Onionlike Spherical Polymer Composites with Controlled Dispersion of Gold Nanoclusters

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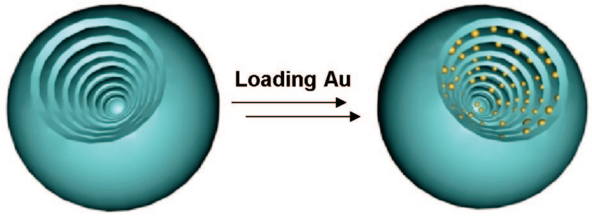
Recently, microspheres with a multilamellar vesicular internal structure have received much attention because of their potential applications in many fields, such as microreactors and as carriers for controlled release system. Until now, different methods have been used to prepare this kind of spheres. Diat et al. have discovered that monodisperse and compactly packed onion phases could be obtained in concentrated solutions of surfactants under controlled mechanical shear.[1] Their applications as carriers for drug delivery[2] and nanoreactors for synthesis of metal nanoparticles[3] have been explored. Through evaporation-induced self-assembly confined in spherical aerosol droplets, Lu et al. have prepared well-ordered particles with multilamellar vesicular structures.[4] This approach has been used to prepare colloidal composites containing inorganic nanoparticles.[5] However, the periodic length of particles produced by above methods was only several nanometers because the low-molecular-weight surfactants were used as structure-directing agents. So, when these particles were applied as microreactors, the incorperated metal inorganic nanoparticles were distributed only randomly inside the nanospheres.[3,5]

Block copolymers have also been used to obtain the onionlike particles. By self-assembly of the amphiphilic block copolymer in solution, the onionlike vesicles have been obtained.[6] Okubo et al. have also produced such particles by seeded dispersion polymerization and solvent absorbing/releasing method.[7] Similarly, Liu et al. dispersed a block copolymer oil solution in water by an emulsion method and the particles with onionlike internal structure were obtained.[8] The polymer onions were also reported in homopolymer/copolymer and copolymer/copolymer blends, where thermodynamic equilibrium plays an important role.[9] Recently, Zhu et al. have designed a novel approach to tailor onionlike polymer crystals using the concept of unbalanced surface stresses.[10] Another facile way to prepare mesostructured spheres is the aerosol-assisted self-assembly of block copolymer, which was first applied by Thomas et al.[11] By this way, droplets of block copolymer solution were produced by an atomizer and the block copolymer self-assembles during the solvent evaporation.

Scheme 1. Cartoon Presentation of Spherical Composite with Au Nanoclusters with Controlled Location[a]



[a] Color layers stand for silica rich cross-linked layers (P2VP layers are not shown); yellow particles stand for gold clusters.

Recently, we also used the aerosol-assisted method to obtain organic/inorganic hybrid mesostructured particles by using a gelable block copolymer, poly(3-(triethoxysilyl)propyl methacrylate)-*b*-polystyrene (PTEPM-*b*-PS),[12] whose concentric PTEPM layers were switched into a cross-linked silica oxide structure by the gelation occurring only in this domain. Herein, we extended this subject to generate the functionalized mesostructured microspheres using a novel gelable functional diblock copolymer, poly(3-(triethoxysilyl)propyl methacrylate)-*b*-poly(2-vinylpyridine) (PTEPM-*b*-P2VP). A kind of functional microspheres with onionlike internal structure was obtained. After cross-linking the PTEPM layers by gelation, we used the microspheres to stabilize the gold nanoparticles within the P2VP layers. Therefore, we have obtained a novel kind of onionlike particles with well-defined alternating layers of Au clusters and silica networks (Scheme 1).

The PTEPM$_{60}$-*b*-P2VP$_{162}$ (gel permeation chromatography (GPC) analysis with standard P2VP calibration (M_n = 24 800, M_w/M_n = 1.20) was synthesized by reversible addition fragmentation chain-transfer mediated radical polymerization (see Experimental Section in the Supporting Information for synthesis and Figures S1 and S2 in the Supporting Information for GPC traces and ^{1}H NMR

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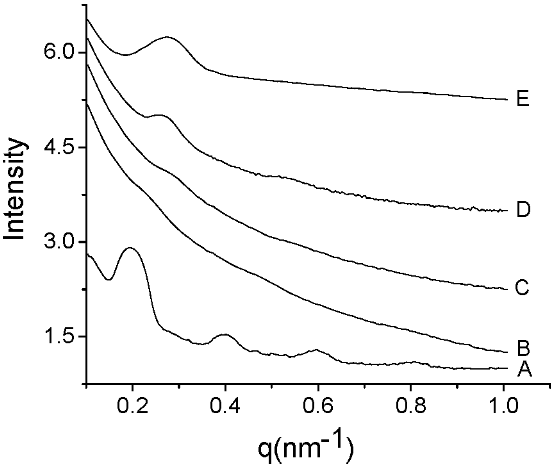

Figure 1. SAXS diagrams of microphase separation of PTEPM$_{60}$-*b*-P2VP$_{162}$ (A) in bulk, (B) in microspheres, (C) in microspheres with cross-linked PTEPM domains, (D) in microspheres with cross-linked PTEPM domains in the presence of ethanol, and (E) in microspheres containing Au nanoclusters.

