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Fabrication of Sno2/Reduced Graphene Oxide Nanocomposite Films for Sensing No2 Gas at Room-Temperature

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Abstract : One-pot polyol process was combined with metal organic decomposition (MOD) method to fabricate a room-temperature NO2 gas sensor based on tin dioxide and reduced graphene oxide (SO2/RGO) nanocomposite films. X-ray diffractometry (XRD) and scanning electron microscopy (SEM) were used to analyze the structure and morphology of the fabricated films. The electrical and NO2 gas-sensing properties of SnO2 to which various amounts of RGO were added were measured in detail as a function of concentration of NO2 gas at room temperature, to elucidate the contribution of RGO to the NO2 gas-sensing capacity. The sensor that was based on a nanocomposite film of SnO2/RGO exhibited a strong response to low concentrations of NO2 gas at room temperature, satisfactory linearity and favorable long-term stability.

Keyword: Tin dioxide (SnO2); reduced graphene oxide (RGO); nanocomposite film; room-temperature NO2 sensor.

1. Introduction

NO_2 generated by combustion facilities and automobiles are known to be extremely harmful to the human body and the environment, so highly sensitive detection is needed for monitoring NO_2 gas. Metal oxides are well known to be effective in detecting various gases with enough sensitivity. Tin dioxide (SnO2), as oxygen-deficient n-type semiconductor with a wide bandgap (Eg = 3.6 eV), much effort has been made to elucidate their ability to detect various toxic and flammable gases [1-3]. According to reports, the SnO_2 sensors operate only at high temperatures, such as 200~500°C. Accordingly, the development of SnO_2 sensors that can operate at lower temperatures, with high sensitivity and low production cost has attracted much attention [4,5].

Graphene consists of a two-dimensional (2D) array of carbon atoms that are covalently connected via sp2 bonds to form a honeycomb sheet [6]. Graphene oxide (GO) sheets have recently become attractive as possible intermediates in the manufacture of grapheme [7]. GO can be chemically or thermally reduced to conductive reduced GO (RGO) [8]. Many methods have been used to prepare metal oxide/graphene composite materials, including the hydro/solvothermal method, solution mixing method, the in-situ growth method and the photoreduction method, all of which have their own advantages and particular conditions of application [9-11]. Among these methods, hydro/solvothermal method is the most widely used to prepare metal oxide/graphene composite because chemical bonds form between metal oxides and graphene, which can improve the electric properties of the composite over those of the same metal oxides or graphene alone. Recently, composite films that are based on SnO_2 nanopowders and graphene have been reported to be as new gas-sensitive materials to reduce further the operating temperature and to improve the sensitivity of sensors based on these materials [12,13]. Neri *et al.* fabricated SnO_2/graphene nanocomposites using the one-pot microwave-assisted non-aqueous sol–gel method for sensing NO_2 [12]. Zhang *et al.* fabricated a more rapidly responding NO_2 gas sensor based on SnO_2 nanoparticles/graphene nanocomposites that were made by the hydrothermal treatment of aqueous dispersion of GO in the presence of Sn salts [13]. The sensing characteristics of these SnO_2/graphene-based NO_2 gas sensors depend on their microstructure, which are determined by their fabrication process. Most NO_2 gas sensors have been fabricated by synthesizing graphene that is decorated with SnO_2 nanomaterial and drop-coating it on a substrate. In this work, SnO_2/RGO nanocomposite films were fabricated by combining the one-pot process with the metal organic decomposition (MOD) method. These films have the advantages of being highly effective, inexpensive and suitable for industrial for mass production. The structural characteristics of the SnO_2/RGO nanocomposite films were investigated by X-ray diffraction (XRD). The surface characteristics of the SnO_2/RGO nanocomposite films were observed using scanning electron microscopy (SEM). The NO_2 sensing performance of SnO_2/RGO nanocomposite films with various amounts of the RGO loaded into the SnO_2 matrix was studied as a function of concentration of NO_2 gas at room temperatuer. Differences in the composition and microstructure were adopted to explain the effect of adding RGO on the sensing mechanism of the SnO_2/RGO nanocomposite films.

