A prototype Ultraviolet Light Sensor based on ZnO Nanoparticles/Graphene Oxide Nanocomposite Using Low Temperature Hydrothermal Method

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Abstract. A new prototype UV nanosensor using ZnO nanoparticles (NPs)/graphene oxide (GO) nanocomposite (ZnO-NP/GO) on silicon substrate is reported in this paper. The hybrid nanocomposite structure has been developed by an optimized hydrothermal process at low growth temperature (~50 °C). In this hybrid nanosensor, the ZnO nanoparticles act as UV-absorbing and charge carrier generating material, while graphene with its superior electrical conductivity has been used as a charge transporting material. Various nanostructure characterization techniques were intensively utilized including SEM, EDX, XRD, FTIR and UV-VIS. Also, the I-V measurement was employed to evaluate the prototype sensor. The morphological SEM analysis showed that the ZnO-NPs (average diameter of 20 nm) were dispersed evenly on the GO sheets. As well, the EDX spectra confirmed the exact chemical composition of the intended structure. The room temperature UV-VIS measurement revealed an enhanced optical absorption of UV-light at an absorption band centered on 375 nm. The improved optical and electrical properties were observed at an optimum relative concentration of 1:10. Under UV light illumination, the measured I-V characteristic of the prototype detector exhibited a considerable photocurrent increase of the ZnO-NP/GO nanocomposite compared to pristine ZnO nanostructure. These results can be promising for future enhanced UV-sensing applications.
1. Introduction

Zinc Oxide (ZnO) is a II-VI semiconductor with a wide band gap (3.37 eV) and a large excitation binding energy of 60 meV at room temperature [1]. It is a non-toxic material, environmentally friendly and has low production cost [2]. These properties make ZnO a desirable material for many applications such as conductive oxides [1], solar cells [3], nanogenerators [4-7], displays and sensors [8-11]. Various UV sensors based on ZnO nanostructures have been reported in literature because this extraordinary nanostructure can enhance the performance of the devices due to the large surface to volume ratio. This enhancement attracted many application fields including flame detection, environmental studies, medical and communication equipment and space exploration [12,13]. Nevertheless, pure ZnO suffers from low operating speed and weak photoresponsivity drawbacks [14,15]. Meanwhile research in graphene is booming due to many remarkable properties comprising good electrical and thermal conductivity, large specific surface area, high mobility of charge carriers, excellent chemical stability and mechanical strength [16]. However, many applications of materials depend greatly on their intrinsic properties. Hybridization of different materials offers a powerful way to enhance the application of graphene by enabling versatile and tailor-made properties with high performance far beyond those of the individual materials. It is expected that ZnO-graphene or graphene oxide nanocomposite will provide a potential for the development of UV detectors with superior response, flexibility and improved stability.

Development of modern high-performance flexible optoelectronics devices such as UV-photodetectors is subjected to the enhancement of several sensor internal key parameters such as: the sensitivity defined \((I_{\text{photo}} - I_{\text{dark}}) / I_{\text{dark}}\) as percentage, spectral responsivity \((R_o)\) defined as, the photocurrent through the device per unit power of irradiation per active area, external quantum efficiency \((\text{EQE})\) defined as, the number of electron detected per light photon and the response speed, which include two values: rise time (the time taken by the sensor to reach 90 % of the max. photocurrent ) and the decay time (the time taken to reach 10 % of the max. photocurrent) [17].

Up to now, there have been a few reports on the development of UV detectors based on ZnO nanocomposites [18]. However, the performance improvement of the UV detector made of ZnO-graphene nanocomposite is still restricted, which is likely due to the absence of effective morphological and interfacial control between ZnO nanostructures and graphene.

In the nanocomposite reported here, ZnO nanoparticles act as UV absorbing and charge carrier generating materials, while graphene is used as a charge transporting and highly conductive material. Many methods have been developed for the preparation of ZnO nanoparticles including chemical vapor deposition (CVD) [19], vapor phase transport process [20], metal-organic vapor phase epitaxy [21], thermal evaporation [22]. These growth techniques are complicated and the operating growth temperatures are comparatively high (> 350 °C).

The hydrothermal process [23-24] has attracted considerable attention because of its unique advantages, such as simplicity, low cost, low temperature (60-100 °C), high yield and more controllable process [25-27] than previously mentioned methods. In this paper, the fabrication of high quality UV nanosensor made of ZnO nanoparticles onto graphene oxide sheets surface, by a simple hydrothermal process, on silicon substrates is reported. The optical, electrical, morphological and structural properties were intensively investigated to assess the improved physical properties of the fabricated UV sensor. The approach presented herein utilizes the superior optical properties of ZnO nanoparticles with the superior electrical and mechanical properties of graphene nano-sheets targeting large values of sensitivity, spectral responsivity and external quantum efficiency.
2. Experimental

2.1 Hydrothermal Synthesis of ZnO nanoparticles

All chemicals used to prepare ZnO nanoparticles were of analytical reagent grade and used as received without any further purification. The ZnO nanoparticles was synthesized using the traditional hydrothermal process. In a typical initial step of the hydrothermal synthesis, a stock solution of zinc acetate dehydrate Zn(CH$_3$CO$_2$)$_2$.2H$_2$O (5 mM) was prepared in 20 ml ethanol under magnetic stirring. Subsequently, 20 ml of NaOH with concentration varying from 0.2 mM to 0.5 mM in ethanol was added to the solution under stirring for 30 minutes. The solution was then transferred into a water path and maintained at a stable temperature in the range of 50-60 °C for 2-3 hours. The obtained ZnO nanoparticles (ZnO-NP) were afterward washed three times with ethanol and distilled water in order to remove any impurities and then dried in air at 50 °C for 24 hours.

