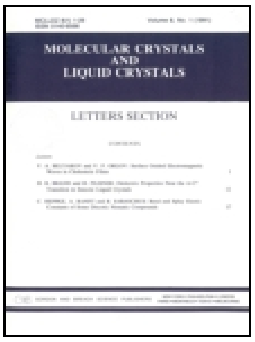

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Molecular Crystals and Liquid Crystals

ISSN: 1542-1406 (Print) 1563-5287 (Online) Journal homepage: http://www.tandfonline.com/loi/gmcl20

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To cite this article: Gil-Ha Jeong, Seok-Jae Kim, Hyun-Seok Ko, Eun-Mi Han & Kyung Hee Park (2015) Electrochemical Properties of Graphene/PEDOT:PSS Counter Electrode in Dye-sensitized Solar Cells, Molecular Crystals and Liquid Crystals, 620:1, 117-122, DOI: 10.1080/15421406.2015.1095272

To link to this article: http://dx.doi.org/10.1080/15421406.2015.1095272

Mol. Crys. Liq. Cryst., Vol. 620: pp. 117–122, 2015
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ISSN: 1542-1406 print/1563-5287 online
DOI: 10.1080/15421406.2015.1095272

Electrochemical Properties of Graphene/PEDOT:PSS Counter Electrode in Dye-sensitized Solar Cells

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The poly(3,4-ethylenedioxythiophene):poly (styrenesulfonate) (PEDOT:PSS) and reduced graphene oxide (rGO)/PEDOT:PSS have been prepared by spin coating as counter electrodes (CEs) for dye-sensitized solar cells. The optimized 1wt% rGO was dispersed in a solution of PEDOT:PSS for the highest electrical conductivity. The cyclic voltammogram result shows that rGO/PEDOT:PSS CE has a good catalytic activity towards the I^-/I_3^- *redox couple compared to Pt CE and PEDOT:PSS CE. The rGO/PEDOT:PSS CE showed a high energy conversion efficiency of 5.1% accompanied by a fill factor of 0.68, which was comparable to those of the Pt CE (4.6%) and PEDOT:PSS (2.4%). Hence, the rGO/PEDOT:PSS is expected to replace the expensive Pt as a promising CE catalyst.*

Keywords PEDOT:PSS; reduced graphene; dye-sensitized solar cells; impedance analysis; counter electrode

1. Introduction

Dye sensitized solar cells (DSSCs) have been attracting considerable attention because of high efficiency, simple fabrication process and low fabrication cost [1, 2]. As an important component of DSSCs, the CE transfers the electrons from the external circuit back to the electrolyte and catalyze the reduction of I_3^- to I^- in the solution. Counter electrodes (CEs) of DSSC are usually made of platinum. Although, Pt has high catalytic activity for I_3^- reduction, high conductivity and stability, it is one of the expensive component materials in DSSCs [3]. While some porous carbon materials and conducting polymer were attempted to replace the Pt electrode [4–6], the conversion efficiency of cells based on carbon CE was relatively low due to the poor catalytic activity for I_3^- reduction per unit area and lower conductivity.

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The conductive polymer poly(3,4-ethylene dioxythiophene) (PEDOT) doped with poly(styrene sulfonate) (PSS) is quite promising as a next-generation transparent electrode material owing to its enormous advantages over other conducting polymers. PEDOT:PSS films have high transparency in the visible range, high mechanical exibility, and excellent-thermal stability and can be fabricated through conventional solution processing. However, pristine PEDOT:PSS films suffer from a very low conductivity of less than 1 S cm^{-1}. Thus, to improve the conductivity of PEDOT:PSS flms is the prerequisite for their application as the counter electrode is added rGO materials in PEDOT:PSS solution. Jo and coworkers [7] have successfully demonstrated a simple and facile approach of preparing a stable aqueous dispersion system of reduced graphene oxide (rGO) nanosheets functionalized with PEDOT:PSS.

In this paper, the $I^-/I_3{}^-$ redox reaction behavirs on the PEDOT:PSS, rGO/PEDOT: PSS CE and Pt CE were characterized in terms of the electrocatalytic properties and charge transfer resistance between these CEs and the $I^-/I_3{}^-$ reox couple. The performances of these CEs were also evaluated by photovoltaic characteristics of the DSSCs.

