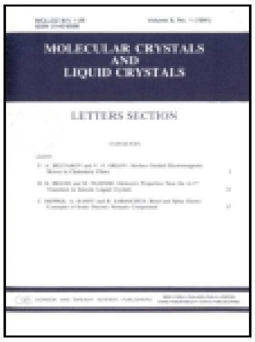

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Polypyrrole and Polypyrrole-Multi Wall Carbon Nanotube for Alternative Counter Electrodes in Dye-sensitized Solar Cells

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In our present study, the composite film of PPy/MWCNT (polypyrrole and multi-wall carbon nanotubes) and PPy were proposed as counter electrodes (CEs) in dye-sensitized solar cells (DSSCs) to replace the precious Pt CE. The PPy and PPy/MWCNT composite films were fabricated on fluorine-doped tin oxide substrates by using a facile electrochemical polymerization route, and served as CEs in DSSCs. The electrochemical impedance spectroscopy and Tafel measurements revealed that the PPy/MWCNT CE possessed more excellent electrocatalytic activity and lower charge transfer resistance of 171.06 Ω in comparison with a PPy CE (338.6 Ω). The DSSC assembled with the PPy/MWCNT CE exhibited a better power conversion efficiency (PCE) of 4.17% under the illumination of 100 mW cm^2, comparable to that of the DSSC based on reference Pt CE (6.86%). Compared with a DSSC using PPy CE with PCE of 3.45%, the PCE of DSSC using PPy/MWCNT CE was increased by 20%. Therefore, the PPy/MWCNT composite film can be considered as a promising alternative CE for DSSC due to its high electrocatalytic performance and excellent electrochemical stability.

Keywords Dye-sensitized solar cells; Pt counter electrode; polypyrrole counter electrode; polypyrrole/multi wall carbon nanotube counter electrode; photovoltaic performance

Introduction

Solar cells have been at the heart of current low-carbon economy and have led to thriving interest in the field of energy and environmental applications because of the pollution and depletion of fossil fuels [1]. Among various solar cells, dye-sensitized solar cell (DSSC) is a promising one owing to its higher power conversion efficiencies over 13% under standard AM 1.5 condition and efforts are now being made toward commercialization [2]. A typical DSSC consists of four components: a dye-sensitizer, TiO_2 photoanode, iodide/triiodide redox electrolyte, and a counter electrode (CE). The CE is a conducting

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layer with electrocatalytic function that serves to catalyze the redox couple regeneration reaction and collect electrons from external circuit. Hereinto, platinum (Pt) CE is preferred because of its high electrocatalytic activity to iodide/triiodide redox reaction and good conductivity. However, Pt is a noble metal; thus, in has resulted in efforts to explore Pt-free CE in DSSC with low cost materials. In this direction, several conducting polymers, such as polyaniline (PANI) [3], poly(3,4-ethylenedioxythiophene) [4] and polypyrrole (PPy) [5] have been applied into DSSC as promising CEs for reducing the oxidized electrolyte. Compared with the most studied PANI and poly(3,4-ethylenedioxythiophene) CEs, there are only few reports on the application of PPy as CE materials in DSSC, although it has been demonstrated one of the most promising candidate in other applications due to its high conductivity, stability and the virtue of easy synthesis in high yield [5, 6]. Nevertheless, its relatively high charge transfer resistance and hindered electron transport between PPy particles would cause the increased overpotential for catalyzing triiodide reduction [7].

Carbon materials such as multi wall carbon nanotubes (MWCNTs) are honored as rapid electron transfer materials accompanied with highly specific surface area, low resistivity, narrow distribution size and excellent mechanical strength [8]. The adhesion of MWCNT to conducting material is necessary to the properties of DSSCs, especially. There is an impression that the simple MWCNT paste printing process might be limited during the drying and firing process. The combination of the MWCNTs with conducting polymer PPy makes their combined composite materials interesting in increasing electrical conduction and therefore overall power conversion efficiency of DSSCs [9].

In this paper, the PPy and PPy/MWCNT composite films were prepared based on PPy system using electrochemical polymerization method and served as CEs in DSSCs. It is expected that photovoltaic performance of the DSSC with PPy/MWCNT electrode can be improved. The electrochemical impedance spectra (EIS) and Tafel measurements have been used to characterize the internal resistances to reveal the origin the increasing of the current and enhancement of the overall efficiency of the DSSC.

Experimental

Materials

Lithium perchlorate ($LiClO_4$) was purchased from Sigma-Aldrich (Japan), and sulfuric acid (H_2SO_4) was purchased from Duksan Korea. Functionalized MWCNT was purchased from Hanwha chemical (Korea). Pyrrole monomer was purchased from TCI Co. LTD., and was distilled prior to use. All the reagents used were reagent grade.

