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Investigation of ammonia gas sensing properties of graphite oxide

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Abstract

In this paper a graphite oxide is investigated as a possible sensing layer of room temperature ammonia chemiresistive gas sensor. The sensing properties were tested in a wide range of ammonia concentrations in air (10-1000 ppm) and under different humidity levels (3-65 %). It was concluded that the graphite oxide based sensor possessed high response to NH_3 in synthetic air ($\Delta R/R_0$ ranged from 2.5 to 7.4 % for concentrations of 100-500 ppm and 3 % relative humidity) with negligible cross-sensitivity towards H_2 and CH_4. It was determined that the sensor recovery rate was improved with ammonia concentration growth. Increasing of ambient relative humidity led to increase of sensor response. The highest response of 22.2 % for 100 ppm of ammonia was achieved at 65 % relative humidity level.

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Keywords: Gas sensor; ammonia; graphite oxide; response, humidity, cross-sensitivity.

1. Introduction

Detection of dangerous and toxic gases in environment, industry or household using miniaturized devices has become a significant task recently. One of the most dangerous gases is ammonia. Ammonia detection at room temperature is therefore of great significance [1], [2]. In comparison to high-power-consuming and high-

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temperature-operated sensors, the room-temperature-operated sensors are associated with many problems to be solved: enhancing sensor response, increasing sensor recovery rate and finding the way for improving the sensing properties. Typically, the ammonia gas sensors are implemented as metal oxide semiconductor gas sensors, however, these sensors operate at relatively high temperatures (200-350°C). The high-temperature power-consuming heating is another problem that could be avoided by the using of novel active materials [3]. Therefore, the creation of room-temperature-operated ammonia gas sensors is a current issue to be solved.

Nowadays, graphene-like compounds are frequently used for ammonia detection. In [4] the authors created Cu-BTC MOF/graphene-based hybrid materials which showed the response of 3.7 % to 500 ppm of NH_3. Katkov et al. [5] developed fluorine functionalized ammonia gas sensors which possessed 10 % response to 10000 ppm NH_3. Graphite oxide (GO) is a special type of graphite-like material that can be utilized for ammonia detection. The excellent ammonia absorption ability of graphite oxide in water was confirmed in [6], and [7]. This material can be successfully used for room temperature detection of ammonia because of good adsorption ability and possibility to enhance the texture characteristics by its reduction. However, the data on its using in an initial non-reduced state as active material for ammonia gas sensors are poorly presented. This work is devoted to the investigation of ammonia gas sensing properties of GO used as the active layer of chemiresistive gas sensor.

2. Experimental

GO synthesized by modified Hummers technique was used for preparation of ammonia gas sensor active layer. The GO synthesis technique was described in details in [8]. Briefly, high purity graphite (20 g) was placed into the flask with 10 g of $NaNO_3$ and 460 mL of concentrated H_2SO_4 (96 %). The mixture was mixed by the magnetic stirrer during 10 min and kept at the temperature of 0°C in ice bath. Anhydrous $KMnO_4$ (60 g) was added 15 min after the beginning of the synthesis and kept for 20 min at 0°C. The resulted suspension was heated to 35°C for 30 min. Then, the mixture was poured into the flask with 230 ml of ice and kept at room temperature (25±2°C) for 15 min. After that, 840 ml of H_2O_2 was added to the mixture and kept another 15 min at room temperature. Prepared GO was washed by deionised water and dried in air at 90°C for 24 hours. GO was investigated by scanning electron microscopy (SEM) using Hitachi S-3400N equipped with energy dispersive spectroscopy (EDX) add-on. The GO chemiresistive gas sensor was obtained by spray coating of GO/DMF suspension (100 mg of GO in 10 mL) between two gold electrodes previously sputtered on a Si/SiO_2 (535/90 nm) substrate to form an active area of 2×4 mm.

The response of the gas sensors was examined using the custom made gas rig. The rig consisted of three gas channels. A synthetic air (80 % N_2, 20 % O_2) was used as gas carrier. The second line was used for analyte: mixture of 5000 ppm NH_3 in air. The third line was used for admixing of wet air for measurements at different relative humidity (RH). The main parameter of the sensors was the sensor response (%):

$$\Delta R/R_0 = (R-R_0) / R_0, \quad (1)$$

where R is the resistance of the sensor exposed to NH_3, (Ω); R_0 is the sensor resistance in synthetic air, (Ω). The investigation of the sensor response was carried out at room temperature (25±2°C). The sensors were examined in a concentration range of 100-1000 ppm. To estimate the sensor selectivity, the sensor response measurements in H_2 and CH_4 (5000 ppm of analyte diluted in air) were also carried out.

