A composite electrode of TiO₂ nanotubes and nanoparticles synthesised by hydrothermal treatment for use in dye-sensitized solar cells

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In dye-sensitized solar cells, highly ordered TiO₂ nanotube arrays provide superior electron transport. However, their low surface area limits the amount of dye loading and thus the photocurrent. In the present work, a hydrothermal treatment of the TiO₂ nanotubes was carried out to form TiO₂ nanoparticles on the tube walls, thereby increasing the surface area for a higher amount of dye loading. The nanotube arrays were prepared by electrochemical anodization and subsequently hydrothermally treated in water at 90 °C. Using the same nanotube length (i.e., 6.5 μm), but different treatment durations, it was found that nanotubes under hydrothermal treatment for 45 min yielded the best photovoltaic performance, due to the combined merits of a high surface area and vectorial electron transport. Under the same treatment duration (i.e., 45 min), but using different nanotube lengths, nanoparticle formation was found to be accelerated in the longer tubes. The parts of the tubes near the bottom were constantly filled with nanoparticles, which limited cell efficiency to about 2.2% when the length was over 16.5 μm. Accordingly, a further efficiency enhancement of up to 3.5% was achieved with tubes of 16.5 μm by adjusting the duration of the hydrothermal treatment.

1 Introduction

Since 1991, dye-sensitized solar cells (DSSCs) have received worldwide attention as a promising and competitive candidate for low-cost photovoltaics. Conventional DSSCs adopt TiO₂ nanoparticles (about 15–30 nm) as the photoanodes. The photoanodes provide a very high surface area for dye adsorption and hence give rise to a high photocurrent, however numerous joints between the particles deteriorate the electron transport process. As such, one-dimensional nanostructures (e.g., nanowires, nanotubes, and nanorods) have been widely studied as alternatives for efficient electron transport. Of particular interest are TiO₂ nanotube arrays fabricated using electrochemical anodization, which yields an oriented alignment suitable for vectorial electron transport. However, in contrast to nanoparticles, the tubes exhibit a lower surface area for dye adsorption, which in turn results in a lower photocurrent and efficiency. Consequently, the most efficient device based on nanotubes yields an efficiency of ~8% in comparison to ~12% for nanoparticles, as detailed in one recent review paper.

Much effort has been made to increase the surface area of the nanotubes, e.g., by exploiting the parallel configuration based on double-sided nanotubes, decreasing the tube diameter, growing bamboo-type tubes, creating hierarchical structure, decorating nanoparticles and so on. A composite electrode of TiO₂ nanotubes and nanoparticles is favorable for efficient DSSCs, as it combines the merits of the individual components, i.e., the high surface area of the nanoparticles and the vectorial electron transport of the nanotubes. Several methods have been exploited to produce the composite electrode. TiCl₄ treatment has been widely employed to precipitate very small nanoparticles (~3 nm) on tube walls before assembling solar cells. To form a desired composite electrode, a concentrated solution is needed, otherwise no obvious changes can be observed after the treatment. Recently, hydrothermal treatment has been reported to form the composite electrode in (NH₄)₂TiF₆ or a P25-nanoparticle-containing aqueous solution. Water soaking is another facile method used to convert nanotubes either partially or entirely into nanoparticles or nanowires. This process is performed without any additional chemicals at room temperature, but it takes a very long period of time (2–3 days) to form the composite architecture. In all
these cases, the obtained structures yield a high surface area for dye loading and hence give rise to an appreciable efficiency enhancement when applied in DSSCs. Nevertheless, the outer tube walls are unlikely to be used any more, as the intertube spaces are filled or blocked by the newly formed nanoparticles. Additionally, electron transport in these electrodes is deteriorated, as the integrity of the tubes has already been destroyed. In view of these problems, it is necessary to figure out the formation process of the composites in order to tailor the configuration for further efficiency improvement.

