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Improved dye sensitized solar cell performance in larger cell size by using TiO₂ nanotubes

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Received 23 October 2012, in final form 26 November 2012

Published 8 January 2013

Online at stacks.iop.org/Nano/24/045401

Abstract

Typical dye sensitized solar cells (DSSCs) exhibit a severe reduction of power conversion efficiency when the cell size is increased. In order to cope with this issue, we have investigated the use of anodized TiO₂ nanotubes on Ti foil in combination with the standard TiO₂ nanoparticle paste coated anode structure. The presence of nanotubes in the anode structure enabled a significant mitigation of the size-dependent deterioration of the DSSC performance, with a trend of much milder decrease of the efficiency as a function of the cell dimension up to 9 cm². The observed improvement is partly attributed to the elimination of fluorine-doped tin oxide glass in the anode structure, as well as the enhanced charge collection via the nanotube coated Ti substrate, resulting from enhanced mechanical and electrical connections and possibly improved light trapping. The introduction of TiO₂ nanotubes on the Ti foil substrate led to a substantial improvement of the J_{sc} current density.

 Online supplementary data available from stacks.iop.org/Nano/24/045401/mmedia

(Some figures may appear in colour only in the online journal)

1. Introduction

Dye sensitized solar cells (DSSCs) have attracted considerable attention in recent years due to their low cost, high energy conversion efficiency, and relatively simple fabrication processes. Since the first report by O'Regan and Grätzel [1] in 1991, a number of investigations have been carried out to improve the performance of DSSCs [2–23]. Over 11% energy conversion efficiency has been achieved in laboratory scale samples [3, 4]. Fluorine-doped tin oxide (FTO) glass has been widely used for the DSSC assembly as the transparent conducting oxide (TCO) because of its high visible light transmittance and good electrical conductivity. However, a noticeable size-dependent efficiency decrease is encountered when the solar cells are scaled up to larger areas for practical applications. As is well known, FTO glass exhibits a high

sheet resistance, which causes Ohmic loss and further leads to a significantly reduced efficiency [5]. In addition, FTO glass is also expensive, adding a substantial cost to the DSSC device [6]. Because of this size related problem, FTO glass based DSSCs are typically constructed with a stop-gap approach of fabricating about one centimeter wide parallel stripes and solder-bond stitching them together to produce larger area cells, for example, with 10–30 cm dimensions. A single cell design without this stitching of narrower cells would be highly desirable for design simplicity and lower cost.

Compared with FTO glass, highly conductive metal based electrodes could be a promising alternative to reduce the resistive loss, device weight and production cost of large size DSSCs. Fan *et al* [7] utilized a stainless steel mesh as the cell photoanode to replace the FTO glass; however,

cells with very low energy conversion efficiencies of $\sim 1.49\%$ were yielded. Onoda *et al* investigated DSSCs with different substrates and they found that a nano-crystalline TiO_2 coated titanium substrate has a higher efficiency than stainless steel and FTO [8]. Metallic Ti has the advantages of low resistivity, low production cost and high temperature stability compared with FTO glass [9–12]. The three-dimensional network film of interconnected TiO_2 nanoparticles has a porous structure and quite a large surface area. While some TiO_2 nanoparticle (TNP) paste tends to show poor adhesion on metal substrates, it has been reported that highly ordered TiO_2 nanotube arrays with a large internal surface area can be grown on Ti foils by an anodization process, and good energy conversion efficiencies have been reported [13–18]. Rustomji *et al* utilized a woven Ti mesh screen with surface TiO_2 nanotubes as the anode basis to obtain $\sim 5\%$ efficiency [18].

Here, we combine low resistance Ti foil, vertically aligned TiO_2 nanotubes and porous film of nano-crystalline TiO_2 particles to reduce the resistive loss and enhance the energy conversion efficiency in larger size single piece DSSCs. The height of anodized, ordered TiO_2 nanotubes (TNTs) was controlled to be around $5\ \mu\text{m}$ by controlled anodization of Ti foil, which was followed by coating with a thin layer of TNPs, about $7\ \mu\text{m}$ thick. The Ti foil substrate gave good electrical conduction after DSSC assembly and the TNTs' nanostructure greatly enhanced the light scattering and the adhesion of the coated TNP paste. The coated TNP layer on top of the nanotubes had a large surface area which could absorb the desired amount of dye molecules. With scaled-up cell sizes from 0.25 to $9\ \text{cm}^2$, it is shown that the size-dependent efficiency loss is substantially reduced in such a metal- and nanotube-containing composite structure in contrast to the traditional FTO glass based DSSC anode design.

