Dye-Sensitized Solar Cells Made with TiO$_2$-Coated Multi-Wall Carbon Nanotubes and Natural Dyes Extracted from Ipomoea

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This paper reports the fabrication of photoelectrode of dye-sensitized solar cells (DSSCs) using TiO$_2$-modified multi-wall carbon nanotubes (MWCNTs). The self-developed nanofluid synthesis system is employed to make TiO$_2$ nanoparticle which has good roundness and uniform size, at an average particle size of 40 nm. The self-prepared TiO$_2$ nanoparticles, after being mixed with TiO$_2$-nanoparticle-modified MWCNTs (TiO$_2$-CNTs) by sol-gel method, are deposited in an indium tin oxide (ITO) conductive glass by electrophoretic deposition method, thus forming a thin film of TiO$_2$/CNTs of 14 μm thick. As seen from the FE-SEM image and Raman spectra, the CNTs adhere well to the TiO$_2$ nanoparticles. In addition, the developed DSSCs make use of the natural dye extracted from ipomoea. The TiO$_2$-nanoparticle-modified MWCNTs prepared by sol-gel method can improve the performance of DSSCs by increasing the short-circuit current density ($J_{sc}$). The enhancement of $J_{sc}$ is attributed to the increased adsorption area of thin films and the improved interconnectivity among TiO$_2$ particles and TiO$_2$-CNTs. Experimental results show that TiO$_2$-modified MWCNTs prepared using natural dye extracted from ipomoea could enhance the light-to-electricity efficiency of DSSCs by as high as 30% (0.278% to 0.359%).

(Received June 15, 2009; Accepted September 25, 2009; Published November 25, 2009)

Keywords: dye-sensitized solar cells (DSSCs), multi-wall carbon nanotubes (MWCNTs), TiO$_2$ nanoparticles, ipomoea

1. Introduction

Dye-sensitized solar cells (DSSCs) have the advantages of easy fabrication and low cost. Recent studies show that the light-to-electricity efficiency of DSSC has exceeded 10–11%. Nevertheless, ever since its initial development, problems of efficiency and stability still need to be overcome. Regarding the preparation of photoanode in cell dye, mainly ruthenium polypyridyl complex nowadays, is employed to sensitize the titanium dioxide (TiO$_2$) semi-conductive porous film of nanoscale crystals. The type of dye being used affects directly the light-to-electricity efficiency of DSSCs. Ruthenium polypyridyl complex has good absorption of visible light, good chemical nature of converting light into electricity, and highly stable excitation state. These advantages lead to its extensive use. However, ruthenium polypyridyl complex contains precious metals, which increase its cost and cause environmental pollution. Researchers have investigated the extraction of natural dyes for DSSCs, which show satisfactory light-to-electricity efficiency. At present, there are many different methods for preparing photoelectrodes in DSSCs, such as physical vapor deposition (PVD) and chemical vapor deposition (CVD). All these methods require high power consumption and vacuum chambers, resulting in higher production cost. In a broad sense, electrophoretic deposition (EPD) is a kind of colloidal manufacturing process. It disperses mainly the charged particles suspended in the colloid solution. Driven by an externally added electric field, the particles move towards the electrode with an opposite charge, and are accumulated on the base to form an even coating. The advantages of EPD include easy manufacturing process, simple equipment, low cost, high deposition speed, good control of deposition thickness and properties, low manufacturing temperature, no restrictions of complicated base shape and wide applicability to diverse materials. In addition, EPD can efficiently prepare thin films of super-micro particles, giving them the advantages of high flatness and consistent thickness.

Carbon nanotubes (CNTs) have excellent mechanical properties, electrical conductivity and thermal conductivity, making them a potential advanced nanocomposite material with more improved functions, including large surface area, stable structure and good conductivity. CNTs also contribute to the electrical conductivity of metal oxide nanocomposites. CNTs can lead to provide higher adsorbed dye quantities, and for interpenetration of electrodes in DSSCs. Several studies have reported that the incorporation of CNTs in a nanocrystalline TiO$_2$ working electrode prepared by blended fabrication with commercial TiO$_2$ (P25) can increase the solar energy conversion efficiency of DSSCs. However, increasing the CNT loading may inhibit the improvement of DSCC performance due to serious aggregation of CNTs in the blending procedure. Some studies have also indicated that the CNTs in DSSCs can improve the electrical conductivity of photoelectrode (TiO$_2$ film) because they can enhance the short-circuit photocurrent ($J_{sc}$) of DSSCs, thus raising its light-to-electricity efficiency. Some studies have reported that Ru(II) dye cannot be adsorbed by single-wall carbon nanotubes (SWNTs). Dye is assumed to be absorbed by TiO$_2$ particles. The adsorption sites, which

