Synthesis of TiO₂ Nanotubes and Their Sensitivity for Toluene Gas

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Abstract TiO₂ nanopowders with anatase structure were firstly prepared by controlling the pH value of a precursor solution without any heat-treatment at room temperature. The prepared TiO₂ nanopowders were hydrothermally treated in 10M NaOH solution at 170°C. Then, the samples were washed in DI water or 0.1M HCl. The TiO₂ nanotubes were characterized by X-ray diffraction (XRD), scanning electron microscope (SEM) and transmission electron microscope (TEM). The gas sensitivity of TiO₂ nanotubes for toluene gas was also investigated. The results show that TiO₂ nanotubes can be prepared by hydrothermal treatment. The morphology of TiO₂ nanotubes prepared by 0.1M HCl washing is destroyed to some extent. TiO₂ nanotubes with DI water washing show better sensitivity than that with 0.1M HCl washing.

Keywords : TiO₂ nanotubes, Hydrothermal treatment, Gas sensitivity, Toluene gas

1. Introduction

Low dimensional titania (TiO₂) nanostructures such as nanotubes, nanowires and nanobelts have attracted much attention in recent years because they have potential applications in electronics, optics, catalysts and gas sensors [1-3].

Many methods have been developed to synthesize one-dimensional titania nanotubes of various dimensions, such as anodization [4], sol-gel [5], and hydrothermal method [6, 7]. The hydrothermal method is a simple and cost-effective method for the large scale production of titania with small diameters.

It is well known that the performance of metal oxide-based gas sensors is largely dependent on the morphology of the sensing layers used [8]. A highly ordered, nanotubular structure that has both size-dependent and surface area-related properties could

further improve gas sensitivity compared with nanoparticle.

In the present study, TiO₂ nanopowders with anatase structure were firstly prepared by controlling the pH value of a precursor solution without any heat-treatment at room temperature. Then, the prepared TiO₂ nanopowders were hydrothermally treated in a sealed teflon-lined stainless autoclave to obtain TiO₂ nanotubes whether DI water washing or 0.1M HCl washing. The gas sensitivity of TiO₂ nanotubes for toluene gas was tested.

2. Experimental

TiCl₄ in toluene (1M), DI water and 3M NaOH solution were used to prepare TiO₂ nanoparticles. TiO₂ nanoparticles were used as starting materials. Then, the nanotubes were prepared by hydrothermal synthesis. The method is basically the

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same as described in previous papers [6]. TiO₂ nanoparticles and 10M NaOH aqueous solution were put into a Teflon-lined stainless autoclaves. The autoclave was heated at 170°C for 24h. After it was cooled down to room temperature. The precipitation was washed by distilled water and 0.1M HCl, respectively. Finally, the precipitation was dried at 80°C for 5h.

The microstructures were observed by Scanning Electron Microscope (SEM) and Transsition Electron Microscope (TEM). The phase composition of the nanotubes was determined by X-ray diffraction (XRD) with continuous scanning mode using Cu K α radiation.

The synthesized nanotubes were mixed with α -terpineol and ethylcellous (1:20), and screen-printed on an alumina substrates. After screen-printing, the sensors were calcined at 500°C for 2h.

The gas sensitivities were tested using toluene gas. The desired concentration levels of gas were obtained with mass flow controllers. Sensitivity is defined as shown in Equation (1).

$$S(\%) = [(R_a - R_g)/R_a] \times 100 \quad (1)$$

where, R_a and R_g are the electric resistances in air and that in a specific concentrated toluene gas, respectively.

Fig. 2. TEM morphology of as-synthesized nanotubes with DI water washing.

3. Results

The SEM morphology of the as- synthesized nanotubes is shown in Fig. 1. It is observed that the nanotubes with a length of several μ m were obtained at very high yield. In addition, the nanotubes tend to form aggregated bundles. However, the morphology of the TiO₂ nanotubes is destroyed after 0.1M HCl washing to some extent. The EDX results show that it contains Na in synthesized nanotubes with DI water washing and no Na exists in those with 0.1M HCl washing, which indicates that Na⁺ is exchanged by H⁺ after 0.1M HCl washing.

Fig. 2 shows a typical TEM morphology of the

Fig. 1. SEM morphologies of as-synthesized nanotubes: (a) DI water washing and (b) 0.1M HCl washing.

Fig. 3. XRD patterns of as-synthesized nanotubes.

Fig. 4. Sensitivities of nanotubes for 5 ppm toluene gas at 400°C.

as-synthesized nanotubes with DI water washing. It can be seen that the nanotubes have a diameter of approximately 10-50 nm and a length of several μm .

Fig. 3 shows the XRD patterns of the as-synthesized nanotubes. The patterns are similar to the results of the earlier works [9]. The characteristic peak at around $2\theta = 10^\circ$ indicates that the nanotubes are composed of a layered titanate. The diffraction peak position ($2\theta = 10^\circ$) of the nanotubes with DI water washing shifts to low angle compared with that with 0.1M HCl washing. This maybe that the radius of Na^+ is larger than that of H^+ . It can be seen that it is made up of $\text{Na}_x\text{H}_{2-x}\text{Ti}_3\text{O}_7 \cdot n\text{H}_2\text{O}$ with DI water washing and $\text{H}_2\text{Ti}_3\text{O}_7 \cdot n\text{H}_2\text{O}$ with 0.1M HCl

washing, respectively.

Fig. 4 shows the sensitivity of the nanotubes sensor for 10 ppm toluene gas at 400°C. It can be seen that TiO_2 nanotubes shows a high sensitivity for toluene gas. Moreover, the sensitivity of TiO_2 nanotubes with DI water washing is better than that with 0.1M HCl washing. The sensor prepared by $\text{H}_2\text{Ti}_3\text{O}_7 \cdot n\text{H}_2\text{O}$ nanotubes shows 5% sensitivity. The sensor prepared by $\text{Na}_x\text{H}_{2-x}\text{Ti}_3\text{O}_7 \cdot n\text{H}_2\text{O}$ nanotubes shows 15% higher sensitivity. The reason is that when the sensor is calcined at 500°C for 2h, as reported in previous work [10], the nanotubes remain as the nanotubes where a lot of Na exist in $\text{Na}_x\text{H}_{2-x}\text{Ti}_3\text{O}_7 \cdot n\text{H}_2\text{O}$ nanotubes. However, some of nanotubes have been destroyed and become particles with less Na in $\text{H}_2\text{Ti}_3\text{O}_7 \cdot n\text{H}_2\text{O}$ nanotubes.

4. Conclusions

The hydrothermal treatment of TiO_2 nanoparticles with NaOH solution produced TiO_2 nanotubes. SEM and TEM observations revealed that the lengths of TiO_2 nanotubes were several μm and the diameters were 10-50 nm. The sensitivity of TiO_2 nanotubes with DI water washing is better than that with 0.1M HCl washing.

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