Single Nanoparticle Localization in the Perforated Lamellar Phase of Self-Assembled Block Copolymer Driven by Entropy Minimization

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ABSTRACT: Although precisely controlled microdomains of block copolymers (BCP) provide an excellent guiding matrix for multiple nanoparticles (NPs) to be controllably segregated into a desired polymer block, localization and positioning of individual NPs have not been demonstrated. Here, we report a unique one-to-one positioning phenomenon of guest Au NPs in the host BCP microdomains; each of polystyrene-functionalized Au NPs is embedded within the perforation domain of hexagonally perforated lamellar (HPL) morphology of poly(dimethylsiloxane-b-styrene) BCP. The local minimization of free energy achieved by the placement of Au NPs into the center of the perforation domain is theoretically supported by the self-consistent field theory (SCFT) simulation. We propose a novel design principle for more precisely controllable nanocomposites by developing a new route of NP arrangement within a polymer matrix.

INTRODUCTION

Because of the quantum size effect and large surface-to-volume ratio, nanoparticles (NPs) exhibit novel properties compared with their bulk counterparts.1 In addition to the various unique properties from the size controllability of NPs, an ordered arrangement of NPs can enhance or alter such properties via synergistic interparticle coupling.2−5 It has been shown that the two-dimensional (2D) or three-dimensional (3D) arrangement of NPs can be controlled by structural or chemical templates.6−20 These approaches have enabled the creation of various nanocomposite materials such as NP−polymer blends, which provide tunable electrical, magnetic, optical, and mechanical properties.20−23 One of the practical templates for the guidance for NP alignment is block copolymers (BCPs) with two chemically dissimilar polymers joined covalently that phase-separate into various nanostructures forming periodic patterns of high resolution (5−100 nm).14−19 By controlling NP dispersions using BCP as a template, highly ordered positioning of NPs within BCP−NP nanocomposite can be achieved, which is essential to the development of potential nanodevices including, but not limited to, sensors,20 plasmonics,21 and photovoltaics.22

Previous studies have demonstrated ex situ BCP−NP blends, in which presynthesized metallic NPs are mixed with BCPs. When the blends are self-assembled, the NPs are spatially distributed either in a selective block of BCP or along the interface of two blocks of BCP as a function of surface chemistry and relative size of NPs.23−28 Also, the phase behavior of BCP−NP nanocomposite as a function of NP concentration was reported.29 Recently, an attempt to locate metallic nanorods in an end-to-end fashion within BCP thin films was reported. The orientation of nanorods under two-dimensional geometric confinement was studied through investigations of various thermodynamic and kinetic factors including the effect of anisotropic shape of NPs.24 In a recent study, the formation of bicontinuous morphology was induced by the insertion of NPs as surfactant at the BCP interfaces.25 In converse to the former approach,24 this study reported the effect of NPs as a modifer of interfacial energy, extensively controlling the orientation and morphology of BCPs.25 Along with various methods for the construction of BCP−NP hybrid structures, attempts to spatially control the NPs on top of BCP nanostructures by postdeposition of NPs were also introduced.30,31

Numerous studies on a mixture of BCPs and NPs have also been carried out using cylindrical or lamellar morphology of BCPs as the main framework to provide one or two-dimensional confinement of the NPs within the BCP matrix.32−34 Furthermore, by attaching the small molecules to the BCPs to make one block stiffer than the other, stronger confinement induced from the conformation entropic effect of chain facilitates better alignment of NPs within BCPs.33,34 Recently, the assembly of large (>10 nm in diameter) NPs in BCP microdomains, based on hydrogen bonding between a brush-type BCP and the ligands on NPs, was also demonstrated.35 However, all of these previous studies focused on the segregation of multiple particles at the domain centers or interfaces, and the isolation and control of individual NPs by
BCP nanotemplates have not yet been demonstrated and still remain a notable challenge. The preparation of isolated NP arrays would enable more extensive tuning on the properties of NPs by modulating interparticle interactions. Moreover, the practical device applications of colloidal nanostructures require the effective principles enabling the accurate positioning of individual nanostructures.

Herein, we report the one-to-one positioning phenomenon of polystyrene-functionalized Au-NPs at the hexagonally perforated lamellar (HPL) structure of a poly(dimethylsiloxane-b-styrene) (PDMS-b-PS) BCP as a useful host template. We show that nanoscale PS perforations containing zero-dimensional hosting sites can efficiently trap the individual Au NPs during one-step solvent-assisted self-assembly of the BCP/NP blend. In order to ensure the selective incorporation of NPs in the PS block of PDMS-b-PS BCP, the Au−NPs were surface-modified with polystyrene (PS) homopolymer through a ligand exchange process (Scheme 1). Although the energetically stable range of HPL morphology is generally narrow,22,23 we discovered that the one-to-one incorporated NPs at the center of each HPL is induced by warm solvent annealing treatment on the spin-cast blend thin film.

