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Synthesis of elastic macrospheres of silica–surfactant nanocomposites

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Abstract

Centimeter sized macrospheres of silica–surfactant nanocomposites were synthesized from tetraethyl orthosilicate (TEOS) and the neutral triblock copolymer Pluronic P123 ($EO_{20}PO_{70}EO_{20}$) or cationic quaternary ammonium surfactants as organic templates under acidic conditions ($pH < 1$), The organic–inorganic hybrid macrosphere is crack-free and possesses high elasticity. The determining factors in the formation of macrospheres include the chemical composition (i.e. TEOS content and surfactant compositions) and the shear rate in the synthetic solution. © 2001 Elsevier Science Ltd. All rights reserved.

1. Introduction

The nanostructured materials of surfactant–silicate composite have received much attention in recent years [1,2]. The interest mainly comes from the community of porous materials researchers. The materials are synthesized by the solution co-condensation of silicate species and amphiphillic organizations. With the templating surfactants removed, one has the very useful mesoporous materials. Among the materials, the mesoporous MCM-41 using the cationic alkyl quaternary ammonium surfactants has been investigated most intensively because of its high thermal and hydrothermal stability, large surface area and tunable pore size (1.5–15 nm) [3–10]. Amphiphillic copolymers can also function as micelle templates as in the SBA-15 materials [11–14]. The porous materials are very useful as adsorption agents or providing a high surface area in catalysis. However, less attention has been paid to the as-synthesized surfactant–silicate as an organic–inorganic composite material [15].

With the organic and inorganic species intimately intertwined in the nanometer scale, one would expect unusual mechanical properties not available to the individual components [16,17]. This kind of investigation is most interesting when a monolithic sample of centimeter scale is available. In the usual synthesis of mesoporous materials, the materials are mostly in powder form and the sizes of the particles are normally of micrometer scale. Of notable exception are the macrospheres obtained by Stucky's group by the method of emulsion templating [18]. However, due to the limitation of the size of emulsion, the diameter of the surfactant/silicate composite spheres seems to be millimeters at the most. Up to the present, mesoporous materials as nanocomposite seem to be mostly limited to films or particles of micron size [19–23].

In this paper, we report a synthesis of centimeter-sized silica–surfactant spheres from two amphiphillic organic templates: (1) the SBA-15 materials from the triblock copolymer surfactant Pluronic123 ($EO_{20}PO_{70}EO_{20}$) and (2) the MCM-41 materials from cationic surfactants mixture of cetyltrimethylammonium bromide (C_{16}TMAB; Merck) and dicetyldimethylammonium (DC_{16}DMAB; Aldrich) bromide under acidic conditions. The silica source is tetraethyl orthosilicate (TEOS). The as-synthesized silica–surfactant spheres show interesting elastic behavior, as in biomimetic organic–inorganic composites.

The macrosphere morphology of the mesoporous materials is also useful as adsorption materials in separation

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applications after calcination to remove the organic templates and surface modifications [24,25]. Thus, we also study the gas adsorption behavior of the macrospheres we synthesize.

2. Experimental

The centimeter-scaled silica–surfactant spheres were prepared by dissolving a suitable amount of amphiphillic triblock copolymer (ethylene oxide)$_{20}$(propylene oxide)$_{70}$(ethylene oxide)$_{20}$ ($EO_{20}PO_{70}EO_{20}$, P123; BASF) or the mixture of cetyltrimethylammonium bromide (C_{16}TMAB; Merck, 99%) and dicetyldimethylammonium (DC_{16}DMAB; Aldrich, 98%) bromide into a desired weight of deionized water. Then, the acid was added into that water solution. Hydrochloric acid (HCl) was used in the P123 system and nitric acid (HNO_3) in the quaternary ammonium surfactant system [25], respectively. After that, the tetraethyl orthosilicate (TEOS; Acrôs) as the silica source was added, consequently polymerizing the silica species to form the rigid spheres under stirring for 7–24 h at 35 or 30°C. Based on our results, the suitable composition in molar ratio to synthesize centimeter-sized silica–surfactant spheres is: 1.0 P123:(96–140) TEOS:1506 HCl:9706 H_2O for P123 block copolymer and 1.0 C_{16}TMAB:(0.25–0.38) DC_{16}DMAB:5.0 TEOS:14.0 HNO_3:760 H_2O for the mixtures of (C_{16}TMAB + DC_{16}DMAB), respectively. The resulting spheres were recovered by filtration, washing with a lot of water and drying at ambient temperature. The organic surfactant templates were removed by calcination at 560°C for 6 h.

