Enhanced Gas Sensing Properties to NO₂ of SnO₂/rGO Nanocomposites synthesized by Microwave-assisted Gas-Liquid Interfacial Method

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Abstract

The detection of nitrogen dioxide (NO₂) is essential for the environment and human health. Tin dioxide (SnO₂) based sensors have demonstrated capabilities to detect NO₂, while their response, response/recover speed and selectivity are not good enough for their practical applications. To address these issues, the SnO₂ nanoparticles doped with reduced graphene oxides (rGO) have been synthesized by using a facile microwave-assisted gas-liquid interfacial solvothermal method in this work. The NO₂ sensing performances have been greatly enhanced after the doping of rGO due to the improved electronic conductivity and the formation of the p-n junction in the as-synthesized SnO₂/rGO nanocomposites. Moreover, our results demonstrate that the sensors based on the SnO₂/(0.3%)rGO nanocomposites (with an average diameter about 10-15 nm) exhibit the best overall performance with the high response of 247.8 to 10 ppm NO₂, fast response/recovery speed (39 s/15 s) and the excellent selectivity at the working temperature of 200 °C. Remarkably, the SnO₂/(0.3%)rGO sensors still exhibit a good gas sensing performance to NO₂ even at room temperature.

Keywords: SnO₂/rGO, Microwave-assisted, Gas-liquid interfacial solvothermal method, Gas sensor, NO₂

1 Introduction

The nitrogen dioxide (NO_2) is a well-known toxic and harmful atmospheric pollutant gas, which primarily comes from burning fuel and exhaust of motor vehicles. Moreover, the exposure of NO_2 can cause some serious diseases of human beings. The exposure limit of NO_2 is 20 ppm as it is immediately dangerous to life or health concentration according to the Center for Disease Control and Prevention of the USA [1]. Therefore, it is of paramount importance to detect the NO_2 gas with high response and selectivity. In industry and medical applications, chemiresistive gas sensors are the most popular devices to monitor the level of the NO_2 gas due to their low cost [2]. Tin dioxide (SnO_2) as an n-type semiconductor is one of the widely used gas sensing materials ascribed to its excellent electrical properties, low cost, high chemical stability [3]. Although the gas sensing performances of SnO_2 are good toward many gases (e.g. H_2S [4], CO [5], NH_3 [6], HCl [7], HCHO [8]), their NO_2 sensing capability still needs to be further enhanced to satisfy the strict requirements for practical applications, such as medical diagnosis based on human breath and gas detection in harsh environments. In these fields, the superior selectivity, a fast response/recovery rate and a low detection limit should be fulfilled simultaneously, which poses great challenges to the commercialization of SnO_2 -based gas sensors.

Nowadays, surface functionalization, the use of heterostructures, and thermal assistance with an external heater or UV-illumination are plausible strategies to improve the response, response/recovery speed and selectivity of gas sensors [9-15]. The recent studies suggests that the combination of SnO_2 -based sensors with reduced graphene oxide (rGO) can be a promising approach to improve their sensing performance [16]. This is because the rGO has the high specific surface area, high electronic conductivity and presence of many chemically active sites for the interaction with gas molecules [17-20]. Additionally, the rGO is a two-dimensional (2D) flat materials, which may provide active sites to uniformly adsorb the precursors of SnO_2 nanoparticles in terms to other carbon materials, such as one-dimensional carbon nanotubes (CNT), as suggested in recent comparative study [21]. The rGO has also been effectively exploited in other applications such as hydrogen production and storage, catalysis, conductive switching and bioimaging [22-25]. To this end, the rGO is selected to interact with SnO_2 to improve its overall NO_2 sensing performance.

In this work, SnO_2/rGO nanocomposites with different mass ratios ($m(\text{rGO})/m(\text{SnO}_2) = 0.0, 0.1, 0.3, 0.5 \text{ wt\%}$) have been successfully synthesized by using a microwave-assisted gas-liquid

interfacial solvothermal method. The gas sensing performances of sensors based on these SnO_2/rGO nanocomposites to different gases (NO_2 , H_2S , CO_2 , CO , H_2 , triethylamine, aniline, diethylether) have been systematically investigated. Our results demonstrate that the sensors based on the $\text{SnO}_2/(0.3\%)\text{rGO}$ nanocomposite exhibits the best overall performance in terms of response, fast response/recovery speed and the selectivity characteristics to NO_2 at the optimal working temperature of 200 °C. Remarkably, this sensor maintains a good gas sensing performance to NO_2 compared with the other previously reported NO_2 gas sensors at room temperature.

