Synthesis of Ba-doped CeO₂ nanowires and their application as humidity sensors

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Abstract
Ba-doped CeO₂ nanowires were obtained from CeO₂ particles through a facile composite-hydroxide-mediated (CHM) route. The products were characterized by x-ray diffraction (XRD), field emission scanning electron microscopy (FE-SEM), transmission electron microscopy (TEM) and high-resolution transmission electron microscope (HRTEM). The formation process of the product was discussed. Humidity sensors based on the source material CeO₂ particles, Ba-doped CeO₂ nanowires grown for 12 and 72 h, were fabricated. The responses to humidity for static and dynamic testing proved that both doping Ba into CeO₂ and converting morphology into a nanowire can improve the humidity sensitivity. The resistance changes from 465 to 3.9 kΩ as the relative humidity (RH) increases from 25% to 88%, indicating promising applications of Ba-doped CeO₂ nanowires in environmental monitoring.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

Nanowires have been attracting great research interest in the last several years. They have been demonstrated to exhibit superior electrical, optical, mechanical and thermal properties, and can be used as fundamental building blocks for nano-scale science and technology, ranging from chemical and biological sensors, field effect transistors to logic circuits [1–7]. Recently, nanowire paper with the function of write-erase-rewrite, made from TiO₂ nanowires, has been produced [8]. Although the methods of synthesizing nanomaterials are diverse, a facile, controllable and low-cost route to prepare nanowires is still a challenge.

The materials for humidity sensors are generally organic polymers or metal oxides. Humidity sensors based on organic polymers have many challenges due to their weak mechanical strength and poor physical and chemical stability. Ceramic types of humidity sensors are superior in performance to the polymeric type, because of their high stability towards a variety of chemical species, a wide range of operating temperatures, and fast response to the changes in humidity. Recent investigations have presented that humidity sensors based on CeO₂ powder show poor sensitivity [9], but that a humidity sensor based on CeO₂ nanowires has shown a fast response [10].

In this paper, to explore the properties of a metal-doped CeO₂ nanowire, first we synthesize Ba-doped nanowires using the CHM approach, which is an effective new approach for synthesizing oxide nanostructures [11–15]. The method is based on the reaction of source materials in a solvent of eutectic composite-hydroxides at a temperature of ~200°C and atmosphere pressure without using an organic dispersant or capping agent. This methodology provides a one-step, convenient, low-cost, nontoxic and mass-production route for the synthesis of nanostructured functional materials. The as-
produced nanocrystals have a clean surface, which is most favorable for further investigating its intrinsic properties and greatly improving its function \[12, 15, 16\], as well as for modifying its surface in bio applications. Second, humidity sensors based on source CeO$_2$ particles, Ba-doped CeO$_2$ nanowires grown for 12 and 72 h, are fabricated and the humidity sensitivity is investigated.

2. Experimental details

The Ba-doped CeO$_2$ is synthesized through the newly invented nanomaterial fabrication route of the CHM method \[11–15\]. In a typical reaction, a 9 g amount of mixed NaOH and KOH with a Na/K ratio of 51.5:48.5 is placed in a 25 ml covered Teflon vessel. A mixture of 1 m mol CeO$_2$ and 1 m mol BaCO$_3$ is added into the vessel as the raw materials for the reaction. Then, the vessel is put in a furnace pre-heated to 200 °C. After the hydroxides are completely molten, the molten reactants are mixed uniformly by shaking the vessel. After reacting for 24–72 h, the vessel is taken out and cooled down to room temperature. The solid product from the reaction is dissolved in deionized water, filtered and washed first by deionized water and then by dilute acid to remove the hydroxide on its surface.

An x-ray diffractometer and energy dispersive x-ray spectroscopy (EDS) are used to investigate its crystalline phase and chemical composition. FE-SEM (Hitachi S-4800) and HRTEM (Hitachi HF-2000) are used to characterize the morphology and the size of the synthesized samples.

