Breath acetone sensor for monitoring ketosis based on polyaniline and silver nanoparticles/polyaniline composite

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Abstract

Ketosis is ketone volatile as metabolic product that released from breath. Acetone is majority metabolic product. Breakdown of body fat is main cause of breath acetone concentrations. Therefore, acetone contained in our exhaled breath is expected to be a good indicator of fat-burning. So, we interested in establishing gas sensor using polyaniline (PANI) and silver nanoparticles-polyaniline composite (AgNPs-PANI) and comparing acetone sensing behavior by electronic nose technique. PANI and AgNPs-PANI are prepared by in-situ chemical oxidation polymerization. Silver nanoparticles are synthesized by reduction of silver nitrate ($AgNO_3$) with sodium borohydride ($NaBH_4$). The sensing behaviors of gas sensors are analyzed at room temperature toward 100 ppm of acetone. The AgNPs-PANI film had exhibited better overall acetone sensing behavior in terms of sensing response when compared with pure PANI. Moreover, the sensing response has affected polymer annealing in differ from incubation time. The highest sensing response has exhibited from 12-hour incubating of AgNPs-PANI sensors. In addition, the resistance of AgNPs-PANI sensors had displayed more stable than pure PANI sensors which is important factor to be as a suitable gas sensor material for acetone exhaled breath sensor development and other applications.

Introduction

The number of breath-based tests approved by the US Food and Drug Administration (FDA) has increased over the past decade. It is well known that the endogenous compounds found in human breath, such as inorganic gases and volatile organic compounds[1]. During fasting, the rate of lipolysis increases leading to the breakdown of triglyceride into glycerol and fatty acid by lipase enzyme. Free fatty acids are transferred to liver for digestion called β-oxidation and produce ATP to be the body's energy then gives by-product namely acetyl-CoA. The acetyl-CoA, originated during the fatty acids β-oxidation which is converted to acetoacetate by HMG-CoA synthase enzyme (mHS, EC 4.1.3.5) is a main role in the synthesis of the ketone bodies. Most of acetoacetate is converted into D-ß-hydroxybutyrate by oxidase enzyme and acetone via decarboxylation. Normally, the pathway produced all of ketone bodies called ketogenesis or ketogenic pathway[2-4]. In addition, acetone is a metabolite derived from fat-burning, produced in the blood, that is expelled through alveoli of the lungs during exhalation[5]. Considering that breath acetone could be a good indicator for monitoring fat metabolism[6], extensive previous work has studied the relationships between breath acetone and diabetes, ketogenic meals, exercise, dieting and hemoglobin A1c[7].

Polyaniline (PANI) is unique among conducting polymers in that its electrical properties could be reversibly controlled both by charge transfer doping and by protonation, which makes it a potential material for applications as chemical and biological sensors, actuators, microelectronic devices, etc[8,9]. Among the family of conducting polymers, polyaniline has been most extensively studied due to its good environmental and chemical stability, ease of synthesis and relatively high electrical conductivity[10,11]. The sensing behaviors of the conducting polymers strongly depend upon the analyte properties and polymer microstructure. The conductivity of PANI could reversibly be controlled by the protonation of the imine sites and the oxidation of the main polymer chain[12].

In the recent years, studies on the synthesis of conducting PANI/metal composite have received great attention due to their enhanced sensing and catalytic capabilities, as compared with those of pure PANI[13]. These properties are very much sensitive to small changes in the metal content and in the size and shape of the nanoparticles[14,15]. The AgNPs-PANI composite nanotubes appear to have better performance in both sensitivity and time response to NH3 gas in comparison with conventional PANI[16,17]. Therefore, it is hopeful to obtain AgNPs-PANI based acetone sensing materials with excellent gas-sensing behaviors.

