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Abstract.

Graphene is a promising material in the field of solid-state gas sensors due to the unique two-dimensional structure. Here, we have shown by fabricating graphene/ZnS-CdS hetero-nanowire structure, the gas sensor sensitivity has a two-fold increase to 20% under 15 ppm gaseous concentration compared to a 10% response in pristine graphene. Spectroscopy and microscopy analysis indicate that the semi-conducting ZnS-CdS hetero-nanowires are 2 nm wide and densely packed on top of graphene. By combining UV illumination, the device approaches a fast response/recovery and high gas sensitivity, thus has a potential to be used in a detection of wide range of gases.

Introduction

Due to the larger surface/volume ratio and low electrical noises, graphene has shown outstanding gas sensing properties [1–4] and even the single molecule detection [5]. Through modifying the carrier density of graphene, the absorbed gaseous molecules perform as electron acceptors or donors and hence change the electrical conductivity of the graphene [4]. Various p- and n-doped gas molecules have been systematically studies to understand the physical sensing mechanism of graphene and it is found that p-doped gases result in an increase in the conductance of the graphene, while the n-doped gases lead to a decrease in the conductance [5]. Among the gas molecules, NO₂ has a rather high charge transfer and exhibits good sensitivity to pristine graphene, thus is commonly used in the electrical gas sensing measurements.

Semi-conductor nanowires have attracted considerable concerns owing to their potential applications ranging from electronics to biology [6–8]. Due to the large surface area and the semiconductor property, they have shown excellent gas sensing performance in a variety of gases [9,10]. In
this work, through the bottom up approach, the gas sensing devices were fabricated by physically attaching well aligned ZnS-CdS nanowires on graphene surface and the electrical gas sensitivity measurements were performed to investigate the modification of the sensitivity. The result indicates that, compared with the response of 10% in pristine graphene, the electrical response of the fabricated devices have shown a two–fold increase to ~20% under the gaseous concentration of 15 ppm. Meanwhile, by employing the UV light improved desorption, the devices show a fast recovery to the initial states. Therefore, the demonstrated gas sensor has the potential to be used in a wide range of gas sensing applications.

**Experimental Details**

2.1 Materials

In this study, large scale graphene synthesized by chemical vapor deposition (CVD) method were used and transferred to a SiO$_2$/Si substrate [11]. The ZnS-CdS hetero-nanowires were synthesized by using a wet-chemical technique in organic medium [12] and the transfer of the ZnS-CdS hetero-nanowires onto graphene surface was done by using a Langmuir–Blodgett film technique [13].

2.2 Device fabrications

Electrical contacts on graphene, as shown in Figure 1a, were fabricated by using a photolithography technique [14], and 10 nm Ti and 150 nm Au were deposited using evaporation followed by a metal lift-off process in acetone. The device after the transfer of the Langmuir-Blodgett self-assembled ZnS-CdS hetero-nanowires is shown in Figure 1b.

2.3 Characterizations

The optical observation, atomic force microscopy, Raman spectroscopy and light absorption spectroscopy were performed in a Olympus light optical microscope, a Bruker Multimode 8 AFM, a Renishaw inVia Raman spectroscopy with 532 nm excitation and a Shimadzu UV-VIS Spectrometer, respectively. The photoconductivity measurement was done by using a DH-2000 Ocean UV-VIS-NIR light source and a Keithley 6430 sub-femtoamp remote sourcemeter. The electrical sensitivity characterization was carried out in a Keithley 6430 sub-femtoamp source-meter in a gas chamber and a mixture of N$_2$ and 15 ppm NO$_2$ was chosen the target gas in the measurement.

![Figure 1](image.png)

**Figure 1.** Light optical microscopy images of (a) graphene with electrical contact, (b) after the ZnS-CdS hetero-nanowires transfer.

**Result and Discussion**

Before and after the ZnS-CdS hetero-nanowires deposition, Raman spectroscopy was carried out to investigate the possible structure modification of the graphene, as shown in Figure 2. It can be seen that both of the spectra consist in two main peaks: 2D peak at at 2700 cm$^{-1}$ and G peak at at 1580 cm$^{-1}$. The sharp 2D peak combing the low intensity of the D peak (at 1350 cm$^{-1}$, that shows the defect density) indicates that the ZnS-CdS nanowires are physically absorbed on graphene surface and no
chemical bond forms, thus the ZnS-CdS hetero-nanowires functionalized graphene should maintain the superior properties of the graphene.

