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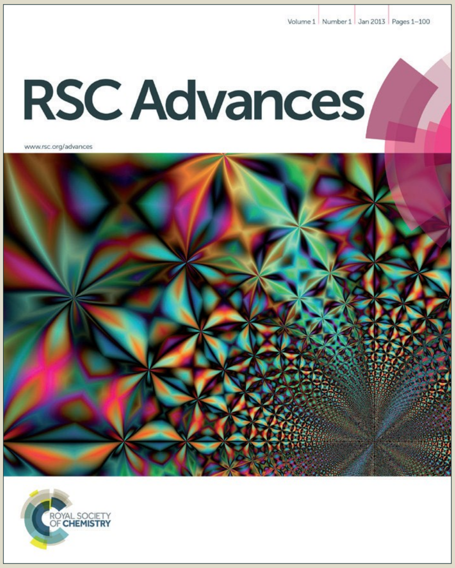

Journal Name

ARTICLE

Hierarchal Multi-lamellar Silica Vesicle Clusters Synthesized through Self-assembly and Mineralization

Received 00th January 20xx,
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

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The self-assembly of nanoparticles to hierarchal structures receives increasing concerns nowadays. In this paper, we report hierarchal silica clusters composed of multi-lamellar silica vesicles (MSVCs) through self-assembly and mineralization. Herein, amphiphilic comb-like polymer with siloxane skeleton and Pluronic P123 were introduced as the co-template, and tetraethoxysilane (TEOS) was the silica source. The flexible templates and gradually solidified silica shell provided the vesicles proper hardness to adapt the shape change during the aggregation and fusion, and the morphology of the MSVCs was fixed by silica finally. The obtained MSVCs were 400~700 nm in dimension, and composed of several multi-lamellar silica vesicles with ca. 105 nm ~ 130 nm in size, respectively. The effect of template ratio, pH value and temperature were discussed to illustrate the proper conditions for preparing hierarchal MSVCs, and the formation of MSVCs was discussed based on time-dependent observation.

Introduction

Fabrication of materials with ordered hierarchal structures through self-assembly is not only a ubiquitous strategy in nature, but also a promising way for developing advanced materials with novel functions.[1-3] In recent years, amphiphilc polymers have received much attention for preparing hierarchal structures via self-assembly and co-mineralization procedure due to their abundant phase behaviors.[4-6] Up to now, many attractive hierarchal structures have been made by polymer micelles, polymer-inorganic hybrids and phase separation.[7-9] However, the construction of polymer vesicle inspired hierarchal structures is still a great challenge.[10-11]

Multi-lamellar vesicles and large compound vesicles are two kinds of hierarchal vesicle structures usually formed by amphiphilic polymer with different strategy.[11-12] Multi-lamellar vesicles could be induced by shear force from a lamellar phase surfactant system, stepwise assembly of polymers, changing solvents, pH value and temperature.[13-15] Large compound vesicles were generally resulted from kinetically controlled aggregation and fusion of small vesicles.[16-19] Inspired by the formation of these two kinds of hierarchal vesicles, multi-lamellar vesicles can hopefully self-assemble to three-dimensional (3D) large compound architecture if the outermost shell of the vesicles is in appropriate hardness, and the morphology can be subsequently fixed by the mineralization of inorganic precursors.[19-24] Besides, the self-assembly of vesicles may result in close packing structures due to their soft nature, which is reported to be the vital factor for fabricating high efficiency photonic crystals with diamond structure by the self-assembly of nanoparticles.[25-26]

In this paper, we present the preparation of multi-lamellar silica vesicle clusters (MSVCs) through facile self-assembly and mineralization procedure. Amphiphilic comb-like surfactant polydimethylsiloxane-*graft*-(poly(propylene oxide)-*block*-poly(ethylene oxide)) (PDMS-*g*-(PPO-*b*-PEO), PSPE) and Pluronic P123 (PEO_{20}-PPO_{70}-PEO_{20}) were applied as co-templates to prepare the MSVCs. The flexible templates could adapt the vesicle aggregation and fusion. In addition, PDMS segment decreased the surface energy and tension between close packed units, consequently improved the stability of vesicles. The hardness of the vesicles could be further tuned with the hydrolysis of silica source so that the vesicles kept their shape while the close packed vesicle clusters were formed. The hierarchal structure was immobilized finally with silica. This strategy paves a promising way to construct vesicle-inspired hierarchal structure directly through efficient self-assembly and mineralization procedure.

