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Optimized reduction of graphite oxide for highly exfoliated silver nanoparticles anchored graphene sheets for dye sensitized solar cell applications

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ABSTRACT

In the present work, we have synthesized graphene sheets by optimizing reduction of graphite oxide (GO) by hydrazine hydrate ($N_2H_4 \cdot xH_2O$) reducing agent and anchored them with silver nanoparticles (Ag NPs). Morphological and spectroscopic studies confirmed the formation of highly exfoliated graphene sheets separated by Ag NPs with improved C/O ratio. The highly electrocatalytic and exfoliated network of graphene sheets/Ag nanocoatings uniformly adhered to FTO substrate has been utilized as platinum (Pt) free counter electrode (CE) in dye sensitized solar cells (DSSC). Fabricated DSSC with only 2.7 μm thick TiO_2 photoanode exhibited photo conversion efficiency ($\eta = 3.44\%$) and short circuit current density ($J_{sc} = 7.03$ mA cm^{-2}) comparable to DSSC containing Pt-CE without any loss of open circuit voltage ($V_{oc} = 0.71$ V) and fill factor (FF = 0.68).

1. Introduction

Among dye sensitized solar cell (DSSC), counter electrode (CE) plays an important role in collection of electrons and reduction of I_3 to I for regeneration of sensitizer after injection of electrons into photoanode. Materials with high conductivity and excellent catalytic activity towards redox electrolyte are pre-requisite for a good CE [1,2]. Irrespective of the high cost, platinum (Pt) based metallic structures loaded on fluorine doped tin oxide (FTO) conducting glass are mostly used as CE, owing to their good conducting and excellent electrochemical activity [3]. The high cost and slow dissolution of Pt in corrosive I/I_3 redox electrolyte lead to exploration of less expensive alternate CE materials like metals [4,5], transition metal sulfides [6,7], conducting polymers [8,9] and carbonaceous materials [10,11]. Carbon based materials including carbon black [12], mesoporous carbon [13], nanocarbon [14,15] and carbon nanotubes [16] have shown appreciable results as CE, although their large amount is needed to maintain comparable efficient DSSC.

Further, graphene a 2D monolayer of sp^2 hybridized carbon atoms, has been explored in DSSC as a conductive transparent photoanode [17] and counter electrode [18] owing to its large surface area, flexibility, high electron mobility, excellent conductivity and high electrochemical stability under prolonged potential cycling [19,20].

Although, graphene has an excellent conductivity and large surface area, but possess limited number of electrocatalytic active sites for the reduction of I_3 that results in sluggish reaction rate. Also, graphene sheet tends to easily aggregate due to strong π-π interaction and hence, reduces the efficiency of DSSC [21].

Here, defect rich graphene has emerged as a suitable candidate for non Pt CE, as the concentration of defects and oxygen containing functional group in graphene significantly affect its electrocatalytic properties [22,23]. Further, higher concentration of defects affects the delocalization of π-electron in graphene and hence reduces its electrical conductivity [24,25]. Thus, there is a need of maintaining appropriate balance between the electrical conductivity and electrocatalytic properties of graphene.

Further, novel graphene composites with metal nanoparticles

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possessing high conductivity and excellent catalytic activity have been proposed [26–28]. The metal nanoparticles with comparatively smaller size and large active area act as nano spacer which not only render superior electrocatalytic activity, but also prevent restacking of graphene layers. Whereas, the presence of abundant grain boundaries and defects between nanoparticles lower their electrical conductivity. The formation of metal nanoparticles/graphene composites overcome the limitations of individual materials and facilitate in maintaining the desired properties of both [29,30]. This has been demonstrated in a range of applications demanding high catalytic activity like, lithium-ion batteries [31–33], fuel cells [34,35], super capacitors [36,37], surface enhanced Raman scattering (SERS) [34] apart from dye sensitized solar cells (DSSC) [38–41].

Pt nanoparticles/graphene composites with comparably lower amount of Pt have been widely studied to open up the possibility of developing economical DSSC with same level of efficiency as with Pt [39,40]. Further to produce completely Pt free DSSC, Ag NPs/graphene composite has been explored as CE and it showed improved performance due to their excellent electrocatalytic and high stability [26,42].

Keeping these observations in consideration, a strategy has been proposed and demonstrated to develop economical DSSC, by utilizing metal nanocoatings on graphene sheets as CE. Here, in this paper, nanocoatings of silver nanoparticles (Ag NPs) on graphene sheets (graphene/Ag NPs) possessing uniform and densely populated growth of Ag NPs on individual graphene sheets have been synthesized by optimized chemical route. The usual chemical route employed for preparing graphene involves the use of hydrazine hydrate ($N_2H_4 \cdot xH_2O$) as reducing agent. However, the amount of $N_2H_4 \cdot xH_2O$ plays a crucial role as its higher amount may be counter-productive, leading to restacking of graphene sheets along with nitrogen doping. Thus, the optimization of $N_2H_4 \cdot xH_2O$ for preparing graphene is of paramount importance for growth of Ag NPs on graphene sheets.

Here, we reported the preparation of Ag NPs coatings on graphene sheets by reduction of graphite oxide (GO) with optimized concentration of $N_2H_4 \cdot xH_2O$ and its application as CE in DSSC. To best of our knowledge, present paper is the first paper on the optimization of $N_2H_4 \cdot xH_2O$ for anchoring of Ag NPs on graphene sheets to produce non-Pt DSSC with comparatively thinner TiO_2 photoanode of 2.7 μm.

