Low Working-Temperature Acetone Vapor Sensor Based on Zinc Nitride and Oxide Hybrid Composites

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Transition-metal nitride and oxide composites are a significant class of emerging materials that have attracted great interest for their potential in combining the advantages of nitrides and oxides. Here, a novel class of gas sensing materials based on hybrid Zn$_3$N$_2$ and ZnO composites is presented. The Zn$_3$N$_2$/ZnO (ZnNO) composites-based sensor exhibits selectivity and high sensitivity toward acetone vapor, and the sensitivity is dependent on the nitrogen content of the composites. The ZnNO-11.7 described herein possesses a low working temperature of 200 °C. The detection limit (0.07 ppm) is below the diabetes diagnosis threshold (1.8 ppm). In addition, the sensor shows high reproducibility and long-term stability.

1. Introduction

Gas sensors based on metal oxide semiconductors (MOS) have stimulated a great deal of interest due to their vital role in environmental monitoring and disease diagnosing. These gas sensors mainly involve surface reactions. However, traditional bare MOSs have some disadvantages, such as low sensitivity, poor selectivity, and high operating temperature. In recent years, great efforts have been introduced to improve the properties of gas sensors, such as doping noble catalysts. However, the scarcity and high cost of noble catalysts greatly hamper their practical application on a large scale. Thus, it is imperative and desirable to develop novel strategies to enhance sensitivity, improve selectivity, and lower the operating temperature.

Acetone in human breath exhaust is a vital marker for noninvasive detection of diabetes. Thus, great efforts have been devoted toward developing high-performance chemoresistive acetone sensors. Pratsinis and co-workers reported an acetone detector based on Si-doped WO$_3$ nanoparticles, which can clearly distinguish healthy humans (≤0.09 ppm acetone) from diabetes patients (≥1.8 ppm acetone). However, the high working temperature of 400 °C restricts its application in many conditions. Kim and co-workers reported that a sensor based on Pt-functionalized WO$_3$ hemitubes showed a gas response of 1.31 for acetone of 120 ppb at a working temperature of 250–350 °C, which offers potential for diabetes diagnosis. However, the relatively high working temperature of the above reported acetone sensor may cause extra damages and may decrease the lifetime of the sensor. Thus, developing novel acetone sensing materials with low working-temperature, as well as appropriate limit of detection, is still a major challenge.

Zinc oxide (ZnO), a multifunctional material, has been widely applied in lithium-ion batteries, as a catalyst, and in various sensing materials. When applied as a gas sensing material, ZnO exhibits sensitivity to many gases, and exhibits satisfactory stability. However, a disadvantage of ZnO-based materials is their high operating temperature. Zinc nitride (Zn$_3$N$_2$) is an n-type group-II nitride semiconductor, having anti-bixbyite structure. In addition, previous studies reported that the electron carrier concentration of Zn$_3$N$_2$ is up to ~1020 cm$^{-3}$ and the electron mobilities could reach approximately 100 cm$^2$ V$^{-1}$ s$^{-1}$. Thus, by introducing Zn$_3$N$_2$ into ZnO, the electron mobility is promoted, resulting in promising enhanced gas-sensing properties of the composite.
materials. These excellent gas sensing properties make new composites consisting of ZnO and Zn$_3$N$_2$ highly desirable.

Herein, we demonstrate a new and generally applicable strategy for the efficient synthesis of ZnNO composites. The ZnNO-based gas sensor (Figure 1a) showed surprisingly excellent performance for detecting acetone vapor with a low detection limit of 0.07 ppm, as well as a low working temperature of 200 °C. Furthermore, a nitrogen content-dependent gas sensing performance was observed, and a promising sensing mechanism is proposed.

