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Self-Assemblies of Diblock Copolymers for the Fabrication of Nanopatterns with Optical Functionalities

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Abstract

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Since the emergence of nanotechnology, which is a field of science that handles the nanoscale materials and objects, the development and fabrication of nanostructured materials have naturally become a key issue. Due to the unique and tunable properties distinct from the bulk counterparts, especially, nanostructures of optically functional materials have been widely used in various fields of nanotechnology, including light harvesting, metamaterials, catalysts and integrated nanodevices. The precise control of the geometry and displacement is crucial for academic investigations and practical applications of these materials, so many approaches have employed various templates to synthesize and construct nanostructures with optically active functions.

Templates mainly refer to prefabricated structures, of which geometry and chemical properties can guide building components to generate defined structures. By using well-designed templates, functional materials from small molecules to colloidal objects can be synthesized or assembled into desired structures through physical restriction or chemical adsorption at specific locations of the templates, enabling the manufacture of functional architectures with specific shapes like dots, lines, and more complex 2D/3D structures. In this regard, nano-sized templates have been spotlighted as a promising tool for fabricating nanostructures of various functional materials, which has become a basis for nanotechnology including both fundamental aspects investigating the unique characteristics of nanomaterials, and application aspects requiring the well-defined nanostructures, such as nanopatterning, biomimetics, and nanodevice fabrication. Especially, templates with nano-sized features in thin films are widely used to fabricate 2D nanomaterials in terms of the handiness of examining the properties of resulting nanostructures and further implementing into nanodevices.

Block copolymer (BCP), consisting of two or more polymers covalently connected, is one of the state-of-art tactics to produce a thin film template. Thin films of BCPs form various periodic nanostructures, including spheres, cylinders, and lamellae, through self-assembly of incompatible polymer blocks, of which the size and the morphology of nanodomains can be controlled by the molecular weight and the block ratio. The use of a BCP film to produce a template is based on the realization of chemically distinct nanodomains by choosing appropriate polymer blocks. This mainly involves a removable polymer block to generate topographic contrast on the film, or a chemically active block to attract and bind other materials. Namely, the self-assembled nanostructures of BCP thin films have the advantages of facile production of nano-sized templates whose physical structures and chemical properties can be adjusted according to the purpose. Moreover, several strategies for orienting BCP nanodomains, including directed self-assembly (DSA), mechanical shear, electromagnetic field, and zone annealing, can also be considered for the practical applications that require aligned and controlled structures, such as optical and electromagnetic devices.

This dissertation proposes the fabrication of BCP templates which can be utilized to construct the nanostructures of optically functional materials via physical confinement or chemical attraction originated from the architectures of templates. Chapter 1 briefly introduces the background and objectives of this work. Chapter 2 demonstrates dichroic plasmon superstructures, which were composed of end-to-end assemblies of Au nanorods (NRs) over a macroscopic area, prepared by utilizing the DSA of BCP thin films. The superstructures exhibited dichroic optical properties under polarized lights in orthogonal directions and also could be transferred onto various substrates without structural deterioration. Chapter 3 presents the macroscopically aligned nanodomains of two different BCPs by a single methodology composed of simultaneous shearing and solvent vapor annealing at room temperature. The shear-aligned nanodomains of each BCP was employed as chemical or physical template, respectively, resulting in the patterns of fluorescent molecules or Au NRs. Finally, chapter 4 describes the facile process using BCP templates for the fabrication of organic-inorganic hybrid perovskite nanopattern with fluorescent properties. BCP templates could provide various nanoscale geometries, and thus enabled the control of the dimension and orientation of perovskite nanopatterns. That is, by the assist of the self-assembled nanostructures of BCP in thin films, nanopatterns with various optical functions could be effectively fabricated and controlled. Thus, this approach is expected to provide broader opportunities to implement and control basis materials for the development and advance of nanooptics and nanodevices.

Keyword: block copolymer, self-assembly, template, nanopattern, optical function **Student Number:** 2012-23033

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Chapter 1

Introduction

Block copolymers (BCPs)

A Block copolymer (BCP) consist of two or more chemically distinct polymer chains, which are covalently connected to each other.^[1,2] For example, when polymer A is covalently connected its chain end with a chain end of polymer B, it forms an A-B type BCP (diblock copolymer, A-*b*-B). If the constituent polymers, usually called "blocks", are immiscible, they exhibit the segregation by the phase separation as in the case of a blend of immiscible homopolymers. Unlike the phase separation in homopolymer blends, however, the covalent connection of the blocks in BCPs prevents the formation of macroscopic domains, so that instead the system minimizes its energy by forming periodic patterns with dimension typically in the range of tens of nanometers. This phenomenon is called microphase separation.^[2-5] The thermostable morphologies of BCPs present various nanostructures, including spheres, cylinders, and lamellae, depending on the degree of polymerization (N, $N = N_A + N_B$ for A-*b*-B), volume fraction of the block ($f_X = N_X / N$, $f_A + f_B = 1$ for A-*b*-B), Flory-Huggins interaction parameter (χ , χ_{AB} for A-*b*-B) between distinguishable block pairs, and the conformational asymmetry of polymer chains.

As in the phase separation of a polymer blend, the thermodynamic basis of microphase separation can be explained in Gibbs free energy of mixing,

(1)
$$\Delta G_{\rm m} = \Delta H_{\rm m} - T \Delta S_{\rm m}$$

where $\Delta G_{\rm m}, \Delta H_{\rm m}, \Delta S_{\rm m}$ is the free energy, enthalpy, and entropy difference between microphase-separated phase (ordered) and homogenous phase (disordered), respectively, and *T* is the temperature. In high *T*, since the enthalpic contribution ($\Delta H_{\rm m}$) is relatively smaller than entropic contribution ($-T\Delta S_{\rm m}$) and the transition to the ordered phase causes negative value of $\Delta S_{\rm m}$, $\Delta G_{\rm m}$ become positive and homogeneous phase is thermodynamically favorable. In contrast, $\Delta H_{\rm m}$, which is usually negative, overwhelms $-T\Delta S_{\rm m}$ in low *T*, resulting in the ordered phase ($\Delta G_{\rm m}$ < 0). Thus, the critical temperature, where the order-disorder transition occurs, is validated when $\Delta G_{\rm m} = 0$ (order-disorder transition temperature, $T_{\rm ODT}$).

Unlike the polymer blend, however, the size of phase-separated domains of each block in a BCP is limited usually less than micron scale, since the distinct polymer blocks in a BCP are covalently connected. When assuming the formation of macroscopic domains like a phase-separated polymer blend, this covalent bond between each block causes the larger entropic penalty from the extended polymer chain than the enthalpic advantage from the reduced interfacial area. Thus, the BCP forming thermodynamically stable phases becomes resided within the radius of gyration (R_g) of polymer chains, which results in the periodic nanostructures with the size in the range of tens to hundreds of nanometers.

In diblock copolymer system (A-*b*-B), the thermodynamic behavior is usually described in terms of χ and *N*. The size of χ , which is strongly related with the contact energy between distinct blocks and thus is usually positive, represents the amount of enthalpic advantage from the decrease in A-B contacts during the microphase separation. This microphase separation is opposed by the loss in system entropy that originated from the localizing A-B joint at interfaces and the stretching of polymer chain to achieve the separated domains with specific size. This entropic loss becomes smaller as *N* becomes larger increasing the possible configuration of polymer segment. Thus, the product χN can be regarded as a nice indicator representing the

thermodynamic factors in the phase behavior of BCPs, so that diblock copolymers with larger χN tend to more easily form periodic nanostructures by microphase separation.

Based on the value of χN , theories which deal with the extent of segregation in microphase separation can be divided into three regimes:^[4,5] (i) strong segregation limit (SSL, $\chi N >> 10$),^[6-8] (ii) weak segregation limit (WSL, $\chi N \sim 10$),^[9-10] and (iii) their intermediate regime.^[11-13] In the SSL regime, the interfaces between each block is narrow and the composition profile at the interfaces changes very rapidly so that almost pure component constitutes each domain of which size is proportional to $N^{2/3}\gamma^{1/6}$.^[8] The morphology, such as spheres, cylinders, lamellae, is only determined by the volume fraction of one block (f) and shows no dependency on temperature. In the WSL regime, the composition fluctuates significantly and shows sinusoidal profiles with relatively thick interfaces. For symmetric diblock copolymers (f = 0.5) in this regime, the system exhibits phase transition from the disordered to the ordered phase (lamellar phase since f = 0.5) as in the SSL regime. But for the case of asymmetric diblock copolymers ($f \neq 0.5$), order-to-order phase transitions (i.e. spheres to cylinders, cylinders to lamellar) are also possible as increasing γN or decreasing temperature. Between these two regimes, the situation becomes more complicated. The overall phase behavior of BCPs including all these regimes can be precisely predictable by adopting self-consistent field theory (SCFT), which also presents more complex morphologies like gyroid phase that exists in the real BCP system. Figure 1-1 shows two phase diagrams of which one is expected from the SCFT approximation and another is obtained from a real BCP.

Thin films of BCPs

BCPs confined in thin films show distinct nanostructures and thermodynamic properties compared to the bulk. In thin film, BCPs tend to form morphologies, which relieve the unfavorable chain stretching/compression caused by limited volume (thickness) and increase favorable interactions at film interfaces. For example, if the thickness (*h*) of a lamellar-forming BCP film is not commensurate with the bulk periodicity L_0 (commensurate when $h = nL_0$, n is an integer), energetically unfavorable chain stretching or compression should be imposed to generate stacked (parallel to the substrate) lamellae while maintaining the flat surface. To avoid this penalty, the film generates terraced structures, such as islands and holes, when the polymer has sufficient mobility to reorganize itself.^[14-17]

In details, the generation of islands and holes is determined by the preference of a block for two possible neighbors, which are usually air and the substrate. When both neighbors prefer the same block, the flat film is only favorable when $h = nL_0$, as in the example described above. When each neighbor like different blocks, $h = (n + 1/2)L_0$ is the condition for the flat film. In the case of sphere- or cylinder-forming BCPs, a minor block, which forms their characteristic structures, cannot fully cover a favorable interface while forming their intrinsic morphology. Instead, a thin layer without specific morphology is formed at the interface, which is usually called brush layer or wetting layer.^[15] So, the formation of islands and holes in those BCPs occurs when the film thickness does not closely match the value $h = nd + \beta$, where *d* is the layer-to-layer distance (e.g. $d = (3^{1/2}/2)L_0$ for cylinder-forming BCPs) and β is the thickness of the brush layers if formed. **Figure 1-2** shows the possible configurations

of thin films described above. In practice, the effects of film thickness and interfacial interactions can be combined with the kinetic aspects, resulting in the significant deviations or complications in final morphologies compared to the bulk counterparts.

These effects also cause the preferential orientation of intrinsic morphologies. In general, each block of BCPs has different interfacial interaction with free surface or substrate, so that one block is selectively located at an interface to minimize the energy of the overall system, resulting in the long axis of the nanodomains parallel to the interface. Orienting the nanodomains normal to the interface requires overcoming these preferential interactions. The details of the controlling the orientation of BCP morphology in a thin film will be introduced in the next section.

A Thin film of BCP is usually prepared from the polymer solution by casting onto a substrate. This as-cast film usually exhibits disordered or poorly organized structures due to the kinetically trapped morphology in nonequilibrium. To generate and enhance the order in thermodynamic equilibrium, the mobility of the polymer chains should be granted to reorganize the nanoscale structures.

The equilibrium structure of BCP can be successfully obtained by using thermal annealing above the limiting glass transition temperature (T_g) of the system.^[18-19] In general, the thermal annealing conditions can be understood by considering the relation between the polymer mobility and the molecular weight, $L_D \propto (\sqrt{t}/N)e^{-C/T}$, where L_D , t, N, C, and T represent polymer diffusion length, annealing time, degree of polymerization, a material-dependent property of polymer, and temperature, respectively.^[19] This relation shows that small increases in T can significantly reduce the annealing time. It also represents that BCPs with higher

molecular weight, which are desirable for the larger size of the nanodomain, show lower polymer mobility within the range of processible temperature, which in turn requires excessively long annealing time or leads to poor ordering. However, in the view of the relatively high demand for smaller nanostructures in nanotechnology fields, the incompatibility of thermal annealing in BCPs with larger molecular weight may not be a major obstacle. Furthermore, there are numerous methods for precisely controlling the temperature, which has made thermal annealing a versatile tool to generate well-controlled nanostructures in laboratories as well as industries.

