Modified carbon nanotube & poly (3-hexylthiophene) nanocomposites integrated in quasi solid-state dye synthesized solar cells

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ABSTRACT
Poly (3-hexylthiophene) (P3HT) and modified (functionalized and silanized) multi wall carbon nanotube (MWNT) nanocomposites have been prepared through in-situ polymerization process in chloroform medium with FeCl$_3$ oxidant at room temperature. The composites (P3HT-MWNT) are characterized through various characterizations to identify the hybrid nanocomposites. Finally, a quasi solid-state dye synthesized solar cells (DSC) with the hybrid P3HT-MWNT composites, an ionic liquid of 1-methyl-3-propyl imidazolium iodide (PMII) are placed between the dye-sensitized porous TiO$_2$ and the Pt counter electrode without adding of iodine and achieved higher cell efficiency (4.1%), as compared to that containing bare PMII (0.29%). The P3HT-MWNT nanoparticles exploits as the extended electron transfer materials and serve simultaneously as a catalyst for the electrochemical reduction of I$_3^-$.

Keywords: Poly(3-hexylthiophene); multi wall carbon nanotubes; quasi solid-state dye synthesized solar cells; functionalized; silanized.

1 INTRODUCTION
Dye-sensitized solar cells (DSC) have introduced significant attention as promising solar-to-electricity power conversion devices due to their higher energy conversion and potential for low-cost production [1,2]. Generally, DSC comprise an electrode consisting of a nanocrystalline titanium dioxide (TiO$_2$) film modified with a dye, a platinum counter electrode 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$^-$/I$_3^-$) couple. Presently, DSC is mainly constructed by using liquid electrolyte as a charge transport material. The charge transport in these liquid electrolytes is typically achieved by using an I$^-$/I$_3^-$ redox reaction in the electrolyte solution. Therefore, long-term durability of DSC is limited by leakage and the volatilization of organic solvent-based electrolytes. Several investigations have been conferred to overcome this drawback, replacing the liquid electrolyte by organic and inorganic hole transport materials [3], polymer and gel electrolytes [4], nanocomposite ionic liquid (IL) electrolytes [5] resulting in a solid-state and quasi-solid state DSC. Imperfect pour filling of the dye coated nanocrystalline TiO$_2$ film with organic and inorganic hole transport materials is resulting 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 nano-composite IL electrolyte can diminish leakages, it is not reasonable, because of high concentration of corrosive and volatile iodine presence in the electrolyte. The introduction of I$_2$ into the electrolytes could enhance the conductivity of the electrolyte via a Grotthuss-type charge carrier exchange transfer mechanism. However, the increasing content of I$_2$ (or I$_3^-$) leads to better 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 DSC 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 [6]. Lee and coworkers reported iodine-free quasi solid-state DSC, containing a conducting polymer loaded carbon black and an ionic liquid, which exhibited a power conversion efficiency 5.8% [7]. Recently, Lee et al. further reported an efficient solid-state DSC using 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 [8]. 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 [9].

In this study, P3HT-MWNT composites were added to the liquid to form the extended electron transfer surface from the counter electrode’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, P3HT-MWNT composites have been used in DSC, and the effect of P3HT-MWNT composites addition in the solvent-free ionic liquid electrolyte without the incorporation of iodine was studied.

2 EXPERIMENTAL PARTS
2.1 General: MWNT (AP-grade, diameter: 10–12 nm, length: 2–20 µm) supplied by Iljin Nanotech Co., Ltd, South Korea was used in as procured form. 3-hexylthiophene (3HT) monomer (97%), chloroform, iron (III) chloride anhydrous (oxidant), 3-aminopropyltriethoxysilane and other organic solvents

purchased from Aldrich as reagent grade were used without further purification.

2.2 MWNT functionalization: Required amount of raw MWNT (rMWNT) were suspended in a 3:1 mixture of concentrated HNO\(_3\)/H\(_2\)SO\(_4\) solution and ultrasonicated in the water bath for 24 h at 60°C using a Branson Sonifier. The resulting acid-treated MWNT were filtered and then washed with water and methanol, subsequently. The functionalized MWNT (fMWNT) were dried in a vacuum oven at 110°C for 24 h.

2.3 Silane modified fMWNT: The acid-treated MWNT were then surface-modified using silane compounds by the following way: necessary amount of fMWNT were suspended in 100 ml of toluene and ultrasonicated in the water bath for 30 min at room temperature. 11.4 mmol of 3-aminopropyltriethoxysilane dissolved in 1 wt.% toluene solution was slowly added in the above solution and refluxed at 75°C with continues stirring for 6 h. The solution was filtered with adding 30 ml of methanol for dilution and washed by deionized water, methanol and acetone. The resultant silane-modified MWNT (siMWNT) powder was collected after vacuum drying at 80°C for 12 h.

