



Electropolymerized polyaniline/graphene nanoplatelet/multi-walled carbon nanotube composites as counter electrodes for high performance dye-sensitized solar cells



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ABSTRACT

Polyaniline (PANI)/graphene nanoplatelet (GNP)/multi-walled carbon nanotube (MWCNT) composite films deposited on fluorine-doped tin oxide (FTO) substrates were successfully fabricated through electrochemical method without pre-treatment of GNP and MWCNT to provide a lower cost counter electrode (CE) for dye-sensitized solar cells (DSSCs). By varying the contents of GNP and MWCNT in the PANI composite CE, the short-circuit current density of DSSC was found to linearly relate to the reduction current density of I^-/I_3^- redox couples measured by cyclic voltammetry. The open-circuit voltage (V_{OC}) is also highly dependent on the reduction potential of redox couples. Besides, the charge transfer resistance at the electrolyte/CE interface measured by electrochemical impedance spectroscopy has an approximately linear relationship with the sheet resistance of PANI composite CE. Notably, the DSSC with the CE fabricated by the weight ratio of PANI/GNP/MWCNT at 1:0.003:0.0045 yielded the highest power conversion efficiency of $7.67 \pm 0.05\%$, which is comparable with the conventional Pt cell ($7.62 \pm 0.07\%$).

1. Introduction

The development of dye-sensitized solar cells (DSSCs) has already reached the commercial stage and is well recognized as the third generation of solar cells in views of their easy processing, fairly high power conversion efficiency (PCE) and low cost for production [1–5]. Conversion of photons to electric current can be achieved through the light absorption by a dye-sensitized mesoporous titanium dioxide (TiO_2) film as photoelectrode. While the electrons generated from the photoexcited dye molecules inject into the conduction band of TiO_2 , the oxidized dye can be recovered by the electrolyte solution inserted between photoelectrode and counter electrode (CE) through the oxidation reaction from I^- to I_3^- ions. The significant role of CE is to transport the electrons from external circuit to the electrolyte and catalyze the reduction reaction of I_3^-/I^- redox couples. Therefore, the selected material of CEs for high performance of DSSCs should possess low sheet resistance and high catalytic power for the reduction reactions of the redox couples.

To date, Pt deposited fluorine-doped tin oxide (FTO) glass is the most commonly used CE in DSSCs. Although Pt exhibits the excellent catalytic activity for I_3^- reduction and high conductivity, high cost and

limited reserve obstruct its application in practice [6,7]. Alternative catalysts for CEs such as carbon black [8,9], carbon nanotube [10,11], graphene [11–17], polyaromatic hydrocarbon [18], and conductive polymers such as polypyrrole [19,20], poly(3,4-ethylenedioxythiophene) [21–24] and polyaniline (PANI) [25–31] have been attempted over the past decades. Among them, PANI has been demonstrated as a promising material for CE due to its desirable properties such as high conductivity, easy synthesis, environmental stability, and high catalytic activity for I_3^- reduction [6,32]. To further improve its performance, PANI was blended with carbon additives such as carbon nanotube [33–36], graphene [37–41], and dual [42,43]. A few researchers even showed that such composite with appropriate amount of additives has better performance than Pt [33,37]. However, the fabrication of these composites were usually required the pre-treatment of carbon additives such as surface oxidation to attain better dispersion.

In this work, we considered that the aromatic ring of aniline and its positive charge provided by sulfuric acid dopant are capable of adsorbing to the surface of graphene nanoplatelet (GNP) and multi-walled carbon nanotube (MWCNT) through π - π and cation- π interactions [44,45]. We polymerized PANI composites from aniline sulfate through electrochemical deposition (ED) method on FTO glass substrate

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with the addition of GNP and MWCNT without further oxidation. The performance of DSSCs could be optimized by choosing a proper polymerization condition as well as the contents of GNP and MWCNT. By varying the contents of GNP and MWCNT in the PANI composite CE, we observed the short-circuit current density of DSSC was linearly related to the reduction current density of I^-/I_3^- redox couples measured by cyclic voltammetry (CV). We also found that the open-circuit voltage (V_{OC}) was highly dependent on the reduction potential of redox couples. Besides, the charge transfer resistance at the electrolyte/CE interface measured by electrochemical impedance spectroscopy (EIS) has a roughly linear relationship with the sheet resistance of PANI composite CE.

2. Experimental

2.1. Materials

Aniline sulfate and sulfuric acid were obtained from Hayashi and Scharlau respectively. Hydrogen peroxide (35% solution in water), isopropanol (99%), titanium isopropoxide (TTIP, 96%), acetonitrile, LiI (99%), I_2 (99.8 + %), 4-tert-butylpyridine (TBP, 99%), guanidinium thiocyanate (GuNCS), 3-methoxypropionitrile (MPN, 98%), tert-butanol and lithium perchlorate ($LiClO_4$) were received from Acros. Hydrochloric acid solution (37%) and ammonium hydroxide (35% solution in water) were obtained from Fisher. 3-Propyl-1-methylimidazolium iodide (PMII, 99.5%) and poly(ethylene glycol) (PEG, $M_w \sim 20,000$) were obtained from Merck. FTO ($\sim 15 \Omega \text{ sq.}^{-1}$) coated glass substrates and *cis*-bis(isothiocyanato)bis(2,2'-bipyridyl)-4,4'-dicarboxylato ruthenium(II) (N3) were acquired from Solaronix. GNP (specific surface area $450 \text{ m}^2 \text{ g}^{-1}$, purity > 99%, average thickness 3 nm, average particle size 0.5–40 μm) and MWCNT (O.D. 10–15 nm, I.D. 2–6 nm, length 0.1–10 μm) were purchased from Uni-Region and Arkema respectively. All chemicals and solvents were used without further purification.