The mobility for the structural reorganization in a BCP film can be also granted by the uptake of solvent molecules lowering the T_g of BCP.^[20-23] In this method called solvent vapor annealing, the BCP thin film is exposed to a vapor of a solvent to form a swollen polymer film. The solvent in the BCP film diminishes unfavorable contact between immiscible blocks. This causes the change of the effective interaction parameter, $\chi_{eff} = \phi_{p\chi}$, where ϕ_p is the volume fraction of the polymer in a solventswollen BCP film. Due to the lowering of T_g and χ which drastically enhances the mobility of BCP, solvent vapor annealing can be used to generate ordered nanodomains of BCPs having high χ or molecular weight, and also provides longrange ordered nanostructures in very short time. In addition, the change of volume and interaction of swollen polymer blocks during solvent vapor annealing can alter the final nanostructures distinct form the intrinsic morphology. ^[22] Figure 1-3 shows a schematic phase diagram with the trajectories of altering morphologies induced by the swelling of BCPs during the solvent vapor annealing. These attractive features make solvent vapor annealing to be utilized as a powerful alternative to generate BCP nanostructures in thin film, although there are some critical obstacles that the appropriate choice and control of solvent vapors are much more challenging compared with the heat control in thermal annealing.^[23]

Orientation of BCP nanostructures

Controlling the orientation of the BCP nanodomains in a thin film is necessary for practical applications, especially in the nanofabrication to create a nanopattern that can be transferred to a substrate for the fabrication of nanoscale devices.^[24] This issue can be divided into two categories: (i) orientation of nanodomains to the substrate/surface, (ii) in-plane (lateral) order and orientation of nanodomains.

As described in the previous section, the major axis of the cylindrical or lamellar nanodomains (for spheres, there is no major axis so that they do not need to be considered) is generally formed parallel to the interfaces due to the preferential interaction between a block and an interface. The control of this preference is a key factor to achieve nanodomains normal to the interfaces.

The most popular approach to control the interfacial interaction is the layer of random copolymers of which chemical components are same with the target BCPs.^[25-27] By adjusting the composition of the random copolymer, the preference of each block to an interface can be balanced (usually called "neutralized") when a layer of this random copolymer is placed between the BCP film and a surface.^[27] This neutralized surface leads to the perpendicular orientation of BCP nanodomains. Other methods for modification of surface characteristics such as self-assembled monolayer,^[28,29] roughened surface,^[30] and chemical prepatterns^[29,31,32] are also

known to induce the perpendicular orientation of BCPs. Instead of controlling the interfacial interaction, perpendicular nanodomains can be also obtained by the application of external compulsions, such as applying electric or magnetic fields across the film, which help to overcome the preferential interactions.^[33,34]

In-plane orientation of BCP nanostructures is another issue in the practical application of the BCP thin film. Due to the self-assembling nature of BCPs, their nanostructures generated on a planar thin film can propagate in any in-plane direction so that generally form randomly oriented structures. For example, in-plane cylinders of BCP on a flat substrate exhibit fingerprint-like shapes without any specific orientation.^[35] So, to achieve the desired nanostructures from the BCP thin film, there should be additional constraints to force the in-plane orientation of BCP nanodomains in a specific direction.

Directed self-assembly (DSA) is the most popular state-of-art technique to handle the lateral order of BCP, which combines bottom-up self-assembly with top-down lithography.^[36-41] Patterns on a substrate generated by conventional lithography, such as e-beam lithography, I-line lithography, and EUV lithography, guide the orientation and the positional order of BCP nanodomains for laterally ordered nanostructures. The DSA is broadly classified into graphoepitaxy^[38,39] and chemoepitaxy^[40] according to the nature of the pre-written pattern on the substrates. Graphoepitaxy utilizes the topographical features of pre-patterned substrates. When a BCP film confined between the walls of topography, the chemical preference of a particular block to the topographic walls induces parallel nanodomains along the walls, resulting in the directional guidance as shown in **Figure 1-4a**. In chemoepitaxy, chemically distinctive patterns with desired orientation are written on the substrate prior to the deposition and self-assembly of BCP film, which induces the selective positioning of each nanodomain of BCP block replicating the underlying patterns as shown in **Figure 1-4b**. Since the current lithography technology can offer from simple to complex patterns, DSA enables well-ordered nanostructures with various geometries to be prepared from BCP thin films.

Mechanical shear is a traditional but fancy tool to obtain BCP nanostructures with a specific orientation.^[41-46] To transmit shear stress and prevent the deterioration during the application of shear stress to the BCP thin film, elastic poly(dimethylsiloxane) (PDMS) pad is typically used. To impart the mobility of polymer chain to form morphology during shearing, annealing process using heat^{[41-^{43]} or solvent vapor^[44-46] is carried out, simultaneously. Directional shear stress is applied from the PDMS pad on the film, and the BCP nanostructures are generated as following the shear direction. The deformation and displacement of the PDMS pad are the source of this directional shear, which is achieved by the lateral drag with vertical press,^[41,42,44] the thermal expansion and contraction,^[43] or the swelling and deswelling of solvent.^[45,46] **Figure 1-5** shows the BCP nanostructures prepared by shearing. Compared to DSA, shearing has the advantages of the selection of substrate and the simplicity, due to the omitting lithography process.}

In addition, various methods including electric fields,^[47] temperature gradient,^[48] and roll casting^[49] have been explored to control and enhance the lateral orientation of BCP nanostructures. Based on this development of techniques controlling the BCP

orientation, BCP nanostructures with well-controlled order promise the realization of many potential nanotechnological applications.

BCP templates

The well-defined nanodomains of BCPs can themselves serve as device materials, such as photonic crystals^[50] or stimuli-sensitive materials.^[51] Moreover, BCP nanostructures in thin films can be used as templates to fabricate nanopatterns of functional materials.^[52,53] Patterned materials with specific properties, such as inorganic nanostructures, nanopores, nanoparticle assemblies, can be prepared for various nanotechnology applications.

One of the most actively studied areas in the BCP templating process is the use of block copolymers as lithographic masks.^[54-57] In conventional lithography, the fabrication of smaller features needs more advanced equipments, resulting in the drastic increment of process cost. Furthermore, small deviations in process condition, such as the resist chemistry, exposure dose, or post-exposure bake temperature, can all lead to relatively large variations in the final structure. However, BCP nanostructures, of which morphology and size are easily tuned and determined by adjusting their molecular weight and composition, are relatively cost-effective due to the self-assembling nature of BCPs. In the lithography process using BCPs, two-dimensional nanostructures of BCPs, including close-packed spheres,^[54,55] in-plane or perpendicular cylinders,^[55,56] and perpendicular lamellae,^[57] can be fabricated on various substrates. By choosing the BCP blocks with different etching sensitivities, those BCP nanostructures can successfully act as an etching mask for an ion-etching

process, which transfers high-resolution periodic nanostructures to the substrate with high fidelity (**Figure 1-6**).

BCP nanostructures in thin films have also been investigated as containers for the spatially defined functional molecules and nanoclusters.^[58-62] Since the BCP is composed of chemically distinct blocks, its nanostructure in thin film naturally can be regarded as a chemical nanopattern for the selective deposition or synthesis of functional materials when using appropriate block pairs. There are two general approaches which differ in the process step when a target functional material is introduced.

In the first, functional molecules,^[58] precursors,^[59] or nanoclusters^[60] are deposited on well-defined BCP nanopatterns. By the chemical affinity, those guest materials are selectively deposited on or incorporated in the preexisting nanodomains of a specific block. After the introduction of the guest materials, a functional nanopattern is the resulting film itself, or be formed by the subsequent synthesis if necessary. Since the functional materials are introduced after the formation of BCP nanostructures, the final structure of functional materials can be easily predicted and targeted by using the BCP template having a desired nanostructure.

The second approach involves the incorporation of functional materials into one of the BCP blocks or homogeneously mixed with the block copolymer, as prior to the fabrication of the film.^[61,62] The subsequent self-assembly process after film casting can give functionality within one of the nanodomains. Naturally, tuning of the quantity is relatively easier since the manufacturer knows the amount of materials introduced. However, there is always a risk that the self-assembling behavior of the

BCP can be altered by the introduced materials causing unwanted final nanostructures. Thus, this approach is usually used when the subsequent self-assembly process is not required, small amount of guest materials is used, or the exact stoichiometry is crucial.

Even overlooking the chemical affinity of BCP nanopatterns, surface topography generated on a BCP thin film can attract and trap the guest materials, physically. Porous or grooved topography with nanoscale features is generated on the BCP thin film by removing or reconstructing nanodomains of one block, selectively. For example, a hexagonally-packed nanoporous film is formed from the perpendicular cylinders of BCP thin film on a substrate, by removing the minor block.^[55] A periodic array of nanogrooves is obtained from the perpendicular lamellar or the parallel (inplane) cylinders.^[55,57] Functional nanostructures that resemble the mother BCP can be simply formed by filling these nano-sized vacancies. Deposition of a material onto an entire film area and lift-off the polymeric residual is the simplest way as in the common lithographic fabrication.^[63,64] Coating of a precursor or nanoparticle solution is another option.^[65] Especially, capillary force generated during spincoating physically drives the solute materials into the compartments, which helps functional nanostructures with desired shape formed without subsequent process. Figure 1-7 shows the examples of various functional nanostructures fabricated by using this physical templating method.

Optical materials in nanostructures

The interaction of materials with electromagnetic waves strongly depends on their size and structures. Especially, when the size and shape of materials is reduced to nanoscale, those optical interaction and properties become distinct and unique from those of bulk counterparts.^[66] Metal nanoparticles are the most commonly known examples showing this nano-sized effect. They exhibit various visible colors available to be tuned by changing their size and shape in nanoscale, which are definitely distinct from their well-known bulk gloss.^[67,68]

These unique appearances of metal nanoparticles arise from the optical interaction called the localized surface plasmon resonance (LSPR) resulted from the collective oscillation of conduction electrons within the metal nanoparticles by incident light with a proper frequency. This induces strong absorption and scattering of light causing the specific color of the nanoparticles in a solution, and the large enhancement of the local electric field, inside and near the nanoparticles. The LSPR behaviors are strongly dependent on the material properties of nanoparticles, including geometrical shape, composition, and surrounding environments of nanoparticles. Moreover, the close approach of these nanoparticles can induce the coupling of LSPRs resulting in the change of resonance energy and also further enhancement of the electric field, so that enables the applications in the numerous aspects, such as photochemical reaction,^[69] plasmon-enhanced spectroscopy,^[70,71] metamaterials,^[72] and photothermal conversion.^[73] In this regard, many researches have been conducted on the synthesis of metal nanoparticles with various geometries
and further arranging or assembling them in proximity into a desired shape, to tune the LSPR characteristics.

light-emitting materials Nanostructured are also attractive optical nanomaterials.^[74] Light-emitting nanomaterials, including quantum dots.^[75] upconversion nanoparticles,^[76] and perovskite nanocrystals,^[77] can present strong emission with various colors by changing their size, shape, and composition. Among these light-emitting nanomaterials, perovskite crystals, which are also promising materials for the solar cell applications, have been widely investigated these days. Perovskites refer to crystalline compounds having orthorhombic crystal structure identical to a calcium titanium oxide mineral (CaTiO₃) found in nature, of which chemical formula can be generally represented as ABX₃. Lead halide perovskite crystals (APbX₃; A = Cs or alkyl ammonium in usual, X = halides) exhibit excellent optoelectric properties required for light-emitting devices, such as high quantum yields, tunable bandgap, narrow emission width. So, they have been synthesized and employed in a variety of light-emitting fields, including lasing,^[78,79] light-emitting diodes,^[79] and photodetectors.^[80]

Beyond the purpose of tuning their unique optical properties, the ability to fabricate nanostructures of optical materials is also essential for practical nanodevices which require precise size and positioning in nanoscale. Templates with nano-sized features can be usually employed for specifying the location of these optical materials to achieve this goal. Also, by synthesizing materials within a template as described in the previous section, the control of the size and location of materials can be achieved at once. Top-down lithography techniques are common methods of preparing templates or even fabricating nanostructures directly, but it always bears the ineffectiveness of high-cost and possible damage risk. In this regard, bottom-up approaches, including self-assembly of BCPs, can be nice alternatives for the fabrication of nanopatterns of optically functional materials.

Aims and objectives

In this dissertation, the fabrication of optically functional nanostructures by the assist of BCP templates is described. In chapter 2, dichroic plasmon superstructures, which are composed of end-to-end assemblies of Au nanorods (NRs) over a macroscopic area, are prepared by utilizing the directed self-assembly of BCP. The superstructures exhibit dichroic optical properties under polarized lights in orthogonal directions and also can be transferred to various substrates without structural deterioration. In chapter 3, macroscopically aligned nanodomains of BCPs in thin films prepared via simultaneous shearing and solvent vapor annealing at room temperature are demonstrated. The shear-aligned nanodomains are utilized as a chemical template for patterning fluorescent molecules and as a physical template for arranging plasmonic NRs. In chapter 4, the fabrication of fluorescent perovskite nanopatterns by the selective deposition of perovskite precursors on BCP templates is presented. By combining perovskite processing and BCP nanopatterning techniques, fluorescent nanopatterns of perovskite with various structures and compositions can be achieved.