Experimental Section

Chemicals and Reagents

All reagents were used as received without further purification. PSPE was provided by the Jilin Petrochemistry

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Electronic Supplementary Information (ESI) available: The analysis of template PSPE, the SEM images of the MSVC products are in the supporting information. See DOI: 10.1039/x0xx00000x

Company. Pluronic P123 (average molecular weight ~5800) was obtained from Aldrich. TEOS was purchased from Sinopharm Chemical Reagent Co., Ltd. The unit parameter of the PSPE copolymer was calculated based on the Gel Permeation Chromatography (GPC) and ^{1}H NMR data (Figure S1, Supporting Information). The number of the PO/EO block units in the side chain is 16/16. The number of grafted units is 8, and the number of dimethyl siloxane units is 29. The formula of the PSPE molecule is shown in Figure S2, Supporting Information in detail.

Typical Synthetic Method of MSVCs

For a typical synthesis, 0.125 g of PSPE and 0.030 g of P123 were mixed first to form a homogeneous viscous liquid. Then 26 g of ultra-pure water was added into the mixture. After stirring for 30 minutes, 0.26 g of TEOS was added in the solution under pH = 3.5. The solution was stirred for another 60 minutes, and then was heated to 65 °C and kept for 24 h. The solid products were collected by centrifugation and lyophilization. The resultant were calcined at 550 °C for 6 h in air to further investigate the pore properties. The mass composition was PSPE:P123:TEOS:H_2O = 1:0.24:2.08:208.

The synthetic conditions were adjusted to investigate the formation of MSVCs. The mass ratio of P123/PSPE was varied from 0.1 to 1.0 by changing the P123 amount, and the pH value was tuned by NaOH or HCl. The synthetic temperatures varied from 40 °C to 80 °C. In time-dependence observation, the samples were dropped on copper mesh and cooled with liquid nitrogen. After being treated under vacuum for 30 min, the samples were observed by TEM directly without calcination.

Characterization Methods

The microscopic characteristics/features of the samples were observed with scanning electron microscopy (SEM) (JEOL JSM-7401F). The accelerating voltage was 1.0 kV. High-resolution transmission electron microscopy (HRTEM) observations were performed using a JEOL JEM-2100 microscope equipped with a LaB6 gun operated at 200 kV (Cs 1.0 mm, point resolution of 2.3 Å). Images were recorded using a TENGRA CCD camera (2304 × 2304 pixels with a 2:1 fibre-optical taper and an effective pixel size of 18 μm^2). The nitrogen adsorption/desorption isotherms were measured at 77 K with Quantachrome Nova 4200E. The surface area was calculated by the Brunauer-Emmett-Teller (BET) method, and the pore sizes were obtained from the maxima of the pore size distribution curve that was calculated by the Barrett-Joyner-Halenda (BJH) method using the desorption branch of the isotherm. The pore volumes were calculated by BJH method base on the nitrogen (N_2) desorption isotherm curves. ^{1}H NMR was performed on a Varian Mercury Plus 400-MHz spectrometer using $CDCl_3$ as solvents at 20 °C. GPC was carried out on a Perkin-Elmer Series 200 GPC Analysis System. The calibration was performed using poly(ethylene glycol) (PEG) based molecular weight standards.

Results and Discussion

The Morphology and Structure of MSVCs

The low magnification scanning electron microscopy (SEM) image of the MSVCs (Figure 1A) showed the morphology of spherical clusters with the diameter between 400~750 nm. The high magnification SEM image of one typical cluster (Figure 1B), which is constructed by close packed polyhedral particles. Different sizes of particles were observed as the building unit. These particle are close packed together and the clear interface can be observed from the adjacent part. Transmission electron microscopy (TEM) image (Figure 1C) showed the cluster was composed of several multi-lamellar silica vesicles. The darker part in the middle of the cluster indicated the interior of cluster also consist of multi-lamellar silica vesicles. Figure 1D showed the multi-lamellar structure in detail. The interlayer distance varied between 2~12 nm, and the thickness of interior layer was ~5 nm. The thickness of outermost shell of the silica vesicle was 17~20 nm.

These results showed that the arrangement of this cluster is similar to the partition of space through the soft spheres with the tetrahedrally close packed (TCP) feature, in which the soft particles were not considered to be perfect spheres but make interface with the surrounding particles to become polyhedral. TCP was formed according to a delicate balance between close packing role, minimum surface area and the total entropy of the soft shell, which have been previously found in Fran and Kasper phases of metals and metallic alloys, mesoporous materials and disordered systems such as soap froths, but this packing structure has not been found in vesicular system, probably because most of the aggregation of vesicles are kinetically controlled, therefore the TCP structure are difficult to hold without appropriate shell hardness. Furthermore, it should be indicated that the vesicles would not always assemble to TCP structure because the vesicles are randomly accumulated to the MSVCs, and there should be several close packing styles in this case.

