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Hydrothermally growth of novel hierarchical structures titanium dioxide for high efficiency dye-sensitized solar cells



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HIGHLIGHTS

• A unique fabrication technology could convert TiO₂ nanorod to "nanomace" directly.

• High density and long branched of hierarchical top micro-corollas and bottom nanoforest.

• Higher dye loading and light harvesting on the basis of fast electron transport.

• Efficiency of fabricated DSSCs are 51% higher than that of bare TiO₂ nanorod arrays.

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ABSTRACT

We report an innovative development of novel double layered photoanodes made of hierarchical TiO2 micro-corollas as the overlayer and TiO2 nanoforest as the underlayer (HTCF), for dye-sensitized solar cells (DSSCs). They are obtained by a facile hydrothermal reaction of TiO2 nanorods array with top microspheres (MS)/FTO (Fluorine-doped tin oxide) glass substrate in an alkaline solution. In this process, the microspheres and nanorods are transformed into micro-corollas and nanotrees, respectively. The photoanodes with HTCF structure can greatly improve the light scattering ability due to their novel structures. Moreover, the enhanced surface area of HTCF can lead to larger dye loading, which achieves the higher light harvesting capacity. Base on the fast electron transport of the interior nanorods, higher light scattering and harvesting capacities, this novel HTCF photoanode realizes tri-functions. The overall power conversion efficiency (PCE) of the HTCF DSSCs are 51% increase in the conversion efficiency compare with those of constructed by bare TiO2 nanorod arrays. In our work, tri-functions of photoanodes are obtained by improving the 1D TiO2 nanostructures (nanorod, nanowire, nanotube et al.). To the best of our knowledge, it is a significant fabrication technology breakthrough for the photoanode of dye-sensitized solar cells.

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1. Introduction

Among third-generation photovoltaic devices, dye-sensitized solar cells (DSSCs) have been drawn intense attention due to its prominent superiority, and recognized as the most potential candidate for high-efficiency solar-to-electricity energy conversion [1–4]. Typically, TiO₂ nanoparticles (NPs) and nanoporous structures (NSs) films were widely used as photoanode in DSSCs to provide large internal surface area for dye molecule adsorption [5–9]. However, further increase in the conversion efficiency has

been limited by energy loss due to random electrical pathway and short electron diffusion length between grain boundaries of nanoparticles where exist enormous defects. On the other hand, one-dimensional (1D) vertically aligned TiO₂ nanostructures such as nanorods (NRs), nanowires (NWs) or nanotubes (NTs) have been estimated to significantly increase electron diffusion length for DSSCs, since they possess the advantages of providing direct electron transfer pathways and effectively suppressing charge recombination [10–15].

However, functional nanostructured photoelectrodes such as above-mentioned 1D nanostructures have been proved to significantly improve the electron diffusion length in the photoelectrode films, because they can provide a direct conduction path way for the rapid collection of photo-generated electrons. But they are not suitable as photoanode materials because of low specific surface

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area, resulting in poor dye adsorption and thereby low light harvesting efficiency [16–22]. It is well known that the fast electron transport, high specific surface area and prominent light scattering ability are indispensable for achieving high performance photo-anode [23–26]. Liao et al. [27] have presented the tri-functional hierarchical TiO₂ spheres for DSSCs. But bilayer TiO₂ grown on the FTO substrate directly, and both layers were hierarchical nanostructure and combine these three beneficial functions have rarely reported.

In this paper, we present a facile and operable hydrothermal strategy for constructing photoanode structure of hierarchical TiO_2 micro-corollas layer upon the nanoforest layer (HTCF), the surface of them were coronal structures with high density and long branched. The HTCF structure photoanodes were used to DSSCs for enhancing the amount of dye adsorption and scattering capability base on fast electron transport, significantly increase the power conversion efficiency. Thereby, this novel structure photoanode display the excellent photoelectrical properties. In our work, trifunctions of photoanodes were obtained by improving the 1D TiO_2 nanostructure (nanorod, nanowire, nanotube et al.). To the best of our knowledge, it is a significant fabrication technology breakthrough for the photoanode of dye-sensitized solar cells (Fig. 1).

