Fabrication of polyaniline coated conductive cotton for ammonia gas detection

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Abstract—Nowadays, ammonia becomes major toxic pollutant. The industrial zones, agricultural zones and mining zones are facing this problem all over the world. Ammonia gives irritating strong smell in the environment and it can affect on the health of human with a long exposure time. Moreover, ammonia is also the biomarker which can indicate the health status of human. For these situations, many ammonia gas sensors are produced. In this work, flexible ammonia gas sensor is prepared based on polyaniline through in-situ polymerization process. We developed a wearable smart textile sensor for ammonia gas detection. 100% cotton which does not irritate the wearer was used for this sensor. The polyaniline-cotton composite was characterized by optical microscope, SEM and FTIR spectroscopy. The morphology of the composites reveal PANI was successfully coated on the cotton. The sensitivity of the gas sensors was monitored directly increasing the concentration of ammonia gas. The resistance changes of the sensors can be seen with increasing the concentration. It could also be proved that the sensor is flexible with bending test. In the future, this flexible PANI-cotton composite sensor can be used for ammonia detection in real applications.

1.Introduction

Ammonia (NH_3) is one of the major toxic pollutants while air pollution is the huge impact on the world today. Ammonia is widely used in chemicals, materials processing, refrigeration and fertilizers etc [1]. In chemical industry, ammonia is used as a main purpose for the production of nitric acid. Because of its ability to cool below 0° C, almost all refrigeration facilities use in mechanical system and food processing make use of ammonia [2,3]. In agriculture sector, farms become to use a lot of fertilizers and animals manures rich of nitrogen based on compounds like ammonia for plant growth and higher yield of fruit and seed production. When fertilizer or manure is spread over the farmland, the smell of ammonia causes the farm very unpleasant smell [4]. Ammonia is the source for ammonium nitrate based on explosives used in mining operations and sodium cyanide (NaCN) used in gold extraction from sulphide ores. On the other hand, creating a safe and cool environment for miners is one of the most important factors. For this reason, ice made by refrigeration is sent down the mine. In that way, the cold melt water is circulated through air cooler and provide cold environment [5].

The long terms exposure of ammonia can cause effect on our eyes, nose, mouth, lungs and throat. Our cardiac system and respiratory system can be damaged by the ammonia in the environment and it might lead to death [6-7]. For dangerous ammonia concentration, a detecting and warning alarm system should be applied in these industries [4].

Ammonia (NH_3) is considered to an important biomarker as it plays a significant role in human body [8,9].

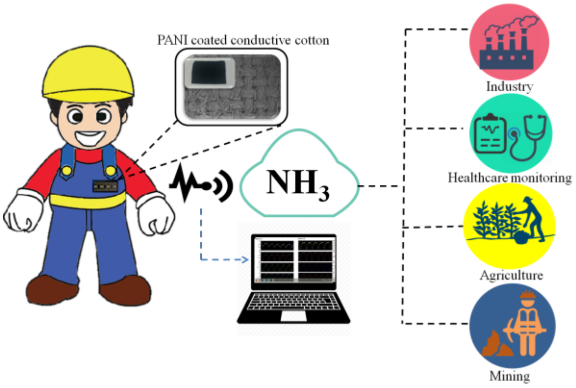

Fig. 1 Schematic diagram of application design for PANI coated conductive cotton as ammonia gas sensor

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Human body excretes ammonia in the form of urea and ammonium salt in urine, some ammonia through sweat glands and breath [10,11]. Patients with kidney failure and ulcers caused by Helicobacter pylori bacterial stomach infection have unbalanced ammonia in their urine and breath [12-14].

In order to detect ammonia (NH_3), sensors with great efficiency and quick response are required. Electronic textiles (e-textiles) can combine the functionality of smart electronic devices with the comfort and the flexibility of stylish clothing [15]. Polyaniline (PANI) is an extraordinary material to work as an active layer in gas sensing applications. Polyaniline (PANI) is the most appropriate conducting polymer for detecting ammonia (NH_3). Polyaniline (PANI) is the most appropriate conducting polymer for detecting ammonia (NH_3), due to its high conductivity, stability, easy synthesis, low cost and high reactivity with gases, such as ammonia [16]. In this work, it aims to fabricate conductive cotton based gas sensor for ammonia detection in industry, agriculture, mining and health care monitoring. Polyaniline (PANI) coated conductive cotton was prepared by in situ polymerization.