2. Experimental procedures

2.1. Synthesis of TiO_2 nanotubes (TNTs)

Highly ordered TiO_2 nanotube arrays were prepared by an anodization process in a two-electrode electrochemical bath. Ti foil (99.5% purity, 0.25 mm thick, Alfa Aesar) with square dimensions was used as a working electrode. Platinum foil was used as the counter-electrode. The voltage was applied by a DC power supply (Agilent, E3612A). A thin TiO_2 nanotube array layer was produced by anodizing the Ti foil in a solution of ethylene glycol (99.8%, JT Baker) containing 0.25% ammonium fluoride (NH_4F , 96%, Alfa Aesar) and 2% H_2O at 60 V for 30 min.

2.2. Preparation of photoanodes

The TNP paste was synthesized by a sol-gel method which was described by previous researchers [19]. The TNP paste was coated onto the surfaces of different sized anodized TNT substrates using a doctor blading method and dried at $130\ ^\circ\text{C}$ for 10 min. Subsequently, all the samples were annealed in a furnace by gradual heating from room temperature to

$500\ ^\circ\text{C}$ ($325\ ^\circ\text{C}/5\ \text{min}$, $375\ ^\circ\text{C}/5\ \text{min}$, $450\ ^\circ\text{C}/15\ \text{min}$ and $475\ ^\circ\text{C}/15\ \text{min}$, with a 10 min ramping time between these steps). For comparison, TNP paste coating on bare Ti foil anodes was also carried out using similar processes. The samples were then treated in 0.04 M TiCl_4 aqueous solution at $70\ ^\circ\text{C}$ for 30 min in order to make good mechanical and electrical contacts between the active Ti oxide nanoparticle layer and the conducting layer, followed by thermal treatment at $500\ ^\circ\text{C}$ for 30 min.

2.3. Fabrication of dye sensitized solar cells

The prepared anode samples were soaked in a 0.3 mM solution of $[\text{Ru}(\text{4-carboxylic acid-4'-carboxylate-2-2 bipyridyl})_2(\text{NCS})_2]$ -[tetrabutylammonium] $_2$ (N719 dye, from Solaronix) in ethanol for 24 h. The cathode counter-electrodes were fabricated by placing a small drop of 5 mM H_2PtCl_6 (from Sigma Aldrich) in isopropanol onto cleaned FTO glass, followed by firing at $400\ ^\circ\text{C}$ for 15 min. The prepared photoanode and counter-electrode were put together into a sandwich cell type structure and sealed with hot-melt gasket of Surlyn. The cell's internal space was filled with electrolyte and the cell was placed in a vacuum chamber to remove the air from inside the cell space and allow the electrolyte to enter. The electrolyte was composed of 0.6 M 1-butyl-3-methylimidazolium iodide (BMII), 0.03 M I $_2$, 0.1 M guanidinium thiocyanate, 0.5 M 4-tert-butylpyridine in acetonitrile and valeronitrile (85:15, v/v). Four identical DSSC samples were made and tested for each condition.

2.4. Characterization

The morphologies of the TNTs and TNPs were determined using an ultrahigh resolution scanning electron microscope (UHR SEM, FEI XL30). The photocurrent density-voltage (J - V) curves were measured using a solar simulator under AM 1.5 G illumination with a 450 W xenon lamp equipped with an AM 1.5 global filter (Newport 81094) and coupled with a Keithley 2420 source meter. The illumination intensity ($100\ \text{mW cm}^{-2}$) was calibrated by a standard Si cell.

