



Heteroatom doped reduced graphene oxide paper for large area perovskite solar cells

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ARTICLE INFO

Keywords:

Self-assembly process
Graphene oxide
Large area
Solar cells

ABSTRACT

Heteroatom (boron) doped reduced graphene oxide (B-rGO) papers were prepared by the simple self-assembly process of graphene oxide through the deoxygenation in argon atmosphere at 400 °C. The phase purity and crystallinity of the B-rGO paper were studied by X-ray diffraction analysis. The wrinkled paper-like morphology was analyzed by scanning electron microscopy (SEM) and the homogeneity by the elemental mapping. The binding energy states of the B-rGO were confirmed by X-ray photoelectron spectroscopy. The shift in zeta potential values also confirms the heteroatom doping in the rGO paper. From the Raman spectra it was observed that the incorporation of boron into the rGO paper exhibits an improved conductivity and mobility. The current-voltage (J-V) characteristics revealed that the B-rGO paper can be effectively used as a hole transport material (HTM) for perovskite solar cells (PSCs). The largest conversion efficiency of 8.96% was achieved for the FTO/TiO₂/CH₃NH₃PbI₃/B-rGO/FTO sandwich structure with an active area of 1 cm².

1. Introduction

Perovskite solar cells (PSC) have attracted enormous interest in recent years with power conversion efficiency (PCE) leaping from 3.8% in 2009 to the current world record of 22% (Wang et al., 2015; Kim et al., 2017). The PSCs are easily processable, cheaper compared to conventional silicon structures and compound semiconductors (Yang et al., 2017; Kojima et al., 2009; NREL chart, 2016). The perovskite materials (CH₃NH₃PbX₃, X = Cl, I or Br) were mostly used in organic-inorganic halide solar cell structures owing to the exceptional properties (Park, 2013; Lee et al., 2012). In the solution process, direct bandgap methylammonium lead iodide (CH₃NH₃PbI₃) based perovskite material was introduced as an alternative to dyes towards enhancing the light harvesting. The perovskite materials also act as electron and a hole conductor to improve the efficiency by combining with a mesoporous titanium dioxide layer (Yella et al., 2014).

A typical PSC consists of a transparent conducting oxide (TCO) layer, a mesoporous or thin compact TiO₂ film as an electron transport layer (ETM), a perovskite layer, a hole transport layer (HTL) and a metal (Au) contact layer (Eperon et al., 2014b). Indium tin oxide (ITO) or fluorine tin oxide (FTO) layers are commonly used as a TCO layer for collecting electrons from the TiO₂ layer. TiO₂ is an efficient n-type material used as an electron transport layer (ETL) in PSC. The 2,2',7,7'-

tetrakis (N,N-di-4-methoxy-phenyl-amino)-9,9'-spiro bi fluorene (spiro-OMeTAD) was predominantly used as HTL to achieve the high PCE. The poor stability and higher design cost of such spiro-OMeTAD material in PSCs necessitate an alternate HTL (Yang et al., 2017; Acik and Darling, 2016; Sum and Mathews, 2014; Eperon et al., 2014a). The reduced graphene oxide (rGO) was used as an HTL layer in the PSC structure (ITO/rGO/CH₃NH₃PbI₃/PC₆₁BM/bathocuproine/Ag) with high stability and PCE of 10.8% (Yeo et al., 2015). The composite form of rGO/spiro-OMeTAD HTL was preferred for PSCs in order to enhance the PCE (Luo et al., 2015). The low-cost inorganic p-type materials like CuI and CuSCN were used as HTL in PSC with PCE of 12.4% and the Sb₂S₃ layer was introduced as a surface blocking layer in the same structure with PCE of 5.24% (Qin et al., 2014; Ito et al., 2014). The higher level of toxicity and low solubility restrict the use of above materials.

