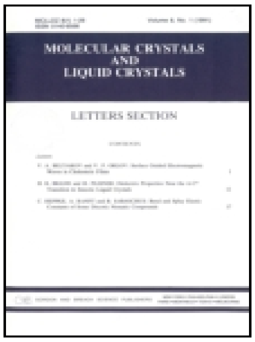

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Graphene/Polyaniline Nanocomposite Multilayer Counter Electrode by Inserted Polyaniline of Dye-Sensitized Solar Cells

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Polyaniline (PANI) conducting polymer and graphene are preferred counter electrode (CE) materials for dye-sensitized solar cells (DSSC). Graphene/PANI nanocomposite multilayer CE is created through the insertion of a PANI layer. It has been demonstrated as a platinum-free counter electrode for cost-efficient DSSCs. Here, graphene/PANI nanocomposite and PANI were synthesized by electro-polymerization from a solution containing aniline monomers and graphene. Graphene/PANI nanocomposite multilayer CE showed improved electrical conductivity, interface charge transfer rate, and catalytic activity on I_3^- *reduction compared with the Pt CE. The high electro-catalytic ability of graphene/PANI nanocomposite multilayer CE was demonstrated by cyclic voltammetry and electrochemical impedance spectroscopy.*

Keywords polyaniline; graphene; dye-sensitized solar cells; electro-polymerization; counter electrode

1. Introduction

The role of the counter electrode (CE) in DSSCs is to transfer electrons from the external circuit back to the redox electrolyte and to catalyze the reduction of I_3^- to I^-. Pt has been preferred as the CE material for DSSCs because of its excellent catalytic activity and corrosion resistance to iodide (I^-) ions present in the redox electrolyte[1]. However, because Pt is a precious metal, it increases the cost of DSSCs. Recently, Pt-free materials with lower cost and good stability have been investigated as catalysts for DSSCs, mainly based on carbon materials[2] and conducting polymers[3, 4].

Polyaniline (PANI) has been used as the CE for DSSCs and high catalytic activity[4]. Graphene is also an atomic-layer-thick and two-dimensional system that has attracted much attention due to its outstanding electronic, optical, thermal, mechanical properties,

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and potential applications[5]. When incorporated into polymers, it has been revealed that graphene can markedly improve the properties of the host materials[6]. The combination of PANI with graphene is expected to give a high electron conduction and to be electrocatalytic through its large surface area.

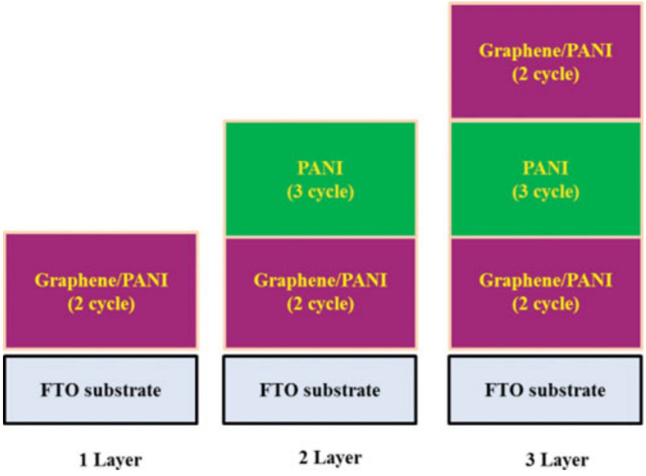
Here, we describe the fabricateion of a graphene/PANI (GP) nanocomposite multilayer CE for DSSCs by a simple and cost-effective electro-polymerization. The multilayer structure can improve electrocatalytic activity by increasing the surface area between CE materials and the electrolyte.

2. Experiment Details

2.1. Preparation of the GP Nanocomposite Multilayer CE

The GP nanocomposite multilayer CE consisted of a bottom GP, PANI, and top GP layers. These layers were deposited continuously on FTO glass by electropolymerizaion. The bottom GP layer was synthesized from an aqueous solution containing 0.2 M aniline, 1.0 M HCl and 1mg/ml graphene oxide aqueous solution. After depositing the bottom GP layer, a PANI layer was synthesized from an aqueous solution containing 0.2 M aniline and 1.0 M HCl. Finally, a top GP layer was synthesized onto the PANI layer under deposited conditions identical to those used for the bottom GP layer. Electropolymerizaion and cyclic voltammetry (CV) was obtained in the potential range of 0 V to +1.5 V using a scan rate of 50 mV s^{-1}.