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Figure 1-1. Phase diagrams for a linear A-*b*-B BCP obtained from: (a) SCFT prediction; (b) real BCP system.^[3]



Figure 1-2. Possible configurations of lamellae in BCP thin films on substrates.^[16]



Figure 1-3. Schematic phase diagram showing the effect of solvent uptake on BCPs (polystyrene-*b*-poly(4-vinyl pyridine) (PS-b-P4VP) with 2-(4'-hydroxybenzeneazo) benzoic acid) in different solvents. Trajectory A – D represent swelling in a nonselective solvent, strongly PS selective solvent, chloroform, 1,4-dioxane, respectively. Trajectory E represents the BCP with larger molecular weight swollen in chloroform.^[22]



Figure 1-4. Control of BCP orientation by DSA techniques: (a) graphoepitaxy;^[39](b) chemoepitaxy.^[40]



Figure 1-5. Directed nanostructures of BCPs by the assist of shearing methods: (a) lateral drag of PDMS pads;^[41] (b) solvent swelling and deswelling of PDMS pads.^[45]



Figure 1-6. The use of BCP nanostructures as etching masks for pattern transfer: (a) by using spherical or cylindrical morphologies;^[55] (b) by using perpendicular lamellar morphology.^[57]



Figure 1-7. Nanostructures fabricated by using BCP thin films as physical templates.^[64,65]

Chapter 2

Dichroic Plasmon Superstructures of Au Nanorods over Macroscopic Areas via Directed Self-Assemblies of Diblock Copolymers[†]

†This chapter is slightly modified version of the published article: <u>H. Kang</u>, S.-S. Kim, S.-I. Yoo, and B.-H. Sohn, *Adv. Mater. Interfaces*, **2019**, *6*, 1901257.

Introduction

Dichroic plasmon superstructures, which exhibit polarization-dependent extinction, have attracted considerable attention because they are intimately related to optoelectronic applications for waveguides,^[1,2] optical switching,^[3] imaging,^[4] and polarization-dependent field enhancement.^[5,6] As dichroism in plasmonic systems is derived from structural anisotropy, Au NRs have been the key elements in many studies. As is well known, Au NRs have two distinct LSPR modes due to the transverse and longitudinal electron oscillations, which correspond to light absorption and scattering along the short (transverse mode) and long (longitudinal mode) axes of the NRs, respectively. As a result, the two LSPR modes of Au NRs can be excited by linearly polarized lights with orthogonal directions, exhibiting an intrinsic dichroic property.^[7-12] While individual Au NRs inherently have an angulardependent plasmonic property, superstructures composed of multiple NRs can strongly enhance the dichroic function.^[6-8,10-23] In particular, end-to-end assemblies of Au NRs can provide directional plasmonic coupling along the NR alignment.^{[6,10-} ^{21]} which is potentially useful for harvesting, propagating, and angulating the energy of light.

In colloidal systems, end-to-end assemblies of Au NRs have been prepared by utilizing site-selective ligand exchange reactions.^[13-19] In an aqueous solution, Au NRs are mostly stabilized by cetyltrimethylammonium bromide (CTAB) surfactants. Interestingly, the local density of CTAB at the ends of NRs is much lower than along the longitudinal side. This can allow selective functionalization at the end of Au NRs by thiol-containing ligands such as bifunctional molecules,^[13-15] polymers,^[16-18] or

proteins.^[19] Subsequently, by promoting specific chemical or physical interactions between the anchored ligands, Au NRs can bind one another into a linear direction. However, even though many research groups have reported the end-to-end assemblies of Au NRs, anisotropic optical properties have not been rarely reported only under specific conditions^[24,25] because of the random orientation of NR assemblies. This indicates that the orientation of NR assemblies must be engineered on a solid substrate at the macroscopic scale for practical measurement and applications.

Wrinkle-assisted templates and BCP thin film may represent the current state-ofart approach for the issue.^[3,5,6,21-23] In the wrinkle-assisted approach, the height variation in the wrinkled structures can exert capillary forces on the colloidal particles during the coating process to deposit them onto the engineered wrinkles.^[3,5,21] Recently, Linear chains of spherical NPs^[3,5] as well as end-to-end oriented NRs^[21] at the centimeter scale were reported, which exhibited polarizationdependent optical properties. In the case of the BCP approach, similar topological BCP templates can be employed to produce end-to-end assemblies of Au NRs.^[6,22,23] However, as the orientation of BCP nanodomains is isotropic in nature, the resulting end-to-end NR assemblies on the substrate did not have anisotropic properties.^[22,23] In this regard, DSA of BCPs is required to engineer the orientation of BCP nanodomains. One of the advantages of DSA is that various nanoscale patterns such arrays, bends, and junctions can be realized beyond wrinkled lines,^[26,27] which is potentially useful for advanced photonics. Recently, linearly oriented end-to-end assemblies of Au NRs by graphoepitaxy of BCPs were reported.^[6] Although they exhibited polarization-dependent surface-enhanced Raman scattering (SERS) enhancement under microscale Raman measurement, large-area macroscopic endto-end assemblies of Au NRs have not yet been reported.

In this chapter, DSA of polystyrene-*block*-poly(methyl methacrylate) (PS-*b*-PMMA) copolymers on lithographic patterns was utilized to exploit the end-to-end alignment of Au NRs at the centimeter scale on the substrate. The prepared end-to-end NR assemblies exhibited strong plasmonic coupling among longitudinal LSPR modes along the alignment direction, which was manifested by an extensive spectral shift in the extinction. Because the resulting NR assemblies had a uniform orientation over the entire substrate, they exhibited a strong dichroic property with polarization-dependent extinction. In particular, both transverse and longitudinal LSPR peaks could be turned on and off under two polarized lights in orthogonal directions. It was further demonstrated that the prepared NR assemblies could be transferred to various substrates such as quartz, flexible poly(ethylene terephthalate), and PDMS elastomers without deteriorating the original alignment, affording opportunities for developing polymer-based dichroic optical systems.

Experimental Section

Materials: CTAB, sodium salicylate, gold chloride trihydrate, sodium borohydride, silver nitrate, ascorbic acid, and toluene were purchased from Sigma Aldrich. PS-*b*-PMMA was purchased from Polymer Source, Inc. The molecular weights of PS and PMMA were 46,100 g mol⁻¹ and 21,000 g mol⁻¹, respectively. The polydispersity index was 1.09.

Synthesis of Au NRs: Au NRs were synthesized by the seed-mediated-growth method with binary surfactants of CTAB and sodium salicylate as described in the literature.^[28] A seed solution was prepared by adding an ice-cold aqueous solution of NaBH₄ (0.6 mL, 0.01 M) to an aqueous mixture solution of HAuCl₄ (0.25 mL, 0.01 M) and CTAB (9.75 mL, 0.1 M). Seed solution (1.6 mL) was then added to the growth solution, which was prepared by mixing surfactants (500 mL of CTAB 0.1 M and sodium salicylate 0.02 M), AgNO₃ (12.0 mL, 0.004 M), HAuCl₄ (500 mL, 0.01 M), and ascorbic acid (2.0 mL, 0.064 M). After 12 h, Au NRs were centrifuged from their aqueous solution and re-dispersed in deionized water several times.

Fabrication of PS-b-PMMA thin films: To fabricate the line-patterned substrate, we used a standard lithography with reactive ion etching on a Si wafer having a SiO₂ layer for production of a line-patterned substrate. All substrates were cleaned in a piranha solution (70:30 v/v of concentrated H₂SO₄ and H₂O₂) at 90 °C for 30 min, thoroughly rinsed with deionized water several times, and then blow dried with nitrogen. PS-b-PMMA was spin-coated onto a cleaned substrate at 4,000–6,000 rpm from its toluene solution (0.9 – 1.0 wt%) and annealed at 230 °C for 8 – 48 h in vacuum. Thereafter, PMMA domains were selectively removed by oxygen plasma (42 mTorr, 80 W, 6 s).

Alignment of Au NRs: After removal of PMMA blocks, Au NRs were spin-coated onto the film at 1,300 – 2,500 rpm for 1 min. To obtain the desirable amount of Au

NRs on the substrate, spin-coating was repeated several times. To transfer aligned Au NRs to other substrates, a thin film of PMMA was coated directly onto Au NRs, delaminated with Au NRs from the substrate by dissolving the underlying SiO₂ layer with an aqueous solution of sodium hydroxide (1.0 M), and floated on water. Then, the PMMA film with Au NRs was transferred to the other substrates such as quartz, flexible poly(ethylene terephthalate), and PDMS elastomers.

Characterization: Field-emission scanning electron microscopy (FE-SEM) was performed on a Hitachi S-4300 at 15 kV. Atomic force microscopy (AFM, Nanoscope IIIA, Digital Instrument) was used in the tapping mode with Si cantilevers. Transmission electron microscopy (TEM) analysis was performed on a Hitachi 7600 operating at 100 kV. UV-Vis absorption spectra were recorded on a Varian Cary-5000 spectrophotometer.

Results and Discussion

To deposit Au NRs on the grooved BCP nanochannels, the experimental parameters such as the physical dimension and surface characteristics of building blocks (namely, NRs and BCPs), concentration of Au NRs, and coating conditions need to be carefully adjusted. As the complete characterization of these experimental parameters is demanding, optimization of the experimental conditions was performed, which could produce the end-to-end NR alignment over the entire substrate with a uniform orientation. To this end, Au NRs were first synthesized by a seed-mediated growth method by employing binary surfactants of CTAB and sodium salicylate. It has been reported that the addition of aromatic additives such as salicylate to the growth solution of NRs significantly increases the structural uniformity of the Au NRs.^[28] As shown in the TEM image (**Figure 2-1a**), the synthesized Au NRs are homogeneous in size and shape. The average diameter and length of the Au NRs were determined as 19 ± 2 nm and 43 ± 3 nm, respectively, leading to the transverse (T) and longitudinal (L) peaks of LSPR at 515 and 618 nm, respectively, in the extinction spectra (**Figure 2-1b**). In principle, the longitudinal LSPR peaks of Au NRs can be engineered over a wide range of wavelengths from the visible to near-IR region by tuning the aspect ratio.^[7-9,28] Nevertheless, NRs with a relatively small aspect ratio = 2.26 were employed because the short NRs would be more suitable for the dense packing on the grooved BCP nanopatterns.

Before investigating the guided NR assemblies on BCP nanopatterns, the colloidal Au NRs were simply spin-coated on a flat substrate. Even though Au NRs are irregularly coated on the substrate (**Figure 2-1c**), they are densely packed inside the agglomerated region as shown in the enlarged SEM image. Interestingly, the Au NRs tended to assemble into either an end-to-end or a side-by-side arrangement, presumably due to their inherent anisotropic geometry, although the overall orientation of NRs was isotropic. The extinction spectrum of the agglomerated NRs exhibited a broad featureless peak above 500 nm (**Figure 2-1d**), which could be ascribed to the uncontrolled plasmon hybridization from randomly orientated NRs in the agglomerated region.

For guided arrangement of Au NRs, a thin film of cylindrical PS-*b*-PMMA copolymers oriented parallel to the substrate was prepared on a Si wafer, and was

exposed to O₂ plasma. It needs to be noted that PS block has a higher etching resistance than a PMMA block.^[29-31] Therefore, the parallel cylindrical patterns in the original PS-*b*-PMMA thin film could be transformed to grooved nanochannel after removing the nanodomains of the PMMA block, which was confirmed by the corresponding FE-SEM image (**Figure 2-2**). The average periodicity and depth of nanochannels were evaluated as 44 ± 3 nm and 5 ± 2 nm, respectively, from AFM analysis (**Figure 2-3**). From the height profile, the average width of the nanochannels was taken as half of the periodicity, the value of which was 22 nm.

Au NRs were spin-coated onto the grooved nanochannel by adjusting the number of coating repetitions, concentration of NR solution, and spinning rate. Initially, the NR solution (5 mg mL⁻¹) was spin-coated for 1 time (2,000 rpm) to examine the feasibility of this approach. Under this condition, Au NRs were mostly placed inside the trench with their long axis aligned in the direction of the nanochannels (**Figure 2-4a**). However, the number of deposited NRs was very small, and the Au NRs were dispersed in a more or less isolated form. To increase the population of deposited Au NRs, the number of coating repetitions was increased to 3 (**Figure 2-4b**) and 7 (**Figure 2-4c**). As confirmed by FE-SEM images, the density of deposited Au NRs noticeably increased with the successive coating processes. In addition, as the orientation of Au NRs was guided by the contour of the fingerprint-like nanochannels, the increased NR density eventually resulted in the end-to-end approach of dissimilar NRs. Further increases in the coating time increased the number of deposited NRs. However, it needs to be noted that some NRs, that were placed out of the trench, behaved as defects during the successive coating processes. As a result, the defect area gradually enlarged with coating repetitions to deteriorate the overall NR alignment. For this reason, the concentration of the NR solution (10 mg mL⁻¹) and the detailed coating conditions were adjusted in a trial-error manner until both the density and the degree of orientation of deposited NRs were maximized. The optimized NR alignment is shown in **Figures 2-4d** and **4e**. From the large-area FE-SEM image (**Figure 2-4e**), it can be observed that Au NRs almost cover the grooved nanochannel as a monolayer without noticeable agglomeration. A closer examination of the NR assemblies further revealed that several Au NRs were closely packed as short chains, which could be referred to as plasmonic oligomers.^[8,15,17,18,20] However, individual oligomers were more or less separated from each other, resulting in a local variation in the gap distance between adjacent NRs. Nevertheless, if only the end-to-end distance of NRs inside the oligomers was considered, an average gap distance of 2.2 nm was evaluated from the FE-SEM image.

