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Organic–Inorganic Nanohybridization by Block Copolymer Thin Films**

By Dong Ha Kim, Zaicheng Sun, Thomas P. Russell, Wolfgang Knoll, and Jochen S. Gutmann*

A simple route for fabricating highly ordered organic–inorganic hybrid nanostructures, using polystyrene-*block*-poly(ethylene oxide) diblock copolymer (PS-*b*-PEO) thin films coupled with sol–gel chemistry, is presented. Hexagonally packed arrays of titania nanodomains were generated by one-step spin-coating from solutions containing a titania precursor and PS-*b*-PEO, where the precursor was selectively incorporated into the PEO domain. The PS-*b*-PEO template was subsequently removed by UV treatment, leaving behind a highly dense array of hexagonally packed titania dots. The size of the dots, as well as the lattice spacing of the array, could be fine-tuned by simply controlling the relative amount of sol–gel precursor to PS-*b*-PEO.

1. Introduction

Surfaces with regularly sized and spaced features on the nanometer length scale are of great interest.^[1,2] Self-assembly is a desirable method for fabricating nanostructured surfaces. In particular, block copolymer systems offer an attractive route for overcoming the limitations of conventional lithographic techniques, owing to their ability to self-assemble into ordered nanoscale morphologies.^[3–6] There have been numerous efforts to use self-assembled block copolymers as a tool for fabricating nanomaterials, and most of the issues have been addressed in bulk states.^[7–22]

Highly ordered semiconductor nanostructures in a confined environment have attracted intense interest owing to their potential applications in optical, optoelectronic, magnetic, and micromechanical devices. The most critical issue is the control of their size, spacing, and size distribution.^[23–30] Sol–gel chemistry using block copolymers as a structure-directing agent has been utilized as a useful approach for generating such nanostructures.^[31–44] However, demands for simple, reproducible, and cost-effective means of fabrication, with exquisite control over the morphology, have been made. Herein, a very simple route, using block copolymer thin films coupled with sol–gel chemistry to fabricate highly ordered organic–inorganic hybrid nanostructures, is presented.

Recently, a rapid route for orienting the cylindrical microdomains of an asymmetric polystyrene-*block*-poly(ethylene oxide) diblock copolymer (PS-*b*-PEO) normal to the surface of a substrate has been reported.^[45,46] Such an amphiphilic PS-*b*-PEO thin film is versatile as a scaffold for various nanostructures, owing to the hydrophilic PEO domain with controlled morphology.^[31,47–50] Kim et al. reported that inorganic oxide nanoparticles could be grown selectively on top of the PEO domains on the surface of PS-*b*-PEO thin film by chemical vapor deposition (CVD).^[47,48] Herein, we report the use of sol–gel chemistry to fabricate hexagonally packed arrays of titania nanodomains via one-step spin-coating from solutions containing titania precursor and PS-*b*-PEO; the precursor was selectively incorporated into the PEO domain. The PS-*b*-PEO template was subsequently removed by exposing to deep UV light, leaving behind an ordered array of titania dots. The scheme for generating such nanostructures is illustrated in Figure 1.

2. Results and Discussion

Figure 2 shows a series of phase-contrast atomic force microscopy (AFM) images of PS-*b*-PEO thin films with different amounts of sol–gel precursor on a silicon wafer. The amounts of precursor relative to the block copolymer (ϕ_p) were 7.1, 10.0, 13.2, and 15.9 % by volume (Figs. 2A–D, respectively). Highly dense, uniform arrays of hexagonally close-packed inorganic domains in a matrix of PS were produced, as evidenced by the harder inorganic domains (brighter areas) in the phase-contrast images.^[45,47,51] From the AFM line scan of the height contrast image (not shown here), the inorganic domains were found to protrude from the PS surface by ≈ 4.0 nm. Any AFM artifact due to the elastic property of the surfaces was ruled out because both phases are rigid. Both the diameter of the inorganic domains (D) and the center-to-center distance between them (d_{c-c}) systematically varied with ϕ_p . The fast Fourier transforms, FFTs, of the AFM images are given in their respective insets in Figure 2: in all cases, the FFTs are full circles, in-

