

Development of ammonia gas sensor based on Ni-doped reduce graphene oxide

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Abstract. The work aims to develop a simple and low cost ammonia gas sensor based on reduced graphene oxide (rGO). Reduced graphene oxide doped with nickel sulfate (NiSO_4/rGO) was used as a sensing material. The sensor was fabricated by a simple drop-cast and spin-coat technique. The performance of the nickel-doped reduce graphene oxide were studied in terms of electrical changes as well as chemical interactions. It was found that after the fabricated sensor was exposed to ammonia vapour for 10 min, the average resistivity was increased to 43% from initial resistance and retained about 8% resistance change upon ammonia removal. The mechanism of the sensor reaction with the ammonia gas is also studied using Fourier Transform Infrared Spectroscopy (FTIR) and is discussed. This preliminary work may help develop the highly sensitive ammonia gas sensor.

1 Introduction

Ammonia is extensively used in several fields of industries including fertilizers, food processing, automotive, rubber, refrigerator and medical diagnostics[1]. High concentration of ammonia greater than 300 ppm can be harmful to human health[2]. It can cause suffocation, severe irritation to respiratory tract, eyes, and skin. Moreover, exposure to over 5,000 ppm can be lethal within 5-10 min [3]. Development of ammonia sensor which is inexpensive, robust and easy to fabricate is noteworthy.

Graphite oxide is the graphite that has been oxidized using strong oxidizers leading to various oxygenated functional groups in its structure. It can be obtained by treating graphite with strong oxidizers. The bulk material disperses in basic solutions to yield monomolecular sheet, known as graphene oxide (GO) by analogy to graphene, the single-layer form of graphite. Graphene oxide sheets have been used to prepare a strong paper-like material, membranes, thin films, and composite materials. Initially Graphene oxide attracted substantial interest as a possible intermediate for the manufacture of graphene. When the graphite stack exfoliated by oxidation[4], the oxidized graphene oxide can be reduced back using chemical or thermal treatment to remove oxygenated functional group, producing materials with large surface area. This state is called reduced graphene oxide (rGO). Transformation of GO to

rGO can be performed either by heat or by chemical treatment. rGO is studied in many applications such as biological engineering[5, 6], optical electronics, absorbent material[7], ultrafiltration, energy storage, and gas sensor[8-10].

Nickel is a lustrous, silvery-white metallic element. Pure nickel, powdered to maximize the reactive surface area, shows a significant chemical activity, but larger pieces are slow to react with air under standard conditions because of an oxide layer formed on the surface preventing further reaction. Nickel(II) sulfate, or just nickel sulfate, usually refers to the inorganic compound with the formula $\text{NiSO}_4(\text{H}_2\text{O})_6$. The yellow anhydrous form, NiSO_4 , is a high melting solid that is rarely encountered in the laboratory. This material is produced by heating the hydrates above 330 °C. It decomposes at still higher temperatures to nickel oxide. Aqueous solutions of $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$ and related hydrates can react with ammonia to give $[\text{Ni}(\text{NH}_3)_6]\text{SO}_4$. Addition of ammonium sulfate to concentrated aqueous solutions of nickel sulfate precipitates $\text{Ni}(\text{NH}_4)_2(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$. This blue-coloured solid is analogous to Mohr's salt, $\text{Fe}(\text{NH}_4)_2(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$.

In this study, nickel sulfate doped reduce graphene oxide is used as an active layer for detection of ammonia vapour by monitoring resistance changes. The mechanism of interaction is also investigated using Fourier-transform infrared spectroscopy (FTIR).

