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Silver sulfide-based sensor for the selective determination of ammonia at room temperature

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ABSTRACT

A novel ammonia sensor was fabricated based on silver sulfide film and its responses to seventeen gases were investigated. The sensor showed high response to NH_3 at room temperature. The most sensitive sensor to NH_3 was the sensor based on Ag_2S prepared with H_2S at 323 K. The response value reached 297 to 7.08% of NH_3 at 2 V operating voltage. The linearity of the response in the NH_3 gas concentration range from 0.084 to 6.08% at 5 V operating voltage suggests the sensor can be reliably used to monitor the concentration of NH_3 gas in this range. The sensor for determination of unknown concentration of ammonia real sample had good consistency with the traditional Nessler's reagent spectrophotometry.

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1. Introduction

Ammonia (NH_3) not only is a foul-smelling toxic gas, but also is an important chemical raw material, intermediate product and completed product in the chemical industry. There is a need for ammonia sensors in many situations including leak-detection in air-conditioning system, environmental sensing of trace amounts ambient NH_3 in air, breath analysis for medical diagnoses [1–4]. Many ammonia detectors based on different principles, such as pulse mode, redox-active and acidbase and resistive polymer have been reported in literatures [5–7]. Miniaturized chemical sensors have played an important role in monitoring the presence of NH_3 gas at low concentrations in the atmosphere [8]. The most common ammonia sensors are solid-state and electrochemical devices [9,10], which are known to be inexpensive and safe. Metal oxide semiconductors have also been used for ammonia sensing and have high sensitivity [11–13]. Ammonia sensors based on copper sulfide has also been reported [14,15]. More recently, highly sensitive ammonia sensors based on a macrocyclic complex (5, 7, 7, 12, 14, 14- hexamethyl- l, 4, 8, 11- tetraazacyclo- tetradeca- 4, 11- diene) nickel(II) iodide complex have been developed [16].

Ammonia sensor has a broad application prospect in the chemical production [17,18]. To achieve automatic control of chemical production involving ammonia (ammonia as raw materials or intermediate products or final products), the change of ammonia concentration must be converted into electrical signals transmitted to the control equipment. Ammonia concentrations are often at the percentage levels in chemical production. However, most of the ammonia sensor is only sensitive to ppm or ppb concentrations of ammonia at present. Therefore, a sensor that is responsive to the percentage concentration ($\sim$% level) of ammonia, need to be developed. In recent years, we have focused on this work. In the present study, a novel ammonia sensor responsive to the percentage concentration of ammonia was fabricated based on silver sulfide film and its responses to ammonia were investigated. Sensitive material selection Ag_2S is mainly the Ag^+ has some empty outer orbits, a strong ability to accept electrons. The investigations have been focused on the NH_3 sensing characteristics of the sensor. The effect of temperature and solid film surface on the gas sensing properties of the sensor was examined. Compared with traditional sensors, the present sensor has many advantages such as high response, wide linear range, without sintering and low working temperature.

2. Experimental

2.1. Material synthesis

2.1.1. Na₂S used as precipitating agent

10 g silver nitrate (AR grade, West Long Chemical Co., Ltd., Shanghai, China) was dissolved in 100 cm^3 of water, and 60 cm^3 of a Na_2S solution (1 mol/dm^3) prepared from analytical reagent (West Long Chemical Co., Ltd., Shanghai, China) was slowly dropped into

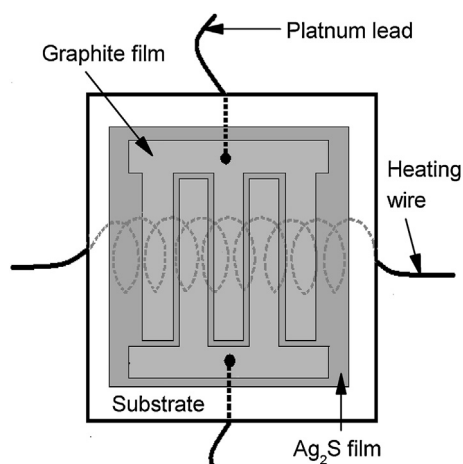* Corresponding author. Tel.: +8615074985299 1.
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Fig. 1. Schematic structure of the sensor.

this silver nitrate solution (0.59 mol/dm^3), stirred at room temperature. The resulting precipitate was washed with distilled water several times and filtered. A replicate sample was prepared in the same manner at 323 K. Finally, two Ag$_2$S materials were dried at a temperature of 393 K for 2.5 h in DHG-9030A electric thermostatic drying oven (Hecheng Instrument Manufacturing Co., Ltd., Shanghai, China).

2.1.2. H$_2$S used as precipitating agent

H$_2$S gas was slowly injected into 100 cm^3 of silver nitrate solution (0.59 mol/cm^3) and vigorously stirred at room temperature. The resulting precipitate was washed with distilled water several times and filtered. Additional Ag$_2$S material was prepared in a similar way, but with a reaction temperature of 323 K. Finally, two Ag$_2$S materials were dried for 2.5 h at a temperature of 393 K. Using Na$_2$S and H$_2$S as a precipitating agent is mainly because they are cheap and easy to get. Synthesis temperature of 323 K was selected mainly taking into account the temperature is the midpoint of the solvent (water) freezing point and boiling point.