Three different structure of CEs were measured for the DSSCs device. The structures of the CEs described in the present work were composed of GP (1 layer), GP/PANI (2 layers), and GP/PANI/GP (3 layers). The designs of the 1-, 2-, and 3-layer CEs are shown in Scheme 1.



Scheme 1. Schematic diagram of the 1-, 2-, and 3-layer CEs.

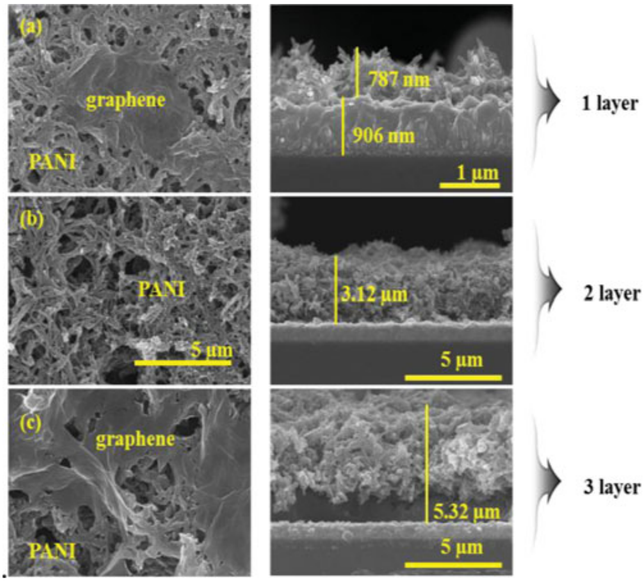


Figure 1. Surface (left) and cross-sectional SEM images (right) of (a) 1 layer CE, (b) 2 layer CEs, and (c) 3 layer CEs on FTO substrates.

2.2. *Fabrication of DSSCs Devices*

The TiO_2 photoelectrodes (PEs) were prepared on a FTO substrate with a thickness of 10-12 μm and a porosity 50-60% by the doctor-blade technique. The TiO_2 film was dried at 180°C for 10 min and immediately sintered at 450°C for 30 min. The TiO_2 PEs were sensitized by dipping them in a 0.5 mM N719 (*cis*-bis(isothiocyanato)bis(2,2′-bipyridyl-4,4′-dicarboxylato)-ruthenium(II) bis-tetrabutylammonium) dye solution (Solaronix Co.) at room temperature for 24 h. The prepared CEs were placed over the dye-adsorbed TiO_2 PE, and assembled by a sandwich type between the TiO_2 PE and GP nanocomposite multilayer CE. The redox electrolyte was injected into the cell through the small holes and sealed with a small square of sealing sheet.

3. Results and Discussion

The morphologies of the 1-, 2-, and 3-layer CEs were studied using SEM. The electrochemically polymerized PANI was composed of nanofibers (Fig. 1(b)). However, a spreading structure was detected in the GP layer (Fig. 1(a), 1(c)), indicating that graphene filled up the pores of the PANI. This structure is expected to enhance the charge transfer between PANI and graphene. The cross-section SEM images show the thicknesses of the CEs. The thicknesses of the 1-, 2-, and 3-layer CEs were 787 nm, 3.12 μm, and 5.32 μm, respectively.

CV was used to evaluate the electrocatalytic activity of the 1-, 2-, and 3-layer CEs on I_3^- reduction. The CV curves scanning from 0 to 1.5 V are shown in Fig. 2. Two couples of redox peaks were observed in the Pt CE. The left one is attributed to the redox reaction of $I_3^- + 2e^- \leftrightarrow 3I^-$, and the right one corresponds to $2I_3^- \leftrightarrow 3I_2 + 2e^-$[7]. It can be seen that the 3-layer CE showed the largest anodic and cathodic current densities for the I_3^-/I^- redox reaction among the four CEs, which can be attributed to its high active surface area.

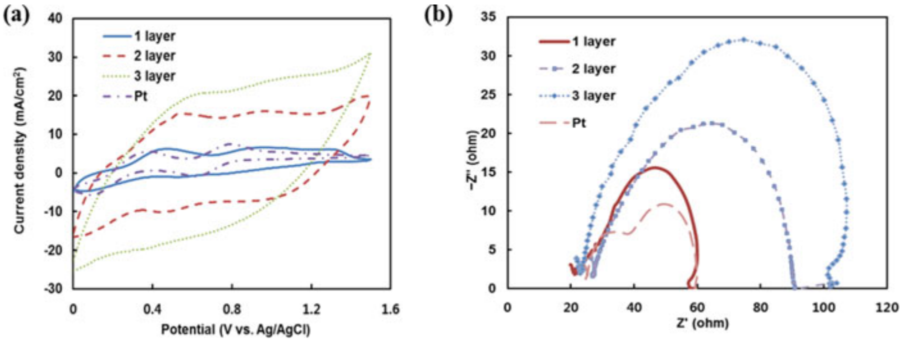


Figure 2. (a) CV curves of the Pt, 1-, 2-, and 3-layer CEs and (b) Nyquest plots of the DSSCs based on the Pt, 1-, 2-, and 3-layer CEs.

