The transparent Schottky junction of reduced graphene oxide/SnO$_2$ nanoarrays towards enhanced broadband photoresponse

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Abstract: The rGO/SnO$_2$ nanoarrays (rGO/SnO$_2$ NAs) Schottky junction is synthesized by a series of RF magnetron sputtering, hydrothermal and electrochemical deposition. The unique transparent junction exhibits the broadband photoelectric responses from the ultraviolet to visible light. As shown, the proper rGO/SnO$_2$ NAs display highly transparency of about ~60% and dramatically enhance photoelectric conversion of about ~100 times than that of the initial Schottky junction. Finally, the mechanism of the Schottky junction is investigated.

1. Introduction
Solar energy [1], as a renewable and clean energy source, is regarded as the ideal replacement of the fossil energy and is used in series of construction, such as solar thermal systems [2], etc. Especially the transparent solar cells, due to the bright prospect for integrating into the windows of buildings [3], etc., would be reported as the most popular issue in current researches.

Nowadays, reduced graphene oxide (rGO) has attracted numerous attentions on the fields of energy storage or electronics, etc. [4-5], owning to the high specific surface area and high electron mobility. Particularly with the remarkable photoelectric performance, the rGO has attracted lots of attentions for applying in the field of transparent conducting electrodes [6]. Meanwhile, with the wide band gap and stable physical-chemical properties, the transparent oxide semiconductors, like ZnO [7] and MoO$_3$ [8], etc., have caused a lot of interests, and are considered as promising candidates for the photoelectric devices, such as Li groups have fabricated the TiO$_2$/ZrO$_2$ mesoscopic layer based perovskite solar cells [9], etc. There, the n-type SnO$_2$, with a wider band gap of 3.6 eV and high transparency in the visible light [10], obtains the great potential in the fields of transparent photoelectric devices. For instance, Xu groups have designed size-controllable SnO$_2$ to explore the gas-sensing properties [11], etc. It is worth noting that, compared to the 2D SnO$_2$ films, the orderly 1D SnO$_2$ NAs obtains the superior photoelectric or optical performance, which could be ascribed to the large specific surface area and efficient pathway for carrier transport, and are particularly beneficial to photoconductivity [12].

Nevertheless, restricted by the rapid recombination of photo-generated carriers and low solar energy conversion, the application of the single material, especially the single SnO$_2$, presents lots of hurdles, and series of strategies have been reported to solve these problems, for instance p-n junctions [13], and heterophase junctions [14], etc. Among these, the Schottky junction is considered as an efficient approach, because it can enhance the photoelectric properties via providing a built-in electric field to accelerate the separation and transportation of the photon-generated carriers. Therefore, the...
SnO$_2$ based Schottky junctions devices have been reported as the hot topic by large numbers of literatures, such as Chetri groups have fabricated the fast response Schottky UV photodetector of Au/Glad-SnO$_2$ nanowire arrays [15], etc. There, the combination of SnO$_2$ NAs and rGO could not only enhance the light harvesting performance, but also improve the photoresponse from the ultraviolet (UV) to visible (VIS) light.

Herein, we have systematically prepared a transparent Schottky junction photoelectronic device via RF magnetron sputtering, hydrothermal and electrochemical deposition method. The results show that the as-prepared transparent photoelectronic device exhibits highly transparency of about ~60% and remarkable photoelectric conversion of 100 times than that of the initial Schottky junction. In addition, the mechanism of the improved photoresponse is discussed.

2. Experiment

2.1 Preparation

**Preparation of the SnO$_2$ NAs:** firstly, a dense SnO$_2$ seed layer was deposited on the FTO glass via RF magnetron sputtering. The cavity background vacuum was 6×$10^{-4}$ Pa, sputtering power was 130W, sputtering temperature was 400°C, sputtering time was 10min. Then, the SnO$_2$ NAs were prepared by a hydrothermal method. Detailed, 2.5mM SnCl$_4$:5H$_2$O, 0.2M (NH$_4$)$_2$CO and 1.5mM EDTA-Na$_2$ were dissolved in deionized water with the presence of 3% of 37% hydrochloric acid. Finally, the solution was transferred into 100 ml Teflon-linked autoclave and the substrate prepared above was immersed into the solution. The autoclave was placed in an oven at 120°C for 48h.

