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UV Light Assisted NO_2Sensing by SnO_2/Graphene Oxide Composite †

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Abstract: Nitric oxide (NO_2) is one of the air pollutants that pose serious environmental concerns over the years. In this study, SnO_2 nanowires were synthesized by evaporation-condensation method and graphene oxide were synthesized using modified Hummers method for low temperature NO_2 detection. Drop cast method was used to transfer graphene oxide (GO), to form composite GO-metal oxide p-n junctions. With integration of reduce graphene oxide (rGO), the UV light absorption was enhanced. This metal oxide composite has shown a reversible response in detecting low concentrations of NO_2 under UV irradiation, with a working temperature range of 50–150 °C. Pure SnO_2 shows 20% response to NO_2 (4 ppm) in dark conditions, while the response increase sup to 60% using UV irradiation at 50 °C. Furthermore, SnO_2/rGO shows a 40% of response in dark, while the response increases to 160% under UV light illumination. This composite exhibits excellent recovery and maintains the baseline under UV light at low temperatures, which effectively overcome the drawbacks of low recovery typically shown by metal oxide gas sensors at low temperature.

Keywords: SnO_2; reduced graphene oxide; metal oxide gas sensors; low temperature gas sensors; NO_2 sensing; SnO_2/rGO heterojunction; UV light irradiation

1. Introduction

Air pollution has become one of the main concerns due to increased usage of automobiles and rapid industrialization. This results in a strong need of environment monitoring, a routine practice to identify and reduce gases that contributes to air pollution. Nitric oxide (NO_2) is considered as one of the most toxic gases that can lead to acid rain and photochemical smog. Significant efforts have been made to detect these toxic gases, including NO_2, due to serious threats they pose on flora and fauna.

Over the past years, many researches have focused in determining efficient methods of detectingNO_2.Metaloxide(MOx)nanostructures,suchasSnO_2nanowires(NWs),canbeconsidered as one of the most widely used materials to detect gases due to their high sensitivity, high stability and simple interface electronics. However, due to their high working temperature, these SnO_2 materials are not considered as the most energy efficient method of detecting NO_2. Graphene and reduce graphene oxide (rGO) are considered as promising sensitive materials for conduct ometric gas sensing owing to their high surface to volume ratio. Therefore, many studies have focused on their

combination for fabricating MOx-rGO composites [1,2], to further improve the sensing performanceofbothmaterials..Thesestudieshaveshownremarkableresponseoffabricated chemical gas sensors in low temperature range. In addition, the use of UV light illumination has a positive effect on sensing properties. rGO shows good optical absorption properties, thus UV light can excite SnO_2/rGO and generate electron-hole pairs on the p-n junction which could significantly improvetheholeconcentrationintherGOtoenhancethesensorresponseanddecreasetherecovery time.

2. Materials and Methods

2.1. Synthesis Method

SnO_2 NWs were prepared by thermal evaporation method, directly on Alumina substrates (99.9% purity, 2 mm × 2 mm, Kyocera, Japan). Alumina substrates were cleaned in acetone using ultrasoundsfor15mintoremovedustparticles, then dried with a synthetic airflow. Afterwards, a thin layer of Au catalyst was deposited on alumina substrates by RF magnetron sputtering (75W argon plasma 5.5×10^{-3} mbar, at room temperature). To synthetize SnO_2 NWs, SnO_2 powder was placed in the middle of a tubular furnace and heated up to 1370 °C to promote evaporation. Alumina substrates were placed into the furnace in a colder region, where the temperature was in the range of 800 °C–950 °C. Argon gas (100 SCCM) was used to transport SnO_2 vapours towards the substrates in order to promote the growth NWs, keeping a constant pressure of 100 mbar inside the tube. GO powder was dissolved in water and stirred in 300 rpm for 15 min, then ultrasonicated for 15 min in order to obtain a homogeneous dispersion. A 5 µL suspension of GO was drop casted on top of the SnO_2 NWs and dried at room temperature.

