Na-Doped ZnO and RGO Composite-Based Flexible Acetone Gas Sensor Operated in Room Temperature

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ABSTRACT Real-time health monitoring is important in disease prediction, prevention, and early treatment. In this study, based on Na-doped ZnO/reduced graphene oxide (RGO) heterojunction, an ultrasensitive flexible room temperature gas sensor was developed for lung cancer surveillance diagnosis. The sensing material was synthesized using a simple solution route. X-ray photoelectron spectroscopy (XPS), X-ray diffraction (XRD), scanning electron microscopy (SEM), and Raman spectroscopy were carried out to investigate the structure and chemical properties. The fabricated material has a surface-to-volume ratio, which was important to the sensing property. The gas-sensing performance was measured from 5 ppm to 200 ppm at room temperature (25 °C). The proposed sensor demonstrated fast response and recovery time, as well as great repeatability and long-term stability. Furthermore, it exhibited mechanical robustness, and can be bent to different angles with almost no resistance change. Moreover, performance investigation at low acetone concentrations (0.2 ppm to 1.0 ppm) revealed its capability of distinguishing acetone gas as low as 0.2 ppm, with good linearity under different acetone concentration. As such, the developed sensor could provide a promising basis for disease monitoring through detecting the concentration of acetone gas exhaled by human.

INDEX TERMS Acetone, flexible sensor, health monitoring, Na-doped ZnO, reduced graphene oxide.

I. INTRODUCTION

As the concern for personal health and environment safety increases, development of intelligent sensors, which can detect specific gases in numerous fields such as industry, agriculture, medicine, and environmental monitoring, has advanced [1]–[6]. Human body health condition can be examined through detecting the type and concentration of exhaled gases [7]. For example, the concentration of acetone gas exhaled by healthy people is generally in the range of 0.3-0.9 ppm, but that of people with lung cancer exceeds 1.0 ppm [1]. Therefore, sensitiveness and low concentration-level detectability are important parameters for a gas sensor.

Various materials are used as sensitive materials for gas sensors including semiconductor metal oxides [8], and vapor sensitive polymers [10]. Nano materials have numerous merits that can affect the gas sensor performance, such as surface-to-volume ratio, specific surface area, surface active sites, size of the nanostructure, and concentration of the energetic carries [10]. Among them, the surface-to-volume ratio plays a decisive role. However, due to the structure of the sensitive material, some conventional gas sensors lack large enough surface-to-volume ratio [11]. The development of nanotechnology in recent years enabled the emergence of a series of new nanomaterials, and allowed them to be used as sensitive materials for gas sensors such as carbon nanotubes, metal nanowires, nanofibers, and nanoparticles [12]–[15].

Graphene, a typical 2D material, has attracted increased attention from different institutions and organizations because of its excellent properties such as mechanical stability [16], biocompatibility, high carrier mobility, and large surface area, due to its unique two-dimensional honeycomb lattice [17]. Therefore, graphene and its composites have
been widely employed among temperature, pressure, and gas sensors [18]–[20]. Zinc oxide (ZnO) has a direct wide band gap (3.37 eV) with a large exciton binding energy (60 meV) [21], and demonstrates good performance in gas-sensing [22], [23] and photoelectronic [24]. Typically, ZnO is an n-type metal oxide semiconductor [25]. However, when group-I elements such as sodium (Na) is incorporated in the ZnO lattice, the n-type ZnO will become a n-type semiconductor without causing any significant lattice distortion and potential variation, while the surface-to-volume ratio of the Na-doped ZnO (NZ) is larger than pure ZnO [26]. Notably, the graphene addition to NZ increases the surface-to-volume ratio. Although there exist many researches focusing on NZ, its production method is complicated, such as pulsed laser deposition [27] and chemical vapor deposition [28]. Besides, the composite of graphene and NZ heterojunction has not been reported yet to the best of our knowledge.

