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A novel ammonia sensor based on high density, small diameter polypyrrole nanowire arrays

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ABSTRACT

A novel sensor based on the PPy nanowire arrays with high density, small diameter (about 50 nm) presented a significantly high surface-to-volume ratio. Conducting polypyrrole (PPy) nanowire arrays were synthesized by electropolymerization in the anodic aluminum oxide (AAO) template which was fabricated by two-step anodizing process. Then, two sides of the PPys/AAO were pasted by Si substrates and the AAO template was etched by HF acid. At last, the gold wires were attached on Si substrates, and the sensor came into being. The sensor was sensitive to ammonia at room temperature and showed relatively high response in low concentration and comparatively short response and recovery time.

1. Introduction

Over the last few decades, conducting conjugated polymers such as polythiophene, polyaniline, and polypyrrole (PPy) which have π-conjugated carbon chains have been investigated intensely, especially on their gas sensing properties. On the one hand, they have many excellent properties such as electrochemical reversibility, relatively environmental stability, high conductivity, good mechanical performance and ease preparation through chemical [1] and electrochemical [2–6] methods; on the other hand, they possess advantages in comparison to metal-oxide gas sensors due to its capability to operate at room temperature [7]. PPy behaves like p-type semiconductors via appropriate doping [8] and can arouse the change of conductivity through interaction with gas or vapor [9–11]. PPys can be used in biosensors, drug delivery [12,13] and chemical sensors. The chemical sensors based on PPy have sensitive properties to many gases such as ammonia, ethanol, methanol, acetone, NO_x, HCl, and volatile aromatic hydrocarbons [8,14–23]. Among these gases, ammonia is a poisonous, colorless one with a pungent smell, which is harmful to our health. The detection of ammonia is of interest in industrial processes and environmental monitoring [24]. It is necessary to develop sensors to detect ammonia rapidly at low concentrations.

To improve the stability, sensitivity and response time of the sensors, PPys composited with different dopants were synthesized [18,21,25–27]. For sensitivity, however, it may be more significant to increase the effective surface area of the polymer because of their poor diffusions of the analyte molecules to the bulk of the polymer. So, Hernandez et al. fabricated a gas sensor based on single PPy nanowire [25]. Reports also showed the sensitivity, to a certain extent, was dependent on the diameter of the one-dimension nanomaterial [9,28]. However, the diameter of the PPy nanowire used as gas sensor is often over hundreds of nanometers. Small diameter and high density PPy nanowire arrays will present a significantly high surface-to-volume ratio which will result in high sensitivity [29,30].

Template-based synthesis method has some special properties, e.g. uniform dimension, high density, high aspect ratio and controllable diameter [31]. That is because the porous AAO template possesses regular, uniform and diameter controllable cylindrical nano-pores [32]. In this paper, PPy nanowire arrays have been synthesized in AAO templates by electrochemical polymerization which is an easy, fast, and green method [4,33]. After depositing a thin layer of Au on the thin PPy film, the two sides of PPys/AAO were pasted with Si substrates and the AAO template was etched by HF acid. At last, the gold wires were attached on the Si substrates. The sensor was sensitive to ammonia at room temperature and showed

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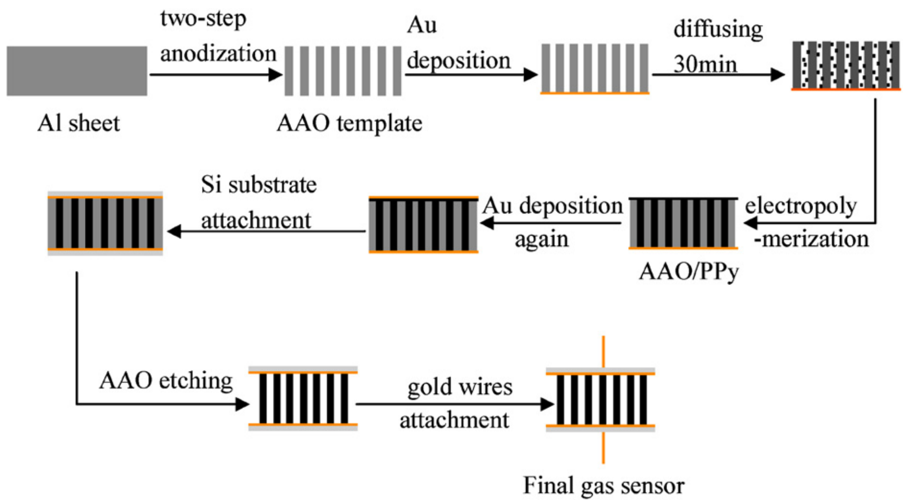

Fig. 1. Schematic diagram of the PPy array sensor fabrication process.

relatively high response in low concentration and comparatively short response and recovery time.