The thin films for humidity sensitivity sensors are prepared from source CeO$_2$ particles, Ba-doped CeO$_2$ nanowires grown for 12 h and 72 h, respectively. The samples are first dispersed in ethanol, and then dropped on top of pre-deposited Au electrodes on the surface of a Si wafer. The dimensions of the film are 5 mm in length, 3 mm in width, and $\sim$20 $\mu$m in thickness. Ohmic contacts for the planar film with copper wires are made by silver paste. The measurements are carried out by putting the sensors in an airproof glass vessel with a volume of 2 l. A hygroscope is placed into the vessel to monitor the relative humidity during the experiment process. The sensor’s resistance is measured by an external testing circuit.

3. Result and discussion

Figure 1(a) shows the XRD pattern of the source material CeO$_2$ (curve 1) and as-synthesized products grown for 12 h (curve 2), 48 h (curve 3), and 72 h (curve 4). All peaks of the source material CeO$_2$ (curve 1) can be indexed as the pure cubic phase ($Fm\overline{3}m$, JCPDS 34-0394) with a lattice constant $a = 0.5411$ nm. It can be seen clearly that, besides the peaks belonging to CeO$_2$ structure, there are some peaks marked in dots belonging to the BaCO$_3$ structure in the spectra of the product grown for 12 h (curve 2). These peaks of the BaCO$_3$ structure are weakened as the growth time increases (curve 3), and at last disappear for the product in the 72 h growth (curve 4), indicating a pure CeF$_2$ structure. The lattice constant of the CeO$_2$ will be expanded when it is doped with Ba. Such an expansion can be detected by XRD measurement because the lattice expansion deduces that diffraction peaks shift toward smaller angles. To explore this point, we compare the 111 peak of the Ba-doped CeO$_2$ sample (solid line) with a source material CeO$_2$ (dot line), as shown in figure 1(b). It can easily be found out that there is a small difference in the 111 peak locations for the Ba-doped CeO$_2$ sample and the source material CeO$_2$, where the former is at 28.34° but the latter is at 28.61°, as is shown in figure 1(b).

Figure 2 shows the typical FE-SEM images of the source material CeO$_2$ (a), and the Ba-doped CeO$_2$ sample grown for 12 h (b), 48 h (c), and 72 h (d). The particle morphology of the source material CeO$_2$, with the diameter ranging from 500 nm to 2 $\mu$m can be seen. When doped with Ba, the particles convert gradually into nanowires, as shown in figures 2(b)–(d). The lengths of the nanowires increase with increasing growing time. Accompanying many anomalous products, only a small number of nanowires forms during the initial 12 h growth. Almost all of the products turned into nanowires with a length of 3–10 $\mu$m after 48 h of growth, except for a few anomalous products. As the growth time is prolonged to 72 h, the length of the nanowires reaches 6–20 $\mu$m without any anomalous particles. Figure 3 exhibits the TEM images (a), the electron diffraction pattern (b) and the HRTEM images ((c), (d)) of the nanowires for a 48 h growth. The electron diffraction pattern of the selected area marked in figure 3(a) is shown in figure 3(b), indicating that the nanowire is a single crystal. The HRTEM images, as shown in figures 3(c) and (d), exhibit the single-crystal structure of the nanowire, and there is no contamination on its surface. The electron diffraction pattern, as well as the HRTEM, implies that the nanowire has the (2 2 0) plane as its growth front. The EDS is taken for a single Ba-doped CeO$_2$ nanowire in figure 3(e), indicating the existence of Ce, Ba, and O in the nanowire, while the Cu and C come from the TEM grid.

The interesting morphological conversion of the CeO$_2$ from anomalous particles into single-crystal nanowires might be explained by a dissolution–recrystallization mechanism \[17\]. The crystal growth experiences first the CeO$_2$ and BaCO$_3$ dissolving in the molten composite alkali solvent, and then CeO$_2$ recrystallizing while some Ba ions dope in, finally crystal growth into a nanowire. This dissolution and
recrystallization process is mainly related to temperature and growth time. In figure 2(b) we can see the CeO$_2$ and BaCO$_3$ dissolution and some short rods forming in the initial 12 h growth. So we presume that dissolution and recrystallization proceed gradually and end in a lack of the reactants.

