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Facile fabrication and characterization of hierarchically porous calcium carbonate microspheres†

Jiaguo Yu,[a,b] Jimmy C. Yu,*[a] Lizhi Zhang,[a] Xinchen Wang[a] and Ling Wu[a]

[a] *Department of Chemistry, The Chinese University of Hong Kong, Shatin, New Territories, Hong Kong, China. E-mail: jimyu@cuhk.edu.hk; Fax: +85 2 2603 5057*

[b] *State Key Laboratory of Advanced Technology for Materials Synthesis and Processing, Wuhan University of Technology, Wuhan 430070, China*

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Higher-order porous calcite microspheres exhibiting high specific surface areas, unusual morphologies and textures were fabricated by a simple precipitation reaction of $CaCO_3$ in the presence of PSMA as a crystal modifier.

A variety of self-organized and hierarchical microscopic skeletal structures composed of inorganic and organic components are produced in nature.[1] Such complex, three-dimensional structures, if fabricated synthetically, could have numerous important applications.[2] For example, porous inorganic microspheres with controlled meso- and macro-porosity might find uses in catalysis, separation technology, and biomedical engineering.[3] A promising approach is to use organic additives and/or templates to control the nucleation, growth, and alignment of inorganic materials. This strategy has led to the formation of a variety of shapes.[4] Such exploration of bioinspired morphosynthesis strategies using self-assembled organic superstructures, organic additives, and/or templates with complex functionalization patterns to template inorganic materials with controlled morphologies and textures has received much attention.[5]

Here, we report for the first time that porous calcium carbonate microspheres with a self-organized hierarchical structure, which have never been seen in natural biominerals nor synthetic $CaCO_3$ materials, were prepared by a simple precipitation reaction in the presence of poly(styrene-*alt*-maleic acid) (PSMA) (sodium salt, 30 wt% solution in water, obtained from Aldrich, average molecular weight ~120 000) as a crystal modifier. The use of amphiphilic copolymers as templates to control the nucleation, growth, and alignment of inorganic particles seems to be a promising strategy.[6] A mechanism involving the self-organization of smaller inorganic particles during the crystallization of calcium carbonate is proposed.

In a typical synthesis, a solution of Na_2CO_3 (0.5 M, 1.28 mL) was added into an aqueous solution of PSMA (100 mL, 1.0 g L^{-1}) and the pH of the solution was adjusted to 10 by using HCl or NaOH. Then a solution of $CaCl_2$ (0.5 M, 1.28 mL) was added quickly into the pH-adjusted solution under vigorous stirring by using a magnetic stirrer. The mixture was stirred for 1 min, and then the solution was kept under static conditions at room temperature for 24 h (unless specified otherwise) before the product was collected for characterization. As a control experiment, the $CaCO_3$ precipitates were also prepared in the absence of PSMA, and all the other conditions were kept the same.

Fig. 1 shows typical scanning electron microscope (SEM, LEO 1450VP) images of the as-prepared samples obtained in the presence of PSMA (1.0 g L^{-1}) after aging at 25 °C for 24 h. The samples exhibit a unique porous spherical superstructure. The microspheres are about 10–20 μm in size and their surface is composed of triangular-shaped calcite subunits that are uniform in size (mean side length = 250 ± 50 nm), and aligned on the surface of the spheres. This implies a multistep growth mechanism where at first small spheres (or nuclei) are formed which is then followed by overgrowth of the spheres by self-organization of smaller particles on their surface. The high-magnification SEM images show that the microspheres appear to be higher-order porous superstructures (as shown in Figs. 1(c) and (d)). The XRD patterns of the obtained samples indicate that the microspheres are pure calcite (shown in the Supporting Information, Fig. S1†). Fig. S1 also reveals a peak broadening of the (104) plane diffraction for calcite prepared in the presence of PSMA. This indicates a poor crystallization and the crystallite size becomes smaller. According to the Scherrer equation, the average crystallite sizes are *ca.* 22.6 and 66.3 nm in the presence and absence of PSMA, respectively. This is probably due to the fact that PSMA suppresses the crystallization of calcite by adsorbing onto the surface of the calcite crystallite.

