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Characterization of magnesium oxalate and cobaltous hydroxide nanostructures prepared through one-step solid-state chemical reaction at low-heating temperature

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Abstract Magnesium oxalate hollow nanostructures and cobaltous hydroxide nanorods have been synthesized successfully by one-step solid-state chemical reaction at low-heating temperature. Magnesium oxalate hollow nanospheres were obtained via directly grinding magnesium acetate and oxalic acid. Cobaltous hydroxide nanorods were also fabricated by means of a suitable surfactant to modify the solid-state reaction. The as-prepared samples were characterized by X-ray diffraction, TEM, and SEM.

Keywords Hollow structure · Nanorods · Solid-state reaction · Magnesium oxalate · Cobaltous hydroxide · Nanomaterials

1 Introduction

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 interest to understand the property variations of material with size, shape, form of aggregation, and dimensionality [3–5]. As an important category, hollow nanostructured materials have aroused extensive attention because of their application as controlled release capsules, artificial cells, chemical sensors, shape-selective catalysts, and absorbents.

In the past few years, studies on hollow structures have focused on sulfides, nitrides, and carbides, such as CdS hollow spheres, peanut-like CdS hollow structures, 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. Furthermore, magnesium oxalate is an important precursor of MgO ceramics materials.

Cobalt hydroxides have recently received increasing attention due to many important applications, such as additives of alkaline secondary batteries, catalysis materials, and reactive templates for highly textured thermoelectric cobaltite ceramics [11–13]. One of the most commonly used techniques to produce cobalt hydroxides is precipitation from homogenous solutions by cobalt salt and bases. However, it is too difficult to obtain $Co(OH)_2$ nanorods. The exploration for a simple synthetic method to obtain $Co(OH)_2$ nanorods would offer the opportunity to further develop their characterization and applications.

It has been confirmed that low-heating-temperature solid-state chemical reaction methods are simple and effective for fabricating coordination compounds [14], cluster compounds [15], solid-coordination compounds [16], and nanomaterials [17–20]. In this paper, we reported the successful preparation of magnesium oxalate hollow nanospheres and nanorods and cobaltous hydroxide nanorods by one-step solid-state chemical reaction at low heating temperature. The novel route can also be adapted to create other functional nanostructures with specific morphology.

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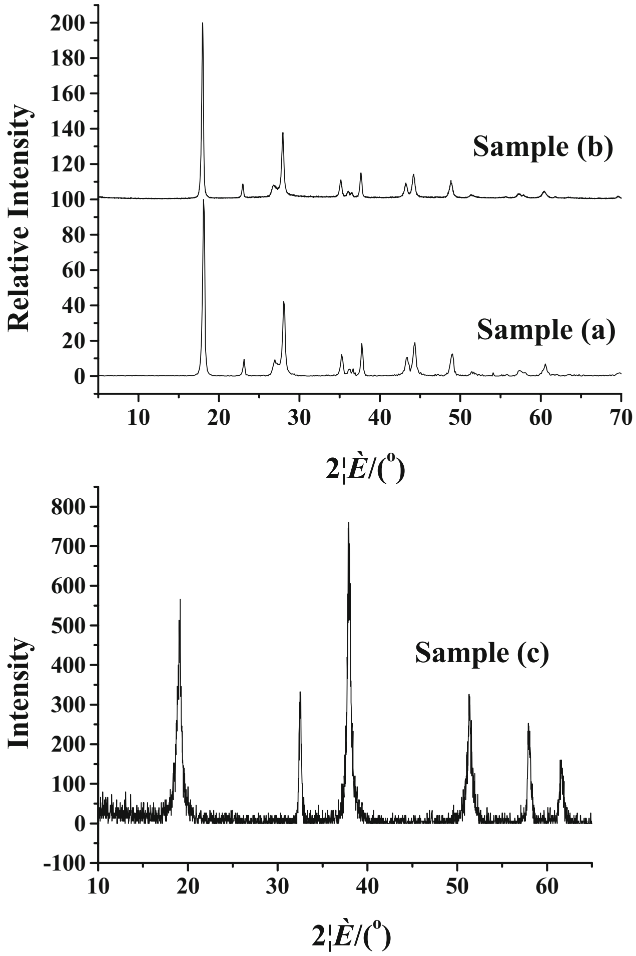

Fig. 1 XRD patterns of as-prepared product samples (a), (b), and (c)

2 Experimental

All the reagents are analytical pure from Shanghai Chemistry and were used without further purification. Reactions were carried out in air. The procedure for synthesizing magnesium oxalate hollow nanostructures is as follows. $MgC_2O_4{\cdot}2H_2O$ hollow nanospheres [sample (a)]: 10 mmol magnesium acetate and oxalic acid were accurately weighed and ground for about 5 min in agate mortar, respectively, then mixed. The mixture was ground for 50 min and heated at 70°C for 2 h to ensure the completeness of the reaction. After further grinding at room temperature, the mixture was washed with water and alcohol in an ultrasonic bath. Finally, the product was dried in air at 70°C for 2 h. $MgC_2O_4{\cdot}2H_2O$ nanorods consisted of hollow nanospheres [sample (b)]: 10 mmol magnesium acetate was accurately weighed and ground for about 5 min in agate mortar, then 4 mL polyethylene glycol (PEG) 400 and 10 mmol oxalic acid fine powder were added. The mixture was ground for 50 min and heated at 70°C for 6 h to ensure the completeness of the reaction. After further grinding at room temperature, the mixture was washed with water and alcohol in an ultrasonic bath. Finally, the product was dried in air at 70°C for 2 h.

