

K₂SO₄ nanowires a good nanostructured template

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Abstract

K₂SO₄ nanowires with the width of 66–100 nm were fabricated by ice-subliming method. Under the heat radiation, the surface of K₂SO₄ nanowires presented ordering K₂SO₄ dots of 3.5 nm and arrays of narrow wires with the width of 3 nm due to the remnant H₂O molecules are released. Using these K₂SO₄ nanowires as the substrate, ZnO nanowires were also fabricated by vapor-phase deposition.
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1. Introduction

Progress in the fabrication and characterization of one-dimensional (1D) nanostructured materials has attracted much interest, owing both to their novel physical properties, which differ from those of bulk materials, and to their potential application in nanodevices [1–7]. Many methods succeed in fabricating nanowires and nanotubes such as metal catalysis [8], carbon nanotube template [9–11] and porous alumina template [12–15]. Because the template and catalysis should be removed for getting the pure 1D materials, it is important to find a template which can be easily removed. In this Letter, K₂SO₄ nanowires template is introduced for its high melting point of 1362 K and being easily washed off. Specially, these K₂SO₄ templates are more suitable to the vapor deposition method due to their loose structure permit the fabrication of the nanowires with different thickness or different materials. In addition, ordering QDs and narrow wires with size of several nanometers can form on the surface of K₂SO₄ nanowires. Be-

cause ZnO is an *n*-type, direct band-gap semiconductor with $E_g = 3.35$ eV [16,17] and particularly interesting for nanodevice applications, ZnO nanowires with ordering QDs is also fabricated.

2. Experimental

The fabrication of K₂SO₄ nanowires by ice subliming method [18]: 0.251 g, 0.0251 g and 0.00251 g K₂SO₄ with AR purity was dissolved in 50 ml water, respectively. After the solution of 0.5 wt% was filled into a 10 ml weighing bottle, it was immersed into liquid nitrogen (77 K). The ice containing K₂SO₄ formed in a minute. Then the weighing bottle was placed into a vacuum chamber before liquid nitrogen had vaporized entirely. Finally the chamber was kept at about 10 Pa by being continually vacuumed with a steady rate of 4 L/s. After this lasted for 24 h, we got the residual white floccules. We also fabricated the products from the solution of 0.05 wt% and 0.005 wt% by the above process.

The fabrication of nanostructured ZnO on K₂SO₄ nanowires: A molybdenum piece between the two electronic rods was used

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as the heat source. ZnO with 99.999% purity was placed on the molybdenum piece. K_2SO_4 white floccules were placed on a copper net ($\varnothing 3$ mm), 5 mm far away above ZnO source. The Mo piece was heated to 1373 K at 1×10^{-3} Pa. ZnO started to grow on K_2SO_4 substrate. The growth process lasted for 30 minutes.

3. Results and discussion

The crystal structure of K_2SO_4 product was characterized by X-ray diffraction (XRD). Fig. 1 is XRD spectrum of the products with the radiation of $Cu K_{\alpha}$. The peaks show an orthorhombic structure with $a = 5.770$ Å, $b = 10.07$ Å and $c = 7.477$ Å (PDF #830681). The morphology was characterized by transmission electron microscopy (TEM) with HITACHI TEM H-8100 IV at 200 kV. Fig. 2 shows the morphology of K_2SO_4 product fabricated by ice subliming method. As shown in Fig. 2(a) (from 0.5 wt% solution), the structure is mainly composed of nanowires with the widths of 66–100 nm and some bridge conjunctions. Fig. 2(b) (from 0.05 wt% solution) and (c) (from 0.005 wt% solution) also show the nanowires with similar width, but they present more fractional segments.

We think the formation of the K_2SO_4 nanowires as follows. When the sample temperature is very low (77 K), the sublimation rate of ice is also low, and the absorbed heat of the sample was larger than the heat loss induced by the sublimation of ice. This led to raise the sample temperature. The final temperature should balance the absorbed heat and the loss heat. The sublimation mainly progressed at this final temperature. The sample temperature in our experiments should be about 273 K for its permitting the high sublimation rate.

