Improvement of dye-sensitized solar cell performance through infiltration of TiO₂ nanoparticles between mesoporous TiO₂ particles

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ABSTRACT

There are two factors on the efficiency of dye-sensitized solar cell (DSSC): one is the amount of dye adsorbed, and the other is contact resistance. In this study, TiO₂ nanoparticles (nano-TiO₂, about 20 nm particle size) were infiltrated between mesoporous TiO₂ (meso-TiO₂) particles with about 300 nm particle sizes, in order to reduce the contact resistance of TiO₂ electrodes. The infiltrated nano-TiO₂ can facilitate electron transfer between meso-TiO₂ particles by filling the empty volume of DSSC electrodes. As a result, the TiO₂ electrode containing 65 wt% of meso-TiO₂ and 35 wt% of nano-TiO₂ exhibited the highest performance of DSSC.

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1. Introduction

Development of alternative energy sources has much attention, as the energy consumption has increased and energy-shortage problem becomes the hottest topic. One of the most promising alternatives is dye-sensitized solar cell (DSSC) which is reasonably high photon to current conversion, inexpensive and easy fabrication, portable, and cost-effective [1,2]. In contrast to DSSC, a conventional semiconductor solar cell, such as a silicon solar cell, shows higher performance, but it should take advantage of ultrahigh pure silicon materials. Moreover, their performances are dependent on the diffused light and the operating temperature under 50 °C [3,4]. The advantages of DSSC are that the performance can be relatively retained under any climate conditions and that it is possible to be applied for flexible substrate resulting in various applications in the future such as on the clothes, accessories, and so on [5,6].

Up to now, there have been considerable efforts to enhance the DSSC performance: depositing a thin tunneling barrier layer on the substrate [7–10], co-sensitizing with different dyes [11], developing a new suitable n-type semiconductor in various ways such as morphology-control and other metal oxides, increasing of dye adsorption amount by mesoporous materials, suppression of the charge recombination, and lowering the contact resistance. Mesoporous TiO₂ (meso-TiO₂) shows high surface area which allows it to adsorb more dyes. However, the overall particle diameters of the meso-TiO₂ are very large compared to that of conventional TiO₂ nanoparticle such as P25 (about 20 nm). Therefore, the DSSC electrodes of meso-TiO₂ particles film contain lots of empty spaces in the DSSC system, resulting that the photoelectron transfer could be suppressed by high contact resistance between the meso-TiO₂ particles. To enhance the DSSC performance and suppress the charge recombination, several research groups have studied about TiCl₄ post-treatment between the TiO₂ surface and sensitizer [12,13]. However, the TiCl₄ post-treatment has disadvantages such as the utilization of new chemicals and further chemical reaction.

In this study, filling the empty spaces between the meso-TiO₂ particles (about 300 nm particle sizes) with smaller TiO₂ nanoparticles (nano-TiO₂, Degussa P25, diameter is about 20 nm) by physical mixing was studied as shown in Scheme 1, in order to reduce the contact resistance between meso-TiO₂ electrodes. x wt% of meso-TiO₂ materials were physically mixed with (100 − x) wt% of nano-TiO₂ (the mixing ratio will be denoted as meso-x), and then pastes were prepared by the mixed TiO₂ powders. The DSSCs prepared with the mixed TiO₂ particles exhibited higher efficiency than those of meso-TiO₂ and nano-TiO₂ (meso-0 and 100).

2. Experimental

2.1. Synthesis of mesoporous titanium dioxide

The meso-TiO₂ was synthesized by the following method. To synthesize titanium glycolate precursor spheres, 2 mL of titanium...
(IV) butoxide (Aldrich, 97%) was mixed with 50 mL of ethylene glycol (Samchun chemicals, 99.9%) and then the solution was stirred at room temperature. After 8 h, a solution containing 510 mL of acetone (Samchun chemicals) and 8.1 mL of deionized water was poured into the mixture, and the final mixture was vigorously stirred for 1 h at room temperature. The white precipitate was centrifuged, washed with ethanol for three times, and dried at 80 °C for 24 h. 1.5 g of titanium glycolate precursor, thus obtained, was mixed with 120 mL of deionized water, and the mixture was heated under reflux conditions for 1 h with vigorous stirring. The white precipitate was collected by centrifugation, washed with deionized water for three times, and dried at 80 °C for 24 h. The diameter of synthesized meso-TiO2 nanoparticle is about 300 nm. For further usage, meso-TiO2 was calcined at 300 °C for 1 h.

