Enhancing NO$_2$ gas sensing performances at room temperature based on reduced graphene oxide-ZnO nanoparticles hybrids

Sen Liu, Bo Yu, Hao Zhang, Teng Fei, Tong Zhang*

State Key Laboratory on Integrated Optoelectronics, College of Electronic Science and Engineering, Jilin University, Changchun 130012, PR China

ABSTRACT

NO$_2$ gas sensor has been constructed using reduced graphene oxide-ZnO nanoparticles (ZnO-rGO) hybrids as sensing materials. Most importantly, the sensor exhibits higher sensitivity, shorter response time and recovery time than those of the sensor based on rGO, indicating that the sensing performances for NO$_2$ sensing operating at room temperature have been enhanced by introduction of ZnO nanoparticles into rGO matrix.

© 2014 Elsevier B.V. All rights reserved.

1. Introduction

Graphene, a rapidly rising star on the horizon of materials science, has fascinated the scientific community in recent years due to its remarkable electronic conductivity, superior mechanical properties, large surface area, and high thermal stability [1–3]. Particularly, the extremely high carrier mobility of graphene nanosheets at room temperature indicates that graphene is a promising candidate for gas sensing operating at room temperature [4]. Additionally, graphene also exhibits detectable change in its electrical resistance after adsorption of guest gases, which further ensures graphene as good candidate for gas sensing [5]. Up to now, graphene-based materials obtained by various methods have been used for detection of gases at low operating temperature, such as, reduced graphene oxide (rGO) obtained by chemical reduction of GO [6,7] and thermal reduction of GO [8,9], graphene prepared by chemical vapor deposition (CVD) [10,11], etc. Particularly, rGO has been attracted much interest due to its great advantages of low cost and bulk quantity production [12]. However, the gas sensors based on pure rGO suffer from some disadvantages, such as low sensitivity, long response and recovery times, which limit their further applications.

Recent research has shown that the electrical properties of rGO can be tuned by doping with other atoms, modification by guest molecules via noncovalent or covalent methods, which provide a new route for preparation of high-performance rGO-based sensing materials [13,14]. For example, rGO-conducting polymers hybrids [15], organic molecules modified rGO [16], nitrogen and silica-doped rGO [17], noble metal modified rGO [18], and rGO-metal oxide hybrids [19] have been successfully used for detection of gases at room temperature. Among them, development of gas sensors based on metal oxides-rGO hybrids has also been attracted considerable attention due to the high-performance for gas sensing by using metal oxides as sensing materials. Indeed, some typical metal oxides, such as SnO$_2$ [20–22], ZnO [19,23], Cu$_2$O [24,25], and WO$_3$ [26,27] have been successfully used for enhancing the sensing properties of rGO-based gas sensors. However, these sensors still suffer from several shortcomings, such as high operating temperature, long response and recovery times, low sensitivity and so on.

ZnO, a typical n-type semiconductor with a direct wide band-gap (3.37 eV) and large excitation binding energy (60 meV), has been widely studied in gas sensing application due to its good response to a variety of reducing or oxidizing gases, low cost, and being friendly to the environment [28,29]. Additionally, recent research has shown that ZnO can be used for enhancing the sensing performance of rGO. For example, Singh et al. have reported that ZnO decorated luminescent graphene exhibits response toward CO, NH$_3$ and NO at room temperature [19]; Huang et al. prepared ZnO quantum dots/graphene nanocomposites for formaldehyde detection with fast response and recovery [22]; Yi et al. synthesized vertically aligned ZnO nanorods and graphene hybrid architectures for flexible gas sensors to detection of ethanol at 300 °C [30]; Zou et al. prepared ZnO nanorods on rGO for detection of ethanol at

* Corresponding author. Tel.: +86 431 85168385; fax: +86 431 85168270.
E-mail address: zhangtong@jlu.edu.cn (T. Zhang).

260 °C [31]. It is obviously seen that these efforts have been devoted to enhancing the sensing properties of graphene-based materials by introduction of ZnO materials. However, these sensors still have more or less disadvantages, such as low sensitivity, high operating temperature. Therefore, it is indeed necessary to develop high-performance gas sensors for detection of gas at mild conditions.

In this study, a new gas sensor was fabricated using ZnO-rGO hybrids as sensing materials for detection of NO_2 operating at room temperature. ZnO-GO hybrids were prepared by *in situ* production of ZnO nanoparticles on the surface of GO, followed by reduction of such hybrids using hydrazine hydrate as reducing agent. Most importantly, the NO_2 sensor based on ZnO-rGO hybrids exhibits higher sensitivity, shorter response time and recovery time than those of pure rGO, indicating enhancing sensing performance of pure rGO by introduction of ZnO nanoparticles.

2. Experimental

2.1. Materials

$Zn(OAc)_2 \cdot 2H_2O$, methanol, $KMnO_4$, H_2O_2 (30 wt%), N,N-dimethylformamide (DMF), $NaNO_3$, and H_2SO_4 (98%) were purchased from Beijing Chemical Corp (Beijing, China). Hydrazine hydrate and KOH were purchased from Shanghai Chemical Corp. (Shanghai, China). 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 sensing materials

GO was prepared from natural graphite powder through a modified Hummers' method [32,33].

