Electrochemical Polymerization of PPy-MWCNT composite as a Counter Electrode for Dye-sensitized Solar Cells

S. AbdulAlmohsin  
*University of Arkansas at Little Rock, samir_mahdi47@yahoo.com*

S. M. Al-Mutoki  
*Technical Institute Of Shatrah*

Z. Li  
*University of Arkansas at Little Rock*

Follow this and additional works at: [http://scholarworks.uark.edu/jaas](http://scholarworks.uark.edu/jaas)

Part of the [Biological and Chemical Physics Commons](http://scholarworks.uark.edu/jaas/vol66/iss1/9)

**Recommended Citation**


Available at: [http://scholarworks.uark.edu/jaas/vol66/iss1/9](http://scholarworks.uark.edu/jaas/vol66/iss1/9)

This article is available for use under the Creative Commons license: Attribution-NoDerivatives 4.0 International (CC BY-ND 4.0). Users are able to read, download, copy, print, distribute, search, link to the full texts of these articles, or use them for any other lawful purpose, without asking prior permission from the publisher or the author.

This Article is brought to you for free and open access by ScholarWorks@UARK. It has been accepted for inclusion in *Journal of the Arkansas Academy of Science* by an authorized editor of ScholarWorks@UARK. For more information, please contact scholar@uark.edu, ccmiddle@uark.edu.
Electrochemical Polymerization of PPy-MWCNT composite as a Counter Electrode for Dye-sensitized Solar Cells

S. AbdulAlmohsin\textsuperscript{1}, S.M. AL-Mutoki\textsuperscript{2} and Z. Li\textsuperscript{1}

\textsuperscript{1}Department of Physics, University of Arkansas, Little Rock, AR 72204, USA
\textsuperscript{2}Electrical Department, Foundation Of Technical Education, Technical Institute Of Shatrah, Shatrah, ThiQar00964, Iraq

Correspondence: samir_mahdi47@yahoo.com

Abstract

Polypyrrole (PPy) - multi wall carbon nanotube (MWCNT) nanocomposites were synthesized by using in situ electrochemical polymerization with different COOH-functionalized MWCNTs. The PPy-MWCNT composites were used as counter electrode in the fabrication of dye sensitized solar cells (DSCs). Compared to the DSC device with PPy counter electrode, the devices with PPy/MWCNT composite electrode offer much higher total photovoltaic conversion efficiency due to the reduced series resistance. These PPy/MWCNT nanocomposite materials proved to be a good alternate to the expensive Pt as counter electrode in DSC.

Introduction

Dye-sensitized solar cells (DSCs) have been attracting attention because of their simple fabrication with low cost materials, high level conversion efficiency (Oregan and Gratzel 1991, Nazeeruddin et al. 1993, Frank et al. 2004, Jayaweera et al. 2008). A typical DSC device consists of three important parts: dye -sensitized nanocrystalline titanium dioxide ($\text{TiO}_2$) or zinc oxide ($\text{ZnO}$), a counter electrode (CE) usually made of platinum film on fluorine-doped tin oxide (FTO) coated glass, and a redox electrolyte (Papageorgiou et al. 1997 and Papageorgiou 2004). The problems with platinum are its expensive cost, inconvenient transportation and limited quantity on the earth (Kay & Grätzel 1996, Murakami et al. 2006, Spath et al. 2003, Okada et al. 2004, Kroon et al. 2007, and Ma et al. 2004). Alternative cheap catalysts and good performance counter electrodes for the DSCs are inexpensive materials, such as carbon black (Murakami et al. 2006), graphene (Roy-Mayhew et al. 2010), carbon nanotubes (Lee et al. 2009), and conductive polymers, like polypyrrole (Wu et al. 2008), polyaniline (PANI) (Sun et al.2010) and poly(3,4-ethylenedioxythiophene) (Kim et al. 2008, Saito et al. 2002, Liu et al. 2010). All of these catalysts are deposited by different techniques such as electrochemical, and spin coating on FTO glass. Polypyrrole counter electrodes can be easily deposited by electrochemical methods with controled conductivity from insulator to metallic depending on concentration of doped salts (Wu et al. 2010). The properties of the PANI film are influenced by the reaction time, initial monomer concentrations, oxidation states, and types of doping acids on the performance of the DSCs (Kim and Wamser 2006).