The selective delivery of NR into the grooved nanochannels could be ascribed to a capillary response.^[6,20-23] When NR solution was dropped on the substrate, Au NRs would have a minor tendency to deposit in the BCP nanochannels by van der Waals (vdW) interactions. However, in general, vdW energy could be negligible compared with thermal energy; therefore, the Au NRs would be mostly in the unbound state in solution.^[32,33] However, during the coating process, as the solvent evaporates, the height variation in the grooved nanochannels can act as pinning sites. The colloidal NR solution would pin in between the adjacent peaks in the nanochannels by forming a meniscus for the capillary interaction.^[6,20,23] It would be worthwhile to note that the capillary energy can be several orders of magnitude larger than thermal energy.^[6,23] In addition, as the capillary energy can be maximized when the long axis of NRs is aligned parallel to the orientation of the nanochannels,^[6,23,34] Au NRs can be deposited along with the grooved nanochannels. The guided NR assembly would be also supported by commensurability between the diameter of NRs (19 nm) and width of (22 nm, half of the periodicity) the nanochannels.

Since Au NRs were deposited along the trench of the nanochannels, they were linearly aligned to induce end-to-end plasmonic coupling. Nevertheless, if the Au NRs in neighboring trenches were considered, a lateral NR assembly could be also recognized, which could contribute to the side-by-side plasmonic coupling. Under this condition, it needs to be noted that the strength of plasmonic coupling is highly sensitive to the proximity of NRs, and exponentially decreases with the gap distance between adjacent NRs according to the plasmon ruler equation.^[10-12,35] As the gap distance in the end-to-end NR assemblies (2.2 nm) determined from the SEM image is much shorter than that in side-by-side NR assemblies (19.8 nm), the guided NR assemblies can be mostly dominated by end-to-end plasmonic coupling. Considering the preferential NR orientation, the extinction spectra of NRs in the grooved nanochannels (Figure 2-4a - 4d) are examined in Figure 2-4f. To clarify the change in LSPR peak, the transverse (530 nm) and longitudinal (615 nm) LSPR peaks of Au NRs are denoted with dashed lines. Upon increasing the NR density in the grooved pattern, the relative intensity of the longitudinal LSPR peak at 615 nm was gradually reduced, and new peaks above 700 nm appeared and increased in intensity. As the longitudinal peak of Au NR has been found to exhibit a strong red-shift with end-toend alignment,^[10-19,21] the appearance of the new peaks can be mostly attributed to

the formation of end-to-end NR assemblies inside the grooved nanochannels. Also note, in comparison with **Figure 2-1b**, transverse LSPR peak was shifted from 515 nm to 530 nm in **Figure 2-4f**. Since lateral (i.e. side-by-side) interaction between adjacent NRs could induce red-shift of transverse LSPR peak,^[10,12] this observation indicated that side-by-side plasmonic coupling could not be completely ruled out in the assembled NRs.

Despite the successful formation of end-to-end NR assemblies, the overall orientation of NRs on the substrate was not uniform because of the isotropic nature of the fingerprint-like patterns. To prepare dichroic plasmon superstructures, the orientation of the initial BCP nanodomains must be engineered before the deposition of Au NRs. In this regard, topological patterns with 500 nm line-width, 50 nm depth and 1000 nm periodicity were fabricated on a Si wafer (patterned area = approximately 9 mm × 9 mm). Onto the Si pattern, PS-*b*-PMMA thin films were spin-coated, thermally annealed, and exposed to O_2 plasma as in the previous conditions. Owing to the preferential interaction between the Si surface and PMMA blocks,^[36-38] the produced BCP nanochannels were linearly oriented parallel to the topological patterns (**Figure 2-5 and Figure 2-6**). In the SEM image, multiple nanochannels were present in each Si trench because the width of Si pattern was much larger than that of BCP pattern. The numbers of BCP nanochannels in a given Si trench were slightly different (12–13 nanochannels in usual), which could be ascribed to the slight variation in the width of Si patterns.^[39-41]

Confirming the directed BCP assemblies, Au NRs were spin-coated on the linearly oriented nanochannels. As shown in **Figure 2-7a** – **7d**, the number of Au NRs inside

the nanochannels can be engineered by adjusting the concentration of NR solution, number of coating times, and spin rate (see figure caption for details). By examining the SEM images, it was determined that Au NRs were placed inside the grooves aligned in the direction of nanochannels. The guided NR assemblies in the nanochannels can also ascribed to the capillary energy as discussed before. As expected, as the number of NRs increases, the gap distance between adjacent NRs in the linear grooves becomes increasingly small, and eventually NRs are tightly packed into an end-to-end configuration. From the SEM image of the optimized sample (Figure 2-7d), the gap distance between adjacent NRs from the end-to-end (in the same nanochannel) and side-by-side (in the different nanochannels) configurations were determined as 2.4 nm and 15.6 nm, respectively. This indicated that the end-to-end plasmonic coupling was the predominant arrangement in the linear assemblies of NRs. Note, the lateral gap distance between NRs decreased slightly compared with that in curved nanochannels (19.8 nm). The observed decrease could be attributed to the change in periodicity of BCP nanochannels in the Si trench to satisfy the commensurability between BCP periodicity and the trench width.[39-41]

In the extinction spectra (**Figure 2-7e**), the longitudinal LSPR peak was gradually red-shifted with the end-to-end plasmon coupling as in the previous case (**Figure 2-4f**). In comparison with the curved NR arrangement, the strength of plasmon coupling was increased in the linear NR assemblies, which could be assessed by the more red-shifted LSPR peaks. For instance, longitudinal LSPR peaks were significantly red-shifted up to 651 nm and 794 nm in **Figure 2-7e**. In principle, the

degree of red-shift is related to the gap distance and the length of end-to-end NR assemblies.^[7,8,10-19] As gap distances between adjacent NRs were quite comparable in **Figure 2-4e** (2.2 nm) and **Figure 2-7d** (2.4 nm), the high degree of red-shifts in the linear assemblies of NRs could be attributed to the enlarged length of NR oligomers. It would be less efficient for NRs to be tightly packed into end-to-end assemblies in the curved grooves in the case of isotropic nanochannels.

Based on the observation, it would be interesting to find the correlation between the degree of red-shifts in the extinction with the length of NR oligomers. Recently, it has been reported that peak position of the red-shifted extinction (λ) follows a single-exponential decay expression of $\lambda = A - Bexp(-N/C)$, where A, B, and C are fitting constants that are associated with the aspect ratio of NRs, and N is the average number of NRs in the end-to-end assemblies.^[15,18] In the literature, the values of A, B, and C, which can be determined by 3D finite element simulations, were reported only for NRs having aspect ratio of integer numbers.^[15] Since the aspect ratio of Au NRs in this study was 2.3, the precise values of A, B, and C could not be directly obtained from the literature. Nevertheless, the aspect ratio of 2.0 was simply used in order to utilize the reported values of A = 816 nm, B = 306 nm, C = 2.2without additional calculation. The peak position of red-shifted extinction of NR assemblies were 730 nm and 794 nm in the curved (Figure 2-4f) and the linear (Figure 2-7e) nanochannels, respectively. By inserting these values in $\lambda = A - A$ Bexp(-N/C), the values of N were determined as 2.8 and 5.8 for oligometric chains in the curved and the linear nanochannels, respectively.

Despite the mismatch in the aspect ratio, the result was in a good agreement with

the closer and tighter packing of Au NRs in linear assemblies. However, it must be noted that the single-exponential equation was obtained by simulating perfectly aligned linear end-to-end NR assemblies with inter-particle gap of 1 nm. However, the prepared NR assemblies was obviously deviated from the perfect order and interparticle gap was 2.2 nm (or 2.4 nm) in this study. Hence, there would be more or less errors on the calculated N values.

Also note, the linear alignment of Au NRs resulted in additional peaks at ~1,033 nm and ~1,516 nm with higher intensities than those of LSPR modes. As these peaks in the near-infrared region were absent in the end-to-end NR assemblies from isotropic patterns (**Figure 2-4f and Figure 2-8**), these were not associated with plasmonic hybridization. Alternatively, these could arise from the diffraction effect of the linear pattern^[42,43] by filling the periodic lines with Au supported by quartz and polymers.

From the large-area SEM image (**Figure 2-9**), it was determined that most of the Au NRs were placed in the trench part of the pattern and only ~5% of deposited NRs were found in the mesa part. We noted that the randomly oriented NRs on the mesa could not be removed by adjusting the coating condition. To quantify the orientation of NRs, the average two-dimensional order parameter (*S*) is calculated as $S = \langle 2 \cos^2 \theta - 1 \rangle$, where θ is the angle of deviation of individual NRs from the direction of BCP nanochannels.^[21] Note, S = 1 corresponds to the perfectly oriented NRs, while S = 0 is an isotropic orientation. By analyzing the orientation angles of Au NRs that were deposited only in the trench region (**Figure 2-10**), the order parameter of S was evaluated as 0.72 with a standard deviation of 0.03. It would be

worthwhile to note that the order parameter was averaged from six independent samples, and the small standard deviation indicated the high level of reproducibility in our method. Also note, the macroscopic extinction spectra, which contains all the contribution from aligned NRs, were basically identical across different samples, validating the uniformity of the NR alignment.

In addition, the end-to-end NR assemblies on the Si pattern can be transferred to various substrates. For this purpose, a thin film of PMMA was coated directly onto Au NRs, delaminated with Au NRs from the substrate, and floated on water. Then, the PMMA film with the aligned NRs was transferred to a TEM grid, transparent quartz, flexible poly(ethylene terephthalate), and PDMS elastomers (Figure 2-11). After the transferring process, it was verified that the alignment of Au NRs was not deteriorated by TEM analysis (Figure 2-12), in which the alignment and population of Au NRs were almost identical to those in the original assemblies on the Si pattern (Figure 2-9). It also needs to be noted that the extinction spectra in Figure 2-7e were measured after being transferred to quartz, and therefore contained the peak of a PMMA support at 315 nm. Since the end-to-end NR assemblies were produced on macroscopic areas, they could exhibit optical anisotropy under differently polarized lights. When the direction of polarized light was orthogonal to the NR alignment (blue line in Figure 2-13), the transverse LSPR peak (denoted as blue arrows) was dominantly excited, while the longitudinal LSPR peaks (red arrows) were turned off. Under parallel polarization with respect to the NR alignment, the opposite trend was observed, in which only longitudinal LSPR peaks were promoted (red lines). It was further noted that the two peaks at wavelengths over 1,000 nm by grating effects also

could be turned on and off under different polarized lights.

Conclusion

A simple approach for the fabrication of dichroic plasmon superstructures over a macroscopic area is demonstrated by utilizing the directed self-assembly of PS-b-PMMA copolymers on lithographic Si patterns. Periodic nanoscale grooves from linearly aligned PS-b-PMMA copolymers facilitated the close packing of Au NRs into plasmonic chains with an end-to-end NR alignment, which induced the selective plasmonic coupling among longitudinal LSPR modes. As the overall orientation of NRs on the substrate was uniform, the prepared plasmonic superstructures exhibited polarization-dependent extinction in a manner which allowed both transverse and longitudinal LSPR peaks to be turned on and off under two polarized lights in orthogonal directions. The observed dichroic property would be further enhanced by increasing the relative portion of the Au NRs inside the trench by preventing the deposition of unaligned NRs on the mesa. In this regard, it would be interesting to decrease the width of mesa by lithographic process to reduce the number of NRs on mesa. In addition, since the capillary forces exerted on the Au NRs would be strongly dependent on the aspect ratio of NRs, the optimization of aspect ratio would further increase the order parameter and population of Au NRs in the trench region. In addition, the plasmonic superstructures could be transferred to various substrates without structural deterioration to allow the implementation of dichroic properties on various materials including flexible platforms. Therefore, this BCP approach for the dichroic plasmon superstructures could provide interesting opportunities for

novel optical systems necessitating plasmonic dichroism, such as polarizationdependent photothermal heating, which can enable thermal switching to control many chemical/physical transformations.

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Figure 2-1. (a, b) Au NRs in a solution state: (a) TEM image; (b) extinction spectrum. (c, d) Au NRs spin-coated on a flat substrate: (c) FE-SEM image; (d) extinction spectrum. The inset scale bar of the enlarged SEM image corresponds to 200 nm.



Figure 2-2. FE-SEM image of grooved nanochannels fabricated from the cylindrical nanostructures of PS-*b*-PMMA after removing PMMA blocks by O₂ plasma.



Figure 2-3. AFM image of nanochannels fabricated from the cylindrical nanostructures of PS-*b*-PMMA on a flat substrate. The height profile corresponds to the white line in the AFM image. The scale bar is100 nm.



Figure 2-4. (a–d) FE-SEM images of Au NRs placed in the grooves of plasmatreated PS-*b*-PMMA thin film with different NR densities. To control the NR density in the grooved pattern, the concentration of NR solution, spin rate, and number of coating processes have been adjusted: (a) 5 mg mL⁻¹, 2,000 rpm, and one time; (b) 5 mg mL⁻¹, 2,000 rpm, and three times; (c) 5 mg mL⁻¹, 2,000 rpm, and seven times; (d) 10 mg mL⁻¹, 1,300 rpm, and four times. (f) Extinction spectra of Au NRs in the grooved patterns with different densities. (e) Large-area FE-SEM image of Au NRs in the grooved pattern shown in (d). The scale bars in (a)–(d) and inset of (e) correspond to 200 nm.