ZnO-rGO hybrids were prepared by *in situ* production of ZnO nanoparticles on the surface of GO, followed by reduction of such hybrids using hydrazine hydrate. In a typical run, 0.054 g of $Zn(OAc)_2 \cdot 2H_2O$ was added into 125 mL of methanol at 60 °C. After stirring for 5 min, 5 mL of GO aqueous dispersion solution (1 mg/mL) was added into the mixture, followed by addition of 65 mL of KOH solution in methanol (0.03 M). After further stirring for 2 h, 200 μL of hydrazine hydrate was added into the mixture and the mixture was heated to 80 °C for 1 h. The ZnO-rGO hybrids were collected by centrifugation at 10,000 rpm for 10 min and washed with water for twice to remove the excessive KOH. The ZnO-rGO hybrids were dispersed into DMF for further use and characterization.

For comparison, pure rGO was prepared by reduction of GO in methanol solution using hydrazine hydrate as reducing agent at 80 °C for 1 h.

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) data were 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. X-ray photoelectron spectroscopy (XPS) analysis was measured on an ESCALAB MK II X-ray photoelectron spectrometer using Mg as the exciting source. 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 DMF dispersion of ZnO-rGO hybrids was used as sensing materials for fabrication of the NO_2 sensors. The sensors were obtained by dip-coating the dispersion onto the ceramic substrate before it was coated with the ZnO-rGO dispersion, two pairs of electrodes were printed on each side as signal electrode and heating electrode, respectively.

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 $S = (R_a - R_g)/R_a \times 100\%$, 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

In the present work, ZnO-rGO hybrids were prepared by an one-pot method using GO and $Zn(OAc)_2 \cdot 2H_2O$ as sources. Fig. 1a shows the XRD patterns of the samples thus obtained, GO and rGO, respectively. It is seen that GO exhibits a strong diffraction peak at 2θ of 10.92° attributed to (0 0 2) diffraction of GO, indicating the formation of GO by Hummers method from graphite. Note that this peak disappears in the rGO and final hybrids, indicating the reduction of GO into rGO in the presence of hydrazine hydrate, a strong reducing agent [12]. Furthermore, compared to XRD pattern of rGO, seven diffraction peaks at 2θ of 31.55, 34.41, 36.25, 47.47, 56.34, 62.61 and 67.75° are observed for the final hybrids, which are indexed as (1 0 0), (0 0 2), (1 0 1), (1 0 2), (1 1 0), (1 0 3) and (1 1 2) diffractions of hexagonal phase with Wurtzite crystal structure of ZnO (space group: C6V (P6₃mc), JCPDS file no. 0-3-0888) [34]. These observations indicate the successful preparation of ZnO-rGO hybrids.

Fig. 1b shows the Raman spectra of ZnO-rGO hybrids, rGO and GO, revealing a D band at about 1355 cm⁻¹ and a G band at about 1605 cm⁻¹, which are attributed to the breathing mode of k-point phonons of A_{1g} symmetry and the first-order scattering of the E_{2g} phonons, respectively [35]. In this work, the intensities of D band to G band for ZnO-rGO hybrids (1.01) and rGO (1.10) are larger than that of GO (0.87), indicating an increased D/G intensity ratio compared to that in GO. This change suggests a decrease in the average size of the sp² domains upon reduction of the exfoliated GO, which can be explained if new graphitic domains were created that are smaller in size to the ones present in GO before reduction, but more numerous in number [2]. All these results confirm the formation of rGO by reduction of GO during the synthesis process for ZnO-rGO hybrids and rGO [35]. It is also found that the intensity of D/G for rGO is also larger than that of ZnO-rGO hybrids, indicating the low disorder degree of ZnO-rGO hybrids, compared to rGO. This observation may be attributed to the interaction of ZnO-GO during the reduction of GO by hydrazine hydrate, which is similar with the previous report on preparation of rGO/SnO₂ [36]. Additionally, the G band for ZnO-rGO hybrids and rGO also changes from 1608 to 1589 cm⁻¹, further confirming the reduction of GO.

The content of the ZnO in ZnO-rGO hybrids was characterized by TGA curve, as shown in Fig. 1c. The weight loss from room temperature to 250 °C is 4.72%, which is attributed to desorption of surface bound water [37]. The weight loss from 250 to 700 is about 16.26%, attributed to the removal of oxygen-containing
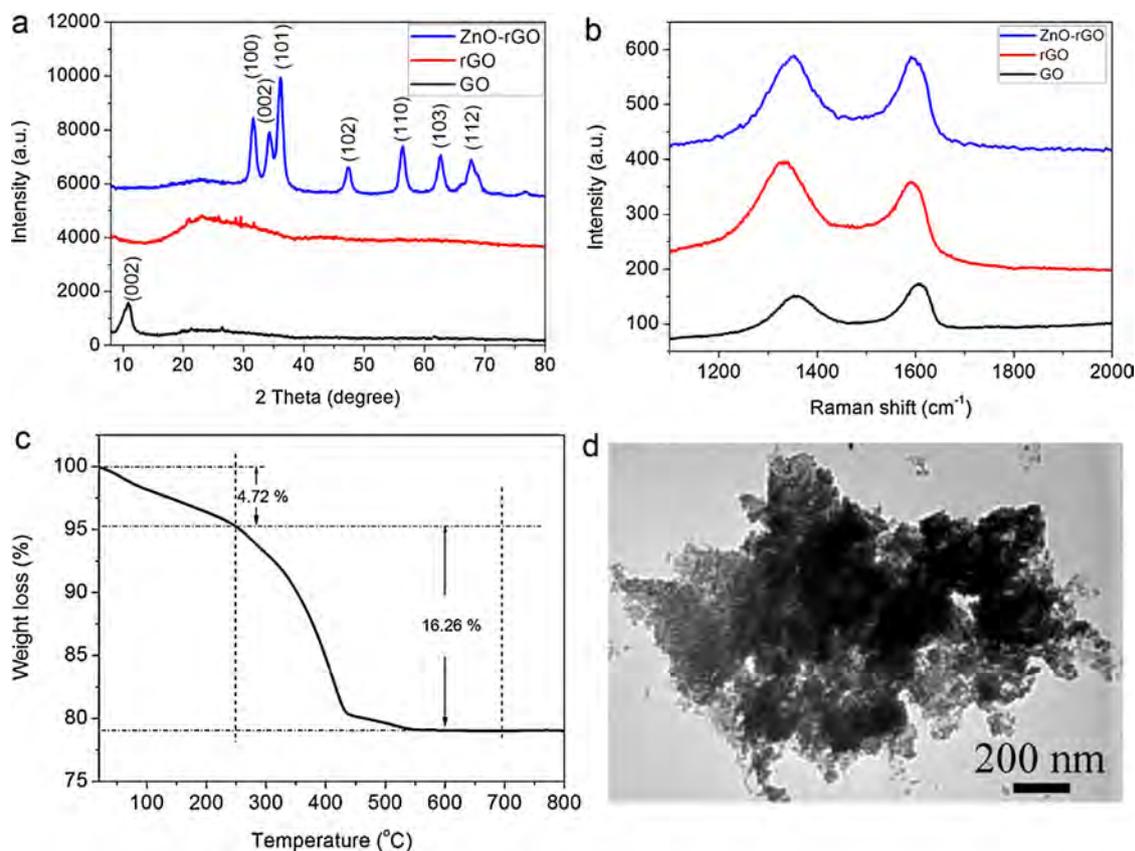
Fig. 1. (a) XRD patterns and (b) Raman spectra of ZnO-rGO hybrids GO and rGO, (c) TGA curve and (d) TEM image of ZnO-rGO hybrids.