Preparation of Counter Electrodes

Electrochemical polymerization of PPy or PPy/MWCNT film onto FTO glass was carried out in a deionized water containing 0.1 M $LiClO_4$, 4 drops of H_2SO_4, 0.1 M pyrrole monomer by using potentiostatic method by applying a potential value of 600 mV for 30 sec. In the case of PPy/MWCNT CE we used 0.01 g of functionalized MWCNT (dispersed in DI water for 30 min using sonication). Prior to the film deposition the solution was stirred for 3 h in an ice bath and then purged with nitrogen. A three-electrode system was used with PPy or PPy/MWCNT film on FTO glass as working electrode, Pt sheet as counter electrode and Ag/AgCl as reference electrode for electrochemical polymerization.

After being polymerization the films were rinsed with copious distilled water followed by ethanol and dried in vacuum for 12 h, the resulting CEs were used in the DSSCs. Pt CE was prepared by thermal reduction of a thin film formed from 7 mM of H_2PtCl_6 in propanol at 450°C for 30 min.

Preparation of TiO_2 Photoanode and Fabrication of Dye-sensitized Solar Cell

FTO glass was cleaned by sequential sonication in methanol, distilled water and acetone. A thin first layer of TiO_2 was deposited by "doctor-blade" technique. The film was dried at 70°C for 30 min, followed by heating to 450°C for 30 min. Then, a second layer of 200 nm-sized light scattering particles was coated on the top of the first layer, also followed by heating to 450°C for 30 min. The electrodes were treated in 40 mM $TiCl_4$ solution at 70°C for 30 min, then rinsing in distilled water and heated at 450°C for 30 min. The TiO_2 electrodes were immersed in a 0.3 mM solution of **N**719 in ethanol at room temperature for 24 h before being removed and rinsed in ethanol immediately before cell fabrication. Cells were fabricated by sandwiching the sensitized TiO_2 photoanode and counter electrodes together with a hot-melt polymer (Surlyn, 60 μm). The electrolyte contains 0.05 M I_2, 0.2 M LiI, 0.7 M 3-propyl-1-methyl imidazoliumiodide and 0.5 M *t*-butylpyridine in acetonitrile.

Characterization and Measurement

The photocurrent-voltage measurement was performed using a Keithley model 2400 Source Meter and a Newport 91192 solar simulator system (equipped with a 1 kW xenon arc lamp, Oriel). Light intensity was adjusted to 1 sun (100 mW/cm^2) with a Radiant Power Energy Meter (model 70260, Oriel). The incident photon-to-current conversion efficiency (IPCE) results were acquired from IPCE G1218a (PV Measurement). This system applies monochromatic light from a 75 W xenon arc lamp (Ushio UXL-75XE) filtered by a dual-grafting monochromator and individual filters onto the test devices. An ellipsoidal reflector collects light from the lamp and focuses on the monochromatic entrance slit via a mechanical chopper to create a small modulated signal. While the modulated, monochromatic light was applied to the test devices, a continuous bias light (ca. 1 sun) was also applied. Electrochemical impedance spectroscopy (EIS) was performed using an electronic-chemical analyzer (Iviumstat Tec.). Tafel curves were recorded on the same workstation by assembling symmetric cell at a scan rate of 10 mV s^{-1}.

Results and Discussions

Fig. 1 illustrates the photocurrent–photovoltage curves of the DSSCs with PPy, PPy/MWCNT and Pt counter electrodes, respectively. Photoelectric parameters such as short-circuit current density (Jsc), open-circuit voltage (Voc), fill factor (FF), and energy conversion efficiency (η) are extracted from J-V curves and are given in Table 1. Since the not good conductivity of Ppy, the DSSC with only PPy as CE yielded power conversion efficiency (PCE) of 3.45% (Jsc = 14.97 mA cm^{-2}, Voc = 0.685 V, and FF = 0.336). However, the cell assembled based on the PPy/MWCNT CE exhibited Jsc of 15.8 mA cm^{-2}, Voc of 0.708 V and FF of 0.37, corresponding to an improved PCE of 4.17%. The improvement in Jsc and FF values for the DSSC based on the PPy/MWCNT CE compared to the one fabricated with PPy CE can be attributed to its superior electrocatalytic activity and low charge transfer resistance (R_{ct}) values (discussed in next section) for I^-/ I_3^- redox couple. Also, the increase of the contact area between PPy/MWCNT CE and

