

See discussions, stats, and author profiles for this publication at: <https://www.researchgate.net/publication/200632782>

Direct Synthesis of Hollow Vaterite Nanospheres from Amorphous Calcium Carbonate Nanoparticles via Phase Transformation

ARTICLE in THE JOURNAL OF PHYSICAL CHEMISTRY C · JULY 2008

Impact Factor: 4.77 · DOI: 10.1021/jp801408k

CITATIONS

31

READS

226

7 AUTHORS, INCLUDING:



X. R. Xu

Zhejiang University

73 PUBLICATIONS 1,639 CITATIONS

SEE PROFILE



Haihua Pan

Zhejiang University

68 PUBLICATIONS 1,538 CITATIONS

SEE PROFILE



Jinhui Tao

Pacific Northwest National Laboratory

41 PUBLICATIONS 919 CITATIONS

SEE PROFILE



Ruikang Tang

Zhejiang University

126 PUBLICATIONS 2,994 CITATIONS

SEE PROFILE

Article

Direct Synthesis of Hollow Vaterite Nanospheres from Amorphous Calcium Carbonate Nanoparticles via Phase Transformation

Anhua Cai, Xurong Xu, Haihua Pan, Jinhui Tao, Rui Liu, Ruikang Tang, and Kilwon Cho

J. Phys. Chem. C, **2008**, 112 (30), 11324-11330 • DOI: 10.1021/jp801408k • Publication Date (Web): 03 July 2008

Downloaded from <http://pubs.acs.org> on November 28, 2008

More About This Article

Additional resources and features associated with this article are available within the HTML version:

- Supporting Information
- Access to high resolution figures
- Links to articles and content related to this article
- Copyright permission to reproduce figures and/or text from this article

[View the Full Text HTML](#)



ACS Publications
High quality. High impact.

The Journal of Physical Chemistry C is published by the American Chemical Society, 1155 Sixteenth Street N.W., Washington, DC 20036

Direct Synthesis of Hollow Vaterite Nanospheres from Amorphous Calcium Carbonate Nanoparticles via Phase Transformation

Anhua Cai,[†] Xurong Xu,^{*,†} Haihua Pan,[†] Jinhui Tao,[†] Rui Liu,[†] Ruikang Tang,^{*,†} and Kilwon Cho[‡]

Department of Chemistry and Centre for Biomaterials and Biopathways, Zhejiang University, Hangzhou, 310027, China, and Department of Chemical Engineering, Polymer Research Institute, Pohang University of Science and Technology, Pohang, 790-784, Korea

Received: February 17, 2008; Revised Manuscript Received: April 25, 2008

A new and simple method for preparation of hollow calcium carbonate nanospheres under mild conditions is developed. Hollow vaterite nanospheres are achieved by water-induced phase transformation of poly(4-sodium styrene sulfonate)-stabilized amorphous calcium carbonate (PSS–ACC) in water–ethanol solution at room temperature. It is found that the sizes of the resulting hollow-structured nanospheres can be easily regulated by the content of PSS and the phase transformation can be greatly affected by the ratio of water to ethanol in the mixed solvent. A combination effect of PSS and water is emphasized in this formation process. It is important to control the amounts of PSS and water in the experiments so that a large scale of hollow vaterite nanospheres with different sizes can be achieved. We suggest that the PSS–ACC particles use themselves as the templates to form the new crystallized shells, and its mechanism is also discussed.

Introduction

There is intense interest in a simple and general strategy to synthesize hollow-structured spheres for their unique structures and properties. Various approaches have been tried by using colloidal/microemulsion templates,¹ sonochemistry,² hydrothermal synthesis, etc.³ Current pathways, which tend to be based on biomimic synthesis of natural nanostructures in mild conditions, have attracted more extensive attention in material sciences. Growing evidence has shown that an amorphous phase such as amorphous calcium carbonate (ACC) plays a crucial and basic role in the formation of biological skeletal tissues.^{4–6} In nature, organisms can produce stable spherical ACC particles, and the colloidal nanoparticles participate as the transient intermediates in the formation of crystallized calcium carbonates, e.g., mollusk shells, sea urchin larva, adult spicules, bellies of woodlice, etc.^{4,6} However, ACC in its pure form is highly unstable in aqueous media, and it needs to be stabilized against spontaneous phase transformation by biological molecules or polyelectrolytes.⁴

Crystallization and morphological control of calcium carbonate have been extensively studied for decades. The hollow-structured calcium carbonate may serve as drug deliverers and diagnostic markers since it provides an excellent biocompatibility. Several strategies have been suggested for the preparation of calcium carbonate hollow spheres. The templates, such as CO₂-bubbles⁷ and organic templates,⁸ are frequently utilized to fabricate hollow calcium carbonates. However, these obtained hollow spheres commonly have large sizes, which are in the microscale, and their morphology is poorly controlled. Another problem of the previous methods is that the yield of hollow structure is always relatively low. Up to now, the preparation of large amounts of nanoscale hollow calcium carbonates has

not been reported. Recently, the water-induced crystallization of alkylbenzene-sulfonate-coated ACC nanoparticles in reverse microemulsions has offered a new idea about the controlled transformation, which reveals that the extent of water penetration into the ACC cores is important to the formation of a complex hybrid structure of calcium carbonate.⁹ Here, we develop a simple but effective method of the direct synthesis of hollow vaterite nanospheres by water-induced transformation from the complex of poly(4-sodium styrene sulfonate) (PSS) and ACC in water–ethanol solutions and we suggest that the PSS–ACC nanospheres themselves can play as the natural templates for the derived hollow structure.

