

A Bio-Inspired Approach to the Synthesis of CaCO_3 Spherical Assemblies in a Soluble Ternary-Additive System

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Two different soluble polymers, poly(ethylene glycol) (PEG) and poly(methacrylic acid) (PMAA), with individual functions were successfully employed in combination with a third additive, sodium dodecyl sulfate (SDS), in one system, and spherical assemblies (e.g., hollow spheres) with multiscale constructs of CaCO_3 were obtained. The variation of polymer concentration drastically changed both the morphology and polymorph of the produced CaCO_3 crystals due to the corresponding transformation of the micelle structure. This study suggests that noncovalent interaction and cooperation between soluble macromolecules play key roles in controlling the growth of biominerals. The results also suggest a novel and facile route toward biomimetic inorganic synthesis.

Natural crystalline materials with their exquisite and highly functional architectures provide an unlimited source of inspiration and concepts for the rational design of artificial crystalline materials, and several areas of materials research have been inspired by the study of biomaterials in recent years.^{1–3} Considerable effort has been devoted to the understanding of natural biomineralization processes typified by the ability of small amounts of organic substances to control the modes of crystallization of certain inorganic materials, in which a range of organic molecules are involved.⁴ Organisms generally utilize complex mixtures of crystal modifiers (rather than a simple additive) to generate a variety of biomaterials.⁵ Analysis of the organic matrix in invertebrate CaCO_3 skeletons such as molluscan shells showed that its soluble fraction includes several acidic proteins and glycoproteins.¹ These proteins are intimately associated with the mineral phase, and in some cases a subset of acidic proteins is actually occluded within the mineral phase. The presence of proteins extracted from the crystal phase of organisms led to the stabilization of this very crystal phase in vitro.^{6,7} But use of just one of these proteins did not produce this phase. Thus, the strong impact from the cooperation of proteins should be stressed in the polymorph control. We could speculate that these soluble acidic proteins are directly involved in controlling mineral formation and may cooperatively function as nucleators of mineral formation or as modulators of mineral growth, in the process of which the noncovalent interaction may play the important role of facilitating the formation of molecular aggregates to provide chemical microenvironments for the deposition of biominerals. Inspired by the biomineralization process, controlled crystallization of calcium carbonate with unusual and complex forms in the presence of organic additives and/or templates is of interest for biomimetic syntheses.^{8–13} Much effort has been devoted to the investigation of the cooperative effect of soluble matrixes and insoluble matrixes.^{10–13} Although the effect of individual soluble molecules in controlling CaCO_3 formation has been identified,^{14–18} there is very little direct in vitro evidence to prove that the soluble macro-

molecules could cooperatively function well as growth modifiers for the crystallization of CaCO_3 , due to the diversity in sizes and morphologies of products. Though Qi and co-workers obtained hollow-structured calcite spheres by introducing specific anions to the amphiphilic block copolymer DHBC solution (the polymer chains of DHBC are covalently bonded together),¹⁹ here we show the well-controlled crystallization of CaCO_3 with multiscale constructs by cooperation of two different soluble synthetic polymers with individual functions used together with a third surfactant in one system. Our strategy is to investigate the noncovalent interaction (e.g., attractive hydrophobic interaction) and cooperation of multiple additives over the nucleation and crystallization of calcium carbonate.

In this work, we demonstrate that the utility of poly(ethylene glycol) (PEG; $M_n = 4600$, Sigma), methacrylic acid (MAA), and sodium dodecyl sulfate (SDS) can cooperatively exert an exceptional control on the crystallization of CaCO_3 by the in situ polymerization²⁰ of MAA monomers through addition of a small amount of HCl as initiator. The crystallization of CaCO_3 was carried out at room temperature (25 °C). A typical procedure was as follows: The SDS concentration was kept at 0.2 mM. A certain volume of HCl was added to the mixed PEG and MAA ([PEG]:[MAA] mass ratio 4:1, total concentration $w = 0.2$ or 0.4 g/L) aqueous solution moderately stirred by using a magnetic stirrer. The initial pH value of the solution was adjusted to 3.5 by using 0.5 M HCl solution. Then SDS, 0.5 M CaCl_2 , and 0.5 M Na_2CO_3 were added in turn. This gave a final CaCO_3 concentration of 4 mM. After addition of the reactants was complete, an evident incubation period was observed before a sudden increase in the turbidity of the solution. When the reaction was finished, the pH value of the solution was about 7. The XRD pattern was determined on a Bruker D8-ADVANCE X-ray powder diffractometer with Cu K α radiation ($\lambda = 1.54178$ Å). The scanning electron microscopy (SEM) images were obtained on a LEO1530VP field-emission (FE) scanning electron microscope. The transmission electron microscopy (TEM) images were obtained on a JEOL JEM-200CX (at 200 kV) instrument. The dynamic light scattering (DLS) measurements were performed on an ALV-5000/E instrument.

