Photocatalytic Printing of Nanostructures on TiO_2 Using Diblock Copolymer

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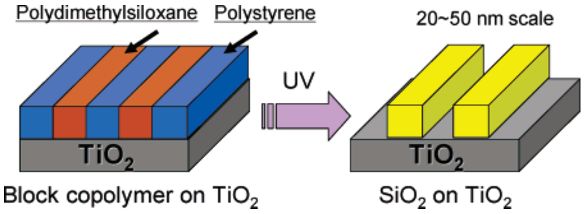
The fabrication of ordered structures in the nanoscale is of significant importance to control the surface properties of materials and to develop arrays of functional materials, leading to high-density devices such as integrated electric circuits and data storages. Besides the conventional "top-down" lithographic approaches, the formation of nanostructures by self-organization of soft materials recently draws much attention.[1] These "bottom-up" approaches could fabricate various surface nanopatterns with uniform sizes and regular shapes by simple procedures and possibly at low cost. It is well-known that block copolymers self-organize into a variety of ordered morphologies in nanometer scales because of the immiscibility between different polymer segments. As a result, the block copolymers could spontaneously form ordered nanoscale structures, such as close-packed spherical, cylindrical, or lamellar, depending on the composition of the polymers. The microphase-separated domains of the block copolymers with the molecular weight of 20−100 kg/mol typically yield periodicities of 20−50 nm, which is the intermediate region between the "top-down" and the "bottom-up" approaches. Recently, the use of block copolymers as structural templates has been studied extensively.[2] Park et al. reported that the selective ozonation of polyisoprene or polybutadiene segments in the block copolymers left the arrays of holes or stripes in the polystyrene (PS) matrixes. They used these porous films as the masks for a reactive ion etching to fabricate dense periodic arrays of holes or dots carved on silicon nitride substrates.[3] Russell et al. reported the fabrication of ultrahigh-density arrays of Co nanowires by using ordered block copolymer films.[4] In their report, a porous polymer film was obtained by the selective etching of one polymer segment in a hexagonally ordered structure of polystyrene-*block*-poly(methyl methacrylate) (PS-*b*-PMMA) and was used as a template for the electrodeposition of Co. They also reported that the selective modification of a hydrophilic segment of polystyrene-*block*-poly(ethylene oxide) (PS-*b*-PEO) with $SiCl_4$ or $TiCl_4$ leads to the formation of SiO_2 or TiO_2 nanodot arrays.[5] Silicon-containing block copolymers were also investigated by taking advantage of the contrast in chemical reactivity between the polymer segments.[6−8] Chan et al. reported the conversion of a silicon containing triblock copolymer film to a three-dimensional nanostructured silicon oxycarbide ceramic.[6] Nanoporous polymer materials were fabricated by selectively removing the silicon-containing block from a bulk block copolymer.[7]

Scheme 1. Schematic Representation of "Photocatalytic Printing" on TiO_2



Photocatalytic TiO_2 is well-known for its strong oxidation power under ultraviolet (UV) light decomposing various organic compounds into CO_2 under ambient conditions.[9] In addition to the photo-induced decomposition reaction, it is known that the surface of TiO_2 becomes highly hydrophilic after UV light irradiation.[10] Much research has been conducted to utilize these abilities of TiO_2 for the applications such as self-cleaning materials, antibacterial materials, and water/air purification.[11]

Herein we report a novel strategy of transferring the nanopatterns of block copolymers into inorganic structures by exploiting the photocatalytic oxidation reaction of TiO_2. The photocatalytic reaction on TiO_2 could transform adsorbed materials into another form with their spatial distribution on the surface conserved, as a result of the mild reaction conditions. Scheme 1 illustrates the idea of what we call "photocatalytic printing" in this work. Polymer segments containing silicon atoms are converted into SiO_2 by the photocatalytic reaction of TiO_2 under mild conditions, while the organic components are decomposed to CO_2. As a result, the nanostructure of the soft block copolymer is transferred to a nanopattern of rigid SiO_2, "printed" on the TiO_2 surface.