Experimental Section

Materials. Poly(4-sodium styrene sulfonate) (MW \approx 70 000 g/mol) and dimethyl carbonate (DMC; AR) were obtained from Aldrich. NaOH (AR), CaCl₂ (AR), and anhydrous ethanol were purchased from Sino Chemical Company, and all chemicals were used directly without further purification. Double-distilled water was used in the experiments.

Preparation of ACC. Hydrolysis of DMC catalyzed by NaOH was used to prepare the ACC powders, according to method 1 (excess of DMC over Ca²⁺) of Faatz et al.¹⁰ Briefly, ACC containing PSS (PSS–ACC) was synthesized as the following: 240 mL of 0.003 mol CaCl₂ aqueous solutions, including 0.015 mol of DMC and 0.003x mol of PSS ($x = 0, 1/4, \text{ or } 1/32$), was quickly mixed with 60 mL of 0.03 mol NaOH aqueous solution. The mixed solution was stirred for reaction about 2.5 min at room temperature. In the preparation, the mole ratio Ca/PSS/DMC/NaOH was 1:x:5:10 in the final mixtures. The precipitates were rapidly separated by centrifugation (8000 rpm) and were washed using anhydrous acetone and ethanol. The obtained solids were dried under a vacuum condition at room temperature for 48 h.

Transformation of ACC. Hollow vaterite nanospheres were formed by water-induced transformation of PSS–ACC. An amount of 15 mg of PSS–ACC was dispersed in 10 mL of

* Corresponding authors. Fax: 86-571-87953736. Tel.: 86-571-87953736. E-mail: rxru@zju.edu.cn (X.X.), rtang@zju.edu.cn (R.T.).

[†] Zhejiang University.

[‡] Pohang University of Science and Technology.

anhydrous ethanol in a 25 mL vial in the presence of an ultrasonic treatment for 1 h. Then different amounts of water, such as 0.5, 1, 2, 4, and 8 mL (the corresponding volume ratios of water to ethanol, R , were 0.5/10, 1/10, 2/10, 4/10, 8/10), were added into the slurry to induce the phase and morphology transformation in a thermostats oscillator at 250 rpm, at a temperature of 25 °C. The samples (1 mL) of the reaction slurry were withdrawn periodically, and the solids were separated by centrifugation (8000 rpm) and were washed using anhydrous ethanol. The obtained solid samples were dried under a vacuum condition at room temperature.

The control experiments were also done as the following: 15 mg of pure ACC powder was dispersed in 10 mL of anhydrous ethanol, and 1 mL water was then added to induce the transformation of ACC in the absence of PSS.

Characterization. All solid samples were examined by using a JEM-200CX transmission electron microscope (TEM) (JEOL, Japan). Scanning electron microscopy (SEM) was performed by a Hitachi S-4800 field emission SEM and SLR10N field emission instrument (FEI, The Netherlands). Powder X-ray diffraction (XRD) was performed by a D/MAX-RA XRD (Rigaku Japan) (Cu K α , $\lambda = 1.5405 \text{ \AA}$). The FT-IR spectra were characterized from 4000 to 400 cm^{-1} in transmission mode by a Nexus-670 spectrometer (Nicolet, U.S.A.). The specific surface area of sample was determined by a BET method, which was measured by an Omnisorp 100CX, (Coulter, U.S.A.).

Results

Preparation of Amorphous Calcium Carbonate. Pure ACC and ACC nanoparticles containing PSS (PSS-ACC) were synthesized according to ref 10. In the presence of PSS, the homogeneous nanoparticles with size of $\sim 80 \text{ nm}$ were obtained at $\text{Ca/PSS} = 4$ (Figure 1, parts a and c). The effect of PSS on the preparation of ACC particles was also examined. Similar to the previous understanding,¹¹ it was found that the presence of PSS could decrease the average size and polydispersity of the resulting ACC particles. With a decrease of PSS amount in the reaction solution, the size of the induced ACC particles increased. For example, at a ratio of $\text{Ca/PSS} = 32$, the average size of the PSS-ACC was $\sim 110 \text{ nm}$ (Figure 1, parts b and d). The amorphous character of the products was examined by selected area electron diffraction (SAED, inset of Figure 1a). However, no diffraction pattern was observed. This result implied that no crystalline phase was detect and these samples should be the amorphous ones. The characteristic FT-IR adsorption peaks of ACC were found in the spectra of pure ACC and the PSS-ACC (Figure 1e): a broad adsorption peak at 866 cm^{-1} , split adsorption peaks at 1421 and 1477 cm^{-1} , and the ν_1 adsorption band around 1074 cm^{-1} . The adsorption bands of PSS, around $1000\text{--}1200 \text{ cm}^{-1}$, were also clearly observed, which confirmed the presence of PSS in the PSS-ACC composites. Thus, the formations of pure ACC and PSS-ACC could be confirmed. The current study also demonstrated that the concentration of PSS could control the particle size of the resulting ACC particles.

