



High performance room temperature NO₂ sensors based on reduced graphene oxide-multiwalled carbon nanotubes-tin oxide nanoparticles hybrids



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ABSTRACT

A facile and effective strategy has been successfully developed to synthesize reduced graphene oxide-multiwalled carbon nanotubes-tin oxide nanoparticles (rGO-CNT-SnO₂) hybrids by hydrothermal method. The combined characterizations of X-ray diffraction, Raman spectrum and Transmission electron microscopy were used to characterize the samples thus obtained, indicating the successful preparation of rGO-CNT-SnO₂ hybrids. A room temperature NO₂ sensor was fabricated by dropping the dispersion of rGO-CNT-SnO₂ hybrids on the surface of ceramic substrate previously printed Au electrodes. Most importantly, the sensor based on rGO-CNT-SnO₂ hybrids shows high response, fast response and recovery rate, high selectivity and good stability, which are much better than NO₂ sensors based on pure rGO and rGO-SnO₂ hybrids.

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1. Introduction

Development of room temperature gas sensors has attracted considerable attention due to their excellent advantages of avoiding high temperature leading to low power consumption, easy integration, good stability, etc. [1]. However, the gas sensors based on semiconductor metal oxides always require high temperature to activate the semiconductor properties of sensing materials for detection of gases, which limit their applications for gas sensing operated at room temperature [2].

Graphene-based materials have been proven as good candidates for fabrication of room temperature gas sensors due to their excellent properties, such as high carrier mobility at room temperature, detectable change in their resistance after adsorption or desorption of guest gases, high surface area, as well as good chemical and physical stability [3,4]. Up to now, the pure graphene materials prepared by various methods, including chemical reduction of graphene oxide (GO) [5,6], thermal reduction of GO [7,8], chemical vapor deposition (CVD) have been used for detection of gases at room temperature [9]. Among them, the reduced graphene

oxide (rGO)-based materials have attracted much attention for gas sensing because of their great advantages of low cost and bulk quantity production, controllable tuning the semiconductor properties by surface modification [10,11]. However, these sensors suffer from the obvious shortcomings of low response, long response and recovery times, which limit their wide applications. Therefore, development of high performance rGO-based room temperature gas sensors is highly required.

It is well known that sensing materials play an important role in the sensing performances of gas sensors. Tuning the semiconductor properties of rGO by surface modification via noncovalent or covalent methods is a promising strategy for fabrication of high performance rGO-based sensing materials. Recently, SnO₂, as a typical n-type semiconductor exhibiting excellent sensing performances, has been used to modify rGO for enhancing sensing performances of rGO-based gas sensors. Although highly aligned SnO₂ nanorods on graphene sheets [12], SnO₂ nanoparticles/rGO [13,14], as well as SnO₂ nanofibers functionalized with rGO [15], have been successfully used for detection of acetone, hydrogen sulfide and nitrogen dioxide (NO₂), relatively high operating temperature is required. Furthermore, the SnO₂-rGO hybrids have also been used for detection of gases at low operating temperature, even room temperature [16–18]. Unfortunately, sensing performances (sensitivity, response time and recovery time) of these sensors still need further enhance to satisfy the criterion for practical applications. More recently, we have fabricated NO₂ sensors using SnO₂-rGO

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hybrids as sensing materials. Although the sensors exhibit better sensing performances than that of rGO, the sensors are also required heating (operated at 50 °C) for detection of gases [19]. In this paper, multiwalled carbon tubes (CNTs) were introduced into the SnO₂-rGO hybrids, and rGO-CNT-SnO₂ ternary hybrids have been successfully prepared by hydrothermal method. Most importantly, the sensing performances have been tremendously enhanced by introduction of CNTs, which are much better than that of pure rGO and SnO₂-rGO hybrids.

2. Experimental

2.1. Materials

SnCl₄·5H₂O, KMnO₄, H₂O₂ (30 wt.%), NaNO₃, and H₂SO₄ (98%) were purchased from Beijing Chemical Corp (Beijing, China). CNTs (10–20 nm in diameter and 10–30 μm in length with purity of 95%) were purchased from Nanjing XFNANO Materials Tech. Graphite powder was purchased from Aladin Ltd. (Shanghai, China). All chemicals were used without any further purification. The water used throughout all experiments was purified through a Millipore system.

2.2. Preparation of rGO-CNT-SnO₂ hybrids

The GO was prepared by the modified Hummers' method according to our previous reports [20]. In a typical synthesis of rGO-CNT-SnO₂ hybrids, 375 μL of GO dispersion (1 mg/mL) and 75 μL of CNTs dispersion (5 mg/mL) were added into 30 mL of H₂O, followed by sonication at room temperature for 30 min. Because GO is a good stabilizing agent for π-rich materials [21,22], a stable GO-CNT dispersion was obtained. After that, 0.036 g of SnCl₄ was added into the above solution, followed by transferring into a 50 mL Teflon-lined stainless steel autoclave and then heated at 180 °C for 12 h. After that, the products were collected by centrifugation, washing by water, and dispersed into water for characterization and further use.

