High Efficient Transparent TiO₂ Nanotube Dye-Sensitized Solar Cells: Adhesion of TiO₂ Nanotube Membrane to FTO by Two Different Methods

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Abstract

In order to fabricate transparent TiO₂ nanotube dye-sensitized solar cells, anodically growth nanotube membranes are detached from Ti substrate by a re-anodization method. The membranes are transferred on FTO glass by two different methods. At the first one, 100mM Ti-isopropoxide is used to make TiO₂ nanoparticles for adhering TiO₂ nanotube membranes to FTO and in the second one a commercial TiO₂ nanoparticle paste is used as connector material. In order to investigate the effect of annealing temperature on the crystallinity of the photoanodes, they were annealed in temperatures from 350 to 650°C. All of the annealed photoanodes show high crystallinity and pure anatase phase in both cases. However nanoparticles with large diameter about 500nm and no homogeneity of dispersion of them at the first method leads to week interconnection between membranes and FTO glasses but good interconnection at the second method leads to high power conversion efficiency of 6.13% under 1 sun illumination without any extra treatment.

1. Introduction

Over the past decades, dye-sensitized solar cells (DSSC) have received considerable attention due to high efficiency and low cost [1,2]. However DSSC with a thick TiO₂ mesoporous film has been demonstrated high power conversion efficiency with optimizing dye molecules and electrolyte composition [3], but random walk of electrons between interconnected nanoparticles limit the electron transport time in these structures [4, 5]. In order to overcome this effect, one dimensional structures such as nanowires [6, 7], nanorods [8, 9] and nanotubes [10-12] are suggested. Among these nanostructures TiO₂ nanotubes are more considerable due to higher surface area than compact oxide film that leads to higher dye loading.
and consequently more light harvesting efficiency [13].

Anodically growth TiO$_2$ nanotubes are amorphous in nature but can be converted to crystalline phases of rutile or anatase by annealing process [14-17]. Since the electron transport is faster in anatase in comparison to rutile phase [18,19], it is tried to omit rutile phase for using TiO$_2$ nanotubes in photovoltaic applications. However it is possible to omit rutile phase in low temperature by ramping annealing, but high temperature annealing usually leads to some percent of rutile phase. This effect can be removed by annealing the membrane after detaching from Ti substrate and transferring on FTO glass in the case of DSSCs.

Front side illumination is another benefit of this approach. The highest power conversion efficiency of a pure TiO$_2$ structure, without TiCl$_4$ treatment, on Ti foil is reported 5.2% to now [20]. One of the reasons that limits transport time and increasing power conversion efficiency in TiO$_2$ nanotube DSSCs is the existence of Ti foil beneath TiO$_2$ nanotubes that excludes front side illumination. Some parts of incident light to cell reflected by Pt cathode and some parts of it absorbs by iodine electrolyte. Some groups have tried to transfer TiO$_2$ nanotube on FTO substrate to have front side illumination [21-23].

In the present work, we prepare TiO$_2$ nanotube membranes [23] and transfer them on fluride-doped tin oxide (FTO) coated glasses to apply them to front side illuminated DSSC configurations. We use two different methods for adhesion of TiO$_2$ nanotube membranes to FTO glasses and compare the effect of them on the photovoltaic characteristics of transparent DSSCs.

2. Experimental procedure

Highly ordered TiO$_2$ nanotube arrays were prepared by anodization of Ti foil (0.125mm thickness, 99.7% purity, Advent) in a two electrode cell by using Pt as counter electrode. Prior to the anodization process the Ti foil was cleaned by sonication in acetone and ethanol followed by rinsing in de-ionized water (DI) and drying under N$_2$ stream. The anodization was performed at 60V at room temperature in a solution of ethylene glycol with 0.15 M NH$_4$F and 3V% water. Different TiO$_2$ nanotube thicknesses were produced by changing the anodization time from 10min to 60min. For producing TiO$_2$ nanotube membranes, the as-prepared TiO$_2$ nanotube samples were annealed in 350° C for 1h. The crystallized TiO$_2$ nanotube samples were anodized again in the first anodization conditions. The ordered TiO$_2$ nanotubes membrane was prepared by immersing the samples in 0.07 M HF solution at 30° C. The freestanding TiO$_2$ nanotube membranes were attached on FTO glasses (7 Ω per square) by two different methods. At the first method three drops of 100 mM Ti-isopropoxide [24] were applied on FTO glass and TiO$_2$ nanotube membrane was transferred on it. At the second method a commercial TiO$_2$ nanoparticle paste (Ti-Nanoxide HT, Solaronix) was coated on FTO glass by doctor-blade technique and membrane was transferred on it. In both cases, after drying the photoanodes in air for about 20 min, they were annealed in the range of 350-650 °C for 1h in a tube furnace.

The annealed photoanodes in 550° C were immersed in a 300 μM dye solution (D719, Everlight, Taiwan) at 40° C for 24h. After dye-sensitization the samples were rinsed with acetonitrile to remove non-chemisorbed dye and dried in N$_2$ stream. Then the photoanodes were sandwiched with a Pt coated FTO glass as a
counter electrode using a hot-melt spacer (25 µm, Surlyn, Dupont). Electrolyte (Io-li-tec, ES-0004) was introduced between the interspace of the DSSCs. The current voltage characteristics were measured under simulated AM 1.5 illumination provided by a solar simulator (300W Xe with an optical filter, Solarlight) applying an external bias to the cell and measuring the generated photocurrent with a Keithley model 2420 digital source meter.