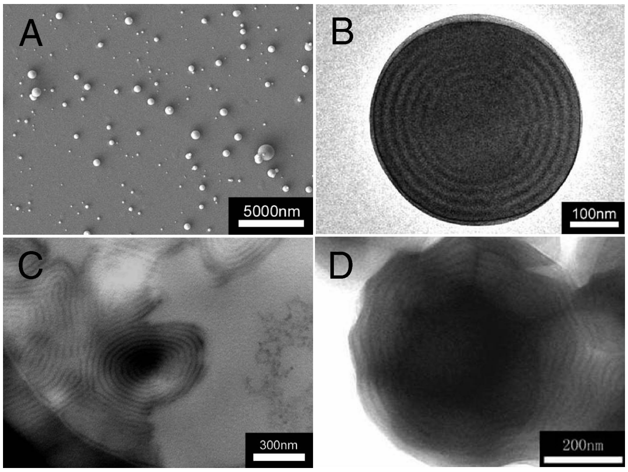

Figure 2. (A) SEM image of the aerosol-assisted spheres formed by PTEPM$_{60}$-*b*-P2VP$_{162}$ collected on a silicon substrate. (B) TEM image of the sphere collected on a copper grid. (C) TEM image of the microtomed slice of spheres. (D) TEM images of the organic/inorganic hybrid spheres after extraction by methanol 3 days.

spectrum, respectively). At an equilibrium state, the bulk microphase separation gave a lamellar morphology with a periodic length of 32.2 nm as confirmed by small-angle X-ray scattering (SAXS) shown in Figure 1, line A. The corresponding transmission electron microscope (TEM) micrograph of microtomed slice is shown in Figure S3 in the Supporting Information.

The aerosol-assisted self-assembly conditions and equipment used here are similar to those described elsewhere.[12] Polymer aerosols were generated from PTEPM$_{60}$-*b*-P2VP$_{162}$ solution in methanol (0.2%, w/v) by an aerosol generator and nitrogen was used as the carrier. After the aerosol passed through a drying chamber at 200 °C, the dried powders were collected by a Teflon filter with apertures of 0.2 μm, or a silicon substrate, or a copper grid coated by carbon film for electron microscope analysis.

As shown by the scanning electron microscope (SEM) micrograph of the particles collected on the silicon substrate (Figure 2A), the particles are spherical and their size ranges from 100 to 1000 nm. The TEM micrograph of a particle collected on the copper grid (Figure 2B) shows the onionlike internal structure. Figure 2C is the corresponding TEM image of the ultramicrotomed slice of particles, further demonstrating the concentric lamellar structure. The dark circle is attributed to the PTEPM layer, whereas the white layer is to the P2VP domain.

Figure 1, line B, is the SAXS curve of the powder collected by a filtrating membrane, from which two weak peaks with the position ratio of 1:2 were observed, and the periodic length was ca. 26.5 nm calculated from the primary peak at the low *q* value. The low peak intensity is because the large surface area of the powder, which strongly scatters X-ray.

To carry out the sol–gel reaction in the PTEPM domains, we put the particles into an atmosphere of hydrochloric acid for 30 min. Completion of the cross-linking reaction was confirmed by analysis of infrared spectrum (see Figure S4 in the Supporting Information).[13] Shown in Figure S5 in the Supporting Information is the TEM image of the microtomed slice of hybrid spheres, from which the concentric layer structure remained its original character after the gelation. The morphology of lamellar structure was also confirmed by SAXS curve (Figure 1, line C) but the periodic length shrank to 23.5 nm because of the cross-linking reaction.

To demonstrate the stability of the patterned hybrid structure, the particles were dispersed into methanol, which was a good solvent for the block copolymer precursor. The layered structure was remained as indicated by TEM image (Figure 2D). Furthermore, SAXS analysis was performed by adding a small amount of ethanol to decrease surface scattering. The intensity of the SAXS peaks (Figure 1, line D) is greatly enhanced and the patterns show a lamellar morphology. It also demonstrated that the particles resisted solvent because the PTEPM layers had been switched into a cross-linked polysilsesquioxane network.