3. Results and discussion

3.1. The morphology of the anodized TNTs and the TNP paste

Figures 1(a) and (b) show the morphology of the TiO_2 nanotubes grown by anodization and utilized as a substrate for coating with a TiO_2 nanoparticle paste layer to fabricate the DSSC solar cell. The vertically aligned TiO_2 nanotubes with $\sim 150\ \text{nm}$ diameter and $\sim 5\ \mu\text{m}$ length were produced by anodization treatment at 60 V for 30 min in a solution of ethylene glycol containing ammonium fluoride (NH_4F). After anodizing, the paste containing $\sim 25\ \text{nm}$ size TiO_2 nanoparticles was coated on top of the TiO_2 nanotube layer, as shown in figures 1(c) and (d). The total thickness of the nanotube and nanoparticle photoanode was around $12\ \mu\text{m}$ (TNT layer $\sim 5\ \mu\text{m}$ and TNP layer $\sim 7\ \mu\text{m}$). The crystal

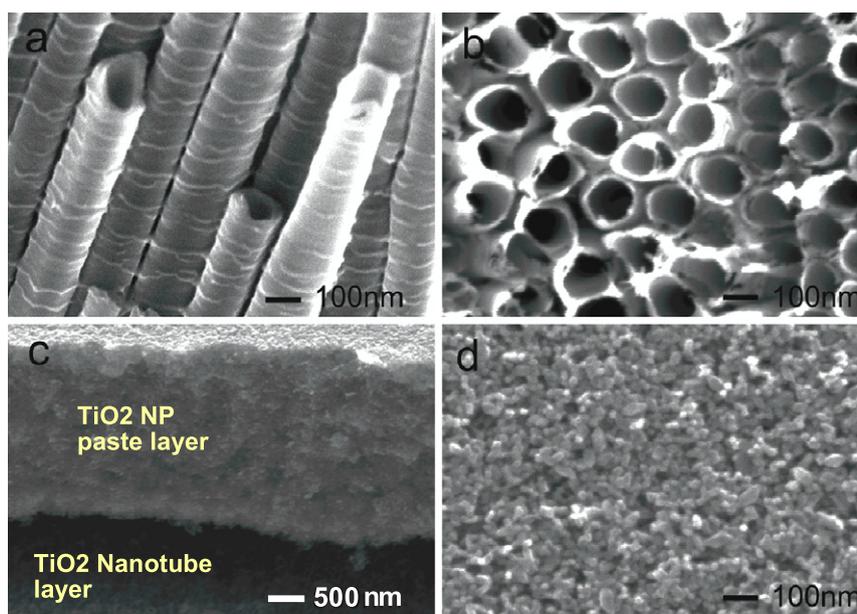


Figure 1. SEM images of anodized TiO₂ nanotubes and coated and baked TiO₂ nanoparticle paste. The TNTs were grown on a Ti foil at 60 V for 30 min. (a) 45° tilted view of the TNTs, (b) top view of the TNTs, (c) 45° tilted cross section of the coated and 500 °C baked paste, and (d) top view of the coated and baked paste.

phase of the TiO₂ nanoparticles and TiO₂ nanotubes has been reported in our previous work [21, 22] to be predominantly the anatase phase after an ~400–500 °C annealing process. Anatase phase TiO₂ is still the main phase utilized in most DSSC related research and applications.

3.2. DSSC performance of a TNP paste-on-Ti versus TNP paste-on-TNT anode

Figure 2 shows the typical, exemplary photocurrent density–voltage (J – V) characteristics of DSSC cells with TNPs coated on bare Ti foil substrate versus those on an anodized TiO₂ nanotube (TNT) layer. The inset shows the DSSC photovoltaic numerical performance data. In contrast to the J – V data for the TNP coated Ti foil (the lower curve in figure 2), which indicate a relatively poor performance with a low short-circuit current density of $J_{sc} \sim 5.20 \text{ mA cm}^{-2}$, the TNP coated TNT structure (the upper curve) exhibits a significantly enhanced photoanode current density of $J_{sc} \sim 9.36 \text{ mA cm}^{-2}$. (Four DSSC samples were made and tested for both types of sample, yielding generally comparable data. For example, the TNP coated Ti foil anode cells exhibited J_{sc} values ranging from 4.59 to 5.20 mA cm^{-2} , while the TNP coated TNT structure produced J_{sc} values ranging from 6.56 to 9.90 mA cm^{-2} .) The results indicate that the DSSC device with anodized TNTs exhibits almost two times higher J_{sc} . As is well known, the porous TNP film absorbs many N719 dye molecules on the large surface area of the 15–20 nm diameter TiO₂ nanoparticles within the TNP layer. There might be some extra dye molecules attached onto the surface of the TiO₂ nanotubes underneath as well; however, the surface area of the ~150 nm diameter nanotubes is expected to be much smaller than that of the TiO₂ nanoparticles in the samples investigated in this study.

