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Transparent and flexible ultraviolet photodetectors based on colloidal ZnO quantum dot/graphene nanocomposites formed on poly(ethylene terephthalate) substrates

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ABSTRACT

Transparent colloidal ZnO quantum-dot (QD)/graphene nanocomposites were formed on poly(ethylene terephthalate) (PET) substrates. Ultraviolet (UV)–visible absorption spectra showed a shoulder peak around 350 nm corresponding to the absorption of ZnO QDs. Optical transmittance of the ZnO QD/graphene/PET multilayer was approximately 80%. High-resolution transmission electron microscopy images showed that the ZnO QDs were distributed along the circumferences of the surfaces on the graphene layers. Current–voltage and current–time measurements on the UV photodetector after bending at 300 K exhibited the ON/OFF switching states and stability resulting from the light-induced conductivity of the flexible graphene layer.

1. Introduction

Large-band-gap ZnO semiconductors have attracted a great deal of interest because of their potential applications in optoelectronic devices due to their excellent physical properties of high chemical stability and large exciton binding energies [1–5]. Nanocomposites based on ZnO quantum dots (QDs) have been particularly attractive because of interest in potential applications in electronic and optoelectronic devices, such as nonvolatile memory devices [6], light-emitting diodes [7], solar cells [8], and ultra-violet (UV) photodetectors [9,10]. The prospect of potential applications of nanocomposites based on ZnO QDs has led to substantial research and development efforts to form several types of nanocomposites acting as active regions [11–13]. Because graphene layers have high conductivity, good transparency, good stretchable, and high chemical and thermal stability [14–16], they have emerged as excellent planar electrodes for promising applications in next-generation electronic and optoelectronic devices [17–19]. The graphene layers play very important roles as carrier transport layers and as electrodes for ultrafast photodetectors [20,21]. Flexible solution-processed UV detectors containing colloidal ZnO nanoparticles formed on graphene/poly(ethylene terephthalate) (PET) sheets have excellent advantages over conventional crystalline semiconductor devices formed via simple fabrication: large area, mechanical flexibility, high transparency, and low cost [22]. Even though some studies concerning UV photodetectors fabricated utilizing ZnO QDs have been performed to achieve high UV photocurrent efficiencies [9,10], very few studies on the transparent and flexible ultraviolet photodetectors based on colloidal ZnO QD/graphene nanocomposites formed on PET substrates utilizing the combined advantages of the high sensitivity of the ZnO QDs and the high conductivity of the graphene have been performed.

This paper reports data for transparent and flexible ultraviolet photodetectors based on colloidal ZnO QD/graphene nanocomposites formed on PET substrates. UV–visible absorption and transmittance of the ZnO QD/graphene/PET nanocomposites were performed to investigate their optical properties. Transmission electron microscopy (TEM) measurements were performed to characterize the structural properties of the ZnO QD/graphene/PET nanocomposites. Current–voltage (I–V) and current–time (I–t) measurements were performed to investigate the electrical properties of the bent photodetector based on ZnO QD/graphene/PET nanocomposites.

2. Experimental details

The UV photodetectors based on colloidal ZnO QDs and graphene layers used in this study were fabricated by using the dropping

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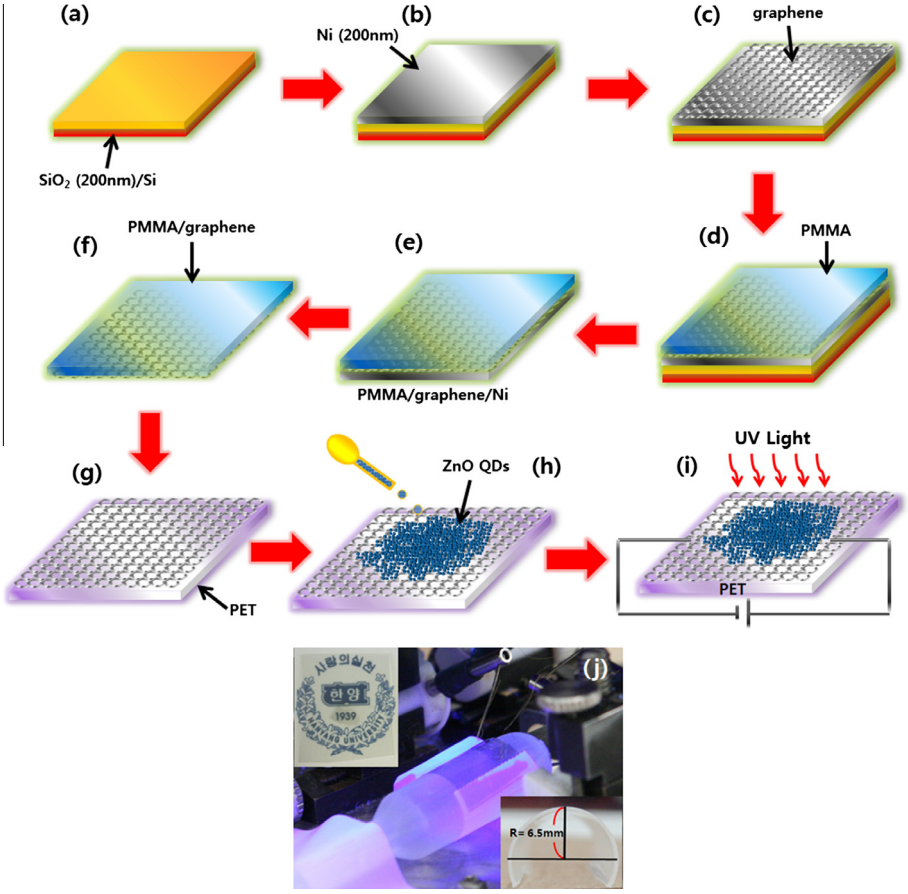

