Synthesis of $\text{BaCO}_3$ Nanowires and Their Humidity Sensitive Property

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Barium carbonate ($\text{BaCO}_3$) nanowires have been synthesized for the first time by using the composite hydroxide mediated (CHM) method. The products are characterized by X-ray diffraction (XRD), field emission scanning electron microscopy (FE-SEM), and transmission electron microscopy (TEM). Humidity sensors based on $\text{BaCO}_3$ nanowires have been fabricated. The response to humidity in static and dynamic measurement proves the ultrasensitive property of the sensors. The resistance changes from 386 M$\Omega$ to 7.1 M$\Omega$ as the relative humidity (RH) increases from 20% to 95%. The response and recovery time of the resistance is 16 s and 56 s versus the changes of relative humidity from 25% to 85%. These results indicate promising applications of $\text{BaCO}_3$ nanowires in a highly sensitive environmental monitoring and humidity control electronic device.

Keywords: Barium Carbonate, Nanowire, Humidity.

1. INTRODUCTION

Nanowires have been attracting great interest in the last decade. Nanowires have exhibited 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. $^1$–$^2$ Barium carbonate exists in nature as a most thermodynamically stable crystal modification among the heavy metal carbonates (ACO$_3$, A = Sr, Pb and Ba). $^3$ $\text{BaCO}_3$ has also been extensively considered as an important material due to its close relationship with aragonite, biomimetic, its wide applications in the ceramic and glass industries as well as its use as a precursor for magnetic ferrites and ferroelectric materials. $^9$ $\text{BaCO}_3$ nanocrystals are commonly obtained via polymer induced synthesis routes. $^{10–14}$ Herein, we take a new strategy to synthesize $\text{BaCO}_3$ nanowires by the composite hydroxide mediated (CHM) method. In addition, humidity sensors based on $\text{BaCO}_3$ nanowires are fabricated and their sensitivity is investigated.

2. EXPERIMENTAL DETAILS

$\text{NaF, BaCl}_2$, $\text{NaOH}$ and KOH were purchased from Chongqing Chemical Reagent Company and all chemicals were of analytical grade and were used as received.

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(from side view of SEM). Ohmic contacts for the planar film consisted of copper wires and silver paste. The electrode gap is about 0.2 mm. The measurements were carried out by putting the sensors in an airproof glass vessel with a volume of 2 L. A hygroscope is placed in the vessel to monitor the humidity change during the experiment. The sensor’s resistance was measured by a Keithley 2400 Source Meter.

3. RESULTS AND DISCUSSION

Figure 1 shows the morphology of the synthesized BaCO$_3$ sample. SEM and TEM images in Figures 1(a–c) illustrate the BaCO$_3$ nanowires with diameters of 100–200 nm and lengths of 5–6 μm. The selected area electronic diffraction indicates that the nanowires are of single crystals. EDS (inset Fig. 1(a)) demonstrates that the composition of the sample are Ba, C and O (Si signal is from the substrate). XRD spectrum shows that all the peaks are perfectly indexed as an orthorhombic phase of BaCO$_3$ (JCPDS-410373) with lattice constants of $a = 6.549$, $b = 5.225$, $c = 8.834$ Å, as shown in Figure 2.

The possible reaction mechanism for the formation of BaCO$_3$ is proposed as follows NaOH and KOH play the same role in the composite hydroxide melts. To simplify the expression for chemical reactions here, we only include NaOH in the formula:

$$\text{BaCl}_2 \rightarrow \text{Ba}^{2+} + 2\text{Cl}^- \quad (1)$$
$$\text{NaOH} \rightarrow \text{Na}^+ + \text{OH}^- \quad (2)$$
$$\text{Ba}^{2+} + 2\text{OH}^- \rightarrow \text{Ba(OH)}_2 \quad (3)$$
$$\text{Ba(OH)}_2 + \text{CO}_2 \rightarrow \text{BaCO}_3 + \text{H}_2\text{O} \quad (4)$$

Reactions (1–3) happen in the composite hydroxide melts in the Teflon vessel at 200 °C, while reaction (4) might occur after the product is removed from the vessel. The Ba(OH)$_2$ obtained from step (3) reacts with CO$_2$ in atmosphere to form BaCO$_3$ thoroughly during the subsequent washing and drying process.

To explore its response to humidity, we built a sensor made from the BaCO$_3$ nanowires (Fig. 3(a)). The experimental setup is shown in Figure 3(b) with the humidity in
the test chamber regulated by a flow controller. Figure 4(a) shows the sensitivity versus relative humidity (RH) in the range of 25–95% at 25°C. Three plots represent three different sensors made from the same BaCO3 nanowires. It can be seen in these sensors that their resistance drops rapidly as the humidity increases. The change of resistance versus RH of these three sensors are similar and are almost of two orders of magnitude as the RH increases from 25% to 85%, illustrating good reproducibility and excellent humidity sensitivity.

It is known that important parameters for sensor devices are response time, recovery time, and reproducibility. To investigate these properties, the dynamic testing of the BaCO3 nanowire device at a constant RH is performed. The response time for the sorption and desorption curves measured at 25°C is shown in Figure 4(b). The response time from 25% to 85% RH is about 16 s, while the recovery time from 85% to 25% RH is about 56 s. Further testing after several additional cycles demonstrates good reproducibility of the sensor. The response and recovery time of the BaCO3 nanowires sensors are much better than that of other sensors made from complex oxides15–17 and simple oxides.18 Therefore, the device made from the BaCO3 nanowires can be regarded as a superior response humidity sensor.

In general, there are two processes of adsorption of water molecules.20,21 First, the chemisorbing of a monolayer of water with proton transfer among hydronium ions (H2O+ → H3O+) and, second, the physisorbing of a multilayer of water with increasing humidity, where both H+ and H3O+ act as charge carriers. According to Anderson’s proton conductivity model,22 when relative humidity is very low, surface coverage of H2O is not complete and protons can form and migrate by hopping from site to site across the surface. When the surface is covered by water, proton transport is dominant, which is confirmed by the characteristics of the resistance dependent on the relative humidity in Figure 4(a). However, the ionic conductivity becomes dominant when relative humidity is high. The shape of the nanowires facilitates the adsorption and desorption of water molecules and results in fast response and recovery to humidity.25

4. CONCLUSIONS

BaCO3 nanowires have been synthesized for the first time by using the composite hydroxide mediated method.
The nanowires are of single crystals with diameters of 100–200 nm and lengths of 5–6 \( \mu \)m and of orthorhombic phase. The investigation of the humidity sensitivity of the sensors made from the BaCO\(_3\) nanowires reveals that the shape of the nanowires facilitates the adsorption and desorption of water molecules resulting in their fast response and recovery to humidity. BaCO\(_3\) nanowires could be an excellent material for applications in highly sensitive environmental monitoring and humidity control electronic devices.

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**References and Notes**


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