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Flexible and conductive cotton fabric counter electrode coated with graphene nanosheets for high efficiency dye sensitized solar cell

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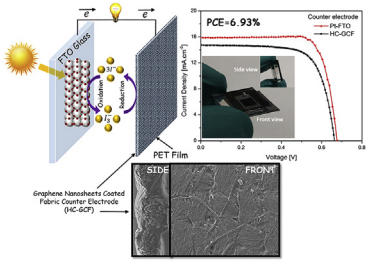
HIGHLIGHTS

- A unique graphene coated-fabric counter electrode is prepared for DSSCs.
- It shows very low surface resistance of only 7 Ω sq^{-1} with excellent flexibility.
- It shows a very low charge transfer resistance of only 1.2 Ω.
- This fabric counter electrode gives a photovoltaic conversion efficiency of 6.93%.

GRAPHICAL ABSTRACT



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ABSTRACT

Textile fabric based electrodes due to their lightweight, flexibility and cost effectiveness, coupled with the ease of fabrication are recently given a huge attention as wearable energy sources. The current dye sensitized solar cells (DSSCs) are based on Platinized-Fluorinated Tin oxide (Pt-FTO) glass electrode, which is not only expensive, but also rigid and heavyweight. In this work, a highly conductive-graphene coated cotton fabric (HC-GCF) is fabricated with a surface resistance of only 7 Ω sq^{-1}. HC-GCF is used as an efficient counter electrode (CE) in DSSC and the results are examined using photovoltaic and electrochemical analysis. HC-GCF counter electrode shows a negligible change of resistance to bending at various bending positions and is also found extremely resistant to electrolyte solution and washing with water. Cyclic voltammogram, Nyquist and the Tafel plots suggest an excellent electro catalytic activity (ECA) for the reduction of tri-iodide (I_3^-) ions. Symmetrical cells prepared using HC-GCF, indicate a very low charge transfer resistance (R_{CT}) of only 1.2 Ω, which is nearly same to that of the Pt with 1.04 Ω. Furthermore, a high photovoltaic conversion efficiency (PCE) of 6.93% is achieved using HC-GCF counter electrode using polymer electrolyte.

1. Introduction

Dye sensitized solar cells (DSSCs) have attained astonishing interest since the last ten years, based on the extremely important energy crises, to shift towards renewable energy sources [1–3]. However, expensive and rare Platinum (Pt) metal, used at the counter electrode (CE) in a typical DSSCs, limits its practical application. Moreover, lack of flexibility, limited availability of the Fluorinated Tin oxide (FTO) glass, used in DSSC and its high cost makes it the most expensive part used in DSSC [4]. Therefore, it is

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extremely important to discover unique materials, which are truly capable of replacing Pt in terms of electro conductivity and electro catalytic activity (ECA) towards the reduction of tri-iodide (I_3^-) ions and on the other hand are also flexible, organic and cost effective.

Recently, a momentous focus is shifted towards the use of Pt-free materials and their composites, in quest of exploring their unique properties to be used at the counter electrode in a DSSC [5,6]. Researchers have used conducting polymers [7–9], carbon materials [10–14] and transition metals based inorganic materials [15,16], Pt-free or low-Pt alloys have also received a growing interest as counter electrode materials in DSSCs, and efficiencies of more than 8% have been achieved using them [17–21]. Yet, the carbon nanotubes (CNT) proved to be most successful and have also given more than 10% efficiencies by using different techniques such as their enzymatic dispersion [22], however commercially available CNT and the metals used in alloys are expensive. Moreover, to replace the FTO glass and to prepare a flexible electrode for DSSC, polyethylene naphthalate (PEN) or polyethylene terephthalate (PET), coated with a very thin layer of Indium Tin oxide (ITO), have also been used [23]; however, not only their conductive coating is sensitive to bending, but also these conductive transparent sheets are not cost effective. Therefore, unique and novel structured electro conductive textiles (e-textiles), with a range of fabrication techniques have gained a lot of attention very recently. Commonly used textiles including, nylon [24], polyester [25], and cotton [26,27], have found their use as flexible and cost effective substrates for the preparation of conductive fabrics, by use of carbon materials and conducting polymers. Amongst these, biodegradable nature of the cotton favors its use in future compared to other fibers. On the other hand, amongst the carbon materials, the two-dimensional graphene with an extremely high electrical conductivity has revolutionized the research recently [28] coupled with the production of graphene in large quantities.

