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Fabrication and electrochemical properties of polypyrol/multi-walled carbon nanotube composites for solar cell applications

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In this study, polypyrrole and multi-walled carbon nanotube (MWCNT) composite film was produced by electrochemical polymerization of pyrrole with MWCNT on ITO surface. The electrochemical properties of composite containing polypyrrole and MWCNT have been investigated. The electrochemical behavior of this composite obtained depends on the electrostatic interactions of the materials in it with each other. The PPy/MWCNT composites were used as counter electrode in the fabrication of dye sensitized solar cells (DSSCs). The solar cell performance results were evaluated by changing the nanotube concentration in the composite film. This composite can also be useful for producing a family of low-cost and easy to prepare solar cell or sensing or energy storage devices.

Keywords: *Multi Wall Carbon Nanotubes, Polypyrrole, electrochemical.*

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1. Introduction

Polypyrrole (PPy) is one of the most intensively studied conducting polymers as counter electrode for DSSCs during the last decade, owing to their high electrical conductivity, interesting redox properties, good catalytic activity for I^{3-} reduction good environmental stability and easy synthesis. [1–4] Due to its poor mechanical properties is usually combined with conductive carbon structures as carbon nanotubes and graphene[5–7]. Composite electrodes formed with conductive polymer and carbon nanotube have recently gained much popularity due to their superior and stable electrochemical properties. [3,8,9] Multiwall carbon nanotubes (MWCNT) has received considerable attention recently have due to their high electrical and thermal conductivity, also extraordinary mechanical properties[6,7]. MWCNTs play important roles in various fields such as electronic devices[10], sensors [7,11], optics [12] and storage of energy [8,13]. The performance of PPy counter electrode can also be enhanced by the combination of PPy with carbon-based nanomaterials, such as, MWCNTs, which have shown high catalytic activity, high surface area, good stability, and rapid electron transport. [9,14,15] Composites obtained with conductive polymer and MWCNT are generally prepared by an in situ polymerization method. Modification of the MWCNT surface provides them with new functions and helps to improve the condition of the conductive polymer/MWCNT interface region, resulting in composites for advanced instrument applications with superior properties.

In this study, we electropolymerize the PPy on the MWCNT-coated indium tin oxide (ITO) substrate by a facile cyclic voltammetry (CV) method to obtain the PPy/MWCNT composite. These composite film studies are critical in the development of dye-sensitized solar cell

(DSSC) to discover new counter electrode (CE) materials to replace expensive and precious platinum (Pt). The resultant composite CE shows that the MWCNT is wrapped with PPy nanoparticles, which takes advantage of the high surface area and good conductivity of the MWCNT and good catalytic activity of the PPy for the reduction of triiodide to iodide, providing the fast electron transport and diffusion channels and plenty of interfacial catalytic active sites. The DSSC based on the PPy/MWCNT composite CE shows an excellent photoelectric conversion efficiency of 2.60% under full sunlight illumination (100 mW cm^{-2}, AM 1.5 G), which is much higher than that of the MWCNT (1.85%) and PPy (2.00%) based DSSCs. The short-circuit current density (I_{SC}) of the DSSCs based different CEs increases in an order of MWCNT<PPy<PPy/MWCNT<Pt which can be explained that the MWCNT can provide high surface area, fast electron transport and diffusion channels and the PPy nano-particles wrapped on MWCNT surface can provide plenty of interfacial active sites. The good photovoltaic performance of the PPy/MWCNT is attributed to the p–p coupling interaction between the PPy and MWCNT, arising from the delocalized electrons of the MWCNT and the aromatic rings of the PPy. The resultant CE can take advantage of the synergic effect of higher electronic conductivity of the MWCNT and superior catalytic activity of the PPy. This can reduce the internal series resistance and enhance FF and ISC values, which in turn lead to higher conversion efficiency. Therefore, this PPy/MWCNT composite structure demonstrates an ideal CE material.

