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Rapid synthesis of zinc oxide nanorods by one-step, room-temperature, solid-state reaction

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Nanorods of zinc oxides were successfully prepared by a simple and novel one-step, room-temperature, solid-state reaction with the assistance of a suitable surfactant. Their morphology was observed through Transmission election microscopy (TEM) and found that the products consist of a pure rod-like structure. They are also characterized by X-ray power diffraction (XRD) patterns and expected to present special magnetic, optical and electrical properties, and facilitate future nanoscale device applications.
Keywords: nanorods; zinc oxides; solid-state reaction; nanostructures

1. INTRODUCTION

The field of nanostructured materials is a fascinating area of chemistry and materials science because of their novel properties that differ from those of bulk materials and potential application in both mesoscopic research and the development of nanodevices [1-3]. One-dimensional (1D) materials are an important category of nano-structured materials and have been widely researched yielding various special structures such as nanotubes, nanorods, nanowires and nanobelts etc[4-6].

Semiconductor materials, metal oxides have aroused extensively interest, as they are capable of being used in optical devices and microelectronic technology. As n-type semiconductor, zinc oxide is expected to process properties having applications in shock resistance, sound insulation, photosensitization, fluorescence, gas sensi-tization and catalysis. Considerable effort has been placed on the synthesis of one-dimensional metal oxides nanostructured materials using laser ablation, template, molecular beam epitaxy and other methods [7-9]. However, these preparation methods usually require complex process control, very high temperature or long synthesis time.

Here we firstly report a novel and rapid route for synthesis of zinc oxide with controllable morphology by means of one-step, room-temperature, solid-state reaction with the assistance of a suitable surfactant. To our knowledge, the solid-state reaction method has been used to prepare many kinds of compounds such as cluster compounds, metal oxides, composite metal oxides, coordination compounds, polymetallates and matastable substances[10-15]. The synthesis methods have shown many advantages such as no need for solvent, high productivity and selectivity, low energy consumption and simple reaction technology.

In the present work, no vacuum system has been used and the reactions were carried out at ambient pressure, which is an advantage of our work. So the synthesis of metal oxide nanorods by room-temperature, solid–state reaction with the presence of a suitable surfactant was especially of great significance. Thus, the method introduced in the present work may provided a new path to fabricate one-dimensional nanostructured materials with a convenient, economical, less energy and material consuming and environmentally friendly way in only one step. The influence of different surfactant is discussed and the surfactant is found to play an important role in the reaction process. The formation mechanism of rod-like morphology was primarily studied.

2. EXPERIMENTAL

All the regents are analytical pure from shanghai chemistry and were used without further purification. Manipulations and reactions were carried out in air.

Our procedure for synthesizing zinc oxides nanorods is as follows. Solid zinc chloride and sodium hydroxide with a molar ratio were ground for 5 min each before mixing together; 5ml of polyethylene glycol (PEG) 400 was then added to the mixture. After 50 min of grinding, the mixture was deposited for 2 h. Then it was further ground and washed with distilled water and alcohol in ultrasonic bath. Finally, the product was dried in air.

The synthesized product was characterized by XRD patterns. XRD were taken on a MAC Science MXP18AHF X-ray diffractometer with graphite-monochromatized CuKα radiation (λ=1.54056Å), employing a sampling width of 0.02°. The morphology of product was determined by TEM. TEM images were made on a Hitachi H-600 transmission electron microscopy with an accelerating voltage of 100KV.

3. RESULTS AND DISCUSSIONS

Fig1. The TEM images of the as-prepared product

Fig.1 illustrates that the typical TEM images of product prepared by one-step, room-temperature, solid-state reaction with the assistance of PEG 400. As can be seen, the product were composed of uniform short nanorods with a diameter of 30nm. It is also found that the nanorods have a snowflake-like morphology, which was piled up by small nanorods.

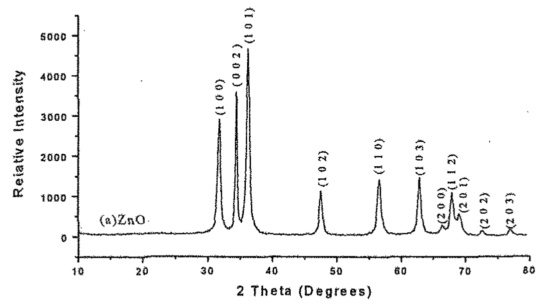

Fig. 2 The XRD patterns of as-prepared product

Fig.2 shows that the XRD patterns of as-prepared nanorods by one-step, room-temperature, solid-state reaction. It can be seen that all of the diffraction peak can be indexed as zinc oxide with hexagonal phase (JCPDS Card file NO.80-0075), although the relative intensity of the peaks of zinc oxide is not consistent with that of bulk zinc oxide. The second intensive peak of bulk zinc oxide is (1 0 0); however, for our sample the second intensive peak is (0 0 2), whereas the other peaks are consistent with that of bulk zinc oxide. The particle sizes calculated from the XRD peak widths by Deby-Scherrer equation are about 10nm. No characteristic peaks of impurities, such as sodium chloride, PEG, and other by-product were observed in zinc oxide nanorods.

Unlike the reactions in the solution, solid-state reactions were directly carried out in the condition of no any medium. So they were preformed in different reaction mechanism from the solution reaction. The products of solid-state reaction are also different from the products from the solution. Metal oxides were obtained through grinding solid metallic salts with sodium hydroxides, which is different from the results of hydroxides in solution. Considering that hydroxides were disposed of by strong reaction heat to produce oxides in the reaction process, we speculate that the reaction of metallic salts with sodium hydroxides to produce oxides is divided into two steps. The first step is to produce hydroxides and the second one is to dehydrate hydroxides to produce oxides.

The formation of rod-like morphology is due to the presence of a suitable surfactant. The influence of different surfactant is discussed and the surfactant is found to play a very important role in the reaction process. In our experiment, polyethylene glycol (PEG) 400 is selected as the surfactant to obtain pure zinc oxide nanorods. Though the PEG 400 was added into the reaction system, it didn't react with the reactant and entirely moved by washing with distilled water and alcohol. XRD data demonstrated that there was no surfactant in the final as-prepared product. During the formation of zinc oxide nanorods, the surfactant, PEG 400 may provide a long chain reaction interface and induce the nanocrystallates to grow in definite direction. Furthermore, the reaction rate was also slow down because the surfactant hindered the touch of the particle of two substrates in the reaction system. Therefore, there is enough time for the small particle to assembly to the rods. The growth process was well controlled through PEG 400, so it was thought that the surfactant was able to act as a template (when PEG wasn't used, no nanorods were formed), with the template action resulting in the growth of the inorganic crystallites in good orientation. Other surfactant, such as tween-60 and span-80, were also tested in our experiments. However, the results show that when they were selected as the surfactant, the products consist of nanospheres in aggregated states. It is very important to selected suitable surfactant for the shape of product in our present work. A detailed study of the growth mechanism of metal oxides nanorods is in process.

4. CONCLUSION

In summary, zinc oxide nanorods with snowflake-like morphology have been successfully prepared by one-step, room-temperature, solid-state reaction methods with the assistance of the surfactant (PEG 400). The key to the formation of the rod-shape formation is the suitable surfactant template which ensures that there is a long-chain reaction interface and there is sufficient time for self-organization of the nanocrystallates. In addition, the present synthesis methods are a simple and facilitate approach for synthesis of one-dimensional materials. With the development of solid-state reaction techniques for morphology control, it is predicted to synthesis other nanostructured materials with a desired morphology.

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