Review Article

One-Dimensional TiO$_2$ Nanostructures as Photoanodes for Dye-Sensitized Solar Cells

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Received 22 December 2012; Accepted 2 February 2013

Academic Editor: Xijin Xu

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Titanium dioxide (TiO$_2$) is a star material due to its remarkable optical and electronic properties, resulting in various applications, especially in the fields of dye-sensitized solar cells (DSSCs). Photoanode is the most important part of the DSSCs, which help to adsorb dye molecules and transport the injected electrons. The size, structure, and morphology of TiO$_2$ photoanode have been found to show significant influence on the photovoltaic performance of DSSCs. In this paper, we briefly summarize the synthesis and properties of one-dimensional (1D) TiO$_2$ nanomaterials (bare 1D TiO$_2$ nanomaterial and 1D hierarchical TiO$_2$) and their photovoltaic performance in DSSCs.

1. Introduction

Titanium dioxide (TiO$_2$) is one of the most extensively studied oxides because of its remarkable optical and electronic properties. Due to its unique physical and chemical properties, TiO$_2$ has been extensively used for various applications, such as dye-sensitized solar cells (DSSCs), lithium ion batteries (LIBs), photocatalysis, water treatment, and gas sensors [1–21].

A typical DSSC consists of a dye-sensitized semiconductor electrode, redox electrolyte, and counter electrode [23, 24]. Once dye molecules absorb light, the excited dye injects electrons to the semiconductor. At the same time, the oxidized dye cation is reduced by the redox electrolyte, which competes with the recombination of injected electrons. Electrons are collected at the semiconductor electrode, pass through the external circuit, and then reenter the cell at the counter electrode to reduce the oxidized electrolyte [25]. A closed circuit is thereby established to continuously convert the solar light to electricity. Nanostructure-based DSSCs show advantages of low cost, high efficiency, and simple in preparation, which is promising as a renewable energy resource for sustainable development of the future [2, 23, 26, 27]. A breakthrough in DSSCs was achieved in 1991, O’Regan and Grätzel firstly introduced wide bandgap semiconductor nanoparticle (TiO$_2$ nanoparticle) into DSSCs as the transporting medium of photo-induced electrons, and conversion efficiency was reached to 7% [2]. Recently the efficiency of DSSCs has been increased to 12.3% [28].

Dye-sensitized semiconductor electrode is usually the efficiency determining component of DSSCs due to the competition between electron separation and recombination accompanying with many electron transfer processes [5, 29, 30]. In brief, semiconductor oxides receive the injected electrons from the excited state of sensitizer dye, and the electrons could be competitively trapped by oxidized dye cation, I$_3^-$ anion in electrolyte, and surface state in TiO$_2$ (e.g., oxygen vacancy) that is known as recombination, before they are transported to an external circuit. The described electron transfer processes in the semiconductor electrode affect essentially conversion efficiency of DSSCs, which depends on the nature and morphology of nanocrystalline semiconductor oxides [31–34].

Wide bandgap semiconductor nanoparticles were the first material used as an efficient photoanode. Due to the small size of the nanoparticles, it can provide a large surface area and a relatively high porosity [2], possible to adsorb enough dye for efficient light harvesting and a relative high...
conversion efficiency. However, TiO$_2$ nanoparticles used in DSSCs are usually as a random network of crystallographically misaligned crystallites, and lattice mismatches at the grain boundaries could influence electron scattering and act as electron trap [31, 34, 35]. This could limit electron transport and reduce electron lifetime. Further improvement of DSSC-based nanoparticle is hindered by the previous drawbacks. One-dimensional TiO$_2$ nanostructures [36–48] have a relatively small amount of grain boundaries and can act as single crystal, which is able to reduce the grain boundary effect and provide fast electron transport. It shows great potential in achieving high performance DSSCs. The recombination rate in TiO$_2$ nanotubes has been found to be 10 times slower than that in nanoparticles [37]. However, it is more difficult for the liquid electrolyte to penetrate into one-dimensional titania than into nanoparticles network, because the one-dimensional titania has usually relatively low surface area, large size, and inefficient intact surface compared with nanoparticles. This usually leads to a large interface charge-transfer resistance for one-dimensional nanostructured materials-based photoanode.