2. Experimental

2.1 Preparation of RGO in glycerol solution

GO was prepared from natural graphite by a modified Hummers method [14]. Briefly, 0.5 g graphite powder was reacted with a mixture of 2 g $NaNO_3$, 12 mL concentrated H_2SO_4 and 3 g $KMnO_4$; then 40 mL deionized water (DIW) and 10 mL H_2O_2 (30%) were added. The resultant mixture was filtered and washed with DIW by centrifuging until the solution attained a pH of 6, and was then sonicated to form a stable suspension of GO in aqueous media. The resulting aqueous GO solution had a concentration of 0.85 mg/mL. The GO was reduced to form RGO in glycerol solution that was prepared as follows: the required amounts of GO were added to 10 g of glycerol and the resultant solution was heated to 190°C for 1 h with vigorous magnetic stirring. The solution was continuously stirred until a stable suspension was obtained.

2.2 Fabrication of gas sensors based on SnO_2/RGO nanocomposite films

An organometallic solution (Sn [OOCCH (C_2H_5) C_4H_9]$_2$,aq.; Tin (II) 2-ethylhexanoate ~ 90 % in 2-ethylhexanoic acid) was used as the precursor in fabricating the gas-sensing material (SnO_2). The organometallic solution was obtained from Strem Chemicals Inc. The solution includes about 28wt% Sn. The SnO_2/RGO nanocomposite films were fabricated as follows: the Tin (II) 2-ethylhexanoate was added and dispersed in the precursor solutions of RGO by ultrasonic vibration for about 2 hours to obtain the well-mixed suspensions. Then, the suspensions were coated onto the surfaces of the Au comb electrodes and the Al_2O_3 substrate by spin coating. The spinning was at 1000 rpm/min and the period of coating was 20 seconds. Thereafter, the coating layers were heated in air using an infra-red dryer at approximately 150°C for 30 minutes, to evaporate the solvents in the coating layers. Finally, the coating layers were sintered at an MOD temperature of 500°C for 4 h, to decompose the coating materials, and obtain SnO_2/RGO nanocomposite films. This sintering process yielded sensing films of appropriate mechanical strength and also conferred thermal stability, as shown in Fig. 1.

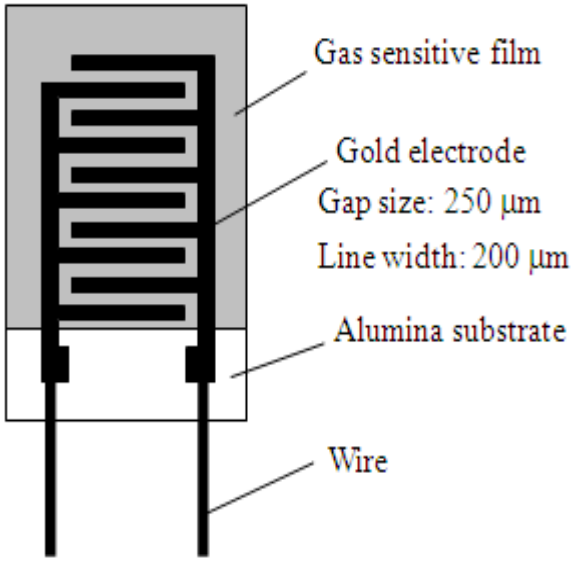

Fig. 1 Structure of NO_2 gas sensor.