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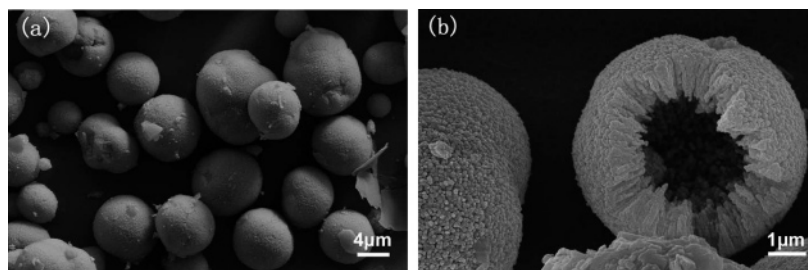


Figure 1. Scanning electron micrographs of CaCO_3 hollow spheres formed in the presence of PEG-PMAA-SDS: (a) low-magnification SEM image of the products; (b) high-magnification SEM image of one typical broken sphere. $w = 0.2$ g/L. $[\text{SDS}] = 0.2$ mM. PMAA was generated through in situ polymerization by using HCl as initiator.

When the polymer concentration (w) was about 0.2 g/L, well-defined hollow spheres were obtained. Figure 1a shows the typical SEM picture of CaCO_3 spheres. It exhibits that the sizes of the spheres range from 4 to 8 μm . We also observed a small fraction of broken hollow spheres. One broken sphere in Figure 1b shows the hollow nature of the spheres. It clearly reveals the hollow structure in high magnification, and shows the rough inner and outer surfaces. From this picture, the wall thickness was estimated to be about 2 μm . We can also see the wall of the sphere was constituted of many rodlike crystals with rounded outer ends along the diameter. The CaCO_3 crystallites appear to be organized in a radially oriented fashion outward from the hollow center of the spheres similar to the hollow calcite/vaterite spheres obtained by Colfen et al.²¹ or Sastry et al.²² TEM images further prove the hollow nature of the spheres (see the Supporting Information). The corresponding X-ray diffraction (XRD) pattern exhibited sharp reflections at 3.04, 2.29, and 2.10, consistent with the characteristic reflections of calcite. Recent studies have established that hollow calcite spheres could be prepared when the PEG-*b*-PMAA block copolymer was used together with SDS as a second additive,¹⁹ or the same block copolymer was used with the gas diffusion method.²³ The present work provides a promising alternative for the synthesis of hollow calcite spheres.

To get some direct information on the formation mechanism of the calcite hollow spheres, some control experiments have been carried out. Under the same experimental conditions mentioned above, if $\text{K}_2\text{S}_2\text{O}_8$ was used as a radical initiator in place of HCl, the product was essentially the same, also with a hollow nature. However, in addition to the hollow calcite spheres, many less-defined particles were also deposited (Figure 2a,b). We suppose that the introduction of SO_4^{2-} may have an influence on the crystallization of CaCO_3 owing to the electrostatic interactions between Ca^{2+} and SO_4^{2-} . This suggests that the HCl initiator not only could perform the same function as $\text{K}_2\text{S}_2\text{O}_8$ but also has the advantage of *avoidance* of introduction of new impurity ions (our precursors contain only Na^+ and Cl^-) that may affect the crystallization of CaCO_3 . Also we tried to follow the morphological development by collecting samples at different crystallization times. At early stages, actually the hollow spheres had already been formed. Parts c and d of Figure 2 show one broken sphere of the sample aged for 4 h. The broken fraction clearly shows the growth mode of the hollow spheres. As shown in Figure 2d, there are clusters of tips in the center. These tips may act as starting points from which the crystallization seems to start in the initial stage of the crystal growth. Then the crystals develop radially outward to construct the spheres.