In this study, a new fabrication method of Na:ZnO/RGO (GNZ) is proposed with a simple solution route using appropriate proportions of graphene oxide (GO), vitamin C, zinc acetate dihydrate (Zn(CH₃COO)·2H₂O), sodium citrate dihydrate (Na₃C₆H₅O₇·2H₂O), and sodium hydroxide (NaOH) under low temperature. Interestingly, NZ presents the shape of a three-dimensional flower while the graphene is two-dimensional. The GNZ is similar to a beautiful flower growing on fertile land. Moreover, the GNZ exhibits a higher surface-to-volume ratio compared to single graphene or NZ, indicating better sensing properties. Subsequently, a flexible acetone sensor is fabricated, which demonstrates high sensitivity, fast response/recovery time, repeatability, and long-term stability.

II. PREPARATION AND CHARACTERIZATION OF MATERIALS
A. PREPARATION OF NA:ZnO HYBRID
All chemical reagents were analytical reagent and without further purification. Here, 16 g of zinc acetate dihydrate (Zn(CH₃COO)·2H₂O) and 70.56 g of sodium citrate dihydrate (Na₃C₆H₅O₇·2H₂O) were dissolved in 50 mL of deionized water (DI) and stirred continuously until the solution became transparent. Afterwards, 0.5 M sodium hydroxide (NaOH) and 5 mL of vitamin C solution were slowly added into the above solution. Next, the mixed solution was stirred at 45 °C for 1 h, and naturally cooled down to room temperature. A gray precipitate was obtained after standing for 30 min, which was then washed with DI water and ethanol several times. Finally, it was annealed at 60 °C for 12 h in a drying oven.

B. PREPARATION OF GNZ COMPOSITES
High purity graphene oxide (GO) was used as the initial material. Additionally, 5 mg of GO nanosheet was added into 30 mL of DI water, followed by 2-h sonication using ultrasonic cleaning machine to evenly disperse the graphene oxide in DI water. Subsequently, the graphene oxide dispersion was mixed with the transparent solution obtained in the previous reports. Then, the prepared Na:ZnO nanoflower was added into the GO solution and dispersed by vigorous stirring. Next, ascorbic acid was added as a reducing agent to reduce GO, allowing the functional groups on the GO surface to be fade away. Finally, the Na:ZnO/RGO hybrid was fabricated. The entire synthetic process is illustrated in Fig. 1.

![Schematic of the synthetic process of GNZ.](image)

C. CHARACTERIZATION
To investigate the structure and composition of the Na:ZnO, the X-ray diffraction (XRD) powder patterns of the samples were captured by Rigaku Smartlab9 powder diffractometer with Cu-Kα1 radiation (λ = 1.54056 Å) at 40 kV and 150 mA. X-ray photoelectron spectroscopy (XPS) was conducted to determine the surface composition of the GNZ sample on a Thermo Fisher Scientific Escalab 250Xi XPS system using a monochromatized Al Kα1 radiation of 1486.6 eV. Moreover, the XPS spectra were charge calibrated according to the adventitious C 1s peak at 284.6 eV. The surface morphology and microstructure of the GNZ sample were observed using a Hitachi SU8010 field emission scanning electron microscope (SEM) at 10.0 kV. Meanwhile, the Raman spectra were obtained using a Renishaw in Via (2000) with a 532 nm laser wavelength.

D. FABRICATION AND MEASUREMENT OF SENSOR
The gas sensor was fabricated by a simple process, as shown in Fig. 2. A polyamide (PI) film was used as the base substrate of the sensor while a copper interdigitated electrode existed on its upper surface. Its fabrication was according to the