In order to overcome these issues, carbon (graphene) based materials were introduced as contact layers. This type of carbon-based materials was not only used as a contact layer and also used to serve as HTM. Graphene, the 2D honeycomb structure with high electron mobility, has been effectively utilized in photovoltaic devices. The multi-layer stacking structure of graphene reduces the recombination rate and improves the efficiency of the solar cell (Liu et al., 2008; Das et al., 2014). Flexible rGO paper-based electrodes were prepared by the self-assembly process from the chemically converted graphene oxide

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material (Selvakumar et al., 2016, 2017a, 2017b). It has been reported that the heteroatom doping can effectively alter the structure of the graphene in photovoltaic device applications (Wang et al., 2012; Chen et al., 2015). The reported PCE with nitrogen-doped graphene in DSSCs based system was 4.75% (Yen et al., 2012). The alternative boron heteroatom was doped with graphene to improve the power conversion efficiency to 6.73% (Fang et al., 2014).

The main objective of the present study was to replace the unstable and high-cost organic hole transport materials with the heteroatom doped graphene oxide paper in PSCs. The freestanding flexible boron doped graphene oxide (B-GO) was fabricated by a cost-effective self-assembly process. The boron doped reduced GO (B-rGO) paper was prepared by annealing the B-GO in an inert atmosphere (argon). The cathodic layer of the photovoltaic device was formed by mixing the chemically converted graphene oxide with B_2O_3 in ethanol. The power conversion efficiency of the PSC fabricated using FTO/ TiO_2 / $CH_3NH_3PbI_3$ /B-rGO paper/FTO device structure has been systematically studied.

2. Experimental methods

2.1. Materials

Graphite powder purchased from Central Drug House, sodium nitrate ($NaNO_3$), potassium permanganate ($KMnO_4$), sulfuric acid (H_2SO_4), hydrogen peroxide (H_2O_2), Di-boron trioxide (B_2O_3) from Merck, titanium di-isopropoxide bis(acetylacetonate) and PbI_2 purchased from Sigma Aldrich and Silane purchased from Spectrochem were used for the synthesis. The fluorine-doped tin oxide (FTO) substrate was purchased from NSG-Pilkington (TEC-15, $t = 2$ mm).

2.2. Preparation of Boron-doped rGO paper

The pure and boron doped rGO papers were prepared by the self-assembly process as reported in our earlier work (Selvakumar et al., 2016, 2017a). By using the same method, the dopant was incorporated in order to prepare the boron doped rGO (B-rGO) paper with B_2O_3 as the boron source. As-synthesized graphene oxide powder and B_2O_3 (10 and 20%) were mixed and mortared for 30 min. The above mixer was sonicated for 3 h to form the boron doped GO gel in an aqueous medium. The gel was poured over the petri-plate and dried at 60 °C overnight. Then the powder was collected and annealed at 400 °C under argon atmosphere to obtain boron doped (10 and 20%) reduced GO (rGO) paper named as B1 and B2 samples respectively.

2.3. Preparation of CH_3NH_3I

For the perovskite material, CH_3NH_3I (MAI) powder was synthesized by the reaction of 13.5 ml of methylamine (33 wt% in absolute ethanol, Sigma) with 15 ml of hydroiodic acid (HI) (57 wt% in water, Aldrich) in a round-bottom flask at 0 °C for 2 h with stirring. MAI was crystallized by rotary evaporation of the solvent at 50 °C. The MAI product was re-dissolved in absolute ethanol and precipitated upon the addition of diethyl ether. After filtration, the step was repeated and the solid was collected and dried at 65 °C in a vacuum oven for 24 h.

2.4. Fabrication of solar cell structure

The perovskite-based solar cell was designed based on the earlier report (Li et al., 2016). The FTO substrate was cleaned with detergent in an ultrasonication bath followed by rinsing with water and ethanol and then dried with UV/O_3 cleaner for 5 min. The dense and compact TiO_2 layer of 50 nm thickness was deposited over the FTO substrate by spin coating at 4000 rpm using titanium di-isopropoxide bis(acetylacetonate) with ethanol (1:9). Then, the films were sintered at 500 °C for 30 min and then cooled to room temperature. The light harvesting

perovskite $CH_3NH_3PbI_3$ layer of thickness 400 nm was deposited onto the TiO_2 layer by mixing PbI_2 and CH_3NH_3I in 2 ml of γ -butyrolactone by spin coating at 4000 rpm using one-step method. After annealing the perovskite film at 100 °C for 30 min, the boron doped rGO paper (B1 & B2) was stuck over the perovskite layer. Finally, a blank FTO plate was fixed on the doped rGO paper.