Here in, we present a novel and unique, highly conductive-graphene coated cotton fabric (HC-GCF) as CE for DSSC. Previously, we have shown to increase the adsorption of graphene oxide nanosheets (GONs) on the cotton fabric by cationizing it [29]. Briefly, both the cotton fabric and GONs carry negative surface charge, therefore, the coating may not be as even and longer lasting as required. Yet through a simple and well-known process of cationization, the surface charge of the cotton fabric was altered, which resulted in self-assembly of GONs on its surface, giving higher amount of loading of GONs and consequently a high electrical conductivity was achieved. This novel and flexible CE is not only cheaper compared to Pt, but also it does not require any high temperature treatment, which is required in the case for activation of Pt. This electrode can be easily prepared in bulk using a simple, dip and dry technique followed by chemical reduction. Therefore, we believe, that HC-GCF electrode will be considered as a strong candidate to replace Pt in future for the further development of low cost, flexible and efficient cells.

2. Experimental

2.1. Materials

Graphite powder was kindly provided by Asbury Carbons (USA) (particles size < 100 μm). Sulfuric acid (H_2SO_4), potassium permanganate ($KMnO_4$), hydrogen peroxide (H_2O_2), hydrochloric acid (HCL), hydrazine monohydrate (N_2H_4), Bovine Serum Albumin (BSA) and nitric acid (HNO_3) were purchased from Sigma-Aldrich (USA). FTO glass (TEC 8, Pilkington Co.), N719 (*cis*-diisothiocyanato-bis(2,20-bipyridyl-4,40-dicarboxylato) ruthenium(II) bis(tetrabutylammonium), Solaronix), chloroplatinic acid hexahydrate (Sigma-Aldrich Co.), Surlyn as spacer (60 μm, Dupont Co.) and Polyethylene oxide (PEO) were used as received, 1-Butyl-3-methylimidazoliumiodide (BMII), iodine (I_2), Lithiumiodine (LiI), 4-*tert*-butylpyridine (TBP) and anhydrous acetonitrile were purchased for the composition of electrolytes by Aldrich Co. For reproducibility, standard cotton fabric (SCF), ISO 105/F, was purchased from Korean Apparel Testing and Research Institute (KATRI). Briefly, it was 100% cotton, weight of the fabric was 115 g m^{-2} with warp 35/cm and weft 31/cm.

2.2. Synthesis of graphene oxide nanosheets

Graphene oxide nanosheets (GONs) were synthesized from graphite powder by the modified Hummer's method [30,31]. Briefly, 5 g of graphite powder was added to 200 mL of concentrated H_2SO_4 in an ice bath with continuous stirring for 30 min. $KMnO_4$ (25 g) was added slowly at temperature no higher than 10 °C. Afterwards, the mixture was allowed to react at 35 °C for 4 h with vigorous stirring. To stop the reaction, the temperature was dropped to 10 °C, with the use of ice, and 250 mL of DI water was added slowly. Later, 5 mL of H_2O_2 (30%) was added and then, the mixture was stirred for 30 more min. Then, this mixture was kept for 2 h followed by rinsing the supernatant, with 10% HCl and then DI water. At that time, 250 mL of water was added to the resulting product to form dispersion and sonicated for 30 min. Un-exfoliated GO was removed by centrifugation for 5 min at 10,000 rpm and to obtain an inorganic salts free GONs, dialysis of the solution was realized for two weeks.

2.3. Cationization of fabric and coating of graphene oxide nanosheets

For the adsorption of GONs onto the cotton fabric, a 1.0% solution of GONs was diluted from the stock solution and bath sonicated for 30 min. The surface charge of the fabric was modified by cationization process, which consists of padding the fabric in 0.15 g L^{-1} BSA solution for 5 min, followed by washing it and then drying at 70 °C for 30 min. After this process, the cotton fabric was cationized, having a positive surface charge. This modification was the basis for the higher attachment of GONs by weight on cotton surface, creating a self-assembly to form an even layer on the fabric. Afterwards, the fabric was soaked in GONs dispersion for 30 min at 80 °C, making it easier for GONs to attach on the surface of fabric by evaporating water in the dispersion slowly. This dip and dry cycle was repeated until there was no change in the sample weight gain.

2.4. Reduction of graphene oxide nanosheets into graphene nanosheets

Chemical reduction method is the most suitable one according to the nature the cotton fabric. The fabric was chemically reduced, using hydrazine monohydrate solution to convert coated GONs to GNs. 100 mM hydrazine monohydrate solution was heated at 90 °C and the fabric was treated in it for 25 min inside a sealed flask. After that, the fabric was washed with plentiful amount of deionized water until the pH of the washing water became neutral. The resulting GNs coated cotton fabric (GCF) was dried at 100 °C in oven for 15 min.

2.5. Preparing photo anode

To prepare the photo anode, Titania nanotubes (TNT) and TiO_2 pastes were prepared and coated on the FTO glass according to our previous work [3,32]. Holed and prewashed FTO glass (15 × 15 mm^2) was immersed in $TiCl_4$ solution (40 mM) for 30 min at 70 °C and washed with water and ethanol. After washing, the