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DMSO modified PEDOT:PSS polymer/ZnO nanorods Schottky junction ultraviolet photodetector: Photoresponse, external quantum efficiency, detectivity, and responsivity augmentation using N doped graphene quantum dots

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ABSTRACT

Schottky junction ultraviolet (UV) photodetector was fabricated by spin coating a hole conducting polymer, poly 3,4-ethylenedioxythiophene: polystyrene sulfonate (PEDOT:PSS) on hydrothermally grown zinc oxide (ZnO) nanorod array. The photodetector performance was improved by increasing the conductivity of PEDOT:PSS polymer using dimethyl sulfoxide (DMSO) additive. The UV detector performance was further enhanced significantly by sensitizing ZnO nanorods with N doped graphene quantum dots (NGQDs). NGQD decorated ZnO NRs/DMSO-PEDOT:PSS Schottky junction device demonstrated superior external quantum efficiency (EQE ~ 90063%), responsivity ($R_\lambda \sim 247$ A/W) and detectivity ($D_\lambda \sim 2.42 \times 10^{11}$ $Hz^{1/2}/W$) at 340 nm wavelength and –1V external bias. The EQE of NGQD modified sample was 56 times higher than pristine PEDOT:PSS/ZnO NR and 4.3 times higher than DMSO modified PEDOT:PSS/ZnO NRs device. NGQD sensitized detector showed superior photocurrent of 80.77 mA/cm^2 at 340 nm wavelength, –1V external bias, which was 2 times higher than DMSO modified and 32 times higher than pristine PEDOT:PSS based device. The photocurrent rise and decay time of NGQD sensitized NRs are very fast compared to other photodetectors.

1. Introduction

Schottky junction photodetectors are attractive due to their simple device geometry, fast response and recovery time, low dark current and high quantum efficiency. [1–6] Such kind of photodetectors has been fabricated by depositing novel metal electrodes with larger work function (φ ~ 4.2 to 6.32eV) such as Au, Ag, Pt, Pd on p or n-type semiconductors [7,8]. Recently, it has been also observed that monolayer graphene film could be an attractive material in order to get Schottky junction for photodetector application [9,10]. Metal/n-type ZnO semiconductor Schottky junctions have been extensively studied for ultraviolet (UV) photodetector applications due to its wide optical band gap (3.2–3.4 eV), easy synthesis process, high gain and overall environmental friendly nature [7,8,11–13]. However, fabrication of metal-semiconductor contacts usually needs high vacuum techniques and several lithographic steps, which raise the fabrication cost of the device. On the other hand, conducting polymer based electrodes are attractive due to its easy and low cost deposition process [14–18]. More importantly, such kinds of polymer based electrodes have potential applications in flexible and wearable electronics [19,20]. Poly 3,4-ethylenedioxythiophene: polystyrene sulfonate (PEDOT:PSS) is a hole conducting conjugated polymer has been widely investigated in organic solar cells [21,22], light emitting diodes [23,24], field effect transistors [25,26], and photodetectors [16,27]. Nowadays, PEDOT:PSS has been utilized as an alternative material for transparent conducting electrodes due to its superior carrier mobility, large work function (5–5.2 eV) and excellent transparency (above 90%) in a wide spectral range (250 nm–800 nm) [16,20]. However, the electrical conductivity (σ) of pristine PEDOT:PSS films is very poor (σ ~ 0.5 to 1 S/cm) [28] compared to conventional transparent conducting oxides (TCO) or metal electrodes (3300 to 10,000 S/cm) [29]. Several research works have been carried out to improve the electrical conductivity and transparency of PEDOT:PSS films by acid treatment or doping with various organic solvents. Xia et al. [28] prepared high conductive PEDOT:PSS films of maximum conductivity ~ 3065 S/cm by treating with concentrated H_2SO_4 and utilized as transparent conducting electrodes in polymer solar cell. Yeon et al. [30] improved the conductivity of PEDOT:PSS up to 4100 S/cm by using HNO_3 treatment. Such high conductive films were used as the counter electrodes for dye sensitized solar cell (DSSC) and they have achieved power conversion efficiency

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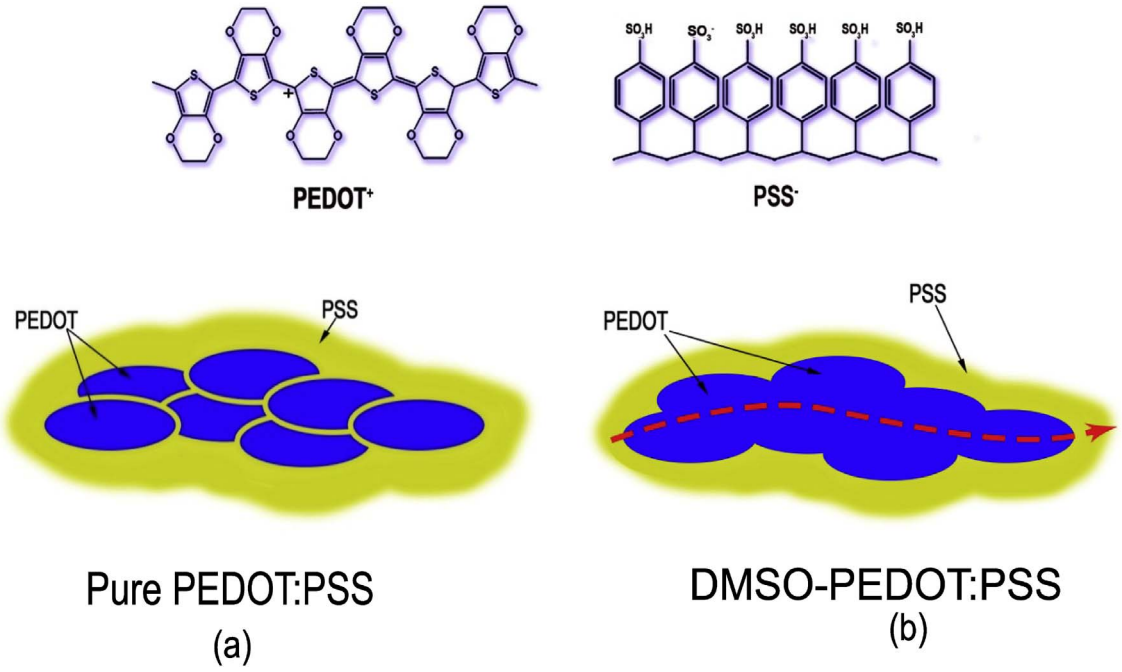