2. Experiment Details

2.1. Preparation of the rGO/PEDOT:PSS Counter Electrode

Poly(3,4-ethylene dioxythiophene):poly(styrene sulfonate) aqueous solution (PEDOT:PSS, Clevios PH 1000) were purchased from Heraeus Ltd. with a PEDOT:PSS concentration of 1.0-1.3% by weight and the weight ratio of PSS to PEDOT was 2.5:1. Graphene oxide(GO) was prepared using a Hummer's method [8] and rGO was prepared under alkaline conditions according to the reported method [9]. We pre-measured to optimize the contents of rGO with PEDOT:PSS solution. From this test, the rGO content in the mixture increased from 0% to 1%, the energy conversion efficiency of the DSSC was increased 2.4% to 5.1%. However, further increasing the weight content of rGO showen little affect. We have produced smooth, highly conductive and transparent films by simply mixing water soluble reduced GO (1 wt.%) with PEDOT:PSS solution. The rGO/PEDOT:PSS films were spin coated at 3000 rpm for 40 s on FTO substrates which were treated with UV/ozone for 15 min prior to spin coating. The films were annealed on a hot plate under ambient atmosphere at 130°C for 30 min. Thicker rGO/PEDOT:PSS films were prepared by spin coating multiple times and annealing after each layer.

2.2. Fabrication of DSSCs Devices and Measurements

TiO_2 paste (Ti-nanoxide D/SP, Solaronix, Swizerland) was screen-printed on an F-doped SnO_2 (FTO) substrate (8 ohm/square, TEC 8, Pillikington) and then sitered at 450°C for 30 min. The film thckness is 12 μm and the amount of adsorbed dye on TiO_2 electrode is about 2.0×10^{-7} mol/cm^2. The dye solution (0.5 mM N719, (*cis*-bis(isothiocyanato)bis(2,2′-bipyridyl-4,4′-dicarboxylato)-ruthenium(II) bis-tetrabutylammonium)) was prepared in anhydrous ethanol solvent. The TiO_2 electrodes were dye-coated by immersing them into a solution of N719 at room temperature overnight. The constituents of the electrolyte were 0.5 M LiI (aldrich), 0.05 M I_2 (aldrich), 0.6 M 1,2-dimethyl-3-propylimidazolium iodide (DMPII, solaronix), and 0.3 M 4-*tert*-butylpyridine (tBP, aldrich) in 3-methoxypropionitrile (MPN, Fluka) solvent. The TiO_2 photoanode and counter electrode were sandwiched together and the space flled with liquid electrolyte.

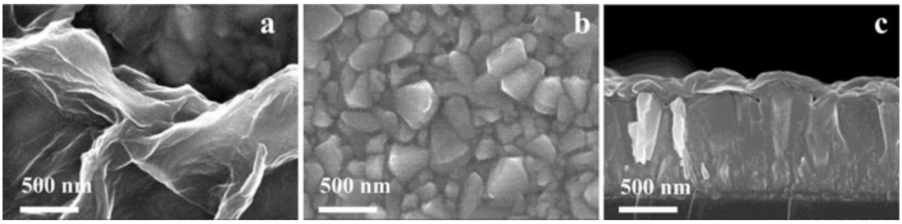

Figure 1. SEM images of a) rGO film, b) PEDOT:PSS coated film on FTO, and c) cross sectional view of rGO/PEDOT:PSS film on FTO substrate.

The surface morphology was characterized by field emission scanning electron microscope (FE-SEM, S-4700). To investigate the electrochemical characteristics of the counter electrodes, cyclic voltammetry (CV) was carried out in a three-electrode system in an acetonitrile solution containing 10 mM LiI, 1 mM I_2, and 0.1 M $LiClO_4$. The PEDOT:PSS/FTO, Pt/FTO or rGO-PEDOT:PSS/FTO electrode served as working electrodes, while the platinum wire and the Ag/AgCl served as the counter electrode and reference electrode, respectively. Electrochemical impedance spectroscopy (EIS) was performed with an electrochemical workstation (CHI660A, USA) with a frequency ranging from 10 mHz to 100 kHz, the magnitude of the alternative signal was 10 mV. An applied bias voltage was set to the open-circuit voltage of the DSSCs in the dark. Photocurrent–voltage characteristics of the DSSCs were recorded using a Keithley 2400 source meter under one sun air mass 1.5 G (100 mV cm^{-2}) illumination provided by a solar light simulator (Thermo Oriel).

3. Results and Discussion

The morphologies of rGO and the rGO/PEDOT:PSS films were invesitigated by FE-SEM. rGO sheets have smooth surfaces with slight wrinkles (figure 1a). As shown Fig.1b, the PEDOT:PSS layer was thin deposited on FTO substrate during spin coating process. Fig.1c show the cross-sectional SEM image of the rGO/PEDOT:PSS film coated on FTO substrate. It is clear from this figure that the graphene sheets were dispersed uniformly in the PEDOT:PSS materix and they were flattened. The thickness of composite film was measured by SEM to be about 50 nm.

