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PAPER

Shape-controlled synthesis of $CdCO_3$ microcrystals and corresponding nanoporous CdO architectures†

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In this paper, we have demonstrated a simple ethylene glycol (EG) mediated solution method for the controlled synthesis of cadmium carbonate ($CdCO_3$) microcrystals. The volume ratios of EG and water have a decisive impact on the morphology of $CdCO_3$. With a decreased water volume, $CdCO_3$ microcrystals transformed from microcubes to nanobelts. Concave microcubes, pinecone-like, and dumbbell-shaped $CdCO_3$ microcrystals were also synthesized with moderate volume ratios of EG and water. The types of cadmium source also has great influence on the formation of $CdCO_3$ microcrystals. Cadmium nitrate and cadmium sulfate are two effective cadmium sources for the preparation of $CdCO_3$ microcrystals. However, pure $CdCO_3$ microcrystals can not be obtained when using cadmium chloride as the cadmium source. The as-prepared $CdCO_3$ microcrystals were an excellent precursor for the fabrication of nanoporous CdO micro/nanostructures *via* a simple thermal transformation process. This simple and controllable solution method opens an important way to fabricate nanoporous CdO micro/nanostructures.

Introduction

Micro/nanostructures have attracted much attention owing to their unique properties.[1–3] Among them, metal oxide micro/nanostructures present very important potential applications in the fields of photocatalysis,[4] solar cells,[5] water treatment,[6] and sensors.[7] CdO, which adopts the centrosymmetric rocksalt structure, has received much attention due to its narrow energy band gap (2.27 eV),[8,9] and good sensing properies.[10–12] For the preparation of CdO, the precursor ($CdCO_3$ and $Cd(OH)_2$) calcination strategy was a very important method, which has been widely reported.[9,13–18] The structures of the obtained CdO greatly depended on the structure of the precursor. So, synthesis of precursors with different morphology plays a key roles in the preparation of CdO nanomaterials. However, to date, it is still a challenge to control the synthesis of $CdCO_3$ using a simple and general method. In our previous work, porous CdO nanowires were prepared by calcining the hydroxy- and carbonate-containing cadmium compound precursor nanowires.[17] Herein, using a simple solution method, the morphology of the $CdCO_3$ precursors were successfully controlled by the volume ratios of ethylene glycol (EG) and water. After calcination, serials of porous CdO nanomaterials with different structures were synthesized. In addition, the types of cadmium source also has a great influence on the structure of the final precursors, which is discussed in detail.

Experimental section

Preparation of $CdCO_3$ precursors

Cadmium nitrate, cadmium sulfate, cadmium chloride, EG, ethanol, and urea were purchased from the Shanghai Chemical Reagents Company, and were of analytical grade and used without further purification. For the synthesis of $CdCO_3$ microcubes, a certain amount of cadmium nitrate was dissolved in the mixture solution of EG and deionized water with volume ratio of 1 : 9 at room temperature. The concentration of the Cd^{2+} was 0.1 mol L^{-1}. After that, urea was added in the above solution, and its concentration was 0.4 mol L^{-1}. After stirring for 10 min, the above solution was transferred into a conical flask with a stopper, and then heated at 100 °C for 10 h and allowed to cool to room temperature naturally. The resulting precipitates were separated by centrifugation and thoroughly washed with distilled water and absolute alcohol several times, and finally dried in an oven at 80 °C.

Synthesis of nanoporous CdO

For the preparation of nanoporous CdO micro/nanostructures, The as-synthesized $CdCO_3$ microcrystals were heated in air (heating rate of 2 °C min^{-1}) and kept at 500 °C for 1 h. The products were allowed to cool naturally to room temperature.

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Characterization

The as-prepared $CdCO_3$ and CdO micro/nanostructures were characterized by field emission scanning electron microscopy (SEM, FEI Sirion 200 FEG, operated at 10 kV), transmission electron microscopy (TEM, JEOL-2010, operated at 200 kV) and X-ray diffraction (XRD, X′Pert ProMPD, Cu-Kα radiation, wavelength 1.5418 Å).

