Synthesis and Enhanced Ethanol Gas Sensing Properties of the g-C₃N₄ Nanosheets-Decorated Tin Oxide Flower-Like Nanorods Composite

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Abstract: Flower-like SnO₂/g-C₃N₄ nanocomposites were synthesized via a facile hydrothermal method by using SnCl₄·5H₂O and urea as the precursor. The structure and morphology of the as-synthesized samples were characterized by using the X-ray powder diffraction (XRD), electron microscopy (FESEM and TEM), and Fourier transform infrared spectrometer (FT-IR) techniques. SnO₂ displays the unique 3D flower-like microstructure assembled with many uniform nanorods with the lengths and diameters of about 400–600 nm and 50–100 nm, respectively. For the SnO₂/g-C₃N₄ composites, SnO₂ flower-like nanorods were coupled by a lamellar structure 2D g-C₃N₄. Gas sensing performance test results indicated that the response of the sensor based on 7 wt. % 2D g-C₃N₄-decorated SnO₂ composite to 500 ppm ethanol vapor was 150 at 340 °C, which was 3.5 times higher than that of the pure flower-like SnO₂ nanorods-based sensor. The gas sensing mechanism of the g-C₃N₄ nanosheets-decorated SnO₂ flower-like nanorods was discussed in relation to the heterojunction structure between g-C₃N₄ and SnO₂.

Keywords: nanocomposites; microstructure; gas sensor; flower-like SnO₂ nanorod; graphitic carbon nitride

1. Introduction

As an n-type metal-oxide semiconductor, tin oxide (SnO₂) has wide applications in many fields, such as lithium-ion batteries [1], photocatalysis [2], and gas sensors [3]. SnO₂ has been investigated as a typical semiconductor gas sensor to ethanol because of its unique chemical properties and crystal structure [4]. As is known, the gas-sensing performance of SnO₂-based sensors can be improved by means of morphology and size control. Hence, diverse shape-controlled SnO₂ nanostructures have been synthesized, such as nanoflower [5], nanoarray [6], nanoplate [7], and nanowire [8]. These SnO₂-based sensors exhibited good sensing properties, including low-cost and fast response and recovery.

However, there are some limitations which prevent the direct application of these sensors, such as poor electrical characteristics, high work temperature, and a low response [9]. Coupling SnO₂ with other semiconductors to construct the heterojunction structure could be an efficient way to overcome these disadvantages. Therefore, many SnO₂-based composites such as SnO₂/r-GO [10–15], SnO₂/ZnO [16–19], SnO₂/Fe₂O₃ [20–23], and SnO₂/NiO [24–26] have been synthesized as...
high-efficiency gas sensors. Graphitic carbon nitride (g-C₃N₄) is a two-dimensional (2D) semiconductor with a 2.7 eV band gap, which possesses good chemical stability and a large surface area. It is available to form an n/n junction structure with SnO₂ [27]. For example, SnO₂/g-C₃N₄ nanocomposites with a strong heterojunction structure were designed and fabricated. The photocatalytic activity of the SnO₂/g-C₃N₄ nanocomposites exhibited enhanced catalytic activity and stable cycle property [28]. Zhang et al. prepared the α-Fe₂O₃/g-C₃N₄ heterostructural nanocomposites as an ethanol gas sensor, and the composites exhibited a high response value (S = 7.76) to 100 ppm ethanol under a working temperature of 340 °C [29]. Zeng et al. successfully fabricated the α-Fe₂O₃/g-C₃N₄ composites for the cataluminescence sensing of H₂S [30]. An efficient dielectric barrier discharge (DBD) plasma-assisted method for the fabrication of the g-C₃N₄-Mn₃O₄ composite was investigated by Hu et al., which displayed a highly selective, sensitive, and linear cataluminescence (CTL) response towards H₂S gas [31]. Sanjay Mathur et al. synthesized SnO₂ nanowires via the CVD method, and the SnO₂ nanowires exhibited an excellent photoresponse performance [32]. Kuang et al. have synthesized high-yield SnO₂ nanowires via an Au catalytic vapor-liquid-solid (VLS) growth process and the SnO₂ nanowire-based humidity sensor displayed a fast response and high sensitivity to relative humidity changes at room temperature [33]. The three-dimensional network’s SnO₂ nanowire was prepared via a flame-based thermal oxidation process (FTS) and applied for ethanol sensing [34]. Oleg Lupan et al. investigated the hybrid networks of heterogeneous shell-core Ga₂O₃/GaN:O₃@SnO₂ nano- and micro-cables with a shell in mixed phases for improving sensor properties [35]. However, to our best knowledge, there is still no research focused on the design and gas sensing application of the g-C₃N₄ nanosheets-decorated SnO₂ flower-like nanorods.

