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Full Length Article

Single-layer graphene/titanium oxide cubic nanorods array/FTO heterojunction for sensitive ultraviolet light detection☆

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ABSTRACT

In this study, we report on the fabrication of a sensitive ultraviolet photodetector (UVPD) by simply transferring single-layer graphene (SLG) on rutile titanium oxide cubic nanorod (TiO_2NRs) array. The cubic TiO_2NRs array with strong light trapping effect was grown on fluorine-doped tin oxide (FTO) glass through a hydrothermal approach. The as-assembled UVPD was very sensitive to UV light illumination, but virtually blind to white light illumination. The responsivity and specific detectivity were estimated to be 52.1 A/W and 4.3×10^{12} Jones, respectively. What is more, in order to optimize device performance of UVPD, a wet-chemistry treatment was then employed to reduce the high concentration of defects in TiO_2NRs during hydrothermal growth. It was found that the UVPD after treatment showed obvious decrease in sensitivity, but the response speed (rise time: 80 ms, fall time: 160 ms) and specific detectivity were substantially increased. It is also found that the speicific detectivity was imporoved by six-fold to 3.2×10^{13} Jones, which was the best result in comparison with previously reported TiO_2 nanostructures or thin film based UVPDs. This totality of this study shows that the present SLG/TiO_2NR/FTO UVPD may find potential application in future optoelectronic devices and systems.

1. Introduction

Photodetectors, in particular ultraviolet photodetector (UVPD) working in UV light region, are receiving increasing research interest lately due to its potential application in a variety of fields including space communication, environmental monitoring, and military surveillance [1–4]. To date, a huge number of semiconductor materials with wide band gap such as III–VI group (e.g. GaN, AlN), II–VI group (e.g. ZnS and CdS), and some metal oxides (ZnO, SnO_2, and TiO_2) have been extensively investigated for fabrication of detectors for sensing UV illumination [5–8]. Among these wide-bandgap semiconductors, TiO_2 nanostructures in one-dimensional fashion (nanorods, nanotubes, nanosheets, *etc.*) are regarded as ideal candidates for realization of highly sensitive UVPD owing to their outstanding chemical, physical and optical properties [9–11]. To date, a number of UVPDs with good performance have been demonstrated. For example, Yang's group reported a double-walled carbon nanotube/TiO_2 nanotubes array heterojunction UVPD. By virtue of the dimensionality difference effect, the device exhibited a high photocurrent-to-darkcurrent ratio and photoresponse at a small bias voltage [12]. Recently, Wang et al. developed an UVPD by directly transferring different layers of TiO_2 nanorods (TiO_2NRs)-assembled cloth onto TiO_2NRs array [13], which was synthesized on conducting FTO coated glass. This devices showed outstanding UV selectivity with a response speed less than 0.3 s. In addition, the quantum efficiency of such an UVPD was as high as 46%. Despite these progresses, the majority of the TiO_2 nanodevices inevitably suffers from slow response speed, high darkcurrent, and poor reproducibility [14,15].

In order to optimize the device performance of TiO_2 based photodetectors, many groups have resorted to metal-semiconductor-metal (MSM) structures instead. Comparatively, the MSM device geometry is usually characterized by superior performance in term of high speed, low dark current and facile fabrication process [16]. What's more, the MSM structure can effectively suppress carrier recombination and enhance carrier transport [17], which is highly beneficial for a high on/off ratio during UV light sensing. Herein,

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we report a new MSM UVPD by replacing metal with graphene, a very good electrode material with high electrical conductivity and transparency, and ultrahigh carrier mobility [18]. The combination of graphene and TiO_2NRs array with strong light trapping effect can simultaneously take advantage of the synergistic effects in photon harvesting and carrier transport, and thus it will greatly enhance the photosensitivity of the device. In order to reduce the defect concentration in the TiO_2NRs, we then adopted an effective wet-chemistry approach [19]. It was found that the SLG/TiO_2NRs/FTO UVPD device after treatment witnessed a great increase in on/off ratio, specific detectivity and response speed, even though the responsivity was reduced simultaneously. This study suggests that the present SLG/TiO_2NRs/FTO UVPD will have great potential for future optoelectronic device application.

2. Results and discussion

The scheme in Fig. 1(a) illustrates the step-wise procedure to fabricate the SLG/TiO_2NRs/FTO nanoheterojunction UVPD. The rutile cubic TiO_2NRs array was grown on FTO glass by a modified hydrothermal method [20]. After growth, a layer of graphene supported by polymethylmethacrylate (PMMA) was directly transferred onto the TiO_2NRs array by an aqueous method [21]. At last, Ag paste was placed directly onto the graphene and FTO side. For convenience, the as-fabricated nano-heterojunction was then assembled onto a printed circuit board (PCB). Fig. 1(c) shows a typical digital camera picture of the SLG/TiO_2NRs/FTO on a PCB, in which the two electrodes are connected to the PCB by wire bonding. Due to their apparent difference in contrast, all components including SLG, FTO and TiO_2NRs can be easily discriminated [Fig. 1(b)].

