

Dye-sensitized solar cells using TiO₂ nanoparticles transformed from nanotube arrays

Yahya Alivov · Z. Y. Fan

Received: 22 September 2009 / Accepted: 27 January 2010 / Published online: 23 February 2010
© Springer Science+Business Media, LLC 2010

Abstract Dye-sensitized solar cells (DSSCs) were fabricated using TiO₂ mesoporous layers obtained by very simple method—transformation of TiO₂ nanotube (NT) films grown by electrochemical oxidation to nanoparticle (NP) films. This transformation is based on thermal annealing of TiO₂ NT arrays formed by anodization of titanium foil in fluorine ambient. Performance of DSSCs fabricated with different size NPs was studied in the range from 35 to 350 nm. Highest nominal efficiency (9.05%) was achieved for DSSC with NP size 65 nm while the lowest nominal efficiency (1.48%) was observed for DSSCs with NP size 350 nm. The dependence of the solar cell parameters with NP size is discussed.

Introduction

Dye-sensitized solar cells (DSSCs) have received considerable attention lately because they are cost-effective and environmentally friendly with efficiencies comparable to those of the traditional silicon based cells [1]. A typical DSSC consists of a dye-sensitized n-type wide band gap semiconductor layer on a semitransparent photon anode, liquid (or solid) electrolyte for hole transport, and a

platinum-covered counter electrode as a cathode. As the heart of the device, the mesoporous semiconductor oxide layer is composed of nanometer-sized particles sintered together for electron transport, and anatase TiO₂ is frequently chosen due to its conduction band energetic, low cost, wide availability, and non-toxicity. Attached to the surface of the mesoporous film is a monolayer of sensitizer dye for light absorption. Photoexcited electrons inject from dye molecules into the conduction band of the oxide and are collected by anode, while the original state of dye is subsequently restored by electron donation from the electrolyte, and hole is transported to the cathode. For DSSC, an overall energy conversion efficiency exceeding 11.0% has been achieved at AM 1.5 sun light (100 mW/cm²) [2, 3]. However, it is still a big challenge to further simplify the solar cell fabrication to get the cost down, and efforts are underway to achieve this goal [4, 5]. Pursuing this goal is the core task for such photovoltaic devices.

Recently, we reported on unique method for fabrication of truncated pyramid shaped TiO₂ nanoparticle (NP) layers by transformation of TiO₂ nanotubes (NTs) through thermal annealing, and the latter was grown by electrochemical anodization of titanium (Ti) foil in ethylene glycol [6]. We found that TiO₂ NTs transformed to NPs when annealing was performed in fluorine ambient at high temperature ramping rate with the opening end of NTs semi-sealed by a supporting plate. The formed NPs had a truncated bipyramid shape with high portion of reactive (001) surface area. The size of NPs depends on fluorine concentration and can be controlled within 20–500 nm range. In this paper, we report on fabrication and characterization of DSSCs fabricated by employing NP layers obtained by such simple method—transformation from NT arrays grown on Ti foils. The highly ordered NT arrays, in turn, are also grown by very simple method—electrochemical oxidation

Y. Alivov (✉) · Z. Y. Fan
Nano Tech Center and Department of Electrical and Computer Engineering, Texas Tech University, P.O. Box 43102, Lubbock, TX 79409-3102, USA
e-mail: yalivov@uci.edu

Z. Y. Fan
e-mail: zhaoyang.fan@ttu.edu

Present Address:
Y. Alivov
University of California, Irvine, CA 92697, USA

of Ti sheets and various pore sizes, lengths, and wall thicknesses can be easily grown by tailoring anodization conditions [7–9]. Because NP layers transformed from NT layers are on conductive Ti sheet they can be directly used for fabrication of DSSCs this method eliminates several steps typical to fabrication conventional TiO₂ NP based DSSCs such as NP paste preparation, deposition on the substrate using blade method, and post-deposition treatments. Thus, DSSCs fabricated using the TiO₂ NP layer transformed from NT array films are expected to be cheaper than existing DSSC devices.

