

Humidity-sensing Performance of Graphene/SnO₂ Nanocomposites

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In this study, a series of humidity sensors based on graphene/SnO₂ (Gr/SnO₂) nanocomposites with different proportions of the sensing material (10, 20, 30, 40, 50, and wt%) have been successfully fabricated by a simple method. The surface design, chemical structural information, and elemental variation of the prepared humidity sensors were investigated using Fourier transform infrared (FTIR) spectroscopy, X-ray diffraction (XRD), energy-dispersive X-ray spectroscopy (EDXS) and transmission electron microscopy (TEM). By measuring the sensitivity, hysteresis, response characteristics of the humidity sensors, it was proved that the obtained 30 wt% Gr/SnO₂-based humidity sensor exhibited outstanding fast response/recovery speeds (28/140 s), small hysteresis (~5% RH), and high humidity sensitivity ($S=80770$) in the 12–90% RH range. Therefore, Gr/SnO₂ can be used as a potential material for real-time humidity-sensing applications.

1. Introduction

Humidity is a key environmental factor affecting environmental protection, precision instrument protection, industrial production, food safety, agricultural manufacturing, wearable electronics, and human health applications in daily life. Thus, it is imperative to monitor the humidity of the surrounding environment for assessing human health.^(1–5) Until now, many efforts have been devoted to developing humidity sensors with flexibility, easy processability, low hysteresis, high sensitivity, low cost, good chemical and thermal stabilities, and capability for the real-time monitoring of humidity, mainly including ceramics, electrolytes, metal oxide semiconductors, polymers, 2D nanomaterials, and proteins.^(6–11) Among them, metal oxide semiconductor nanomaterials such as ZnO, ZrO₂, SnO₂, WO₃, and TiO₂ have been generally recognized as preferred choices owing to their advantages of cost-effectiveness, chemical stability, and high sensitivity.^(12–17) In recent years, as a typical n-type oxide semiconductor, SnO₂ has been widely investigated as a sensitive material for humidity detection application.

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However, SnO_2 has some shortcomings such as low sensitivity and slow response, which seriously hindered the development and application of humidity sensors.^(18–20) To solve this problem, numerous research studies have been devoted to improving the humidity-sensing performance of SnO_2 -based sensors. As a typical carbon material, graphene has a large specific surface area and excellent electrical performance, and can be considered as an ideal material to improve the sensing performance of SnO_2 humidity sensors.^(21,22) Notably, reports have demonstrated that graphene decorated with metal oxide nanoparticles is effective for constructing high-performance sensors. Although there are humidity sensors prepared using SnO_2 , graphene and derivatives, most of them reflect humidity changes based on the change in capacitance.⁽²³⁾ However, the difference in this paper lies in the use of a dynamic flow system and the change in impedance to reflect humidity.

In this study, a Gr/ SnO_2 nanomaterial-based humidity sensor is proposed. The electrical characteristics, chemical structure, surface morphology, and humidity-sensing properties of the prepared Gr/ SnO_2 humidity sensor were studied using Fourier transform infrared (FTIR) spectroscopy, X-ray diffraction (XRD), energy-dispersive X-ray spectroscopy (EDXS), transmission electron microscopy (TEM), and chemical impedance analyses. The results of the experiment showed that the prepared Gr/ SnO_2 humidity sensor demonstrates outstanding performance for humidity detection, which is dated in terms of response in a quick/short recovery period, small drift in humidity, and high humidity sensitivity.

2. Sensor Fabrication

2.1 Components used

Graphene with high purity (>99%) was purchased from UniRegion Bio-Tech. Ethanol (anhydrous) was purchased from Echo Chemical Corporation Limited, Taiwan. Polyvinyl alcohol (PVA) and sodium stannate ($\text{Na}_2\text{SnO}_3 \cdot 3\text{H}_2\text{O}$) were purchased from Sigma–Aldrich Co. Ltd. (USA). Distilled and deionized (DI) water was collected from a Milli-Q water purification system (Millipore Corp.). All the purchased materials were used as is and without further processing or treatment.

