Dye-Sensitized TiO₂ Nanotube Solar Cells: Rational Structural and Surface Engineering on TiO₂ Nanotubes

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Abstract: Owing to well-defined structural parameters and enhanced electronic properties, highly ordered TiO₂ nanotube arrays have been employed to substitute TiO₂ nanoparticles for use in dye-sensitized solar cells. To further improve the performance of dye-sensitized TiO₂ nanotube solar cells, efforts have been directed toward the optimization of TiO₂ photoanodes, dyes, electrolytes, and counter electrodes. Herein, we highlight recent progress in rational structural and surface engineering on anodic TiO₂ nanotube arrays and their effects on improving the power conversion efficiency of dye-sensitized TiO₂ nanotube solar cells.

Keywords: dye-sensitized solar cells • electrochemistry • nanostructures • surface chemistry • titanium

1. Introduction

Dye-sensitized solar cells (DSSCs) composed of nanostructured photoanodes (e.g., TiO₂ nanoparticle (NP) films), dyes, redox electrolytes, and counter electrodes have received considerable interest in the past two decades owing primarily to their high solar-to-electricity conversion efficiency at a very competitive fabrication cost.[1] They present an attractive alternative to conventional silicon-based solar cells. Tremendous efforts have been concentrated on improving device performance and stability by optimizing each component in the DSSCs and the design of device configuration to realize their significant commercial potentials.[2] Recent years, highly ordered TiO₂ nanotube (NT) arrays, fabricated by electrochemical anodization of titanium in fluorine-containing electrolytes,[3] have been utilized as photoanodes for DSSCs and shown improved charge-collection efficiency and enhanced light scattering compared with commonly used TiO₂ NP films (TPs).[1a,2b,3e,4] Vertically oriented TiO₂ NT arrays (TNAs) with well-defined structural parameters, including pore size, tube length, wall thickness, and surface chemistry, can be obtained by tuning the conditions of electrochemical anodization.[3c,4] In comparison to electron hopping between TiO₂ NPs in conventional TiO₂ photoanodes, vertically aligned TiO₂ NTs provide a vectorial charge-transport pathway along the long axis of the NTs, thereby imparting longer electron lifetimes and reduced charge recombination (Scheme 1).[2b,4c,5] However, the overall power conversion efficiency of dye-sensitized TiO₂ NT solar cells remained relatively low as a result of incomplete coverage of dye molecules on the TiO₂ NT surface and insufficient infiltration of electrolyte into NTs. Clearly, the optimization of structural parameters and surface properties of TNAs is of key importance to achieve larger surface areas for increased dye loading, better electronic interaction between dye and TiO₂ surface, and more efficient charge transport.

Herein, we aim to highlight recent progress in improving the performance of dye-sensitized TiO₂ NT solar cells through rational structural and surface engineering on TiO₂ NTs. First, we discuss the effects of structural modification on TNAs on the performance of the resulting solar cells, including the integration of TiO₂ NPs with TNAs, the formation of hierarchically structured TiO₂ NTs, the construction of 3D NT arrays on Ti wire and mesh, and new designs of dye-sensitized double-sided NT arrays. Subsequently, we assess the influence of surface engineering (i.e., TiCl₄ treatment, oxygen plasma activation, and the doping of TNAs with a secondary species) on the photovoltaic performance of dye-sensitized TiO₂ NT solar cells.

