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Hybrid TiO_2-Graphene nanoribbon photoanodes to improve the photoconversion efficiency of dye sensitized solar cells

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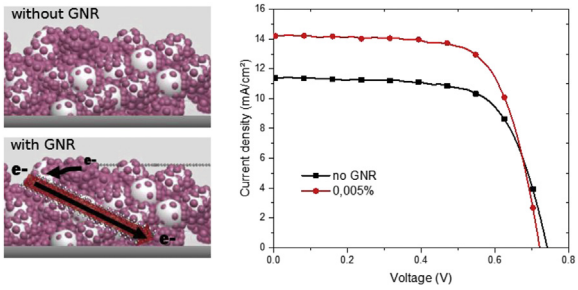
HIGHLIGHTS

- Effect of different loading of GNR in TiO_2 are analyzed for solar cells.
- Dye sensitized solar cells performance intially improved at lower GNR loading.
- At 0.005 wt % of GNR, hybrid device yields the PCE of 20% higher than bare one.
- Addition of GNR in TiO_2 enhances the dye loading and electron lifetime.
- Optimized amount of GNR in TiO_2 is much lower than the other carbon allotropes.

GRAPHICAL ABSTRACT



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ABSTRACT

We report the effect of incorporating different loadings of graphene nanoribbons (GNR) into a standard photoanode made of TiO_2 sensitized with dye molecules. The GNRs are observed to significantly improve the photoconversion efficiency (PCE) of dye-sensitized solar cells (DSSCs). The TiO_2-GNR hybrid photoanodes were prepared using the doctor-blade method. The presence of GNR in the composite photoanode was characterized by scanning electron microscopy, transmission electron microscopy and Raman spectroscopy. Our results highlight that, at an optimum loading of 0.005 wt%, GNR increases the PCE of DSSCs up to values 20% higher than the PCE of control devices. This improvement is mainly attributed to improved dye loading, enhanced electron lifetime and reduced carrier recombination, as confirmed by quantitative measurements of dye loading, transient photovoltage decay and electrochemical impedance spectroscopy results, respectively.

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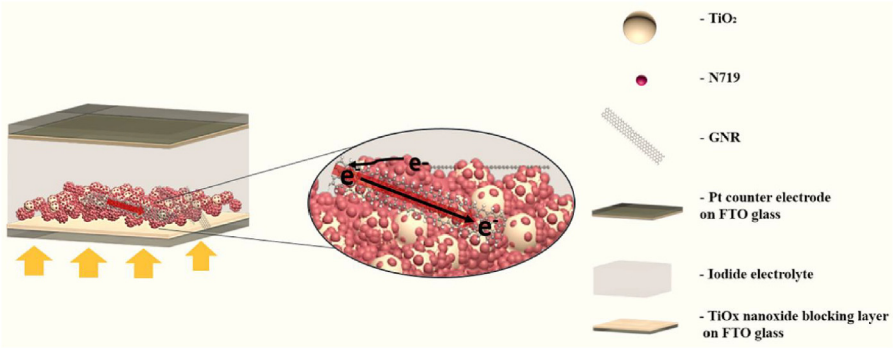

Fig. 1. Schematic of DSSCs components with TiO_2-GNR hybrid photoanodes highlighting preferred electrons transport through mesoporous film toward FTO.

1. Introduction

The energy crisis is one of the most critical challenges of modern society, due to excessive use of fossil fuels and the consequent environmental pollution and climate change [1]. Addressing this challenge requires the development of efficient, economic and eco-friendly alternative energy resources [2]. Since the pioneering work by O'Regan and Grätzel in 1991 [3], Dye Sensitized Solar Cells (DSSCs) have been widely studied and considered as a promising, low-cost, large scalable and environmentally friendly alternative to commercially available silicon solar cells [4]. A typical DSSC consists of a photoanode of a wide band gap semiconductor (typically a mesoporous film of metal oxide nanoparticles) sensitized with dye molecules, a redox couple electrolyte as a hole transport medium and a counter electrode (CE), which is usually a platinum-coated fluorine doped tin oxide (FTO) [5,6] glass as shown in Fig. 1. To date, the highest photoconversion efficiency (PCE) of liquid junction DSSCs is 14.3% [7], still lower than typical values of commercial silicon solar cells due to undesirable photogenerated carrier recombination at anode/dye/electrolyte and cathode/electrolyte interfaces [8–10].

