Highly Sensitive and Portable Gas Sensing System Based on Reduced Graphene Oxide

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Highly Sensitive and Portable Gas Sensing System Based on Reduced Graphene Oxide

Wentian Mi, Shih-Wen Chiu, Tao Xue, Yuanquan Chen, Hanyu Qi, Yi Yang, Kea-Tiong Tang, and Tian-Ling Ren*

Abstract: Graphene has been widely used in gas-sensing applications due to its large specific surface area and strong adsorption ability. Among different forms of graphene used as gas-sensing materials, reduced graphene oxide is one of the most convenient and economical materials to integrate with Si-based electronics, which is very important to graphene-based gas sensors. In addition, the stacking structure of graphene oxide flakes facilitates absorption and detection of gas molecules. Based on reduced graphene oxide, a highly sensitive and portable gas-sensing system was demonstrated here. Solution-based graphene oxide was cast on a chip like a TF memory card and then reduced thermally. A signal acquisition system was designed to monitor resistance variation as a sign of gas concentration. This miniature graphene-based gas sensor array demonstrates a new path for the use of graphene in gas-detection technologies. And the creation of a sensitive and portable graphene gas sensor also shows great potential in fields such as medicine and environmental science.

Key words: reduced graphene oxide; gas sensor; signal acquisition system; thermal reduction

1 Introduction

Graphene has been an active research focus in various areas due to its unique two-dimensional (2-D) crystal structure[1–3] and excellent electrical[4–6], thermal[7, 8] and mechanical[9, 10] properties. Gas sensing is one of the most attractive applications of graphene due to its large specific surface area, strong absorption ability, and high sensitivity to surface adsorbates[11]. Different forms of graphene, such as graphene composites[12], graphene foam, and graphene quantum dots, have been used for gas sensing applications. Among them, Graphene Oxide (GO) is particularly prominent. Mass production of GO can be achieved via oxidative exfoliation of graphite[11]. Because of this, GO is heavily oxidized and introduces many oxygen-containing functionalities, leading to the high conductance of GO[13]. These oxygen-containing functionalities can be removed to reduce the conductance of GO[14]. The electrical properties of reduced GO (rGO) are inferior to those of pristine graphene when used as channel material in a transistor[13, 15]. The specific surface area, absorption ability, and sensitivity to surface adsorbates of rGO are similar to those of pristine graphene[16–18]. Hence, a number of studies have focused on the gas sensing application of rGO[19–26].

Though rGO does not perform as well as pristine graphene in transistor applications, rGO has an advantage as a functional material for gas sensing. rGO can be easily produced in high volume by inexpensive reagents via simple chemical processes. Due to its
substantial oxygen-containing functionalities, GO can be evenly dispersed in water\cite{27}. The GO water dispersion provides a convenient way to fabricate GO film for integration with Si-based electronics. There are many GO reduction methods and the process can be easily controlled, which means the properties of GO that depend on the reduction degree, such as conductivity and tensile strength, can be finely tuned by the reduction conditions\cite{28, 29}. Meanwhile, gaps in the stacking structure of rGO flakes enhance the absorption of gas molecules, which makes rGO a better platform for gas sensing than pristine graphene\cite{23}.

Recently, some studies on gas-sensing applications of rGO were released\cite{19, 21–23, 26}. rGO-based gas sensors that can detect different gases\cite{19–21, 26} were discussed in several papers. Typically, the response and recovery times of these rGO-based gas sensors are tens of seconds. The sensitivity of rGO gas sensors for some warfare agents and explosive gases can be up to parts-per-billion levels, which indicates their great potential for security uses. In addition, various modifications in both the physical structure of the sensor\cite{30} and the chemical structure of rGO have been studied in recent works.

Despite the superiorities of rGO in gas-sensing applications, there are still many improvements in these devices that remain challenging. To maximize the advantages of rGO in gas-sensing applications and improve the practicality and portability of rGO-based gas-sensing systems is of vital importance for the implementation of such devices.

Here, a highly sensitive and portable gas-sensing system based on reduced graphene oxide is demonstrated. A substrate similar in size to a TF card is applied. A 5-unit array of interdigital electrodes is fabricated on the front end of the substrate. A very small quantity of GO dispersion (~10 μL) is dropped onto the interdigital electrodes as the gas-sensing material. Then the GO is thermally reduced in a rapid thermal processing system to a proper reduction degree for gas sensing. The interface circuits convert the conductance variation of rGO to voltage signals, which are acquired by a multi-channel AD converter and processed by LabView in a PC. The interdigital electrodes detect the conductance variation of the rGO, which results in high sensitivity of the gas-sensing system. And the multi-unit design of the rGO gas sensor can minimize the impact of variations in the rGO film, which also supports the device’s sensitivity. Moreover, the portable and miniaturized design of rGO-based gas-sensing systems provides a new vista for the implementation of rGO gas sensors in various applications.

2 Experiments

2.1 Substrate chip

Portability and usability are of vital importance for rGO-based gas-sensing systems. Therefore, the substrate chip of the rGO gas sensor is designed to be similar to a TF memory card, as shown in Fig. 1. There are 7 units on the front end of the substrate chip, which perform as separate rGO gas sensors. The signals from these rGO gas-sensor units can be wired out through different pads on the end of the chip. The eighth pad is used for the reference signal. The substrate chip can be inserted into a TF card reader, and the signals from the rGO gas sensors on the chip can be acquired thereby.

The pads, interconnects, and electrodes are made of Au deposited onto a SiO$_2$/Si substrate and patterned by lift-off technology. Then a parylene layer is deposited on the top to cover the interconnects and expose the gas-sensor unit and contact pads for gas detection and signal wiring.