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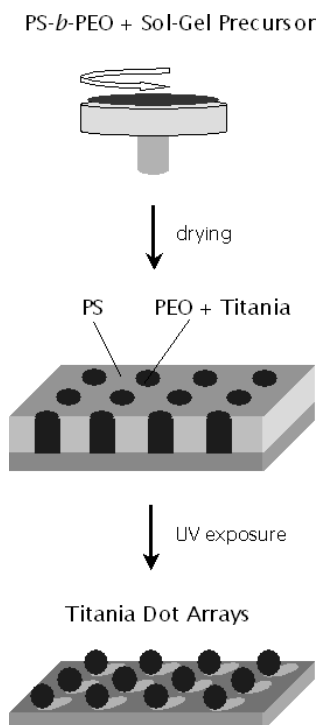


Figure 1. Schematic diagram of the process used to generate a nanopatterned titania dot array templated by a PS-*b*-PEO/sol-gel film. A toluene solution of PS-*b*-PEO was mixed with the desired amount of sol-gel precursor solution, and the solution was spin-coated onto a silicon wafer. Subsequent UV treatment removed the PS-*b*-PEO template and generated ordered arrays of titania dots.

dicating large grains of hexagonally packed domains oriented in different directions. The lattice spacing, which is inversely proportional to the peak position in the FFT image, decreased with increasing ϕ_p . These results show that the hexagonally packed inorganic nanodomains were preserved, and that the spacing of the nanodomains decreased with increasing ϕ_p .

The corresponding series of field-emission scanning electron microscopy (FESEM) images of the thin films with different ϕ_p are shown in Figures 3A–D. The histograms of the distribution of the inorganic domain sizes in the images were constructed using Scion image analysis software, and the Gaussian fits to them are given in Figure 4A. The average domain size, D (the center position of each Gaussian fit), and the values of d_{C-C} calculated from the images are summarized in Figure 4B; both D and d_{C-C} decreased with increasing ϕ_p . The D values are ≈ 19.5 , 18.8, 14.6, 13.5, and 12.1 nm and the d_{C-C} values are ≈ 36.2 , 33.2, 29.5, 23.6, and 22.4 nm, for samples with ϕ_p values of 4.6, 7.1, 10.0, 13.2, and 15.9 %, respectively. A morphological transition of the block copolymer domains was not observed even with high values of ϕ_p , in contrast to other systems.^[31–33,38,49]

The following model describes the above experimental results. The initial solution is homogeneous, because PS, PEO, and the sol-gel precursor are soluble in the mixed solvent of toluene and isopropanol. As the toluene evaporates, micelles are formed, in which the hydrophilic core, PEO, and the titania oligomer are surrounded by the PS corona and the micelles get closer, forming ordered cylindrical domains. If the film is sufficiently thin (e.g., its thickness is comparable with the bulk peri-