2. Experimental section

2.1. Synthesis

The hierarchical TiO_2 with top micro-corollas and bottom nanoforest structure is grown by two steps hydrothermal growth processes. The first step: growth of the bottom 1D vertically aligned nanorods array and top microspheres. 30 mL of deionized water



Fig. 1. Schematic illustration of the fabrication process of the hierarchical top microcorollas and bottom nanoforest structure TiO_2 photoanodes via two steps of hydrothermal reactions.

was mixed with 30 mL of concentrated hydrochloric acid (36.5–38% by weight) to reach a total volume of 60 mL in a Teflonlined stainless steel autoclave (100 mL volume). The mixture was stirred at ambient conditions for 5 min before the addition of 0.75 mL titanium isopropoxide (98%Aladdin). After stirring for another 5 min, FTO substrate was placed into the bottom of the Teflon-lined with the conducting side facing up. The hydrothermal synthesis was conducted at 200 °C for 4 h. The system was then allowed to cool to ambient temperature. The FTO substrate was taken out and rinsed extensively with deionized water and allowed to dry in ambient air. Finally, the FTO substrate was calcined at 450 °C for 2 h with a heating rate of 2 °c min⁻¹ in air, and collected for next step. The second step: generating of the nanomeshes. According to our previous report, the method to directly convert commercial P25 powders into 3D nanomesh and urchin-like spheres structures [28,29]. Herein, the nanoforest films could be obtained by refreshing the hydrothermal process. 4-8 mL hydrogen peroxide (30%) was added into 27 mL of 10 M NaOH solution, after the solution was stirred for 3 min mildly, the solution was transfered the Teflon-lined. Then, the TiO2 nanorods film (product of the first step) was placed at the bottom of the Teflonlined with the nanorods side facing up, maintained at 150 °C for 2 h, and then allowed to cool to room temperature naturally. The as-prepared TiO₂/FTO films were washed with distilled water thoroughly and underwent an ion exchange process in 0.1 M HCl, following a heat treatment in a muffle furnace at 450 °C for 2 h.

2.2. Characterizations of materials

The morphology and microstructure were examined by fieldemission scanning electron microscopy (FESEM, JEOL JSM-7500F, operated at an acceleration voltage of 15 kV). Transmission electron microscopy (TEM) measurement was obtained on a JEOL JEM-2100 microscope operated at 200 kV. The crystal structure of the asprepared product was investigated by X-ray diffraction (XRD) (Rigaku TTRIII, with CuK α 1 radiation).

2.3. DSSCs fabrication

The TiO₂ NRs were treated with a TiCl₄ solution. TiO₂ NR grown substrates were immersed into the 0.05 M TiCl₄ at 70 °C for 30 min and then sintering at 450 °C in air for 30 min [30], finally, the TiO₂ NR grown substrates were loaded with dye by immersing into 0.4 mM Ru-dye (cis-dithiocyanate-N, N'-bis (4-carboxylate-4 tetrabutyl ammoniumcarboxylate-2,2'-bipyridine) ruthenium (II) (known as N719, Solaronix) for 24 h at room temperature. Dyeanchored NRs were capped by a Pt-coated FTO, acetonitrile/valeronitrile (85/15v/v) electrolyte containing 0.6 M 1,2-dimethyl-3-propylimidazolium iodide, 0.03 M I₂, 0.1 M guanidinium thiocyanate, and 0.5 M 4-tert-butylpyridine (Aldrich) for making a DSSC by a vacuum filling method. The working electrode film area for solar cell performance test was controlled by a mask representatively 0.25 cm².