![Fabrication process of the acetone sensor.](image)
III. RESULTS AND DISCUSSION

A. STRUCTURE AND MORPHOLOGICAL ANALYSES OF GNZ

To investigate the structural and chemical, the GNZ is characterized by SEM, XPS, Raman spectra, and XRD, which are illustrated in Fig. 3. Fig. 3(a) shows the result of the SEM image of GNZ. There are some three-dimensional (3D) flower-like structures on the two-dimensional sheet structures. The flower-like structure is NZ, while the two-dimensional sheet structure is RGO. The NZ growing on the RGO resembles beautiful flowers growing on fertile land. Fig. 3(b) demonstrates the partial enlargement of the structure of Fig. 3(a). It can be observed that the diameter of the flower-like structure is approximately 1.3 µm. Meanwhile, GNZ possesses a large surface area compared to single NZ and RGO; thus, many boundaries are also included. Hence, GNZ is predicted to have outstanding performances in gas sensing. In the Fig. 3(c), it is the SEM image of NZ, and Fig. 3(d) is the enlarge image which contains Na. And Fig. 3(e) is SEM image of RGO, it is seen RGO shows layered structure. In the Fig. 3(f), it is the result of the EDS mapping of different elements. The surface compositions and chemical state of GNZ are investigated using XPS. A survey XPS spectrum is given in Fig. 3(g), in which, each peak is found to be consistent with the corresponding element. Fig. 3(h) shows the Na 1s spectrum, whose peak is at 1071.6 eV, indicating the presence of Na-O bonding states [29]. The presence of Na-O is attributed to Na3C6H5O7·2H2O and NaOH. When they dissolve in DI water, they ionize sufficient sodium ions, which are doped into the ZnO lattice as n-type doping during zinc oxide crystal lattice formation [30]. Subsequently, the O 1s spectrum is acquired to prove the formation of ZnO, as shown in Fig. 3(i). The three peaks of O 1s are 530.64 eV, 531.84 eV, and 532.68 eV, which indicate the presence of a metal-oxygen bonding state, oxygen atoms in the vicinity of oxygen vacancies, and hydroxyl groups, respectively [31]. Furthermore, the C 1s spectrum can be deconvoluted into four Gaussian peaks centered at binding energy of 284.7 eV, 285.68 eV, 286.82 eV, and 289.4 eV in Fig. 3(j). The bending energy at 284.7 eV corresponding to the C-C probably originated from RGO, whereas the bending energies at 285.68 eV, 286.82 eV, and 289.4 eV are associated with C-O, C=O, and O-C=O, respectively, in Fig. 3(j). These characteristic peaks may be derived from the RGO production process. There are some remnant oxygen and hydroxyl groups remaining on the surface of the reduced graphene oxide [18]. Meanwhile, the Raman spectra reveals an increasing I_D/I_G intensity ratio (from 1.03 to 0.99) in Fig. 3(k), which also indicates successful reduction of GO. In Fig. 3(l), all the diffraction peaks correspond well with the hexagonal wurtzite structure of ZnO (JCPDS card No.36-1451), which proves that the NZ is highly crystallized and Na doping has a negligible influence on the ZnO crystalline structure. Besides, a diffraction peak appeared at 27.62°, indicating that the graphene oxide has been reduced. Moreover, XRD is carried out to investigate the crystalline structure of GNZ.

B. PERFORMANCE OF GAS SENSOR

To test the performance of the gas sensor, the fabricated sensor is exposed to different concentrations of acetone gas. Here, the sensitivity, response time (T_{res}), and recovery
FIGURE 4. (a) Response of the sensor when it was in different acetone gas concentrations, from 5 ppm to 200 ppm, at room temperature (25°C); (b) Experimental data and fitting line of the sensor under different concentrations ranging from 5 to 200 ppm. (c) Response time and recovery time at 100 ppm of acetone gas; (d) Repeatability of the sensor when the GNZ sensor was exposed to 100 ppm of acetone gas for 6 times; (e) Response of the sensor to low concentrations of acetone (0.2, 0.4, 0.6, 0.8, and 1 ppm); (f) Experimental data and fitting line of the sensor under different concentrations ranging from 0.2 to 1 ppm. (g) Repeatability of the sensor when exposed to 1 ppm of acetone gas for 5 times; (h) Relative resistance changes of gas sensor in response to the exposure of acetone at 0, 1, 10, 50, and 100 ppm for up to 10 days. (i) Responses of the GNZ sensor to acetone and other gases.

VOLUME 8, 2020 171571

where, \( R_g \) and \( R_a \) are the sensor resistances in air and target gas at room temperature (25°C), respectively [32].

