Fabrication of electrospun LaFeO₃ nanotubes via annealing technique for fast ethanol detection

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A B S T R A C T
Developing a simple method for fabricating nanotube materials is highly desired in nanomaterials research. In this work, LaFeO₃/polyvinylpyrrolidone (PVP) composite nanofibers were prepared by a single spinneret electrospinning method. Then, LaFeO₃ nanotubes were obtained via a rapid annealing technology. The gas sensors based on LaFeO₃ nanotubes were fabricated for investigating their gas sensing properties. The results show that the LaFeO₃ nanotubes gas sensor is of good response and selectivity to ethanol, and the fast response/recovery times are about 2/4 s to 100 ppm ethanol at 160 °C. We expect that LaFeO₃ nanotubes can be used to fabricate ethanol gas sensors, and the preparation method of LaFeO₃ nanotubes can provide new ideas for synthesizing other nanotube materials.

1. Introduction

Nowadays, numerous hollow structural materials such as nanotubes, hollow nanofibers, and hollow spheres are emerging in the fields of electrocatalysts, gas sensors, capacitors and batteries due to their high surface area, porosity, active sites and unique carriers transport properties [1–4]. However, the most of previous hollow structural materials syntheses involve the use of templates, surfactants, toxic organic solvents, and tedious procedures, which are not very environment-friendly and efficient for practical applications [5]. Compared with other methods, the coaxial electrospinning as an effective and widely applied method is reported to prepare hollow nanofibers materials, but it is difficult to select a suitable inner solvent, accurately control electrospinning parameters and completely eliminate the core material [6,7]. In order to overcome the shortcomings of coaxial electrospinning, researchers are trying to explore the appropriate annealing technology for fabricating electrospun hollow nanofibers [2]. Although the single spinneret electrospinning has been reported to synthesize hollow nanofibers with diameters of 145–250 nm [2,7–9], it is still a challenge to prepare hollow nanomaterials with finer diameter, such as nanotubes.

Previously, we have synthesized LaFeO₃ nanofibers for gas detection via electrospinning [10]. On the basis of electrospinning technology, this work aims at preparing LaFeO₃ nanotubes via annealing technology with a fast heating rate, further investigating its gas sensing properties. The results show that the as-prepared LaFeO₃ nanotubes can be effectively applied in the field of ethanol detection, and the preparation method of LaFeO₃ nanotubes can offer a guidance for synthesizing other nanotube materials.

2. Experimental

All the reagents are analytical grade and used as received without further purification. First, 0.002 mol La(NO₃)₃ 6H₂O, 0.002 mol Fe(NO₃)₃ 9H₂O and 0.004 mol citric acid were dissolved in 5 ml deionized water, and the mixed solution was magnetically stirred at 80 °C for 4 h to obtain clear and transparent homogeneous precursor solution A. Meanwhile, 1 g polyvinylpyrrolidone (PVP, MW: 1,300,000) was added in 5 ml ethanol and stirred to form a homogeneous viscous solution B. Second, solution A was poured into solution B to form mixed solution C and stirred for about 10 h at room temperature. Third, the solution C was loaded into a plastic syringe (10 ml) with a spinneret (inner diameter: 0.6 mm). The schematic diagram of electrospinning setup and annealing procedure are depicted in Fig. 1(a–b). The electrospinning parameters are as follows: the applied voltage is +18 kV on spinneret and −5 kV on aluminum foil, the distance between the spinneret and aluminum foil is 20 cm, the propulsion speed is 0.2 ml/h, the temperature and relative humidity of electrospinning ambient are maintained at about 35 °C and 35% RH by the control regulator. Finally, the LaFeO₃ nanotubes were obtained by annealing the LaFeO₃/PVP composite nanofibers at 600 °C for 120 min with the...
heating ratio 10 °C/min. The crystalline structures and morphologies of LaFeO$_3$ nanotubes were characterized by X-ray diffraction (XRD; Brukers, D8 Advance) with Cu K$_\alpha$ radiation (\(\lambda = 0.15418 \text{ nm}\)), field-emission scanning electron microscope (FE-SEM, Hitachi S4800) and transmission electron microscopy (TEM; JEOL, JEM-2100). Fig. 1(c) shows the photograph and structure schematic of gas sensor. The details for fabrication and measurement of gas sensor referred to our previous work [10]. The current-voltage (I-V) curves were tested by a semiconductor parameter tester (NS-400P, Beijing Zhongke Micro-Nano Networking Technology Co., Ltd.) and the gas sensing properties were investigated by a CGS-8 intelligent gas sensing analysis system (Beijing Elite Tech Co., Ltd, China). The values of R$_g$/R$_a$ (R$_g$: resistance in gas; R$_a$: resistance in air) are defined as the response for p-type LaFeO$_3$ material in detecting reductive gases, and the response/recovery times are defined as the time spans to reach a 90% variation in resistance upon exposure to gas and air [11].