Figure 2-5. FE-SEM image of linearly aligned grooves of plasma-treated PS-*b*-PMMA thin film on the lithographic pattern. The scale bar is 1 μ m.



Figure 2-6. AFM image of nanochannels fabricated from the cylindrical nanostructures of PS-*b*-PMMA on a patterned substrate. The height profile corresponds to the white line in the AFM image. The scale bar is 100 nm.



Figure 2-7. FE-SEM images of Au NRs placed in the aligned grooves of plasmatreated PS-*b*-PMMA thin film with different NR densities. To control the NR density in the aligned grooves, the concentration of NR solution, spin rate, and number of coating processes have been adjusted: (a) 3 mg mL⁻¹, 2,000 rpm, and four times; (b) 7 mg mL⁻¹, 2,000 rpm, and two times; (c) 7 mg mL⁻¹, 2,000 rpm, and three times; (d) 15 mg mL⁻¹, 2,500 rpm, and two times. (e) Extinction spectra of Au NRs in the aligned grooves with different densities. The scale bars correspond to 200 nm.



Figure 2-8. extinction spectrum of end-to-end NR assemblies in the isotropic nanochannels, measured in wide-range of wavelength.



Figure 2-9. Large-area FE-SEM image of Au NRs in linearly aligned grooves of plasma-treated PS-*b*-PMMA thin film shown in **Figure 2-5**. The scale bar is 1 μm.



Figure 2-10. (a) Color-mapped SEM image of **Figure 2-9** based on the angle between the long axis of each Au NR and nanochannel of the image; (b) histogram of the angles.



Figure 2-11. Photographs of transferred Au NRs to various substrates.



Figure 2-12. TEM image of aligned Au NRs embedded in a PMMA support for transferring them onto a quartz substrate. The scale bar is $1 \mu m$.



Figure 2-13. Polarization-dependent extinction spectra of aligned Au NRs on quartz substrate. The incident light is linearly polarized parallel (red line) and perpendicular (blue line) to the direction of NR alignment.

Chapter 3

Shearing with Solvent Vapor Annealing on Block Copolymer Thin Films for Templates with Macroscopically Aligned Nanodomains[†]

†This chapter is slightly modified version of the published article: <u>H. Kang</u>, K. Kim and B.-H. Sohn, *Nanotechnology*, **2020**, *31*, 455302.

Introduction

A strategy of template-assisted fabrications has been widely applied to the efficient creation of functional nanopatterns with electronic,^[1] optical,^[2] or magnetic constituents.^[3] For example, a nanoscale template with a well-defined geometry manufactured by e-beam lithography enabled plasmonic nanoparticles in a specific order to generate abnormal coupling of plasmonic resonances,^[4, 5] which would not be available without a guiding template.

A template constructed on a large area can also be an effective medium for macroscopic arrangements of nanoparticles in a particular orientation to deliver anisotropic characteristics in photonic or electronic functions.^[6,7] Especially, DSA of BCP nanodomains confined in lithographical patterns can provide a large-area template in a microscopic controlled order with a macroscopic specified orientation.^[8-10] In previous chapter, a template by the DSA technique allowed the anisotropic alignment of Au NRs in the nanogrooves originated from BCP nanodomains, leading to the polarization-dependent plasmonic extinction.^[11] In addition to a template based on physical confinement, BCP nanodomains can offer a chemical affinity of selective attraction to molecules^[12,13] or colloids^[14,15] so that a variety of applications as chemical templates can be expected with well-ordered BCP nanodomains.

To orient BCP nanodomains macroscopically, various techniques such as DSA,^[8,9] mechanical shearing,^[16,17] electric or magnetic field,^[18,19] and zone annealing^[20,21] have been developed. Especially, shearing method is suitable for a large-area thin film and eliminates the necessity of pre-patterned substrates. A pad of PDMS placed

on a BCP film can be simply displaced parallel to the film surface at an elevated temperature, resulting in the shear-induced orientation of BCP nanodomains. In order to guarantee chain mobility of BCP during the shearing process, thermal annealing above the glass transition temperature of BCP is usually favored. Since annealing at a high temperature would occasionally cause undesirable oxidation or degradation of heat-sensitive moieties in BCP or attached to BCP such as fluorophores containing carbon double bonds, solvent vapor annealing can be an alternative to lower an annealing temperature. Solvent molecules infiltrated to BCP can reduce the glass transition temperature and also bring down the effective interaction parameter.^[22] Recently it was reported that solvent annealing improved the quality of aligned BCP nanodomains obtained by thermal shearing.^[23] There are several reports on simultaneous shearing and solvent annealing on BCP thin films^{[24-} ^{26]} Even with solvent annealing, however, shearing on a large-area BCP film at room temperature is limited because it requires a proper choice of solvent, which should be miscible with both blocks of BCP and volatile at room temperature with an ability of swelling a PDMS pad.

In this chapter, the large-area orientation of BCP nanodomains by simultaneous shearing and solvent vapor annealing at room temperature with an appropriate solvent or mixture to the corresponding BCP was demonstrated. Then, the shear-aligned nanodomains were applied to a chemical template for patterning of fluorescent molecules and a physical template for positioning of Au NRs.

Experimental Section

Materials: Polystyrene-*b*-poly(4-vinyl pyridine) (PS-*b*-P4VP) and PS-*b*-PMMA were purchased from Polymer Source, Inc. The number-average molecular weight (M_n) of PS-*b*-P4VP and PS-*b*-PMMA were 69,000 g mol⁻¹ ($M_n^{PS} = 51,000$ g mol⁻¹; $M_n^{P4VP} = 18,000$ g mol⁻¹) and 67,100 g mol⁻¹ ($M_n^{PS} = 46,100$ g mol⁻¹; $M_n^{PMMA} = 21,000$ g mol⁻¹), respectively. All other chemicals were purchased from Sigma-Aldrich.

Synthesis of BODIPY-functionalized PS-b-P4VP and Au NR: 4,4-difluoro-4-bora-3a,4a-diaza-*s*-indacene (BODIPY) with alkyl bromide was synthesized as described in our previous publication.^[27] BODIPY (760 mg, 54% yield) was firstly synthesized and then modified with alkyl bromide, resulting in an orange-red crystalline solid (470 mg, 86% yield). BODIPY with alkyl bromide (6 mg) was mixed to a toluene solution of PS-*b*-P4VP (1.0 wt%, 5.0 g). The solution was heated at 75 °C for 6 h and then poured slowly in hexane (50 mL). The precipitate of BODIPYfunctionalized PS-*b*-P4VP was purified and dried at 50 °C for 24 h. As explained in previous chapter,^[11] Au NRs were also synthesized by the seed-mediated-growth method with binary surfactants of CTAB and sodium salicylate.

Preparation of thin films and templates: Silicon wafers and quartz substrates were cleaned using piranha solution (70:30 v/v of concentrated sulfuric acid and hydrogen peroxide), thoroughly rinsed with deionized water, and then dried with N₂. Quartz substrates were used only for the measurement of extinction spectra. A thin film of PS-*b*-P4VP or BODIPY-functionalized PS-*b*-P4VP was spin-coated from its toluene

solution (0.9 wt%) onto a cleaned substrate at 3,000 rpm for 30 s. A spin-coated film was exposed to chloroform vapor in a glass jar for 30 min at room temperature. A jar (125 mL) with chloroform (10 mL) was first sealed for 1 day. Then, a spin-coated film on a substrate was placed in the sealed jar. After 30 min, the film was taken out from the jar. For shearing, a PDMS pad of ~ $1.3 \times ~1.3 \text{ cm}^2$ was swollen with chloroform and placed on a BCP film with an additional weight (500 g) on it. Then, shear stress (~13 kPa) was applied to the PDMS pad for 5 s in the lateral side by using a weight (230 g) in the downward direction. (**Figure 3-1**) For PS-*b*-PMMA, a mixed solvent of acetone and cyclohexane (1:1 v/v) was used. Shear stress (~16 kPa) was applied for 10 min. In addition, a shear-aligned film of PS-*b*-P4VP was immersed in 0.05 mM BODIPY in ethanol for 1 h, thoroughly rinsed, and then dried. For PS-*b*-PMMA, PMMA block was selectively etched by oxygen plasma (42 mTorr, 80 W, 6 s). Au NRs were also spin-coated (1,500 rpm, 60 s) on a PMMA-etched film.

Characterizations: FE-SEM was performed on a Hitachi S-4300 at 15 kV. AFM (Nanoscope IIIA, Digital Instrument) was used in tapping mode with a Si cantilever. TEM analysis was performed on a Hitachi 7600 operating at 100 kV. UV-Vis absorption spectra were recorded on a Varian Cary-5000 spectrophotometer. For extinction spectra with the polarized incident light, a linear polarizer was inserted between the sample and the light source of the spectrometer. The polarizer was adjusted to make the polarized incident light parallel or perpendicular to the shear direction of the sample.

Results and discussion

PS-b-P4VP, which has 24 vol% of the P4VP block, was employed to obtain cylindrical P4VP nanodomains in a PS matrix. Firstly, a morphology of PS-b-P4VP in a thin film after solvent vapor annealing was investigated. By spin coating, a film with a thickness of ~31 nm was prepared and then annealed in chloroform vapor. It should be note that that chloroform is a non-selective solvent for PS and P4VP, which dissolves both blocks. Since the surface of the annealed film was almost flat, it was necessary to enhance the topographic contrast on the film for SEM characterization. The film was briefly dipped in ethanol, a selective solvent for P4VP, and dried in air, which resulted in collapse of P4VP nanodomains by selective swelling and subsequent deswelling.^[15] Figure 3-2 shows a fingerprint-like pattern, in which dark lines (~10 nm wide) correspond to the collapsed P4VP blocks. Thus, the collapsed P4VP blocks are clearly distinguished from bright lines (~43 nm wide) of the PS blocks in the SEM image. In addition, a fingerprint-like pattern is associated with a monolayer of in-plane cylinders because the film thickness (~31 nm) is smaller than the domain period (~53 nm). From Fast Fourier Transform (FFT) of the image (shown as an inset in Figure 3-2), two concentric rings indicate isotropic orientation of the cylinders with a regular periodicity (53 nm averaged from two rings). Thus, by solvent vapor annealing, in-plane cylinders having a regular spacing were produced in isotropic orientation.

To induce anisotropic orientation of in-plan cylindrical nanodomains of BCPs, shear force can be typically applied to a copolymer film at an elevated temperature. Since in-plane cylinders of PS-*b*-P4VP were induced by vapor annealing with a

choice of a co-solvent, simultaneous shearing and annealing at room temperature could be applied on a thin film (~31 nm thick) of PS-*b*-P4VP, by using a PDMS pad swollen with chloroform. After shearing, the film showed a featureless surface in a SEM image, implying that P4VP cylinders are imbedded inside the film. To visualize the P4VP cylinders, the topographic contrast on the film was induced by collapsing the P4VP block with ethanol. Figure 3-3 is a large area SEM image of a thin film of PS-b-P4VP after shearing, in which dark P4VP cylinders (~10 nm wide) are well aligned along the shear direction (marked by the arrow) and parallel each other with a defined separation (~42 nm), although there are some defects. The same orientation of the cylinders was observed all over the sheared film without a fingerprint-like pattern. The FFT in the inset of **Figure 3-3** shows vertically-aligned sharp spots as a characteristic of parallel structures and gives the periodicity of 52 nm in average. In addition, the orientation parameter S is 0.98, which was calculated from $S = 2\langle \cos^2 \rangle$ θ - 1 with an angle θ of a local part along a cylinder with respect to the shear direction, indicating an excellent orientation. Note, S = 1 corresponds to the perfect orientation, while S = 0 is an isotropic orientation.^[7] Thus, shearing with solvent vapor annealing is effective at room temperature to produce well-aligned cylindrical nanodomains.

Since the pyridine unit of the P4VP block can coordinate functional molecules such as fluorescent dyes and precursors of nanoparticles, functionality can be selectively localized in the P4VP nanodomain of PS-*b*-P4VP. In other words, an active function on large-area aligned nanodomains can be imposed by attaching a suitable group to PS-*b*-P4VP. Particularly, organic fluorophores are vulnerable to elevated temperatures so that shearing with vapor annealing at room temperature is advantageous to generate fluorescent and aligned nanodomains with PS-*b*-P4VP. Thus, green-fluorescent BODIPY with alkyl bromide was attached to the P4VP block by quaternization as shown in **Figure 3-4**. 0.6 mol% of the dye molecule to the pyridine unit was attached, which was large enough to provide measurable fluorescence but small enough not to disturb forming nanodomains. The emission spectrum of BODIPY-functionalized PS-*b*-P4VP exhibited the emission maximum at 513 nm, which was almost identical to that of BODIPY before attached to the P4VP block (**Figure 3-5**).