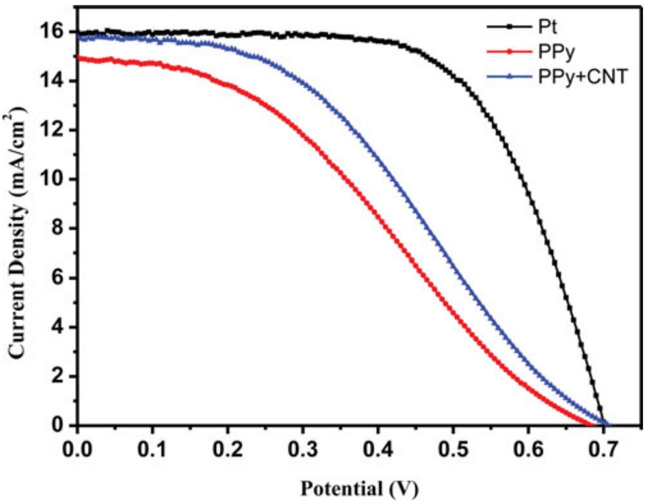

Figure 1. Currentdensity-voltage (J-V) curves for DSSCs employing different counter electrodes.

electrolyte was accountable for improving the Jsc in DSSC [10]. One of the reasons for increased conversion efficiency of the PPy/MWCNT -based DSSC was due to the significantly increased Jsc value. This result agreed well with the IPCE values as shown in Figure 2. On the other hand, compared to the DSSCs based on the only PPy and PPy/MWCNT CE, the Pt based DSSC exhibits an improved FF value and along with a slightly higher Jsc value, resulting in a much higher PCE. This can be ascribed to that the decreased charge transfer resistance (discussed in the following section) for the Pt CE.

To illuminate electrocatalytic activity of the CE for the I_3^- reduction reaction, charge-transfer resistance was measured using the EIS. This is an important index representing the electrocatalytic performance of CE. Fig. 3 gave the Nyquist plots of the Pt, PPy and PPy/MWCNT CEs and the resultant EIS parameters came from the EIS spectra were depicted in Table 2. The R_s describes mainly the resistance of the two identical electrodes and the electrolytic resistance. The R_{ct} measures the electrode's catalytic activity for reducing triiodide (I_3^-) to iodine (I^-) and the R_w describe the Warburg impedance. [9]. From Fig. 3, it is also found that the R_{ct} of PPy- only electrode is high to 338.6 Ω. By preparing MWCNT layer onto PPy substrate, the R_{ct} dramatically decreased to 171.06 Ω. The plots suggest qualitatively that R_{ct} of a cell increased in the order of Pt < PPy/MWCNT < PPy. The R_{ct} changed in this study essentially referred to the component of resistance against electron transfer from the counter electrode to I_3^-. The smallest R_{ct} value of the Pt cell compared to only PPy and PPy/MWCNT cells could be the reason for high Jsc and FF values of the corresponding DSSC. On the other hand, the smaller R_{ct} value of the PPy/MWCNT

Table 1. Photovoltaic parameters of DSSCs with different counter electrodes

Sample	Jsc (mA/cm^2)	Voc (V)	FF (%)	Efficiency (%)
Pt	15.98	0.702	61.15	6.86
PPy	14.97	0.685	33.64	3.45
Ppy + CNT	15.8	0.708	37.28	4.17

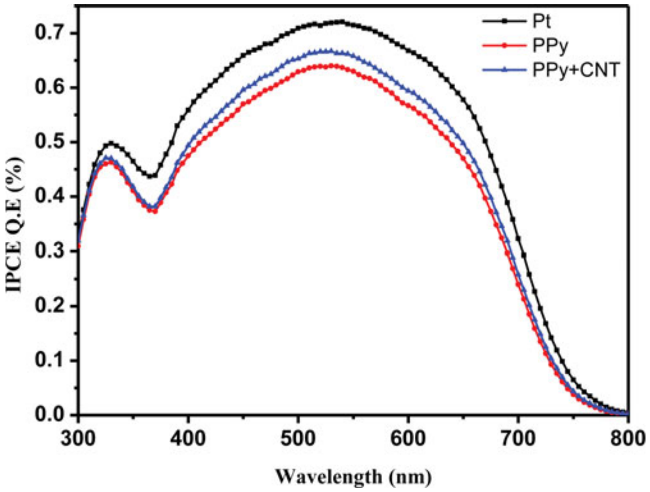

Figure 2. IPCE curves of DSSCs employing different counter electrodes.

cell compared to only PPy cell correlated well with the higher Jsc and FF values of the corresponding DSSC. This illuminates that PPy electrode has poor catalytic activity for the reduction of I_3^-, however, the composite film of PPy/MWCNT efficiently induced the reduction of I_3^- to I^- in the electrolyte owing to the contribution of the high surface area and porous structure which can considerably improve the catalytic activity of the CE. The main contribution of the synergistic influence of the PPy and MWCNTs can remarkably increase the performance of PPy/MWCNT counter electrode.

Fig. 4 presented the Tafel curves for cells similar to the ones used in the EIS measurement to investigate the electrocatalytic activity of the PPy/MWCNT CE. Theoretically, the Tafel curve can be divided into three zones. The curve at very high potential is attributed to the limiting diffusion zone, which depends on the transport of I_3^- and I^- in the electrolyte.