X-ray powder diffraction (XRD) patterns were taken on the Wiggler-A beamline ($\lambda = 0.1326$ nm) of the Synchrotron Radiation Research Center, Hsinchu, Taiwan and the Scintag X1 diffractometer using CuKα ($\lambda = 0.154$ nm). The N_2 adsorption–desorption isotherms were collected at 77 K on a Micromeritics ASAP 2010 apparatus. Before the analysis, the calcined samples were outgassed at 250°C for about 6 h in 10^{-3} torr. The pore size distribution was obtained from the analysis of the adsorption branch of the isotherms by using the BJH (Barrett–Joyner–Halenda) method. The surfactant content of the as-synthesized mesoporous silicas was measured by thermogravimetric analysis (TGA). TGA were conducted with a ULVAC TGA-7000RH thermogravimetric system. In a typical experiment, ca. 10 mg of sample was heated to 800°C at 10°C/min under dried air. The surfactant content was determined from the weight loss between the temperature range of 140–250°C for P123 and 280–400°C for quaternary ammonium surfactants. The weight remaining above 600°C was attributed to the silica.

3. Results and discussion

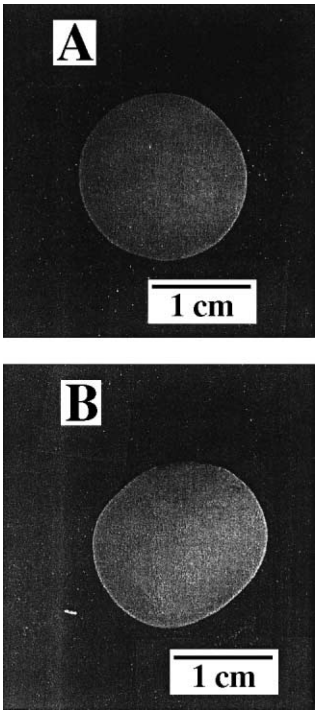

Fig. 1. The photographs of the as-synthesized centimeter-sized sphere obtained from A. P123–TEOS–H_2O–HCl system. B. (C_{16}TMAB + DC_{16}DMAB)–TEOS–HNO_3–H_2O system.

Fig. 1A shows a photograph of the centimeter-sized spheres prepared from the P123–TEOS–H_2O–HCl system with neutral surfactant and Fig. 1B shows the spheres made from the cationic surfactant (1.0 C_{16}TMAB + 0.25 DC_{16}DMAB)–TEOS–H_2O–HNO_3 compositions. One can see clearly that they are crack-free spheres, and the diameters are about 1.5 cm. To our knowledge, they are the largest mesoporous silica–surfactant spheres so far. If the stirring rate and composition is not adjusted properly, one obtains a powdered form of the composite materials. The particle size of the powder is mostly in the micron-scale. The balancing of the flow and chemical composition is often delicate. Too low a shear rate would not be enough to generate the inward compression, and too high a rate may break apart the floc. It seems the surface of the acid-synthesized small particles is pretty ‘sticky’, the flocculation brings together the particles and further siloxane condensation make the floc grow into big balls.

We ground the materials into powder to analyze their powder X-ray diffraction patterns. X-ray diffraction result (Fig. 2A) confirms, which possesses the 100, 110 and 200 sharp peaks, the hexagonal structure for the macrosphere of P123, but the mesostructure of (C_{16}TMAB + DC_{16}DMAB)– silica sphere is lamellar in structure with distinct 100 and 200 XRD peaks (Fig. 2B). After calcination for surfactant elimination, the silica sphere obtained from P123 was intact in outer appearance and the hexagonal

