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Counter electrodes from conducting polymer intercalated graphene for dye-sensitized solar cells

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HIGHLIGHTS

- Conducting polymers are intercalated into graphene.
- The intercalated electrodes are used for DSSC applications.
- The intercalated electrodes have superior catalytic activity.
- The efficiencies are markedly enhanced for intercalated electrode based DSSCs.

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ABSTRACT

Creation of cost-effective and platinum-free counter electrodes (CEs) is persistent for developing advanced dye-sensitized solar cells (DSSCs). We present here the fabrication of conducting polymers such as polyaniline (PANi), polypyrole (PPy), or poly(3,4-ethylenedioxythiophene) (PEDOT) intercalated reduced graphene oxide (rGO) CEs on flexible Ti foil or polyethylene-terephthalate substrate for liquid-junction DSSC applications. The ration architecture integrates the high electron-conducting ability of graphene and good electrocatalytic activity of a conducting polymer into a single CE material. The preliminary results demonstrate that the resultant CEs follow an order of rGO/PPy > rGO/PANi > rGO/PEDOT > rGO. A maximal cell efficiency of 6.23% is determined on the optimized solar cell device, yielding 104.9% enhancement in comparison to rGO based device.

1. Introduction

Dye-sensitized solar cell (DSSC) converting solar energy into electricity by complicated photoelectrochemical reactions is one of the promising solutions to energy crisis and environmental pollution [1]. A typical DSSC device comprises of a counter electrode (CE) for reducing triiodide ions in the electrolyte, a photoanode having a wide bandgap semiconductor for dye absorption, and a redox electrolyte having iodide/triiodide (I^-/I_3^-) couples. An efficient CE can accelerate I^- generation for dye recovery and reduce recombination reaction within a real DSSC [2–4]. Up to date, precious platinum (Pt) has been a preferred CE material for DSSC due its reasonable catalytic activity toward redox electrolyte as well as good electrical conductivity and chemical stability. The high dosage of Pt material is a burden for commercial DSSC. Therefore, many efforts have been placed on searching CE candidates such as carbonaceous materials [5–12], conducting polymers [13–15], compounds [16–19], and alloys [20–22] to replace Pt for DSSC. It is noteworthy that conducting polymers such as polypyrole (PPy), polyaniline (PANi), or poly(3,4-ethylenedioxythiophene) (PEDOT) are promising CE electrocatalysts because of their simple synthesis,

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cost-effectiveness, and superior electrocatalytic activity. However, the ability of collecting reflux electrons from external circuit is still unsatisfactory in comparison with Pt-based materials, leading to photocurrent loss and reduced photovoltaic performances. Moreover, conducting polymers can be further oxidized into fully-oxidized state when exposed in air, allowing for reduced electrical and electrochemical performances.

Apart from conducting polymers, graphene is another well-considered CE catalyst because of excellent electrical conduction, chemical stability, and high specific surface area in two-dimensional conjugated structure [23–26]. One of the drawbacks of graphene is its unsatisfactory redox behaviors toward I_3^- reduction reaction. A rising strategy is to combine graphene with conducting polymers, allowing for formation of graphene-based composites with superior rapid charge transfer ability and redox performances [27–29]. Early works in this field focused on the electrodeposition, chemical deposition, and spin-coating of graphene/polyaniline composite [16], carbon fiber/PEDOT:PSS [17], chemically converted graphene/polyaniline [30] et al. Another effective way is the intercalation of conducting polymers into graphene, which can avoid further oxidation of conducting polymers and therefore improve the stability of CE materials.

Flexible electrodes are promising in self-powered systems in wearable electronic devices [31–34]. Therefore, one of the persistent topics is to create flexible electrodes for photovoltaic devices [35–38]. Titanium (Ti) foil and polyethylene terephthalate (PET) are widely utilized as flexible substrates in organic electronics applications [39]. We launch here a new strategy of synthesizing PPy, PANi, or PEDOT intercalated reduced graphene oxide (rGO) on Ti foil or PET substrate as Pt-free CE for DSSC applications.

2. Experimental

2.1. Synthesis of conducting polymers and GO

The doped PANi was synthesized by a chemical method using the procedures in literature [40,41], while the doped PPy and PEDOT were prepared according to the procedures in Refs. [42,43]. The GO was synthesized from natural graphite powder by a modified Hummers and Offema method [44–46].

2.2. Preparation of CEs

0.2 g of GO was thoroughly dispersed in 100 mL of deionized water to form a homogeneous solution 10 mL of GO aqueous solution was mixed with 10 mL of saturated PPy, PANi, or PEDOT aqueous solution, and ultrasonicated for 2 h to from a stable dispersion (Fig. S1). 4 mL of the above mentioned dispersion was filtrated and moulded on Ti foil and PET substrate to form a film with an average thickness of ~5 μm. To improve the electrical conductivity of the GO films, the GO/PPy, GO/PANi and GO/PEDOT CEs were reduced by concentrated ethanol solution of HI (30 vol%) for 15–20 h at room temperature [46]. After being rinsed with ethanol, the rGO/PPy, rGO/PANi, rGO/PEDOT CEs are dried and utilized as CEs catalysts for DSSC, as shown in Fig. S2.

