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Emulsion-phase synthesis of honeycomb-like $Mg_5(OH)_2(CO_3)_4{\cdot}4H_2O$ micro-spheres and subsequent decomposition to MgO

Guo Gao[a,b], Lan Xiang[b,*]

[a] Department of Bio-Nano-Science and Engineering, National Key Laboratory of Nano/Micro Fabrication Technology, Key Laboratory for Thin Film and Microfabrication of Ministry of Education, Institute of Micro-Nano Science and Technology, Shanghai Jiao Tong University, Shanghai 200240, China

[b] Beijing Key Laboratory of Green Reaction Engineering and Technology, Department of Chemical Engineering, Tsinghua University, Beijing 100084, China

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ABSTRACT

Herein we report a simple emulsion-phase route for the synthesis of honeycomb-like basic magnesium carbonate (BMC, $Mg_5(OH)_2(CO_3)_4{\cdot}4H_2O$) micro-spheres at 80 °C. Magnesium(II) salts in water are precipitated by sodium carbonate in the presence of cetyltrimethylammonium bromide (CTAB). Scanning electron microscopy shows the obtained BMC samples are composed of a lot of micro-spheres (diameter ranging from 8 to 10 μm) which are interweaved by a lot of nano-sized thin sheets (thickness of 20–30 nm and length >1 μm). The BMC micro-spheres prepared by this approach are porous and appear to be hollow structures. The size and shape of BMC are related to the CTAB concentration and temperature. The lower concentration of CTAB resulted in the decrease of the micro-spheres sizes. When the temperature was elevated to 110 °C, hexagonal tablets (thickness of 20 nm, length of each side varies from 400 to 600 nm) can be prepared. After the calcinations for BMC at 600 °C for 2 h, BMC are almost completely converted to MgO. Transmission electron microscopy indicates that the obtained MgO samples have a poly-crystalline feature. The possible formation mechanism of BMC micro-spheres has been discussed.

1. Introduction

In recent years, synthesis and assembly of nano-sized building components into curved crystalline frameworks (e.g., spherical and tubular) have attracted much technological and scientific attention due to their structure-dependent properties which are far from those of planar architectures [1–4]. Many strategies, such as hard/soft template synthesis, chemical vapor deposition and thermal oxidation, have been developed to the synthesis of such structure [5–9]. Although these methods have successfully prepared diverse crystalline structures [e.g., nano-tubes and micro-spheres], the study of organizing building units into well-organized curved structures has been still a strategic subject of long-term and active efforts [4,10,11].

Magnesium oxide (MgO) is an important materials which have been widely used in areas such as toxic waste remediation, paint, catalyst, refractory and superconductor [12,13]. Chen and Jordan [14] prepared porous and high surface area MgO micro-spheres via a wet precipitation method. He [15] reported the synthesis of nano-structured MgO micro-spheres via an interfacial reaction in a solid-stabilized emulsion solution. Niu et al. [16] suggested one-step assembly route for the synthesis of coral-like MgO micro-crystals from porous nano-particles.

Currently, the driving mechanisms for the assembly of curved structures involve capillary effect, hydrophobic and hydrophilic actions, surface tension, and geometric constrains of building blocks [3]. It is widely accepted that the size and shape of micro/nano-sized products are close related to their precursor's structures. To fully understand and exploit the assembly process of curved crystalline structures, we report a simple emulsion-phase strategy for the assembly of nano-sized BMC thin sheets into well-weaved micro-spheres. After calcinations for the precursors at 600 °C for 2 h, corresponding MgO samples can be obtained. The possible formation mechanism of BMC micro-spheres has been proposed to the cooperation action of the geometric constrains of BMC shin sheets and the dimension-oriented arrangement assisted by CTAB. As far as we know, we are the first to prepare the well-weaved honeycomb-like BMC micro-spheres and to observe the BMC micro-spheres have coreless feature.