2. Structural Engineering on TNAs

2.1. Integration of TiO₂ NPs with TiO₂ NTs

Integrating a TP with highly ordered TNAs has yielded two typical configurations of photoanode in DSSCs: a TP–TNA bilayer[6] and TNAs filled with TiO₂ NPs.[7] Zheng et al. constructed a layer-by-layer hierarchical photoanode consisting of a TP and free-standing TNAs for DSSCs (Figure 1), which exhibited increased light-harvesting efficiency, longer electron lifetimes, and more efficient electron extraction than those in single NP-film- or NT-array-based devices.[8] Notably, TiO₂ NPs used in this work were prepared by breaking crystallized TNAs with high intensity ultrasonication because crystalline TiO₂ NTs were composed of small TiO₂ nanocrystals and could be deformed by strong mechanical force.[9] With the optimum thickness of the TP (8 μm) and TNAs (9 μm) in the FTO-TP-TNA (FTO = fluorine-doped tin oxide) configuration, an overall power con-
version efficiency, (PCE), of 8.80% was obtained under AM 1.5 simulated sunlight (Figure 1, right), whereas for the FTO-TNA-TP configuration the highest PCE was 6.03% (Figure 1, left). It was suggested that electron extraction from TP to the FTO glass was better than that from TNA to the FTO substrate as a result of less interfacial resistance.\[6a\] Using a similar FTO-TP-TNA configuration of photoanode, Lin et al. demonstrated greatly increased PCE by opening the closed bottom of the TNAs through oxalic acid etching.\[6b\] Compared with the closed-end TiO\textsubscript{2} NT, open-end TiO\textsubscript{2} NT allowed the redox electrolyte to easily reach the TP layer, thereby leading to more efficient light harvesting and electron transport along the NTs. As a result, a PCE of 9.1% (AM 1.5, front illumination mode) was achieved when open-end TNAs were utilized to construct the DSSC, corresponding to a 70% enhancement in efficiency relative to the device made with closed-end TNAs (PCE = 5.3%).

Infiltrating TiO\textsubscript{2} NTs with TiO\textsubscript{2} NPs was investigated to increase the surface area on the TiO\textsubscript{2} photoanode for higher dye loading. Figure 2 shows the SEM images and illustrations of TiO\textsubscript{2} NTs before and after infiltration with 14 nm TiO\textsubscript{2} NPs. When using TNAs impregnated with TiO\textsubscript{2} NPs as the photoanode in DSSCs, a 30% increase in PCE was yielded (i.e., increase from PCE = 3.46 to 4.56%), which was attributed primarily to enhanced photocurrent as a result of increased dye loading. The device performance was further improved to PCE = 5.39% by coating the TiO\textsubscript{2} photoanode with a thin layer of strontium oxide, which acted as a potential barrier layer to improve the open-circuit voltage, $V_{oc}$.\[7a\] Infiltration of TiO\textsubscript{2} NPs into TiO\textsubscript{2} NTs can be achieved by vacuum filling by utilizing a colloidal solution of TiO\textsubscript{2},\[7a–c\] ultrasonication-assisted filling, \[7d\] and electrophoretic deposition.\[7e\]

2.2. Hierarchically Structured TNAs

By adjusting the electrochemical anodization conditions or by applying hydrothermal treatment on TiO\textsubscript{2} NTs, hierarchically structured TNAs can be produced; these exhibited improved device performance when used as photoanodes in DSSCs owing to the greatly increased surface area for more efficient dye loading and improved light management.

Kim et al. reported the fabrication of bamboo-type TNAs by exploiting appropriate alternative voltage cycling (Figure 3).\[8\] The formed TiO\textsubscript{2} NTs exhibited much larger surface areas because of increased surface roughness, thereby enhancing dye loading (i.e., $L_{dye} = 52$ (NT; Figure 3b), 69 (B-NT1; Figure 3c), and 78 a.u. (B-NT2; Figure 3d), and
thus, improved PCE in the dye-sensitized TiO$_2$ NT solar cells (i.e., PCE = 1.90 (NT), 2.48 (B-NT1), and 2.96% (B-NT2)).

Yip et al. developed a one-step approach to fabricate a bilayer structure composed of a photonic crystal (PC) layer and a TiO$_2$ NT layer (Figure 4).

First, the PC layer was obtained on titanium foil through periodic current pulse anodization, followed by the formation of a smooth TiO$_2$ NTs layer by single constant-current anodization. The PC layer on top of TiO$_2$ NTs can enhance light harvesting within the absorption range of the dye. The axial lattice constant of the PC layer can be readily tuned by adjusting the parameters for pulsed current pulse anodization. DSSCs fabricated with a PC–NT bilayer photoanode had a larger PCE than that of the device made with NT only, that is, PCE = 5.61% for a photoanode with a purple PC layer compared with PCE = 3.66% for a reference cell without a PC layer.

