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On the sensitivity of conductimetric acetone gas sensor based on polypyrrole and polyaniline conducting polymers

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ABSTRACT

Polypyrrole (PPy) and polyaniline (PANi) synthesized onto the Au/Al_2O_3 by chemical oxidation-casting (COC), chemical vapor deposition (CVD) and impregnated oxidation (IO) techniques are employed to monitor the level of acetone in gas phase. With PPy prepared by CVD (PPy(CVD)) as the sensing material, the sensitivity of acetone gas sensor is found to be 5.20×10^{-7} ppm^{-1}. The sensitivity of acetone gas sensor based on PANi is greater than that of PPy. The maximum sensitivity and minimum response time are obtained for PANi prepared by IO technique. With PANi(IO)/Au/Al_2O_3 as the sensing electrode, the sensitivity, response and recovery times of acetone gas sensor are 5.908×10^{-4} ppm^{-1}, 1.0–3.0 and 3.0–10.0 min, respectively. The detection limit of acetone gas sensor based on PANi(IO) is 29 ppm.

1. Introduction

Acetone has been widely applied in medical, pesticide and paint industries, and used as solvent, reagent, and extractant. When emitted, it is harmful to the environment and humans. Slight irritation of noses, throats, lungs and eyes in the presence of 300–500 ppm acetone has been reported. Human exposed to 2000 ppm acetone environment suffer nausea and vomiting symptoms [1]. Acetone is also a flammable gas with lower explosive limit (LEL) and upper explosive limit (UEL) of 2.6 and 12.8%, respectively. Hence, analyzing the concentration of acetone in the environment is very important to our health and industrial safety. Furthermore, many diseases are accompanied with characteristic components in the patient's breath [2]. The level of acetone in normal human breath is in the range of 10–50 ppm. However, the concentration of acetone in a diabetic patient's breath is increased to 50–400 ppm [3–5]. The analysis of acetone concentration in the breath has great potential for non-invasive diagnosis of the diabetic state [6].

Usually, semiconductors are used as the sensing materials for conductimetric acetone gas sensors. In general, the n-type semiconductors used for detecting the level of acetone are metal oxides, such as ZnO [7,8], TiO_2 [9], SnO_2 [10], and WO_3 [1]. If the reducing (oxidizing) substances are adsorbed and reacted with the n-type sensing semiconductors, the conductivity will be increased (decreased). On the other hand, the conductivity is increased (decreased) when the oxidizing (reducing) substances are adsorbed and reacted with the p-type sensing materials. For sensing acetone, the main p-type sensing materials are conducting polymers, such as polypyrrole (PPy) [11–21], polyaniline (PANi) [16,21,22], poly-N-methylpyrrole [16], poly-5-carboxyindole [16], poly(p-xylylene) (PPX) [23], and functionalized ferrocenecarboxymethylated polymers [24]. Polypyrrole (PPy) prepared by the chemical oxidation method and then casted onto the Pt–Pd alloy/Al_2O_3 is used as sensing electrode to monitoring acetone [17]. PPy/Pt–Pd interdigitated electrode prepared by the chemical vapor deposition (CVD) method is used to sensing methanol [19]. Acetone, ethyl acetate, methanol and ethanol are detected based on PPy/Au/inert substrate prepared by CVD method [20]. The study on the effect of doping anions on the sensing properties of PPy composite polymers found that composite materials doped with α-naphthalene sulfonic ion (α-NS^-) have maximum sensitivity [13]. The dopants and doping level can affect the surface morphologies, chemical/physical properties, surface energy and crystallinity [13,25,26]. Hence the electrical conductivity is affect by the dopants and doping level. Four kinds of conducting polymers (PPy, PANi, poly-N-methylpyrrole and poly-5-coboxyindole) prepared on the Au microelectrode are employed to detect five volatile organic gases, namely methanol, ethanol, acetone, ether and toluene [16]. The PPy sensor array with various thicknesses is used to detect diabetic patient's breath in terms of principal component analysis (PCA) method [17]. Four kinds of ferrocenecarboxymethylated polymers are used for conductimetric monitoring methanol and acetone

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vapors, and the structural effect on electrical properties is also investigated [24]. However, the effects of conducting polymers prepared with various techniques on acetone-sensing characteristics are seldom reported in the literature.

PPy- and PANi-conducting polymers synthesized onto interdigitated and four-electrode Au/Al_2O_3 electrodes by chemical oxidation-casting (COC), chemical vapor deposition (CVD) and impregnated oxidation (IO) techniques are utilized to monitor the level of acetone in the gas phase. The surface morphologies of the conducting polymers and the sensing properties for detecting acetone are systematically investigated.

2. Experimental

2.1. Preparation of Au/Al_2O_3 electrodes

The alumina plate was first immersed and washed with 3.0 M NaOH aqueous solution in an ultrasonic bath for 30 min, and then flushed several times with deionized (DI) water. Then it was washed with 3.0 M HCl aqueous solution, flushed again several times with DI water, and finally, dried in a 70 °C oven. The interdigitated (ID) and four-electrode (FE) Au patterns were sputtered on the alumina plate in terms of shadow masks for preparing Au(ID)/Al_2O_3 and Au(FE)/Al_2O_3-based electrodes. The ID electrode was designed with six teeth and each tooth with size of 10 mm × 1 mm. The size of each electrode of the FE was designed to be 12 mm × 1 mm.