2.3 Instruments and analysis

The surface microstructure of the SnO_2/RGO nanocomposite films coated on an alumina substrate was investigated using a field emission scanning electron microscope (FEI company, Nova NanoSEM™ 230). The XRD powder pattern of the SnO_2 film and SnO_2/RGO nanocomposite films were measured using Cu K_α radiation (Shimadzu, Lab XRD-6000). The electrical and sensing characteristeristics were measured using a static state system at room temperature, as shown in Fig. 2. Each sensor was connected in series with a load resistor and a fixed 5V tension (DC mode) was continuously supplied to the sensor circuit from a power supply (GW, PST-3202). The resistance of the sensor was determined from the voltage at the ends of the load resistor using a DAQ device (NI, USB-6218) in various concentrations of gas. The concentration for standard NO_2 and NH_3 gases were 100,000 and 1000. The required various gas concentrations were produced by diluting the known volume of standard gas with dry air and then were injected into the chamber. The desired various gas concentrations were measured using a calibrated gas sensor system (Dräger, MiniWarn). The interfering experiment was performed by measuring the resistance of the sensor exposure to NH_3 and H_2O gases, respectively. The volume of the chamber is 18 liters. The gas inside the chamber was uniformly distributed using a fan. After some time, the chamber was purged with air and the experiment was repeated for another cycles. All experiments were performed at room temperature, which was about 23.0 ± 1.5°C and the relative humidity was 40% RH. The sensor response (S) was calculated by the following equation:

$$S(\%) = \frac{(R_{gas} - R_{air})}{R_{air}} \times 100\% = \frac{(\Delta R)}{R_{air}} \times 100\% \quad (1)$$

where R_{gas} and R_{air} are the electrical resistances of the sensor in the tested gas and air, respectively.

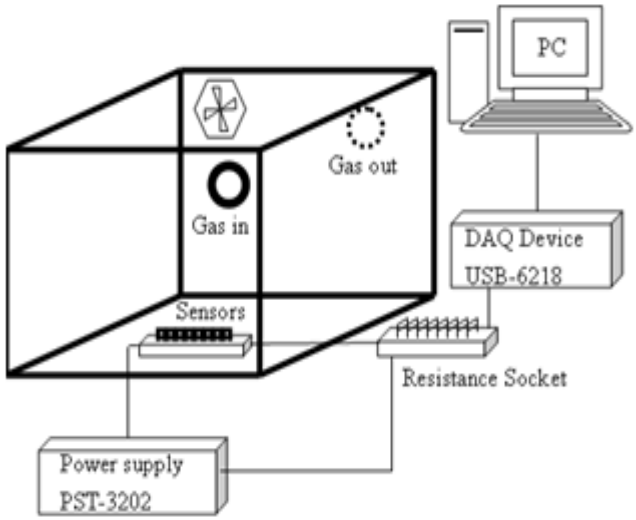

Fig. 2 Measurement system for testing gas sensors

3. Results and discussion

3.1 Morphology observations

Figure 3 presents SEM images of the SnO_2 film and the SnO_2/RGO nanocomposite films that were formed by MOD at 500°C. The SnO_2 film exhibited a flat and needle-shaped surface (Fig. 3(a)). When the RGO was added into the SnO_2 matrix, the surface of the SnO_2/RGO nanocomposite film exhibited a flat covered with granules. Moreover, no naked RGO was present on the surface of the intentionally fractured SnO_2/RGO nanocomposite film, even when the amount of added RGO was increased to 0.05 g. The RGO were embedded in the SnO_2 matrix and uniformly dispersed therein (Fig. 3(b)).

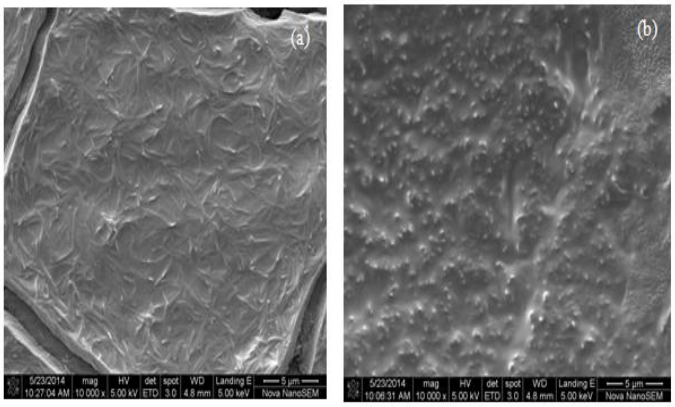

Fig. 3 FE-SEM images of (a) SnO_2 film and (b) SnO_2/RGO nanocomposite film that were fabricated by one-pot process and MOD at 500°C.