2. Experimental

2.1 Reagents and Materials

Aniline hydrochloride 97% was obtained from Aldrich, and used as received. Ammonium peroxy-disulfate, analytical grade, from Ajax Finechem Pty Ltd; was used. Sodium hydroxide (NaOH) was from RCL Labscan Limited. Undyed 100% cotton was employed as substrates in the experiments.

2.2 Preparation of PANI coated conductive cotton

Fig. 2 shows the fabrication of PANI coated conductive cotton. 100% cotton was prepared into five different sample sizes (1cmx1cm, 2cmx2cm, 3cmx3cm, 4cmx4cm and 5cmx5cm). The cotton samples were dipped in aqueous 5 M NaOH solution for 5 minutes for mercerizing, rinsed twice and dried before PANI coating.

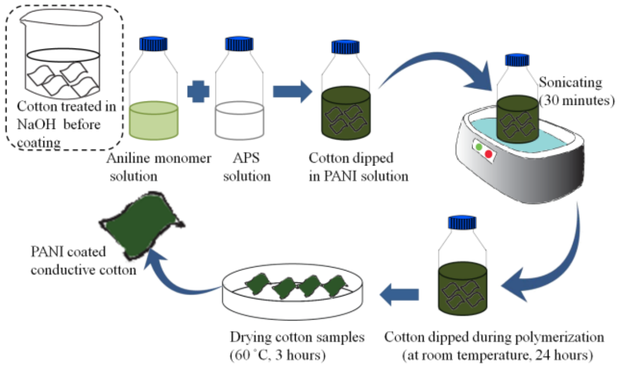

Fig. 2 Schematic diagram shows fabrication of PANI coated conductive cotton

PANI solution is made with monomer/oxidant molar ratio 1:2. Aniline hydrochloride (1.296 g) was dissolved in 50 mL DI water in a flask. Next, ammonium peroxydisulfate (APS) (2.738 g) was dissolved in 50 mL DI water. The solutions were mixed in a bottle and the cotton pieces were immersed in the mixed solution at that time. The mixture was sonicated for 30 minutes and left at room temperature for 24 hours to polymerize. After 24 hours, the cotton pieces were taken out of the solution and dried by heating in the oven at 60 C for 3 hours

3. Results and Discussions

3.1 Optical microscope

Fig. 3 shows optical microscope images of PANI coated cotton with different lengths (1cm-5cm). It can be observed the interlaced structure of warp and weft yarn clearly from the low magnification version of optical microscope images.

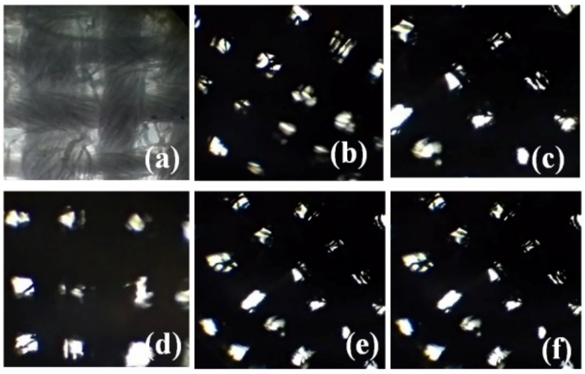

Fig. 3 Optical microscope images of (a) normal cotton and PANI coated conductive cotton (b) 1cmx1cm (c) 2cmx2cm (d) 3cmx3cm (e) 4cmx4cm (f) 5cmx5cm

The deposited PANI causes the white cotton surfaces turned to dark green. Therefore, the polyaniline coated cotton in figure (b) to (f) tends to dark green colour indicating the well dispersion of PANI. It was shown that PANI can be successfully deposited on the cotton surface by in-situ chemical polymerization of aniline. Furthermore, polyaniline deposition process is the convenient way to reduce the surface hairiness of cotton as shown in the optical microscope images of PANI coated conductive cotton.