2 Experimental

2.1 Synthesis of rGO

In this study, all chemicals were purchased with the analytical grade and used as purchased. The graphene oxide (GO) as a starting material for the preparation of the rGO was synthesized using a modified Hummers method [26]. Typically, 2 g graphite was re-suspended in 100 mL conc. H_2SO_4 with 1 g NaNO_3 in an ice bath. 8 g KMnO_4 was added while the temperature was kept below 4 °C. After being stirred for 2.5 h, the reaction system was transferred to a water bath and stirred for 1 h at 35 °C. The mixture was diluted with 100 mL deionized water and stirred for 30 min at 98 °C. Next, 100 mL deionized water and 20 mL of 30% H_2O_2 were added. After being stirred 30 min, the brownish yellow precipitate was obtained through the centrifugation. The precipitate was immersed in the 2M HCl aqueous solution for about 10 h. And then, the suspension was centrifuged and washed with deionized water. At last, the GO was obtained by the ultrasonic exfoliation and freeze drying. The rGO was synthesized via the chemical reduction. At first, the GO was completely dispersed in deionized water via ultrasonication. Then, the excess ammonia solution and hydrazine hydrate were slowly added to the GO suspension solution. Subsequently, the suspension solution was in the thermostat water at 90 °C for 90 min. The as-made products were dialyzed and dried with vacuum freezing drying for about 12 h. Finally, the black rGO nanosheets were attained.

2.2 Synthesis of SnO_2/rGO

SnO_2/rGO nanomaterials were synthesized by using microwave-assisted gas-liquid interfacial solvothermal method. Firstly, 1.4594 g of $\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$ was dissolved in 10 ml ethylene glycol (EG) with stirring for 1 h. At the same time, rGO (0.0 wt%, 0.1 wt%, 0.3 wt%, 0.5 wt%) was dispersed in

30 ml of EG by ultrasonic cell disruption for about 40 min. After that, the rGO solution was dropwise added to the $\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$ solution under continuously stirring. The above mixture solution was kept in a beaker and transferred into a 200 ml Teflon-lined autoclave which contained a dilute ammonia solution (15 ml ammonia solution mixed with 15 ml deionized water) and heated from room temperature to 180 °C for 20 min. Finally, the system was kept under the autogenous pressure for 60 min. The experiment was performed on a MWave-5000 multifunctional microwave chemical reaction apparatus (Sineo Microwave Chemistry Technology Company, Shanghai, China), as shown in our previous article [27]. By employing the microwave-assisted gas-liquid interfacial solvothermal method, the growth of nanoparticles occurs at the interface between NH_3 gas and EG solution due to the poor solubility of NH_3 in EG. Using this specific method, the nanoparticles were synthesized with a narrow size-distribution. The products were then centrifuged and washed with ethanol and deionized water for several times, and dried at 105 °C in air for 8 h. The as-synthesized products were further calcined at 550 °C with the protection of Ar for 2 h to produce SnO_2/rGO nanocomposites with different mass contents of rGO (0.0, 0.1, 0.3 and 0.5 wt%).

2.3 Characterizations

The components of the samples were identified by using the X-ray diffraction (XRD, Bruker D8 Advance diffractometer with Ni-filtered $\text{Cu-K}\alpha$ radiation) in the 2θ range of 10° to 80°. The field emission scanning electron microscopy (FESEM) images were taken on the JEOL JSM-7100F microscope. The transmission electron microscopy (TEM), high resolution TEM (HRTEM), and selected-area electron diffraction (SAED) investigations were performed on a JEOL JEM-2100F microscope with an accelerating voltage of 200 kV. The FT-IR spectra were measured by using the Thermo Scientific Nicolet 6700 instrument in the frequency range of 400-4000 cm^{-1} . The Raman spectra were measured by using the Renishaw In Via spectrometer with a 532 nm wavelength laser of 2000-100 cm^{-1} . The surface and pore characterizations of the microspheres were determined through the N_2 adsorption/desorption at -196 °C by using an ASAP 2020 surface area and porosity analyzer (Micromeritics Instrument Corporation, USA). The X-ray photoelectron spectroscopy (XPS) investigations were carried out by using the SECA Lab2200i-XL spectrometer with an unmonochromated Al $\text{K}\alpha$ (1486.6 eV) X-ray source.

2.4 Gas sensing measurements

The gas sensing measurements were conducted by using the WS-30A (Hanwei Electronics Co., Ltd., Henan, China). The temperature varied in the range of room temperature to 300 °C. The tested gases atmosphere were under the laboratory condition of 30 RH% and 25 °C. The sensor response is defined as $S_r = R_g/R_a$ (oxidizing gases) or $S_r = R_a/R_g$ (reducing gases), respectively. Here, R_a and R_g refer to the resistances of sensors in air and in target gas, respectively. The response and recovery time (t_{resp} and t_{reco}) are defined as the time required to reaching 90% variation of the sensor resistance upon exposure to the analyte gas and air, respectively.

3 Results and discussion

3.1 Characterization results

To determine the components and their crystalline phases of the as-prepared composites, SnO₂ and SnO₂/rGO nanoparticles were investigated by using the XRD. The pure SnO₂ sample was synthesized using the same method without doping rGO for the control experiment. As shown in **Fig. 1**, the **(A-D)** samples have almost identical XRD patterns, which demonstrate that all samples have a tetragonal structure (JCPDS card NO. 41-1445). The diffraction peaks observed at 2θ of 26.611°, 33.893°, 37.949°, 51.780° are attributed to (110), (101), (200) and (211) planes of the tetragonal rutile phase, respectively. A hump in **Fig. 1(E)** between 2θ values of 23–26° indicates the presence of rGO. There are no apparent XRD peaks in **Figs. 1(B-D)** for rGO, which indicates that its amount is small in all the considered SnO₂/rGO composite. The mean sizes (D) of SnO₂ and SnO₂/rGO nanoparticles were calculated based on Scherrer equation (as shown in equation (1)) using the 2θ and half peak width of their most intensive (110) peaks.

$$D = \frac{K\lambda}{\beta \cos\theta} \quad (1)$$

where λ is the X-ray wavelength ($\lambda=0.154056$ nm), β is the full-width at half maximum (FWHM) intensity, θ is the diffraction angle, and K is Scherrer constant ($K=0.89$). The D values of the different samples are listed in **Table 1**. The results suggest that the mean sizes of nanoparticles positively correlate to the amount of rGO. And the SnO₂ nanoparticles without doping rGO have the smallest mean size. This may be due to the pre-adsorption of Sn⁴⁺ on the surface of rGO, which causes the formation of larger SnO₂ nanoparticles.