Synthesis of Hollow Vaterite Nanospheres. An amount of 15 mg of PSS-ACC ($\text{Ca/PSS} = 4$) was dispersed in 10 mL of anhydrous ethanol under an ultrasonic treatment for 1 h, then 1 mL of double-distilled water was added to induce the transformation at 25 °C. Large-scale and uniform hollow nanospheres (Figure 2a) were finally obtained after 2 days. The TEM study showed that their size was approximately 80 nm and the thickness of the shell was around 20 nm. It was interesting that the sizes of the hollow nanospheres corresponded to the original

sizes of PSS-ACC. The nanospheres were also examined using SEM (Figure 2c). However, it was found that the shells of the spheres were not complete and the holelike structures always appeared on the shells. This phenomenon was clearly demonstrated by a high-magnification SEM image (Figure 2c, inset). Through the hole, we could also confirm that the sphere had a hollow structure. The previous studies suggested that such a hollow-structured nanoparticle with an open pore had numerous potential industrial applications as catalysts, lightweight fillers, low-dielectric materials, drug-release vectors, etc.^{3,7,8a}

The main crystal phase of the products was vaterite, which was a metastable phase of calcium carbonate. A trace amount of calcite was also detected by XRD (Figure 2d) and FT-IR (Figure 5) in the resulting hollow spheres. However, it was important that the crystal phase of the individual nanosphere was pure vaterite, which was determined by SAED (Figure 2b). The data could match the vaterite lattice well, and all the diffraction dots were assigned to (112), (116), (200), (201), (302), and (304) crystal planes of vaterite (Figure 2b). And it was interesting that the calcite phase was not detected in spheres by SAED. Actually, the rhombohedra-shaped calcite single crystals were sometimes observed separately and their ratio was extremely low, around 3 mol %, calculated from the XRD result according to a method introduced by Dickinson and McGrath.¹² Thus, we concluded that the resulting hollow-structured nanospheres were pure vaterite.

Role of PSS in the Transformation of ACC. To clarify the effect of PSS, a control experiment was preformed under the same condition in the absence of PSS. In comparison to PSS-ACC, the pure ACC particles had larger sizes, about 500 nm. The hollow nanostructure was not observed after the water-induced transformation. However, the large solid spheres were obtained after 2 days under $R = 1/10$ (Figure 3a). Both the studies of SAED and FT-IR indicated that the resulting particles were vaterite. SEM examination confirmed that the formed vaterite spheres were solid, which were found by the aggregation of numerous small particles, and their surfaces were extremely rough (Figure 3b). It could be seen that the hollow-structured particles were not evolved by using pure ACC. This control experiment clearly demonstrated that the involvement of PSS was crucial during the formation of the hollow-structured vaterite nanospheres. Without the involvement of PSS, the solid ACC spheres turned into the solid vaterite spheres directly during the water-induced transformation.

As mentioned above, the size of PSS-ACC nanoparticles could be controlled by an adjustment of the PSS amount. Since the particles used themselves as the template to form the hollow vaterite spheres by the controlled phase transformation, the sizes of the hollow nanospheres could be easily regulated by the PSS concentration (Figure 4, parts a and b). When the mole ratio of Ca to PSS was 32, the size of formed hollow nanospheres was about 110 nm, which was similar to the original PSS-ACC particles too. Another important role of PSS in this system was to stabilize the ACC phase against spontaneous phase transformation. Therefore, the decreasing of PSS amount in the ACC system would result in the decreasing of the evolved hollow spheres. In contrast to $\text{Ca/PSS} = 4$, a lower percentage of the hollow nanospheres was detected with the lesser PSS under the similar experimental conditions (Figure 4b).

Role of Water in the Transformation of ACC. Li and co-workers⁹ reported the effect of water on the formation of the emergent nanostructure of calcium carbonate in a reverse microemulsion. The important role of the water amount in the formation of hollow nanospheres was also found in the present