2.3. Characterizations

Raman spectra were obtained on J-YT64000 Raman spectrometer with 514.5 nm wavelength incident laser light. Powder X-ray diffraction (XRD) datum was recorded on a RigakuD/MAX 2550 diffractometer with Cu Kα radiation (λ = 1.5418 Å). A Perkin-Elmer TGA 7 unit was used to carry out the thermogravimetric analysis (TGA) in air at a heating rate of 10 °C/min. Transmission electron microscopy (TEM) measurement was made on a HITACHI H-8100

electron microscopy (Hitachi, Tokyo, Japan) with an accelerating voltage of 200 kV.

2.4. Preparation of gas sensors

The aqueous dispersion of rGO-CNT-SnO₂ hybrids was used as sensing materials for fabrication of NO₂ sensors. The sensors were obtained by dip-coating the dispersion onto the ceramic substrate before it was coated with the rGO-CNT-SnO₂ dispersion; two pairs of electrodes were printed on each side as signal electrode and heating electrode, respectively. For the dropping the sensing materials onto the electrode, 0.3 μL of rGO-CNT-SnO₂ aqueous dispersion was dropped on the surface of electrode, followed by dryness at room temperature. Gas sensing properties were measured using a static test system. Saturated target vapor was injected into a test chamber (about 1 L in volume) by a microinjector through a rubber plug. After fully mixed with air (relative humidity was about 25%), the sensor was put into the test chamber. When the response reached a constant value, the sensor was taken out to recover in air. The electrical properties of the sensor were measured by CGS-8 intelligent test meter (Beijing Elite Tech. Co., Ltd., China). The response of the sensor was defined as $S = R_a/R_g$, where R_a is the resistance of the sensor in the air and R_g is the resistance of the sensor in target gas. The time taken by the sensor to achieve 90% of the total resistance change was defined as the response time in the case of adsorption or the recovery time in the case of desorption.

3. Results and discussion

The structure of the products was first examined by XRD pattern. Fig. 1a shows the XRD pattern of rGO-CNT-SnO₂ hybrids. It is seen that the samples exhibit eight peaks at 2θ of 26.75, 33.77, 37.99, 51.75, 61.96, 65.23, 71.13 and 78.72°, which are attributed to the (1 1 0), (1 0 1), (2 0 0), (2 1 1), (3 1 0), (3 0 1), (2 0 2) and (3 2 1) planes of tetragonal rutile SnO₂ (JCPDS File No. 41-1445), indicating the formation of SnO₂ crystals [23]. Furthermore, no peaks associated with CNT or rGO are observed for the samples, which may be attributed to the low content of CNT and rGO in the final hybrids.

It is well known that the Raman spectrum is an effective technique to examine the structure change from GO to rGO. Fig. 1b shows the Raman spectra of GO and SnO₂-containing hybrids. Normally, the rGO-based materials exhibit a D band at about 1350 cm⁻¹ and a G band at about 1600 cm⁻¹, which are attributed to arising from a breathing mode of κ-point phonons of A_{1g} symmetry, and the first order scattering of the E_{2g} phonon of sp² C atoms, respectively [24]. It is seen that GO exhibits D peak at 1352 cm⁻¹ and G band at 1606 cm⁻¹, which are the same to GO previously reported [25]. In contrast, after hydrothermal treatment, the hybrids show a D band

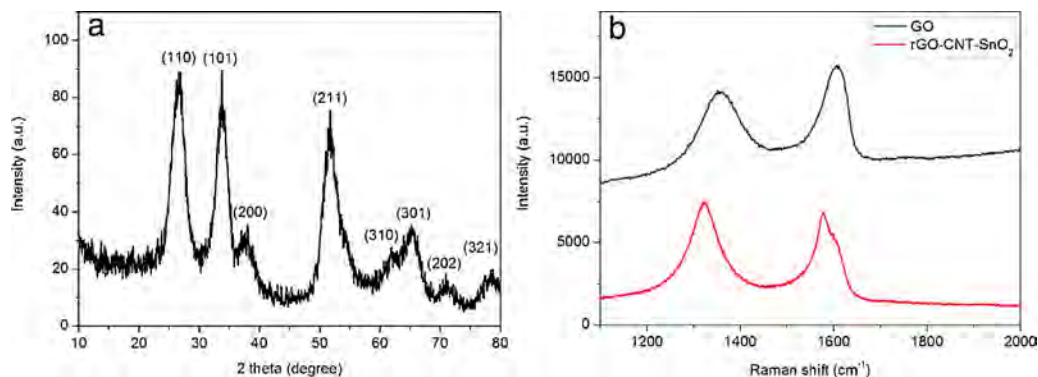


Fig. 1. (a) XRD pattern of the samples obtained by hydrothermal treatment of GO-CNT dispersion in the presence of SnCl₄, and (b) Raman spectra of GO and rGO-CNT-SnO₂ hybrids.

