Mesoporous TiO₂ Nanowire Film for Dye-Sensitized Solar Cell

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In this work, TiO₂ nanowire arrays were grown on fluorine-doped tin oxide (FTO) glass substrate, and then were converted into mesoporous nanowires (MNWs). The TiO₂ MNWs are about 5–30 nm in length and 30–200 nm in diameter, with mesopores size of 5–30 nm randomly distributed on the NW surface. X-ray diffraction pattern reports show that the NWs are single crystallized rutile TiO₂ and oriented grown along [001]. Through further characterization of FT-IR and TG-DSC, we proposed a reasonable explanation for pore existence. After dye-sensitized solar cells (DSSCs) assembly, the photoelectric conversion efficiency (PCE) of MNWs based DSSC achieved 3.2%. It means tenfold enhancement of photoelectric property compare with the as-grown NWs. Furthermore, dye absorb capacity of MNWs can reach up to 4.11 × 10⁻⁸ mol/cm². However, such MNWs can not only provide quick and efficient electron transmission channel, but also owns big specific surface area to absorb abundant dyes, thus conducive to fabricate solar cell with a high PCE.

Keywords: Dye-Sensitized Solar Cell, Hydrothermal, Mesopore, TiO₂ Nanowires.

1. INTRODUCTION

Dye-sensitized solar cells (DSSCs) have been thought to be one of the most promising photovoltaic devices among the third generation solar cells for the low cost and relatively high photovoltaic conversion efficiency.¹,² As a key part in DSSCs, photoanode acts as both the dye scaffold and electrons transfer media from the excited dyes to the conductive glass substrate.³,⁴ Generally, the conventional TiO₂ nanoparticle photoanodes show the disadvantage of electron scattering and trapping at the grain boundaries among nanoparticles, which might be the major obstacle for the further efficiency improvement of DSSCs.⁵⁻⁸ One-dimensional (1D) nano-structures have proven to be an effective way to facilitate electron transport in DSSCs. The electron transport rate of a 1D nano-structured film is improved by several orders of magnitude greater than that of a nanoparticle film for DSSCs, thus resulting in an improvement of short-circuit current density.⁹,¹⁰

However, the specific surface area of the 1D nano-structured films is still low. In order to increase the specific surface area, strategies such as converting TiO₂ nanorods to nanotubes,¹¹ preparing hierarchical TiO₂ nanodendrite/nanoparticle composite film on the base of TiO₂ nanowire (NW) arrays¹² and TiCl₄ after treatment on the surface of TiO₂ nanorods¹³ have been reported. The excellent electron transfer property of 1D material is generally benefited by good crystallization. In order to obtain good crystalline and to guarantee large surface area at the same time, Smith prepared a kind of mesoporous combined single-crystallized TiO₂ bulk structure using template method. The mesoporous single crystal TiO₂ prepared by them displayed higher conductivity and electron mobility than conventionally used nanocrystalline TiO₂, thus record high efficiency of 7.2% was obtained in their solid-state solar cells.¹⁴
Considering the excellent advantages of combining good crystalline and large specific surface area of the TiO$_2$-based photoanode, mesopore combined NWs arrays were successfully synthesized in this work. TiO$_2$ nanowires arrays were directly grown on FTO, which can effectively provide perpendicular electron transfer channel. Single-crystalline of the TiO$_2$ NWs can facilitate effective electron transfer with less crystalline boundaries. Furthermore, the randomly distributed mesopores on NWs can greatly improve specific surface area of the as-prepared NWs arrays, which can tremendously enhance the dye absorption ability of TiO$_2$ MNWs-based photoanode for DSSCs. Owing to large specific area and good crystalline, the DSSCs with the TiO$_2$ MNWs-based photoanode can achieve a photoelectric conversion efficiency of 3.2%.

2. EXPERIMENTAL DETAILS

2.1. Materials
Titanium(IV) isopropoxide was used as titanium source. Hydrochloric acid and ethanol (C$_2$H$_5$OH, analytical reagent grade (AR), ≥ 99.7% (wt)) were purchased from Beijing Chemical Works. Commercial FTO substrate was used. 5 × 10$^{-4}$ M ethanol solution of ruthenium 535-bisTBA (N719 dye, Wuhan Geao) was obtained by dissolving N719 powders in ethanol. The Pt-coated FTO counter electrode (thermo decomposition, Wuhan Geao) was used as received. The electrolyte use here is a solution containing of 0.5 M LiI, 0.05 M I$_2$, 0.5 M 4-tert-butyl pyridine (TBP) and 0.3 M 1,2-Dimethyl-3-propylimidazolium Iodide (DMPII) in 10 ml acetonitrile.

