Solid-State Method Synthesis of SnO₂-Decorated g-C₃N₄ Nanocomposites with Enhanced Gas-Sensing Property to Ethanol

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Abstract: SnO₂/graphitic carbon nitride (g-C₃N₄) composites were synthesized via a facile solid-state method by using SnCl₄·5H₂O and urea as the precursor. The structure and morphology of the as-synthesized composites were characterized by the techniques of X-ray diffraction (XRD), field-emission scanning electron microscopy (FESEM), transmission electron microscopy (TEM), energy dispersive spectrometer (EDS), thermogravimetry-differential thermal analysis (TG-DTA), X-ray photoelectron spectroscopy (XPS), and N₂ sorption. The results indicated that the composites possessed a two-dimensional (2-D) structure, and the SnO₂ nanoparticles were highly dispersed on the surface of the g-C₃N₄ nanosheets. The gas-sensing performance of the samples to ethanol was tested, and the SnO₂/g-C₃N₄ nanocomposite-based sensor exhibited admirable properties. The response value (Ra/Rg) of the SnO₂/g-C₃N₄ nanocomposite with 10 wt % 2-D g-C₃N₄ content-based sensor to 500 ppm of ethanol was 550 at 300 °C. However, the response value of pure SnO₂ was only 320. The high surface area of SnO₂/g-C₃N₄-10 (140 m²·g⁻¹) and the interaction between 2-D g-C₃N₄ and SnO₂ could strongly affect the gas-sensing property.

Keywords: 2-D graphitic carbon nitride; SnO₂; nanocomposite; ethanol; gas-sensing performance

1. Introduction

With the development of social industrialization, the leakage and pollution of poisonous gas occur frequently in people’s daily life. It brings a serious threat to human health [1-5]. Hence, the development and research of gas sensors have become urgent work [6]. In the past several years, various metal oxide semiconductors (MOS) materials, such as SnO₂ [7], ZnO [8], CuO [9], α-Fe₂O₃ [10], Co₃O₄ [11], MnO₂ [12], WO₃ [13], In₂O₃ [14], and NiO [15], were used to prepare gas sensors, which possess the outstanding advantages of low cost, controllable size, high-response value, and fast response and recovery time. For example, Yogendra Kumar Mishra et al. successfully prepared a novel ZnO tetrapod network structure, and the fabricated device structures exhibited excellent sensing behaviors toward H₂ at 400 °C [16]. Hybrid 3-D networks of ZnO-T with Zn₂SnO₄ were synthesized using the FTS approach, and the ZnO-T with Zn₂SnO₄-based sensor showed the highest response value (S = 29.3) toward CO gas at 275 °C [17]. Aerographite/nanocrystalline ZnO hybrid network materials were prepared and exhibited strong visible light scattering behavior and broadband photo absorption [18]. As is typical of n-type metal oxide semiconductors, SnO₂ is widely used as a candidate in the gas-sensing field for its wide band gap of 3.6 eV, good chemical stability, and...
physical properties. However, when taking into consideration their practical application in gas sensing, there are many defects exposed to us. For example, high working temperature, long response and recovery time, and poor stability and aggregation restrict their gas-sensing development. Therefore, many attempts have been made to improve their gas-sensing properties, such as enhancing the specific surface area and the electrical properties by using two-dimensional (2-D) materials [19–23].

Graphene, a representative of 2-D material, has been a focus of scientific research because of its unique property and structure with a unilaminar sp²-hybridized carbon atom configuration. In recent years, graphene and reduced graphene oxide (r-GO) have been widely used for gas-sensing investigation due to their large specific surface area and excellent conductivity [24–30]. Many researchers reported that metal oxide-decorated graphene nanocomposite-based sensors exhibited superior sensibility to different gases [31–37]. However, as we know, the preparation process of GO and r-GO is complicated and consumptive. Hence, it is necessary to explore a similar novel structure material with graphene.