Herein, the hydrothermal method was utilized for the first time to synthesis the g-C₃N₄ nanosheets-decorated SnO₂ flower-like nanorods for the ethanol sensing application. It was found that the g-C₃N₄ nanosheets-decorated tin oxide flower-like nanorods composite possesses a much higher response value, repeatability, and stability to ethanol vapor than pure flower-like SnO₂ nanorods.

2. Results and Discussion

2.1. Sample Characterization

The pure SnO₂ and SnO₂/g-C₃N₄ composites with 5, 7, and 9 wt % g-C₃N₄ contents were synthesized by a facile hydrothermal method. Also, the as-prepared samples were marked as SnO₂/g-C₃N₄-5, SnO₂/g-C₃N₄-7, and SnO₂/g-C₃N₄-9, respectively. Figure 1 displays the XRD patterns of the synthesized SnO₂, g-C₃N₄, and g-C₃N₄ nanosheets-decorated tin oxide flower-like nanorods (SnO₂/g-C₃N₄) composites with different g-C₃N₄ contents. One can see from the XRD pattern that two diffraction peaks at 13.1° and 27.5° can be observed for pure g-C₃N₄, these two peaks were accorded to the (100) plane and (002) plane of g-C₃N₄, which could be due to the inter-layer structure of the tri-s-triazine unit with interplanar spacing and the conjugated aromatic system, respectively [36]. The XRD patterns of SnO₂/g-C₃N₄ composites show some diffraction peaks at 26.61°, 33.89°, 37.94°, and 51.78°, which could be assigned to the (110), (101), (200), and (211) planes of the tetragonal rutile structure SnO₂ (JCPDS Card No. 41-1445). However, the diffraction peaks of g-C₃N₄ are not observed in the SnO₂/g-C₃N₄ composites. This could be due to the small content of g-C₃N₄.

The microstructure and morphology of the synthesized samples were verified by using FESEM and TEM. One can see clearly from Figure 2a that the morphology of the as-prepared g-C₃N₄ possesses many wrinkles with overlaps at the edges, demonstrating the existence of the two dimensional (2D) nano-lamellar structure. It can be observed from Figure 2b that the pure SnO₂ product displays the unique 3D flower-like microstructure assembled with many uniform nanorods. The lengths and diameters of a single nanorod are about 400–600 nm and 50–100 nm, respectively. For the g-C₃N₄ nanosheets-decorated SnO₂ flower-like nanorods composite, as shown in Figure 2c, the SnO₂ flower-like nanorods were closely coupled by g-C₃N₄ nanosheets. A proposed growth mechanism of SnO₂ flower-like nanorods can be summarized by crystal growth and nucleation.
theory. The SnO$_2$ nanocrystals nucleation points are generated in different orientations. Therefore, the SnO$_2$ nanorods grow in irregular directions and finally formed into 3D flower-like structures. Figure 2f displays the typical TEM image of pure g-C$_3$N$_4$, and g-C$_3$N$_4$ possesses two dimensional nanosheets structure with many wrinkles. The TEM images of g-C$_3$N$_4$ nanosheets-decorated tin oxide flower-like nanorods composites are displayed in Figure 2d,e, and SnO$_2$ flower-like nanorods were coupled by a lamellar structure, which is 2D g-C$_3$N$_4$. Thus, we can conclude that g-C$_3$N$_4$ nanosheets-decorated SnO$_2$ flower-like nanorods composites were successfully synthesized by the hydrothermal method combining the above analysis results offered by XRD, FESEM, and TEM.