To check the quality of both materials, the morphology, crystallinity and chemical composition of both graphene and cubic TiO_2NR were examined. Fig. 2(a) shows the Raman analysis of the chemical vapor deposition (CVD) derived graphene, from which one can find two strong peaks: one at ~1511 cm^{-1} (G-band) and another at ~2633 cm^{-1} (2*D*-band). Additionally, there is also a very weak peak at 1346 cm^{-1}, which can be attributed to the *D*-band. The intensity ratio of 2.12 (I_{2D}/I_G) and the relatively weak *D*-band corroborates the single-layer feature with a little quantity of defects [22,23]. The Fig. 2(b) corresponds to scanning electron microscopy (SEM) image of the SLG at Si/SiO_2 wafer. Obviously, there are some wrinkles which were usually unavoidable during the transfer of graphene at water [24]. The representative top-view SEM image of the TiO_2NRs was shown in Fig. 2(c). It's clear that all the TiO_2NRs have a well-defined rectangular cross-section. The diameters were in the range from 50 to 140 nm, with an average value of about 100 nm [Fig. 2(d)]. According to the high-resolution transmission electron microscopy (HRTEM) image and the selected area electron diffraction (SAED) pattern shown in Fig. 2(e), the as-prepared TiO_2NRs were single crystalline of rutile phase, with a preferred growth orientation along the [001] direction [25].

Fig. 3(a) plots the *I–V* curve of the SLG/TiO_2NRs/FTO UVPD. Obviously, it displays a typical nonlinear behavior, as often in conventional MSM structure. Given the negligible contact barrier of both the Ag/SLG and Ag/FTO contacts (Fig. S1, Supporting Information), such a nonlinear *I–V* characteristics can be exclusively attributed to two Schottky junctions assembled in a back-to-back fashion [inset of Fig. 3(a)]: one is formed at FTO/TiO_2NRs interface, and the other one at the SLG/TiO_2NRs interface, which is different from other graphene-like 2D material-semiconductor heterojunction based devices [26,27]. Our optoelectronic analysis finds that this SLG/TiO_2NRs/FTO nanoheterojunction is virtually blind to white light illumination, but exhibits pronounced sensitivity once it was shined by UV illumination with wavelength of 365 nm [Fig. 3(b)], suggesting potential application for UV detection. Fig. 3(c) compares the photoresponse of three heterojunctions assembled from cubic TiO_2NR with different diameters. It is apparent that when the TiO_2NR diameter gradually increases from 100 to 180 nm, the photocurrent on the contrary decreases from 3.83 to 2.65, and 0.78 mA at a bias voltage of −5 V. This relatively high photoresponse for 100 nm TiO_2NR device is associated with the better light absorption capability, as we will discuss later. Further study found that the photoresponse of the UVPD is determined by the UV light intensity as well. Fig. 3(d) shows the *I–V* curves of the device under UV light radiation with varied intensities, from which one can observe that the photocurrent increases gradually with the increase of the UV intensity.

Besides diameter of TiO_2NR and wavelength of incident light, the photoresponse of the present nanoheterojunction UVPD is also found to be determined by bias voltage. Fig. 3(e) plots the photoresponse of the device at different negative bias voltages. At all bias voltages, the UVPD device showed good UV photosensivity when the 365 nm light was alternately switched on and off. Moreover, with the increase of the bias voltage (absolute value), the photocurrent will increase monotonically, possibly due to the increase in drift velocity and suppression in recombination possibility [28,29]. This bias voltage dependent photocurrent is slightly different from the case at forward bias voltage, under which the present device similarly shows pronounced sensitivity to UV illumination. Nonetheless, the darkcurrent is relatively higher than that at negative bias voltage (Fig. S2). In light of this, negative bias voltage will be applied on the UVPD in the following optoelectronic characterization. As a matter of fact, the obvious photoresponse at negative bias voltage can be explained by the energy band diagram shown in Fig. 3(f). Due to the different Schottky barrier heights (SBH), the two back-to-back Schottky junction was asymmetric, with a relatively larger built-in electric field at SLG/TiO_2NRs interface than that at FTO/TiO_2NRs. When applied by a negative bias voltage (the graphene side is negatively biased and the FTO side is positively biased), the SBH at SLG/TiO_2NRs interface will increase, while that of FTO/TiO_2NRs heterojunction will on the contrary decrease, as shown by red line. In this case, the electrons were difficult to flow from the TiO_2 side to the graphene in dark condition, leading to a low dark current. Upon UV light illumination, the photo-generated electron and holes could be separated by the electric field in opposite directions, forming photocurrent in the circuit.

In order to unveil the underlying reason for the aforementioned diameter dependent photosensitivity, the optical properties of TiO_2NRs array with different diameters under 365 nm UV illumination was then examined. Fig. 4(a–c) illustrate the distribution of electric field energy density distribution and the corresponding SEM of the TiO_2NRs with varied diameters. Obviously, the electric field distributions of TiO_2NRs array without SLG coverage (W/O) is almost identical to that of TiO_2NRs with SLG coverage (W/), consistent with the high transparency of single layer graphene [30]. Meanwhile, all the cubic TiO_2NRs display very good light trapping effect: That is, the incident photon energy will be efficiently confined within the nanostructures. The hot spot with high field intensity is about hundreds of nm below the SLG/TiO_2NRs interface, which is beneficial for the photosensing process. Such a light trapping effect is further confirmed by the simulated absorption spectrum of both TiO_2NRs array and its planar counterpart. As displayed in Fig. 4(d), in comparison with the cubic TiO_2NRs array, the planar TiO_2 shows relatively weak light absorption in the UV region due to the strong reflectance. Furthermore, among the three kinds of TiO_2NRs, the 100 nm TiO_2NR shows the highest light absorption than planar TiO_2 at around 365 nm, which is in good agreement with the previous result.