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Microwave-assisted synthesis of cobalt oxalate nanorods and their thermal conversion to Co_3O_4 rods

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Abstract

Cobalt oxalate nanorods have been successfully synthesized by a simple microwave-assisted solution approach using an ionic liquid 1-*n*-butyl-3-methyl imidazolium tetrafluoroborate. Upon thermal decomposition at 400 °C, cobalt oxalate nanorods could be converted to Co_3O_4 rods consisting of nanoparticles. The products were characterized using X-ray powder diffraction, transmission electron microscopy, thermogravimetric analysis and differential scanning calorimetric analysis.

Keywords: A. Nanostructures; A. Oxides; B. Chemical synthesis

1. Introduction

Transition metal oxides have many applications due to their interesting properties [1,2]. Among these oxides, spinel type Co_3O_4 displays unique electronic and chemical properties. In particular, Co_3O_4 is an important ceramic oxide with electrochemical [3], magnetic [4], and catalytic applications [5]. Co_3O_4 with a variety of morphologies, for example, nanotubes [6–8], nanoparticles [9], nanocubes [10], nanofibers [11], and hollow spheres [12] have been reported.

Room temperature ionic liquids (RTILs) are a new class of solvents with advantages such as high fluidity, low melting temperature, extended temperature range in liquid state, high ionic conductivity,

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thermal stability and importantly negligible vapor pressure [13]. RTILs can be used in catalysis [14], electrochemistry [15], and polymer synthesis [16]. RTILs have also received increasing attention for their applications in inorganic materials synthesis [17,18]. The application of microwave heating in synthetic chemistry is a fast-growing area of research [19,20]. Microwave heating has been accepted as a promising method for rapid volumetric heating, higher reaction rates and reduction in reaction times compared with conventional heating methods. RTILs are excellent microwave-absorbing agents due to their high ionic conductivity and polarizability, thus leading to a high heating rate and a significantly shortened reaction time. Recently, microwave-assisted ionic liquid (MAIL) method has been applied in synthesis of Te nanowires and nanorods [21], flowerlike ZnO [22,23], CdS and ZnS nanoparticles [24], Bi_2S_3 and Sb_2S_3 nanorods [25], and $PbCrO_4$ nanorods [26]. The MAIL method is a fast and environment-friendly route to the preparation of a variety of nanostructured materials. However, there have been no reports on the preparation of cobalt oxalate nanorods using RTILs. Here we demonstrate the successful example of the extension of this method to the synthesis of cobalt oxalate nanorods.

In this paper, we report our recent effort in synthesis of cobalt oxalate nanorods by microwave assisted solution method using an ionic liquid 1-*n*-butyl-3-methyl imidazolium tetrafluoroborate ([BMIM][BF_4]). We demonstrate that cobalt oxalate nanorods could be converted to rods consisting of Co_3O_4 nanoparticles upon thermal decomposition at 400 °C.

2. Experimetal

2.1. Chemicals and apparatus

Cobalt acetate ($Co(CH_3COO)_2 \cdot 4H_2O$), sodium hydroxide (NaOH), [BMIM][BF_4] and oxalic acid ($H_2C_2O_4$) were purchased and used without further purification.

The microwave oven (2.45 GHz, maximum power 300 W) used for sample preparation was a focused single-mode microwave synthesis system (Discover, CEM, USA). The system was equipped with a magnetic stirrer and a water-cooled condenser. Temperature was controlled by automatic adjusting of microwave power. X-ray powder diffraction (XRD) patterns were recorded using a Rigaku D/max 2550 V X-ray diffractometer with high-intensity Cu Kα radiation ($\lambda = 1.54178$ Å) and a graphite monochromator. The transmission electron microscopy (TEM) was taken on Hitachi H–800 electron microscope with an accelerating voltage of 200 kV. Thermogravimetric analysis (TG) and differential scanning calorimetric analysis (DSC) of samples were carried out on a NETZSCH STA 409 PC thermal analyzer with a heating rate of 10 °C/min in alumina crucibles in flowing air.