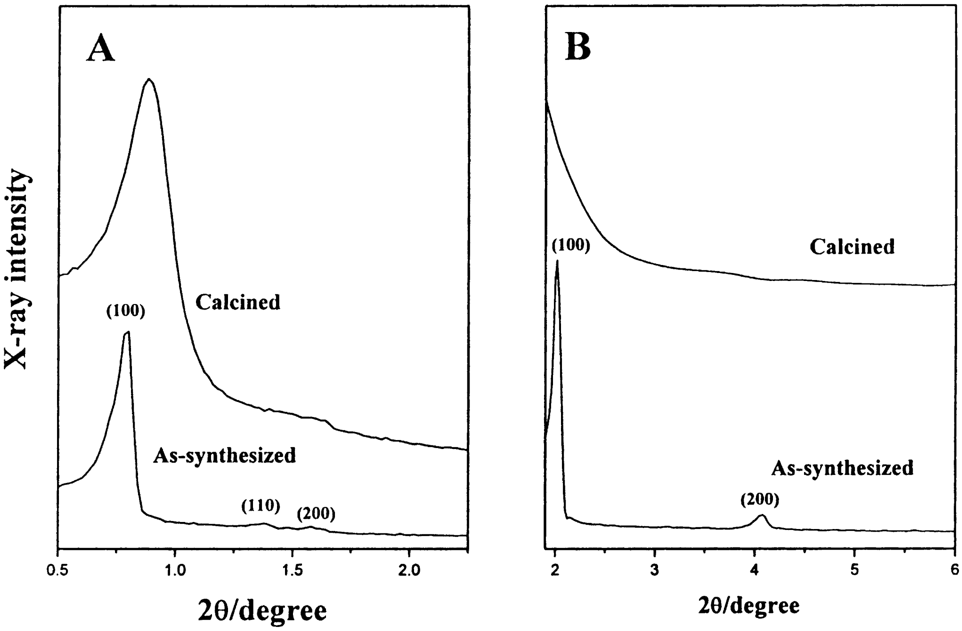

Fig. 2. XRD patterns of the as-synthesized and calcined centimeter-sized macro spheres of Fig. 1. A: P123 (the wavelength of the X-rays is 0.1326 nm); B: $C_{16}MAB + DC_{16}DMAB$ (the wavelength of the X-rays is 0.154 nm).

structure was still maintained (Fig. 2A). In contrast, the lamella-structured macrosphere synthesized from (1.0 $C_{16}TMAB + 0.25\ DC_{16}DMAB$) was cracked and the lamellar mesostructure completely collapsed to amorphous silica (Fig. 2B) [2].

Porosity data determined from nitrogen adsorption for the calcined P123-silica sphere are shown in Fig. 3. The pore size distribution is narrow, indicating good structure order. The large BET surface area (about 732 m^2/g), pore size (about 5.2 nm) and thick wall (4.7 nm) make this silica sphere potentially useful in catalysis support, adsorbence and chromatography.

Controlling properly the cooperation condensation between inorganic and organic surfactants template, which is crucial in designing morphologies and sizes of inorganic–organic composites, depends strongly on the compositions. In neutral surfactant P123-silica systems, the proper ratios of the TEOS/surfactant in the range of 96–140 are necessary to obtain the macrospheres. The TEOS content plays a significant role in determining the binding strength with the P123 surfactant mesostructures. Below or above this narrow composition range, various micrometer-scaled silica–surfactant fibers, spheres, gyroids and other morphologies were produced as previously reported [27–30]. Compared to other synthetic methods, our procedure and compositions are simple and convenient.

For the cationic $C_{16}TMAB + DC_{16}DMAB$ surfactant–silica case, the ratio of $DC_{16}DMAB/C_{16}TMAB$ must be in the range of 0.25–0.38 to prepare the macrospheres. Because the $DC_{16}DMA^+$ surfactant possesses higher hydrophobilicity and the nitrate ion has a stronger binding affinity towards the quaternary ammonium surfactant (S^+) [26], the $DC_{16}DMA^+$, $C_{16}TMA^+$ and NO_3^- combination promotes a low-curvature mesostructure ($S^+NO_3^-$) formation, e.g. the lamellar mesophase. Without the addition of $DC_{16}DMAB$, the product's size is only micrometer-scaled and in gyroidal sphere form or silica ropes morphology [31–33]. Moreover, $DC_{14}DMAB$ or $DC_{12}DMAB$ as the hydrophobicity-increasing agents can also have an ability to result in centimeter-sized sphere formation, but the proper amount needed for producing the lamellar mesophase sphere increases with decrease of chain-length of DC_nDMAB [34]. In brief, the adjustment of hydrophobicity controls the shape and dimension of the silica–cationic surfactant composite.

Examining the TGA plots of these two mesoporous silica surfactant spheres, we can get the surfactant/silica weight ratio in the products. The surfactant/silica ratio is about 1.0 for P123-silica spheres and near 2.0 for the $C_{16}TMAB + DC_{16}TMAB$–silica spheres (Fig. 4). Since the spheres consist of inorganic–organic compositions, the spheres could have interesting elastic properties and mechanical stability similar to those in natural bio-ceramics. A simple elasticity test was observed. We free drop the spheres (as in Fig. 1A), made from P123, on to a copper plate from the height of 1 m. It bounces back to a height between 50 and 80 cm. Similar elasticity was also observed for the spheres made from cationic surfactants as in Fig. 1B, but they are less resistant to cracking, e.g. easier to break. More careful measurements of the elastic modulus and its relationship to synthesis condition are to be reported in the future.