Results and discussion

Fig. 1 presents the SEM images of the products synthesized using cadmium nitrate as cadmium resource, with a 1 : 9 volume ratio of EG and water. It is clear that well-faceted cubelike and oblique cubelike microcrystals were obtained. The microcrystals with flat surfaces and sharp edges/corners are evidently shown in the high-magnification SEM image in Fig. 1b–d. The XRD pattern shown in Fig. S1† suggests the microcrystals were $CdCO_3$.

At high temperature, CO_2 was given off owing to the hydrolysation of urea, and then CO_3^{2-} was formed. So, the formation of $CdCO_3$ resulted from the reaction between Cd^{2+} and CO_3^{2-}. In formamide aqueous solution, Yu *et al.* reported an interesting top-down solid-phase approach for the fabrication of cubelike well-faceted $CdCO_3$ microcrystals on cadmium foils.[13] When using a liquid-phase precipitation method, cubelike $CdCO_3$ microcrystals with flat surfaces and sharp edges/corners can not be obtained anymore. The proposed growth mechanism suggested that the concentration of carbon dioxide has a great influence on the structures of the products. The results of the present work demonstrate that *in situ* decomposition of urea is a promising strategy for the growth of $CdCO_3$ microcrystals with flat surfaces and sharp edges/corners.

The obtained $CdCO_3$ microcrystals were excellent precursors for the preparation of CdO. Fig. 2 shows the SEM images of the products after calcination of the $CdCO_3$ microcrystals at 500 °C for 1 h in air. The obtained products still maintain the cubelike and oblique cubelike characters, as shown in Fig. 2a and b. Fig. 2c suggests that the flat surfaces and sharp edges/corners were also preserved. The obtained products were composed of nanoparticles, which resulted from the decomposition of $CdCO_3$. At the same time, nanoporous structures were formed throughout the cube, as shown in Fig. 2c and d. The formation of the pores was due to the generated CO_2, which resulted from the decomposition of $CdCO_3$.[13] The TEM image shown in the inset of Fig. 2d suggests that the nanoparticles were about 40–50 nm in diameter. The XRD pattern (Fig. S2†) confirmed that the obtained nanoporous cubelike structures were the cubic phase of CdO.

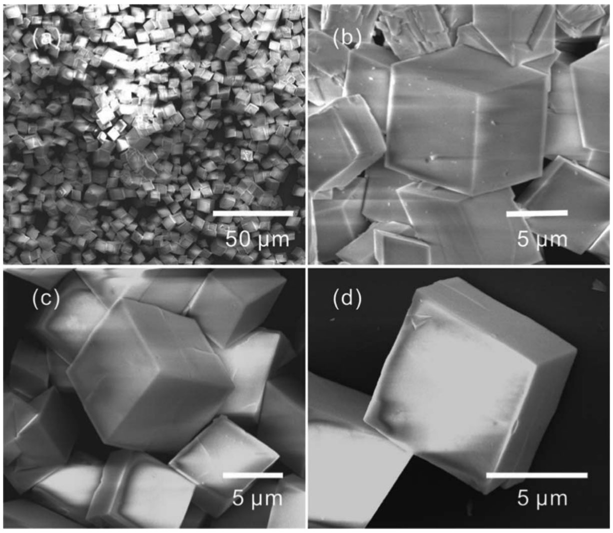

Fig. 1 Low-magnification (a) and high-magnification (b–d) SEM images of the cubelike and oblique cubelike $CdCO_3$ microcrystals.