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increase apparently with uniform immobilization of TiO$_2$ on multi-wall carbon nanotubes (MWCNTs), can result in a larger surface area for dye adsorption. Many studies have indicated that the efficiency of $e^-$/$h^+$ recombination is an important factor affecting the photoelectron conversion efficiency of DSSC.\textsuperscript{15,16} MWCNTs that are bound to be immobilized by TiO$_2$ can also conduct electricity to photo-electrons easily since electrons are generated from TiO$_2$ under light irradiation.\textsuperscript{17,18} Thus, the efficiency of the electron-hole recombination in the nanocomposite can be possibly decreased.

This study employs EPD technology to prepare a TiO$_2$/CNT film by mixing self-prepared TiO$_2$ particles with the modified TiO$_2$-CNTs in an electrophoretic tank. The TiO$_2$/CNT film thus prepared then becomes the photoelectrode of DSSCs. In addition, the natural dye used as dye sensitizer in the fabrication of DSSCs is extracted from ipomoea.

2. Experimental Principles and Methods

2.1 Preparation of TiO$_2$ nanofluid

This research used a novel processing technology to produce a nanocomposite nanofluid,\textsuperscript{19,20} which comprises primarily a cooling system, an arc discharge generator system, a vacuum system, an ultrasonic vibration system, a nanofluid collector and a pressure balance system. To fabricate the TiO$_2$ nanofluid, two pure Ti rods of the same size are used as the anode and cathode electrodes inside the vacuum chamber. The dielectric fluid in the vacuum chamber was deionized water. The vacuum pressure of this experiment was set to be 4 × 10$^3$ Pa. The vacuum level of the vacuum chamber was reduced to around 4 × 10$^3$ Pa, with processing starting upon the setting of voltage, current, pulse-on and pulse-off time. In addition, the nanofluid collector was attached to a vortex generator, so the nanoparticles could be evenly stirred. Field-emission scanning electron microscope (FE-SEM, LEO-1530) images were taken to measure and analyze the structure and morphology of the prepared TiO$_2$ nanoparticles. X-ray diffraction (XRD) pattern was also employed to analyze the structure of the fabricated TiO$_2$ nanoparticles.

2.2 Preparation of TiO$_2$-CNT

The MWCNTs (QF-MCNTs-30, Yong-Zhen Technomaterial Co. Ltd., Taiwan) used in this study were 10–30 nm in diameter, 10–15 μm in length, prepared by chemical vapor deposition (CVD), and had a purity of over 95%. The sol-gel solution was prepared by blending titanium tetra-isopropoxide (Ti(OC$_3$H$_7$)$_4$) (Wako Pure Chemical Industries Co. Ltd., Japan), isopropanol (IPA, First Chemical Co. Ltd., Taiwan), nitric acid (First Chemical Co. Ltd., Taiwan), and distilled water. The weight ratio for preparing the sol-gel solution was kept at 1 : 10 : 1 : 0.2 for Ti(OC$_3$H$_7$)$_4$ : IPA : H$_2$O : HNO$_3$.\textsuperscript{21} The solution was under reflux at the temperature of 80°C for 1 h using a magnetic stirrer. For each sample, 0.5 g of MWCNT was mixed with 50 mL of sol-gel solution, and stirred in closed vials for 3 h. The impregnated MWCNTs were separated from the solution by filtration. The blended solution was baked in an oven at 80°C for 1 h, and then sintered in a furnace at 600°C for 1.5 h, thus yielding the composite powder of TiO$_2$-CNT.

2.3 Preparation of natural dye

Ten grams of fresh ipomoea (Taiwan) were placed in 200 mL of 95 mass% ethanol solution. Under different preset temperatures (20–80°C), ipomoea was heated by indirect hydronic heating in boiling water for 20 minutes to extract its chlorophyll. The solid residue in the solution was poured through the filter paper in a clean and light-free working environment to remove impurities of the dye solution, thus giving a pure and natural dye solution.