Hydrothermal treatment on ordered TNAs is an alternative approach to construct hierarchically structured TNAs, resulting in greatly increased surface roughness for more efficient dye loading. Ye et al. demonstrated increased roughness on the TiO$_2$ NT surface by hydrothermally treating TiO$_2$ NTs in an aqueous solution containing (NH$_4$)$_2$TiF$_6$, in which smooth TiO$_2$ NTs transformed into rough NTs deo-
rated with small TiO$_2$ NPs. Such structural transformation resulted from competition between two reactions, namely, hydrolysis of Ti$^{4+}$, which favored the formation of TiO$_2$ NPs, and chemical etching (i.e., dissolution) owing to the presence of F$^-$. As a result, the dye loading increased and a PCE value of over 7% was obtained. By hydrothermal processing of TNAs in an aqueous solution containing hydrochloric acid and titanium tetraisopropoxide (TTIP), Hu et al. grew TiO$_2$ nanorod branches on a TiO$_2$ NT surface (Figure 5). Compared with untreated TNAs, the obtained TiO$_2$ nanorods branched on the TNAs exhibited enhanced dye adsorption capability (i.e., dye loading increased from 66 to 88 mm$^3$). Consequently, the PCE value improved from 1.87 to 3.18% under AM 1.5G simulated sunlight conditions.

### 2.3. TNAs Grown on a Structured Ti Electrode

In addition to the growth of well-ordered TNAs on flat substrates, such as titanium foil and FTO glass, the fabrication of TiO$_2$ NTs on titanium wires and titanium meshes were also reported. The resulting intriguing cylindrical core/shell-like TNAs were directly used as photoanodes in DSSCs.

Figure 6 shows the structural characterization of cylindrical TNAs fabricated by electrochemical anodization of titanium wire in ethylene glycol containing a small amount of ammonium fluoride. Highly ordered TNAs were grown uniformly on the surface of the titanium wire, thus forming cylindrical Ti@TiO$_2$ core/shell wires. Figure 7 depicts a fiber-type DSSC (F-DSSC), capitalizing on cylindrical TNAs as the photoanode, in which the titanium wire core served as an electrode for the collection of electrons and a platinum wire wrapped around the Ti@TiO$_2$ wire acted as a counter electrode. Semi- or all-solid-state electrolyte was placed between dye-sensitized TNAs and the surrounding platinum wire. The PCE values of the semisolid and all-solid F-DSSC were approximately 1.5 and 0.21%, respectively.
Titanium mesh was also anodized in fluorine containing an electrolyte to yield a 3D array of TiO$_2$ NTs (Figure 8). Vertically oriented TiO$_2$ NTs with tunable pore sizes and thicknesses were produced on the surface of titanium wires by adjusting the electrochemical anodization conditions. It is noteworthy that the ability to form TNAs on flexible titanium mesh opens up new opportunities to fabricate lightweight and flexible DSSCs. An overall PCE of 5.0% was achieved with optimum structural parameters (i.e., tube diameter, length of NT, and size of the Ti mesh).

2.4. Double-Sided Anodic TNAs

During electrochemical anodization, both sides of a flat titanium foil can be anodized to obtain a TiO$_2$ NT/Ti foil/TiO$_2$ NT three-layer thin film (i.e., double-sided TNAs), which has been utilized as a photoanode to construct dye-sensitized TiO$_2$ NT solar cells with improved dye loading and PCE values.

The configuration of a bifacial dye-sensitized TiO$_2$ NT solar cell, capitalizing on a TiO$_2$ NT/Ti foil/TiO$_2$ NT film as the photoanode and the characteristic current density–voltage curves with one- and double-sided illumination, are shown in Figure 9. Under double-sided illumination, the photocurrent density was almost twice that of one-sided illumination (i.e., 11.9 vs. 6.05 mA cm$^{-2}$). Clearly, a new design of device configuration is necessary to achieve simultaneous double-sided illumination for viable applications.

In this context, recently Sun et al. demonstrated a new parallel configuration of DSSCs using double-sided TNAs as the photoanode and a dielectric mirror for light reflection. The latter allowed illumination on both sides of the device with sunlight coming in one direction (Figure 10). An average 70% increment in photocurrent and 30% enhancement in PCE were obtained relative to those of the single cells; this was due to markedly increased surface area and highly reduced series resistance. Although the PCE value was relatively low (PCE = 1.74%), the use of a dielectric mirror to obtain simultaneous double-sided illumination was intriguing and provided insight into the design of DSSCs with optimized photoanode structures.