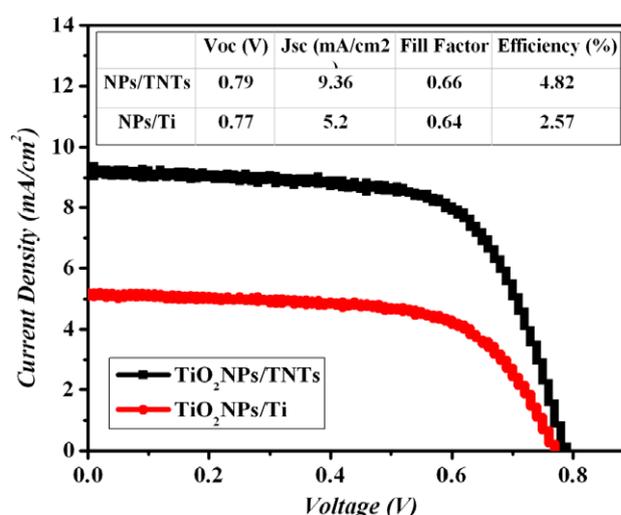


Figure 2. Comparative photocurrent density–voltage (J – V) characteristics of the (TNP-on-Ti foil) anode versus the (TNP-on-TNT on Ti foil) anode. The anode size is $0.5 \times 0.5 \text{ cm}^2$ for both types of DSSC cell.

The photoelectrons generated from the dye molecules are transferred to the TiO₂ nanoparticles for eventual collection by the conductive substrate to produce electric current and generate power. The improved DSSC performance by the addition of the TiO₂ nanotube layer between the traditional TiO₂ nanoparticle layer and the Ti foil (figure 2) is tentatively attributed to one or more of the following factors.

- (i) A more robust mechanical locking of the active TNP layer material (see the schematics of figure 3) and less tendency for local microcracking or local delamination of the TNP layer from the Ti foil as the TNPs and metallic

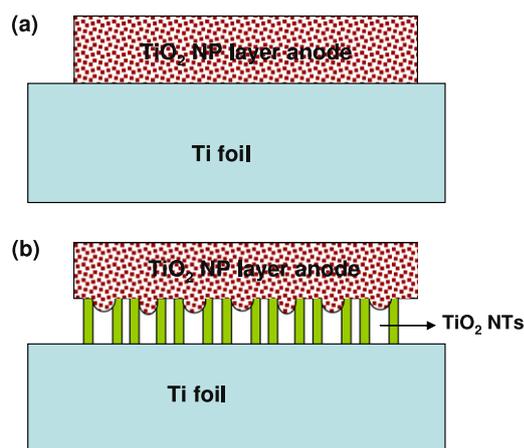


Figure 3. Schematic illustration of the mechanical and electrical connections of the TiO₂ anode layer to the Ti foil. (a) A TiO₂ nanoparticle (TNP) layer without a TiO₂ nanotube layer, and (b) with a TiO₂ nanotube (TNT) layer.

Ti have different elastic moduli and thermal expansion behavior.

- (ii) TNTs, having fewer interfacial boundaries due to their vertically aligned array and continuous electrical conduction paths to the Ti metal conductor underneath, most likely allow more efficient electron transfer from the TiO₂ nanoparticle layer, thus reducing the chance of charge recombination, which also means that the electrons may have longer lifetimes to contribute to the higher photocurrent [20, 23].
- (iii) Increased sunlight absorption and reduced reflection due to the topographically rough, vertically aligned nanotube structure which may help to trap the sunlight better (see figure 4).