groups and the decomposition of carbon framework from the composites [38]. Based on the about results, the content of ZnO in ZnO-rGO hybrids is about 79.02%. Furthermore, the TEM image of ZnO-rGO hybrids (Fig. 1d) exhibits a typical the morphology similar to graphene-based materials. Furthermore, numerous nanoparticles are decorated on the surface of rGO, indicating the formation of ZnO-rGO hybrids.

The structure of ZnO-rGO hybrids was further characterized by XPS technique. Fig. 2a shows the XPS spectra of ZnO-rGO hybrids and GO, respectively. It is seen that both samples exhibit two peaks at 284.6 eV and 532.0 eV, which are attributed to C1s and O1s bands, respectively. Note that ZnO-rGO hybrids also exhibit several bands associated with Zn2p, Zn3s, Zn3p and Zn3d bands, which further confirms the presence of Zn element in the final samples. Fig. 2b–d shows the C1s spectra of GO rGO, and ZnO-rGO hybrids. It is seen that both samples exhibit several peaks, which can be deconvoluted into three peaks at 284.5 eV, 286.6 eV, and 288.4 eV, associated with C—C, C—O, and C=O, respectively. It is obviously seen that the peak intensity of C—O and C=O is strong in GO (Fig. 2c). In contrast, the peak intensity of C—O and C=O in rGO and ZnO-rGO hybrids tremendously decreases, and the content of C—C correspondingly increases dramatically. Fig. 3 shows the Zn2p spectrum of ZnO-rGO hybrids, revealing two bands at 1021.7 eV and 1044.8 eV, indicating the production of ZnO. All these observations further confirm that ZnO-rGO hybrids have been successfully prepared.

To demonstrate the sensing application of the ZnO-rGO hybrids, a room temperature NO_2 gas sensor was constructed by deposition of ZnO-rGO dispersion on the surface of the microelectrode. In addition, the NO_2 gas sensor was also constructed by using rGO as sensing materials. Fig. 4a shows the schematic structure of the microelectrode used for gas sensing in the present work, which is the same to our previous work [22]. Fig. 4b shows the

current–voltage (I–V) curves of ZnO-rGO and rGO on the microelectrodes at room temperature, respectively. It is seen that rGO is a typical p-type semiconductor, which is the same to previously reported publication [8,9]. After introduction of ZnO nanoparticles (a typical n-type semiconductor) into rGO matrix, the hybrids are also a typical p-type semiconductor. Furthermore, the current of the sensor based on ZnO-rGO hybrids is much lower than that of rGO, indicating the increasing the resistance of rGO. This could be explained by the fact that the deposited ZnO NPs result in a hole depletion region of the rGO sheet near the interface with n-type ZnO NPs, which leads to a decrease in the rGO electrical conductivity [39]. This observation is agreement with previous report on metal oxide modified graphene-based materials, indicating the successful modification of rGO by ZnO nanoparticles. A recent study has reported that p-type SnO_2-rGO hybrids have been successfully obtained by introduction of relatively amount of SnO_2 into rGO matrix, where the increasing the amount of SnO_2 (about 80 wt%) results in formation of n-type hybrids [40]. Although the amount of ZnO in ZnO-rGO hybrids is similar to that of SnO_2-rGO hybrids, the ZnO-rGO hybrids exhibit a typical p-type semiconductor, which is attributed to that there are other factors effecting on the semiconductor properties of rGO-metal oxide hybrids, such as the structure of rGO, the structure of metal oxides. Indeed, in our previous work, p-type SnO_2-rGO hybrids have been prepared with wide ranges of SnO_2 content ranging from 57.3 to 92.1 wt% [22]. The introduction of ZnO NPs into rGO matrix can tune the semiconductor properties of rGO, which may make effect on the sensing performance of rGO.