Recently, graphitic carbon nitride (g-C₃N₄) with its graphite-layered structure, which is similar to graphene, has been studied for various applications, including photo degradation and photocatalysis, due to its large specific surface area and high chemical stability [38–41]. Until now, there are few reports about the application of gas sensors in the presence of g-C₃N₄. Zeng et al. successfully prepared a α-Fe₂O₃/g-C₃N₄ nanocomposite using a facile refluxing method for the cataluminescence sensing of H₂S [42]. In our previous work, cocoon-like ZnO-decorated graphitic carbon nitride nanocomposites were synthesized, which showed an impressive response toward ethanol [43]. As far as we know, there is no related report about the application of SnO₂/g-C₃N₄-based sensors in the gas-sensing field.

In our study, we synthesized SnO₂/g-C₃N₄-nanocomposites with different mass ratios of SnO₂ and g-C₃N₄ using a facile solid-state reaction method. The gas-sensing properties, including selectivity, stability, and sensitivity of SnO₂/g-C₃N₄ to ethanol, were investigated. As a result, the SnO₂/g-C₃N₄ nanocomposite-based sensor exhibited a higher response value and better selectivity to ethanol than pure SnO₂ nanoparticles.

2. Materials and Methods

2.1. Materials

Urea, Tin (IV) chloride pentahydrate (SnCl₄·5H₂O, 99.0%), sodium hydroxide (NaOH), and polyethylene glycol 400 (PEG-400) were purchased from Sinopharm Chemical Reagent Co., Ltd. (Beijing, China). All chemicals were used as received without further purification.

2.2. Preparation of g-C₃N₄

Graphitic carbon nitride (g-C₃N₄) was synthesized by pyrolysis of urea in a muffle furnace; 20 g urea was put into an alumina crucible with a cover, then heated to 250 °C within 110 min and kept at 250 °C for 1 h. The further treatment was performed at 350 and 550 °C for 2 h, respectively. The heating rate of the whole reaction was 2 °C·min⁻¹. The yellow power (g-C₃N₄) was collected. The collected amount of the g-C₃N₄ was about 1 g.

2.3. Synthesis of the SnO₂/g-C₃N₄ Nanocomposites

SnO₂/g-C₃N₄ nanocomposites were synthesized using a facile solid-state reaction method. In a typical synthesis procedure, 10 wt % 2-D g-C₃N₄ in the composites (SnO₂/g-C₃N₄-10) were prepared using the following method. 3.5 g of SnCl₄·5H₂O, 0.167 g of g-C₃N₄ and 3 mL of PEG-400 were mixed by grinding in an agate mortar. Then, 1.6 g NaOH was slowly added to the mixture, which was ground for another 30 min. An emission of water vapor and heat during the addition of NaOH was observed. The resulting product was separated by centrifuging and washed several times with distilled water and absolute ethanol. Then, the obtained product was dried at 60 °C for 12 h. Finally, the product was ground to powder. SnO₂/g-C₃N₄ nanocomposites with 7 wt % and
13 wt % g-C3N4-decorated SnO2 were also prepared in accordance with this method and marked as SnO2/g-C3N4-7 and SnO2/g-C3N4-13, respectively. For comparison, the same method was used to synthesize pure SnO2 nanoparticles in the absence of g-C3N4.

2.4. Characterization

The crystal microstructure of the sample was identified by X-ray diffractometry (XRD, Bruker-AXS D8, Bruker, Madison, WI, USA) using Cu Kα radiation with a wavelength of 0.154 nm. X-ray photoelectron spectroscopy (XPS) measurements were taken on a Perkin-Elmer PHI 5600 spectrophotometer (Perkin Elmer Limited, Waltham Mass, Waltham, MA, USA) with Mg Kα (1253.6 eV) radiation. Scanning electron microscope (SEM) images were observed by field-emission scanning electron microscopy (FESEM, Quanta™250 FEG) (FEI, Eindhoven, The Netherlands). Transmission electron microscopy (TEM) analysis was performed on a JEOL JEM-2100 microscope (JEOL, Tokyo, Japan) operating at 200 kV. Thermal gravity and differential thermal analysis (TG–DTA) was carried out on a TA-SDT Q600 (TA Instruments, New Castle, DE, USA) at a heating rate of 10 °C·min⁻¹ under an air atmosphere. Nitrogen adsorption–desorption isotherms were obtained on a Quantachrome Autosorb-iQ sorption analyzer (Quantachrome, Boynton Beach, FL, USA). Before carrying out the measurement, the samples were degassed at 150 °C for more than 6 h. The specific surface areas (SBET) of the samples were calculated following the multi-point BET (Brunauer-Emmett-Teller) procedure. The pore size distributions were determined from the adsorption branch of the isotherms using the DFT method.