Fig. 1. Schematic representation of carrier transport in PEDOT:PSS polymer. (a) unmodified PEDOT:PSS, conductive PEDOT grains (blue) are surrounded by an insulating PSS shell (green) (b) thinning of PSS layer after addition of DMSO solvent, which creates better carrier transport. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

~8.59%. Ouyang et al. [31] reported the improvement of electrical conductivity of PEDOT:PSS polymer using organic solvents such as ethylene glycol (EG), dimethyl sulfoxide (DMSO) and sorbitol. The maximum conductivity of the films was obtained σ~ 1057 S/cm after DMSO doping [32].

Recently, UV photodetectors using n-type ZnO/PEDOT:PSS conducting polymer based Schottky junction have been attracted much attention due to its high sensitivity, low cost and easy fabrication process [16,17]. But the poor electrical conductivity of PEDOT:PSS polymer decreases the carrier collection, which gives rise to slower photoresponse and lowering device performance.

On the other hand, attachment of semiconductor quantum dots (e.g., CdS, CdSe, CdTe, PbS) with ZnO nanorods also improve the photoconductivity and suppress carrier recombination of the photodetectors [27,33,34]. However, most of the Quantum dots (QDs) are highly toxic and may create many health related issues [35,36]. Recently, the photoconductive properties of ZnO nanorods have been enhanced several times by sensitizing with graphene quantum dots (GQDs) [37,38]. These carbon nanomaterials have been utilized instead of semiconductor QDs due to their size tuneable optical absorption, emission properties and favourable band alignment [37,39,40]. More importantly, such new kinds of QDs are made from most abundant and nontoxic elements on earth with minimal low synthesis cost [41,42]. Doping with several elements like nitrogen, sulphur, boron etc. strengthen optical absorption of GQDs from ultraviolet to visible range [43–45].

In our previous report, we have studied ZnO nanorod/PEDOT:PSS based Schottky junction UV detectors with high external quantum efficiency (EQE~1617%), detectivity (D_λ~3 × 10^{11}Hz$^{1/2}$/W) and responsivity (R_λ~4.4A/W) [46]. The photodetector performance was further enhanced after sensitizing the nanorods with graphene quantum dots (GQDs), which has strong UV photoabsorption (EQE~13167%, D_λ~ 1.29 × 10^{12} Hz$^{1/2}$/W and R_λ~36A/W). However, in ZnO nanorod/PEDOT:PSS junction, the poor electrical conductivity of pristine PEDOT:PSS polymer increases interfacial resistance and decreases the carrier collection, which give rise to slower photoresponse and lowering device performance. The detector performance of the Schottky junction device could be improved further by increasing the electrical conductivity of PEDOT:PSS polymer. Simultaneously, sensitization of ZnO NRs with doped GQDs can also boost the photoabsorption and increase photogenerated carriers.

In this article, we have improved the UV photoresponse properties of ZnO Nanorods/PEDOT:PSS Schottky junction by enhancing the electrical conductivity of PEDOT:PSS polymer using DMSO solvent. The conductivity enhancement of PEDOT:PSS polymer layer has been verified by four probe method along with STM analysis. The UV photodetector performance was further enhanced by attaching nitrogen doped graphene quantum dots (NGQDs) as UV sensitizer on ZnO nanorods (ZnO NRs) surface. The key photodetector parameters such as EQE, detectivity, responsivity, response and recovery time have been studied in details.

2. Material and methods

2.1. Growth of nanorods (NRs)

ZnO NRs were synthesized hydrothermally on fluorine-doped tin oxide (FTO) coated glass substrates. The detailed growth procedure has been reported elsewhere [46,47]. Prior to the growth of ZnO NRs, patterned FTO coated glass substrates were ultrasonically cleaned in DI water, followed by acetone and isopropyl alcohol. ZnO nanoparticle seed layer solution was prepared by adding 0.01M of zinc acetate dehydrate (Merck 99%) in 50 ml isopropyl alcohol (Merck 99%) followed by heating and stirring at 65^{O}C for 1 h. Afterwards, 0.02M of diethanolamine (Merck 99.5%) was added to the above solution. The solution was cooled to room temperature and spin coated on the cleaned FTO coated glass substrate followed by annealing at 200^{O} C for 1hr. Nanorods were grown by dipping the seeded substrates in a Teflon lined stainless steel hydrothermal reactor, containing zinc nitrate (0.05M) (Sigma Aldrich 98%) and HMTA (0.05M) (Sigma Aldrich 99%) solutions. The reaction temperature of the solution was maintained at 90^{O}C for 4 h. The grown nanorods were cleaned with DI water and annealed at 400^{O}C for 2 h for further use.