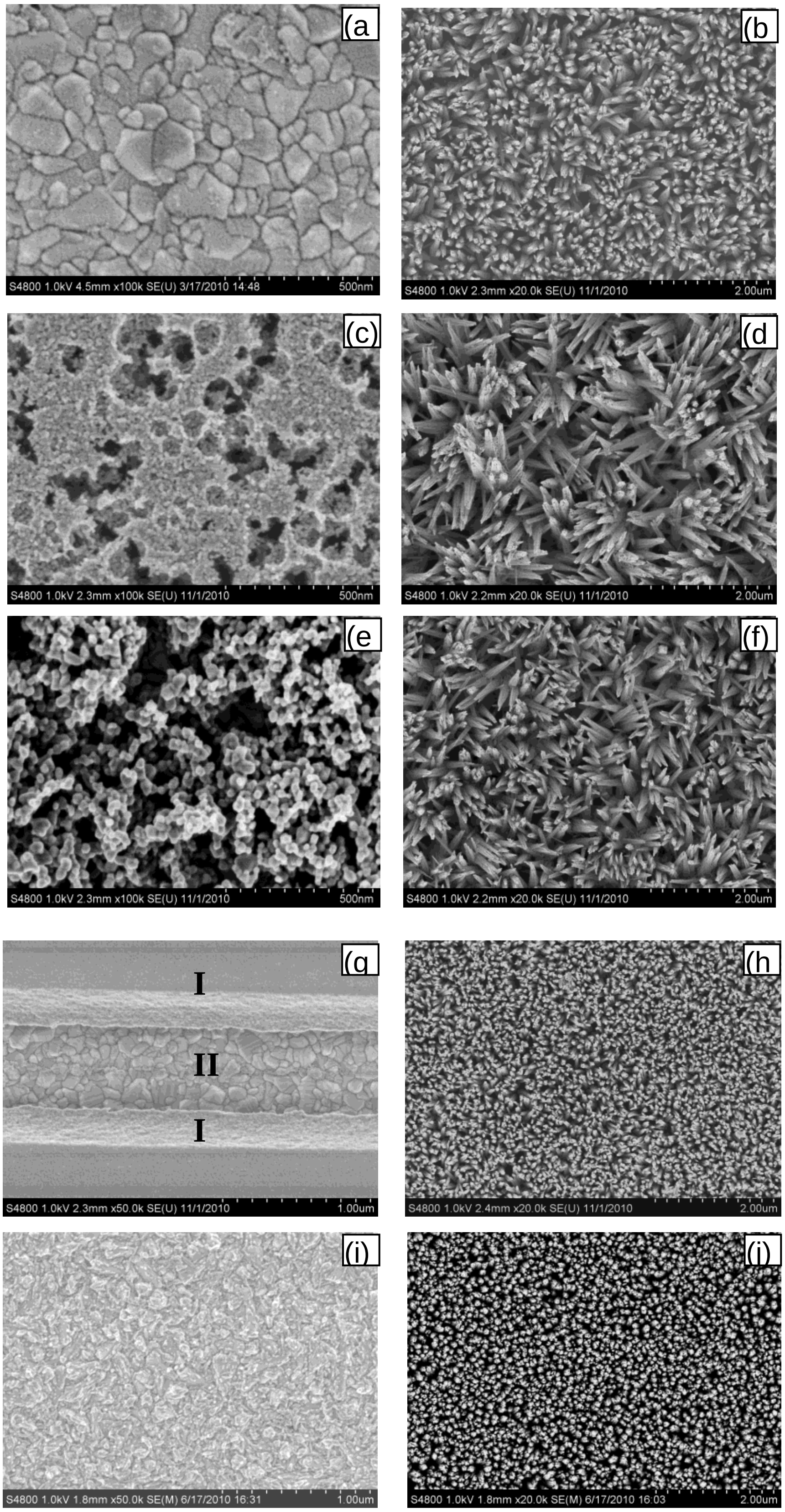

Figure 2. FE-SEM images of various modified substrates and TiO_2 nanowire arrays fabricated on them: (a, b) unpretreated FTO glass and corresponding TNA, (c, d) spin-coated by 6 nm particles and corresponding TNA, (e, f) spin-coated by 25 nm particles and corresponding TNA, (g, h) 0.05M $TiCl_4$ isopropanol solution and corresponding TNA, (i, j) 0.05M TiCl4 aqueous solution and corresponding TNA

Adhesion strength at the FTO-TiO_2 interface is not as strong as that at the TiO_2-TiO_2 interface, so TNA on unpretreated FTO glass is confronted with a peeling problem, while TNA on modified substrate doesn't encounter this problem.