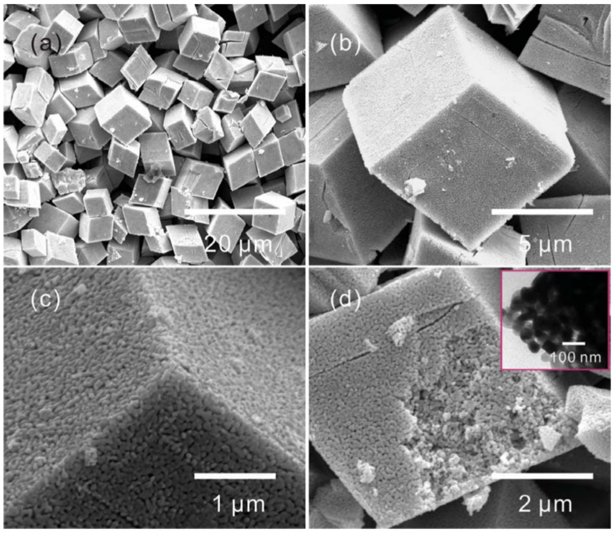

Fig. 2 Low-magnification (a) and high-magnification (b–d) SEM images of CdO nanostructures after heating the $CdCO_3$ microcrystals at 500 °C for 1 h in air. The inset of (d) is the TEM image of the CdO micro/nanostructures.

It is well known that polyalcohols are a very important ligand for forming coordination complexes with metal cations.[19,20] Polyalcohol based metal coordination complexes have been proven to be excellent precursors for the fabrication of metal oxide nanostructures.[19–23] In the present work, the volume ratios of EG and water has a great influence on the structures of the $CdCO_3$. The cubelike $CdCO_3$ microcrystals prepared with pure water were non-uniform and defective (Fig. S3†). With volume ratios of 2 : 8, similar cubelike $CdCO_3$ microcrystals were obtained. On further decreasing the volume of water, the structures of the products were clearly changed (Fig. S4†). The cubelike products were obviously decreased with the increased EG volume. Furthermore, a small amount of nanobelts were observed on increasing the volume ratios to 5 : 5. On further increasing the volume of EG, more and more nanobelts were obtained (Fig. S5†). The results suggest that the $CdCO_3$ microcrystals were transformed from microcubes to nanobelts with decreasing water volume. The intermediate products include concave cubelike, pinecone-like, and dumbbell-shaped $CdCO_3$ microcrystals. Fig. 3 presents SEM images of the products obtained after calcining the $CdCO_3$ microcrystals, which were prepared with a 3 : 7 volume ratio of EG and water. It is clear that, besides the cubelike products, some porous concave cubic, pinecone-like, and dumbbell-shaped CdO structures were obtained.

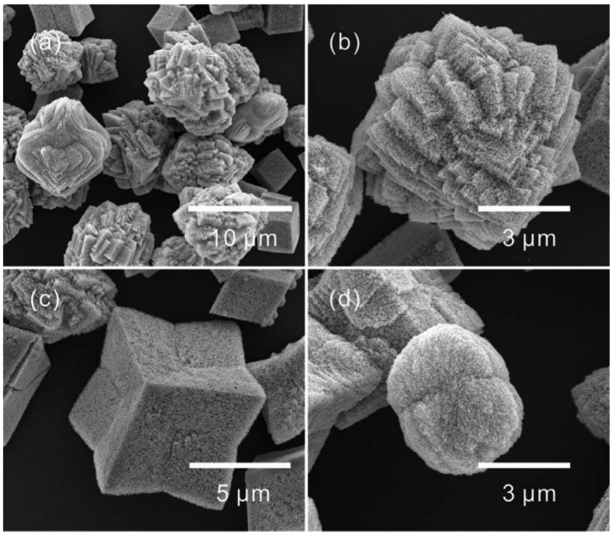

Fig. 3 SEM images of CdO micro/nanostructures after heating the $CdCO_3$ microcrystals, synthesized with a 3 : 7 volume ratios of EG and water, at 500 °C for 1 h in air.

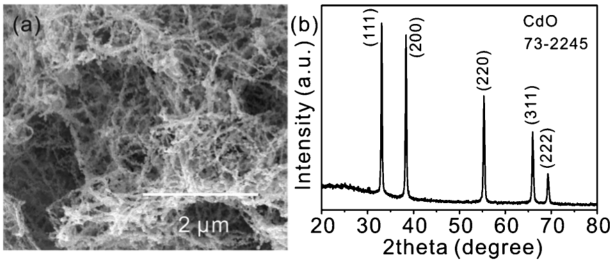

Fig. 5 SEM image (a) and XRD pattern (b) of CdO nanowires after heating the $CdCO_3$ nanobelts at 500 °C for 1 h in air.