**Experimental Section**

**Au−Nanoparticle (Au−NP) Synthesis.** Monodisperse and size-tuned Au-NPs were synthesized using the procedure reported by the Swihart group.36 Under an inert gas atmosphere (Ar), 5 mL of oleylamine (OLM, Aldrich, technical grade) was refluxed at 150 °C. 0.3 mmol of gold(III) chloride trihydrate (HAuCl₄·3H₂O, Aldrich, 99.9+%)) was mixed with 1 mL of OLM. The mixture was then quickly injected into the refluxed OLM and was kept at 150 °C for 1.5 h. After cooling the solution to room temperature, 4 mL of methanol (OCI, 95%) was added to the solution to precipitate the NPs, and the mixture was centrifuged at 6000 rpm for 10 min. The NPs were dispersed in 3 mL of toluene (OCI, 99%, EP-1L) for the subsequent ligand exchange process. 0.01 g of thiol-terminated polystyrene (PS-SH, Polymer Source Inc., MW = 31 kg/mol) was fully dissolved in 2 mL of toluene, which was then mixed with the NP solution. The mixture was kept for 2 h with magnetic stirring; sufficient time was provided for the ligand-exchange reaction. Again, to precipitate the Au-PS NPs, 3 mL of methanol was added, and the mixture was centrifuged at 6000 rpm for 10 min. A small portion of the NPs was dispersed in toluene and dried on copper mesh grid (300 mesh Cu, Ted Pella Inc.), which was imaged using a transmission electron microscope (TEM, JEOL JEM-ARM200F microscope at 200 kV).

**BCP−NP Blend Self-Assembly.** 0.6 wt % poly(styrene-b-dimethylsiloxane) (PS-b-PDMS, Polymer Source Inc., MW = 36 kg/mol, fPDMS = 38%) in toluene:heptane=propylene glycol methyl ether acetate (mixing ratio = 1:1:1, Junsei, Aldrich) solution was added to the presynthesized Au−PS NPs. BCP−NP blend solution samples with different weight fractions of the Au NPs were prepared. PS-brush-functionalized Si substrates were prepared by spin-coating 2.0 wt % hydroxyl-terminated PS homopolymer (PS-OH, Polymer Source Inc., MW = 43 kg/mol) and thermal-annealing the substrates at 150 °C for 2 h in a vacuum oven. After removing the PS homopolymer remnant using toluene, BCP−NP solution was spin-coated at 5000 rpm for 20 s. Subsequently, a warm solvent annealing (WSA) procedure (45 °C, 5 min) was used for fast and effective self-assembly of the BCP−NP blend using a varied toluene:heptane (T:H) ratio (total solvent...
volume = 25 mL). Using RIE, the annealed samples were etched under CF₃ plasma (20 s at 50 W) followed by O₂ plasma (30 s at 60 W). The oxidized PDMS nanostructures with Au−NPs were imaged using a scanning electron microscope (SEM, Hitachi S-4800).

Self-Consistent Field Theory (SCFT) Simulation. A hybrid particle field theoretic simulation was utilized to simulate the blends of NPs and flexible BCP chains. To obtain a perforated lamellar phase, parameters (\(\gamma N = 20, f_{PS} = 0.675\)) of a gyroid-forming block copolymer were used, and the simulation was performed under a thin film condition. The bottom of the simulation box attracts the PS block while the top surface of the simulation box attracts the PDMS block to mimic the PDMS preferred air surface in the experiments. To plot the free energy curve as a function of deviation from the center of pore, grid refinement technique optimized on the GPU cluster was used. The size of NPs is set to 0.2\(L_\infty\) which corresponds to actual NP size of around 13 nm.

### RESULTS AND DISCUSSION

We hypothesized that one-to-one matched assembly between BCP microdomains and NPs can be realized with a BCP morphology containing zero-dimensional points with energetic instability. Such points can provide strong confinement to the NPs, and the BCP/NP blend can be energetically stabilized via one-to-one self-assembly. In this sense, the HPL phase can provide appropriate sites where NPs can reside. In the bulk state, the HPL phase of BCPs has been reported to be a metastable state of the gyroid (G) phase; however, under thin film confinement conditions, one-dimensional confinement provides stability of the phase. The findings of our previous study, where we demonstrated a one-to-one matched host−guest self-assembly between HPL and sphere BCP phases, suggest that a monolayer HPL is a highly effective candidate template for NPs to be three dimensionally confined. Because of the curved interface at the perforation, energetically unstable points in the matrix block can arise due to the significantly stretched polymer chains above and below the perforations in the lamellar plane; when the two stretched points in the vertical axis are simultaneously contacted and filled by corona chains from another sphere-forming BCP, free energy minimization and uniform microphase separation between the two BCPs can be achieved. This morphological advantage was a key factor in selecting HPL as the template for NP localization as in the case of BCP blends.

