Research Article

Quasi Solid-State Dye-Sensitized Solar Cell Incorporating Highly Conducting Polythiophene-Coated Carbon Nanotube Composites in Ionic Liquid

Mohammad Rezaul Karim, 1 Ashraful Islam, 1, 2 Surya Prakash Singh, 2 and Liyuan Han 2

1 Center of Excellence for Research in Engineering Materials (CEREM), College of Engineering, King Saud University, Riyadh 11421, Saudi Arabia
2 Photovoltaic Materials Unit, National Institute for Materials Science (NIMS), 1-2-1 Sengen, Tsukuba, Ibaraki 305-0047, Japan

Correspondence should be addressed to Mohammad Rezaul Karim, mkarim@ksu.edu.sa
and Ashraful Islam, islam.ashraful@nims.go.jp

Received 30 April 2011; Accepted 13 June 2011

Academic Editor: Ahmed El-Shafei

Copyright © 2011 Mohammad Rezaul Karim et al. This is an open access article distributed under the Creative Commons Attribution License, which permits unrestricted use, distribution, and reproduction in any medium, provided the original work is properly cited.

Conducting polythiophene (PTh) composites with the host filler multiwalled carbon nanotube (MWNT) have been used, for the first time, in the dye-sensitized solar cells (DSCs). A quasi solid-state DSCs with the hybrid MWNT-PTh composites, an ionic liquid of 1-methyl-3-propyl imidazolium iodide (PMII), was placed between the dye-sensitized porous TiO2 and the Pt counter electrode without adding iodine and higher cell efficiency (4.76%) was achieved, as compared to that containing bare PMII (0.29%). The MWNT-PTh nanoparticles are exploited as the extended electron transfer materials and serve simultaneously as catalyst for the electrochemical reduction of I−.

1. Introduction

Dye-sensitized solar cells (DSCs) have attracted significant attention as promising solar-to-electricity power conversion devices because of their higher energy conversion and potential for low-cost production [1–6]. In general, DSCs comprise an electrode consisting of nanocrystalline titanium dioxide (TiO2) films modified with a dye, a platinum counterelectrode, and an electrolyte solution in between the electrodes. Photoexcitation of the dye results in the injection of an electron into the conduction band of the oxide. The original state of the dye is subsequently restored by electron donation from a redox system, such as the iodide/triiodide (I−/I3−) couple. At the present, DSCs are mainly constructed by using liquid electrolyte as a charge transport material. The charge transport in these liquid electrolytes is typically achieved by using I−/I3− redox reaction in electrolyte solution. Therefore, long-term durability of DSCs is limited by leakage and the volatilization of organic solvent-based electrolytes. Numerous investigations have been conferred to overcome this drawback, replacing the liquid electrolyte by organic and inorganic hole transport materials [7–9], polymer and gel electrolytes [10–14], and nanocomposite ionic liquid (IL) electrolytes [15–20] resulting in solid-state and quasi solid-state DSCs. Imperfect pour filling of the dye-coated nanocrystalline TiO2 film with organic and inorganic hole transport materials results in a poor device efficiency. Moreover, the ionic conductivity for the majority of the amorphous polymer electrolytes is too low (<10−5 S cm−1), limiting the device efficiency. Although nanocomposite IL electrolyte can reduce leakages, it is not satisfactory, because of the high concentration of corrosive and volatile iodine present in the electrolyte. The introduction of I2 into the electrolytes could increase the conductivity of the electrolyte via a Grotthuss-type charge carrier exchange transfer mechanism. However, the increasing content of I2 (or I3−) leads to enhanced light absorption even in the visible range by the electrolyte. The increased absorption of visible light by the electrolyte, the enhanced dark current, and the reduced ionic conductivity of the electrolyte contribute to
the performance variation of the corresponding DSCs with increasing I$_2$ concentration.