2.5. Characterization

The crystallinity of the pure and boron doped rGO papers were studied using RIGAKU MINIFLEX II-C X-ray diffraction system with Cu K α radiation. The morphology of rGO and B-rGO papers was characterized using TESCAN VEGA 3 SBU Scanning Electron Microscope (SEM) and the element mapping by FEI Quanta FEG 200 High-Resolution SEM. The elemental compositions of the samples were further investigated using SPECS X-ray photoelectron spectroscopy (XPS) with PHIBOS100 energy analyzer and Al ($K\alpha$: 1486.61 eV). Raman spectra were recorded using HORIBA JOBIN YVON LABRAM HR micro-Raman system with an excitation wavelength of 488 nm of the argon-ion laser. Electrical properties of boron doped rGO paper-based electrodes were studied using Hall effect measurement system (HMS-5000). UV/Visible (UV/Vis) absorption spectra were recorded in a Hitachi (Model U-4100) UV/Vis NIR spectrophotometer. The photocurrent density-voltage (J - V) characteristics were analyzed by applying a forward bias to 1.0 cm^2 area of the sample illuminated with a solar simulator (1.5 AM, 100 $mW\ cm^{-2}$) equipped with a 500 W Xe lamp (YSS-100A, Yamashita Denso).

3. Results and discussion

The mechanism of heteroatom (boron) doped rGO paper reveals that the boron atoms sit at the interstitial sites of graphene lattice. Since the trivalent impurity has insufficient electrons in its orbit, doping with rGO paper leads to an increase in the bond length. The doping of heteroatom significantly enhances the conductivity and increases the energy conversion (Fang et al., 2014). Fig. 1(a) shows the as-synthesized 10% boron doped rGO paper (B1) with rectangular shape ($5 \times 12\ cm^2$) and Fig. 1(b) shows the corresponding mechanism of B-rGO paper. The functional groups correspond to pure and boron doped rGO paper were identified from the FTIR spectra as shown in Fig. S1. The shift in the lower wavelength of DRS-UV spectra (Fig. S2) also identifies the doping of heteroatom. The zeta potential values shift towards the positive side for the boron doped rGO paper (Fig. S3). The increase of surface roughness is also confirmed from AFM images (Fig. S5).

The crystallinity of the as-prepared boron doped rGO papers was ensured by XRD analysis. Fig. 2 shows the XRD pattern of pure and boron doped rGO papers. A minor shift in the peaks at the 2θ value of 25.24° towards the higher angle of 25.5° (for 10% B-rGO paper) and 25.72° (for 20% B-rGO paper) was observed confirming the boron doping in the rGO matrix. The shoulder peak at $2\theta = 27.74^\circ$ is due to the un-reacted B_2O_3 in the sample. The shoulder peak is also shifted to higher angle for boron doped samples (Fang et al., 2014; Li et al., 2016). The inter-layer spacing of the pure rGO paper was estimated to be 3.52 Å. For boron doped rGO papers (B1 & B2), the values were 3.47 & 3.51 Å, respectively. The trivalent impurities significantly reduce the interlayer spacing of the rGO paper.

The morphology of pure and boron doped rGO papers are shown in Fig. 3. Pure rGO paper (Fig. 3(a)) exhibits wrinkled paper-like morphology. The boron doping has not altered the morphology of the rGO paper as shown in Fig. 3(b) and (c). However, change in the surface roughness has been observed in boron doped rGO paper. Elemental mapping of the B1 sample shown in Fig. 4 confirms the presence of carbon (C) and oxygen (O). Since the boron is a light element, it was not detected in the elemental mapping. The presence of oxygen in the B1 sample (Fig. 4) was due to the oxygen functional groups in the hexagonal carbon structure.

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