Supporting Information (SI)

Graphene-Modified ZnO Nanostructures for Low-Temperature NO$_2$ sensing

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Thermogravimetric (TG) analysis of ZnO/rGO-0.5

Thermogravimetric analysis of typical sample ZnO/rGO-0.5 is shown in the Figure S1. From room temperature to 160 °C the mass loss of about 2 wt% is associated with the release of physical absorption of water.¹ From 160 to 440 °C owing to the burning decomposition of oxygen-containing groups attached to graphene oxide layers and ZnO, the mass loss of about 1.5 wt%. From 440 °C to 660 °C, can be summed up in combustion of carbon skeleton decomposition and mass loss of about 0.5 wt%.²
Gas-sensing performance of ZnO/rGO nanocomposites

Figure S2 compares the NO$_2$-sensing response ($R_a/R_g$) of the ZnO/rGO-$x$ nanocomposites ($x=0$, 0.5, 1 and 1.5) as a function of operating temperature. One can see that the pure ZnO sample has the highest NO$_2$-sensing response (~29.61) operating at 160 °C, the ZnO/rGO-0.5 sample has the highest NO$_2$-sensing response (~61.57) operating at 100-130 °C, the ZnO/rGO-1 sample has the highest NO$_2$-sensing response (~30.74) operating at 130 °C and the ZnO/rGO-1.5 sample has the highest NO$_2$-sensing response (~28.99) operating at 130 °C. The optimum response temperature of the pure ZnO sample is much lower than that of the GO-doped ZnO samples, indicating that the addition of GO nanosheets improved the gas-sensing properties especially at a low operating temperature.
Figure S2. NO$_2$-sensing response as a function of operating temperature in the presence of ZnO/rGO nanocomposites ([NO$_2$] =50 ppm).

To check the effect of operating temperature on the NO$_2$-sensing performance of the ZnO/rGO-0.5 sample, we placed an emphasis on comparing the $R$-$t$ curves of its NO$_2$-sensing performance under various operating temperatures. Figure S3 shows the detailed results. From Figure S3a, one can see that the sensor based on the ZnO/rGO-0.5 nanocomposite exhibits an obvious response to NO$_2$ gas during an operating temperature range of 70–200 °C, but the optimum operating temperature is 130–160 °C. For the NO$_2$ gas with a concentration of 0.5 ppm, the ZnO/rGO-0.5 sensor can work at 70 °C and exhibits a weak gas response. At the optimum operating temperature of 130 °C, the detection limit of NO$_2$ concentration of the ZnO/rGO-0.5 sensor can be expected to extend to ppb-level if the measuring accuracy of sampling NO$_2$ is allowed. Figure S3b shows the response of the ZnO/rGO-0.5 sensor under different operating temperatures to a 50 ppm NO$_2$ gas. One can see that the NO$_2$-sensing response operating at 130 °C reaches a summit of 62.

Figure S3. Detailed NO$_2$-sensing data of the ZnO/rGO-0.5 sample: (a) $R$-$t$ response curves obtained at various operation temperatures, and (b) typical response to 50 ppm NO$_2$ at various temperatures.
Figure S4. Response and recovery times of the ZnO and ZnO/rGO sensors upon exposure to NO$_2$ gas operating at 130 °C: (a) Various samples upon exposure to 50 ppm NO$_2$ according the $R$–$t$ curves in Figure 6c, (b) ZnO and (c) ZnO/rGO-0.5 upon exposure to NO$_2$ gases with various concentrations.

Figure S5. Comparisons of the $R$–$t$ curves of the ZnO/rGO-0.5 sensor obtained by different synthetic methods: ultrasonic spray and traditional precipitation.

A large amount of rGO weakens the NO$_2$ gas sensitivity of ZnO/rGO. We tested the gas sensitivity of ZnO/rGO-2 and ZnO/rGO-3, as shown in Figure S6. It can be seen that the response of ZnO/rGO nanocomposites decreases with the increase of rGO, and the $R$–$t$ curve of ZnO/rGO-3 shows a straight line. With the increase of rGO, the resistance of gas-sensitive materials decreases and tends to conductor. The mass of rGO is relatively light, and the mass fraction of ZnO and rGO is used as the comparison in the synthesis, so rGO with 3wt % has a high molecular weight.
Figure S6. Comparisons of the $R-t$ curves of the ZnO/rGO-0.5, ZnO/rGO-2 and ZnO/rGO-3 sensor exposure to NO$_2$ gases with various concentrations (0.5–50 ppm) operating at 130 °C.