Interestingly, when the homopolymer PMAA was directly employed (the total polymer concentration was kept at 0.2 g/L, and the mass ratio of PEG to PMAA was 4:1), different products were obtained. As shown in Figure 3a, only spherical calcite

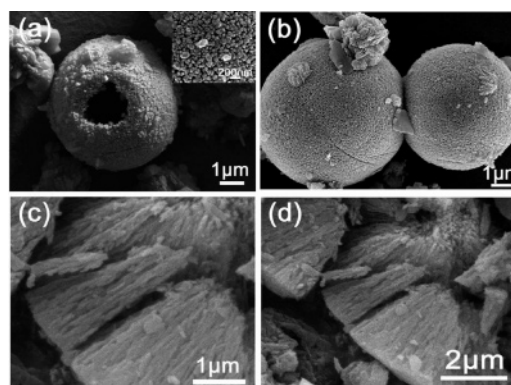


Figure 2. (a) SEM image of one typical hollow sphere. The inset shows the surface morphology of these spheres. (b) SEM image of the intact spheres. (c, d) SEM images of one typical broken sphere of the sample aged for 4 h. $w = 0.2$ g/L. $[\text{SDS}] = 0.2$ mM. The PMAA was generated through in situ polymerization by using (a, b) $\text{K}_2\text{S}_2\text{O}_8$ as initiator and (c, d) HCl as initiator.

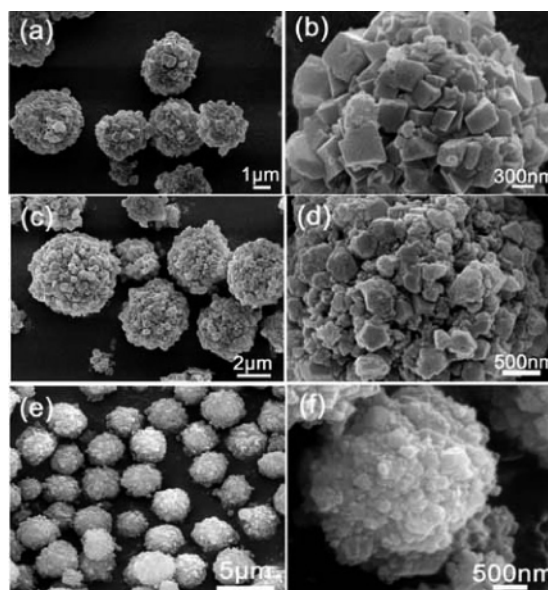


Figure 3. SEM images of CaCO_3 spheres formed in the presence of PEG-PMAA-SDS when homopolymer PMAA was directly used. (a, b) $M_n = 1270$, (c, d) $M_n = 1270$, pH 3.5. (e, f) $M_n = 5880$, pH 3.5. (a, c, e) Low-magnification SEM images. (b, d, f) High-magnification SEM images.

aggregates constituted of rhombohedral particles were obtained in the presence of a PMAA ($M_n = 1270$), PEG, and SDS mixture solution. So we consider the pH variation or the length of PMAA polymer chains may play a crucial role in controlling the final structures of the products. However, as the pH value of the solution and the length of PMAA polymer chains were varied, no significant change in the assembly of calcite spherical

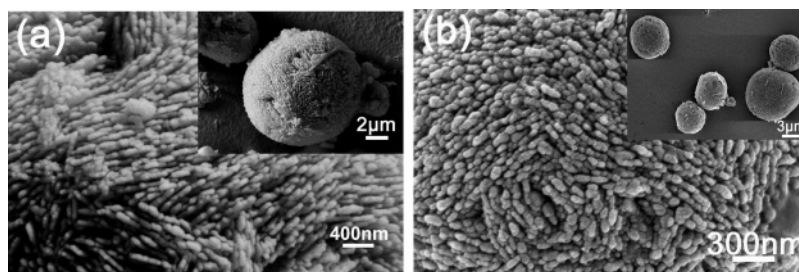


Figure 4. SEM images of CaCO_3 spherical assemblies obtained in the presence of PEG–PMAA–SDS with an aging time of 24 h (a) and 4 h (b). The inset of (a) shows one whole sphere of the sample after an aging time of 24 h. $w = 0.4$ g/L. $[\text{SDS}] = 0.2$ mM. PMAA was generated through in situ polymerization by using HCl as initiator.