The surface composition and element analysis for $\text{SnO}_2/(0.3\%)\text{rGO}$ nanocomposites were investigated by using the XPS. There are relatively weak peaks at 26 eV, 716 eV (shown in **Fig. 2(A)**) and two relatively strong peaks at 486.9 eV, 495.3 eV (can be seen in **Fig. 2(B)**), which are associated with Sn 4d, Sn $3p_{3/2}$, Sn $3d_{5/2}$, and Sn $3d_{3/2}$, respectively [28]. In the high-resolution O 1s XPS spectrum (**Fig. 2(C)**), four peaks at 530.6 eV, 531.0 eV, 531.8 eV and 532.5 eV are observed, which are related to O species from Sn-O, C-O and absorbed hydroxyl groups from the moisture, respectively [28, 29]. The high-resolution C 1s XPS spectrum (**Fig. 2(D)**) shows three peaks at 284.6, 285.0 and 285.4 eV, which account for the C atoms in the C-C, C-O and C-OH groups [30, 31]. These XPS results demonstrate that rGO is successfully integrated into the SnO_2 nanoparticles.

The FT-IR spectrum of $\text{SnO}_2/(0.3\%)\text{rGO}$ composite is shown in **Fig. 3(A)**. A prominent peak at 629 cm^{-1} in the spectrum reveals the presence of the vibration mode of O-Sn-O from the SnO_2 in SnO_2/rGO . In addition, the Raman spectrum of $\text{SnO}_2/(0.3\%)\text{rGO}$ shows two peaks at 580 and 477 cm^{-1} , which represent the A_{1g} and E_g vibration modes of SnO_2 nanoparticles [32]. Thus, the existence of SnO_2 in $\text{SnO}_2/(0.3\%)\text{rGO}$ nanocomposites are further determined. The spectrum also portrays the C=C (sp^2 -hybridization) peak at 1622 cm^{-1} and C-H stretching and bending vibration peaks at 2853 and 2922 cm^{-1} , respectively [33, 34]. Furthermore, the stretching vibration band at 3433 cm^{-1} is attributed to the adsorption peak of O-H ($\nu(\text{OH})$) in hydroxide radical (-OH), which is attributed to the absorbed water molecules [35]. The significant structural changes occurring during the chemical processing from SnO_2 and rGO to $\text{SnO}_2/(0.3\%)\text{rGO}$ are reflected in their Raman spectra (**Fig. 3(B)**). There are two distinctive peaks in Raman spectra. The D- and G-bands are observed at 1347 cm^{-1} and 1591 cm^{-1} , respectively. The D-band is ascribed to the disorder of carbon materials due to the sp^3 hybridization of C atoms in the grain boundary and defects [36]. The G-band corresponds to the E_{2g} vibration of sp^2 hybridization graphite [37]. The I_D/I_G of SnO_2/rGO is 0.79 indicates the high degree of the reduction of GO.

The morphology and structure of samples have been characterized by using the FESEM and TEM. As shown in **Figs. 4(A)** and **(B)**, the SnO_2 and $\text{SnO}_2/(0.3\%)\text{rGO}$ nanocomposites are ultrasmall and uniform nanoparticles. This can be ascribed to the viscosity of ethylene glycol solution, which can be used to control the morphology of the products during the solvothermal process [38]. At the interface between gas and liquid, a small amount of Sn^{4+} ions react with the ammonia gas to generate precipitations at high temperature and high pressure. The introduction of ethylene glycol solvent can

lead to the slow precipitation of SnO₂ nanoparticles to the bottom of beaker without aggregation. After the rGO is introduced in the synthesis process, Sn⁴⁺ ions are first adsorbed on the surface of rGO before they react with the ammonia gas. Thus, a large amount of SnO₂ nanoparticles are formed on the rGO sheet, which can lead to the aggregation of nanoparticles to reduce the surface tension and create a coarsening of grains [39]. Consequently, the mean sizes of SnO₂ nanoparticles increase along with the increase of rGO content in the SnO₂/rGO. This trend is consistent with the XRD results in **Table 1**. The TEM images (**Figs. 4(C)** and **(D)**) further demonstrate that SnO₂/(0.3%)rGO nanocomposites is ultrasmall. And the existence of SnO₂ crystals is supported by their characteristic interplanar spacing of 0.335 nm which corresponds to the lattice distances of the (110) plane of rutile SnO₂ [40]. The SAED pattern (the inset in **Fig. 4(D)**) also supports the single crystalline nature of SnO₂ nanoparticles. Yet, there are no rGO observed in the HRTEM image. This can be attributed to the small amount of rGO used in this work.

