研究快报

草酸镁空心纳米结构的一步低热固相化学合成

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Synthesis of Magnesium Oxalate Hollow Nanostructures by One-step, Low Heating Temperature Solid-state Chemical Reaction

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Abstract: Magnesium oxalate hollow nanostructures have been synthesized successfully by one-step, low heating temperature solid-state chemical reaction. Magnesium oxalate hollow nanospheres were obtained though grinding directly grinding magnesium acetate and oxalic acid. And magnesium oxalate nanorods consisted of hollow nanospheres were also fabricated by means of a suitable surfactant to modify the solid-state reaction mentioned above. The as-prepared samples were characterized by XRD, TEM and SEM.

Key words: hollow structure; solid-state reaction; magnesium oxalate; nanomaterials

Nanostructured materials are a focused research field due to their unusual properties and potential applications ranging from mesoscopic research to the development of nanodevices[1,2]. Especially, all sorts of nanoscale materials with specific structure or interesting morphology have prompted considerable interests to understand the property variations of material with size, shape, form of aggregation and dimensionality[3~5]. As an important category of that, hollow nanostructured materials have aroused extensive attention because of applications such as controlled release capsules, artificial cells, chemical sensors, shape-selective catalysts and absorbents.

Within the past few years, studies on the hollow structures have been focused on sulfides, nitrides and carbides such as CdS hollow spheres, peanut-like CdS hollow structure, BN nanobamboos and SiC hollow nanospheres[6~10]. However, to the best of our knowledge, there is no report on the synthesis of magnesium oxalate with hollow nanostructures.

Low heating temperature solid-state chemical reaction is a simple and effective method to fabricate coordination compounds[11], Cluster compounds[12], solid-coordination compounds [13] and nanomaterials[14~17]. In this communication, we report the successful preparation of magnesium oxalate hollow nanospheres and nanorods by one-step, low heating temperature solid-state chemical reaction. The novel route can also

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be adapted to create other functional nanostructures with specific morphology.

1 Experimental

All the reagents were A.R. grades from Shanghai Chemical Reagent Company and were used without further purification. Reactions were carried out in air.

The procedure for the synthesis was as follows: $MgC_2O_4 \cdot 2H_2O$ hollow nanospheres (sample A): 10 mmol magnesium acetate and oxalic acid were weighed accurately and ground for about 5 min in agate mortar, respectively, then mixed. The mixture was ground for 50 min and heated at 70 ℃ for 2 h to ensure the completeness of reaction. After further grinding at room temperature, the mixture was washed with alcohol in ultrasonic bath. Finally, the product was dried in air at 70 ℃ for 2 h. $MgC_2O_4 \cdot 2H_2O$ nanorods consisted of hollow nanospheres (sample B): 10 mmol magnesium acetate were weighed accurately and ground for about 5 min in agate mortar, then was added 4 mL polyethylene glycol (PEG) 400 and 10 mmol oxalic acid fine powder. Then the mixture was treated the same as for sample A above to obtain the final product.

XRD was taken on a MAC Science MXP18AHF X-ray diffractometer with graphite-monochromatized Cu $K\alpha$ radiation (λ=0.154 056 nm). TEM images were made on a Hitachi H-600 transmission electron microscopy with an accelerating voltage of 100 kV. SEM images were performed on a LEO1430VP scanning electron microscopy.

2 Results and discussion

Fig.1 shows the XRD patterns of the as-prepared products. It can be seen that the diffraction peaks of two samples can be indexed as magnesium oxalate hydrate ($MgC_2O_4 \cdot 2H_2O$, JCPDS No.28-0625). No characteristic peaks of impurities such as reaction substrates and other by-products were observed in two samples.

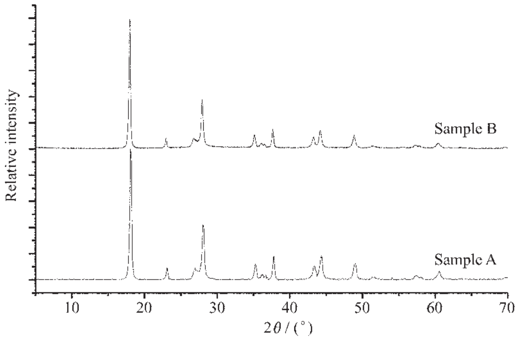

Fig.1 XRD patterns of as-prepared products

The transmission electron microscopy (TEM) images are shown in Fig.2. It can be observed obviously that two samples have hollow structures. The strong contrast between the dark edge and pale center is the evidence for their hollow nature. Sample A consisted of hollow nanospheres with a diameter of 50~100 nm. Sample B was composed of hollow nanorods with a diameter of 100~200 nm and a length up to several micron. The scanning electron microscopy (SEM) images were shown in Fig.3. It can be seen that two samples have sphere-like and rod-like morphology, respective-

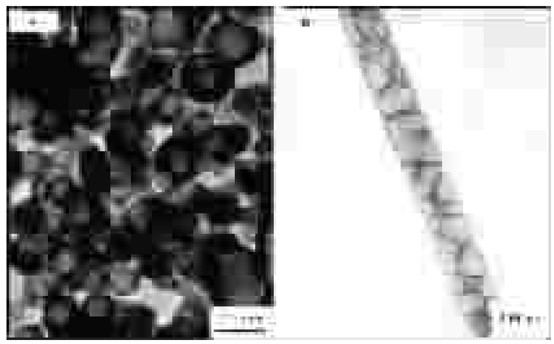

Fig.2 TEM images of sample A and sample B

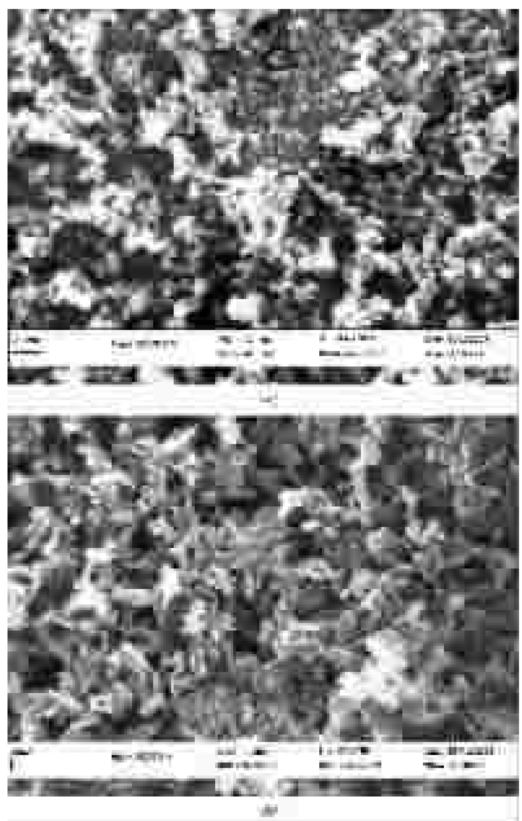

Fig.3 SEM images of two solid-state samples (a) sample A and (b) sample B

ly. This result is fairly in agreement with that of TEM.

In the experiment, the surfactant played an important role in the process of shape-formation. When no surfactant was used in the reaction process, only nanospheres were observed. So it can be thought that the surfactant may act as a soft template and induce the nanocrystallites to grow in good orientation. A detailed growth mechanism of nanorods is in under study. In addition, with the development of solid-state reaction techniques for morphology control, it could be expected that other functional nanostructured materials with a desired morphology might be synthesized.

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