2.2. Preparation of cobalt oxalate nanorods

In a typical procedure, $Co(CH_3COO)_2 \cdot 4H_2O$ (13 mg) was dissolved in a mixture of deionized water (0.3 mL) and [BMIM][BF_4] (0.2 mL) (sample 1) or in deionized water (0.5 mL) (sample 2). Then solid $H_2C_2O_4$ (6 mg) and NaOH aqueous solution (0.1 mL, 1 M) were added. Pink precipitate appeared immediately. The mixture was heated at 90 °C for 10 min by a microwave oven and cooled down to room temperature naturally. The product was separated by centrifugation, washed with deionized water and absolute ethanol and dried in vacuum. Sample 3 was obtained under the same experimental conditions as sample 1 except that oil bath was used instead of microwave heating.

2.3. Preparation of Co_3O_4 rods

For the preparation of Co_3O_4 (sample 4), sample 1 was heated at 400 °C in air for 2 h, and black Co_3O_4 powder was obtained.

3. Results and discussion

Fig. 1(a) shows the XRD pattern of sample 1 prepared by the microwave assisted solution method. It indicates that the product consisted of a single phase of cobalt oxalate (JCPDS No. 25-0250). After thermal decomposition of cobalt oxalate precursor at 400 °C for 2 h (sample 4), a single phase of well-crystallized Co_3O_4 with the cubic structure (JCPDS No. 80-1541) was obtained (Fig. 1(b)).

Fig. 2 shows TEM micrographs of samples 1–3. From Fig. 2(a–c), one can see that sample 1 consisted of cobalt oxalate nanorods with diameters of about 50 nm and lengths up to several micrometers. Most nanorods were aligned together (Fig. 2(b)) and thus appeared thicker in a low-magnification TEM micrograph (Fig. 2(a)). Fig. 2(b) displays a magnified TEM image, showing the assemblies of nanorods. Besides aligned nanorods, some nanorods grew into bundles in a few cases (Fig. 2(c)). Cobalt oxalate nanorods were also obtained in ethanol by a solvothermal method at 120 °C for 12 h [27]. In our experiments, cobalt oxalate nanorods could be quickly obtained under microwave heating at 90 °C for 10 min.

Without using $[BMIM][BF_4]$ (sample 2), different morphologies were observed. As shown in Fig. 2(d), sample 2 exhibited irregular rod-like morphology. The average diameters of these rods were about 100 nm and lengths were several hundred nanometers. When keeping the preparation condition identical to sample 1 but oil bath was used instead of microwave heating (sample 3), rod-like cobalt oxalate could also be obtained (Fig. 2(e)) and the morphologies were similar to that of sample 2. However the assemblies of rods were not observed in both samples 2 and 3. One can see that the diameters of rods in both samples 2 and 3 were larger than those of sample 1. This indicates that both the $[BMIM][BF_4]$ and microwave heating play an important role in the formation of cobalt oxalate nanorods. $[BMIM][BF_4]$ consists of larger cation $[BMIM]^+$. The high ionic conductivity and polarizability of $[BMIM]^+$ make it an excellent microwave-absorbing agent, thus leading to a high heating rate and a significantly shortened

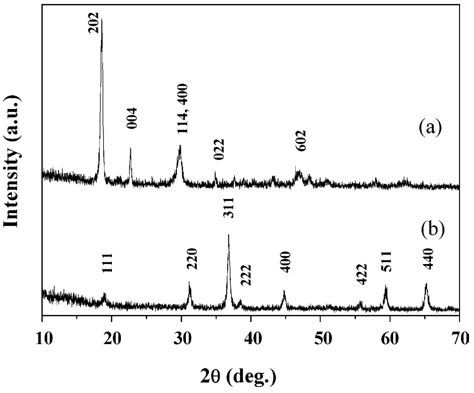

Fig. 1. XRD patterns of the products. (a) Cobalt oxalate nanorods (sample 1); (b) Co_3O_4 rods (sample 4).

