Nanolithography through mixture of block copolymer micelles

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Abstract
Block copolymer micelle lithography is known for producing ordered and uniform nanostructures. In this report, we have combined different types of block copolymer to produce two interpenetrating lattices of micelle nanoreactors, further extending the capacity of block copolymer micelle lithography. Using polystyrene-block-poly(acrylic acid) and polystyrene-block-poly(4-vinylpyridine), we have generated hexagonally packed hybrid micelles. Metal species can preferentially sequester into poly(acrylic acid) and poly(4-vinylpyridine) cores respectively by immersion of the micelle coated substrates into the metal precursor solution. As a result, metal containing nanoparticle hybrids, such as smaller zinc oxide nanoparticles surrounding larger gold nanoparticles, can be generated.

1. Introduction
Metal and semiconductor nanoparticles exhibit unique, size-dependent properties. Their technological potential in biomolecular recognition, catalysis, molecular electronics and photonics has fueled the synthesis effort [1–10]. The block copolymer template approach, regarded as a powerful nanofabrication enabler [3, 11, 12], offers the capacity of generating periodically ordered and uniform nanoparticles with tunable composition, size, and spacing simultaneously at low cost and high throughput.

Compared to templates prepared by self-assembled block copolymer thin films, the solution-based block copolymer micelle template is robust and versatile [3, 4, 6, 11–13]. Amphiphilic block copolymers, similar to low molecular weight surfactants, form micelles above the critical micelle concentration. When a non-polar solvent is used, the insoluble polar blocks will collapse together to form a core while the soluble non-polar blocks will be organized into the corona. These highly stable micelles, thermodynamically favored, can then be assembled into closely packed structures. Upon casting them on flat substrates, surface micelles arrange in a hexagonal configuration. If precursors for magnetic and optical nanoparticles can be ‘sequestered’ into micellar cores, periodically ordered functional nanoparticles with even size distribution can be fabricated [6–10, 13–16].

Recently, blending block copolymers with either a homopolymer or different type of block copolymer has been explored to further expand the capacity of block copolymer micelle lithography [1, 17, 18]. New types of micelle of different sizes and spacings can be formed without the need for the synthesis of a new polymer system. Hybridized micelles, with a size intermediate between the sizes of micelles formed by the two block copolymers, have been prepared [18]. Tuning catalyst density on a surface has been achieved by mixing one type of micelle loaded with catalyst species and another type of micelle without catalyst species [17]. It can be envisioned that a mixture of nanoparticles with different properties can be prepared by employing two different types of block copolymer micelle which can be selectively loaded with one kind of nanoparticle precursor. For example, a substrate with a mixture of two different types of ordered nanocrystal will exhibit either the combined optical properties and/or new properties if they are in close proximity. It is therefore possible to grow two different 1D nanostructures in close proximity by using arrays of different nanocatalysts.

In this communication, we report that ordered surface micelle arrays consisting of two different types of micelle in terms of lattice constant, size and property, can be readily formed by the deposition of solution micelles
of polystyrene-block-poly(4-vinylpyridine) (PS-b-P4VP) and polystyrene-block-poly(acrylic acid) (PS-b-PAA). By varying the ratio of these two polymer micelle systems, polystyrene-block-poly(4-vinylpyridine) and poly(styrene-block-acrylic acid), a variety of morphologies can be constructed. We employed surface micelles as templates to prepare functional nanoparticles. We found that the kinetics of nanoparticle formation were largely dependent on the solubility of the 'reactive' micelle core and the thickness of the 'passive' micelle corona. More significantly, surface micelles can sequester inorganic species of interest much faster than solution micelles can. For example, it takes less than 10 min for zinc cations to be incorporated into PS-b-PAA surface micelles, as opposed to 24 h for zinc cations to be incorporated into PS-b-PAA solution micelles. We have shown that nanoparticle blends, consisting of gold (Au) and zinc oxide (ZnO), can be produced by selectively sequestering Au anions into protonated P4VP cores of PS-b-P4VP and Zn cations into PAA cores of PS-b-PAA. Furthermore, we have demonstrated that swelling hybrid micelles by solvent vapor annealing, production of larger nanoparticles in closer proximity can be generated, thus extending the capacity of block copolymer micelle lithography. It is expected that this new class of functional nanoparticle can be explored for controllable 1D nanomaterial growth, e.g. two different sizes or types of nanowire. More broadly, this new approach of creating highly ordered photonic, magnetic and semiconducting ordered uniform nanoparticles of different kinds will pave a new pathway for generating novel functional material platforms to enhance existing applications and enable new ones.

2. Experimental procedure

2.1. Materials and micelle blending

We employed two amphiphilic block copolymers: polystyrene-block-poly(4-vinyl pyridine) (PS-b-P4VP) and polystyrene-block-poly(acrylic acid) (PS-b-PAA). The solution of PS-b-PAA, M_n, 109 000 g mol^{-1} for PS and 20 700 g mol^{-1} for P4VP) purchased from Polymer Source Inc., Dorval, Canada. Their polydispersity indices (PDI) are 1.2 and 1.15 respectively. The block copolymers were dissolved separately in toluene overnight at a concentration of 3 mg ml^{-1}. The solution of PS-b-PAA was heated to 140 °C for 30 min to promote the formation of micelles [1]. The two different polymer micelle solutions were then mixed to form binary micelles. A monolayer of surface micelles on a Si(100) surface was deposited by spin coating (1000 rpm/30 s) immediately after mixing. Selected binary micelles were then annealed using a purpose-built solvent chamber for 3 days.

