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Morphology and size control of calcium carbonate crystallised in reverse micelle system with switchable surfactants

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A series of $CaCO_3$ particles with different morphologies, such as, rhombohedra, sphere, dendrite-like, etc. were successfully prepared in CO_2/N_2 switchable surfactant (N'-dodecyl-N, N-dimethyl acetamidine bicarbonate) reverse micelles.

Biologically mineralized materials have gained much attention in recent years because of their unusual properties arising from their complex shape, hierarchical organization, and various polymorphs of the constituent minerals. [1-5] As one of the most common biological minerals, calcium carbonate ($CaCO_3$) has attracted considerable attention due to its wide application in industrial and scientific fields. $CaCO_3$ crystals exist in three main crystalline polymorphs (calcite, vaterite and aragonite) and in amorphous material as well. Calcite and aragonite are the main forms existing in organisms, and calcite is more stable than aragonite from the perspective of thermodynamics. The properties and applications of $CaCO_3$ depend on the morphology, polymorph, particle size, and chemical purity of the crystals. [6-10]

Currently, water-in-oil (W/O) microemulsions have been given considerable attention for its soft template effect, reproducibility, and simple maneuverability.[11] W/O microemulsions are composed of nanometer-sized water droplets that are dispersed in a continuous oil medium and stabilized by surfactant molecules. Such thermodynamically stable systems are heterogeneous on a molecular scale and able to serve as nanoreactors, which favor the growth of small crystallites with a desired narrow size distribution and morphology. [12, 13] However, this method requires a certain amount of oil phase and surfactant. How to efficiently separate, recover and simply remove the surfactant is an important issue to be solved.

As a switchable surfactant can undergo reversible inter-conversions between active and inactive forms, [14] it is possible to recover and re-use the surfactant afterwards and to easily remove it from the system. Jessop et al. have reported a switchable surfactant using CO_2/N_2 as a trigger, [15-17] where in the hydrophobic long-chain alkyl amidines (inactive) can be protonated and become water-soluble surfactants upon the addition of CO_2, and the amidinium ions (active) can then be deprotonated by bubbling N_2. Both CO_2 and N_2 are inexpensive and environmentally benign.

Here we attempt to find a relatively simple, mild, low-cost and environmentally friendly strategy to synthesize $CaCO_3$ nanoparticles. A series of $CaCO_3$ particles were successfully synthesized in a CO_2/N_2 switchable surfactant (N'-dodecyl-N, N-dimethyl acetamidine bicarbonate) reverse micelles. The switchable surfactant can form reverse micelles in the oil phase spontaneously. In the completion of the reaction, N_2 is introduced to switch off the “active” buttom. Particles can be obtained by simply washing to remove the adsorbed surfactants, which simplifying the tedious traditional separation process. [18, 19]

Reverse micellar solutions were prepared by adding aqueous solution of either $CaCl_2$ or Na_2CO_3 to a certain concentration of N'-dodecyl-N, N-dimethylethyl amidine bicarbonate/n-heptane/n-hexanol mixtures. Then the two micellar solutions, containing respectively $CaCl_2$ and Na_2CO_3, were mixed and stirred for 6 h at room temperature (Scheme 1). After completion of the reaction, the mixture was heated to 65 ℃ and bubbled by N_2 for 30 min until the system became turbid. Calcium carbonate was separated with centrifugation (8000 r / min). The separated calcium carbonate particles were washed by ethanol and acetone alternately for 2-3 times and dried before characterization.

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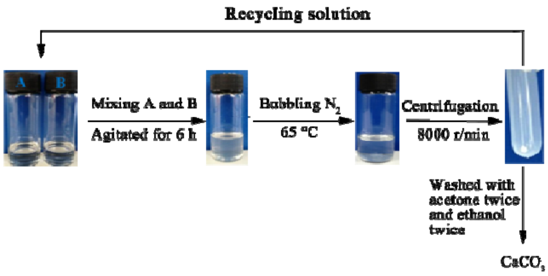

Scheme 1. Synthesis of $CaCO_3$ in CO_2/N_2 switchable surfactant reverse micelles (A refers to reverse micelle of $CaCl_2$; B refers to reverse micelle of Na_2CO_3).