2.4. Measurements of DSSCs' performance

The current–voltage (I-V) characteristics were measured by using a Keithley 2400 Source Meter under one sun AM1.5G (100 mW cm⁻²) illumination with a solar light simulator (Newport, Model: 94023A). A 450 W xenon arc lamp (Newport, Model: 6280NS) was served as a light source and its incident light intensity was calibrated with an NREL-calibrated Si solar cell equipped with a optical filter to approximate AM1.5Gone sunlight intensity before each measurement. The incident photontocurrent efficiency (IPCE) spectra were measured as a function of wavelength from 350 to 800 nm with a spectral resolution of 5 nm on the basis of a Spectral Product Zolix DSC300PA. Diffuse-reflectance spectra were measured on the same film samples on a Perkin–Elmer UV/Vis spectrophotometer (SHIMADZU 2550). Intensity-modulated photovoltage spectroscopy (IMVS) and intensity-modulated photocurrent spectroscopy (IMPS) measurements were carried out on an electron lifetime and dispersion test system (PSL-100) with a diode laser light source with variable intensities at 620 nm.

3. Results and discussion

3.1. Characterization of materials

The products' structure and morphology of the step-one and step-two were observed by field emission scanning electron microscopy (FE-SEM). After the first step hydrothermal growth process, the images at different locations and magnifications reveal that the entire surface of the FTO substrate is covered very uniformly TiO₂ nanorod (NR) arrays, and there were a mass of microspheres (MS) on the top of them, the MS constituted by nanorods (shown in Fig. 2a, b and f, the photoanode was designated as T1), the average length of nanorod arrays film, as determined from Fig. 2a inset is 6 um. Fig. 2a and b reveal the average diameter of MS is about 8 um. The vertically oriented first generation TiO₂ NRs can be used as the backbone of the next hydrothermal reaction. After the second step hydrothermal growth, the oriented nanostructure is still maintained, which eventually leads to TiO₂ nanostructure are corroded the surface with holistic (both NR arrays and MS). Fig. 2c and g; Fig. 2d, h, e and i displays the products after adding 4 mL, 6 mL and 8 mL of hydrogen peroxide to 10 M sodium hydroxide solution, respectively. As can be seen from Fig. 2g-i, the top view figures reveal that the surface of the NR appears araneose structures, and have a good porosity and connectivity, we call them nanomesh [28]. With the increase in the amount of hydrogen peroxide, the nanomesh density, branched length and connectivity are also increase. The top MS eventually became a hierarchical micro-corollas structure (see Fig. 2c-e, the photoanodes were designated as T2, T3 and T4, respectively). In addition, the TiO₂ nanorod (NR) arrays were transformed into nanoforest finally.

Nanoforest with the hierarchical top micro-corollas and bottom tree-like TiO₂ (T4) could be easily grown on a large area (Fig. 3a). The quality of the TiO₂ NRs has been characterized by scanning electron microscope (SEM) and transmission electron microscope (TEM). The cross sectional scanning electron microscopy (SEM) images of T4, the mean diameter and length of T4 observed from SEM (Fig. 3a and inset) are 600 nm and 6.8 μ m, respectively. The individual first generation backbone TiO₂ NR (T1) is shown in Fig. 3e and f, the diameter is 200 nm, and the individual NR with HRTEM shows that they are completely crystalline along their



Fig. 3. SEM and TEM pictures of TiO_2 nanoforest: (a) cross section view, (b, c) magnified view of SEM and TEM for single TiO_2 nanotree, (d) HRTEM of the nanotree crown, (e, f) magnified view of SEM and TEM for backbone, (g) HRTEM picture and selected area electron diffraction pattern of backbone.

entire lengths. Lattice fringes with inter planar spacings, $d_{110} = 0.32$ nm and $d_{001} = 0.29$ nm are clearly imaged and are consistent with the rutile phase (Fig. 3g and inset). Fig. 3b and c suggest that the TiO₂ NR with hierarchical tree crown (indicated by the blue dotted lines in Fig. 3b) grow coated to the vertically oriented first generation backbone TiO₂ NRs surface (indicated by the red dotted lines in Fig. 3b). As can be seen from Fig. 3c, the thickness of hierarchical tree crown indicates a highly crystallized rutile phase structure (Fig. 3d).