To resolve the drawbacks of the nanoparticles and 1D nanostructures, 1D hierarchically structured materials were designed by combining nanoparticles and nanorods or nanowires. They have been used to take advantage of both the large surface area of nanoparticles and efficient charge transport of 1D nanostructures [50]. The interpenetration of electrolyte in the 1D hierarchical structure could be improved, and the interfacial area could be increased which might leads to more electron separation and fast transport [31, 34, 35, 51–57]. Compared with the nanoparticles and 1D nanostructures, the photovoltaic properties of 1D hierarchical structure are superior. This indicate a potential approach to overcome the limitations of nanoparticles and one-dimensional nanostructures as photoanode materials, though the increase of the grain boundary effect is inevitable in a hybrid structure matrix due to the formation of grain boundaries between nanoparticles and nanorods or nanowires.

In this paper, we review the recent developments in using of one-dimensional (1D) nanostructures as photoanodes for efficient DSSCs. Various randomly oriented and vertically aligned 1D nanostructures, and their composites with nanoparticles used in DSSCs are discussed, for which the order is randomly oriented 1D nanotubes and nanorods, vertically aligned 1D nanotubes and nanorods, randomly oriented 1D hierarchical TiO$_2$ and vertically aligned 1D hierarchical TiO$_2$.

2. Applications in DSSC Photoanode

The photoanode shows significant effects on the photocurrent and photovoltage of a DSSC. As a key material in photoanode, fast electron transfer kinetics of TiO$_2$ are necessary to avoid photoelectron recombination, which usually depends strongly on the micromorphology and crystallographic structure of TiO$_2$. Therefore, it is very important to synthesize controllably titania nanomaterials with specific structures and big surface area with optimized electron transfer kinetics.

2.1. Randomly Oriented 1D TiO$_2$

2.1.1. Randomly Oriented 1D TiO$_2$ Nanotube. To overcome the electron transport limit of nanoparticles, TiO$_2$ nanotubes were the first reported 1D nanomaterial for use as a bifunctional photoanode material, which exhibiting both efficient generation of photon-generated electrons and good light-scattering property. Uchida et al. [58] have developed a facile one-step hydrothermal method to synthesize TiO$_2$ nanotube [59]. The nanotube is 100 nm long with an outer diameter of...
8 nm. The specific surface area can reach to 270 m$^2$/g. DSSC with such nanotube showed a 2.9% conversion efficiency, which was not better than that of nanoparticles. The main reason for the previous result may due to the aggregate of the TiO$_2$ nanotube, which could reduce electricity contact and increase impedance between TiO$_2$ nanotube and conductive glass. And the nanotube wall here could also block the diffusion of the $I^-/I_3^-$.

To synthesize TiO$_2$ nanotube with high dispersion and crystallization could improve the photoelectrochemical
properties. Adachi et al. [60] and Ohsaki et al. [22] have reported such TiO$_2$ nanotubes (TNTs) with large aspect ratio and large specific surface area. The conversion efficiency could reach to 6.4% (Figure 1). After treating with the TiCl$_4$, the conversion efficiency could increase to 7.1%. Single crystal of TiO$_2$ facilitates the fast transport of electron. And large aspect ratio of TiO$_2$ nanotubes could help to reduce the grain boundary effect. The research also indicated that the increased electron density and electron lifetime in the photoanode could be beneficial for the improved photoelectrochemical properties.

Our group [16] also reported the protonated TiO$_2$ nanotube prepared from one-step hydrothermal method with anatase TiO$_2$ and 10 M NaOH solution as the starting materials [15, 61]. After being calcined at 400°C, single crystal of TiO$_2$(B) nanotube was obtained (Figure 2). Although nanotubes have the advantage in morphology and surface area for enhancing photoelectrochemical performance, TiO$_2$(B) nanotubes in this work showed relatively poor photovoltaic properties with the $n$ value of only 1.05%. The poor performance here was mainly related to the serious recombination in numerous surface defects and a relatively open tunnel structure of TiO$_2$(B) [15]. Higher temperature calcination would reduce the surface defects, but the tube morphology could not exist.