2. Materials Method

2.1. Reagents

All chemicals and reagents used in the study were purchased from Sigma Aldrich and pyrrole was purchased from Alfa Aesar. Also, all chemicals were used as received without any further purification. All aqueous solutions were prepared with distilled water.

2.2 Characterizations and Apparatus

The electrochemical studies were performed using an Ivium Compactstat Potentiostat. Electropolymerization of pyrrole monomer was performed in a three-electrode system with a ITO as the working electrode, coupled with a Pt wire counter and Ag/AgCl reference electrode. The PPy/MWCNT composite structure was analysed by Fourier transform infrared spectra (FT-IR) (Nexus 670 model spectrophotometer). UV–vis absorption measurement was carried out with an Agilent 8453 UV–vis diode array spectrophotometer. Device studies were also evaluated under N_2 ambient in glove box using Keithley 2400 sourcemeter with AM1.5 light source using as solar simulator.

2.3. Preparation of PPy/MWCNT composite film

Multiwall carbon nanotubes (MWCNT) were prepared by chemical vapour deposition (CVD) technique according to literature procedures ***[16–19].*** MWCNT (5 mg) in 2 mL N,N-Dimethylformamide (DMF) was dispersed in ultrasonicator for 2 h. Then, electropolymerization of PPy film onto ITO/MWCNT was carried out in 0.1 M LiClO4/ACN (lithium perchlorat/acetonitrile) containing 0.015 M Pyrrole by cyclic voltammetry (CV) method with the potential scanning range of -1.0 to +1.0 V at 100 mV/s scan rate for 6 cycles. The PPy/MWCNT composite was coated on ITO electrode by electrodeposition. Electrochemical studies were performed using a potentiostat (Ivium Compactstat Potentiostat). Surface area of the working electrode (ITO) was 1.2 cm^2 (0.6 cmx2 cm). The counter electrode was Pt wire, and the reference electrode was a Ag/AgCl. Also, electrochemical studies on the composite were carried out on the ITO electrode surface and the DSSC device application on the FTO surface.

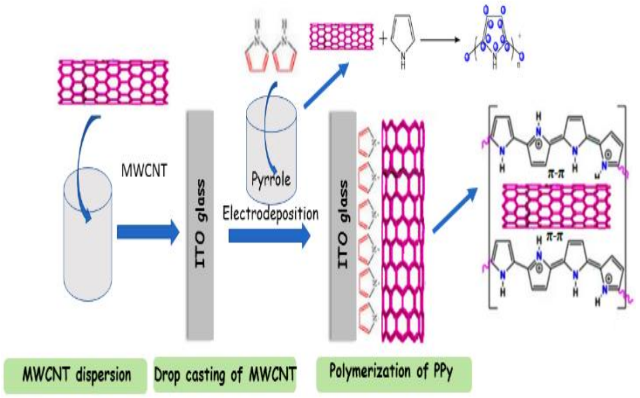

Figure 1. Schematic diagram of the PPy/MWCNT composite film preparing on the ITO substrate.

2.4. Investigation of spectroelectrochemical properties

Spectroelectrochemical analyzes was carried out to understand the band structure of composite. For spectroelectrochemical analyzes and the preparation of polymer films, 0.037 M PPy dissolved in 0.1 M LiClO4/ACN was deposited between −1.0 V and 1.0 V for 4 cycles on MWCNT coated ITO. UV spectrum of the PPy/MWCNT film was studied at different applied potentials in monomer free 0.1M LiClO4/ACN electrolyte/solvent couple system. Transmittance percentage (%T) wavelengths of the composite films were obtained by UV–Vis spectrophotometer.