Thanks to the unique electrical, mechanical, optical properties of carbon nanotube (CNT), many researchers incorporated CNT into PPy nanocomposite in order to improve the mechanical, electrical, optical performance (Peng et al. 2011). PPy/CNT nanocomposites have superior electrical, capacitance, magnetic properties and thermal stability (Zdenko et al. 2010, Wang et al. 2007). Here, we report the electrochemical polymerization of polypyrrole with different percentage weight of MWCNTs that are functionalized by the carboxylic group COOH. The flexible polypyrrole /carbon composite was employed as counter electrode in DSCs, and the photovoltaic performance of the DSC devices was evaluated.

Methods

Pyrole monomer, (99.8 %, from Aldrich), MWCNTs functionalized by COOH (99.9 %, from Cheap Tube) were used as purchased without further treatment. Pyrole monomer was first dissolved in sulfuric acid (0.1 M) and different percentage weight of COOH functionalized MWCNTs was added into the solution. The electrochemical polymerization was carried out by using galvanostatic step method at a constant voltage of 2 V (Chen et al. 2011). The working electrode was a commercial FTO-glass with a surface area of 1.5 cm$^2$. A platinum wire electrode was used as a counter electrode. The amount of the electrodeposited polypyrrole was estimated by weighing the working electrode before and after the electrode deposition. The schematic diagram of the
The electrochemical cell is displayed in Figure 1.

![Figure 1. Schematic description of the electrochemical cell.](image)

For comparison, the Pt/FTO electrode was made by thermal decomposition of H₂PtCl₆ (30 mM in isopropanol) using centrifugation (1000 rpm) for 30 sec, then annealing FTO glass at 385°C on hot plate for 30 min. The redox electrolyte I/III is used for transferring electrons from counter electrode to the excited dye.

**Characterization techniques**

The structure and the morphology of the as-prepared polypyrrole/MWCNT were characterized by scanning electron microscopy (SEM, JSM 7000F). UV-vis spectra of the coatings were obtained in transmission mode on a LAMBDA 750 UV-vis spectrophotometer. A 23 W mercury arc UV lamp with a wavelength of 365 nm was used with a lamp-to-sample distance of 10 cm. The current density–voltage (J-V) characteristics were recorded with a Keithley 2400 Source Meter. Current was continuously measured as a function of voltage using a semiconductor characterization system (Keithley Instruments) to obtain the J-V characteristics, examine the I-V curves and explore the reverse breakdown voltage, respectively.

**Results and Discussion**

**Morphology.** Figure 2 shows the surface morphology of PPY, MWCNTs, and PPY/MWCNT composite. As shown in Fig. 2C, the PPY/MWCNT nanocomposite has a large roughness. The rough surface would help to increase the surface interfacial area between the electrolyte and the counter electrode. This would increase transfer of electrons between the PPY and the dye through the redox electrolyte.

![Figure 2. (A) SEM images of PPY, (B) MWCNTs, and (C) PPY/MWCNT composite with 10% MWCNT concentration.](image)

Figure 3 demonstrates the optical absorption spectra of PPY and PPY/MWCNT composites obtained with different COOH functionalized

---

*S. AbdulAlmohsin, S.M. AL-Mutoki and Z. Li*
MWCNT percentage weight (0 wt%, 2 wt%, 5 wt%, and 10 wt%). As shown in Figure 3, the shape and positions of absorption peaks of PPY and PPY/MWCNT composite remain almost the same. The PPY/MWCNT composites increase their photon absorption with increase in MWCNT concentration.