2.4 Preparation of photoelectrode for DSSC

The self-developed arc discharge nanofluid synthesis system was utilized to prepare a TiO$_2$ nanofluid with an average particle size of 40 nm. The prepared TiO$_2$ fluid was pumped dry by vacuum to become a nanopowder. After blending 0.35 g of self-prepared TiO$_2$ with 100 mL of IPA, followed by addition of TiO$_2$-CNT (0.001–0.02 g) composite powder of different proportions, an electrophoretic suspension was made. The electrophoretic suspension was shaken in an ultrasonic vibrator for 1 h. After that, EPD was performed at 14°C. Figure 1 shows the schematic diagram of the
experimental setup for preparing TiO$_2$/CNT thin film by EPD. As can be seen, the anode (aluminum plate) and cathode [$7\Omega$/sq, indium tin oxide (ITO) conductive glass] were placed parallel at a distance of 1 cm in the electrophoretic suspension. The voltage was set to be 40 V. In Fig. 1, there are two electrophoretic baths. Hence, two TiO$_2$/CNT thin films can be formed for the subsequent measurement. A TiO$_2$/CNT film of around 14 \(\mu\)m thick was deposited. The thin film had to undergo sintering treatment at 400°C for 2 h to increase its compactness. Finally, the TiO$_2$/CNT film was immersed in natural ipomoea dye for 24 h, allowing the natural dye molecules to be absorbed by the surface of TiO$_2$/CNT film.

2.5 Assembly and test of DSSC

After dye absorption by TiO$_2$ electrode, the photoelectrode surface was cleaned using acetonitrile to remove any natural dye that had not been absorbed by the TiO$_2$/CNT nanoparticle surface. Then the DSSC was placed in quiescence and dried to develop the photoelectrode of DSSC. In addition, the oxidation-reduction electrolyte at I$^-$/I$_3^-$ was poured into the counter-electrode cracks and then coated with platinum. The TiO$_2$ electrode and counter electrode were tightly bonded and fixed by a binder clip to prevent the production of air bubble, and a sandwich DSSC was thus formed. In the performance test of the prepared DSSC, xenon (Xe) light of 150 W was selected to simulate the sunlight (AM 1.5), and an I-V curve analyzer (Keithley 2400) was employed to measure the light-to-electricity efficiency of the prepared DSSC.

Before the test, the distance between light and the sample was adjusted, and the light density was set to be 100 mW/cm$^2$. The measured results was plotted in an I-V curve, from which the data of $V_{OC}$ (V), $J_{SC}$ (mA/cm$^2$), fill factor (FF) and $\eta$% could be further acquired.

3. Experimental Results and Discussion

The process parameters were vacuum pressure, $4 \times 10^3 \text{ Pa}$; peak current, 4 A; pulse-on and pulse-off time, 6 \(\mu\) s; and breakdown voltage, 220 V. Figure 2(a) shows the FE-SEM image of TiO$_2$ nanoparticles fabricated using the abovementioned working parameters. The TiO$_2$ nanoparticles thus produced have a mean particle size of around 40 nm. After the reaction of sol-gel solution was completed, the MWCNTs were modified by TiO$_2$, and their FE-SEM images are shown in Fig. 2(b). The crystal structure of the fabricated TiO$_2$ nanoparticles could be determined using an X-ray diffractometer (M03XHF22, X-ray diffractometer with Cu Ka radiation). When producing the samples, a vacuum funnel was first utilized to filter out the particles from the nanofluid. After desiccation, the acquired desiccated powder could serve as the produced sample. Comparing the XRD pattern after examination of the standard spectrum of a JCPDS (Joint Committee on Powder Diffraction Standards) card shows that the crystal structure of the fabricated particles was anatase TiO$_2$ (JCPDS card no. 21-1272). Since the rutile phase of TiO$_2$ had better light scattering, the rate of light utilization could be increased, thus enhancing the light-to-electricity efficiency of DSSCs accordingly. The modified MWCNTs had to undergo sintering treatment at 600°C to change the crystallized structure of TiO$_2$. The recorded XRD spectra of pure MWCNTs and the thermally treated TiO$_2$-CNTs at 600°C are shown in Fig. 3. The most intense peaks at 26° reflection (Fig. 3, pattern (a)) correspond to the (002) plane for MWCNTs. As seen in pattern (b) of Fig. 3, the intense peaks at 27.8, 36.2, 41.2, 54.5 and 56.7 correspond to the (110), (101), (111), (211) and (220) planes, respectively.
(JCPDS card no. 21-1276). They clearly reveal that the crystalline phase of the immobilized TiO$_2$ is rutile phase. However, as observed from pattern (b) in Fig. 3, the crystalline phase of anatase at the intense peak is 25.4, corresponding to the (101) plane (JCPDS card no. 21-1272). This result indicates that the surface of MWCNTs is almost modified by the rutile phase of TiO$_2$. Furthermore, the peak of 26.0 at 20 position, which is the characteristic of CNT, is not observed in the XRD patterns. A reason for this phenomenon is that the main peak of MWCNT at 26.0 may overlap with the main peak of anatase TiO$_2$ crystallites at 25.4 since these two peaks are very close. Moreover, the crystallinity of TiO$_2$ is much higher than that of MWCNT, thus making TiO$_2$ peaks surpass those of MWCNT. Figure 4 shows the Raman spectra (RENISHAW in Via) of the purified CNT and the thermally treated TiO$_2$-CNT powder at 600°C. Comparing these two diagrams reveals that the TiO$_2$-CNT powder shows five Raman peaks, as seen in pattern (b) of Fig. 4, with the Raman peaks of 274 cm$^{-1}$, 449 cm$^{-1}$ and 616 cm$^{-1}$ meeting the Raman peak of the rutile phase, and the other two Raman peaks of 1352 cm$^{-1}$ (D band) and 1586 cm$^{-1}$ (G band) are MWCNT peaks. As shown from Fig. 4, the D-band and G-band pertaining to the MWCNT of TiO$_2$-CNT powders show blue-shifts by 5 and 4 cm$^{-1}$, respectively, with respect to that of pristine MWCNT at about 1347 and 1582 cm$^{-1}$. These blue-shifts can be attributed to the strain effects at the TiO$_2$/CNT interfaces, which may influence the vibrational frequencies. Furthermore, these Raman spectral changes of MWCNT are due to the adherence of TiO$_2$ nanoparticles to the CNTs.