Thin films of anatase TiO_2 were prepared on Corning no. 1737 glass by dip-coating using a commercial titanium isopropoxide solution (NDH-510C, Nippon Soda Co., Ltd.). The dip-coated samples were dried at 120 °C for 40 min, heated to 500 °C for 1 h, and calcined at 500 °C for 30 min in air. The TiO_2 substrates were cleaned ultrasonically in an aqueous detergent solution for 1 h. Polystyrene-*block*-poly-

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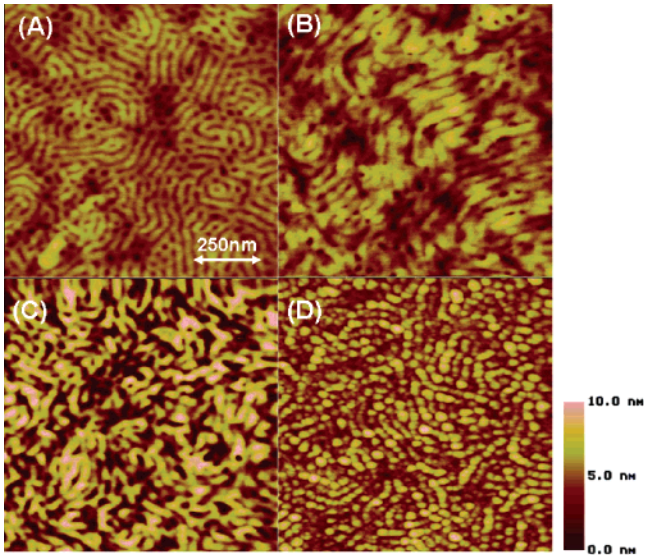

Figure 1. AFM height images of PS-*b*-PDMS-1 block copolymer thin films deposited on TiO_2 films (A) before and (B) after UV irradiation for 20, (C) 68, and (D) 216 h.

(dimethylsiloxane) (PS-*b*-PDMS) diblock copolymers (Polymer Source, Inc.) were spin-cast on the substrates from 7.5 mg/mL solution in toluene at 3000 rpm. The thicknesses of the films were in the range of 30−50 nm, evaluated by spectral ellipsometry (H-VASE with M-2000, J. A. Woollam Co., Inc.) using the films deposited on silicon wafers under the same coating conditions. PS-*b*-PDMS-1 has number-average molecular weights (M_n) of 31 000 and 11 000 g/mol for the blocks of PS and PDMS (volume fraction of 28.4% PDMS), respectively, with a polydispersity of 1.1. PS-*b*-PDMS-2 has M_n values of 43 000 and 8500 g/mol for the blocks of PS and PDMS (volume fraction of 19% PDMS), respectively, with a polydispersity of 1.04. The surface morphologies of the block copolymer films were observed using atomic force microscopy (AFM; Nanoscope 31, Digital Instruments, Inc.) in tapping mode under ambient conditions. Field-emission scanning electron microscopy (FE-SEM; S-900 Hitachi, Inc.) was conducted with an acceleration voltage of 5 kV. The samples were prepared without any metal sputtering. The block copolymer films on TiO_2 were irradiated in air using a fluorescent black light bulb (FL10BLB, NEC Co., Ltd., Tokyo, Japan; maximum wavelength, 365 nm) with a UV light intensity of 1 mW/cm^2 at the film surface. The conversion reaction of PDMS to SiO_2 and the decomposition of PS were investigated by X-ray photoelectron spectroscopy (XPS; model 5600, Perkin-Elmer with a Mg Kα X-ray source). Ti $2p_{3/2}$ peaks at 461.25 eV were used to calibrate the chemical shifts of Si 2p.

Figure 1A shows the AFM height image of a PS-*b*-PDMS-1 film spin-cast on a TiO_2 substrate. The film shows a wormlike structure with a periodic length of about 40 nm, indicating the microphase separation between the PS and the PDMS segments in the film. The morphology shown in Figure 1A is assigned to cylinders of PDMS oriented parallel to the substrate, considering the volume fraction of PDMS (28.4%) and some recent works on PS-*b*-PDMS.[12,13] The receding (darker) and the protruding (brighter) areas could be attributed to the PDMS and the PS segments, respectively. This assignment is also supported by a phase contrast in the AFM phase images (see Supporting Information).

When the films were irradiated by UV light, the surface morphology of the films drastically changed. Figure 1B,C shows the AFM height images after the UV irradiation for 20 and 60 h, respectively. In these figures, one of the components in the nanostructures gradually receded and the height contrasts became enhanced in the course of the UV irradiation. The change was completed after 216 h, and the AFM image of the final state is shown in Figure 1D. While a slight globular deformation in the structure is observed, Figure 1D reproduces the wormlike structure with the width of about 40 nm similar to the one before the UV irradiation in Figure 1A. In other words, the spontaneously generated pattern of the block copolymer in Figure 1A was transferred to the nanostructure with an enhanced height contrast in Figure 1D by the UV irradiation. The root mean square (rms) of the height profiles in AFM represents the enhancement of the height contrast, changing from 0.87 nm (Figure 1A) to 1.9 nm (Figure 1D) after the UV irradiation.[14] A FE-SEM image of the PS-*b*-PDMS-1 film after the UV irradiation for 216 h is shown in Figure 2. A wormlike structure with the width of 40 nm is clearly seen, corresponding to the AFM image of Figure 1D.