2.5. Sensor Fabrication and Measurements

The gas-sensing performance of the as-synthesized samples to ethanol was tested using the intelligent gas-sensing analysis system of CGS-4TPS (Beijing Elite Co., Ltd., Beijing, China). Figure 1 shows a brief device schematic diagram. In the process of the gas-sensing test, the relative humidity in the test chamber is 25%. The gas sensors were prepared in a usual way [44]. A small amount of the as-prepared samples were fully ground in an agate mortar with a few drops of ethanol, which served as the agglomerant to form starchiness. Afterwards, the pastes were equally spread on a ceramic substrate (13.4 mm × 7 mm) with interdigitated Ag-Pd electrodes to form the thin film. Before carrying out the test, the substrate was aged at 60 °C for 2 h and at 150 °C for 12 h to improve the stability and repeatability of the gas sensors. The response of the sensors was defined as the ratio of Rg/Ra, where Ra and Rg were the resistances of the sensor measured in air and in test gas, respectively.

![Image](image_url)

**Figure 1.** The appearance diagram (a) and the internal structure diagram (b) of the CGS-4TPS gas-sensing test system, and the structure of the gas sensor substrate (c).

3. Results and Discussion

3.1. Sample Characterization

Figure 2 shows the XRD patterns of as-prepared g-C3N4, pure SnO2 nanoparticles, and SnO2/g-C3N4 nanocomposites. From Figure 2a, there are two obvious diffraction peaks around 13.1° and 27.5°, which
were accorded to the (100) and (002) planes of g-C₃N₄. These two peaks are likely to be attributed to the structure of the tri-s-triazine unit with interplanar spacing and the conjugated aromatic system, respectively [39]. It can be concluded that g-C₃N₄ was synthesized successfully. As seen from the other curves, there are four distinct diffraction peaks around 26.61°, 33.9°, 51.7°, and 65.9°, which correspond to the (110), (101), (211), and (301) planes of the tetragonal rutile SnO₂ (JCPDS Card No.41-1445), respectively. However, Figure 2c–e shows that there are no diffraction peaks of g-C₃N₄ observed in the curves. This is due to the relatively small content of g-C₃N₄ in the nanocomposites or the peak around 27.5° of g-C₃N₄ is covered by the peak around 26.61° of SnO₂.

![Figure 2. X-ray diffraction (XRD) patterns of the graphitic carbon nitride (g-C₃N₄), SnO₂, and SnO₂/g-C₃N₄ nanocomposites with different g-C₃N₄ contents.](image)

