Fabrication of Metallized Nanoporous Films from the Self-Assembly of a Block Copolymer and Homopolymer Mixture

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Received January 30, 2007. In Final Form: April 24, 2007

Inorganic compound HAuCl₄, which can form a complex with pyridine, is introduced into a poly(styrene-block-2-vinylpyridine) (PS-b-P2VP) block copolymer/poly(methyl methacrylate) (PMMA) homopolymer mixture. The orientation of the cylindrical microdomains formed by the P2VP block, PMMA, and HAuCl₄ normal to the substrate surface can be generated via cooperative self-assembly of the mixture. Selective removal of the homopolymer can lead to porous nanostructures containing metal components in P2VP domains, which have a novel photoluminescence property.

Introduction

Films of block copolymers have been recognized as promising candidates for the preparation of various functional nanostructures, which may be used in surface patterning, lithography, and templating for the fabrication of organic—inorganic electronic, optical, and magnetic devices.1-7 To this end, well-aligned microdomains, especially those in an orientation normal to the substrate, are desirable.8,9 However, without further constraint, the perpendicular alignment of the domains is difficult to obtain because of the preferential interactions of one of the blocks with the substrate and air interfaces.10-12 In recent years, numerous research efforts have been devoted to improving the alignment of cylindrical domains of block copolymers. A block copolymer film with oriented microdomains can be obtained by several approaches such as the “neutral surface” of the solid substrate,13 an external electric field,14 solvent-induced orientation,15,16 solvent prewetting,17 directional crystallization,18 the introduction of geometric substrate anisotropy,19 and a polymeric supramolecular assembly with a low molar mass additive.20,21 After the removal of one of the blocks in block copolymer films with cylindrical microdomains perpendicular to the substrate via UV exposure or plasma etching methods,22 ordered nanoporous films can be fabricated.

It has been demonstrated that the addition of a homopolymer or low-molecular-weight additives to a block copolymer is another simple route to producing porous nanostructures with multiple length scales.8,23 The addition of the low-molecular-weight compounds may change the properties of one of the blocks or the interactions at interfaces, resulting in improvement of the orientation of microdomains. Well-ordered nanostructured thin polymer films have been fabricated from the assembly of poly(styrene-block-4-vinylpyridine) (PS-b-P4VP) and 2-(4′-hydroxybenzeneazo) benzoic acid (HABA). The alignment of the cylindrical nanodomains formed by P4VP-HABA associates is insensitive to the composition of the confining surface. After removal of HABA, a nanomembrane is obtained.8

Recent computer simulations have predicted that the synergistic interactions between self-organizing particles and a self-assembling matrix material can influence the phase behavior and ordering of the block copolymers.24 In experiments, Kramer’s group reported a nanoparticle-induced phase transition in a block copolymer thin film as well as the formation of different structures of gold nanoparticles.25 Russell’s group showed that the cooperative, coupled self-assembly of mixtures of diblock

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copolymers and surface-active nanoparticles could orient the copolymer domains normal to the surface in thin films, even when one of the blocks was strongly attracted to the substrate.\textsuperscript{26a} Very recently, the same group also showed that the complexation of alkali halide or metal salts with the poly(ethylene oxide) (PEO) block of a PS-\textit{b}-PEO copolymer could greatly affect the ordering process of the copolymer films during solvent annealing, and the microdomains of the block copolymer were found to orient normal to the surface of the film with markedly enhanced lateral order.\textsuperscript{26b} Wei’s group observed a morphological transformation of PS-\textit{b}-P4VP from a hexagonally packed cylindrical structure to a lamellar structure upon sequestering CdS nanoparticles in the P4VP block. The binding of CdS nanoparticles into the P4VP domains is caused by the formation of hydrogen bonds between them.\textsuperscript{27a} It is also found that the dispersion of TiO\textsubscript{2} nanoparticles affects the block copolymer’s luminescence at different wavelengths.\textsuperscript{27b}