N_2 adsorption-desorption isotherm of the calcined sample displays type IV curves with H2-type hysteresis loops in the range of P/P_0 = 0.4~0.8, indicating the existence of the ink-bottle style mesochannel structure (Figure 2A). The PDMS chains can be oxidized into silica during calcination step, which forms ink-bottle shape channel structure and results in the H2-type hysteresis loops. This phenomenon is often observed in the porous materials synthesized by the silicone-type surfactants.[27] The adsorption branch shows a broad pore size distribution, suggesting the inhomogeneous distribution of the cavity size, however, the pore entrance size calculated by the BJH method was ca. 4.0 nm based on the desorption branch of the isotherm. Besides, the isotherms shows a sharp increase at $p/p_0 < 0.1$ and a plateau when $p/p_0 > 0.1$, suggesting the existence of micropores in the material, which is attributed to the PEO segments embedded in the silica matric.[28]

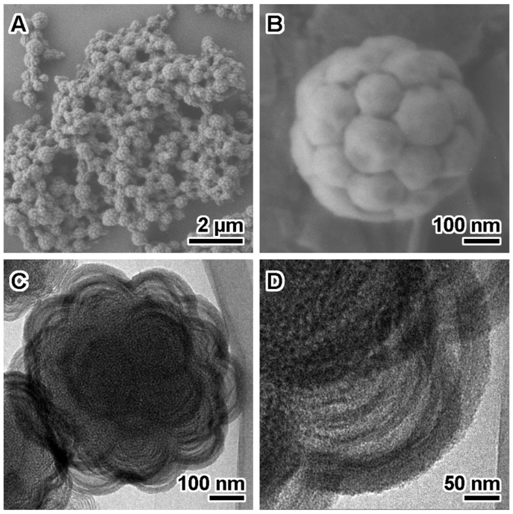


Figure 1. SEM images (A, B) and TEM images (C, D) of the MSVCs; The synthesis was carried with the synthetic mass ratio of PSPE:P123:TEOS:H_2O = 1:0.24:2.08:208 at 65 °C.

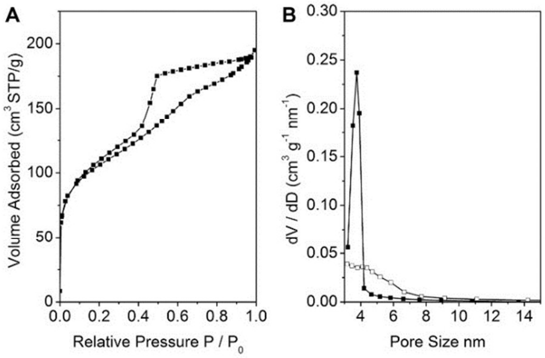


Figure 2. N_2 adsorption/desorption isotherms and pore size distribution curves calculated based on the desorption (solid square) and adsorption (hollow square) branches of the MSVC.

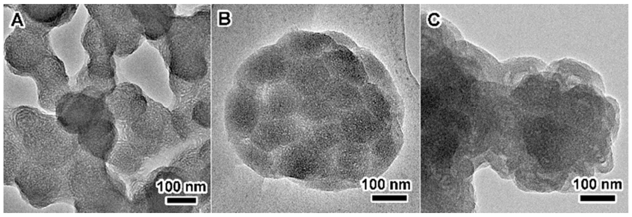
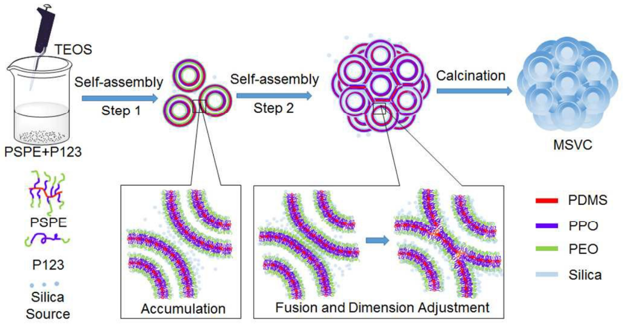


Figure 3. TEM images of the time-dependence observation in preparing MSVCs at 1 h (A), 2 h (B) and 4 h (C). The synthesis was carried with the synthetic mass ratio of PSPE:P123:TEOS:H_2O = 1:0.24:2.08:208 at 65 °C.