In the present work, the reduction of GO for ZnO-rGO hybrids was carried out in the presence of ZnO nanoparticles methanol, which is different from the previously reported preparation of rGO by hydrazine hydrate [41]. Based on the results of Raman spectra of rGO and ZnO-rGO, it is deduced that the ZnO nanoparticles
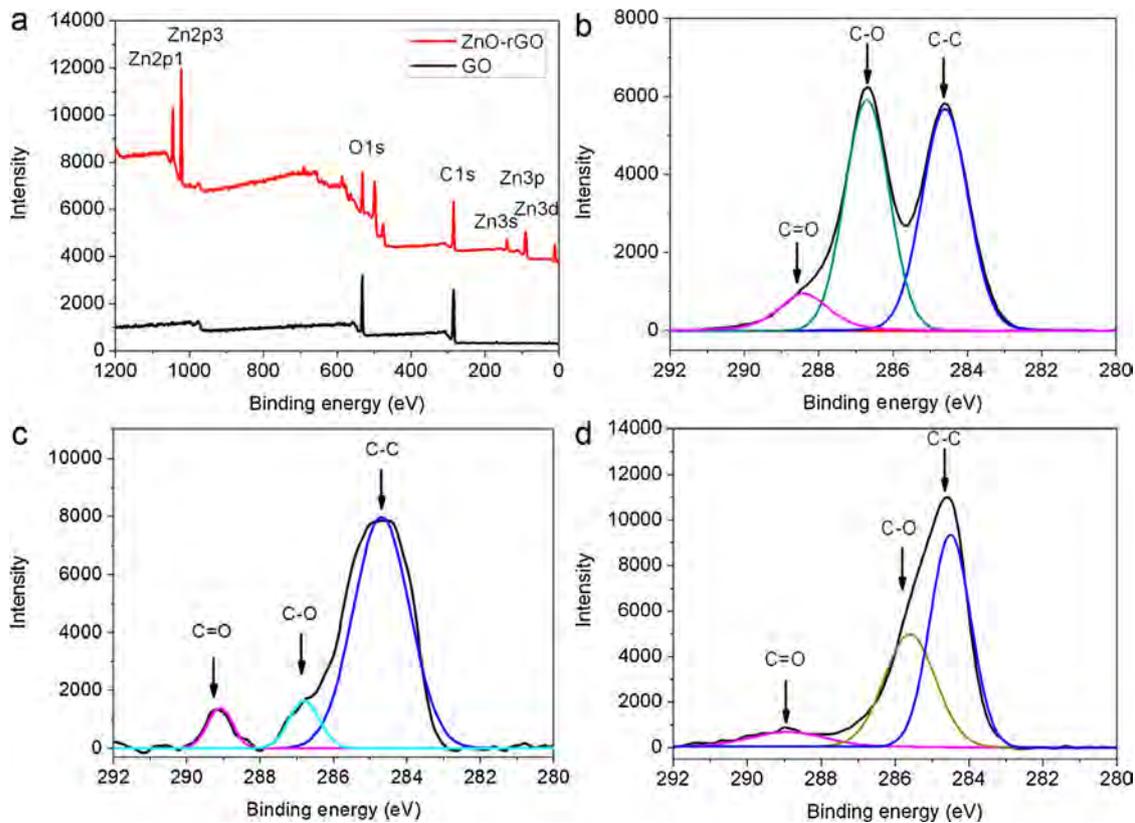
Fig. 2. (a) XPS spectra of ZnO-rGO hybrids and GO and C1s spectra of (b) GO, (c) rGO, (d) ZnO-rGO hybrids.

participate in the reduction of GO. Although the preparation of rGO form GO by using ZnO as photocatalyst under UV-light [42] or alcohol as reducing agent at high temperature [43] has been reported, the process for ZnO-rGO hybrids was performed at relatively wild conditions, such as, no strong UV-light and low temperature. Thus, the reduction of GO is attributed to the strong removal of oxygen containing group in GO by hydrazine hydrate and there may be no electron transfer from the ZnO nanoparticles to the GO.

The sensing performances were first examined by detection of NO_2 at room temperature. Fig. 4c shows the response and recovery curve of the sensor based on ZnO-rGO hybrids towards 5 ppm NO_2 operating at room temperature. It is seen that an obvious decrease of resistance is observed by introduction of the sensor into 5 ppm NO_2, indicating ZnO-rGO exhibit ability for detection

Fig. 3. Zn2p spectrum of ZnO-rGO hybrids.

of NO_2. The resistance of the senor can be recovery to the initial value after putting the sensor back to air and the response to 5 ppm NO_2 is 25.6%. The response time and recovery time towards 5 ppm are 165 s and 499 s, respectively. Furthermore, the sensing performance for detection of NO_2 by rGO is also examined. However, no obvious response is observed by introduction of the sensor into 5 ppm NO_2 (data not shown). Fig. 4d shows the response and recovery curve of the sensor based on rGO to 25 ppm NO_2, giving a response about 12.12%. The response time and recovery time towards 25 ppm NO_2 are 14.4 min and 82.0 min, respectively. The sensing performances indicate that enhancing NO_2 sensing performance of rGO is obtained by modification of rGO by ZnO nanoparticles.

