Freestanding flexible polypyrrole nanotube membrane for ammonia sensor

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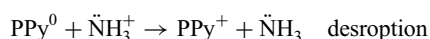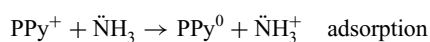✉ *E-mail: csufangdong@gmail.com; liyg2010@wtu.edu.cn*

A simple self-sacrificed template method was used to prepare a polypyrrole (PPy) nanotubes sensor for the detection of ammonia (NH_3). Scanning electron microscopy (SEM) and transmission electron microscopy (TEM) were used to analyse the morphology of the fabricated membrane. The results show that pyrrole was uniformly polymerised around the sodium vanadate ($Na_5V_{12}O_{32}$) nanowires, and the $Na_5V_{12}O_{32}$ nanowires along with Ti foil were subsequently dissolved thoroughly with citric acid (0.5 M) and hydrofluoric acid (10%, v/v) to obtain a freestanding flexible PPy nanotube membrane. The resulting PPy membrane was sensitive to NH_3 and exhibited rapid and reproducible response at room temperature.

1. Introduction: Environmental contamination has greatly increased due to modern industrialised society. In most industrially developed countries, strict ambient air quality standards for toxic gases have been established. Increasing industrialisation makes it necessary to constantly monitor and control contaminations in the environment. To protect the environment and to prevent humans from being harmed, the detection of toxic gas has become increasingly important. For this reason, much recent effort has been devoted to the development of gas sensors [1–4] with widespread applications in physical and chemical analysis, gas detection and environmental monitoring. Effective sensors should be highly sensitive, stable and disposable and there is a need for novel materials for use in improved gas sensors.

Conducting polymers have been tested for function as a gas sensor, and allow room temperature operation, low cost, flexibility and easy processability [5–9]. Among various conducting polymers, polypyrrole (PPy) has attracted much particular interest for use in gas sensing because of its good environmental stability, lightweight, chemically tunable properties and easy synthesis [10, 11]. Chemical sensors based on PPy have sensitivity to many gases such as ammonia (NH_3), ethanol, methanol, acetone, NO_x, HCl and volatile aromatic hydrocarbons [12–14]. Among these gases, NH_3 is detrimental to human health, poisonous, colourless, and has a pungent smell. PPy sensors have been developed and tested for ability to detect the NH_3. The contact of NH_3 with PPy will result in the decrease the charge-carrier concentration of the polymer and the formation of neutral polymer backbones. After the removal of NH_3, the PPy will return to its original state [11, 15]. Su *et al.* [15] used the in situ self-assembly of PPy on plastic substrates to form a novel flexible NH_3 sensor that exhibited a strong response to NH_3. Similar results also have been reported by Sandra *et al.* [12] and Carquigny *et al.* [16]. The following reactions are possibly involved in the NH_3 sensing process [17]:

$$PPy^+ + \ddot{N}H_3 \rightarrow PPy^0 + \ddot{N}H_3^+ \quad \text{adsorption}$$
$$PPy^0 + \ddot{N}H_3^+ \rightarrow PPy^+ + \ddot{N}H_3 \quad \text{desroption}$$

Although the basic gas-sensing mechanism (adsorption and desorption of gas molecules) remains the same, compared to the conventional sensors based on flat films, one-dimensional gas sensors (with high surface-to-volume ratio) and exhibit many inspiring characteristics [18]: (i) ultra sensitivity and fast response time, (ii) higher selectivity and stability, (iii) light weight, and (iv) low-temperature operations. Due to these advantages, there is intensive interest in the development of one-dimensional gas sensors. To fabricate one-dimensional PPy (nanowires or nanotubes), Zhang *et al.* [14] used an electropolymerisation method and anodic aluminium oxide as the template. PPy nanowires can also be synthesised through template-free electropolymerisation [19].

In this Letter, PPy nanotubes were synthesised on sodium vanadate ($Na_5V_{12}O_{32}$) nanowire templates by electrochemical polymerisation, an easy, fast, and green method. After depositing a thin PPy layer, the Ti foil substrate and the $Na_5V_{12}O_{32}$ nanowires template were etched by hydrofluoric (HF) acid and citric acid. Finally, the achieved PPy nanotube membrane sensor was sensitive to NH_3 at room temperature and showed relatively high response at low concentration with a comparatively short response and recovery time.

2. Experimental

2.1. Preparation of $Na_5V_{12}O_{32}$ nanowires: All reagents were analytical-reagent grade and used without further purification. In a typical preparation, NH_4VO_3 and NaCl (molar ratio of 1 : 6) were dissolved in deionised water under room temperature [20]. Next, the homogeneous solution was transferred into stainless steel autoclave. Then a piece of Ti foil was put into the solution described above. The hydrothermal reactions were carried out at 150°C for 1 h. After that, the autoclave naturally cooled to room temperature, and the Ti foil was washed with deionised water and dried at 80°C in air for 12 h.