**Preparation of the rGO/SnO$_2$ NAs:** Graphene oxide was synthesized by the improved Hummers’ method. The graphene oxide is dispersed by freeze-dried to obtain the graphene oxide powder. Further, the electrolyte for electrodeposition of rGO was 0.3M graphene oxide and 0.1M LiClO$_4$ mixture solution with -1.2V (vs Ag/AgCl) for 5, 10, 20 minutes at room temperature. The as-prepared samples with different ratio of the rGO were marked as rGO/SnO$_2$-1, rGO/SnO$_2$-2, rGO/SnO$_2$-3, respectively.

2.2 Characterization

Micromorphology and microstructure of the samples were investigated by field emission scanning electron microscopy (FESEM, Hitachi S-4800, Japan) and transmission electron microscopy (TEM, JEM-2100, Japan). The crystallographic information and phase were characterized by X-ray diffraction (XRD, Bruker AXS D8-discover, Germany). Optical properties were determined from the ultraviolet-visible spectroscopy absorption (U-3900 Hitachi). The photosresponse was evaluated by electrochemical workstation (ZAHNER IM6, Germany). The illumination was obtained by a xenon lamp at 100mW/cm$^2$. The photocurrent-voltage properties were performed on Keithley 4200.

3. Results and Discussion

As revealed in Figure 1a, the TEM displays that the rGO thin films are multilevel and wrinkled. Figure 1b illustrates the XRD of the rGO/SnO$_2$ NAs Schottky junction on the FTO substrate. There, the intensive diffraction peaks at 26.6°, 37.9°, 51.7°, 57.9° and 65.0° correspond to the (110), (111), (211), (022) and (112) crystalline planes of the SnO$_2$ (PDF#71-0652). As shown, the narrow FWHM (full width at half maximum) and the strong diffraction peaks indicate the high crystal quality of the SnO$_2$ film. Further, the characteristic peak at 23° is the typical diffraction peak of the rGO. Moreover, the other diffraction peaks mainly originate from the FTO substrate. Therefore, results of the XRD demonstrate that the successful fabrication of the rGO/SnO$_2$ NAs.
Figure 1 (a) The TEM of the rGO film, (b) the XRD of the rGO/SnO$_2$ NAs Schottky junction.

Figure 2 The SEM of the rGO/SnO$_2$ Schottky junction at different stage, (a) the SnO$_2$ NAs, (b) the rGO, (c) the rGO on SnO$_2$ NAs, (d) the cross section of the rGO/SnO$_2$ Schottky junction.

Figure 2a reveals the highly dense, orderly and uniform SnO$_2$ cubic nanoarrays. As shown, the diameter of nanoarrays is about ~40nm, which can be deemed as the efficient pathway for charge carrier transport and the effective electrical contact between the SnO$_2$ NAs and rGO film. Figure 2b is SEM of the rGO deposited on FTO substrate. As revealed, the ultrathin rGO films with the decent flexibility are a typical two-dimensional material, which is beneficial to improve the optical transmittance. In this work, the rGO film was synthesized by simultaneously electrochemical depositing and reducing GO films on the top of the SnO$_2$ NAs. Figure 2c displays the rGO films deposited on the SnO$_2$ NAs. There, the SnO$_2$ NAs covered by the rGO film could be observed clearly, which indicates that the rGO/SnO$_2$ Schottky junction obtains a high transparency. Figure 2d illustrates the cross section of the as-prepared sample, which indicates that the transparent Schottky junction is formed by the rGO films and SnO$_2$ NAs with length of about ~200 nm.