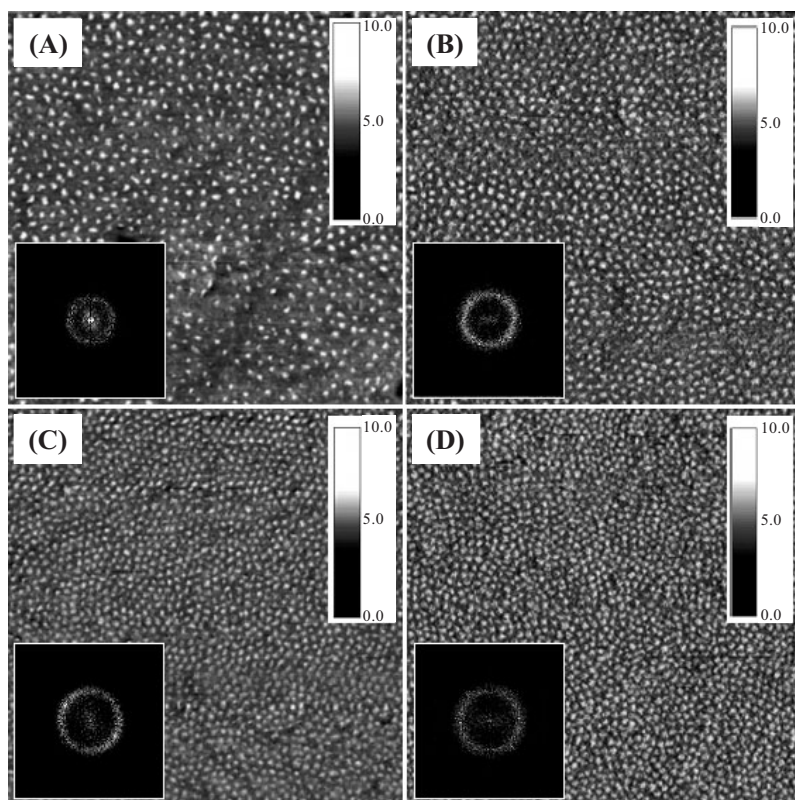


Figure 2. Phase-contrast AFM images of PS-*b*-PEO films with different amounts of sol-gel precursor: A) 7.1 %; B) 10.0 %; C) 13.2 %; D) 15.9 %. All AFM images are $1 \mu\text{m} \times 1 \mu\text{m}$ in size. The inset in each AFM image (lower left) is a fast Fourier transform (FFT) of the respective AFM image. The scale of all the FFT images was chosen to represent the same area in Fourier space, in order to allow direct comparison.

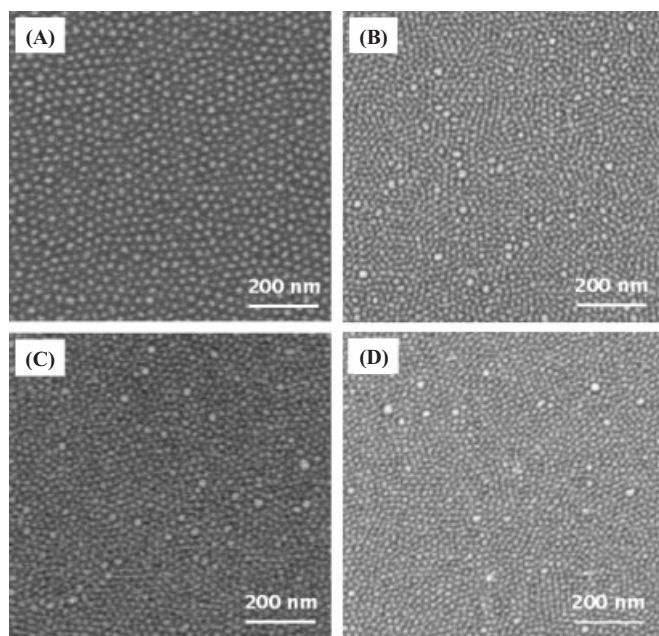


Figure 3. FESEM images of PS-*b*-PEO films with different amounts of sol-gel precursor: A) 7.1%; B) 10.0%; C) 13.2%; D) 15.9%. The film thicknesses were about 48.0 ± 5 nm.

