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

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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 Grätzel 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 (TiO₂) or zinc oxide (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 controlled 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

Pyrrole monomer, (99.8 %, from Aldrich), MWCNTs functionalized by COOH (99.9 %, from Cheap Tube) were used as purchased without further treatment. Pyrrole 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 cm². 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

electrochemical cell is displayed in Figure 1.

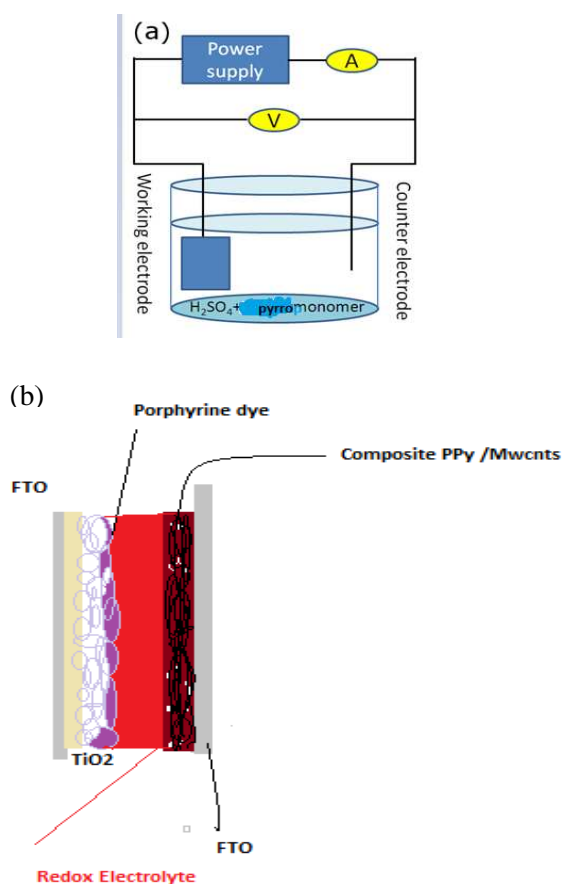


Figure 1. Schematic description of the electrochemical cell.

For the counter electrodes used in DSCs, PPy/MWCNTs nanocomposite electrodes were prepared under different percentage weight of MWCNTs (including 0 wt %, 1 wt %, 5 wt %, and 10 wt %, respectively). The electrochemical method used to prepare the PPy/MWCNT nanocomposite electrode was based on published procedures, except for using Pyrrole Monomer instead of 3-hexial Thiophen (Park et al. 2008). For the photoanode, FTO glass was first rinsed with acetone, 2- propanol and de-ionized (DI) water, and then the TiO₂ solution (50:25:20:5) (TiO₂ anatase : DI-water : ethanol : acetic acid) was airbrushed onto the clean FTO glass under heating of 300 °C. A 7 μm thick transparent layer of anatase TiO₂ particles was heated to 500 °C for 1 hour. The temperature was then reduced to 80 °C and the coated FTO glass was immersed in 0.2 mM porphyrin (Tetra 4-carboxyphenyle porphyrin in ethanol) overnight. The dye-sensitized electrodes were washed with ethanol then DI-water and dried by blowing with nitrogen gas.

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⁻/I₃⁻ 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.

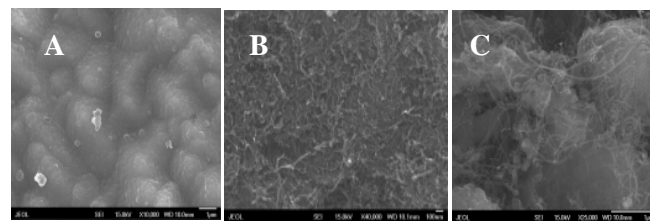


Figure 2. (A) SEM images of PPy, (B) MWCNTs, and (C) PPy/MWCNT composite with 10% MWCNT concentration.

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

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

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.

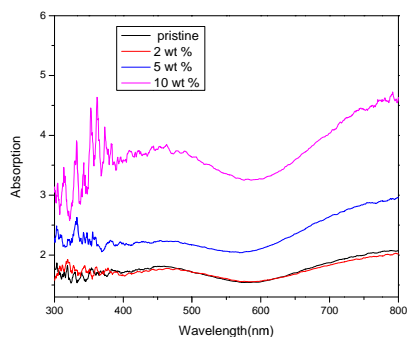


Figure 3. UV-vis absorption spectra of pristine PPy and PPy/MWCNT nanocomposite deposited by electrochemical polymerization (see Materials and Methods).