Methodology

Synthesis of AgNPs-PANI nanocomposites

Silver nanoparticles were synthesized by chemical reduction of silver cations using sodium borohydride. A 10-mL volume of 1.0 mM silver nitrate was added dropwise (about 1 drop second) to 30 mL of 2.0 mM sodium borohydride solution that had been chilled in an ice bath. The reaction mixture was stirred vigorously on a magnetic stir plate. The solution turned light yellow after the addition of silver nitrate[18]. The AgNPs-PANI nanocomposite was prepared by *in-situ* oxidative polymerization of aniline monomer in the presence of silver nanoparticle colloidal solution. In a typical synthesis process[19], 2.59 g of aniline hydrochloride was added to the prepared silver nanoparticles. The aqueous solution of 5.71 g ammonium persulfate was added to the above mixture. The reaction was allowed to continue for 12 hours under constant stirring at 1–2 °C. The resultant product was filtered and washed with DI water and methanol and then dried in vacuum for overnight. The pure PANI was synthesized using same chemical polymerization method as described above in the absence of silver colloid. Silver nanoparticles were characterized by UV-vis spectroscopy.

Fabrication of PANI and AgNPs-PANI based sensor

7 mg of PANI or AgNPs-PANI nanocomposites were dissolved in 1 mL of tetrahydrofuran (THF) and then material solutions were sonicated for 15 minutes to obtain the homogeneous solution of mixture. The films of these solutions were spin coated layer-by-layer (LbL) at 1500 rpm on micro-gap interdigitated electrode. The films are spin-coated in order to obtain a measurable resistance. After the coating of the polymer films, they were kept at 80 °C for 3 hours and 12 hours to remove moisture and THF solvent. The heating temperature is selected after a careful examination of the respective material properties of THF and PANI. The films were measured resistance after incubation again, the electrical resistivity was approximately 1-35 kΩ in order to act as a gas sensor array for gas sensing analysis and this electrical resistance is suitable range using by our electronic nose system. Nanocomposite materials act as electrical pathways. Changes in electrical resistance of these gas sensors depends on the physical and chemical adsorption of the volatile compounds onto/into the polymer composite film, causing them to swell and change in the electrical resistance.

Gas Sensing Measurement

The gas sensitivity of pure PANI and AgNPs-PANI nanocomposite sensors was evaluated by dynamic measurement using electronic nose systems. The method of dynamic measurement act as a working system of artificial nose is mimicked by switching the flow of reference gas and the sample gas into a pocket of the gas sensors as well as it can select the cycle number of measurement. In this set-up, the reference gas and sample gas have been stored and allowed to flow from two separate bottles. Ambient air is used as reference gas. The flow rate of ambient air was 40 mL/min. The responses of the sensor are presented in terms of R_r (%), R_r was calculated as percentage change in electrical resistance where R_f and R_i denote the resistance of the sensor measured in presence of acetone and ambient air, respectively.

$$R_r (\%) = [(R_f - R_i)/R_i] \times 100 = (\Delta R/R_i) \times 100 \qquad (1)$$

This experiment examines sensing response comparison between pure PANI and AgNPs-PANI sensors over acetone gas. The effect of incubation time in sensor fabrication process was investigated that we studied at 80 °C for 3 hours and 12 hours as well as interested the sensing response of gas sensor when odor in different concentrations of acetone (viz., 100, 300 and 500 ppm). Electronic nose system is acquired via a DAQ card USB which recorded the change of electrical resistances in real time and visualized it on a computer screen via a user interface software programmed under LabVIEW program.

Results and Discussion

UV-vis spectroscopy was used to confirm silver nanoparticles formation. Fig. 1A, demonstrated clear yellow solution of synthesized AgNPs by silver nitrate and sodium borohydride. The UV-vis absorption spectra were recorded in the range of 300 to 700 nm. As shown in Fig. 1B, the absorption spectra of AgNPs solution exhibited a maximum absorption band around 422 nm, which is a characteristic plasmon resonance band for silver nanoparticles. The results indicated the formation of silver nanoparticles prepared with sodium borohydride as a reducing agent.
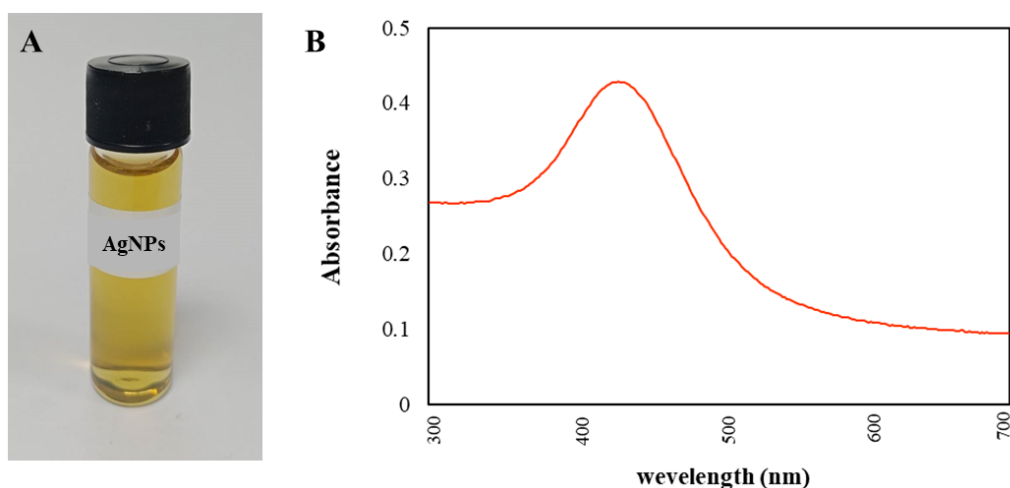
**Figure 1.** (A) Colloidal silver and (B) UV–vis absorption spectra of AgNPs.