XPS analysis was carried out to confirm the surface chemical composition and the formation of heterojunction in the SnO₂/g-C₃N₄ sample; the result is shown in Figure 3. Figure 3a displays the survey scan spectra of g-C₃N₄, SnO₂, and SnO₂/g-C₃N₄-10. It is observed that Sn, O, C, and N exist in the SnO₂/g-C₃N₄ composite, and Sn, O, and C exist in SnO₂. The spectra of g-C₃N₄ show only C and N elements. The C 1s peak from SnO₂ is due to the adventitious carbon. As shown in Figure 3b, two signal peaks of Sn 3d in pure SnO₂ at binding energies of 486.68 eV and 495.08 eV correspond to Sn 3d₃/₂ and Sn 3d₅/₂, respectively. However, the two signal peaks of Sn 3d in SnO₂/g-C₃N₄-10 had a shade of shift, in which the peak position shifted to 486.58 eV of Sn 3d₃/₂ and 494.98 eV of Sn 3d₅/₂, respectively. This phenomenon can be attributed to the interactions between g-C₃N₄ and SnO₂ and to the heterojunction of the interface region between g-C₃N₄ and SnO₂. For the high-resolution XPS spectra shown in Figure 3c, there are few distinctions of O 1s between SnO₂ and SnO₂/g-C₃N₄-10. Figure 3d displays the high-resolution XPS spectra of C 1s. The three signal peaks for the C 1s binding energies exist at 284.4, 285.82, and 287.9 eV, respectively. As is well known, the signal at 284.4 eV corresponds to sp² C–C bonds, while the signal at 285.82 eV is identical to the combination of C–N groups. And the signal at 287.9 eV comes from the sp² C atoms from the aromatic rings N–C=N. As is seen in Figure 3e, there are three signals with binding energies at 398.5, 399.8, and 400.7 eV, respectively. The peak at 398.5 eV is ascribed to sp²-hybridized aromatic N bonded to C atoms, and the peak at 399.8 eV comes from the tertiary N bonded to C atoms in the form of N–(C)₃. The peak at 400.7 eV is related to the N–H structure. From the above analysis, the interactions between Sn and g-C₃N₄ enhance the electrical conductivity of the nanocomposite, which could be of benefit for the gas-sensing performance.
Figure 3. X-ray photoelectron spectroscopy (XPS) survey of g-C$_3$N$_4$, SnO$_2$, and SnO$_2$/g-C$_3$N$_4$-10 samples: (a) the general scan spectrum; (b) Sn 3d spectrum; (c) O 1s spectrum; (d) C 1s spectrum; and (e) N 1s spectrum.

TG-DTA analysis was carried out to reveal the weight change situation of g-C$_3$N$_4$. The temperature range was from room temperature to 700 °C, and the heating rate was 10°/min. As is shown in Figure 4, the first peak was between 100 °C and 300 °C, which is due to the desorption of moisture and solvent. The second peak was between 400 °C and 600 °C, which is due to the combustion of g-C$_3$N$_4$ in air. This result demonstrates that g-C$_3$N$_4$ was not decomposed at the optimum temperature of 300 °C in the process of testing for gas-sensing properties.

The SEM images of g-C$_3$N$_4$, SnO$_2$, and SnO$_2$/g-C$_3$N$_4$ composite are shown in Figure 5. Figure 5a displays the SEM image of g-C$_3$N$_4$. On the edge of the thin layers, many wrinkles can be clearly seen, which are representative of 2-D materials. Figure 5b shows many SnO$_2$ nanoparticles agglomerated together with different size. As shown in Figure 5c, plenty of particles are highly decentralized on the g-C$_3$N$_4$ sheets. This could be beneficial to improving the gas-sensing properties.
The percentage composition of the four elements of C, N, Sn, and O is 35.63 wt %, 42.06 wt %, 5.39 wt %, and 16.92 wt %, respectively. The energy dispersive spectrometer (EDS) mapping of the area that was observed in Figure 6b, where the peaks of Sn, O, C, and N are simultaneously existent.

**Figure 4.** Thermogravimetry–differential thermal analysis (TG–DTA) profiles of g-C3N4.

**Figure 5.** Scanning electron microscope (SEM) images of (a) g-C3N4; (b) SnO2; and (c) SnO2/g-C3N4-10 samples.

Figure 6a displays the typical spectra of SnO2/g-C3N4-10 composite recorded from the surface area that was observed in Figure 6b, where the peaks of Sn, O, C, and N are simultaneously existent. The percentage composition of the four elements of C, N, Sn, and O is 35.63 wt %, 42.06 wt %, 5.39 wt %, and 16.92 wt %, respectively. The energy dispersive spectrometer (EDS) mapping of the four elements Sn, O, C, and N are shown in Figure 6c, Figure 6d, Figure 6e, and Figure 6f, respectively. The distributions of these four elements are clearly observed. According to Figure 6, the structural feature of the SnO2/g-C3N4-10 composite is that 2-D g-C3N4 and SnO2 particles are effectively combined. It can be concluded that the SnO2/g-C3N4 composites were synthesized successfully using the solid-state method, which is applicable to large-scale production.