3.2 Scanning Electron Microscope (SEM)

The SEM images of the PANI coated cotton samples were taken at different magnifications with 100 X (Fig. 4) and 1000 X (Fig. 5). In SEM image of untreated cotton, it shows a very smooth surface. The presence of PANI can clearly be seen on PANI cotton. The non-smooth surface in figures shows evidently that PANI did not cover uniformly. It can still be seen non-uniform PANI coated areas although some areas of the fabric were fully coated. However, PANI perforation in the fabric yarn provided the cotton to be conductive.

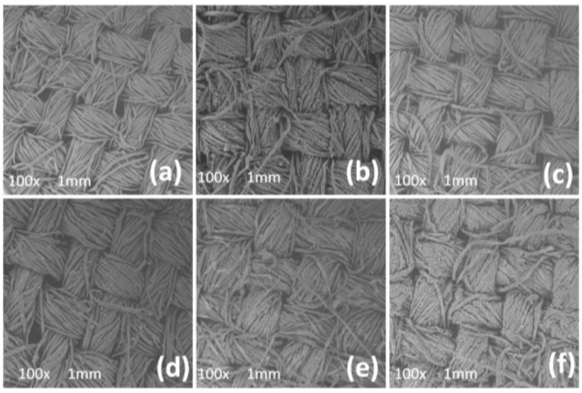

Fig. 4 Scanning Electron Microscope (SEM) images of (a) untreated cotton and PANI coated cotton (b) 1 cmx1cm (c) 2cmx2cm (d) 3cmx3cm (e) 4cmx4cm (f) 5cmx5cm

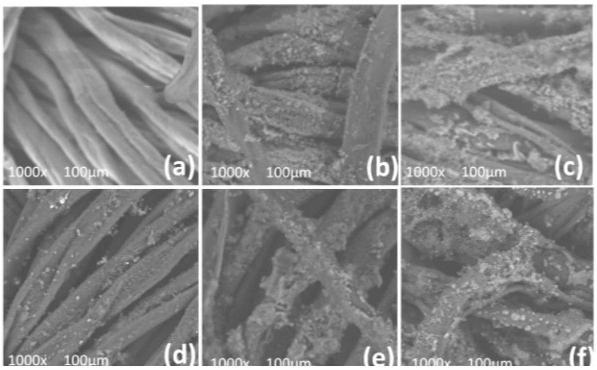

Fig. 5 Scanning Electron Microscope (SEM) images of (a) untreated cotton and PANI coated cotton (b) 1 cmx1cm (c) 2cmx2cm (d) 3cmx3cm (e) 4cmx4cm (f) 5cmx5cm

3.3 FTIR Spectroscopy

The FTIR spectra for untreated cotton and PANI coated cotton with different ranges which were recorded in the range of 400-4000 cm^{-1} are shown in Fig.6. The peak at 3337.4 cm^{-1} in the spectrum of untreated cotton was characteristics of CH_2 antisymmetric stretching vibrations of the secondary CH_2OH groups present in the glucose units of cellulose[17]. At this area of spectra of PANI coated cotton samples, the absence of this peak may be due to the decreasing of secondary CH2OH groups after PANI inclusion. At 2837.4 cm^{-1} of untreated cotton, the peak was CH_2 symmetric stretching band.

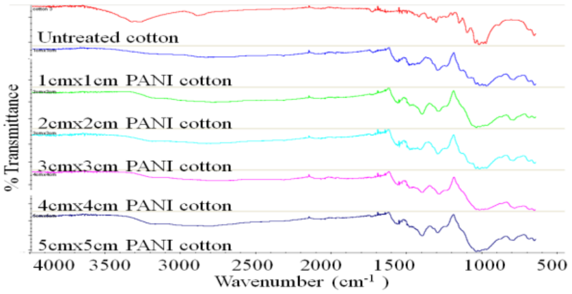

Fig. 6 FTIR spectra of untreated cotton and PANI treated cotton samples

The spectra of the PANI cotton with different ranges were the same as all of the samples were prepared under the same condition. The characteristic of PANI peaks were observed in the spectra of PANI coated cotton. The peak at 1403.9 cm^{-1} was attributed to the C=N stretching modes of quinoid rings and 1305.1 cm^{-1} peak represented to the C-N stretching of benzenoid rings. The N=Q=N stretching of the quinonoid units of PANI was observed at 1148cm^{-1}. This peak was due to electron delocalization. There was still small peaks in the PANI coated cotton spectra. It means that all of CH_2OH groups in the glucose units of cellulose coud not interact completely with conductive PANI.