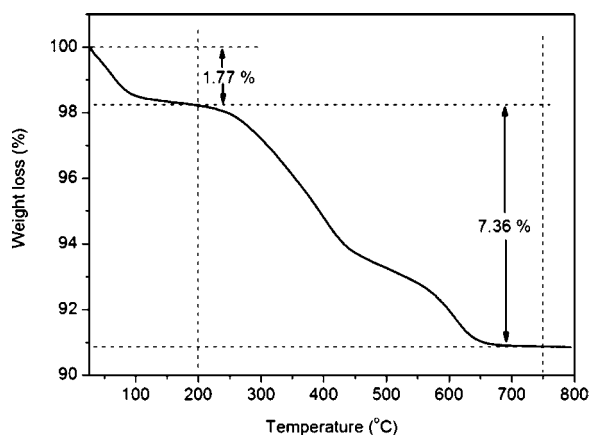


Fig. 2. TGA curve of rGO-CNT-SnO₂ hybrids heated in air by increasing the temperature from room temperature to 800 °C.

at 1323 cm⁻¹, which is lower than that of GO, and the shift of the D band is attributed to the assembly of GO and CNTs through the π - π interaction [26]. Additionally, the hybrids also exhibit a G band with a strong peak at 1577 cm⁻¹ and a broad peak at 1601 cm⁻¹, which is also attributed to the modification of rGO by CNTs [27]. According to our previous report, rGO can be obtained by reduction of GO through the hydrothermal method [19]. Based on the above results, it is deduced that rGO-CNT-SnO₂ hybrids have been successfully prepared by the hydrothermal treatment of GO-CNT dispersion in the presence of SnCl₄.

To examine the content of CNT and rGO in the hybrids, the rGO-CNT-SnO₂ hybrids were characterized by TGA. Fig. 2 shows the TGA curve of the rGO-CNT-SnO₂ hybrids by heating in air from room temperature to 800 °C at a heating rate of 10 °C/min. A weight loss of 1.77% is observed by heating the hybrids from room temperature to 200 °C, which is attributed to desorption of guest molecules including water and gases adsorbed by the hybrids. Further increasing the temperature from 200 °C to 700 °C, the hybrids show the weight loss of 7.36% attributed to the loss of the functional groups in rGO as well as the combustion of rGO and CNTs [11]. Based on the results of TGA, the content of SnO₂ in the hybrids is 90.87%.

Fig. 3 shows the TEM images of rGO-CNT-SnO₂ hybrids. It is seen that the hybrids exhibit typical plat morphology, which is similar with the rGO-based materials (Fig. 3a). Compared to the pure rGO, the hybrids consist of numerous nanoparticles on the surface, indicating the formation of SnO₂ nanoparticles on the

rGO, further confirmed by corresponding high magnification TEM image (Fig. 3b). It is also found that CNT is obviously observed on the surface of rGO sheet, indicating the successful introduction of CNT into the rGO-SnO₂ hybrids, as shown in Fig. 3b. It is also found that the diameter of CNT and SnO₂ nanoparticles is about 10–15 nm and 5–8 nm, respectively. It should be noted that the structure of the hybrids can be analyzed as the immobilization of SnO₂ nanoparticles on the surface of rGO decorated with CNTs, although the content of rGO in hybrids is relatively small. The successful modification of rGO by SnO₂ and CNTs could tune the semiconductor properties of rGO, leading to a new way for improving the sensing performances of rGO-based materials for gas sensing operating at room temperature.

The gas sensor based on rGO-CNT-SnO₂ hybrids was firstly tested to detection of NO₂ at room temperature and the structure of the electrode is shown in Fig. 4a and the detailed structure of the electrodes is also shown in Fig. 4b. It should be noted that the dropping method is different from the conventional dip-casting method for preparation of metal oxide-based gas sensors. It is seen that the concentration of the dispersion containing sensing materials and the volume dropped onto the electrode could be controlled accurately, and thus good reproducibility of the sensor fabrication process is obtained. The present work is focused on the fabrication of rGO-based NO₂ sensor operated at room temperature, where rGO-CNT-SnO₂ hybrids were used as sensing materials. Although the room temperature in theory is 25 °C, the temperature in our lab may be higher or lower than 25 °C in various seasons. To remain the temperature constant for gas sensing, a slightly high temperature (32 °C) is adopted. Thus, a heater was integrated into the electrode for detection of NO₂.

Fig. 5a shows the response and recovery curve of this sensor toward 5 ppm NO₂. The resistance of rGO-CNT-SnO₂ hybrids on the electrode is 205 M Ω , which is much higher than that of pure rGO, indicating the successful modification of rGO by SnO₂. The resistance of the sensor decreases rapidly by placing the sensor into the vessel containing of 5 ppm NO₂, and the resistance of the sensor recovers to the initial value after removing the sensor in air. It is clearly seen that rGO-CNT-SnO₂ hybrids exhibit a typical the p-type semiconductor property. The response of the sensor to 5 ppm NO₂ is 2.53, and the response time and recovery time of the sensor toward 5 ppm NO₂ are 8 s and 77 s, respectively. It should be noted that sensing performances of the sensor based on rGO-CNT-SnO₂ hybrids are much better than the previously reported NO₂ sensors based on rGO-based materials, and the detailed comparison of the sensor based on rGO-CNT-SnO₂ hybrids and other