X-ray diffraction (XRD) of $CaCO_3$ synthesized in reverse micelles at different reactant concentrations are shown in Figure 1. The result demonstrated that pure calcite was produced when the reactant concentration is 0.2 M and 0.3 M. With the increase of reactant concentration, the relative intensity of each peak was enhanced. When the concentration arrives at 0.5 M, a mixture composed of calcite and vaterite was fabricated (Table 1).

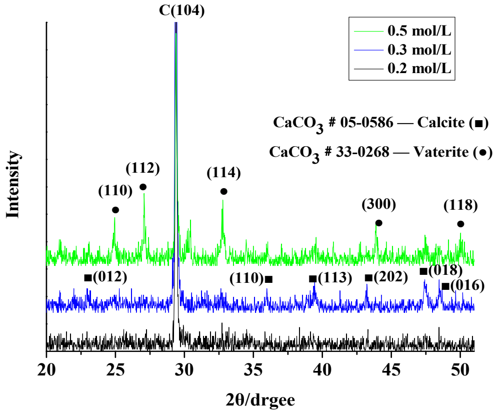

Figure 1 XRD patterns of $CaCO_3$ prepared at different reactant concentrations

Table 1 Crystal form content of $CaCO_3$ prepared at different reactant concentrations [a]

reactant concentrations (mol/L)	calcite (%)	vaterite (%)
0.2	100	0
0.3	100	0
0.5	67.8	32.2

[a] the surfactant concentration is 0.07 M; the concentration of $CaCl_2$ and Na_2CO_3 is same; molar ratio $[CaCl_2]/[Na_2CO_3]=1$.

Although calcite is more stable than other polymorphs at ambient temperature and atmospheric pressure, precipitates may be found as a mixture of polymorphs or with one of the forms predominating. [20] Ostwald proposed that the solid first formed on crystallisation of a melt or a solution would be the least stable polymorph. [21]. Therefore, in this experiment, the first phase precipitates out of the supersaturated solution was amorphous calcium carbonate and then transformed into vaterite as a metastable (more soluble) phase. The transformation of vaterite into calcite may be suggested that the more soluble vaterite crystals dissolve while the less soluble calcite crystals nucleate and grow.[22] When the concentration of reactant was high, vaterite precipitated in appreciable amounts, confirming that vaterite formation favors high (relative) concentrations of Ca^{2+}.[23]

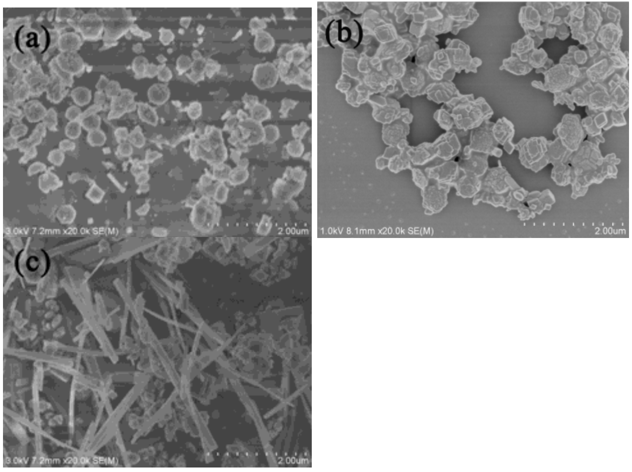

Figure 2 SEM images of $CaCO_3$ prepared at different reactant concentrations (a)0.5 mol•L^{-1}, (b)0.3 mol•L^{-1}, (c)0.2 mol•L^{-1}