Table S1. Comparison of NO$_2$ gas-sensing performance of the present work with literatures

| Material system | Synthetic process | Concentration of NO$_2$ | Response | Reference |
|-----------------|-------------------|--------------------------|----------|-----------|
| rGO/ZnO         | Assembly          | 120 ppb                  | 1.875    | 3         |
| rGO/MoS$_2$     | Reflux            | 40 ppm                   | 48.4     | 4         |
| rGO/SnO$_2$     | Hydrothermal      | 5 ppm                    | 65.5     | 5         |
| Phosphorus      | Calcination       | 40 ppb                   | 25       | 6         |
| WO$_3$          | Magnetron sputtering | 16 ppb               | 26       | 7         |
| Fe/WO$_3$       | Hydrothermal      | 1 ppm                    | 4.7      | 8         |
| Phosphorus      | Calcination       | 200 ppm                  | 229      | 9         |
| Boron/Graphene  | Calcination       | 2 ppm                    | 8        | 10        |
| Cu$_2$O/rGO     | Self-assembly     | 1 ppm                    | 5.8      | 11        |
| rGO/ZnO USS     | USS               | 50 ppm                   | 63       | This work |

The response of ZnO/rGO-0.5 to 50 ppm NO$_2$ gas at relative humidity of 35% and 65% is shown in Figure S7. The response of ZnO/rGO-0.5 to NO$_2$ gas was reduced by increasing humidity, and the specific response was reduced from 63 (35%) to 11 (65%). At high relative humidity, the adsorption of water molecules prevents the adsorption of oxygen on the sensor surface, and the adsorption layer can be used as a barrier between the surface of ZnO sensor and NO$_2$ gas.\(^\text{12}\)

Figure S7. $R$-$t$ curves of the ZnO/rGO-0.5 sensor to 50 ppm NO$_2$ operating at 130 °C under relative humidity of 35% and 65%.

Gas-sensing preliminary data ($U$-$t$ curve) of ZnO/rGO nanocomposites

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The gas sensitivity test of ZnO/rGO nanocomposite is mainly based on voltage test method, which indirectly reflects the change of component resistance. The basic principle is shown in Figure 1. The entire circuit is made up of a series of load resistors \((R_0, 100–50000 \, \text{KΩ})\) and ZnO/rGO nanocomposite resistors \((R)\). The temperature of the gas sensing test is controlled by adjusting the voltage of the other loop. It is known from Figure 1 that the voltage tested by the system is the voltage of the load resistor, and the Resistance-time curve \((R–t)\) in the text is calculated according to Equation 5; Figure S8, Figure S9, Figure S10, Figure S11 and Figure S12 are the original Voltages-time curves \((U–t)\). The response is obtained from the voltage change across the load resistor, and the change in device resistance is indirectly calculated to analyze and calculate the response of the device.

Figure S8. \(U–t\) curves of the ZnO/rGO nanocomposites \((\text{ZnO/rGO-x, } x=0, 0.5, 1 \text{ and } 1.5)\) to NO\(_2\) with various concentrations \((0.5–50 \, \text{ppm})\) at different operating temperatures: (a) 70 \(^{\circ}\)C, (b) 100 \(^{\circ}\)C, (c) 130 \(^{\circ}\)C, (d) 160 \(^{\circ}\)C, and (e) 200 \(^{\circ}\)C.
Figure S9. $U$-t curve of the ZnO/rGO-0.5 sensor exposure to NO$_2$ gases with various concentrations (0.01–50 ppm) operating at 130 °C.

Figure S10. $U$-t curves of the ZnO/rGO-0.5 sensor upon exposure to NO$_2$ gases with various concentrations (0.01–50 ppm) operating at various temperatures.

Figure S11. $U$-t curves of the ZnO/rGO-0.5 sensor operating at 130 °C upon exposure to VOCs, CH$_4$, CO, H$_2$S, H$_2$, NO$_2$, and SO$_2$. 
Figura S12. Comparisons of the $U$-$t$ curves and their corresponding responses of the ZnO/rGO-0.5 sensor obtained by different synthetic methods: ultrasonic spray and traditional precipitation.

Notes and references

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