aggregates was observed. The surface of the spherules is found to be very rough, with small calcite subunits establishing the superstructures. But some variation in the morphology and crystal size of the subunits was evident. Parts c and e of Figure 3 represent the products obtained as a consequence of pH variation (pH 3.5) and length change of PMAA polymer chains ($M_n = 5880$; the pH value of the solution was about 3.5), respectively. The SEM images at even higher magnification in Figure 3b,d,f show the surface structures in more detail. A general observation for the pH value's variation and the length change of PMAA polymer chains was the enhanced control of the morphology and crystal size of the subunits of aggregates, not the final structure of the products. But from these above results we can speculate that the PMAA, PEG, and SDS could form complex micelles for the assembly of calcite spherical aggregates. A comparison between the experiment in which the in situ generated PMAA was utilized and the one in which homopolymer PMAA was directly employed suggests that the pH value and length of PMAA polymer chains were not the main factors for controlling the final structure of CaCO_3 ; the in situ radical polymerization of MAA in aqueous solution may have a significant effect on the final morphology of the product. It has been documented that the in situ polymerization of polymeric additives plays an important role in controlling the final crystal phase by varying the onset of radical polymerization with respect to CaCO_3 .²⁰ With the combination of the ternary-additive strategy and in situ polymerization, this system should take charge of the polymorph and morphology of the calcite hollow spheres by fully utilizing the dynamic nature of the soluble organic matrixes. It is difficult to fully understand the mechanism implication of the effect of in situ polymerization of MAA over the crystallization of CaCO_3 , and this will be the subject of further work.

Further doubling the total concentration of polymers in the mixed solution to 0.4 g/L (SDS concentration was kept at 0.2 g/L), resulted in relatively bigger solid spheres instead of hollow spheres. Figure 4a clearly shows the typical SEM images of the unique crystals with unusual lamellar structure. From these images we can see the spheres were constituted of lamellar subunits, the thickness of which was estimated to be about 60 nm, and the lamellar subunits seem to be composed of oriented fused primary particles. Surprisingly, the X-ray diffraction pattern of this sample shows weak diffraction peaks from calcite, in addition to the sharp diffraction peaks from vaterite, the metastable polymorph of CaCO_3 . The d spacings (nm), 0.429 (002), 0.356 (100), 0.329 (101), 0.273 (102), 0.206 (110), 0.182 (104), and 0.164 (202), are consistent with the vaterite polymorph, and those of 0.380 (102), 0.303 (104), 0.228 (113), and 0.191 (108) suggest the existence of calcite. This indicates that these spherical particles consist predominantly of vaterite and partly calcite. These results suggest that the variation of polymer concentration drastically changes both the morphology and