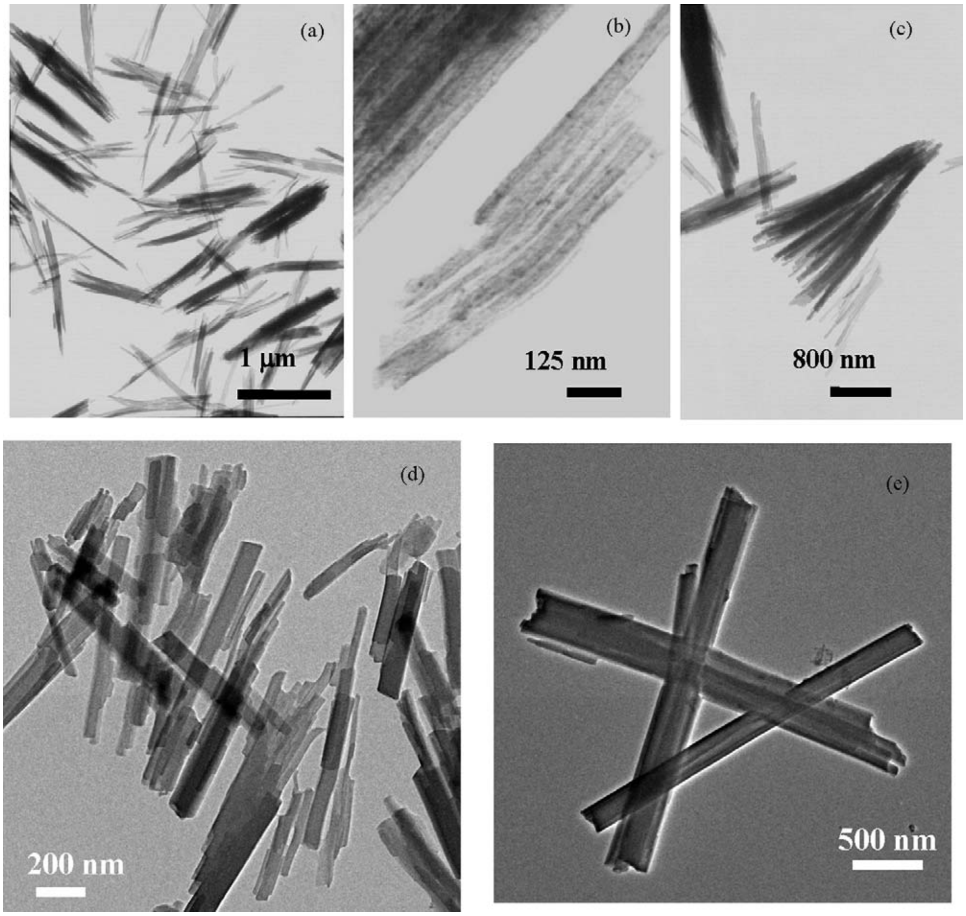

Fig. 2. TEM micrographs of samples 1–3. (a–c) Sample 1; (d) sample 2; (e) sample 3.

reaction time [21]. The movement and polarization of ions under the rapidly changing electric field of the microwave result in transient, anisotropic microdomains for the reaction system, favoring the formation of assemblies of nanorods.

The decomposition temperature of cobalt oxalate was determined according to the results of TG and DSC measurements. When cobalt oxalate nanorods were heated in air at 400 °C for 2 h, Co_3O_4 rods consisting of nanoparticles were observed (Fig. 3). The SAED (selected area electron diffraction) pattern (the inset of Fig. 3(b)) shows polycrystalline nature of Co_3O_4 rods. The rings of the SAED pattern can be indexed as (1 1 1), (2 2 0), (3 1 1) and (4 0 0) reflections which match well with the reported values of the spinel phase of Co_3O_4 [28]. During the thermal decomposition, the elimination of hydroxyl and oxalate groups caused the disruption of the original rodlike morphology, and the template confinement of cobalt oxalate nanorods resulted in the formation of Co_3O_4 rods consisting of nanoparticles. Similar strings of Co_3O_4 nanoparticles were also reported by calcination of cobalt-basic-carbonate ($Co(OH)_x(CO_3)_{0.5(2-x)}\cdot nH_2O$) nanorods [29] and cobalt oxalate nanorods [27]. Xu and Zeng [29] found that Co_3O_4 nanoparticles interconnected along the original longitudinal directions of the cobalt-basic-carbonate nanorods have a predominant assembling direction of [1 1 1].