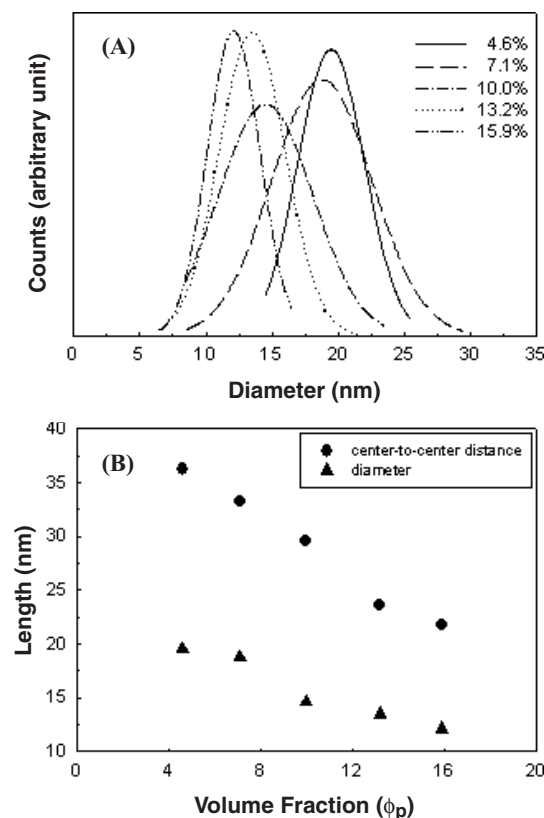


Figure 4. A) Gaussian fits to the distribution of inorganic domain sizes in the FESEM images. B) Diameter of the inorganic domains and center-to-center distance between the domains as functions of the amount of sol-gel precursor.

od of the block copolymer), the cylindrical domains are oriented normal to the substrate surface via self-assembly induced by solvent evaporation.^[45,46]

The decrease in D and d_{C-C} (Fig. 4B) can be understood in terms of the complex micellization behavior of amphiphilic diblock copolymers in mixed solvents. In general, the size and shape of amphiphilic diblock copolymer micelles depends on the interfacial tension between the two solvated blocks. If one uses a mixed solvent system, such as the toluene/isopropanol system employed in this study, at least one of the blocks will typically be preferentially solvated by one solvent component. In these cases, the resulting interfacial tension and thus, the micelle size, is a function of the solvent composition. Seo et al. investigated the micellization of a PS-*b*-PEO copolymer with the inverse morphology of the system in our study (i.e., the weight-average molecular weight, M_w , of the PEO block is much larger than the PS block and the majority of the solvent is hydrophilic);^[52] it is reasonable to assume that our system shows a similar behavior and exhibits a decrease in micelle size as a function of cosolvent addition. It is thus qualitatively understandable that the domain size of the resulting titania particle decreases with increasing ϕ_p , if one views the isopropanol/sol-gel solution as a “cosolvent” and assumes a preferential mixing of this cosolvent with the PEO block of the PS-*b*-PEO.

With a concentration-dependent decrease of domain size, the decrease in interparticle distance between the dots with increasing ϕ_p can be interpreted in terms of the distribution of added precursor molecules inside the PEO domain.^[53] If the precursor is uniformly distributed in the micellar domain, the number of block copolymers at the interface per unit area will decrease, that is, the number of PS-*b*-PEO chains constituting one micelle decreases, leading to a decrease in d_{C-C} .

The chemical identity of the generated inorganic materials was confirmed by X-ray photoelectron spectroscopy (XPS) at a takeoff angle of 15° . The characteristic peak of titanium, Ti($2p^3$), was observed at ≈ 459 eV and the peaks for C(1s) and O(1s) were observed at ≈ 285 and ≈ 538 eV, respectively, in the survey spectra (not shown here).^[54–56] Figure 5A shows a series of high-resolution O(1s) XPS spectra of PS-*b*-PEO films with different values of ϕ_p . The peaks at ≈ 533 and ≈ 530 eV are attributed to oxygen atoms bound to carbon and titanium atoms, respectively. It is clear that the intensity of the peak at ≈ 530 eV relative to the peak at ≈ 533 eV increases with increasing ϕ_p , indicating that more titania is incorporated into the PS-*b*-PEO film. The atomic ratios, Ti/C and O/C, measured from the survey spectra are summarized in Figure 5B; the values increase with increasing ϕ_p initially and show a saturation behavior.