The nitrogen adsorption-desorption isotherms of SnO₂/(0.3%)rGO was conducted to measure the specific surface area (SSA) of as-synthesized materials as shown in **Fig. 5**. This is confirmed by the corresponding pore-size distribution that shows one peak for SnO₂/(0.3%)rGO mesopores about 14 nm (inset of **Fig. 5**). And the average pore width is about 16.23 nm. The two isotherms are very similar and be identified as type IV with an obvious hysteresis loop in the P/P_0 range of 0.7 to 1, according to the classification by the International Union of Pure and Applied Chemistry (IUPAC). The BET SSA of the SnO₂/(0.3%)rGO is 39.7 m²/g. This SSA is quite high compared to the other metal oxide nanoparticles reported in previous studies [5, 27, 30]. The high BET SSA and ultrasmall nanoparticles of the SnO₂/(0.3%)rGO nanocomposites are beneficial to the gas sensing performance [5].

3.2 Gas sensing properties

The optimal operation temperatures on the gas sensing responses of the sensors based on different SnO₂/rGO nanocomposites to 50 ppm NO₂ have been first detected, as shown in **Fig. 6(A)**. The volcano curves are identified for all the sensors with the best performance at about 200 °C. It suggests that there is absorption-desorption dynamic equilibrium at the working temperature 200 °C. As the temperature further increases, the balance shifts in the direction of desorption. As such, the amount of adsorbed NO₂ molecules decreases. Hence, the responses of sensors gradually decline beyond 200 °C (shown in **Fig. 6(A)**). The response of the SnO₂/(0.3%)rGO sensor reaches the

maximum value of 1296.53 at 200 °C. **Fig. 6(B)** displays the gas sensing performance of the sensor based on SnO₂/(0.3%)rGO nanocomposite at different concentrations of NO₂. The response increases with the concentration of NO₂ (1, 5, 10 and 20 ppm) at the optimal working temperature of 200 °C. The response and recovery time of the SnO₂/(0.3%)rGO nanocomposite to 10 ppm NO₂ are 39 s and 15 s, respectively (shown in **Fig. 6(C)**). Remarkably, even at room temperature, this sensor still possesses a good gas sensing performance to NO₂ with response of 2.02 and response/recovery time of 171 s/254 s, respectively (shown in **Fig. 7**). Compared to the previous results, the sensor based on the SnO₂/(0.3%)rGO nanocomposite exhibits the higher response and the fast response and recovery rate (**Table 2**) [41-46].

The selectivity is another important parameter used to evaluate the performance of gas sensors [47]. Herein, the responses of eight different target gases (triethylamine, diethyl ether, H₂S, CO, H₂, CO₂, aniline and NO₂) have been measured using the SnO₂/(0.3%)rGO-based sensor (shown in **Fig. 6(D)**). The concentration of these target gases is 100 ppm except NO₂, which is 10 ppm. The response to 10 ppm NO₂ is 4.5 times higher than that to the second most sensitive gas (100 ppm trimethylamine). Therefore, our results demonstrate that this sensor has an outstanding selectivity to NO₂ sensing. To test the operational stability of the SnO₂/(0.3%)rGO sensor, its sensing performance to NO₂ at 200 °C was investigated over a period of time. **Fig. 6(E)** presents the response of the sensor based on SnO₂/(0.3%)rGO to 10 ppm NO₂ at 200 °C after one week and three months from an initial test. The response of the sensor remained unchanged after three months, but the response speed slightly increased. The long-term stability of the sensor based on SnO₂/(0.3%)rGO shows a very promising prospect for practical applications.

3.3 Discussion

The improved gas sensing performance of SnO₂/rGO based sensors can be ascribed to the synergetic interaction between metal oxide nanocrystals and the rGO sheets. Herein, the rGO sheets act as a template to prepare the ultra-small SnO₂ nanoparticles. During the synthesis process, the rGO can provide active sites for the adsorption of Sn⁴⁺, which is the key step for the preparation of SnO₂/rGO nanoparticles. Meanwhile, the excessive Sn⁴⁺ in the solution can also form ultra-small SnO₂ nanoparticles. Since the amount of rGO sheets is much smaller in terms of that of SnO₂ nanoparticles, the rGO sheets have a discrete configuration, which is evidenced by the SEM and TEM images with the absence of noticeable rGO nanosheets (can be seen in **Fig. 4**). So, the

conductive rGO nanosheets can connect with neighboring SnO₂ nanoparticles as bridges to reduce the total resistance of the nanocomposites [48]. The reduced resistance with the increase of rGO amount experimentally demonstrated here (**Fig. 8**) can not only enhance the response of the sensors for the change of the resistance, but also reduces the power consumption. To this end, the introduction of rGO nanosheets can be greatly beneficial to the practical applications of sensors.

When the gas sensors are placed in fresh air, oxygen molecules can be adsorbed on the surface of n-type SnO₂ surface to extract electrons from their conduction band to form negatively charged oxygen species (O₂⁻, O⁻ and O²⁻). As a result, an electron depletion layer (EDL) is formed on the SnO₂ surface (as illustrated in **Fig. 9**) [49].