The Formation of MSVCs

Time-dependence TEM observation were carried out to investigate the formation of MSVCs. The TEM image of the sample synthesized for 1 hour (Figure 3A) showed some spherical vesicles with multi-lamellar structure, but the MSVCs were not yet observed. The average size of the particles was approximately 120 nm, which is between the dimensions of vesicles in the final clusters showed in Figure 1. In addition, due to the soft nature of these vesicles in the early stage of the reaction, the outermost shell was as thin as the interior layer. After 2 hours, the clusters could be observed (Figure 3B). However, the multi-layer structures could hardly be identified except the edge region since the low condensation of the silica source and the overlapping of the clusters. Finally, MSVC was observed after 4 hours hydrothermal treatment (Figure 3C). The outermost shell of the particle became thicker and the lamellar structure appeared clearly, indicating high condensation of the silica source.



Scheme 1. Schematic illustration for the formation of MSVC.

According to the time-dependence observation, the formation of MSVCs could be described by a two-step self-assembly procedure (Scheme 1). The first step was the co-assembly of silicone surfactant, P123 and partly hydrolysed silica source. The hydrophobic PDMS segments were compatible with the PPO segments, as well as the hydrolysed TEOS were compatible with the hydrophilic PEO segments. During the early stage of the hydrothermal process, the multi-lamellar polymer-organosilicone vesicles have been formed in the solution. The second step included the aggregation and fusion of the vesicles along with the condensation of hydrolysed TEOS. The aggregated vesicles underwent shape changes to polyhedral vesicles to adapt the surrounding vesicles so that they could accomplish minimum surface in a vesicle cluster. In this stage, the adjacent vesicles were fusing to form common outermost layers. Benefited from the soft hydrophilic and hydrophobic part, the dimension and shape of these vesicles could be further adjusted effectively during the fusion to accomplish ordered close packing. With concisely controlled synthesis conditions, both the shape of polyhedral vesicles and clusters were immobilized by silica before further fusion. After calcination, the MSVCs were obtained.

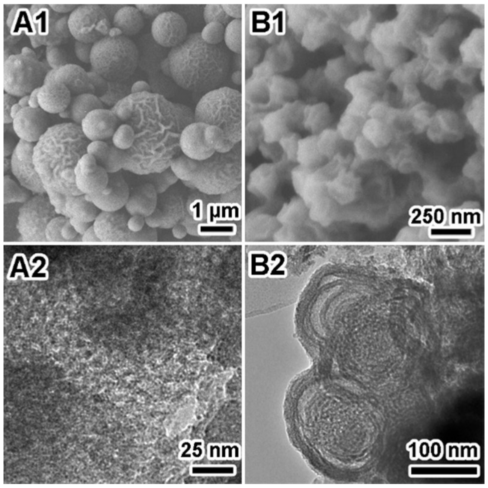


Figure 4. SEM and TEM images of the as-synthesized samples prepared with the molar ratio of P123 to PSPE was 0.1 (A) and 0.5 (B), while other conditions were maintained as the synthesis of MSVCs.

The Investigation of Synthesis Condition

The conditions to obtain MSVCs were investigated by changing the co-template ratio, pH value and temperature. As shown in Figure 4A1, when the ratio of P123 to PSPE was 0.1, silica spheres with a wide size distribution were obtained. The TEM image (Figure 4A2) showed the interior of these particles were disordered mesoporous structures. When the ratio of P123 to PSPE was increased to 0.5, small silica particles around 100 nm in diameter with wrinkled surface were observed (Figure 4B1). TEM image (Figure 4B2) showed the particles were yolk-shell structure with multi-lamellar shell and mesoporous core. The structural and morphological changes indicate the amount of P123 affected the hydrophobicity of the co-template. With the addition of P123, the assembly structure transformed from micelle to multi-lamellar vesicles, but more P123 might give rise smaller vesicle with several layers, and the excessive P123 assembled with TEOS to form a mesoporous core during the hydrothermal treatment.

The pH value affected not only the hydrolysis and condensation rate of TEOS, but also the hydrophilicity of templates. Under pH=5.0, collapsed vesicles with multi-lamellar interior structure were obtained (see Figure 5A). Since the hydrolysis rate of TEOS was relatively low, the vesicles were still too soft to keep their spherical shape in calcination even though have been hydrothermal treated for one day. The collapsed vesicles were much larger than the vesicles formed under pH = 3.5. It was because that the deprotonation of the PEO moieties decreased their hydrophilicity, thus the templates tended to form larger vesicles. By increasing the pH value to 8.0 (Figure 5B), collapsed single layer vesicles with diameter at around 100 nm were observed. The wall of the vesicles were very thin and soft because the interaction between PEO and negatively charged silanol are quite weak. Further, the transformation from multi-lamellar vesicle to single-lamellar vesicle might be attributed to the low hydrophilicity of PEO blocks in alkali environment.