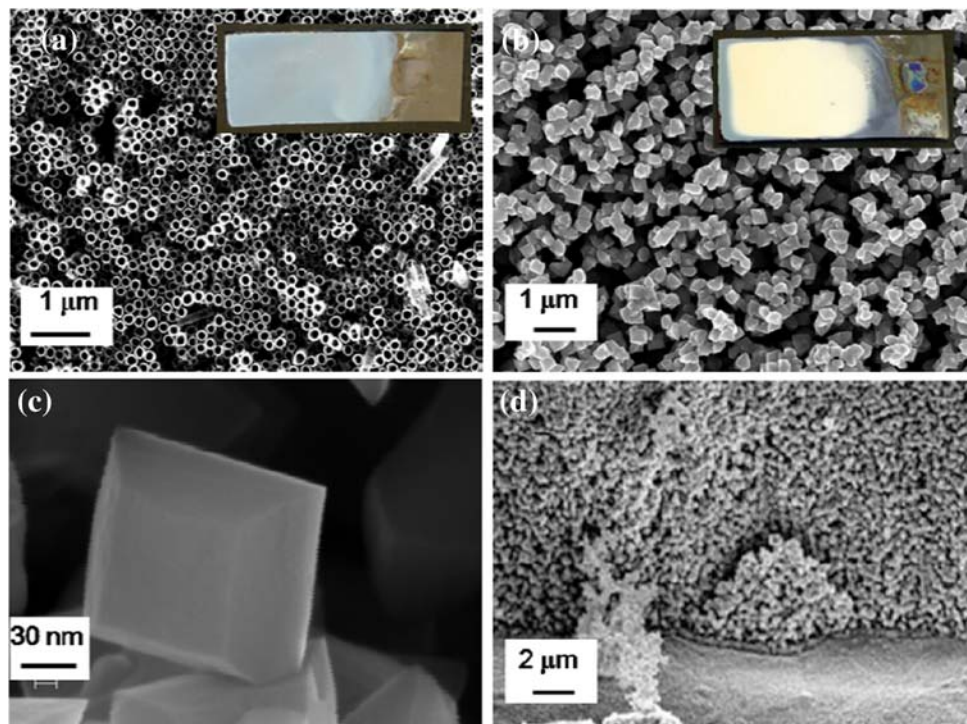
Experimental section

Ti sheets with 0.25 mm thickness and 99.97% purity was used for electrochemical oxidation in electrolyte prepared using NH₄F (98%) and ethylene glycol (99.8%). Anodization was carried out in DC voltage ranging from 30 to 60 V with NH₄F concentration varied in a range of 0.1–2 wt%. A 10% water (H₂O) was added to the electrolyte to increase the growth rate [10, 11]. A well-defined tubular structure was observed as can be seen from Fig. 1a, which presents scanning electron microscope (SEM) images of top view of as-grown sample. NT arrays grew on both sides of the Ti sheet without noticeable differences in NT depth, diameter, wall thickness, and surface morphology. Both sides of nanotubes arrays have the same gray color as shown by the photo camera picture in inset of Fig. 1a. Supported by a

microscope glass slide, the sample was thermal annealed in an oven with air ambient in temperature range from 500 °C to 800 °C for 60 min with a temperature ramping rate of 16 °C/min from room temperature. After thermal treatment, the amorphous TiO₂ nanotubes on the side opposite to the underlying glass slide retained the NTs morphology with the same gray color, but transformed to anatase phase. On the other hand, NTs facing the glass slide were transformed to NPs as shown in Fig. 1b and the color of the surface changed from gray to yellow as shown in inset of Fig. 1b. NPs have a shape of truncated bipyramids as shown by zoom-in image in Fig. 1c. The formed NPs are concatenated into porous NP films which are mechanically stable and do not change in morphology and thickness after treatment in ultrasonic cleaning, implying a good electrical contact between NPs. The thickness of NP side was found to be 13–17 μm against 56–60 μm of the thickness of original NT films. Such a reduction of the NT film thickness by 4–5 times was explained by a collapse of the original hollow NTs with amorphous structure and densification and crystallization into NPs [12]. Figure 1d shows cross-section of the converted NP layer after annealing at 500 °C for 1 h, from which a sharp boundary between NP layer and Ti foil can be seen. The NP size depended on the fluorine concentration during annealing and was controlled within 20–350 nm size range in this study [6]. Crystal properties of both NT and NP sides of the samples were studied by X-ray diffraction.