It is expected that nanoporous thin films of block copolymers may exhibit novel electronic and optical properties if a metal or semiconductor component is introduced.\textsuperscript{9a} Nanoporous thin films containing Ru have been obtained using metallosupramolecular block copolymers.\textsuperscript{9a} Here, we report a simple method to fabricate functional nanoporous thin films containing Au using mixtures of asymmetric PS-\textit{b}-P2VP block copolymers and PMMA homopolymers. Usually, the cylindrical microdomains of P2VP parallel to the substrate surface are formed by the preferential interaction of P2VP with the substrate surface. Chloroauric acid, which can form a complex with pyridine units in this block copolymer, is introduced to adjust the interaction between P2VP and the substrate surface. The alignment of the cylindrical nanodomains formed by P2VP, HAuCl\textsubscript{4}/PMMA has been produced after the introduction of HAuCl\textsubscript{4}. Selective removal of the homopolymer can generate porous nanostructures containing Au in P2VP blocks, which have a novel optical property. The scheme to generate a nanoporous film containing tiny gold spots is illustrated in Figure 1.

\textbf{Experimental Section}

\textbf{Materials.} Polystyrene-block-poly(2-vinyl pyridine) (PS-\textit{b}-P2VP) with a polydispersity index of 1.07 was purchased from Polymer Source, Inc. The number-average molecular weights of the PS and P2VP blocks were 54,900 and 18,600 g/mol, respectively. PMMA of \(M_n = 23,600\) was obtained from Polymer Source, Inc. Tetra-chloroauric(III) acid (HAuCl\textsubscript{4}/H\textsubscript{2}O\textsubscript{2}) was purchased from Fluka and used as received. Analytical-grade tetrahydrofuran (THF) was purchased from Laborbedarf GmbH.

\textbf{Substrates.} Silicon (Si) and SiO\textsubscript{2} wafers with a native oxide layer (ca. 2.5 cm \(\times\) 2.5 cm) were cleaned in piranha solution (70/30 v/v concd H\textsubscript{2}SO\textsubscript{4}/30% H\textsubscript{2}O\textsubscript{2}) at 80 \(^\circ\)C for 30 min, thoroughly rinsed with Milli-Q water, and then blown dry with nitrogen gas. \textbf{Caution!} Piranha solution reacts violently with organic compounds and should not be stored in a closed container. The gold substrates were prepared by first evaporating a 2 nm chrome layer and then a 50 nm gold layer on silicon substrates.

\textbf{Film Preparation.} Given amounts of PS-\textit{b}-P2VP, PMMA (5 wt \% PMMA, relative to the P2VP block), and HAuCl\textsubscript{4}/H\textsubscript{2}O\textsubscript{2} were dissolved in THF and stirred for at least for 24 h to make a homogeneous solution. The molar ratio of HAuCl\textsubscript{4}/2VP was 0.5. Polymer films were produced simply by spin coating from the 1.0 wt \% THF solution onto silicon (with native oxide on the surface), SiO\textsubscript{2}, and gold substrates at 2000 rpm. The film thickness measured by a surface profiler (Tencor P-10, KLA Tencor) was about 60 nm. Gold salts in the mixture films were reduced by UV exposure or were dipped into 1 wt \% NaBH\textsubscript{4} solutions for 10 s.\textsuperscript{28,29} To remove the PMMA, the film was exposed to deep UV irradiation and then washed with acetic acid.\textsuperscript{22} To obtain the AFM image of the bottom surface of the mixture film containing gold after treatment with UV irradiation and acetic acid, the film was floated onto the surface of a 2 wt \% HF water solution, transferred to a water bath to remove HF, and then transferred to a Si substrate with the bottom of the film up.

\textbf{Characterization.} SFM height and phase contrast images were obtained using a Digital Instruments Dimension 3100 scanning force microscope in tapping mode with an Olympus cantilever with a spring constant ranging from 33.2 to 65.7 N/m and a resonance frequency of 277.3–346.3 Hz (as specified by the manufacturer). X-ray photoelectron spectroscopy (XPS) was performed on a Perkin-Elmer-Physical Electronics 5100 with Mg K\textsubscript{x} excitation (400 W). Spectra were obtained at a takeoff angle of 15\(^{\circ}\). Photoluminescence (PL) spectra were measured using a Spex Fluorolog II (212) instrument at an excitation wavelength of 350 nm.