The plateau in Figure 5B can be interpreted in terms of a macrophase separation between the block copolymer and precursor molecules added. When precursor is added into the selective PEO domain, the domain size increased at lower values of ϕ_p . With increasing ϕ_p , macrophase separation occurs at a certain point. It has been reported that there is a high tendency for macrophase separation as the repulsion between added component and PS matrix increases.^[53] This is evidenced by the

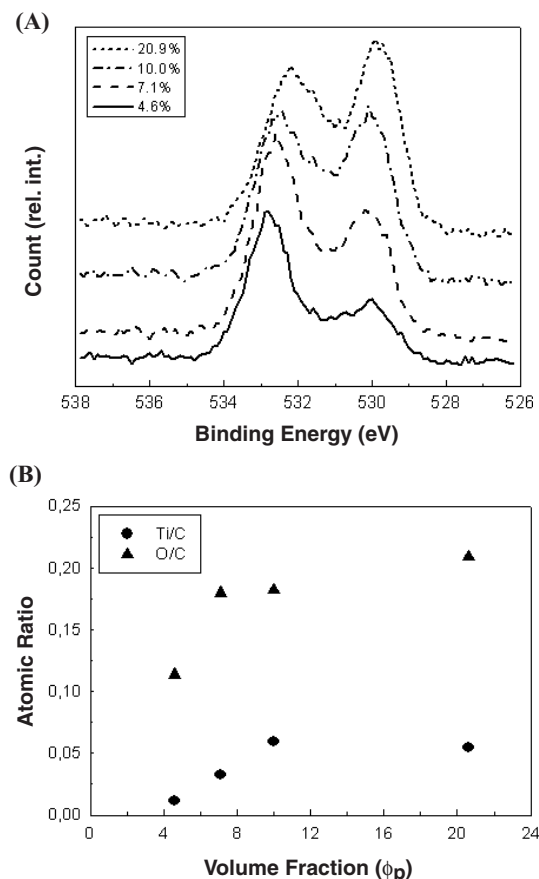


Figure 5. A) High-resolution O(1s) XPS spectra of PS-*b*-PEO films with different amounts of sol-gel precursor; acquired at a takeoff angle of 15°. B) Atomic ratios for PS-*b*-PEO films with sol-gel precursor as a function of the amount of sol-gel precursor.

existence of large domains observed in the SEM images of PS-*b*-PEO with higher ϕ_p . Thus, not all the precursor molecules might be incorporated into the dissolved PS-*b*-PEO before filtration and subsequent spin-coating steps if more than a certain amount of precursor is added.

It is a necessary and intriguing task to generate patterned arrays of pure titania on a silicon wafer from the precursor-containing films for possible applications. To this end, thin films of PS-*b*-PEO with ϕ_p values of 35.0 and 15.0 % were exposed to deep UV light to remove the PS-*b*-PEO matrix. It is known that free radicals and activated species, which have been generated in situ from atmospheric oxygen by UV light, remove organic polymer.^[42,57,58] Figure 6A clearly shows that highly dense arrays of titania dots were generated over the wide area of the surface, keeping the lateral positional and orientational order. The height of the dots estimated from the side view (Fig. 6B) was much lower than the initial film thickness, which is attributed to the collapse of PEO during the UV-exposure step. More in-depth investigation into the solid-like titania structure by X-ray diffraction analysis is in progress.