In order to consider the possible surface area effect that influences the amount of dye absorption and DSSC efficiency, we calculated the total surface area of the 5 μm tall nanotubes utilized and compared with that for the 7 μm thick TiO₂ nanoparticle layer. For the nanotubes, assuming an average OD (r_o , outer diameter) of 150 nm and ID (r_i , inner diameter) of 130 nm, and a 20 nm gap between adjacent nanotubes, the total inner surface area + outer surface area per 1 cm² area of the 5 μm tall TNT array structure is calculated to be $\sim 0.015 \text{ m}^2$. For the 7 μm thick nanoparticle layer, assuming a uniform 20 nm diameter and face-centered-cubic close packing, the total surface area is calculated to be $\sim 0.156 \text{ m}^2$, which is one order of magnitude larger than that for the 5 μm tall nanotubes. Therefore, even assuming that all the inner and outer surface of the nanotubes are coated with adsorbed dye and utilized, the contribution of the dye reaction from the nanotube portion is much smaller than that from the nanoparticle portion.

By substituting a part of the nanoparticle layer material with the nanotube material layer (i.e., instead of 12 μm thick TiO₂ nanoparticles, we used 5 μm thick nanotubes + 7 μm thick nanoparticles), we actually sacrificed about 40% of the surface area. Nevertheless, we observed a significant

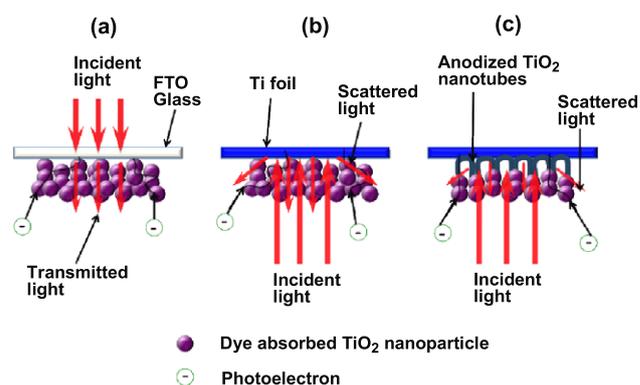


Figure 4. Schematic of the electron transfer paths and the utilization of incident light in the different substrate based DSSC anodes: (a) FTO glass, (b) Ti foil, and (c) anodized Ti (on Ti foil). More sunlight capture with reduced light transmission or reflection can be achieved by structure (c).

improvement in the DSSC performance. We attribute this phenomenon to the enhanced light scattering by the presence of the TNT structure underneath the TNP structure, which is in agreement with Zhu *et al*'s published results [23].

For the TNT-only DSSC cells without the TNP layer, we typically see $\sim 2\text{--}3\%$ lower efficiency than for the TNP-only DSSC cells with a comparable material thickness (data not shown). As discussed above, the TNT layer that we utilize has an order of magnitude smaller surface area than the TNP layer and the dye absorption is thus expected to be much smaller than for the TNP cells, with the DSSC efficiency also expected to be somewhat limited. Further research is required to have a more thorough understanding of the mechanisms for the observed DSSC performance enhancement, and the possible contribution of each of the factors listed above.

Comparative schematic illustrations of the possible electron transfer and light paths for three types of anode structure—based on FTO, Ti metal, or anodized Ti substrates—are shown in figure 4. In traditional FTO solar cells, light passes through the anode FTO glass, then some of the light is absorbed by the dye molecules. The transmitted sunlight is not utilized since it passes through the cell, as illustrated in figure 4(a). In the Ti foil based solar cell, the photoanode substrate is replaced with a metallic titanium sheet, so some of the sunlight can be reflected by the Ti substrate and then be used again. For the anodized TNT based solar cell, the light can be scattered by the three-dimensional topography of the highly ordered TiO₂ nanotubes. This leads to an increase of the optical path length in the TiO₂ film, thus allowing more light to be recycled by the dye molecules for additional photocurrent generation. As reported previously [23], anodized TNTs show more light harvesting due to the enhanced light scattering off the oriented nanotube structure. This scattered light can be used again in the DSSC anode, which helps to improve the conversion efficiency. Furthermore, compared to the TiO₂ nanoparticle type anode structure, the vertically aligned and continuous nanotubes have fewer interfaces for easier electron transport with a reduced chance of charge recombination, which could further enhance the conversion efficiency of TNT based DSSCs.