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2 Materials and Method

2.1 Materials

Graphene oxide (GO) used in this study was synthesized according to the Hummers' method [11]. In brief, 1.5 g of sodium nitrate and 3 g of graphite powder were mixed with 23 ml of sulphuric acid in a beaker in an ice bath. Potassium permanganate (KMnO₄, 9 g) was slowly added and heated to 35°C for 30 minutes. After that, 138 ml of deionize water was added and temperature maintained at 80°C for 30 minutes. Finally, 420 ml of the deionized water (DI) was added together with 50 ml of hydrogen peroxide (6%) in order to stop the reaction. The obtained products were washed with 5% hydrochloric acid and deionized water four and three times respectively, and centrifuged at 4000 rpm for 10 minutes, and dried in a vacuum oven at 40°C for 48 hr. The obtained graphene oxide was further ball-milled to reduce the particle size using ball milling (Retsch, Emax) at 800 rpm, 5 mm bead size and 30 minutes at 20 mg/mL concentration in DI water. Nickel sulfate (20 mg/ml) was added to the GO grinder solution (NiSO₄/GO) at the 1:1 (w/w) ratio, mixed together and used as active compound for fabricating NiSO₄/rGO sensor. In another set of active sensing compound, multi-wall carbon nanotube (MWNT, synthesized using arc discharge, from Nanogenstore [12]) was mixed with GO solution in the 1:1 ratio.

2.2 Preliminary selection of active compounds

Three active compounds have been initially tested for their responses to ammonia vapour which are reduced graphene oxide (rGO), carbon nanotube doped reduce graphene oxide (MWNT/rGO) and nickel sulfate doped reduce graphene oxide (NiSO₄/rGO). For the preliminary testing, drop cast technique have been used. The sensor is fabricated by dropping a solution of active compounds (10 mg/ml) onto a glass slide which has two aluminium electrodes separated by a gap of 0.5 mm. The sensor is then dried and GO thermally reduced using an oven at 180°C for 2 hr. The sensors are exposed directly to ammonia vapour from 30% ammonia solution (LOBA), for 75 minutes. This preliminary screening is to select the materials which show high response and quick recovery for further sensor fabrication.

Fig. 1. shows percent resistance change of the sensor upon exposure to ammonia atmosphere of:)a(reduce graphene oxide (rGO),)b(MWNT-doped rGO and)c(nickel sulfate (NiSO₄) doped rGO to ammonia vapour during 75 minutes)left(and after ammonia vapor removed)right(, nickel sulfate-doped reduce graphene oxide has almost a 100% change in sensing and also good recovery than the reduce graphene oxide alone which has some response and but cannot fully recovered to the initial resistance. The MWCT-doped reduced graphene oxide shows the highest response but cannot be recovered into the initial resistance too. As a result, nickel sulfate-doped reduce graphene oxide was chosen for further testing.

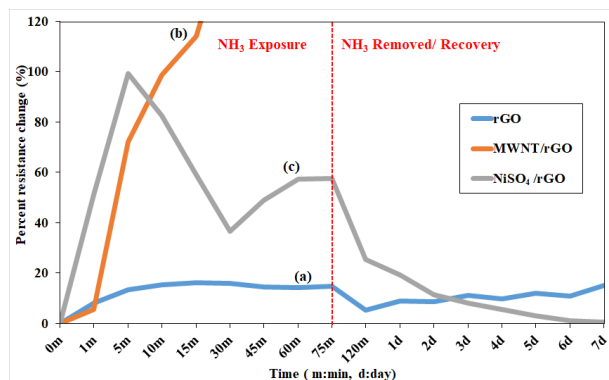


Fig. 1. Percent change of (a) reduce graphene oxide, (b) carbon nanotube doped reduce graphene oxide and (c) nickel sulfate doped reduce graphene oxide to ammonia vapor in the first 120 minutes (left), and after ammonia vapor removed (right).

2.3 Sensor fabrication

For fabrication of ammonia detection gas sensors, Fig. 2. shows the interdigitate electrodes with a 0.1 mm interdigitate spacing that was fabricated by sputtering an aluminium interdigitated pattern onto an alumina ceramic substrate.

The active sensor layer was prepared by spin casting a 50 µL of NiSO₄/GO solution onto the above interdigitated substrate at 5000 rpm for 30 seconds and dried in two steps: first on a hot plate at 50°C for 10 minutes, then in an oven at 200°C for 2 h to transform the NiSO₄/GO film into its reduced form (NiSO₄/rGO).