2.2 Preparation of ZnO-NP/GO nanocomposite sensor

ZnO-NP/GO nanocomposite was synthesized using a customary hydrothermal method. The synthesis was started by dispersing of (1 mg/mL) graphene in 10 mL of sulfuric acid and sonicated at room temperature for 10 minutes. Similarly, 0.1 g of ZnO was dispersed and sonicated in 10 mL of distilled water. After that, 10 mL of graphene solution was added to 10mL of ZnO solution and the mixture was sonicated for 5 minutes. A layer of the prepared mixture was then deposited on a cleaned n-Si substrate at room temperature to fabricate the sensor. Finally, a thin layer of Ag was printed over the mixture in a specific pattern as shown in the Figure 1. The Cu electrodes were fixed over Ag using heat and a duct tape.

![Figure 1. Schematic diagram of the ZnO-NP/GO UV sensor](image-url)
3. Results and discussion

The successful preparation of the ZnO-NPs/GO hybrid structure was evaluated using various standard characterization techniques including scanning electron microscope (SEM), electron dispersive X-ray (EDX), ultra-violet visible (UV–VIS) and Fourier transform infra-red (FTIR). These techniques can assess the morphological, optical as well as the structural properties of the hybrid structure. Likewise, the I-V characteristics were utilized to evaluate the behavior of the newly developed nanosensor.

3.1 UV-VIS Spectroscopy

Room temperature UV–vis absorption spectra were carried out for diverse range of ZnO(NPs)/GO concentrations to consider the finest optical properties of the hybrid structure, see Figure 2a. The first UV-vis measurement was performed for the unmodified ZnO-NPs and GO. Typical ZnO UV-vis spectrum revealed two absorption bands centered near the wavelengths of 265 nm and 375 nm. Conversely, the transparent graphene oxide exhibits a weaker absorption band centered nearby 290 nm. On the other hand, the hybrid ZnO-NP/GO with relative concentrations of 1:1000, 1:100 and 1:50 showed no absorption peaks at the considered wavelength range, as shown in Figure 2a. Most probably this is due to the very low concentration of the ZnO-NPs, which acts as an inefficient UV absorber. Oppositely, a clear enhanced absorption band centered at a wavelength close to 375 nm was observed for the samples with ZnO-NPs/GO relative concentrations of 1:10 and 1:1. Among the diverse studied samples, it was observed that these samples with concentrations of 1:10 and 1:1 have the intended optical behavior with a single absorption band centered at a wavelength of approximately 375 nm. Consequently, further investigation on the sample with a concentration of 1:10 was executed and analyzed. Figure 2b displays the spectrum of the hybrid ZnO-NP/GO sample with the concentration of 1:10 accompanied by the unmodified samples of ZnO NPs and GO. The figure revealed a considerable quench in the 375 nm and the 265 nm peak intensities as compared with the unmodified ZnO-NPs. This quench may be attributed to the effective electron transfer from the conduction band of ZnO to GO during the nanocomposite combination, which indicates that the effective charge transfer can reduce the charge recombination and increase the photocatalytic activity of ZnO nanoparticles.
Figure 2a: UV-Vis absorption spectra of all samples with different ZnO-NP/GO ratios

Figure 2b: UV-Vis absorption spectra for GO, ZnO and ZnO-NP/GO (ratio 1:10)
3.2 XRD Analysis

The XRD spectra of ZnO-NP/GO nanocomposite films are shown in Figure 3. All major ZnO reflections are clearly observed at 2θ = 31.6°, 34.4°, 36.4°, 47.3°, 56.8°, 62.7°, 68.3°, 72.5° and 76.8°, which correspond, respectively, to the (100), (002), (101), (102), (110), (103), (201), (004) and (202) planes of ZnO (Joint Committee on Powder Diffraction Standards 36-1451). All peaks in the ZnO-NPs can be indexed to hexagonal wurtzite structure with space group P63mc and lattice parameters of a = 0.3251 nm and c = 0.5208 nm, which indicates that ZnO-NPs are oriented to some extent. Moreover, a quite strong peak appeared at a 2θ value of about 26.5°, which is corresponded to the (002) plane of the GO. Because only one GO peak was observed, this confirms the partial reduction of the GO to a Gr sheet. Additionally, the absence of any extra diffraction peaks of other phases on both XRD patterns demonstrating the phase purity of the nanocomposite. The maximum diffraction peak of the GO was marked with asterisk in Figure 3.