The Brunauer–Emmett–Teller (BET) surface areas (with corresponding porosities) (Micromeritics ASAP 2010) of the $CaCO_3$ powder samples obtained in the presence and absence of PSMA are 123.1 $m^2\ g^{-1}$ (21.5%) and 1.6 $m^2\ g^{-1}$ (0.5%), respectively. This indicates that the former are porous powders and the latter are solid powders (see Fig. 2S†).[4e] Fig. 2 shows the pore size distribution curve calculated from the desorption branch of a nitrogen isotherm by the BJH method using the Halsey equation.[7] The inset shows the corresponding nitrogen isotherms of $CaCO_3$ powders prepared in the presence of PSMA. The isotherm is a combination of types I and IV (BDDT classification) with two very distinct regions. At low relative pressure, the isotherm exhibits high adsorption, indicating that the powder contains micropores (type I). However, at high relative pressures between 0.3 and 0.9, the curve exhibits a hysteresis loop indicating the presence of mesopores (type IV).[7] The pore size distribution curve shows that the powders contain micropores (<2 nm) and mesopores with a maximum pore diameter of *ca.* 3.8 nm. It can be concluded from the above BET and SEM results that the obtained porous $CaCO_3$ microspheres contain at least three kinds of pores: micropores

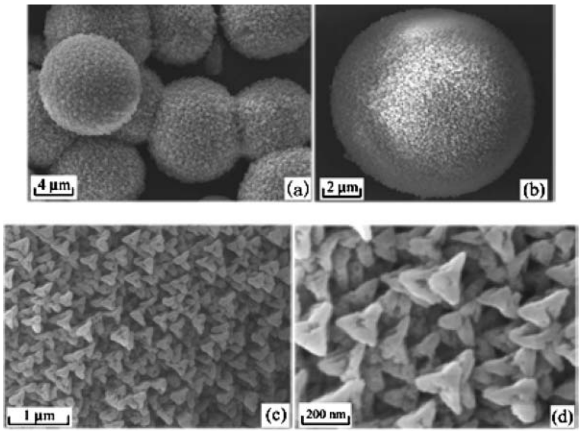

Fig. 1 (a) SEM images of $CaCO_3$ particles obtained in the presence of PSMA, (b) intact porous calcite microsphere, (c)–(d) higher-magnification SEM images of (b) showing detailed textures and porosities.

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† Electronic supplementary information (ESI) available: Figs. S1–S4: XRD patterns, SEM image, TEM images and formation mechanism of porous microspheres. See http://www.rsc.org/suppdata/cc/b4/b406839d/

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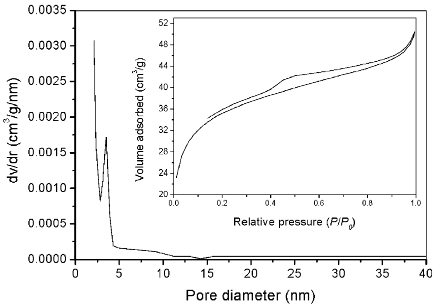

Fig. 2 Pore size distribution curve and the corresponding isotherms (inset) of $CaCO_3$ powders obtained in the presence of PSMA.

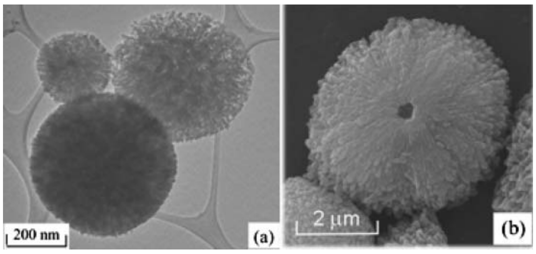

Fig. 3 (a) TEM image of $CaCO_3$ particles obtained in the presence of PSMA (1.0 g L^{-1}) after aging at 25 °C for 10 min, (b) SEM image of a broken calcite microsphere.