Dye-sensitized solar cells (DSSCs) were fabricated using conventional approach [1, 2]. NP films, attached on

Fig. 1 Representative SEM images of TiO₂ nanotubes and transformed NPs: **a** top view of NT arrays, inset is photo-camera picture of NT side of the sample (size 0.5 in. × 1 in.); **b** top view of NP side of the sample; inset shows photo-camera picture of NP side (size 0.5 in. × 1 in.). Most of the NPs have a shape of truncated pyramid and bi-pyramid as shown in (c). **d** cross-section of the NP layer on Ti foil



the original Ti foils, were dye sensitized by immersion in 0.3 M ethanolic solution of N719 dye for 24 h. The TiO₂ photon electrodes (anodes) and semitransparent Pt-coated ITO counter electrodes (cathodes) were sandwiched together using 60 μm thick hot-melt Surlyn spacers. The liquid electrolyte solution, composed of 0.3 M LiI, 0.05 M I₂, 0.5 M 4-tertbutylpyridine, and 0.6 M 1-propyl-2,3-dimethylimidazolium in 3-methoxypropionitrile was introduced between the sensitized and counter electrodes by using syringe. The solar cell area filled with the electrolyte was 5 × 5 mm². It is important to note that since the part of the electrolyte evaporated before and during solar cell measurements despite the sealing, the current density was calculated using the remained with electrolyte area. The evaporated area varied from sample to sample (possibly depending on the sealing quality) and changed from quarter to half of the initial area. The photovoltaic properties of fabricated DSSCs were studied by photocurrent–photovoltage (*I*–*V*) characterization under illumination using AM 1.5 solar simulator (Photo Emission Tech Inc.) through the semitransparent Pt counter electrode.

Results and discussion

Representative SEM images of NP patterns of different grain sizes are shown in Fig. 2. In this figure, another approach, sealing the NT samples in a glass container, is also adopted for annealing. In all cases truncated pyramid

Fig. 2 Representative SEM images of different size NPs formed from NTs using different NH₄F concentrations: **a** 25 nm, annealed in sealed glass container at 2% NH₄F, **b** 60 nm, annealed on glass slide at 1% NH₄F, **c** 220 nm annealed in sealed glass container at 0.1% NH₄F, and **d** 350 nm annealed on glass slide at 0.5% NH₄F

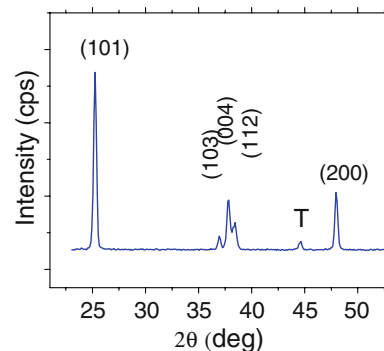
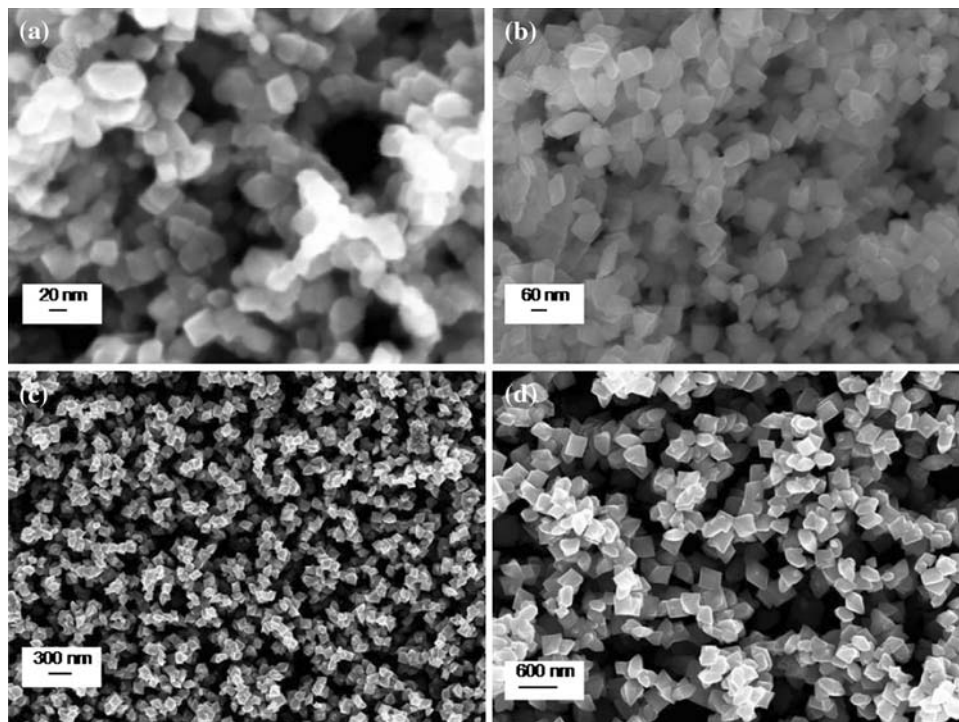


Fig. 3 GAXRD spectrum of anatase NP films transformed from NTs. *T* refers to the diffraction peak of Ti foil

shape of NPs were observed regardless of NP size. Figure 3 presents the XRD spectrum of the NP layer transformed from NT film. As seen it consists of anatase (101), (103), (004), (112), and (200) diffraction peaks at 25.3°, 36.95°, 37.75°, 38.45°, and 47.95°, respectively. A diffraction peak at 44.55° refers to the Ti sheet peak. Anatase–rutile transformation temperature for NP side was higher by 100 °C compared to that for NT side, being 750 °C and 650 °C, respectively. Photoluminescence spectroscopy also demonstrated the crystalline quality of the NP film to be much better than anatase NT film [12].