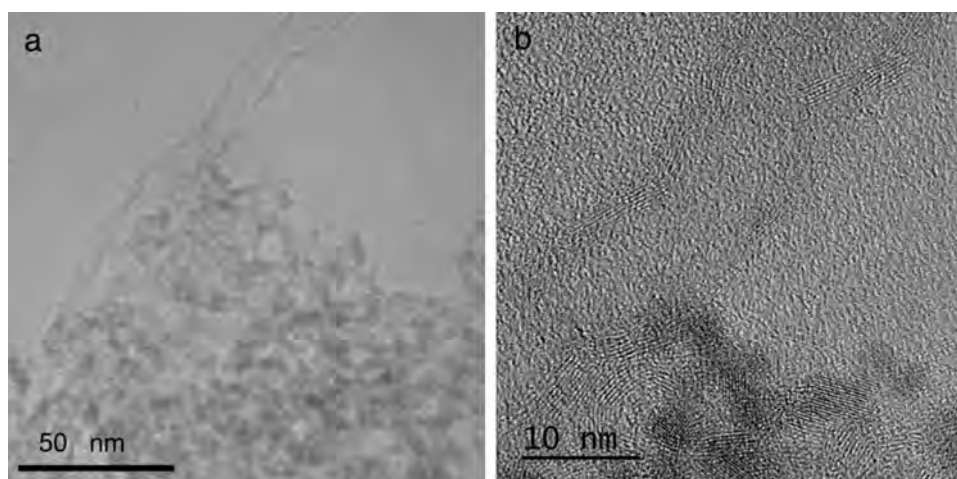


Fig. 3. (a) Low and (b) high magnification TEM images of rGO-CNT-SnO₂ hybrids.

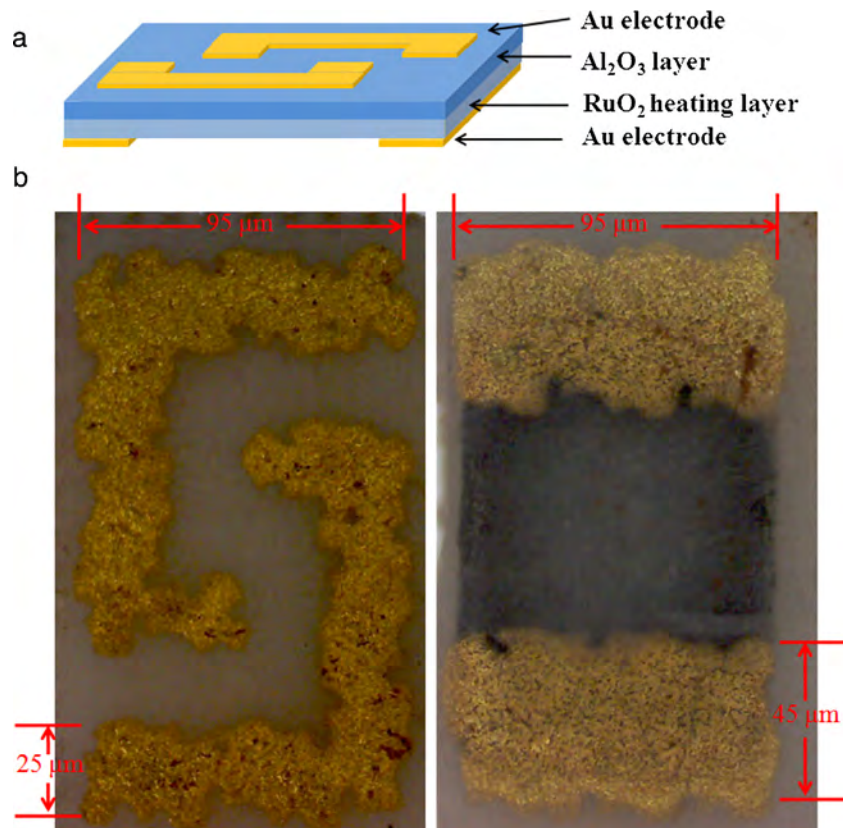


Fig. 4. (a) The schematic illustration of device for fabrication of room temperature NO_2 sensors based on rGO-CNT-SnO₂ hybrids and (b) the photographs of the electrodes.