Figure 1. X-ray powder diffraction (XRD) patterns of the synthesized SnO$_2$, g-C$_3$N$_4$, and g-C$_3$N$_4$ nanosheets-decorated tin oxide flower-like nanorods composites (SnO$_2$/g-C$_3$N$_4$-5, SnO$_2$/g-C$_3$N$_4$-7, and SnO$_2$/g-C$_3$N$_4$-9).

Figure 2. Field-emission scanning electron microscopy (FESEM) images of pure g-C$_3$N$_4$ (a); SnO$_2$ flower-like nanorods (b); SnO$_2$/g-C$_3$N$_4$ nanocomposite (c); and transmission electron microscopy (TEM) images of the SnO$_2$/g-C$_3$N$_4$ composite (d,e) and pure g-C$_3$N$_4$ (f).
Figure 3 exhibits the FT-IR spectra of g-C₃N₄, SnO₂, and SnO₂/g-C₃N₄-7 samples. As can be seen from Figure 3b, the broad absorption peaks could be observed at wave-numbers of 570 cm⁻¹ and 660 cm⁻¹, which could be assigned to the Sn–O characteristic peaks. In Figure 3a,c, the peaks in the range of 1240–1637 cm⁻¹ are ascribed to the C–N and C=N stretching vibration modes, and the peak at 808 cm⁻¹ corresponds to the triazine units. These two sets of characteristic vibration peaks are characteristic of g-C₃N₄. As is shown in Figure 3c, all the characteristic peaks of SnO₂ and g-C₃N₄ can be observed clearly. These results make up for our XRD analysis, in which g-C₃N₄ and SnO₂ are coexisting in the SnO₂/g-C₃N₄ composites. Compared with pure g-C₃N₄, there is a slight red shift in the bands of g-C₃N₄ in the composite. This result indicates that there is an interaction between SnO₂ and g-C₃N₄ [27], which is beneficial to the gas sensing application.

Figure 3. Fourier transform infrared spectrometer (FT-IR) spectra of g-C₃N₄ (a); SnO₂ (b); and SnO₂/g-C₃N₄-7 (c) nanocomposite.

TG analysis was investigated by heating up from room temperature to 800 °C at a heating rate of 5 °C·min⁻¹ to reveal the weight change of g-C₃N₄. It can be seen from Figure 4 that the weight of g-C₃N₄ is set constant at temperature below 500 °C. When the temperature increases to 510 °C, the weight of g-C₃N₄ starts to decrease (the combustion of g-C₃N₄ in air). The weight stays at the same level when the temperature exceeds 655 °C. It can be concluded that g-C₃N₄ is stable at low temperature and burn at high temperature. This phenomenon demonstrates that g-C₃N₄ could stably exist in the composite under the operating temperature in the range of 200–400 °C in the gas-sensing test process.

Figure 4. Thermogravimetry (TG) analysis for heating the g-C₃N₄ from room temperature to 800 °C.
2.2. Sensing Performance Tests