In this study, composite electrodes of nanotubes and nanoparticles were prepared by hydrothermal treatment of the nanotubes in water at 90 °C for short periods (<5 h). The composites were systematically investigated and applied in dye-sensitized solar cells by either changing the treatment duration or tube length. The results indicate that, with an optimized treatment duration for a particular tube length, an optimal composite structure can be produced to utilize both the inner and outer tube walls while maintaining the tube features, thus increasing the power conversion efficiency.

2 Experimental

2.1 Anodization and hydrothermal treatment

Highly ordered TiO2 nanotube arrays were fabricated by electrochemical anodization using titanium foil (0.25 mm, 99.5% purity, Alfa Aesar) as the working electrode (back side unprotected23) and a platinum gauze as the counter electrode. Prior to the anodization, the foils were degreased in acetone, ethanol and deionized (DI) water for 20 min each and dried using a stream of air. The distance between electrodes was set at 22 mm. The electrolyte solution was ethylene glycol (extra pure, Merck) containing 0.3 wt% ammonium fluoride (98+% reagent, Sigma-Aldrich) and 5 vol% DI water. All of the anodizations were conducted at 50 V and at room temperature (~20 °C).

The resultant nanotubes were ultrasonically cleaned in ethanol/DI water (1 : 1, v/v) for 30 min to remove the nanowires accumulated on tube tops.20 Prior to ultrasonication, the as-anodized nanotubes were annealed at 200 °C for 2 h to increase the adhesion strength between the tubes and the titanium substrate. Subsequently, the cleaned and top-opened nanotubes were immersed in 20 mL DI water inside a Teflon-lined stainless steel autoclave for the hydrothermal treatment. The autoclave was kept in an oven at 90 °C for different durations (<5 h). After cooling down to room temperature in the oven, the samples were rinsed with DI water and dried in air.

2.2 Solar cell assembly

To obtain fully crystallized TiO2 nanotube arrays for use in DSSC devices, the pristine and hydrothermally treated nanotubes were subjected to thermal annealing at 450 °C for 3 h in air. Thereafter, the nanotubes were sensitized by soaking in a 0.3 mM solution of N719 dye (cis-diisothiocyanato-bis[2,20-bipyridyl-4,4’-dicarboxyato]ruthenium(II)bis(tetrabutylammonium), Solaronix) in acetonitrile/tert-butanol (1 : 1, v/v) solvent for 48 h. The sensitized nanotube arrays were assembled into DSSCs with platinized FTO glasses acting as the counter electrode, which were prepared by the thermal decomposition of a H2PtCl6 solution (0.6 mM) at 400 °C for 15 min. The two electrodes were separated using hot-melt films (SX1170, Solaronix, Switzerland) with a thickness of 25 μm. The electrolyte (EL HPE, Dyesol) containing an iodide/tri-iodide redox couple was introduced from one hole on the counter electrode under a partial vacuum. The active area of the cells was 0.26 cm2.

2.3 Characterizations

Top and cross-sectional views of the nanotube arrays were characterized by field emission scanning electron microscope (FESEM, JEOL, JSM-7600F). The morphology and structure of a single tube attached with nanoparticles were obtained by transmission electron microscopy (TEM, JEOL, JEM-2010, 200 kV). The phase compositions were examined with glancing angle X-ray diffraction (GAXRD, PANalytical Empyrean, Cu-Kα radiation).

The photocurrent–voltage characteristics of DSSCs were measured with a digital source meter (Keithley 2400) under simulated AM 1.5 illumination (100 mW cm−2) from a solar simulator (1 kW xenon with AM 1.5 filter, Müller). The amount of dye loading for the nanotube films was determined by measuring the UV-vis absorption spectra of the desorbed dye solutions. The dye molecules were desorbed by immersing the sensitized samples in a 0.1 M solution of NaOH in a mixed solvent system (water/ethanol = 1 : 1, v/v).

3 Results and discussion

3.1 Synthesis of the composite electrodes by hydrothermal treatment

Fig. 1(a, b) shows the pristine smooth TiO2 nanotubes with pore diameter of 92 ± 5 nm. The top-opened tubes are obtained after clearing away the undesired nanowires from the tube tops.20 Compared with conventional nanoparticles used in DSSCs, the large diameter tubes provide a much lower surface area for dye adsorption. In order to increase the

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**Fig. 1** FESEM images of the top (a, c, e) and cross-section (b, d, f) of the TiO2 nanotube arrays of 6.5 μm, without (a, b) and with hydrothermal treatment for 30 min (c, d) and 45 min (e, f).
surface area, the nanotubes were therefore subjected to hydrothermal treatment in water at 90 °C.

