Fabrication of rGO/Cuprous Oxide Nanocomposites for Gas Sensing

Zhekun Wu 1,2, Yanyan Wang 1,2,*, Shuyang Ying 1,3, Manman Huang 1,2 and Changsi Peng 1,2

1School of Optoelectronic Science and Engineering & Collaborative Innovation Center of Suzhou Nano Science and Technology, Soochow University, Suzhou 215006, People's Republic of China
2Key Lab of Advanced Optical Manufacturing Technologies of Jiangsu Province & Key Lab of Modern Optical Technologies of Education Ministry of China, Soochow University, Suzhou 215006, People's Republic of China

*Corresponding author email: yywang@suda.edu.cn

Abstract. We report a simple fabrication of a gas sensor using a nanohybrid composite of reduced graphene oxide/cuprous oxide (rGO/Cu2O). The deoxidation of GO occurs meanwhile with the synthesis of Cu2O. The Cu2O component of the nanohybrid material has a linear morphology and a micron size, which is homogeneously mixed with rGO. The rGO/Cu2O gas sensor can effectively detect ppm level of NO2 gas, showing an outstanding reusability. Because rGO/Cu2O has a large specific surface area, it is more conducive to gas adsorption on its surface. Its good effect on detecting NO2 proves that the sensor has good commercial prospects.

1. Introduction

Nowadays, rapid development of industry and agriculture is one of the main causes of air pollution [1,2]. Therefore, the detection of harmful gases is particularly important not only for environmental protection but also for everybody’s health. Nitrogen dioxide (NO2) is one of the main gases that causes air pollution. It can not only erode the ozone layer but also cause smog and acid rain. In addition, NO2 gas at ppb level will also have harmful effects on human health [3]. The US Environmental Protection Agency stipulates that the gas standard of NO2 inhalation is 53 ppb [4]. Therefore, how to prepare a highly efficient, sensitive and controllable gas sensor is particularly important.

The sensors are usually composed of various materials. The most presentative is the p-type oxide semiconductors. Among them, Cu2O has attracted plenty of attentions due to its oversimplified preparation, non-toxicity and convenient production cost[5,6]. At the same time, another graphene-based composite material with high conductivity and fast electron transport is also a hot research topic. Graphene oxide (GO) is generally obtained by oxidation of graphite and is widely used in composite materials [7,8]. Additives such as rGO can help to form specific morphological structures of Cu2O. According to recent studies, rGO is more active than GO since the oxidizing group in rGO can effectively enhance chemical modification to form rGO flakes. Simultaneously, its excellent ductility and stability made rGO a popular scaffold material. According to investigations, it is proved that rGO inclines to form composites with semiconductor materials using hydrothermal synthesis [9]. Besides, owing to its synergy with the semiconductor structures, its sensing performance can be significantly improved [10].
During this paper, we reported such new type of gas sensor composed of rGO/Cu$_2$O composite material made by a simple synthesis route. It was manifest that the sensor demonstrated excellent response and suitable response/recovery time, superior to that shown by the rGO nanosheets or Cu$_2$O alone. The excellent sensing properties made the rGO/Cu$_2$O nanohybrid sensor a promising alternative for monitoring low concentrations of NO$_2$.

2. Experiment

2.1. Preparation of Graphene Oxide
The graphene oxide was obtained by the optimized Hummer’s method. The preparation process is as follows: first, 2 g of natural graphite was mixed with 50 ml of concentrated H$_2$SO$_4$ in a 250 ml beaker and stirred with a magnetic stirrer at 200 rad/min for 30 min. Then, 1 g of sodium nitrate was added to the reaction solution to generate nitric acid in situ in the solution. Keep it stirred in an ice bath at a speed of 320 rad/min for 2 h. Subsequently, 7.1 g of potassium permanganate was added to the mixed solution, then the reaction solution was stirred and reacted in a 35 °C water bath for 2 h to further complete the oxidation intercalation. Then, 150 ml of deionized water was slowly added to the mixed solution and stirred for 30 min to generate heat to further increase the layer spacing. Afterwards, 55 ml of 4% hydrogen peroxide solution was dropped to the above solution and stirred for 30 min to further oxidize and consume excess potassium permanganate. By suction, washing three times with dilute hydrochloric acid (3%, 100 ml) and centrifuging three times, a brown-yellow GO suspension was obtained, then the solution was dissolved in deionized water and placed in a dialysis bag for dialysis for one week. After drying in an oven at 40 °C, graphene oxide is finally obtained.