2. Experimental

2.1. Materials

Graphite flakes (~100 mesh, 99.95%), potassium permanganate ($KMnO_4$, 99%), sodium nitrate ($NaNO_3$, 99%), sulfuric acid (H_2SO_4, 98%), hydrogen peroxide (H_2O_2, 30%), hydrazine hydrate ($N_2H_4 \cdot xH_2O$, 82%)), silver nitrate ($AgNO_3$), sodium borohydride ($NaBH_4$), cetyl trimethylammonium bromide (CTAB), transparent conducting fluorine doped tin oxide (FTO) substrates, titanium tetrachloride ($TiCl_4$), lithium iodide (LiI), lithium perchlorate ($LiClO_4$), iodine (I_2) and di-tetrabutylammoniumcis-bis(isothiocyanato)bis(2,2-8bipyridyl-4,4dicarboxylato) ruthenium (II) (N719) dye were procured from Sigma Aldrich. Titanium dioxide paste (TiO_2), platinum paste and electrolyte containing I_3/I as redox couple in 3-methoxypropionitrile (EL-HSE) were procured from Dyesol, Australia.

2.2. Synthesis of graphene and graphene/silver nanoparticle composite

Graphite oxide (GO) was prepared by using Hummer's method [43]. Here, 4 g of graphite flakes, 2 g of $NaNO_3$ and 12 g of $KMnO_4$ were added in 100 ml of concentrated H_2SO_4 and stirred continuously for 2 h in an ice bath. After removing the ice bath, DI water was added to above solution to maintain it at 98 °C, followed by addition of H_2O_2 to remove impurities. Further it was washed and filtered with warm water until its pH becomes 7 and centrifuged at 5500 rpm for 20 min. The residue was GO, which was then heated in oven at 80 °C for 24 h to obtain it in the powder form. The 20 mg of GO powder was added to 50 ml of DI water and subjected to sonication for 15 min until the formation of a clear solution which was further reduced with reducing agent hydrazine hydrate ($N_2H_4 \cdot xH_2O$). To optimize the reduction of GO, different amount of $N_2H_4 \cdot xH_2O$ ranging from 0.5 μl (0.2 mM) to 3.0 μl (1.2 mM) in steps of 0.5 μl have been added to above prepared GO solution separately and heated in oil bath at 100 °C under a water cooled condenser for 24 h. The product was dried at 80 °C for 12 h and the resulting samples were named as G_X; X = 1 to 6.

Silver nanoparticles (Ag NPs) were prepared by making a solution of 1.0 mM aq. $AgNO_3$ (5.0 ml) and 0.2 g of CTAB surfactant, which was added drop by drop to 20 ml aq. $NaBH_4$ solution (2 mM) while stirring for 1 h. To the resulting solution, 50 ml of chloroform in conjunction with 0.1 g of NaCl was added and obtained organosol was separated with separating funnel and dried at room temperature to obtain Ag NPs [44]. Further, to prepare nanocoatings of Ag NPs on graphene, different amount of Ag NPs (1.0, 2.0 and 3.0 mg) and 10 mg of G_4 were added in 50 ml of DMF separately and heated at 100 °C under continuous magnetic stirring for 20 h. Finally, G_4/Ag nanocoatings with different amount of Ag NPs were collected by centrifugation and further washed with distilled water to remove the unbounded Ag NPs and dried under a continuous air flow. Here, these samples have been named as G_4/Ag1, G_4/Ag2 and G_4/Ag3.

2.3. Fabrication of CEs and assembly of DSSC

The FTO substrates firstly were cleaned with detergent solution, isopropyl alcohol and DI water using ultra-sonication for 15 min. Here, 2.0 mg of prepared samples were added in 5 ml of ethanol separately and ultra-sonicated for 1 h to form a well dispersed solution. For preparing nearly 2.0 μm thick counter electrode, the as-prepared solution was drop casted on the FTO substrates using a micro pipette and dried at 100 °C for 2 h in a vacuum oven. The adhesion of these samples on FTO was further improved by annealing at 300 °C for 30 min. In order to avoid the back recombination through the direct contact of electrolyte with the FTO, a blocking layer was introduced between FTO and mesoporous TiO_2 layer by dipping FTO in aqueous solution of $TiCl_4$ (40 mM) for 30 min in an oil bath at 70 °C followed by annealing at 450 °C. Further, 2.7 μm thick transparent film of TiO_2 paste was spread on the compact film using doctor blading method and allowed to dry at room temperature, tailed by annealing at 450 °C. These electrodes were dipped in 0.3 mM solution of N719 dye in ethanol for 24 h. The CEs of different samples (Pt, G_X and G_4/Ag nanocoatings) and a dye sensitized porous TiO_2 thin film based photoanode (area $0.6 \times 0.6\ cm^2$) was assembled together and redox I_3/I electrolyte was poured between them to prepare DSSC.

2.4. Characterization

Fourier transform infrared spectroscopy (FTIR) analysis of samples was carried out on Perkin Elemer (Frontier C92035) spectrometer. Morphological analysis of the samples was studied using Carl Zeiss (Supra 55) Field emission scanning electron microscope (FESEM) and JEOL (JEM-2100) high resolution transmission electron microscope (HRTEM). Raman spectroscopy was performed with Renishaw (In-Via Reflex) micro-Raman