2. Results and Discussion

Scheme 1 illustrates the growth mechanism of ZnNO. In the first step, the Zn$_3$N$_2$ hollow microspheres were formed by the heat treatment of zinc powder under NH$_3$ atmosphere. Typically, under standard atmospheric pressure, the melting point of Zn is 420 °C and the boiling point of Zn is 907 °C. At 600 °C, the vapor pressure of Zn is 0.014 atm, so Zn has already reacted with NH$_3$ and has been changed to Zn$_3$N$_2$ at the surface of the Zn powder. That is to say, the surface of Zn powder was wrapped with solid Zn$_3$N$_2$ by effect of reaction with ammonia gas, and the interior of it was filled with liquid Zn. Furthermore, it is in instability, with plenty of Zn vaporizing from the interior of the Zn powder because the Zn in the core sublimes at such high temperature. When the outer layer cannot withstand the pressure, the weaker part of the surface can be broken. Thus, the zinc nitride with a hollowed-out sphere/hemisphere structure is obtained. Afterward, thermal calcination is applied, during which the Zn$_3$N$_2$ hollow microspheres can be converted into ZnNO composites.

To confirm the nitrogen content of different ZnNO, thermal gravimetric analysis (TGA) measurement was performed, which is shown in Figure S1 of the Supporting Information. According to the data, the contents of nitrogen in ZnNO were calculated to be about 0.3%, 5.3%, 11.7%, 19.8%, 35.6%, 54.5%, and 99.8%, respectively. Thus, these ZnNO samples were correspondingly designated ZnNO-0.3, ZnNO-5.3, ZnNO-11.7, ZnNO-19.8, ZnNO-35.6, ZnNO-54.5, and ZnNO-99.8.

The phase composition and purity of the as-synthesized ZnNO samples were characterized by powder X-ray diffraction (XRD). Figure 1b shows the XRD patterns of ZnNO-99.8 and ZnNO-11.7 samples. It can be seen that each peak fairly corresponds with the reported data for cubic Zn$_2$N$_3$ with lattice constant $a = 9.813$ Å or hexagonal wurtzite ZnO with lattice constant $a = 3.260$ Å and $c = 5.209$ Å, respectively.

For the zinc nitride, all hkls correspond to $h + k + l = 2n$ and we can find $l = 2n'$ in all (hhl) types, which means that the zinc nitride belongs to body centered cubic crystal system and has the x axis glide symmetry, conforming with Partin’s model.[12] According to this, the zinc nitride has the antibixbyte structure, in which the metal atoms occupy the tetrahedral sites of an approximately cubic closely packed array of N atoms belonging to Ia 3 space group. We also found that the content of zinc oxide improved with an increase in the oxidation temperature and the diffraction peaks of zinc oxide can be readily indexed to hexagonal P6$_3$mc ZnO phase. When the oxidation temperature was raised to 600 °C, the zinc nitride can be converted into zinc oxide completely. So, we can synthesize various ratios of zinc nitride/oxide composites by setting the oxidation temperature from 300 to 600 °C. The XRD patterns of ZnNO with different nitrogen contents are shown in Figure S2 of the Supporting Information.

It is acknowledged that gas sensing performance is greatly dependent on morphology. Thus, the zinc nitride samples were characterized by scanning electron microscopy (SEM) (Figure 2) and transmission electron microscopy (TEM) (Figure S3, Supporting Information), before and after oxidation, to confirm their morphologies. It can be observed from Figure 2a that the zinc nitride grew into a hollowed-out sphere/hemisphere structure with diameters in the range of
2–6 µm. The hollowed-out sizes and shapes on the surface are different and random. In addition, it can be calculated that the thickness of the hollowed-out sphere was about 60 nm. After oxidation, we can confirm from SEM observation (Figure 2b) that the morphology of the ZnNO showed hardly any changes when compared with Zn$_3$N$_2$. They also approximately maintained hollowed-out sphere/hemisphere structure, but there was some needle-like ZnO appearing on the surface. In addition, it can be observed from Figure S3 of the Supporting Information that the ZnNO composites were formed at the interface of ZnO and Zn$_3$N$_2$, forming abundant heterojunction at the interface of ZnO and Zn$_3$N$_2$.