In order to investigate the gas sensing performance of the synthesized samples-based sensor to ethanol, a series of tests were performed. The response values \( \frac{R_a}{R_s} \) of the g-C\textsubscript{3}N\textsubscript{4} nanosheets-decorated tin oxide flower-like nanorods composite and the pure flower-like SnO\textsubscript{2}-based gas sensors toward 500 ppm ethanol vapor were measured under different operating temperature. With the increase of operating temperature, one can see from Figure 5a that all of the samples exhibited the similar variation tendency. Also, the response values of the SnO\textsubscript{2}/g-C\textsubscript{3}N\textsubscript{4}-based sensors reached the maximum value at 340 °C, while the maximum value of pure SnO\textsubscript{2} was 70 at 360 °C. This result shows that the optimum operating temperature of SnO\textsubscript{2}/g-C\textsubscript{3}N\textsubscript{4} decreased compared with that of pure SnO\textsubscript{2}. This result may be due to the fact that the chemisorbed oxygen species can achieve the required energy and effectively react with ethanol vapor molecules on sample surface varying the resistance significantly [37]. The response value of the SnO\textsubscript{2}/g-C\textsubscript{3}N\textsubscript{4} composite-based sensor is much higher than pure SnO\textsubscript{2}. The response values increased with adding the content of g-C\textsubscript{3}N\textsubscript{4} from 5 wt. % to 7 wt. % and decreased with further increase of g-C\textsubscript{3}N\textsubscript{4} content. The response values of the pure SnO\textsubscript{2}, SnO\textsubscript{2}/g-C\textsubscript{3}N\textsubscript{4} composites with g-C\textsubscript{3}N\textsubscript{4} contents of 5, 7, and 9 wt. % to 500 ppm ethanol vapor at 340 °C are 43, 125, 150, and 135, respectively, indicating that the addition of g-C\textsubscript{3}N\textsubscript{4} has a great influence on enhancing the gas sensing performance. When the mass percentage of g-C\textsubscript{3}N\textsubscript{4} in the composites is 7 wt. %, the response reaches the maximum value. A suitable content of g-C\textsubscript{3}N\textsubscript{4} in the composite is beneficial to form the preferable heterojunction structure in the interface region between flower-like nanorods SnO\textsubscript{2} and 2D g-C\textsubscript{3}N\textsubscript{4}. However, much higher addition of g-C\textsubscript{3}N\textsubscript{4} may result in the formation of the connection of bulk. This will further decrease the specific surface area of the sample and reduce the active sites for oxygen and ethanol gas adsorption, further leading to the degradation of sensing performance. Hence, the optimum operating temperature is 340 °C and the optimum g-C\textsubscript{3}N\textsubscript{4} content is 7 wt. % for this g-C\textsubscript{3}N\textsubscript{4} nanosheets-decorated SnO\textsubscript{2} flower-like nanorods nanomaterial. Therefore, all of the further research was carried out by using SnO\textsubscript{2}/g-C\textsubscript{3}N\textsubscript{4}-7 composite sensor at 340 °C. Figure 5b displays the response values of the four samples to different ethanol vapors in the concentration range of 100–3000 ppm at 340°C. With the increase of ethanol concentration, the response values increased for all of these four sensors. The curves increased rapidly in the range of 100–500 ppm and increased slowly with the increasing concentrations from 500 ppm to 3000 ppm.

![Figure 5](image_url)

Figure 5. The response values of the SnO\textsubscript{2}, SnO\textsubscript{2}/g-C\textsubscript{3}N\textsubscript{4}-5, SnO\textsubscript{2}/g-C\textsubscript{3}N\textsubscript{4}-7, and SnO\textsubscript{2}/g-C\textsubscript{3}N\textsubscript{4}-9 to 500 ppm ethanol (a) under different operating temperatures; (b) for different concentrations of ethanol at 340 °C.

Figure 6a shows the real time response curves of the pure SnO\textsubscript{2} and SnO\textsubscript{2}/g-C\textsubscript{3}N\textsubscript{4}-7 to ethanol in the range of 100–3000 ppm at 340 °C. All of the response-recovery cycles were measured about 300 s with a response interval and a recovery interval of 150 s, respectively. We can observe from
Figure 6a that the two samples show a similar trend: the response values increase with increasing ethanol concentration. To the same concentration of ethanol, SnO$_2$/g-C$_3$N$_4$-7 exhibited much higher response value than that of pure SnO$_2$. The response value of the SnO$_2$/g-C$_3$N$_4$-7 composite-based sensor towards 500 ppm ethanol vapor was about 150, about four times higher than pure SnO$_2$. As is known, response-recovery time is another very important influential factor on the application of gas sensor. Figure 6b shows the response-recovery time curve of the SnO$_2$/g-C$_3$N$_4$-7 composite toward 500 ppm ethanol vapor. As seen from the curve, when the sensor was exposed and separated to ethanol, the response increased rapidly (31 s) and also decreased rapidly (24 s), respectively.

