Synthesis and characterization of nanostructures of ZnO and ZnO/Graphene composites for the application in hybrid solar cells

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ABSTRACT

As an n-type inorganic semiconductor, ZnO has been widely used in hybrid solar cells (HSCs) due to its numerous characteristics such as low cost, easy synthesis, non-toxicity and good optoelectronic properties. In this work we have synthesized the ZnO nanostructures/nanoparticles via wet chemical route having Zinc Acetate Dihydrate (ZnADH) as precursor, Poly (Ethylene Glycol) block poly (Propylene Glycol) block poly (Ethylene Glycol) (PEG-PEG-PEG/P123) as template directing agent. Graphene oxide (GO) was prepared by the Modified Hummer's Method through the oxidation of graphite flakes and $KMnO_4$ was used as an oxidizing agent. ZnO/Graphene nanocomposites were prepared via sonication process. Oxidation peaks of graphite showed by the UV—Vis spectroscopy were around 216 nm and all composite films were observed to be appeared in visible region. A considerable reduction in bandgap of ZnO from 3.1eV to 2.9eV was observed due to incorporation of graphene oxide which was confirmed with both UV—Vis bandgap analysis method and cyclic voltammetry (CV). Measureable progress in the performance of IV characteristics of hybrid solar cells was achieved using the ZnO/Graphene composite as electron collector in active layer along with P3HT:PCBM in an inverted hybrid photovoltaic device. Short circuit current was observed to be improved by approximately four times then its original value in these devices along with the increase in the concentration of GO whereas open circuit voltage showed a decreasing trend.

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1. Introduction

Polymer organic photovoltaic devices offer a cheap and attractive alternative for silicon based solar cells because the polymer materials having both conducting and semiconductor properties has led to new and elating possibilities in the field of optoelectronic devices. However, the photoexcitation in the polymer leads to the formation of strongly bound electron-hole pair or an exciton is created whereas its results in the formation of free charge carriers in the case of inorganic semiconductors [1]. The exciton generated in the polymeric material can only be separated into free charge carriers at the interface of organic and inorganic semiconductors which are known as donor (n-type) and acceptor (p-type) materials in the photovoltaic devices. Life time of exciton and their respective diffusion length are generally limited so the only excitons created in the vicinity (5—15 nm) of donor acceptor interface will give rise to free charge carriers. This limitation is overreached in bulk heterojunction hybrid solar cells by closely mixing donor and acceptor materials which creates multiple junctions in the active layer increasing the interfacial area between both donor and acceptor materials. This ensures the generation of charges from photogenerated excitons. In recent years various bulk-heterojunction photovoltaic devices have been reported that uses conjugated polymer in combination with inorganic semiconductors [2—4]. Such hybrid polymer/inorganic nanocomposite material may unite the benefits of both materials including the solution processing of organic semiconductors and high electron mobility of inorganic semiconductors. The inorganic electron acceptor material can provide further advantages to the device, while still keeping the low cost processability, such as inorganic materials are more environmentally stable than organic materials [5]. Addition of these materials to OPV devices could overcome one of the biggest downfalls of the technology, which is the photo induced degradation of the conjugated organic semiconductors. Most commonly used acceptor material in these devices is (6,6) phenyl C61 butyric acid methyl ester (PCBM). The light absorption contribution of PCBM is smaller than absorption process in an inorganic

semiconductor in organic photovoltaic (OPV) devices [6,7]. Moreover, the quantum confinement, which results in modification of the size and shape of the inorganic nanoparticle, varies the bandgap of the nanoparticle and also its absorption profile [8]. Absorption of light in these devices is also controlled by the thickness of the active layer. It increases with increasing thickness but a thick active layer effects charge carrier transport because of space charge effects and/or charge recombination. This is defined in terms of increased series resistance and reduced efficiency [9].

To overcome the problem different structures, like mesoporous, nanorod, and nanostructure are introduced [10–13]. ZnO is a good n-type material for the application in photovoltaic (PV) devices due to its better optical, electrical, structural and environment-friendly properties, which includes high electron mobility and ease of control of its size and shape. The devices based on ZnO nanoparticles have a larger specific interfacial area as compared to those based on other nanostructures i.e. nanorods, which makes them efficient. Moreover their efficiency could be enhanced if band gap of ZnO may be narrowed down, as it possesses the wide band gap (3.2–3.4eV) and absorbs more light in UV region as compared to the visible region [14,15]. Graphene, a 2D carbon nanostructure, possesses high electron mobility (exceeding 2000 cm^2/V). Addition of graphene in inorganic semiconductor material has shown enhancement in the charge transfer rate of electrons. This in turn increases the photocurrent by reducing the recombination of photogenerated electron−hole pair due to $\pi-\pi$ interactions of graphene [16,17].

