

Hierarchically Structured Colloids of Diblock Copolymers and Au Nanoparticles

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Composites of polymers and nanoparticles have received much attention due to their enhanced optical and electronic properties relative to pure polymeric materials.¹ Spatial control of nanoparticles in different polymeric domains is of great interest for practical applications such as solar cells,² photonic crystals,³ and high density magnetic storage media.⁴ In particular, block copolymers offer the possibility of precise control of nanoparticle organization at the nanoscale,^{3,5} especially by exploiting the rich phase behavior of multiblock copolymer systems and mixtures with homopolymers.⁶ Furthermore, confinement of those nanoscale hierarchical structures can lead to the development of new colloidal composite particles, which may show unusual response to external optical, magnetic, or electric field depending on their structures. Therefore, they may pro-

vide opportunities for the development of plasmonic meta-materials,⁷ spherical optical cavities,⁸ conducting particles for anisotropic conductive films,⁹ contrast agents for biomedical imaging,¹⁰ and catalytic systems.¹¹ A few groups have started developing schemes for composites spheres with multilayered nanoparticles on the surface of colloidal spheres or monolayered nanoparticle shell inside colloidal spheres.¹² However, it is still challenging to create a hierarchical structure of nanoparticles over the whole colloidal sphere.

Recently, we have demonstrated a simple and robust method for making block copolymer colloidal particles with nanoscale internal structures and controllable overall shapes.^{6b,c} Other approaches for making structured colloids from block copolymers have also been demonstrated, including using aerosol droplets and inverse opal as templates,^{13,14} or precipitation of block copolymers in a nonsolvent.¹⁵ In this communication, we report simple route for fabrication of hierarchically structured multilayer composite spheres, which were produced by introducing polymer-coated gold nanoparticles into spherically confined phases of block copolymers. To start, the block copolymer and nanoparticles were dissolved in toluene (oil), which was then emulsified in water using a high-speed mechanical homogenizer. Particles were formed by slow evaporation of the toluene by heating (see Scheme S1 in the Supporting Information). Because a symmetric poly(styrene-*b*-butadiene) (PS-*b*-PB) diblock copolymer was used as the matrix for the composite particles, spherically confined layered “onionlike” structures were produced, with the gold nanoparticles encapsulated inside. We demonstrate that the location of the nanoparticles within block copolymer domains can be systematically controlled by varying the

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Table 1. Physical Properties of Block Copolymers

polymers	M_p (g/mol)	M_w/M_n	f_{PS} (wt %)
85k PS- <i>b</i> -PB	85 000	1.05	55
180k PS- <i>b</i> -PB	178 500	1.08	50
300k PS- <i>b</i> -PB	297 700	1.07	52
PS- <i>b</i> -PEO	20 200	1.03	18
PB- <i>b</i> -PEO	25 000	1.06	20 (f_{PB})

lamellar domain spacing and the areal density Σ of polymer chains on the Au-nanoparticles.

As a stabilizer for the emulsion and composite particles, amphiphilic diblock copolymers, either poly(styrene-*b*-ethylene oxide) (PS-*b*-PEO) or poly(butadiene-*b*-ethylene oxide) (PB-*b*-PEO) were used. Their physical properties are listed in Table 1. Au nanoparticles with PS ligands were synthesized and filtered with a membrane for purification as described in previous reports.^{5,16} The areal density of PS chains on the Au surface and the size of the Au nanoparticles were controlled by the initial mole feed ratio f of PS ligands (MW = 1.1 kg/mol) to (Au atoms + PS ligands).⁵ Two different PS-Au nanoparticles were prepared, with effective diameters of 5.76 and 4.98 nm and areal chain densities Σ of 1.43 and 2.04 chains/nm², respectively. The prefix of PS-Au nanoparticles (e.g., 5-PS-Au) indicates the approximate effective diameter in nanometers.

As shown in the TEM image in Figure 1a, microspheres formed with an onionlike structure of block copolymer. The cross-sectional TEM images b and c in Figure 1 show that PS-Au nanoparticles were confined within the polystyrene layers. As in a previous report,^{6c} the outermost layer of the composite particles was determined by amphiphilic copolymer surfactant used (images b and c in Figure 1). However, when triblock copolymers of ethylene oxide and propylene oxide (F108, BASF) or sodium dodecyl sulfate were used as surfactants, most of the PS-stabilized Au nanoparticles were observed at the surface or outside of the composite particles (see Figure S2 in the Supporting Information). We speculate that the Au nanoparticles were captured at the surface because of the affinity between PS chains on Au nanoparticles and PS-*b*-PEO surfactant chains. When PB-*b*-PEO copolymer was used as a surfactant instead, the outermost PB layer suppressed the loss of PS-Au nanoparticles as shown in Figure 1b. Because gold nanoparticles are sufficiently covered with PS ligands, all Au nanoparticles- (5-PS-Au) are located near the center of PS domain, shown in images b and c in Figure 1. Interestingly, at the outmost layer, gold nanoparticles in Figure 1c were not located at center of domain but near the surface of composite microsphere. In the case of outermost PS layer of the composite spheres, an interface between PS-*b*-PB and surfactant, PS-*b*-PEO, is close to the surface due to small molecular weight of the PS block in the PS-*b*-PEO (~3600 g/mol). Notably, when PS-*b*-PEO or PB-*b*-PEO copolymer surfactant was used, all nanoparticles were incorporated into our block copolymer microspheres and we have not found any noticeable variation of