Cobaltous hydroxide nanorods [sample (c)]: 20 mmol of solid $Co(Ac)_2{\cdot}4H_2O$ was weighed and ground for about 5 min in agate mortar, then 5 mL of PEG 400 was added. After mixing completely, 30 mmol of solid NaOH was added to the mixture, which was ground for 30 min and then laid at room temperature for 2 h. Finally, the mixture was washed with distilled water and EtOH in an ultrasonic bath. The product was dried in air.

X-ray diffraction (XRD) were taken on a MAC Science MXP18AHF X-ray diffractometer with graphite-monochromatized CuKα radiation (λ=1.54056 Å). Transmission electron microscopy (TEM) images were made on a Hitachi H-600 transmission electron microscope with an accelerating voltage of 100 KV. Scanning electron microscopy (SEM) images were performed on a LEO1430VP scanning electron microscope. Thermal analysis (TG-DTA) was examined in air on a NETZSCH STA449C thermal analyzer at a heating rate of 10°C/min from 30°C to 700°C.

3 Results and discussion

Figure 1 shows the XRD patterns of the as-prepared products. It can be seen that the diffraction peaks of two samples [sample (a) and sample (b)] can be indexed as magnesium oxalate hydrate ($MgC_2O_4{\cdot}2H_2O$, JCPDS NO.

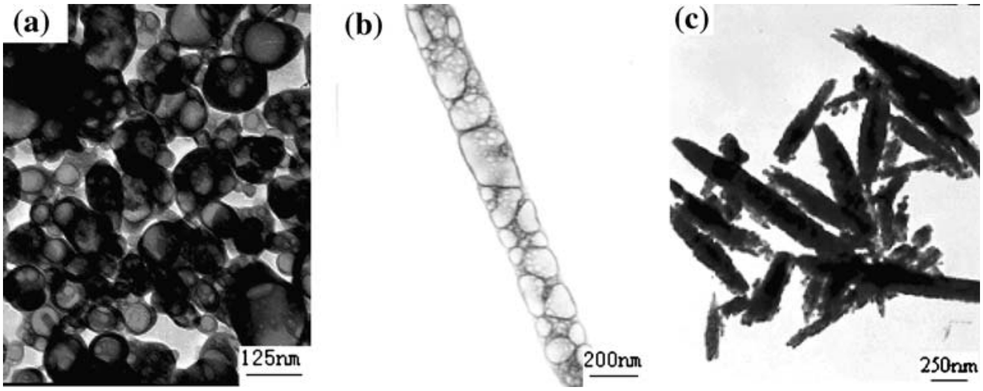

Fig. 2 TEM images of sample (a), sample (b), and sample (c)

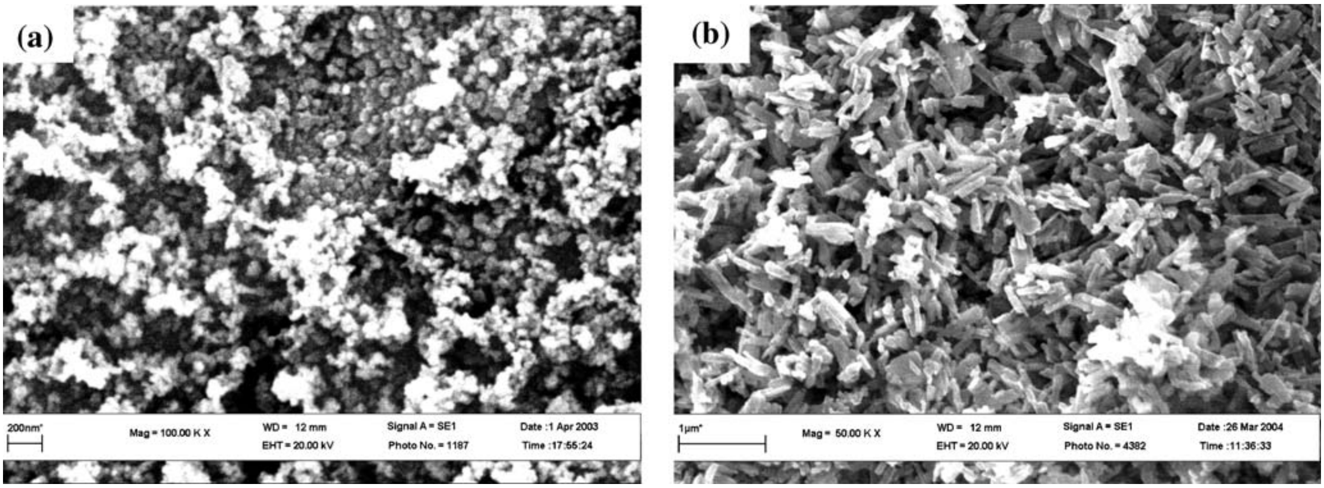

Fig. 3 SEM images of sample (a) and sample (b)

