

## Enhancement of Ammonia Gas Sensing by Tin Dioxide-Polyaniline Nanocomposite

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Received: 28 June 2022, Revised: 20 July 2022, Accepted: 28 July 2022, Published: 4 November 2022

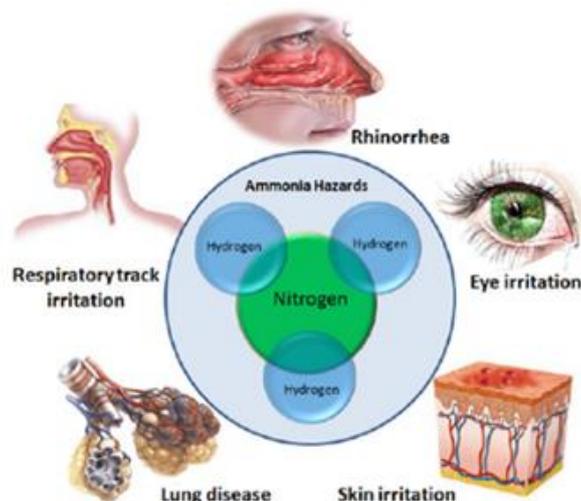
### Abstract

Ammonia (NH<sub>3</sub>) gas is an important chemical in many industries. Employees working in such industrial areas may be exposed to a certain concentration of NH<sub>3</sub> which could cause various symptoms such as irritation of skin and eyes and problems in respiratory system. The development of new NH<sub>3</sub> sensing material has attracted great attention. In this study, porous tin dioxide nanofibers (SnO<sub>2</sub> NFs) were successfully fabricated by electrospinning. The SnO<sub>2</sub> NFs were composited with polyaniline (PANI), conducting polymer. The tin dioxide nanofibers@polyaniline nanocomposite (SnO<sub>2</sub> NFs@PANI) was examined and showed improved and desirable sensing for NH<sub>3</sub> gas, which includes high sensitivity, quick response and fast recovery times at room temperature.