2.5. Fabrication of a dye-sensitized solar cell (DSSC) with PPy/MWCNT composite film

The cleaning process for fluorine-doped tin oxide glass (FTO) substrate was performed using an acetone and isopropanol by an ultrasonic bath. FTO (SnO_2:F, Pilkington TEC-15; Rsheet:15O/&, dimension of 0.5×0.5 cm^2), electrically conductive oxide-coated glasses preferred as transparent electrodes. The MWCNT suspension with a concentration of 0.5 mg/mL in DMF was spin coated on the FTO glass substrate. The coated surface was dried in a drying oven at 80 ° C for 1 hour. The PPy/MWCNT counter electrode (as an alternative to hydrogen hexachloroplatinate (H_2PtCI_6)) on FTO substrate was fabricated by electrodeposition of the PPy on the MWCNT. As the working electrode, a nanocrystalline TiO_2 layer of 20 mm thickness was prepared by spin coating method. This prepared electrode was sintered and annealed at 70° C for 1 hour. After the electrodes were coated with TiO2, they were sintered at 450 ° C for 1 hour, and then decreased to 80°C. It was immersed in 0.3 mM solution of the di-tetrabutylammonium cis-bis(isothiocyanato)bis(2,2′-bipyridyl-4,4′-dicarboxylato)ruthenium(II) (N719) dye previously reported in the literature [20] in a mixture of dehydrated acetonitrile and tert-butanol with volume ratio of 1:1 and left in this solution for 12 hours. The DSSC was produced by sandwiching the redox electrolyte without any sealing between the dye sensitive TiO2 anode and the counter electrode (PPy/MWCNT). To complete the fabrication of the DSSC cell, the cathode with a Surlyn frame as spacer and the counter electrode were sealed at a pressure of about 0.2 MPa and ensuring good adhesion. A redox electrolyte solution containing 0.5 M lithium iodide (LiI), 0.05 M iodine (I2) and 0.5 M 4-tert-butyl-pyridine in anhydrous acetonitrile was then introduced through the back holes of the counter electrode. [5,21]

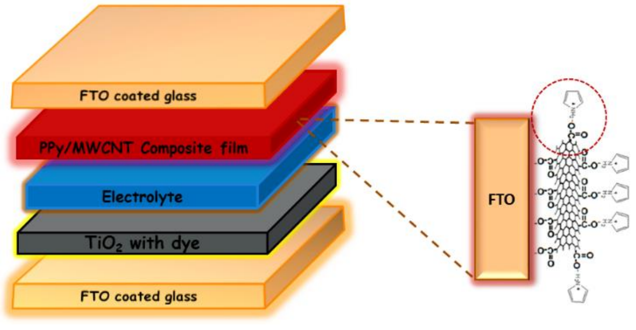

Figure 2. The structure of a dye-sensitized solar cell using PPy/MWCNT composite film as a counter electrode.

3. Results and discussion

3.1. Characterization

Fig. 3a shows the FT-IR spectra of the PPy, MWCNT, and PPy/ MWCNT, respectively. In the PPy curve, the peaks at 1522 and 1408 cm^{-1} are from the fundamental stretching vibrations of pyrrole rings, indicating the ring structure was not affected by polymerization. The bands at 1060 and 763 cm^{-1} can be attribute to the N-H deformation vibration and C-H wagging vibration, respectively. The presence of strong bands at about 1161 and 847 cm^{-1} indicates the formation of the doped PPy. The low absorption band at 689 cm^{-1} is due to the C-H out of plane bending of the pyrrole moiety in the PPy [5,8,22]. In the MWCNT curve, the absorption bands at 1581 and 1205 cm^{-1} are associated with stretching of the carbon nanotube backbone. Two bands appearing at 1720 and 1401 cm^{-1} can be attributed to the C=O stretching vibration and hydroxyl group (-OH) bending deformation of the carboxylic group (-COOH) from the acid oxidized MWCNT, respectively [23]. All the characteristic bands of the PPy and MWCNT are reserved in the spectrum of the PPy/MWCNT composite, demonstrating that the backbone structure of the PPy and MWCNT was not damaged and the PPy/MWCNT composite was successfully prepared by the electrochemical polymerization. The band shift can be interpreted by covalent interactions (probably the p–p coupling interaction) between the PPy and MWCNT [23,24], which is expected to give a facile electron transport between the PPy and MWCNT.