3. Results and discussion

SEM images of the synthesized GO sample are shown in Figure 1. GO sample is represented by rough particles with a micron size.

From the SEM images shown in Fig. 1 it is clear that strong treatment of graphite made the material more defective and the particles' surface was covered by platelets of GO. According to EDX data, there are three main elements presented in the prepared material: C (70.44 at. %), O (22.46 at. %) and S (7.1 at. %). The C:O ratio of 3.1 confirms the high content of oxygen-containing functional groups. The appearance of sulphur can be linked with the presence of S=O and S-O groups on the GO surface [6].

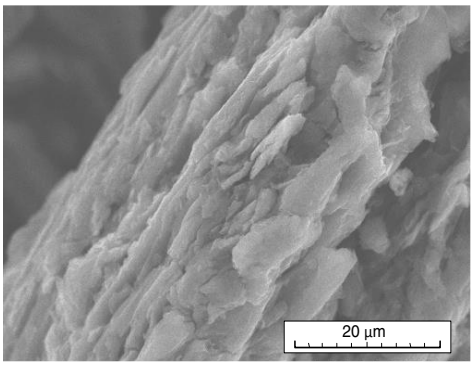

Fig. 1. SEM image of the GO sample.

The GO sensor response to ammonia varied from 2.5 to 10 % in the concentration range from 100 to 1000 ppm (see Fig. 2a). The sensor showed relatively high response in comparison with carbon nanotubes and graphene-like materials [9]. The sensor exhibited weak recovery rate at relatively low concentrations of ammonia (e.g. 100 ppm). The increase of NH_3 concentration induced enhancement of the recovery rate.

Current-voltage curves of the sample are shown in Fig. 2b. The sensor exhibited linear I-V characteristics. The addition of NH_3 to air resulted in a slight change of the curve slope.

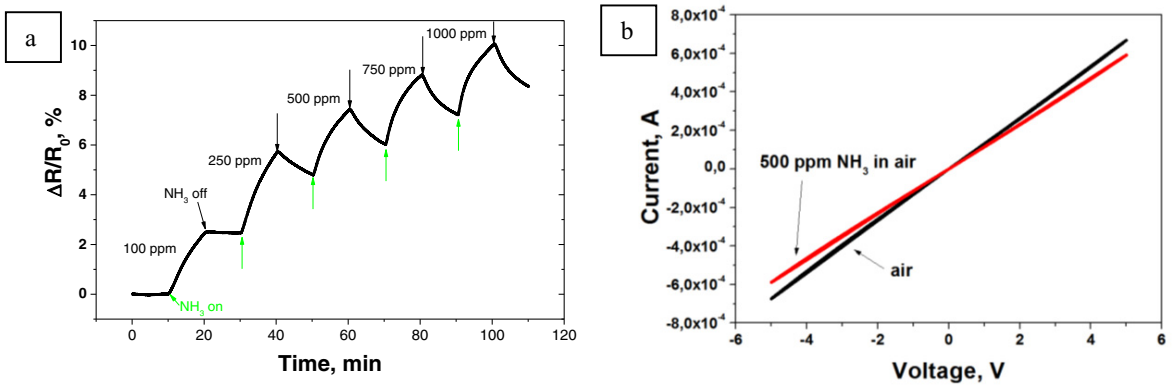

Fig. 2. (a) GO based chemiresistive sensor response to ammonia at room temperature for concentration range from 100 ppm to 1000 ppm; (b) current-voltage characteristic of GO based chemiresistive sensor measured in air atmosphere and in 500 ppm of ammonia in air mixture at room temperature.

To estimate the influence of RH on GO sensor characteristics, the measurements with RH of 3 %, 27 % and 65 % were carried out (see Fig. 3a). Increasing of RH led to increase of sensor response. The highest response was achieved for 65 % RH (22.2 %, 22.5 %, 29.6 % for 100 ppm, 250 ppm, and 500 ppm, respectively). This effect can be linked with the improved adsorption of ammonia on the humidified GO surface.

According to cross-sensitivity measurement the sensors we prepared show higher response to ammonia in a comparison with H_2 and CH_4 (see Fig. 3b). The response curve of GO sample to H_2 and CH_4 indicated weaker adsorption of these gases in a comparison with NH_3 due to the nature of these compounds where ammonia is the strongest electron-donating compound. As the sensors show good selectivity towards ammonia, they can be possibly utilized for detection of ammonia in air or N_2 in industrial processes (absorption or desorption of NH_3 in chemical industry, oil-refining and petrochemical industry).