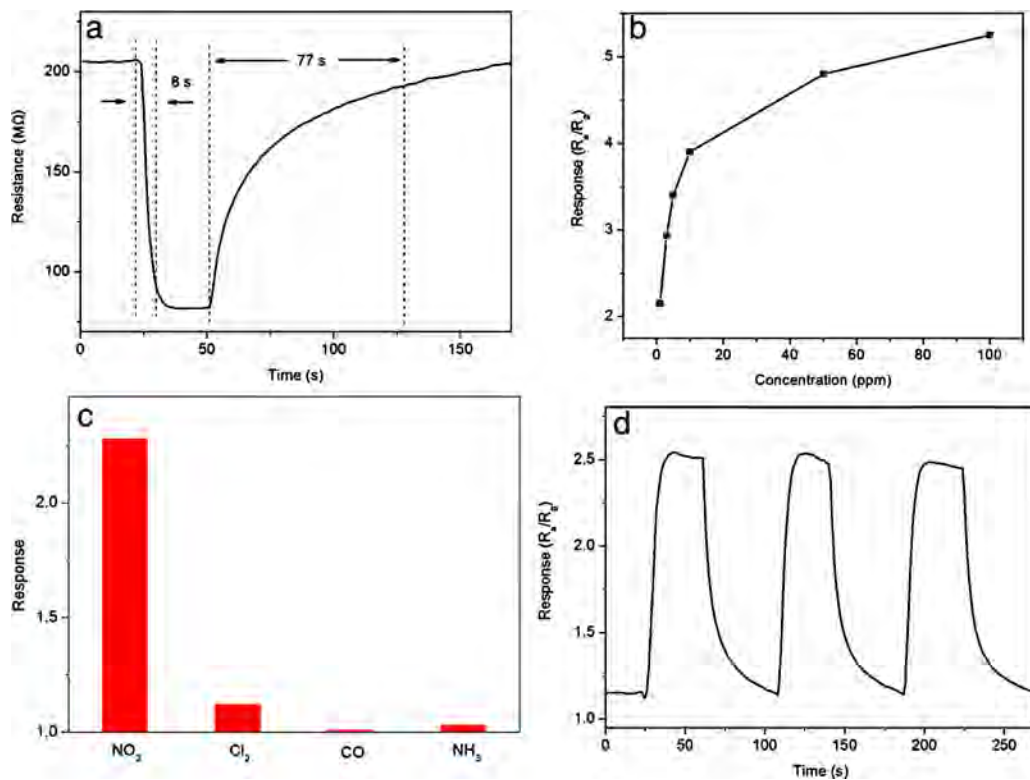


Fig. 5. (a) The response and recovery curve of the sensor based on rGO-CNT-SnO₂ hybrids to 5 ppm NO_2 operated at room temperature. (b) The responses of the sensor based on rGO-CNT-SnO₂ hybrids toward the NO_2 concentrations ranging from 1 ppm to 100 ppm at room temperature. (c) The selectivity of the sensors based on rGO-CNT-SnO₂ hybrids toward 5 ppm gases, including NO_2 , Cl_2 , CO and NH_3 at room temperature. (d) The reproducibility of temporal response of rGO-CNT-SnO₂ hybrids exposed to 5 ppm NO_2 at room temperature.

Table 1
Comparison of sensing performances of our proposed NO₂ sensor with other published NO₂ sensors based on metal oxide-rGO hybrids.

Materials	Concentration (ppm)	Operating temperature (°C)	Response	Response/recovery times (s/s)	Reference
ZnO-rGO	5	RT	25.6%	165 s/499 s	[11]
rGO-SnO ₂ nanoparticles	5	50	3.31	135 s/200 s	[19]
Cu ₂ O nanowires-rGO	2	RT	67.8%	-/-	[27]
WO ₃ nanorods-rGO	1	300	61	-/-	[33]
WO ₃ -rGO	5	250	133	25–200 s/ 25–200 s	[34]
NiO nanosheets-rGO	5	200	~4.7	-/-	[35]
Co ₃ O ₄ -rGO	60	RT	80%	-/no recovery	[36]
rGO-CNTs-SnO ₂	5	RT	2.53	8 s/77 s	This work

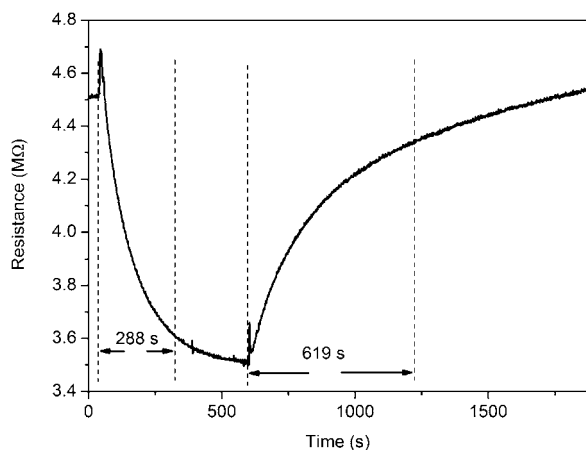


Fig. 6. The response and recovery curve of the sensor based on rGO-SnO₂ hybrids to 5 ppm NO₂ operated at room temperature.

rGO-based sensors is shown in Table 1. Furthermore, this sensor also exhibits faster response time (8 s) and recovery time (77 s) than that of rGO-SnO₂ nanocomposites (288 s and 619 s) as shown in Fig. 6, indicating the improvement of sensing performances of rGO-based NO₂ sensors by introduction of SnO₂ nanoparticles together with CNTs. Compared to the previously reported NO₂ gas sensing based graphene nanomesh [28] and Au nanoparticles-rGO [29], the sensor based on rGO-CNT-SnO₂ hybrids shows fast recovery rate, which is attributed to the modification of rGO by SnO₂ nanoparticles, leading to the fast recovery rate through the interactions between NO₂ molecules and SnO₂ nanoparticles; While the slow recovery rate is attributed to the special interactions between NO₂ molecules and the defect of rGO for the conventional rGO-based gas sensors. Indeed, SnO₂ nanocrystals prepared by the electrospinning method show fast response and recovery for detection of NO₂ at room temperature [30]. Furthermore, the fast response and recovery rate is also attributed to introduction of CNT into rGO-SnO₂ hybrids. Firstly, the presence of CNT could prevent the restacking of rGO layers, indicating improvement of the surface area due to the formation of microstructure [31]. Secondly, the introducing of CNT could also improve the electron-transfer rate during the process of NO₂ sensing, where the conductivity of CNT is much better than rGO as well as SnO₂ nanoparticles [32].

