



Self-assembly of graphene oxide/polyaniline multilayer counter electrodes for efficient dye-sensitized solar cells



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ABSTRACT

Layer-by-layer (LbL) assembly provides a facile approach in fabricating well-defined nanoarchitectures with electrical and electrochemical properties. Research on electrical and electrochemical performances of the LbL membranes from graphene oxide would be profound in modern photovoltaic nanodevices. We demonstrate here the LbL self-assembly of polyaniline-(graphene oxide/polyaniline)_n [PANI-(GO/PANI)_n] (*n* represents the deposition cycle) multilayer films with good electrical and electrochemical behaviors and employment as counter electrodes (CEs) in dye-sensitized solar cells (DSSCs). The resulting multilayer films give a linear growth in bulk conductivity and increased electrocatalytic activity toward triiodides. Careful examination of data and characterizations indicates that the electrical and electrochemical properties are impressive to fulfill the task of PANI-(GO/PANI)_n CEs. A promising power conversion efficiency of 7.41% (measured under standard AM1.5 test conditions) is obtained in PANI-(GO/PANI)₄ CE in comparison with 6.37% from PANI-(GO/PANI)₁ CE. This strategy provides new opportunity for the fabrication of efficient DSSCs, and the efficiency record is expected to be surpassed by scalable technique and components.

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1. Introduction

With the rapid development of the low-carbon economy, grave concerns about security of energy supplies and the environmental consequences of greenhouse gas emissions have spurred governments to support the development of new renewable energy sources [1–3]. For that reason, solar energy is expected to play a crucial role as a future energy source [4,5]. Dye-sensitized solar cells (DSSCs) represent a promising next-generation photovoltaic technology for the production of renewable, clean, and affordable energy [6–8]. A typical DSSC is always by sandwiching electrolyte containing the iodide/triiodide (I^-/I_3^-) redox couples between a photoanode comprising TiO_2 nanocrystals sensitized by dye molecules and a counter electrode (CE). During the operation of a DSSC device, photosensitizers (i.e. dye molecules) on the surface of the nanostructured titanium oxide (TiO_2) are excited by incident light and then release electrons to conduction band of TiO_2 nanocrystalline. After being collected by a current collector (fluorine-doped tin oxide, FTO), the excited electrons can form current and arrive CE [9]. The oxidized dye molecules can be recovered by I^-/I_3^- redox couples, whereas triiodides will be reduced by a CE under the participation of reflux electrons. Platinum is a preferred CE material for the electroreduction reaction of triiodides

due to its superior conductivity, electrocatalytic activity, and stability. However, high cost of Pt material has prevented it from being widely used in commercial DSSCs. Therefore, it is a prerequisite to exploit substitutes for Pt in order to reduce the overall cost and simultaneously keep the performances of DSSCs [10–13].

The combination of carbon materials and conducting polymers are believed as an efficient route. Early works in this field focused on the electrodeposition, chemical deposition, and spin-coating of graphene/polyaniline composite [14], carbon fiber/PEDOT:PSS [15], graphene/polyaniline hybrid [16], graphene/PEDOT:PSS [17], chemically converted graphene/polyaniline [18], et al. The chemically, physically or electrochemically codeposited conducting polymer/carbon materials give a crucial drawback for using CEs of DSSCs: the interfacial resistance between conducting polymer and carbon material is relatively high because of their unsatisfactory bonding, which gives a low charge-transfer kinetics. Therefore, carbon/conducting polymer CEs do not fulfill their excellent function in enhancing conversion efficiency of DSSCs. To the best of our knowledge, power conversion efficiency of ~7% has been obtained from the DSSCs using carbon/conducting polymer CEs, not to mention highly efficient DSSCs from carbon/conducting polymer multilayer CEs.

Herein, we present a facile layer-by-layer (LbL) self-assembly process to generate (graphene oxide/polyaniline)_n [(GO/PANI)_n] conducting multilayer CEs with good electrochemical properties for applications in DSSCs. LbL self-assembly is a simple and cost-effective process with alternating deposition using complementary

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functionality, which engendered tremendous interfaces and highly ordered architectures [19]. GO is known as a partially oxidized two-dimensional graphite layer, which is honored by high electrical conductivity and good stability, but poor electrocatalytic activity toward electrolytes. However, PANi, a typical conducting polymer, is characterized by an excellent redox behavior and easy synthesis, whereas the electron-conduction ability is relatively low in comparison with that of carbon materials. The combination of positively charged PANi with negatively charged GO by a self-assembly technique is expected to give a high electron-conduction, increased interfacial area, and good charge-transfer ability. The resultant (GO/PANi)_n conducting multilayer CEs can be controlled over the thickness, morphology and chemical components. This work indicates that the LBL assembly structures can facilitate the electrocatalytic and conducting activities, and the (GO/PANi)_n conducting multilayer CEs possess their distinctive electronic properties, interesting chemical behaviors, and potential applications in DSSCs.

2. Experimental

2.1. Synthesis of positively charged PANi and negatively charged GO

The polyaniline was synthesized by a chemical method using ammonium persulfate (APS) as oxidant [20,21]. Under magnetic stirring, an aqueous solution of APS was slowly dropped into the solution comprising 1 mL of aniline monomer (molar ratio of APS to aniline monomer was 1: 1) and 1 mM of hydrochloric acid (HCl) aqueous solution. Keeping the mixture sustaining polymerized for 30 min at room temperature, the reactant was placed at 0 °C for 12 h to obtain well soluble PANi. After pump filtration, deionized water washing, and vacuum drying at 50 °C, the anhydrous PANi powders were obtained and subsequently prepared for a 0.5 M aqueous solution.