Over the last few years, considerable efforts have focused on improving the light harvesting capacity by molecular engineering of specific donor in the sensitizers [11] and carrier transport within the photoanodes, either by modifying the morphologies of the wide band gap semiconductor [12–18] or by band edge engineering of TiO_2, ZnO with doping of Zr^{4+} and Co^{2+} [19] and using a combination of TiO_2, ZnO and SnO_2 in a nanocomposite network (ZnO-TiO_2, ZnO- SnO_2, SnO_2-TiO_2 etc) [20–22]. Recently, the incorporation of carbon allotropes such as carbon nanotubes (CNTs), graphene sheets, graphene oxide, fullerene, graphenized carbon nanofiber, and carbon black [23–28] in the wide band gap semiconductor have proven to significantly enhance the charge carrier transport and also loading amount of dye molecules, leading to an increase of the overall PCE [27–30].

The major bottleneck for the use of carbon allotropes, such as CNTs and graphene sheets, in the photoanode is related to undesirable agglomeration of these materials, caused by their extended surface and significant Van der Waals forces inside of most commonly used solvents [31,32]. This tendency to aggregate into bundles consequently leads to a lower interaction with TiO_2 nanoparticles that contributes to reducing the beneficial effects of the carbon allotropes as additives. There are few reports on the surface modification of these carbon allotropes as a possible solution to enhance the solubility to obtain homogenous dispersion into TiO_2. Although surface modification significantly improves solubility, the procedure can introduce defects on the carbon surface, reducing their efficiency [33].

Recently, a top-down approach for producing a new carbon allotrope called Graphene Nanoribbon (GNR) has been developed. This lithographic method produces large arrays of quasi 1-D nanoribbon structures by lengthwise unzipping of MWCNTs sidewalls with the help of potassium intercalation [34,35]. GNRs offer promising features such as high electron mobility (200 000 $cm^2 V^{-1} s^{-1}$) as well as high theoretical specific surface area (2600 $m^2 g^{-1}$), which depends on the ribbon width [36], the shape of the ribbon edges (combination of zigzag and armchair shapes) and the presence of dangling bonds at ribbon edges [37]. Due to these appealing properties and a lesser chance of agglomeration, GNRs could be a better candidate than other carbon allotropes (CNTs and graphene sheets) for insertion in the anode to improve the performance of DSSCs. Until now, few studies have reported the application of GNR in Li-ion batteries electrodes [38–40], in dielectric polymers [41,42], in counter electrodes [43,44], and additive in electrolyte [45] of DSSCs to improve device performance.

Herein, we describe the incorporation of small amounts of GNRs in TiO_2 mesoporous films and demonstrate that this procedure doubles the electron life time in DSSCs. The TiO_2-GNR hybrid photoanodes with different GNR (wt.%) concentrations were prepared using a doctor-blade method [27,28]. The device's functional performance initially improved at low GNR concentration yet was found to decline with further increase in GNR concentration inside the TiO_2 active layer. At the optimum GNR concentration (0.005 wt %), the DSSC yields the highest PCE of 7.18%, under one simulated sunlight at AM 1.5G (100 mW/cm^2), which is 20% higher than the PCE of the control device made of a bare TiO_2 photoanode. This enhanced PV performance is systematically investigated by quantitative dye loading, transient photovoltage decay and electrochemical impedance spectroscopy (EIS) measurements. In addition, the optimized amount of GNRs reported in this study is much lower than that of other carbon allotropes-TiO_2 hybrid photoanodes based DSSCs [27–30], reducing the overall device fabrication cost.

2. Experimental

2.1. Materials

FTO conducting substrates with sheet resistance 15 Ω/square were supplied by Xop Glass (Spain). The TiO_2 nano-oxide blocking layer solution was purchased from Solaronix. The transparent mesoporous TiO_2 paste composed of 20 nm sized anatase particles (Code 18 NR-T) and scattering paste of 150–200 nm nanoparticles sized were supplied by Dyesol, Australia. The redox couple electrolyte (consisting of iodine and tri-iodide I^-/I_3^-) and the Ruthenium based N719 dye were purchased from Solaronix. GNR of several micrometers length and below 100 nm width, Dimethylformamide (DMF), methanol, acetone, ethanol and isopropanol (IPA) solvents were obtained from Sigma-Aldrich Inc. All the chemicals are used as received without any purification.

2.2. TiO_2-GNR hybrid film deposition

The GNR suspension was dispersed in DMF, an aprotic solvent that has a high efficiency for the exfoliation of carbon nanomaterials [46]. A thin and compact TiO_2 blocking layer was deposited on ultrasonically