### 2.1.2. Randomly Oriented 1D TiO$_2$ Nanorod

One-dimensional TiO$_2$ nanorods have a relatively small amount of grain boundaries and can act as single crystal, which is able to reduce the grain boundary effect and provide fast electron transport [51–53]. And the rod could keep the rod morphology with higher temperature calcination. Many researches were focused on TiO$_2$ nanorods.

Jiu et al. [49, 62] have reported single crystalline anatase TiO$_2$ nanorods synthesized by surfactant-assisted hydrothermal method. Short rods with the diameter 20–30 nm and length 100–150 nm have been obtained (Figure 3). The clear lattice strips indicated that the nanorods with high crystallinity and fewer defects have been obtained, which is beneficial for the transfer of electrons in the rods. A high light-to-electricity conversion yield of 7.06% was achieved by applying the TiO$_2$ nanorods as thin film of dye-sensitized solar cells. The nanorod shows the same advantages as nanotubes: the fast electron transport, the reduced recombination, and the long lifetime.

We also fabricated such small size nanorods with a special method different from the tradition. The nanorods were obtained by calcination of protonated TiO$_2$ nanotube at 600°C for 2 h [16]. It is much thicker and shorter with a diameter of 15–30 nm and a length of about 100 nm. The interference fringe spacing of the nanorods is about 0.35 nm, corresponding to the interplanar distance of the (101) plane in the anatase phase. And the conversion efficiency could reach to 7.71%. IMPS and IMVS were used to investigate further the electron transport and recombination processes, as shown in Table 1. Compared with nanotube calcined at 400°C, nanorods calcined at 600°C show a longer lifetime, which is over 10-fold longer than that for TiO$_2$(B) nanotube and a shorter electron transport time only half of the TiO$_2$(B) nanotube. This indicates that anatase nanorods with a good crystallinity are beneficial to a faster electron transport and a longer electron lifetime. In fact, it is considered that the

#### Table 1: Detailed IMPS/IMVS parameters of the DSSC with titanate nanotubes calcined at different temperatures [16].

<table>
<thead>
<tr>
<th>Calcination temperature</th>
<th>$\tau_a$ (ms)$^a$</th>
<th>$\tau_n$ (ms)$^a$</th>
<th>$D_n$ (cm$^2$/s)$^a$</th>
<th>$L_n$ ((\mu)m)$^a$</th>
</tr>
</thead>
<tbody>
<tr>
<td>400°C</td>
<td>1.83</td>
<td>14.2</td>
<td>3.5 × 10$^{-4}$</td>
<td>22.3</td>
</tr>
<tr>
<td>500°C</td>
<td>1.18</td>
<td>53</td>
<td>5.4 × 10$^{-4}$</td>
<td>53.6</td>
</tr>
<tr>
<td>600°C</td>
<td>0.94</td>
<td>106</td>
<td>6.8 × 10$^{-4}$</td>
<td>85</td>
</tr>
<tr>
<td>700°C</td>
<td>1.47</td>
<td>17.7</td>
<td>4.4 × 10$^{-4}$</td>
<td>278</td>
</tr>
</tbody>
</table>

![Figure 4](image-url)
good crystallinity and the cylindrical geometry could allow the nanorods to support radial electric fields, which could keep the electrons away from the nanorods surface, thereby reducing surface electron densities and recombination.

2.2 Vertically Aligned 1D TiO$_2$. Randomly oriented 1D TiO$_2$ nanomaterial undoubtedly plays as the “electron speedways”; however, these nanotubes and nanorods are disordered and random. It has not realized the direct electron transport. So, it is significant to design and study the vertically aligned 1D TiO$_2$ nanomaterial would be much more significative.