On further increasing the volume ratio to 9 : 1, a large number of nanobelts that were tens of microns in length were obtained, as shown in Fig. 4 and Fig. S6†. The ringlike structure resulted from the curved nanobelts shown in Fig. 4c and d suggest the obtained nanobelts were very soft. No cubelike products were observed. So, the results mean that the morphology of $CdCO_3$ was well controlled by the change in the volume ratio of EG and water. The XRD pattern (Fig. S6c†) confirmed that the obtained products were $CdCO_3$. Fig. 5 presents the SEM image and XRD pattern of the products after calcination of the $CdCO_3$ nanobelts. It is clear that one-dimensional CdO nanowires were obtained.

The results discussed above suggest that the transformtion of $CdCO_3$ products from cubelike to nanobelt resulted from the presence of EG. It is well known that EG can react with metal cations to form linear complexes upon heating.[19,24] So, herein, EG could serve as a ligand to form long chain-like coordination complexes with Cd^{2+} (Fig. S7†). At the same time, with the hydrolysation of urea, the concentration of CO_3^{2-} was increased. Then, Cd^{2+} in chain-like complexes reacted with CO_3^{2-} to form $CdCO_3$ products, which then precipitated out from the reaction medium in the form of uniform nanobelts.

A different cadmium source, cadmium sulfate rather than cadmium nitrate, was used to prepare $CdCO_3$ using the same solution method with a 1 : 9 volume ratio of EG and water. To our surprise, $CdCO_3$ microspheres rather than cubelike products were obtained (Fig. S8†). The diameter of the microspheres was about 10–20 μm. Their surfaces were obviously coarser than those of the $CdCO_3$ microcubes. The results suggest that the morphology of the $CdCO_3$ microcrystals also depended on the anions of the cadmium salt. In addition, most of the obtained $CdCO_3$ microspheres were not perfect. Some concaves were clearly observed. The formation of the concaves was due to the growth of other small spheres (Fig. S8b†). After calcination, CdO microspheres were obtained, as shown in Fig. 6. The surface and the cross-sectional images shown in Fig. 6c and d confirm that the obtained CdO were porous throughout the sphere.

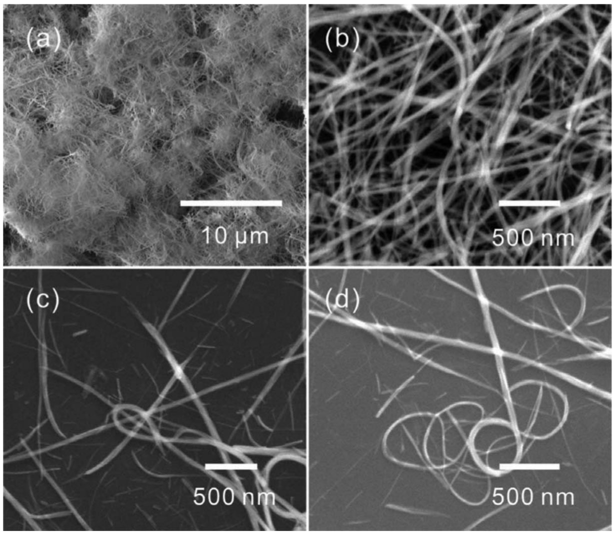

Fig. 4 Low-magnification (a) and high-magnification (b–d) SEM images of the $CdCO_3$ nanobelts synthesized with a 9 : 1 volume ratio of EG and water.