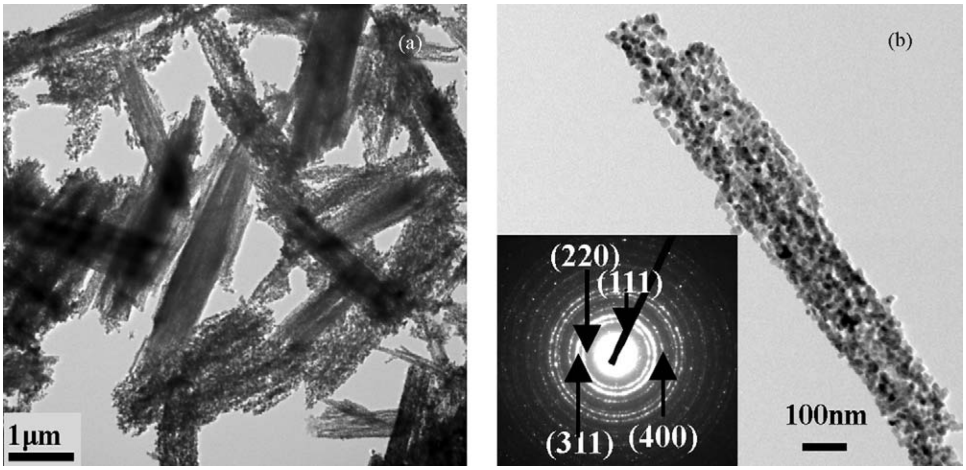

Fig. 3. TEM micrographs of samples 4. The inset of (b) shows the corresponding SAED pattern.

We investigated the thermal behavior of cobalt oxalate nanorods (samples 1 and 2) by TG and DSC. Fig. 4 shows TG and DSC curves of samples 1 and 2 with a heating rate of 10 °C/min in air. One can see that the two samples have similar thermal behavior. The first weight loss occurred at around 150–210 °C, owing to the removal of structural water [29]. As the temperature increased, a well-defined DSC peak due to the decomposition of cobalt oxalate precursor at 378 °C for sample 1 (Fig. 4(a)) and 288.9 °C for sample 2 (Fig. 4(b)) were observed and accompanied the larger weight loss in TG curves.

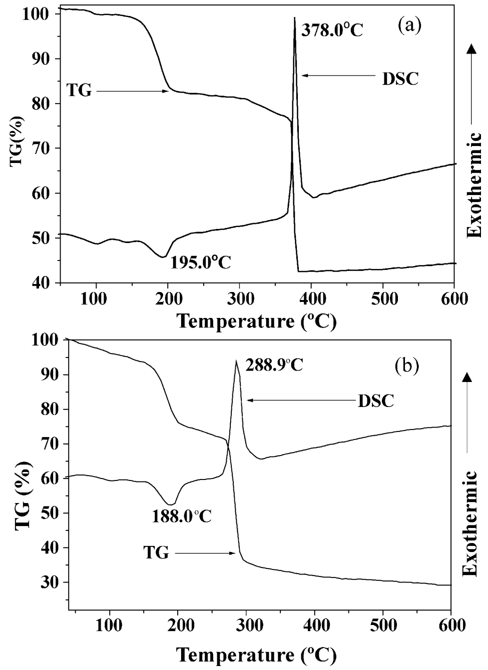

Fig. 4. TG/DSC curves of the samples. (a) Sample 1; (b) sample 2.

The decomposition temperature of cobalt oxalate increased about 90 °C when the ionic liquid was used. It is known that the decomposition temperature of [BMIM][BF_4] is about 360 °C [30,31]. When [BMIM][BF_4] was used, [BMIM][BF_4] may adsorb on the surface of cobalt oxalate nanorods, thus increasing the decomposition temperature of cobalt oxalate.

4. Conclusions

In summary, we have successfully synthesized cobalt oxalate nanorods with diameters of about 50 nm by the microwave-assisted ionic liquid method at 90 °C for 10 min using an ionic liquid [BMIM][BF_4]. This method is a fast, and environment-friendly route. Both the [BMIM][BF_4] and microwave heating play an important role in the formation of cobalt oxalate nanorods. Upon thermal decomposition at 400 °C, cobalt oxalate nanorods could be converted to Co_3O_4 rods consisting of nanoparticles.

Acknowledgments

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