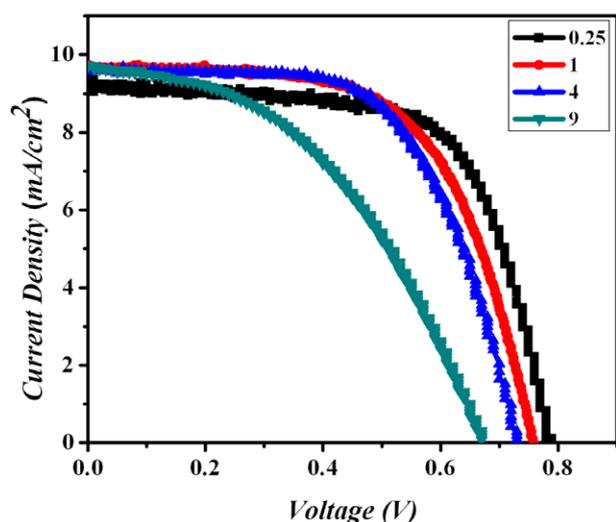


Figure 5. Photocurrent–voltage (J – V) characteristics of TiO_2 particles coated on different sized anodized TNT substrates. The cell sizes (in cm^2 active area) are marked in the inset.

Table 1. The photovoltaic performance of DSSCs with TNP paste coated on TNTs with four different active cell areas.

Active area (cm^2)	V_{oc} (V)	J_{sc} (mA cm^{-2})	Fill factor	Efficiency (%)
0.25	0.79	9.36	0.66	4.82
1	0.75	9.69	0.61	4.50
4	0.73	9.68	0.61	4.35
9	0.67	9.72	0.45	2.92

3.3. DSSC performance of different sized TNP paste-on-TNT cells

The photovoltaic characteristics of DSSCs with TNP paste coated on TNTs (figure 4(c) structure) with four different active cell areas are shown in figure 5 and table 1. Four identical samples were prepared and tested for each cell size, with the results indicating comparable DSSC performance from sample to sample. The average data are shown in the table. The typical example J – V curves shown in figure 5 indicate that the TiO_2 nanoparticle coated, anodized TNT cells have efficiency values of 4.82%, 4.50% and 4.35% for cell sizes of 0.25 cm^2 , 1 cm^2 and 4 cm^2 , respectively. When the cell size is further increased to 9 cm^2 , the efficiency is slightly lower (2.92%) than for the other three sizes. However, the fill factor (0.45) is improved by $\sim 80\%$ compared to identical sized traditional FTO glass based photoanode solar cells (see figure S1 and table S1 in the supporting information available at stacks.iop.org/Nano/24/045401/mmedia) due to the reduced series resistance of the Ti-containing photoanode.

The noticeably higher fill factor results in almost 50% enhancement of the energy conversion efficiency over that of the same size traditional FTO glass solar cell. In contrast to FTO glass based TNP solar cells, the efficiency of the TNP anodized TNT–Ti foil solar cell does not exhibit a significant drop when the size of the solar cell is increased. For comparison, the photovoltaic characteristics of traditional DSSCs based on FTO glasses are presented in figure S1

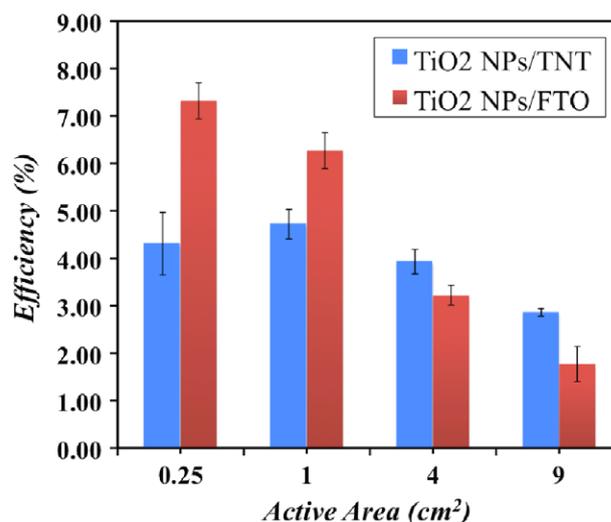


Figure 6. The size dependence of the DSSC efficiency for TiO_2 nanoparticle based cells with nanoparticle paste coated on an FTO substrate versus a TNT substrate.