Conducting polymer-coated carbon nanotube composites are extremely good conducting hybrid materials, which are often used in organic field effect transistor, solar cells, sensors, electrochromic devices, and light emitting diodes [21–24]. Lee and coworkers reported iodine-free quasi solid-state DSCs, containing a conducting polymer loaded carbon black and an ionic liquid, which exhibited a power conversion efficiency of 5.8% [25]. Recently, Lee et al. further reported an efficient solid-state DSC using a hybrid carbon nanotubes-binary ionic liquid containing 1-ethyl-3-methylimidazolium iodide (EMII) and 1-methyl-3-propylimidazolium iodide (PMII), without the addition of iodine and TBP [26]. Besides, Wang et al. and Ikeda et al. have reported separately a solid-state electrolyte without the incorporation of volatile iodine and achieved high device efficiency [27, 28].

In our earlier work, we reported highly conducting cable-like PTh-MWNT composites, composed of conducting polyiophene (PTh) with the host filler multiwalled carbon nanotube (MWNT), synthesized by the gamma-radiation-induced in situ chemical polymerization method [29]. In this study, core-shell MWNT-PTh composites were added to ionic liquid to form the extended electron transfer surface (Scheme 1) from the counterelectrode's surface to the bulk electrolyte, in order to facilitate electron transfer and, thereby, decrease the dark current from the working electrode to the electrolyte. For the first time, MWNT-PTh composites have been used in DSSC, and the effect of MWNT-PTh composites addition in the solvent-free ionic liquid electrolyte without the incorporation of iodine was studied.

2. Experimental

2.1. Materials. The following chemicals were purchased and used without further purification: iodine (I$_2$, from Merck), 1-methyl-3-propyl-imidazolium iodide (MPII, from Merck), tert-butyl alcohol (Fluka), acetonitrile (ACN, 99.99%, Aldrich), tert-butyl alcohol (Fluka), acetonitrile (ACN, 99.99%, Aldrich), anhydrous iron (III) chloride (FeCl$_3$, Aldrich), and chloroform (CHCl$_3$, Aldrich). Thiophene monomer (99+%, Aldrich) was distilled under a reduced pressure and kept below 0°C prior to use. MWNT (>95 vol. grade, produced by the CVD method; diameter: 10–20 nm, length: 10–50 μm) was supplied by Iljin Nanotech Co., Ltd., Republic of Korea.

2.2. Composite Electrolyte. The conducting MWNT-PTh hybrid composites were synthesized as per our reported work [29]. The instruments used for the characterization of MWNT-PTh hybrid composites included a field-emission scanning electron microscope (FE-SEM) (Hitachi Model S-4300) and a transmission electron microscope (TEM) (Philips model CM 200) with an Acc. Voltage of 200 kv. The room-temperature conductivity of the pressed pellets was measured by the four-point probe method using a Jandel engineering instrument, Model CMT-SR1060N. The composite electrolyte was prepared by mixing the solid powder of MWNT-PTh, PMII, and ACN in a weight ratio of 1 : 7 : 7. ACN was added to the composite to improve the mixing, and was removed on a hot plate at a temperature of 90°C.
2.3. Fabrication of Dye-Sensitized Solar Cell. Nanocrystalline TiO$_2$ photoelectrodes of 15 μm thickness (area: 0.25 cm$^2$) were prepared on conducting glass using a variation of a previously reported method [30]. Fluorine-doped tin oxide-coated glass electrodes (Nippon Sheet Glass Co., Japan) with a sheet resistance of 8–10 ohm$^{-2}$ and an optical transmission of greater than 80% in the visible range were used. Anatase TiO$_2$ colloid pastes (particle size ~25 nm and ~400 nm) were obtained from commercial sources (Solaronix). The nanocrystalline TiO$_2$ thin films of approximately 15 μm thickness were deposited onto the conducting glass by screen printing. The film was sintered at 500°C for 1 h. The film thickness was measured with a Surfcom 1400 A surface profiler (Tokyo Seimitsu Co. Ltd.). The electrodes were impregnated with a 0.05 M titanium tetrachloride solution and sintered at 500°C. A dye solution of $3 \times 10^{-4}$ M N719 was prepared in 1:1 acetonitrile and tert-butyl alcohol solvents. Deoxycorticolic acid (20 mM) was added to the dye solution as a cosorbent to prevent aggregation of the dye molecules [31, 32]. The electrodes were immersed in the N719 solution and then kept at 25°C for 20 h to adsorb the dye onto the TiO$_2$ surface. Photovoltaic measurements were performed in a two-electrode sandwich cell configuration. The dye-deposited TiO$_2$ film and a platinum-coated conducting glass were used as the working electrode and the counter electrode, respectively. A 30 μm thick surlon spacer was put on the dye-deposited TiO$_2$ electrode and attached by heating. The MWNT-PTh/PMII hybrid composite electrolyte was then put onto the dye-sensitized TiO$_2$ film at 85°C to ensure that the PMII can penetrate well into the porous structure and remove the residual ACN. The dye-deposited TiO$_2$ electrode with the MWNT-PTh/PMII hybrid composite electrolytes was assembled with a platinum-coated conducting glass electrode and sealed by heating the polymer frame. The electrolytes used for liquid cell were composed of 0.6 M dimethylpropylimidazolium iodide (DMPII), 0.05 M I$_2$, and 0.1 M LiI in acetonitrile.