In order to characterize real time electrical phenomenon of PANI and PANI composite by electronic nose system. The change of electrical resistances in real time via a user interface was recorded while the set-up measurement is switching the flow of ambient air and acetone gas into a pocket of the gas sensors. Changing in electrical resistance of gas sensors depends on the physical and chemical adsorption of the volatile compounds onto/into the polymer

composite film, causing them to swell and change in the electrical resistance. As shown in Fig. 2, the result indicated that increase of resistance when exposed to 100 ppm of acetone gas and then switch flow to ambient air showed slight steady electrical resistance until became to acetone was injected again. Electrical resistance of ambient air after acetone exposure was not return to baseline but exhibited slight steady. From this result lead to calculation method of sensing response when has more than one of cycle measurement, the resistance of the sensor measured in presence of ambient (R_i) should be use previous cycle resistance before switch flow to sample gas.
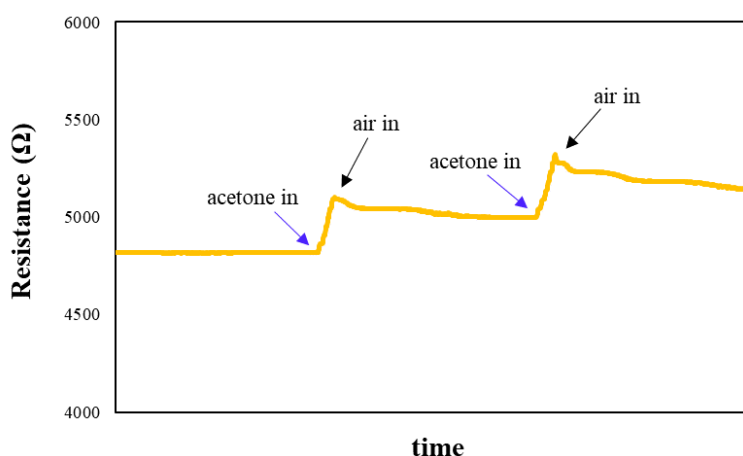

Figure 2. Electrical resistance of PANI sensor upon exposure 100 ppm of acetone.