2. Experimental

In a typical experiment, an aqueous solution containing 25 ml $MgSO_4{\cdot}7H_2O$ (0.23 M) and 20 ml cetyltrimethylammonium bromide (CTAB, 0.10 M) was stirred continuously at room temperature for 1 h. Then the above mixed solution and another 50 ml Na_2CO_3 (0.27 M) was simultaneously added into 100 ml Na_2SO_4

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* Corresponding author at: Beijing Key Laboratory of Green Reaction Engineering and Technology, Department of Chemical Engineering, Tsinghua University, Beijing 100084, China. Tel.: +86 10 62788984; fax: +86 10 62772051.

E-mail addresses: gaogaoguoguo@yahoo.com.cn (G. Gao), xianglan@mail.tsinghua.edu.cn (L. Xiang).

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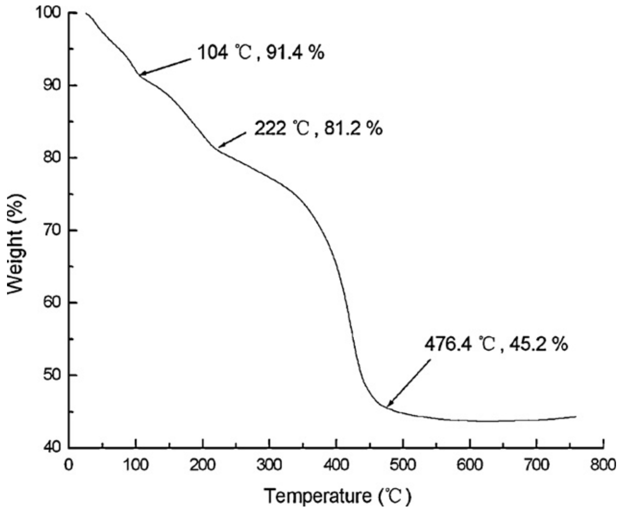

Fig. 1. TG curve of the samples obtained at 80 °C.

(0.12 M) aqueous solution respectively. The mixture solution of basic magnesium carbonate (BMC) was elevated temperature to 80 °C for 4 h. After reaction, the solution was naturally cooled to room temperature. The resulting products were washed by de-ionized water and ethanol, separated in a centrifuge and dried in a vacuum oven. After the calcinations for precursors at 600 °C for 2 h, the precursors are almost completely converted to MgO.

The crystallographic information and composition of all samples were examined by X-ray diffractometer (XRD; Japan, Rigaku, Cu Kα radiation) and an X-ray energy dispersive spectrometer (EDS, EDAX Genesis 2000, USA). The shape and structure of the samples were characterized by a scanning electron microscopy (SEM) and a transmission electron microscopy (TEM, JSM-2010, JEOL, Japan). A thermo-gravimetric (TG, Netzsch STA409C, Germany) analyzer was used to better understand the thermal stability and decomposition behavior of the precursors.

3. Results and discussion

It is known that basic magnesium carbonate (BMC, $Mg_5(OH)_2(CO_3)_4{\cdot}4H_2O$) is the general form for the resulted products between the reaction of magnesium sulfate and sodium carbonate in aqueous solution. In order to analyze the thermal stability and decomposition behavior of BMC, the obtained precursors were characterized by TG analysis. Fig. 1 shows the TG curve of samples obtained at 80 °C in the presence of 0.1 M CTAB. The mass decrease within the temperature interval of 25–104 °C was related to the loss of adsorbed water on the samples surface. At the temperature region of 104–222 °C, the weight loss decreased from 91.4 to 81.2% was resulted in the thermal decomposition of magnesium hydroxide ingredient. In the temperature range of 222–476.4 °C, about 36% of mass loss may be attributed to thermal decomposition of magnesium carbonate ingredient. At temperatures beyond 476.4 °C, the weight loss almost kept at a constant value of 43.6% (600 °C), suggesting that the BMC were almost all decomposed into MgO.