It should be noted that the gas response of a chemiresistor type gas sensor depends strongly on the working temperature. A lower working temperature will reduce power consumption of the device as well as danger when detecting inflammable and explosive gas. Thus, the optimum operating temperature of the ZnNO-11.7 sensor was determined firstly. Figure 2 shows the responses of ZnNO-11.7 sensor to 20 ppm acetone at various operating temperatures (140–240 °C). The optimum operating temperature of the ZnNO-11.7 sensor is suggested to be 200 °C. The relatively low response at low temperature is mainly attributed to the small amount of adsorbed oxygen and the targeted gas molecules not having enough thermal energy to react with the oxygen species adsorbed on the surface of the sensing materials. The reason for the increase of response with the operating temperature increasing is that the increasing amount of adsorbed oxygen leads to more excited electrons, and the targeted gas molecules have enough energy to overcome the activation energy barrier to react with the surface oxygen species. With a further increase of operating temperature, the high temperature will lead to low gas adsorption ability, resulting in the decrease of response.\[^{13}\] It has been acknowledged that one of the greatest disadvantages of ZnO-based materials is the high working temperature, which is usually above 300 °C.\[^{14}\] Thus, the ZnNO-11.7 shows great improvement in lowering the working temperature. This is mainly attributed to that ZnNO-11.7 has a lower resistivity, which can stimulate adequate electrons at a relative low working temperature. A comparison between other reported ZnO-based materials and our materials is summarized in Table S1 of the Supporting Information.

Excellent response and recovery properties will enable a device to detect gases in real-time. To check the real-time detection performance of the device, the dynamic response of the ZnNO-11.7 sensor toward various concentrations of acetone at 200 °C was measured and the result is shown in Figure 3a. It can be observed that with the increase of acetone concentration, the response of the sensor also exhibits an increase trend. The response of the sensor exhibits an almost linear increase when exposed to acetone of concentration from 1 to 500 ppm (Figure 3b). The detection limit of the ZnNO-11.7 sensor for acetone is measured to be approximately 0.07 ppm based on signal-to-noise ratio of 3 (calculation details in Supporting Information), which is far below the diabetes diagnosis threshold (1.8 ppm). In addition, the sensor shows excellent reversibility properties with a response/recovery time of less than 20/30 s, regardless of the acetone concentration (Table S2, Supporting Information).

Electrical resistivity of the ZnNO can be tuned by changing the nitrogen content of the composites, which could significantly affect the sensitivity of the sensor. In order to probe the trend of the sensitivity versus the nitrogen content of ZnNO, and to achieve the optimum range of nitrogen content for sensing, we measured the acetone vapor sensing performance of ZnNO of different nitrogen contents. An obvious higher sensitivity was observed with increasing the nitrogen content, until about 11%. Then, the sensitivity began to decrease dramatically, indicating that the sensitivity of ZnNO was tightly dependent on the nitrogen content. Figure 3c plots the trend line of the response dependence on the nitrogen content. It can be obviously observed that the sensitivity significantly increased when the nitrogen content fell in the range of 5% to 15%, and achieved the maximum response at around 11.7%. It is well understood that Zn$_3$N$_2$...
has low resistivity and thus could work at low working temperature. However, pure Zn$_3$N$_2$ shows relatively low response to acetone. Thus, we introduced ZnO into Zn$_3$N$_2$ to increase the amount of adsorption (target gas and oxygen), resulting in an increase in response. However, when the content of ZnO is increased further, the composites will need higher working temperature to stimulate more electrons to the conduction band. Thus, at the same working temperature, the response of the ZnNO with high content of ZnO decreased.

The optimum working temperatures of ZnNO-5.3 and ZnO (Figure S4, Supporting Information) were 240 and 320 °C, respectively, which confirm our speculation for the nitrogen-dependent gas sensing properties of ZnNO composites.