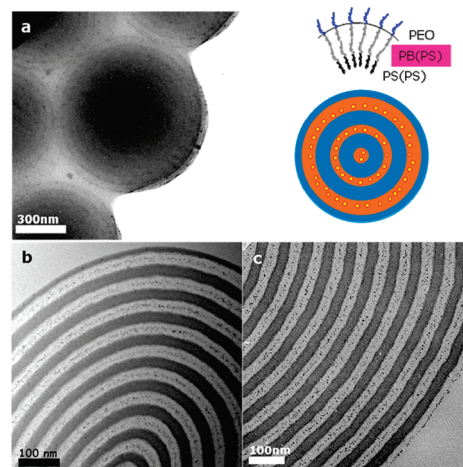


Figure 1. (a) Bright-field and (b) cross-sectional TEM image of composite particles of PS-*b*-PB (MW = 85 kg/mol) and 5-PS-Au particles with PB-*b*-PEO stabilizer. (c) Cross-sectional TEM image of a composite particle of PS-*b*-PB and 5-PS-Au particles with PS-*b*-PEO stabilizer. Lighter layers are the PS domains.

nanoparticle concentration from colloid to colloid in the TEM images. From TEM images, the spatial distribution of Au nanoparticles from the outermost lamellar layer to the internal lamellar layer near the core region was nearly uniform, presumably because the curvature (κ) even at the core region was not high enough to change the spatial distribution of Au nanoparticles.

We have also investigated the effect of particle size relative to domain thickness on particle location in the PS domain by changing domain size of the PS phase, which is controlled by molecular weight of PS-*b*-PB block copolymer. By increasing the molecular weight of PS-*b*-PB from 85 to 300 kg/mol, the PS domain thickness increased from 19 to 39 nm, as shown in the TEM images of Figure 2a–c. The distribution of gold nanoparticles in the PS domain changed dramatically with increasing domain thickness, as shown in insets of the TEM images. As in previous theoretical work,¹⁷ the change of nanoparticle distribution in polymer domain can be characterized using the invariant polymerization index, which is given by

$$\bar{N} = \rho_0^2 a^6 N$$

where ρ_0 is the melt segment density, N is the degree of polymerization, and a is the statistical segment length.

For the diblock copolymers used in this study, the invariant polymerization indices (\bar{N}) were 7.6×10^3 , 1.7×10^4 , and 2.8×10^4 for PS-*b*-PB with 85, 180, and 300 kg/mol, respectively. For $\bar{N} = 7.6 \times 10^3$ (85 kg/mol, PS-*b*-PB), 5-PS-Au nanoparticles were only observed near the center of PS domains (Figure 2a). When \bar{N} is increased from 7.6×10^3 to 2.8×10^4 , the location of PS-Au nanoparticles was changed from the center to the interface because relative ratio of particle diameter to domain size is decreased (Figure 2c).¹⁷ Because the number of ligands per particles has a Poisson distribution, particles could be located in both

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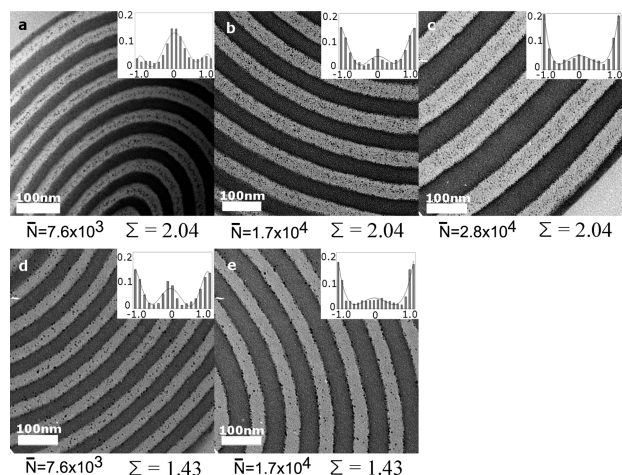


