Novel Self-Assembled MgO Nanosheet and Its Precursors

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A novel self-assembled microstructure, nestlike $Mg_5(CO_3)_4(OH)_2{\cdot}4H_2O$ spheres, is formed by a self-assembly of nanosheets in the hydrothermal process. MgO with the similar morphology can be obtained by calcination of nestlike $Mg_5(CO_3)_4(OH)_2{\cdot}4H_2O$. MgO precursors with a uniform, ellipsoid-shaped, and smooth surface or flowerlike architecture, built by individual thin sheets, can be well-obtained by carefully controlling pH values of the initial reaction solution. The nestlike MgO exhibits a unique geometrical shape; its surface is composed of uniform MgO nanosheets. The unique MgO microstructure with high surface areas may possess promising applications as the sorbent for chemisorption and destructive adsorption of various pollutants.

Introduction

A challenge in materials engineering is the controlled assembly of purposefully designed molecules or ensembles of molecules into meso-, micro-, and nanostructures to provide an increasingly precise control at molecular levels over the structure, properties, and function of materials.[1] Recently, self-assembly of meso-, micro, and nanostructured building blocks has become an active research field in materials synthesis and device fabrication.[2−6] Chemical synthesis of functional materials, especially for those with the self-assembly of artificial building blocks into various curved single-layer superstructures, provides an important way for material architectures.[7,8] Some methods such as catalyst- or template-based methods[9] have shown the possibility of successfully controlling the assembly of primary building units into curved structures. We believe that direct methods in which synthesis and self-assembly are coupled in situ to produce highly ordered structures have potential applications in this regard, due to the fact that the introduction of templates or catalysts to the reaction system can be effectively avoided. Hydrothermal synthesis may be a useful tool for the synthesis of one-dimensional materials due to its various advantages such as a single-step process at low temperatures, wide selection of composition, and morphological control.[10]

Many important applications for magnesium oxide (MgO) have been found for use in catalysis, refractory material industries, paint, and superconductors.[11−13] MgO is also a potential catalyst and catalyst support for various reactions as well as a promising sorbent for chemisorption and destructive adsorption of various pollutants, as a high surface area of the mesoporous and shaped form of MgO is desirable for these applications. MgO is unique in its basicity with an isoelectric point of about 12, and it forms a class apart from other supports and sorbents such as alumina, zeolites, active carbon, silica, etc., which are acidic, neutral, or amphoteric. Generally, high surface area MgO was prepared mainly by calcination of the low surface area $Mg(OH)_2$, obtained either by precipitation or by MgO hydration.[14] Normally, MgO with 307−397 $m^2\ g^{-1}$ can be regarded as possessing a high surface area, while $Mg(OH)_2$ with 20−60 $m^2\ g^{-1}$ is regarded as possessing a low surface area.[14] Over the past few years, numerous work has been done to study the morphology of magnesium salts and MgO,[15,16] which is an interesting topic for general research.

Hydrated magnesium carbonate hydroxide ($Mg_5(CO_3)_4(OH)_2{\cdot}4H_2O$) is widely used in rubber, plastics, and fire retardants.[17,18] $Mg_5(CO_3)_4(OH)_2{\cdot}4H_2O$ may also be used as a precursor to prepare MgO. In this paper, we present a novel self-assembled microstructure, nestlike spheres, which are formed by self-assembly of nanosheets in the hydrothermal process. The nestlike MgO exhibits unique geometrical shapes, as its surfaces are composed of nanosheets. Such a unique MgO microstructure with a high surface area may lead to important applications as a kind of promising sorbent.

Experimental Procedures

All chemical reagents used in this experiment were of analytical grade. The detailed synthesis procedures are described as follows: 0.08 mol of magnesium chloride was dissolved in deionized water, followed by the addition of 0.24 mol of urea. An HCl solution (2 M) or the $NH_3{\cdot}H_2O$ (25 wt %) solution was added to the vigorously stirred mixture with the aim of adjusting the pH value to the desirable range of 3−10. The mixture was transferred to a Teflon-lined autoclave of 80 mL capacity. The autoclave was then filled with water up to 70% of the total volume. The autoclave was sealed to an electric oven and maintained at 423 K for 4 h at a pressure of 0.6 to ∼0.8 MPa. After cooling to room temperature naturally, the white powder was collected, filtered off, and washed with deionized water and absolute ethanol several times, respectively. Finally, the sample was dried in air at 353 K for 4 h. The ellipsoid-shaped MgO precursor with a smooth surface was obtained at pH = 3 to ∼4, the nestlike $Mg_5(CO_3)_4(OH)_2{\cdot}4H_2O$ composed of small one-dimensional nanosheets can be synthesized at pH = 6 to ∼7, and the flowerlike MgO precursor built from individual thin sheets can be synthesized at pH = 9 to ∼10. The MgO sample was then prepared by calcination of the nestlike $Mg_5(CO_3)_4(OH)_2{\cdot}4H_2O$ in air at 973 K for 3 to ∼4 h. The as-prepared samples were characterized by X-ray diffraction (XRD) on a Rigaku-DMax 2400 diffractometer equipped with graphite monochromatized CuKα radiation in the 2θ angle