**Keywords:** Tin dioxide, Polyaniline, Ammonia, Sensor, Nanocomposite

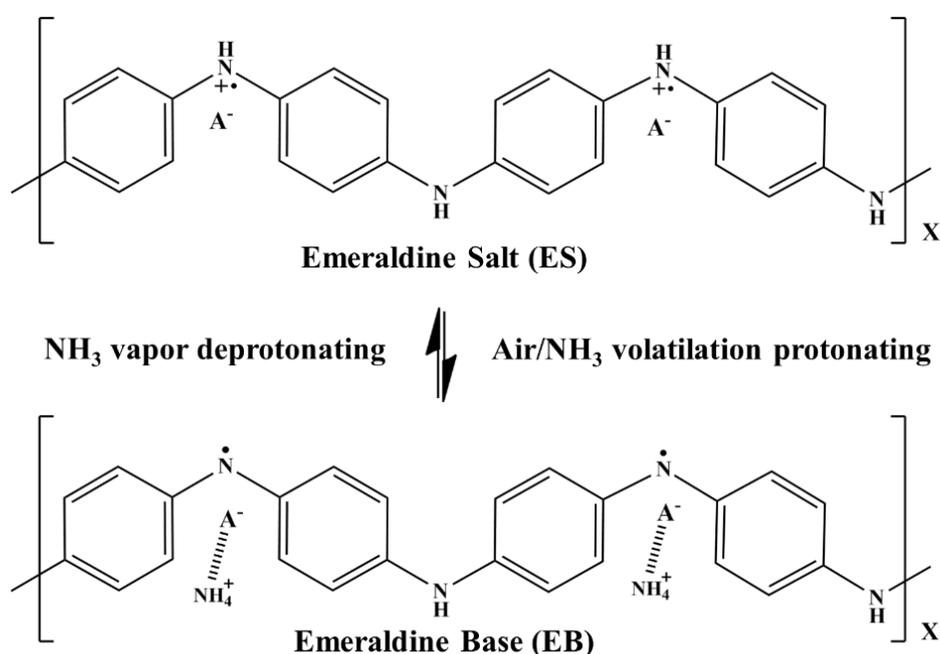
### Introduction

Ammonia (NH<sub>3</sub>) gas is an inorganic compound with pungent smell, classified as toxic gas that is corrosive to some materials. The gas affects living organisms and is dangerous to humans. Ammonia gas is an important chemical resource in many chemical industries such as fertilizer production industry, automobile industry, cleaning products industry, pharmaceutical industry, plastic and polymer manufacturing industry and herbicide manufacturing industry. Employees who work in such industrial areas are at risk to be exposed to some concentration of NH<sub>3</sub> for a long-term which may cause various symptoms such as irritation of skin and eyes and problems in respiratory system as shown in **Figure 1** [1]. In atmosphere, ammonia presents lower than 1 - 5 ppb [2]. According to the Occupational Safety & Health Administration (OSHA), human exposure to ammonia gas should not exceed 8 h and 15 min when the concentrations are 25 and 35 ppm [2], respectively.



**Figure 1** Effects of ammonia gas exposure [1].

The ammonia gas can be detected by many of spectroscopic methods [3-5] or solid-state sensing methods [6-10]. Among those methods, solid-state probe composed of conducting polymer film made of polyaniline (PANI) [11-13] polypyrrole (PPy) [14] or poly(3,4-ethylenedioxythiophene) (PEDOT) [15], is widely employed for the measurement at room temperature because the device is inexpensive and easy-to-handle. Although, those conducting polymers yield a fair sensitivity to  $\text{NH}_3$  gas, their sensitivity and efficiency can be improved when functionalized with metal-oxide [16-18]. Indium oxide ( $\text{In}_2\text{O}_3$ ) and titanium dioxide ( $\text{TiO}_2$ ) are examples of metal-oxide that were doped in polyaniline (PANI) nanofiber [19] and silk fiber [20], respectively, to enhance both sensitivity and limit of detection (LOD) for ammonia gas measurement. The solid-state-probe readout is oftenly on a basic of resistance-to-voltage conversion [21]. In this work, tin dioxide ( $\text{SnO}_2$ ) and PANI are of interested. The PANI, shown in **Figure 2**, is a conducting polymer that can electrically exchange charges with  $\text{NH}_3$  gas [22]. Its resistance alters when  $\text{NH}_3$  gas presents. For  $\text{SnO}_2$ , it is a metal-oxide that has a wide energy bandgap which resulting in good thermal stability. Not only, it is low-cost and easy to synthesize but it also is an electrochemically favor [23-27]. A fabrication method for  $\text{SnO}_2$  NFs doped in PANI has been reported in this work, along with its verification for promoting the  $\text{NH}_3$  gas detection.



**Figure 2** Schematic illustration of the interaction of  $\text{NH}_3$  gas with PANI occurring at the continuous chain (N) on the polymer structure.

## Materials and methods

### Chemicals and materials

Tin (II) chloride dihydrate ( $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ , purity 99 %), tin oxide powder ( $\text{SnO}_2$ ), aniline (purity 98.5 %), dimethylformamide (DMF), ammonium peroxydisulphate (APS, purity 99 %), polyacrylonitrile (PAN, MW = 150,000), hydrochloric acid (HCl, 37 %) and ethanol (95 %) were purchased from Sigma-Aldrich Co., USA. Acetone ( $\text{C}_3\text{H}_6\text{O}$ ), methanol ( $\text{CH}_3\text{OH}$ ) and toluene ( $\text{C}_6\text{H}_5\text{CH}_3$ ) were purchased from Merck Co., Germany. Formaldehyde ( $\text{CH}_2\text{O}$ ) was purchased from Quality Reagent Chemical Co., New Zealand. All chemicals were analytical grade and used as received.