2.2.1 Vertically Aligned 1D TiO$_2$ Nanotube. Vertically aligned TiO$_2$ nanotubes provide a vertical pathway for electron transport along the tube and thus minimize electron loss during diffusion process, and the vertically ordered tubular structure will facilitate the filling of new sensitizer or electrolyte for a further increase in efficiency. As such, self-aligned TiO$_2$ nanotube arrays have been widely studied for applications as photoanodes in DSSCs [65–74].

Mor et al. [38] have reported a highly ordered 360 nm long TiO$_2$ nanotube arrays, made by anodization of thick-film titanium foil (Figure 4). After treating with TiCl$_4$ and
Figure 7: (a) Schematic diagram of the dye-sensitized solar cell with the one-dimensional hierarchical titania as photoanode on FTO, showing the processes involved in current generation. (b, c) TEM images of the one-dimensional titania with hierarchical structures after calcination at 300°C (b) and 700°C (c). (d, e) The electron lifetime ($\tau_n$) (d) and electron transport time ($\tau_d$) (e) for DSSCs of titania with hierarchical structures, nanorods, and nanoparticles [50].
calcining at 450°C, a highly ordered photoanode was obtained. The DSSC exhibited a $J_{sc}$ of 7.87 mA/cm$^2$, a $V_{oc}$ of 0.75 V, and an overall conversion efficiency of 2.9%. This result was no better than nanoparticles. A low surface area with a length of only 360 nm could be responsible for the result of insufficient dye-loading and low light-harvesting efficiency. However, highly ordered arrays showed a long lifetime and excellent electron transport path compared to nanoparticles. To resolve the problem of the low surface area, many efforts were done. Nanotubes with lengths up to 100 μm have been produced to increase the surface area for dye-loading [63, 75]. Shankar et al. [63] even obtained ultralong TiO$_2$ nanotubes with length over 200 μm (Figure 5), which delivered significantly improved DSSC efficiency of 6.89%. However, synthesis of these ultralong nanotubes costs much time (more than 10 h) and electricity for anodization process, and the reported efficiencies of TiO$_2$-nanotube-array-based DSSCs are still lower than DSSCs based on mesoporous TiO$_2$ films due to the relative low internal surface area for dye-loading of nanotube arrays [44, 76, 77].

### 2.2.2. Vertically Aligned 1D TiO$_2$ Nanorod

Different from 1D nanotube array, DSSCs based on 1D TiO$_2$ nanorods array remain a challenge [43, 78–86], which is mainly owing to the low dye-loading ability resulting from the insufficient specific surface area. Liu and Aydil [44] reported a facile, hydrothermal method for the first time to grow oriented, single-crystalline rutile TiO$_2$ nanorod films on transparent conductive fluorine-doped tin oxide (FTO) substrates (Figure 6). The growth parameters, such as growth time, growth temperature, initial reactant concentration, acidity, and types additives, could effectively influence the diameter, length, and density of the nanorods. A small lattice mismatch between the FTO substrate and rutile TiO$_2$ is key in driving the nucleation and growth of the rutile TiO$_2$ nanorods on FTO. 4 μm long TiO$_2$ nanorod films were obtained through the previous method. After treating with TiCl$_4$, a light-to-electricity conversion efficiency of 3% was achieved.

Many efforts have done to modify the oriented rutile TiO$_2$ nanorod to improve the photoelectrochemistry properties. Lv et al. [87] have reported a densely aligned TiO$_2$ nanorod arrays (NRAs) with high surface area. Theses densely aligned TiO$_2$ NRAs with tunable thickness were grown directly on transparent conductive fluorine-doped tin oxide (FTO) substrates by hydrothermal method. Dilute hydrochloric acid was used as chemical etching liquid to further increase the specific surface area of the TiO$_2$ NRAs. TiO$_2$ nanorods were split into secondary nanorods with a reduced diameter during the etching treatment. And the inner surface area of the TiO$_2$ NRAs was markedly enlarged. Finally, a conversion efficiency of 5.94% was achieved by using such NRAs. It is so far the best reported results for the 1D rutile TiO$_2$ NRA films.