3.2 XRD characterization

Figure 4 shows the XRD spectra of the SnO_2 film and SnO_2/RGO nanocomposite films that were prepared by the combined one-pot process and MOD method. The XRD patterns of SnO_2 film show three main peaks at 2θ = 26.56, 33.82, 51.50 and 65.42°, which are identified as corresponding to (1 0 0), (1 0 1), (2 1 1) and (1 1 2) planes of tetragonal rutile SnO_2, indicating the formation of SnO_2 crystals. For the SnO_2/RGO nanocomposite, the XRD patterns showed no appreciable difference between the orientations and phases of SnO_2 and SnO_2/RGO samples, probably due to the reduction of GO by glycerol [15] or RGO was embedded in the SnO_2 matrix and so could not be easily detected by X-ray diffraction.

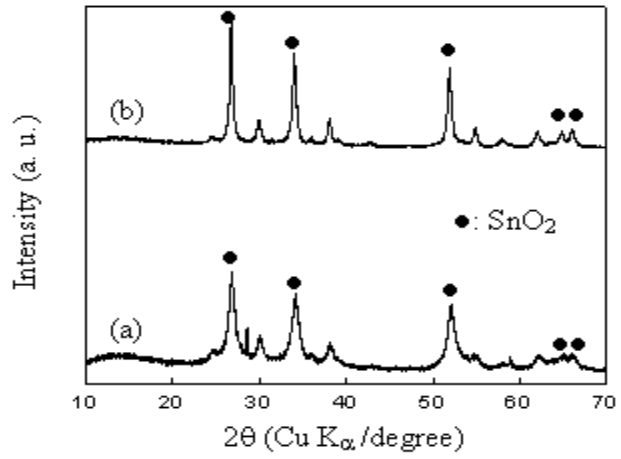

Fig. 4 XRD patterns of (a): SnO_2 film and SnO_2/RGO nanocomposite films that were fabricated by one-pot process and MOD at 500°C.

3.3 Gas sensing characteristics of SnO_2 film and SnO_2/RGO nanocomposite films

Figure 5 plots the responses of the sensors that were based on SnO_2 film and SnO_2/RGO nanocomposite films that were prepared using various amounts of RGO, to various concentrations of NO_2 gas at room temperature. Clearly, the responses (S) of the sensors that were made of the SnO_2/RGO nanocomposite films were significantly stronger than that of the sensor that was made of the pure SnO_2 film. The NO_2 gas sensor that was made of the SnO_2/RGO nanocomposite film that was doped with 0.01 g of RGO was chosen to study further its other gas sensing characteristics because this sensor exhibited the highest response.

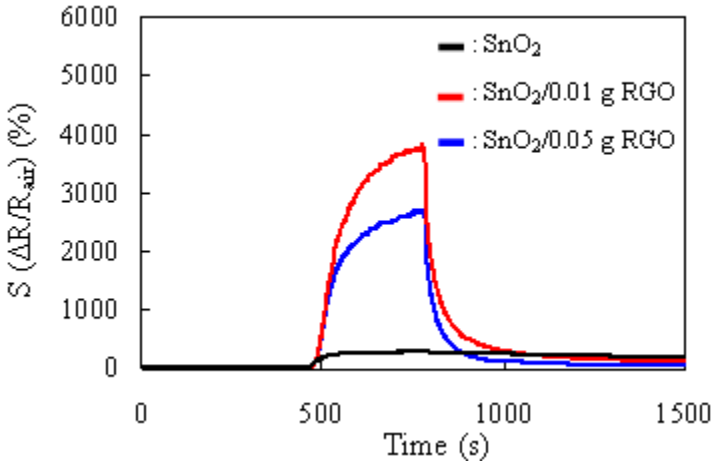

Fig. 5 Response (S) of NO_2 gas sensors based on SnO_2 film and SnO_2/RGO nanocomposite films that were prepared by one-pot process and MOD at 500°C for 4 h with various amounts of added RGO in response to 5 ppm NO_2 gas.