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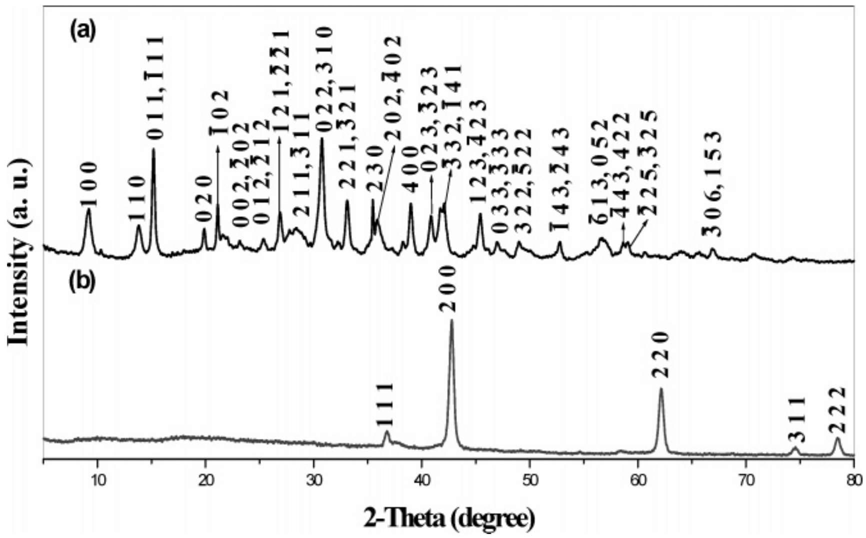

Figure 1. XRD patterns of: (a) nestlike $Mg_5(CO_3)_4(OH)_2{\cdot}4H_2O$ precursor and (b) MgO samples obtained by calcination of nestlike $Mg_5(CO_3)_4(OH)_2{\cdot}4H_2O$.

ranging from 5 to 80° as well as scanning electron microscopy (SEM, JSM-5600LV, JEOL).

Results and Discussion

X-ray Analysis. As shown in Figure 1a, all peaks in the XRD pattern can be indexed as a pure monoclinic structure, and the cell parameters calculated from these diffraction data are a = 10.07, b = 8.90, c = 8.32 Å, and β = 113.57°, which are in a good agreement with the reported data (JCPDS 70-0361). The XRD pattern of the obtained MgO sample is shown in Figure 1b. All strong peaks may be indexed as the cubic MgO phase with the cell constant a = 4.21 Å, which is in good agreement with the value in the literature (JCPDS, 75-0447). The sharp diffraction peaks imply a good crystallinity of our target compound, MgO.

SEM Observation. The micro- to nanostructural characteristics of the as-prepared samples are further examined by SEM. Figure 2 shows SEM images of the as-prepared nestlike $Mg_5(CO_3)_4(OH)_2{\cdot}4H_2O$ samples. From Figure 2, it is evident that $Mg_5(CO_3)_4(OH)_2{\cdot}4H_2O$ particles mainly consist of nanosheetlike structures. Interestingly, $Mg_5(CO_3)_4(OH)_2{\cdot}4H_2O$ particles are self-assembled into spherical assemblies with a tunnel appearance. In our work, $Mg_5(CO_3)_4(OH)_2{\cdot}4H_2O$ particles can be well-controlled as this morphology, with a diameter in the range of 10−20 μm.

MgO microspheres are obtained from nestlike $Mg_5(CO_3)_4(OH)_2{\cdot}4H_2O$ particles by calcination, and the general morphology of the as-prepared MgO samples is clearly shown in Figure 3. It is interesting that both MgO and its precursor possess the same morphology; even such a transformation has a chemical process. It can be found that MgO microspheres are smaller than $Mg_5(CO_3)_4(OH)_2{\cdot}4H_2O$ microspheres, the density of the former being higher than that of the latter. That is, MgO nanosheets are formed more tightly. MgO microspheres are in fact built from small one-dimensional nanosheets in a highly close-packed assembly. These nanosheets are aligned with one another perpendicularly to the more compact MgO spherical surface. Careful observation may find that the nestlike nanostructures consist of conformed nanosheets with a diameter of 200−400 nm.