To obtain better insight into the dynamics of the interfacial charge transfer process within the DSSCs, electrochemical impedance spectroscopy (EIS) was performed. Figure 2(b) shows the Nyquist plots of the DSSCs based on the Pt, 1-, 2-, and 3-layer CEs. The semicircle decreases clearly from the 3-layer CE to the 1-layer CE. This means the diffusion of the redox couples within the multilayer structure is accelerated by the elevated interfacial area. Because charge transfer resistance (R_{ct}) varies inversely with the electrocatalytic activity for the reduction of I^-/I_3^- redox species, the large decrease demonstrates that the 3-layer CE has the highest electrocatalytic activity.

Figure 3 shows the current density-voltage (J-V) curves of the DSSCs based on the Pt, PANI, 1-, 2-, and 3-layer CEs. The extracted characteristic values of power conversion efficiency (PCE), open-circuit voltage (V_{oc}), short-circuit current (J_{sc}), and fill factor (FF) are summarized in Table 1. The PCE decreased with the increase in layers, resulting in an increase in R_{ct} with the increase in layers. The resulting electrode with a high surface area

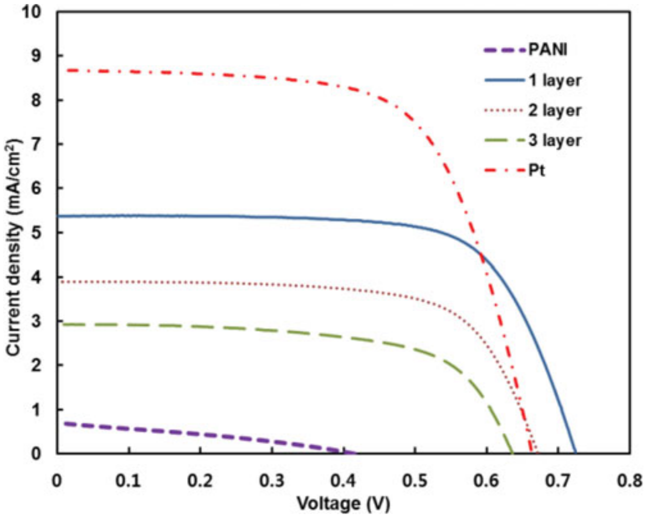


Figure 3. Photocurrent density-voltage curves of the DSSCs based on the Pt, PANI, 1-, 2-, and 3-layer CEs.

Table 1. Photovoltaic parameters of DSSCs with Pt, PANI, 1-, 2-, and 3-layer CEs

Sample	V_{oc} (V)	J_{sc} (mA/cm^2)	FF	PCE(%)
PAN1	0.42	0.70	0.31	0.09
1 layer	0.72	5.39	0.70	2.72
2 layer	0.67	3.90	0.68	1.79
3 layer	0.64	2.93	0.63	1.18
Pt	0.70	9.06	0.65	3.75

can exhibit high electrocatalytic activity. However, due to the increased film thickness, the resisting force of the electrolyte diffusion in the electrode/electrolyte interface was also increased consequently. The cell with a 1-layer CE was shown to have the largest PCE among the 1-, 2-, and 3-layer CEs. The cell with a 1-layer CE exhibited a PCE of 2.72%, up to 73% of that with the Pt CE.

4. Conclusions

We demonstrated the fabrication of GP nanocomposite multilayer CEs by electropolymerization. The GP nanocomposite exhibited promising properties in terms of electrocatalytic activity in the CE of the DSSCs. The resulting electrode with high surface area can exhibit high electrocatalytic activity. However, due to the increased film thickness, the resisting force of the electrolyte diffusion in the electrode/electrolyte interface was increased consequently. The DSSCs from the 1-layer CE provided an impressive PCE of 2.72%, in comparison with that of 1.18% from the 3-layers CE. The research presented here can help in achieving higher-performance CEs for DSSCs based on other sensing conducting polymers.

Acknowledgments

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