Figure 5(a) shows the FE-SEM image of the surface morphology of TiO$_2$ thin film acquired with no TiO$_2$-CNT powder added in the EPD process. Figure 5(b) and Fig. 5(c) show the FE-SEM images of the surface morphology of TiO$_2$/CNT thin films acquired after adding 0.001 g and 0.02 g of TiO$_2$-CNT powder, respectively in the EPD process. The excessive CNT-TiO$_2$ content might cause aggregation of MWCNTs, which undermines the separation of TiO$_2$ particles, thus leading to larger cracks formed. Moreover, with increase in quantity of TiO$_2$-CNT powder, the number of cracks on the surface of the films increased accordingly, and the increase in number of these cracks might decrease dye adsorption. The dye molecules staying in cracks and having no bonding with TiO$_2$ would be lost in the electrolyte solution. Hence, there were not sufficient dye molecules to transmit electrons to the semi-conductive oxide, resulting in reduced conversion efficiency of DSSCs.

Figure 6 shows the FE-SEM image of TiO$_2$/CNT thin film prepared by the EPD process. As shown from the prepared
photoelectrode film in Fig. 6(a), there are many TiO$_2$ nanoparticles coated on the surface of CNT. The particles around the TiO$_2$-CNT thin film are the TiO$_2$ nanoparticles prepared by the arc discharge nanofluid synthesis system developed by the authors. Figure 6(b) shows the cross-section image of the photoelectrode film after being sintered at 400°C. As can be seen, the prepared TiO$_2$/CNT thin film is of 14 μm thick and is highly compact. Figure 7 shows the UV-vis (V-650, Jasco, Japan) transmittance spectra of the composite electrode. As can be seen, within the range of visible light wavelength, when more TiO$_2$-CNT nanopowder is added to prepare the CNT/TiO$_2$ thin film, the transmittance intensity falls due to the increase in CNT content in the CNT/TiO$_2$ thin film. Figure 8 shows the acquired absorption spectrum of ipomoea leaf extract after UV/Vis illumination. As seen from the curves of the spectrum, the absorption of ipomoea extract fluid peaked at the wavelength of 410 nm. The amount of dye-sensitizer adsorbed by the as-prepared TiO$_2$ thin film and the TiO$_2$/CNT (0.001 g) thin film are $1.66 \times 10^{-8}$ mol cm$^{-2}$ and $5.32 \times 10^{-8}$ mol cm$^{-2}$ respectively.

