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Platinum/graphene hybrid film as a counter electrode for dye-sensitized solar cells

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ABSTRACT

A platinum nanoparticles/graphene nanosheets (PtNP/GN) film was prepared on rigid fluorine-doped tin oxide substrate by using a facile one step electrochemical deposition method, and the film was used as counter electrode for dye-sensitized solar cell (DSSC). The cyclic voltammetry, electrochemical impedance spectroscopy and Tafel curves measurements indicated that the PtNP/GN CE has higher conductivity and better electrocatalytic activity for I_3^-/I^- redox reaction, lower charge transfer resistance on the electrolyte/electrode interface for I_3^-/I^- redox reaction than that of Pt electrode, which is due to that the synergistic effect combined platinum nanoparticles with graphene nanosheet intrinsic characteristic. As a result, the DSSC based on the PtNP/GN counter electrode achieved a high power conversion efficiency of 7.88% under AM1.5 illumination of 100 mW cm^{-2}, which is higher 21.04% than that of the DSSC based on Pt electrode.

1. Introduction

Since the breakthrough work by Grätzel and O'Regan in 1991 [1], dye-sensitized solar cell (DSSC) has attracted considerable attention as an alternative to conventional silicon solar cells for their low cost, low energy consumption, simple fabrication process, and high power conversion efficiency [2,3]. Traditionally, a DSSC consists of TiO_2 photoanode, I^-/I_3^- electrolyte and platinum (Pt) counter electrode (CE). The photo-induced oxidation of a dye molecule on TiO_2 electrode and the oxidized dye molecule is reduced by I^- in the process. The oxidized species diffuses from the surface of the dye to the Pt CE and regenerates I^-. Pt, as the conventional catalyst for DSSC, induces an electrocatalytic activity for the iodide/triiodide redox reaction. The traditional Pt film were prepared on rigid fluorine-doped tin oxide (FTO) substrate by sputtering or thermal vapour deposition technique, which consumed a large amount of expensive Pt. Many reports have displayed several options by thermal decomposition or electrochemical reduction to replace the expensive and not transparent Pt-based sputtered layer [4–6]. The method decrease Pt loading (10–100 mg cm^{-2}) and the cost of the divice, however, the power conversion efficiency of the DSSC are also decreased [7,8].

Many carbonaceou materials including carbon black [9], activated carbon [10,11], graphite [11], carbon nanotubes [12,13] and graphene [14] have been attempted as alternative counter electrode materials. Among them, graphene maybe is the most promising potential CE material in DSSC due to its inherent features of large surface area, high optical transmittance, excellent electrical conductivity and thermal conductivity [15,16]. Choi et al., [17] prepared graphene CE by electrophoretic deposition method, the conversion efficiency of the DSSC based on the graphene CE was 5.69%. Kavan et al. [18] demonstrated that the graphene nanoplatelet surpassed Pt as the electrocatalyst in cobipyridine-mediated DSSC. Recently, Pt incorporated graphene based materials have been introduced into DSSCs. For example, Gong et al. [19] self-assembled a monolayer of graphene/Pt as counter electrode for DSSC; Tjoa et al. [20] demonstrated a facile route to synthesize graphene oxide–Pt nanoparticle hybrid by light assisted spontaneous coreduction of graphene oxide and chloroplatinic acid without reducing agent, and obtained an efficiency of 6.77%; Bajpai et al. [21] using pulsed laser deposition deposited Pt nanoparctile on micrometer-sized graphene sheets, and the DSSC fabricated based on this electrode exhibits better performance than that obtained from Pt; Guo et al. [22] prepared graphene/Pt hybrid by an one-step, microwave-assisted heating reduction.

In the present work, a novel platinum/graphene (Pt/GN) film was prepared on fluorine-doped tin oxide substrate by using a facile one step electrochemical deposition method. Based on the synergistic effect combined the excellent conductivity and high specific surface area from Pt nanoparticles with the electrocatalytic activity and facile electron transport from graphene nanosheet, it is expected that the photovoltaic performance of the DSSC based on the Pt/GN CE could be improved.