Acrylic was purchased from Ekasilpbangkok Co., Thailand. Ceramic, screen-print graphene electrode (SPGE) and screen-print carbon electrode (SPCE) were in-lab fabrication. Ceramic obtained from a calcination of aluminum oxide ( $\text{Al}_2\text{O}_3$ ) at 1,050 °C. The SPGE and SPCE were screened with conductive inks; carbon inks (Gwent Electronic Materials Ltd., UK.) and graphene inks (Sun Chemical Co., USA.), respectively. Hantek 365F PC USB Digital Multimeter (Hantek.eu., Czech) was employed as a resistance recorder.

### Preparation of SnO<sub>2</sub> nanofibers

A 3.5 g polyacrylonitrile (PAN) was dissolved in 5 mL DMF at 80 °C with a stirring for 2 h. A 0.5 g SnCl<sub>2</sub>·2H<sub>2</sub>O was further added into the solution and stirred for 1 h. The prepared solution was then loaded into a syringe which connected to a 0.5 mm diameter stainless-steel needle. The needle tip was set 15-cm away from a rotating collector that was wrapped with aluminum foil. An electrospinning was carried out by applying 16 kV electric field across the needle and rotating collector while 13 μL/min feeding rate was applied on to the syringe. The obtained nanofiber was then calcinated at 600 °C in air for 2 h, in order to remove the organic constituents of PAN and further crystalize the SnO<sub>2</sub>.

### Synthesis of NH<sub>3</sub>-sensing materials

#### Pure PANI

Solution A was prepared by sonicating 46.34 μL of 10.79 M aniline monomer in 15 mL 1 M HCl for 30 min. Solution B was prepared by adding 0.114 g of ammonium peroxydisulphate (APS) into 15 mL of 1 M HCl and stirred for 30 min. Then, solution A and solution B were mixed and stirred for 30 min. An in-situ chemical polymerization took place at room temperature within 1 h. Finally, the pure PANI was obtained after being filtered and washed with 95 % ethanol and 1 M HCl, respectively. The precipitates were collected and dried in air for 24 h.

#### SnO<sub>2</sub>/PANI

The SnO<sub>2</sub>/PANI was prepared by the same procedure for the pure PANI except the composition in solution A. To prepare SnO<sub>2</sub>/PANI, solution A was prepared by sonicating 1 mg SnO<sub>2</sub> powder in 15 mL of 1 M HCl for 10 min. Then, 46.34 μL of 10.79 M aniline monomer was added and continue sonicated for another 30 min.

#### SnO<sub>2</sub> NFs@PANI

The SnO<sub>2</sub> NFs@PANI was prepared by the same procedure for the SnO<sub>2</sub>/PANI except the composition in solution A. To prepare SnO<sub>2</sub> NFs@PANI nanocomposite, 1 mg SnO<sub>2</sub> nanofiber synthesized in 2.2 was added, instead of SnO<sub>2</sub> powder.

### Measurement of NH<sub>3</sub> gas

To fabricate a sensor, each of NH<sub>3</sub> sensing materials; pure PANI, SnO<sub>2</sub>/PANI or SnO<sub>2</sub> NFs@PANI was weighted (5 mg) and dispersed in 1 mL DMF. Then, 60 μL of the mixture was drop-casted on different substrates; acrylic, ceramic, SPCE or SPGE and dried at 55 °C for 20 min.

In the gas measurement, the fabricated sensor was placed in a closed system and was connected to the digital multimeter. Resistances were continuously recorded, at room temperature (30 ± 5 °C) when the closed system was filled by a desire concentration of NH<sub>3</sub> and when the NH<sub>3</sub> was flush out by air. The response (S) of the fabricated sensor was defined as the following equation [28,29];