During the process of the sublimation, the pressure of the vacuum chamber kept at 10 Pa. It was far lower than the saturated vapor pressure of the ice at the experimental temperature.

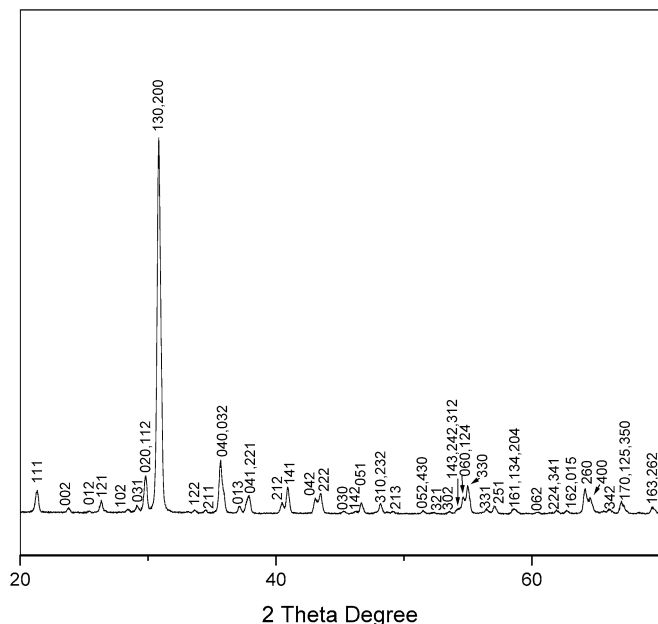


Fig. 1. XRD spectrum of K_2SO_4 nanowires.

This showed that the process of the sublimation was mainly limited by the surface of the sample. That is to say, there was a need for increasing the surface area. Just this led to the spontaneous formation of the nanostructures of 66–100 nm for it can multiply the surface many times.

K_2SO_4 nanowires from the 0.5 wt%, 0.05 wt% and 0.005 wt% K_2SO_4 solutions showed the nanowires with the similar width. So, we think the width of the K_2SO_4 nanowires may be determined by the critical thickness with which the ice- K_2SO_4 layers were strong enough to support themselves.

We can image the formation of K_2SO_4 nanowires. With the ice subliming, a groove first formed on the surface of the ice- K_2SO_4 layer, and the residual K_2SO_4 are dusted on to the two edges. These K_2SO_4 prevented the covered ice from subliming. And the nearest groove could only form on the other side of these residual K_2SO_4 bars. When this process took place all over the surface, a spacing structure of K_2SO_4 bar-groove formed. From Fig. 2(a), the groove can be validated by the white light strips on the middle of the nanowires with the width large than 100 nm. With the ice sublimation, the grooves were penetrated and K_2SO_4 nanowires formed.

Because some H_2O may be embedded in K_2SO_4 nanowires for a low fabrication temperature of about 273 K, the effect of electron radiation on the morphology of K_2SO_4 nanowires was studied. When an electron beam with acceleration voltage of 200 kV and beam current of 15 μA were projected on the K_2SO_4 nanowires, some small holes formed on the surface of the wires. As shown in Fig. 3, these holes were not random but they were arranged in rows. This indicates that H_2O molecules were on the position of rows were easy to be picked off. The selective evaporation of H_2O molecules on the surface of K_2SO_4 nanowires may be related with the crystal structure of K_2SO_4 and heat conduction of the surface. Details research is undergoing.

With the increase of electron radiation, some ordered K_2SO_4 dots form on the surface of K_2SO_4 nanowires. As shown in Fig. 4, the even size of the dots is about 3.5 nm and the distance between two QDs is about 7.8 nm. With the further increase of electron radiation, as shown in Fig. 5, an array of narrow wires with diameter of about 3 nm can also form on the surface of K_2SO_4 nanowires.

