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Ultraviolet, visible, and near infrared photoresponse properties of solution processed graphene oxide

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ABSTRACT

The photoresponse properties of solution processed graphene oxide (GO) ranged from ultraviolet–visible–near infrared regime are studied. Photoelectrochemical results indicate that the as-prepared GO devices have excellent sensitivity, high-speed and superior reproducibility as a visible and near infrared photodetector. Especially, the responsivity and external quantum efficiency are found to be about 95.8 mA/W and 26.2%, respectively, for incident wavelength of 455 nm at 0.8 V bias voltage. Resulting from the degradation of GO under UV irradiation, the GO devices exhibit unstable photoresponse performance, as well as high UV photosensitivity.

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1. Introduction

Graphene is considered to be promising building block for electronic and optoelectronic devices due to its special geometry, high carrier mobility, zero band-gap, linear energy dispersion relation, and remarkable photon absorption over a wide wavelength range from ultraviolet to the visible and infrared regimes [1–7]. Recently, the photoresponse properties of graphene have been wildly investigated [1], and a substantial amount of interesting results, such as ultra-broad bandwidth [8,9], error-free high-speed optical communication [10], plasmonic resonant enhancement [11], position dependence [12], hot-carrier dominated transport [13,14] were reported. Unfortunately, difficulty in synthesizing high-quality mass produce graphene inhibits its further application.

As an oxidation product of graphene, graphene oxide (GO) is a layered materials consisting of graphene sheet decorated with oxygen in the form of carboxyl, hydroxyl or epoxy groups [15,16]. There are many interesting consequences of the unique structure such as photoluminescence, tailored electronic and optoelectronic properties [17–19]. In addition, the noticeable technological advantages of films prepared from solution processed GO, including ease of material processing, low cost of fabrication, mechanical flexibility, and compatibility with various substrates make them more

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attractive for large-area devices. GO based thin films have been successfully used as transparent and flexible materials for electronic and optoelectronic devices [20–23]. Most recently, Ho et al. reported that GO could be an attractive candidate for near infrared photodetector [24]. However, the photoresponse properties of GO under ultraviolet and visible irradiation have not been addressed. Here, the photoresponse performances of solution processed GO ranged from ultraviolet–visible–near infrared regime are studied. A comparison of the different properties has also been discussed.

2. Experimental details

Graphene oxide was synthesized from graphite powder by the modified Hummers' method using a mixture of H_2SO_4 , NaNO₃, and KMnO₄ [25]. The morphologies and chemical structures of the solution processed GO were characterized using atomic force microscopy (AFM, SPI3800N) and Fourier transform infrared spectrum (FTIR, PE Spectrum One). The morphologies of the GO device were investigated using scanning electron microscopic (SEM, JEOL, JSM-6360).

Photoelectrochemical test systems were composed of a CHI 660D electrochemistry workstation, an illumination source, and a homemade three-electrode cell using platinum as counter electrode, saturated calomel electrode as reference electrode, and Na_2SO_4 (0.5 M, 98.0%) as electrolyte. The working electrode was prepared on glassy carbon electrode. The GO solution (0.5 mg/ml) was dropped onto the glassy carbon electrode, dried at 60 °C for

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Fig. 1. In the front of (a) is AFM image showing surface morphology of GO thin film, the red line and the blue line are the height profiles of the (I) and (II). (b) FTIR spectra of solution processed graphene oxides. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.)

several hours. GO sensor was illuminated under a diode laser with three kinds of wavelengths (λ = 455, 655, and 980 nm, respectively) at the spot size of raw beam around 1 mm, as well as a high pressure UV lamp with a cut-off filter with the radiation from 280 nm to 350 nm.