![Figure 2. Raman comparison of the pristine graphene (black) and functionalized graphene (red).](image)

The ZnS-CdS hetero-nanowires were prepared by a wet chemical approach [12], where the structure sketch is shown in the inserted image of Figure 3. The hetero-nanowires consist of periodic constituent blocks of semiconductor ZnS and CdS. The absorption property in solution status was investigated and shown in Figure 3. UV-VIS absorption spectrum exhibits that the absorption onsets are at 340 nm and 440 nm, corresponding to the ZnS bandgap of 3.65 eV and CdS bandgap of 2.82 eV, respectively. The nanowires then were transferred onto graphene surface by using a Langmuir–Blodgett film technique [13]. The surface topography [15–17] was studied by using AFM and the high resolution height and peak force error images are shown in Figure 4. It can be seen that the ZnS-CdS hetero-nanowires after transfer are ~2 nm in diameter and were densely packed on the surface.

![Figure 3. UV absorption spectrum of the ZnS-CdS hetero-nanowires](image)
Figure 4. AFM height (a) peak force error (b) image of the ZnS-CdS hetero-nanowires

Due to the semi-conductor property of the ZnS-CdS hetero-nanowires, under UV light illumination, photoelectron can be generated and contribute to the current, which is confirmed in the photoconductivity measurement shown in Figure 5. In this experiment, under the bias voltage of 1 mV, the initial current of the functionalized graphene was 1.08 μA and increases to 1.13μA under illumination.

Figure 5. Photoconductivity measurement of the ZnS-CdS hetero-nanowires functionalized graphene under the bias voltage of 1mV.

Figure 6 shows the normalized conductance response of the pristine graphene and functionalized graphene under the exposure of 15 ppm NO$_2$ in N$_2$. The electrical response magnitude $S$ was expressed as:

$$S = \left( \frac{G}{G_0} - 1 \right) \times 100\%$$

where $G_0$ is the measured conductance of graphene prior to the NO$_2$ exposure, i.e. when exposing to pure N$_2$ gas and $G$ is the measured conductance of graphene under the NO$_2$ exposure. When the pristine graphene is exposed to NO$_2$ gas, the electrical conductance of the graphene has a significant increase of 10% and this is because of the electron acceptor role of NO$_2$ in the sensing, where the electrons are transferred to the NO$_2$ molecules from graphene and finally leading to an increase in the hole density of graphene. The response time in graphene gas sensing was found to be ~1000s and, to accelerate the recovery process, the UV light illumination was employed to desorb the NO$_2$ molecules to initialize the device [4]. As for the ZnS-CdS hetero-nanowires functionalized graphene, the
sensitivity has a dramatic increase to 20%, which is two-fold as high as pristine graphene, and the response time is decreased to ~300s, which is one third as compared to pristine graphene. Therefore, the demonstrated gas sensor has considerably enhanced the response time as well as the sensitivity of pristine graphene.

This improved sensing performance of the ZnS-CdS hetero-nanowires functionalized graphene can be explained from the perspective of absorption energy and surface sites. According to the work of Tamvakos et al [10], the NO$_2$ is tended to bond to Zn atoms due to a high absorption energy. Thus, the faster response in the functionalized graphene can be well explained considering the comparably low absorption energy between NO$_2$ molecules and pristine graphene. Moreover, the large surface area of the ZnS-CdS hetero-nanowires provide a large amount of sites for the NO$_2$ molecules to position, combining with the higher absorption energy, thus the sensitivity is dramatically enhanced as well.

![Figure 6. Normalized conductive response of graphene gas sensors.](image)

**Figure 6.** Normalized conductive response of graphene gas sensors.

**Conclusion**

In our work, the ZnS-CdS hetero-nanowires functionalized graphene were successfully synthesized and incorporated into the gas sensor device. The semiconducting ZnS-CdS hetero-nanowires show the absorption onsets of 340 nm and 440 nm corresponding to the band gap of 3.65 eV for ZnS and 2.82 eV for CdS, respectively. Raman spectroscopy and AFM analysis indicates that the 2 nm wide nanowires are physically arranged on graphene surface and there is no chemical bond formed. Through the electrical gas sensing measurements, it is found that the hybrid material shows much faster response and the normalized conductive response of the ZnS-CdS hetero-nanowires functionalized graphene has a two-fold increase to 20% compared with the response of pristine graphene of 10%. Combing the UV illumination to accelerate the molecule desorption process, the devices exhibit fast response and recovery and, thus, has the possibility to be used in application of wide range of gases detection.

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