The humidity sensitivity experiments are performed with humidity sensor devices made from the source material CeO$_2$, Ba-doped CeO$_2$ samples grown for 12 and 72 h, as shown in figure 4(a), while the experimental setup is shown in figure 4(b). The humidity in the vessel is controlled by mixing...
the dry air and the wet air. The relative resistances \( \frac{R_{RH}}{R_0} \) of the devices versus relative humidity (RH) are shown in figure 5(a), where \( R_{RH} \) and \( R_0 \) denote the resistance of the sensors in different humidity environments and in a humidity of 25%, respectively. Plots A, B and C in figure 5(a) represent the \( \frac{R_{RH}}{R_0} \) response to RH for the devices of the source CeO₂ (A), and Ba-doped CeO₂ nanowires grown for 12 h (B) and 72 h (C) in static air of 25–90% RH at 25°C respectively. It can clearly be seen that the resistance of the device made of the source material CeO₂ changes little with the humidity increase, while the resistance of the devices made of Ba-doped CeO₂ nanowires grown for 12 and 72 h both decrease with the increase of RH. The resistance of the device made of the 72 h sample decreases much more rapidly, and the resistance of the device in 25% RH is 465 MΩ, which is 119 times that (3.9 MΩ) in 88% RH. The static testing results indicate that both doping Ba into CeO₂ and converting the morphology into a nanowire can improve the humidity sensitivity.

Furthermore, to prove some important parameters for a sensor device (response time, recovery time, and reproducibility), dynamic testing of the device in a certain RH is performed in figure 5(b), in which we call dry air DA and wet air WA for short. The device is put in the vessel with an initial RH of 55% and an initial resistance of about 175 MΩ. When wet air of about 85% RH is switched into the vessel, the resistance of the device decreases rapidly. After 2 min, the resistance of the device is reduced to 8 MΩ and then changed slowly. Then dry air of about 25% RH is switched into the vessel and the resistance recovered to about 175 MΩ in 2 min. At the same time, another three circles follow after the previous one, proving good reproducibility of the sensitivity.

A few mechanisms have been proposed to explain the surface conductivity change in the presence of water vapor [18–20]. In general, it experiences first the chemisorbing of monolayer water with proton transfer among hydronium (H₃O⁺), where the electrical response depends on the number of water molecules adsorbed on the sensor surface; and then the physisorbing of multilayer water with increasing humidity, where H₃O⁺ appears in the physisorbed water and serves as a charge carrier. H⁺ ions can move freely in the physisorbed water according to Grotthuss’s chain reaction [21–23]. Electrolytic conduction takes the place...
of protonic conduction at high humidity. This is further confirmed from the characteristics of the resistance versus relative humidity of the sensor in figure 5(a). The resistance decreases nonlinearly with increasing humidity, implying ion-type conductivity as the humidity-sensing mechanism [24–26]. From figure 5(b), we can see that the response speed is faster than the recovery speed. This may contribute to the humidity sensitivity. Ba-doped CeO$_2$ nanowires could be a potential material for humidity detecting applications.

4. Conclusions

In summary, Ba-doped CeO$_2$ nanowires can be obtained from CeO$_2$ particles through the CHM approach. The morphology conversion of the products could be explained by a dissolution-recrystallization mechanism. Test results for humidity sensitivity based on source CeO$_2$ particles, and Ba-doped CeO$_2$ nanowires grown for 12 and 72 h indicate that both doping Ba into CeO$_2$ and converting the morphology into a nanowire can improve the humidity sensitivity. Considering the excellent chemical and thermal stability, Ba-doped CeO$_2$ nanowires could be a potential material for humidity detecting applications.

Acknowledgments

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