



NH₃ gas sensor based on Pd/SnO₂/RGO ternary composite operated at room-temperature



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ABSTRACT

Novel room-temperature NH₃ gas sensors based on Pd, tin oxide (SnO₂) and reduced graphene oxide (RGO) ternary nanocomposite (Pd/SnO₂/RGO) film were fabricated by the one-pot route. The Pd/SnO₂/RGO ternary nanocomposite films were characterized by Fourier transform infrared spectroscopy (FTIR), Raman, X-ray diffractometry (XRD), scanning electron microscopy (SEM) and atomic force microscopy (AFM). Microstructural observations revealed that the Pd and SnO₂ nanoparticles easily and homogeneously attached to the surface of RGO. The sensor that was based on a Pd/SnO₂/RGO ternary nanocomposite film responded strongly to low concentrations of NH₃ gas at room-temperature. Its better sensor sensitivity than that of the pristine of SnO₂ and SnO₂/RGO nanocomposite film was related to the higher conductivity and catalytic activity of the Pd/SnO₂/RGO ternary nanocomposite film.

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1. Introduction

Ammonia (NH₃), a highly toxic gas, is commonly used in agriculture, the food industry and the chemical industry and is known to be extremely harmful to the human body and the environment, so very sensitive detection is required to monitor it. Semiconducting metal oxides are well known to be effective in sensitively detecting various gases. Among these semiconducting metal oxides, tin oxide (SnO₂) is used for detecting NH₃ gas sensing with high sensitivity, but it is effective at high temperatures; has high power consumption [1]. Therefore, a few works on nanostructural SnO₂-based sensors that can sense NH₃ at room-temperature have been published; these sensors are produced by forming a nanocomposite with multi-walled carbon nanotubes (MWCNTs) [2] or alkaline-earth metals [3], because these materials have large surface areas for the adsorption/desorption of gas molecules, and are therefore exhibit favorable gas-sensing performance at room-temperature.

Graphene comprises two-dimensional (2D) arrays of carbon atoms that are covalently connected via sp² bonds to form a honeycomb sheet that has unique thermal, mechanical and electrical properties, and so is useful in various sensing systems [4,5]. Recently, graphene was used as a filler in the formation of SnO₂/graphene nanocomposite materials [6,7] and

polypyrrole/graphene for monitoring NH₃ gas [8]. Many methods have been utilized to prepare metal oxide/graphene composite materials, including the hydro/solvothermal method, the 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]. Of these methods, hydro/solvothermal method is the most extensively used to prepare metal oxide/graphene composite because chemical bonds form between metal oxides and graphene, improving the electrical properties of the composite over those of the same metal oxides or graphene alone. Furthermore, the sensing performance of NH₃ gas sensors that are made of ZnO, SnO₂ and reduced graphene oxide (RGO) films can also be greatly improved by modifying them with noble metals Pd, Pt and Ag, respectively [12–14]. Recently, Xu et al. [15] fabricated Au/SnO₂/graphene ternary nanocomposite using the one-pot route. However, no attempt has been made to fabricate an NH₃ gas sensor that is based on a noble metal/metal oxide/graphene ternary nanocomposite. This work concerns Pd/SnO₂/RGO ternary nanocomposite for sensing NH₃ gas at room-temperature. Pd/SnO₂/RGO ternary nanocomposites were prepared by the one-pot route, whereby thin films thereof were fabricated directly on an alumina substrate. This method is very simple; wastes only a little material and consumes little power. In the one-pot approach, the simultaneous reduction of graphene oxide to RGO and PdCl₂ to Pd nanoparticles and the conversion of SnO₂ nanoparticles from SnCl₂ precursors are performed simultaneously. The Pd/SnO₂/RGO ternary nanocomposites were

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characterized by Fourier transform infrared spectroscopy (FTIR), Raman, X-ray diffraction (XRD), atomic force microscopy (AFM) and scanning electron microscopy (SEM). The NH_3 sensing performance of Pd/SnO₂/RGO ternary nanocomposites in which various amounts of RGO was loaded into the SnO₂ matrix and Pd was added, was studied.

2. Experimental method

2.1. Materials

Graphene powder, stannous chloride dihydrate (SnO₂·2H₂O), palladium(II) chloride (PdCl₂), polyvinylpyrrolidone (PVP; average mol wt. 40,000) and hydrochloric acid (HCl) were obtained from Sigma–Aldrich. All reagents used were analytical grade. All used deionized water (DIW) was prepared using a Milli-Q Millipore (Bedford, MA, USA) purification system, and the resistivity of water was above 18.0 MΩ cm⁻¹.