(<2 nm), mesopores (2–6 nm) and macropores (>50 nm). The micropores and mesopores are ascribed to the interstitial voids of the packed primary particles (or crystallites) within the aggregates (or triangular-shaped particles).[7] The macropores come from the interstitial spaces formed among the triangular-shaped particles (as shown in Figs. 1(c)–(d)).

The growth process of the porous calcite microspheres was investigated with TEM by examining the early stages of the crystal growth. As shown in Fig. 3(a), spherical porous calcium carbonate particles (*ca.* 200–600 nm) appear after aging in the solution for 10 min, and the texture of the sphere is quite loose. After aging for 20 min, the particles grow larger to a size of about 1 µm and become dense (Fig. S3†). Furthermore, many small calcium carbonate particles grow out radially on the outer surface of the spheres showing an incipient stage of the final porous microspheres. The corresponding XRD results (not shown here) indicate that the samples in the early stage consist of both calcite and vaterite in a 77% to 23% ratio.[8] With increasing aging time, the content of vaterite decreases gradually. It is all calcite after aging for 8 h. According to the above results, a possible two-step formation mechanism is proposed (Fig. S4†). In the first step, the chains of PSMA accumulate electrostatically a large amount of Ca^{2+} and carbonate ions. Then nucleation occurs at an outburst speed forming a large number of small calcite and vaterite particles. These particles aggregate by the covalent interactions between Ca^{2+} ions on the surface of $CaCO_3$ and carboxylate groups on the polymer chains.[9] When the growth of $CaCO_3$ particles reaches a critical size, the inorganic/organic composite particles separate from solution due to phase separation and generally adopt a spherical morphology because this gives the minimum total surface energy for a given volume. In the second step, the acidic macromolecules are adsorbed and self-assembled on the surface of the as-formed composite microspheres. This kind of environment may be more suitable for the growth of rhombohedral calcite crystals, which are often nucleated on a small triangular (001) face at a rigid substrate surface.[10] Such secondary nucleation would result in the formation of many small calcite crystals with a trigonal pyramidal morphology.[11] The deposition of the precise array of calcite crystals on the surface of composite microspheres is ascribed to the controlled nucleation at the interface between the crystals and the adsorbed acidic macromolecules. To further understand the formation mechanisms of microspheres, an ultrasonic experiment was carried out to fragment the spherules in order to better observe the internal structures. A few broken microspheres were clearly observed when the samples were sonicated in an ultrasonic cleaning bath (Bransonic ultrasonic cleaner, model 3210EDTH, 47 kHz, 120 W, USA) for 1 h. Fig. 3(b) shows the three-part internal structure of the microspheres: a cavity of about 200 nm at the center of the spheres, a large middle section of a radially grown and layered crystal structure, and an outside surface layer containing many triangular-shaped particles. The internal textures of the spheres further support the above proposed mechanism. The nuclei of the spheres have higher polymer content and their structures are loose. Therefore, the nuclei are less stable and they collapse during sonication. Of course, the detailed formation mechanism needs to be further investigated.

The above-described porous microspheres exhibit higher-order superstructures in at least four different length scales. They are crystalline at the unit level, uniform triangular-shaped calcite particles in the nano-size range, self-organized nano-particles on the mesoscopic/submicrometre scale, and spheroidal at the micrometre and macroscopic levels, respectively.

In conclusion, higher-order porous calcite microspheres exhibiting high specific surface areas, unusual morphologies and textures have been produced by a simple precipitation reaction of $CaCO_3$ in the presence of PSMA as a crystal modifier. PSMA plays an important role of control on the nucleation, growth and alignment of calcium carbonate particles. Such self-organized hierarchical structure formation in the submicrometre scale is unusual. The use of an amphiphilic copolymer in the biomimetic fabrication of hybrid materials offers new insights into the control of structure and morphology under easily attainable reaction conditions.

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