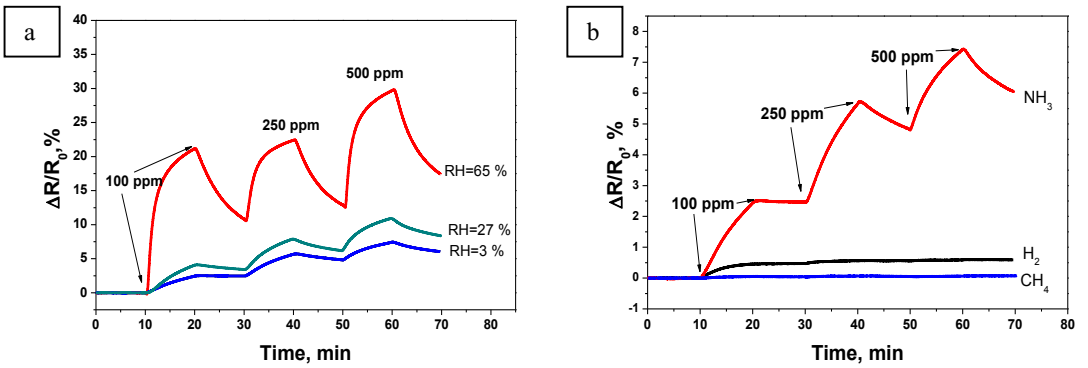

Fig. 3. (a) influence of RH on sensor response; (b) sensor response towards different gases measured at room temperature.

4. Conclusion

The presented results show the efficiency of GO as the active material for room temperature ammonia gas sensors. The GO based sensor possessed high response to NH_3 in air ($\Delta R/R_0$ ranged from 2.5 to 7.4 % for concentrations of 100-500 ppm). It was determined that the sensor response increases during grow of the relative humidity. The highest response was achieved for 65 % relative humidity (22.2 %, 22.5 %, 29.6 % for 100 ppm, 250 ppm and 500 ppm, respectively). The prepared sensor shows much higher response towards NH_3 in comparison with H_2 and CH_4.

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References

[1] H.-Q. Nguyen, J.-S. Huh, Behavior of single-walled carbon nanotube-based gas sensors at various temperatures of treatment and operation, Sensors Actuators B Chem. 117 (2006) 426–430.
[2] N. A. Travlou, M. Seredych, E. Rodríguez-Castellón, T. J. Bandosz, Activated carbon-based gas sensors: effects of surface features on the sensing mechanism, J. Mater. Chem. A 3 (2015) 3821–3831.
[3] N. N. Gedam, P. R. Padole, S. K. Rithe, G. N. Chaudhari, Ammonia gas sensor based on a spinel semiconductor, Co0.8Ni0.2Fe2O4 nanomaterial, J. Sol-Gel Sci. Technol. 50 (2009) 296–300.
[4] N. A. Travlou, K. Singh, E. Rodríguez-Castellón, T. J. Bandosz, Cu–BTC MOF–graphene-based hybrid materials as low concentration ammonia sensors, J. Mater. Chem. A 2 (2015) 2445–2460.
[5] M. V. Katkov, V. I. Sysoev, A. V. Gusel'nikova, I. P. Asanov, L. G. Bulusheva, A. V. Okotrub, A backside fluorine-functionalized graphene layer for ammonia detection, Phys. Chem. Chem. Phys. 17 (2014) 444–450.
[6] M. Seredych, A. V. Tamashausky, T. J. Bandosz, Graphite oxides obtained from porous graphite: The role of surface chemistry and texture in ammonia retention at ambient conditions, Adv. Funct. Mater. 20 (2010) 1670–1679.
[7] M. Seredych, T. J. Bandosz, Combined role of water and surface chemistry in reactive adsorption of ammonia on graphite oxides, Langmuir 26 (2010) 5491–5498.
[8] A. G. Bannov, A. A. Timofeeva, V. V. Shinkarev, K. D. Dyukova, A.V. Ukhina, E. A. Maksimovskii, S. I. Yusin, Synthesis and studies of properties of graphite oxide and thermally expanded graphite, Prot. Met. Phys. Chem. Surfaces 50 (2014) 183–190.
[9] J.-W. Han, B. Kim, J. Li, M. Meyyappan, A carbon nanotube based ammonia sensor on cellulose paper, RSC Adv. 4 (2014) 549.