Growth Mechanism. Generally speaking, the shape of a single-crystalline nanostructure is often determined by the intrinsic symmetry of corresponding lattices. The shape of a crystal can also be considered in terms of growth kinetics, by which the fastest growing plane should disappear to leave behind the slowest growing plane as the facets of the sample. In the present work, we have investigated effects of different synthetic conditions on the morphology of MgO precursor crystallites such as the nest- and flowerlike architectures shown in Figures 2 and 4.

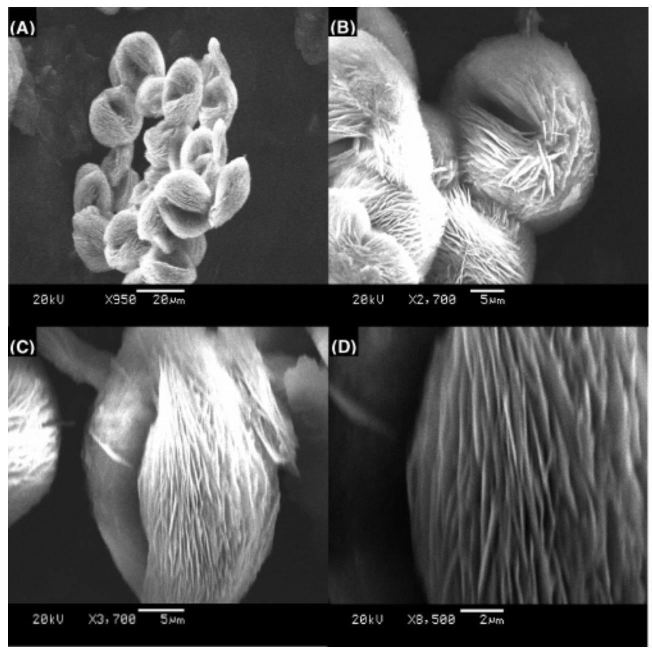

Figure 2. SEM images of $Mg_5(CO_3)_4(OH)_2{\cdot}4H_2O$ synthesized at pH = 6 to ~7. (A) Panoramic morphologies. (B and C) Individual spheres. (D) Detailed view on an individual sphere.

It has been observed that a pH variation of the initial reaction solution drastically changes the morphology of the obtained particles. Figure 4 shows SEM images of MgO precursors at the standard conditions and various pH values. It can be seen that the uniform ellipsoid-shaped particles with the diameter of 10−20 μm, which exhibit a smooth surface, are produced by adjusting the pH from 3 to 4 (Figure 4A,B). When the pH value is increased from 6 to ~7, nestlike $Mg_5(CO_3)_4(OH)_2{\cdot}4H_2O$ crystallites with a diameter of 10−20 μm can be obtained, which

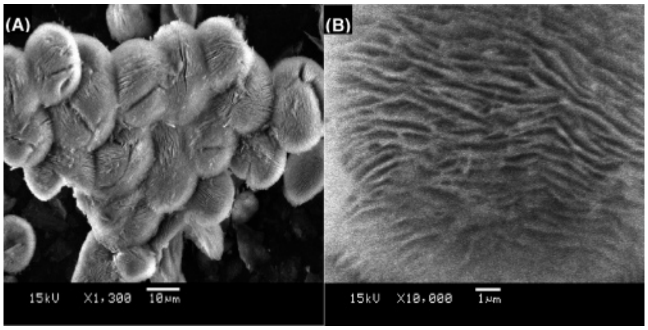

Figure 3. SEM images of MgO by calcination of the nestlike $Mg_5(CO_3)_4(OH)_2 \cdot 4H_2O$. (A) Overall product morphology. (B) Detailed surface view on an individual MgO sphere.