Hundreds of species of volatile organic compounds (VOCs) in human breath are exhaled from the blood through exchange in the lungs.$^{[15]}$ Gas chromatography/mass spectrometry studies have shown that several volatile organic compounds, such as toluene and xylene, typically have levels of 1–20 ppb in healthy human breath.$^{[16]}$ Thus, an excellent acetone sensor should have the ability to particularly recognize acetone in the complex atmosphere of human breath. To quantify the selectivity of the ZnNO-11.7 sensor against other interference gases, the ratios between the response to 100 ppm acetone and other test gases were calculated and plotted, as shown in Figure 4a. The higher the value of $S_{acetone}/S_{test\ gas}$, the better the selectivity of the sensor. From the inset of Figure 4a, we can observe that the values of $S_{acetone}/S_{test\ gas}$ are all over 3, indicating that the ZnNO-11.7 sensor exhibited excellent selectivity. To further study the thermal stability cycle of the sensor, the sensitivity of

Figure 3. a) Dynamic sensing performance and b) calibration curves of ZnNO-11.7 sensor toward various concentrations of acetone at 200 °C. c) Trend line for the nitrogen content-dependent responses.

Figure 4. a) Dynamic sensing performance of ZnNO-11.7 sensor toward 100 ppm of various gases. Inset: The ratio between the response to acetone and to other test gases. b) Stability measurement of the ZnNO-11.7 sensor to 20 ppm acetone at 200 °C within a week. c) Sensor response of ZnNO-11.7 sensor at 200 °C upon exposure to 0.9 ppm acetone concentration at various relative humidity (RH).
the sensor was measured for 7 d once a day. Figure 4b shows that the ZnNO-11.7 sensor exhibited good thermal stability. Besides, in realistic condition, the influence of humidity on the gas sensing properties could not be ignored. Thus we conducted the measurement of response of the sensor based on ZnNO-11.7 to 1 ppm acetone under different humidity condition, and the results were shown in Figure 4c. Due to the water molecule will occupy the reacting sites, thus with the humidity increasing, the response will be decreased. However, the response of the sensor to 900 ppb still reached 1.89 regardless of the high humidity of 90 RH%, which was far higher than that in human breath.

The working mechanism of the chemiresistive sensor at high working temperature lies in the conversion of electrical resistance because of the surface reactions of the gas sensing materials.\[17\] ZnO is an n-type semiconductor, and when exposed to air, the oxygen will adsorb on the surface of ZnO to form ionic oxygen species by capturing electrons from the conduction band of ZnO. Reducing (oxidizing) gases can change the surface carrier concentration by capturing or releasing electrons from or to the conduction band of ZnO, acting as electron-donating groups. It is obvious that the amount of adsorbed oxygen species plays an indispensable role in the performance of the sensor. The ZnO and Zn$_3$N$_2$ based sensors exhibit hardly any sensitivity to acetone at 200°C, which may be due to the small coverage of adsorbed oxygen as well as a small change in resistivity below the limit of detection. Nevertheless, the sensitivity of ZnO will be significantly enhanced by compositing with Zn$_3$N$_2$.

Typically, the electrons will transfer from Zn$_3$N$_2$ to ZnO when forming heterojunction at the interface because of the lower work function of ZnO (as shown in Figure 5a).\[18\] After transferring to the surface of ZnO, the electrons from Zn$_3$N$_2$ will be captured by oxygen molecules. Since the ZnO shows hardly any response to acetone at 200°C, we assume that the trapped electrons by adsorbed oxygen species on the surface of ZnO in the composites are mainly the transferred electrons form Zn$_3$N$_2$. Thus, the amount of adsorbed oxygen on the surface of ZnO is mainly determined by the density of transferred electrons from Zn$_3$N$_2$. However, the electrons will be trapped at the interface region (the space-charge region) when transferring from Zn$_3$N$_2$ to ZnO. The density of adsorbed oxygen can be described by the following equation (the deduction process can be seen in the Supporting Information)

\[
r_2N_{d1} \exp \left( - \frac{e(Q_s + Q_i)^2}{2eTN_{d1}} \right) = 3Q_s
\]