and table S1 (available at stacks.iop.org/Nano/24/045401/mmedia). The samples in figure S1 and table S1 (available at stacks.iop.org/Nano/24/045401/mmedia) were fabricated in an essentially identical manner to the cells with TNP paste on a Ti foil anode in this study, except that FTO glass was used in the anode without any Ti foil involved.

The dependence of the DSSC photovoltaic performance of FTO and TNT based cells on the active area is shown in figure 6. When the anode area is small, for example, 0.25 cm^2 , the FTO based solar cell shows a much higher J_{sc} of 16.42 mA cm^{-2} than that for the TiO_2 nanotube/Ti foil based cell, exhibiting a J_{sc} value of 10.1 mA cm^{-2} . A similar behavior is seen for the 1 cm^2 size cells. However, when the size is increased the trend reverses at a cell area of 4 cm^2 , at which point the nanotube-containing metal anode cell (TNP-on-TNT) already exhibits an efficiency above that for the TNP on FTO cell. When the cell size is further increased to 9 cm^2 , the J_{sc} of the FTO based cells dramatically decreases to ~ 6 mA cm^{-2} (see figure S1 and table S1 available at stacks.iop.org/Nano/24/045401/mmedia), while the nanotube-containing cell still maintains a higher efficiency than the FTO based cell. The fill factor of the FTO based cell also shows a noticeable decrease from 0.54 to 0.26. Furthermore, the power conversion efficiency of the FTO based cell drops remarkably from more than 7% to below 1.5% when the anode size is made larger. Therefore, it is shown that in order to prepare the desired, larger sized DSSC cell (a full sized cell, not a stitched line array cell), use of the TiO_2 nanotubes and removal of the FTO glass are very beneficial.

The sheet resistance of the FTO glass substrate is 12.4 Ω/sq at room temperature, which is increased to 15.4 after sintering at 450 $^\circ\text{C}$ for 30 min, while the Ti substrate maintains a low resistance of $\sim 1.0 \times 10^{-3}$ Ω/sq , which is four orders of magnitude smaller than that of the FTO glass [24]. The electrical resistance of the substrate plays a very important role in the factors determining the DSSC

cell performance, especially when the cell size is scaled up. Therefore, the efficiency of TNP coated, anodized Ti cells exhibits a much higher performance stability with respect to increased active area size than FTO based cells. It should be noted that while the anode FTO glass was eliminated in this work, the cathode structure still utilized FTO glass. Our ongoing research effort to also eliminate the cathode FTO glass and replace it with a metallic structure is likely to further reduce the size dependence of solar cell performance in larger DSSC cells, which will be reported in future publications.

4. Conclusions

In order to mitigate the severe performance deterioration in larger size DSSC solar cells, we have investigated the use of anodized TiO₂ nanotubes (TNTs) on Ti foil in combination with the standard TiO₂ nanoparticle coating. The presence of nanotubes in the DSSC anode as well as the removal of the FTO glass from the anode structure enabled a significant improvement in the size-dependent deterioration of the DSSC with a much milder decrease of the efficiency as a function of the cell dimensions up to 9 cm², greatly surpassing the performance of standard TiO₂ nanoparticle based solar cells. The observed improvement is partly attributed to the elimination of the highly resistive FTO glass in the anode structure, as well as the enhanced charge collection via the nanotube coated Ti substrate, resulting from improved mechanical and electrical connections, electron conduction and possibly improved light trapping.

Acknowledgments

The authors wish to acknowledge COSMO and COSMO-America, Iwama fund (SJ), and a National Research Foundation (NRF) grant through the World Class University Program (R33-2008-000-10025-0) for financial support of this research. The fellowship support of the China Scholarship Council (for YZ) is also acknowledged.

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