After 30 min treatment, only a few small particles of several nanometers form on both the inner and outer tube walls, as presented in Fig. 1(c, d). As the duration of the treatment is increased to 45 min, more particles of a larger size (ca. 20–40 nm) are obtained, as shown in Fig. 1(e, f). The newly formed particles on the tubes will enlarge the available surface area for dye adsorption. Meanwhile, the preserved tubular structure can provide a vectorial pathway for electron transport. Hence, the composite electrode will combine the merits of nanoparticles and nanotubes, which is desirable for efficient DSSCs. This is the most intriguing feature, which is in contrast to other reported composite structures16,21,22 where the integrity of the tubes is destroyed.

As the duration of the hydrothermal treatment increases to 1 h, the tubes almost convert into nanoparticles completely such that the top surface nearly loses its tube-like features, as presented in Fig. 2(a). Although the vertical alignment is still discernible in Fig. 2(b), the relevant magnifications reveal that the integrity of tube walls is nearly destroyed and each tube is composed of numerous nanoparticle segments, as detailed in the insets of Fig. 2(b). Fig. 2(c)–(e) shows that the upper part of the tubes are still hollow while the middle part is partially blocked and the lower part is completely filled with nanoparticles. This is ascribed to the abundant TiO2 source near the tube bottoms for nanoparticle formation, which is due to the V-shaped tube inner pores. When further increasing the duration (e.g., to 3 or 5 h), the nanotube arrays exhibit a similar morphology.

Accompanying the morphological evolution, the structure of the TiO2 nanotubes also changes with the duration of the hydrothermal treatment, as shown in Fig. 3(a). For the pristine nanotubes, only titanium peaks from the substrate are detected. Therefore, the original TiO2 nanotubes are still amorphous after annealing at 200 °C for 2 h to increase the adhesion between the nanotubes and the titanium substrate. Upon hydrothermal treatment, an anatase phase emerges and the peak intensity increases with treatment duration. It can be concluded that the hydrothermal process in water induces the phase transformation from amorphous to anatase, in line with the results reported elsewhere.21,24 For application in DSSCs, all of these nanotubes were annealed at 450 °C for 3 h. Fig. 3(b) reveals that all of the nanotubes entirely convert into the anatase structure upon annealing.

To gain further insight into the tube evolution upon hydrothermal treatment, the relevant nanotubes were characterized using transmission electron microscopy (TEM). Fig. 4(a) displays the representative morphology for one pristine nanotube, which exhibits a smooth hollow tubular structure with thick walls. The corresponding selected area electron diffraction (SAED) pattern indicates that the pristine tubes are amorphous. After hydrothermal treatment for 30 min, the tube walls are partially converted into nanoparticles while keeping the hollow tube structure, as illustrated in Fig. 4(b). The corresponding SAED pattern shows weak diffractions, confirming the presence of crystallites. This is
consistent with the pertinent XRD patterns shown in Fig. 3(a). When further prolonging the duration of the treatment to 45 min, the original tubular structure is still discernible with the tube being filled with big particles, as shown in Fig. 4(c), and more crystallites are thus formed (see the relevant inset). After 1 h, the tubes are transformed into nanoparticles completely, losing the tubular structure, as depicted in Fig. 4(d). The corresponding SAED pattern shows the typical features seen from nanocrystals. The TEM results are in fairly good agreement with the morphology and phase evolutions that are presented in Fig. 1–3.