Figure 3a presents the optical transmittance of the rGO/SnO$_2$ NAs with different deposition durations. There, the maximum transmittance of about ~80% is achieved by 5 min deposition. It’s obvious that the transparency decreases with the increased deposition. As revealed, the rGO/SnO$_2$-2 with 10 min deposition displays a transmittance of about ~60% in range of 400-800 nm, which is considered as a high transparency for such Schottky junction (inset in Figure 3a). Further, the optical absorptions of the pure SnO$_2$ NAs and the rGO/SnO$_2$-2 are displayed in Figure 3b, there, the sharp absorption edges of the SnO$_2$ NAs and rGO/SnO$_2$-2 are around ~350nm. By calculation, the optical bandgap of the as-prepared rGO/SnO$_2$ is about 3.297 eV (inset in Figure 3b), and corresponds to the intrinsic bandgap of the SnO$_2$. It’s interesting that the rGO/SnO$_2$ NAs exhibit indiscriminate optical absorption in visible light, so that the bandgap of rGO/SnO$_2$ NAs could still maintained at 3.297 eV (inset in Figure3b), which is another advantage for the rGO Schottky junction.
Figure 3 (a) The optical transmittance of the different samples. Insets: photograph, (b) UV-vis absorption spectra of the SnO$_2$ NAs and rGO/SnO$_2$-2. Insets: the optical bandgap.

Figure 4 the photovoltaic conversion properties of the different rGO/SnO$_2$ Schottky junctions.

Figure 4 is the photovoltaic conversion properties of the different rGO/SnO$_2$ NAs under 0 V bias. The photocurrents of rGO/SnO$_2$-1, rGO/SnO$_2$-2 and rGO/SnO$_2$-3 are $2.81 \times 10^{-9}$, $3.67 \times 10^{-7}$ and $3.10 \times 10^{-7}$ A, respectively. It is worth noting that the photocurrent runs placidly during the cycle process, which indicates that the transparent photoelectric device owns a good repeatability. As revealed, with the increase of the rGO, the photovoltaic response of the rGO/SnO$_2$ NAs exhibits an obvious improvement of about ~100 folds, and then decrease. There, the rGO/SnO$_2$-1 demonstrates a lower photocurrent, which is ascribed to that the little rGO would lead to the partial interface Schottky junctions. Then, with the increasing of the rGO, the rGO/SnO$_2$-2 reveals the best performance due to the formation of the high-quality interface Schottky junctions. However, the excess rGO (rGO/SnO$_2$-3) could not only lead a lower transparency, but also cause the decreased photocurrent.

The as-prepared heterojunction demonstrates an excellent rectifying behavior (Figure.5a), which is ascribed to the formation of the Schottky junction between the rGO and SnO$_2$ NAs. Figure 5b is I–V around the origin. As revealed, an open circuit voltage is about ~0.17 V and a short circuit current is about ~0.57 A, which indicates the great photovoltaic effect of the transparent Schottky junctions.

Figure 5 (a) I-V of the rGO/SnO$_2$-2, inset: the log curve, (b) the curve in detail around the origin.
As shown in Figure 6a, the as-prepared sample is a typical Schottky junction that fabricated by the rGO and SnO$_2$ NAs. Figure 6b illustrates the bandgap diagram of the Schottky junction under illuminations. Herein, the electrons in the SnO$_2$ valence band would be excited to form the electron-hole pairs. Driven by the built-in electric field, these photon-generated electron-hole pairs would separate and transfer to the rGO continuously, which could enhance the photocurrent of the sample efficiently. Due to the higher charge carrier mobility of the rGO, the recombination of the photon-generated electron-hole pairs would decrease dramatically, which is benefit for enhancing the photoelectric performance. In addition, the SnO$_2$ could hardly use the visible light (Figure 3b) due to the wide bandgap of 3.297 eV, but with the indiscriminate optical absorption of the rGO in visible light, this sample could enhance the light capture to improve the photoelectric conversion efficiently.

4. Conclusion

In summary, we prepared the transparent rGO/SnO$_2$ NAs Schottky junction by an efficient and simple method of hydrothermal and electrochemical deposition. By calculation, the as-prepared transparent rGO/SnO$_2$ NAs Schottky junction exhibits a high transparency of about ~60% and excellent photoelectric performance enhancement of about ~100 folds than that of the initial Schottky junction, which is attributed to the formation of the Schottky junction between the rGO and the SnO$_2$, that the nano-arrays could provide a efferent transmission channel for electrons transferring, and the rGO with the indiscriminate optical absorption in the visible light could improve the solar energy utilization.

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