where $r_2$ is the radius of ZnO hemispheres, and $N_{d1}$ is the donor density. $Q_s$ and $Q_i$ are the density of adsorbed oxygen and the interface state, respectively. $e$ is the dielectric constant of Zn$_3$N$_2$, $k$ is the Boltzmann constant, and $T$ is the temperature (K). From Equation (1), we can come to the conclusion that the adsorbed oxygen is largely dependent on the donor density of Zn$_3$N$_2$ ($N_{d1}$), the interfacial contact area, as well as the interface state density ($Q_i$). Thus, when the amount of ZnO in the composite is very little, the amount of chemical bonds at the interface is also too sparse to allow enough electrons to transfer to the surface of ZnO, resulting in a small amount of adsorbed oxygen on the surface of ZnO, which was illustrated in Figure 5b. When the electrical contact between ZnO and Zn$_3$N$_2$ is perfect, the potential barrier induced by the interface state is low enough to make the amount of electrons transferring across the large interface, resulting in an increased amount of adsorbed oxygen species, and then enhanced gas sensing properties (Figure 5c). However, when the amount of ZnO in the composites is increased further, the interface density will decrease, which will decrease the adsorbed oxygen on the surface of ZnO, resulting in a decrease of response of the composites.\[19\] The proposed mechanism could be consistent with our experimental results and the usually observed sintering-neck model.\[20\]

![Image](image_url)

**Figure 5.** a) Band alignment between Zn$_3$N$_2$ and ZnO. Schematic of the ZnNO composites with small amount b) and large amount c) of ZnO and the gas sensing process.
3. Conclusion

In conclusion, we successfully synthesized hybrid Zn₃N₂ and ZnO composites through a simple strategy and innovatively applied them as gas sensing materials. The ZnNO-based sensor exhibited sensitivity and high selectivity to acetone vapor as well as a low working temperature of 200 °C. The sensitivity was dependent on the nitrogen content of the ZnNO, and the sensor exhibited the best sensitivity when the nitrogen content was 11.7%. Overall, the superior acetone vapor sensing performance of the ZnNO-based sensor supplies exciting opportunities for disease diagnosing. Furthermore, we expect our findings to bring up new promising gas sensing materials, and to inspire rational synthesis of other transition metal nitride and oxide hybrids for high-performance gas sensors.

4. Experimental Section

Sample Preparation: All chemicals were used as received without further purification. 0.5 g zinc powder was loaded in a rectangular alumina boat and shifted to the center of an alumina tube mounted in a horizontal tube furnace. The furnace was set to reach 11.7% nitrogen concentration in the gas phase. Then, the furnace was cooled to room temperature naturally, and a black powder was obtained. The pure zinc nitride was oxidized in an ambient environment at temperatures of 300–600 °C for 0 to 24 h with a ramp rate of 1 °C min⁻¹. ZnO with different nitrogen contents were obtained.

Characterization: XRD analysis was conducted on a Rigaku MiniFlex 600 powder X-ray diffractometer with Cu Kα radiation (λ = 1.5418 Å). SEM images were performed on a JSM-7800F (Japan) instrument. TGA was examined on a Mettler Toledo 825e analyzer.

Gas Measurement: Gas sensing performances were measured by a homemade sensor testing system (a cylindrical glass chamber with a volume of 100 mL). A gas mixing line equipped with mass flow controllers was designed to prepare target gases at specific concentrations in the testing chamber as shown in Figure S5 of the Supporting Information. The resistance changes of sensor in air or tested gas were monitored by a high-resistance meter (Victor, 86E, China). Typically, 50 mg mL⁻¹ ZnNO-composites-ethanol solution was deposited on the surface of the device and calcined at 150 °C for 3 h. In this study, S is defined as the relative resistance change (S = Rgas/Rair), where Rair is the initial resistance of the sensor and Rgas is the measured resistance after exposure to test gas. Rres and Rrecov are defined as the time taken by the sensor to achieve 90% of the total resistance change in the case of response and recovery, respectively.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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