2.2. Preparation of Pd/SnO₂/RGO ternary nanocomposites

The graphene oxide (GO) that was used herein was prepared using Hummer's method [16]. Pd/SnO₂/RGO ternary nanocomposite was prepared using a method similar to that described by Xu et al. [15]. In a typical synthesis, the required amounts of GO were added to 3 mL DIW and was sonicated to form a stable suspension of GO in aqueous media. Then, 0.1 g PVP, 150 μL HCl (36–38%), 0.225 mmol SnO₂·2H₂O, and 1.5 mL PdCl₂ (10 mg/mL) were added into the above suspension of GO solution and the as-prepared mixing solution was stirred for 2 h. The amounts of GO dopant were varied 0.1, 0.2 and 0.3 g.

2.3. Fabrication of gas sensors based on Pd/SnO₂/RGO ternary nanocomposite and measurement of sensing properties

Fig. 1 displays a picture of the structure of NH_3 sensors fabricated on an alumina substrate. The interdigitated gold electrodes were made by screen printing. The as-prepared Pd/SnO₂/RGO ternary nanocomposite precursor solution was drop-coated on an alumina substrate with a pair of comb-like electrodes. Then, it was dried by heating at 60 °C. The electrical and sensing characteristics were measured using a bench system at room-temperature, as shown in Fig. 2. Each sensor was connected in series with a load resistor and

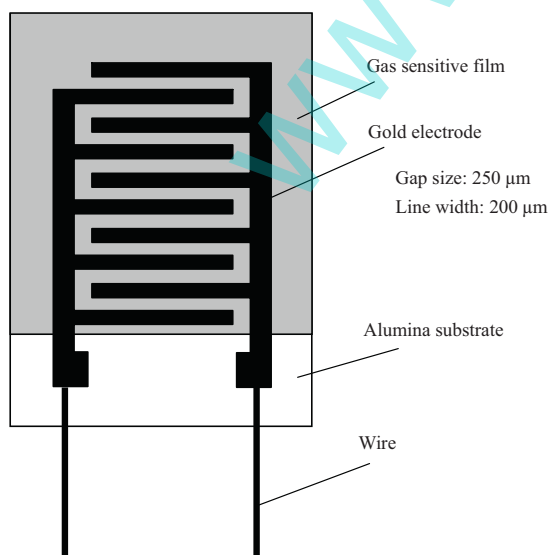


Fig. 1. Structure of NH_3 gas sensor.

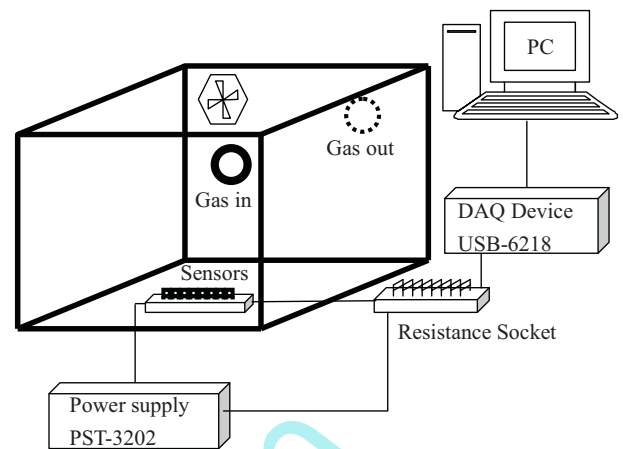


Fig. 2. Measurement system for testing gas sensors.

a fixed 5 V 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 standard NH_3 (1000 ppm) gas was purchased from Shen Yi Gas Co. (Taiwan). 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 volume of the chamber is 18 L. 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.

2.4. Characterization of Pd/SnO₂/RGO ternary nanocomposite

A Fourier transform infrared spectrometer (FTIR, Nicolet 380) was used to obtain the IR spectra of the GO, PVP and Pd/SnO₂/RGO ternary nanocomposite. A Raman spectrometer (OLYMPUS BX41) was used to obtain the Raman spectra of the as-prepared GO and Pd/SnO₂/RGO ternary nanocomposite. The surface microstructure of the SnO₂/RGO film and Pd/SnO₂/RGO ternary nanocomposite films coated on an alumina substrate was investigated using a field emission scanning electron microscope (FEI company, Nova NanoSEM™ 230) equipped with an energy dispersive spectrometer (EDS) and an atomic force microscope (AFM, Ben-Yuan, CSPM 4000) in tapping mode which the horizontal and vertical resolution are 0.26 and 0.10 nm, respectively. The XRD powder patterns of the GO, SnO₂/RGO and Pd/SnO₂/RGO ternary nanocomposite were measured using Cu K_α radiation (Shimadzu, Lab XRD-6000).

3. Results and discussion

3.1. Preparation and structural characteristics of Pd/SnO₂/RGO ternary nanocomposite films

Fig. 3 presents the simultaneous chemical reduction of GO and Pd²⁺ and the formation of SnO₂ nanoparticles by the one-pot process. SnCl₂ was used as a reducing agent in the simultaneous reduction of GO and PdCl₂ to RGO and Pd nanoparticles, respectively. This method typically generates Pd and SnO₂ nanoparticles that grow in situ homogeneously on the surface of the RGO.