Figure 4 presents *I*–*V* characteristics, and Table 1 summarizes the open-circuit voltage (*V*_{oc}), short-circuit current density (*I*_{sc}), calculated fill factor (FF), and

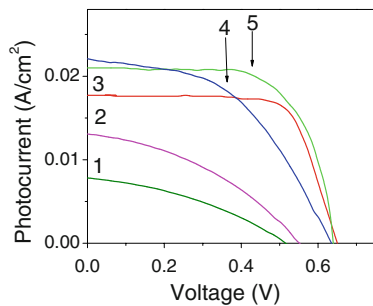


Fig. 4 Photocurrent–photovoltage characteristics of DSSCs fabricated using different TiO₂ NP size layers: (1) 350 nm; (2) 220 nm; (3) 100 nm; (4) 65 nm; and (5) 35 nm

Table 1 A summary of photovoltaic properties of DSSCs fabricated using different size TiO₂ NP layers

Sample number	NP size (nm)	V _C (V)	I _{sh} (mA/cm ²)	FF	η (%)
1	35	0.65	17.7	0.72	8.45
2	65	0.64	21.0	0.68	9.05
3	90	0.65	22.7	0.48	6.75
4	220	0.54	12.9	0.39	2.78
5	350	0.51	7.8	0.37	1.48

efficiency (η) of all DSSCs fabricated using different NP size layers. As was mentioned above (“[Experimental section](#)”), current density I_{sc} was calculated using the remained with electrolyte area. However, we believe that some “invisible” electrolyte present in the “empty” area could give some contribution to the measured current thus giving error to the real current density I_{sc} , and therefore, to the efficiency. Therefore, the I_{sc} and efficiency values given in this paper, unlike open circuit voltage V_{oc} and fill factor FF, are nominal rather than actual used to compare samples with different NP size. Three sets of samples were prepared for each NP size, in Fig. 4 I – V curves of the solar cells with the highest performance for each NP size are shown. The reproducibility of results was within 30%.

It was found that the efficiency of DSSCs greatly depended on NP size d varying in the range 1.45%–9.05%. It had maximum value (9.05%) for DSSCs with NP with $d = 65$ nm, and decreased with d to 1.45% corresponding to $d = 350$ nm as can be seen from Fig. 5a, which plots the efficiency as a function d . The efficiency η corresponding to $d = 35$ nm was 8.45% and was slightly less than that for sample with $d = 65$ nm. Open circuit voltage, V_{oc} , was about 0.65 V until $d = 90$ nm, and then decreased with d until 0.51 V that corresponds to $d = 350$ nm (Fig. 5a). Short-circuit current, I_{sc} , first increased from 17.7 mA/cm² to 22.7 mA/cm² when d increased from 35 nm to 90 nm (Fig. 5b), and then started decreasing with further increase of d , reaching 7.8 mA/cm² that corresponds to

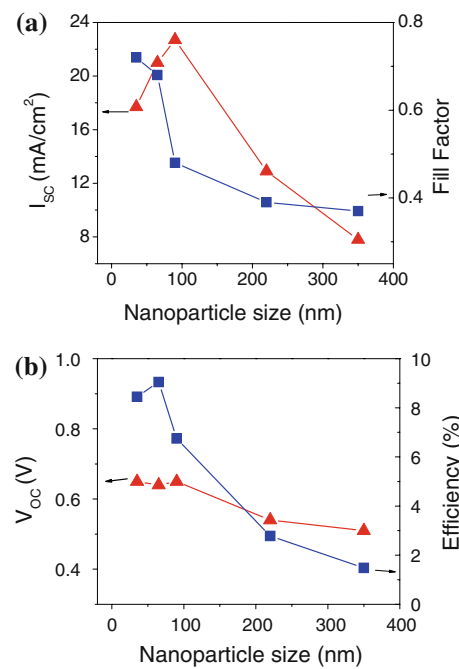


Fig. 5 **a** Short-circuit current (I_{sc}) and fill factor (FF) as a function of NP size, **b** the same plots for open-circuit voltage (V_{oc}) and the efficiency