A thin film of BODIPY-functionalized PS-*b*-P4VP was sheared by the same method and condition used for pristine PS-*b*-P4VP. The film again showed a featureless surface after shearing so that the topographic contrast was enhanced by ethanol. The image of well-aligned cylindrical nanodomains shown in **Figure 3-6** is almost exchangeable with that in **Figure 3-3**, implying that the fluorescent dye attached to the P4VP block did not affect the orientation of cylindrical nanodomains. Thus, well-ordered nanodomains having BODIPY dyes were effectively produced with an assist of shearing and vapor annealing at room temperature. It is noted that the characteristics of domain width, periodicity, and FFT are identical to those of the sheared film of pristine PS-*b*-P4VP. However, the orientation parameter *S* shows a less ordered value of 0.88, because of possible reduction of the mobility of P4VP blocks due to a large molecule of BODIPY. The sheared film of BODIPY-functionalized PS-*b*-P4VP exhibited green fluorescence with a slightly red-shifted emission maximum at 520 nm, compared to that of BODIPY itself (inset in **Figure**

3-6). Since BODIPY dyes were localized in the large-area oriented nanodomains, polarization-dependent emission could be expected.^[28] However, there was no polarized emission from the sheared film, probably because the orientation of nanodomains would not induce the ordering of the dye molecules attached to them

(Figure 3-7).

Instead of attaching the BODIPY to the P4VP block before shearing and annealing, we can introduce BODIPY fluorophores in the P4VP nanodomains in a sheared film of pristine PS-*b*-P4VP. By the chemical affinity between the alky bromide of the modified BODIPY and the pyridine unit of the P4VP block, selective infiltration of BODIPY to pre-aligned P4VP cylinders can be attained. Therefore, we can employ a sheared film of pristine PS-*b*-P4VP shown in **Figure 3-3** as a chemical template for patterning functional molecules in nanoscale and orienting them in macroscale. We simply dipped a sheared film of PS-*b*-P4VP in a BODIPY solution, followed by rinsing and drying. There was no visible damage or deformation on the film after dipping. Thus, the image after loading of BODIPY shown in **Figure 3-8** is essentially unchanged from that in **Figure 3-3**. Accordingly, all physical values of domain width, periodicity, FFT, and orientation parameter *S* were preserved. In addition, we observed the identical green emission from the film (inset of **Figure 3-8**), confirming an effective chemical template of a sheared film of PS-*b*-P4VP. We note that no polarized emission was observed from a BODIPY-loaded film (**Figure 3-9**).

In previous chapter, a physical template of PS-*b*-PMMA was demonstrated, which guided Au NRs into an end-to-end configuration with minimizing their side-by-side aggregation. In order to develop cylindrical nanodomains in a thin film of PS-*b*-

PMMA, thermal annealing was required at a high temperature. Furthermore, for large-area orientation of cylindrical nanodomains, the directed self-assembling technique was necessary with a lithographically patterned substrate. In contrast, well-aligned cylindrical nanodomains in a thin film of PS-*b*-P4VP were produced simply by shearing simultaneously with solvent vapor annealing at room temperature. Thus, we applied the same protocol to a thin film of PS-*b*-PMMA for the purpose of obtaining well-aligned cylindrical nanodomains to be used as a physical template to guide Au NRs.

To develop a morphology by simultaneous shearing and annealing, a solvent should dissolve both PS and PMMA blocks and be volatile at room temperature to deliver enough vapor during a short period of shearing process. In addition, a PDMS pad should be swollen by this solvent. A mixed solvent of acetone and cyclohexane met these criteria. Without shearing, we first annealed a thin film (~30 nm thick) of PS-*b*-PMMA by vapor of this mixed solvent at room temperature. As performed in previous chapter, cylindrical PMMA nanodomains were etched by oxygen plasma and transformed into grooved nanochannels, which were confirmed as dark lines in a fingerprint-like pattern shown in the SEM image of **Figure 3-10**. The average periodicity was calculated as 40 nm from the FFT (inset of **Figure 3-10**). The depth of the grooves was also evaluated as ~5 nm by AFM analysis (**Figure 3-11**).

A thin film of PS-*b*-PMMA was sheared by the same method used for PS-*b*-P4VP except a mixed solvent of acetone and cyclohexane. After shearing, we transformed cylindrical nanodomains into grooved nanochannels by etching the PMMA blocks with oxygen plasma. **Figure 3-12** is a large area SEM image of the nanochannels

fabricated from a sheared film of PS-*b*-PMMA. Nanochannels appear dark and wellaligned along the shear direction. The ordering evaluated by the orientation parameter *S* (0.97) is as good as that of PS-*b*-P4VP (0.98), indicating that the technique of shearing with vapor annealing has a potential to be a universal method for aligning nanodomains of BCPs with a suitable choice of solvent. We note that the average periodicity (40 nm) and the depth (~5 nm) of the grooved nanochannels were not affected by shearing process. We also counted the number of defects including dislocations per area (μ m²) in the shear-aligned cylinders, which is 6.4 for of PS-*b*-P4VP and 2.8 for PS-*b*-PMMA (**Figure 3-13**). With consideration of a short duration of shearing, this defect density is reasonable, compared to that in thermally sheared BCPs (< 10 μ m⁻²).^[16,17]

We utilized a thin film having well-aligned nanochannels created by simultaneous shearing and annealing for a physical template to guide Au NRs. It is worthy of note that nanochannels are uniformly formed over the entire film compared to them only on the patterned area by the directed self-assembling technique used in previous chapter.^[11] We synthesized Au NRs of ~19 nm in diameter and ~40 nm in length by the seed-mediated growth method, which show the transverse and longitudinal peaks of LSPR at 518 nm and 621 nm, respectively (**Figure 3-14**).

The synthesized Au NRs were deposited onto the grooved nanochannels on a quartz substrate by spin-coating. We note that Si and quartz substrates did not make any difference in the nanochannels obtained by simultaneous shearing and annealing. In **Figure 3-15** of the large-area SEM image, bright Au NRs are registered on the nanochannels so that they are not agglomerated, although there are several spots of

clustering. In the enlarged image (inset of **Figure 3-15**), we clearly find that Au NRs are deposited in the direction of the grooved nanochannels. The lateral aggregation of Au NRs was effectively prevented by the gap (~20 nm) between the nanochannels, which would be pronounced without a physical template to guide Au NRs. We note that the selective deposition of Au NRs into the grooves can be ascribed to the capillary force occurred in the solvent evaporation during the coating process as explained in the previous reports.^[10,11] In addition, Au NRs in each nanochannel assembled into an end-to-end configuration, which resulted in the strong LSPR peaks at 600 nm and 706 nm, particularly in the extinction spectrum with the polarized incident light parallel (||) to the aligned direction (inset of **Figure 3-15**). Two peaks at 600 nm and 706 nm correspond to the longitudinal LSPR from the long axis of Au NRs and the coupled LSPR from end-to-end assemblies of Au NRs, respectively.^[11] With the perpendicularly polarized light (\perp) , however, these two peaks were diminished but the transverse LSPR peak from the short axis of Au NRs became noticeable at 525 nm due to the end-to-end assemblies of Au NRs on a macroscopic area. Thus, the Au NRs guided on the aligned nanochannels exhibited the plasmonic anisotropy with respect to the polarized light. We note that both longitudinal and coupled LSPR peaks were still observable with the perpendicularly polarized light, presumably because of imperfect alignments of Au NRs. It is worthwhile to note that we completely eliminated the diffraction effect due to the patterned substrate, which was necessary in previous chapter using the directed self-assembling method,^[11] because simultaneous shearing and annealing produced a uniform template of nanochannels over the entire film.

Conclusions

We demonstrated that simultaneous shearing and solvent vapor annealing was an effective method to obtain large-area alignments of cylindrical nanodomains in thin films of both PS-b-P4VP and PS-b-PMMA. With an appropriate solvent, a roomtemperature process of shearing was achieved, which is desirable for BCPs containing heat-sensitive groups such as organic fluorophores. Then, shear-aligned nanodomains of PS-b-P4VP were utilized as a template for nanoscale patterning of green fluorescent BODPIY, which was directly attached to the P4VP block before shearing or incorporated into the P4VP nanodomain after shearing. From both thin films, we observed the green fluorescence of BODIPY without deterioration. By the same shearing method, large-area aligned nanodomains of PS-b-PMMA were produced at room temperature and then converted to the grooved nanochannels by etching the PMMA blocks. The nanochannels effectively worked as a physical template for guiding Au NRs to end-to-end assemblies on a macroscopic area, resulting in the polarization-dependent plasmonic extinction. The technique of shearing with solvent vapor annealing demonstrated here can extend potential applications of BCPs where macroscopically oriented nanopatterns are needed.

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[†]This publication corresponds to the contents of chapter 2.



Figure 3-1. Schematic diagram of the shearing setup.



Figure 3-2. SEM image of a thin film of PS-*b*-P4VP after annealing in chloroform vapor and followed by dipping in ethanol for the topographic contrast. The inset is the Fast Fourier Transformation (FFT) of the image. The scale bar is 1 µm.



Figure 3-3. Large-area SEM image of a thin film of PS-*b*-P4VP after shearing by a PDMS pad swollen with chloroform. The inset is the FFT of the image. The arrow shows the shear direction. The scale bar is 1 µm.



Figure 3-4. Functionalization of PS-*b*-P4VP with green fluorescent BODIPY.


Figure 3-5. Absorption (dashed line) and emission (solid line) spectra in chloroform: (a) green fluorescent BODIPY; (b) BODIPY-functionalized PS-*b*-P4VP. The excitation wavelength was 442 nm.



Figure 3-6. Large-area SEM image of a thin film of BODIPY-functionalized PS-*b*-P4VP after shearing by a PDMS pad swollen with chloroform. Two insets are the FFT of the image and the emission spectrum from the film. The excitation wavelength was 442 nm. The scale bar is 1 μ m.



Figure 3-7. Emission spectra from the sheared films of BODIPY-functionalized PS*b*-P4VP with the polarizer parallel (\parallel) or perpendicular (\perp) to the shear direction. The emission spectrum with the parallel (\parallel) polarizer is vertically shifted for clarity.



Figure 3-8. Large-area SEM image of a shear-aligned thin film of PS-*b*-P4VP after dipping in an ethanol solution of BODIPY. Two insets are the FFT of the image and the emission spectrum from the film. The excitation wavelength was 442 nm. The scale bar is 1 μ m.



Figure 3-9. Emission spectra from the sheared PS-*b*-P4VP film dipped in a BODIPY solution with the polarizer parallel (\parallel) or perpendicular (\perp) to the shear direction. The emission spectrum with the parallel (\parallel) polarizer is vertically shifted for clarity.



Figure 3-10. SEM image of a thin film of PS-*b*-PMMA after annealing in mixed vapor of acetone and cyclohexane. The PMMA domain was removed by oxygen plasma for the topographic contrast. The inset is the FFT of the image. The scale bar is $1 \mu m$.



Figure 3-11. AFM images of nanochannels after removal of PMMA nanodomains in thin films of PS-*b*-PMMA: (a) by solvent vapor annealing; (b) by shearing with solvent vapor annealing. The height profile corresponds to the red line in each image. The scale bars are 200 nm.



Figure 3-12. Large-area SEM image of a thin film of PS-*b*-PMMA after shearing by a PDMS pad swollen with a mixed solvent of acetone and cyclohexane. The inset is the FFT of the image. The arrow shows the shear direction. The scale bar is 1 µm.



Figure 3-13. SEM image of defects (marked by circles) on shear-aligned thin films: (a) PS-*b*-P4VP; (b) PS-*b*-PMMA. The scale bars are 200 nm. A number of defects was counted in an area of $6 \,\mu m \times 8 \,\mu m$.



Figure 3-14. Au NRs: (a) TEM image; (b) Extinction spectrum. The scale bar is 100

nm.



Figure 3-15. Large-area SEM image of a shear-aligned thin film of PS-*b*-PMMA after depositing Au NRs in the nanochannels. Three insets are the FFT of the image, the extinction spectra with the polarized incident light parallel (\parallel) and perpendicular (\perp) to the aligned direction, and an enlarged image (0.5 µm × 0.5 µm). The scale bar is 1 µm.

Chapter 4

A Facile Fabrication of Fluorescent Organic-Inorganic Hybrid Perovskite Nanopatterns by Using Block Copolymer Templates

Introduction

In recent few years, organic-inorganic hybrid lead halide perovskites (APbX₃, A = alkyl ammonium cation, X = Cl, Br, I) have been intensively studied as optoelectronic materials due to the extraordinary advantages, such as low cost, processability, high quantum yield, narrow full width at half maximum, and tunable band gap, and so on.^[1,2] Numerous works implanted these "promising materials" into various applications including solar cells,^[3] photodetectors,^[4] lasers,^[5] and light-emitting diodes.^[5] In this flow, the need for perovskite patterned into micro- or nanosize naturally arose, since those offer the feasibility in integrated device fabrication as well as novel optoelectronic functions.^[6-10] Moreover, in the field of light-emitting applications, smaller perovskite architectures have been preferred to limit the diffusion and dissociation of excitons which resulted in the enhanced radiative recombination.^[11]

To tailor the perovskite into patterned structure, however, conventional top-down lithography techniques are hard to be applied directly, due to the possible degradation of novel properties during the process. In order to overcome this limitation, nondestructive techniques, such as soft imprinting,^[12] inkjet printing,^[13] selective crystallization,^[14] and template-assisted growth,^[15] are employed for the patterning of perovskite films. These methods can effectively produce perovskite patterns with micron or submicron size. However, the fabrication of nanosized perovskite patterns is still challenging because it is difficult to prepare appropriate templates or control the growth of perovskite crystals at the nanoscale.