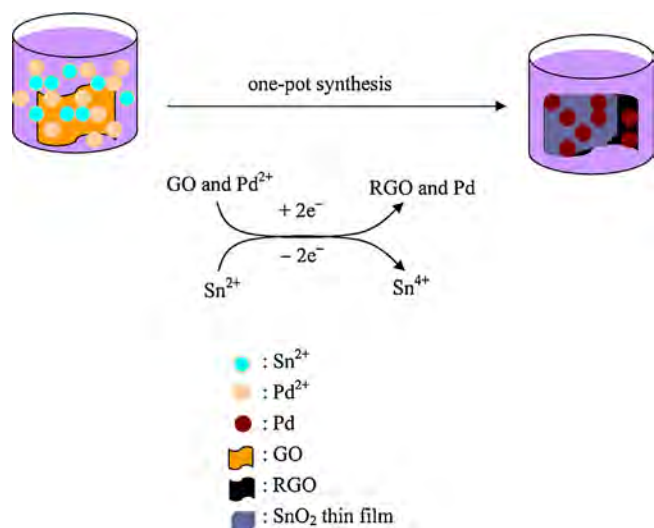


Fig. 3. Schematic illustration for the synthesis of the Pd/SnO₂/RGO ternary nanocomposite by one-pot process.

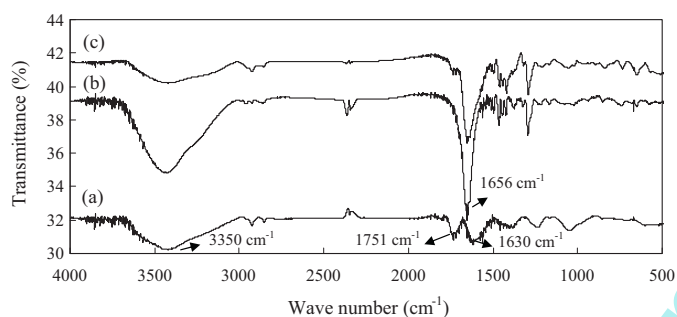


Fig. 4. IR spectra of (a) GO, (b) PVP and (c) Pd/SnO₂/RGO ternary nanocomposite that was fabricated by one-pot process.

3.1.1. IR spectra

The IR spectrum of the GO in Fig. 4(a) includes a peak at 3350 cm⁻¹, which is attributable to the O–H stretching vibration and peaks at 1751 and 1630 cm⁻¹, which are attributable to the C=O stretching vibrations. Fig. 4(b) presents the C=O stretching vibration of the PVP (1656 cm⁻¹). The heights of the peaks at 1751 and 1630 cm⁻¹ that were obtained from the Pd/SnO₂/RGO ternary nanocomposite were lower when the one-pot process was used with SnCl₂ as a reducing agent (Fig. 4(c)), suggesting the successful reduction of GO. Accordingly, partially reduced GO was formed in the Pd/SnO₂/RGO ternary nanocomposite.

3.1.2. Raman spectra

The Raman spectrum of the as-prepared GO in Fig. 5(a) exhibited two prominent peaks at 1598 cm⁻¹ and 1335 cm⁻¹ corresponding to the well documented G and D bands. The G band is related to the graphitic hexagon-pinch mode, while the D band corresponds to defects in the graphene oxide. The intensities ratio of the D and G bands of the Pd/SnO₂/RGO ternary nanocomposite obviously increased in comparison with those of the as-prepared GO in the same test conditions, indicating the reduction of GO in the Pd/SnO₂/RGO ternary nanocomposite (Fig. 5(b)) [17,18].

3.1.3. XRD characterization

Fig. 6 shows the XRD spectra of the GO, SnO₂/RGO and Pd/SnO₂/RGO ternary nanocomposite that were prepared by one-pot processes. GO yielded a sharp diffraction peak (002) appears at 10.75°, revealing that most of the graphite powder was oxidized

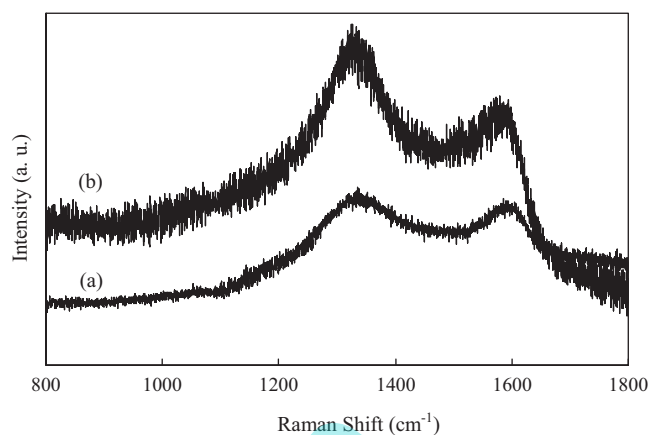


Fig. 5. Raman spectra of (a) GO, (b) Pd/SnO₂/RGO ternary nanocomposite that was fabricated by one-pot process.