\textbf{Results and Discussions}

It is well known that P2VP cylindrical microdomains orient parallel to the substrate surface in thin block copolymer films because of the preferential interaction of P2VP with the substrate and low surface energy of PS with the air interface.\textsuperscript{26c} It has been reported that a mixture of a PS-\textit{b}-PMMA with a small amount

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of PMMA homopolymer can change the phase behavior of the system and enhance the orientation of the PMMA cylindrical microdomains normal to the surface. However, the enhancement effect of the orientation by the addition of a homopolymer is relatively weak for the PS-\textit{b}-P2VP system because of the strong interaction between VP units and the OH groups at the SiO$_x$ substrate surface. Figure 2 shows the AFM height and phase contrast images of the PS-\textit{b}-P2VP/PMMA blend films on silicon substrates before (Figure 2A,B) and after (Figure 2C,D) the removal of PMMA. Brighter dots and darker areas in the phase image of Figure 2B correspond to the cylindrical microdomains normal to the substrate and the PS matrix, respectively. After UV irradiation and acetic acid treatment (to cross-link PS-\textit{b}-P2VP and remove PMMA), a mixed morphology of perpendicular and parallel orientations was observed (Figure 2C,D). The results indicate that the addition of a small amount of PMMA produces only part of the cylindrical microphase-separated domains of P2VP and PMMA normal to the substrate. Similar behaviors were observed for PS-\textit{b}-P2VP/PMMA blend films on SiO$_2$ and gold substrates. It is well known that at low homopolymer concentration or when the molecular weight of the homopolymer is below or comparable to that of one solubilizing block, the homopolymer is solubilized in the copolymer microdomains. For PS, PMMA, and PVP, the PMMA–PVP interaction parameter ($\chi_{\text{PMMA–PVP}} = 0.007$) is much lower than the values for PS–PVP ($\chi_{\text{PS–PVP}} = 0.1$) and PS–PMMA ($\chi_{\text{PS–PMMA}} = 0.02$). The molecular weight of PMMA is larger than that of the P2VP block. In terms of the interaction parameters and the molecular weight of PMMA, it is reasonable to deduce that the added PMMA is located in P2VP microdomains and surrounded by P2VP.

With the addition of a gold (Au) precursor, HAuCl$_4$, to the PS-\textit{b}-P2VP/PMMA mixtures, it is found that the perpendicular orientations of the microphase domains are markedly enhanced. Figure 3A–D shows the AFM height and phase contrast images of the PS-\textit{b}-P2VP/PMMA/HAuCl$_4$ films before and after removal of PMMA. The height variation and phase contrast are relatively small for the as-prepared film. However, arrays of pores with an average diameter of $\sim$38 nm on the film surface were observed (Figure 3C) after the removal of PMMA, illustrating that nanoscopic cylindrical domains are perpendicular to the film surface. It has been reported that deep UV irradiation of the mixture cross-links PS and P2VP, degrades PMMA, and reduces HAuCl$_4$. Though it is not clear if UV irradiation can promote the microphase separation between PMMA and Au-containing P2VP domains, nanoporous block copolymer films containing a Au component in the P2VP blocks (Figure 3C), which are

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different from the porous films generated from neat PS-\textit{b}PMMA,\textsuperscript{22,23} are obtained.

To investigate further if the cylindrical microdomains are normal to the substrate surface, the bottom surface of the PS-\textit{b}-P2VP/PMMA/HAuCl\textsubscript{4} mixture film on the SiO\textsubscript{2} substrate after the removal of PMMA with UV irradiation and acetic acid treatment was examined with AFM. The height and phase images shown in Figure 3E,F imply that the cylindrical microdomains containing P2VP, PMMA, and Au span the entire film thickness. The average center-to-center distance of the pores is measured to be about 50 nm. As we know, the PVP block has a preferential interaction with the polar substrate, and the PS block prefers an air interface because of its lower surface energy. Thus, lamellae parallel to the substrate with an asymmetric wetting configuration have to be induced during the high-temperature annealing process.\textsuperscript{29} However, after thermal annealing in vacuum at 170 °C for 2 days, UV irradiation, and acetic acid treatment, a porous film is also observed (Figure 4), indicating that the orientation of the cylindrical domains normal to the substrate is induced by the introduction of HAuCl\textsubscript{4}. X-ray photoelectron spectroscopy

**Figure 3.** AFM height (A, C) and phase images (B, D) of films of PS-\textit{b}-P2VP/PMMA/HAuCl\textsubscript{4} mixtures: (A, B) as spin cast and (C, D) after UV irradiation and treatment with acetic acid. AFM height (E) and phase (F) images of the back side of the film of PS-\textit{b}-P2VP/PMMA/HAuCl\textsubscript{4} mixtures after UV irradiation and treatment with acetic acid.
(XPS) measurements were carried out on the mixture films after the reduction of Au salts. The characteristic Au 0 peaks at ~84.0 eV (Au 4f 7/2) and ~87.7 eV (Au 4f 5/2) are clearly observed (Figure 5). From the results, one can conclude that the Au salts become metallic Au after reduction.