2.2. Preparation of PANI composite CEs

All PANI composite films were deposited on FTO glass substrates by polymerization through ED method in an aqueous solution containing 0.5 M aniline sulfate, 1 M sulfuric acid, and various amounts of GNP and MWCNT (see Table 1) in a three-electrode system as described below. At first, FTO glass substrates were sequentially cleaned with an acid solution (volume ratio of $H_2O:H_2O_2:HCl_{(aq)} = 6:1:1$), alkaline solution (volume ratio of $H_2O:H_2O_2:NH_3(aq) = 5:1:1$) and isopropanol each for 20 min. The cleaned FTO glass, a Pt wire, and a saturated Ag/AgCl were used as the working electrode, counter electrode and

reference electrode respectively. Carbon additives were pre-added into the solution through sonication for 2 h and subsequently stirring for 12 h. The CE sample codes and their corresponding component ratios were listed in Table 1. ED process was carried out by a computer-controlled potentiostat instrument (PGSTAT 302 N, Autolab) with a constant potential of 0.8 V (vs. Ag/AgCl) and the electric charge densities set at 20, 30, and 40 mC cm^{-2} respectively. The as-formed PANI composite films were washed with 1 M sulfuric acid to remove the unreacted chemicals. The thickness of resulting PANI films was $\sim 100 \text{ nm}$ as measured by SEM

2.3. Fabrication of DSSCs

The photoelectrodes for DSSCs were fabricated as follows. TiO_2 precursor paste was synthesized by sol-gel method according to the literature [4]. The TiO_2 paste was then coated on FTO glass by using doctor-blade method and subsequently sintered at 450 $^\circ\text{C}$ for 30 min. Then, coating and sintering process were repeated to achieve a desired thickness of $\sim 18 \mu\text{m}$ as measured by SEM. An active area of 0.25 cm^2 selected from the sintered film was then immersed into a N3 dye ($3 \times 10^{-4} \text{ M}$) in a mixed solvent of acetonitrile and *tert*-butanol for 24 h. The dye-adsorbed photoelectrode was then rinsed with acetonitrile and dried in air. The liquid electrolyte containing 0.6 M PMII, 0.1 M LiI, 0.05 M I_2 , 0.1 M GuNCS, and 0.5 M TBP in MPN was injected into a gap between photoelectrode and PANI composite CE separated by a 60 μm spacer. A FTO glass sputtered with $\sim 100 \text{ nm}$ thick Pt as CE was also prepared for comparison

2.4. Measurements

Fourier-transform infrared (FTIR) spectra were recorded on a Thermo Nicolet NEXUS470 ATR-FTIR spectrometer and JASCO FT/IR-410. Thermogravimetric analysis (TGA) was conducted using a TA Instruments Q50 at a heating rate of 10 $^\circ\text{C min}^{-1}$ under N_2 . A four-point probe with a Keithley 2400 sourcemeter was used to measure the sheet resistance of prepared PANI composite CEs. JEOL JSM-6300 SEM was used to investigate the morphology of PANI composites. CV measurements were carried out in the acetonitrile solution containing 0.01 M LiI, 0.001 M I_2 and 0.1 M $LiClO_4$ by using a potentiostat/galvanostat (PGSTAT 302N, Autolab) with PANI composite film as working electrode, a saturated Ag/AgCl as reference, and a Pt wire as the auxiliary electrode. The potential range was from -0.5 V to 1.2 V at a scan rate of 50 mV s^{-1} . The photocurrent-voltage characterizations of all the DSSCs were recorded on PGSTAT 302 N under 100 mW cm^{-2} with a 1000 W ozone-free Xenon lamp equipped with a water-based IR filter and AM 1.5 filter (Newport Corporation). EIS data were recorded

Table 1
Properties of PANI/GNP/MWCNT composite films prepared by ED method.

Composite films	ANI/GNP/MWCNT Weight ratio ^a	Carbon additive content in film (wt%) ^b	Film weight (mg cm^{-2}) ^c	Sheet resistance ($\Omega \text{ sq.}^{-1}$) ^d
Pt	NA	NA	NA	4.69 ± 0.04
PANI	1/0/0	0	0.38 ± 0.04	15.02 ± 0.12
PANI-G1	1/0.0030/0	10.36	0.43 ± 0.04	11.08 ± 0.10
PANI-G2	1/0.0045/0	14.85	0.48 ± 0.03	9.36 ± 0.11
PANI-G3	1/0.0060/0	11.96	0.46 ± 0.02	10.76 ± 0.11
PANI-C1	1/0/0.0030	6.86	0.41 ± 0.02	13.40 ± 0.15
PANI-C2	1/0/0.0045	12.62	0.47 ± 0.04	12.10 ± 0.10
PANI-C3	1/0/0.0060	9.25	0.46 ± 0.05	12.92 ± 0.11
PANI-G1C1	1/0.0030/0.0030	N/A	0.46 ± 0.05	9.46 ± 0.15
PANI-G1C2	1/0.0030/0.0045	N/A	0.45 ± 0.02	7.65 ± 0.11
PANI-G1C3	1/0.0030/0.0060	N/A	0.46 ± 0.04	8.25 ± 0.14

^a Ratio of the major components in the solution for electropolymerization.

^b Weight percentage of carbon additives in the PANI composite estimated by TGA shown in Fig. 2.

^c Estimated by TGA data shown in Fig. 2.

^d Measured by four-point probe method.

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