### 2.3. 1D Hierarchical TiO$_2$ Nanomaterial

TiO$_2$ nanoparticles used in DSSCs have its limitations, such as influencing the electron scattering and acting as an electron trap. 1D nanostructured TiO$_2$ could reduce the grain boundary effect and provide fast electron transport. However, it is more difficult for the liquid electrolyte to penetrate into one-dimensional titania than into nanoparticles network. And the small surface area would block the improving of the photoelectrochemistry properties. In general, fast reaction kinetics (fast electron transport, long electron lifetime, and less recombination) together with large specific surface area are the essential properties of the superior photoanode materials with excellent photoelectrochemical properties.

#### 2.3.1. Randomly Oriented 1D Hierarchical TiO$_2$

To achieve highly efficient DSSCs, one-dimensional hierarchical composites were designed as show in Figure 7 [50], which combine the high electron transport from 1D nanostructures and large surface area to attach enough dyes from nanoparticles. A proposed electron transfer model is shown in the following; the injected electrons in the nanoparticles standing on nanorods are subject to transfer into the nanorods and then are rapidly transported to FTO substrate due to the single-crystal feature of the nanorods. The results indicate that one-dimensional hierarchical titania cannot only provide a matrix similar to the hybrid structure matrix but also avoid forming a large amount of grain boundaries with optimized fast reaction kinetics: low charge-transfer resistance, fast electron transport, and long electron lifetime. And the existed nanoparticles greatly improve the surface area of the nanorods. The conversion efficiency of one-dimensional
hierarchical titania can reach to 4.46%, which is about 5 times higher than that of their corresponding nanorods.

2.3.2. Vertically Aligned 1D hierarchical TiO$_2$: Pan et al. [64] have reported vertically aligned 1D hierarchical TiO$_2$. 10 nm size of TiO$_2$ NPs were uniformly coated on the side walls of NTs through infiltration with TiCl$_4$ solution and hydrothermal synthesis (Figure 8). Compared with the bare NT structure, dye-loading of mixed NT and NP structure was two times doubled. The larger surface area resulted in more recombination which slightly reduced the electron lifetime. However, the diffusion length was still longer than the tube length used. This means most electrons are collected.

3. Summary

In this paper, we have summarized the using of 1D TiO$_2$ nanostructures as electrode materials for DSSC photoanode. Randomly oriented 1D TiO$_2$ (nanotubes and nanorods) with cylindrical geometry could support radial electric fields that could keep the electrons away from the nanorods surface, thereby reducing surface electron densities and recombination. And large aspect ratio of TiO$_2$ would help to reduce the grain boundary effect. The electron lifetime would also increase. All these advantages could be beneficial for the improved photoelectrochemical properties. However, randomly oriented 1D TiO$_2$ nanomaterial are disordered and random. It has not realized the direct electron transport. Vertically aligned TiO$_2$ nanotubes provide a vertical pathway for electron transport along the tube and thus minimize electron loss during diffusion process, and the vertically ordered tubular structure will facilitate the filling of new sensitizer and electrolyte for a further increase in efficiency. However, the small surface area made the photoelectrochemistry properties worse than the randomly oriented 1D TiO$_2$ nanomaterial. In general, fast reaction kinetics (fast electron transport, long electron lifetime, and less recombination) together with large specific surface area are the essential properties of the superior photoanode materials with excellent photoelectrochemical properties. To achieve highly efficient DSSCs, 1D hierarchical TiO$_2$ were designed. Both randomly oriented and vertically aligned 1D nanostructures have been used as the photoanode materials. Detailed study showed that this 1D hierarchical TiO$_2$ could combine the high electron transport from 1D nanostructures and large surface area to attach enough dyes from nanoparticles. Furthermore, the bigger pores inside the hierarchical structured films are also beneficial for the permeation and diffusion of electrolyte in the photoanode, forming good ohmic contact. The results provide a potential approach to obtain highly effective solar conversion materials.

Acknowledgments

This work has been supported by the Chinese National Science Funds (no. 51202094); the Priority Academic Program Development of Jiangsu Higher Education Institutions; the Natural Science Foundation (no. 12KJB150010 and no. 12KJB430001) of Jiangsu Education Committee of China.

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