



Graphene coated alumina-modified polypyrrole composite films as an efficient Pt-free counter electrode for dye-sensitized solar cells



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ABSTRACT

Polypyrrole (PPy) with graphene coated Al_2O_3 (GCA) composite films with different levels of graphene were fabricated via a two-step process. GCA was first prepared. A dispersed solution of monomeric pyrrole and GCA was deposited on a fluorine doped tin oxide film by one-step electrodeposition and used as an electrocatalyst on the counter electrodes (CEs) for dye-sensitized solar cells (DSSCs). The DSSCs fabricated from these CEs were characterized by the current density-voltage, incident photon-to-current conversions efficiency, cyclic voltammetry, electrochemical impedance spectroscopy, and Tafel measurements. The DSSCs containing the 3 wt.% PPy/GCA (PPy/GCA) CE exhibited an efficiency of 7.33%, whereas the DSSCs with a CE having Pt as the catalytic material showed an efficiency of 7.57%. The results show that the PPy/GCA composite film is a potential catalyst for replacing the expensive, conventional Pt in DSSCs.

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1. Introduction

The structure of a dye-sensitized solar cell (DSSC) consists of a dye-adsorbed photoanode, liquid electrolyte, and a counter electrode (CE) [1]. Comprehensive descriptions of each component can be found in a recent book edited by Kalyanasundaram [2]. As the energy conversion efficiency depends on the redox reaction at the redox electrolyte/CE interfaces, CE would play an important role in reducing the oxidized electrolyte species, and determining the conversion efficiency [3]. A thin Pt film is generally used as the catalytic layer on the CE because of its excellent electrocatalytic ability and high conductivity. The Pt is normally coated on a transparent conductive oxide glass, e.g., fluorine-doped tin oxide (FTO) or indium-doped tin oxide (ITO) for preparing the CE of a DSSC. Owing to the expense of Pt, alternative materials, such as carbon materials or conducting polymers, have been assessed in recent years as potential catalytic materials for the CEs in DSSCs.

Carbonaceous materials, in the form of single-walled carbon nanotubes (SWCNTs), multi-walled carbon nanotubes (MWCNTs), graphite, activated carbon, and graphene, have been used as potential alternative counter electrode materials on account of

their high electronic conductivity, corrosion resistance towards I_2 , high reactivity for I_2 reduction and low-cost [3–8]. Among them, graphene, which is an atomic planar sheet of hexagonally-arrayed sp^2 carbon atoms, has been demonstrated to be a promising and efficient counter electrode material for DSSCs [9,10] because of its high surface area, excellent thermal conductivity, strong mechanical strength, and good electric conductivity [11–15]. In addition, conducting polymers, such as polypyrrole (PPy) [16–22], poly(3,4-ethylenedioxythiophene)-poly(styrene sulphonate) (PEDOT:PSS) [23–25], and polyaniline (PANI) [26–28], have also been incorporated into the CEs for DSSCs. Among them, PPy has attracted considerable interest because of the simple process, mass production and low cost [29]. Jeon et al., have prepared PPy nanoparticles and utilized them to the CE of DSSCs, which achieved a remarkable efficiency of 7.73% [30]. Bu et al., have prepared stable and transparent PPy CE of bifacial DSSCs and obtained impressive power conversion efficiencies of 5.74% and 3.06% corresponding to front- and rear-side illumination, respectively [31].

Composites of carbon materials and conducting polymers have been used as the catalytic layers on the CEs of DSSCs [32–38]. In these composite films, the conducting polymer and carbon material function as the conductive support and catalyst, respectively; thus, the superior conductivity and electro-catalytic activity of such catalytic layers render high performance to the DSSCs. For instance, Gong et al., have prepared rGO@PPy and used it as the CE of DSSCs to obtain a cell efficiency of 8.14% [20].

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Chen et al., have prepared a composite film of PPy and graphene quantum-dot as the catalytic layer on the CE in DSSC, and achieved a cell efficiency of 5.27% [39]. Gao et al., synthesized nitrogen doped graphene by pyrolysis of graphene polypyrrole composites and used it as the CE of DSSCs to obtain a cell efficiency of 6.8% with high reliability and durability, which is comparable to that of Pt CE (7.0%) [40]. Previously, to prevent sheet aggregation, the inactive material, Al₂O₃, was first coated with graphene oxide (GCA) and the coated particles were then mixed with the photoanode (TiO₂), where they were heat treated [41]. In this paper, a composite film of PPy/GCA was coated on the FTO glass by electropolymerization, using an aqueous solution containing GCA particles and pyrrole monomer. The FTO glass coated with the PPy/GCA composite films were used as the CEs in a DSSC. Scanning electron microscopy and transmission electron microscopy were applied to confirm the successful incorporation of GCA in the PPy/GCA composite thin film. The electro-catalytic ability of the CE with PPy/GCA was characterized by cyclic voltammetry (CV), electrochemical impedance spectroscopy (EIS), and Tafel plots. The PPy/GCA CE shows an efficiency of 7.33%, which is 13% higher than the pristine PPy (6.48%) CE and comparable to that based on noble metal Pt (7.57%) CE highlighting the potential in low cost and efficient DSSC. Moreover, the DSSCs employing PPy/GCA as CE exhibit better long-term stability than the case using pristine PPy and Pt as CEs.