Fig. 2(A) indicates the SEM images of BMC obtained at 80 °C in the absence of CTAB. We note that the samples involve many irregular loose-packed aggregates with a diameter changing from 500 nm to several microns. The high magnification SEM image in Fig. 2(B) shows these irregular aggregates are built from a lot of nano-sized thin sheets. Fig. 2(C) shows the general SEM images of BMC obtained at 80 °C in the presence of CTAB. SEM results show that the samples are composed of numerous micro-spheres, and the diameter of the micro-spheres is about 8–10 μm. Fig. 2(D) shows the micro-spheres are in fact assembled by a lot of nano-sized thin sheets (thickness of 20–30 nm and length of greater than 1 μm). These building units are aligned perpendicularly to the spherical surface, pointed toward a common center and interweaved together, forming a honeycomb-like architecture. Interestingly, we found that a few micro-spheres prepared by this approach presented coreless with a hollow cavity, as suggested in Fig. 2(E) and (F). Fig. 2(G) shows the high magnification SEM image of a selected cavity. It was evident that these micro-spheres appear to be hollow inside, and they were composed of well-weaved shell walls. The thickness of the outer shell wall is about hundreds of nanometers. The above results reveal that CTAB is supposed to play an important role in the shape formation by kinetically controlling the assembly of building blocks.

We also study the influence of CTAB concentration on the size and shape of the BMC micro-spheres. Fig. 3(A) shows the samples obtained at 80 °C with a lower concentration of CTAB (0.02 M). We found that the micro-spheres are still built from a lot of thin sheets, and these micro-spheres are well-interweaved and presented a honeycomb-like structure. Although the morphology of the micro-spheres has no obvious change, the size of them has an evident decrease changing from 8–10 μm (0.1 M CTAB) to about 6 μm (0.02 M CTAB). This evolution suggests that CTAB serves as not only a dispersive agent but also a cohesive agent. When the concentration of CTAB is low, the assembly from building units of BMC thin sheets into micro-spheres is ineffectively capped.

We also study the influence of temperature on the morphology of BMC micro-spheres, and find that the BMC micro-spheres can be fabricated at a wide temperature interval changing from 60 to 90 °C. Our best results were obtained at 80 °C, in the presence of 0.1 M CTAB. After calcinations for the BMC micro-spheres at 600 °C for 2 h, the well-weaved structure of the micro-spheres has been destroyed, as depicted in Fig. 3(B). This evolution can be explained that when calcining BMC at 600 °C to prepare MgO, CO_2 and H_2O gas will be escaped from the component nano-sheets, and then numerous gas channels will be produced due to the release of inner stress. If the crack width of gas channels reached a certain value, the component nano-sheets will be disassembled from the matrix frameworks, destroying the well-weaved micro-spheres structures. The results indicated that the micro-spheres are unstable at a high calcined temperature (600 °C).

XRD pattern of the calcined samples is shown in Fig. 4(A). The diffraction peaks can be indexed to the cubic lattice of MgO (JCPDS No. 4-829). The EDS data (not shown) reveal that the atomic ration of Mg to O in our calcined samples is close equal to 1:1. The corresponding selected area electron diffraction (SAED) pattern in Fig. 4(B) indicates that the obtained MgO samples have a polycrystalline feature.

When the mixed solution of BMC obtained at 80 °C was transferred into a Telfon cell and elevated the temperature to 110 °C for 6 h, hexagonal tablets (Fig. 5) can be obtained. The thickness of tablets is about 20 nm. The length of each side varies from 400 to 600 nm. This morphological evolution may be explained in the following: first, an increase in temperature accelerated the decomposition of BMC, and thus accelerated the burst of bubbles (CO_2 and H_2O gas) and the migration/diffusion rates of inorganic species (e.g., H_2O and $SO_4{}^{2-}$) into and from the cavity of micro-spheres, resulting in the disassembly of micro-spheres. Second, the increase of temperature also triggers the reassembly process for the component nano-sheets. It is possible that the capping agent of CTAB may favor preferential adsorption to (1 1 0) and (1 0 0) crystal planes while allowing the formation of hexagonal structures. The morphological evolution can be divided into two steps: disassembly and reassembly process.