Fig. 2. (a, b, f) SEM images of the bare TiO₂ nanorods arrays base on FTO substrates with different locations and magnifications. (c, d, e) top corollas microspheres (MS) and (g, h, i) bottom TiO₂ nanoforest with 4 mL, 6 mL and 8 mL of hydrogen peroxide adding, respectively.

The X-Ray Diffraction (XRD) pattern of the as-prepared TiO₂ NRs (b) and hierarchical tree crown TiO₂ NRs (c) grown on FTO substrates, and the bare FTO glass substrate (a) are shown in Fig. 4. Evidently, the SnO₂ peaks were observed for all three XRD curves, which illustrated that the prepared products were constructed on FTO substrates. The well-defined and sharp Bragg peaks with high intensity indicate the good crystallinity of b and c. All identified peaks can be perfectly indexed to rutile TiO₂ with a = 4.566 Å and c = 2.948 Å, which is consistent with the standard data file (JCPDS card No.88-1172).

3.2. Photovoltaic performances

The four kinds of different TiO₂ NRs and nanoforest structure formed on FTO substrates are further used as a photoanode in DSSCs. In order to distinguish, the four kinds of TiO₂ NRs and nanoforest structure photoanodes were named as T1-Film, T2-Film, T3-Film and T4-Film. Under illumination of AM 1.5 simulated sunlight with a power density of 100 mW cm⁻¹ [2], the typical photocurrent density-photovoltage (J–V) curves of DSSCs based on the four films (T1-Cell: T1-Film; T2-Cell: T2-Film; T3-Cell: T3-Film; T4-Cell: T4-Film) are shown in Fig. 5, and the corresponding photovoltaic parameters are summarized in Table 1. In order to make the results significant and reliable, the statistical efficiency with standard deviation of four independent measurements for DSSCs based on different photoanodes were therefore show cased in Table 1 as well.

As shown in Fig. 5 and Table 1, the fill factor (FF) and opencircuit photovoltage (V_{oc}) varied little among the four TiO₂ NRs structure cells, the variation of the energy conversion efficiency (η) mainly came from the change in the short-circuit photocurrent density (J_{sc}) . The short-circuit current density (J_{sc}) increases from 8.19, to 9.51, to 10.60–11.72 mA cm⁻² as the film varied from T1, T2, T3 and T4, leading to the efficiencies of the DSSCs based on different TiO₂ NRs structures are 3.90%, 4.66%, 5.35% and 5.89%, respectively. It is noteworthy that the most efficient photovoltaic performance of 5.89% is achieved for T4-Cell, exhibiting that 11.72 mA cm⁻² in I_{sc} , 728 mV in V_{oc} and 0.69 in FF. Furthermore, both the J_{sc} and η of the T4-Cell improve by 43% and 51% respectively compared to T1-Cell. As expected, the J_{sc} largely depended upon the dye adsorption amount and light scattering capabilities of the NRs arrays, which will be discussed later in detail. In order to facilitate comparison, the photovoltaic data of P25-Cell is also revealed in Fig. S1, and Table S1, ESI[†].



Fig. 4. XRD patterns of the FTO glass substrate (a), the bare TiO_2 nanorods array on FTO substrate T1 (b) and the TiO_2 nanoforest on FTO substrate T4 (c).



Fig. 5. *I*−*V* curves of the DSSCs based on different photoanodes measured under one sun illumination (AM1.5 G,100 mW cm⁻²).-●- T1-Cell, -▼- T2-Cell, -◆- T3-Cell and -■- T4-Cell.

It is well known that the TiO₂ photoanode as a carrier of the dye, and the dye as a harvester of the photon, the photocurrent is strongly related to the light harvesting capability of TiO₂ photoanode [31–33]. Therefore, to promote dye loading and light scattering of the electrodes are two equally important tasks for light harvesting. Excellent specific surface area photoanode materials leading to high dye adsorption amount, the amounts of N719 dye adsorbed on these four films were investigated by thorough desorption in 1 mM NaOH solution, and then obtained by measuring the UV-Vis absorption spectra of the solutions. As shown in Table 1, the increasing amounts of dye uptakes were achieved for TiO₂ NRs with increasing tree crown density. The dye loading of T2-Cell, T3-Cell and T4-Cell are 1.4 times, 2.5 times and 3.3 times higher than that of T1-Cell, respectively. The higher dye loadings of the formers are ascribed to the larger specific surface area of the films with increasing tree branched density.