2.2. Preparation of PPy hollow nanotube membrane: The $Na_5V_{12}O_{32}$@PPy nanocomposite nanowires were prepared through the polymerisation of pyrrole (Py) on the $Na_5V_{12}O_{32}$ nanowires surface by electrodeposition method in a three-electrode system. In brief, the electrodeposition solution contains 0.01 M of pyrrole monomer (Py), 0.01 M sodium dodecylbenzenesulfonate and 0.01 M NaCl. The electrochemical deposition was carried out between 0.2 and 0.7 V with a scanning rate of 1 mV s^{-1} by cyclic voltammetry. After electrodeposition, the as-prepared $Na_5V_{12}O_{32}$@PPy nanocomposite was washed with water and

acetone [20]. The PPy hollow nanotube membrane was achieved by dissolved the $Na_5V_{12}O_{32}@PPy$ nanocomposite on Ti foil in 0.5 M solution of citric acid and 10% (v/v) HF acid solution.

2.3. Characterisation:
Field-emission scanning electron microscopy (SEM) images were obtained on a Zeiss Ultra Plus microscope. Transmission electron microscopy (TEM) images were taken on a JEM 2100F Microscope.

2.4. Gas sensing:
The gas-sensing properties of the samples were determined in a static flow system (CGS-4TPs, Beijing Elite Tech. Co., Ltd, China). The as-prepared samples were further ground into fine powders and mixed with absolute ethanol in a weight ratio of 4 : 1 to form paste, then the paste was dropped onto the cleaned Al_2O_3 (10 mm × 20 mm × 0.635 mm) substrate with interdigitated gold electrodes to form a sensing film and its thickness is about 100 μm. Test NH_3 was injected into the test chamber (1.8 L in volume) using a microliter syringe through the sample inlet. After the test NH_3 material was injected onto the hot evaporation stage, the target vapour was formed. When the sensor response reached a constant value, the test chamber was opened and the system exposed to an ambient atmosphere to measure its recovery in air. The resistance values of the gas sensors were measured at different operating temperatures adjusted by heating the sensor unit through a Thermo controller. The test was performed in a temperature range of 30–80°C. The ratio of change in the resistance (response, S) of sensing materials under a certain gas level relative to the resistance in the absence of gas was defined as

$$S(\%) = \frac{R_g - R_a}{R_a} \times 100 \qquad (1)$$

where R_g is the sensor response to the NH_3 and R_a is the baseline resistance. The response time of senor can be analysed by the following equation:

$$t_r = t_{90\%max} - t_{initial} \qquad (2)$$

where $t_{90\% max}$ is the time point when resistance reached 90% of the maximum value, $t_{initial}$ is the time point when the gas is introduced [21].

3. Results and discussion:
The synthesis of the PPy nanotube membrane is illustrated in Fig. 1. First, Ti foil was employed as the substrate to grow the precursor ($Na_5V_{12}O_{32}$) nanowire arrays via a facile hydrothermal method. Second, electrochemical deposition technique was used to coat the PPy on the surface of $Na_5V_{12}O_{32}$ nanowires, which produced the $Na_5V_{12}O_{32}@PPy$ nanocomposite. To obtain the PPy nanotube membrane, the nanocomposites were dissolved in citric acid and HF acid solution to remove the $Na_5V_{12}O_{32}$ nanowires and Ti foil, respectively.
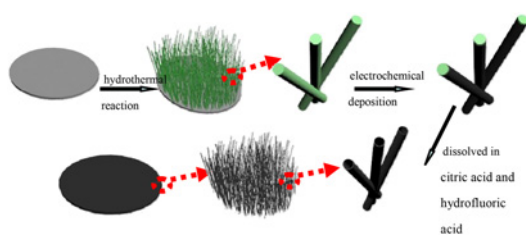

Fig. 1 *Schematic illustration of the synthesis procedure of the PPy nanotube membrane*

The morphology of the as-prepared products was investigated by SEM (Figs. 2a and b), which revealed uniform growth of the nanowires grown on the Ti foil surface. The nanowires were about 4 μm in length and about 90 nm in diameter. Figs. 2c and d show the SEM images of the PPy nanotube membrane and the inset in Fig. 2c shows the digital images of the flexible PPy nanotube membrane. It can be seen from these figures that we have successfully obtained freestanding flexible PPy nanotubes with a larger diameter of ~272 nm. Fig. 2e depicts the cross-section image of the PPy nanotube membrane, which shows that the PPy is hollow and the thickness of the membrane is about 4.0 μm. The tubular structure was investigated by TEM, as shown in Fig. 2f, with results that are consistent with the SEM image (Fig. 2e). The thickness of the PPy wall is ~42 nm (Fig. 2f).