Here, O₂⁻ species can be formed at low temperature (equation (3)). And the more stable O⁻ can be formed at operating temperature of 200 °C (equation (4)) [50]. When the sensors are exposed to the NO₂ gas, NO₂ can react either with adsorbed negatively charged oxygen species or directly with the n-type SnO₂ surface (as shown in equation (5) and (6)). After that, adsorbed NO₂ can be reduced on the surface of SnO₂/rGO nanocomposites (as shown in **Fig. 9**). As a result, the width of the EDL increases, which can increase the resistance of the gas sensing materials.

Based on this mechanism, the width of EDL on the sensor materials play a crucial role in the enhancement of the response of sensors. Since the work function of p-type rGO (5.4 eV) [51] is higher than that of n-type SnO₂ (4.8 eV) [30], the electron can transfer from SnO₂ to rGO, which can increase the width of the EDL. Thus, the formation of p-n heterojunctions after the introduction of p-type rGO nanosheets can have positive effects on the sensing performance. In summary, the introduction of rGO can improve the conductivity and lead to the formation of p-n junction, which can enhance the gas-sensing performance of SnO₂-based nanocomposites to NO₂.

On the other hand, the XRD analyses demonstrate the increase of the amount of rGO leads to the

increase of SnO₂ nanoparticles, which suggests a reduced SSA. As a result, the performance of sensors would decrease when the amount of rGO is too high. In this regard, the concentration of rGO need to be optimized to achieve the best overall sensing performance. Using the microwave-assisted gas-liquid interfacial method, we find that the optimal amount of rGO is 0.3 wt% for NO₂ sensing.

4 Conclusion

In this work, SnO₂/rGO nanocomposites doped with different amount of rGO (0.0, 0.1, 0.3, 0.5 wt%) were synthesized via a microwave-assisted gas-liquid interfacial solvothermal method. And the gas sensors based on these nanocomposites showed excellent NO₂ gas sensing properties in the temperatures range of RT to 300 °C. A higher response of 247.8 to 10 ppm NO₂ with a short response time (39 s) and recovery time (15 s) was achieved based on the SnO₂/(0.3%)rGO nanocomposite at 200 °C. Moreover, even at room temperature and low concentration, the gas sensing performance of these gas sensors are still very good. In this sensor, the response and response/recovery speed have been greatly enhanced after the doping of rGO. The intrinsic resistance of SnO₂ apparently decreases with the doping of rGO. The active sites of rGO for the pre-concentration of the precursor of SnO₂ nanoparticles combined with its high electronic conductivity and the formation of the p-n heterojunction in the composite are contributed to the improved overall sensing performance. However, a high concentration of rGO can lead to the aggregation of SnO₂ nanoparticles, which reverses effect on the sensing performance. The results demonstrate that the SnO₂/(0.3%)rGO exhibit the best overall performance, which is promising to be used in the novel highly efficient NO₂ gas sensors.

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References

- [1] <https://www.cdc.gov/niosh/idlh/10102440.html>.
- [2] A.A. Mane, M.P. Suryawanshi, J.H. Kim, A.V. Moholkar, Fast response of sprayed vanadium pentoxide (V₂O₅) nanorods towards nitrogen dioxide (NO₂) gas detection, *App. Surf. Sci.* 403 (2017) 540-550.