GO was prepared according to the procedures in our previous reports [22,23].

2.2. Assembly of (GO/PANi)_n ultrathin films

(GO/PANi)_n multilayer CEs were fabricated on FTO glass substrates (sheet resistance 12 Ω·cm⁻², purchased from Hartford Glass Co., USA). Prior to assembly, the substrates were first cleaned with deionized water and anhydrous ethanol. FTO substrates were immersed in a piranha solution [7/3 (v/v) of H₂SO₄/H₂O₂ at room temperature] for 1 h. To assemble CE, the pretreated FTO glass was immersed in PANi aqueous solution for 5 min, rinsed with deionized water for 1 min and dried by N₂ gas stream, then immersed in GO aqueous solution (7 ~ 10 mg·mL⁻¹) for 5 min, then rinsed again by deionized water for 1 min and dried by N₂ gas stream; After that, the substrate was further immersed in PANi solution for 5 min, then rinsed again for 1 min and dried by N₂ gas stream, thus we obtained FTO-PANi-(GO/PANi)₁ monolayer film. By repeating the previous procedures, we can obtain FTO-PANi-(GO/PANi)_n multilayer CE (*n* represents the deposition cycle).

2.3. Electrochemical characterizations

The electrochemical properties of FTO-PANi-(GO/PANi)_n multilayer CEs were characterized using a three-electrode method. The electrical behaviors were evaluated by recording the as-impedance spectroscopy on a CHI660E Electrochemical Workstation in a frequency range of 0.1 Hz ~ 1 MHz and an ac amplitude of 10 mV at room temperature in 0.5 M H₂SO₄ solution. Glassy carbon pole ($\varphi = 3$ mm) coated by PANi-(GO/PANi)_n films were employed as working electrode, Pt sheet with a size of 1 × 1 × 0.3 cm³ was

counter electrode and Ag/AgCl was reference electrode. The ohmic resistance associated with the film was determined from high-frequency intersection of the spectrum with the Z' axis, from which the conductivity can be calculated based on dimensional information. Cyclic voltammetry (CV) was also conducted on the same equipment. Before the measurement, the electrolyte was deoxygenated by nitrogen bubbling for 5 min.

2.4. Assembly of DSSCs

A layer of TiO₂ nanocrystal anode film with a thickness of 10 μm and active area of 0.09 cm² was prepared by coating the TiO₂ colloid using a screen printing technique, followed by sintering in air at 450 °C for 30 min. Subsequently, the TiO₂ film was soaked in a 0.5 mM N719 [cis-di(thiocyanato)-N,N'-bis(2,2'-bipyridyl)-4-carboxylic acid-4-tetrabutylammonium carboxylate, purchased from Dyesol LTD, Australia] ethanol solution for 24 h to uptake N719 dye for the fabrication of dye-sensitized TiO₂ photoanode. The DSSC was fabricated by sandwiching liquid electrolyte between a dye-sensitized FTO-TiO₂ photoanode and multilayer CE.

2.5. Other characterizations

Ultraviolet-visible (UV-vis) absorption spectra were recorded with a Mapada 3200 UV-Visible spectrometer. The morphology of GO was observed on a TEM (JEM2010, JEOL). The cross-sectional and top-view scanning electron microscope (SEM) images of the resultant FTO-PANi-(GO/PANi)_n CE were observed and photographed by a Zeiss Ultra plus field emission scanning electron microscope. Incident photo-to-current conversion efficiency (IPCE) curves were obtained at the short-circuit condition on an IPCE measurement systems (MS260). The light source in this case was a solar simulator (PEC-L11, AM1.5G, Peccell Technologies, Inc.); Light was focused through a monochromator onto the photovoltaic cell. The monochromator was moved in steps from 400 to 700 nm to generate the IPCE as defined in equation:

$$IPCE(\lambda) = 1240(J_{sc}/\lambda\varphi) \quad (1)$$

where λ was the wavelength, J_{sc} is the short-circuit photocurrent density (mAcm⁻²), φ was the incident radiative flux (mWcm⁻²) measured using an optical detector. In order to obtain the IPCE spectra, the anodes were sensitized by N719 dye.

3. Results and discussion

Fig. 1a shows a low-magnification TEM image of as-synthesized GO nanosheet from Hummers method, suggesting that the GO presents transparent and thin rolled feature. However, a great deal of lattice distortions and plenty of defects can be detected at high-magnification, as shown in Fig. 1b, indicating that partial conjugated structures of GO have been destroyed within oxidation process for access of functional groups, such as -COOH, -C=O, -O-. Fig. 1c shows the top-view SEM image of PANi-(GO/PANi)₁₀ CE. The GO nanosheets are adsorbed onto the former layer of PANi with a poor directionality and a rough surface. From the cross-sectional SEM photograph, as shown in Fig. 1d, one can find the CE material display a multilayer structure with an average thickness of each GO/PANi bilayer at about 8 nm. The layered structure is expected to provide enormous interfacial area for I⁻/I₃⁻ transportation and redox reactions.

Self-assembly of the multilayers has a dependence on adsorption time, as shown in Fig. 2a. The UV-vis spectra of the multilayer films display three characteristic features that can be used as a means of identification: a shoulder at ~317 nm (→ π* transitions of C=O bonds) [24,25], and two maximum bands at 440 and 900 nm

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