Figure 2. Cross-sectional images of a composite particle with various combinations of block copolymer and PS-Au nanoparticles for PB-*b*-PEO surfactant. (a) PS-*b*-PB with 85 kg/mol and 5-PS-Au particles; (b) PS-*b*-PB with 180 kg/mol and 5-PS-Au particles; (c) PS-*b*-PB with 300 kg/mol and 5-PS-Au particles; (d) PS-*b*-PB with 85 kg/mol and 6-PS-Au particles; (e) PS-*b*-PB with 180 kg/mol and 6-PS-Au particles. Insets show particle frequency versus normalized distance.

regions, as shown in a previous report.¹⁸ Comparing the previous work for PS-*b*-P2VP (the critical areal chain density >3 chains/nm²),¹⁸ Au nanoparticles were positioned away from the center of the PS domain to the interface because of their relatively weak affinity with PS-*b*-PB interface because of the low areal chain density ($\Sigma \approx 2.04$) of these 1.1 kg/mol PS ligands. Cross-sectional TEM images of a PS-*b*-PB film on a gold substrate (see Figure S3 in the Supporting Information), demonstrate that PB rather than PS, just as P2VP rather than PS, is attracted to Au.

Similarly, the fraction of 6-PS-Au nanoparticles segregated along the PS/PB interface increased for larger \bar{N} (images d and e in Figure 2), which is consistent with the theoretical prediction.¹⁷ Interestingly, the histogram of particle distributions in Figure 2 reveals that fewer 6-PS-Au nanoparticles were found near the center of PS domain at a given \bar{N} because the attraction between nanoparticle surface and PB chains is stronger for lower areal chain density ($\Sigma \approx 1.43$) in the 6-PS-Au particles.

We could also change the internal morphology by using mixtures of PS-*b*-PEO and PB-*b*-PEO as emulsion stabilizers, as demonstrated previously.^{6c} Mixing ratio (f_s) of PS-*b*-PEO to PB-*b*-PEO in water is related with the interfacial affinity with block copolymers, which controls the internal phase morphology and the particle shape. As shown in Figure 3, when $f_s = 0.46$, a mixture of block copolymer and 6-PS-Au nanoparticles also formed stacked lamellar structure inside oblate composite particles since the interface for a mixing ratio of $f_s = 0.46$ produced neutral interface that equally attracted both PS and PB blocks. In the TEM images a and c in Figure 3, most of the 6-PS-Au nanoparticles segregated along the center of the PS domain, where \bar{N} was 7.6×10^3 (85 kg/mol, PS-*b*-PB). However, when \bar{N} of the PS-*b*-PB was increased to 1.7×10^4 , more particles were observed at PS/PB

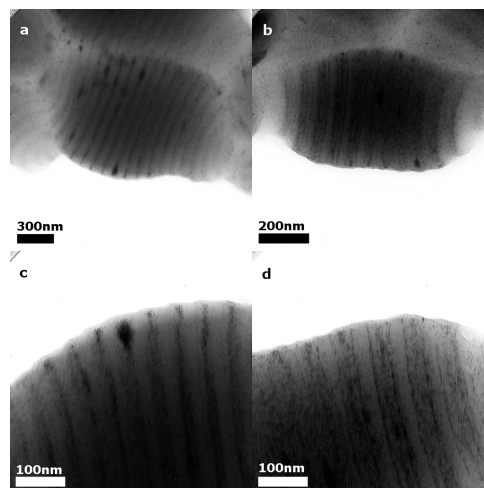


Figure 3. Nonspherical composite particles for mixed surfactant of PS-*b*-PEO and PB-*b*-PEO at the mixing ratio of 50:50. (a) PS-*b*-PB with 85 kg/mol and 6-PS-Au particles; (b) PS-*b*-PB with 180 kg/mol and 6-PS-Au particles; (c, d) magnified images of a and b.

interface as shown in TEM images b and d in Figure 3. Notably, when gold nanoparticles are introduced, the composite particles are more easily deformed, as shown in Figure 3a, because small gold nanoparticles with PS ligands can cause the glass transition temperature of the PS block to be lower than that of the PS block of the pure block copolymer. Similar effects were also observed when we added homopolymer PS with low molecular weight.

In summary, we have shown that composite particles of block copolymers and PS-stabilized gold nanoparticles were successfully prepared by using amphiphilic block copolymers as surfactants. The location of PS-Au nanoparticles was controlled systematically by varying \bar{N} and the areal chain density. As \bar{N} decreased, the fraction of PS-Au particles with intermediate values of Σ at the PS/PB interface decreased. As the areal chain density increased, the location of PS-Au nanoparticle in PS domain with the same \bar{N} was shifted from the interface to the center. Our experimental technique can be expanded to high-performance colloidal materials by introducing other functional nanoparticles with desirable optical, electrical, and magnetic properties into such nanostructured microspheres. Furthermore, much more unusual morphologies in terms of internal shape and external shape can be explored.

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Supporting Information Available: Experimental procedure, characterization of Au nanoparticles, and TEM images of composite particles with F108 surfactants and a block copolymer film on a Au substrate (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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