![Figure 6a](image1.png) ![Figure 6b](image2.png)

**Figure 6.** (a) The real time response curves of the SnO$_2$ and SnO$_2$/g-C$_3$N$_4$-7 composite sensors toward ethanol vapor; (b) response-recovery time characteristics of the SnO$_2$/g-C$_3$N$_4$-7 based sensor to 500 ppm ethanol vapor at 340 °C.

The repeatability and stability are both crucial influence factors of gas sensing performances. As is shown in Figure 7a, the response values of these four response-recovery cycles of SnO$_2$/g-C$_3$N$_4$-7 sensor stay almost the same (165, 160, 167, and 155) toward 500 ppm ethanol at 340 °C. This result indicated that the synthesized SnO$_2$/g-C$_3$N$_4$-7 composite possesses an admirable repeatability for ethanol vapor detection. Figure 7b displays the stability test result of SnO$_2$/g-C$_3$N$_4$-7 composite sensor toward 500 ppm ethanol vapor at 340 °C, and the response values were kept at a stability of around 155 after 30 days test, indicating that the synthesized g-C$_3$N$_4$ nanosheets-decorated SnO$_2$ flower-like nanorods composite possesses an excellent stability.

![Figure 7a](image3.png) ![Figure 7b](image4.png)

**Figure 7.** (a) Repeatability and (b) stability measurements of the SnO$_2$/g-C$_3$N$_4$-7-based sensor to 500 ppm ethanol at 340 °C.
As is well known, the selectivity of the sensor for the different gases is one of the most important factors for its practical application. Figure 8 displays the selectivity test results of SnO$_2$ flower-like nanorods and SnO$_2$/g-C$_3$N$_4$-7 composite to methanol, ethanol, toluene, formaldehyde, and acetone with the concentration of 500 ppm. The test results indicated that the sample possesses the superior selectivity to ethanol vapor at the operating temperature of 340 °C. The high selectivity to ethanol maybe come from the fact that when reacted with the absorbed oxygen, ethanol is more likely to lose electrons, and hydroxyl group (–OH) is easy to oxidize under the optimum operating condition.

![Figure 8](image-url)

**Figure 8.** Comparision of the response values of the flower-like SnO$_2$ nanorods and the SnO$_2$/g-C$_3$N$_4$-7 composite toward 500 ppm different gases at 340 °C.

Table 1 lists the sensing performances of different materials to ethanol vapor. One can observe from Table 1 that the RGO/hollow SnO$_2$ nanoparticles [11], hollow ZnO/SnO$_2$ spheres [16], tubular α-Fe$_2$O$_3$/g-C$_3$N$_4$ [29], and Au/3D SnO$_2$ microstructure [38] samples possess the response values to ethanol of 70.4, 78.2, 7.76, and 30, respectively. In our research, the 7 wt. % 2D g-C$_3$N$_4$ decorated SnO$_2$ flower-like nanorods composite possesses the response value of 85 to 100 ppm ethanol vapor at 340 °C, indicating a great potential application of the synthesized sample to ethanol detection.