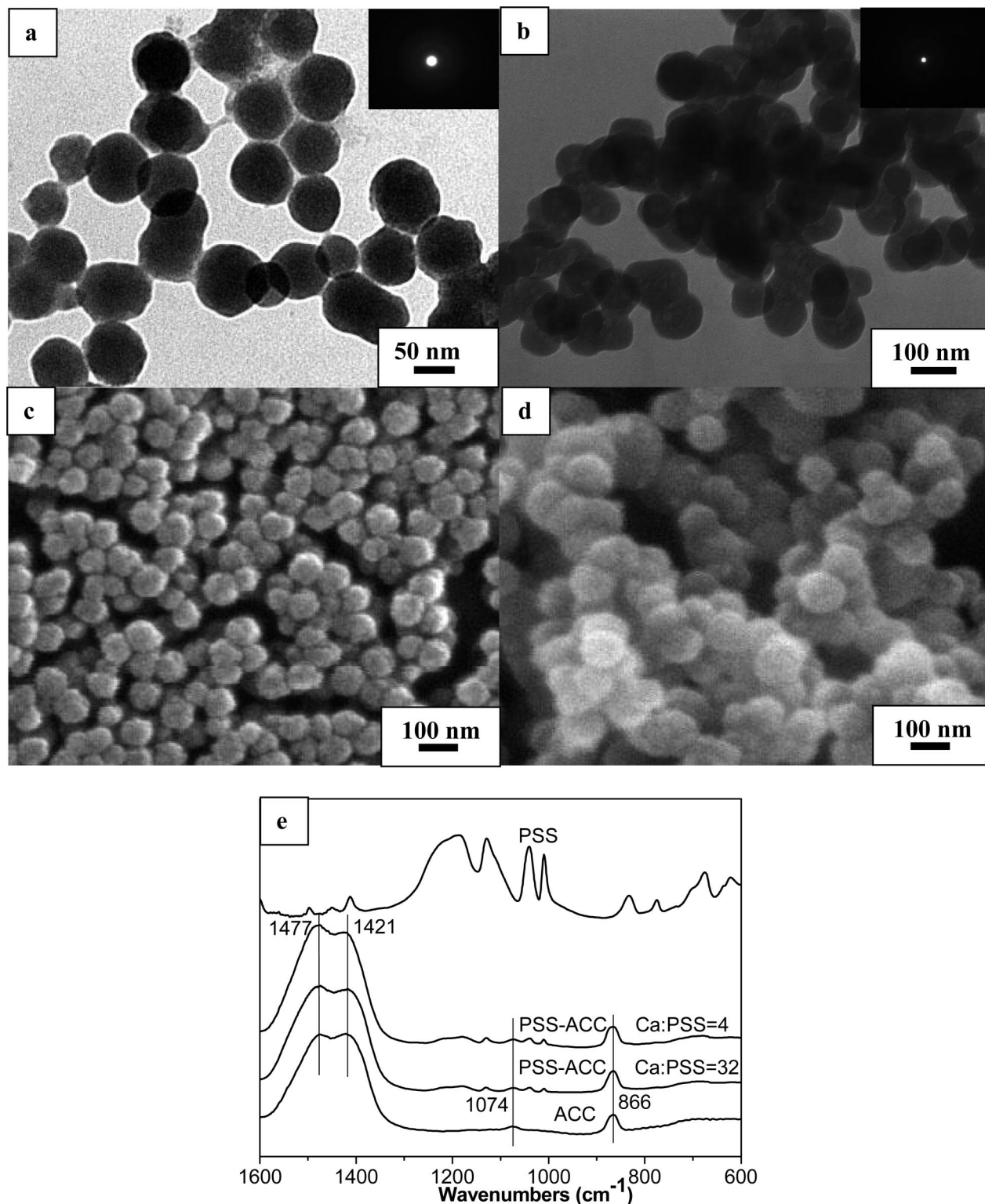


Figure 1. PSS-ACC at Ca/PSS = 4: (a) TEM image and SAED (inset) and (c) SEM image; PSS-ACC at Ca/PSS = 32: (b) TEM image and SAED (inset) and (d) SEM image; (e) FT-IR of pure ACC, PSS-ACC at Ca/PSS = 4 or 32, and PSS, showing PSS-ACC containing PSS.

work. In our experiments, R , the volume ratio of water/ethanol, was changed in a range of 0.5/10 to 8/10. FT-IR results showed that the content of calcite in the final products increased obviously when R was increased. The adsorption peak at 712 cm⁻¹ represented the presence of calcite, and its relative intensity was gradually strengthened by the increasing of R from 1/10 to 8/10. Additionally, the characteristic adsorption band of vaterite, a split peak at 1440 and 1490 cm⁻¹, turned into the characteristic adsorption of calcite at 1418 cm⁻¹ (Figure 5). It was well-known

that water could promote the transformation of PSS-ACC to the most stable phase of calcium carbonate, calcite, directly and quickly. An increasing of water amount would result in a formation of less hollow vaterite nanospheres. With the increasing of R , the population of hollow vaterite nanospheres reduced; more and more calcite rhombohedra crystals were obtained. At a high level of R (4/10 and 8/10), the hollow nanospheres could be hardly found, and most products were the calcite rhombohedra. Simultaneously, with the increasing of experimental time,