The formation of ordering QDs were explained as follows. When the K_2SO_4 nanowires were under the electron radiation, the remnant H_2O molecules on the surface are heated and get rid off. This resulted in many vacancies appearing on the surface. The surface became instable. So it spontaneously formed K_2SO_4 crystallites of about 3.5 nm. Now, the heat radiation could only get rid off the remnant H_2O molecules around the crystallites of about 3.5 nm. These new vacancies then compressed the crystallites to form a compact arrange, the ordered dots. When the dots were dense enough to be continuous with the neighboring dots in a line, instead of separate crystallites the residual K_2SO_4 formed narrow wires for the small crystallites being jointed with the neighboring ones. And the surface presented the narrow wires array.

The remnant H_2O molecules have been validated by the differential thermal analysis (DTA) measure on the fresh product.

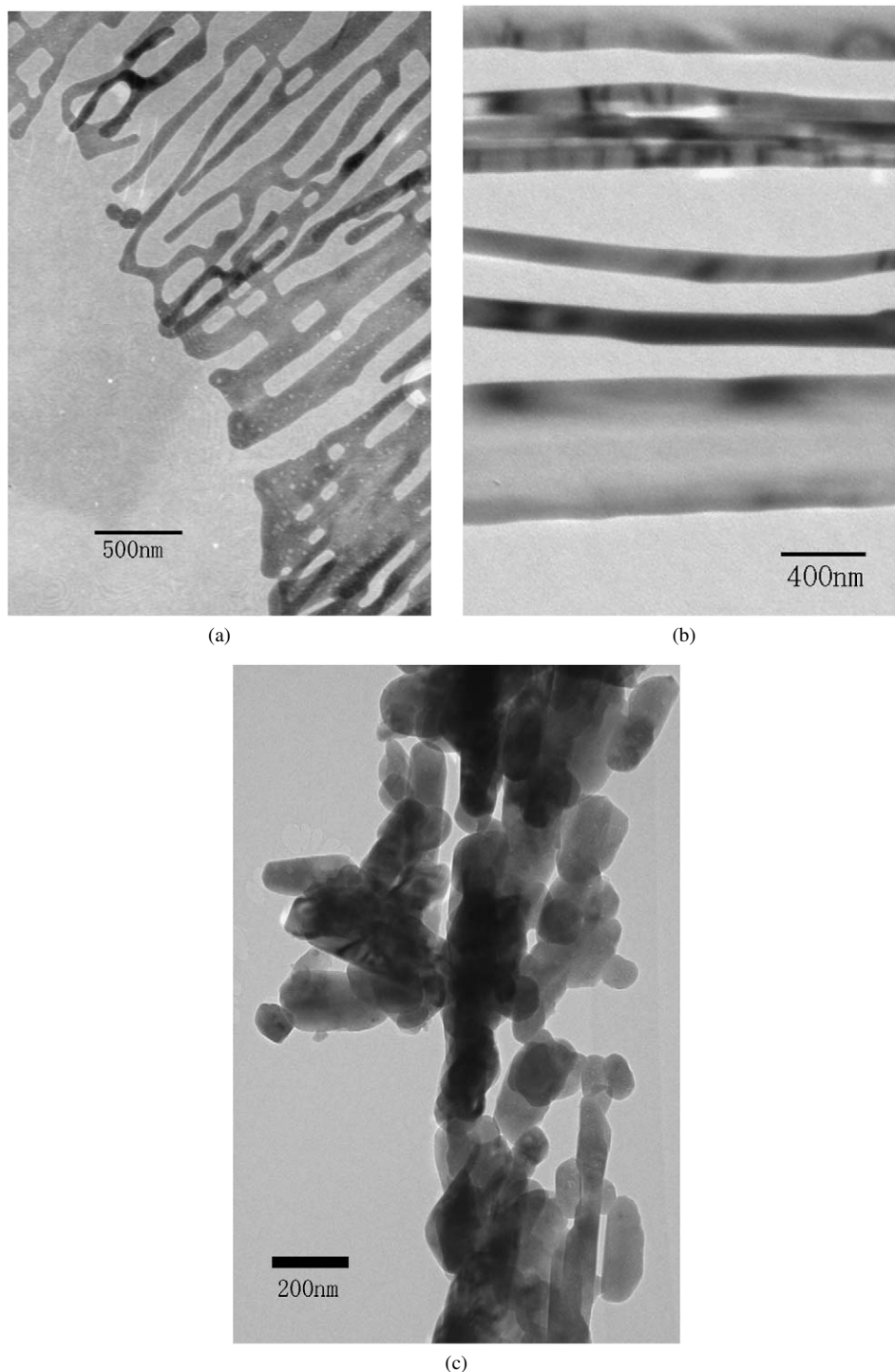


Fig. 2. (a) TEM image of K_2SO_4 nanowires from 0.5 wt% solution. (b) TEM image of K_2SO_4 nanowires from 0.05 wt% solution. (c) TEM image of K_2SO_4 nanowires from 0.005 wt% solution.