2.3. Assembly of DSSC

Mesoporous TiO_2 film with a thickness of 10 μm was prepared by coating sol-thermal synthesized TiO_2 colloid on FTO glass substrate by a doctor-blade technique. Subsequently, the film was sintered at 450 °C for 30 min in ambient atmosphere, which were finally sensitized with a 0.5 mM ethanol solution of N719 dye. The DSSC with an active area of 0.25 cm^2 was fabricated by combining the dye-sensitized TiO_2 anode and PET or Ti foil supported rGO, rGO/PANi, rGO/PPy or rGO/PEDOT CE, filled with a I^-/I_3^- redox electrolyte in acetonitrile.

2.4. Characterization and measurements

The cross-sectional morphologies of the rGO/PPy, rGO/PANi, and rGO/PEDOT were captured by a field emission scanning electron microscope (SEM, Hitachi S-4800). X-ray diffraction (XRD) profiles were determined on a Bruker D8 instrument using Cu Kα radiation at a scan rate of 10° min^{-1}.

Cyclic voltammetry (CV) was carried out in 10 mM I_2, 50 mM LiI, and 500 mM $LiClO_4$ in acetonitrile. The rGO, rGO/PPy, rGO/PANi, or rGO/PEDOT with active area of 0.25 cm^2 served as working electrodes, while a platinum foil and an Ag/AgCl were used as counter and reference electrodes, respectively. Electrochemical impedance spectroscopy (EIS) characterizations were carried out on a traditional electrochemical workstation at an ac amplitude of 10 mV. The recorded EIS plots were fitted with Z-view software to extract corresponding electrochemical parameters. Tafel polarization curves were determined by assembling symmetric dummy cells with a CE|electrolyte|CE architecture.

The characteristic photocurrent-voltage (*J-V*) curves were determined on the same electrochemical workstation under 100 mW cm^{-2} irradiation. Before measurement, the DSSC was covered with a black mask with an area of 0.25 cm^2 to avoid stray light.

3. Results and discussion

Fig. 1 shows the cross-sectional SEM morphologies of PANi, PPy, and PEDOT intercalated rGO on Ti foils. Apparently, the rGO nanosheets have been stacked into laminated structure filled with conducting polymers. This architecture is beneficial to providing gigantic surface area for I_3^- absorbing and conducting electrons from rGO to conducting polymers for I_3^- reduction. Moreover, the rGO/conducting polymer catalysts have a close contact with Ti substrate, allowing for good electron collection from external circuit to CE material.

The XRD patterns of rGO/PPy, rGO/PANi, and rGO/PEDOT composite as well as pristine rGO are presented in Fig. 2. The peak position at $2\theta = 24^\circ$ for (002) plane of rGO can be detected on the as-prepared rGO/PPy, rGO/PANi, and rGO/PEDOT catalysts. However, the intercalation of conducting polymers into stacked rGO results in the weakening and broadening of the diffraction peak at $2\theta = 24^\circ$ [47,48].

Fig. 3a,b show *J-V* characteristics of the DSSCs based on rGO/PPy, rGO/PANi, and rGO/PEDOT on Ti foil or PET substrate. The corresponding photovoltaic and electrochemical parameters including open-circuit voltage (V_{oc}), short-circuit current density (J_{sc}), fill factor (*FF*), cell efficiency (η), and charge-transfer resistance (R_{ct}) are summarized in Table 1. For example, the DSSC with a PET supported rGO/PPy CE yields a remarkable $\eta = 4.41\%$, $J_{sc} = 14.2$ mA cm^{-2}, $V_{oc} = 0.589$ V, and $FF = 0.527$, which are much higher than the photovoltaic parameters obtained with pristine rGO CE based solar cell. It is noteworthy that the V_{oc}, J_{sc}, and *FF* values for the DSSC based on rGO/PPy CE are also higher than corresponding data of other DSSCs. The may be attributed to the rapid conversion from I_3^- to I^-, accelerating the dye recovery and persistent electron photogeneration. It is noteworthy to mention that the determined cell efficiencies are higher than 3.52% from pristine Pt based DSSC on a flexible PET substrate [49] but lower than 8.36% for carbon black nanoparticles/sulfonated-poly(thiohene-3-[2-(2-methoxyethoxy)ethoxy]-2,5-diyl) [50], 6.8% for nitrogen doped graphene, as well as ~7.5% for metal selenides [51,52] electrode based solar cells. However, the launched strategy