$d = 350$ nm. Such a dependence of I_{sc} with NP size can be explained by a competition of recombination losses and photoelectron generation in TiO₂. At smaller NP size, the total surface area is higher resulting in a higher electron harvesting but results in enhanced recombination rate due to increased grain boundaries. With an increase of NP size recombination losses decrease faster than does electron generation that result in the peak position observed in Fig. 5b. Unlike other solar cell parameters, fill factor monotonically decreases from 0.72 to 0.37 (Fig. 5b) when d increased from 35 nm to 350 nm. As was mentioned above (“[Experimental section](#)”) the current density was calculated by estimating visually the area covered with the electrolyte after partial evaporation.

As was seen above the highest short-circuit current $I_{sc} = 22.7$ mA/cm² was observed for sample with NP size $d = 90$ nm (Table 1, Fig. 5b). However, due to its low fill factor 0.48 the resulting efficiency is less than that for samples with 65 nm and 35 nm NP size (9.05% and 8.45%, respectively.) As seen from Fig. 5a, b, all solar cell parameters V_{oc} , I_{sc} , FF, and η decrease as NP size increases. Previously all solar cell parameters were reported to degrade with an increase of recombination rate [13]. The degradation of DSSC performance in our experiments could be attributed to increase of recombination rate due to increase of uncoated part of the Ti electrode with an increase NP size (TiO₂ NPs were formed on Ti metal foil). When the liquid electrolyte comes into direct contact with

the exposed Ti metal anode, electrons in the anode could recombine with the oxidized redox species [14]. To reduce this effect, different thin oxide barrier layers such as ZrO_2 , TiO_2 , MgO , Al_2O_3 , Y_2O_3 have been employed in the literature [15]. Poor attachment of dye molecules to bottom uncovered electrode is also reported to be a cause for reduction of solar cell parameters, and this may be another reason for DSSC performance decrease with an increase of NP size [15].

Conclusion

In conclusion, in this work we demonstrated DSSCs fabricated using NP layers converted from electrochemically grown NT array films by annealing in fluorine ambient. NP layers transformed from NT layers can be directly used for fabrication of DSSCs without need for paste preparation, deposition, thermal treatments this method makes DSSCs cheaper than conventional DSSCs. Maximum nominal efficiency (9.05%) has been achieved for solar cells with NP size 65 nm. Although the efficiency of DSSCs demonstrated in this work is less than the highest efficiency reported in literature optimization of fabrication process and proper engineering could lead to improvement of performance of DSSCs fabricated by this method.

References

1. Grätzel M (2001) *Nature* 414:338
2. Grätzel M (2005) *Inorg Chem* 44:6841
3. Nazeeruddin MK, De Angelis F, Fantacci S, Selloni A, Viscardi G, Liska P, Ito S, Takeru B, Grätzel M (2005) *J Am Chem Soc* 127:16835
4. Nishino J, Teekateerawej S, Nosaka Y (2004) *J Mater Sci* 39:3813. doi:10.1023/B:JMSE.0000030746.52141.55
5. Han H, Zan L, Zhong J, Zhao X (2005) *J Mater Sci* 40:4291. doi:10.1007/s10853-005-3880-9
6. Alivov Y, Fan ZY (2009) *J Phys Chem C* 113:12954
7. Zwillig V, Aucouturier M, Darque-Ceretti E (1991) *Electrochim Acta* 45:921
8. Macak JM, Schmuki P (2006) *Electrochim Acta* 52:1258
9. Alivov Y, Pandikunta M, Nikishin S, Fan ZY (2009) *Nanotechnology* 20:225602
10. Paulose M, Shankar K, Yoriya S, Prakasham HE, Varghese OK, Mor GK (2006) *J Phys Chem B* 110:16179
11. Shankar K, Mor GK, Prakasham HE, Yoriya S, Paulose M, Varghese OK, Grimes CA (2007) *Nanotechnology* 18:065707
12. Alivov Y, Fan ZY (2009) *Nanotechnology* 20:405610
13. Bisquert J, Cahen D, Hodes G, Rühle S, Zaban A (2004) *J Phys Chem B* 108:8106
14. Gregg BA, Pichot F, Ferrere S, Fields CL (2001) *J Phys Chem B* 105:1422
15. Kay A, Grätzel M (2002) *Chem Mater* 14:2930