Figure 6 plots the response (S) as a function of concentration of NO_2 gas for the sensor that was made of the SnO_2/0.01 g RGO nanocomposite film. The sensitivity ($\frac{\Delta S}{\Delta C}$) is determined from the slopes of the plots of response vs. gas concentration.

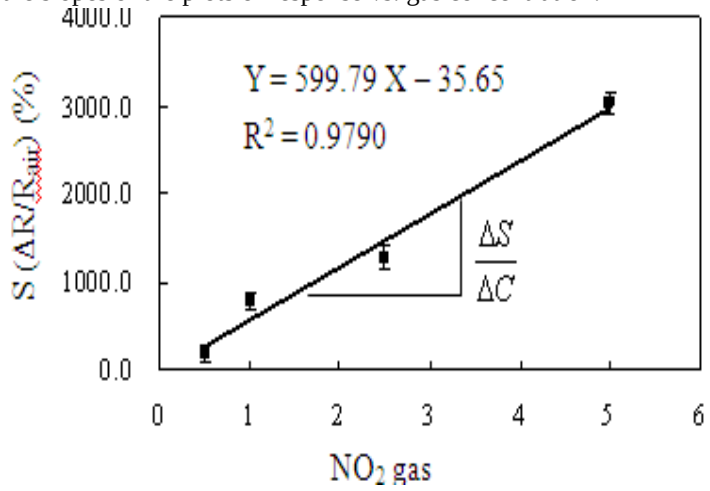

Fig. 6 Linear dependence of response of NO_2 gas sensor based on SnO_2/0.01 g RGO nanocomposite film on concentration of NO_2 gas at room temperature. Sensitivity ($\frac{\Delta S}{\Delta C}$) is determined from the slope of the linear curve.

The response time is defined as the time required for the sensor to reach 90% of the maximum change in resistance following exposure to a given NO_2 gas. The recovery time is defined as the time required for the sensor to recover 90% of the decrease in resistance after the sensor is exposed to a dry gas. The response and recovery times of the NO_2 gas sensor were 4.9 and

6.0 min, respectively, at a testing concentration of NO_2 of 5 ppm. Figure 7 plots the results concerning the interfering effects of NH_3 gas on the NO_2 gas sensor. NH_3 gas may be regarded as having unobvious interference effects with NO_2 at a testing NO_2 concentration of 2.5 ppm.

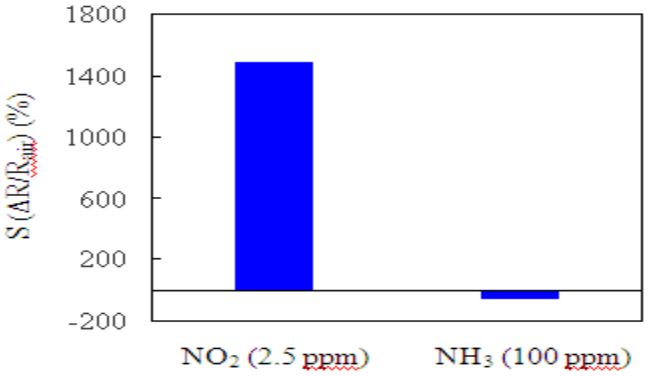

Fig. 7 Response (S) of NO_2 gas sensors based on SnO_2/0.01 gRGO nanocomposite film to interfering gas NH_3.

Figure 8 plots the effect of ambient humidity on the response (S) of the NO_2 gas sensor at a testing NO_2 concentration of 5 ppm. The response (S) of the NO_2 gas sensor decreased as the ambient humidity increased, because the physisorbed water occupied the active sites of the sensing materials.