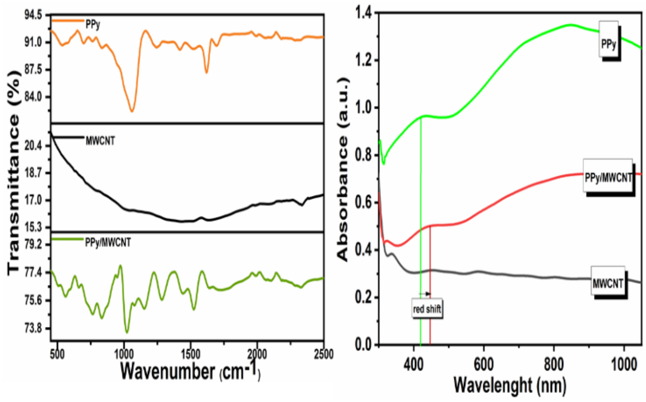

Figure 3. (a) FT-IR spectra and (b) UV–vis absorption spectra of the PPy, MWCNT and PPy/MWCNT.

The UV–vis absorption spectra of PPy, MWCNT, and PPy/ MWCNT CEs are shown in Fig. 3b. The PPy CE exhibits a characteristic absorbance peak at 432 nm, which is associated with p–p* electron transition of conjugated PPy chains. And a broad absorption onset ranging between 850 and 1000 nm, that could be related to the conductive form of PPy (dication) [5,25]. An absorption peak appears around 465 nm in the spectrum of the PPy/MWCNT composite. Compared with the single PPy at 432 nm, the red shift is a typical characteristic of a delocalization of electrons, which might resulting from the p–p coupling due to the doping of MWCNTs [26]. At the same time, an increase in the electronic density of the p band after polymerizing the PPy film has been reported [5,26]. The delocalized electron facilitates the transfer of charges that the catalytic reaction rate at the interface of electrolytes and electrodes could be enhanced.

3.2. Cyclic voltammogram of PPy/MWCNT composite film

Fig. 4 shows the comparison of second cycle of bare ITO, PPy and PPy/MWCNT composite film in CV. When all conditions were the same in 0.1 M ACN/LiClO$_4$ solution, the current rises PPy/MWCNT composite film increments were found to be higher than bare PPy. This large size of integrated CV areas depend on the amount of charge loaded on the ITO electrodes.

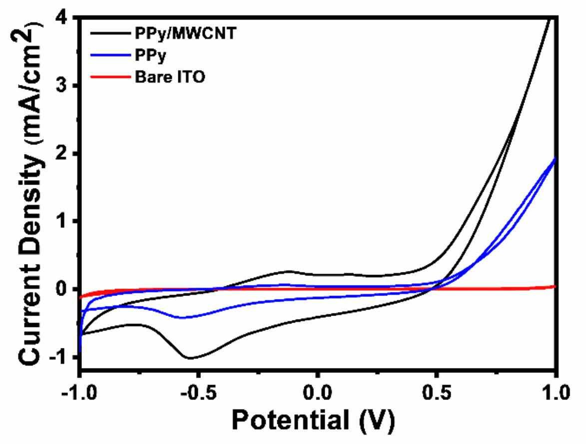

Figure 4. Cyclic voltammograms for PPy/MWCNT and PPy -coated ITO at a scan rate of 100 mV/s in 0.1 M LiClO4/ ACN without monomer.