Fig. 5a shows the effect of the operating temperature on the sensing performances to 5 ppm NO_2 for the sensor based on ZnO-rGO hybrids. By increasing the operating temperature from room temperature to 60 °C, the responses decrease slightly and the recovery times increase. By further increasing the operating temperature to 80 °C, the response is slightly increases to 26.3% and the recovery time also decreases. However, according to the effect of powder consumption on the application of gas sensors, detection of NO_2 by the sensor based on ZnO-rGO hybrids was performed at room temperature. Fig. 5b shows the response and recovery curve of the sensor based on ZnO-rGO hybrids to various NO_2 concentrations ranging from 1 to 25 ppm, where the responses are 13.1%, 15.2%, 25.6%, 34.9% and 45.2%, respectively, indicating that the NO_2 sensor thus constructed can be used detection of NO_2 with a wide concentration ranges. The selectivity of the sensor based on ZnO-rGO hybrids towards NO_2 is also examined, as shown in Fig. 5c. It is seen that the response of the sensor to 5 ppm NO_2 is 25.6%, which is much larger than those of the sensor to 5 ppm other gases, such as Cl_2, NO and CO, indicating that the NO_2 sensor based on ZnO-rGO hybrids exhibits good selectivity and can
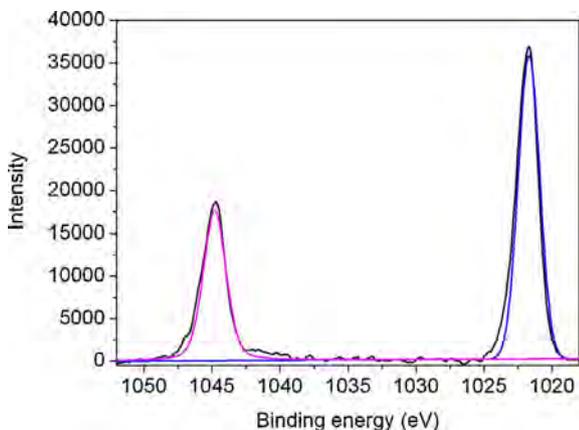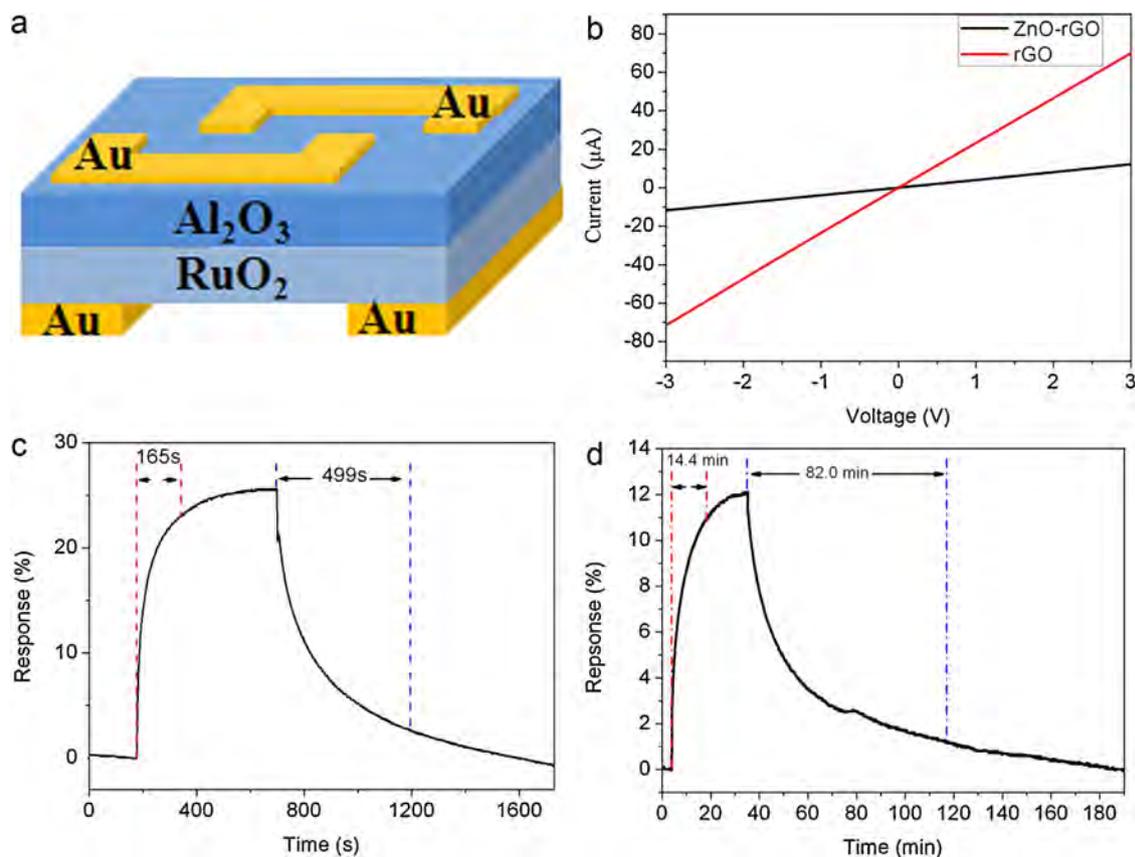
Fig. 4. (a) A scheme to illustrate the structure of microelectrode used for room temperature detection of NO_2 in this work; (b) Current–voltage curves of the sensors based on ZnO-rGO hybrids and rGO; and (c) response and recovery curve of sensor based on ZnO-rGO hybrids towards 5 ppm NO_2; and (d) response and recovery curve of sensor based on rGO towards 25 ppm NO_2. (All the sensing performances were performed at room temperature.).

be used for selective detection of NO_2. The high response to NO_2 can be attributed to its high electron-donating power, compared to other gases. Fig. 5d shows the reproducibility of temporal response of ZnO-rGO hybrids exposed to 5 ppm NO_2 at room temperature. It is seen that the sensors maintain its initial response amplitude without a clear decrease upon three successive sensing tests to 5 ppm NO_2, indicating that the ZnO-rGO hybrids possesses good repeatability. All these observations indicate that ZnO-rGO hybrids are good candidate for development of high performance NO_2 sensor operating at room temperature. The long-term stability of the NO_2 sensor based on ZnO-rGO hybrids is also examined by periodical measurements of the sensor responses to 5 ppm NO_2. The variation of the response decreases to about 97% of its initial response on the 10th day. The response decreases to about 95% and 90% on the 20th and 30th day, respectively. All these results indicate the good stability of the NO_2 sensor based on ZnO-rGO hybrids.