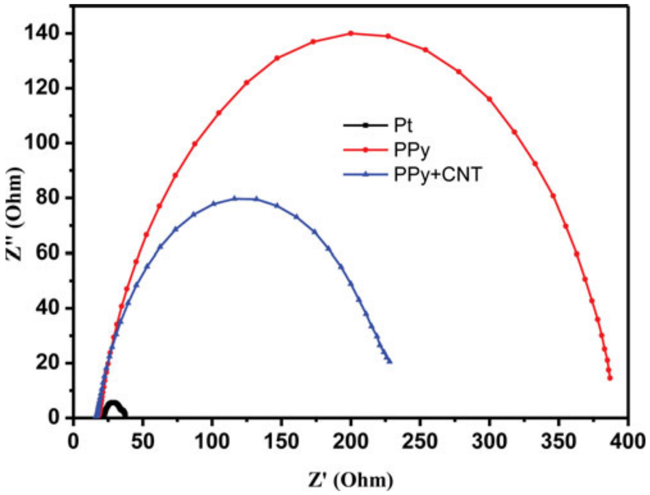

Figure 3. Nyquist plots showing the effect of different counter electrodes.

Table 2. Electrochemical impedance analysis of different counter electrodes

Sample	Rs (Ohm)	R_{ct} (Ohm)	R_w (Ohm)
Pt	17.5	12.15	3.1
PPy	17.26	338.6	33.95
Ppy + CNT	15.95	171.06	38.6

The curve at relatively low potential but higher than 125 mV corresponds to the Tafel zone, where the voltage is a linear function of log J. The curve at very low potential is polarization zone, arising from the electrochemical reaction. In Tafel zone, we can collect information on the exchange current density (J_0, obtained by the intersection of cathodic branch and equilibrium potential line) [11]. Since J_0 mainly depends on two factors, the concentration of the oxidized species and the electrocatalytic performance of CE. The PPy/MWCNT CE exhibited a larger slope than the PPy CE, which demonstrated the presence of a larger J_0 for the PPy/MWCNT composite CE. This meant that the PPy/MWCNT CE was as sufficient as Pt to catalyze the reduction of I_3^- to I^-. This was generally in accordance with those presented in the EIS measurement according to the following equation.

$$J_0 = RT/nFR_{ct}$$

Where R is the universal gal constant, T is the absolute temperature, n is the number of electrons contributing to the charge transfer at the interface, and F is Faraday's constant. In comparison with PPy-only CE, the enhanced J_0 from PPy/MWCNT complex ones derives from the rapid charge-transfer.

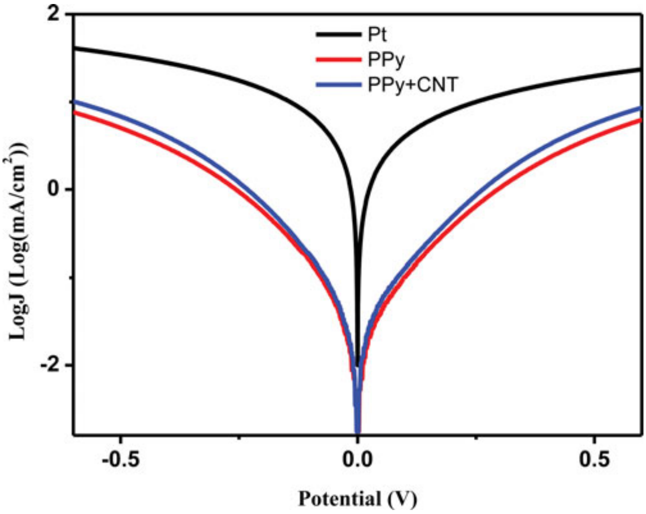

Figure 4. Tafel curves of various symmetrical cells that are similar to the ones used for the EIS measurement.

Conclusions

In summary, PPy and PPy/MWCNT were prepared and coated on a FTO glass to construct PPy and PPy/MWCNT counter electrodes (CE) used in dye-sensitized solar cells (DSSCs). The electrochemical analyses of PPy/MWCNT CE made from EIS measurements indicated the better electrocatalytic activity for the I^-/ I_3^- redox shuttle and low R_{ct} at the interface between electrolyte and CE. Tafel measurements have been carried out to determine the enhancement in charge-transfer kinetics and electrocatalytic activity toward iodides. The main advantage is that the preparation process can be carried out in ambient atmosphere and application can be achieved in large-scale. Under the similar fabrication conditions, the DSSC from PPy/MWCNT CE provides an impressive power conversion efficiency of 4.17% in comparison with that of 3.45% from PPy-based CE. The present work suggests that the PPy/MWCNT CE shows a great potential as a low-cost and high-efficient alternative to Pt in DSSCs.

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