2.2 Synthesis

A known amount of $\text{Na}_2\text{SnO}_3 \cdot 3\text{H}_2\text{O}$ was dissolved in an anhydrous ethanol solution (20 ml) and then sonicated for 0.5 h. Subsequently, a stoichiometric amount of graphene was sonicated with the aforementioned solution for 1 h. The solution was kept in an electric oven at 50 °C for 24 h. The desired product was obtained by calcination at 400 °C for 2 h. Graphene/ SnO_2 abbreviated as Gr/ SnO_2 was the final composite obtained. Tests were performed on nanocomposite sensing materials fabricated using graphene at various ratios (10, 20, 30, 40 and 50 wt%).

2.3 Characterization

Structural and particle size analyses, TEM, and FTIR spectroscopy were performed to characterize the samples. Structural analysis was conducted using XRD from Shimadzu (Model no. 6000) over a range of $10\text{--}80^\circ$ (2θ) at 2°min^{-1} using Cu K α 1 radiation ($\lambda = 1.5404 \text{ \AA}$) at 35 kV and 35 mA. Average particle size was evaluated using $\kappa\lambda/\beta\cos\theta$ for Gr/SnO₂. The samples were suspended in ethanol using ultrasound and dispersed in a copper grid prior to TEM analysis using an electron microscope from JEOL (Model no. JEM2010) to visualize the surface morphology. For FTIR spectroscopy, the samples were pulverized with KBr prior to analysis. An Agilent Cary Fourier transform spectrometer that covered the wavelength range from 400 to 4000 cm^{-1} was used to obtain the spectra.

2.4 Fabrication of humidity sensor

The clips for sensors were fabricated by dip-coating (Binder: PVC) the prepared material on an alumina substrate ($10 \times 5 \text{ mm}^2$; rotation speed, 1000 rpm), which appeared like a pair of comb-like gold electrodes. Subsequently, the gas-sensitive layer was dried at 80°C for 30 min, followed by calcination at 300°C for 4 h. Two wires were used to connect the two gold electrodes to the sensor circuit.

2.5 Humidity-sensing measurements

Figure 1 shows a schematic diagram of the experimental setup used for measuring the electrical response of the sensor, which was investigated using a dynamic flow system equipped with a thermo-hygrometer for temperature and relative humidity (RH) monitoring. The humidity sensor was optimized according to Taiwan's Center of Measurement Standard/Industrial Technology Research Institute (ITRI) standards. The designed sensors were placed inside an

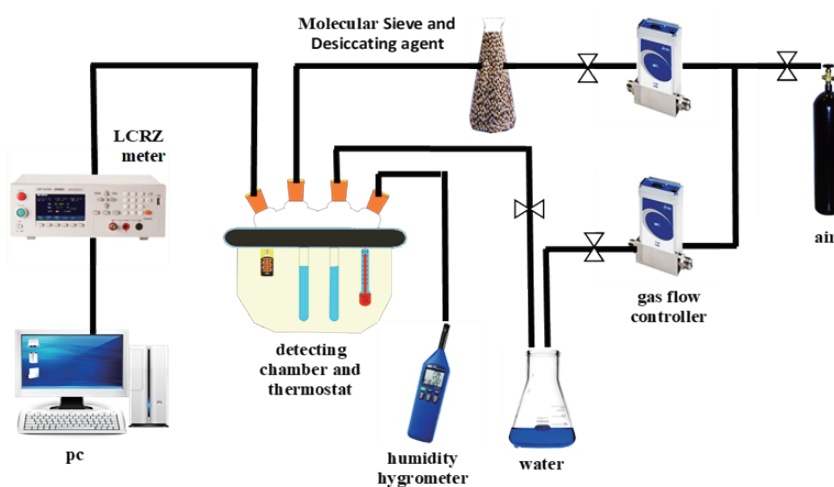


Fig. 1. (Color online) Experimental setup.