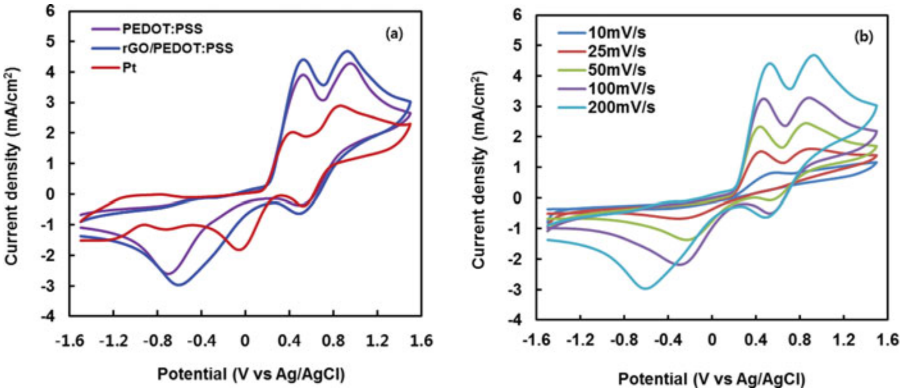

Figure 2. (a) CVs of the various CEs with an electrolyte of 10 mM LiI, 1mM I_2 and 0.1M $LiClO_4$ in ACN at a scan rate of 50 mV/s (b) CVs with various scan rate of rGO/PEDOT:PSS CE.

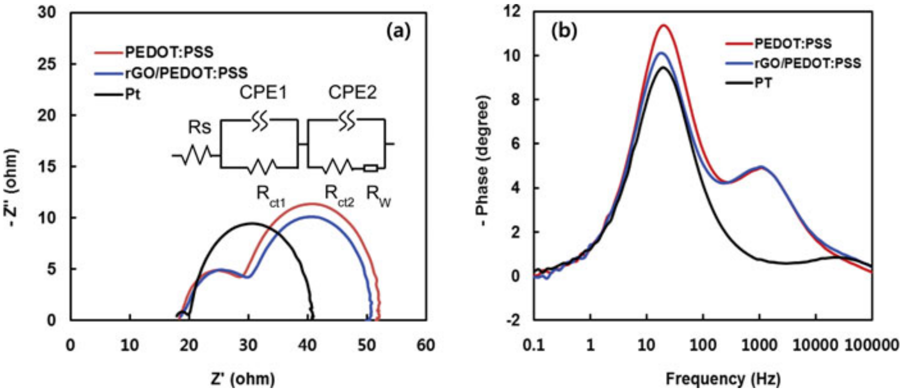

Figure 3. EIS results of (a) Nyquest plots and (b) Bode plots in the DSSCs with various CEs.

The electrocatalytic ability for the various Ces can be obtained from the CV measurement. Fig. 2 shows the CV curves of the Pt, PEDOT:PSS, and rGO/PEDOTPSS CEs. In Fig. 2a, the 10wt% rGO/PEDOT:PSS CE shows a higher redox current density than that of the PEDOT:PSS and Pt CEs, which implies that the rGO/PEDOT :PSS CE possesses better electrocatalytic activity for reduction of the I_3^- ions. The CV measurements shown in Fig. 2 reveal that the electrocatalytic ability PEDOT:PSS can be improved by the addition of rGO materials. Yeh. *et al.* reported that higher electrocatalytic activity of the electrode with PEDOT:PSS/materials could be attributed not only to the inherent superior properties of matrials like rGO for electrical conductivity and catalytic ability, but also to the high electrochemical surface area of the composite film owing to its high surface roughness and porous morphology [10].

For the I^-/I_3^- redox couple, the major electrochemical reduction at the CE can be represented as $I_3^- + 2e^- \rightarrow 3I^-$. Fig. 2b shows cyclic voltammograms of the I^-/I_3^- redox couple on the rGO/PEDOT:PSS CE with various scan rate in acetonitrile. This results shows the adsorption of iodide species is little affected the redox reaction at the rGO/PEDOT:PSS CE surface as well as Pt surface, and this also suggest that no specific interaction between I^-/I_3^- redox couple and PEDOT:PSS CE as is the case of Pt CE [11].