| Materials                               | Ethanol Vapor Concentration (ppm) | Temperature (°C) | Response ($R_a/R_g$) | Ref.       |
|-----------------------------------------|----------------------------------|-----------------|----------------------|------------|
| RGO/hollow SnO$_2$                      | 100                              | 300             | 70.4                 | [11]       |
| Hollow ZnO/SnO$_2$ spheres              | 100                              | 225             | 78.2                 | [16]       |
| α-Fe$_2$O$_3$/g-C$_3$N$_4$               | 100                              | 340             | 7.76                 | [29]       |
| Au/3D SnO$_2$ microstructure            | 150                              | 340             | 30                   | [38]       |
| SnO$_2$/g-C$_3$N$_4$                    | 100                              | 340             | 85                   | this work  |

2.3. Mechanism Discussion

SnO$_2$ flower-like nanorods have been synthesized via a hydrothermal reaction method, and the schematic diagram of the synthesis of the g-C$_3$N$_4$ nanosheets-decorated SnO$_2$ flower-like nanorods is displayed in Figure 9. Many researchers hold the point that the diameter of the SnO$_2$ nanorods is changed by varying the Sn$^+/\text{OH}^-$ ratio in solution [39]. However, Vuong et al. declared that the diameter of SnO$_2$ nanorods decreased with the increase of the stannic chloride amount. A proposed
growth mechanism of SnO$_2$ flower-like nanorods can be summarized by crystal growth and nucleation theory. The synthesis process includes two sections of nucleation and crystal growth. In the hydrothermal condition, the Sn(OH)$_6^{2-}$ nucleus is formed via the following chemical reactions in the process of nucleation stage [40]:

\[
\begin{align*}
Sn^{4+} + 4OH^- & \leftrightarrow Sn(OH)_4 \\
Sn(OH)_4 + 2OH^- & \leftrightarrow Sn(OH)_6^{2-} \\
Sn(OH)_6^{2-} & \rightarrow SnO_2 + H_2O + 2OH^- 
\end{align*}
\]

Figure 9. The schematic diagram of the synthesis of the g-C$_3$N$_4$ nanosheets decorated SnO$_2$ flower-like nanorods.

In the process, nucleation plays an important role not merely in the morphology formation but also in the quantity of the final product. At the initial stage of the chemical reaction, the Sn$^{4+}$ ions start to react with the redundant OH$^-$ ions and further form the [Sn(OH)$_6$]$^{2-}$ coordination ions. Meanwhile, a small quantity of SnO$_2$ nanocrystals can be generated due to the decomposition of the [Sn(OH)$_6$]$^{2-}$ coordination ions. These initial SnO$_2$ nanocrystals play an important role as seeds in the next hydrothermal stage. The [Sn(OH)$_6$]$^{2-}$ coordination ions could be accelerated to decompose and form plenty of SnO$_2$ nanocrystals in the later hydrothermal reaction condition, which can be aggregated into SnO$_2$ nanoparticles. At the same time, these SnO$_2$ nanocrystals nucleation points around [Sn(OH)$_6$]$^{2-}$ can be oriented to grow into the rod-like structures. The SnO$_2$ nanocrystals nucleation points are generated in different orientations. As a result, the SnO$_2$ nanorods grow in irregular directions and finally form into 3D flower-like structures. This phenomenon can be explained by the fact that the surface-free energy of the rutile structure of crystalline SnO$_2$ faced an increase in the order of (110) < (100) < (101) < (001), which lead to the crystal growth on the faces of (001) or (101). However, the other faces have no exceptions [41,42].