Moreover, to investigate the scattering efficiency in detail, the UV/Vis reflectivity of each film was also evaluated. As shown in Fig. 6, the reflectance of T2-film, T3-film and T4-film are much higher than the T1-film, suggesting better light scattering capabilities for such a kind of the hierarchical top corollas MS and bottom nanoforest structure photoanode compared with a bare NR photoanode in the visible and near-infrared regions, T4-film has the most outstanding light scattering performance among them, which can be attributed to the following fact. The dense the hierarchical tree crown and corollas MS enable them to reflect the transmitted light back to the under layer, which effectively prolongs the optical transfer length of the photoanode. The higher the tree crown density, the more transmitted light was reflected, resulting in enhanced light harvesting efficiency.

Table 1

Photovoltaic data of five different TiO₂ structure films, measured under AM 1.5 G one sun illumination (100 mW cm⁻²) as shown in Fig. 5. J_{sc} : short-circuit photocurrent density. V_{oc} : open-circuit photovoltage; η : total power conversion efficiency; FF: fill factor, η^* : the efficiency with standard deviation which is calculated from 4 independent cells.

Sample	$J_{\rm sc}$ (mA cm ⁻²)	$V_{\rm oc}({ m mV})$	FF (%)	η (%)	$\eta^*(\%)$	Dye adsorbed (nmol cm ⁻²)
T1-Cell	8.19	722	0.66	3.90	3.90 ± 0.11	30.2
T2-Cell	9.51	731	0.67	4.66	4.66 ± 0.18	41.8
T3-Cell	10.60	731	0.69	5.35	5.35 ± 0.22	76.5
T4-Cell	11.72	728	0.69	5.89	5.89 ± 0.21	98.6

From I-V measurements and UV-Vis adsorption.



Fig. 6. The UV–Vis reflection of four films without dye loading. — T1-Film, — T2-Film, — T3-Film and — T4-Film.

Fig. 7 shows the incident photon-to-current conversion efficiency (IPCE) spectra as a function of wavelength for those four DSSCs. The IPCE spectra of the DSSCs using four kinds of photoanodes and same dye (N719) display maximums at same wavelength (about 525 nm). T4-Cell possesses the highest IPCE values over the whole of the spectral region. Compared to the T1-Cell, the IPCE of the T4-Cell increased from 27% to 53% at around 525 nm (7% higher than that of P25-Cell at around 525 nm, shown in Fig. S2, ESI†). The higher IPCE of T4-Cell over a wide range (350–800 nm) contributed to the increase in the efficiency of light harvesting (larger dye molecular loading and higher light-reflectance), which could lead to a higher short-circuit current density. It is worth noting that the IPCE data of T4-Cell shows an obvious red-shift to a longer wavelength (600–750 nm) compared to the T1-Cell due to the better light scattering ability for the former.

After carefully analyzing the dye loading and light scattering performance, electron transport and recombination properties are equally important factors for DSSCs. In order to obtain better insight into the electron transport and recombination properties within DSSCs, the intensity-modulated photocurrent spectroscopy (IMPS) and intensity-modulated photovoltage spectroscopy (IMVS)



Fig. 7. Incident photon to current conversion efficiency (IPCE) curves of the TiO₂ electrodes prepared from four TiO₂ samples.-●-T1-Cell, -▼- T2-Cell, -♦- T3-Cell and -■- T4-Cell.