2.2. Preparation of MNW Films
The TiO$_2$ nanowire arrays were grown by hydrothermal method. 0.41 ml titanium isopropoxide (≥97%, Aldrich) was added into 35 mL 5 M hydrochloric acid solution. After stirring for 10 mins, the precursor was transferred into a 50 mL autoclave with Teflon liner. The FTO-coated glass substrate (15 U/Omega · cm$^{-2}$, Wuhan Geao) was cladded with a thin compact TiO$_2$ seed layer. The autoclave was heated at 180 °C for 10 hrs, and the TiO$_2$ NW film was obtained. Then as-grown TiO$_2$ NW films were converted into etched nanowires (ENWs) film by etching in 30 mL 6 M hydrochloric acid at 150 °C for 3 hours. Finally, MNWs were obtained by annealing the ENWs at 500 °C for 30 mins.

2.3. Assembling of DSSCs
All the TiO$_2$ films were immersed into a 5 × 10$^{-4}$ M ruthenium 535-bisTBA (N719 dye) ethanol solution at 45 °C for 24 hrs. Then, the electrodes were rinsed with anhydrous ethanol to remove the redundant dyes at room temperature. The DSSC was assembled by clamping dye-sensitized photoanode and a transparent Pt-coated FTO counter electrode using a face-to-face layout. The active area of solar cells was 0.25 cm$^2$. A drop of electrolyte was injected into the interspace between the two electrodes before test.

2.4. Characterization
The crystal structure of NWs was examined by X-ray Diffractometer (XRD, D8 ADVANCE, Cu Kα radiation, λ = 1.54 Å, tube voltage = 40 kV, tube current = 30 mA). A field emission scanning electron microscope (FESEM, FEI Quanta200F, Operating voltage: 30 kV) and a transmission electron microscope (TEM, JEOL JEM-2000FX, Japan) with selected-area electron diffraction (SAED) analyses were used to observe the microstructures of TiO$_2$ NW films. Fourier transform infrared spectroscopy (FT-IR, Perkin Elmer, Spectrum 100) was used to investigate the chemical bonding of the samples surface at a resolution of 0.5 cm$^{-1}$. The thermal properties of the TiO$_2$ films were studied by NETZSCH STA 449C thermogravimetry-differential scanning calorimetry (TG-DSC) analysis in air from room temperature to 700 °C at a ramping rate of 10 °C/min with Al$_2$O$_3$ as reference. The photocurrent density–voltage characteristics of the DSSCs were evaluated by a source meter (Keithley 2400) under a solar simulator (Oriel 92250A-1000, Newport, 100 mW cm$^{-2}$). The amounts of absorbed dye were measured using an ultraviolet visible (UV-Vis) spectrophotometer (UV-2450, J. Nanosci. Nanotechnol. 15, 1–6, 2015

Figure 1. FESEM images of TiO$_2$ NWs. The (a), (c), (e) are top views of as-grown NWs, ENWs and MNWs, respectively. The (b), (d), (f) are cross-sectional views f as-grown NWs, ENWs and MNWs.
Figure 2. TEM images of the as-grown NWs (a), ENWs (b) and MNWs (c), (d) is the SAED pattern of the MNWs.

3. RESULTS AND DISCUSSION

It can be observed from Figures 1(a) and (b) that highly ordered NW arrays were obtained after hydrothermally grown at 180 °C for 10 hrs. These NWs form highly aligned TiO2 NW cluster arrays with a length of about 5 μm and an average diameter of about 290 nm. Usually, a cluster contains tens of NWs. The NW assembling was due to the large ratio of length to diameter ratio of individual NW.15–17 Figures 1(c) and (d) are the top and cross-sectional SEM images of the ENW arrays respectively. It clearly shows that TiO2 NW cluster arrays were successfully split up by the etching process. The diameter of the clusters decreased to about 50 nm while the length of NWs was unchanged. Figures 1(e) and (f) show the top and cross-sectional SEM images of MNWs arrays after annealing at 500 °C, respectively. It indicates that the separated NWs tend to partially combine together again during the anneal process.

