Synthesis and application of graphene–silver nanowires composite for ammonia gas sensing

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Abstract
Graphene, consisting of a single carbon layer in a two-dimensional (2D) lattice, has been a promising material for application to nanoelectrical devices in recent years. In this study we report the development of a useful ammonia (NH\textsubscript{3}) gas sensor based on graphene–silver nanowires ‘composite’ with planar electrode structure. The basic strategy involves three steps: (i) preparation of graphene oxide (GO) by modified Hummers method; (ii) synthesis of silver nanowires by polyol method; and (iii) preparation of graphene and silver nanowires on two electrodes using spin and spray-coating of precursor solutions, respectively. Exposure of this sensor to NH\textsubscript{3} induces a reversible resistance change at room temperature that is as large as \( \Delta R/R_0 \sim 28\% \) and this sensitivity is eight times larger than the sensitivity of the ‘intrinsic’ graphene based NH\textsubscript{3} gas sensor (\( \Delta R/R_0 \sim 3\%, 5\% \)). Their responses and the recovery times go down to \( \sim 200 \) and \( \sim 60 \) s, respectively. Because graphene synthesized by chemical methods has many defects and small sheets, it cannot be perfectly used for gas sensor or for nanoelectrical devices. The silver nanowires are applied to play the role of small bridges connecting many graphene islands together to improve electrical properties of graphene/silver nanowires composite and result in higher NH\textsubscript{3} gas sensitivity.

Keywords: graphene, Hummers method, silver nanowires, polyol method, ammonia gas sensing

Classification numbers: 4.08, 5.15

1. Introduction
Graphene has attracted extensive attention in various research fields since the discovery of its monolayered structure because of its unique electrical properties such as high carrier mobility, ambipolar field effect and quantum Hall effect [1]. This 2D-nanostructure holds great promise for potential applications in many technological fields such as nanoelectronics, sensors, nanocomposites, batteries, liquid crystal devices (LCDs) and solar cells [1].

In today’s modern world, there are many various threats from gases that originate from laboratories and factories. To maintain safety, effective detection systems or sensors are required. Therefore, gas sensors based on graphene material are in urgent demand. Recently, the use of chemically reduced graphite oxide (rGO) for chemical sensors with satisfactory results has been reported [2–6]. These excellent sensor properties of rGO are due to two important facts: (i) its 2D structure makes every carbon atom a surface atom so
that electron transport through rGO can be highly sensitive to adsorbed molecules; and (ii) rGO is conductive and has chemically active defect sites making it a promising candidate for the active material in molecular sensors.

In most of the above publications, the sensing device was fabricated by spin-coating method, the GO suspension spun onto metal interdigitated electrodes with both finger width and interfinger spacing source–drain separation of about 1 µm. The GO was subsequently reduced using chemical agent and/or heating [2–5]. Despite the growing interest and rapid progress in graphene/rGO sensors, there were, however, technical challenges that needed to be addressed before they could be practically employed. That was fabrication of metal interdigitated electrodes using an e-beam lithography process.

In this study we report the development of a useful ammonia (NH₃) gas sensor based on graphene–silver nanowires ‘composite’ in which silver nanowires played a connecting bridges role among small rGO sheets (for overcoming the technical challenges in e-beam lithography process). For sensing signal measurement, we used two silver planar electrode arrays with 6 mm distance between them that were deposited by thermal evaporation method (for inexpensive, fast and facile purposes).

2. Experiment method

2.1. Synthesis of reduced graphene oxide (rGO) and silver nanowire materials

2.1.1. Synthesis of rGO. The basic method for preparation of rGO involves three steps: exfoliation of natural graphite by microwave irradiation, chemical oxidation of exfoliation graphite to GO by using the mixture of KMnO₄/NaNO₃/H₂SO₄ (modified Hummers method), reducing GO by chemical and heat method to graphene. More details about the three steps of synthesis of graphene were presented in our previous papers [1,7].