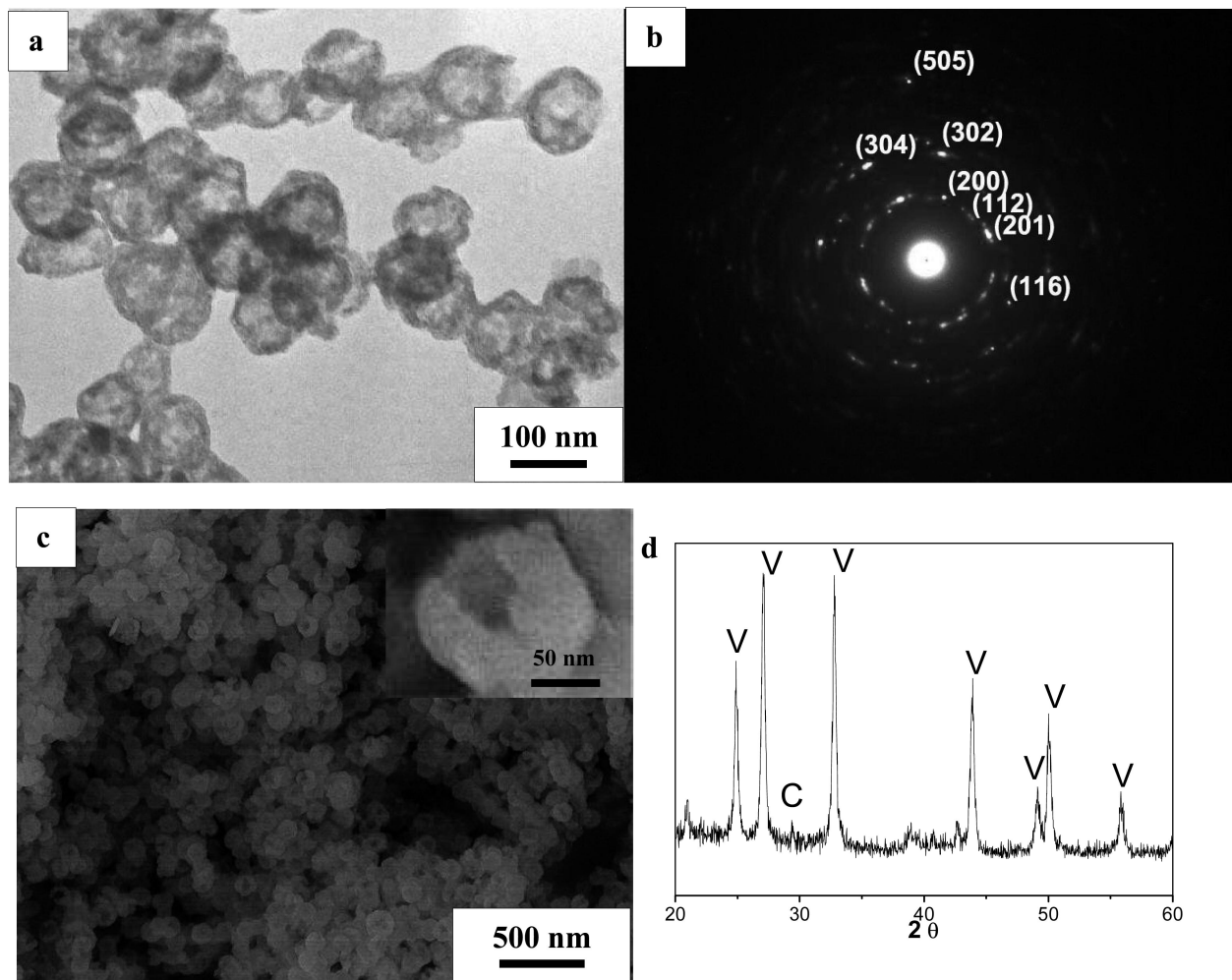


Figure 2. (a) TEM; (b) SAED pattern of (a); (c) SEM images for PSS-ACC obtained after transforming for 2 days under $R = 1/10$ at $\text{Ca/PSS} = 4:1$ (inset, high magnification of the hollow nanospheres); (d) XRD pattern of the product of hollow vaterite nanoparticles at $\text{Ca/PSS} = 4:1$ (V, vaterite; C, calcite).

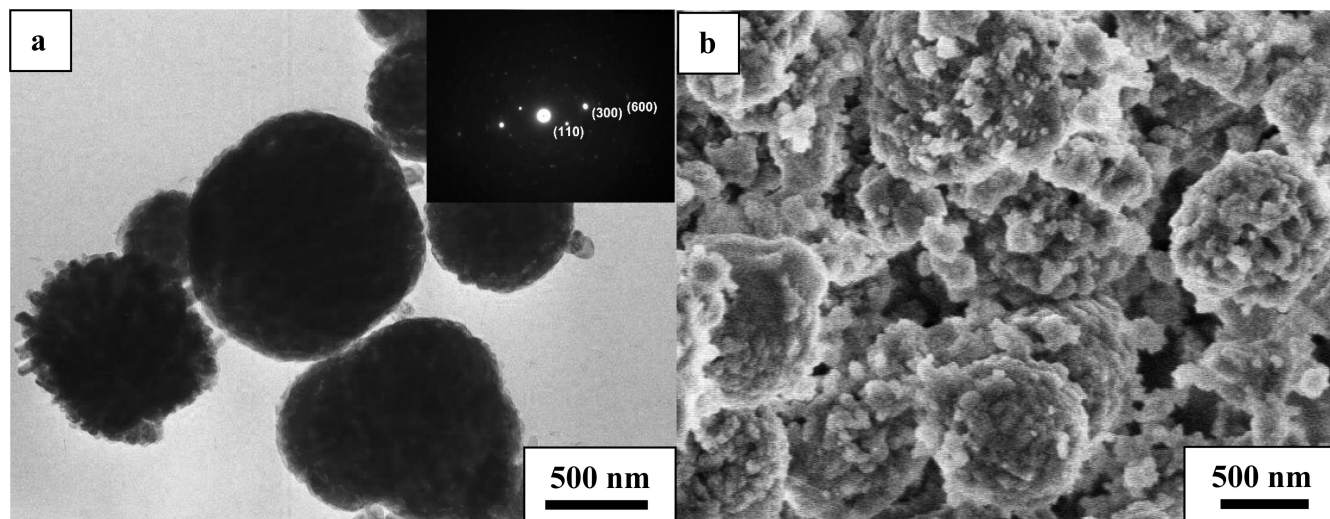


Figure 3. (a) TEM (inset, SAED pattern) and (b) SEM images of pure ACC in the presence of 1 mL of water after transforming for 2 days.

the percentage of vaterite nanospheres decreased and the other phases such as aragonite and calcite were detected. As an expectation, the total amount of aragonite and calcite in the resulting samples increased with the experimental time. It was easy to understand that vaterite would slowly transform into more stable aragonite or calcite with a long experimental time period since vaterite was a thermodynamically metastable phase

of calcium carbonate in the aqueous solutions. However, this result indicated that the water amount in solution was another important factor during the formation of hollow vaterite nanospheres.