As shown in Figure 4, the photoluminescence spectrum of porphyrin on TiO₂ exhibits two peaks, the main peak at 663.909 nm and another at 722.937 nm, corresponding to the fluorescence region of porphyrin (Brazier 1990). Thus, the porphyrin is very optically active in the visible range, and can be a good dye sensitizer material. The optical absorption of porphyrin on TiO₂ was displayed in Figure 5. The main absorption peak is located around 420 nm with the half width at maximum of about 100 nm. The extended π-conjugated system in the porphyrin structure is responsible for its high optical absorption due to the high mobility of π-electrons.

The photovoltaic performance of the devices was evaluated under illumination AM1.5 (~100mW/cm²). As shown in Figure 6 and Table 1, the device made of pristine PPY as the counter electrode has low short circuit current (Jsc=3.7 mA/cm²) and open circuit voltage (Voc=0.34 V), and thus low photovoltaic conversion efficiency (0.46%). However, the Jsc increases significantly to 6 mA/cm² with addition of 2 wt% MWCNT in the PPY/MWCNT composite. For the DSC device with PPY/MWCNT (10 wt%) nanocomposite as counter electrode, both the Voc and Jsc are close to those of the Pt device, and this efficiency (around 0.88 %) is also comparable to that of the Pt electrode (the efficiency about 1 %).

As seen from Table 1, the serial resistance of the pristine PPY counter electrode is 55.9 Ω. But the resistance decreases with increase of MWCNT concentration in the PPY/MWCNT composite counter electrode, say for 2 wt% is 33.7 Ω, and 5 wt% is 31.76 Ω. At the MWCNT concentration of 10 wt%, the PPY/MWCNT composite counter electrode is 30Ω, which is close the platinum electrode (28 Ω). So, the
Table 1: Photovoltaic Parameters Obtained from Figure 6

<table>
<thead>
<tr>
<th>Counter Electrodes</th>
<th>Jsc (mA/cm²)</th>
<th>Voc (Volt)</th>
<th>FF</th>
<th>Series Resistance (Ω)</th>
<th>Efficiency (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pt</td>
<td>6.9</td>
<td>0.41</td>
<td>0.33</td>
<td>28.0</td>
<td>1.04</td>
</tr>
<tr>
<td>Pristine PPy</td>
<td>3.7</td>
<td>0.34</td>
<td>0.36</td>
<td>55.9</td>
<td>0.46</td>
</tr>
<tr>
<td>PPy/MWCNT (2 wt%)</td>
<td>6.4</td>
<td>0.38</td>
<td>0.40</td>
<td>33.7</td>
<td>0.78</td>
</tr>
<tr>
<td>PPy/MWCNT (5 wt%)</td>
<td>6.1</td>
<td>0.38</td>
<td>0.37</td>
<td>31.8</td>
<td>0.86</td>
</tr>
<tr>
<td>PPy/MWCNT (10 wt%)</td>
<td>6.0</td>
<td>0.42</td>
<td>0.35</td>
<td>30.0</td>
<td>0.88</td>
</tr>
</tbody>
</table>

increase of MWCNT concentration improves efficiency for DSCs because of the decreased internal resistivity. In our devices, the large surface area and high mobility of nanotubes could be beneficial to exciton dissociation and charge carrier transport, thus improving the overall power conversion efficiency. Thus, the PPy/MWCNT nanocomposite can be as counter electrode for DSC.

Conclusions

We prepared PPy-MWCNT nanocomposite with different MWCNT percentage by using in situ electrochemical polymerization. The electrochemical polymerization technique proved to be an effective method to fabricate a conductive polymer composite with COOH functionalized MWCNTs. For the DSC devices with PPy-MWCNT as counter electrode, the total photovoltaic conversion efficiency increases with the MWNT concentration due to the reduced series resistance. We found that these nanocomposite materials can be used for counter electrode as a catalyst in DSC to replace the expensive Pt electrode.

Literature Cited


Electrochemical Polymerization of PPy/MWCNT composite as a Counter Electrode for Dye-sensitized Solar Cells