It is well known that the pure rGO exhibits relatively weak response and long response and recovery times for detection of NO_2

at room temperature [8,9]. Thus, the improvement of NO_2 sensing performance is attributed to the introduction of ZnO nanoparticles for modification of rGO matrix. Indeed, the gas sensing performance of rGO materials can be enhanced by modification of metal oxide nanoparticles. However, the exact sensing mechanism of ZnO-rGO hybrids for detection of NO_2 is not completely understood at present time and requires further study. The sensing performance of the NO_2 based on ZnO-rGO hybrids was also compared with the previously reported NO_2 sensors based on rGO-based materials, as shown in Table 1. Although the response of ZnO-rGO to NO_2 is lower than that of SnO_2-rGO [22], WO_3-rGO [27,44] and NiO-rGO [45], the operating temperature for ZnO-rGO is much lower than them. It is also found that the response to NO_2 is also lower than other NO_2 sensors based on Cu_2O-rGO [24] and Co_3O_4-rGO, however, ZnO-rGO hybrids exhibit faster response time and recovery time. To satisfy the practical applications for detection of NO_2 operating at room temperature, additional work is also required to further enhance the sensing performances of NO_2 sensor based on ZnO-rGO hybrids.

Table 1
Comparison of sensing performances of our proposed NO_2 sensor with other published NO_2 sensors based on metal oxide-rGO hybrids.

Materials	Concentration (ppm)	Operating temperature (°C)	Response	Response/recovery times (s/s)	Reference
SnO_2 nanoparticles-rGO	5	50	3.31	135/200	[22]
Cu_2O nanowires-rGO	2	RT	67.8%	–/–	[24]
WO_3 nanorods-rGO	1	300	61	–/–	[27]
WO_3-rGO	5	250	133	25–200/25–200	[44]
NiO nanosheets-rGO	5	200	~4.7	–/–	[45]
Co_3O_4-rGO	60	RT	80%	–/no recovery	[46]
ZnO-rGO	5	RT	25.6%	165/499	This work
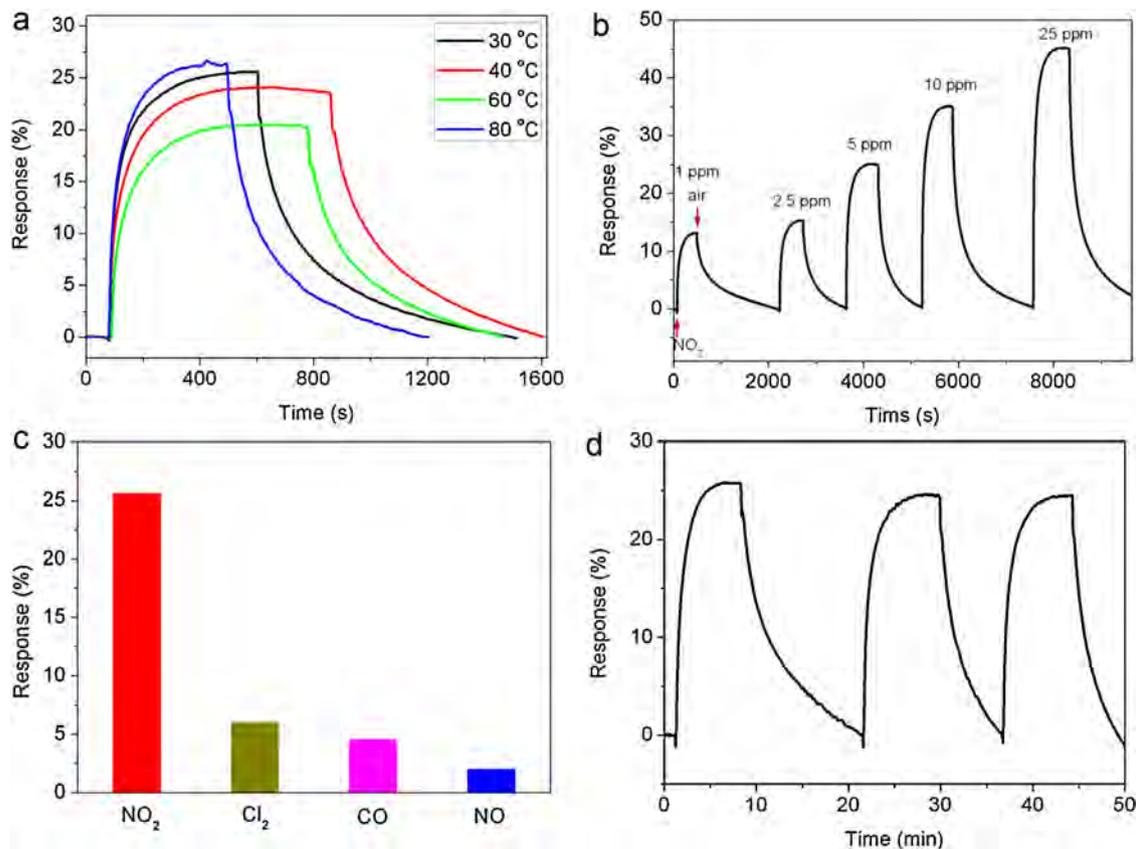
Fig. 5. (a) Response and recovery curves of the sensor based on ZnO-rGO hybrids to 5 ppm NO$_2$ operating at 30 °C, 40 °C, 60 °C and 80 °C; (b) response and recovery curve of the sensor based on ZnO-rGO hybrids to various NO$_2$ concentrations of 1 ppm, 2.5 ppm, 5 ppm, 10 ppm and 25 ppm at room temperature; (c) the selectivity of the sensors based on ZnO-rGO hybrids toward 5 ppm gases, including NO$_2$, Cl$_2$, NO and CO at room temperature; (d) the reproducibility of temporal response of ZnO-rGO hybrids exposed to 5 ppm NO$_2$ at room temperature.