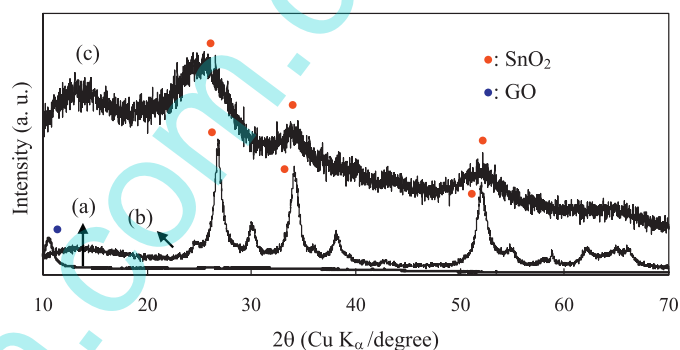


Fig. 6. XRD patterns of (a) GO, (b) pure SnO₂ and (c) Pd/SnO₂/RGO ternary nanocomposite that was fabricated by one-pot process.

to GO with an increase in the d-spacing to 6.70 Å [19]. The XRD patterns of SnO₂ include three main peaks at $2\theta = 26.56^\circ$, 33.82° and 51.50° , corresponding to the (1 0 0), (1 0 1) and (2 1 1) planes of tetragonal rutile SnO₂, revealing the formation of SnO₂ crystals [20]. The Pd/SnO₂/RGO nanocomposite exhibited no appreciable difference between the orientations and phases of SnO₂ probably owing to the reduction of GO by SnCl₂ or the fact that RGO was embedded in the SnO₂ matrix and so could not be easily detected by X-ray diffraction. Additionally, the diffraction peaks of the Pd/SnO₂/RGO nanocomposite were very broad, indicating a disordered and poor crystalline structure.

3.1.4. AFM and SEM analyses

Fig. 7 presents the surface morphology of the GO film and the Pd/SnO₂/RGO ternary nanocomposite film that was prepared by the one-pot route, obtained using tapping-mode AFM. The size of each image was 5 μm × 5 μm. The Pd/SnO₂/RGO ternary nanocomposite film (Fig. 7(b)) had a rougher surface than did the GO film (Fig. 7(a)), revealing that the Pd and SnO₂ nanoparticles easily attached to the surface of RGO. The FE-SEM images and EDS spectra in Fig. 8 further present the surface morphologies of the SnO₂/RGO and Pd/SnO₂/RGO ternary nanocomposite films that were prepared by one-pot processes. In the SnO₂/RGO film (Fig. 8(a)), the SnO₂ nanoparticles were deposited only on the RGO sheets with high density and high uniformity. The high-magnification SEM image (inset in Fig. 8(a)) reveals that SnO₂ nanoparticles were firmly attached to the RGO sheets and their average size was 20 nm. The composition of the SnO₂/RGO film was obtained by EDS (Fig. 8(b)), which revealed clearly that the SnO₂/RGO film comprised Sn, C and O elements. Many bright nanoparticles were observed on the

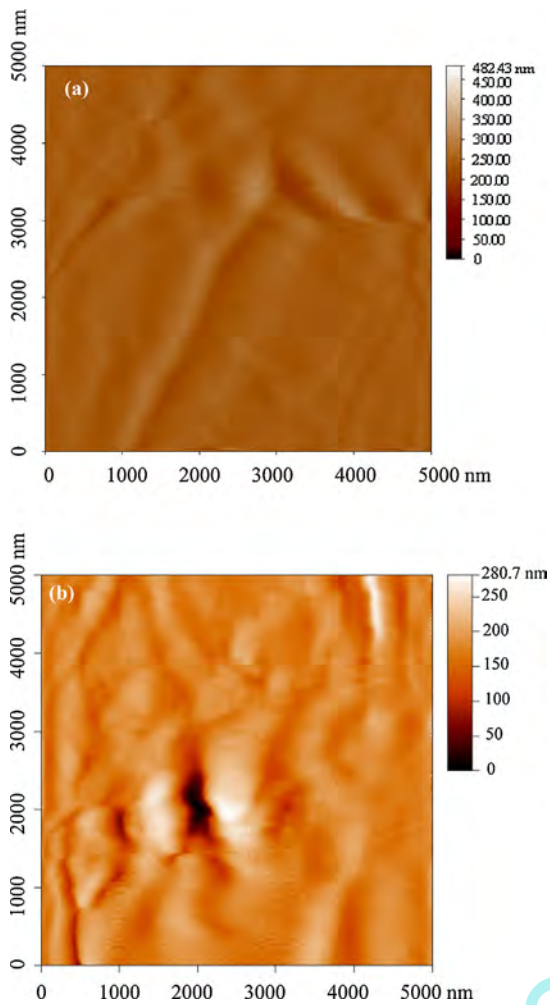


Fig. 7. AFM images of (a) GO film and (b) Pd/SnO₂/RGO ternary nanocomposite film that was fabricated by one-pot process.