2.2. Preparation of rGO/Cu$_2$O Nanohybrid Composite
The rGO/Cu$_2$O nanohybrid composite was based on copper acetate monohydrate as the reaction precursor, graphene oxide as the coating layer, pyrrole as the reducing agent and structure-directing agent, and hydrothermally reduced at 120 °C under a weak acid condition. First, 0.2 g of copper acetate monohydrate was dissolved in 40 ml of deionized water and sonicated for 10 min until it was completely dissolved. Then, 20 mL of about 1.5 mg/mL of GO solution was added. The mixture was ultrasonically mixed for about 3 h. Then, we use a micropipette to take 0.075 ml of pyrrole monomer and dissolve it in 10 ml of deionized water. Next, 0.15 mL of acetic acid was dropped to the above solution. Afterward, the mixed solution was heated at 120°C for 12 h. When it was cooled down to room temperature, the resulting products were centrifuged and washed with water and ethanol several times. Finally, the rGO/Cu$_2$O nanohybrids were obtained. The graphene content was shown to make a significant impact on the gas sensing response of the composite material. Thus, by controlling the amount of graphene, rGO/Cu$_2$O composites with different graphene content were prepared.

2.3. Preparation of Gas Sensor
The interdigital electrode of the gas sensor used in the experiment was prepared by the lift-off process. First, the coating photoresist was spinned on a clean silicon wafer. Secondly, we designed a well-structured mask, and exposure and development were made by it. Lastly, interdigital electrodes were prepared after gold sputtering and de-glue stripping. In order to fabricate the sensing device, a micro-syringe was used to extract 0.1 µL rGO/Cu$_2$O colloid and deposit it on the electrode gap.

2.4. Characterization
Scanning electron microscopy (SEM) images were acquired using Sigma 300 at 3 kV. The X-ray diffractograms (XRD) were captured by Cu-K@ radiation diffractometer of $\lambda = 1.5418\text{Å}$ in the range of 5°-80°(2$\theta$) at room temperature. The Raman spectroscopy was acquired by using HR-800 with the excitation wavelength of 632.8 nm He-Ne laser.
3. Results and Discussion

Figure 1(a) and (b) depicted the SEM images of the as-prepared GO and rGO/Cu$_2$O nanohybrids, respectively. From Figure 1(a), we could see that GO had plenty of wrinkles stacked at the edges, demonstrating the presence of evenly distributed GO sheets. Figure 1(b) showed that Cu$_2$O exhibited a wire-like morphology with an average length of over a few micrometers. Moreover, it was well-mixed with rGO nanosheets, which were seen to be uniformly distributed. The rGO nanosheets and the Cu$_2$O nanowires formed a tightly knit cross-connected composite.

![SEM images of GO and rGO/Cu$_2$O nanohybrid composites.](image)

XRD was to clarify the microstructure and phase componential features of the rGO/Cu$_2$O nanohybrids (Figure 2). There existed a broad diffraction peak at 23°, attributed to the (002) plane of rGO, demonstrating the whole oxidation of GO. Furthermore, peaks could be assigned to (1 1 0), (1 1 1), (2 0 0), (2 2 0), (3 1 1), and (3 2 2) planes of copper oxide/cuprite phase (JCPDS card No. 78-2076). Moreover, there were no significant peaks of GO, indicating that GO was completely transformed to rGO.

![XRD pattern of rGO/Cu$_2$O nanohybrid samples.](image)

The carbonaceous compound of the rGO/Cu$_2$O nanohybrid composite was investigated by Raman spectroscopy. The well-known peaks of D and G bands were found in both samples. The source for the D peak was generally related to the breakage, formation or introduction of defects in the chemical bond during oxidation or reduction. Furthermore, the G band represented the intrinsic peak of graphene. As Figure 3 showed, in the case of both GO and the rGO/Cu$_2$O nanohybrids, there were two intense peaks located at 1350 and 1582 cm$^{-1}$ assigned to the D band and the G band. The enlargement of the I_D/I_G value represented the increase of disorders in the structure. Besides, by the reduction of pyrrole, the ratio of D peak to G peak increased from 1.088 to 1.127, which was closely related to the reduction's degree of GO, inducing fewer defects in the rGO/Cu$_2$O nanohybrids.
Figure 3. Raman spectra of (a) GO and (b) the rGO/Cu$_2$O nanohybrid composite.

When the gas is going through the sensor, the concentration of holes inside the gas-sensitive material will increase due to the adsorption of the gas and the gas-sensitive material. The resistance of the material will decrease correspondingly. The gas-sensitive response is calculated by calculating the changing resistance in the I-T curve, the calculation formula is as follows: \( S(\%) = \frac{(R-R_0)}{R_0} \). Among them, \( R_0 \) is the initial resistance of the sensor, \( R \) is the real-time resistance when NO$_2$ gas is introduced.