The structure of a single gas-sensing unit on the substrate chip is shown in Fig. 2. The interdigital electrodes in the center of the unit are for detection of the rGO conductance variation. The two terminals of the interdigital electrodes are connected to the common reference channel and the independent signal channel separately. The thickness of the parylene layer is 45 μm, which makes the unit a small container for GO dispersion and restricts the GO dispersion drop and

Fig. 1 The substrate chip for the rGO gas sensor is similar to a TF memory card. The serial numbers of units are marked.
2.2 Reduced graphene oxide

The form and properties of GO (rGO) have great influence on the performance of rGO-based gas-sensing systems. And the integration of GO with Si-based electronics is also a bottleneck for the development of the rGO-based gas sensors.

To simplify the fabrication of the rGO-based gas sensor, a precise pipette is used for the casting of GO dispersion onto the substrate. As the parylene layer forms a small container in the gas sensor unit, a 1.2 μL droplet of GO dispersion dropped by pipette can remain on top of the interdigital electrodes without spreading out on the surface of the substrate. A GO film is formed after the evaporation of the water on the interdigital electrodes, which is shown in Fig. 3.

After all the gas-sensor units on the chip are covered with GO film, the whole chip is placed in a rapid thermal processor for reduction of the GO. Then, the chip was heated at 500 °C for 105 s. The GO film after the heating is shown in Fig. 4. The resistance of the GO film measured through the interdigital electrodes decreases to thousands of ohms.

2.3 Signal acquisition and processing

The gas adsorbates on the rGO film lead to resistance variation. The resistance signal is converted to voltage signals for further processing.

Taking advantage of the substrate chip’s similarity to TF memory cards, the chip can be inserted into a TF card reader for signal acquisition, as shown in Fig. 5. Signals from different gas sensor units are read out separately through the TF card reader and wired out by the bus line for signal conversion and processing.

Interface circuits to convert resistance signals from the rGO gas sensors to voltage signals are shown in Fig. 6. The voltage reference LM4140 and the 2000 Ω $R_{ref}$ work as a potential divider for the signal conversion. To guarantee the stability of the potential divider, the operation amplifier LM324N isolates the potential divider from a following AD converter.

Then the voltage signals from all the channels are input into a multi-channel AD converter for further
signal processing. The AD converter is then connected with a PC and the converted digital signals are processed with LabView. An overview of the whole gas-sensing system is shown in Fig. 7.

3 Results and Discussion

3.1 Graphene oxide reduction

Reduction conditions have a great impact on the form and conductivity of the rGO film. They should be precisely controlled to guarantee the quality of the rGO-based gas sensor.

The temperature is the primary condition for GO reduction. A higher temperature usually leads to faster reduction and better conductivity of the rGO film.

However, the GO film used here is prepared by drop casting, which means the thickness may be over 1 μm. Some oxygen-containing functionalities in GO film are converted to oxygen during the heating process, which leads to the loose stacking structure of rGO compared with GO. A higher reduction temperature means faster release of oxygen, which may destroy the rGO film.

Figure 8 shows the form of the rGO film after reduction under 800 °C for 105 s. In contrast to the rGO film reduced under 500 °C shown in Fig. 4, the rGO film here has obviously peeled off from the substrate, which results in bad contact with the interdigital electrodes. The suspended rGO film even broke, which is detrimental to the performance of the gas sensor. Therefore, during the fabrication of the rGO gas sensor, 200 °C is selected as the reduction temperature.

Because the temperature has great influence on the form of the rGO film, reduction time is the only control parameter for rGO film resistance. The resistance of the rGO film is important to the gas-sensing system. An excessively high resistance signal is difficult to acquire and process. And excessively low resistance of the rGO film may lead to high power consumption; the resistance should be monitored in real time. Thus, the resistance of the rGO film should be controlled to kΩ level.

The resistance of the GO film during the annealing process under 500 °C was measured and plots are shown in Fig. 9. The curve shows that the resistance of all 7 gas sensor units decreases to under 10 kΩ after 105 s. Thus, the reduction time in this experiment is set to 105 s.

![Fig. 6 Signal conversion circuit for every channel.](image1)

![Fig. 7 Overview of the gas-sensing system based on rGO.](image2)

![Fig. 8 rGO film reduced under 800 °C. The rGO film peeled off from the substrate and broke due to the excessive reduction temperature.](image3)

![Fig. 9 The resistance variation of the GO film during the reduction process.](image4)
3.2 Gas-sensing performance
To test the gas-sensing performance of the rGO-based gas-sensing system, the alcohol was injected into a heated chamber to generate alcohol gas. The resistance variation of the rGO is monitored and its plots are shown in Fig. 10.

The mole fraction of the alcohol gas is \(2.63 \times 10^{-3}\). Their alcohol injections were performed, at 0 s, 1.0 \(\times 10^4\) s, and 2.5 \(\times 10^4\) s. All 7 channels of the rGO gas sensors showed obvious resistance variations up to 23%, which demonstrates the high sensitivity of the rGO-based gas sensor.

After the resistance variation of the rGO attained a peak value, dry air was pumped into the chamber to realize the desorption of the gas molecules. The resistance of the rGO gradually returns to its original value. However, the resistance cannot be fully recovered, due to gas molecules absorbed in the deep layers of the rGO. Thus, after the desorption process, the resistance variation remains \(\sim 5\%\).

4 Conclusion
In summary, a highly sensitive and portable gas-sensing system based on reduced graphene oxide is proposed. The resistance variation of the rGO-based gas sensors can be up to 23% when exposed to alcohol gas. The miniaturized design of the gas-sensor array and the easy preparation method of rGO film provide great potential for implementation of rGO-based gas sensors in the future. This result highlights the potential of highly sensitive rGO-based gas sensors for various applications.

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References

Fig. 10 The gas-sensing performance of the rGO-based gas sensors.


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