The surface microstructure evolution of the samples was further observed by TEM. Over-lapped TiO2 NW bundles can be observed in the as-grown NWs (Fig. 2(a)). After in-situ hydrothermally etching in HCl solution at 150 °C for 3 hrs, the as-grown TiO2 clusters were split up into individual NWs with diameter of ~10 nm (Fig. 2(b)). The surface morphology (Fig. 2(c)) shows numerous mesopores on the NWs. They randomly distributed on the NWs after the ENWs were calcination at 500 °C. The mesopores were 5~30 nm in size. It is worth noting that mesopores on TiO2 NW surfaces can only be formed by the combination of etching and calcination processes. Reversing the order of this two steps or missing either one cannot produce mesopores. No pore traces were found on samples of calcination as-prepared NWs first then etching and directly calcination as-prepared NWs. Furthermore, the select area electron diffraction patterns of MNWs (Fig. 2(d)) shows clearly single crystal diffraction spots pattern, which proves that our MNWs are well crystallized.

To further study the crystal structure of the TiO2 samples, the XRD patterns are shown in Figure 3. The strongest peak at 62.74° can be indexed as (002) planes of tetragonal rutile TiO2 (JCPDS, file No. 21-1276: a = 4.593 Å, c = 2.959 Å; space group: P42/mmm (136)). After etching, the (002) peak intensity of the ENWs and MNWs decreases. The strongest (002) peaks of all three samples indicate that all the NWs, ENWs and MNWs grow preferentially along the [001] direction.

Figure 3. XRD patterns of FTO substrate, as-grown NWs, ENWs and MNWs.

Figure 4. FT-IR spectra of as-grown NWs, ENWs and MNWs.
FT-IR spectra of as-grown NWs, ENWs and MNWs are shown in Figure 4. For the as-grown NWs (Fig. 4(A)), one obvious absorption peak is observed at 658 cm$^{-1}$. The broad band within 750–400 cm$^{-1}$ corresponds to the flexural vibration of Ti–O and Ti–O–Ti groups. In the FT-IR spectra of ENWs, there are three different peaks located at 500–750 cm$^{-1}$, 1025 cm$^{-1}$ and 1626 cm$^{-1}$. After etching process (Fig. 4(B)), there is more Ti complex on the surface of NWs, so one small peak at 500–750 cm$^{-1}$ appear, which is attributed to the Ti–O vibration of amorphous titanium oxide. The peak at 1025 cm$^{-1}$ is probable attributed to the C–H band and –Cl groups vibration. Another peak located at 1626 cm$^{-1}$ attributes to deformation vibrations of hydroxyl groups (–OH) and H$_2$O on the TiO$_2$ surface. After calcination (Fig. 4(C)), the signal related to Ti–O bonds in amorphous titanium oxide, –Cl groups and –OH are disappeared. Calcination can significantly improve surface condition of TiO$_2$ nanowires, further change configuration of surface, thus can make contribution to pore forming.

Figure 5 shows the TG-DSC curve of the ENWs. There was a steady weight loss process of etched TiO$_2$ NWs from 70 °C to 500 °C in the TG curve, with a total weight loss of about 3%. There are three endothermic peaks in the DSC curve at 100 °C, 220 °C and 350 °C. It was known that there are –OH and amorphous Ti–O exist on the etched NWs. The endothermic peaks located at 100 °C mainly attribute to the elimination of absorbed water. Then, the endothermic peaks around 220 °C is probably due to the combustion decomposition of some organic matters. Endothermic peak start from 350 °C possibly resulted from the desorption of the hydroxyl –OH group on the surface of TiO$_2$ and phase conversion from amorphous TiO$_2$ to crystallized rutile phase. This result agreed with that shown in the above FT-IR spectra analysis.