In summary, we found that the hollow-structured vaterite nanospheres could be conventionally synthesized when R values were 0.5/10–2/10 within 2 days. The crystallinity⁹ of the formed

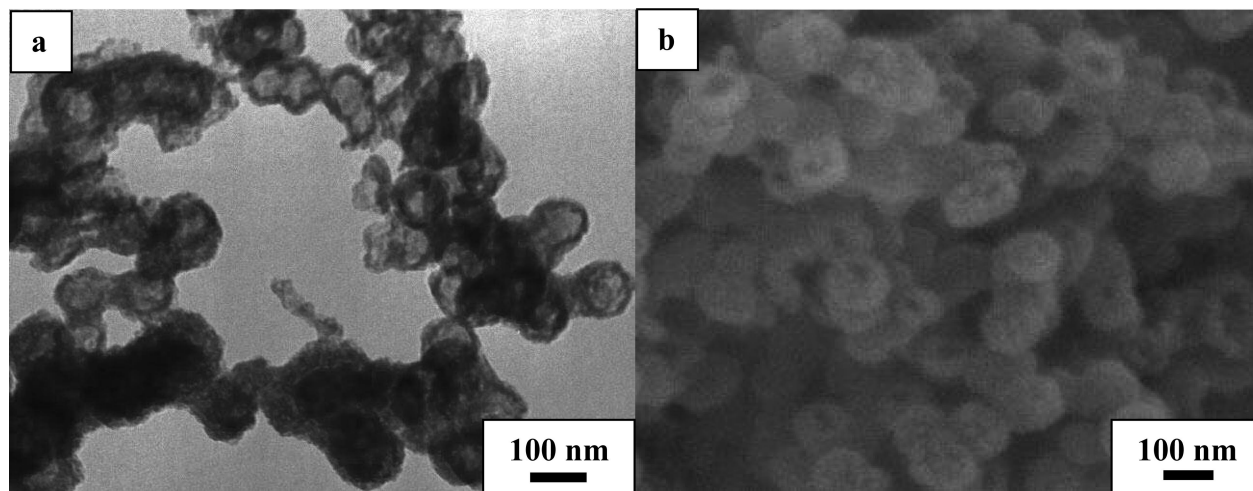


Figure 4. (a) TEM and (b) SEM images of PSS-ACC (Ca/PSS = 32) obtained after transforming for 2 days.

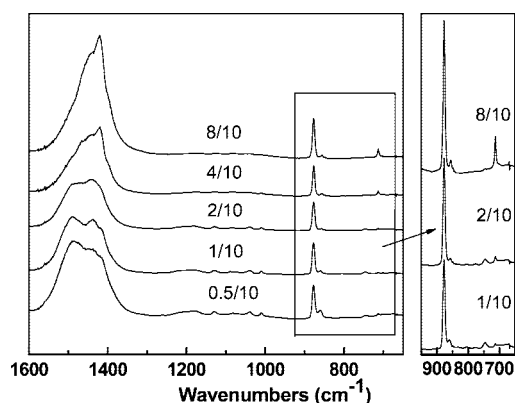


Figure 5. IR spectra of the products under the different R values (the inset is the enlargement curves of some samples from wavenumbers of 950–650 cm^{-1}).

nanospheres could be improved by increasing the water amount (Figure 6); however, more calcite or aragonite could be induced accordingly.

Discussion

PSS is a kind of polyelectrolyte with high density of negatively charged sulfonate groups. PSS is often used to regulate the crystallization of calcium carbonates in the studies of biomineralization. Generally, the direct addition of PSS into the supersaturated calcium carbonate solution cannot result in the precipitation of the hollow-structured vaterite. However, it can stabilize the vaterite phase and reduce the size of particles in the solution.¹¹ Cölfen and co-workers¹³ have suggested that the strong interaction between PSS and calcium ions changes the pathway of mineralization from the conventional ion-by-ion growth to the mesoscale assembly. Although ACC precursors are also formed in their experiments, the formation of the hollow structure is not reported.¹³ Li and co-workers⁹ have studied the transformation of surfactant-stabilized ACC in microemulsion, but there is no formation of hollow calcium carbonate although a surfactant of alkylbenzene sulfonate is used. We note that 5 nm ACC particles are used in their experiment, which is much smaller than our PSS-ACC composites. However, Yu et al.³ have reported the preparation of microscale hollow calcium carbonate spheres by self-transformation in the presence of PSS at high temperature (at 70 °C). In our work, PSS-ACC precursors are used and the

formation of hollow nanoscale vaterite spheres can be easily regulated. It is highlighted that our preparations are performed at room temperature. Another highlight of the present study is that the formation of hollow vaterite nanospheres is self-templated by their original PSS-ACC precursors.

The combination of PSS and water plays a key role in the formation of hollow vaterite nanospheres. The strong interaction of polyanionic sulfonate groups of PSS with calcium ion can influence the nucleation of calcium carbonate. The polymer adsorptions onto the ACC surfaces inhibit the aggregation and growth of the particles. Thus, the obtained PSS-ACC nanospheres always have smaller and more uniform dimensions than the pure ACC. Another important effect of PSS is the inhibition of phase transformation of vaterite into calcite, which is widely accepted in many literatures.^{3,9} These effects become more obvious when the content of PSS is increased in the PSS-ACC complex. In the experiment, we demonstrate that the higher content of PSS promotes the formation of hollow vaterite nanospheres with smaller sizes under the same experimental condition of water amount. In the absence of PSS, only irregular vaterite solids are obtained (Figure 3).

Our experimental results also suggest that the nanospheres originate from a dissolution–recrystallization process of PSS-ACC in the presence of water. Water has another remarkable effect on the formation of the hollow vaterite nanospheres. In the presence of PSS, no hollow spheres can be found if a large amount of water, e.g., 8 mL, is added into the PSS-ACC suspension. However, when a little water is used, such as $R = 1/10$, PSS-ACC can be transformed into the hollow-structured vaterite. With the increasing of the water amount, the transformation of PSS-ACC into the rhombohedral-shaped calcite is promoted. In general, lower water amount and higher PSS content are two key factors to reduce the crystallization rate of PSS-ACC, which can improve the formation of the hollow nanospheres.