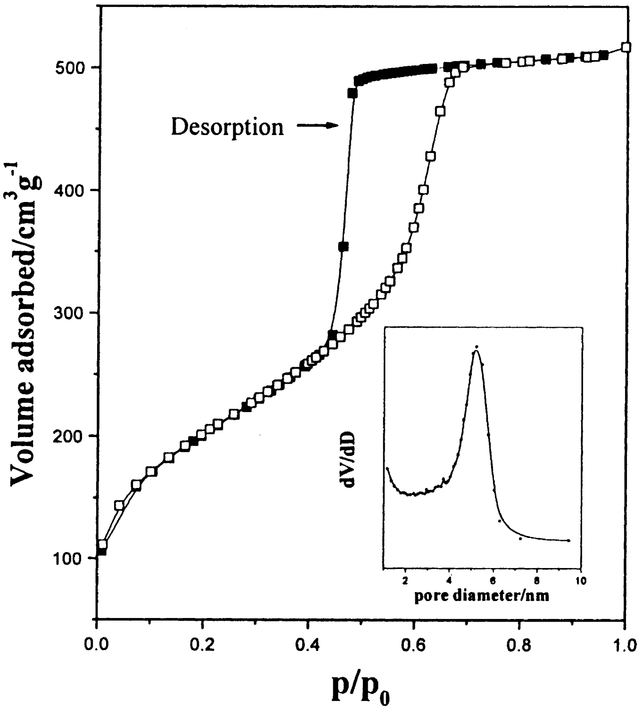

Fig. 3. N_2 adsorption–desorption isotherm of a sphere synthesized from P123. Inset: pore size distribution plot calculated from the adsorption branch by the BJH method.

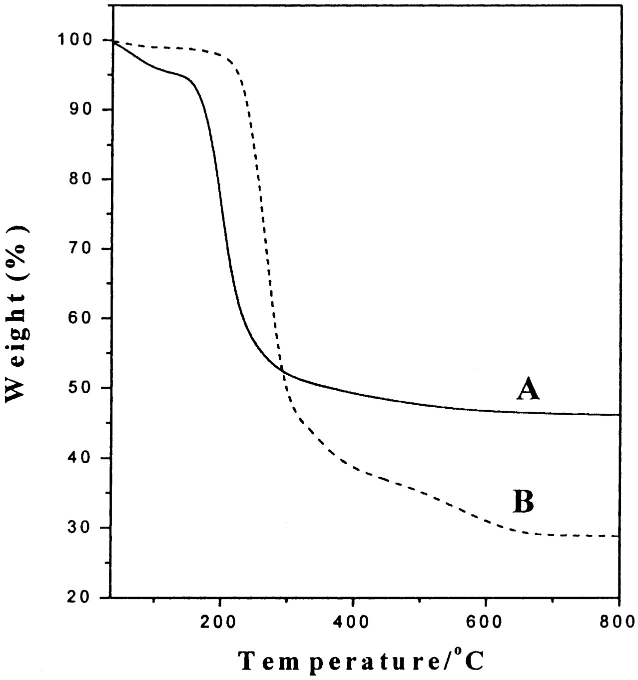

Fig. 4. TGA plots of the as-synthesized macrospheres of Fig. 1. A: P123; B: $C_{16}MAB + DC_{16}DMAB$.

The inorganic–organic composites possess both the rigidity of the inorganics and the flexibility of the organic surfactants to exhibit the novel elastic properties. The elasticity of the spheres reflects high storage capacity of elastic energy and little dissipation due to creeping. This is really an unusual material because the elasticity one observes in polymeric rubber is normally due to the entropy of the polymer configuration. Here, the effect is due to the bending elasticity of the hexagonal or the lamellar mesophase of the surfactant–silicate nanocomposite. As nature teaches us, the hexagonal arrangement of honeycomb gives a light and elastic structure. We have succeeded in making similar architecture in the nanometer scale from surfactant and silicate and the monolith in an unprecedented macroscale. Our synthesis employed the hydrodynamic shear flow for 'snowballing' the sticky surfactant–silica nanocomposite. Apparently, there should be no intrinsic upper bound to the size of the materials.

After calcinations to remove the organic templates, the spheres preserve the original shape, but the surfactant-removed spheres completely lose their elastic property and are easily broken into powder. Losing the elastic property of the organic part, one is left with only a brittle porous silica macrosphere. Nonetheless, it would be a nice configuration for chromatographic and adsorption applications.

4. Conclusions

One can develop synthetic control of the organized intermingling of inorganic and organic components of composite materials to obtain artificial materials that are analogous to biological materials in their structural complexity, morphologies and properties for applications. The nanocomposite is unique in exhibiting elastic behavior which is due to the fine balancing of the rigidity of inorganic silica and the flexibility of the organic substrate. The synthesis is a low temperature sol-gel reaction which is amenable to other flow processing to obtain various geometric forms other than the simple macrosphere reported in this paper.

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