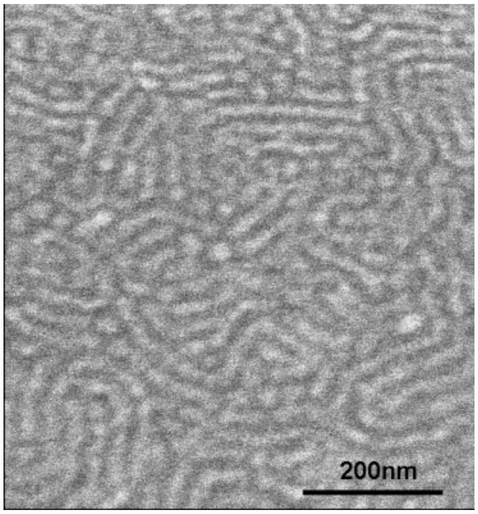

Figure 2. FE-SEM image of a PS-*b*-PDMS-1 block copolymer thin film deposited on the TiO_2 film after UV irradiation for 216 h.

After the UV irradiation, the observed surface structures were not removed by washing with organic solvents, indicating the chemical transformation of the polymer. It is also important to note that the polymer films on bare glass substrates did not change their morphologies under the same irradiation conditions. These observations indicate that the changes of the morphologies in the polymer films were induced by the photocatalytic reaction of TiO_2. The PS segment was decomposed because of the strong oxidizing ability of TiO_2 under the UV irradiation, while the soft PDMS segment was oxidized to rigid SiO_2.[15] It results in transferring the initial structure of the microphase separation into the inorganic nanopattern on the TiO_2 surface (Scheme 1).

To confirm the chemical transformation of the film after the UV irradiation, the compositions of the films were

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(14) The image of Figure 1D is totally different from a pristine TiO_2 surface, which consists of 20 ± 3 nm grains of crystalline TiO_2, and was relatively flat with 1.2−1.4 nm of rms.

(15) It has been reported that TiO_2 photocatalyst is capable of oxidizing silicon-containing organic compounds adsorbed on the surface into SiO_2: Sun, R. D.; Nakajima, A.; Watanabe, T.; Hashimoto, K. *J. Photochem. Photobiol., A* **2003**, *154*, 203.

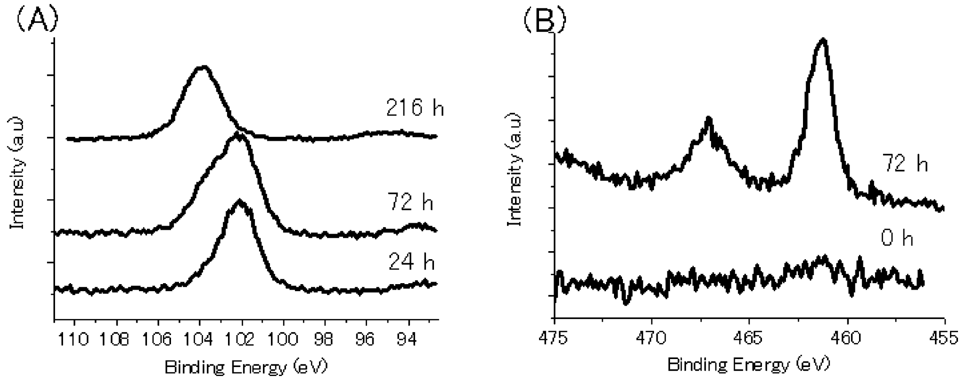

Figure 3. XPS profile changes of PS-*b*-PDMS-1 in the (A) Si 2p and (B) Ti 2p regions in the course of the UV irradiation.

