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Morphological control in synthesis of cobalt basic carbonate nanorods assembly

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Abstract

Cobalt basic carbonates (CBC) with different morphologies have been synthesized by using urea as a hydrolysis-controlling agent. A variety of means, such as XRD, FT-IR, TG, SEM and TEM, were performed to characterize the as-synthesized samples. As evidenced by XRD, the samples are $Co(OH)_{1.0}(CO_3)_{0.5}$ with orthorhombic crystal phase (space group $P22_12$), which is further supported by FT-IR and TG analysis. SEM and TEM observations show that the sample of nanorods aggregate possesses bundle shape without using sodium dodecyl sulfate (SDS) as structure-directing agent, while the sample has pinecone-like shape at the presence of SDS. It is expected that SDS coordinated to CBC nanocrystals may retard the growth of small nanoparticles into bigger ones, and that SDS may be adsorbed on the side face of nanorods and also retards the aggregation of nanorods into bundles, finally forming the pinecone-like shape of nanorods aggregate.

Keywords: Nanomaterials; Thermal properties; Structure-directing agent; Morphology control

1. Introduction

Monometal or mixed-metal basic salts have been extensively studied over the last two decades due to the important electric, magnetic and catalytic properties of themselves or their derivative metal oxides.[1–8] As a result, a substantial amount of information is now available on crystallography, structural chemistry, thermal reactivity, and surface properties of these materials. Recently, Xu [9] reported the morphological control of cobalt–basic-salt nanorods by varying synthetic parameters. To the best of our knowledge, however, no attention has been paid to further assembly of dispersed nanorods into larger aggregates with different morphologies. Here, we firstly report the synthesis of pinecone-like or bundle shape of nanorods aggregates with or without the assistance of structure-directing agent under hydrothermal conditions.

2. Experimental

Pinecone-like cobalt basic carbonate was prepared using $CoCl_2 \cdot 6H_2O$ (AR grade; AJAX Chemicals, Australia), Sodium Dodecyl Carbonate (SDS) (>99% pure; Sigma Chemicals, USA), urea (AR grade; AJAX Chemicals, Australia) and distilled water in the mass of 2, 16, 16 and 10 g, respectively. These mixtures were stirred at room temperature for 2 h to yield a homogeneous solution, and then transferred to the oven at 353 K for 24 h. The hydrolysis rate of cobalt species was controlled by the slow hydrolysis of urea. The resulting precipitation was cooled down and separated by centrifugation. Then, the precipitated products were washed with ethanol extensively and then dried in air at 323 K overnight. The sample thus obtained was referred to as CBC-P. For comparison purposes, the sample synthesized without SDS was referred to as CBC-B.

The as-synthesized samples were characterized by a variety of means. Infrared spectra were recorded on a PE2000 Fourier transform infrared (FTIR) spectrophotometer using KBr pellets, containing 1% weight sample in KBr, which is dried in oven at

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373 K overnight before measurement. Thermogravimetric analysis (TGA, Shimadzu TGA 50H) was performed with a heating-rate of 2 K/min. X-ray diffraction (XRD) measurements were carried out at a speed of 0.01 s^{-1} by a Bruker Axs diffractometer (Germany) with CuKα radiation generated at 40 kV, 30 mA. SEM (JEOL 6400F) and TEM (JEOL 2010, 200 KV) were used to image samples at high resolution.

3. Results and discussion

3.1. X-ray diffraction

The XRD spectra of samples synthesized with or without using SDS are shown in Fig. 1. As can be seen from Fig. 1, CBC-B has stronger diffraction peak intensity than CBC-P, which indicates that the crystallinity of CBC-B is higher than CBC-P. The diffraction peaks of CBC-B agree well with that of $Co(OH)_{1.0}(CO_3)_{0.5}$ with orthorhombic crystal phase (space group $P22_12$). [7] Cell parameters of CBC-B, a, b and c, are calculated to be 0.879 nm, 0.102 nm and 0.443 nm, respectively. On the other hand, at the presence of SDS, the synthesized sample, CBC-P, has much weaker diffraction peaks compared to CBC-B. But we can still identify that these two samples have the same crystal phase. It is expected that dodecyl sulfate anions were adsorbed on some crystal face of CBC nanoparticles, which may decrease the growth rate of CBC crystals. [10] Hydroxide and carbonate anions in the CBC samples are thought to be from the hydrolysis of urea according to reactions(1) and (2).