As to the TNAs grown on substrates modified by 6 nm and 25 nm nanoparticles, the vertical orientations are even worse, as shown in Fig. 2(d, f). XRD patterns of these two samples illustrate that six crystal planes of nucleation sites expose to the solution, and TNA can grow along any plane, which may result in the poor vertical orientation. FTO glass modified by a drop of 0.05 M $TiCl_4$ isopropanol solution is covered by a compact film, as shown part I in Fig. 2(g). By cutting through the film, FTO glass beneath the compact film can be seen, as shown part II in Fig. 2(g). The compact film leads to a good vertical orientation of TiO_2 growth in Fig. 2(h). For the TNAs grown on substrates modified by being immersed in 0.05 M $TiCl_4$ aqueous solution, as shown in Fig. 2(j), it shows excellent vertical orientation. In the image only the head of nanowire can be seen, but not the lateral side of nanowire, which indicates the TNA grows totally perpendicular to the substrate. All the samples have the same single nanowire width of 20-30 nm, indicating it's an inherent property for rutile TiO_2—nanowire of this size owing the best stability.

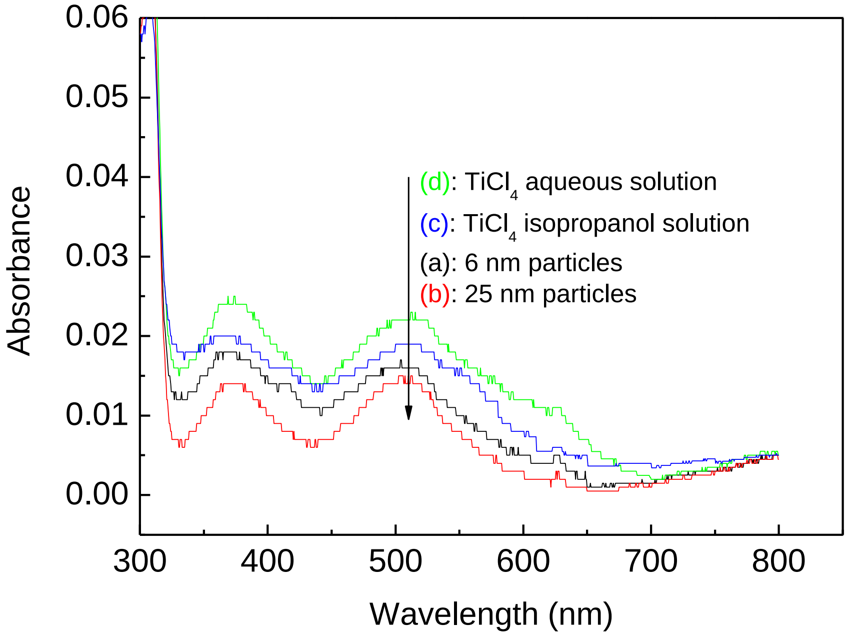

Figure 3. UV-vis adsorption spectra of dye N719 adsorbed on TNAs fabricated on various modified substrates: (a) spin-coated by 6 nm particles, (b) spin-coated by 25 nm particles, (c) 0.05M $TiCl_4$ isopropanol solution, (d) 0.05M $TiCl_4$ aqueous solution

The dye N719 adsorbed on various TNA photoanodes were measured by UV-vis adsorption spectrometry, as shown in Fig. 3. All the four adsorption peaks appear at around 515 nm, which are typical characteristics of dye N719. Dye adsorption peaks for TNAs on the substrates pretreated by 6 nm and 25 nm particles are very close, and also the lowest in these four samples. For the sample corresponding to 0.05M $TiCl_4$ isopropanol solution, the intensity of adsorption increases. As to the sample prepared on substrate pretreated by 0.05M $TiCl_4$ aqueous solution, it owns the highest adsorption peak, illustrating the most dye on it.