3. Results and discussion

Fig. 2(a) shows the XRD patterns of the LaFeO$_3$ nanotubes. All the diffraction peaks match well with the standard JCPDS card of LaFeO$_3$ (No. 37-1493) and no impure peaks can be observed in Fig. 2(a), indicating orthorhombic perovskite structure and high purity of LaFeO$_3$ [10]. The FE-SEM image of LaFeO$_3$/PVP composite nanofibers before calcination is shown in Fig. 2(b). The diameter of LaFeO$_3$/PVP composite nanofibers is about 100 nm. Fig. 2(c) shows the FE-SEM image of LaFeO$_3$/PVP composite nanofibers after calcination at 600 °C with the heating ratio 10 °C/min. It can be seen that the LaFeO$_3$ nanotubes with an average outer diameter of about 50 nm are interlaced and the hollow structure can be clearly observed in the ruptured sections. To observe the details of LaFeO$_3$ nanotubes, TEM image is shown in Fig. 2(d). The clear nanotubes structure with the inner diameter ranging from 15 to 30 nm can be seen from TEM image. The formation process LaFeO$_3$ nanotubes can be concluded as follows: During an appropriate fast heating rate, LaFeO$_3$ nanoparticles will move toward the outside of nanofibers driven by the expanded gas produced by PVP decomposition [2]. The uneven inner wall of LaFeO$_3$ nanotubes can be also reasonably explained by the random expanded gas. The selected area electron diffraction (SAED) pattern (inset of Fig. 2(d)) shows the LaFeO$_3$ nanotubes are of polycrystalline structure. The above results indicate the annealing technique with an appropriate fast heating rate can produce uneven inner cavities in nanofibers and form nanotubes. The uneven inner wall of LaFeO$_3$ nanotubes can dramatically increase the amount of active sites and improve the gas sensing performance.
Fig. 3(a) shows typical I-V curves of the gas sensor at different working temperatures from 100 to 280 °C. As observed, all the currents are increased linearly with the applied voltages (−3 V to 3 V), revealing that the good ohmic contacts are formed between the sensing layer and electrodes, and upcoming gas sensing behaviors are caused by LaFeO3 nanotubes [12]. For investigating the gas sensing properties of LaFeO3 nanotubes, the responses of the gas sensor to 100 ppm different reductive gases at different operating temperatures are measured as shown in Fig. 3(b). The maximal responses of the gas sensor to 100 ppm ethanol, acetone and formaldehyde are about 9.4, 4.3, and 3.5 at 160 °C, respectively. The response of the gas sensor to ammonia is only 1.3 at 180 °C. The results show that LaFeO3 nanotubes gas sensor is more appropriate for detecting ethanol compared with other reductive gases above. The inset of Fig. 3(b) shows the response/recovery times to 100 ppm ethanol at different temperatures. The response/recovery times are temperature-dependent and decrease with the temperature ascending. The temperature only has a little influence on the response values. So the subsequent gas sensing tests are focused on ethanol at 160 °C. Fig. 3(c) shows dynamic response/recovery curve to different concentrations ethanol. All the response and recovery cycles are stable and reversible at the range of 5–1000 ppm ethanol. From the inset of Fig. 3(c), it can be clearly seen the gas sensor exhibits fast response/recovery times of about 2/4 s to 100 ppm ethanol. The response versus ethanol concentrations curve is shown in Fig. 3(d). With the ethanol concentration increasing, the response increases rapidly below 100 ppm while slowly beyond 100 ppm, and reaches a stable value at about 1000 ppm due to the response saturation of the gas sensor. In addition, the inset of Fig. 3(d) shows the linear fitting curve to 5–100 ppm ethanol, which can be represented as $Y = 0.07453X + 2.2824$, $R^2 = 0.96583$, where $Y$ is response, $X$ is ethanol concentration, $R^2$ is the correlation coefficient, indicating the gas sensor is of good linearity to 5–100 ppm ethanol at 160 °C. Fig. 3(e) shows the repeatability of the gas sensor on successive exposure to 100 ppm ethanol, indicating the gas sensor is of good repeatability in the continuous switching measurements. The stability of the gas sensor to 100 ppm ethanol at 160 °C for a month is measured as shown in Fig. 3(f). The response values exhibit no significant change for a month, indicating a good stability of the gas sensor. Compared with the previous report of LaFeO3 nanobelt ethanol sensor [11], LaFeO3 nanotubes ethanol sensor is of better performance on the response values and response/recovery speeds.

### 4. Conclusions

In summary, on the basis of single spinneret electrospinning method, the LaFeO3 nanotubes were successfully synthesized via annealing technology with a fast heating rate. The clearly hollow structure is formed in the LaFeO3 nanotubes, and the average outer diameter is about 50 nm. Furthermore, the gas sensor based on LaFeO3 nanotubes shows good response, selectivity and rapid response/recovery speeds to ethanol at 160 °C. The facile preparation method of LaFeO3 nanotubes can also provide new ideas for the synthesis of other nanotube materials.
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References