airtight glass chamber prefilled with water. The RH inside the chamber was controlled by injecting air into the water, generating water vapor. The system was allowed to reach equilibrium for 15 min. The RH response (S) of the sensor and the error in the hysteresis of humidity (H) were calculated using the following equation:

$$S = \frac{R_d}{R_h} \quad (1)$$

Here, R_d is the 12% RH-produced resistance, which can be under dry conditions, and R_h is the specific-humidity-produced resistance.

$$H = \frac{\Delta f_{max}}{ffs} \quad (2)$$

Here, Δf_{max} is the maximum hysteresis error and ffs is the full-scale response output. RH was varied from 12 to 90%, then back to 12% to evaluate the humidity hysteresis properties of the sensors. When the total impedance can have a drift of 90%, the time was estimated as the response time. Different ratios of air to water and RH at 12 and 90% were used to estimate the sensor behavior under dynamic conditions. RH was monitored using a Rotronic hygrometer. The impedance response of the sensing material to ambient humidity was measured using a chemical impedance analyzer (Delta United, USA Model no. 6010); the input voltage and frequency were 1 V and 1 kHz, respectively.

3. Results and Discussion

3.1 Structure characterization

The FTIR investigation was conducted to determine the structural information of the functional groups of different contents for Gr/SnO₂ nanocomposites as presented in Fig. 2. The FT-IR spectra of graphene exhibit a band at 2363 cm⁻¹ associated with the C=O stretching mode, which may have resulted from the environmental adsorption of CO₂ on the graphene surface.⁽²⁴⁾ Broad and weak bands at 856 and 1450 cm⁻¹, respectively, indicate the occurrence of O-Sn-O bonding.⁽²⁵⁾ The wide band at 3400–4000 cm⁻¹ might be caused by the vibration of water molecules on the surface of the Gr/SnO₂ nanocomposite.

Figure 3 shows the XRD patterns of the samples. All the as-synthesized samples have a diffraction peak at about 26.3 and 54.0°, which can be attributed to the (002) and (004) crystal planes of graphene.⁽²⁶⁾ In all the as-synthesized Gr/SnO₂ samples with different SnO₂ contents, the prominent diffraction peaks at 26.7, 33.9, 51.8, 54.6, 57.5, 64.5, and 65.7° can respectively be ascribed to the (110), (101), (211), (220), (002), (112), and (301) planes of SnO₂ related to the standard value (JPCDS 41-1445).⁽²⁷⁾ The synthesis produced a high-purity material as no other crystalline phase was observed.

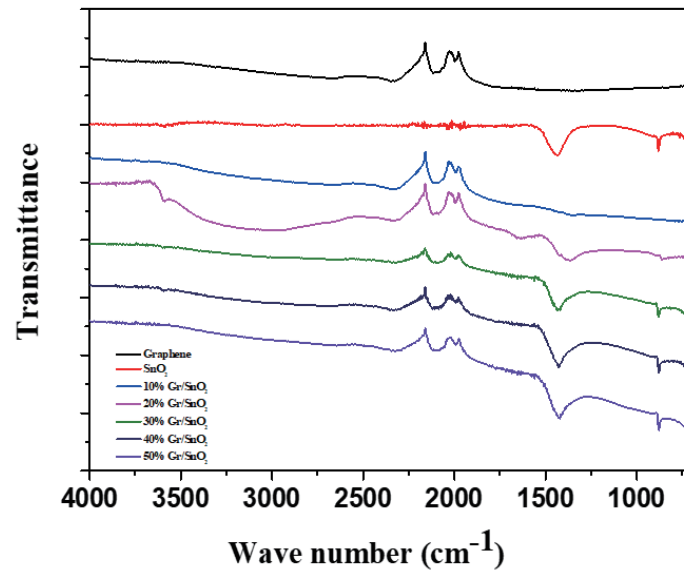


Fig. 2. (Color online) FT-IR spectra of different contents for Gr/SnO₂ nanocomposites.