2.4. Photovoltaic Characterization. The working electrode was illuminated through a conducting glass. The current-voltage characteristics were measured using a solar simulator (AM-1.5, 100 mW/cm$^2$, WXS-155S-10: Wacom Denso Co., Japan). Monochromatic incident photon-to-current conversion efficiency (IPCE) for the solar cell, plotted as a function of excitation wavelength, was recorded on a CEP-2000 system (Bunkoh-Keiki Co., Ltd.). Incident photon-to-current conversion efficiency (IPCE) at each incident wavelength was calculated from (1), where $I_c$ is the photocurrent density at short circuit in mA cm$^{-2}$ under monochromatic irradiation, $q$ is the elementary charge, $i$ is the wavelength of incident radiation in nm, and $P_0$ is the incident radiative flux in W m$^{-2}$:

$$\text{IPCE}(\lambda) = 1240 \left( \frac{I_c}{q \lambda P_0} \right).$$  (1)

3. Results and Discussion

Room temperature ionic liquids have several qualities as compared with other choices since they have negligible volatility, high thermal stability, a wide electrochemical potential window, and satisfactory ionic conductivity [33, 34]. Ionic liquids have limited ion diffusion because of their high viscosity. The conductivity of ionic liquid electrolytes is further improved by increasing iodine concentration resulting in a polyiodide formation thus facilitating electron-exchange-type conductivity [35]. Increasing of iodine concentration is, however, limited by strong visible light absorption by iodine itself. Therefore, iodide ionic liquids in combination with moderately high iodine concentration only make a satisfactory electrolyte for DSCs. Moreover, it was reported that the carbon material in the iodine-free composite electrolyte serves simultaneously as a charge transporter in the electrolyte and as a catalyst for electrochemical reduction of I$_3^-$ ions [25]. The iodide anion-based IL can provide sufficient I$^-$ for the regeneration of oxidized dye under illumination; I$^-$ in turn oxidizes to I$_3^-$, which can be reduced back to I$^-$ at the carbon material.

A main component of DSCs is the electrolyte that fills the space between the dye-coated porous nanocrystalline TiO$_2$ electrode and the counterelectrode. In the vast majority of cases the electrolyte contains I$^-$/I$_3^-$ redox couple. In general, iodide salt and iodine are the source of the I$^-$/I$_3^-$ redox couple. In the electrolyte, I$_2$ exists in the form of polyiodides such as I$_3^-$ or I$_5^-$ (2). Photoexcitation of the dye results in the injection of an electron into the conduction band of the TiO$_2$. The oxidized state of the dye (dye$^+$) should be regenerated efficiently by electron donation from I$^-$ (3). The efficient regeneration of oxidized dye is crucial for obtaining good electron collection yields and a high cycle life of the sensitizer. Meanwhile, the electrons accumulated at the counterelectrode by the external circuit will lead to concentration over potentials for the electrolyte at the counterelectrode and loss of energy of the DSCs if the electrons are not transferred by I$_3^-$ efficiently (4). Apart from recapture by the oxidized dye, the electrons can be lost to the electrolyte by reaction with the I$_5^-$ (5). Therefore an efficient transport of iodide and triiodide in the electrolyte is necessary for good performance of the DSCs. Meanwhile, the increase of the I$_3^-$ concentration in the electrolyte results in an increasing dark current of the DSCs and thus decreases the device performance:

$$I^- + I_2 \rightarrow I_3^- + I_2 \rightarrow I_5^- \quad \text{(electrolyte solution)} \quad (2)$$

$$3I^- + 2\text{dye}^+ \rightarrow I_3^- + 2\text{dye} \quad \text{(TiO}_2\text{ electrode)} \quad (3)$$

$$I_3^- + 2e^- \rightarrow 3I^- \quad \text{(counterelectrode)} \quad (4)$$

$$I_5^- + 2e^- \ cb \quad \text{(TiO}_2\text{ electrode)} \rightarrow 3I^- \quad (5)$$

Conducting polymer-coated carbon nanotubes are notable materials, which are being widely studied because of their extraordinary electronic and mechanical properties. Considering these aspects, combustible and nonvolatile PMII and MWNT-PTh composites, were incorporated into
DSCs for this study (Scheme 1). The presence of redox-active PMII ionic liquid fills the nanoporous TiO₂/dye interface, where no space is available for MWNT-PTh composites to occupy. It is expected that this IL would allow perfect contact at the interface between the dye-coated porous TiO₂ and the conducting polymer-coated carbon material [19], that is, MWNT-PTh composites.

A typical morphology of MWNT-PTh composites synthesized by the radiolysis polymerization method was investigated using scanning electron microscopes (Figure 1). In Figure 1(a), the FE-SEM image shows a uniform view of the MWNT-PTh composites. The tubular morphology of the MWNT-PTh composites was also imaged by the TEM, as shown in Figure 1(b). Structural characterizations showed that there was clear indication of interfacial entrapment between the PTh and MWNT; the conducting polymer is coated on the surface of the carbon nanotube. Here, the tubular inner part (core) is mainly the compound of MWNT and the outer coated surface (shell) is conducting polythiophene with variable thicknesses (20–50 nm diameters), and their external surfaces are not smooth.

Figure 2 shows the energy dispersive spectroscopy (EDS) analysis of MWNT-PTh composites (data are given in the table). The atomic percents of the C and S are 58.78 and 11.75, respectively, for MWNT-PTh composites which reveal that carbon nanotube and polythiophene are both present in the sample. In general, electrical conductivity may be taken as a function of the conjugation length of the polymer and the amount of active dopant present in the polymer, as the number of charge carriers depends upon the extent of the dopant concentration, provided that other factors remain unchanged. A powder sample of 0.02 g was loaded and pressed into a pellet 1.2 cm in diameter and a pressure of 170 atm by a manual hydraulic press for 10 min. Then, the electrical conductivity of the pellets was measured by a standard four-point probe method, connected to a Keithley.

**Figure 1:** (a) FE-SEM and (b) TEM images of MWNT-PTh composites.

**Figure 2:** Representative EDS analysis data of MWNT-PTh composites.
Table 1: Photovoltaic properties of the DSCs with MWNT-PTh/PMII composite electrolyte and with bare PMII electrolyte using Pt/ITO and bare ITO as counterelectrode.