The gas-sensing response of the rGO/Cu$_2$O nanohybrid composite for NO$_2$ was studied for different gas concentrations (Figure 4). We found that, regardless of the concentration range of NO$_2$, the rGO/Cu$_2$O nanohybrids showed an excellent response. For 50 ppm of NO$_2$ gas, the response was about 43.5%, the response time and recovery time were about 350 and 250 s, respectively. By decreasing the concentration of NO$_2$, the response dropped to about 28.3% for 5 ppm and about 17.7% for 500 ppb. The large specific surface area was beneficial for NO$_2$ adhesion, enabling the rGO/Cu$_2$O nanohybrids to show excellent NO$_2$ sensing performance.

Figure 4. Response curves of the rGO/Cu$_2$O gas sensor towards unequal concentrations of NO$_2$ gas.

4. Conclusions
In this research, we fabricated a novel rGO/Cu$_2$O gas sensor via a facile synthesis approach. The samples showed good dispersibility. NO$_2$ gas sensing experiments showed that the rGO/Cu$_2$O nanohybrid composite exhibited outstanding gas sensing properties. Even at room temperature, the produced gas sensor's detection limit was as low as 500 ppb. According to the published results, after
more nuanced structural modulation of the rGO/Cu$_2$O nanohybrid composites, these prepared sensors would show a more competitive NO$_2$ detection in future applications.

Acknowledgments
The authors gratefully acknowledge financial supports by the National Natural Science Foundation of China (no. 61871281 and 51302179), the Postgraduate Research & Practice Innovation Program of Jiangsu Province (SJCX19_0799), the International Cooperation Project by MOST of China (SQ2018YFE010343), and the Priority Academic Program Development (PAPD) of Jiangsu Higher Education Institutions.

References
[1] Ou, J. Z.; Ge, W.; Carey, B.; Daeneke, T.; Rotbart, A.; Shan, W.; Wang, Y.; Fu, Z.; Chrimes, A. F.; Wlodarski, W.; Russo, S. P.; Li, Y. X.; Kalantar-zadeh, K. (2015) Physisorption-based charge transfer in two-dimensional SnS$_2$ for selective and reversible NO$_2$ gas sensing. ACS Nano, 9, 10313-10323.
[2] Xiao, Y.; Yang, Q.; Wang, Z.; Zhang, R.; Gao, Y.; Sun, P.; Sun, Y.; Lu, G. (2016) Improvement of NO$_2$ gas sensing performance based on discoid tin oxide modified by reduced graphene oxide. Sens. Actuators, B., 227, 419-426.
[3] Casals, O.; Markiewicz, N.; Fabrega, C.; Gra cia, I.; Cane , C.; Wasisto, H. S.; Waag, A.; Prades, J. D. (2019) A parts per billion (ppb) sensor for NO$_2$ with microwatt power requirements based on micro light plates. ACS Sens., 4, 822-826.
[4] Zhou Y, Wang Y, Guo Y. (2019) Cuprous oxide nanowires/nanoparticles decorated on reduced graphene oxide nanosheets: sensitive and selective H$_2$S detection at low temperature. Mater Lett, 336-339.
[5] Wang, M. Y.; Huang, J. R.; Tong, Z. W.; Li, W. H.; Chen, J. (2013) Reduced graphene oxide-cuprous oxide composite via facial deposition for photocatalytic dye-degradation. J. Alloys Compd., 568, 26-35.
[6] Abulizi, A.; Yang, G. H.; Zhu, J. J. (2014) One-step simple sonochemical fabrication and photocatalytic properties of Cu$_2$O-rGO composites. Ultrason. Sonochem, 21, 129-135.
[7] Tang, N.; Chen, B.; Xia, Y.; Chen, D.; Jiao, X. (2015) Facile synthesis of Cu$_2$O nanocages and gas sensing performance towards gasoline. RSC Adv., 5, 54433-54438.
[8] Li W, Guo J, Cai L, et al. (2019) UV light irradiation enhanced gas sensor selectivity of NO$_2$ and SO$_2$ using rGO functionalized with hollow SnO$_2$ nanofibers. Sens. Actuators, B., 290, 443-452.
[9] Clfen, H.; Mann, S. (2003) Higher-order organization by mesoscale self-assembly and transformation of hybrid nanostructures. Angew. Chem., Int. Ed., 42, 2350-2365.
[10] Liang, Y.; Li, Y.; Wang, H.; Zhou, J.; Wang, J.; Regier, T.; Dai, H. (2011) Co$_3$O$_4$ nanocrystals on graphene as a synergistic catalyst for oxygen reduction reaction. Nat. Mater., 10, 780-786.