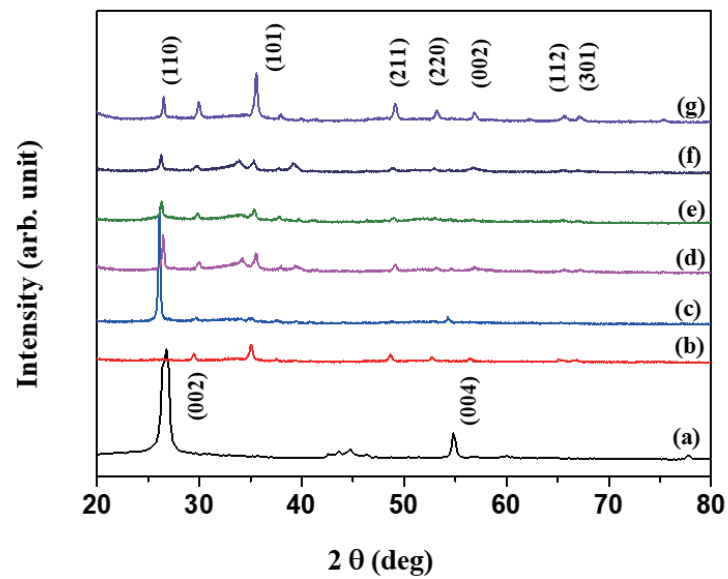


Fig. 3. (Color online) XRD analyses of (a) graphene, (b) SnO₂, and (c)–(g) 10, 20, 30, 40 and 50 wt% Gr/SnO₂ nanocomposites.

In the case of the Gr/SnO₂ nanocomposite, it is very difficult to find the peak at 26.3 and 54.0° because SnO₂ is highly crystalline, whereas that of the graphene nanosheet may provide the disordered stack nature in the nanocomposite.

The morphologies of SnO₂, graphene, and Gr/SnO₂ materials were visualized using TEM, as illustrated in Figs. 4(a)–4(d). Figure 4(a) shows that the SnO₂ material exhibits inconsistent