2. Experimental

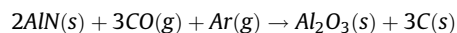
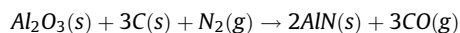
2.1. Materials

Perchloric acid (HClO₄, 70%) and sodium dodecyl sulfate (>99%) were purchased from Sigma–Aldrich, and carbon (HIBLACK30) was obtained from Orion Engineered Carbons. α-Al₂O₃ (AM-21, 99.7%) was acquired from Sumitomo Chemical Co. Pyrrole monomer was supplied by TCI Co. LTD., and distilled prior to use. All reagents used were of reagent grade.

2.2. Preparation of counter electrodes

Among the other conducting polymers available, PPy and its derivatives have attracted particular interest, because of their high conductivity and stability. The ease of synthetic procedures and the availability of the initial monomer are also attractive features of PPy.

The GCA nanoparticles were synthesized according to the following reactions:



Firstly, AlN powder was prepared by calcining a mixture of alumina and carbon at 1300 °C for 5 h under a flow of nitrogen [42]. As prepared AlN powder was placed in an alumina crucible. Then the crucible was placed in an alumina tube and heated to 1400 °C at 5 °C min⁻¹ in a gas mixture containing argon and 10 vol. % CO at a flow rate of 200 ml min⁻¹. Thus the graphene-coated Al₂O₃ particles could be synthesized by calcining the AlN powder at 1400 °C for 20 h under a flow of 10 vol.% CO/Ar [43].

Electrochemical polymerization of PPy onto fluorine doped tin oxide (FTO) glass was carried out in deionized (DI) water (50 mL) containing 4 drops of perchloric acid (HClO₄), 0.1 M pyrrole monomer using a potentiostatic method by applying a potential of 0.6 V for 45 sec. In the case of PPy/GCA CEs, the above-prepared GCA with various loadings with respect to pyrrole monomer (0.1 M), such as 1.5 wt.%, 3.0 wt.%, 4.5 wt.%, and 6.0 wt.%, were dispersed. The 3 wt.% composite gave the best photovoltaic

performance (Table S1). Therefore, this ratio was selected for further experiments. The solution was stirred for 3 h in an ice bath and then purged with nitrogen. Prior to film deposition, the composite solution was sonicated for 5 min to achieve a good dispersion of GCA. A three-electrode system was used with FTO glass as the working electrode, Pt sheet as the counter electrode and Ag/AgCl as the reference electrode for electrochemical polymerization. After polymerization, the films were rinsed with distilled water, followed by ethanol and dried in a vacuum for 12 h. The resulting CEs were used in the DSSCs. Pt CE was prepared by the thermal reduction of a thin film formed from 7 mM of H₂PtCl₆ in propanol at 450 °C for 30 min.

2.3. Preparation of the TiO₂ photoanode and the fabrication of dye-sensitized solar cell

FTO glass was cleaned by sequential sonication in methanol, distilled water and acetone. A thin first layer of TiO₂ was deposited using the doctor-blade technique. The film was dried at 70 °C for 30 min, followed by heating to 450 °C for 30 min. Subsequently, a second layer of 200 nm-sized light scattering anatase particles was coated on the top of the first layer, which was followed by heating to 450 °C for 30 min. The electrodes were treated in a 40 mM TiCl₄ solution at 70 °C for 30 min, and rinsed in distilled water, followed by ethanol, and heated at 450 °C for 30 min. The TiO₂ electrodes were immersed in a 0.3 mM solution of N719 in ethanol at room temperature for 24 h. The electrodes were then removed and rinsed with acetonitrile immediately before cell fabrication. The cells were fabricated by sandwiching the sensitized TiO₂ photoanodes and counter electrodes together with a hot-melt polymer (Surlyn, 60 μm). The electrolyte contained 0.05 M I₂, 0.2 M LiI, 0.7 M 3-propyl-1-methyl imidazoliumiodide and 0.5 M *t*-butylpyridine in acetonitrile.

2.4. Characterization and measurement

The morphology and structure of the materials were investigated by transmission electron microscopy (TEM, FEI Tecnai F20) and field emission scanning microscopy (FESEM, Hitachi S-4800). The photocurrent-voltage measurements were performed using a Keithley model 2400 Source Meter and a Newport 91192 solar simulator system (equipped with a 1 kW xenon arc lamp, Oriel). The light intensity was adjusted to 1 sun (100 mW cm⁻²) with a Radiant Power Energy Meter (model 70260, Oriel). The incident photon-to-current conversion efficiency (IPCE) results were acquired using an IPCE G1218a (PV Measurement). This system applies the monochromatic light from a 75 W xenon arc lamp (Ushio UXL-75XE) filtered by a dual-grating monochromator and individual filters onto the test devices. An ellipsoidal reflector collects the light from the lamp and focuses it on the monochromatic entrance slit via a mechanical chopper to create a small modulated signal. While the modulated, monochromatic light is applied to the test devices, a continuous bias light (ca. 1 sun) is also applied. The electrochemical behavior of the samples was examined by cyclic voltammetry (CV) using three-electrode cells with Ag/AgCl and a platinum sheet as the reference and counter electrodes, respectively. The electrolyte was 0.1 M LiClO₄, 0.001 M I₂ and 0.01 M LI in an acetonitrile solution. Electrochemical impedance spectroscopy (EIS) was performed using a computer-controlled Ivium IviumStat and the impedance spectra were interpreted using a nonlinear least-square fitting procedure obtained using commercial software (ZView 2, Scribner Associates Inc.). The Tafel polarization curves were recorded on the same workstation by assembling a symmetric cell. The curves were recorded by scanning the potential window of -0.5 to 0.5 V at a scan rate of 10 mV s⁻¹.

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