2.2. Bimodal zinc oxide nanoparticle synthesis via surface sequestration and characterization

Hydrogen tetrachloroaurate(III) hydrate (HAuCl_4) and zinc(II) chloride (ZnCl_2), precursors for gold and zinc oxide (ZnO) nanoparticles respectively, were purchased from Sigma-Aldrich. To generate nanoparticles, monolayer micellar films were first immersed in freshly prepared 0.01 M solutions in deionized water. Subsequently, the block copolymer micelle template was removed by oxygen plasma to yield nanoparticles.

2.3. Micelle and nanoparticle characterization

Atomic force microscopy (AFM, Park System Corporation, Santa Clara, CA) was used to study surface micelle morphology. The particle size was estimated by AFM height analysis. X-ray photoelectron spectra (XPS) were obtained from an upgraded PHI-5000C ESCA system (Perkin-Elmer). The monochromatic Mg Kα with photon energy of 1253.6 eV was selected as the x-ray source. After annealing at 500 °C for 1 h, photoluminescence characterization was studied using a QuantaMaster® 50 (Photon Technology International, Birmingham, NJ) with the excitation wavelength of 350 nm.

3. Results and discussion

3.1. Hybrid surface micelles: PS-b-P4VP /PS-b-PAA

It is known that PS-b-P4VP and PS-b-PAA form reverse micelles in toluene. PS blocks are assembled to form the corona while the polar blocks, P4VP blocks or PAA blocks are collapsed into a core. We found that solution micelles that were stable can maintain their integrity during the spin coating process. Figure 1 is a set of AFM topographic images prepared using block copolymer blends and corresponding pure block copolymers. Due to the tip convolution [19–25] inherent in scanning probe microscopy, we use only the height measurements to determine feature sizes. The surface micelles formed by PS-b-PAA were uniform, with an average size of 7 nm, while surface micelles generated by PS-b-P4VP were less uniform, with small 13 nm and large 20 nm micelles. Nevertheless, the size differences between micelles formed by these two polymers were significant for this investigation. Since both polar P4VP and PAA core blocks are nearly kinetically frozen in the non-polar toluene environment, chain interchange should not take place [16]. The AFM height characterization indicated that the heights of PS-b-PAA surface micelles and PS-b-P4VP surface micelles when they are mixed together are similar to the heights of surface micelles prepared from pure block copolymers. This result suggests that inter-diffusion was minimal. Binary surface micelles with varied morphologies were successfully formed, as demonstrated by the set of AFM height images in figure 1.

3.2. Inorganic nanoparticle formation

3.2.1. Nanoparticles formed by surface micelles of PS-b-PAA

After the formation of surface micelles by simple spin coating, the sequestration of inorganic species of interest was carried out by soaking the substrates in a precursor solution, e.g. aqueous ZnCl_2, as depicted in figure 2(a). Since the water used to dissolve metal salts is also a favorable solvent for PAA, the swollen core promotes the kinetics of zinc ion.
incorporation. This was further facilitated by a relatively thin corona shell formed by PS, as the number average molecular weight of PS is 16 000 g mol\(^{-1}\). Figure 2(b) is a set of AFM height images and corresponding line traces indicating that nanoparticles were uniform, with the average diameter of nanoparticles being 1.5 nm to 3 nm after immersion for 3 and 5 min (respectively) in 0.01 M ZnCl\(_2\). This is in stark contrast to the solution-based approach, which takes more than 24 h for zinc species to be localized into the core to form 3 nm nanoparticles. This corroborated with published results by other groups [14, 26]; uniform and ordered nanoparticles were generated within 10 min. The slow kinetics is due to the combination of ‘frozen cores’ that can hinder metal ions from diffusion and incorporation, with limited solubility of zinc chloride in toluene. Figure 3 contains comparative AFM height images of zinc oxide nanoparticles prepared by PS-\(b\)-P4VP and PS-\(b\)-PAA. Poorly defined nanoparticles smaller than 0.5 nm are formed by PS-\(b\)-P4VP in figure 3(b), whereas 2 nm nanoparticles are formed by PS-\(b\)-P4VP in figure 3(b), whereas 2 nm nanoparticles are formed by PS-\(b\)-P4VP in figure 3(a). This result shows the importance of corona thickness and the degree of core solvation for effective nanoparticle preparation.