The possible mechanism of the formation of hollow vaterite nanospheres is assumed (Scheme 1). The low amount of water first triggers the phase transformation of the external surface of PSS-ACC spheres to crystallize into vaterite, then the PSS in the particles inhibits the further transformation of vaterite into stable calcite. Meanwhile, the ACC located in the center of the spheres can be gradually dissolved since ACC has a high solubility in the water phase. The dissolved parts leave the spheres from the defects of the shells, or the holes. Thus, the outside ACC becomes vaterite and the inner ACC is

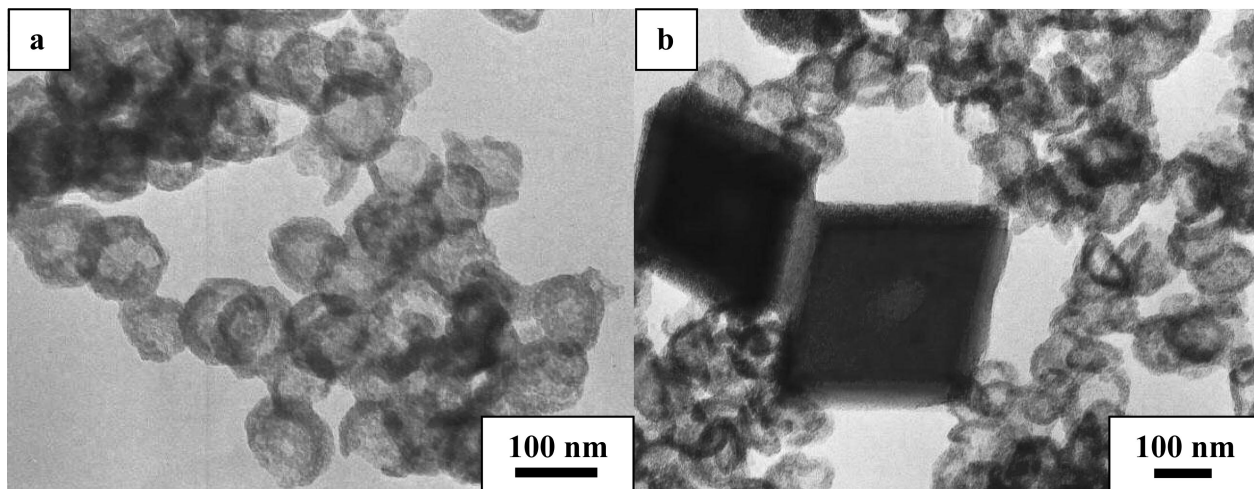
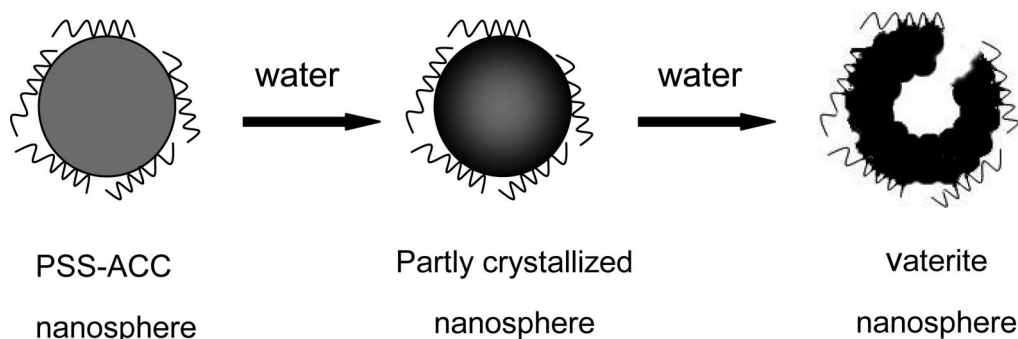


Figure 6. TEM image of hollow vaterite nanospheres obtained after transforming 2 days. (a) $R = 0.5/10$; (b) $R = 2/10$; the typical calcite single crystals are also induced as the water amount is increased.

SCHEME 1: Evolution of the Hollow Vaterite Nanospheres from the ACC Solid Particles under the Controls of PSS and Water



removed, which resulted in the observed hollow structure. It is emphasized that all of the processes must be slow and stepwise so that the newly formed vaterite can use the original PSS-ACC particles as the templates (Figures 1a and 2a). Yu et al.¹⁴ has suggested a similar process for calcite hollow microspheres through a vaterite precursor. On the basis of the mechanism, the crystallinity of the shell must be greatly improved from the original amorphous phase, which is confirmed by the bright- and dark-field images of TEM. The result shows that the shell

is an improved crystalline phase than the other parts, which are still amorphous (Figure 7). It is emphasized that only the cooperative effects of less amount of water and the involvement of PSS can guarantee such a formation of hollow vaterite nanospheres.