Prior to exploring the self-assembly behavior of the BCP−NP blend, the important solvent annealing parameters to achieve a uniform monolayer HPL structure of neat BCP were investigated. First, controlling the BCP film thickness and swelling ratio is important to achieve a stable HPL monolayer because the expanded thickness of BCP film due to solvent swelling should be commensurate with the equilibrated thickness. Second, to achieve one-to-one isolation of NPs in BCP microdomains, the effective volume fraction of each polymer block should be systematically controlled by adjusting the composition of mixture solvent vapor and the volume fraction of NPs in the blend. During the warm solvent annealing (WSA) of the blend, a mixture of toluene and heptane, which selectively swells PS and PDMS, respectively, was used; fine-tuning of the ratio between toluene and heptane allows the control of effective volume fraction \(f_{PS}^B\) of each block, leading to the morphological transitions of the BCP.

Figure S1 in the Supporting Information maps the morphology transition from cylinder to lamellar phase of the PDMS-b-PS BCP. The selective existence of Si in the PDMS block enables the facile observation of HPL nanostructures using SEM after the removal of PS matrix via plasma oxidation. Stable and ordered HPL morphology was obtained with an annealing temperature of 45 °C, annealing time of 5 min, and a toluene:heptane (T:H) ratio between 10:1 and 7:1. Although the HPL-forming annealing conditions are different when Au−NPs are added to BCPs due to the added volume of Au−NP to the PS block, these preliminary observations on the BCP phase behavior served as a useful reference for the morphology control of the BCP/NP blend. Figure 1 and Figure S3 demonstrate the phase behavior of self-assembled BCP-NP blend as a function of T:H mixing ratio and the weight fraction of NPs in the blend. The WSA treatment time was fixed at 5 min. The increase of the heptane volume fraction in the mixture solvent increases the effective volume fraction of the...
PDMS block ($f_{\text{PDMS}}^{\text{eff}}$), whereas the increase in NP concentration increases the effective volume fraction of the PS block ($f_{\text{PS}}^{\text{eff}}$). At NP fraction of 40%, macrophase separation between NPs and BCPs and separation between NP and BCP layers were observed. However, for a NP concentration of 20%, both NPs and BCPs were stabilized as a monolayer structure, where multiple NPs are confined in single PS perforation. When the NP concentration is further tuned down to approximately match the number of perforations (NP wt % = 10%), delicate localization of a single NP inside a single perforation was predominantly observed.

The statistical distribution of NP insertion in the PS perforations is demonstrated in Figure 2. In addition to the representative SEM images in Figure 1, raw data from 10 points of each sample were processed to obtain the statistical data. At a low NP fraction of 3%, only 29% of the perforation were occupied by NPs, and the majority of them were empty without NPs. However, for a NP fraction of 10%, one-to-one insertion was observed in more than 60% of the perforations, and more
than 84% of occupied perforations showed one-to-one accommodation of NPs. If the number of perforations and that of NPs become equal through extremely delicate tuning of the NP fraction in the blend, the percentage of empty perforations is expected to be significantly reduced. The statistics represent the promising result of delicate localization of single NP within each pore of HPL phase. At a NP fraction of 20%, the average number of NPs within one perforation increased to 5.54. As the NP concentration further increases to 30%, agglomeration of a large number of NP dominates, leading to a significant increase in the number of empty perforations without NPs. At the optimized condition of NP fraction and T:H ratio, single NP insertion in a BCP microdomain is predominantly achieved, indicating favorable microphase separation between NPs and BCPS.

In order to investigate the kinetics of microphase separation phenomenon and to determine the best timeline for the quenching of the one-to-one NP-inserted morphology, the time evolution of the BCP–NP blend morphology as a function of WSA time was monitored, and the results are shown in Figure 3. We previously reported the fast self-assembly of PDMS-b-PS BCP facilitated by WSA treatment on the basis of the thermal activation effect combined with plasticization by incorporated solvent molecules.37 The as-spun sample showed spherical BCP microdomains mixed with well-dispersed individual Au NPs. The initial BCP microdomains were then significantly reconstructed into an equilibrium HPL morphology within approximately 5 min of WSA treatment. During the BCP phase transition, NPs were captured inside the PS perforations, as shown in the SEM images. The best one-to-one matching was obtained for a WSA time of 6 min, as shown in Figure 3c. However, at the later stage of annealing after 8 min, gradual separation between NPs and BCP was observed, suggesting metastability of the one-to-one matched morphology. It was also observed that, as the macrophase separation proceeds, regions of low NP density transformed to the cylinder phase because the stabilization effect of HPL phase upon loading NPs disappears.