polymorph of the resulting CaCO_3 crystals. Usually, the coexistence of calcite and vaterite polymorphs is an indication of a metastable state,²⁴ and the vaterite polymorph will be changed into calcite on extended aging time through a solvent-mediated process^{24–27} in solution. However, even though our samples were aged in solution for long times (e.g., 7 days), the XRD and SEM analyses exhibited almost the same phase structure and morphology. This indicates that the vaterite polymorph can be stabilized under this experimental condition. According to atomic surface structure modeling, the (001), (101), and (110) planes are positively charged and contain exposed Ca ions; thus, negatively charged polymer groups can adsorb on the plane.²⁸ It is understandable given that higher polymer concentration (namely, the increase of the concentration of carboxyl groups (PMAA)) could translate into better CaCO_3 binding efficiency and adsorption ability. Thus, the preferential adsorption of the polymer on vaterite relative to calcite that can at least balance the relative loss in the crystallization energy²⁴ could result in the crystallization of vaterite. Though these planes would be blocked for further growth, the stabilization of the vaterite surface by the carboxyl groups of polymers in aqueous solution may prevent phase transformation, which might account for the kinetic promotion of the metastable polymorph owing to the interaction between Ca^{2+} and the carboxyl groups.^{29,30} To get additional evidence for the formation mechanism of these complicated morphological spheres, we also collected samples at early stages of formation from the solution. Figure 4b shows the SEM image of the 4 h old sample. As shown in Figure 4b, the spheres obtained exhibited the lamellar structure in embryo, and it confirmed that the lamellar subunits were constituted of primary particles and the thickness of these lamellar subunits was about 60 nm. Presumably, these primary particles that were directionally fused together evolve into the lamellar subunits of the spheres. The lamellar particles have a uniform thickness throughout the whole sphere, which implies that the thickness is controlled at the initial stages of crystallization, and the side faces are blocked from growth by polymer adsorption. In addition, we believe that the emergence of lamellar particles implies that there exists a preferential direction aligned along the surface of lamellar subunits. We found that the XRD result of this sample clearly shows the relative intensification of (002) vaterite reflections. This goes well with the observation that single-crystal vaterite disks that can be prepared under a stearic acid monolayer by Mann et al.³¹ or in the DHBC and surfactant mixture solution by Qi et al.¹⁹ lie on the (001) plane. Though the lamellar subunits would exhibit a polycrystalline nature owing to the primary-particle-containing structure, it is reasonable to assume that the preferential plane also exists due to the exhibition of an anisotropic structure of the lamellar particles and the lamellar particles may also lie on the (002) plane.

As we know, under similar conditions, the presence of pure PEG has no effect on the crystal morphology and only large

ill-defined irregular-shaped aggregates consisting of rounded particles were obtained in the presence of PMAA.²⁴ Also only calcite solid spheres were produced in mixed PMAA–SDS solutions, whereas rhombohedral calcite crystals were formed in mixed PEG–SDS solutions.¹⁹ In the presence of PEG and PMAA (in situ polymerization initiated by HCl) or the presence of PEG, MAA, and SDS, close-packed assemblies of rhombohedral calcite particles which were embedded mutually were deposited in our control experiments (see the Supporting Information). FTIR analyses of the products indicated the formation of poly(methacrylic acid). All these results mentioned above indicate that the copresence of PEG and PMAA together with the anionic surfactant significantly influences the polymorphism selectivity of CaCO_3 and enhances the morphological modification effect.

According to Bailey, PEG can interact with PMAA and form a hydrogen bond in aqueous solution, promoting the segregation of polymer from water to form complexes.³² This point was further proved by the evidence that aggregated products were obtained only in the presence of PEG and PMAA. Also the homopolymer PEG can interact strongly with anionic SDS to form PEG–SDS complex micelles with EG groups intermingling in the headgroup region of the SDS micelles,¹⁹ and that interaction between polyelectrolytes and surfactants of the same charge is believed to be weak or nonexistent.^{33–35} The investigation of interaction between SDS and polystyrene-*b*-poly(acrylic acid) block copolymer (PS-*b*-PAA) showed that ionic headgroups of SDS repel the charged PAA chains and only hydrocarbon chains of SDS partition into the PS core of the polymer aggregates.³⁶ Thus, we could speculate that the mixture of PEG, PMAA, and SDS could form complex micelles with a core–shell structure similar to that of the PEO-*b*-PMAA–SDS complex¹⁹ in mixed solutions. Owing to the repulsion of the ionic headgroups of SDS, PMAA as a shell may be just adsorbed on the surface of the core which was constituted of PEG and SDS with PEG incorporated into the headgroup region of the SDS micelles through the interaction between the PMAA and PEG. DLS measurements were carried out to investigate the aggregation properties of this ternary-additive system in the original aqueous solution. When the polymer concentration was 0.2 g/L, the mean diameter of the complex micelles was about 180 nm, and as the polymer concentration increased to 0.4 g/L, the mean size increased to about 200 nm. Therefore, the aggregate size seems much smaller than the inner diameter of the hollow spheres or that of the spheres with lamellar structure. It is interesting to note that the same phenomenon has been observed by Qi et al.¹⁹ According to Qi's results, the presence of salts has a considerable effect on the size of the complex micelles, and both the presence of the reactants in the solution and the development of the inorganic structure could perturb the organic template, resulting in an adaptive construction.¹⁹ So these complex micelles may function as templates and provide the microenvironment in which nucleation and growth of CaCO_3 occur. In the presence of polymers, an organic–inorganic interface region would perform the function as the chemical microenvironment where nucleation of CaCO_3 occurs. In this work, PEGs seems to function as the bridges between PMAAs and the SDS micelles; PMAAs would provide the nucleation sites for the crystallization of CaCO_3 owing to the interaction of PMAA and Ca^{2+} , which leads to a high local supersaturation of Ca^{2+} covering the periphery of the micelles. The crystallization of CaCO_3 starts from these nucleation sites on the surface of the micelles, and then the crystals develop outward until they collide with each other, leading to the final