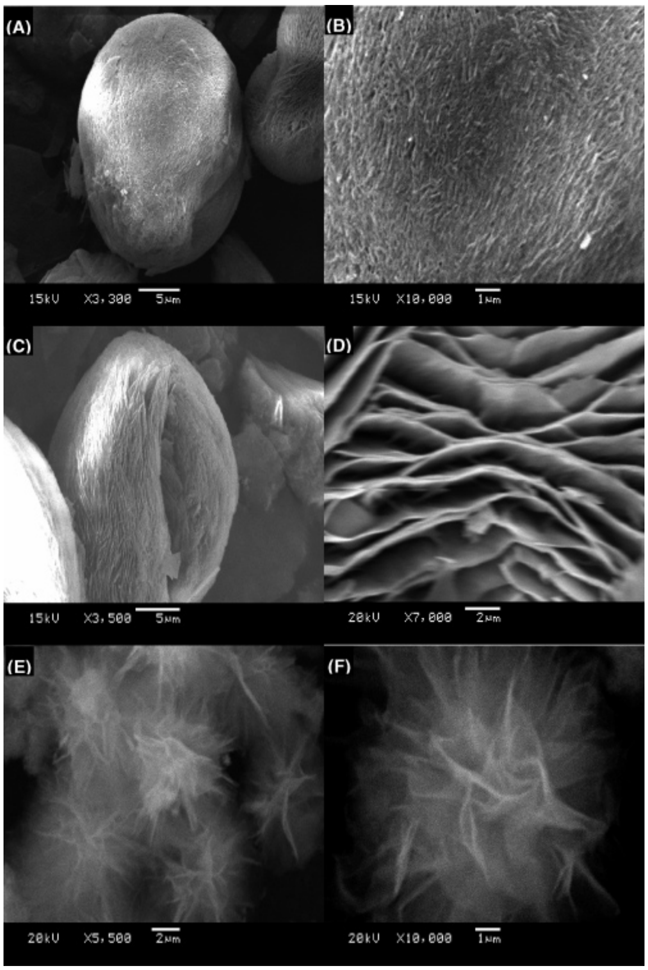

Figure 4. SEM images of MgO precursors. (A and B) Uniform and ellipsoid-shaped MgO precursor with a smooth surface synthesized at pH = 3 to ~4. (C and D) Nestlike $Mg_5(CO_3)_4(OH)_2 \cdot 4H_2O$ composed of small one-dimensional nanosheets synthesized at pH = 6 to ~7. (E and F) Flowerlike MgO precursor built by individual thin sheets synthesized at pH = 9 to ~10.

are composed of small one-dimensional nanosheets in a highly close-packed assembly (Figure 4C,D). When the pH value is up to 9 to ~10, the flowerlike MgO precursor can be obtained (Figure 4E,F). Careful observation shows that the flowerlike MgO precursor is built from individual thin sheets, as its surface is different from that of ellipsoid-shaped and nestlike particles. Therefore, for better governing of the morphology of MgO precursors, the growth stage in the hydrothermal process should be precisely controlled by carefully adjusting the pH value of the initial reaction solution.

A possible growth mechanism of nestlike $Mg_5(CO_3)_4(OH)_2 \cdot 4H_2O$ crystallites may be regarded as an assembly process. The nanoscale formation of sheetslike building units can be realized by the homogeneous precipitation, which can also be organized into the $Mg_5(CO_3)_4(OH)_2 \cdot 4H_2O$ microspheres via an aggregation. The major chemical reactions for the formation of $Mg_5(CO_3)_4(OH)_2 \cdot 4H_2O$ compounds in the aqueous solution can be formulated as

$$CO(NH_2)_2 + H_2O \rightarrow CO_2 + NH_4^+ + OH^- \quad (1)$$

$$Mg^{2+} + CO_2 + OH^- \rightarrow Mg_5(CO_3)_4(OH)_2 \cdot 4H_2O \quad (2)$$

The homogeneous precipitation of OH^- ions and CO_2 released from urea (as shown in eqs 1 and 2) results in the direct assembly of nestlike $Mg_5(CO_3)_4(OH)_2 \cdot 4H_2O$ crystals. OH^- ions are formed as a result of the reaction of H_2O with NH_3 and CO_2, which is produced by the decomposition of urea. Subsequently, $Mg_5(CO_3)_4(OH)_2 \cdot 4H_2O$ nuclei form rapidly, which controls the growth speed of $Mg_5(CO_3)_4(OH)_2 \cdot 4H_2O$ nuclei by OH^- and CO_2 slowly released by urea. The newly formed $Mg_5(CO_3)_4(OH)_2 \cdot 4H_2O$ crystallites are self-assembled on the existing nuclei to form the nestlike spheres. Our time-dependent experiments agree well with the previous assembly mechanism (see Supporting Information).

Conclusions

In conclusion, we report a novel nestlike $Mg_5(CO_3)_4(OH)_2 \cdot 4H_2O$ formed by self-assembly of nanosheets, which is fabricated by the hydrothermal process. Single-crystalline nestlike $Mg_5(CO_3)_4(OH)_2 \cdot 4H_2O$ is successfully prepared through a simple homogeneous precipitation reaction. MgO with the similar morphology can be formed by the thermal decomposition of nestlike $Mg_5(CO_3)_4(OH)_2 \cdot 4H_2O$. The uniform ellipsoid-shaped MgO precursor with a smooth surface and the flowerlike MgO precursor built by individual thin sheets can be obtained by carefully controlling pH values of the initial reaction solution. The nestlike $Mg_5(CO_3)_4(OH)_2 \cdot 4H_2O$ exhibits a unique geometrical shape, as its surface is composed of nanosheets. The unique MgO microstructure with a high surface area may find important applications as a promising sorbent.

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Supporting Information Available: Assembling process of nestlike $Mg_5(CO_3)_4(OH)_2 \cdot 4H_2O$. This material is available free of charge via the Internet at http://pubs.acs.org.

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