Additionally, the surface properties of hollow vaterite nanospheres are also studied by nitrogen adsorption-desorption. The Brunauer-Emmett-Teller (BET) surface areas of original PSS-ACC and hollow nanospheres are ca. 61.91 and 90.91

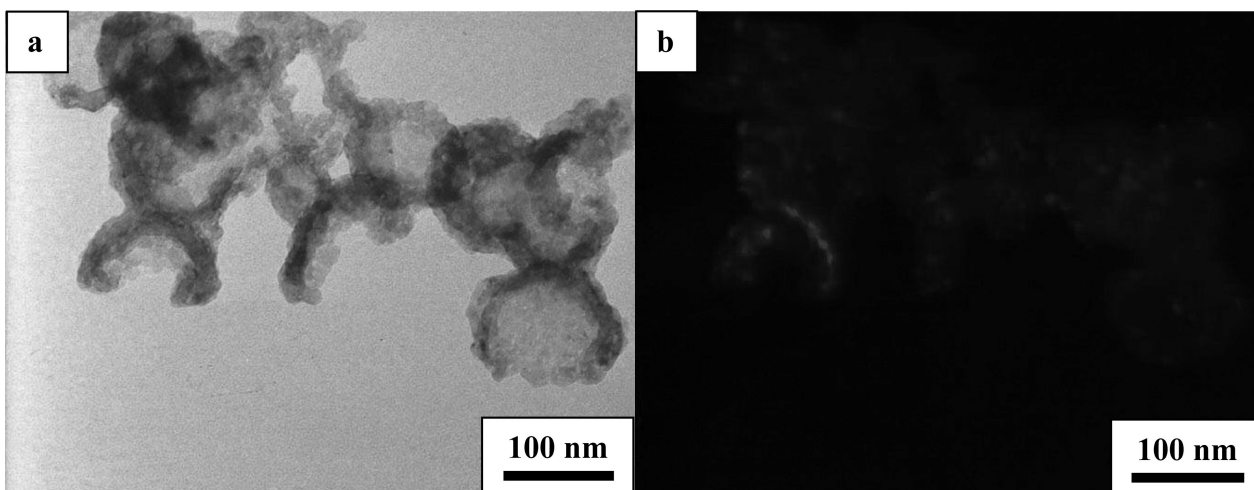


Figure 7. TEM image of hollow vaterite nanospheres, when $R = 1/10$, obtained after the phase transformation for 12 h: (a) the bright field; (b) the dark field.

m²/g, respectively. As the expectation, the special surface area of the hollow nanospheres is obviously larger than that of the solid ACC particles although their average sizes are similar. These data can also confirm the formation of hollow structures by the controlled phase transformation. It is also agreed that the hollow-structured nanospheres have great potential application as catalyst carriers, fillers, targeted drug delivery, gene carriers, etc.

Conclusion

PSS–ACC nanospheres are synthesized, and their sizes can be adjusted by the concentration of PSS. The phase transformation of the metastable ACC spheres can be induced by water, which is controlled by a combination effect of PSS and water. Thus, a large scale of hollow vaterite nanospheres can be obtained under a mild experimental condition. However, the control of the Ca/PSS/water ratio in the experiments is a key step. It is demonstrated that a high content of PSS in the PSS–ACC complex and less amount of water are preferred during the formation of hollow-structured nanospheres of vaterite. This study shows an easy but effective pathway to synthesize hollow vaterite spheres with different sizes.

Acknowledgment. The work was supported by the National Science Foundation of China (Grant Nos. 20601023 and 20571064) and the Project sponsored by SRF for ROCS, SEM.

Cho is thankful for the support from the “Center for Nano-structured Materials Technology” under “the 21st Century Frontier R&D Programs” of the Ministry of Science and Technology of Korea (Grant No. 06K1501-01010).

References and Notes

- (1) Walsh, D.; Mann, S. *Nature* **1995**, *377*, 320.
- (2) Cai, Y. R.; Pan, H. H.; Xu, X. R.; Hu, Q. H.; Li, L.; Tang, R. K. *Chem. Mater.* **2007**, *19*, 3081.
- (3) Yu, J. G.; Gao, H. T.; Davis, S. A.; Mann, S. *Adv. Funct. Mater.* **2006**, *16*, 2035.
- (4) Addadi, L.; Raz, S.; Weiner, S. *Adv. Mater.* **2003**, *15*, 959.
- (5) Nassif, N.; Pinna, N.; Gehrke, N.; Antonietti, M.; Jäger, C.; Colfen, H. *Proc. Natl. Acad. Sci. U.S.A.* **2005**, *102*, 12653.
- (6) Politi, Y.; Arad, T.; Klein, E.; Weiner, S.; Addadi, L. *Science* **2004**, *306*, 1161.
- (7) Hadiko, G.; Han, Y. S.; Fuji, M.; Takahashi, M. *Mater. Lett.* **2005**, *59*, 2519.
- (8) (a) Xu, A. W.; Qiu, Y.; Dong, W. F.; Antonietti, M.; Cölfen, H. *Adv. Mater.* **2005**, *17*, 2217. (b) Ma, Y. R.; Qi, L. M.; Ma, J. M.; Cheng, H. M. *Langmuir* **2003**, *19*, 4040.
- (9) (a) Li, M.; Mann, S. *Adv. Funct. Mater.* **2002**, *12*, 773. (b) Li, M.; Lebeau, B.; Mann, S. *Adv. Mater.* **2003**, *15*, 2032.
- (10) Faatz, M.; Gröhn, F.; Wegner, G. *Adv. Mater.* **2004**, *16*, 996.
- (11) Jada, A.; Verraes, A. *Colloids Surf., A* **2003**, *219*, 7.
- (12) Dickinson, S. R.; McGrath, K. M. *Analyst* **2001**, *126*, 1118.
- (13) (a) Wang, T. X.; Cölfen, H.; Antonietti, M. *J. Am. Chem. Soc.* **2005**, *127*, 3246. (b) Wang, T. X.; Antonietti, M.; Cölfen, H. *Chem. Eur. J.* **2006**, *12*, 5722.
- (14) Yu, S. H.; Cölfen, H.; Antonietti, M. *J. Phys. Chem. B* **2003**, *107*, 7396.

JP801408K