Figure 9 shows the J-V characteristics of the prepared DSSCs for the as-prepared TiO$_2$ thin film and the TiO$_2$/CNT thin films prepared by mixing TiO$_2$ nanoparticles with TiO$_2$-CNTs at different proportions in the EPD process. In Fig. 9, the required electrophoretic suspension is added 0.001 g, 0.01 g and 0.02 g of TiO$_2$-CNTs, respectively to 0.35 g of self-prepared TiO$_2$ nanoparticles and 100 mL of IPA. Table 1 shows the data acquired from measuring the light-to-electricity properties of DSSCs, which were obtained after blending TiO$_2$-CNTs at different proportions with the self-prepared TiO$_2$ in the electrophoretic solution. The data include short-circuit photocurrent density ($J_{sc}$), open-circuit voltage ($V_{oc}$), and power conversion efficiency ($\eta$).
Table 1 Photoelectrochemical parameters of TiO$_2$-CNT after incorporating TiO$_2$-CNTs in DSSCs.

<table>
<thead>
<tr>
<th>TiO$_2$-CNTs</th>
<th>$V_{oc}$ (V)</th>
<th>$J_{sc}$ (mA/cm$^2$)</th>
<th>$\eta$ (%)</th>
<th>FF</th>
<th>Cell area (cm$^2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0 g</td>
<td>0.545</td>
<td>0.91</td>
<td>0.278</td>
<td>0.56</td>
<td>0.25</td>
</tr>
<tr>
<td>0.001 g</td>
<td>0.56</td>
<td>1.14</td>
<td>0.359</td>
<td>0.56</td>
<td>0.25</td>
</tr>
<tr>
<td>0.01 g</td>
<td>0.56</td>
<td>1.06</td>
<td>0.319</td>
<td>0.54</td>
<td>0.25</td>
</tr>
<tr>
<td>0.02 g</td>
<td>0.545</td>
<td>1.01</td>
<td>0.295</td>
<td>0.54</td>
<td>0.25</td>
</tr>
</tbody>
</table>

Voltage ($V_{oc}$), fill factor (FF), and energy conversion efficiency ($\eta$). As seen in the table, the open-circuit voltage increased from 0.54 to 0.56. Furthermore, for 0.001 g of TiO$_2$-CNTs, the value of short-circuit photocurrent density ($J_{sc}$) was found to increase by 25% from 0.91 to 1.14 mA/cm$^2$ when compared with the prepared TiO$_2$ electrode. However, $J_{sc}$ decreases from 1.14 to 1.01 mA/cm$^2$ with the subsequent increase in TiO$_2$-CNTs from 0.001 g to 0.02 g. Such a gradual decrease in $J_{sc}$ with increase in TiO$_2$-CNTs can be attributed to the increased number of cracks on the surface of the porous TiO$_2$ electrode. Consequently, the addition of TiO$_2$-CNTs enhanced the electrical conductivity of porous TiO$_2$ electrode, but decreased the adsorption area of ruthenium dye and created cracks on the TiO$_2$ film. Thus, the TiO$_2$-CNTs (0.001 g) containing TiO$_2$ electrodes had conversion efficiency increased by 30% (0.278% to 0.359%), which was higher than that of the prepared TiO$_2$ electrode of DSSCs (Table 1). However, the subsequent increase in concentration of TiO$_2$-CNTs (from 0.001 to 0.02 g) did not further help increase the conversion efficiency. The photoelectrodes in DSSCs had their CNTs modified by TiO$_2$ to become TiO$_2$-CNT composite powder. The CNTs added could enhance the short-circuit current density ($J_{sc}$), providing more efficient electron transfer effect and enhancing the efficiency of photoelectrode. In addition, mixing the self-prepared TiO$_2$ nanoparticles with the TiO$_2$-CNT composite powder in the electrophoretic solution also helps improve the interconnectivity between TiO$_2$ particles and TiO$_2$-CNTs, and further enhances the overall light-to-electricity efficiency of DSSCs.

4. Conclusions

From the abovementioned experimental results and discussion, the following conclusions can be drawn.

(1) This study prepared successfully highly efficient photoelectrode of DSSCs using electrophoresis technology to mix the modified TiO$_2$-CNT composite powder with the self-prepared TiO$_2$ nanoparticles in the electrophoretic solution and with natural dye extracted from ipomoea.

(2) Compared with the conventional TiO$_2$ cell, the TiO$_2$-modified cell (0.001 g of TiO$_2$-CNTs) achieved an increase in conversion efficiency of 30%.

(3) In the photoelectrode of DSSCs, TiO$_2$ is modified by CNTs. The short-circuit current density ($J_{sc}$) can be enhanced to provide more efficient electron transfer effect.

Acknowledgement

This study was supported by the National Science Council of Taiwan, Republic of China under the project grant: NSC 97-2221-E-027-046.

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