3. Results and discussions

To investigate the quality of the solution processed GO flakes, the topography and chemical structures of raw GO sheets were characterized using AFM and FTIR, respectively. Fig. 1(a) is the typical AFM image of GO sheet onto 300 nm SiO₂/Si substrate, it is clearly indicated that the sheet has very clean surface with a uniform thickness across the lateral dimensions. The thickness distribution for GO sheet is obtained by scanning a substrate area of $1 \,\mu m \times 1 \,\mu m$ and the height profiles corresponding to the dashed line-cut are shown in the right frame. Large nanosheet with uniform thicknesses about 1-2 layer can be clearly seen from the height profiles. Further FTIR spectrum (Fig. 1(b)) is recorded to confirm the chemical structure of as-prepared sample, and the following functional groups are identified in the GO sample [26]: the strong peak of 1730 cm⁻¹ attributes to the C=O stretching vibrations of the –COOH groups, the peak of 1620 cm⁻¹ assigns to the C=C from unoxidized sp² CC bonds, the peaks at 1384 and 1224 cm⁻¹ determine to the C-OH stretching vibrations, and the other peaks are due to OH, C–O and C–O–C stretching at 3392, 1052 and 856 cm⁻¹, respectively.

Photoelectrochemical tests were performed in a $0.5 \text{ M} \text{ Na}_2\text{SO}_4$ electrolyte using a typical three-electrode electrochemical cell configuration. The schematic setup is shown in Fig. 2. The glassy carbon loaded on with the as-prepared GO flakes were used as the working electrode. From the inset SEM image of the surface of working electrode, it is clearly observed that the loading GO flakes were uniform distribution and presenting a warping appearance caused by the hydrophobic nature of glassy carbon [27]. Typical *I–V* characterizations of the photodetector based on GO devices in the dark (squares) and under illumination (circles) at 980 nm with 240 mW are exhibited in Fig. 3(a), which is shown that the



Fig. 2. A schematic diagram of the photoelectrochemical test systems with SEM image of GO on glassy carbon electrode.

current under illumination is lager than that in the dark when the voltage is sweeping ranged from 0 V to 0.8 V. The current changing under with different illumination intensities is also investigated. Fig. 3(b) represents the photoresponse for one of the devices under a bias voltage at 0.8 V, where all of the light-state current with various illumination intensities are efficiently enhanced and the enhancement is increased with the intensity increase. The photoresponse performance of the GO sensor is mainly attributed to the separation of the photo-generated electron-hole pairs under an electric field. When the intensity of the light is higher, more photons are absorbed by the GO sensor and generate more exciton, resulting in a larger photocurrent.

In order to demonstrate the reproducibility of the data with time, the illumination source is turned on and off at a given interval. As shown in Fig. 3(c), the current value increases immediately after switching on the light and it reaches its original quickly after switching off, confirming the excellent behavior of the device under continuous cycling. Various illumination sources are used to further expose this effect in detail. From Fig. 3(d), it is observed that the current changes as the wavelength of 980 nm as illuminant and the shorter of the wavelength the larger of current changed. All of above results imply that the GO can be acted as a photodetector for visible, and near infrared lights.

The performances of GO sensor are evaluated based on the parameter of current responsivity (R_{λ}) and external quantum efficiency (EQE). Thereinto, current responsivity is defined for the photocurrent generated per unit power of the incident light on the effective area of a photodetector, and the EQE is expressed as the number of electrons detected [28–30]. The higher values of R_{λ} and EQE mean high sensitivity. R_{λ} and EQE can be calculated as $R_{\lambda} = I_{\lambda}/(P_{\lambda}S)R_{\lambda}$ [31,32] and EQE = $hcR_{\lambda}/(e\lambda)$ [33,34], where, I_{λ} represents the magnitude of current change between light illumination on and off, P_{λ} is the light intensity, *S* indicates the effective illuminated area, *h* is the Planck's constant, *c* is the velocity of light, *e* is the electronic charge, and λ represents the wavelength of the incident light. According to the experimental results, all of the calculated parameters are listed in Table 1. Current responsivity of GO devices is 95.8 mA/W, 20.8 mA/W, and 17.5 mA/W, respectively,

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