Hydrothermal generation of TiO₂ nanoparticles is based on a dissolution–precipitation process in which water molecules play an essential role.²¹,²⁴,²⁵ The as-anodized TiO₂ nanotubes are amorphous and thermodynamically unstable in water. Water molecules adsorb onto the surface of the amorphous titania to combine with the basic octahedral titania unit of TiO₆²⁻. Subsequently, the dehydration of water leads to a regular arrangement of the octahedral unit and crystallization. Noticeably, stably crystallized tubes barely induce the dissolution–precipitation process, resulting in limited changes to the tube morphology and structure.²² In this process, the ambient temperature and pressure affect the nucleation and growth of the crystallites, influencing the final electrode configuration. Under the current experimental conditions, i.e., hydrothermal treatment at 90 °C, the size and amount of the nanoparticles increase with treatment duration. For short durations (below 1 h), amorphous tube walls partially dissolve and precipitate to form crystalline nanoparticles on the tubes. For long durations (above 1 h), the whole tube converts into a columnar structure consisting of nanoparticles and no discernible morphology change is observed for further prolonged treatment. Meanwhile, the relevant crystallinity enhances with the treatment duration, as can be seen from the increased intensity of the XRD (Fig. 3(a)) and SAED patterns (Fig. 4). It demonstrates that the morphological evolution and phase transformation occur simultaneously during the dissolution and precipitation process. As compared to previous reports,¹⁸,²¹ the hydrothermal treatment at elevated temperature (i.e., 90 °C) in this study drastically shortens the transformation time (i.e., ~1 h vs. 2–3 days). Furthermore, the nanoparticle size is much larger than that formed at room temperature (i.e., 20–40 nm vs. 3–10 nm)²¹ because the higher temperature and pressure facilitate the particle growth.

### 3.2 Application of the composite electrodes in DSSCs

The pristine and hydrothermally treated TiO₂ nanotubes were subsequently exploited as photoanodes in DSSCs. The photocurrent–voltage characteristics are shown in Fig. 5(a). Compared to solar cells based on pristine nanotubes, those based on the treated nanotubes exhibit a higher power conversion efficiency. The efficiency as a function of hydrothermal treatment duration is summarized in the inset of Fig. 5(a). It shows that the efficiency dramatically increases from 1.04% to 2.04% and then slightly drops to 1.63% as the duration increases. The enhancement in efficiency can be
ascribed to the nanoparticle formation under hydrothermal treatment, which enhances the dye adsorption properties. Fig. 5(b) shows the relevant dye loading study. From 30 min to 45 min, the remarkable increase in the amount of dye loading contributes to the abrupt efficiency enhancement, which in turn originates from the enlarged surface area from forming big nanoparticles (see Fig. 1 and 4). Further increase in the treatment duration has little influence on the dye amount, as the tubes convert into nanoparticles completely around 1 h (see Fig. 2 and 4). In addition, the filled tube bottoms and intertube spacing after long treatment durations (see Fig. 2) reduce the surface area for dye adsorption, thus lowering the photocurrent and power conversion efficiency. Moreover, the destroyed integrity of the nanotubes may deteriorate the charge collection process and therefore affect the cell performance, as shown from the decreased photocurrent with increased treatment duration (from 45 min to 5 h in Fig. 5(a)) under a similar amount of dye loading (see Fig. 5(b)). A detailed study of the electron transport and recombination in these composite nanostructures is currently under way. Eventually, the nanotubes under hydrothermal treatment for 45 min exhibit the highest efficiency in the present study, since they combine the advantages of nanoparticles and nanotubes.