surface of the Pd/SnO₂/RGO ternary nanocomposite film (Fig. 8(c)). The composition of the nanoparticles was obtained by EDS, which yielded the spectrum that is presented in Fig. 8(d). The EDS analysis revealed that the Pd nanoparticles surely grew on the Pd/SnO₂/RGO ternary nanocomposite film.

3.2. Gas sensing characteristics of Pd/SnO₂/RGO ternary nanocomposite films

The sensor response (*S*) was calculated by the following equation:

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

Table 1

Comparison of performance of NH₃ gas sensor developed herein with the literature.

Sensing material	Fabrication method	Operating temperature (°C)	Response (%)	References
MWCNTs/SnO ₂	Mixing process	25	8 ^a	[2]
Sr/SnO ₂	Electrospinning method	25	10 ^b	[3]
Graphene/SnO ₂	Hydrothermal method	25	15.9 ^c	[6]
Pt/SnO ₂	Sputtering method	230	25.7 ^d	[21]
Pd/SnO ₂ /RGO	One-pot synthesis under ultrasonication	25	7.6 ^e	This work

^a The sensor in response to 60 ppm NH₃ gas.

^b The sensor in response to 10 ppm NH₃ gas.

^c The sensor in response to 50 ppm NH₃ gas.

^d The sensor in response to 450 ppm NH₃ gas.

^e The sensor in response to 5 ppm NH₃ gas.

where R_{air} and R_{gas} are the electrical resistances of the sensor in the air and tested gas, respectively. The inset 1 in Fig. 9 plots the response (*S*) of the NH₃ gas sensor that was based on SnO₂/RGO film to 100 ppm NH₃ gas. The response (*S*) was weak (about 0.016) at an NH₃ testing concentration of 100 ppm because the SnO₂/RGO film exhibited a poor crystalline structure. The inset 2 in Fig. 9 plots the response (*S*) of the NH₃ gas sensor that was based on Pd/SnO₂ film to 100 ppm NH₃ gas. The response of the sensor that was based on Pd/SnO₂ was about 8 at an NH₃ testing concentration of 100 ppm. This observation was thought to arise from the fact that the Pd nanoparticles can exhibit favorable catalytic activity. Introducing RGO and Pd nanoparticles effectively improved the sensitivity of the Pd/SnO₂/RGO ternary nanocomposite film. To improve the NH₃ gas-sensing characteristics of the SnO₂/RGO film that was fabricated by the one-pot route, the film was decorated with Pd nanoparticles during the one-pot process. Fig. 9 plots the responses of the sensors that were based on Pd/SnO₂/RGO ternary nanocomposite films that were prepared using various amounts of GO, to 100 ppm NH₃ gas at room temperature. Clearly, the responses (*S*) of the sensors that included the Pd/SnO₂/RGO ternary nanocomposite films were significantly stronger than that of the sensors that were made of the SnO₂/RGO and Pd/SnO₂ films, suggesting that catalytic activity of Pd nanoparticles critically affects the response of the Pd/SnO₂/RGO ternary nanocomposite film responding to NH₃ gas. Additionally, the response (*S*) of the sensors that were based on a Pd/SnO₂/RGO ternary nanocomposite film increased with the amount of added RGO. 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 concentration of 100 ppm NH₃ gas. The recovery time is defined as the time required for the sensor to recover 90% of the decrease in resistance following its exposure. The response and recovery times of the NH₃ gas sensor that was made of the Pd/SnO₂/0.1 g RGO ternary nanocomposite were 7 and 50 min, respectively, at an NH₃ testing concentration of 100 ppm. However, when the amount of added RGO was increased to 0.2 g, the recovery of the sensors was rather slow (>100 min). Therefore, the other gas sensing characteristics of the NH₃ gas sensor that was made of the Pd/SnO₂/RGO ternary nanocomposite film that was doped with 0.1 g of RGO were studied further, because this sensor exhibited favorable sensitivity even at a low testing concentration of NH₃ (5 ppm) and a short recovery time. Fig. 10(a) plots the responses (*S*) of the sensor that was made of the Pd/SnO₂/0.1 g RGO ternary nanocomposite film to various concentrations of NH₃. The sensor exhibited a good reversibility and a response of 7.6% even at a low NH₃ testing concentration of 5 ppm. Fig. 10(b) plots the response (*S*) versus NH₃ gas for the sensor that was made of the Pd/SnO₂/0.1 g RGO ternary nanocomposite film. The sensitivity ($\Delta S/\Delta C$) is determined from the slopes of the plots of response versus gas concentration. The linear sensing characteristics in the ranges 5–150 ppm and 150–300 ppm differed. A rapid decrease in slope was observed from 150 to 300 ppm of NH₃ gas, and the sensitivity at 5–150 ppm NH₃ gas exceed that at 150–300 ppm. This result was related to the adsorption of NH₃ gas molecules onto