hollow structure. When the total polymer concentration is too large, the sizes of the complex micelles become larger. This can be attributed to the expansion of the PEG region of the core caused by the association of more PEG on SDS micelles. As the PEG region increases, PMAA molecules may be capable of penetrating into the PEG region. In addition to the complex micelles, there would be many free polymer molecules that could function as potent inhibitors in the solution. Therefore, nucleation and growth of CaCO_3 would occur under the cooperative effect of the complex micelles and free molecular inhibitors. Probably the formation of primary particles would occur among the shells along the chains of PMAAs, leading to a preferential growth direction. As the specific adsorption of polymer occurs on specific planes, the attractive hydrophobic interactions between the alkyl tails would lead to particle fusion and structural rearrangement,³⁷ and finally the formation of lamellar particles. As the formation of lamellar particles occurs around the complex micelles, the products exhibit the final morphology with lamellar subunits and a spherical superstructure. In addition, the hydrophobic association²² between the lamellar particles may promote the formation and stabilization of such spherical assemblies with lamellar structures. It should be noted that control over CaCO_3 phase formation could be performed by dendrimer/surfactant templates.^{38,39} In combination with protonation of only half of the surfactant in the aggregates assembled by poly(propyleneimine) dendrimers and octadecylamine, the extremely high rigidity of the aggregates will limit the possibilities of the templates to adapt themselves so as to match a specific crystal face, which could possibly account for the formation of amorphous CaCO_3 rather than a crystalline phase. This is different from our ternary-additive system that could adopt adaptive constructions which finally lead to the formation of unusual CaCO_3 spherical assemblies.

In conclusion, both PEG and PMAA additives are indispensable to the multiscale structures of the CaCO_3 spherical assemblies together with the SDS surfactant. These results above demonstrate the importance of the noncovalent interaction and cooperation between the multiple additives to the formation of inorganic superstructures, and indicate that the functions of these soluble organic additives are related not only to their structures, but probably also to their neighboring macromolecules and the microenvironments in which they are located.⁴ With respect to the presence of organic molecules, it is possible that their functional groups and the chemical microenvironment they build, in which the functional groups can act through a specific chemical interaction with the growing crystal, both play pivotal roles in controlling the crystallization of inorganic minerals. They coordinate with each other, and their cooperative function contributes to the final polymorph and morphology of CaCO_3 . The production of well-defined hollow calcite spheres and unusual spherical assemblies with lamellar superstructures in an aqueous system of soluble ternary additives represents a novel and potentially useful route to the biomimetic synthesis of inorganic crystals with complex structures. Although the formation mechanism is not yet fully understood, here we have provided a new concept of the biomimetic synthesis of inorganic structures. The major requirement seems to be the selection of the multiple components that are able to construct well-defined aggregates so as to provide an appropriate chemical microenvironment where the precipitation of inorganics occurs. If suitable multiple components are available, the potential of this route is clear. It is believed that such multiadditive systems may offer a whole new range of possibilities to control the inorganic form and could be extended to other inorganic systems.

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Supporting Information Available: Scanning electron micrographs of CaCO₃ spheres formed in the presence of PEG–PMAA and PEG–MAA–SDS, XRD pattern of products obtained in the presence of PEG–PMAA–SDS, transmission electron micrographs of CaCO₃ hollow spheres formed in the presence of PEG–PMAA–SDS, and DLS result of the formation of ternary-additive PEG, PMAA, and SDS complex micelles in aqueous solution. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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