The response of the sensor based on rGO-CNT-SnO₂ hybrids to various concentrations of NO₂ is also examined, as shown in Fig. 5b. It is seen that the response to NO₂ increases rapidly with increasing the concentrations of NO₂ ranging from 1 ppm to 10 ppm, and the response increases slowly by further increasing the NO₂ from 10 ppm to 100 ppm. Additionally, the response of the sensor toward 1 ppm NO₂ is 1.60, suggesting that the sensor thus fabricated can be used for detection of NO₂ at relatively low concentration of NO₂. All these observations indicate that the sensor

based on rGO-CNT-SnO₂ hybrids can be used for detection of NO₂ with a wide detection range from 1 ppm to 100 ppm. Furthermore, a good linearity of response curve of this sensor is observed for detection of NO₂ with concentration from 1 ppm to 10 ppm.

The selectivity is also a very important parameter for gas sensor, and the sensor based on rGO-CNT-SnO₂ hybrids is also examined, as shown in Fig. 5c. It is well known that the rGO-based sensors are sensitive to NO₂ and NH₃, because they are strong electron donor and electron acceptor, respectively. In addition, due to the strong oxidation ability, Cl₂ is also an interference for detection of NO₂. As shown in Fig. 5c, it is seen that the response of the sensor toward 5 ppm NO₂ is 2.53, while the response to 5 ppm Cl₂, NH₃ and CO are no more than 1.20, indicating the good selectivity of the sensor based on rGO-CNT-SnO₂ hybrids. It should be noted that the poor response of the sensor to NH₃ is observed, which is different from the previously reported rGO-based gas sensor [37]. The poor response to NH₃ may be attributed to the presence of SnO₂, which could change the active sites on the surface of the sensing materials, as well as tune the semiconductor property of rGO.

Fig. 5d shows the reproducibility of temporal response of rGO-CNT-SnO₂ hybrids exposed to 5 ppm NO₂. Notably, the sensor maintains its initial response amplitude without a clear decrease upon three successive sensing tests to 5 ppm NO₂, indicating that the rGO-CNT-SnO₂ hybrids possess good repeatability. All these observations indicate that rGO-CNT-SnO₂ hybrids are good candidate for development of high performance room temperature NO₂ sensor.

The sensing mechanism of the sensor based on rGO-CNT-SnO₂ toward the detection of NO₂ is also discussed. It is seen that rGO-CNT-SnO₂ hybrids exhibit high response, fast response time and recovery time than that of rGO-SnO₂ hybrids, as shown in Figs. 5a and 6, which are also better than that of pure rGO. The improvement of sensing performances is attributed to the tuning the structure of sensing materials by introduction of SnO₂ nanoparticles and CNT, and the possible reasons for enhancing the sensing performances may be proposed as follow. Firstly, the modification of rGO by SnO₂ nanoparticles not only tunes the surface active sites for adsorption and desorption of target gas, but also tunes the semiconductor properties by formation of p-n heterojunction structure between n-type SnO₂ and p-type rGO. Secondly, the introduction of CNT could improve the electron-transfer rate due the good electrical conductivity of CNT, as well as the increases the surface area of the sensing materials due to the one-dimension structure.

As shown in the above data, the SnO₂-CNTs-rGO hybrids show a typical p-type semiconductor property, which is different from the previously reported the gas sensors based on SnO₂-based materials [38]. Two different depletions layers coexist in the hybrids, where one is on the surface of SnO₂ nanoparticles and the other one is the interface between SnO₂ nanoparticles and rGO sheets [14]. Due to the high coverage of SnO₂ on rGO and good sensing performance compared to that of pure rGO, thus the sensing performance is performed by adsorption/desorption of NO₂ on the surface of SnO₂. It is

well known that the numerous oxygen adsorbates (O^{2-} , O^- or O_2^-) are formed on the surface of SnO_2 nanoparticles after adsorption of oxygen by SnO_2 nanoparticles, where due to electron transfer from the conduction band (CB) of the SnO_2 to oxygen [39]. By exposition of the hybrids into NO_2 , a strong electron donor, the electrons were injecting into the hybrids, leading to the decreasing the resistance of the hybrids. In contrast, after the sensor inserting into air, the NO_2 molecule desorbed from the surface of hybrids, the resistance of the sensor increases and recovers to the initial resistance. The presence of p-n hetero-junction could increase the electron transfer rate during the detection process, due to the high conductivity of rGO, compared to SnO_2 nanoparticles [27,34]. However, the exact sensing mechanism of rGO-CNT- SnO_2 hybrids for detection of NO_2 is not completely understood at present time and requires further study.

4. Conclusions

In conclusion, a new NO_2 sensor has been successfully fabricated by using rGO-CNT- SnO_2 hybrids as sensing materials, which were prepared by hydrothermal treatment of GO-CNT dispersion in the presence of $SnCl_4$. Most importantly, the sensor based on rGO-CNT- SnO_2 hybrids exhibits high response, fast response and recovery rate, good selectivity as well as good stability for detection of NO_2 at room temperature, which are much better than the previously reported rGO-based NO_2 sensors. Our present study is of importance because it provides a new sensing material for fabrication of high-performance room temperature NO_2 sensors.