As reported previously, the incorporation of HAuCl₄ results in local protonation of the pyridine units followed by electrostatic interaction of the quaternary ammonium species with AuCl₄⁻ anions (i.e., complexation between HAuCl₄ and the pyridine units). The complexation of HAuCl₄ to the pyridine units leads to the change in interaction between P2VP and the substrate interface and finally to a change in the structure of the film. The same results obtained from films on Au, Si, and SiO₂ substrates illustrate that the alignment of the cylindrical nanodomains in the mixture film is insensitive to the surface energy of the substrates because of P2VP-HAuCl₄ complexation, which is consistent with the results of the PS-b-P2VP/HABA system.

To understand the optical properties of the nanoporous films containing Au, photoluminescence (PL) measurements were carried out. For comparison, PL spectra of pure Au nanoparticles fabricated from PS-b-P2VP/HAuCl₄ micelles combined with oxygen plasma etching are also shown in Figure 6. One can see that pure Au nanoparticles exhibit a broad band with the main peak centered at 330 nm at an excitation wavelength of 260 nm and another broad band with the main peak at 440 nm at an excitation wavelength of 350 nm. In comparison, a strong PL band consisting of two emission peaks (330 and 367 nm) is observed for the nanoporous film containing Au at an excitation wavelength of 260 nm. The peak at 330 nm is in agreement with that obtained for pure Au nanoparticles, and the peak at 367 nm is a new one and is observed for the first time from this type of Au nanostructure with extraordinary morphology.

It has been reported that small Au nanoparticles (~5 nm) show PL at 440 nm with an excitation wavelength of 230 nm, which is assigned to the radiative recombination of Fermi-level electrons and sp- or d-band holes. When the size of bare Au nanoparticles is larger than ~5 nm, PL has not been observed. Surface-passivated Au nanoclusters (~1.2 nm) also exhibit...
emission in the near-IR, red, and blue.\textsuperscript{38} A weak light emission (530 nm) from relatively large Au nanoparticles (\textasciitilde 25 nm) is attributed to the interactions between surface plasmons and incident photons, which occur simultaneously with the thermal electron relaxation,\textsuperscript{39} and the emission process was suggested to be due to electron–electron and electron–surface scattering processes.\textsuperscript{40} In our case, the physical origin of the peak at 330 nm from pure Au nanoparticles and nanoclusters in PS-\textit{b}-P2VP films may be understood by the same mechanism and may be ascribed to the radiative recombination of Fermi-level electrons and sp- or d-band holes. However, the peak at 367 nm resulting from the nanoporous film containing gold nanoclusters was different from that fabricated by the simple mixture of PS-\textit{b}-P2VP and HAuCl\textsubscript{4}. The geometry of the ringlike nanostructures composed of Au nanoclusters and PVP domains in the film may have a critical influence on the PL band, and the in-depth mechanism needs to be further investigated in future studies.

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Conclusions

A simple method used to fabricate a metallized nanoporous block copolymer film by the introduction of an inorganic compound into a block copolymer/homopolymer mixture is demonstrated. The degree of orientation of the cylindrical microdomains of block copolymer perpendicular to the substrate can be enhanced by the addition of inorganic compounds. Selective removal of the homopolymer can generate porous nanostructures containing metal component in one of the blocks, which shows a novel optical property. The metallized nanoporous films can be fixed permanently after cross-linking with UV irradiation. This may open up possibilities for the design of novel nanostructured, functional hybrid materials with diverse composition at low cost.

Acknowledgment. This work was funded by the National Natural Science Foundation of China (20674030), the Shandong Natural Science Foundation (Y2006B02), and the Doctorial Foundation of the University of Jinan (B0541). This work was supported by the Seoul Research and Business Development Program (10816).