For morphological characterization, a field-emission scanning electron microscope (FE-SEM, Hitachi SEM FE 4800) were used. X-ray diffraction analysis (XRD) was performed with an X’pert Philips MPD with a PanalyticalX´celerator detector using graphite monochromized Cu Kα radiation (wavelength 1.54056 Å).

3. Results and discussion

Figure 1 (a-d) shows cross sectional SEM images of freestanding TiO₂ NT membranes with different thicknesses. The insets show back side of the membranes. It can be seen from these figures that the bottom of the tubes are opened in some parts.

To investigate the effect of annealing temperature on crystallinity of the tubes, two different configurations were annealed in air at temperatures from 350 to 650°C. Figure 2(a-b) show crystallinity of the tubes in 350 to 650°C.

![Fig. 1. The FE-SEM images (a-d) of TiO₂ nanotubes with thicknesses from 4 to 30 µm, the insets show back side view of the membranes.](image)

![Fig. 2. XRD pattern of 20µm nanotube membrane annealed in temperatures from 350 to 650°C attached on FTO by Ti-isopropoxide method (a) and by 2µm commercial nanoparticle paste (b).](image)
Fig. 3. (a, b) The J-V curves of DSSCs consisted of different thicknesses of TiO$_2$ nanotube membranes attached on FTO by Ti-isopropoxide method and annealed in 550°C.

Table 1. The photovoltaic parameters of DSSCs consisted of different thicknesses of TiO$_2$ nanotube membranes attached on FTO by Ti-isopropoxide method and annealed in 550°C.

<table>
<thead>
<tr>
<th>Tube Thickness</th>
<th>$V_{oc}$</th>
<th>$I_{sc}$</th>
<th>$\eta$ (%)</th>
<th>$ff$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>15µm</td>
<td>0.57</td>
<td>0.29</td>
<td>0.05</td>
<td>30</td>
</tr>
<tr>
<td>20µm</td>
<td>0.60</td>
<td>0.51</td>
<td>0.11</td>
<td>36</td>
</tr>
<tr>
<td>30 µm</td>
<td>0.49</td>
<td>0.37</td>
<td>0.05</td>
<td>27</td>
</tr>
</tbody>
</table>

Front side illumination:

<table>
<thead>
<tr>
<th>Tube Thickness</th>
<th>$V_{oc}$</th>
<th>$I_{sc}$</th>
<th>$\eta$ (%)</th>
<th>$ff$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>15µm</td>
<td>0.65</td>
<td>0.60</td>
<td>0.17</td>
<td>43</td>
</tr>
<tr>
<td>20µm</td>
<td>0.66</td>
<td>0.92</td>
<td>0.23</td>
<td>38</td>
</tr>
<tr>
<td>30 µm</td>
<td>0.52</td>
<td>0.69</td>
<td>0.12</td>
<td>33</td>
</tr>
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These two kinds of illumination are schematically shown in Fig. 4.

Fig. 4. Schematic representation of back side (a) and front side (b) illumination in transparent TiO$_2$ nanotube DSSCs.

Table 1 shows that however the open circuit voltages are enough high but low short circuit currents leads to low power conversion efficiencies in this method. The highest power conversion efficiency is 0.23% that is occurred in 20µm tubes. This power conversion efficiency is very low even with comparison to TiO$_2$ nanotubes on foil. Low current density might be because of weak interconnection between TiO$_2$ nanotube membrane and FTO glass. In order to remove this effect a commercial TiO$_2$ nanoparticle paste was used.

Figure 5 shows the photovoltaic characteristics of DSSCs consisted of different thicknesses of TiO$_2$ nanotube membranes on 2 µm nanoparticle paste. Similar to the previous one, the photoanodes are annealed at 550°C. As can be seen from this figure, however the open circuit voltages are in the same order of the Ti-isopropoxide case but short circuit currents are considerably more. This high $I_{sc}$ and also high fill factor leads to high power conversion efficiency in this case. So that a high power conversion efficiency of 6.13% in 20 µm nanotube membrane in front side illumination is occurred. This power conversion efficiency is very high without any TiCl$_4$ treatment in comparison to DSSCs consisted of TiO$_2$ nanotubes on foil.
The J-V curves of DSSCs consisted of different TiO$_2$ nanotube array on 2µm nanoparticle paste annealed in 550°C. Figure 6(a) shows the nanoparticles that are produced by Ti-isopropoxide method. It can be understood that big diameter of nanoparticles between 400 nm to 500 nm and weak homogeneity of dispersion of them can be resulted in weak interconnection between membranes and FTO glasses. As can be seen in figure 6(b), nanoparticles with diameter of 10 nm in the commercial paste lead to a compact and good interconnection between TiO$_2$ nanotube membranes and FTO glasses.

It can be concluded that 20 µm is an optimized thickness for the membranes in transparent DSSCs. Table 2 shows that however increment in thickness leads to higher J$_{sc}$ because of more dye-loading and consequently higher light harvesting efficiency but decrement of V$_{oc}$ and fill factor resulted to lower power conversion efficiency. In comparison a commercial TiO$_2$ nanoparticle...
paste with diameter about 10 nm as connector leaded to high $J_{sc}$ and power conversion efficiency of 6.13% without any TiCl$_4$ treatment. Annealed photoanodes in different temperatures show pure anatase phase in both cases.

References