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References

- [1] J. Kong, N.R. Franklin, C.W. Zhou, M.G. Chapline, S. Peng, K.J. Cho, H.J. Dai, Nanotube molecular wires as chemical sensors, *Science* 287 (2000) 622–625.
- [2] Q. Wan, Q. Li, Y. Chen, T. Wang, X. He, J. Li, C. Lin, Fabrication and ethanol sensing characteristics of ZnO nanowire gas sensors, *Appl. Phys. Lett.* 84 (2004) 3654–3656.
- [3] F. Schedin, A.K. Geim, S.V. Morozov, E.W. Hill, P. Blake, M.I. Katsnelson, K.S. Novoselov, Detection of individual gas molecules adsorbed on graphene, *Nat. Mater.* 6 (2007) 652–655.
- [4] D.-T. Phan, G.-S. Chung, Characteristics of resistivity-type hydrogen sensor using palladium-graphene nanocomposite, *Int. J. Hydrog. Energy* 39 (2014) 620–629.
- [5] J.D. Fowler, M.J. Allen, V.C. Tung, Y. Yang, R.B. Kaner, B.H. Weiller, Practical chemical sensors from chemically derived graphene, *ACS Nano* 3 (2009) 301–306.
- [6] F. Ricciardella, E. Massera, T. Polichetti, M.L. Miglietta, G.D. Francia, A calibrated graphene-based chemisorption sensor for sub parts-per-million NO_2 detection operating at room temperature, *Appl. Phys. Lett.* 104 (2014) 183502.
- [7] G. Lu, L.E. Ocola, J. Chen, Reduced graphene oxide for room-temperature gas sensors, *Nanotechnology* 20 (2009) 445502.
- [8] J. Wang, B. Singh, S. Maeng, H.-I. Joh, G.-H. Kim, Assembly of thermally reduced graphene oxide nanostructures by alternating current dielectrophoresis as hydrogen-gas sensors, *Appl. Phys. Lett.* 103 (2013) 083112.
- [9] F. Yavari, Z. Chen, A.V. Thomas, W. Ren, H.-M. Cheng, N. Koratkar, High sensitivity gas detection using a macroscopic three-dimensional graphene foam network, *Sci. Rep.* 1 (2011) 166.
- [10] W. Yuan, A. Liu, L. Huang, C. Li, G. Shi, High-performance NO_2 sensors based on chemically modified graphene, *Adv. Mater.* 25 (2013) 766–771.
- [11] S. Liu, B. Yu, H. Zhang, T. Fei, T. Zhang, Enhancing NO_2 gas sensing performances at room temperature based on reduced graphene oxide-ZnO nanoparticles hybrids, *Sens. Actuators B* 202 (2014) 272–278.
- [12] Z. Zhang, R. Zou, G. Song, L. Yu, Z. Chen, J. Hu, Z. Zhang, R. Zou, G. Song, L. Yu, Z. Chen, J. Hu, Highly aligned SnO_2 nanorods on graphene sheets for gas sensors, *J. Mater. Chem.* 21 (2011) 17360–17365.
- [13] G. Giovannini, S.G. Leonardi, M. Latino, N. Donato, S. Baek, D.E. Conte, P.A. Russo, N. Nicola, G. Neri, S.G. Leonardi, M. Latino, N. Donato, S. Baek, D.E. Conte, P.A. Russo, N. Pinna, Sensing behavior of SnO_2 /reduced graphene oxide nanocomposites toward NO_2 , *Sens. Actuators B* 179 (2013) 61–68.
- [14] C. Marichy, P.A. Russo, M. Latino, J.-P. Tessonnier, M.-G. Willinger, N. Donato, G. Neri, N. Pinna, Tin dioxide-carbon heterostructures applied to gas sensing: structure-dependent properties and general sensing mechanism, *J. Phys. Chem. C* 117 (2013) 19729–19739.
- [15] S.-J. Choi, B.-H. Jang, S.-J. Lee, B.K. Min, A. Rothschild, I.-D. Kim, Selective detection of acetone and hydrogen sulfide for the diagnosis of diabetes and halitosis using SnO_2 nanofibers functionalized with reduced graphene oxide nanosheets, *ACS Appl. Mater. Interf.* 6 (2014) 2588–2597.
- [16] S. Mao, S. Cui, G. Lu, K. Yu, Z. Wei, J. Chen, Tuning gas-sensing properties of reduced graphene oxide using tin oxide nanocrystals, *J. Mater. Chem.* 22 (2012) 11009–11013.
- [17] P.A. Russo, N. Donato, S.G. Leonardi, S. Baek, D.E. Conte, G. Neri, N. Pinna, Room-temperature hydrogen sensing with heteronanostructures based on reduced graphene oxide and tin oxide, *Angew. Chem. Int. Ed.* 51 (2012) 11053–11057.
- [18] Q. Lin, Y. Li, M. Yang, Tin oxide/graphene composite fabricated via a hydrothermal method for gas sensors working at room temperature, *Sens. Actuators B* 173 (2012) 139–147.
- [19] H. Zhang, J. Feng, T. Fei, S. Liu, T. Zhang, SnO_2 nanoparticles-reduced graphene oxide nanocomposites for NO_2 sensing at low operating temperature, *Sens. Actuators B* 190 (2014) 472–478.
- [20] S. Liu, J. Tian, L. Wang, H. Li, Y. Zhang, X. Sun, Stable aqueous dispersion of graphene nanosheets: noncovalent functionalization by a polymeric reducing agent and their subsequent decoration with Ag nanoparticles for enzymeless hydrogen peroxide detection, *Macromolecules* 43 (2010) 10078–10083.