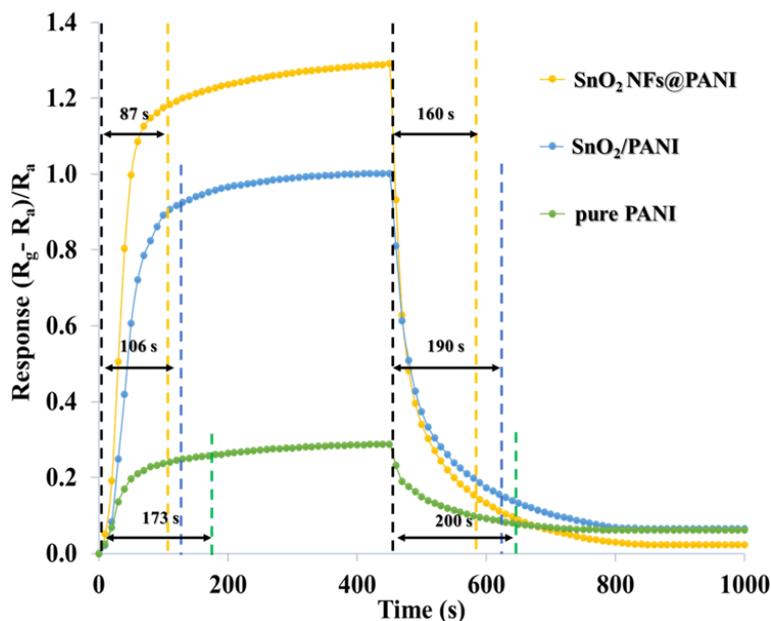
$$S = (R_g - R_a)/R_a$$

The R<sub>g</sub> represents resistance of the sensor in NH<sub>3</sub> gas and R<sub>a</sub> is a resistance of the sensor in air. The response and recovery times are defined as the time required for the sensor to achieve 90 % of stable resistance, when the fabricated sensor was exposed to the NH<sub>3</sub> gas and air, respectively.

## Results and discussion

### Effect of sensing materials and its substrate

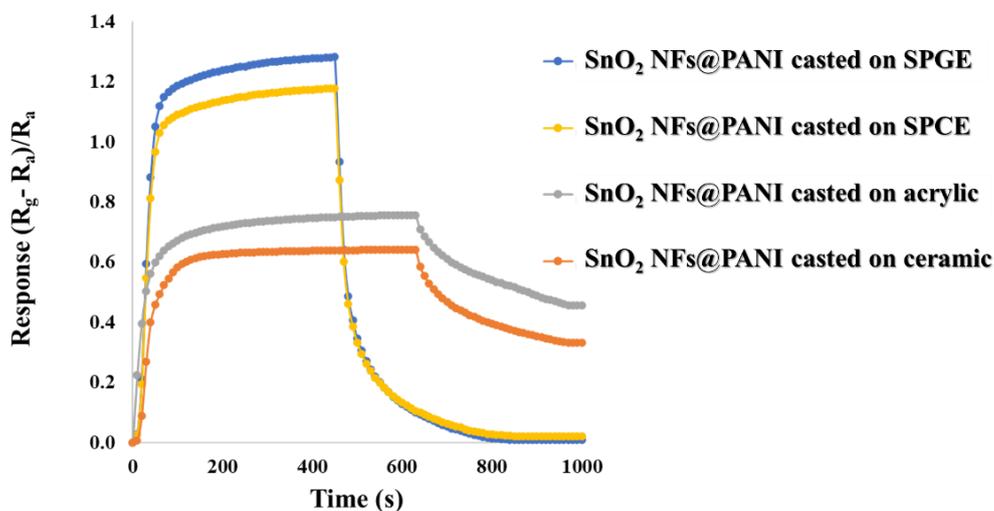
At room temperature, the NH<sub>3</sub> gas sensors made of PANI, SnO<sub>2</sub>/PANI or SnO<sub>2</sub> NFs@PANI casted on SPCE substrate were compared (**Figure 3**). The responses for 0.6 ppm NH<sub>3</sub> were 0.2873, 1.0015 and 1.2885 on the PANI, SnO<sub>2</sub>/PANI and SnO<sub>2</sub> NFs@PANI sensors, respectively. Among the 3 sensors, SnO<sub>2</sub> NFs@PANI gave the highest and fastest response to NH<sub>3</sub> gas as well as the fastest recovery time when compares to the PANI and SnO<sub>2</sub>/PANI sensors. The response and recovery times on the SnO<sub>2</sub> NFs@PANI sensor were 87 and 160 s, respectively.