BCPs can provide fascinating templates, which have advantages of generating

various nanostructures by self-assembly and restricting the growth and position of perovskite crystals in their nanostructures. The synthesis of perovskite using BCP nanostructures have been mostly carried out in BCP micelles in a solution.^[16-18] By employing the core block capable of attracting perovskites or their precursors, such as poly(2-vinyl pyridine) (P2VP) or P4VP, BCP micelles can be utilized to synthesize and encapsulate the perovskite nanocrystals in their cores. Nanopatterned perovskite could be achieved by casting these BCP micelle containing perovskite crystals into a thin solid film, in which the position of perovskite crystals was determined by the arrangement of BCP micelles formed during the casting process.^[17,18]

But interestingly, the fabrication of perovskite nanopatterns using the BCP morphologies in solid state have been rarely reported. Recently, methyl ammonium lead bromide (MAPbBr₃) perovskite crystals confined in various morphologies of PS-*b*-P2VP thin film were reported, which was achieved by blending precursors of MAPbBr₃ with PS-*b*-P2VP.^[19] The Lewis acid-base interaction of the precursor ions with the P2VP caused the selective positioning of perovskite into P2VP nanodomains, of which formed periodic nanostructures, such as spheres, cylinders, and lamellae, by self-assembling nature of BCPs. Although, it showed the fancy combination of perovskite synthesis with BCP nanopatterning in simplest way, this approach always possesses the risks that the incorporation of perovskite precursors hinders or alters the morphology evolution of the BCP so that causes unexpected structures and defects, which is widely known behavior in the blend system of BCP.^[20,21]

In this study, we demonstrated the selective deposition of perovskite precursors

on the self-assembled nanostructures PS-*b*-P4VP thin films to the fabricate MAPbBr₃ nanopatterns. By spin-coating of PbBr₂ and subsequent vapor deposition of MABr on PS-*b*-P4VP thin films, MAPbBr₃ perovskite nanopatterns replicating the shape and size of P4VP domains could be achieved, which exhibited strong green fluorescence. Since the self-assembly process of BCP and synthesis of perovskite was combined but operated separately, PS-*b*-P4VP nanostructures with various dimensions and morphologies could be utilized as templates to fabricate perovskite nanopatterns inheriting the structures of mother templates. Furthermore, our approach was also extended to employing iodide precursors to generate red-emitting perovskite fields demanding patterned structures.

Experimental Section

Materials: PS-*b*-P4VPs were purchased from Polymer Source, Inc. The numberaverage molecular weight (M_n) of PS-*b*-P4VPs were 32,000 g mol⁻¹ ($M_n^{PS} = 25,000$ g mol⁻¹; $M_n^{P4VP} = 7,000$ g mol⁻¹, denoted as 25k-7k), 69,000 g mol⁻¹ ($M_n^{PS} = 51,000$ g mol⁻¹; $M_n^{P4VP} = 18,000$ g mol⁻¹, denoted as 51k-18k), 136,000 g mol⁻¹ ($M_n^{PS} = 109,000$ g mol⁻¹; $M_n^{P4VP} = 27,000$ g mol⁻¹, denoted as 109k-27k), respectively. All other chemicals were purchased from Sigma-Aldrich.

BCP templates: Silicon wafers and quartz substrates were cleaned using piranha solution (70:30 v/v of concentrated sulfuric acid and hydrogen peroxide) at 90 $^{\circ}$ C for 30 min, thoroughly rinsed with deionized water, and then dried with nitrogen

stream. Quartz substrates were used only for the measurement of extinction spectra. Each PS-*b*-P4VP was dissolved in toluene, which was stirred for 24 h at room temperature and for 3 h at 85 °C and then cooled to room temperature. For micelle templates, 0.3 wt% of PS-*b*-P4VP in toluene was spin-coated onto a cleaned substrate at 3,000 rpm for 30 s and used without further treatment. For PS-*b*-P4VP templates with 4VP cylinders, PS-*b*-P4VP was spin-coated from its toluene solution (0.8 - 0.9 wt%) onto a cleaned substrate at 3,000 rpm for 30.5 s and used without further treatment.

Perovskite nanopatterns: Solutions of PbX₂ (X = Br, I) were prepared by mixing an excess amount of PbX₂ with methanol and stirring for 1 day at 60 °C. Clear solutions saturated with PbX₂ were obtained after decanting and filtering, and further kept in 60 °C until use. The vapor deposition chamber for methyl ammonium halides (MAXs) was prepared by putting 0.2 g of MAX in a fresh glass jar (60 ml-volume) with a Si lid. To prepare PbBr₂ nanopatterns on PS-b-P4VP template, warm PbX₂ solution was spin-coated onto a PS-*b*-P4VP template at 2,000 rpm for 30 s. Then, the film was heated for 10 min at 90 °C in ambient atmosphere. Subsequently, the film was directed toward MAX powder at the bottom, and heated for 1 h at 150 – 180 °C to convert PbX₂ into MAPbX₃ perovskite.

Characterizations: FE-SEM was performed on a Hitachi S-4300 at 15 kV. AFM (4, Nanoscope IIIA, Digital Instrument) was used in tapping mode with a Si cantilever.

Common TEM images were obtained on a Hitachi 7600 operating at 100 kV. TEM analysis for energy dispersive spectroscopy (EDS) was performed on a JEOL JEM-F200 at 200 kV. UV-Vis absorption spectra were recorded on a Varian Cary-5000 spectrophotometer. The PL spectra of the films were measured using an Acton SpectraPro with He-Cd laser (442 nm).

Results and Discussion

Figure 4-1 illustrates the overall process to fabricate fluorescent nanopatterns of MAPbBr₃ perovskite by using a BCP template. The main idea of our approach is the selective deposition of PbBr₂ within the nanodomain of one block of BCP film, and grow MAPbBr₃ perovskite from those PbBr₂ nanopatterns. We utilized thin films of PS-*b*-P4VP as a BCP template, which has 24 vol% of the P4VP block producing cylindrical P4VP nanodomains. The pyridine unit of P4VP block can bear ionic salts thus localizes PbBr₂ to generate nanopatterns. A thin film of PS-*b*-P4VP was firstly fabricated by spin-coating on a SiO₂/Si substrate and then solvent vapor annealing was performed on the film to generate morphology by putting it in a closed chamber filled with chloroform vapor. We note that chloroform is a non-selective solvent for PS and P4VP, which dissolves both blocks, thus can generate in-plane cylindrical morphology of P4VP block.^[22]

To deposit PbBr₂ into the P4VP cylinders, we simply spin-coated a PbBr₂ solution onto the PS-*b*-P4VP template. In this step, the choice of appropriate solvent is also a crucial issue since the solution should show proper wetting behavior on the film surface to ensure uniform coating,^[23] while maintaining the morphology of PS-*b*- P4VP. Methanol, which is a selective solvent for P4VP and thus shows adequate wetting behavior without damaging the film, is well suited for this purpose. Also, the preference of methanol on P4VP could help the migration of PbBr₂ toward P4VP domains during spin-coating process.^[24,25] Although PbBr₂ is hardly soluble in alcohols, we noticed that even a trace amount of PbBr₂ dissolved in methanol was enough to form nanopatterns in a PS-*b*-P4VP template. Thus, PbBr₂ nanopatterns on a PS-*b*-P4VP template could be prepared by the spin-coating of PbBr₂ saturated in methanol on a PS-*b*-P4VP thin film having in-plane cylinders of P4VP.

MABr was then introduced on the PbBr₂ nanopatterns to convert PbBr₂ into MAPbBr₃ perovskite. Unlike the deposition of PbBr₂, vapor phase deposition was employed to introduce MABr because any solution process could harm the PbBr₂ and PS-*b*-P4VP, including the dissolution of PbBr₂ and underlying template. To this end, MABr powder was heated at 150 °C in a glass jar to produce MABr gas while PbBr₂ nanopatterns was placed up-side down at the lid. The grown MAPbBr₃ also inherited the structure of mother PS-*b*-P4VP template resulting in the patterned structures of MAPbBr₃. These MAPbBr₃ nanopatterns exhibited the same green fluorescence as the MAPbBr₃ perovskite crystals,^[17,19] thus the formation of fluorescent MAPbBr₃ nanopatterns could be confirmed.

Figure 4-2a shows the TEM image of a PS-*b*-P4VP film after annealed in chloroform vapor, in which periodic in-plane cylinders of P4VP were shown in slightly darker but not clearly distinct from surrounding PS domains. The average periodicity of P4VP cylinders was measured as ~52 nm. In AFM measurement, the surface of the annealed S4VP film was found to be almost flat (**Figure 4-2b – 2c**).

After the spin-coating of PbBr₂ on the PS-*b*-P4VP film, the contrast between PS and P4VP domains in the TEM image was significantly enhanced and shown as darker P4VP cylinders (~21 nm wide) surrounded by PS (**Figure 4-3a**), which indicates that high atomic number Pb was mainly located at P4VP sites. The surface of film was also changed from flat to 10 nm-height corrugation, as shown in AFM results (**Figure 4-3b** – **3c**). To confirm the selective deposition of PbBr₂ on P4VP sites without infringing PS domain, we removed PS-*b*-P4VP template by applying O₂ plasma to identify the exact location of inorganic Pb components. As shown in **Figure 4-4**, remained Pb resembled the structures of periodic P4VP cylinders, which indicates the selective deposition of PbBr₂ nanopatterns on the PS-*b*-P4VP template.

After the vapor deposition of MABr, these PbBr₂ nanopatterns were converted to MAPbBr₃ inheriting the periodic nanostructures, of which whole film exhibited green fluorescence excited by UV light (**Figure 4-5**). AFM analysis confirmed that the corrugation of the film surface was increased from ~10 nm to ~15 nm, indicating the incorporation of MABr into the lattice of PbBr₂ to form perovskite structures causing the volume expansion (**Figure 4-5b** – **5c**).^[26] It was found that there was no penetration or migration of perovskite crystal into PS domains during the vapor deposition process, as confirmed in large-area FE-SEM image of MAPbBr₃ after removing polymeric template (**Figure 4-6**). EDS mapping of the TEM image, which visualizing the distribution of Pb and Br, also indicates the selective deposition of PbBr₂ and MABr on P4VP cylinders without penetrating PS domain during the whole process (**Figure 4-7**).

The selective deposition of PbBr₂ on the PS-*b*-P4VP template mainly be ascribed to the preference of PbBr₂ toward to pyridine units of P4VP cylinders. Since the nitrogen atoms of pyridines can attract Pb ions by the Lewis acid-base interaction,^[19] PbBr₂ migrates and is deposited on P4VP domains as solvent evaporation during spin-coating process. Furthermore, the solvent, methanol, also prefers P4VP rather than PS so that dewetting of solution film from the PS surface during spin-coating might help the migration of the solution itself toward P4VP, as in other reports using the selective wetting and dewetting on chemically heterogeneous patterns for the pattern replication.^[24,25] Thus, in-plane P4VP cylinders generated by self-assembly of the S4VP thin film could be employed as a chemical template for fabricating patterned PbBr₂ which resulted in MAPbBr₃ perovskite nanopatterns after vapor deposition of MABr.

The formation of MAPbBr₃ perovskite nanopatterns was further tracked by UVvis spectroscopy (**Figure 4-8**). As more MABr was deposited, the absorption gradually increased especially at the wavelength range below 500 nm. After 1 h of growth, the characteristic band edge of MAPbBr₃ perovskite crystals at ~520 nm was clearly observed,^[19] indicating the growth and formation of MAPbBr₃ perovskite nanopatterns was achieved by the vapor deposition of MABr. We note that the change of absorption is not originated from the absorption of MABr itself, which was confirmed from the absorption spectrum of PS-*b*-P4VP template undergoing MABr deposition without PbBr₂ (**Figure 4-9**).

The growth of MAPbBr₃ perovskite on PbBr₂ was also investigated by the change in photoluminescence (PL) characteristics (**Figure 4-10**). When MABr was deposited for 15 min or more, each film exhibited green PL of which intensity was dramatically enlarged and the maximum wavelength was red-shifted from 510 nm to 527 nm, as the deposition time increased. We note that the PL of 15 minute-deposition case was very weak, but detectable (**Figure 4-11**).

The structure of PS-*b*-P4VP templates can be tuned by changing the molecular weight and adopting appropriate self-assembly techniques, which is expected to result in various kinds of MAPbBr₃ nanopatterns. For example, quasi-hexagonal arrays of P4VP nanodots could be achieved by spin-coating of PS-*b*-P4VP micelles dissolved in toluene and using without further annealing process. The size and center-to-center distance of P4VP nanodots are governed by the length of P4VP core block and PS corona block.^[27] In this regard, we prepared micelle templates by using PS-*b*-P4VP with three different molecular weights (25k-7k, 51k-18k, and 109k-27k), and adopted our perovskite process.