Based on the above results, the as-anodized TiO₂ nanotubes with different tube lengths were subjected to hydrothermal treatment for 45 min in order to study the length effect. The corresponding photocurrent–voltage characteristics are given in Fig. 6(a). It shows that the cell photocurrent increases with tube length from 1.90 mA cm⁻² at 3.5 μm to 6.77 mA cm⁻² at 20.5 μm. This trend is in good agreement with the measurement of the amount of dye loading, as exhibited in Fig. 6(b). The amount of dye absorbed is in turn influenced by the available surface area of the nanotubes. For the shortest tubes of 3.5 μm, it shows that only a few small nanoparticles are on the tube surface while the tube walls are still smooth, as shown in Fig. 7(a, b). When the tube length increases to 6.5 μm, many big nanoparticles of 20–40 nm decorate the tube walls, after the same treatment duration (Fig. 1(e, f)). In this case, the surface area is greatly enlarged. This explains why the dye loading and efficiency are nearly tripled when tube length increases from 3.5 μm to 6.5 μm. For longer tubes of 16.5 μm, the whole of the tube is converted into nanoparticles (see Fig. 7(c, d)) which leads to a further increase in surface area and higher amount of dye loading. However, at the part nearest the tube bottom, it is evident that the original tubes have been completely filled with nanoparticles and become solid nanocolumns, as depicted in the inset of Fig. 7(d). As the length increases to 20.5 μm, the treated nanotube tops are almost completely covered with nanoparticles, as compared to that of the 16.5 μm long tubes, as illustrated in Fig. 7(e, f). The solid structures at the lower parts of tubes make it difficult for dye to attach. This is why the amount of dye loading does not increase greatly with longer nanotubes. Additionally, with longer tubes (>16.5 μm), the photovoltage is reduced due to increased electron recombination in the longer tubes. The reduction in voltage offsets the increase in photocurrent and eventually results in a similar conversion efficiency for solar cells with a tube length of over 16.5 μm (~2.2%). Therefore, nanoparticle formation under hydrothermal treatment is accelerated in longer tubes, due to the abundant titania source allowing the dissolution–precipitation process to occur. Consequently, for longer tubes (>6.5 μm), the hydrothermal treatment duration should be adjusted accordingly to obtain

![Fig. 6 Photocurrent–voltage characteristics of DSSCs based on TiO₂ nanotubes of different lengths (a) and the corresponding dye loading amount (b) under hydrothermal treatment of 45 min.](image)

![Fig. 7 FESEM images of top (a, c, e) and cross-sectional (b, d, f) morphologies for the TiO₂ nanotube arrays treated for 45 min, with lengths of 3.5 μm (a, b), 16.5 μm (c, d), and 20.5 μm (e, f). The inset of (d) shows the bottom part of the corresponding tubes.](image)
the preferred composite electrode of nanotubes and nanoparticles. This has been proved in Fig. 8, where nanotubes of 16.5 μm in length were treated for less than 45 min. The photovoltaic device exhibits the best performance when the treatment duration is reduced to around 15 min. All the characteristics are improved when compared to the devices with tubes treated for 45 min (photocurrent: 8.82 vs. 6.04 mA cm⁻², photovoltage: 0.70 vs. 0.67 V, fill factor: 0.57 vs. 0.55). Eventually, a power conversion efficiency of 3.54% is achieved. Therefore, an optimal treatment duration exists for a particular tube length. For long tubes, the treatment duration should be shortened to obtain an optimized composite structure, which makes full use of both outer and inner tube walls while also conserving the tube features.

**4 Conclusions**

It is facile and effective to create TiO₂ nanoparticles on anodic nanotubes using a hydrothermal treatment in water. The tube morphology and structure evolve with the duration of the hydrothermal treatment. For tubes with a length of 6.5 μm, within 1 h titania nanoparticles form on both the inner and outer tube walls while keeping the integrity of the tubes. At prolonged times exceeding 1 h, the nanotubes are entirely converted into nanoparticles. At 45 min, the best efficiency of 2.04% is obtained due to the combined effect of a high surface area from the nanoparticles and the vectorial electron transport from the still preserved nanotubes. For tubes of different lengths under the same treatment duration (i.e., 45 min), the efficiency of solar cells increases with tube length up to 16.5 μm, but this stays nearly constant over 16.5 μm. This is owing to the accelerated nanoparticle formation in longer tubes, which fill the lower parts of the tubes and hence reduce the available surface area for dye attachment. Accordingly, a further efficiency enhancement of 3.54% is achieved using nanotubes of 16.5 μm by shortening the treatment duration to only 15 min.

**Acknowledgements**

We thank Yong Mei Yoke of the Materials Lab of School of Mechanical and Aerospace Engineering, Nanyang Technological University, for her assistance in TEM measurements. This work is also supported by CISRI grant: 11020990A.

**References**