3.4 Measuring the sensitivity of gas sensors

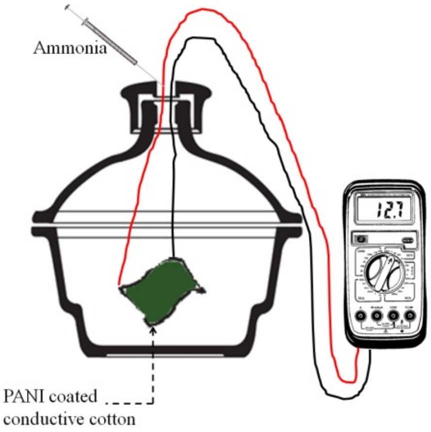

Fig. 7 Schematic measurement system for NH_3 detection

For measuring gas sensors performance, the measurement system for NH_3 gas detection is as shown in Fig. 7 The specially prepared gas chamber (24000 cm3) was used. The PANI coated cotton was put inside the gas chamber and the two edges of the cotton were attached with the clips of digital multimeter. In order to get the desired gas concentration for measuring, the measured amount of ammonia gas was injected with a syringe. The changing resistance values of the PANI coated cotton were monitored continuously using a digital multimeter.

Fig. 8 shows the sensitivity of PANI coated cotton gas sensor to ammonia gas from 25 ppm to 100 ppm. The sensitivity of the composite gas sensor is defined as

$$\% S = [(R - R_0) / R_0] \times 100 \qquad (1)$$

where R and R_0 are the resistances of the sensor after and before VOCs exposure, respectively.

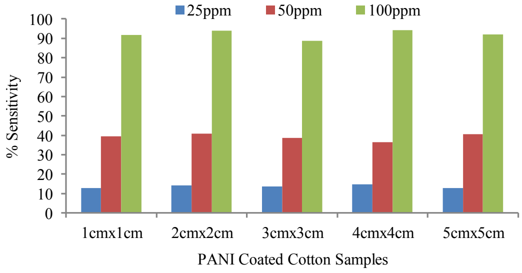

Fig. 8 The sensitivity of PANI coated cotton gas sensor

The results reveal that the resistance values of PANI coated cotton changed according to the concentrations of the ammonia gas. The resistance increased with the increasing concentration (25ppm-100 ppm). However, the length of the cotton cannot affect on the sensitivity of the sensors. There is not too much difference in sensitivity of the PANI cotton with various lengths.

When the ammonia gas passes through the sensor,the interactions between the reactive sites of PANI and ammonia molecules occur. As ammonia has electron donating nature, it accepts hydrogen from PANI backbone and form ammonium ion. So, PANI looses H^+ ion and its electron density increases. In that way, the resistance of the gas sensors become increased.

3.5 Flexibility Experiment

Table I. The resistance of PANI coated cotton gas sensor sample in various condition.

Cotton samples	Initial State	Bending	Normal
1cmx1cm	43 kΩ	40 kΩ	43 kΩ
2cmx2cm	48 kΩ	45 kΩ	48 kΩ
3cmx3cm	24 kΩ	20 kΩ	24 kΩ
4cmx4cm	19 kΩ	16 kΩ	19 kΩ
5cmx5cm	31 kΩ	28 kΩ	31 kΩ

4. CONCLUSIONS

PANI-cotton composite gas sensors have been successfully prepared with in-situ polymerization process. The morphology of the PANI-cotton showed that PANI can be successfully deposited on the cotton. The PANI based gas sensor can be operated efficiently at room temperature to detect ammonia with various concentrations. Varying the length of the cotton cannot affect on the sensing performance of the sensor. We hope that this wearable smart textile sensor will be very useful in real applications of ammonia gas detection in industry, agriculture and mining areas and for providing health status of the patients with kidney failure and stomach infection.

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