The response and recovery time were the time spent by the sensor to achieve 90% of the total resistance change during the absorption and releasing process [33]. The initial resistance of GNZ was 2782 \( \Omega \). The GNZ sensor was placed in the air chamber to exploit its sensitive features, with its test process being relatively simple. First, dry air was continuously introduced into the air chamber for 10 min, followed by a continuous introduction of certain acetone gas concentration as long as the resistance of the GNZ sensor was stable. Afterward, the dry air was introduced into the air chamber until the resistance was stabilized again. By repeating the above steps, the sensor performance in different acetone concentrations were achieved. The dynamic sensitive of the GNZ sensor was illustrated in Fig. 4(a) when exposed under different acetone concentrations of 5, 10, 20, 50, 100, and 200 ppm at room temperature (25°C). As the concentration of acetone gas increased, the resistance of the GNZ sensor increased gradually. Experiment data under different concentration were extracted and linearly fitted, the slope is about 0.019 ppm\(^{-1}\). Considering 100 ppm acetone as an example, it can be clearly observed from Fig. 4(c) that the response time (\( T_{res} \)) of the GNZ sensor was 80 s, while the recovery time (\( T_{rec} \)) was around 135 s. The response of the GNZ sensor after being exposed to 100 ppm of acetone gas three times is shown in Fig. 4(d). Notably, the GNZ sensor resistance was observed to be almost unchanged. The concentration of acetone gas exhaled by normal people is generally less than 1 ppm. Conversely, for some people with diseases such as lung cancer, it could be higher than 1 ppm. Therefore, experiments were carried out for the GNZ sensor under different acetone gas concentrations of 0.2, 0.4, 0.6, 0.8, and 1 ppm; their results are shown in Fig. 4(e). It was observed that the GNZ sensor could distinguish very low concentrations of acetone gas. Although the response was not particularly high, the GNZ sensor presented a possibility for human disease detection.

And the linear fitting result is shown in Fig. 4(f).

Fig. 4(g) shows the repeatability of the sensor under 1 ppm, and it can be seen that the sensor shows good performance at room temperature. Moreover, the stability of the sensor is another important factor index, as shown in Fig. 4(h), it is the result of the sensor under different concentration acetone for 10 days. Sensors should be insensitive to other gases except the target gas. Hence, some different volatile organic vapors, including ethanol, methanol, and isopropanol, were used to
FIGURE 5. The different humidity effect of the gas sensor on the 50 ppm acetone.

test the performance of the GNZ sensor. The test environments were in accordance with the test condition of acetone, and the concentrations of different types of gases were all 100 ppm. As can be seen from Fig. 4(i), the sensitivity towards acetone was higher than other gases, demonstrating the great sensitivity to acetone gas of the GNZ sensor.

To study the humidity effect on the gas test process, we performed the gas sensor at 50 ppm under different humidity, ranged from 10 %RH to 80 %RH, and the result of the humidity effect is shown in Fig. 5.

C. GAS SENSING MECHANISM

The acetone gas sensing mechanism of the Na:ZnO/RGO gas sensor depends on the adsorption/desorption of the target gas, which could change the resistance of the sensor. When Na:ZnO/RGO was exposed in the air atmosphere, oxygen molecules was absorbed on the surface of the Na doped ZnO, which forms adsorbed oxygen ions species (O$_2^-$) by extracting conduction band electron and creating a space charge conduction region.

Physical adsorption is achieved by Van der Waals force between Na:ZnO and RGO, which is generally small and poorly selective. Chemical adsorption is achieved by chemical reactions. Gas molecules reacted chemically with some substances on the surface of sensitive material, causing chemical bonds, which are much more powerful than Van der Waals forces, to break and recombine [35]. One possible sensitive principle is that the sensitive material (GNZ) prepared in this experiment adsorbed acetone gas through simultaneous physical and chemical adsorption. First, RGO has a significantly large surface-to-volume ratio, which can quickly adsorb acetone gas to its surface through physical adsorption, and greatly improve the utilization efficiency of sensitive materials. The adsorbed gas then chemically reacts with GNZ, which is a p-n heterojunction semiconductor with large number of holes and small number of electrons. The surface of GNZ has a layer of hole accumulation (thickness is $h_1$). When the GNZ is placed in the air, it will adsorb an oxygen-containing substance to form O$_2^-$ on its surface [36], as shown in Fig. 6(a). When the sensor is placed in acetone, the acetone gas will react with O$_2^-$ of the GNZ as follows:

\[
\text{CH}_3\text{COCH}_3 + 4\text{O}_2^- \rightarrow 3\text{CO}_2 + 3\text{H}_2\text{O} + 4e^-.
\]