2D g-C$_3$N$_4$ nanosheets-decorated SnO$_2$ flower-like nanorods composites were synthesized via a facile hydrothermal method as a high-property gas sensor for detecting ethanol. In order to understand the gas-sensing process, the schematic diagram of the test gas that reacted with SnO$_2$/g-C$_3$N$_4$ composite was shown in Figure 10a. As is known, the similar principle of gas sensor is the surface-adsorbed oxygen theory. When the sensor was exposed in the air condition, the oxygen molecules were adsorbed on the SnO$_2$ surface and capture electrons from the conduction band of SnO$_2$. Furthermore, the adsorbed oxygen molecules were ionized into O$_2^-$, O$^-$, and O$_2^-$ (Equation (4)), and formed a depletion layer with a certain width ($W_s$) of the hole accumulation ($h^+$) on the SnO$_2$ surface [43,44]. When the sensor was exposed in ethanol gas, the reduced gas ethanol
molecules were oxidized into acetaldehyde and finally turned into carbon dioxide and water by these oxygen anions (Equations (5) and (6)) [10]. As a result, the trapped electrons were released back to the SnO$_2$ depletion layer, where the width ($W_s$) of depletion area of the hole accumulation ($h^+$) became thinner and led to the decrease of the resistance by the transfer of electrons between ethanol molecules and oxygen anions. As is well known, the electrons transfer may affect the great change of the composite resistance. In addition, the improved ethanol-sensing performances of the g-C$_3$N$_4$ nanosheets-decorated flower-like SnO$_2$ nanorods composite could be attributed to the structure of SnO$_2$ nanorods coupled by 2D g-C$_3$N$_4$ nanosheets and the heterojunction of interface region between flower-like SnO$_2$ nanorods and 2D g-C$_3$N$_4$.

\[
O_2 + e^- \rightarrow O_2^- \tag{4}
\]

\[
2CH_3CH_2OH + O_2^- \rightarrow 2CH_3CHO + 2H_2O + e^- \tag{5}
\]

\[
2CH_3CHO + 5O_2^- \rightarrow 4CO_2 + 4H_2O + 5e^- \tag{6}
\]

In general, the large specific area of 2D g-C$_3$N$_4$ nanosheets can provide more active sites to adsorb oxygen molecules and ethanol molecules. The interconnecting network structure created by

![Figure 10](image)

**Figure 10.** (a) The schematic diagram of air and ethanol react with the synthesized composite; and (b) the band diagram of SnO$_2$/g-C$_3$N$_4$ before and after the combination.

In general, the large specific area of 2D g-C$_3$N$_4$ nanosheets can provide more active sites to adsorb oxygen molecules and ethanol molecules. The interconnecting network structure created by
SnO$_2$ nanorods and 2D g-C$_3$N$_4$ nanosheets could supply more channels for the gas adsorption and diffusion and further enhance the interaction between SnO$_2$ and ethanol molecules. The energy band model (Figure 10b) was used to explain the energy change of SnO$_2$/g-C$_3$N$_4$ for ethanol detection. Figure 10b shows that the g-C$_3$N$_4$ and SnO$_2$ have the structure of valence band and conduction band (E$_v$ and E$_c$) and the Fermi level (E$_f$) is between these two bands. When flower-like SnO$_2$ nanorods and 2D g-C$_3$N$_4$ nanosheets were combined together, a heterojunction structure was formed. When ethanol molecules pass through the interface between g-C$_3$N$_4$ and SnO$_2$, the electrical property at the heterojunction was changed. SnO$_2$ and g-C$_3$N$_4$ are all n-type semiconductors with band gaps of 3.6 eV and 2.7 eV, respectively. Since the work function of g-C$_3$N$_4$ is smaller than that of SnO$_2$, the electrons will inflow from the conduction band of g-C$_3$N$_4$ to the conduction band of SnO$_2$, leading to a higher potential barrier. The Fermi level is aligned when the electronic transmission achieves a new dynamic balance. The electrons may go over the low energy barriers and the schottky barrier is 0.4 eV. As a result, the electrons and holes are separated [27,43]. Meanwhile, the heterojunction structure may suppress the recombination of electron-hole and urge electrons to transfer quickly from ethanol vapour to the surface of SnO$_2$/g-C$_3$N$_4$. Therefore, this leads to a higher response because of the increased conductivity of the heterojunction structure [29].

3. Materials and Methods

3.1. Chemicals

Analytical-grade purity SnCl$_4$·5H$_2$O (99.0%), NaOH, and absolute ethyl alcohol were purchased from Shanghai Macklin Biochemical Co., Ltd, Shanghai, China and were used without further purification.