4. Conclusions

In summary, room temperature NO$_2$ sensor has been successfully constructed using ZnO-rGO hybrids as sensing materials, and the sensor thus obtained exhibits better sensing performances than those of rGO. Our present work provides a novel method for development of high performance gas sensors using graphene-based materials.

Acknowledgments

References

[1] 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.

[2] S. Stankovich, D.A. Dikin, R.D. Piner, K.A. Kohlhaas, A. Kleinhammes, Y. Jia, Y. Wu, S.T. Nguyen, R.S. Ruoff, Synthesis of graphene-based nanosheets via chemical reduction of exfoliated graphite oxide, Carbon 45 (2007) 1558–1565.

[3] X. Huang, X. Qi, F. Boey, H. Zhang, Graphene-based composites, Chem. Soc. Rev. 41 (2012) 666–686.

[4] J. Wang, Y. Kwak, I. Lee, S. Maeng, G.-H. Kim, Highly responsive hydrogen gas sensing by partially reduced graphite oxide thin films at room temperature, Carbon 50 (2012) 4061–4067.

[5] R. Ghosh, A. Midya, S. Santra, S.K. Ray, P. Guha, Chemically reduced graphene oxide for ammonia detection at room temperature, ACS Appl. Mater. Interf. 5 (2013) 7599–7603.

[6] J.T. Robinson, F.K. Perkins, E.S. Snow, Z. Wei, P.E. Sheehan, Reduced graphene oxide molecular sensors, Nano Lett. 8 (2008) 3137–3140.

[7] 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.

[8] G. Lu, L.E. Ocola, J. Chen, Gas detection using low-temperature reduced graphene oxide sheets, Appl. Phys. Lett. 94 (2009) 083111.

[9] G. Lu, L.E. Ocola, J. Chen, Reduced graphene oxide for room-temperature gas sensors, Nanotechnology 20 (2009) 445502.

[10] 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.

[11] A. Salehi-Khojin, D. Estrada, K.Y. Lin, M.-H. Bae, F. Xiong, E. Pop, R.I. Masel, Polycrystalline graphene ribbons as chemiresistors, Adv. Mater. 24 (2012) 53–57.

[12] 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.

[13] W. Yuan, G. Shi, Graphene-based gas sensors, J. Mater. Chem. A 1 (2013) 10078–10091.

[14] Y. Xu, H. Bi, G. Lu, C. Li, G. Shi, Flexible graphene films via the filtration of water-soluble noncovalent functionalized graphene sheets, J. Am. Chem. Soc. 130 (2008) 5856–5857.

[15] L. Al-Mashat, K. Shin, K. Kalantar-zadeh, J.D. Plessis, S.H. Han, R.W. Kojima, R.B. Kaner, D. Li, X. Gou, S.J. Ippolito, W. Wlodarski, Graphene/polyaniline nanocomposite for hydrogen sensing, J. Phys. Chem. C 114 (2010) 16168–16173.

[16] 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.

[17] F. Niu, J.-M. Liu, L.-M. Tao, W. Wang, W.-G. Song, Nitrogen and silica co-doped graphene nanosheets for NO$_2$ gas sensing, J. Mater. Chem. A 1 (2013) 6130–6133.

[18] W. Li, X. Geng, Y. Guo, J. Rong, Y. Gong, L. Wu, X. Zhang, P. Li, J. Xu, G. Cheng, M. Sun, L. Liu, Reduced graphene oxide electrically contacted graphene sensor for highly sensitive nitric oxide detection, ACS Nano 5 (2011) 6955–6961.

[19] G. Singh, A. Choudhary, D. Haranath, A.G. Joshi, N. Singh, S. Singh, R. Pasricha, ZnO decorated luminescent graphene as a potential gas sensor at room temperature, Carbon 50 (2012) 385–394.

[20] 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.

[21] Q. Lin, Y. Li, M. Yang, Tin oxide/graphene composite fabricated via a hydro-thermal method for gas sensors working at room temperature, Sens. Actuators B 173 (2012) 139–147.

[22] 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.

[23] Q. Huang, D. Zeng, H. Li, C. Xie, Room temperature formaldehyde sensors with enhanced performance, fast response and recovery based on zinc oxide quantum dots/graphene nanocomposites, Nanoscale 4 (2012) 5651–5658.

[24] 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$_2$O nanowire mesocrystals for high-performance NO$_2$ gas sensor, J. Am. Chem. Soc. 134 (2012) 4905–4917.