$$H_2N\text{–}CO\text{–}NH_2 + 3H_2O \Leftrightarrow 2NH_4^+ + OH^- + HCO_3^- \quad (1)$$

$$OH^- + HCO_3^- \Leftrightarrow CO_3^{2-} + H_2O \quad (2)$$

3.2. FT-IR and TG (thermal gravimetric) analysis

The FT-IR investigations also confirm the formation of cobalt basic carbonate. Fig. 2 presents the FT-IR spectra of CBC-B and CBC-P. The wide bands at 3585 cm^{-1} are assigned to the stretching vibration of the OH^- of CBC samples, noting that the peaks at 1613–1635 cm^{-1} is due to the bending mode of OH^-. The vibration appearing at 3353–3365 cm^{-1} is attributed to the OH^- interacting with carbonate anions. As shown in Fig. 2, these OH^- related peaks of CBC-P are relatively stronger than that of CBC-B, which means that CBC-P with smaller crystallite size may contain more surface hydroxide groups than CBC-B. The presence of CO_3^{2-} in the samples is evidenced by its vibration bands from middle to lower wavenumbers, which suggests the mono- or poly-dentate carbonate ligand. The broad bands around 1500 cm^{-1} are assigned to stretching vibration of CO_3^{2-}. The sharp peak present at 828 cm^{-1} is attributed to $\delta(CO_3)$, and the rest of the minor bands at around 1073, 751–758, and 689 cm^{-1} can be assigned to ν(C═O), δ(OCO), and ρ(OCO), respectively, while the bands at 947 cm^{-1} are ascribed to δ(M–OH) bending modes.

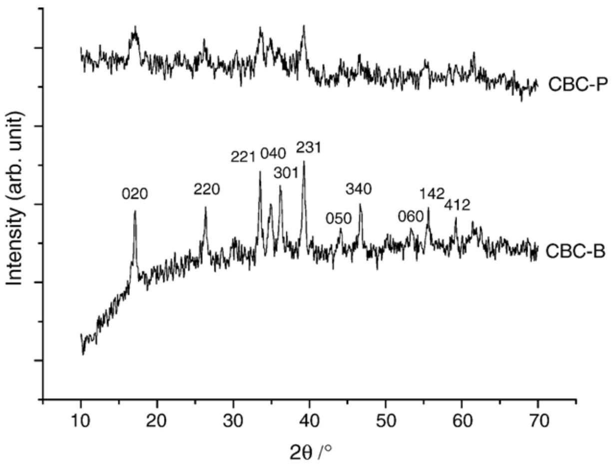

Fig. 1. XRD spectra of CBCs.

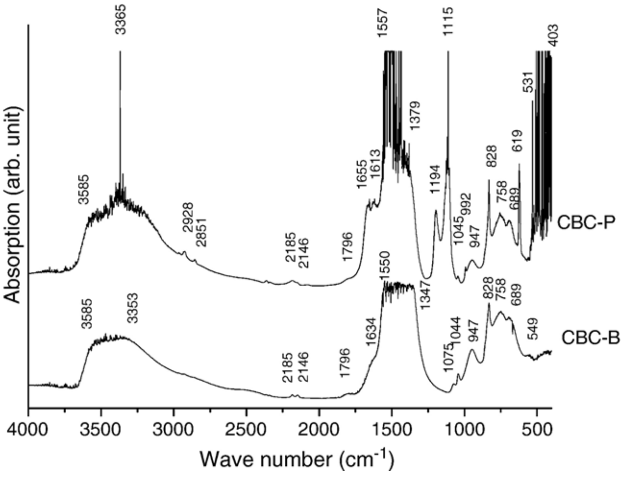

Fig. 2. FT-IR spectra of CBCs.

For CBC-P, FT-IR spectrum shows that SDS is not completely removed by ethanol wash. Some peaks from the surfactant are present in the spectrum. For instance, the peaks at 2928 and 2851 cm^{-1} can be assigned to the C–H stretching vibration and series of strong peaks around 1500 cm^{-1} are due to the C–H bending vibrations; peaks at 1194 and 1115 cm^{-1} are ascribed to the C–C stretching and bending vibrations. This indicates that dodecyl sulfate anions have some strong action with cobalt cations in this sample and cannot be easily washed away with ethanol.

TG analysis (not shown here) showed that CBC-B and CBC-P have different behaviors of thermal pyrolysis. DrTG curve of CBC-B presents a well-defined peak at 523 K with small shoulder peak at 547 K, owing to a consecutive removal of carbon dioxide and structural water by decomposition of carbonate anions and dehydroxylation. The weight loss of CBC-B reaches 27% at 773 K, which is quite close to stoichiometric value of weight loss, 25% (providing the pyrolysis product is Co_3O_4). As for CBC-P, only one well-defined peak is observed at 561 K, and there is no other shoulder peak observed. The decomposition temperature of CBC-P is relatively higher as compared to that of CBC-B, which is due to the protection effects of SDS that adsorbed on the surface of CBC-P. The weight loss of this sample reaches 37.5% at 773 K, which is apparently higher than the stoichiometric value of weight loss. This could be ascribed to the uncleaned SDS and more surface hydroxyl group contained in CBC-P with smaller crystallite. Supplementary experiment also demonstrated that the decomposition temperature of SDS is around 553 K, which indicates that the decomposition peak of SDS is superposed with the decomposition peak of CBC-P. This again showed that SDS adsorbed on the sample surface may protect the CBC-P, to some extent, from thermal decomposition.