![Figure 3. XRD pattern of ZnO-NP/GO nanocomposite](image-url)
3.3 Morphology and size Analysis

The morphologies and compositions of the ZnO-NP/GO nanocomposite for the sample with a concentration of 1:10 were characterized by a scanning electron microscope SEM equipped with an energy dispersive X-ray (EDX). The EDX analysis of the chemical composition, as-prepared ZnO-NPs/GO nanocomposite on Si substrate, shows that only Zn, O, C and Si signals were detected, see Figure 4a. The existence of only these signals indicates that the hybrid structure indeed made up of Zn, O, C and Si elements. Also, since there is no any signals of the secondary phase or impurity were detected, this may suggest the high-purity of the grown structure. In addition, the morphological SEM analysis showed that the ZnO-NPs with an average diameter of almost 20 nm were dispersed evenly on the GO sheets, see Figure 4b.

![Figure 4](image)

(a) EDX pattern (a) and SEM image (b) for ZnO-NP/GO sample (ratio 1:10)

3.4 FTIR Spectroscopy

The surface modifications of the functional groups of ZnO-NPs/GO after the hydrothermal process were investigated by FTIR spectroscopy. Figure 5 shows the FTIR spectrum of the absorption bands of ZnO-NPs/GO nanocomposite with the relative concentration of 1:10. All oxidized samples exhibit an absorption band centered at 440 cm\(^{-1}\); this is related to the stretching mode of Zn-O bond vibration [1]. The peaks at 3450, 1740, 1680 and 720 cm\(^{-1}\) are assigned to O-H stretching vibration, C=O stretching, C=C bond stretch in alkenes and C-H rock, respectively [2-4]. The acquired FTIR spectrum.
for the sample confirms the existence of ZnO-NPs/GO, which is in agreement with the identical contents obtained by the XRD and EDX analysis.

![Figure 5: FTIR spectrum of ZnO-NP/GO nanocomposite (sample with ratio 1:10)](image)

3.5 I-V characteristics

Figure 6 shows the typical I-V characteristics of ZnO-NPs/GO sensor for the sample with the concentration of 1:10 under dark and UV light illumination. Usually, for the UV detectors, the dependences of photocurrent is defined as the difference between the photoexcited and dark current ($I_{ph} = I_{light} - I_{dark}$). The UV light employed for characterization has a wavelength of 365 nm and power density of 10 mW/cm$^2$ at the bias of 6 V. As observed in Figure 6, the sensor shows an increase in the photocurrent when exposed to the UV light as compared with the dark condition. The sensor response exhibited power-law behavior as a function of the biased voltage with quite good hysteresis properties. The increased in the $n$-type ZnO conductivity may be attributed to the role of intrinsic defects (i.e. native defects), which are a result of the growth conditions and impurity atoms of the ZnO nanostructures under study. Moreover, it is well known that the weak photon absorption and fast carrier kinetics of the GO limit its application for photodetection. This limitation can be overcome by introducing photosensitive nanostructures such as ZnO-NPs to GO for a hybrid nanostructure. However, in spite of extensive research for many years, the role of these intrinsic defects is still not perfectly clear at present. In the dark, the oxygen molecules adsorbed on the surface of ZnO-NPs capture free electrons of the $n$-type semiconductor. As a result, a depletion layer near the nanoparticle surface is produced, resulting in an upward band bending near the surface. Due to the
large surface-to-volume ratio, the adsorption of oxygen significantly reduces the conductivity of the nanowires. UV light illumination with photon energy higher than the energy gap of ZnO generates electron–hole pairs in the ZnO. Subsequently, the holes tend to migrate to the nanoparticle surface along the band bending line and recombine with O$_2$-trapped electrons, thus releasing oxygen from the surface. Therefore, adsorbed oxygen and the photogenerated hole contribute to local charge neutrality and free up the photogenerated electrons, which enhances the conductivity of the sensor.

![Figure 6: I–V curves of the ZnO-NR/GO (ratio 1 detector in darkness and in UV illumination of 10 mW/cm$^2$.](image)

4. Conclusions

The synthesis of high quality hybrid ZnO-NPs/GO nanocomposites via simple and cost-effective method by mixing of GO solution and ZnO-NPs solution was achieved and characterized successfully. The operation of an efficient prototype sensor based on ZnO-NPs/GO nanocomposite at room temperature was also demonstrated confidently. The UV sensor of the hybrid nanocomposite was considerably enhanced under the UV light illumination. This enhancement is mainly attributed to the adsorbed oxygen on the ZnO-NPs surface and the photogenerated holes, which ultimately can contribute to the local charge neutrality and free up the photogenerated electrons thereby enhancing the conductivity of the sensor. The sensitivity of the fabricated detector is comparable to the conventional metal oxides-based detectors in the literature. The present study provides a distinctive platform for designing metal/wide band gap semiconductor/graphene oxides nanocomposites to enhance the UV detection.
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