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Electrocatalytic porous nanocomposite of graphite nanoplatelets anchored with exfoliated activated carbon filler as counter electrode for dye sensitized solar cells

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ABSTRACT

A unique graphite nanoplatelet (GnP) composite synthesized with a synchronized distribution of exfoliated activated carbon (AC) filler is proposed for promising Pt-free dye sensitized solar cells. The defect rich morphology of the exfoliated activated carbon filler is designed with graphite nanoplatelets to enhance its electrocatalytic activity and electron pathways, and for this purpose different percentages of AC fillers were incorporated into the GnP matrix. The proposed GnP/AC composite shows a more defect-rich morphology synchronized with high electronic conductivity which greatly enhances the electrocatalytic activity and electron transfer mobility (R_{CT} of 2.19 Ω). A DSSC fabricated with the proposed GnP/AC composite exhibited a high conversion efficiency rate of 8.478%, similar to that of the Pt electrocatalyst. The high catalytic activity of GnP/AC is attributed to the synergistic effect of the high electron affinity of GnP and the structural distortion caused by the AC filler material. This high-performance catalyst can be a promising material for efficient energy storage and harvesting applications.

1. Introduction

Dye-sensitized solar cells (DSSCs) are among the most promising energy-conversion devices capable of addressing the ever-increasing challenges related to energy harvesting due to their high efficiency and robustness (O'regan and Grätzel, 1991; Grätzel, 2001, 2004). AC has been investigated as a promising filler material for carbon composite structures for cathode materials for DSSCs (Arbab et al., 2016a,b; Memon et al., 2017). Activated carbon has a high surface area and maintains a multi-edge defect-rich porous morphology to endure the generation of active sites for charge storage and electrochemical reactions (Wang et al., 2015; Saha et al., 2014). AC is perhaps the most explored class of porous carbons, and it have been traditionally employed as a replacement for the Pt catalyst (Yoon et al., 2013). Moreover, AC and Pt have similar electron affinities and band-gap energies (Arbab et al., 2016b). AC has much higher ion diffusion than that of the Pt catalyst (Gong et al., 2009; Arbab et al., 2015). Furthermore, the high porosity and surface area of activated carbon are likely higher than those Pt and other types of carbon used as cathodes (Lee et al., 2008). However, due to the more defect-rich morphology and the poor chemical stability of activated carbon, the injection of tri-iodide ions from the electrolyte to the cathode can be blocked (Lee et al., 2012). Such defect-rich aggregates are detrimental to the performance of carbon-based DSSCs because they fill the electron pathways of activated carbon and reduce the electrolyte/cathode interference mechanism. Therefore, they can be effective filler materials for use in carbon composite structures.

Various strategies have been devised to fabricated different types of composite structures with activated carbon fillers so as to enhance the catalytic characteristics of the carbon matrix. To date, activated charcoal has been exfoliated and used as a filler material for various composite structures. Examples include titania (Li et al., 2010), zinc oxide (Xin et al., 2011) and metal oxide materials (Liao et al., 2013; Salunkhe et al., 2015; Zheng et al., 2014) created by various techniques, such as

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sol-gel synthesis, hydrothermal/solvothermal chemical deposition, ultra-sonication and electrochemical deposition. The photovoltaic performance rates of these types of composite cathodes range from 5 to 7% (Joshi et al., 2009; Yen et al., 2011; Lin et al., 2011). The rationale for different types of composites along with activated carbon as a filler material has brought considerable change to the electrocatalytic properties of cathodes and subsequently the photovoltaic performance capabilities of DSSCs. A matrix of thin forms of graphite nanostructures such as GnP can provide a direct conduction pathway for the rapid collection of tri-iodide ions at the collector cathode. The induction of GnP fills the porous channels of activated carbon and can enhance electronic stability and ion diffusion capacity of composite structures (Sahito et al., 2017). GnP, a thin form of graphite, has recently received widespread attention due to its electronic conductivity and morphology (Sahito et al., 2016). The thickness of GnP close to that of graphene is suitable for the development of functional and structural nanocomposites. Therefore, a new form of carbon electrocatalyst synchronized with GnP and activated must be developed to fulfil the need for optimized surface area and fast electron transport outcomes.

In this paper, we report the fabrication of a GnP matrix/AC filler composite structure for promising Pt-free DSSCs. The synthesis technique involves the functionalization of a graphite material to incorporate the effective oxygen moieties required for the reduction reaction followed by the addition of activated charcoal processed by ultra-sonication and an acidic dispersion method. The sonication technology shakes the GnP dimensions and fills the gaps of the charcoal vacancies. In this way, a high surface area with high electronic conductivity can be achieved. The proposed system of carbon cathode materials showed higher electrocatalytic activity and rapid electronic transport with very low charge transfer resistance values ($R_{CT} = 2.19\,\Omega$). The photovoltaic performance of the proposed system of the GnP/AC composite is 8.478%. This unique combination of defect-rich AC with the fine dimensions of GnP can provide new approaches towards the fabrication of functionalized carbon composites for DSSCs. Different morphologies of composites were fabricated by altering the percentage of the AC filler. AC filler in amounts of 0–120% was incorporated into the GnP composite cathode material, and the electrochemical behavior and photovoltaic performance outcomes were investigated. Comparative studies with a Pt electrode were also done to ascertain the performance capabilities of the GnP/AC composite.