3.2.3. Nanoparticles formed using hybrid surface micelles of PS-\(b\)-P4VP versus PS-\(b\)-PAA. Effective solvation of micellar cores is needed to facilitate the metal species incorporation process. Unlike homogeneous surface micelles of PS-\(b\)-P4VP, which were incapable of effective incorporation of zinc ions, the surface micelles generated by PS-\(b\)-P4VP in a hybrid system can localize zinc ions into the P4VP micelle cores. Figure 4(a1) is a set of representative AFM images of surface micelles and corresponding nanoparticles formed by using surface micelles. Hybrid nanoparticles with two distinct sizes were synthesized successfully. The associated line trace displayed in figure 4(a2) indicates that the size of nanoparticles produced from PS-\(b\)-PAA was 3 nm while those from PS-\(b\)-P4VP were 11 nm. We speculate that partial proton transfer from PAA blocks onto P4VP blocks during mixing of the two kinds of micelles in solution before deposition would lead some of the pyridine moieties in the PS-\(b\)-P4VP micelles to be protonated. This will render the P4VP cores to be more polar, and thus able to accept zinc ions. Another contributing factor is that, in the binary micelle configuration, each PS-\(b\)-P4VP provides a 4 nm corona layer [29]. The thicker corona layer is expected to impede the diffusion of zinc ions from the solution into P4VP cores. Moreover, water that is used for the ZnCl\(_2\) precursor cannot solvate P4VP cores, whereas PAA is soluble in water, thus impairing the zinc incorporation. Figure 4 contains comparative AFM height images of zinc oxide nanoparticles prepared by PS-\(b\)-P4VP and PS-\(b\)-PAA.
micelle is surrounded by many PS-\textit{b}-PAA micelles. This configuration should disrupt the thick continuous hydrophobic corona formed by the PS-\textit{b}-P4VP micelles, as illustrated in figure 4(c). The solvated cores, coupled with the thinner corona barriers, are expected to promote Zn impingement into the P4VP cores in PS-\textit{b}-P4VP.
3.2.4. Effect of solvent annealing. Ethanol vapor was used to enlarge P4VP and PAA cores resulting from favorable interaction between these polar polymer blocks and ethanol. Figure 4(b) is a series of AFM characterizations of surface micelles after solvent vapor treatment and the corresponding ZnO nanoparticles produced from ‘wet’ surface micelles. Using solvent-swollen surface micelles, larger ZnO nanoparticles with bimodal distributions centered at 5 and 20 nm were produced. For comparison, ‘dry’ micelle templates yielded 3 and 11 nm nanoparticles, as shown in figure 4(a). Larger diameters and more closely packed nanoparticles were generated using swollen micelles. This process can further extend the nanoparticle fabrication capability.

3.2.5. Formation of hybrid nanoparticles. Chloroauric acid (HAuCl₄) can be selectively incorporated into P4VP because the protons in chloroauric acid render the P4VP to be positively charged to attract gold anions, AuCl₄⁻. On the other hand, the negatively charged acrylic acid (COO⁻) repels gold anions. Figure 5(a) is the AFM height analysis of the resulting gold nanoparticles prepared from hybrid micelles using PS-b-P4VP:PS-b-PAA = 4:1 (weight ratio). It is clearly seen that gold nanoparticles were formed at the location where PS-b-P4VP micelles reside. Instead of stripping the polymer template after soaking it in the gold solution, the substrate was rinsed with water followed by immersion in a ZnCl₂ solution. As a result, zinc oxide nanoparticles formed in the region where PS-b-PAA micelles reside. The XPS spectra, shown in figure 5(b), indicate the formation of hybrid nanoparticles: Au nanoparticles were preferentially produced by the PS-b-P4VP surface micelles, whereas Zn ions were mainly localized into PS-b-PAA micelles. By employing selective interaction of metal precursor species with functional groups in polymer repeat units, hybrid nanoparticles with different size and composition were formed by this straightforward method, further extending the nanoparticle fabrication capability.

If the two different types of nanoparticle possess different optical properties, then combining them together it is expected that added or new phenomena will be generated [30]. In order to realize photonic applications, physical structure guided annealing or chemical and mechanical influence annealing can be used to attain a long-range order [31–34].

4. Conclusions

The surface micelle approach is a highly effective method to fabricate well-ordered nanoparticles. The composition
and structure of block copolymer micelles are important. Thin coronas and solvated cores are required to facilitate inorganic species incorporation and nanoparticle formation. This is a high-throughput method. Due to simple kinetics, nanoparticles can be produced in a significantly shorter time period, less than 10 min, in comparison to the lengthy time, 24 h, required for the solution micelle approach. We have shown that using hybrid micelle templates, binary nanoparticles with the same composition but differing in size, or differing in both size and composition, can be formed controllably. Furthermore, by employing solvent vapor annealing, the nanoparticle size can be adjusted. The added nanoparticle fabrication capability paves a pathway for the exploration of hybrid nanoparticles for a series of technological applications, including catalysts for the formation of 1D nanomaterials with different properties in close proximity, semiconducting nanoparticle arrays to sense multiple chemical species, and photonics.

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Figure 5. (a) AFM height images of surface micelles and height analysis of as-synthesized Au and ZnO nanoparticles using the templates made of 4:1 = PS-b-P4VP:PS-b-PAA, (scan area = 0.5 μm × 0.5 μm, height scale bar is −4–16 nm) and (b) XPS analysis with a Mg Kα photon energy of 1253.6 eV.