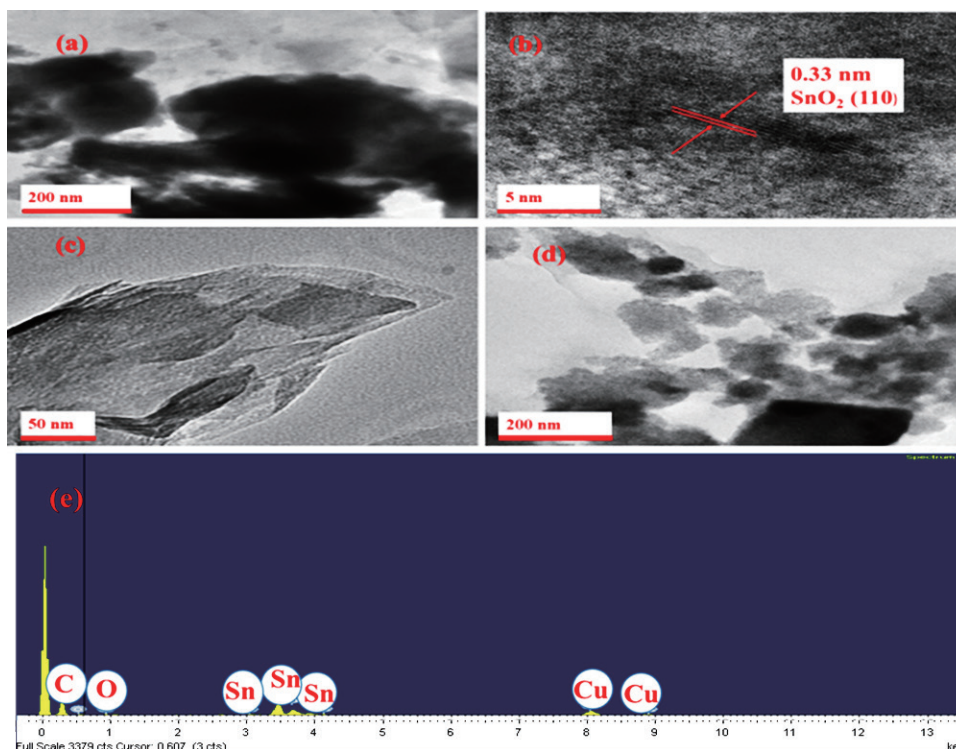


Fig. 4. (Color online) TEM images of (a and b) SnO_2 , (c) graphene, (d) 30 wt% Gr/SnO_2 , and (e) EDX spectrum of 30 wt% Gr/SnO_2 nanocomposite.

morphology and particle agglomeration. Figure 4(b) shows the fringe spacing (0.33 nm) indexed to the (100) crystallographic planes of SnO_2 .⁽²⁸⁾ Figure 4(c) shows the stacking behavior with the irregularities of assembled graphene sheets. Figure 4(d) shows the aggregation of SnO_2 on the surface of the 30 wt% Gr/SnO_2 nanocomposite. The presence of tin, carbon, and oxygen was estimated from the EDX spectra in Fig. 4(e) for the Gr/SnO_2 composite prepared in 30 wt% ratio. These results confirmed the phase purity and formation of nanocomposites in the samples.

3.2 Humidity-response properties of as-prepared samples

The as-prepared Gr/SnO_2 nanocomposite samples with different graphene contents have been used as humidity sensors, and their humidity sensing properties under various RH have been measured. The measurements were carried out at a suitable AC voltage of 1 V and frequency of 1 kHz. The impedance values of the as-prepared samples (SnO_2 , graphene, and Gr/SnO_2 with different graphene contents) decreased with increasing RH values as shown in Fig. 5(a). In addition, 30 wt% Gr/SnO_2 exhibited the highest sensitivity (80770) in the RH range of 12–90% (a change of approximately four orders of magnitude), as shown in Fig. 5(b).

When humidity sensors are utilized in the adsorption and desorption processes, the most important characteristic that should be evaluated for humidity sensor reliability is the difference in maximum RH. This property is known as humidity hysteresis. Compared with previously