As shown in Fig. 6, the results show that the main absorption of heat presents a concave step, the beginning of which is near 373 K. It is according to the H_2O boiling point. The curve shows flat shape at the range of 373–861 K, and an absorption peak appears at 861 K. Then the curve raises its tail. This indicates that above 861 K, the heat absorption of the sample becomes weak. For the thermogravimetry (TG) curve, it shows clear decrease above 373 K. This indicates that the remnant

H_2O molecules are gradually being get rid off. Above 861 K, the weight loss more and reach a new stage. The whole weight loss is 1.4 wt%. So the fresh K_2SO_4 nanowires contain the remnant H_2O of at least 1.4 wt%.

K_2SO_4 nanowires template has two advantages. One is that K_2SO_4 nanowires can be used as the template of nanostructured materials fabricated at high temperature for the melting point of K_2SO_4 being 1362 K. The other is that it is easy to get pure

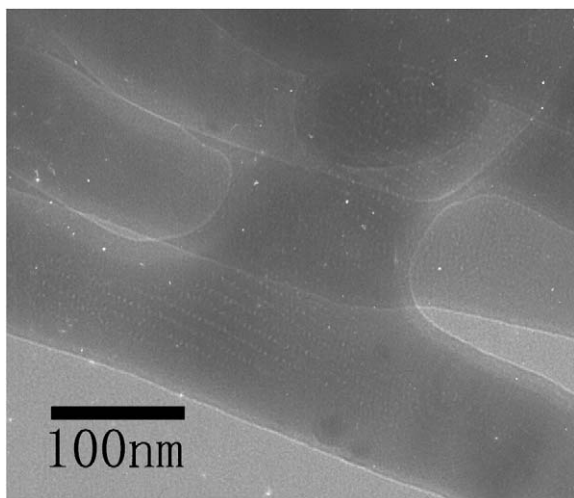


Fig. 3. Small holes formed on the surface of K_2SO_4 nanowires.

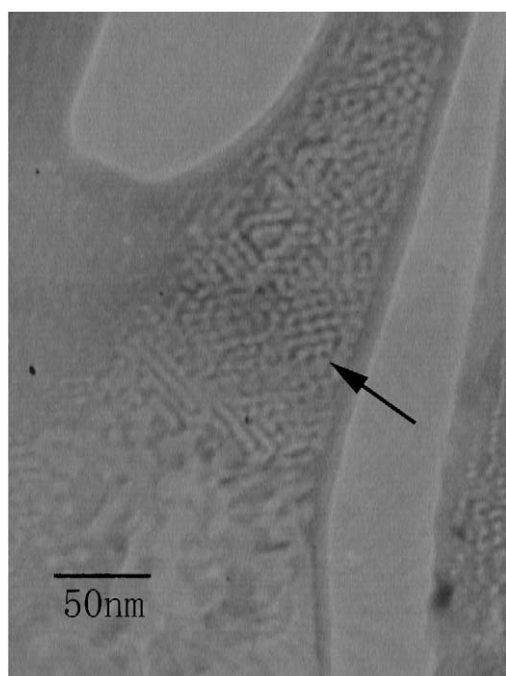


Fig. 4. The ordering dots formed on the surface of K_2SO_4 nanowires.