Fig. 8. (a) Electron diffusion coefficients and (b) electron lifetimes as a function of open-circuit voltage for the four DSSCs. - ● -T1-Cell, - ▼ - T2-Cell, - ◆ - T3-Cell and - ■ - T4-Cell.

measurements were further carried out under an illumination of 620 nm from an LED light source [34–36]. Fig. 8 represents the main results in the form of the electron diffusion coefficient (D_n) and electron lifetime (τ_r) as a function of open-circuit voltage (V_{oc}) for these four DSSCs based on different photoanode structures (T1-Film, T2-Film, T3-Film and T4-Film). Clearly recognized are the power law dependences of the electron diffusion coefficient (D_n) and τ_r on V_{oc} , which are inaccordance with the well-known trapping-detrapping model customarily used to describe electron transport/recombination in DSSCs [37]. Notably, whereas τ_r appears to be insensitive to the morphology of our photoanode films, D_n depends very much on the morphology [38,39].

Fig. 8a can notice that the D_n curve of the T4-Cell which lies the highest, confirming faster electron transit capability. It is thus clear that such novel HTCF structure photoanode possess prominent electron transport properties. From this result, several aspects merit attention. First, it is believed that electron transport depends very much on the morphology. The fast electron transport rate for the T4-Film can be ascribed the hierarchical TiO₂ tree crown being assembled from the nanomesh building units. This hierarchical nanostructure has been proven to have fewer surface trapping sites and defects for impeding electron recombination with I_3 in the electrode [40,41]. In the mean time, the surface of NRs with

intelligently tree crown structure, results in good neighboring contacts among adjacent NRs with close linkage of tree crown, which builds a sort of highway to boost electron transport. Second, unlike other double layered films fabricated from subsequent overlayer TiO₂ materials with different nanostructures which covered in the nanorods, the present nanotree crown overlayer was obtained via in situ hydrothermal growth and transformation by using the nanorods as raw materials. Hence, the seamless connection between the hierarchical TiO₂ tree crown outer layer and the TiO₂ nanorods inner layer is clearly recognizable. This junction type between the two layer scan further promote the D_n of T2-Cell, T3-Cell and T4-Cell with varying degrees.

The electron lifetime in the nanorod and HTCF structure TiO₂ films are shown in Fig. 8b. Compare with the diffusion coefficient, the lifetime in the different DSSCs is very similar except the pure NR based DSSC (T1-Cell). However, the curve of T1-Cell lies the lowest, this is strange, since the single crystalline NR is expected to decrease recombination rate due to its fast transportation and less trapping sites. So we speculate that the lower lifetime of the pure NR based DSSC (T1-Cell) results from the backward electron transfer from the FTO to the electrolyte [42]. If the electrolyte is in contact with the FTO in the NR based DSSC, faster transport of the electron in the NR accelerates the recombination of the electron in the FTO with iodine ions in the electrolyte [43]. However, the backward electron transfer is significantly reduced when the surface of the NR grow tree crown, as shown in Fig. 8b.The higher the tree crown density, the harder the electrolyte is in contact with FTO. Last but not least, it is reported that electron lifetime is related to the internal trapping and detrapping through bulk traps within DSSCs. The higher the bulk traps density, the longer the electron lifetime. This is because quick trapping and slow releasing of the electrons by the bulk traps could effectively delay the sacrifice of injected electrons [43,44]. The hierarchical tree crown on the outer layer can efficiently passivate the surface states and increase the density of bulk traps and thus enlarge the lifetime of the electrons.

4. Conclusions

A unique fabrication technology could change TiO₂ nanorods into coronal based on FTO substrates. The novel HTCF photoanode structure was used to DSSCs, which showed higher dye loading and light harvesting abilities, significantly increased the power conversion efficiency of the DSSCs. The power conversion efficiency was 5.89% ($J_{sc} = 11.72 \text{ mA cm}^{-2}$, $V_{oc} = 728 \text{ mV}$, FF = 0.69) which indicated a 51% increase in the conversion efficiency compared to those of bare TiO₂ NRs (PCE = 3.90%: $J_{sc} = 8.19 \text{ mA cm}^{-2}$, $V_{oc} = 722 \text{ mV}$, FF = 0.66). This is a significant fabrication technology breakthrough to achieve tri-functions by improving the 1D TiO₂ nanostructure (nanorod, nanowire, nanotube et al.) photoanodes.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.jpowsour.2014.05.118.

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