2.4 Preparation of P3HT and P3HT-MWNT Nanoparticles: A typical in-situ chemical oxidative polymerization for the 3HT and 3HT-MWNT was carried out. The synthesis for the composite consists of following steps: 100 ml of CHCl\(_3\) solution containing MWNT (required amount of rMWNT, fMWNT and siMWNT individually) was added to a 250 ml double-neck, round bottomed flask carrying a magnetic Teflon-coated stirrer. The mixture was sonicated for 1 h at room temperature in order to disperse the MWNT. 4 mmol of FeCl\(_3\) in 100 ml CHCl\(_3\) solution was added to the above solution and further sonicated for 30 min. 3HT monomer (1 mmol) in a 25 ml CHCl\(_3\) solution was taken in a condenser and added drop wise to the MWNT and FeCl\(_3\) solution with constant stirring. The reaction mixture was stirred for an additional 24 h under the same conditions. The resultant P3HT-MWNT composite was precipitated in methanol, filtered using a Buchner funnel and then carefully washed several times with methanol, 0.1 M HCl, deionized water and acetone. The obtained black powder was dried under a vacuum dryer at room temperature for 24 hrs. The bulk polymer (P3HT) was synthesized following the similar procedure by using the same monomer and oxidant ratio.

2.5 Composite electrolyte: The composite electrolyte was prepared by mixing the solid powder of P3HT & P3HT-MWNT composites, 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.

2.6 Fabrication of dye-sensitized solar cell: A 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 [10]. 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 (SolaRox). 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 1400A 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 3x10\(^{-4}\) M N719 was prepared in 1:1 acetonitrile and tert-butyl alcohol solvents. Deoxycholic acid (20 mM) was added to the dye solution as a coadsorbent to prevent aggregation of the dye molecules [11]. The electrodes were immersed in the N719 solution and then kept at 25°C for 20h 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 surlyn spacer was put on the dye-deposited TiO\(_2\) electrode and attached by heating. The P3HT & P3HT-MWNT/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 P3HT & P3HT-MWNT/PMII hybrid composite electrolytes was assembled with a platinum-coated conducting glass electrode and the edges were sealed by UV glue.

2.7 Characterizations: FE-SEM was studied in a dried film of the polymer and composites was platinum coated and was observed through a Field Emission Scanning Electron Microscope (Hitachi S-4200) at 20 kV. The photovoltaic performance measurements was as follows: 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 equation 1, where Isc is the photocurrent density at short circuit in mA 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 equation 1, where Isc is the photocurrent density at short circuit in mA cm\(^{-2}\).

\[
\text{IPCE} (\lambda) = \frac{1240 (I_{sc}/q\lambda P_0)}{E_{a} - E_{c}}
\]
Ionic liquids have limited ion diffusion because of its 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 [13]. 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 DSC. 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 [7]. The iodide anion based IL can provide sufficient I$_3^-$ for the regeneration of oxidized dye under illumination; I$_3^-$ in turn oxidizes to I$_5^-$, which can be reduced back to I$_2^-$ at the carbon material.

A main component of DSC is the electrolyte that fills the space between the dye coated porous nanocrystalline TiO$_2$ electrode and the counter electrode. In the vast majority of cases, the electrolyte contains I$_3^-$/I$_2^-$ redox couple. In general, iodide salt and iodine are the source of the I$_3^-$/I$_2^-$ redox couple. In the electrolyte, I$_2^-$ exists in the form of polyiodides such as I$_5^-$ or I$_3^-$ (eq. 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$^+\$) should be regenerated efficiently by electron donation from I$_2^-$ (eq. 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 counter electrode by the external circuit will lead to concentration over potentials for the electrolyte at the counter electrode and loss of energy of the DSC if the electrons are not transferred by I$_2^-$ efficiently (eq. 4). Apart from recapture by the oxidized dye, the electrons can be lost to the electrolyte by reaction with the I$_3^-$ (eq. 5). Therefore an efficient transport of iodide and triiodide in the electrolyte is necessary for good performance of the DSC. Meanwhile, the increase of the I$_3^-$ concentration in the electrolyte results in an increasing dark current of the DSC and thus decreases the device performance.

\[
\Gamma + I_2 \rightarrow I_2^- + I_2 \rightarrow I_5^- \text{ (electrolyte solution)} \quad (2)
\]

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

\[
I_3^- + 2e^- \rightarrow 3\Gamma \text{ (counter electrode)} \quad (4)
\]

\[
I_3^- + 2e^- \text{cb (TiO}_2\text{ electrode)} \rightarrow 3\Gamma \quad (5)
\]

Conducting polymer coated carbon nanotube are notable materials, which are being widely studied because of their extraordinary electronic and mechanical properties. Considering these aspects, an incombustible and non-volatile PMII and P3HT-MWNT composites was incorporated into DSC for this study. The presence of redox-active PMII ionic liquid fills the nanoporous TiO$_2$/dye interface, where no space is available for P3HT-MWNT composites to occupy. It is expected that this IL would allow perfect contact at the interface between the dye-coated porous TiO$_2$ and the conducting polymer coated carbon material [5], i.e., P3HT-MWNT composites.