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2. Experimental

2.1. Materials

$H_2PtCl_6{\cdot}6H_2O$, hydrochloric acid (HCl), isopropanol, 4-*tert*-butyl-pyridine (TBP), acetonitrile and titanium tetrachloride ($TiCl_4$) were purchased from Shanghai Chemical Agent Ltd., China. Graphene nanosheets (UNI-ONWARD Corp., 99.9%, Taiwan). The organometallic compound sensitized dye N-719 [RuL_2 (NCS)2:2 TBA, L = 2,2-bipyridyl-4,4-dicarboxylic acid, TBA = tetrabutylammonium] was obtained from Solaronix SA (Switzerland). All reagents are of analytical reagent grade and used without further purification. FTO glass substrates (8 Ω cm^{-2}, Hartford Glass Co., USA) were cut into 2.5 cm × 1.5 cm carefully and ultrasonically cleaned sequentially in detergent, acetone and distilled water for 10 min, respectively; and then stored in isopropyl alcohol.

2.2. Preparation of the Pt/GN CE

In brief, the preparation of the Pt/GN CE using an electrodeposition method outlined below. The electrodeposition was carried out with an electrochemical analyzer system (CHI660D, Shanghai Chenhua Device Company, China). All experiments were implemented in a three-electrode cell, including a Pt foil as counter electrode, an Ag/AgCl electrode as reference electrode and FTO glasses with an exposed area of 1 cm^2 as the working electrode. The base plating solution consisted of 0.01 M of H_2PtCl_6 and 14 wt.% of HCl in 50 ml deionized water. The used weight of graphene nanosheets was set as 0 g, 0.025 g, 0.05 g, 0.075 g, 0.1 g and 0.125 g, and then added them into the base plating solution in weights ranging from 0 wt.%, 0.05 wt.%, 0.10 wt.%, 0.15 wt.%, 0.20 wt.% to 0.25 wt.%, respectively. Of the above finally obtained base plating solution was sonicated for 30 min and refluxed for 12 h. A constant current density of 10 mA cm^{-2} was served for electrodeposition. The FTO glasses covered with Pt/GN hybrid materials were put into an oven at 200 °C for 30 min, then the Pt/GN CE was obtained. For comparison, a Pt electrode was prepared without graphene under the same condition.

2.3. Fabrication of DSSC

A TiO_2 anode was prepared as described previously [23–25]. In brief, a thin TiO_2 blocking layer was deposited on the FTO substrate by immersing the FTO in the 0.15 M of $TiCl_4$ isopropanol solution for 12 h, followed by sintering at 450 °C for 30 min in air. Subsequently, the TiO_2 layer with particle size of 10–20 nm was coated onto the blocking layer by using doctor blade method, and then sintered at 450 °C for 30 min in air. The dye was loaded by immersing the TiO_2 anode in the 0.3 mM of dye N719 ethanol solution for 24 h. Thus the dye-sensitized TiO_2 anode with thickness of 6–8 μm was obtained. The DSSC was fabricated by injecting the liquid electrolyte (0.05 M of I_2, 0.1 M of LiI, 0.6 M of tetrabutylammonium iodide and 0.5 M of TBP in acetonitrile) in the aperture between the dye-sensitized TiO_2 electrode and the CE. The two electrodes were clipped together and wrapped with thermoplastic hot-melt Surlyn.