Figure 4-12 show FE-SEM images of MAPbBr₃ perovskite nanodot arrays from each micelle template, treated by O₂ plasma to reveal the position of MAPbBr₃. The synthesized MAPbBr₃ nanodots were located in a quasi-hexagonal arrangement, but the center-to-center distance between adjacent nanodots was gradually increased with the size of the PS block and measured as 35 nm, 42 nm, and 66 nm, respectively. Likewise, the average size of synthesized MAPbBr₃ nanodots also became larger with increasing the size of P4VP block and measured as 21 nm, 23 nm, and 28 nm, respectively. Notably, PLs from these MAPbBr₃ nanodot arrays (**Figure 4-13**) were almost identical to that of MAPbBr₃ fabricated by the P4VP cylinder template. We believe that the size of nanodots was not in the regime of confinement effect, so that the PL characteristics was not significantly altered in spite of the change in dimension of MAPbBr₃ perovskite.^[28]

Tuning the dimension of synthesized perovskite by adjusting the molecular weight could be also applied to P4VP cylinder templates. **Figure 4-14** shows MAPbBr₃ perovskite nanopatterns synthesized on a PS-*b*-P4VP template having narrower and denser arrays of P4VP cylinders, which was accomplished by using lower molecular weight PS-b-P4VP (25k-7k). The synthesized perovskite exhibited smaller overall dimension, of which width and periodicity were measured as ~16 nm and ~33 nm, respectively. In addition, we were also able to achieve MAPbBr₃ nanopatterns directed in a single orientation (**Figure 4-15**) by employing well-aligned P4VP cylinders prepared via shear-alignment technique of BCPs.^[22] These series of results show the versatility of our process, which can be utilized to produce various kinds of MAPbBr₃ nanopatterns by combined with the preexisting BCP patterning techniques.

In addition to MAPbBr₃, we could extend our approach to fabricating MAPbI₃ perovskite nanopattern by using iodide precursors (PbI₂ and MAI). As in the case of PbBr₂, a small amount of PbI₂ is soluble in methanol, which could be spin-coated on the PS-*b*-P4VP template to implement PbI₂ nanopatterns. By employing the same process, PbI₂ nanopatterns (**Figure 4-16a**) and MAPbI₃ nanopatterns (**Figure 4-16b**) could be fabricated. Compared to the MAPbBr₃ nanopatterns, the synthesized MAPbI₃ exhibited PL at longer wavelength (maximum at 755 nm) ranging from dark red to near IR (**Figure 4-16c**). It should be noted that higher temperature (180 °C) in vapor deposition is necessary to obtain fluorescent MAPbI₃ perovskite.

Since the process also worked with iodide precursors as well, one can expect the perovskite nanopatterns composed of mixed halides, which are usually used to tune the PL wavelength by changing the composition of two or more halides in perovskites.^[29] It could be accomplished by spin-coating PbBr₂ on a PS-*b*-P4VP template and subsequently depositing MAI instead of MABr. **Figure 4-17** shows the PL emission spectrum of the perovskite nanopatterns composed of two different halides, Br and I, of which maximum wavelength (687 nm) located between that of each single halide perovskite (527 nm for MAPbBr₃, 755 nm for MAPbI₃). It should be noted that when the ionic pairs of each precursor were switched (use PbI₂ and MABr, instead of PbBr₂ and MAI), no PL was observed. We suspect that the heavier I atoms in PbI₂ are hard to be reorganized so that inhibit MABr from penetrating into PbI₂ lattices and forming crystalline structures of perovskite.

Conclusion

We presented a facile process for the fabrication of organic-inorganic hybrid perovskite nanopattern by employing the self-assembled nanostructures of PS-b-P4VP thin films as templates. Chemical affinity of P4VP toward ionic species helped the selective deposition of lead halides on P4VP domains by simple spin-coating process, which further led to the formation of perovskite nanopatterns mimicking the nanostructures of mother BCP templates. The fabricated perovskite nanopatterns exhibited strong fluorescence, of which wavelength could be tuned by using the precursors with different halides. One advantage of our approach is based on the separating the self-assembly of BCP and perovskite processing, which make possible to implant the self-assembled nanostructures of BCPs into perovskites without harm or altering the intrinsic nanostructures of BCPs. In the same viewpoint, it also enabled adopting preexisting BCP nanopatterning techniques granting BCP templates with various nanoscale geometries, resulting in the perovskite nanopatterns with controlled dimension and orientation. As such, our approach can be considered as a facile combination of two well-established fields which are still developed magnificently, thus is expected to be a potential tool in the field of perovskite requiring nanopatterned structures.

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[†]This publication corresponds to the contents of chapter 3.



Figure 4-1. Process for the fabrication of fluorescent MAPbBr₃ nanopatterns on a PS-*b*-P4VP template.



Figure 4-2. PS-*b*-P4VP template. (a) TEM image; (b) AFM height image; (c) height profile of the surface obtained from (b). All scale bars are 100 nm.



Figure 4-3. PbBr₂ nanopatterns on a PS-*b*-P4VP template. (a) TEM image; (b) AFM height image; (c) height profile of the surface obtained from (b). All scale bars are 100 nm.



Figure 4-4. FE-SEM image of $PbBr_2$ nanopatterns after O_2 plasma treatment. The scale bar is 100 nm.



Figure 4-5. MAPbBr₃ nanopatterns on a PS-*b*-P4VP template. (a) TEM image; (b) AFM height image; (c) height profile of the surface obtained from (b). The inset in (a) is a photograph of the whole film under 365 nm excitation source. All scale bars are 100 nm.



Figure 4-6. Large-area FE-SEM image of MAPbBr₃ perovskite nanopatterns after O_2 plasma treatment. The scale bar is 1 μ m.



Figure 4-7. EDS elemental mapping images for MAPbBr₃ nanopatterns. All scale bars are 100 nm.



Figure 4-8. Absorption spectra of MAPbBr₃ perovskite nanopatterns formed by different deposition time of MABr.


Figure 4-9. Absorption spectra of pristine PS-*b*-P4VP template (black solid line), PbBr₂ spin-coated on PS-*b*-P4VP template (dashed line), MABr deposited on PS-*b*-P4VP without PbBr₂ (dotted line), and MAPbBr₃ fabricated on PS-*b*-P4VP template (green solid line).



Figure 4-10. Emission spectra and corresponding photographs of MAPbBr₃ perovskite nanopatterns formed by different deposition time of MABr. The excitation was 442 nm.



Figure 4-11. Emission spectrum of MAPbBr₃ perovskite nanopatterns formed by 15 min of vapor deposition, corresponding to the purple line in **Figure 4-10**.



Figure 4-12. FE-SEM images of MAPbBr₃ perovskite nanopatterns fabricated from the templates of PS-*b*-P4VP: (a) 25k-7k micelles, (b) 51k-18k micelles, (c) 109k-27k micelles. All scale bars are 200 nm.



Figure 4-13. Emission spectra of MAPbBr₃ perovskite nanopatterns fabricated from the PS-*b*-P4VP micelle templates with different molecular weights.



Figure 4-14. FE-SEM image of MAPbBr₃ perovskite nanopatterns fabricated from the template of PS-*b*-P4VP (25k-7k) cylinders. The scale bar is 200 nm.



Figure 4-15. Large-area FE-SEM image of MAPbBr₃ perovskite nanopatterns fabricated from the shear-aligned PS-*b*-P4VP (51k-18k) template. The scale bar is 1 μ m.



Figure 4-16. Formation of MAPbI₃ perovskite nanopatterns. (a) TEM image of PbI₂ on a PS-*b*-P4VP template. (b) TEM image of MAPbI₃ perovskite nanopattern. (c) Emission spectrum of MAPbI₃ nanopattern excited at 442 nm. The scale bars are 100 nm.



Figure 4-17. Emission spectrum of perovskite nanopatterns with mixed halides by using PbBr₂ and MAI as precursors. For comparison, PL maximum wavelengths of pure MAPbBr₃ and pure MAPbI₃ are presented in green and red dashed lines, respectively.

국문 초록(Abstract in Korean)

이중블록공중합체의 자기조립을 통한 광기능성 나노패턴의 제조

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나노크기의 물질 및 물체를 다루는 나노기술의 출현 이후로 나노크기 의 소재를 개발하고 제조하는 것은 자연스럽게 주요 관건이 되었다. 특 히 광기능성 물질의 나노구조는 벌크 상태와는 차별화되어 나타나는 조 절 가능한 독특한 특성으로 인해 광포집, 메타물질, 촉매 및 집적소자와 같은 여러 나노기술 분야에서 널리 사용되어 왔다. 학술적 연구 및 실제 응용을 위해서는 이러한 물질들의 구조 및 위치의 정확한 제어가 중요하 기에, 많은 방법들이 템플릿을 활용하여 광학 활성을 가진 나노구조를 합성 및 구현하고 있다.

템플릿은 빌딩 블록들이 특정한 형태를 형성하도록 유도할 수 있는 구 조 또는 화학적 특성을 가진 틀이다. 작은 분자에서 콜로이드에 이르는 기능성 소재들은 잘 설계된 템플릿 상의 특정 위치에서 물리적 제한 또 는 화학적 흡착을 통해 원하는 구조로 합성되거나 조립될 수 있으며, 이 를 통해 점, 선 및 복잡한 2차원/3차원 구조 등의 특정 형태를 갖는 기 능성 아키텍처를 구현 가능하다. 이와 관련하여, 나노크기의 템플릿은 다양한 기능성 소재의 나노구조를 제조하기 위한 유망한 수단으로서 주 목 받아왔으며, 이는 나노물질의 고유한 특성을 탐구하는 기초 연구적 측면과 더불어 나노패터닝, 생체모방, 나노소자 제조와 같이 잘 구성된 나노구조를 필요로 하는 응용적 측면에까지 나노기술의 한 축을 담당해 왔다.

공유 결합으로 연결된 둘 이상의 고분자로 이루어진 블록공중합체를 활용하는 것은 박막 형태의 템플릿을 제조하는 최신 전략 중 하나이다. 블록공중합체의 박막은 고분자 블록들의 자기조립을 통해 구. 실린더 및 판상 구조와 같이 다양한 주기적 나노구조를 형성하며, 이러한 나노구조 의 크기 및 모폴로지는 분자량과 블록비를 조절하여 제어할 수 있다. 블 록공중합체 박막을 템플릿으로 활용하는 것은 블록공중합체를 구성하는 고분자 블록의 종류를 적절하게 선택함으로써 화학적으로 구별되는 나노 도메인을 구현하는 것을 기반으로 한다. 이는 주로, 박막에 높낮이 대비 를 형성할 수 있도록 제거 가능하거나, 또는 다른 소재들을 유인하고 결 합시킬 수 있는 화학적 활성을 가진 블록을 활용함으로써 이뤄진다. 즉. 블록공중합체 박막의 자기조립 나노구조는 활용 목적에 맞춰 물리적 구 조 및 화학적 특성이 조절된 나노크기의 템플릿을 쉽게 제조할 수 있다 는 장점이 있다. 또한, 유도자기조립(directed self-assembly, DSA), 기계적 전단, 전자기장 및 구역 어닐링(zone annealing)과 같이 블록공 중합체의 나노도메인을 정렬할 수 있는 여러 전략들을, 정렬되고 제어된 구조를 필요로 하는 광학 및 전자기 장치와 같은 실제 응용 분야에 고려 할 수도 있다.

본 학위논문은 물리적 구속 또는 화학적 인력을 통해 광기능성 재료의 나노구조를 구성하는 데 사용할 수 있는 블록공중합체 템플릿의 제조를 다룬다. 1장에서는 이 연구의 배경 지식과 목적을 간략하게 소개한다. 2 장에서는 블록공중합체 박막의 DSA를 활용, 금 나노막대의 종단간조립 (end-to-end assembly)을 통해 대면적에서 형성된 이색성 플라즈몬 초구조(dichroic plasmon superstructure)를 소개한다. 해당 초구조는 직교 방향의 편광 하에서 이색성 광학 특징을 보였으며 구조적 열화 없 이 다양한 기판에 전사 가능하였다. 3장에서는 서로 다른 두 블록공중합 체의 나노도메인을 용매 증기 어닐링과 전단을 동시에 가하여 상온에서 대면적으로 정렬할 수 있는 단일 방법론을 제시한다. 전단 정렬된 각 블 록공중합체의 나노도메인은 각각 화학적 또는 물리적 템플릿으로 사용되 어 형광 분자 또는 금 나노막대의 패턴을 구현 가능하였다. 마지막으로, 4장에서는 블록공중합체 템플릿을 사용하여 형광 특성을 나타내는 유기 -무기 하이브리드 페로브스카이트의 나노패턴을 제조하는 손쉬운 공정 을 소개한다. 블록공중합체 템플릿이 제공하는 나노크기의 다양한 형태 들을 통해 구조의 크기 및 방향이 제어된 페로브스카이트 나노패턴을 구 현하였다. 종합하자면, 블록공중합체 박막에서의 자기조립 나노구조를 이용하여 다양한 광학적 기능을 가진 나노패턴을 효과적으로 제작, 제어 할 수 있었다. 본 접근법은 나노광학 및 나노소자의 개발 및 발전을 위 한 기초 재료를 구현하고 제어할 수 있는 폭 넓은 기회를 제공할 것으로 기대된다.

주요어: 블록공중합체, 자기조립, 템플릿, 나노패턴, 광기능성

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