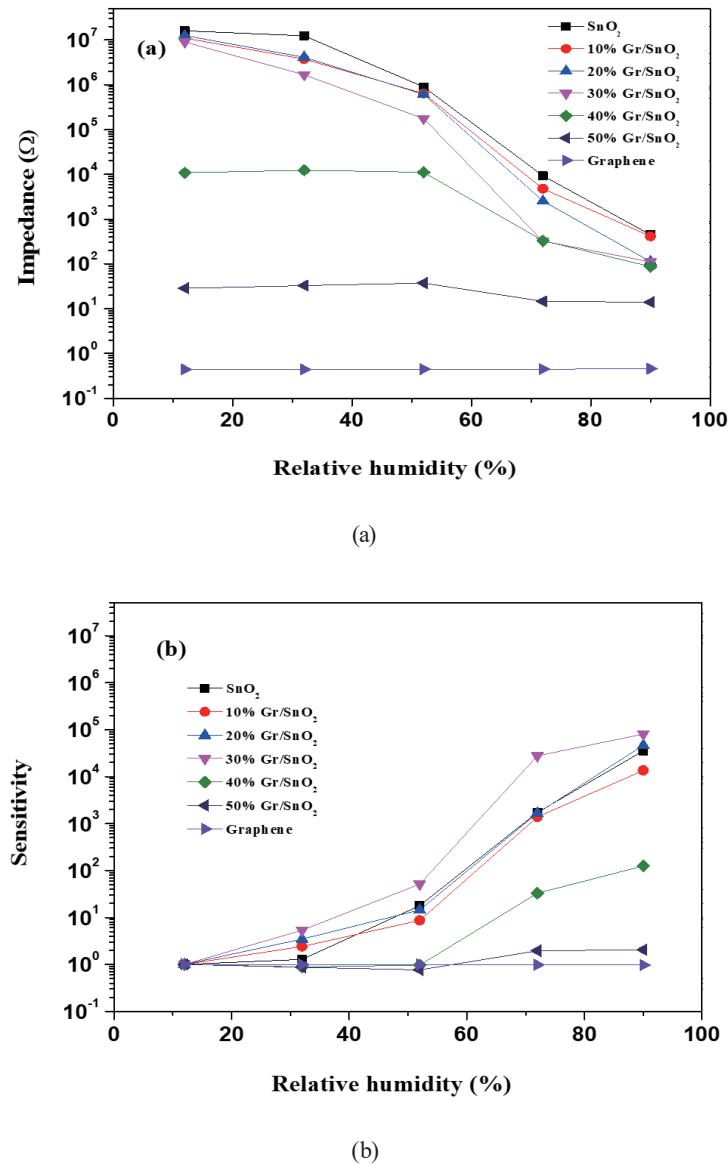


Fig. 5. (Color online) (a) Variations in impedance with RH (%) of as-prepared samples. (b) Variations in sensitivity with RH (%) of as-prepared samples.

reported sensors,⁽²³⁾ Table 1 shows that 30 wt% Gr/ SnO_2 displayed good humidity hysteresis (the maximum humidity hysteresis was 5.48%) in the RH range of 12–72%.

Response and recovery times can be regarded as one of the crucial characteristics for the assessment of humidity sensor performance and practical applications. Figure 6 shows that the impedance of 30 wt% Gr/ SnO_2 abruptly changed inversely with increasing RH and then returned to its original value with decreasing RH. In addition, Fig. 6 also shows that the response and recovery times of 30 wt% Gr/ SnO_2 were 28 and 140 s, respectively, when the RH range between 12 and 90%.

Table 1

Maximum humidity hysteresis errors of 30 wt% Gr/SnO₂ under various RH values.

RH (%)	Maximum hysteresis error (%)
12	0.13
32	1.12
52	5.19
72	5.48

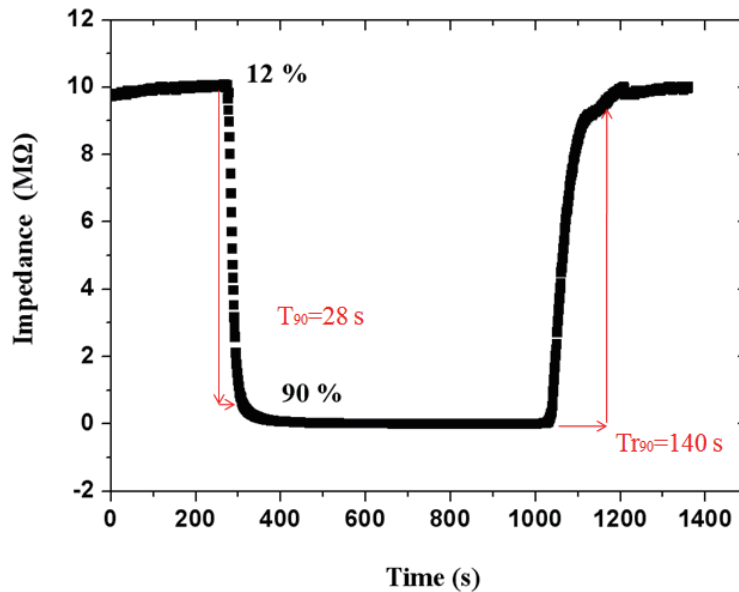
Fig. 6. (Color online) Response and recovery characteristics of 30 wt% Gr/SnO₂ nanocomposite.

Table 2 shows the response and recovery times of 30 wt% Gr/SnO₂ sensors from this work and previous works.^(18,29–32) Moreover, compared with the reported humidity sensor based on SnO₂ in Table 2, the 30 wt% Gr/SnO₂ sensor shows good performance with response and recovery times of 28 and 140 s, respectively.