- [21] V.C. Tung, J.-H. Huang, I. Tevis, F. Kim, J. Kim, C.-W. Chu, S.I. Stupp, J. Huang, Surfactant-free water-processable photoconductive all-carbon composite, *J. Am. Chem. Soc.* 133 (2011) 4940–4947.
- [22] S. Liu, J. Tian, L. Wang, Y. Luo, X. Sun, Production of stable aqueous dispersion of poly(3,4-ethylenedioxythiophene) nanorods using graphene oxide as a stabilizing agent and their application for nitrite detection, *Analyst* 136 (2011) 4898–4902.
- [23] C.-H. Kwak, H.-S. Woo, J.-H. Lee, Selective trimethylamine sensors using Cr_2O_3 -decorated SnO_2 nanowires, *Sens. Actuators B* 204 (2014) 231–238.
- [24] X. Huang, X. Qi, F. Boey, H. Zhang, Graphene-based composites, *Chem. Soc. Rev.* 41 (2012) 666–686.
- [25] S. Liu, J. Tian, L. Wang, X. Sun, A method for the production of reduced graphene oxide using benzylamine as a reducing and stabilizing agent and its subsequent decoration with Ag nanoparticles for enzymeless hydrogen peroxide detection, *Carbon* 49 (2011) 3158–3164.
- [26] K. Sablok, V. Bhalla, P. Sharma, R. Kaushal, S. Chaudhary, C.R. Suri, Amine functionalized graphene oxide/CNT nanocomposite for ultrasensitive electrochemical detection of trinitrotoluene, *J. Hazard. Mater.* 248–249 (2013) 322–328.
- [27] S. Deng, V. Tjoa, H.M. Fan, H.R. Tan, D.C. Sayle, M. Olivo, S. Mhaisalkar, J. Wei, C.H. Sow, Reduced graphene oxide conjugated Cu_2O nanowire mesocrystals for high-performance NO_2 gas sensor, *J. Am. Chem. Soc.* 134 (2012) 4905–4917.
- [28] R.K. Paul, S. Badhulika, N.M. Saucedo, A. Mulchandani, Graphene nanomesh as highly sensitive chemiresistor gas sensor, *Anal. Chem.* 84 (2012) 8171–8178.
- [29] V. Tjoa, W. Jun, V. Dravid, S. Mhaisalkar, N. Mathews, Hybrid graphene-metal nanoparticle systems: electronic properties and gas interaction, *J. Mater. Chem.* 21 (2011) 15593–15599.
- [30] C. Jiang, G. Zhang, Y. Wu, L. Li, K. Shi, Facile synthesis of SnO_2 nanocrystalline tubes by electrospinning and their fast response and high sensitivity to NO_x at room temperature, *CrystEngComm* 14 (2012) 2739–2747.
- [31] Q. Tang, M. Sun, S. Yu, G. Wang, Preparation and supercapacitance performance of manganese oxide nanosheets/graphene/carbon nanotubes ternary composite film, *Electrochim. Acta* 125 (2014) 488–496.
- [32] Y. Du, X. Gao, X. Ye, Z. Zheng, Q. Feng, C. Wang, K. Wu, Composition and architecture-engineered Au- SnO_2 /GNS-SWCNTs nanocomposites as ultrasensitive and robust electrochemical sensor for antioxidant additives in foods, *Sens. Actuators B* 203 (2014) 926–934.
- [33] J. Qin, M. Cao, N. Li, C. Hu, Graphene-wrapped WO_3 nanoparticles with improved performances in electrical conductivity and gas sensing properties, *J. Mater. Chem.* 21 (2011) 17167–17171.
- [34] S. Srivastava, K. Jain, V.N. Singh, S. Singh, N. Vijayan, N. Dilawar, G. Gupta, T.D. Senguttuvan, Faster response of NO_2 sensing in graphene- WO_3 nanocomposites, *Nanotechnology* 23 (2012) 205501.
- [35] L.T. Hoa, H.N. Tien, V.H. Luan, J.S. Chung, S.H. Hur, Fabrication of a novel 2D-graphene/2D-NiO nanosheet-based hybrid nanostructure and its use in highly sensitive NO_2 sensors, *Sens. Actuators B* 185 (2013) 701–705.
- [36] N. Chen, X. Li, X. Wang, J. Yu, J. Wang, Z. Tang, S.A. Akbar, Enhanced room temperature sensing of Co_3O_4 -intercalated reduced graphene oxide based gas sensors, *Sens. Actuators B* 188 (2013) 902–908.
- [37] N. Hu, Y. Wang, L. Zhang, Y. Wang, X. Huang, H. Wei, L. Wei, Y. Zhang, Ultrafast and sensitive room temperature NH_3 gas sensors based on chemically reduced graphene oxide, *Nanotechnology* 25 (2014) 025502.
- [38] L. Yin, D. Chen, X. Cui, L. Ge, J. Yang, L. Yu, B. Zhang, R. Zhang, G. Shao, Normal-pressure microwave rapid synthesis of hierarchical SnO_2 @rGO nanostructures with superhigh surface areas as high-quality gas-sensing and electrochemical active materials, *Nanoscale* 6 (2014) 13690–13700.
- [39] J. Cao, T. Zhang, F. Li, H. Yang, S. Liu, Enhanced ethanol sensing of SnO_2 hollow micro/nanofibres fabricated by coaxial electrospinning, *N. J. Chem.* 37 (2013) 2031–2036.

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