2.1.2. Synthesis of silver nanowires (Ag NWs). The Ag NWs material was synthesized through polyol method. This process needed two steps: seeding process and nanowires-growing process. First, AgNO₃ was reduced to form the nucleus seeds at a quite low concentration. Then the newly generated silver atom would selectively deposit onto the seeds to induce the 1D growth at a relatively high concentration. More details about synthesis of Ag NWs were presented in our previous paper [8].

2.2. Preparation of gas sensing devices and measurement system

The gas sensor reported herein was fabricated on a quartz wafer with thermal evaporation and two silver electrodes (figure 1). The GO solution was spin-coated directly onto a clean quartz wafer. Subsequently, these dry GO films were exposed to hydrazine and heated to 800 °C in the high vacuum of ~10⁻⁶ Torr to reduce to rGO films. After that, two silver planar electrode arrays were deposited on the rGO films using thermal evaporation method with 6 mm distance between them. Finally, we used spray-coating method to disperse Ag NWs arranged between two electrodes to complete our gas-sensing devices.

The as-fabricated rGO–Ag NWs composite devices with two planar electrodes were sensitive to gaseous species without any further treatment and were used for gas detection by simply measuring the resistance change of the device upon exposure to various gases.

Besides, to obviously estimate and compare the gas sensitivity of rGO–Ag NWs composite in our subject, the gas sensing devices based on intrinsic rGO material (without Ag NWs) were also fabricated for a reference sample. Thus, for the reader’s convenience we refer to two kinds of sensing sample: gas sensing rGO device and gas sensing rGO–Ag NWs device (figure 1) in the following presentation.

Relying on the popular gas sensor testing systems, that were designed by equipment manufacturers and laboratories, the homemade NH₃ gas testing equipment was set up to
measure the sensing properties of the as-fabricated devices (such as: sensitivity, stability, response time and recovery time of the devices). Our measurement system included an Ar gas tank, gas hoses and solenoids system, two flowmeters, a bubbler with NH₃ solution and an airtight test chamber connected with collect-store data DAQ component. The Ar gas played a role as carrier gas, dilution gas and purge gas [9].

The device was mounted in the test chamber with electrical feedthroughs. The measurement included two processes: absorption and desorption. In absorption process, the flowing NH₃ target gas (consisting of Ar carrier gas) from the bubbler into the test chamber for the period time and the change in resistance of sensor were recorded in that time. Moreover, we let the Ar purge gas flow through the test chamber to re-establish the rGO initial resistance. That step will give information about desorption ability of sensor in desorption process. All of the above procedures were controlled by computer.

3. Results and discussion

3.1. Degree of graphene–Ag NWs composite

UV–Vis spectroscopy was used to monitor the combination of rGO and Ag NWs into a composite. The spectra were characterized by two absorbance peaks at 270 and 375 nm (figure 2) which were characteristic peaks of rGO and Ag NWs material, respectively [1,7,8].

Besides, AFM images (figure 3) revealed that rGO synthesized by chemical methods had small sheet dimensions (called an island). The Ag NWs were used to play the role of bridges connecting together many rGO islands to improve electrical properties of rGO–Ag NWs composite. The results were much higher conductance (∼3.5 kΩ for rGO sheets and ∼0.5 kΩ for rGO–Ag NWs composite) but their transparency in both of cases is unchanged (∼80%).

In sensor devices, the contact resistance normally existing between the sensing material and the metal electrode further distorted the conventional sensitivity formulation. Figure 4 shows linear and symmetric I–V curves. This indicates that contact areas in our devices, including rGO sheets—silver electrodes and rGO sheets—Ag NWs contacts, are possibly Ohmic contacts. Therefore, we believe that the electrical contacts do not play a significant role in our devices and the data are most consistent with simple charge transfer.

3.2. Gas sensing characteristics of devices

Electronic measurements of the gas sensing devices revealed that NH₃ gas sensitivity of rGO material was improved by spray-coating of Ag NWs on its surface. This conclusion was proved by combining several facts that were confirmed under experimental conditions (i.e. room temperature and atmospheric pressure) from the as-fabricated devices [6] as follows:

Firstly, the sensitivity ability of sensing rGO devices (figure 5(a)) was investigated. The experiment consisted of the introduction of the (NH₃/Ar) target gas for 600 s,
Figure 5. (a) Response of the rGO sensors to NH$_3$ gas; (b) comparison between response of the rGO sensors and rGO–Ag NWs composite to NH$_3$ gas.