This research work is based on firstly synthesizing new nanostructures of ZnO so that to increase the interfacial area between donor and acceptor material. Secondly, Graphene, having a work function of 4.5eV, is explored for its effect on the band gap of ZnO thin films and also on photocurrent which is generated in such structures. In the past, much of the research have been performed with making for enhancement of photocatalytic activity of ZnO using graphene nanosheets, such as preparing composites through ultrasonic treatment [18], UV-assisted photocatalytic reduction [19], hybridization [20], spin casting [21], hydrothermal method [22] etc. These methods have successfully shown increase in the photocatalytic activity by the composites; however, none of the work actually reported the effect of graphene on the band gap of the semiconductor material. So this work was hence developed to report the change in electrical properties of ZnO by incorporation of graphene nanosheets. ZnO nanostructures were prepared by adopting the wet chemical route using Poly (Ethylene Glycol) block poly (Propylene Glycol) block poly (Ethylene Glycol) (PEG-PEG-PEG/P123) as template directing agent and graphene was dispersed in the sol through sonication. Thin films were obtained using spin coating composites on the glass and ITO substrates followed by the water bath process and subsequent heat treatment. Thirdly, to use these pure ZnO films and ZnO/Graphene composite films in hybrid solar cells and then studying their IV characteristics.

2. Experimental work

2.1. Synthesis of ZnO nanostructures and ZnO/Graphene composites

A sol gel of ZnO was obtained using the wet chemical route. All the chemicals were purchased from Sigma Aldrich and then were used as obtained. Firstly, zinc acetate dihydrate (ZnADH 99%) (3.636 g) and Poly (Ethylene Glycol) block poly (Propylene Glycol) block poly (Ethylene Glycol) (PEG-PEG-PEG/P123) (Mw 5800) (0.72 g) were dissolved in 2-methoxyethanol (2MeEtOH 99.9+ %) (21 ml) then ethanolamine (EA 99+ %) (1 ml) and hydrochloric acid (HCl 37%) (3.2 ml) were further added. The solution was stirred for 3 h for 4 h and 5 h respectively. This variation in stirring time was

done to study difference in the morphology of ZnO nanostructures with respect to stirring time. Modified Hummer's method was used for the oxidation of graphite flakes into graphene oxide (GO) having KMnO$_4$ as an oxidizing agent reported elsewhere [23].

The solution of 0.5mg/1 ml of graphene oxide in 2-methoxyethanol was prepared followed by sonication in ultrasonic water bath for 50 min. This process was done to ensure that the graphene oxide nanosheets are homogenously dispersed in the solution. This GO solution in two different concentrations i.e. 1.25 ml and 2.5 ml was added separately with all three kinds of ZnO sols i.e. 3hr stirred sol, 4hr stirred sol and 5hr stirred sol (Table 1). The resulting mixture was sonicated for 50 min before thin film deposition [24].

For the thin film deposition, cleaning of ITO substrate was done firstly by distilled water followed by acetone, 2-isopropanol, and de-ionized water. SCS|G3-8 spin coat machine was used for making films by spin coating. Firstly, the solution of pure ZnO films (3hr stirred, 4hr stirred and 5hr stirred) and then composite films was spread on the substrate uniformly and then the substrate was allowed to spin slowly till 2000 rpm and let it spin for 30 s to dry out the coating. After deposition the films were placed in the dust free place for drying at room temperature for 30 min. Dried films were then placed in pre heated water in the water bath (BM210 water bath) at 80 °C for 14 h; the process is called as water bath process. After that samples were annealed at 500 °C at a heating rate of 2 °C min^{-1} for 2 h in Nabertherm Gmbh N17/HR-400V Muffle heating furnace to achieve the ZnO nanostructures and reduced graphene oxide RGO [25].

2.2. Device fabrication

The blend of P3HT (Mark lisicon SP001): PCBM (Ossila Ltd) was prepared by dissolving them with molar ratio of 1:0.7 in 0.5 ml chlorobenzene acting as solvent. This solution was stirred for 24 h at room temperature in order to achieve the homogenous solution. The solution was spread on ZnO coated film by spin coating at 3000 rpm for 30 s. The sample was annealed at 90 °C for 10 min on hot plate to remove the stresses in the morphology of films. The PEDOT:PSS layer was spin coated on P3HT/PCBM layer at 5000 rpm for 30 s. The film was annealed on hot plate at 90 °C for 10 min. After that the films were placed in the mask which was made up of copper. The aluminum electrodes with work function 4.3eV were deposited on the films through thermal electrode deposition method for electrical connections.

3. Results and discussion

Figs. 1 and 2 shows the scanning electron microscope (SEM) images of ZnO nanostructures having some mushroom like morphology and ZnO nanoparticles. The images show homogenously distributed nanostructures and nanoparticles in the range of

Table 1
ZnO/GO composite sols.

Precursor composite sol	ZnO sol	GO (5 mg ml^{-1})
ZnO 3Hr str. Pure	2.5 ml	0 ml
ZnO 3Hr str. 1.25 ml GO	2.5 ml	1.25 ml
ZnO 3Hr str. 2.5 ml GO	2.5 ml	2.5 ml
ZnO 4Hr str. Pure	2.5 ml	0 ml
ZnO 4Hr str. 1.25 ml GO	2.5 ml	1.25 ml
ZnO4Hr str. 2.5 ml GO	2.5 ml	2.5 ml
ZnO 5Hr str. Pure	2.5 ml	0 ml
ZnO 5Hr str. 1.25 ml GO	2.5 ml	1.25 ml
ZnO 5Hr str. 2.5 ml GO	2.5 ml	2.5 ml