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Low dark current and improved detectivity of hybrid ultraviolet photodetector based on carbon-quantum-dots/zinc-oxide-nanorod composites

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ABSTRACT

In this study, we fabricated an ultraviolet (UV) photodetector by blending a hybrid photoactive layer (HPL) that is composed of a hybrid structure containing Carbon Quantum Dots (CQDs) and Zinc Oxide Nanorods (ZnO NRs). To observe the effective photo-inducing abilities of CQDs and ZnO NRs, we analyzed the electrical properties of a UV photodetector using an HPL of CQDs/ZnO NRs. Under an illumination of 365 nm UV light with an intensity of 1 mW/cm^2, the UV photodetector exhibited a high detectivity of 8.33×10^{12} Jones, which is higher than that of a UV photodetector using a HPL of blended poly-*n*-vinylcarbazole (PVK) and ZnO NRs. Experimental results show that an HPL of blended CQDs/ZnO NRs can induce efficient charge extraction from CQDs and ZnO NRs. In addition, CQDs act as charge controllers that enable hole-electron separation in the device upon UV illumination. These results indicate that synthesized CQDs can substitute for a charge transport polymer (i.e., PVK) and that a UV photodetector using CQDs can exhibit high detectivity.

1. Introduction

An ultraviolet (UV) photodetector has a wide range of applications including in environmental and biological research, sensing, detection, and the launching of missiles [1]. To date, most of the commercial photodetectors are fabricated by means of film growth from single-crystalline Si, SiC, GaN, and ZnO, which requires vacuum processing [2–5]. Recently, UV photodetectors based on nanomaterials such as semiconductor quantum dots, carbon materials, and gold nanoparticles (NPs) have become particularly attractive because of their potential applications in next-generation optoelectronic devices [6–8]. As a wide-band-gap semiconductor material, ZnO has drawn considerable attention because of its unique optical and electrical properties, one of which is a wide band gap (3.37 eV) [9–11]. In particular, various ZnO nanomaterials have been used to fabricate UV photodetectors with high photoconductive gain and high responsivity [12,13]. Unfortunately, these UV photodetectors suffer from poor transient response, which has been attributed to surface defects such as the grain boundaries of ZnO nanomaterials [14]. Thus, recent research on UV photodetectors based on hybrid material with carbon material-ZnO-NP composites has attracted much attention because of their efficient charge extraction. This has been attributed to the collection efficiency of the ZnO-based UV photodetector, a quality that contributes to high responsivity and a fast transient response.

The incorporation of carbon materials has received considerable attention because of the tunable surface functionalities, outstanding optical properties, thermal stability, and low toxicity of these materials. Carbon materials have been widely used in photoelectronics, biotechnology, and chemical and biological sensing [15,16]. Specifically, Carbon materials synthesize the bottom-up

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method such as graphene quantum dots (GQDs), and reduced graphene oxide (rGO). Son et al. studied UV photodetectors using the wet spin-coating for ZnO NPs and a transfer method for the graphene sheet [17]. Current-voltage measurements of the UV photodetector at 300 K showed that the ratio of photocurrent to dark current was approximately 1.1×10^4. Shao et al. introduced a photodetector fabricated from a ZnO QDs-graphene composite and polymers. The photodetector demonstrated high sensitivity to UV light with a maximum photoresponsivity of 247 A/W at 325 nm [18]. The high photoresponsivity of this device was attributed to the high active surface to volume ratio of the ZnO QDs-graphene composite. Zhan et al. studied a new type of self-powered, visible-light photodetector fabricated from a thermal rGO-ZnO NPs hybrid nanostructure [19]. The distinct and fast photoresponse of this device was a direct result of enhanced charge transfer between rGO and ZnO NPs, as well as the excellent electric properties of rGO sheets.

Guo et al. fabricated UV photodetectors having lateral structures by employing ZnO- NPs/carbon-quantum-dots (CQDs) hybrid films and synthesized the CQDs using a top-down method [20]. The researchers found that CQDs can improve the surface defects of ZnO NPs and the carrier separation at the CQDs/ZnO-NPs interface. However, this UV photodetector has not been reported in a performance comparison of charge transport polymer/ZnO NPs with CQDs/ZnO NPs. In addition, it was fabricated using a lateral structure of a sapphire substrate. The lateral-structured UV photodetector using sapphire substrate was more expensive than the vertical-structured UV photodetector based on CQDs/ZnO NPs that have yet to be reported.

In this work, we analyzes the electrical properties to compare poly-*n*-vinylcarbazole (PVK)/ZnO NRs and CQDs/ZnO-NRs-based UV photodetector. In addition, to fabricate a low-cost UV photodetector, we propose a vertical structure using CQDs/ZnO NRs. Our device simply consists of four layers excluding an electron-conducting layer, and can be produced by means of all solution processes. We find that the performance of a UV photodetector using CQDs can be improved to the carrier separation at the hybrid interface of CQDs/ZnO NRs. Thus, CQDs can be a good substitute for a charge transport polymer such as PVK and the detectivity of the UV photodetector can be improved.