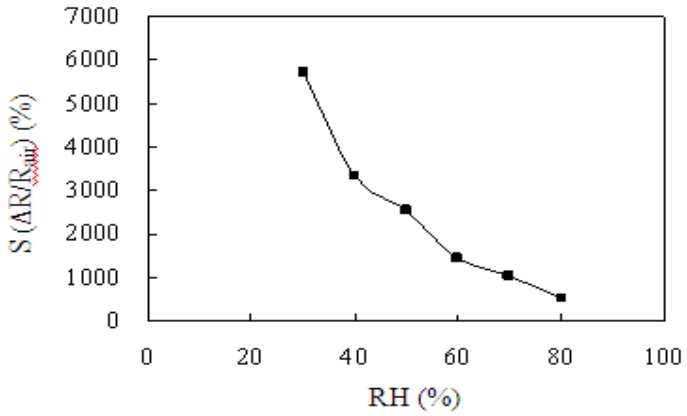

Fig. 8 Effect of ambient humidity on response of the NO_2 gas sensor based on WO_3/0.01 g RGO nanocomposite film to 5 ppm of NO_2 gas at room temperature.

Figure 9 plots the long-term stability. The response (S) of the NO_2 gas sensor did not significantly vary for at least 50 days in a testing NO_2 concentration of 2.5 ppm.

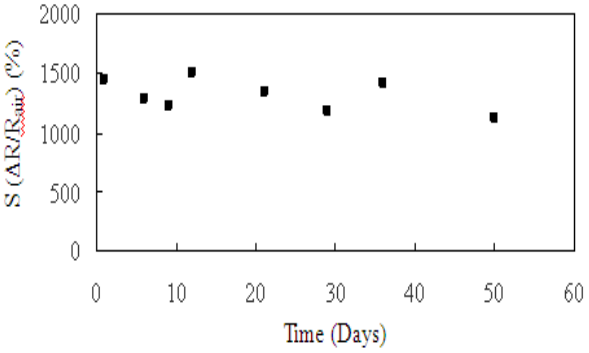

Fig. 9 Long-term stability of response of the NO_2 gas sensor based on SnO_2/0.01 g RGO nanocomposite film in 2.5 ppm of NO_2.

Table 1 compares the performance of NO_2 gas sensor that is developed herein with that of the NO_2 gas sensor that was based on the RGO/SnO_2 nanocomposite sensing matetilas. The response of the NO_2 gas sensor that is developed herein was higher than of those reported literatures.

Table 1 Comparison of performance of NO_2 gas sensor developed herein with the literatures.

Sensing material	Fabrication method	Response (%)	References
RGO was embedded in the SnO_2 matrix	one-pot process combined with MOD	1271[a]	This work
SnO_2 nanoparticles decorated on the surface of graphene	one-pot microwave-assisted non-aqueous sol–gel	900[b]	[12]
SnO_2 nanoparticles decorated on the surface of graphene	hydrothermal	75[c]	[13]

[a] The sensor in response to 2.5 ppm NO_2 gas at room temperature.
[b] The sensor in response to 8 ppm NO_2 gas at 100°C.
[c] The sensor in response to 5 ppm NO_2 gas at 100°C.

4. Conclusion

A new SnO_2/RGO nanocomposite gas sensor was developed herein with high sensitivity and favorable recovery properties in detecting NO_2 gas at room temperature. The new SnO_2/RGO nanocomposite gas sensor solves the problems of conventional SnO_2 sensors that cannot detect NO_2 gas at room temperature. The preparation of the SnO_2/RGO nanocomposite sensor was simple. The fabrication procedure involves the heat treatment of SnO_2 with RGO, which are initially dispersed in an organometallic solution. This new gas sensor will be adapted in the near future to a NOx gas sensor that uses less power than current NOx gas sensors.

This work found that the sensitivity of the new SnO_2/RGO nanocomposite sensor to NO_2 increases dramatically if only a few RGO are added as dopants to the SnO_2 substrate.

The NO_2 gas sensor that was based on a SnO_2/RGO film exhibited very sensitive with acceptable linearity ($Y = 599.79 X – 35.5$; R^2=0.9790) between 0.5 and 5 ppm, good reversibility and long-term stability (at least 50 days) when used at room temperature. NH_3 gas may be regarded as having unobvious

interference effects with NO_2 at a testing NO_2 concentration of 2.5 ppm. Ambient humidity significantly affected the NO_2 gas sensor.

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