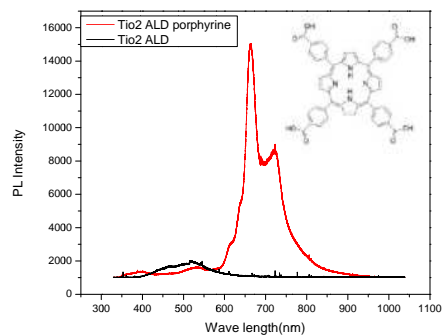


Figure 4. Photoluminescence spectra for TiO₂ and porphyrin/TiO₂.

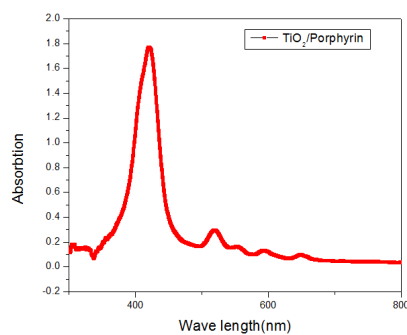


Figure 5. UV-absorption spectrum of TiO₂/Porphyrin.

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.

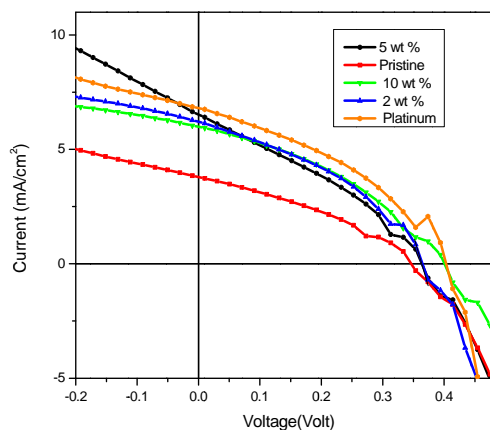


Figure 6. Photocurrent-voltage characteristics of the DSCs using different counter electrode including Pt, PPy, PPy/MWCNT with different MWCNT concentration.

The photovoltaic performance of the devices was evaluated under illumination AM1.5 ($\sim 100\text{mW}/\text{cm}^2$). As shown in Figure 6 and Table 1, the device made of pristine PPy as the counter electrode has low short circuit current ($J_{sc}=3.7\text{ mA}/\text{cm}^2$) and open circuit voltage ($V_{oc}=0.34\text{ V}$), and thus low photovoltaic conversion efficiency (0.46%). However, the J_{sc} increases significantly to $6\text{ mA}/\text{cm}^2$ 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 V_{oc} and J_{sc} 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 $55.9\ \Omega$. But the resistance decreases with increase of MWCNT concentration in the PPy/MWCNT composite counter electrode, say for 2 wt% is $33.7\ \Omega$, and 5 wt% is $31.76\ \Omega$. At the MWCNT concentration of 10 wt%, the PPy/MWCNT composite counter electrode is $30\ \Omega$, which is close the platinum electrode ($28\ \Omega$). So, the

Table 1: Photovoltaic Parameters Obtained from Figure 6

| Counter Electrodes | J_{sc} (mA/cm ²) | V_{oc} (Volt) | FF | Series Resistance (Ω) | Efficiency (%) |
|-----------------------|-----------------------------------|--------------------|------|--------------------------------|----------------|
| Pt | 6.9 | 0.41 | 0.33 | 28.0 | 1.04 |
| Pristine PPy | 3.7 | 0.34 | 0.36 | 55.9 | 0.46 |
| PPY/MWCNT (2 wt%) | 6.4 | 0.38 | 0.40 | 33.7 | 0.78 |
| PPY/MWCNT (5 wt%) | 6.1 | 0.38 | 0.37 | 31.8 | 0.86 |
| PPY/MWCNT (10 wt%) | 6.0 | 0.42 | 0.35 | 30.0 | 0.88 |

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.

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