**Figure 6. Cont.**
Figure 6. Energy dispersive spectrometer (EDS) spectra (a) and SEM image (b) of the SnO$_2$/g-C$_3$N$_4$-10 nanocomposite, and EDS mappings of the Sn (c), O (d), C (e), and N (f) element related to (b).

Figure 7 shows the TEM and HRTEM images of g-C$_3$N$_4$, SnO$_2$ and of the SnO$_2$/g-C$_3$N$_4$ nanocomposite. As shown in Figure 7a, it can be seen that there are plenty of gauffers in the floccules. Figure 7b shows that the pure SnO$_2$ samples consist of many nanoparticles. Meanwhile, as can be seen from Figure 7c, the SnO$_2$ nanoparticles are highly dispersed on the surface of g-C$_3$N$_4$. From Figure 7d, the lattice fringes with interplanar spacings of 0.26 and 0.34 nm can be assigned to the (101) and (110) planes of the g-C$_3$N$_4$-supported SnO$_2$ nanoparticles.

Figure 7. Transmission electron microscopy (TEM) images of (a) g-C$_3$N$_4$; (b) SnO$_2$; and (c) SnO$_2$/g-C$_3$N$_4$-10; and (d) HRTEM image of the SnO$_2$/g-C$_3$N$_4$-10 composite.
Figure 8 depicts the N\textsubscript{2} adsorption–desorption isotherms and the corresponding pore size distribution of the as-prepared g-C\textsubscript{3}N\textsubscript{4}, SnO\textsubscript{2}, and SnO\textsubscript{2}/g-C\textsubscript{3}N\textsubscript{4}-10 samples. It can be seen from Figure 8a that the isotherms of the three samples show type IV, which is the typical characteristic of mesoporous material according to the IUPAC. The well-defined hysteresis loop of the SnO\textsubscript{2}/g-C\textsubscript{3}N\textsubscript{4}-10 sample belongs to the H\textsubscript{3}-type, indicating the presence of an aggregation of laminated structure with narrow slits formed by g-C\textsubscript{3}N\textsubscript{4} and SnO\textsubscript{2} nanoparticles. The corresponding pore size distributions of these three samples are shown in Figure 8b. It can be clearly seen that the pore diameters of SnO\textsubscript{2} and SnO\textsubscript{2}/g-C\textsubscript{3}N\textsubscript{4}-10 are relatively small, and the majority concentrate upon about 2 nm according to the DFT method. The BET-calculated results show that the specific surface areas of g-C\textsubscript{3}N\textsubscript{4}, SnO\textsubscript{2}, and SnO\textsubscript{2}/g-C\textsubscript{3}N\textsubscript{4}-10 samples are 60.7 m\textsuperscript{2}·g\textsuperscript{-1}, 173.2 m\textsuperscript{2}·g\textsuperscript{-1}, and 140.0 m\textsuperscript{2}·g\textsuperscript{-1}, respectively. The high specific surface area could be in favor of enhancing gas-sensing properties.

![Figure 8](image)

**Figure 8.** (a) N\textsubscript{2} adsorption–desorption isotherms and (b) the corresponding pore size distribution curves of the g-C\textsubscript{3}N\textsubscript{4}, SnO\textsubscript{2}, and SnO\textsubscript{2}/g-C\textsubscript{3}N\textsubscript{4}-10 samples. The dV/dD value was shifted by 0.05 and 0.1 units for the curves of data sets SnO\textsubscript{2}/g-C\textsubscript{3}N\textsubscript{4}-10 and SnO\textsubscript{2}, respectively.