As shown in Figure 2, the reactant concentration had also a strong influence on the shape of crystals. When the reactant concentration is 0.5 M, the $CaCO_3$ is spherical (typical vaterite morphology) (Figure 2a), accompanied by few rhombohedral crystals (typical calcite morphology),[24] which is corresponding to XRD patterns. Under 0.3 M, the obtained $CaCO_3$ is almost rhombohedra, with smaller ones gather together forming a larger one. This is mainly due to the high surface energy of fine calcium carbonate crystals, tending to aggregate into large particle to reduce the surface energy. When the concentration decreased to 0.2 M, the rod-like particles appeared. It has to be pointed out that the exact growth mechanism is still unknown, although some explanation was given in the literature based on two kinds of rates, which denote the rate of nucleation and growth outward at the ends of rod-like primary crystals (r_1) and the rate of nucleation and growth along the rod axes of rod-like primary crystals (r_2), respectively. When r_1 is much smaller than r_2, rod-like or ellipsoid crystals will be obtained[25, 26].

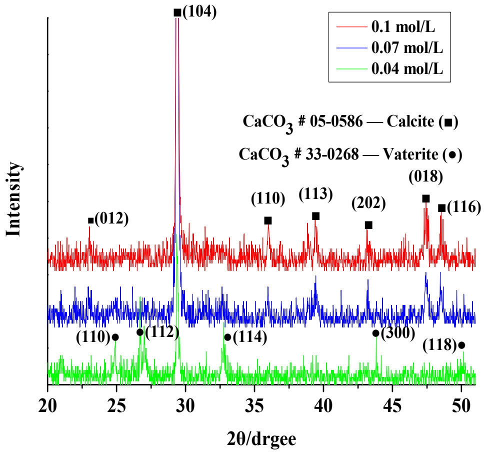

Figure 3 XRD patterns of $CaCO_3$ prepared at different surfactant concentrations

Table 2 Crystal form content of CaCO3 prepared at different surfactant concentrations[a]

surfactant concentration (mol/L)	calcite (%)	vaterite (%)
0.04	78.5	21.5
0.07	100	0
0.1	100	0

[a] the reactant concentration is 0.3 M; molar ratio [$CaCl_2$]/[Na_2CO_3]=1.

Figure 3 shows XRD patterns of $CaCO_3$ prepared at different surfactant concentrations. It indicates that when the surfactant concentration is 0.04 M, the calcite and vaterite crystalline mixture was obtained. With the increase of surfactant concentration, the mixed polymorph turns into pure calcite. This may be due to electrostatic interaction. The cationic surfactant is easily adsorbed on the negatively charged surface, the crystal tends to be the most stable crystalline form of calcite, and excessive surfactant will adsorb on the surface of calcium carbonate, resulting in polymorph changes.

The aggregation number of micelles varies with the different surfactant concentrations, thus the constitute of the "pool" size and shape are different. When the surfactant concentration is 0.1 M, the dendritic structure composed of needle-like aggregates can be observed in Figure 4(a). From the magnified picture, the diameters of the branches are under 200 nm. Aggregates with the same morphology are also obtained by β-CD and DTAB. [27] In the present research, unique morphology was obtained in an appropriate concentration without any complexes or additives. When surfactant concentration is higher, the degree of supersaturation of Ca^{2+} will increase, especially on the side of needles. This tends to cause the two-dimensional nucleation, forming dendritic morphology. The mixture of rhombohedra and hollow pie-like particles exist in 0.04 M. Similar hollow structure of vaterite crystal type has also been reported.[28]