3.2. Sample Preparation

Graphitic carbon nitride (g-C$_3$N$_4$) was synthesized by our previous reported method [45]. Typically, 7 wt. % g-C$_3$N$_4$ nanosheets-decorated SnO$_2$ flower-like nanorods (SnO$_2$/g-C$_3$N$_4$-7) were synthesized by the hydrothermal method: 0.17 g g-C$_3$N$_4$ powder was dispersed into 200 mL ethanol under ultrasonic treatment for 2 h. 5.259 g SnCl$_4$·5H$_2$O was added into 200 mL of NaOH solution (0.81 M). Subsequently, the g-C$_3$N$_4$ solution was added into this mixture solution with magnetic stirring until it formed a white suspension. Finally, the mixture was transferred into a 500 mL stainless-steel Teflon-lined autoclave, then put into an oven and further heated at 200 °C for 48 h. The final product was washed with deionized water and ethanol several times and dried at 60 °C. According to this method, the SnO$_2$/g-C$_3$N$_4$ composites with 5 and 9 wt. % g-C$_3$N$_4$ content were also synthesized and marked as SnO$_2$/g-C$_3$N$_4$-5 and SnO$_2$/g-C$_3$N$_4$-9, respectively. The pure flower-like SnO$_2$ nanorods were also synthesized by the same method.

3.3. Characterizations

X-ray diffraction (XRD) analysis was carried out on Bruker-AXS D8 (Bruker, Madison, WI, USA) with CuKα radiation at 40 kV and 25 mA. Fourier Transform Infrared Spectrometer (FT-IR) was recorded on a Bruker Tensor 27 (Bruker, Madison, WI, USA). Thermogravimetry (TG) analysis was completed on a NETZSCH STA449C Simultaneous Thermal Analyzer (NETZSCH, Selb, Germany) at a heating rate of 10 °C·min$^{-1}$ under air atmosphere. Field-emission scanning electron microscopy (FESEM) (Quanta™ 250 FEG, FEI, Eindhoven, The Netherlands) was used to observe the structure and morphology of the sample. Transmission electron microscopy (TEM) analysis was done on a JEOL JEM-2100 microscope (JEOL, Tokyo, Japan) operating at 200 kV.

3.4. Gas Sensor Fabrication and Analysis

Gas-sensing performance test of the synthesized sample was carried out on an intelligent gas-sensing analysis system of CGS-4TPS (Beijing Elite Tech. Co., Ltd., Beijing, China). Figure 11 shows
with the relative humidity of 40%. The operating temperature was set in the range of 200 °C. The gas sensing test process, the test gas was first injected into the closed 0.018 m³ volume chamber by a microinjector with the relative humidity of 40%. The operating temperature was set in the range of 200 °C to 400 °C. The gas response (S) was defined as the ratio of $R_a/R_g$, where $R_a$ and $R_g$ were the resistances of sensor in air and in the test gas, respectively. The response and recovery times were defined as the time required for a change in response to reach 90% of the equilibrium value.

![Figure 11. (a) The schematic diagram of the CGS-4TPS gas-sensing test system and (b) the gas sensor structure.](image)

**4. Conclusions**

In summary, the g-C₃N₄ nanosheets-decorated tin oxide flower-like nanorods (SnO₂/g-C₃N₄) composite was successfully synthesized by using a facile hydrothermal method. The as-prepared sample possesses flower-like nanorods and a lamellar structure. Compared with pure SnO₂, the g-C₃N₄ nanosheets-decorated SnO₂ flower-like nanorods exhibited an obvious improvement of gas sensing performance to ethanol, and the response value was 150 to 500 ppm ethanol at 340 °C. The improved sensing properties are mainly attributed to the high surface area of the sample and the heterojunction between SnO₂ and g-C₃N₄. Considering the effective synthesis approach and the high sensing performance, the as-prepared SnO₂/g-C₃N₄ composite could be an ideal candidate for ethanol detection application.

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