2.4. Measurements

The micromorphology of Pt/GN film was observed by using a JSM-7600F field emission scanning electron microscope (FESEM). Cyclic voltammetry measurement (CV) were conducted, in which an as-prepared CE was taken as the working electrode in a three-electrode one-compartment cell, a 4-cm^2 Pt sheet auxiliary electrode and an Pt wire reference electrode in an acetonitrile solution consisting of 10 mM LiI, 1 mM I_2, and 0.1 M $LiClO_4$. The electrochemical impedance spectroscopy (EIS) measurement was carried out with two identical electrodes, which were sealed with a thermoplastic hot-melt Surlyn leaving an exposed area of 0.64 cm^2. The electrolyte used in the device tests was also injected into the EIS symmetric cells. The EIS tests were carried out simulating open-circuit conditions at ambient atmosphere, and using an electrochemical measurement system (CHI660D, Shanghai Chenhua Device Company, China) at a constant temperature of 20 °C with AC signal amplitude of 20 mV in the frequency range from 0.1 to 10^5 Hz at 0 V DC bias in the dark. The complex nonlinear least square analyses of the Nyquist plots were made with the ZSimdemo version 3.30d. Transmittance of sample was measured using an Optizen (3100UV) spectrophotometer.

The photovoltaic testing of the DSSC was carried out by measuring photocurrent-photovoltage (*J-V*) characteristic curves under white light irradiation of a 100 mW cm^{-2} (AM1.5) from a solar simulator (XQ-500W, Shanghai Photoelectricity Device Company, China) in ambient atmosphere. The fill factor (FF) and the power conversion efficiency (η) of the DSSC was calculated according to the following equations [2]:

$$\eta\ (\%) = \frac{V_{max} \times J_{max}}{P_{in}} \times 100\% = \frac{V_{OC} \times J_{SC} \times FF}{P_{in}} \times 100\% \quad (1)$$

$$FF = \frac{V_{max} \times J_{max}}{V_{OC} \times J_{SC}} \quad (2)$$

where J_{SC} is the short-circuit current density (mA cm^{-2}); V_{OC} is the open-circuit voltage (V), P_{in} is the incident light power and J_{max} (mA cm^{-2}) and V_{max} (V) are the current density and voltage at the point of maximum power output in the *J–V* curves, respectively.

3. Results and discussion

3.1. Morphology analysis

Fig. 1 shows the morphologies of the graphene nanosheets, Pt particles and Pt/GN film. From Fig. 1a, it can be seen that the graphene nanosheets possess a lamellar structure, which provide a large specific surface area. The Pt particles shown in Fig. 1b have a diameter of 100–200 nm and are even distributed on the surface of substrate. From Fig. 1c, it can observe that the graphene nanosheets are covered on the surface of Pt particles. The EDS analysis of the Pt/GN film (presented in Fig. 1d) indicates the presence of C and Pt elements. This result further confirms the formation of Pt/GN film.

3.2. Cyclic voltammetry analysis

In order to investigate the conditions of the redox reaction of the iodide ions at the CE for DSSC, the electrolyte solution containing iodide/triiodide was used in the CV measurements. Fig. 2a shows the CVs for the Pt and Pt/GN CEs at the scan rate of 10 mV s^{-1}, in which two pairs of redox peaks can be observed for both of the CEs. The left redox peak marked with ⋆ is due to the reaction $I_3^- + 2e^- \rightarrow 3I^-$ [26,27]. This is the reaction that takes place at the CE of the DSSC and is vital for its operation. The right peaks marked with ☆ in CV corresponding to $3I^- \rightarrow I_3^- + 2e^-$ [26,27] and is insignificant in the context of DSSC. Thus the magnitude of the cathodic current density reduction peak (I_{pc2}) and cathodic potential position (V_{pc2}) at the left are directly proportional to the ability of the CE to reduce the I_3^- species. It can be clearly observed from Fig. 2a that the absolute value of I_{pc2} for the Pt/GN CE is conspicuously larger and the V_{pc2} is more positive compared to the Pt CE, indicating an improved conductivity and electrocatalytic activity for the Pt/GN CE compared to Pt electrode. Fig. 2b shows the influences of the weights of graphene nanosheets on the Pt/GN CE at the scan rate of 10 mV s^{-1}. The relationships between the various