3. Surface Engineering on TNAs

Rational surface engineering on TiO$_2$ NTs prior to dye loading, including TiCl$_4$ treatment, oxygen plasma activation, and doping with metal or metal oxide, has been particularly beneficial for increasing surface roughness, enhancing dye
adsorption, and improving electronic interactions between the dye and TiO₂, thereby promoting the overall PCE of dye-sensitized TiO₂ NT solar cells.[3d,5,19]

TiCl₄ treatment on TNAs leads to increased surface roughness by forming small TiO₂ NPs on the TiO₂ NT surface, which provides a larger surface area for the adsorption of more dye molecules. TiCl₄ treatment could also improve electronic interactions between dye molecules and TiO₂, thereby enabling more efficient charge injection from the excited dye to the conduction band of TiO₂.[3d,5,6b,12,19k] TiCl₄ treatment is usually carried out by immersing the TNA in an aqueous solution of TiCl₄ at a slightly increased temperature, followed by annealing at high temperature to create crystalline TiO₂ NPs on the NT surface.[19h] Figure 11 shows SEM images of TNAs before and after TiCl₄ treatment; the increased surface roughness is clearly evident. Significantly higher dye loading on TiO₂ NT treated with TiCl₄ resulted and a doubling of the PCE from 1.9 to 3.8% was achieved.[19h]

Oxygen plasma exposure on TNAs substantially promotes the surface hydrophilicity of TiO₂ by increasing the number of hydroxyl groups on the TiO₂ surface; this facilitates dye adsorption.[5,12,19b] The increased surface hydrophilicity is also beneficial for the infiltration of dye solution (i.e., dye dissolved in ethanol) all the way into TiO₂ NTs, favoring increased dye loading.[5,19b] Characteristic I–V curves of dye-sensitized TiO₂ NT solar cells, as a result of surface treatments with TiCl₄ and oxygen plasma exposure, are shown in Figure 12. The thickness of the TNAs was 14 μm. The PCE was improved upon a longer period of oxygen plasma exposure time, and the maximum PCE was obtained with 10 min oxygen plasma activation (Figure 12c).[5] Intriguingly, the device performance decreased upon lengthy exposure to oxygen plasma (Figure 12d), which may be attributed to the decreased surface hydrophilicity of TiO₂ after longer oxygen plasma treatment.[20]

It is worth noting that TNAs can be modified through doping with a beneficial secondary species, such as boron,[19c,e] nitrogen,[19g,l,n,21] niobium,[19j] and magnesium,[19f] which effectively improves the electronic properties of TiO₂, leading to enhanced device performance. Figure 13 shows the effect of niobium doping on the PCE of dye-sensitized TiO₂ NT solar cells, in which niobium was added to the TNAs by directly anodizing the Nb–Ti alloy in fluorine-containing electrolyte.[19] The device performance improved up to 30% with less than 1 wt% niobium in the TNAs compared with nondoped TiO₂ NTs.

A thin layer of MgO deposited on the TiO₂ NT surface by a simple hydrothermal approach improved both the photocurrent and photovoltage in dye-sensitized TiO₂ NT solar cells.[19l] The formation of a MgO layer on the TiO₂ NT surface not only increased the surface area for more efficient dye loading, but also acted as an energy barrier layer to...
reduce charge recombination between TiO$_2$ and the electrolyte.

4. Summary and Outlook

We have highlighted recent efforts to improve the performance of dye-sensitized TiO$_2$ NT solar cells through rational structural and surface engineering on anodic TNAs. A wide range of approaches have been developed to structurally modify TiO$_2$ NTs, including the introduction of TiO$_2$ NPs with NTs, the formation of hierarchically structured TiO$_2$ NTs, the construction of 3D NT arrays on titanium wire and mesh, and a new design of dye-sensitized double-sided TNAs. Judicious surface engineering on TNAs can be realized by TiCl$_4$ treatment, oxygen plasma activation, and doping with a secondary species. Such advantageous modifications on TNAs have led to significantly improved PCE values in the resulting dye-sensitized TiO$_2$ NT solar cells. In parallel with progress being made in seeking the optimization of dyes, electrolytes, and counter electrodes, these development activities may yield even higher photovoltaic performances.

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Figure 13. J–V characteristics of dye-sensitized TiO$_2$ NT solar cells fabricated with Nb-doped TiO$_2$ NTs with different annealing temperatures and concentrations of Nb: a) TiO$_2$ NTs and 0.1 Nb–TiO$_2$ annealed at different temperatures; and b) TiO$_2$ NTs doped with different concentrations of Nb. (Reprinted with permission from Ref. [19].)