Large amounts of electrons are generated through the reaction formula (2). As shown in Fig. 6(b), these electrons will react with the surface holes of GNZ, and greatly reduce their number, resulting in a thin hole layer (thickness is $h_2$, and $h_2 < h_1$), which in turn increases the sensor resistance.

FIGURE 6. GNZ sensor sensitivity mechanism. (a) Sensitive material; (b) three-dimensional structure of the GNZ; (c-e) band diagram of GNZ heterojunction before and after contact (in air and acetone).
When the sensor is exposed to the air, the $O_2$ in the air will react with the electrons produced by the chemical reaction in the previous step:

$$O_2 + e^- \rightarrow O_2^-$$ (3)

Through this reaction, the $O_2^-$ on the GNZ surface will be replenished, while the reduction of electrons will restore the hole layer and sensor resistance to their initial states. The GNZ flexible acetone gas sensor achieves accurate sensing of acetone gas by the above two reactions.

Figs. 6 (c–e) illustrate the GNZ heterojunction. Fig. 6(c) is the schematic of the band gap of the GNZ heterojunction in the air. The Na doped ZnO nanostructures and GNZ heterojunction increased the sensing by the property synergistic. Firstly, Na doped in the ZnO nanostructures provides more active sites for the chemical adsorption compared to pristine ZnO, which leads to a larger change of sensor resistance. Conversely, the high sensitivity of the sensor can also be influenced by the p-n heterojunction between the p-type RGO and n-type Na:ZnO. Due to the difference in the Fermi level, the work function of RGO is higher than ZnO, as shown in Fig. 6(c).

It is well known that RGO has zero bandgap that demonstrates metallic features. As the p-type, holes are the majority charge carriers in the RGO. In contrast, as the n-type, electrons are the majority charge carriers in the Na:ZnO. In the RGO and Na:ZnO heterojunction, the holes are transferred from RGO to ZnO, resulting in the electron conduction in the interface between Na:ZnO and RGO. From the aspect of band diagram of Na:ZnO and RGO, both charge carriers are migrated until Fermi level, as shown in Fig. 6 (d-e). When the charge carrier transferred to Fermi level, band bending occurs due to the formation of the Schottky barrier at the heterojunctions. When the Na:ZnO/RGO heterojunction is exposed to air, the electrons are extracted from the conduction band, increasing the space charge region width at the heterojunction as oxygen molecules are adsorbed on both Na:ZnO and the defect RGO site. When GNZ is exposed to the acetone gas, the acetone molecules react with the absorbed $O_2^-$, and release electrons from the RGO to Na:ZnO. Furthermore, on the RGO surface, there exist a significant number of defect sites and functional groups, which increases the gas response and high performance of the selectivity.

IV. CONCLUSION

In this study, a three-dimensional Na-doped ZnO grown on two-dimensional reduced graphene oxide was synthesized using a simple solution route. Based on this material, a flexible acetone sensor was fabricated, which demonstrated good performance. Furthermore, the sensor has a fast response and recovery time, and exhibited great repeatability and long-term stability. The gas-sensing properties of the sensor have been measured from 5 ppm to 200 ppm at room temperature (25 °C). Moreover, the performance of the sensor at low acetone concentrations (0.2 ppm to 1.0 ppm) was examined. It was found that the response was not particularly high at low acetone concentrations, but there exists a possibility for disease detection by detecting the concentration of acetone gas exhaled by a person. The sensor showed mechanical robustness, and can be bent to different angles without affecting its own performance. Hence, the proposed sensor can be utilized in many applications, such as health and environmental monitoring, as well as chemical

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