Thermal stability of the hybrid spheres could also be improved because of the formation of the silica oxide network in the PTEPM domains. As shown in line A of Figure S6 in the Supporting Information, the un-cross-linked particles began to loss their weight at the temperature of 265 °C because of initiation of the sol–gel reaction in PTEPM domains caused by heating. However, the onset weight loss temperature of cross-linked spheres shown in line B of Figure S6 in the Supporting Information increased to 340 °C, which is the decomposed temperature of organic parts of the hybrid spheres.

Through self-gelation of the PTEPM domains, the organic/inorganic hybrid spheres are obtained and have a good thermal stability and solvent resistance. The most interesting thing is that the concentric uniform P2VP layers are isolated by the cross-linked silica layers. This structure allows us to make use of P2VP to capture the functional species from the outside, i.e., the present functional spheres can be used as microreactors. Herein, we tried to encapsulate gold

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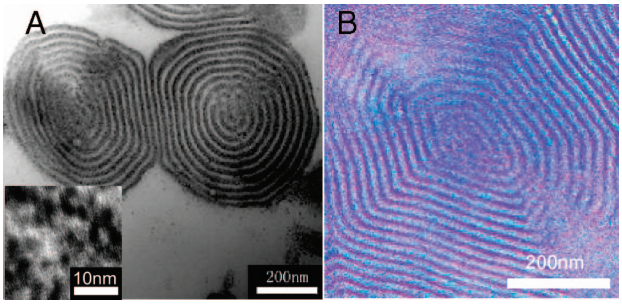

Figure 3. TEM images of (A) the microtomed hybrid spheres containing Au nanoclusters (inset is the magnified P2VP domain) and (B) EELS map of the corresponding microtomed hybrid spheres containing Au nanoclusters.

nanoparticles to demonstrate this concept. The cross-linked hybrid particles were immerged into a water solution of $NaAuCl_4$ (ca. 50 mg/mL) for about 24 h and then washed with water several times to remove excess $AuCl_4$ ions free from complexation in the spheres. It was found that the color of the pink powders turned pale yellow, indicating that the Au ions had been captured by the spheres. These particles were then transferred into a freshly prepared aqueous solution of sodium borohydride (100 mg/mL) with stirring, and the color of the particles turned dark brown immediately, indicating the formation of small Au nanoclusters.

Figure 3A is the TEM of the microtomed slice of hybrid spheres containing Au nanoclusters, from which one may learn that the original onionlike structure was maintained. It is noteworthy that the darker layers contain huge amounts of small black particles, whereas lighter layers do not, implying that the Au particles are enriched only into P2VP domains. The inset image in Figure 3A is the magnification of P2VP domain, which shows that the size of Au nanocluster is ca. 2.4 nm. Furthermore, the SAXS curve of particles containing Au nanoclusters (Figure 1E) gave a primary scattering peak. Compared with Figure 1C, the periodic length of the particles containing Au particles remained unchanged.

To further support that the Au nanoclusters and the silica oxide network were distributed as alternative layers in the spheres, we performed electron energy loss spectroscopy (EELS) of the same microtomed slice sample. In this way, elemental composition of different domains can be visualized by analyzing the energy losses due to the electron scattering of different elements. As shown in Figure 3B, lamellae with alternant color are observed, in which the cyan layer is attributed to the P2VP domain containing the Au nanoclusters and the fuchsia layer is the silica-rich domain. The powder X-ray diffractogram of the hybrid spheres containing Au nanoclusters (see Figure S7 in the Supporting Information) also matched well with the Au nanoclusters from the JCPDS card (04-0784). The broad peak is due to the small size of nanoclusters, ca. 2 nm calculated by the profile fitting method, which is similar to the data obtained by TEM.

To estimate the number of Au nanoclusters contained in these spherical particles, we also performed thermogravimetric analysis of the hybrid spheres with Au nanoclusters, which is shown in line C of Figure S6 in the Supporting Information. Compared with line B, the weight percent of Au nanoclusters could reach as high as about 40% in the obtained nanocomposite materials. This result is remarkable because gold nanoclusters of such high amounts can be loaded into the microspheres and their dispersions are still controlled.

In summary, the three-dimensional confined microphase separation of a novel functional diblock copolymer containing P2VP was studied using an aerosol-assisted process. By selective gelation of the PTEPM domains in the aerosols, robust organic/inorganic hybrid functional microspheres with highly ordered concentric curved lamellar structure were obtained. Such hybrid mesostructured spheres were then used as microreactors to incorporate Au nanoclusters in P2VP domains. Therefore, we have successfully prepared a novel kind of onionlike particles with well-defined alternative distribution of Au nanoclusters and silica oxide networks in different layers. This novel kind of particle materials is expected to find application in many fields.

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Supporting Information Available: Experimental section containing the materials, characterization, polymer preparation, and Figures S1−S7 (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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