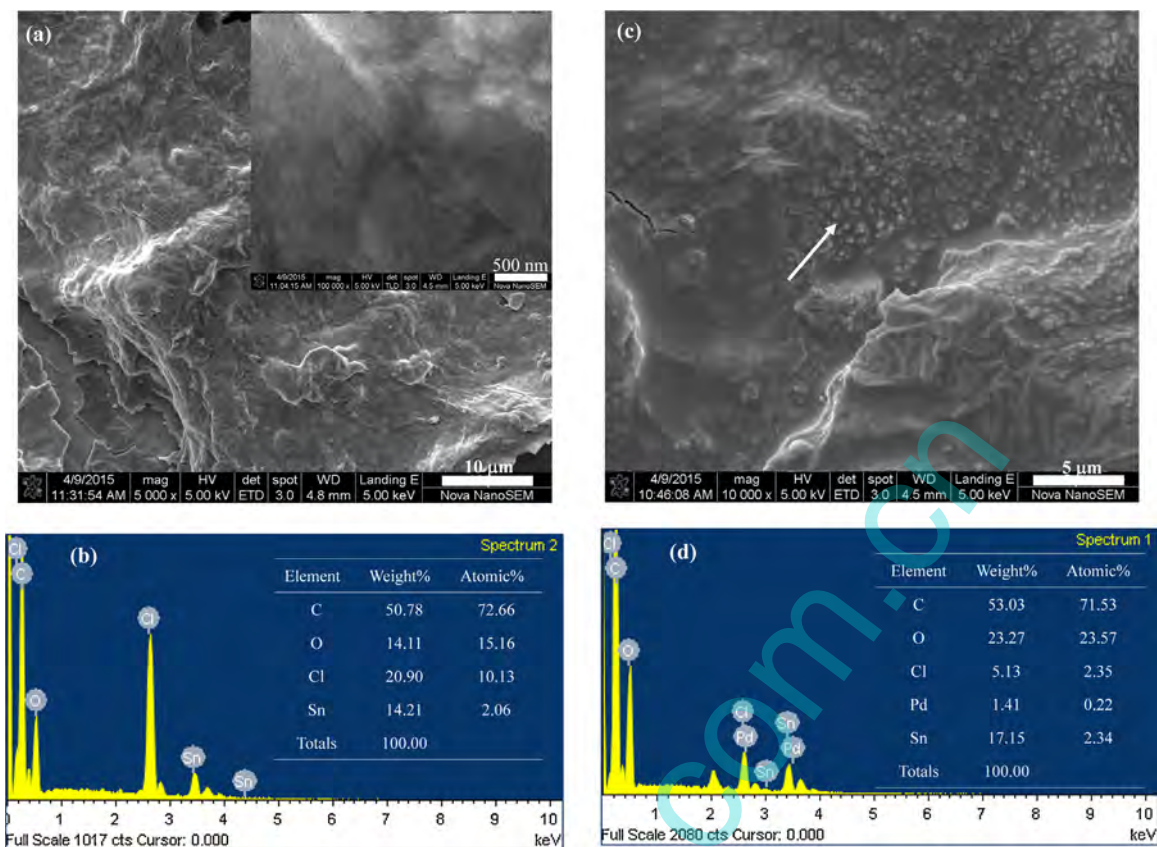


Fig. 8. FE-SEM images and EDS spectra of (a) SnO₂/RGO film, (b) EDS spectra of SnO₂/RGO film, (c) Pd/SnO₂/RGO ternary nanocomposite film that was fabricated by one-pot process and (d) EDS spectra of nanoparticles on the surface of the Pd/SnO₂/RGO ternary nanocomposite film.

the surface of the Pd/SnO₂/RGO ternary nanocomposite film. As the concentration of NH₃ increased (150–300 ppm), the number of active sites for adsorption declined, causing the rapid decrease in the slope. Fig. 11 plots the long-term stability of the sensor that was made of the Pd/SnO₂/0.1 g RGO ternary nanocomposite film. The average and relative standard deviation (RSD) of the response (*S*) of the NH₃ gas sensor at a testing concentration of 100 ppm of NH₃ for 58 days were 19.6 and 2%, respectively. Table 1 compares the NH₃ gas-sensing properties of the present NH₃ sensor were compared with those in the literature [2,3,6,21]. The NH₃ sensor that was made of Pd/SnO₂/0.1 g RGO ternary nanocomposite film exhibited the strongest response (*S*) because the Pd exhibited a high energy of adsorption (chemisorption) of NH₃ gas and the embedded RGO generated effective carrier transfer paths in the SnO₂ matrix.