2.2. Gas Testing

Gas testing was carried out in a homemade gas chamber. Interdigitated Pt contacts and Pt heaters were deposited on alumina substrates by DC magnetron sputtering. Afterwards, these alumina substrates were mounted on TO packages using electro-soldered gold wires. The devices were placed inside a homemade test chamber to investigate the conductance variation as a function of chemical species. A fixed voltage (1V) was applied to the sensors and the total gas flow was set to 200 SCCM with 40% relative humidity. Samples were tested in 50–150 °C temperature ranges and were stabilized for 10 h for each temperature before the introduction of the test gases. Sensors were exposed to the gas for 20 m in with fixed concentration, and then the synthetic air flow was restored to recover the base line signal. The response for the variation of conductance was calculated using following formulae, for reducing and oxidizing gases, respectively

$$\text{Response} = \left(\frac{G_{Gas} - G_{Air}}{G_{Air}}\right)\% \quad (1)$$

$$\text{Response} = \left(\frac{G_{Air} - G_{Gas}}{G_{Gas}}\right)\% \quad (2)$$

where, G_{Air} is the base line conductance of the sensor and G_{Gas} is the conductance of the sensor in presence of the target gas.

3. Results

3.1. Characterization and GasTesting

Figure 1 shows scanning electron microscope images of the NWs grown on the Au catalyst: thin, long and dense NWs were obtained by thermal evaporation method. It shows that rGO exhibits a gauze-like sheet morphology on top of the SnO_2NWs. Figure 1b shows that rGO sheets successfully decorate SnO_2 nanowires: their surface and edges can be easily distinguished.

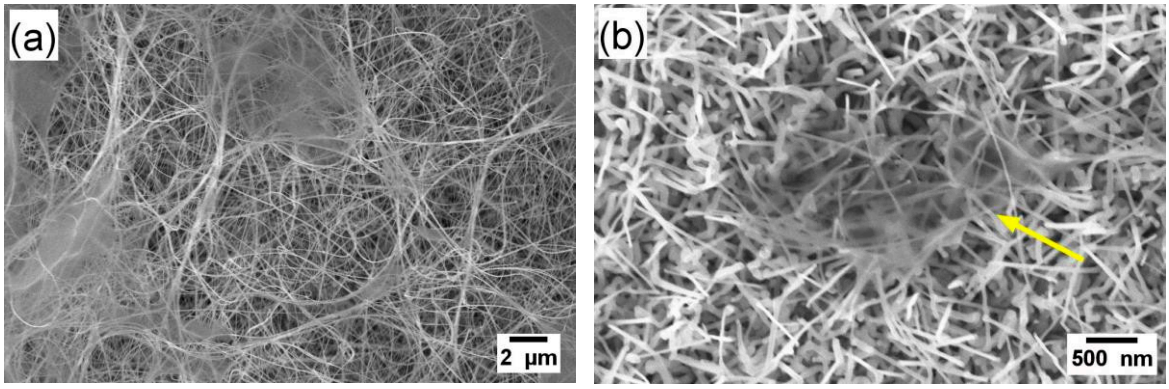

Figure 1. SEM imagers of SnO_2/rGO composite in different magnifications.(**a**) Low magnification; (**b**) High magnification.

Figure 2a shows the dynamic response of the SnO_2/rGO toward NO_2 in the concentrations range of 1–4 ppm under UV and without UV irradiation. Upon exposure to NO_2 gas, the electrical conductance of the composites decreases, which is a typical behaviour of n-type semiconductor. It clearly shown that the SnO_2/rGO composite increases the response at 50 °C under UV irradiation. Figure 2b reports the sensor response at different temperatures: the responses at 50–100–150 °C, are 153, 113 and 104 when the NO_2 concentration is 4 ppm. The response is two times higher than SnO_2/rGO composite, and more than eight times higher than SnO_2 NWs. Figure 3 shows the influence of the temperature towards both response and recovery time. SnO_2/rGO has a recovery time of about 25 min in dark, which decreases to 8 min under UV irradiation.