The EIS spectra of symmetric cells based on the various CEs are shown in Fig. 3. The electrochemical properties of the various CEs, including the solution resistance (R_s) and charge transfer resistance (R_{ct1}), were obtained by fitting the equivalent circuit shown in the inset of Fig. 3a and are summarized in Table 1. The R_s values of PEDOT:PSS CE and rGO/PEDOT:PSS CE are 18.03 Ω and 20.35 Ω, respectively, both of them are higher than that of Pt CE (17.94 Ω), which may be caused by the slightly lower conductivity of

Table 1. Photovoltaic parameters of DSSCs based on Pt, PEDOT:PSS and rGO/PEDOT: PSS counter electrodes

CE	J_{SC} [mA/cm^2]	V_{OC} [V]	FF	η [%]	R_s(Ω)	R_{ct1}(Ω)
PEDOT:PSS	8.8	0.67	0.41	2.4	18.03	15.83
rGO/PEDOT:PSS	10.4	0.73	0.68	5.1	20.35	11.90
Pt	10.9	0.68	0.63	4.6	17.94	1.74

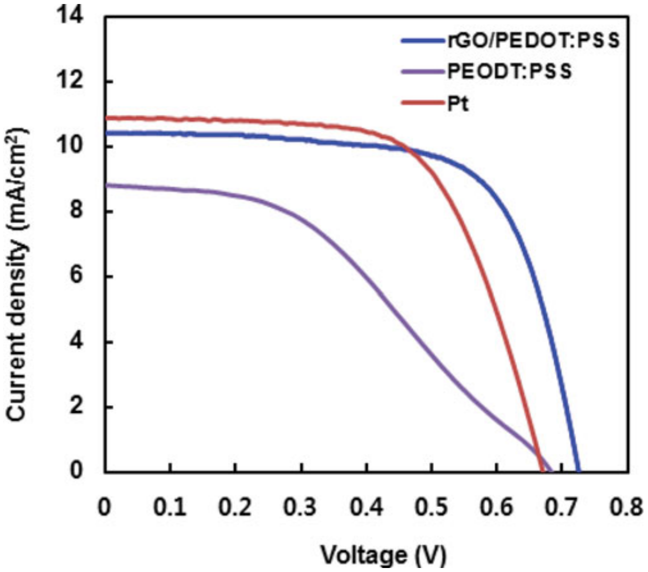

Figure 4. Photocurrent density-voltage curves of the DSSCs with the various CEs.

PEDOT:PSS film compared to Pt (Fig. 3b). The R_{ct1} can be calculated from the radius of the first corresponding semicircle. In Table 1, the rGO/PEDOT:PSS composite CE improves charge transfer at the FTO substrate/composite electrode interface with a slightly lower R_{ct1} value of 11.90 Ω cm^2, compared to the PEDOT:PSS CE (15.87 Ω cm^2). This is attributed to the enhancement of electrical conductivity and catalytic ability due to the presence of rGO materials. However, R_{ct1} value the rGO/PEDOT:PSS composite CE is higher than that of Pt CE (1.74 Ω cm^2).

The photocurrent density-voltage (J-V) characteristics of the DSSCs with the various CEs are shown in Fig. 4. The rGO/PEDOT:PSS CE reached a cell conversion efficiency of 5.1%, Voc of 0.73V, Jsc of 10.4 mA cm^{-2} and FF of 0.68. Compared to PEDOT–PSS film, the addition of a small amount of rGO effectively increased the short-circuit photocurrent densities and fill factors of the cells. This is mainly due to that the high specific surface area and many chemical defects of ultrathin graphene sheets provide them with high catalyzation activity toward reduction of iodine.[12] As shown in Fig. 4, the rGO/PEDOT:PSS CE generally provides a higher open-circuit voltage (Voc) than those of the PEDOT:PSS and Pt CEs. Moreover, the increased FF (0.68) in the case of the cell with rGO/PEDOT:PSS, compared to those of the cells with PEDOT:PSS (0.41) and Pt (0.63), is consistent with their corresponding charge transfer resistances. Finally the rGO/PEDOT:PSS CE cell achieved a higher efficiency, a higher FF and Voc. The corresponding photovoltaic parameters are summarized in Table 1.

4. Conclusions

The rGO/PEDOT:PSS counter electrode was prepared by spin coating method. The attractive electrochemical properties and photovoltaic parameters of DSSCs with the rGO/PEDOT:PSS CE, as compared to those with either PEDOT:PSS or a Pt CE, are attributed to the better electrocatalytic activity of rGO and good adherence of the PEDOT:PSS materials to the FTO substrate. The rGO/PEDOT:PSS CE could be a promising substrate for the expensive Pt CE considering low-cost fabrication, the possibility of large-scale production and high cell efficiency.

Acknowledgments

This research was supported by the Basic Science Research Program through the National Research Foundation of Korea (NRF) funded by the Ministry of Science, ICT & Future Planning (2012R1A1A3010655).

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