Based on the microstructure observation and analysis above, a schematic illustration of the MNWs growth process is proposed in Figure 6. Firstly, TiO$_2$ NW arrays are grown on the FTO substrate by the hydrothermal process. As grain boundaries and surface crystal defects have higher reactivity than other places in the as-prepared NWs, the etching treatment split off the original NW clusters and resulted in the inhomogeneous surface of NWs. After the subsequent calcinations process, numerous randomly distributed mesopores were formed on the surfaces of NWs, which is the result of the synergistic effects of recrystallization, inhomogeneous surface tension, and removement of residual water, –OH, and other organic group within the NW arrays.
To investigate the effect of etching and annealing treatment on the photoelectric property of TiO$_2$, DSSCs with as-prepared NWs, ENWs and MNWs as photoanode were fabricated respectively. Figure 7 shows the photocurrent–voltage ($I$–$V$) curves of these cells. The results are summarized in Table I. It is interesting to find that the efficiency increases from 0.26% to 1.98% after the NWs had been etched. After the ENWs were converted to the MNWs, the efficiency further increases to 3.2%, providing a tenfold improvement compared to the as-grown NWs. Typically, the open circuit voltage ($V_{oc}$), short-circuit current density ($J_{sc}$) and fill factor (FF) of the DSSCs with MNW TiO$_2$ are 0.66, 10.36 mA/cm$^2$ and 0.47, respectively, which presents the highest power conversion efficiency of 3.2% among three kinds of DSSCs.

By converting TiO$_2$ NWs to MNWs, the specific surface areas of the TiO$_2$ anode increases, this can directly increase the dye adsorption amount. From the $I$–$V$ result, we can see that the most important parameter which brings about photoelectron property improvement is current density. The increase of current density is usually attributed to two reasons: the more dye absorption and effective electron injection.$^{31}$ The amount of absorbed dyes was measured by UV-Vis absorption spectrum of dye desorption solution after dipping the dye-sensitized photoanode into a 0.1 M NaOH aqueous solution for 30 mins.$^{32,33}$ The dye loading amount on the NWs is only $1.61 \times 10^{-8}$ mol/cm$^2$, while the ENWs obtain a highest dye loading amount of $5.06 \times 10^{-8}$ mol/cm$^2$. However, the MNWs just acquire a dye loading amount of $4.36 \times 10^{-8}$ mol/cm$^2$, which is about 86% of the ENWs. Although dye absorption amount are nearly proportional to short current density, there are two kinds of dye loading way: chemically bonding and physically absorbing. The MNWs show lower dye absorption amount but much higher short circuit density than ENWs may be ascribed to more efficient chemically bonded dye amount. It was reported that anneal process can significantly enhance the surface status of the etched NWs.$^{26}$ The dye molecules can be chemically adsorbed onto the surface of TiO$_2$ NWs more effectively via the formation of ester-like bonding between the carboxylic acid groups and –OH groups on the TiO$_2$. Therefore, the ENWs possess better dye absorption capacity, but worse electron transfer ability than MNWs. Thus it makes sense that the MNW photoanode performed best in DSSCs.

### Table I. The $I$–$V$ characteristics of the DSSCs consist of as-grown NWs, Etched NWs and MNWs.

<table>
<thead>
<tr>
<th>Photoanode</th>
<th>$J_{sc}$/mA cm$^{-2}$</th>
<th>$V_{oc}$/V</th>
<th>FF</th>
<th>Dye absorption$/\times 10^{-8}$ mol/cm$^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>As-prepared NWs</td>
<td>0.89</td>
<td>0.55</td>
<td>0.58</td>
<td>0.28</td>
</tr>
<tr>
<td>ENWs</td>
<td>5.05</td>
<td>0.61</td>
<td>0.64</td>
<td>1.98</td>
</tr>
<tr>
<td>MNWs</td>
<td>10.36</td>
<td>0.66</td>
<td>0.47</td>
<td>3.20</td>
</tr>
</tbody>
</table>

Figure 7. $I$–$V$ curves of the DSSCs consist of as-grown NWs, ENWs and MNWs.

Figure 8. UV–vis absorption spectra of N719 dye in 0.1 M NaOH aqueous solution, desorbed from the TiO$_2$ electrodes made with as-grown NWs, ENWs and MNWs.

4. CONCLUSIONS

In summary, a novel mesopore combined TiO$_2$ NW arrays were in-situ prepared on FTO substrate. By etching with HCl solution and then calcinations of the original as-prepared TiO$_2$ NWs, numerous randomly distributed mesopores were formed on the surfaces of the TiO$_2$ NWs. A tenfold enhancement of PCE in the DSSCs with mesoporous TiO$_2$ was obtained compared to that of the as-grown NWs. Large surface areas offered $4.11 \times 10^{-8}$ mol/cm$^2$ dye absorbed amount. The findings of the present research provide a new choice for combining both good electron transfer ability and large specific surface area in film materials.

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References and Notes

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