Table 1. Mass of dye and mass of dye per area for TNAs fabricated on various modified substrates

	Mass of dye (g)	Mass of dye per area (g cm^{-2})
6 nm particles	6.7×10^{-6}	2.7×10^{-5}
25 nm particles	5.9×10^{-6}	2.4×10^{-5}
0.05M $TiCl_4$ isopropanol solution	8.0×10^{-6}	3.2×10^{-5}
0.05M TiCl4 aqueous solution	9.7×10^{-6}	3.9×10^{-5}

Table 1 reveals the amount of dye adsorped on the surface of TiO_2 photoelectrodes, the cell cutting area was fixed at 0.25 cm^2. TNA fabricated on FTO glass pretreated by 0.05M $TiCl_4$ aqueous solution contains 9.7×10^{-6} g dye molecules, i.e. 3.9×10^{-5} g cm^{-2} on TiO_2 photoelectrodes, much higher than the other three samples. This is probably due to superiority of crystal vertical orientation. From Fig. 2, it can be concluded that the four samples have almost the same nanowire width, nanowire bundle width and nanowire length, so For TiO_2 grown in poor vertical orientation, which can be seen in Fig. 2(d, f), the neighboring nanowire will intersect with each other, hindering dye molecule to diffuse to the bottom of the TNA, thus resulting in poor dye loading. Regarding TNA with excellent vertical orientation, as shown in Fig. 2(j), nanowire grows perpendicular to the substrate, it is believable the neighboring nanowires are parallel and will not intersect with each other, so dye molecule can infiltrate and adsorb to the bottom of the TNA, and ultimately a significantly higher dye adsorption spectra is achieved.

Fig. 4 shows the typical current density versus voltage curves of the DSSCs assembled with TiO_2 nanowire arrays fabricated on diverse modified substrates. TNA grown on unpretreated FTO glass tends to peel off from the substrate so it's not workable for solar cell use. The short-circuit current density (J_{sc}) of the cells based on substrates pretreated by 6 nm and 25 nm particles are relatively low, 2.30 and 2.03 mA cm^{-2}. The value increases to 3.16 mA cm^{-2} for substrates pretreated by a drop of 0.05 M $TiCl_4$ isopropanol solution. As to the cell based on substrates immersed in 0.05 M $TiCl_4$ aqueous solution, J_{sc} increases to as high as 3.75 mA cm^{-2}. This enormous increment is probably due to improvement of dye adsorption. Correspondingly, the open circuit voltage (V_{oc}) increases from 0.738 V、0.728 V to 0.761 V to 0.767 V. Higher V_{oc} is obtained at larger J_{sc}. Fill factor (FF) of these four samples are determined by the following equations:

$$FF = V_mJ_m/V_{oc}J_{sc} \qquad (2)$$

where V_m and J_m are the voltage and current density at maximum power output. The calculation using the J-V curves yield FF at 0.57, 0.57, 0.60 and 0.63, respectively, the cell based on substrates immersed in 0.05 M $TiCl_4$ aqueous solution also shows the highest value. The overall photoelectric conversion efficiency of the four corresponding cells are 0.96%, 0.84%, 1.45% and 1.81%. Solar cell based on substrates immersed in 0.05 M $TiCl_4$ aqueous solution exhibits the best conversion efficiency due to the excellent vertical orientation.

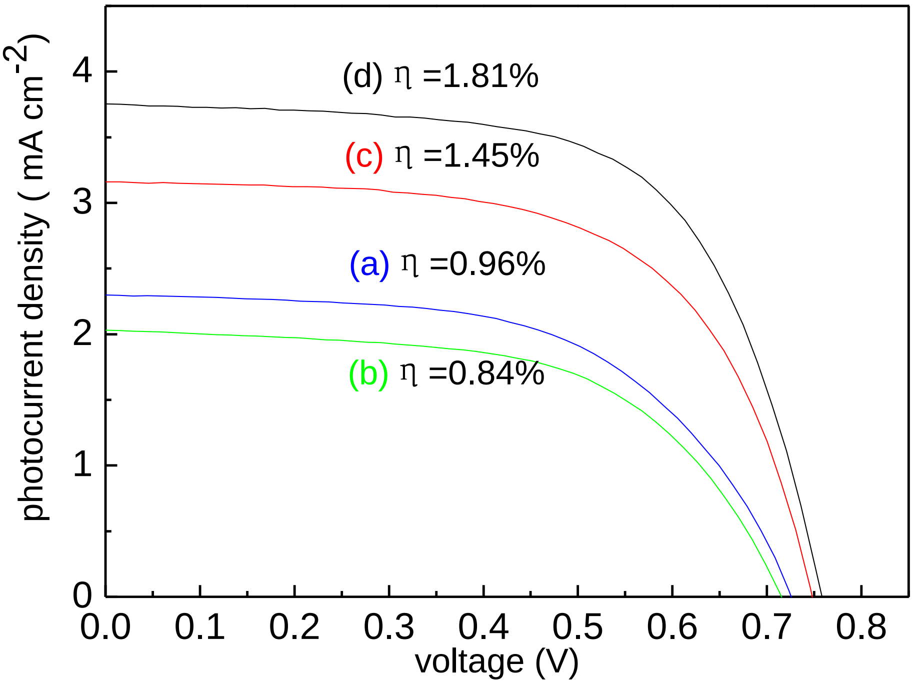

Figure 4. Current density-voltage curves of DSSCs assembled with TiO_2 nanowire arrays fabricated on various modified substrates: (a) spin-coated by 6 nm particles, (b) spin-coated by 25 nm particles, (c) 0.05M $TiCl_4$ isopropanol solution, (d) 0.05M $TiCl_4$ aqueous solution