28-0625) and sample (c) can be indexed as cobaltous hydroxide (JCPDS NO. 30-0443). No characteristic peaks of impurities such as reaction substrates and other by-product were observed in three samples. The results indicate that the two solid-state systems have reacted completely.

The TEM images are shown in Fig. 2. It can be observed that two samples [sample (a) and sample (b)] have hollow structures. The strong contrast between the dark edge and pale center is the evidence for their hollow nature. It was seen that sample (a) consists of hollow nanospheres with diameters of 30–60 nm. Sample (b) was composed of nanorod-assembled hollow nanospheres with diameters of 100–200 nm and lengths of up to several microns. Sample (c) was composed of nanorods with diameters of 150–250 nm and lengths of up to 300–1,000 nm.

The SEM images are shown in Fig. 3. It can be seen that two magnesium oxalate samples have sphere-like and rod-like morphologies. The observational results are consistent with those of the TEM.

To provide more information on the composition and structure of the product, we carried out thermal analyses of as-prepared $Co(OH)_2$. The corresponding TG/DTA curves are shown in Fig. 4. It is observed that $Co(OH)_2$ nanorods follow two-step decomposition. The first weight loss of about 18.12% before 290°C is consistent with the loss of one structure of water [$Co(OH)_2 \rightarrow CoO + H_2O$, calc. 19.39%]. It is accompanied by an exothermic peak at 205.4°C. The second one occurs in a wide temperature range of 290–550°C and corresponds to decomposition of CoO leading to the formation of the metal Co.

It is worth noting that the suitable surfactant plays an important role in the process of shape-formation of magnesium oxalate hollow nanostructures and cobaltous hydroxide nanorods. When no surfactant was used in the reaction process, only nanospheres were observed. After introducing a suitable surfactant – PEG 400 – to the

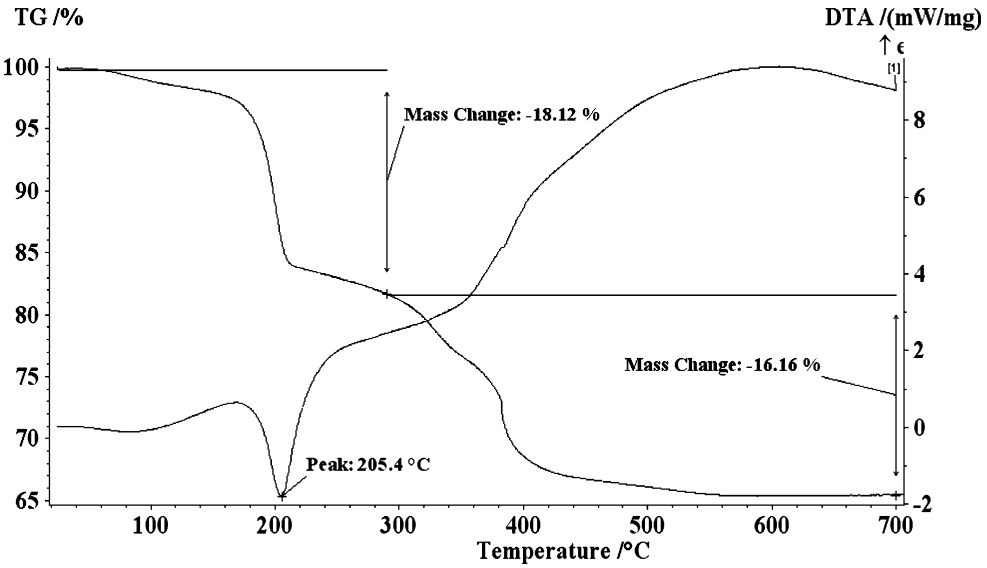

Fig. 4 The TG–DTA curves of $Co(OH)_2$ nanorods

reaction system, the nanorod-like structure was obtained. Other surfactants such as Tween-60 and Span-80 were also tested in our experiments. However, no nanorods were formed. Therefore, it can be thought that the surfactant (PEG) may act as a soft template and induce the nanocrystallites to grow in good orientation. A detailed study of the growth mechanism of nanorods is in process. In addition, with the development of solid-state reaction techniques for morphology control, it is predicted to synthesize other functional nanostructured materials with desired morphologies.

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