nanostructured materials for the K_2SO_4 template being easily washed off. To prove K_2SO_4 nanowires being able to work as a nanostructured template, ZnO nanostructure was fabricated on K_2SO_4 nanowires substrate by vapor-phase deposition. The morphology of the sample whose K_2SO_4 nanowires substrate had been washed off by water was characterized by TEM. As shown in Fig. 7, the width of ZnO nanowires is about 100–150 nm, the concaves resulted from the K_2SO_4 nanowires can be seen clearly. This shows that during the growth process, the growth of ZnO was confined on the wires and conjunctions of the K_2SO_4 substrate and the nanostructured ZnO has a negative shape to the K_2SO_4 wires. Specially, some ordering QDs formed on the inner surface of nanostructured ZnO. As shown in inset, the average size of QDs is about 3.5 nm and a , the constant of the plane hexagonal lattice composed of QDs, is

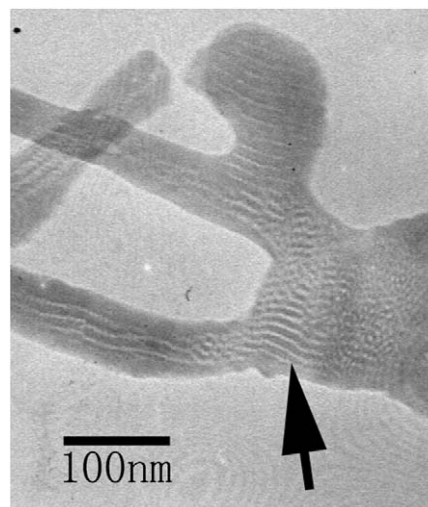


Fig. 5. Array of narrow wires formed on the surface of K_2SO_4 nanowires.

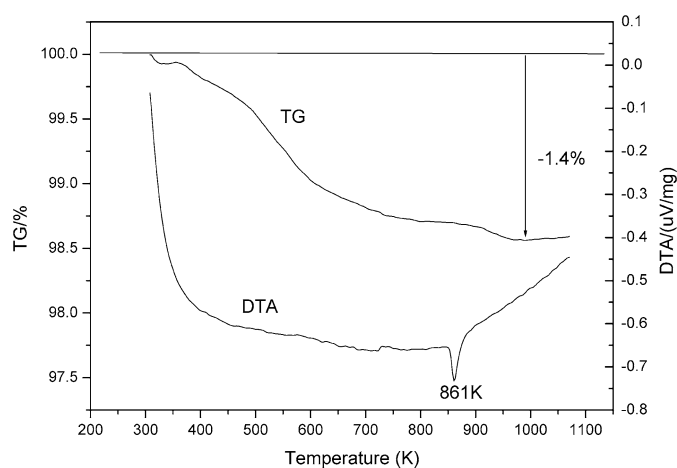


Fig. 6. The differential thermal analysis (DTA) and the thermogravimetry (TG) of the fresh product.

about 7.8 nm. In addition, an array of ZnO narrow wires is also found on other inner surface. As shown in Fig. 8, the width of ZnO narrow wires is about 3 nm and the distance between two narrow wires is also about 3 nm. These show that the fine nanostructure spontaneously formed on the surface of K_2SO_4 wires can be copied into the nanostructured materials grown on them.

For knowing the relation of the fine nanostructure and the ZnO nanowires, TEM image of ZnO nanostructure was taken at a side angle. As shown in Fig. 9, a double layer structure can be seen clearly. It is composed of a thin layer of small nanoparticles with several nanometers and a thick layer of anisotropic grains with the diameter of less 30 nm. The thin layer formed at the beginning of the growth and the fine nanostructures also formed in this thin layer. Then via a buffer composed of particles with the size of 3–30 nm, the continuous thick layer was grown on the thin layer. This makes the fine nanostructures be fixed on the thick layer. The complex will be hard enough to stand independently for the thickness of the thick layer can be adjusted by growth time. This double layer structure of the complex is important to extend the application of K_2SO_4 nanowires