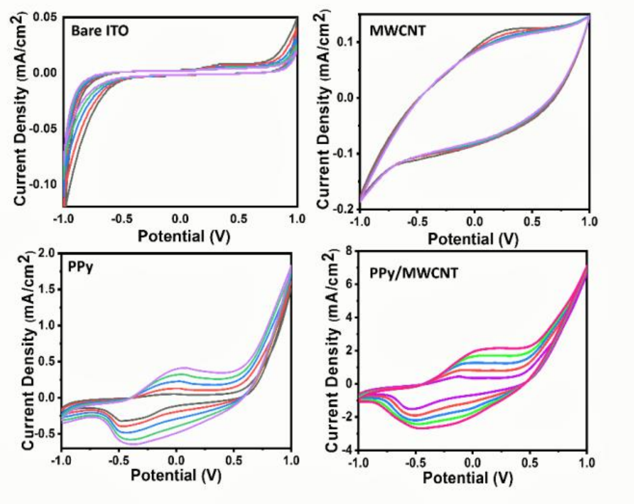

Figure 5. Cyclic voltammogram of electrodeposition of polypyrrole on (a) bare ITO (b) PPy (c) MWCNT (e) PPy/MWCNT coated electrodes in 0.1M LiClO4/ACN electrolyte–solvent couple.

3.3. Stability of PPy/MWCNT composite films

Cyclic voltammetry can be used to investigate the long-term electrochemical stability of conductive polymers. To determine the stability of the PPy/MWCNT-ITO composite, the composite film prepared by electrochemical polymerization was subjected to 200 cycles of CV with a scanning speed of 100 mV /s between -1.0 V and +1.0 V in a monomer-free solvent system. For this purpose, we obtained the PPy/MWCNT composite by non-stop cycling process between −1.0 V and +1.0 V at scan rate of 100 mV/s in 0.1 M monomer free solution. The stability of PPy/MWCNT–ITO composite film between first (area of the integration: 0.656) and last cycles (area of the integration: 0.577) was 86.40. In this composite, polypyrrole is a good electron donor, MWCNT is considered to be an acceptor. Also, MWCNT facilitates charge ransfer from units of PPy to MWCNT leading to increase the stability of the composite.

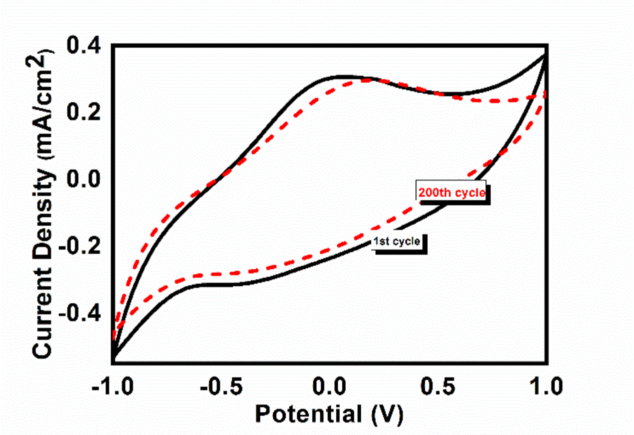

Figure 6. Stability graph of PPy/MWCNT coated electrode in 0.1 M LiClO4/ACN electrolyte–solvent couple.

As shown in Figure 5, the CV of the electrodeposited PPy/MWCNT-ITO composite was examined in 0.1 M monomer free solution. The redox current has increased at a scan rate varying between -1.0 and +1.0 V s. Hence, the anodic peak is shifted towards a positive potential, while the cathodic peak is shifted towards a negative potential. This indicates that the redox process is not diffusion controlled and the polypyrrole film adheres well to the ITO electrode surface and the composite is successfully obtained.

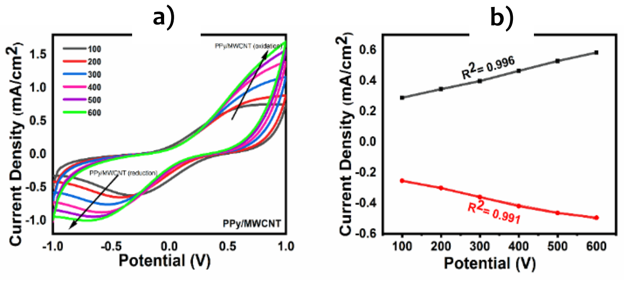

Figure 7. a) Cylic voltammogram with scan rates ranging from 0.1 to 0.6 V/s in monomer free solution. b) Relationship of anodic and cathodic current peaks as a function of scan rate.