Considering the building blocks for the formation of well-weaved BMC micro-spheres, the organizing scheme by pre-aligning them in a correct organization order is deemed as the possible formation mechanism, as depicted in Fig. 6. In the initial stage of the reaction, an emulsion system of oil in water (O/W) was formed

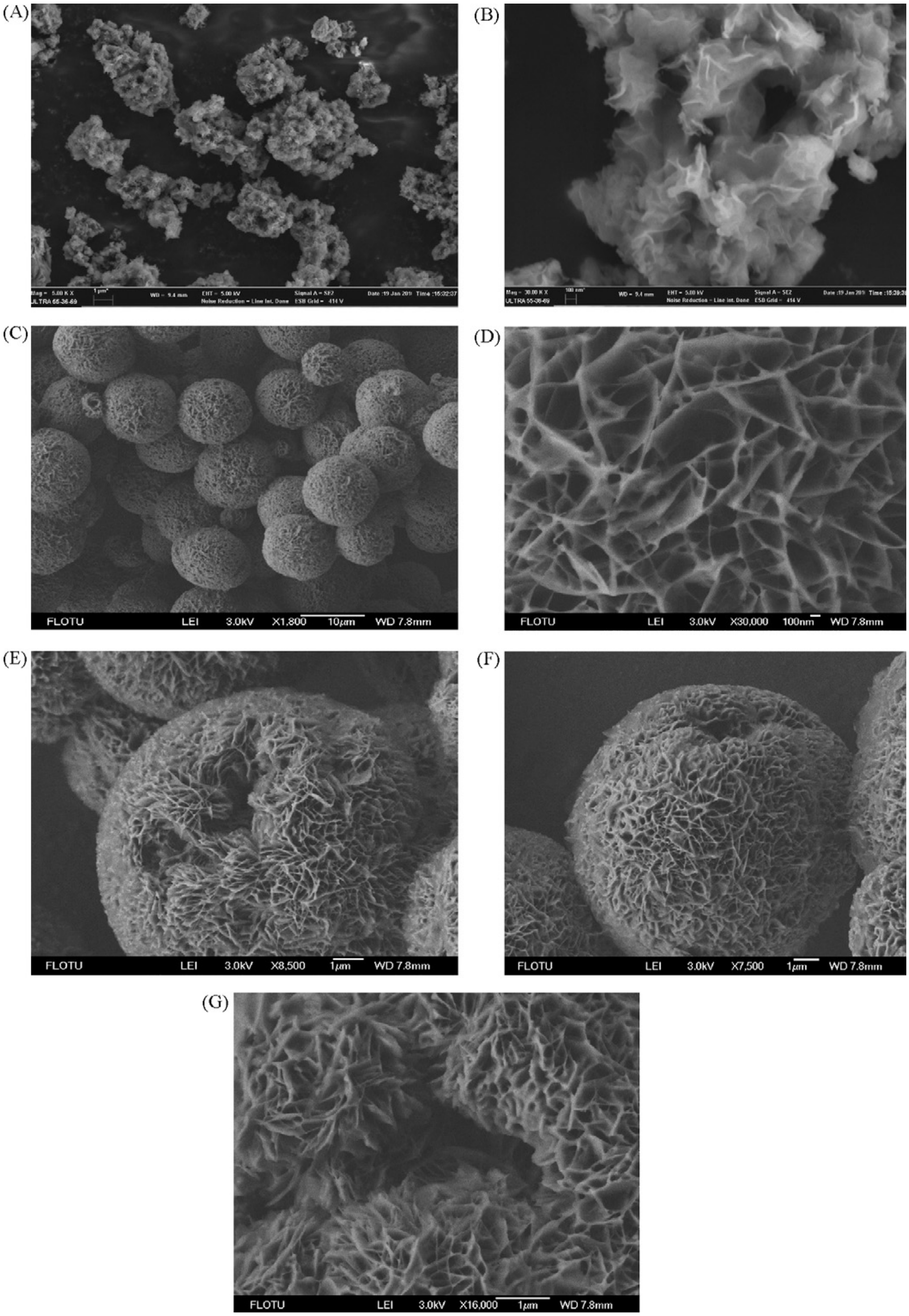

Fig. 2. General SEM images of basic magnesium carbonate micro-spheres obtained at 80 °C in the absence (A), high SEM image (B) and presence of 0.1 M CTAB (C), a detailed view on an individual micro-sphere (D), the selected micro-spheres with a hollow cavity (E and F), a detailed view on the cavity (G).

when CTAB was mixed with magnesium sulfate solution. In order to obtain a homogeneous O/W emulsion system, thorough stirring for 1 h is essential. At this stage, the positive Mg^{2+} ion will react with CTAB molecule and subsequently form the Mg^{2+}–CTAB complex. When the mixture and another 50 ml Na_2CO_3 solution were simultaneously added