In order to achieve sensing response efficiently of AgNPs-PANI composite sensor. The effect of incubation time on sensor fabrication was studied to optimize time for removing moisture and THF solvent. The sensing response (R_r) of pure PANI and AgNPs-PANI which both types of nanomaterial were incubated at 80 °C for 3 and 12 hours. Sensing response were calculated while the sensing material exposed to 1,000 ppm of acetone certain in 0.5 L of bottle and the measurement was conducted for 3 cycles. Fig. 3 showed sensing response of pure PANI and AgNPs-PANI sensor as well as exhibited of total number cycle measurement. The results showed highest sensing response in first cycle all of sensor types however 12 hours incubated AgNPs-PANI sensor displayed highest sensing response was 22.48% at first cycle of measurement and exhibited decrease slightly of 3 hours incubated AgNPs-PANI sensor, 12 hours and 3 hours incubated pure PANI sensor, respectively. Moreover, pure PANI sensor had no stable of electrical resistance property both of 3 and 12 hours incubation lead to these sensors were ineffective to allow as a suitable gas sensor characteristic (data not show).
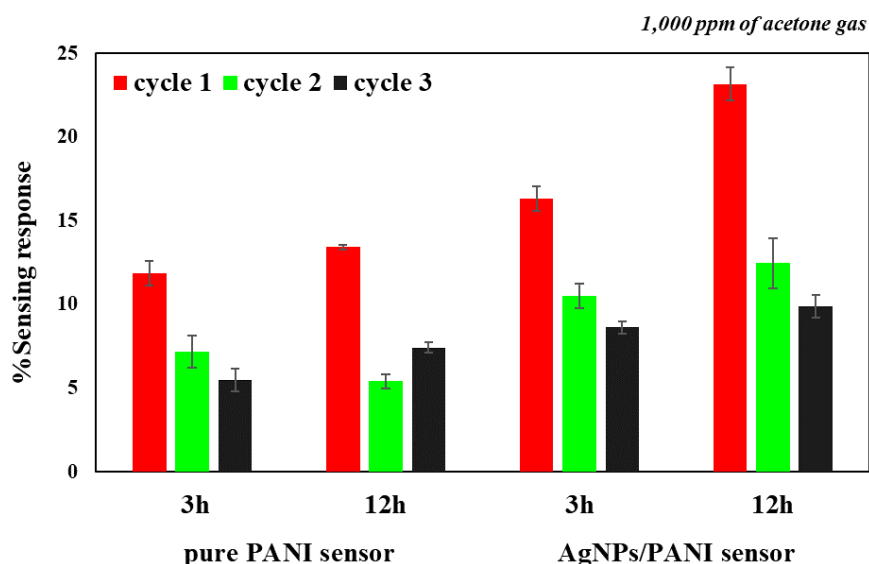
Figure 3. Sensing response of pure PANI and AgNPs-PANI sensors all of 3 number cycle over 1,000 ppm of acetone.

Therefore, AgNPs-PANI sensors were kept for 3 and 12 hours incubation were selected to determine sensing response against different concentrations of acetone (viz., 100, 300 and 500 ppm). As the result Fig. 4 showed increase of sensing response in both types of AgNPs-PANI sensors while concentration of acetone was increasing. In addition, these sensors exhibited higher sensing response of 12 hours than 3 hours incubation. Thereby, the sensing response has affected polymer annealing in differ incubation time.
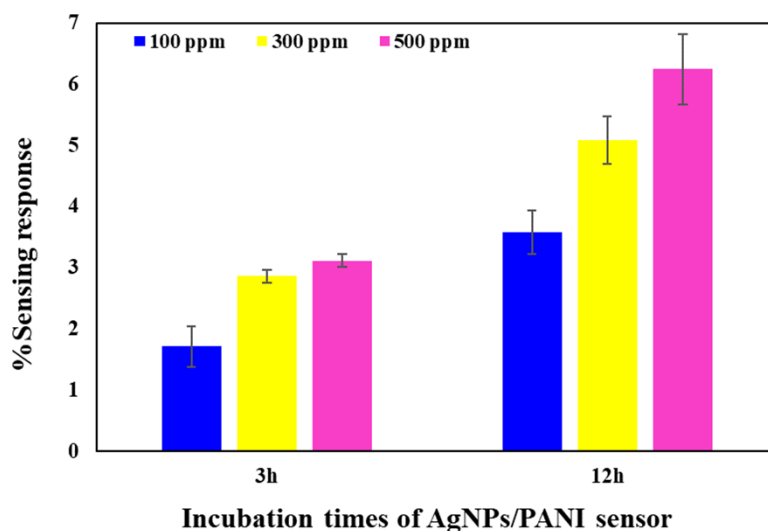
Figure 4. The sensing response of 3 hours and 12 hours incubated AgNPs-PANI sensor against 100, 300 and 500 ppm of acetone.

Conclusion

The AgNPs-PANI composite sensor exhibited better overall acetone sensing behavior in terms of sensing response when compared with pure PANI. The sensing response has affected polymer annealing in differ from incubation time. The highest sensing response has exhibited from 12-hour incubating of AgNPs-PANI sensors. In addition, the resistance of AgNPs-PANI sensors had displayed more stable than pure PANI sensors which is important factor to be as a suitable gas sensor material for acetone exhaled breath sensor development and other applications.

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