3.3. Electrical properties and sensing mechanism of NH₃ gas sensors based on Pd/SnO₂/RGO ternary nanocomposite film

Exposure to NH₃ gas reduced the electrical resistance of the Pd/SnO₂/RGO ternary nanocomposite film herein. Since NH₃ is an electron-donating gas, the decrease in the sensor resistance is hypothesized to be caused by the fact that the prepared Pd/SnO₂/RGO ternary nanocomposite film herein exhibited the electrical behavior of an n-type semiconductor. Upon exposure to NH₃ gas, the adsorbed electron-donating NH₃ molecules compensate for the electron carriers in the n-type Pd/SnO₂/RGO ternary nanocomposite film, causing the electrical resistance of the Pd/SnO₂/RGO ternary nanocomposite film to decrease as the concentration of NH₃ increases. Fig. 12 plots the *I*–*V* characteristics of the prepared Pd/SnO₂/0.1 g RGO ternary nanocomposite film. The

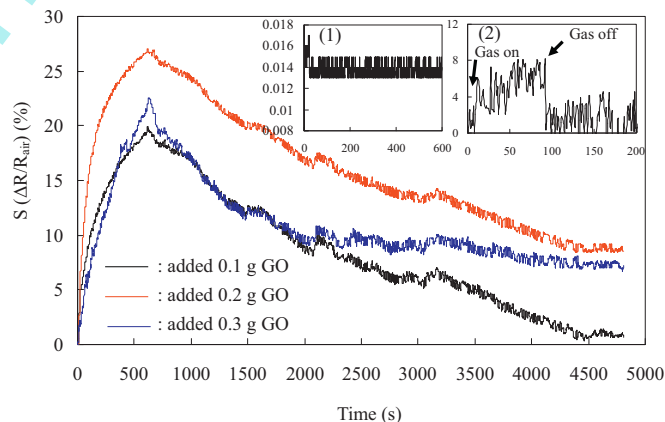


Fig. 9. Response (*S*) of NH₃ gas sensors based on Pd/SnO₂/RGO ternary nanocomposite films that were prepared by one-pot process with various amounts of added RGO to 100 ppm NH₃ gas at room-temperature. Inset 1: Response (*S*) of NH₃ gas sensors based on SnO₂/RGO film. Inset 2: Response (*S*) of NH₃ gas sensors based on Pd/SnO₂ film.

I–*V* relationship was linear between –5 and 5 V, revealing good ohmic contact.

Gas-sensing mechanism of semiconducting metal oxides is well known to involve gas adsorption, charge transfer and gas desorption. Therefore, reactions at room-temperature have been suggested to be responsible for changes in resistance upon the adsorption of NH₃. The following are used from the reports of Li et al. [3] and Gupta et al. [21].



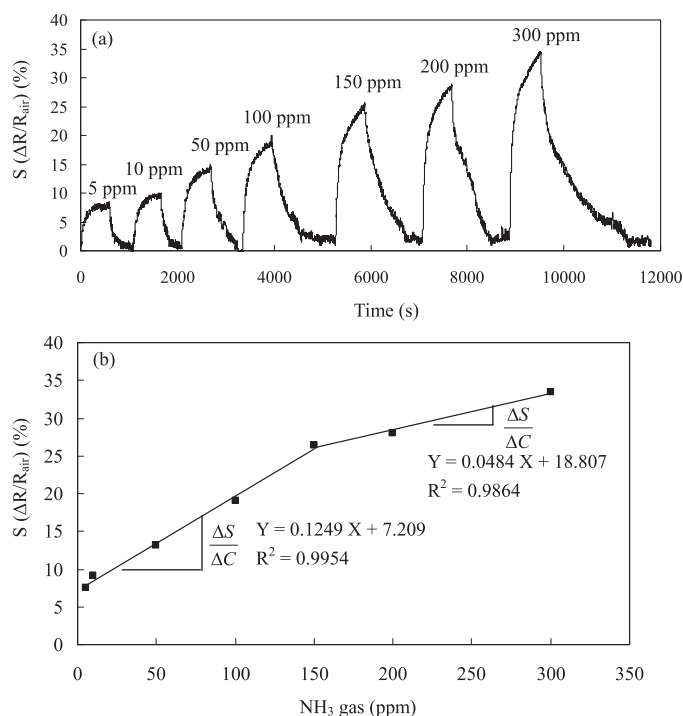


Fig. 10. (a) Response (S) of NH₃ sensor based on Pd/SnO₂/0.1 g RGO ternary nanocomposite film that was prepared by one-pot process to various concentration of NH₃ gas at room-temperature and (b) linear dependence of response (S) of NH₃ gas sensor based on Pd/SnO₂/0.1 g RGO ternary nanocomposite film on concentration of NH₃ gas at room temperature. Sensitivity ($\Delta S/\Delta C$) is determined from the slope of the linear curve.