Fig. 2. (a) the interdigitated pattern with a 0.1 mm interdigitate spacing on an alumina substrate, and (b) NiSO₄/GO mixed solution for spin coating onto the electrode

2.4 Ammonia vapour testing

Fig. 3. shows diagram of a gas-test setup. Ammonia gas was generated by bubbling a 300 mL ammonia solution at various flow rates. This vapour is mixed with air zero for dilution at the ratio of 50% for the initial acclimatization, 50% for the 1st duty cycle, 25% for the 2nd duty cycle, and 12.5% for the 3rd duty cycle each with the interval of 10 min exposure to the ammonia gas and 30 min under air flow (air zero) for sensor recovery. The sensor response, or percent resistance change, may be calculated using equation (1),

$$\text{Percent resistance change (\%)} = (R - R_0) \times R_0 / 100 \quad (1)$$

where R_0 is the sensor's initial resistance, and R is the sensor's resistance during gas exposure taken to be the value after the burn-in period (the 1st exposure period to ammonia vapor), just before the 2nd exposure to ammonia vapor.

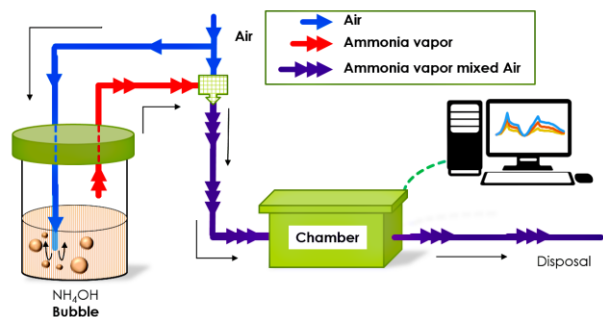


Fig. 3. Schematic diagram of the gas test set-up

3 Result and Discussion

3.1 Sensor's percent resistance change

Resistance of the nickel sulfate doped reduce graphene oxide (NiSO_4/rGO) sensor on an alumina substrate was measured in each sample for four duty cycles. Fig. 4. displays the percent change of electrical resistance during exposure to the ammonia vapour which is allowed to flow in consecutive stages as follows: the burn-in period or the first time the sensor is exposed to ammonia vapour at 50% ratio (mixing with air zero) for 10 min, followed by a recovery period by flowing air-zero for 30 min. During this period, the sensor resistance values change a lot and not completely recovered to the initial resistance value. The new resistance after 30 min recovery is taken as a baseline resistance of the sensor.

During the next duty cycle, taken as actual operating cycle, the sensor resistance change is increased to about 43%. In the following recovery period in air-zero flow, the resistance change of the sensor falls back to about 6% from the baseline value. In the 3rd duty cycle, ammonia vapour is reduced to 25%, the resistance change is increased to about 38%, and the sensor can recover to about 8% above the baseline value within 30 min after the ammonia gas turned off. In the 4th duty cycle, ammonia vapour concentration is reduced to 12.5% and the resistance change is increased to about 30%, the sensor can also recover very well with the resistance back to about 8% above the baseline value. From this result, it seemed that the sensors still change a little bit even after 4th cycles. The 8% retention of resistance may indicate some irreversible reaction of ammonia with sensor. The baseline resistance, or the resistance after ammonia removed, seemed to be quite stable after the 3rd cycle. The longer burn-in period may be needed to help stabilize the sensor performance.

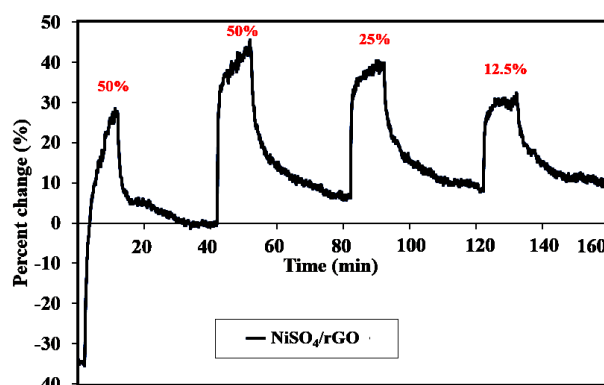


Fig. 4. Percent change response of NiSO_4/rGO exposure to ammonia bubble vapor for four duty cycles, the first cycle was taken as a burn-in period.