As can be seen from the CV graph in Fig. 7a, charge density increases when MWCNT is coated on ITO, which causes the PPy-MWCNT-ITO composite to have higher charge and current density. The absolute values of the cathodic and anodic peak current densities gradually increased and their locations also regularly shifted to the negative and positive directions with the scan rate increasing. Simultaneously, the good linear relationship between square root of the scan rates and peaks current densities was also illustrated in Fig. 7b.

3.4. Photovoltaic performance of PPy/MWCNT composite film

Figure 6 shows the current-voltage curves of the MWCNT and PPy/MWCNT composite electrode cells. In Table 1, I_{sc} (short circuit current), V_{oc} (open-circuit voltage), FF (filling factor) and efficiency values of these cells are summarized. The photoelectric parameters of DSSC of PPy/MWCNT composite electrode are higher than that of single MWCNT electrode. When using PPy/MWCNT composite film as counter electrode, the efficiency of DSSC reaches 2.60%. This value is approximately 40.54% higher than MWCNT. Considering these results, the composite electrode coated with PPy captures the liquid electrolyte in very small pores, providing a large active surface area and excellent stability on the electrode. The increase in $I^{3-/}I^{-}$ redox reaction rate with the increase of PPy/MWCNT composite electrode surface area also improves the photoelectric performance of DSSCs.

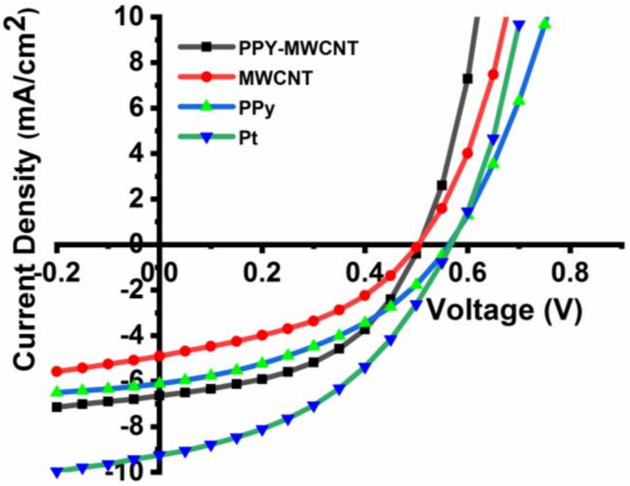

Figure 8. Photocurrent–voltage curves of DSSCs with different counter electrodes under illumination of AM 1.5 (100 mW cm^{-2}) at effective area of 0.5×0.5 cm^2.

Material	I_{SC}	V_{OC}	FF	Efficiency (η)
Pt	9.25	550	0.434	3.68
PPy	6.11	550	0.416	2.00
MWCNT	4.90	500	0.410	1.85
PPy/MWCNT	6.63	500	0.481	2.60

Table 1. The solar cell performance of PPy/MWCNT and MWCNT as counter electrode.

4. Conclusion

In this study, the energy conversion efficiency of dye sensitive solar cells (DSSCs) was increased by using polypyrrole (PPy)/multi-walled carbon nanotube (MWCNT) composite film instead of Pt. MWCNT film was attached tightly to FTO. The porous structure of PPy electrodeposed in MWCNT improved the roughness and specific surface area of the MWCNT and increased the electronic transmission capacity of PPy. In the CV curves, the higher catalytic ability of MWCNT/PPy was observed. When the efficiencies of DSSCs prepared with MWCNT and PPy/MWCNT are compared, an increase of 40.54% has been observed in efficiency. PPy/MWCNT electrode has excellent photoelectric properties, simple preparation process and low cost, alternative counter electrode to Pt can be recommended in DSSCs.

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