### 3.2. Gas-Sensing Property

The gas-sensing properties of the as-prepared samples to ethanol vapor were investigated, in detail. Figure 9a shows the response values of pure SnO\textsubscript{2} and SnO\textsubscript{2}/g-C\textsubscript{3}N\textsubscript{4}-based sensors to 500 ppm of ethanol at different operating temperatures. It can be clearly observed that the response values increased with the increase of the operating temperature. However, the response values decrease when the temperature is above 300 °C. The maximum response of SnO\textsubscript{2}/g-C\textsubscript{3}N\textsubscript{4}-10 is R\textsubscript{a}/R\textsubscript{g} = 555 at 300 °C, which is much higher than that of the pure SnO\textsubscript{2}-based sensor. It reaches the maximum response when the mass percentage of g-C\textsubscript{3}N\textsubscript{4} in the composites is 10%. From the curves, the response value of SnO\textsubscript{2}/g-C\textsubscript{3}N\textsubscript{4}-13 sample is lower than that of the pure SnO\textsubscript{2}-based sensor. The high content of g-C\textsubscript{3}N\textsubscript{4} may lead to the connection of the g-C\textsubscript{3}N\textsubscript{4} nanosheets, which could form the micro-electric bridges on the surface. The micro-electric bridges may result in the semiconductor’s resistance being reduced. Figure 9b,c display the response values of the four samples (SnO\textsubscript{2}, SnO\textsubscript{2}/g-C\textsubscript{3}N\textsubscript{4}-7, SnO\textsubscript{2}/g-C\textsubscript{3}N\textsubscript{4}-10, and SnO\textsubscript{2}/g-C\textsubscript{3}N\textsubscript{4}-13) at 300 °C to different concentrations of ethanol. As shown in the curves, the response values increased with increasing ethanol concentrations. The slope of the curves increased rapidly when the concentration range of ethanol was from 50 ppm to 500 ppm. However, it increased slowly with increasing concentrations in the range of 500–2000 ppm. It can be concluded that the adsorption to ethanol has approached saturation value when the concentration reaches 2000 ppm. To evaluate the gas-sensing performances of SnO\textsubscript{2}/g-C\textsubscript{3}N\textsubscript{4} composite, the comparison between this work and other literature is summarized in Table 1. As can be observed, the SnO\textsubscript{2}/g-C\textsubscript{3}N\textsubscript{4} composite exhibits superior performances compared with other SnO\textsubscript{2}-based sensors.
Figure 9. (a) Response values of the sensors based on SnO\textsubscript{2}, SnO\textsubscript{2}/g-C\textsubscript{3}N\textsubscript{4}-7, SnO\textsubscript{2}/g-C\textsubscript{3}N\textsubscript{4}-10, and SnO\textsubscript{2}/g-C\textsubscript{3}N\textsubscript{4}-13 to 500 ppm of ethanol as a function of operating temperature; (b,c) the responses of sensors (SnO\textsubscript{2}, SnO\textsubscript{2}/g-C\textsubscript{3}N\textsubscript{4}-7, SnO\textsubscript{2}/g-C\textsubscript{3}N\textsubscript{4}-10, and SnO\textsubscript{2}/g-C\textsubscript{3}N\textsubscript{4}-13) operated at 300 °C versus different concentrations of ethanol.

Table 1. Comparison of the performance of various SnO\textsubscript{2}-based gas sensors toward ethanol.

| Sensing Materials | Ethanol Concentration (ppm) | Temperature (°C) | Response (Ra/Rg) | Reference |
|-------------------|-----------------------------|-----------------|------------------|-----------|
| RGO-SnO\textsubscript{2} | 100 | 300 | 70 | [45] |
| Ni-doped SnO\textsubscript{2} | 100 | 260 | 30 | [46] |
| Fe\textsubscript{2}O\textsubscript{3}/SnO\textsubscript{2} | 100 | 300 | 30 | [47] |
| Au/SnO\textsubscript{2} | 150 | 340 | 30 | [48] |
| SnO\textsubscript{2}/g-C\textsubscript{3}N\textsubscript{4}-10 | 100 | 300 | 230 | this work |