2.2. Preparation of PPy(COC)/Au/Al_2O_3 electrode

First, 30 ml 0.263 M ammonium persulphate ($(NH_4)_2S_2O_8$) (APS) aqueous solution was slowly added into 40 ml 0.7 M pyrrole and 0.7 M α-naphthalene sulfonic acid (α-NSA) aqueous solution, and stirred with 600 rpm at 0 °C for 12 h. PPy powder (doped with α-NS^- and $SO_4{}^{2-}$) obtained by filtrating the reaction solution was washed several times with 50 ml DI water and 50 ml methanol in series till the neutral aqueous filtrate was obtained. The as-prepared PPy powder was dried in a 30 °C vacuum oven for 48 h, and then undoped by immersing in 1.0 M NH_4OH aqueous solution for 48 h. Finally, PPy powder doped with α-NS^- was obtained by immersing the undoped PPy into α-NSA solution for 48 h.

Then, 0.2 g PPy powder (doped with α-NS^-) was added into 4.0 ml toluene and agitated in an ultrasonic bath for 30 min. The PPy(COC)/Au/Al_2O_3 electrode was obtained by casting 15 μl PPy toluene slurry onto the as-prepared Au/Al_2O_2 electrode, and then dried in a room-temperature vacuum oven.

2.3. Preparation of PPy(CVD)/Au/Al_2O_3 electrode

The Au(ID)/Al_2O_3 electrode was immersed in 0.1 M $FeCl_3$ aqueous solution for 1 h, and then dried at room temperature. The $FeCl_3$/Au(ID)/Al_2O_3 electrode was put faced down and covered on the top of a beaker containing a suitable amount of PPy toluene solution (v/v ratio of 1/1), which was stirred with a magnetic bar at room temperature. When the evaporated PPy vapor contacted with $FeCl_3$ (oxidant) on the electrode surface, PPy film was formed on the surface of Au(ID)/Al_2O_3. The procedure was repeated several times to obtain a desired thickness of PPy film, and then the PPy(CVD)/Au(ID)/Al_2O_3 (PPy(VD)-ID) electrode was washed with DI water to remove the residual $FeCl_3$ and PPy monomer.

2.4. Preparation of PANi–PMMA(COC)/Au/Al_2O_3 and PANi(IO)/Au/Al_2O_3 electrodes

First, 200 ml 1.0 M $HClO_4$ and 0.75 M APS aqueous solution was slowly added into 209.3 ml 0.48 M aniline aqueous solution sparged with N_2, and stirred at 5 °C for 2 h with 600 rpm. By filtrating the reaction solution, the obtained PANi powder doped with $ClO_4{}^-$ and $SO_4{}^{2-}$ was washed several times with DI water. The as-prepared PANi was dried in a 50 °C vacuum oven for 48 h. The procedures for undoping and doping with the other anions of PANi were the same as those for PPy as described above.

Then, 0.2 g as-prepared PANi powder was added into 4.0 ml NMP (n-methyl-2-pyrrolidone) containing 0.238 g PMMA (polymethylmethacrylate) as binder, and ultrasonically agitated for 60 min to prepare the PANi slurry. The PANi–PMMA (COC)/Au(ID)/Al_2O_3 (PANi–PMMA(COC)-ID) electrode was prepared by casting 15 μl PANi slurry onto the Au(ID)/Al_2O_3 electrode, followed by drying in a 50 °C vacuum oven for 24 h.

The Au(ID)/Al_2O_3 electrode was vertically immersed into a 25 ml 0.25 M aniline and 1.0 M HCl aqueous solution, which was agitated with 150 rpm at 5 °C. Then 25 ml 0.375 M ASP aqueous solution was added drop by drop, and agitated for 1 h to prepare the PANi(IO)/Au(ID)/Al_2O_3 (PANi(IO)-ID) electrode. The as-prepared PANi(IO)-ID electrode was washed several times with DI water and dried in a 50 °C vacuum oven.

2.5. Characterization of sensing electrodes

The surface morphologies and the functional groups of the conducting polymers on the sensing electrodes were analyzed by scanning electron microscope (SEM) (JEOL JSM 5400) and Fourier transform infrared spectrometer (FTIR) (Bio-Rad FTS-40 with resolution of 0.5 cm^{-1}), respectively.

The home-made sensing electrode was placed in a gas chamber and sealed with two PMMA plates by four screws as indicated in Fig. 1. The distance between the gas inlet tube and the electrode surface was kept at 1.0 cm. A desired flow rate of N_2 was introduced through three Erlenmeyer flasks loaded with acetone in series to ensure saturation of acetone in N_2 gas stream. The desired concentration of acetone was obtained by diluting the saturated acetone gas stream with a suitable N_2 gas flow rate using a mass flow rate control system. By setting a constant current to the sensing electrode, the resistances of the sensing electrode were calculated according to the response voltages for various sensing conditions.

Using PPy and PANi prepared with various techniques as the sensing materials, the potential drops and the resistances between electrodes were measured under the constant DC applied current. The ratio of change in the resistance (response, S) of sensing materials under a certain acetone level relative to the resistance in the absence of acetone was defined as

$$S = \frac{R_a - R_0}{R_0} \tag{1}$$

where R_a and R_0 were the resistances of sensing materials at a certain level of acetone and at the background gas environment (in the absence of acetone), respectively. The resistances of the sensing electrodes measured in the sensing procedures were located in the range of 10–100 Ω. The response time (t_{90}) and the recovery time (t_{10}) were defined as the time for reaching 90% equilibrium response and 10% background signal, respectively. The sensitivity (ppm^{-1}) of the acetone gas sensor was defined as the slope of the response S against the concentration of acetone.

3. Results and discussion

3.1. Surface morphologies of conducting polymers

The texture of the substrate (alumina plate) (Fig. 2(a)) reserved in the surface morphology of PPy (CVD)-ID electrode (Fig. 2(b)) indicated that a thin PPy film was obtained by using CVD technique. A thin nano-sized PPy fibrillar structure was covered on the granular structure of alumina substrate. On the other hand, the granular