A typical FE-SEM image of the P3HT and P3HT-MWNT nanocomposites are presented in Fig. 1. By comparing them one can see the well-buried MWNT in the polymer matrix taking tubular structures.

![Fig. 1: FE-SEM images of (a) P3HT and composites of (b) P3HT-siMWNT, (c) P3HT-fMWNT, & HR-TEM image of (d) P3HT-siMWNT.](image)

The photovoltaic performances of the DSC under AM 1.5G simulated solar light at a light intensity of 100 mW cm$^{-2}$ using P3HT & P3HT-MWNT/PMII composite electrolytes and using bare PMII as electrolyte are shown in Table A. The cell efficiency of P3HT/PMII device is 1.1%, which is 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. All devices with composite electrolytes of P3HT-MWNT/PMII show a high efficiency of 3.7-4.1%, which is remarkably higher than that of both P3HT/PMII composite and bare PMII device. The presence of composite materials facilitates electron transfer from counter electrode to I$_5^-$ ions in P3HT-MWNT/PMII composite devices.

![Table A. Photovoltaic properties of the DSSC with P3HT & P3HT-MWNT/PMII composite electrolytes and with bare PMII electrolyte using Pt/ITO as counter electrode.*](table)

<table>
<thead>
<tr>
<th>Sensitizer</th>
<th>IPCE$_{max}$ ($\text{mA cm}^{-2}$)</th>
<th>$V_{oc}$ (V)</th>
<th>FF</th>
<th>$\eta$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PMII</td>
<td>5</td>
<td>1.3</td>
<td>0.680</td>
<td>0.33</td>
</tr>
<tr>
<td>P3HT-sMWNT</td>
<td>56</td>
<td>8.0</td>
<td>0.755</td>
<td>0.616</td>
</tr>
<tr>
<td>P3HT-siMWNT</td>
<td>63</td>
<td>10.0</td>
<td>0.764</td>
<td>0.520</td>
</tr>
<tr>
<td>P3HT-fMWNT</td>
<td>72</td>
<td>11.9</td>
<td>0.730</td>
<td>0.472</td>
</tr>
<tr>
<td>P3HT</td>
<td>21</td>
<td>3.5</td>
<td>0.700</td>
<td>0.440</td>
</tr>
</tbody>
</table>

*Conditions: sealed cells; dye, N719; coadsorbate, DCA 40 mM; photoelectrode, TiO$_2$ (15 $\mu$m 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; $\eta$, total power conversion efficiency.
Fig. 2 (i) shows a photocurrent density-voltage curve of a sealed solar cell based on P3HT & P3HT-MWNT composites/PMII under AM 1.5G simulated solar light at a light intensity of 100 mW cm\(^{-2}\). Device with P3HT-fMWNT/PMII composite electrolyte shows a high short-circuit photocurrent density, \((J_{sc})\) of 11.9 mA cm\(^{-2}\), an open circuit potential of 0.73 V, and a fill factor of 0.47, corresponding to an overall conversion efficiency (\(\eta\)) of 4.1%. Fig. 2 (ii) shows the monochromatic incident photon to current conversion efficiency (IPCE) for DSCs based on P3HT-MWNT/PMII composite. P3HT-fMWNT/PMII device shows 72% IPCE at 520nm. An inefficient charge transport properties in the composite electrolyte may be responsible for the low conversion efficiency in the P3HT-rMWNT & P3HT-siMWNT/PMII electrolyte based device. Further study will target the development of a high-performance quasi solid 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.

Fig. 2: i) Solar cells performance and ii) IPCE data of (a) bulk P3HT/PMII and P3HT-MWNT/PMII composites of (b) P3HT-rMWNT/PMII, (c) P3HT-siMWNT/PMII, & (d) P3HT-fMWNT/PMII.

4 CONCLUSIONS

P3HT and P3HT-MWNT composite could be synthesized through in-situ polymerization procedure using FeCl\(_3\) oxidant for photovoltaic cells applications. A 4.1% of light-to-electricity conversion efficiency of the solid-state DSC is fabricated using hybrid P3HT & P3HT-MWNT/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 solid-state DSC incorporating highly conducting P3HT-MWNT composite is an order higher than that of bare PMII device (0.29%). It is assumed that the hybrid P3HT-MWNT composite plays a key role for both charge transportation in the composite electrolyte and the catalytic activities for electrochemical reduction of I\(_3^−\).

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5 REFERENCES