Figure 10a displays the real-time response curves of the pure SnO\textsubscript{2} and SnO\textsubscript{2}/g-C\textsubscript{3}N\textsubscript{4}-10 to ethanol in the range of 50–2000 ppm at 300 °C. As shown in the curves, the response values of the both sensors increased with the increasing concentration of ethanol in the range of 50–2000 ppm. The response value of the SnO\textsubscript{2}/g-C\textsubscript{3}N\textsubscript{4}-10-based sensor is much higher than that of the pure SnO\textsubscript{2}-based sensor to the same concentration of ethanol. The response values of pure SnO\textsubscript{2} and SnO\textsubscript{2}/g-C\textsubscript{3}N\textsubscript{4}-10 to 2000 ppm of ethanol are 800 and 2400, respectively. The response–recovery time curve of SnO\textsubscript{2}/g-C\textsubscript{3}N\textsubscript{4}-10 to 2000 ppm of ethanol is shown in Figure 10b. It can be clearly observed that the response increased and decreased promptly when the SnO\textsubscript{2}/g-C\textsubscript{3}N\textsubscript{4}-10-based sensor was exposed to and separated from ethanol, respectively. The response time and the recovery time are 10 s and 47 s, respectively. The relatively rapid response and recovery time could be due to the unique structure of the 2-D g-C\textsubscript{3}N\textsubscript{4}-supported SnO\textsubscript{2} nanoparticles.
The hydroxyl group (–OH) is much easier to oxidize at the optimum operating temperature. It is more likely to lose electrons in the process of a redox reaction with the absorbed oxygen, and the gas sensing.

Repeatability and stability are both crucial influence factors of gas-sensing properties. Figure 11a reveals the repeatability of the SnO$_2$/g-C$_3$N$_4$-10 sensor to 500 ppm of ethanol at 300 °C. As shown in the curves, the response values of the four response–recovery cycles are almost the same, namely 570, 565, 554, and 566, respectively. It can be concluded that the as-prepared SnO$_2$/g-C$_3$N$_4$-10 sensor has an admirable repeatability for ethanol gas sensing. A durable response value was measured to explore the stability of the SnO$_2$/g-C$_3$N$_4$-10 sensor. Figure 11b displays the test result for every five days, and the response values to 500 ppm of ethanol at 300 °C are maintained around 550. Hence, the conclusion may be drawn that the SnO$_2$/g-C$_3$N$_4$-10-based sensor has an unexceptionable stability for ethanol gas sensing.

It is well known that selectivity is another key criteria for measuring the quality of gas sensors. Figure 12 shows the selectivity test results of the pure SnO$_2$ and SnO$_2$/g-C$_3$N$_4$-10 sensors to five different gases of 500 ppm, including methanol, ethanol, toluene, formaldehyde, and acetone. It can be seen that the SnO$_2$/g-C$_3$N$_4$-10 sensor has a selectivity to ethanol superior to that of other gases compared to the pure SnO$_2$ sensor at 300 °C. The higher response to ethanol may be because ethanol is more likely to lose electrons in the process of a redox reaction with the absorbed oxygen, and the hydroxyl group (–OH) is much easier to oxidize at the optimum operating temperature.
would adsorb on the surface of SnO$_2$ and SnO$_2$ heterojunction changes when ethanol gas molecules pass through the interface region between g-C$_3$N$_4$ and SnO$_2$. Both SnO$_2$ and g-C$_3$N$_4$ are n-type semiconductors. The band gaps are 3.71 eV and 2.7 eV, respectively. The conduction band level of g-C$_3$N$_4$ is more negative than that of SnO$_2$. When SnO$_2$ and g-C$_3$N$_4$ were combined, they formed a heterojunction structure. The electrons will inflow prevent the aggregation of SnO$_2$ nanoparticles. Consequently, this unique structure with large specific surface area is beneficial to the mass of oxygen molecules adsorbed on to the surface of SnO$_2$ and to the adsorption and diffusion of ethanol molecules, leading to an enhanced reaction between ethanol gas molecules and oxygen anions. Beyond that, the improved gas-sensing performances may also be attributed to the heterojunction of the interface region between g-C$_3$N$_4$ and SnO$_2$ and to the interactions between Sn and g-C$_3$N$_4$ verified in the XPS results. The electrical property at the heterojunction changes when ethanol gas molecules pass through the interface region between g-C$_3$N$_4$ and SnO$_2$. Both SnO$_2$ and g-C$_3$N$_4$ are n-type semiconductors. The band gaps are 3.71 eV and 2.7 eV,