**Figure 3** Responses, response times and recovery times of 0.6 ppm  $\text{NH}_3$  on pure PANI (green line),  $\text{SnO}_2/\text{PANI}$  (blue line) and  $\text{SnO}_2$  NFs/PANI (yellow line) sensing materials casted on SPCE.

**Figure 4** shows responses of 0.6 ppm  $\text{NH}_3$  measured by the  $\text{SnO}_2$  NFs@PANI that was casted on 4 different substrates: acrylic, ceramic, SPCE and SPGE. Noted here that during the sensor fabrication, low contact angle of a DMF drop containing sensing material was observed on the acrylic and ceramic substrates. This indicates a poor contact between the  $\text{SnO}_2$  NFs@PANI and the substrate surfaces which causes damage in the sensing material framework due to the extended of the drop. Moreover, a slowly penetration of  $\text{SnO}_2$  NFs@PANI was also found on both substrates revealing a loss of some sensing material from the substrate surfaces. These lead to a low response in  $\text{NH}_3$  gas detection on acrylic and ceramic substrates.

Compare to the  $\text{SnO}_2$  NFs@PANI that was casted on the SPCE and SPGE substrates, higher responses were recorded. This reveals a good contact between conductive inks and  $\text{SnO}_2$  NFs@PANI. A higher contact angle of the DMF drop on both substrates resulted in a gather of the sensing material within the drop area. No penetration of  $\text{SnO}_2$  NFs@PANI was found on the SPCE and SPGE. **Figure 4** shows that the  $\text{SnO}_2$  NFs@PANI cased on the SPGE gave the highest response to the  $\text{NH}_3$  gas.



**Figure 4** Responses of 0.6 ppm  $\text{NH}_3$  measured by  $\text{SnO}_2$  NFs@PANI casted on acrylic (grey line), ceramic (orange line), SPCE (yellow line) and SPGE (blue line).