- [3] I.S. Hwang, J.K. Choi, S.J. Kim, K.Y. Dong, J.H. Kwon, B.K. Ju and J.H. Lee, Enhanced H_2S sensing characteristics of SnO_2 nanowires functionalized with CuO , *Sens. Actuators B* 142 (2009) 105-110.
- [4] W. Nakla, A. Wisitsora-at, A. Tuantranont, P. Singjai, S. Phanichphant, C. Liewwhitan, H_2S sensor based on SnO_2 nanostructured film prepared by high current heating, *Sens. Actuators B* 203 (2014) 565-578.
- [5] L.N. Xu, W.G. Chen, L.F. Jin, W. Zeng, A novel SnO_2 nanostructures and their gas-sensing properties for CO , *J. Mater. Sci.* 27 (2016) 4826-4832.
- [6] X.Y. Zhu, Y.C. Guo, H. Ren, C. Gao, Y. Zhou, Enhancing the NO_2 gas sensing properties of rGO/SnO_2 nanocomposite films by using microporous substrates, *Sens. Actuators B* 248 (2017) 560-570.
- [7] W. Xu, L. Xia, J.G. Ju, P. Xi, B.W. Cheng, Y.X. Liang, Preparation and low-temperature gas-sensing properties of SnO_2 ultra-fine fibers fabricated by a centrifugal spinning process, *J. Sol-Gel Sci. Technol.* 78 (2016) 353-364.
- [8] N.A. Zaidi, M.W. Tahir, P.P. Vinayaka, W. Lang, Detection of ethylene using gas chromatographic system, *Procedia Engineering* 168 (2016) 380-383.
- [9] J. Zhang, Z. Qin, D. Zeng, C. Xie, Metal-oxide-semiconductor based gas sensors: screening, preparation, and integration, *Phys.Chem.Chem.Phys.*, 19 (2017) 6313-6329.
- [10] Q. Sun, K. Diao, T. Sun, M. Li, X. Cui, H. Tian, B. Xiang, Enhanced gas-sensing performance of $\text{SnO}_2/\text{Nb}_2\text{O}_5$ hybrid nanowires, *RSC Adv.*, 6 (2016) 105317-105321.
- [11] F.H. Saboor, T. Ueda, K. Kamada, T. Hyodo, Y. Mortazavi, A.A. Khodadadi, Y. Shimizu, Enhanced NO_2 gas sensing performance of bare and Pd-loaded SnO_2 thick film sensors under UV-light irradiation at room temperature, *Sens. Actuators B* 223(2016) 429-439.
- [12] F. Schütt, V. Postica, R. Adelung, O. Lupan, Single and Networked ZnO -CNT Hybrid Tetrapods for Selective Room-Temperature High-Performance Ammonia Sensors, *ACS Appl. Mater. Int.* 9 (2017) 23107-23118.
- [13] N. Joshi, L.F. da Silva, H.S. Jadhav, F.M. Shimizu, P.H. Suman, J.C. M'Peko, M.O. Orlandi, J.G. Seo, V.R. Mastelaro, O.N. Oliveira Jr, Yolk-shelled ZnCo_2O_4 microspheres: Surface properties and gas sensing application, *Sens. Actuators B* 257 (2018) 906-915.
- [14] J. Zhang, X.H. Liu, G. Neri, N. Pinna, Nanostructured Materials for Room-Temperature Gas Sensors, *Adv. Mater.* 28(2016) 795-831.
- [15] H.L. Tian, H.Q. Fan, G.Z. Dong, L.T. Ma, J.W. Ma, NiO/ZnO p-n heterostructures and their gas sensing properties for reduced operating temperature, *RSC Adv.* 6(2016) 109091-109098.
- [16] P. Tyagi, A. Sharama, M. Tomar, V. G, A comparative study of $\text{RGO}-\text{SnO}_2$ and $\text{MWCNT}-\text{SnO}_2$ nanocomposites based SO_2 gas sensors, *Sens. Actuators B*, 248 (2017) 980-986.
- [17] H. Song, X. Li, P. Cui, S.X. Guo, W.H. Liu, X.L. Wang, Sensitivity investigation for the dependence of monolayer and stacking graphene NH_3 gas sensor, *Diam. Relat. Mater.* 73 (2017) 56-61.
- [18] Sh. Nasresfahani, M.H. Sheikhi, M. Tohidi, A. Zarifkar, Methane gas sensing properties of Pd-doped SnO_2 /reduced graphene oxide synthesized by a facile hydrothermal route, *Mater. Res. Bull.* 89 (2017) 161-169.
- [19] C.M. Zhang, L. Li, J. Ju, W. Chen, Electrochemical sensor based in graphene-supported tin oxide nanoclusters for nonenzymatic detection of hydrogen peroxide, *Electrochim. Acta* 210 (2016) 181-189.
- [20] D.Z. Zhang, H.Y. Chang, P. Li, R.H. Liu, Q.Z. Xue, Fabrication and characterization of an ultrasensitive humidity sensor based on metal oxide/graphene hybrid nanocomposites, *Sens. Actuators B* 225 (2016) 233-240.
- [21] V. Srivastava, K. Jain, At room temperature graphene/ SnO_2 is better than $\text{MWCNT}/\text{SnO}_2$ as NO_2 gas sensor, *Mater. Lett.* 169 (2016) 28-32.
- [22] N.M. Musyoka, J. Ren, H.W. Langmi, B. C. North, M. Mathe, D. Bessarabov, Synthesis of $\text{rGO}/\text{Zr-MOF}$ composite for hydrogen storage application, *J. Alloys Compd.* 724 (2017) 450-455.