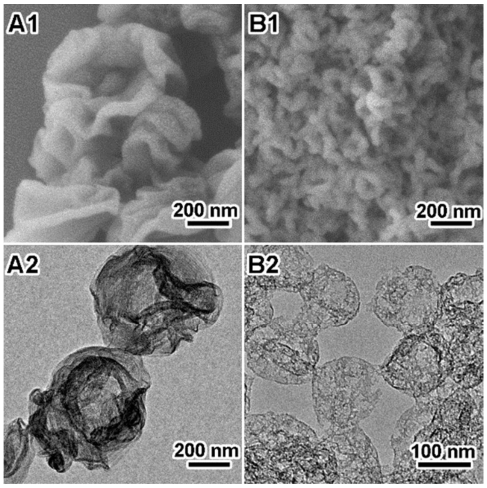


Figure 5. SEM and TEM images of the as-synthesized samples synthesized under the pH value of 5.00 (A) and 8.00 (B), while other conditions were maintained as the synthesis of MSVCs.

Temperature was also a key factor to the synthesis. At low temperature of 40 °C, the resulting product was mesoporous silica spheres with ca. 1~5 µm diameter (Figure 6A1 and A2). By increasing the temperature to 55 °C, silica spheres with wrinkled surface were obtained (Figure 6B1 and B2). The diameter of these spheres was ca. 300 nm, and the interior of the spheres was solid. While the synthesis temperature was increased to 80 °C, raspberry-like silica clusters with ca. 400 nm in dimension could be observed (Figure 6C1). The raspberry-like silica clusters were composed of several small unilamellar silica vesicles with ca. 100 nm in diameter (Figure 6C2). The morphology and structure transformation with different temperature could be explained in terms of the hydrophobicity of the templates. The hydrophobicity of PDMS, PEO and PPO segments turned stronger with the increasing of temperature, therefore, the self-assembly of the templates changed from micelle to multi-lamellar vesicle, and finally to smaller vesicle. In addition, the hydrolysis and condensation rate of TEOS were also accelerated with the increasing of temperature, therefore the condensation of vesicles at earlier stage prevented the vesicles from further arrangement to close packing.

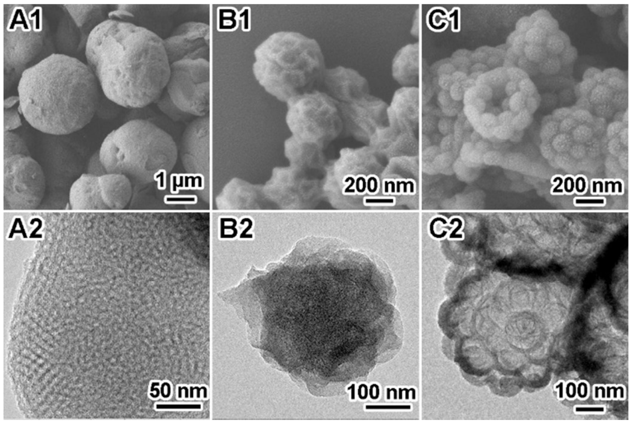


Figure 6. SEM and TEM images of the as-synthesized samples synthesized under the temperature of 40 (A), 55 (B) and 80 °C (C), while other conditions were maintained as the synthesis of MSVCs.

Conclusions

To the best of our knowledge, this is the first example of preparing hierarchical silica vesicle clusters with close-packed architecture and multi-lamellar interior structure through self-assembly and mineralization. The hierarchal structure was the result of several factors including the amphiphilic nature of the PSPE and P123 templates, the flexibility of the hydrophobic segments, suitable hardness of the vesicles, and appropriate temperature, pH value and template ratio. These results point toward exciting opportunities for further fabricating high efficiency photonic crystals via soft particles' self-assembly directly.

Acknowledgements

This research was supported by the National Natural Science Foundation of China No. 51573088, No. 21571128, No.21101106 and No.21201120; the National Excellent Doctoral Dissertation of China No.201454, the Youth Natural Science Foundation of Shanghai No.12ZR1445100, the Project Sponsored by the Scientific Research Foundation for the Returned Overseas Chinese Scholars, State Education Ministry, and the "Chenguang" Program of the Shanghai Educational Development Foundation No.12CG10. The authors also thank Evonik Industries for the financial supporting.

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