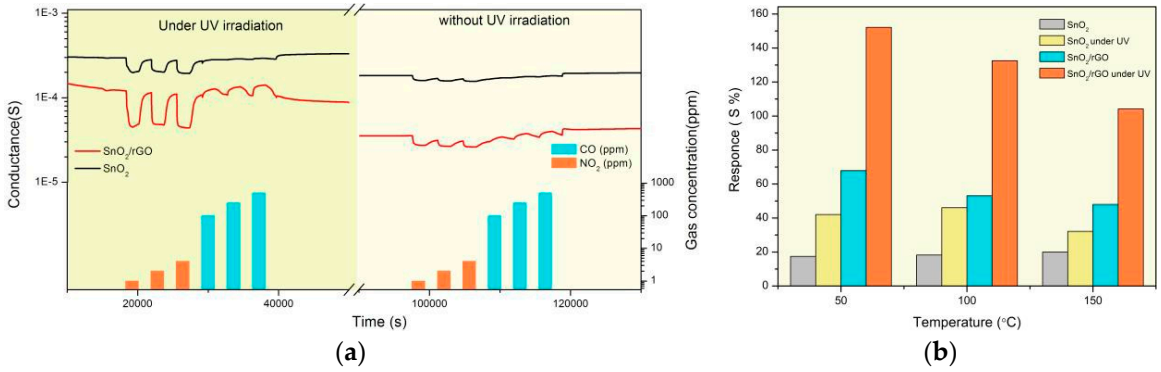

Figure 2. (**a**) Dynamic response of SnO_2, SnO_2/rGO composite toward NO_2 (1, 2. 5, 4 ppm), CO (100, 250, 500 ppm) at 50 °C and RH = 40%; (**b**) Sensor responses toward NO_2 (4 ppm) in different working temperature and RH = 40%.

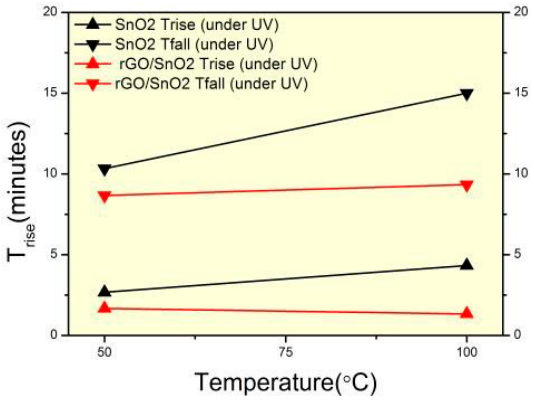

Figure 3. Response time and recovery time of the SnO_2/rGOcomposite.

3.2. Gas SensingMechanism

Under UV irradiation, incident light is absorbed by SnO_2 and rGO, generating electron-hole pairs. These photo-generated electrons and holes can be separated due to the effect of heterojunction, which rapidly increases the electron concentration in the SnO_2 conduction band [3]. When the composite is exposed to air, oxygen molecules are easily adsorbed on the surface capturing the photo-generated electrons from the conduction band as shown in following equations [4,5].

$$\upsilon \rightarrow h^{+} + e^{-} \quad (3)$$

$$O_2 + e^{-}_{(h\upsilon)} \rightarrow O^{-}_{2(h\upsilon)} \quad (4)$$

The sensing mechanism of the SnO_2/rGO composite can be explained as follows: on the one hand, rGO sheet provides many adsorption sites for NO_2 molecules owing to their high surface area, and it provides preferential pathways for the charge transport; on the other hand, SnO_2 can react with NO_2 molecules thanks to the high reactivity of photo generated $O^{-}_{2(h\upsilon)}$. The chemical reaction between NO_2 and oxygen species on the surface explained through the following Equation (4):

$$NO_2 + O_2^{-} + 2e^{-} \rightarrow NO_2^{-} + 2O_2^{-} \quad (5)$$

4. Conclusions

In this study, SnO_2 nanowires were synthesized by thermal evaporation method and GO was drop casted on top of the SnO_2 nanowires to form SnO_2/GO composite. Annealing process were conducted to form SnO_2/rGO and these SnO_2/rGO composites show good response to NO_2 under UV irradiation. Furthermore, UV light enhanced response time and recovery time: this composite can be used for low-temperature NO_2 gas detection.

Author Contributions: The authors contributed equally.

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Conflicts of Interest: The authors declare no conflict of interest.

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