<table>
<thead>
<tr>
<th>Electrolyte</th>
<th>Counterelectrode</th>
<th>J_{sc} (mA cm^{-2})</th>
<th>V_{oc} (V)</th>
<th>FF</th>
<th>η(%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PMII</td>
<td>Pt/ITO</td>
<td>1.3</td>
<td>0.68</td>
<td>0.33</td>
<td>0.29</td>
</tr>
<tr>
<td>MWNT-PTh/PMII</td>
<td>Pt/ITO</td>
<td>10.2</td>
<td>0.73</td>
<td>0.64</td>
<td>4.76</td>
</tr>
<tr>
<td>PMII</td>
<td>ITO</td>
<td>1.0</td>
<td>0.49</td>
<td>0.27</td>
<td>0.13</td>
</tr>
<tr>
<td>MWNT-PTh/PMII</td>
<td>ITO</td>
<td>7.6</td>
<td>0.62</td>
<td>0.60</td>
<td>2.83</td>
</tr>
<tr>
<td>Liquid electrolyte</td>
<td>Pt/ITO</td>
<td>15.4</td>
<td>0.70</td>
<td>0.73</td>
<td>7.86</td>
</tr>
</tbody>
</table>

*Conditions: sealed cells; dye: N719; coadsorbate: DCA 40 mM; photoelectrode: TiO_2 (15 μm thickness and 0.25 cm^2); irradiated light: AM 1.5 solar light (100 mW cm^{-2}). J_{sc}: short-circuit photocurrent density; V_{oc}: open-circuit photovoltage; FF: fill factor; η: total power conversion efficiency.

The photovoltaic performances of the DSCs under AM 1.5 G simulated solar light at a light intensity of 100 mW cm^{-2} using MWNT-PTh/PMII composite electrolyte and using bare PMII as electrolyte are shown in Table 1. The cell efficiency of MWNT-PTh/PMII device is 4.76%, which is remarkably higher than that of bare PMII device (0.29%). The low device efficiency of bare PMII device is due to significant decrease in both J_{sc} and FF. The presence of PTh-MWNT facilitates electron transfer from counterelectrode to I_3^- ions in MWNT-PTh/PMII composite device. Recently, Lee et al. reported, based on electrochemical impedance spectroscopy (EIS) analysis, that the presence of carbon materials in IL facilitates electron transfer from counterelectrode to I_3^-, which enables the I^-/I_3^- redox couple to work more efficiently than they would in the absence of carbon materials [25]. An analogous explanation is also assumed for the MWNT-PTh/PMII composite electrolyte systems as well.

Figure 3 shows a photocurrent density-voltage curve of a sealed solar cell based on MWNT-PTh/PMII under AM 1.5 G simulated solar light at a light intensity of 100 mW cm^{-2}. The MWNT-PTh/PMII electrolyte containing solar cell showed a photocurrent density of 10.2 mA cm^{-2}, a no-open-circuit potential of 0.73 V, and a fill factor of 0.64, corresponding to an overall conversion efficiency (η) of 4.76%. In the same experimental condition, liquid electrolyte device shows an overall conversion efficiency (η) of 7.86% with a high photocurrent density of 15.4 mA cm^{-2} (Table 1). Figure 4 shows the monochromatic incident photon to current conversion efficiency (IPCE) for DSCs based on MWNT-PTh/PMII composite and liquid electrolytes. Liquid-electrolyte-based device shows the maximum IPCE of 74% at 540 nm, while the MWNT-PTh/PMII device shows only 59% IPCE at 540 nm. Inefficient charge transport properties in the composite electrolyte may be responsible for the low...
conversion efficiency in the MWNT-PTh/PMII-electrolyte-based device. Further study will target the development of a high-performance quasi-solid-state solar cell through improvement of charge transport properties in the composite electrolyte and also the catalytic activity of the electrolyte for electrochemical reduction of I$_3^-$ ions.

4. Conclusion
A 4.76% of light-to-electricity conversion efficiency of the quasi solid-state DSCs is obtained using hybrid MWNT-PTh/PMII composites electrolyte without the addition of iodine under the radiation of 100 mW cm$^{-2}$ (AM1.5 full sunlight). The cell efficiency of the quasi solid-state DSCs incorporating highly conducting MWNT-PTh composite is one order higher than that of bare PMII device (0.29%). It is assumed that the hybrid MWNT-PTh composite plays a key role in both charge transportation in the composite electrolyte and the catalytic activities for electrochemical reduction of I$_3^-$.

Acknowledgment
The authors gratefully acknowledge the financial support from NPST program by King Saud University of project no. 10-NAN1021-02.

References