2. Experimental methods

2.1. Synthesis of Carbon Quantum Dots

The CQDs were synthesized using a previously proposed bottom-up method [21] that employs anhydrous citric acid (CA, Sigma-Aldrich) as the carbon precursor, octadecene (ODE, Sigma-Aldrich) as the noncoordinating solvent, and oleylamine (OA, Acros Organics) as the surface passivation agent, all of which are shown in Fig. 1. A total of 15 ml of ODE and 2 ml of OA were loaded into a 50 ml three-neck flask, and degassed with argon for 30 min. When temperature was raised to 200 °C, 1 g of anhydrous CA was quickly injected into the reaction flask. After 20 min, the synthesized solution was naturally cooled to room temperature. The resulting dark-yellow solution was purified by being precipitated with ethanol and was subjected to centrifugation at 4000 rpm for 10 min to obtain jelly-like CQDs. After being twice purified with ethanol, the CQDs were dried at room temperature. Finally, the CQDs were dissolved in chlorobenzene.

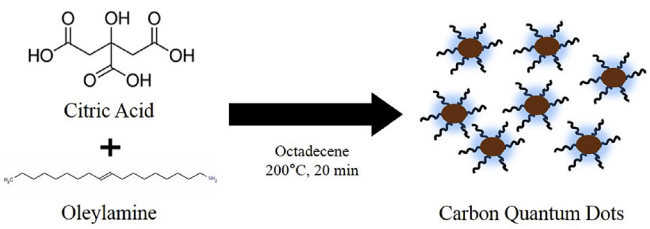

Fig. 1. Schematic of the synthesis of Carbon Quantum Dots.

2.2. Synthesis of ZnO NRs

To synthesize ZnO NRs, we used an optimized sol-gel method [22,23]. A total of 11.5 mmol of zinc acetate dihydrate [Zn(CH3COO)2·2H2O, Sigma-Aldrich] was dissolved in 62.5 ml of anhydrous methanol and 2 ml of DI water was added to a 100 ml three-neck flask. The solution was heated to 60 °C by means of magnetic stirring. Then, 19.6 mmol of lithium hydroxide (LiOH, Sigma-Aldrich) was added to 32.5 ml of anhydrous methanol by gradual injection (1 ml/s). After 5 h, the mixed solution became turbid and ZnO NRs were grown. The synthesized ZnO NRs were then precipitated by centrifuging, washed repeatedly with anhydrous methanol twice, and finally dispersed in chlorobenzene, forming a translucent solution.

2.3. Fabrication of device

We fabricated a solution-processible UV photodetector as a vertical-structure device. The UV photodetector consisted of an anode (ITO), hole extraction layer (HEL), hybrid photoactive layer (HPL), and aluminum (Al) cathode. Fig. 2 provides schematic and energy band diagrams of the proposed UV photodetector. The energy levels of the CQDs can be found in Ref. [24]. And the thickness of each layer in these devices measured using a Focused ion beam (FIB) as shown in Fig. 2. A patterned glass substrate of 150 nm indium tin oxide (ITO), a typical anode material, was cleaned ultrasonically in acetone, methanol, and 2-propanol. An HEL of poly(ethylene-dioxythiophene):polystyrenesulphonate (PEDOT:PSS, Clevios™ PVP AI 4083, USA) was spin-coated on a pretreated ITO-patterned glass substrate at 1500 rpm for 30 s, and annealed at 150 °C on a hot plate for 10 min, which gave a HEL film thickness of approximately 80 nm. To prepare the CQD/ZnO-NRs hybrid HPL, We blended the CQDs and ZnO-NRs solution in a ratio of 1:1 (by volume). The HPL was deposited on the PEDOT:PSS film using the spin-coating method at 1500 rpm for 30 s and was annealed at 110 °C for 30 min in a vacuum oven. The HPL had a thickness of approximately 370 nm. A 150 nm Al cathode was thermally deposited under high-vacuum conditions. The photoactive area was 9 mm^2. In addition, the device based on the PVK/ZnO NRs was fabricated to compare it with a device that used CQD/ZnO NRs. The PVK/ZnO NRs had a thickness of approximately 400 nm. In our UV photodetector, all layers, excluding the electrodes were simply fabricated by spin coating.

2.4. Evaluation of device performance

To evaluate the device performance, we measured the current density-voltage (J-V) characteristics under a UV light source having a radiation power of 1.0 mW/cm^2 and a 365 nm wavelength. The J-V data were measured using a computer-controlled voltmeter (Keithley 2400 series sourcemeter, Keithley Instruments Inc., USA) and LabVIEW software (National Instruments, USA). UV–Vis absorption was recorded by means of a UV–Vis spectrophotometer (SHIMAZU UV-1700). The morphology of HPL was examined using an atomic force microscope (AFM) (Park Systems, Republic of Korea), and the transient response was measured with an oscilloscope (Tektronix), which was used to record the voltage variation in the resistor.