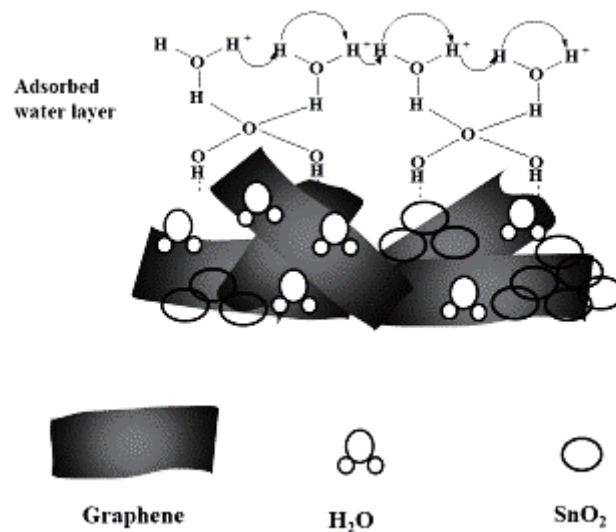
3.3 Sensing mechanism

Figure 7 shows the humidity-sensing mechanism models of adsorption for 30 wt% Gr/SnO₂ nanocomposite. The sensor exhibits both high conductance and extremely high impedance as shown in Fig. 5. The adsorption occurs via two adsorption processes: water molecules are absorbed through physical and chemical adsorption processes via van der Waals forces⁽²⁸⁾ and hydrogen bonding.⁽¹³⁾ At low humidity, only a few H₂O or H₃O⁺ molecules were adsorbed on the surface of Gr/SnO₂; thus, it is difficult to transport conduction ions. Upon increasing RH, the sensor surface exhibits a continuous adsorption of H₂O molecules, which further forms hydrogen bonds with the existing primary water layers. The Gr/SnO₂ nanocomposite surface with irregularly stacked smooth graphene sheets is filled with water owing to capillary

Table 2

Summary of Gr/SnO₂ sensor performance from this work and previous works.

Material	Fabrication method	Meas. range	Res./rec. time	Ref.
Al/SnO ₂ Co-doped	Hydrothermal	11–95%RH	100 s/88 s	(18)
SnO ₂ /RGO	Spin-coating	11–95%RH	52 s/100 s	(29)
RGO/SnO ₂	Hydrothermal	11–97%RH	6–102 s/6–9 s	(30)
RGO/SnO ₂	Hydrothermal	11–97%RH	100 s/100 s	(31)
SnO ₂ nanowire	Hydrothermal	30–85%RH	120–170 s/20–60 s	(32)
Gr/SnO ₂	Hydrothermal	12–90%RH	28 s/140 s	This work

Fig. 7. Adsorption models for 30 wt% Gr/SnO₂ nanocomposite.

condensation when RH is significantly high. The transfers of H₂O and H₃O⁺ were accelerated by the serial water layers. Agmon⁽³³⁾ and Casalbore-Miceli *et al.*⁽³⁴⁾ showed H₂O/H₃O⁺ transfers on the serial layers with the following chemical reaction: $\text{H}_2\text{O} + \text{H}_3\text{O}^+ \rightarrow \text{H}_3\text{O}^+ + \text{H}_2\text{O}$.

Therefore, the conductivity of Gr/SnO₂ nanocomposites is enhanced by the free movement of conductive ions. The Gr/SnO₂ nanocomposites have fast and high sensing response and recovery times.

4. Conclusions

In this study, the humidity-sensing properties of a Gr/SnO₂ nanocomposite were determined by experiment studies. The experimental results revealed that the nanocomposite with 30 wt% Gr/SnO₂ provided a high sensitivity ($S = 80770$), which is a change of approximately four orders of magnitude. Compared with previously reported sensors, the proposed sensor exhibits fast response/recovery (28/140 s) and good hysteresis (~5% RH). The results indicate that Gr/SnO₂-based humidity sensors are good candidates for humidity-sensing applications (e.g., precision instrument protection, food safety, and agricultural manufacturing).

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