2.2. Sensor fabrication

Sensors fabrication process is as follows: Silver sulfide materials were mechanically milled in a PVA solution (polyvinyl alcohol, 0.1 wt%) medium using LNMN-120 electric agate ball mill (Liaoning Heishan Xinli Tun Agate Craft Factory, China) and grinded for 4.5 h to form a paste. The paste was sprayed by electro-motion spray gun onto an aluminum oxide substrate on which a pair of interdigited electrodes made of graphite film. Graphite film was previously coated on the substrate by direct friction. Graphite has a high chemical stability, good electrical conductivity and low cost. This is the reason to use it as an interdigited electrode. Resistance of the graphite film was 20 Ω per cm. The total size of the interdigited electrode was 4 × 4 mm^2 and the interelectrode gap was 0.1 mm. Platinum wires were used for contacts to graphite. The size of the gas-sensing film was 5 × 5 × 0.015 mm^3. Gas-sensing film thickness was controlled by the spraying time. The square Al$_2$O$_3$ substrate size is 6 × 6 × 3 mm^3. The element was dried at a temperature of 393 K for 3 h in DHG-9030A electric thermostatic drying oven, and then was naturally cooled to room temperature in the air. A platinum heating wire having a 0.1 mm diameter was included in the substrate to form a side-heated gas sensor. It is shown in Fig. 1. Finally, the sensing element was soldered on a pedestal with a vent hole, and then was cased in a plastic vessel with a reticulate vent [19]. Four Ag$_2$S were used to make the sensors under the same process conditions.

2.3. Measurement techniques

The measurements of gas sensing properties of the sensor were carried out using a system with an airtight chamber of 10 dm^3 in the present experiment. To ensure the environment in the airtight chamber was nearly at atmospheric pressure, a dilatation film was connected to the airtight chamber. The dilatation film could be distended when the chamber was excessively filled with sample gases. An adjustable speed miniature fan was installed in the chamber for accelerating the gas mixing and eliminates the error of the response time. The sensor was exposed to sample gas of variable concentration, containing a known amount of air. During the sensing measurement, the sample gas concentration was altered by injecting sample gases into the airtight chamber using SGC-LR-10000 sample injector (Hongsheng Instruments Co., Ltd., Shenzhen, China). The sample is a liquid at room temperature (such as CH$_3$OH, C$_2$H$_5$OH, and other organic reagents), it was first vaporized into a gas, and then tested the response of the sensor to its vapor as follows: a known amount of liquid sample was injected into a vacuum container with a known volume using 10 μl (minimum scale 0.1 μl) micro sample injector (Rui Xin Instrument Co., Ltd., Wenzhou, China), to fully evaporate as a gas. The concentration of vapor was obtained from the calculation. Then a precise volume of vapor was extracted using sample injector, and injected into the test chamber. Heating and operating voltage for the test were provided by a WY-30-2A power supply (Optoelectronic Information Co. Ltd., Hangzhou, China). DC operating voltages (V_O) were applied across the circuit, and the output voltage (V_S) across the sampling resistor (R_S) was recorded. The transformational relation between the resistance (R) of a sensor and the output voltage of the sampling resistor in circuit is given by the following formula:

$$R = (V_O − V_S)R_S/V_S \tag{1}$$

The electrical resistance of a sensor was measured in sample gases and in air. When the sensor worked at a different operating voltage or different temperature, the output voltage of the baseline might be different in the ambient air. Therefore, the sampling resistor was designed as an adjustable resistor. By adjusting the resistance value of the sampling resistor, the output voltage can be controlled to the same baseline. This approach ensured the accuracy and comparability of measurement results.

Seventeen sample gases such as ammonia (NH$_3$, 99.99%, Shiyuan Gas Co., Ltd., Guangzhou, China), water vapor (H$_2$O), hydrogen sulfide (H$_2$S, 99.99%), sulfur dioxide (SO$_2$, 99.9%, Shiyuan Gas Co., Ltd., Guangzhou, China), nitrogen dioxide (NO$_2$, 99%, Yanglilai Chemical Gas Co., Ltd., Beijing, China), formaldehyde (HCHO), methanol (CH$_3$OH), ethanol (C$_2$H$_5$OH), acetone (CH$_3$COCH$_3$), benzene (C$_6$H$_6$), toluene (C$_7$H$_8$), ethyl ether (C$_4$H$_{10}$O), tetrahydrofuran (C$_4$H$_8$O), chloroform (CHCl$_3$), propylamine (C$_3$H$_9$N), dimethylformamide (C$_3$H$_7$NO) and aniline (C$_6$H$_7$N) (All organic reagents were AR grade) were tested. The sensor responses to seventeen sample gases were measured at working temperatures 298, 303, 313, 323, 333, 343 and 353 K and operating voltages continuously increased from 1 to 15 V in steps of 1 V for each temperature. The concentration of sample gas in the test chamber was changed from 0.001 to 7.5% (the ratio of sample gas volume to air volume) divided into 14 times, with different step length.

The response time is the time for the output voltage change to reach 90% of the total change from air to the sample gas. The recovery time of the sensor was recorded as a duration in which the output voltage changes to reach 90% of the total change when sensor was moved from the test gas into the air. In order to reduce the diffusion time of the sample gas in the large-volume Chamber, improve the accuracy of the response time. An adjustable speed miniature fan was installed in the chamber for accelerating the gas mixing and eliminates the error of the response time.