2. Experimental details

2.1. Materials

Activated carbon powder (charcoal with a 100 mesh size, Sigma Aldrich Co.) was selected for the formation of the conductive matrix. GnP powder (carbon content > 99.5, C-300, 300 m^2/g, xGnP Co.) was selected as the conductive network. Nitric acid (60%, Matsunoen Chemicals) was used for the oxidative functionalization of the carbon content. For the formation of the carbon paste, polymer carboxymethyl cellulose (a sodium salt of MW 250,000 g, Sigma Aldrich Co.) was used as a binding agent. Conductive transparent glass (FTO TEC 8, Pilkington Co.) substrates were used. The dye sensitizer purified N719, cis-diisothiocyanato-bis (2,2′-bipyridyl 4,4′dicarboxylato) ruthenium (II) bis (tetra butyl ammonium), D719, was purchased from Everlight Co. TiO_2 (P25 by Degussa Co.), 20 nm in size, and titania nanotubes (TNT, self-synthesized (Qadir et al., 2015, 2016; Sun et al., 2014) were used as photoanodes. The ionomer surlyn, 60 µm thick, was purchased from Solaronix. Other laboratory grade reagents were purchased from Sigma Aldrich Co.

2.2. Route for the synthesis of activated-carbon-decorated graphite nanoplatelet composite cathode materials

Fig. 1 shows a schematic illustration of the fabrication process of the activated-carbon-filled graphite nanoplatelet (GnP/AC) composite materials used for the DSSCs. The composite fabrication process involves sonication and acidic dispersion combined with a high-speed shear mixing technique, where 1 g of GNPs are initially functionalized with 100 mL of nitric acid for two hours. Additionally, activated charcoal is added to the nitric acid/GNP slurry and subjected to high-speed shear sonication so as to exfoliate the activated carbon filler material. The high-shear sonication process for a prolonged time caused the fragmentation of the activated carbon fillers, assisting with the intercalation of exfoliated fillers in the GnP network. GnP nano-composites with different weight percentages of the filler varying from 0 to 120% were prepared. This slurry was washed in pure H_2O while shacked and filtrated to neutralize the pH. The composite cake obtained by vacuum filtration was transformed into a paste by grinding in a ceramic mortar with 15 mL of CMC as a binder (1 wt% in H_2O). The resulting paste was held at a standard temperature and pressure for one day. Square FTO glass samples ($1.5 \times 1.5\,cm^2$) were used as counter-electrode substrates. The prepared paste was coated onto these substrates by a bar coating method using 3 M Magic tape, followed by drying under warm air at 50 °C. The prepared counter electrodes were dried for 30 min in a 60 °C air-circulating oven. The resultant counter electrodes were prepared as 0%, 30%, 60% and 120% GnP/AC composites. As a reference material, Pt-coated FTO glass samples were also prepared. Pt counter electrodes were prepared by drop-casting a 10 mM H_2PtCl_6 solution (in isopropyl alcohol) onto single-hole FTO glass while annealing at 400 °C for 20 min in a hot air blower.

2.3. DSSC fabrication

For the fabrication of the DSSCs, first, the photoanodes were fabricated. The $15 \times 15\,mm^2$ dimension square cut FTO glass samples were cleaned with acetone, water and ethanol in that order. The cleaned and $TiCl_4$-treated FTO glass samples were then coated with a double layer (12 µm) of titania nanotubes. The designed TNT overlayer is described in our previous works (Qadir et al., 2015, 2016; Sun et al., 2014). The dye-covered photoanodes ($4 \times 5\,mm^2$) were washed to remove any unfixed dye using ethanol and then dried under flowing nitrogen. The photoanodes and counter electrodes were sandwiched together with an ionomer spacer by hot-pressing at 80 °C for 20 s. After pressing, the electrolyte solution was injected into the cells from the holed counter electrode by means of the capillary vacuum effect. The cells were then sealed by an ionomer cover. For the fabrication of quasi-solid-state DSSCs, a high-density polymeric electrolyte was prepared. For the preparation of the polymeric gel electrolyte, 0.6 M 1-butyl-3-methyl-imidazolium iodide (BMII), 0.05 M iodine (I_2), 0.1 M lithium perchlorate (LiI), 0.1 M guanidine thiocyanate (GuNCS), 0.5 M 4-*tert*-butyl pyridine (TBP) and 3 wt% of polyethylene oxide polymer (Mw 30,000) were mixed in an acetonitrile solution.

2.4. Characterization

In order to assess the surface morphology, field-emission scanning electron microscopy (FE-SEM, JEOL JSM-6700F) at an accelerating voltage of 15 kV was utilized. Coating with was also conducted on the carbon samples to obtain clear images. Furthermore, the GnP and AC composition was confirmed by an X-ray photon spectroscopy (XPS) analysis using the Multi-Lab ESCA 2000 system VG from Thermo Scientific, USA. For XPS, monochromatized Al Kα radiation with an energy step size of 0.05 eV was used. The crystalline structure of the proposed GnP/AC nanocomposite was investigated with wide-angle X-ray diffraction (WAXD) using a Rigaku Denki X-ray generator (Rigaku, D/Max-2500) equipped with CuKα radiation ($\lambda = 1.54181$ A) at 40 kV and 60 mA. WAXD data were collected with a step interval of 0.02° and at a measuring speed of $5^\circ\,min^{-1}$ in the 2 theta range of 10° to 80°. The porous and defect-rich morphology of the proposed nanocomposite was investigated using Raman spectrometry (Jasco NRS-3100) with an