2. Experimental

2.1. Preparation of nanoporous AAO template

Nanoporous alumina templates with pore diameters about 50–80 nm were prepared by a two-step anodizing process [34]. Highly pure aluminum sheet (99.99%) was degreased under ultrasonication by acetone, distilled water and anhydrous ethanol, respectively, following annealed at 500 °C in N_2 gas atmosphere for 5 h. Then the sheet was electropolished under the constant voltage of dc 10 V in a mixture of anhydrous ethanol and $HClO_4$ (9:1 in v/v) until a mirror shining surface appeared. The aluminum sheets were firstly anodized at constant potential of 40 V using platinum foil as a counter electrode in 0.3 M $H_2C_2O_4$ solution for 4 h and then moved into H_3PO_4 (6%) and H_2CrO_4 (1.8 wt%) solution at 60 °C for 6 h to dissolve the oxide membrane. After washed by distilled water several times, the Al sheets were anodized again in the same anodizing conditions for 12 h. Then the backside of Al layer was removed via a reaction with a saturated $SnCl_4$ solution. The barrier layer at the bottom of the AAO membrane was removed by placing the sample in 6% H_3PO_4 until the barrier layer was dissolved. After washing and drying, the AAO template with nano-pores was obtained.

2.2. Preparation of PPy nanowire arrays and the fabrication of gas sensor

The schematic diagram of fabrication process of nanowire array sensor, gold layer and silicon substrate outside is illustrated in Fig. 1. Electrochemical polymerization of pyrrole was carried out in a one-compartment cell at room working temperature by the use of a Model LK2005 electrochemistry workstation. Briefly, one planar surface side of the AAO template with nano-pores was firstly deposited a thin layer of Au (about 25 nm), and then contacted to copper to serve as working electrode during the electrodeposition. A Pt plate was used as counter electrode and Ag/AgCl (KCl saturation solution) electrode as reference electrode. The template was immersed in the solution which contains 0.55 M pyrrole monomer and 1.1 M $LiClO_4$ for 30 min before electropolymerization, allowing the monomer to diffuse into the template pores. The PPy nanostructure was obtained by potentiostatically polymerizing in the pores of the AAO template at 1.0 V vs. Ag/AgCl for about 650 s and a thin film of PPy formed. The sample was cleaned by distilled water and anhydrous ethanol and then dried in air.

The gas sensor was fabricated as follows: thin layer (about 25 nm) of Au was sputter-deposited onto the thin film of PPy which was synthesized in nano-pores in order to increase the electrical conductivity and strengthen the device. Then the two sides of template were attached to the silicon substrates with silver glue and heated at 180 °C for 20 min to get the silicon fastened. After that, the array device was dipped into 10% HF at room temperature. Following that, the gold wires were fixed onto silicon substrates using the same method. Finally the gold wires were soldered on the electrodes by indium. Then the PPy nanowire arrays were fabricated. With prolonged electrochemical polymerization time, PPy could deposit not only inside but also outside of the pores of AAO, offering the possibility of making the electric contact with a conducting tip from external power supply circuit and improving the fastness of the structure of sensor.

2.3. Characterization of PPy nanowires

The morphologies of PPy nanowires were investigated by a field emission scanning electron microscope (FEI Quanta 200 FEG). The FTIR (NICOLET IS10, America) spectra of the PPy nanowires were measured in KBr discs.

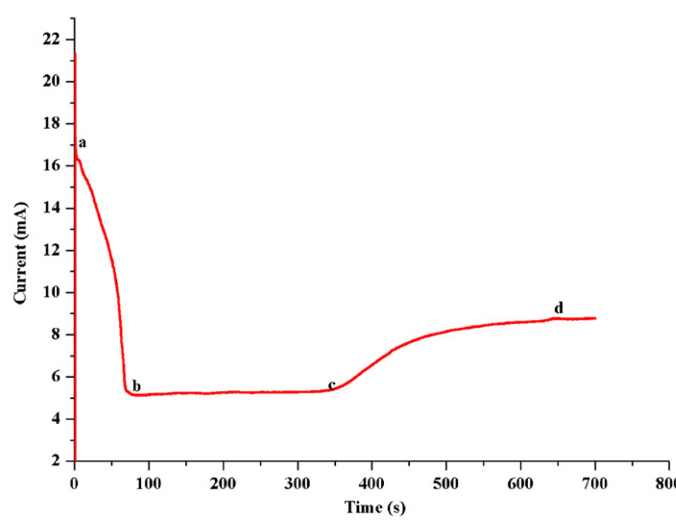

Fig. 2. Current–time curve of PPy synthesized at 1.0 V vs. Ag/AgCl in 0.5 M pyrrole + 0.2 M $LiClO_4$.