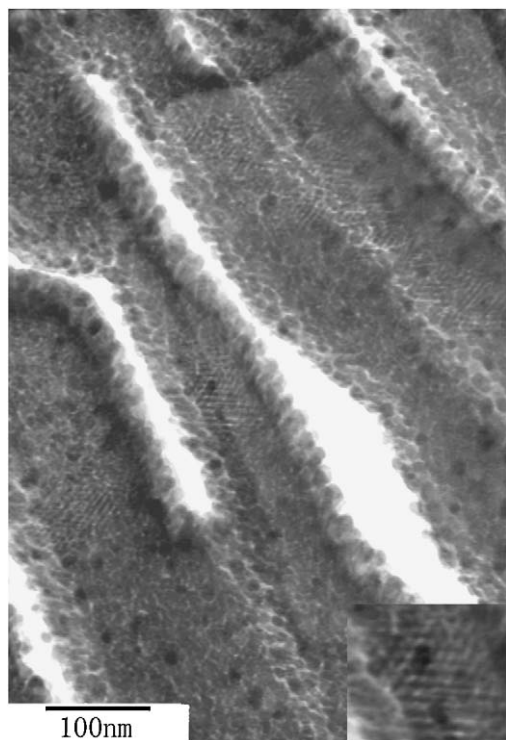


Fig. 7. ZnO nanowires with ordering QDs fabricated on the K_2SO_4 nanowires template.

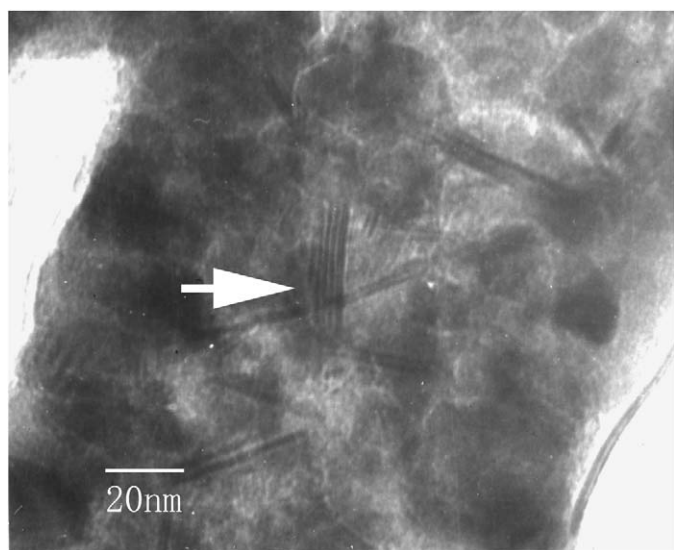


Fig. 8. An array of ZnO narrow wires.

template by forming fine nanostructure of a material and using other materials to fix them.

4. Conclusion

K_2SO_4 nanowires were fabricated by ice-subliming method, the product was composed of nanowires of 66–100 nm and some bridge conjunctions. Under the electron radiation, ordering dots of 3.5 nm and array of narrow wires with width of 3 nm

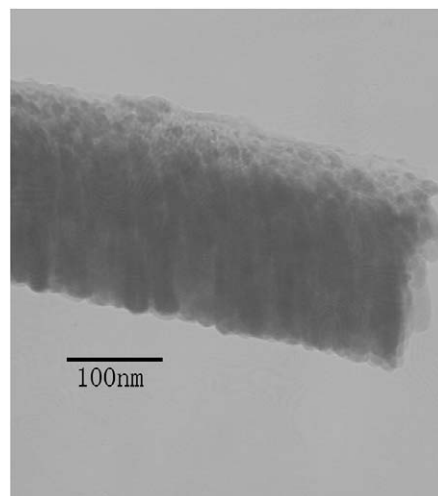


Fig. 9. TEM image of ZnO nanostructure taken at a side angle.

formed on the surface of K_2SO_4 nanowires. K_2SO_4 nanowires will be a good template for its high melting point of 1362 K and being easily washed off. ZnO nanostructure was fabricated on K_2SO_4 nanowires substrate by vapor-phase deposition. Besides ZnO nanowires formed on the K_2SO_4 nanowires template, ZnO fine nanostructures also formed on the inner surface of ZnO nanowires. Because of the loose structure, K_2SO_4 nanowires can work as the template not only for vapor method but also for liquid method such as ethanol system. In a summary, K_2SO_4 nanowires can be a good template for nanowires, nanotubes and QDs assembly.

Acknowledgements

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