As is well known, SnO$_2$ is a typical n-type metal oxide semiconductor, and there are several different types of gas-sensing mechanisms. Generally, the surface-controlled type can be used to explain the mechanism of the SnO$_2$/g-C$_3$N$_4$ composite towards ethanol. The resistance changes when the sensor is exposed to different types of gases. When the sensor was exposed in air, oxygen molecules would adsorb on the surface of SnO$_2$ and capture electrons from the conduction band of SnO$_2$. Then, oxygen molecules were ionized to O$^{2-}$, O$^-$, and O$_2^-$, and the formation of depletion layers led to an increase in resistance of the composite sensor. However, when the sensor was exposed to the ethanol gas under high temperature, the ethanol molecules would react with oxygen ions absorbed on the surface of the sensor. As a result, the ethanol molecules were oxidized into acetaldehyde and eventually oxidized into carbon dioxide and water. The trapped electrons were released back to the depletion layer of the sensing film, resulting in a decrease in the resistance of the composite-based sensor, as is shown in Figure 13.

Figure 12. Responses of SnO$_2$ and SnO$_2$/g-C$_3$N$_4$-10-based sensors to 500 ppm of different reducing gases at 300 °C.

![Figure 12](image)

Figure 13. Schematic diagram of test gas reaction with the as-prepared nanocomposite.

The SnO$_2$/g-C$_3$N$_4$ composites exhibit better gas-sensing properties than pure SnO$_2$ nanoparticles. In this nanocomposite, g-C$_3$N$_4$ served as a support and stuck to SnO$_2$ nanoparticles. This support can prevent the aggregation of SnO$_2$ nanoparticles. Consequently, this unique structure with large specific surface area is beneficial to the mass of oxygen molecules adsorbed on to the surface of SnO$_2$ and to the adsorption and diffusion of ethanol molecules, leading to an enhanced reaction between ethanol gas molecules and oxygen anions. Beyond that, the improved gas-sensing performances may also be attributed to the heterojunction of the interface region between g-C$_3$N$_4$ and SnO$_2$ and to the interactions between Sn and g-C$_3$N$_4$ verified in the XPS results. The electrical property at the heterojunction changes when ethanol gas molecules pass through the interface region between g-C$_3$N$_4$ and SnO$_2$. Both SnO$_2$ and g-C$_3$N$_4$ are n-type semiconductors. The band gaps are 3.71 eV and 2.7 eV,
respectively. The conduction band level of g-C_3N_4 is more negative than that of SnO_2. When SnO_2 and g-C_3N_4 were combined, they formed a heterojunction structure. The electrons will inflow from the conduction band of g-C_3N_4 to the conduction band of SnO_2, leading to a higher potential barrier. As a result, the electrons and holes are separated. Meanwhile, the heterojunction structure may suppress the recombination of the electron–hole pair and urge electrons to quickly transfer from the ethanol vapor to the surface of SnO_2/g-C_3N_4. Therefore, this leads to a higher response because of the increased conductivity of the heterojunction structure [49].

4. Conclusions

In summary, we demonstrated an ethanol gas sensor based on a SnO_2/g-C_3N_4 nanocomposite, which was synthesized by a facile solid-state method using a grinding treatment at room temperature. The SnO_2 nanoparticles were highly distributed on the g-C_3N_4 sheets. The gas-sensing properties of the SnO_2/g-C_3N_4 nanocomposite-based sensors exhibited enhanced gas-sensing properties compared to pure SnO_2, including sensitivity and selectivity. The ameliorative sensitivity may be due to the large specific surface area and the interaction between 2-D g-C_3N_4 and SnO_2 nanoparticles. As a result, the SnO_2/g-C_3N_4 nanocomposite is a promising candidate for high-performance ethanol gas-sensing application.

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