3.2 FTIR spectra

Fourier-Transform Infrared (FTIR) spectroscopy was used to examine the chemical characteristics as well as the interaction of NiSO_4/rGO with ammonia during exposure and recovery. The FTIR spectra of samples were measured in the attenuated total reflectance (ATR) mode using diamond head with the deuterated, L-alanine doped triglycine (DTGS) detector (Thermo Scientific, Nicolet iS5 FT-IR). FTIR spectra were obtained over the average of 32 scans from 3700 cm^{-1} to 570 cm^{-1} , with spectral resolution of 4 cm^{-1} .

Fig. 5. shows FTIR results compared to spectra of initial GO, NiSO_4 , and NiSO_4/rGO sample used for gas ammonia sensing. Major peaks of GO spectrum were at 1718 , 1618 , 1220 , and 1043 cm^{-1} which can be assigned to the C=O, C=C, and C-O of epoxy and ether vibrations, respectively [13]. For nickel sulfate, the major peaks were at 3409 , 1600 , 1070 , 776 and 610 cm^{-1} which can be assigned to the O-H stretching, OH bending, SO_4 and Ni-O stretching, respectively [14]. After heat treatment, NiSO_4/GO is transformed into NiSO_4/rGO , the intensity of the bands representing graphene oxide decreases and peak of NiSO_4 still remained at 3405 , 1070 and 610 cm^{-1} [13].

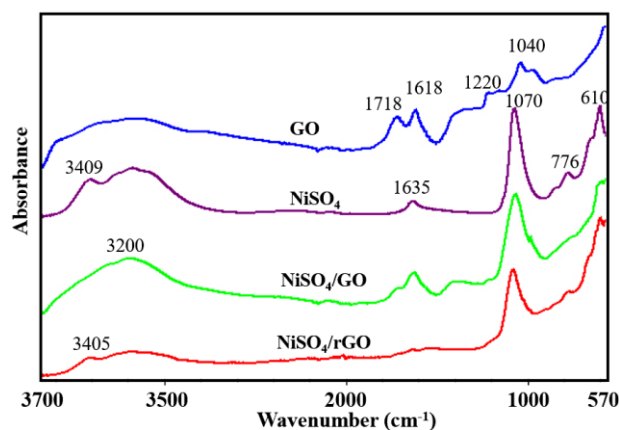


Fig. 5. FTIR results compared among spectra of initial GO, NiSO_4 , NiSO_4/GO and NiSO_4/rGO sample used for gas ammonia sensing.

Fig. 6. shows the FTIR spectra of NiSO₄/rGO sample upon exposure to ammonia vapour, major peaks of acid-base reactions between ammonium and reduce graphene oxide were observed at 3300, 3200, and 1240 cm⁻¹. New emerging peak at 1440 cm⁻¹ also shows up after sample's recovery under air flow. This bond is formed due likely to the ammonia desorption from the sensor's film. Upon re-exposure to ammonia vapor, this peak is suppressed again showing specific reversible interaction of ammonia gas with the sensor. The presence of the 3344 cm⁻¹ upon ammonia exposure in both 1st and 2nd exposure is likely from the ammonium, which indicates that the ammonia gas may have been adsorbed onto the sensor's surface in the form of ammonium.

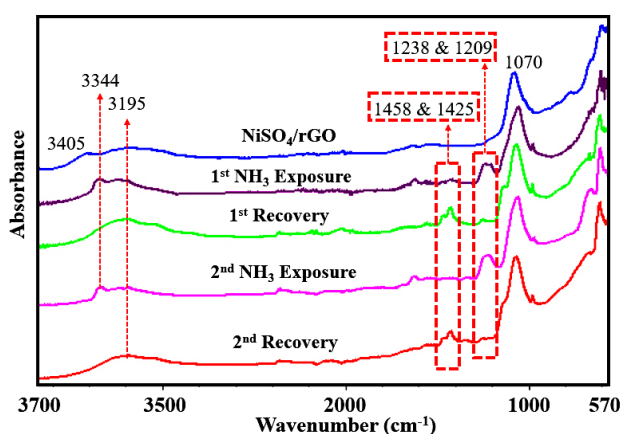


Fig. 6. FTIR of NiSO₄/rGO interaction with ammonia vapor for 5 minutes in two duty cycle.