Figure 6. (a) Response of the rGO–Ag NWs composite to NH$_3$ gas (changing volume of Ag NWs solution spray-coated onto rGO surface); (b) the rGO and rGO–Ag NWs devices show repeatable response to NH$_3$ gas.

and (Ar) purging gas for 300 s. The result indicated that intrinsic sensing of gas sensing rGO devices was low electrical response upon exposure to NH$_3$ gas (sensitivity 3–4%) and this material could not be completely restored at room temperature. The flow of testing gas (NH$_3$ 0.1%/Ar) was held the same in all experiments.

Analysis of the gas sensing curves in figure 5 can be divided into two parts: the ‘rapid’ (steep slope) and ‘slow’ (shallow slope) response. The rapid response arises from molecular adsorption onto low-energy binding sites, such as sp$^2$-bonded carbon, and the slow response arises from molecular interactions with higher energy binding sites, such as vacancies, structural defects, and oxygen functional groups [3,4].

For the next step, the sensitivity ability of rGO–Ag NWs composite was studied and the whole above experiment process was repeated. The data in figure 5(b) shows that the presence of Ag NWs can improve the sensing properties of rGO sheets, namely the sensitivity increases from ~3.5% (rGO) to ~28% (rGO–Ag NWs), the response time decreases from 600 s (rGO) to ~200 s (rGO–Ag NWs) and the recovery time goes down from 300 s (rGO) to ~60 s (rGO–Ag NWs). In particular, complete NH$_3$ molecular desorption on the surface of rGO–Ag NWs composite took place at room temperature. Through suggestions, we can guess that connecting together individual rGO sheets by Ag NWs caused the increase of the mobility of carriers in rGO sheets and led to higher gas sensing properties of rGO. In addition, due to the appearance of Ag NWs bridges, the number of the sites with high binding energies in rGO sheets decreases while the number of those with low binding energies increases. Because the molecular gas was mainly absorbed at the sites with low binding energies, the appearance of Ag NWs bridges led to the complete desorption ability of rGO–Ag NWs composite.

Finally, we measured gas sensitivity of rGO–Ag NWs composite with the change of the Ag NWs content corresponding to the volume of solution spray-coated onto the same rGO surface. From the results, the greater the volume of Ag NWs solution used, the higher the sensitivity of devices that was reached, while the response and recovery times decreased (figure 6(a)), meaning that Ag NWs continue to improve the sensing properties of rGO. However, if we continuously increased the volume of Ag NWs solution, the sensing properties of rGO could decrease. To explain this phenomenon we guess that the greater the volume of Ag NWs solution used, the larger the area of the rGO sheets that was covered. This cover prevented the touch between molecular gas and rGO sheets and led to the decrease of sensing properties of devices.
Additionally, from figure 6(b) the excellent repeatable response of devices to NH$_3$ gas with ten cycles was measured. This showed sensor stability and it offered an opportunity to explore the cycle-to-cycle variation for sensors. The room temperature sensing performance of the rGO–Ag NWs devices under atmospheric pressure was very encouraging for practical applications when considering the simplicity and low cost of fabricating these devices, and the potential opportunities for optimization.

4. Conclusions

In this study rGO–Ag NWs composite was used for fabricating chemical sensors. These sensors had extremely simple structure and they responded to NH$_3$ gas at room temperature and atmospheric pressure. Using Ag NWs improved sensitivity of our gas sensing devices from $\sim$3.5% (rGO) to $\sim$28% (rGO–Ag NWs) while the response and recovery time decreased ($\sim$200 and 60 s, respectively). This phenomenon can be deduced by playing the role of the bridges connecting together many rGO islands of the Ag NWs, and high binding energy sites of rGO sheets were reduced with the appearance of Ag NWs. We suggest that the work reported here (including the simplicity of device fabrication and the sensor signal processing method) is a significant step toward the practical application of rGO-based chemical sensors.

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