Fig. 3a shows the response of the sensor upon exposure to NH_3 gas at different concentrations. The response time of the PPy nanotubes sensor is 77, 75, 74, 61, 46, and 42 s for the 50, 100, 200, 300, 500, and 1000 ppm NH_3, respectively. Once NH_3 gas was introduced, the resistance of the sensor increased sharply with time until it reached a plateau and remained constant. Then, after the NH_3 was cut-off, the resistance slightly decreased. When the NH_3 concentration increased, the resistance also increased. The results demonstrate that the sensor has a surprisingly high and quick response to NH_3. The increasing resistance of the PPy nanotubes device upon exposure to NH_3 gas is caused by the electrical interaction of NH_3 molecules absorbed on the surface of the PPy nanotubes. When PPy is exposed to NH_3 gas, the gas molecules easily absorb on the surface of the nanotubes and the PPy nanotubes lose electrons by the nitrogen's doublet of some nitrogen atoms of the polymer backbone, leading to the formation of NH_3^+ radical groups. This electron transfer between the NH_3 molecule and the polymer's positive hole decreases the positive charge density which leads to a decrease in the conductance. Consequently, after adsorption of NH_3, the polymer becomes less conducting, and the measured conductance decreases. In contrary, during desorption of the NH_3 molecules, the sensor's conductance increases [13, 15, 16]. As shown in Fig. 3b, the response grows almost linearly with an increase of the NH_3 concentration ranging from 50 to 1000 ppm at room temperature. As shown in Fig. 3c that the resistance of the PPy nanotubes could return to its conductive state after the removal of NH_3, as the response in the first and fifth circles
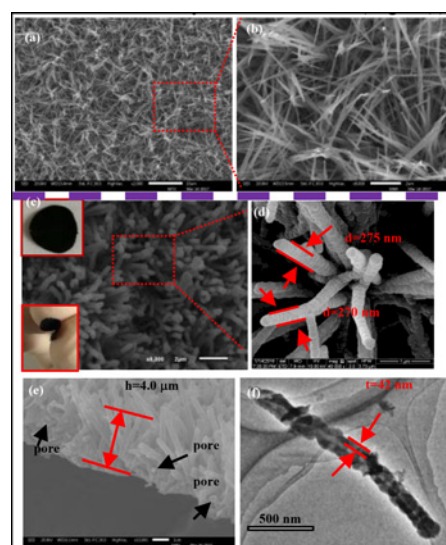

Fig. 2 *Tubular structure. Inset in (c) shows the digital images of the flexible PPy nanotube membrane*
a, b SEM images of $Na_5V_{12}O_{32}$ nanowires
c–e SEM images of the PPy nanotubes array
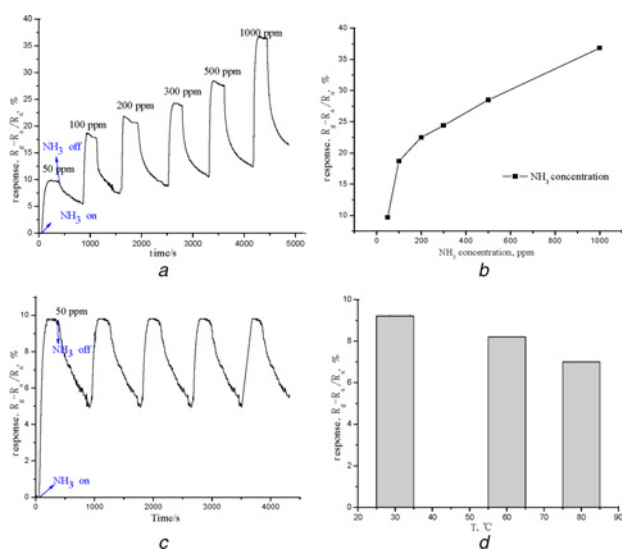*f* TEM image of the PPy nanotubes array

Fig. 3 *Response of the sensor*

a The time-dependent change of the resistance at room temperature: the response to NH_3 at different gas concentrations

b The response of the as-fabricated sensor to NH_3 with different concentrations

c Five reversible cycles of exposure to 50 ppm NH_3 at room temperature

d Sensor response to 50 ppm NH_3 at different working temperatures

returned nearly to the same baseline, which illustrating the strong reproducibility of the sensor. Fig. 3*d* represents the gas response of the gas sensors at operating temperatures from 30 to 80°C. The resistance of PPy decreased with increased heating temperature. As discussed above, the sensing process involves two steps: adsorbing the analyte molecules in sensing film and then the reaction of these molecules with the sensing film. Temperature can influence both of these steps. Adsorption is favoured at low temperature and increasing temperature will shift the equilibrium to desorption. When adsorption/desorption is the main step, sensitivity will dwindle down as temperature increases [22]. The interaction between the conducting polymer and gas analyte is rather strong at room temperature, likely explaining the determination that the best sensitivity was observed at room temperature.

4. Conclusions: The SEM and TEM analyses consistently indicate that the successful preparation of PPy nanotube membrane has been achieved by removing the $Na_5V_{12}O_{32}$ template and Ti foil. The prepared membrane exhibits a higher response to NH_3 gas at room temperature. The PPy nanotube membrane is a promising NH_3 gas sensor due to its low cost, easy fabrication and high response sensing properties.

6 References

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