### Sensing mechanism of SnO<sub>2</sub> NFs@PANI to NH<sub>3</sub>

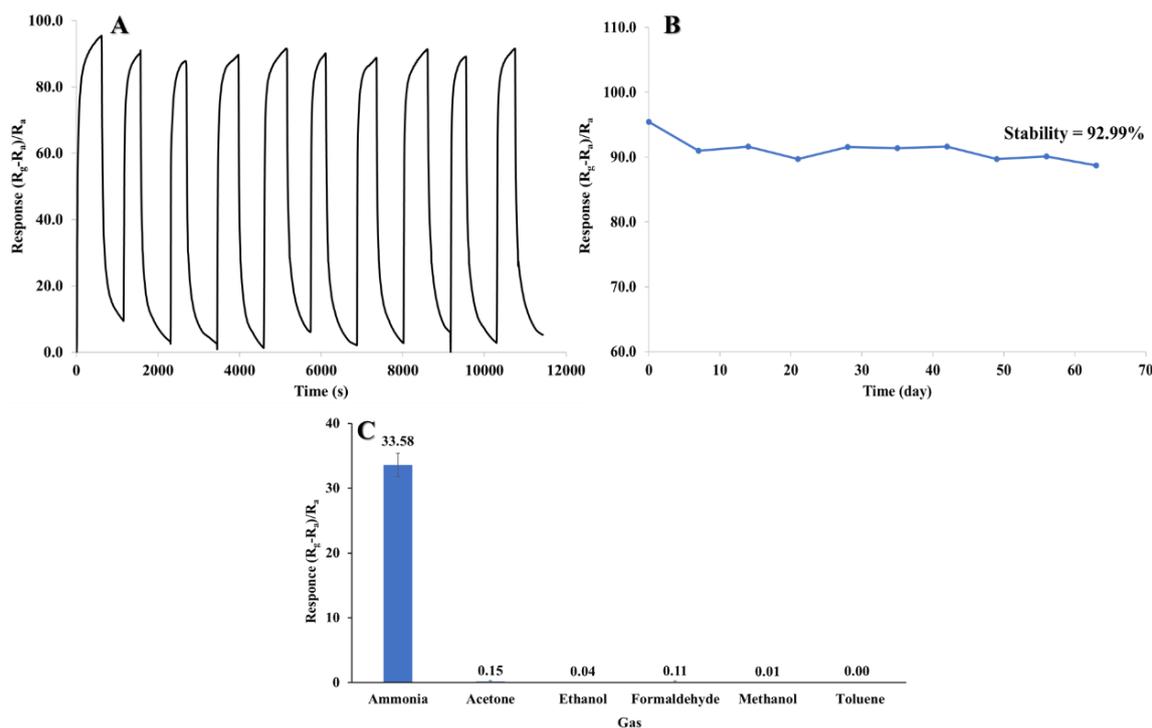
The SnO<sub>2</sub> NFs@PANI sensor is a p-n junction at the interface between PANI and SnO<sub>2</sub> nanofibers. Typically, PANI is considered as p-type semiconductor that exhibits holes conductivity. It can be interpreted as the deprotonation/protonation process via adsorption/desorption of NH<sub>3</sub> gas. As NH<sub>3</sub> gas is presented on PANI, the lone pair electron of NH<sub>3</sub> gas adsorbed on coordination bonding with the proton resulting in deprotonation of nitrogen atoms on PANI (**Figure 2**). As a result of the deprotonation, the charge carriers disappears and hence the electrical conductivity decreases. This causes the transformation of PANI from emeraldine salt (ES) to emeraldine base (EB), which led to the increase of resistance [30]. In contrast, after the sensor was exposed to air, PANI transforms back to ES again, which causes the resistance of PANI decreased. SnO<sub>2</sub> nanofiber acts as a n-type semiconductor which electron is the majority carrier. At the interface, the electrons of SnO<sub>2</sub> nanofibers recombine with holes in PANI until the p-n junction reaches the equilibrium state. The depletion region is then formed at the interface between the p-type PANI and n-type SnO<sub>2</sub> nanofibers [31,32]. The gas was introduced, NH<sub>3</sub> molecules are adsorbed on the surface of the sensor, based on SnO<sub>2</sub> NFs@ PANI nanocomposite withdrawal of protons from PANI, which leads to a decrease of holes concentration in PANI and the depletion layer at the interface. Thus, the resistance of the SnO<sub>2</sub> NFs@ PANI sensor further increased. Therefore, the formation of the p-n junction structure and the nanostructure of the SnO<sub>2</sub> NFs@ PANI sensor can improve the NH<sub>3</sub> gas sensing performance.