into Na_2SO_4 aqueous solution, a homogeneous nucleation process occurs. An order array of the nuclei assisted by CTAB (Fig. 6(A)) will easily generate numerous thin sheets (Fig. 6(B)) via the interface reaction of O/W emulsified droplets. It is known that the morphological evolution is determined by the relative growth rate of different crystallographic planes and their crystal habit relied on the relative order of surface energy. As for the preferential crystal growth direction, it is speculated that the crystal orientation are (1 0 0) and (0 1 0) facets. When the temperature was elevated to the range of 60–90 °C, the cooperation action of the geometric constrains of shin sheets and the dimension-oriented arrangement assisted by CTAB may be easily generated spherical structures (Fig. 6(C)). The roles of CTAB on the formation of spher-

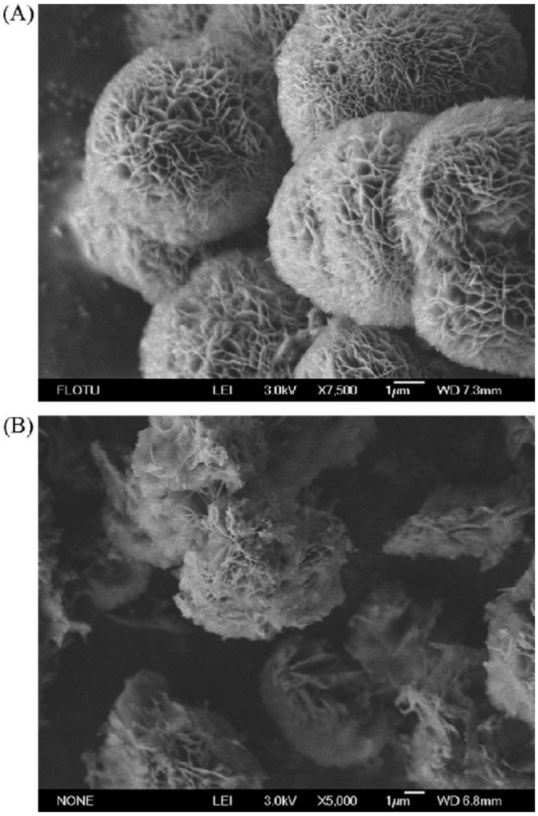

Fig. 3. SEM image of the products obtained at 80 °C with 0.02 M CTAB (A) and the calcined samples at 600 °C for 2 h (B).