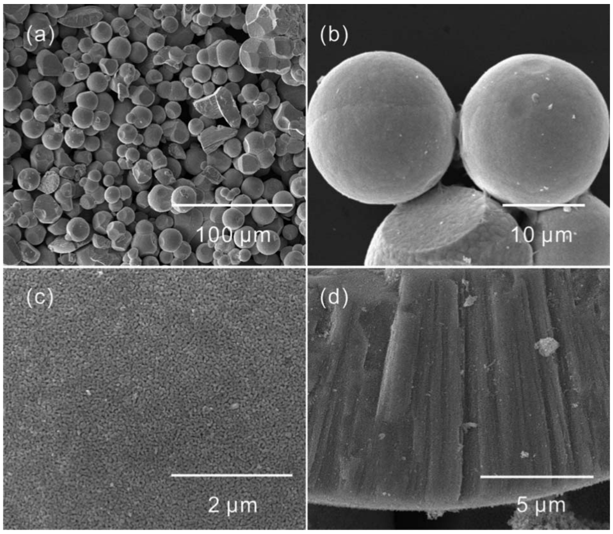

Fig. 6 Low-magnification (a, b) and high-magnification (c, d) SEM images of the CdO nanostructures after heating the $CdCO_3$ spheres, prepared with a 1 : 9 volume ratio of EG and water, at 500 °C for 1 h in air.

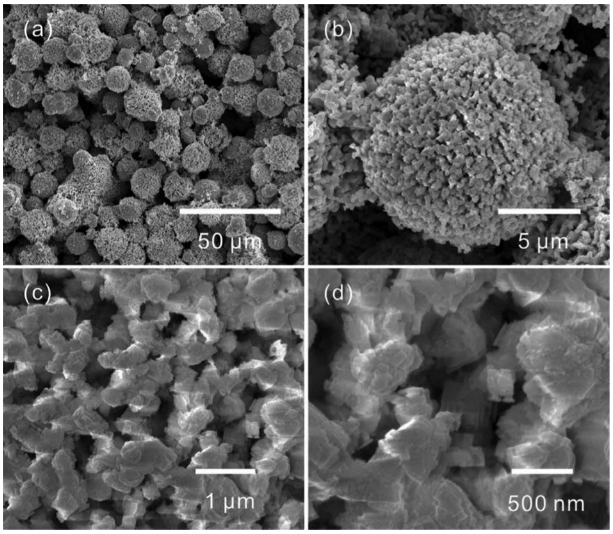

Fig. 7 Low-magnification (a, b) and high-magnification (c, d) SEM images of nanostructures after heating the microcrystals at 500 °C for 1 h in air. The microcrystals were synthesized with a 9 : 1 volume ratio of EG and water using $CdCl_2$ as the cadmium source.

To further investigate the role of the anions of the cadmium salt, cadmium chloride was chosen as the cadmium source. The volume ratio of EG and water also has a great influence on the morphology of the products. With the volume ratio of 9 : 1, sphere like products composited with nanoplates were obtained. Rod-like products were prepared with the volume ratio of 1 : 1 (Fig. S9†). When the volume of water was increased, cube-like and pinecone-like products were synthesized. Furthermore, only some irregular particles were formed in pure water (Fig. S10†). The sphere-like products were calcined at 500 °C for 1 h in air, and the obtained products are shown in Fig. 7. It is clear that porous spheres were obtained. However, the XRD pattern suggests that the above porous spheres were composed of CdO and $Cd_3O_2Cl_2$ (Fig. S11b†). In addition, the corresponding precursor was composed of $CdCO_3$, CdOHCl, and $Cd_4Cl_3(OH)_5$ (Fig. S11a†). The results suggest that cadmium chloride was not an effective candidate for the synthesis of pure $CdCO_3$ precursors.

Conclusions

In summary, this work demonstrated a simple EG assisted controlled synthesis for fabricating $CdCO_3$ microcrystals. The morphology and structures of the $CdCO_3$ microcrystals were controlled well by the volume of EG and water, and by the types of cadmium sources. Using the obtained $CdCO_3$ microcrystals as precursors, nanoporous CdO micro/nanostructures with different morphologies were successfully prepared by thermal treatment.

Acknowledgements

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