- [23] J. Song, S. W. Kang, Y. W. Lee, Y. Park, J. Kim, S. W. Han, Regulating the catalytic function of reduced graphene oxides using capping agents for metal-free catalysis, *ACS Appl. Mater. Interfaces*. 9 (2017) 1692-1701.
- [24] J. Wei, Z. Zang, Y. Zhang, M. Wang, J. Du, X. Tang, Enhanced performance of light-controlled conductive switching in hybrid cuprous oxide/reduced graphene oxide ($\text{Cu}_2\text{O}/\text{rGO}$) nanocomposites, *Opt. Lett.* 42 (2017) 911-914.
- [25] Z. Zang, X. Zeng, M. Wang, W. Hu, C. Liu, X. Tang, Tunable photoluminescence of water-soluble AgInZnS -graphene oxide (GO) nanocomposites and their application in-vivo bioimaging, *Sens. Actuators B* 252 (2017) 1179-1186.
- [26] W.S. Hummers, R.E. Offeman, Preparation of graphitic oxide, *J. Am. Chem. Soc.* 80 (1958) 1339-1339.
- [27] Y.H. Gui, J.B. Zhao, H.Y. Wang, J.F. Tian, H.Z. Zhang, Microwave-assisted gas-liquid interfacial synthesis of WO_3 precursor and nano- WO_3 for gas-sensing application, *J. Mater. Sci.: Mater. Electron* 27 (2016) 6445-6451.
- [28] M. Fondell, M. Gorgoi, M. Boman, A. Lindblad, An HAXPES study of Sn, SnS, SnO and SnO_2 , *J. Electron Spectrosc.* 195 (2014) 195-199.
- [29] X.L. Li, H.L. Wang, J.T. Robinson, H. Sanchez, G. Diankov, H. Dai, Simultaneous nitrogen doping and reduction of graphene oxide, *J. Am. Chem. Soc.* 131 (2009) 15939-15944.
- [30] Y. Xiao, Q.Y. Yang, Z.Y. Wang, R. Zhang, Y. Gao, P. Sun, Y.F. Sun, G.Y. Lu, Improvement of NO_2 gas sensing performance based on discoid tin oxide modified by reduced graphene oxide, *Sens. Actuators B* 227 (2016) 419-426.
- [31] L. Huang, Y. Liu, L.C. Ji, Y.Q. Xie, T. Wang, W.Z. Shi, Pulsed laser assisted reduction of graphene oxide, *Carbon* 49 (2011) 2431-2436.
- [32] R. Sriramprabha, M. Divagar, D. Mangalaraj, N. Ponpandian, C. Viswanathan, Formulation of SnO_2 /graphene nanocomposites modified electrode for synergistic electrochemical detection of dopamine, *Adv. Mater. Lett.* 6 (2015) 973-977.
- [33] J. Wang, R. Ran, J.K. Sunarso, C. Yin, H.G. Zou, Y. Feng, X.B. Li, X. Zheng, J.F. Yao, Nanocellulose-assisted low-temperature synthesis and supercapacitor performance of reduced graphene oxide aerogels, *J. Power Sources* 347 (2017) 259-269.
- [34] J. Song, K.J. Huang, N. Wang, Gas-sensing properties and in situ diffuse-reflectance Fourier-transform infrared spectroscopy study of diethyl ether adsorption and reactions on SnO_2/rGO film, *J. Mater. Res.* 31 (2016) 2035-2045.
- [35] S.R. Bansode, R.T. Khare, K.K. Jagtap, M.A. More, P. Koinkar, One step hydrothermal synthesis of SnO_2 -RGO nanocomposite and its field emission studies, *Mater. Sci. Semicond. Process.* 63 (2017) 90-96.
- [36] J.J. Shi, Z.X. Cheng, L.P. Gao, Y. Zhang, J.Q. Xu, H.B. Zhao, Facile synthesis of reduced graphene oxide/hexagonal WO_3 nanosheets composites with enhanced H_2S sensing properties, *Sens. Actuators B* 230 (2016) 736-745.
- [37] P.G. Su, L.Y. Yang, NH_3 gas sensor based on $\text{Pd}/\text{SnO}_2/\text{RGO}$ ternary composite operated at room-temperature, *Sens. Actuators B* 223 (2016) 202-208.
- [38] G.Z. Shen, D. Chen, K.B. Tang, F.Q. Li, Y.T. Qian, Large-scale synthesis of uniform urchin-like patterns of Bi_2S_3 nanorods through a rapid polyol process, *Chem. Phys. Lett.* 370 (2003) 334-337.
- [39] M.A. Mahmud, N.K. Elumalai, M.B. Upama, D. Wang, B. Puthen-Vettil, F. Haque, M. Wright, C. Xu, Controlled Ostwald ripening mediated grain growth for smooth perovskite morphology and enhanced device performance, *Sol. Energ. Mat. Sol. C* 167 (2017) 87-101.
- [40] P. Sun, W. Zhao, Y. Cao, Y. Guan, Y. Sun, G. Lu, Porous SnO_2 hierarchical nanosheets: hydrothermal

- preparation, growth mechanism, and gas sensing properties, *Cryst. Eng. Comm.* 13 (2011) 3718-3724.
- [41] H. Zhang, J.C. Feng, T. Fei, S. Liu, T. Zhang, SnO₂ nanoparticles-reduced graphene oxide nanocomposites for NO₂ sensing at low temperature, *Sens. Actuators B* 190 (2014) 472-478.
- [42] L. Li, S.J. He, M.M. Liu, C.M. Zhang, W. Chen, Three-dimensional mesoporous graphene aerogel-supported SnO₂ nanocrystals for highperformance NO₂ gas sensing at low temperature, *Anal. Chem.* 87 (2015) 1638-1645.
- [43] J.H. Lee, A. Katoch, S.W. Choi, J.H. Kim, H.W. Kim, S.S. Kim, Extraordinary improvement of gas-sensing performances in SnO₂ nanofibers due to creation of local p-n heterojunctions by loading reduced graphene oxide nanosheets, *ACS Appl. Mater. Interfaces* 7 (2015) 3101-3109.
- [44] X. Liu, J.S. Cui, J.B. Sun, X.T. Zhang, 3D graphene aerogel-supported SnO₂ nanoparticles for efficient detection of NO₂, *RSC Adv.* 4 (2014) 22601-22605.
- [45] P.G. Su, C.H. Wei, W.L. Shiu, Fabrication of SnO₂/reduced graphene oxide nanocomposites films for sensing NO₂ gas at room-temperature, *Int. J. Sci. Eng. Technol.* 4 (2015) 268-272.
- [46] S. Mao, S.M. Cui, G.H. Lu, K.H. Yu, Z.H. Wen, J.H. Chen, Tuning gas-sensing properties of reduced graphene oxide using tin oxide nanocrystals, *J. Mater. Chem.* 22 (2012) 11009-11013.
- [47] M.S. Yao, W.X. Tang, G.E. Wang, B. Nath, G. Xu, MOF thin film-coated metal oxide nanowire array: significantly improved chemiresistor sensor performance, *Adv. Mater.* 28 (2016) 5229-5234.
- [48] Q.X. Feng, X.G. Li, J. Wang, Percolation effect of reduced graphene oxide (rGO) on ammonia sensing of rGO-SnO₂ composite based sensor, *Sens. Actuators B* 243 (2017) 1115-1126.
- [49] V.L. Patil, S.A. Vanalakar, P.S. Patil, H.K. Jin, Fabrication of nanostructured ZnO thin films based NO₂ gas sensor via SILAR technique, *Sens. Actuators B* 239 (2017) 1185-1193.
- [50] Z.Y. Wang, Y. Zhong, S. Liu, T. Zhang, Preparation of Ag nanoparticles-SnO₂ nanoparticles-reduced graphene oxide hybrids and their application for detection of NO₂ at room temperature, *Sens. Actuators B* 222 (2016) 893-903.
- [51] P.V. Kumar, M. Bernardi, J.C. Grossman, The impact of functionalization on the stability, work function, and photoluminescence of reduced graphene oxide, *ACS Nano* 7 (2013) 1638-1645.