Fig. 1. Schematic diagram of the formation process for the ZnO QD/graphene nanocomposites: (a) SiO_2/Si substrate; (b) Ni formation on the SiO_2/Si substrate by using an e-beam evaporation process; (c) graphene layer formation on the Ni/SiO_2/Si substrate by using the chemical vapor deposition process; (d) PMMA polymer growth on the Ni/SiO_2/Si substrate by using a spin-coating technique; (e) separation of the PMMA/graphene/Ni and the SiO_2/Si substrate in a HF etching solution; (f) separation of the PMMA/graphene and the Ni in a TGF etching solution; (g) transfer from the PMMA/graphene to the PET substrate and dissolvation of the PMMA protecting layer in acetone; (h) dropping ZnO QDs in a DMF solution onto the graphene/PET sheets; (i) UV photodetector fabricated with colloidal ZnO QDs on the graphene/PET sheet. (j) Photographs of the equipment and the device. A blue color emblem of Hanyang University, which was under the photodetector, was clearly seen through the transparent PET films. The sheets of the device were perfectly transparent in the visible light region. The bottom left insert shows a flexible UV photodetector sheet bent at $R = 6.5$ mm, where R is the radius of curvature.

and the attachment methods. The formation and the transfer methods for the graphene sheets on Ni/SiO_2/Si substrates are described elsewhere [23]. Photodetectors based on colloidal ZnO QDs/graphene sheets were fabricated by using the following procedure: (i) synthesis of colloidal ZnO QDs, (ii) synthesis of large-area graphene, and (iii) transfer of the graphene to the substrate.

2.1. Synthesis of colloidal ZnO QDs

Solutions were formed by dissolving zinc acetate dehydrate ($Zn(CH_3COO)_2{\cdot}H_2O$) powder (1 wt%) in precise proportion into a dimethylformamide (DMF) solution. After the $Zn(CH_3COO)_2{\cdot}H_2O$ and DMF solutions had been stirred for 10 min at 27 °C, the $Zn(CH_3COO)_2{\cdot}H_2O$/DMF mixture was heated to 105 °C at a heating rate of 2 °C/min and was then maintained at 105 °C for 5 h. When the mixture had cooled to 27 °C, colloidal ZnO QDs had formed. The detailed syntheses of colloidal ZnO QDs are described elsewhere [24].

2.2. Synthesis of large-area graphene

The SiO_2-coated Si substrates were cleaned by using a routine chemical cleaning procedure of sonification in an acetone and methanol solution and a rinse in deionized water. Then, the chemically-cleaned SiO_2-coated Si substrates were dried by using N_2 gas, followed by the deposition of a 200-nm-thick Ni layer on each SiO_2-coated Si substrate by using thermal evaporation. After the substrates had been mounted onto a susceptor in a custom-built chemical vapor deposition chamber, the substrates were heated to 850–1000 °C and then sustained at that temperature for 30–60 s in a H_2 and Ar atmosphere. As soon as the thermal annealing process had been finished, 50 sccm of methane (CH_4) was introduced into the processing chamber for 10 min. The samples were then cooled to room temperature at a cooling rate of 10 °C/s. The carbon atoms that had segregated from the Ni films formed large-area, continuous graphene sheets during cooling [22].

2.3. Transfer of the graphene to the substrate

The transfer method for the graphene sheets deposited on Ni/SiO_2/Si substrates is similar to that previously reported [22]. After a polymethylmethacrylate (PMMA, MicroChem, 950,000 MW, 9–6 wt% in anisole) layer had been spun coated onto a graphene/Ni/SiO_2/Si substrate, the PMMA/graphene/Ni layer was separated from the SiO_2/Si substrate in a HF etching solution. Subsequently, the Ni layer was removed in a TFG etching solution. The freestanding PMMA/graphene films with hydrophobic surfaces floated on the etching solution and were then transferred to the PET