2.2. Fabrication of dye-sensitized solar cell

The pastes of TiO2 electrode composed of x g meso-TiO2 and \((0.1 - x)\) g nano-TiO2 were prepared. Total 0.1 g of TiO2 powder was mixed with 0.53 mL of ethylene glycol, and then 0.05 g hydroxypropyl cellulose (Aldrich, \(M_w = 370,000\)) was added. The fluorine-doped tin oxide (FTO) glass was washed sequentially by sonicating in deionized water with surfactants, deionized water with ethanol, and deionized water baths for 30 min. The prepared pastes were deposited on the clean FTO glass (1.5 cm × 1.5 cm) by using two 5 μm thick spacers (3 M) to control the thickness of TiO2 film as 10 μm by the doctor blade method. After removing the spacers, the electrodes were dried at 80 °C for 12 h and then sintered under air conditions at 450 °C for 45 min.

Dye adsorption of the TiO2 films was preceded by immersion in a 0.3 mM dye ethanol solution for 24 h. N719 (Solaronix) was used in this study as a dye molecule. For counter electrode, platinum (Pt)-coated FTO glass was prepared by coating with 5 mM H2PtCl6 isopropanol solution on clean FTO glass and sintering it at 380 °C for 30 min subsequently. The cell was fabricated by sandwiching the paste-coated FTO glass and Pt-coated FTO glass with hot-melt film (SX1170-60, Solaronix). The ionic liquid electrolyte containing 0.1 M LiI, 0.05 M I2, 0.5 M TBP, 0.62 M DMPII, 0.44 M 3-amino-5-methylthio-1H-1,2,4-triazole, and acetonitrile was injected into the space between two electrodes through the holes and then finally the cell was sealed.

2.3. Characterization

X-ray diffraction (XRD) patterns were obtained from Rigaku Ultima IV instrument with Cu Kα source at 40 kV and 30 mA. Photocurrent–voltage (I–V) curves were measured by using a Keithley model source measure unit. A solar simulator (Newport, ORIEL Sol3A) was used as a light source, and the light intensity was adjusted with a Si solar cell (VLSI Standard Incorp., SRC-1000-TC-KG5) for 1-sun condition. Incident photon to current conversion efficiency (IPCE) was measured as a function of wavelength from 400 nm to 800 nm using a specially designed IPCE system (ORIEL IQE 200 TM). A Xe lamp (Dolan-Jenner industries, DC-950) was used as a light source for generating a monochromatic beam. Field emission scanning electron microscopy (FE-SEM) images were taken using a Hitachi UHR S 5500 at 30 kV. Transmission electron microscopy (TEM) images were taken using a JEOL JEM-2100F at 300 kV. N2 adsorption–desorption isotherms and Barrett–Joyner–Halenda (BJH) pore size distribution curves were measured with Micromeritics Tristar 3020 at liquid N2 temperature.

3. Results and discussion

3.1. Characterization of mesoporous TiO2 materials

XRD patterns in Fig. 1 indicate that the nano-TiO2 has mainly anatase phase with small rutile phase, whereas the meso-TiO2 material exhibits purely anatase phase. The grain sizes, calculated using Scherrer’s formula, of the nano-TiO2 and meso-TiO2 are about 17.8 nm and 10 nm, respectively.

Fig. 2 shows the N2 adsorption–desorption isotherms and the corresponding BJH pore size distribution. As shown in Fig. 2A, the meso-TiO2 exhibits typical type-IV isotherm with hysteresis loop, which is the characteristics of mesoporous materials. The BJH pore size distribution curve (Fig. 2B) obtained from the adsorption branches indicates the pores size of meso-TiO2 was about 10 nm. In contrast, the nano-TiO2 has no mesopores.
As depicted in Fig. 3A, the SEM image shows that the meso-TiO₂ materials exhibit spherical morphology, uniform particle size of about 300 nm, and rough surfaces due to the existence of mesopores. Fig. 3B (TEM image) shows that the aggregation of primary TiO₂ particles results in a larger secondary meso-TiO₂ particle. Therefore, the meso-TiO₂ particles have disordered mesostructure and mesopores are derived from the empty space between the primary TiO₂ particles.

N₂ adsorption–desorption isotherms of meso-x mixed powders are shown in Fig. 4 and BET surface areas are summarized in Table 1. The surface area of meso-x powders increases sequentially as the ratio of meso-TiO₂ increased, and surface area of meso-100 is as twice as that of meso-0. The meso-0 sample (nano-TiO₂) has no pores and relatively low surface area. The higher surface area of a TiO₂ material helps it to adsorb more dye molecules, which might enhance the DSSC performance.

3.2. Solar cell performance

The meso-TiO₂ particles with high surface area seem to allow the particles to adsorb more dye molecules for enhancing the DSSC performance. However, the diameter of meso-TiO₂ particles is about 300 nm that is enough to generate the large empty space between meso-TiO₂ particles, resulting in the high contact resistance in a DSSC system. Here, the design concept of TiO₂ electrodes (Scheme 1) is infiltration of nano-TiO₂ particles (about 20 nm) between the meso-TiO₂ particles in order to decrease the contact resistance in the DSSC system. The TiO₂ electrodes were fabricated using the mixture of meso-TiO₂ and nano-TiO₂ particles with different weight ratios as shown in Fig. 4.