Here, it is important to note that the time scale of BCP self-assembly and phase stabilization is faster than that of NP aggregation, which allows stabilization of the HPL phase by capturing well-dispersed NPs inside the PS perforations prior to the macrophase separation of Au NPs. At the same time, the HPL phase helps the localization of NPs by providing three-dimensional local confinement. This aspect will be analyzed and explained based on our SCFT simulation. WSA offers clear advantages in these circumstances because the time required for BCPS to reach equilibrium is significantly reduced compared to that of RT solvent annealing.37,45 This technique provides an appropriate time window for NP trapping, during which the nanostructure can be quenched to stop further macrophase separation of NPs.

Regardless of the unique structure of HPL, its functional application rarely has been demonstrated. One of the reasons is that the fact that the allowed ranges of $\chi N$ and volume fraction for equilibrium HPL phase are relatively narrow compared to that of cylindrical and lamellar phases. An attempt to stabilize HPL morphology in bulk by modifying the polydispersity of the

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**Figure 4.** SCFT simulation results for the HPL BCP/NP blend. (a) Unit cell structure of the SCFT simulation. The green contour represents the boundary layer between PS and PDMS, and the red contour represents a nanoparticle. A single NP is then moved to the $X'$ and $Y'$ direction to calculate the free energy landscape. Snapshots of simulation when NP is moved by 8 nm toward (b) $Y'$ direction and (c) $X'$ direction. For both cases, perforated lamellar phase breaks. (d) Helmholtz free energy (units of $kT$) map as a function of deviation of NP position from the center ($X'$ and $Y'$). Local energy minima exists at the center.
minority poly(methyl acrylate) (PMA) block of poly(styrene-b-methyl acrylate) (PS-b-PMA) was reported. It was also reported that blending AB BCP with a homopolymer stabilizes new morphologies including HPL. Both studies emphasized the necessity to alleviate the "energetic defects" that exist in the HPL phase. The present study also discovered that the narrow volume fraction range for the HPL phase can be extended by the addition of NPs. While the neat BCP sample presented the HPL morphology in a range of T:H ratio of 10:1 to 7:1, the HPL phase was observed for a wider range (30:1 to 2.5:1) in the case of the BCP/NP blend sample, as shown in Figure S5. The energetic stabilization of the HPL phase by the addition of NPs is consistent with the host–guest self-assembly between HPL and spherical microdomains, which was reported in a previous paper.

Local confinement of NPs within the perforated lamellar phase of BCPs and consequent reduction of free energy can be explained using a SCFT simulation. Figure 4a shows a snapshot of NPs located at the centers of pores of the PDMS region. A simulation of four NPs per simulation box was carried out to reduce the finite size effect of the system. After the system reaches equilibrium, a single NP was moved from the center of the pore, and free energy as a function of deviation coordinate from the center (X and Y in Figure 4a) was calculated and plotted in Figure 4d, showing the local energy minima for the central placement of NPs in the PS perforation. When the nanoparticle position deviates less than 6 nm from the pore center, a free energy well with a potential barrier confines the NP in the PS perforation. However, when the NP moves more than 6 nm from the center, the perforated lamellae breaks (see Figures 4b and 4c) and significantly lowers the free energy of the blend system. A large content (50–60%) of solvent in the swollen BCP/NP blend during the solvent vapor treatment may allow the significant fluctuation of NPs inside the confinement volume. These results explain how the perforated lamellar phase of BCPs can locally confine the well-dispersed individual NPs at the initial WSA treatment stage and how the NPs and BCPs gradually macrophase-separate at the later stage. We also calculated energy well depths with varying NP radius and the length of the polymer ligands, the interparticle distance of the NPs can be systematically controlled, which could in return tune the plasmonic coupling of the NPs. Also, such a system may open the possibility of realizing a 3D hybrid NP system using a 3D BCP template for enhanced plasmonic properties. Moreover, individual NPs captured by BCP host domains introduce the influence of a distinct material between neighboring particles. Tuning of NP size and NP to BCP distance as well as possible variation of the confining material from an organic to an inorganic material could be used as tools to precisely investigate the behavior of NP plasmonics.

ASSOCIATED CONTENT

Supporting Information

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Experimental details and characterization data (PDF)

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