### NH<sub>3</sub> gas sensing performance

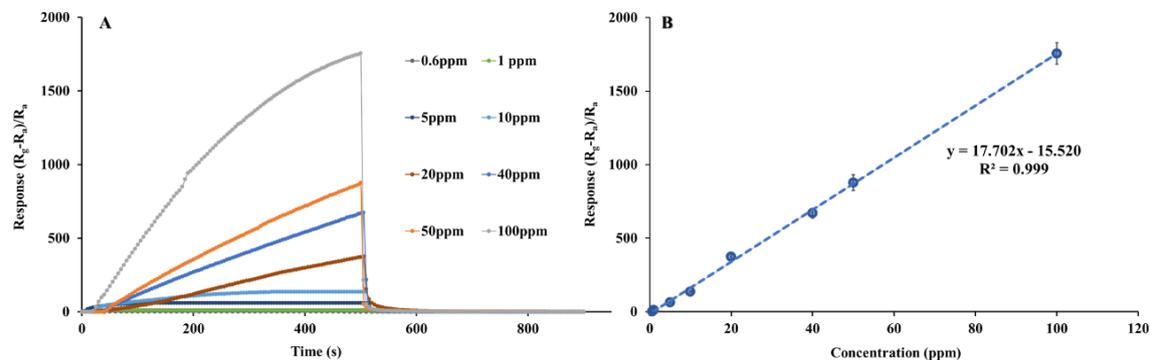
Stability of the fabricated sensor, SnO<sub>2</sub> NFs@PANI casted on SPGE, was examined in terms of inter- and intra-day. **Figure 5A** shows 10 repeatedly measurements of 10 ppm NH<sub>3</sub> gas. Small fluctuated response (SD = 2.11) was observed in the result. The response quickly rose up when the sensor exposed to NH<sub>3</sub> gas and fell back to the initial value when the NH<sub>3</sub> gas was replaced by air. This behavior indicates a typical p-n junction of a semiconductor with excellent reversibility. The same sensor was, further, tested for an inter-day stability. Daily averaged responses of 10 ppm NH<sub>3</sub> gas measurement were plotted in **Figure 5B**. A slightly decrease in the response was found in the first 7 days which could be due to the film aging and disappearance of unstable adsorption sites. After day seventh, a stable response was observed for about 2 months. These results suggest good repeatability and long-term use of the SnO<sub>2</sub> NFs@PANI sensor.

Selectivity against different kinds of gas was evaluated. In compared to NH<sub>3</sub> gas, very low responses to 10 ppm acetone, ethanol, formaldehyde, methanol and toluene gases were detected by the SnO<sub>2</sub> NFs@PANI sensor (**Figure 5C**). This indicates an excellent selectivity of the SnO<sub>2</sub> NFs@PANI sensor toward the NH<sub>3</sub> gas.

Response of the sensor on various NH<sub>3</sub> concentrations was performed and displayed in **Figure 6**. A fine linear relationship between the measured responses and NH<sub>3</sub> concentrations was formed in a range of 0.6 to 100 ppm NH<sub>3</sub> gas, with a good correlation coefficient ( $R^2$ ) of 0.999. The results showed an excellent sensing of the SnO<sub>2</sub> NFs@PANI sensor to wide concentration range (0.6 - 100 ppm) of NH<sub>3</sub> gas.



**Figure 5** A) Ten repeatedly responses of the SnO<sub>2</sub> NFs@PANI sensor to 10 ppm NH<sub>3</sub>, B) Long-term stability of SnO<sub>2</sub> NFs@PANI sensor response to 10 ppm NH<sub>3</sub> at room temperature, C) Selectivity of the SnO<sub>2</sub> NFs@PANI sensor to 10 ppm of various gases.



**Figure 6** A) Dynamic response of the SnO<sub>2</sub> NFs@PANI sensor to 0.6 - 100 ppm of NH<sub>3</sub> at room temperature, B) Response of the SnO<sub>2</sub> NFs@PANI sensor at room temperature as a function of NH<sub>3</sub> concentration.

## Conclusions

In this work, we successfully fabricated an NH<sub>3</sub> sensor based on tin dioxide nanofibers@polyaniline nanocomposite (SnO<sub>2</sub> NFs@PANI) that was prepared by electrospinning, calcination and in-situ chemical polymerization methods. The results showed that the SnO<sub>2</sub> NFs@PANI sensor gave higher response and faster recovery time compared to the pure PANI and PANI/SnO<sub>2</sub> sensing materials. The SnO<sub>2</sub> NFs@PANI casted on the SPGE shows the highest response compared to those casted on ceramic, acrylic and SPCE substrates. The SnO<sub>2</sub> NFs@PANI sensor performance showed great repeatability, good stability, excellent selectivity and exhibited an ability to detect a wide NH<sub>3</sub> concentration range (0.6 - 100 ppm).

## Acknowledgements

This work is financially supported by Electrochemistry and Optical Spectroscopy Center of Excellence (EOSCE), Department of Chemistry, Chulalongkorn University, Bangkok, Thailand.

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