Fig. 5 shows the photovoltaic efficiencies of DSSCs thus prepared, and the results are summarized in Table 1. As the amount of nano-TiO₂ between meso-TiO₂ particles increase up to...
65 wt%, the short-circuit currents ($J_{SC}$) and fill factors increase from 7.5 to 10.8 mA/cm$^2$ and from 65% to 72%, respectively, whereas the open-circuit voltages ($V_{OC}$) are almost retained. The cell efficiency of meso-65 (6.1%) is much larger than those of meso-0 (3.5%) and meso-100 cells (4.5%). The $J_{SC}$ values and efficiencies of DSSCs decrease as the amount of meso-TiO$_2$ increase from 65 wt% to 100 wt%. Fig. 6 shows that the meso-100 cell exhibits higher $J_{SC}$ (about 1.0 mA/cm$^2$), $V_{OC}$ (about 40 mV), FF (4%) and the efficiency (1%), compared with those of meso-0 cell. This is probably because meso-100 cell are composed with the meso-TiO$_2$ particle with large surface area that can adsorb more dye molecules than the nano-TiO$_2$ electrode. Thus, more photoelectrons can be generated from dye molecules. After the treatment, clearly, those values were enhanced more than meso-0 cell, and meso-100 cell (meso-30–90 cells). As shown in Fig. 4 and Table 1, a higher surface area of TiO$_2$ electrode has an effect on the enhanced efficiency, $J_{SC}$, $V_{OC}$, and fill factor. Especially, the meso-65 cell has the highest efficiency among all the meso-$x$ cells, even though its adsorptive ability to dye molecules is lower than that of meso-100. It implies that the contact resistance is a key factor to enhance the DSSC performance, which can be reduced by infiltration of nano-TiO$_2$ particles within the empty spaces between the meso-TiO$_2$ particles.

Dye molecule, N719, has the maximum absorption wavelength ($\lambda_{max}$) around 500 nm. IPCE measurement gives the information of how many photons at each wavelength could be absorbed and the cell generates and transfers electrons well. The IPCE curves in Fig. 7 show the highest intensity of quantum efficiency ($I_{QE}$) at 530 nm. For easier comparison, 5 samples are selected (meso-0, 30, 65, 90, and 100). The meso-0 cell shows the lowest $I_{QE}$, whereas the meso-65 cell the highest $I_{QE}$. The meso-30, 90, 100 cells have the $I_{QE}$ values between $I_{QE}$ values of the meso-0 and meso-65 cells. It means that infiltrated nano-TiO$_2$ particles in the electrode of meso-65 cell decreases the contact resistance in the most efficient way, and allow the photoelectrons to transfer faster and easier than in cases of other cells.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$J_{SC}$ (mA/cm$^2$)</th>
<th>$V_{OC}$ (mV)</th>
<th>FF (%)</th>
<th>$\eta$ (%)</th>
<th>$S_{BET}$ (m$^2$/g)</th>
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<tr>
<td>Meso-0</td>
<td>7.5</td>
<td>754.4</td>
<td>64.8</td>
<td>3.6</td>
<td>43</td>
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<tr>
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<td>70.0</td>
<td>4.9</td>
<td>52</td>
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<tr>
<td>Meso-20</td>
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<td>756.0</td>
<td>68.7</td>
<td>4.5</td>
<td>55</td>
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<tr>
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<td>10.2</td>
<td>766.7</td>
<td>69.6</td>
<td>5.6</td>
<td>62</td>
</tr>
<tr>
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<td>64.9</td>
<td>5.1</td>
<td>65</td>
</tr>
<tr>
<td>Meso-50</td>
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<td>777.2</td>
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<td>5.1</td>
<td>69</td>
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<tr>
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<td>5.4</td>
<td>71</td>
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<tr>
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<td>71.9</td>
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<tr>
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<td>68.8</td>
<td>4.5</td>
<td>90</td>
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</table>
4. Conclusion

In summary, the infiltration of nano-TiO$_2$ between meso-TiO$_2$ particles allows the electrode film to have higher surface area and reduce the contact resistance. In this study, the DSSC containing 65 wt% of meso-TiO$_2$ particles shows the highest efficiency, which is because the contact resistance is lower than the others. The synergetic effect coming from increase in the amount of adsorbed dye molecules and lowering the contact resistance of TiO$_2$ particles can be obtained for the optimized TiO$_2$ electrode condition of DSSC. The present design concept could be helpful to enhance photovoltaic device performance.

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