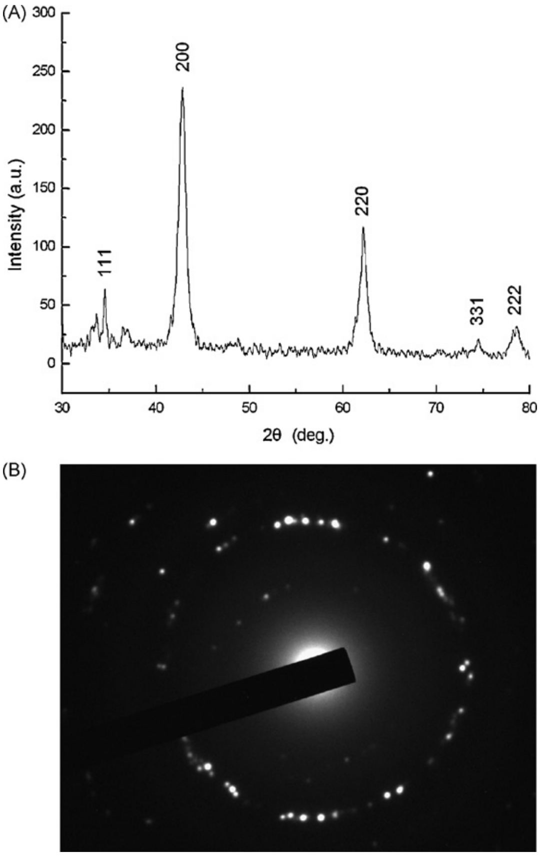

Fig. 4. XRD (A) and SAED (B) patterns of the calcined samples.

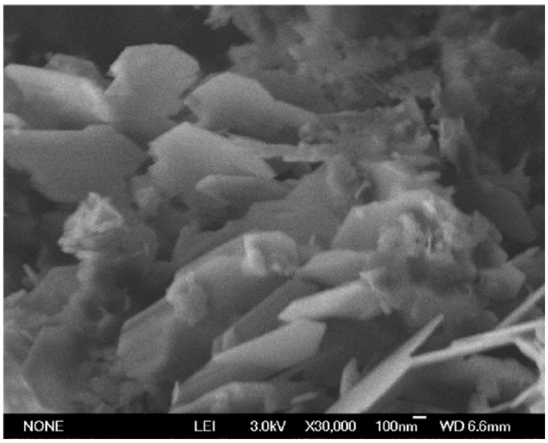

Fig. 5. SEM image of the BMC samples obtained at 110 °C.

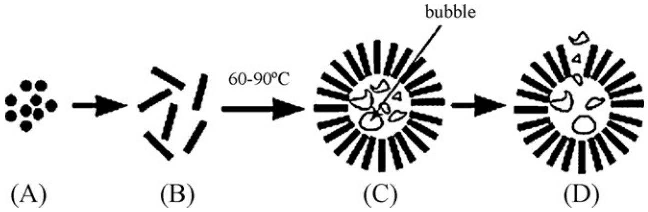

Fig. 6. The possible formation mechanism of the BMC micro-spheres.

ical architectures have been discussed extensively in the reported literatures [17,18]. Another interesting phenomenon is the micro-spheres appear to be coreless structure. This reason for such a hollow structure was related to the cavitation bubbles (CO_2 and H_2O gas) released by the thermal decomposition of BMC during the elevated process, and generate the observed hollow cavity (Fig. 6(D)).

4. Conclusions

In summary, we reported a simple emulsion-phase route for the synthesis of well-weaved basic magnesium carbonate (BMC) micro-spheres with a honeycomb-like structure at 80 °C. The micro-spheres prepared by this method are porous and appear to be hollow structures. The micro-spheres (diameter ranging from 8 to 10 μm) are built from a lot of nano-sized thin sheets (thickness of 20–30 nm and length >1 μm). The cooperation action of the geometric constrains of BMC shin sheets and the dimension-oriented arrangement assisted by CTAB is believed to play a key role in the assembly of honeycomb-like micro-spheres. It is expected that the current driving mechanism for the curved frameworks may be contributed to the “building blocks” of materials assembly.

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