[25] L. Zhou, F. Shen, X. Tian, D. Wang, T. Zhang, W. Chen, Stable Cu$_2$O nanocrystals grown on functionalized graphene sheets and room temperature H$_2$S gas sensing with ultrahigh sensitivity, Nanoscale 5 (2013) 1564–1569.

[26] X. An, J.C. Yu, Y. Wang, Y. Hu, X. Yu, G. Zhang, WO$_3$ nanorods/graphene nanocomposites for high-efficiency visible-light-driven photocatalysis and NO$_2$ gas sensing, J. Mater. Chem. 22 (2012) 8525–8531.

[27] 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.

[28] J.-Q. He, J. Yin, D. Liu, L.-X. Zhang, F.-S. Cai, L.-J. Bie, Enhanced acetone gas-sensing performance of La$_2$O$_3$-doped flowerlike ZnO structure composed of nanorods, Sens. Actuators B 182 (2013) 170–175.

[29] C.W. Na, S.-Y. Park, J.-H. Lee, Punched ZnO nanobelt networks for highly sensitive gas sensors, Sens. Actuators B 174 (2012) 495–499.

[30] J. Yi, J.M. Lee, W.I. Park, Vertically aligned ZnO nanorods and graphene hybrid architectures for high-sensitive flexible gas sensors, Sens. Actuators B 155 (2011) 264–269.

[31] R. Zou, G. He, K. Xu, Q. Liu, Z. Zhang, J. Hu, ZnO nanorods on reduced graphene sheets with excellent field emission, gas sensor and photocatalytic properties, J. Mater. Chem. A 1 (2013) 8445–8452.

[32] W.S. Hummers Jr., R. Offeman, Preparation of graphitic oxide, J. Am. Chem. Soc. 80 (1958) 1339.

[33] S. Liu, B. Yu, T. Zhang, Preparation of crumpled reduced graphene oxide–poly(p-phenylenediamine) hybrids for the detection of dopamine, J. Mater. Chem. A 1 (2013) 13314–13320.

[34] Q. Ding, Y. Miao, T. Liu, Morphology and photocatalytic property of hierarchical polyimide/ZnO fibers prepared via a direct ion-exchange process, ACS Appl. Mater. Interf. 5 (2013) 5617–5622.

[35] 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.

[36] B. Zhao, G. Zhang, J. Song, Y. Jiang, H. Zhuang, P. Liu, T. Fang, Bivalent tin ion assisted reduction for preparing graphene/SnO$_2$ composite with good cyclic performance and lithium storage capacity, Electrochim. Acta 56 (2011) 7340–7346.

[37] J. Wang, Z. Shi, J. Fan, Y. Ge, J. Yin, G. Hu, Self-assembly of graphene into three-dimensional structures promoted by natural phenolic acids, J. Mater. Chem. 22 (2012) 22459–22466.

[38] Y. Feng, N. Feng, Y. Wei, G. Zhang, An in situ gelatin-assisted hydrothermal synthesis of ZnO-reduced graphene oxide composites with enhanced photo-catalytic performance under ultraviolet and visible light, RSC Adv. 4 (2014) 7933–7943.

[39] 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.

[40] 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.

[41] D. Li, M.B. Mueller, S. Gilje, R.B. Kanner, G.G. Wallace, Processable aqueous dispersions of graphene nanosheets, Nat. Nanotechnol. 3 (2008) 101–105.

[42] G. Williams, P.V. Kamat, Graphene-semiconductor nanocomposites: excited-state interactions between ZnO nanoparticles and graphene oxide, Langmuir 25 (2009) 13869–13873.

[43] D.R. Dreyer, S. Murali, Y. Zhu, R.S. Ruoff, C.W. Bielawski, Reduction of graphite oxide using alcohols, J. Mater. Chem. 21 (2011) 3443–3447.

[44] 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 grapheme-WO$_3$ nanocomposites, Nanotechnology 23 (2012) 205501.

[45] 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.

[46] N. Chen, X. Li, X. Wang, J. Yu, J. Wang, Z. Tang, S.A. Akbar, Enhanced room temperature sensing of Co$_3$O$_4$-intercalated reducedgraphene oxide based gas sensors, Sens. Actuators B 188 (2013) 902–908.

Biographies

Sen Liu received his B.S. degree in 2005 in Chemistry and PhD degree in 2010 in Inorganic Chemistry from Jilin University. During the period of 2010 to 2012, he worked in Prof. Xuping Sun's group as a postdoctoral research associate in State Key Lab of Electroanalytical Chemistry, Changchun Institute of Applied Chemistry, Chinese Academy of Sciences. He joined in College of Electronic Science and Engineering at Jilin University in 2012. Now he is an associate professor in Jilin University and his current research is focused on the preparation of functional materials and their sensing applications.

Bo Yu received his BS degree from the College of Electronics Science and Engineering, Jilin University, China in 2012. As an MS student, his research interests include sensing functional materials and devices.

Teng Fei received his BS degree in 2005 in chemical engineering and technology and PhD degree in 2010 in polymer chemistry and physics from Jilin University, China. He is currently a lecturer in the College of Electronics Science and Engineering, Jilin University. His research interests include sensing functional materials and devices.

Tong Zhang completed her MS degree in semiconductor materials in 1992 and her PhD in the field of microelectronics and solid-state electronics in 2001 from Jilin University. She was appointed as a full-time professor in the College of Electronics Science and Engineering, Jilin University in 2001. Her research interests are sensing functional materials, gas sensors, and humidity sensors.