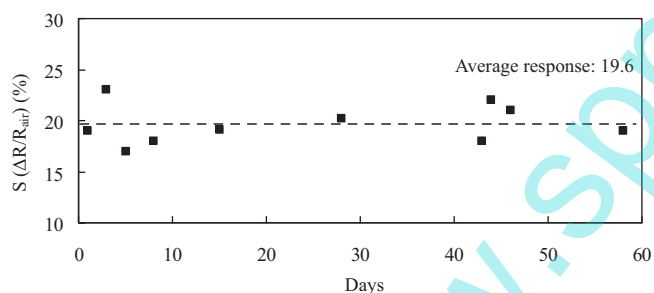


Fig. 11. Long-term stability of response of the NH₃ gas sensor based on Pd/SnO₂/0.1 g RGO ternary nanocomposite film that was fabricated by one-pot process in 100 ppm of NH₃ gas.

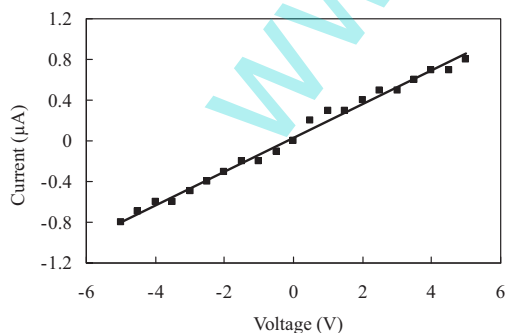
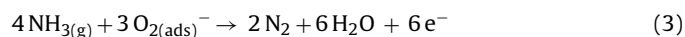


Fig. 12. $I-V$ characteristics of Pd/SnO₂/0.1 g RGO ternary nanocomposite film.



Semiconductor gas sensors are commonly used in air at atmospheric pressure, so atmospheric oxygen on the surface adsorbs electrons from the conduction band of the n-type Pd/SnO₂/RGO

ternary nanocomposite film, forming $\text{O}_2(\text{ads})^-$ and an electron-depleted layer at the surface of the film (Eq. (2)). In this work, as NH₃ gas was adsorbed, and electrons were released into the conduction band according to Eq. (3), reducing resistance. Additionally, the excellent response of the NH₃ sensor that was made of Pd/SnO₂/RGO ternary nanocomposite film at room-temperature is analyzed by considering two main phenomena. First, according to some investigations [12,21,22], adding Pd to the surface of the Pd/SnO₂/RGO ternary nanocomposite film forms weak-bonded complex between Pd atoms and adsorbed oxygen molecules at room-temperature, causing the weak complex easily dissociated to form additional oxygen species, activates the reaction between NH₃ and the adsorbed oxygen species, enhancing the sensitivity of the Pd/SnO₂/RGO ternary nanocomposite film. Second, the pristine SnO₂ film exhibits high resistance at room-temperature. Doping with RGO reduced the resistance of the SnO₂/RGO nanocomposite film to $\sim 100\text{ k}\Omega$, revealing that the added GO was reduced to conductive RGO, which formed new electrical paths in the Pd/SnO₂/RGO ternary nanocomposite film and facilitated the transfer of electrons, and so adding RGO improved the response of the Pd/SnO₂/RGO ternary nanocomposite film. Therefore, NH₃ gas was easily detected at room-temperature using the Pd/SnO₂/RGO ternary nanocomposite film herein, owing to the combination of its catalytic activity and favorable charge transfer.

4. Conclusions

Novel room-temperature NH₃ gas sensors, based on Pd/SnO₂/RGO ternary nanocomposite films, were successfully fabricated by the one-pot route. FTIR, Raman, SEM-EDS and AFM revealed that the SnCl₂ not only was the precursor of SnO₂ but also simultaneously reduced both GO and PdCl₂ to RGO and Pd nanoparticles, respectively. Based on the experimental results, introducing RGO and Pd nanoparticles enhanced the response of the Pd/SnO₂/RGO ternary nanocomposite film to NH₃ gas, especially at low concentrations. The NH₃ gas sensor that was based on a Pd/SnO₂/RGO ternary nanocomposite film that was doped with 0.1 g of RGO had high sensitivity even at a low testing concentration of NH₃ (5 ppm), good linearity ($Y = 0.1249 X + 7.209$; $R^2 = 0.9954$) between 5 and 150 ppm, good reversibility, a short response time (7 min), a short recovery time (50 min) and long-term stability (of at least 58 days) at room-temperature.

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