4. CONCLUSIONS

TiO_2 nanowire arrays were synthesized directly on the transparent conducting substrate by solvothermal procedure without any template. The morphology and vertical orientation of the as-prepared TNAs have been detailedly studied upon various substrate modifications. The essential structure of the synthesized TNAs is single nanowires, and several nanowires bundle together to form a larger secondary structure, namely a nanowire bundle. TNA grown on unpretreated FTO glass tends to peel off from the substrate so it's not workable for solar cell use. The peeling problem can be resolved by modification of a TiO_2 nanoparticle layer. TNAs on substrate modified by 6 nm and 25 nm particles suffer from a bad vertical orientation, and corresponding solar cell exhibits relatively low conversion efficiency. By using the substrate pretreated by a drop of 0.05 M $TiCl_4$ isopropanol solution, the crystal vertical orientation and conversion efficiency improves significantly. As to the substrate modified by being immersed in 0.05 M $TiCl_4$ aqueous solution, the as-prepared TNA owns excellent vertical orientation and thus shows a photoelectric conversion efficiency as high as 1.81%.

Our study has therefore opened the great possibility for rutile TiO_2 nanowire arrays with excellent crystal vertical orientation to apply in many fields including dye sensitized solar cell [6], photocatalysis [15], gas sensors [16] and hydrogen generation by water photoelectrolysis [17].

ACKNOWLEDGEMENT
This work is financially supported by the National High Technology Research and Development Program (863 program, No. 2009AA033701) and Science & Technology Commission of Shanghai Municipality (08DZ2270500), China.

References

1. B. O’Regan and M. Grätzel, *Nature,* 353 (1991) 737.
2. M. Grätzel, *Nature*, 414 (2001) 338.
3. M. Gratzel, *J. Photochem. Photobiol*. A, 168 (2004) 235.
4. G. K. Mor, K. Shankar, M. Paulose, O. K. Varghese and C. A. Grimes, *Nano Lett*., 6 (2006) 215.
5. X. Feng, K. Shankar, O. K. Varghese, M. Paulose, T. J. Latempa and C. A. Grimes, *Nano Lett*., 8 (2008) 3781.
6. B. Liu and E.S. Aydil, *J. Am. Chem. Soc*., 131 (2009) 3985.
7. A.I. Hochbaum and P. Yang, *Chem. Rev*., 110 (2010) 527.
8. W. Ho, J. C. Yu and J. G. Yu, *Langmuir,* 21 (2005) 3486.
9. M. Paulose, K. Shankar, S. Yoriya, H. E. Prakasam, O. K. Varghese, G. K. Mor, T. A. Latempa, A. Fitzgerald and C. A. Grimes, *J. Phys. Chem*. B, 110 (2006) 16179.
10. S. K. Pradhan, P. J. Reucroft, F. Yang and Dozier, *J. Cryst. Growth*, 256 (2003) 83.
11. Z. R. Tian, J. A. Voigt, J. Liu, B. Mckenzie and H. Xu, *J. Am. Chem. Soc*., 125 (2003) 12384.
12. Z. S. Wang, H. Kawauchi, T. Kashima and H. Arakawa, *Coord. Chem. Rev*., 248 (2004) 1381.
13. M. Abd-Lefdil, R. Diaz, H. Bihri, M. A. Aouaj and F. Rueda, *Eur. Phys. J. Appl. Phys*, 38 (2007) 217.
14. C. J. Howard, T. M. Sabine and F. Dickson, *Acta Crystallogr. Sect*. B, 47 (1991) 462.
15. Q. Zhang, A. K. Chakraborty and W. I. Lee, *J. Phys. Chem. Solids*, 69 (2008) 1450.
16. M. Paulose, O. K. Varghese, G. K. Mor, C. A. Grimes and K. G. Ong, *Nanotechnology*, 17 (2006) 398.
17. G. K. Mor, K. Shankar, M. Paulose, O. K. Varghese and C. A. Grimes, *Nano Lett.*, 5 (2005) 191.