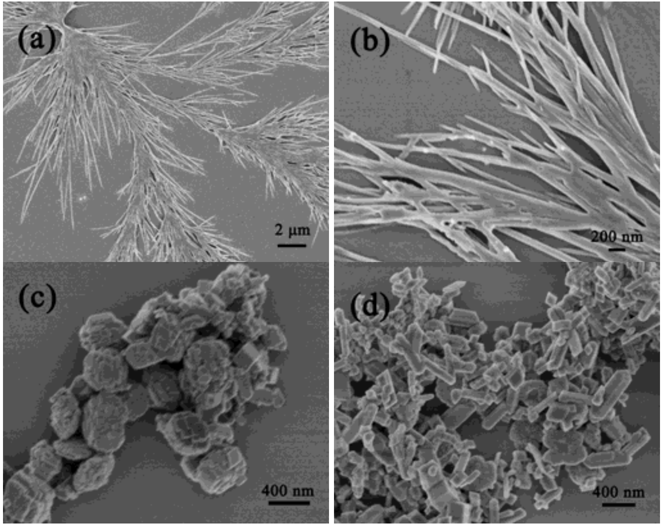

Figure 4 SEM images of $CaCO_3$ prepared at different surfactant concentrations (a)0.1 M，(b) Magnification of 0.1 M，(c)0.07 M，(d) 0.04 M

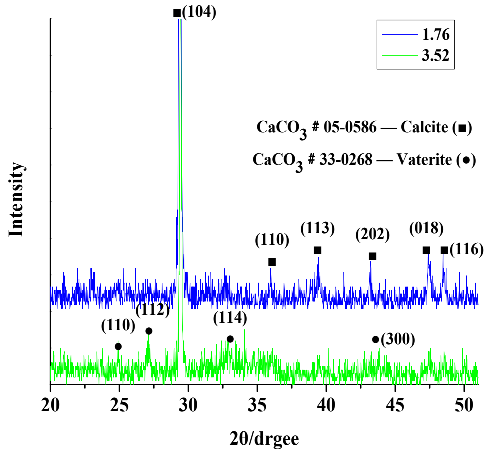

Figure 5 XRD patterns of $CaCO_3$ prepared at different ω. The reactant concentration is 0.3 mol/L and molar ratio [$CaCl_2$]/[Na_2CO_3]=1; the surfactant concentration is 0.07 M.

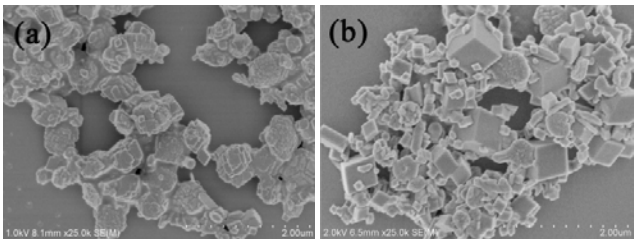

Figure 6 SEM images of $CaCO_3$ prepared at different ω (a)1.76，(b)3.52

Surfactants, with hydrophilic and hydrophobic parts, dissolved in organic solvents form spheroidal aggregates called reverse micelles. Water is readily solubilized in the polar core, forming a so-called "water pool," characterized by ω, that is molar ratio of water to surfactant. [29] The size of "water pool" increases with ω. Since the calcium carbonate particle generated in the "pool", the size of it is directly determines the size of the calcium carbonate particles. Figure 5 shows XRD patterns of $CaCO_3$ obtained with different ω. When ω reaches 3.52, $CaCO_3$ particle shows a mixed crystal type of vaterite and calcite. From the corresponding SEM images in Figure 6 (b), larger size of rhombohedras appear, which is not the smaller ones unite together forming a large one. In addition, the change of ω also affects the strength of reverse micelle interfacial membrane. Generally, as ω increases, interfacial membrane strength becomes smaller.[30] As a result, the interface membrane is easily broken because of the collision between the reverse micelles, and the particle size becomes large and difficult to control.

Conclusions

In conclusion, switchable surfactant N'-dodecyl-N,N-dimethylethyl amidine bicarbonate reverse micelle was used as soft template to prepare submicron fine calcium carbonate. Particles with rhombohedra, sphere, dendrite-like, etc. were obtained by changing the reactant concentration, surfactant concentration, ω. Compared with other methods, the reaction conditions are relatively mild. This research provides new insights into facile preparation of calcium carbonate particles and might well be extendable to the morpho-synthesis of other novel inorganic materials.

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