Table 1 The location (2θ) and the full-width at half maximum (FWHM) intensity of the (110) peak measured from the XRD images of SnO₂ and SnO₂/rGO nanocomposites and their calculated mean crystallite size.

Sample	2θ	FWHM	Crystallite size (nm)
SnO ₂	26.447	0.655	12
SnO ₂ /(0.1%)rGO	26.636	0.308	26
SnO ₂ /(0.3%)rGO	26.651	0.218	37
SnO ₂ /(0.5%)rGO	26.365	0.183	44

Table 2 Comparison of the sensing properties of various NO₂ sensors based on SnO₂/(0.3%)rGO

Materials	T (°C)	NO ₂ (ppm)	Response	t _{Resp} /t _{Reco} (s/s)	Ref.
SnO ₂ /rGO	50	5	3.31	135/200	[36]
SnO ₂ /rGO	55	100	1.08	-/373	[37]
SnO ₂ /(1.4%)rGO	75	1	696	-/-	[23]
SnO ₂ /rGO	200	1	15	-/-	[38]
SnO ₂ /(0.3%)rGO	200	10	247.80	39/15	This work
SnO ₂ /rGO	RT	50	-	190/224	[39]
SnO ₂ /rGO	RT	5	-	294/360	[40]
SnO ₂ /rGO	RT	100	2	295/-	[41]
SnO ₂ /(0.3%)rGO	RT	10	2.021	171/254	This work

Fig. 1. XRD pattern of SnO₂/rGO nanocomposites doped with different contents of rGO: (A) SnO₂, (B) SnO₂/(0.1%)rGO, (C) SnO₂/(0.3%)rGO, (D) SnO₂/(0.5%)rGO, (E) rGO

Fig. 2. (A) The XPS spectra, (B) high resolution XPS of Sn 3d, (C) high resolution XPS of O 1s, and (D) high resolution XPS of C 1s of $\text{SnO}_2/(0.3\%)\text{rGO}$

Fig. 3. (A) FTIR spectra of SnO₂/(0.3%)rGO nanocomposites and (B) Raman spectra of SnO₂, SnO₂/(0.3%)rGO and rGO

Fig. 4. SEM images of SnO₂ nanoparticles (A) SnO₂ and (B) SnO₂/(0.3%)rGO nanocomposites; TEM images of SnO₂/(0.3%)rGO (C and D). The inset in (D) is the corresponding SAED pattern

Fig. 5. Nitrogen adsorption-desorption isotherm of $\text{SnO}_2/(0.3\%)\text{rGO}$.

The inset is the corresponding pore-size distribution

Fig. 6. (A) Temperature-sensitivity curve of SnO_2/rGO with different mass of rGO, (B) Response of $\text{SnO}_2/(0.3\%)$ rGO to different concentration (1, 5, 10 and 20 ppm) of NO_2 at 200 $^{\circ}\text{C}$, (C) Response-recovery curve of $\text{SnO}_2/(0.3\%)$ rGO to 10 ppm NO_2 at 200 $^{\circ}\text{C}$, (D) Selectivity of $\text{SnO}_2/(0.3\%)$ rGO sensor, (E) Operational stability of the $\text{SnO}_2/(0.3\%)$ rGO sensor for 10 ppm NO_2 at 200 $^{\circ}\text{C}$

Fig. 7. The response curve of SnO₂/(0.3%)rGO to 10 ppm NO₂ at RT

Fig. 8. The relationship of resistance and temperature

Fig. 9. Schematic diagram of SnO₂/rGO nanocomposites showing the sensing mechanism

Enhanced Gas Sensing Properties to NO₂ of SnO₂/rGO Nanocomposites synthesized by Microwave-assisted Gas-Liquid Interfacial Method

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