4 Conclusion

Nickel-doped reduced graphene oxide ammonia sensor has been successfully fabricated using interdigitated sensors. The sensor can successfully detect ammonia gas generated by bubbling ammonia aqua solution with about 43% increase in the sensor's resistance during 10 min exposure (after initial burn-in period). Upon ammonia gas removal, the sensor's resistance can be almost fully recovered to about 6% above the baseline value in about 30 min. The sensors can be used for many cycles of ammonia gas exposure although the baseline shifted up slightly after each recovery indicating that some irreversible interactions also occurred. From the FTIR spectra, NiSO₄/rGO show interaction with ammonia vapor, causing the peak to appear at 3300, 3200, 1240 cm⁻¹ indicating that the ammonia gas may have been adsorbed onto the film in the form of ammonium. The exact interaction mechanism remains to be further investigated.

This study was supported by the Center of Excellence in Materials and Plasma Technology (CoE M@P Tech), and Low Carbon Technology grant, Bangchak Petroleum Public Company. Thanva is grateful to TAIST-Tokyo Tech scholarship. Authors thank Thitima M. Daniels for helpful supports and guidance on equipment.

References

- Mani, G.K. and J.B.B. Rayappan, Applied Surface Science. *Selective detection of ammonia using spray pyrolysis deposited pure and nickel doped ZnO thin films.* **311**: p. 405-412 (2014).
- Zhang, D., C. Jiang, and Y.e. Sun, Journal of Alloys and Compounds. *Room-temperature high-performance ammonia gas sensor based on layer-by-layer self-assembled molybdenum disulfide/zinc oxide nanocomposite film.* **698**: p. 476-483 (2017).
- Timmer, B., W. Olthuis, and A.v.d. Berg, Sensors and Actuators B: Chemical. *Ammonia sensors and their applications—a review.* **107**(2): p. 666-677 (2005).
- Dimiev, A.M. and J.M. Tour, ACS Nano. *Mechanism of Graphene Oxide Formation.* **8**(3): p. 3060-3068 (2014).
- Sun, P., et al., ACS Applied Materials & Interfaces. *Small Temperature Coefficient of Resistivity of Graphene/Graphene Oxide Hybrid Membranes.* **5**(19): p. 9563-9571 (2013).
- Vuorinen, T., et al., Sci Rep. *Inkjet-Printed Graphene/PEDOT:PSS Temperature Sensors on a Skin-Conformable Polyurethane Substrate.* **6**: p. 35289 (2016).
- Tippo, N., et al., *Slow Release of Menthol Using Sorbents Developed from Microwave Graphene Oxide.* 2017.
- Bannov, A.G., et al., Sensors (Basel, Switzerland). *Investigation of Pristine Graphite Oxide as Room-Temperature Chemiresistive Ammonia Gas Sensing Material.* **17**(2): p. 320 (2017).
- Seekaew, Y., et al., Organic Electronics. *Low-cost and flexible printed graphene-PEDOT:PSS gas sensor for ammonia detection.* **15**(11): p. 2971-2981 (2014).
- Verma, S. and R.K. Dutta, RSC Advances. *A facile method of synthesizing ammonia modified graphene oxide for efficient removal of uranyl ions from aqueous medium.* **5**(94): p. 77192-77203 (2015).
- Marcano, D.C., et al., ACS Nano. *Improved Synthesis of Graphene Oxide.* **4**(8): p. 4806-4814 (2010).
- Singjai, P., S. Changsarn, and S. Thongtem, Materials Science and Engineering: A. *Electrical resistivity of bulk multi-walled carbon nanotubes synthesized by an infusion chemical vapor deposition method.* **443**(1): p. 42-46 (2007).
- Onuki, K., et al., Bulletin of the Chemical Society of Japan. *Kinetics of the Thermal Decomposition of Nickel Sulfate.* **56**(11): p. 3294-3296 (1983).
- Sharma, A.K., et al., *Extraction of Nickel Nanoparticles from Electroplating Waste and Their Application in Production of Bio-diesel from Biowaste.* Vol. 6. 2014.