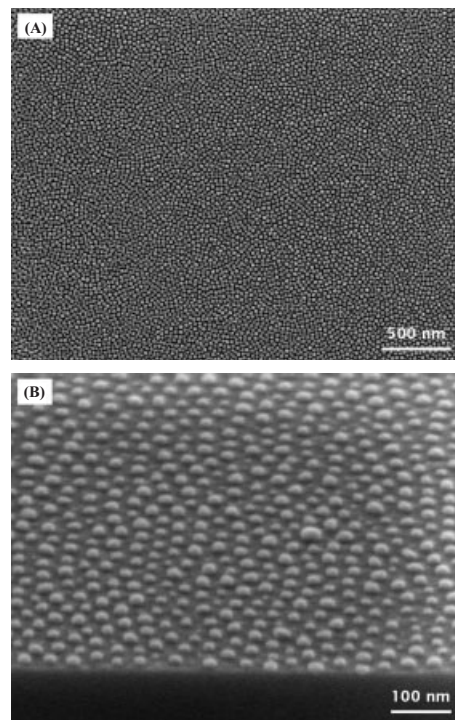


Figure 6. FESEM images of titania dot arrays prepared from PS-*b*-PEO films with A) 35.0 % and B) 15.0 % sol-gel precursor, after exposure to UV light at room temperature for 6 h in air.

3. Conclusions

A very simple route to highly dense arrays of hexagonally packed inorganic materials using thin-film block copolymers with sol-gel chemistry was presented. Thin films of asymmetric PS-*b*-PEO with a titania precursor in a cylindrical PEO domain were obtained by one-step spin-coating. Subsequent UV treatment of the films resulted in a nanoscopically patterned surface of an array of titania dots with tunable domain size and spacing. Such nanostructured titania surfaces have promise for use as binding matrices for sensory applications or optical devices through which quantitative analysis can be done in terms of the effect of size and spacing.^[54,59–61]

4. Experimental

An asymmetric diblock copolymer of polystyrene and poly(ethylene oxide) with a molecular weight of 11 217 g mol⁻¹ and a polydispersity of 1.11 was synthesized by sequential anionic polymerization of styrene monomer followed by ethylene oxide monomer [62]. The volume fraction of PEO was 0.33. Another commercial PS-*b*-PEO (molecular weight 25 400 g mol⁻¹; polydispersity 1.05) with a PEO volume fraction of 0.25 (Polymer Sources Inc.) was used to generate a titania dot array by UV exposure (Fig. 6) to verify the general validity of the experimental findings. Titanium tetra-isopropoxide (TTIP, 97 %) was purchased from Aldrich. Analytical grade isopropanol, HCl (37 %), and toluene were purchased from Fisher Scientific and Laborbedarf GmbH.

A solution of PS-*b*-PEO in toluene (10 mg mL⁻¹) was stirred for at least 1 h to ensure complete dissolution. Sol-gel precursor solutions were prepared by adding TTIP (0.125 mmol) dropwise into isopropanol (5 mL) containing HCl (0.125 mmol) under vigorous stirring for at least 1 h. The desired amount of sol-gel precursor solution was added into a PS-*b*-PEO solution and stirred for 5 min. The films were prepared on a silicon wafer by spin-coating, at 2500 rpm for 120 s, using a SÜSS Delta 80BM spin-coater. The film thicknesses, determined by a Tencor P-10 surface profiler, were about 48.0 ± 5 nm. The obtained films were dried under ambient conditions to induce crosslinking of the sol-gel precursor. The samples were irradiated by UV light at 254 nm with a dose of 25 J cm⁻² (XX-15S; UVP, Inc.) at room temperature for 6 h in air to remove the organic matrix, leaving behind titania domains.

AFM images were obtained using a Digital Instruments Dimension 3100 scanning force microscope in tapping mode with an Olympus cantilever (spring constant in the range 33.2–65.7 N m⁻¹ and resonant frequency of 277.3–346.3 kHz).

FESEM images were obtained using a field-emission scanning electron microscope (LEO 1530 "Gemini") under 1 kV accelerating voltage. The images were analyzed using Scion image software (Scion Corporation) to determine *D* and *d*_{C-C}; the average values in a 512 nm × 512 nm area were taken.

XPS were recorded on a VG Escalab 200I-X2 from VG scientific with Al K α excitation (1486.6 eV). Spectra were obtained at a takeoff angle of 15° (between the plane of the surface and the entrance lens of the detector optics).

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