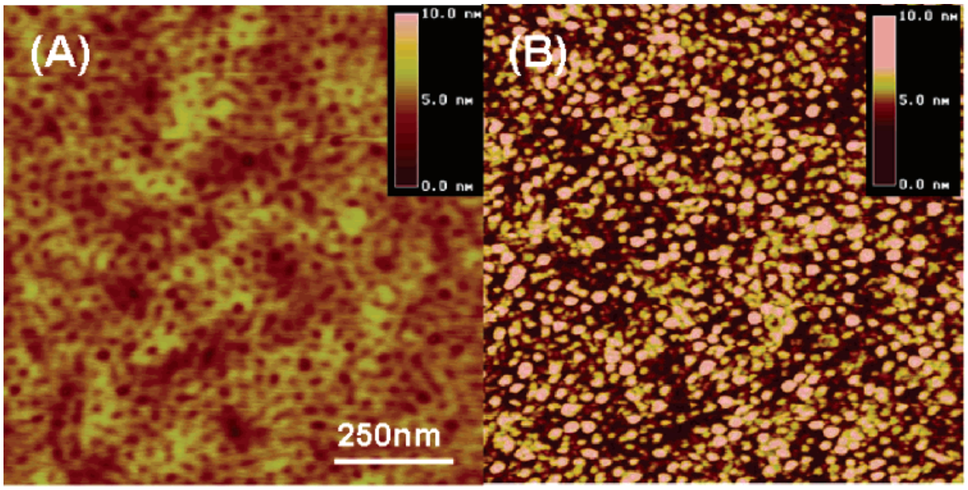

Figure 4. AFM height images of PS-*b*-PDMS-2 block copolymer thin films deposited on TiO_2 films (A) before and (B) after UV irradiation for 216 h.

analyzed by XPS. The atomic composition ratio of carbon decreased by 95% during the UV irradiation, and the carbon concentration was nearly the same as the contaminant level on TiO_2 after 216 h, suggesting the complete decomposition of the organic components.[16] The conversion of PDMS segments to SiO_2 was monitored in the Si 2p region (Figure 3A). Si 2p peak corresponding to the Si−O bond shifted toward higher binding energy from 102.1 to 103.7 eV after 216 h of the UV irradiation, indicating the conversion of PDMS to SiO_2.[17] In contrast, no peak was observed in the Ti 2p region before the UV irradiation because of the complete coverage of TiO_2 by the polymer film (Figure 3B). After the UV irradiation for 72 h, however, both the Ti $2p_{1/2}$ and the Ti $2p_{3/2}$ peaks corresponding to Ti−O bonds in TiO_2 were observed at 461 and 467 eV, respectively. These XPS results clearly show the decomposition of the organic components in the polymer and the conversion of PDMS to SiO_2 by photocatalytic oxidation of TiO_2, accompanied by the partial exposure of the TiO_2 substrate surface.

Because a block copolymer adopts a variety of nanostructures depending on its segment ratio, it is possible to control the morphology of the SiO_2 nanopattern by changing the starting block copolymer. Figure 4A is an AFM height image of a PS-*b*-PDMS-2 film spin-cast on a TiO_2 substrate. It shows round-shaped darker (lower) areas with diameters of 20−30 nm. Considering the volume fraction of PDMS in PS-*b*-PDMS-2 (19%), the darker areas could be attributed to the PDMS spherical microdomains and the bright areas could be attributed to the PS matrix (see Supporting Information). After 216 h of UV irradiation, the height contrast was enhanced and the bright dots with the sizes of 20−50 nm were clearly seen in Figure 4B. It is concluded that the structure in Figure 4A was transferred into the structure in Figure 4B as a negative image in terms of the height contrast in AFM. This result suggests that the concept of “photocatalytic printing” in Scheme 1 can be applied to the various microphase separated patterns.

In conclusion, we have successfully transferred the nanostructures of the block copolymers into SiO_2 patterns on the surface, taking a new approach by exploiting the photocatalytic oxidation on TiO_2 as presented in Scheme 1. The method reported here is virtually one step and has an advantage of the easiness in the fabrication. Because the surface wettability of TiO_2 could be greatly affected by the surface structures,[18,19] the detailed investigation into the surface properties could lead to the relationship between surface nanostructure and the photoinduced hydrophilicity of TiO_2. Furthermore, the nanostructures of SiO_2 could be used as bases for chemical modifications of the surface in the existence of an exposed TiO_2 surface. The idea of photocatalytic printing might also be applied to metal containing polymers such as Co and Fe to obtain the high-density arrays of the various metal oxides under mild conditions.

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(16) To confirm the complete decomposition of the organic components, the irradiated sample was heated at 550 °C to remove the remaining organic components. No change of the carbon peak intensity was observed in XPS spectra before and after the heating, suggesting that the conversion was completed after 216 h of the UV irradiation.

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Supporting Information Available: AFM phase images of the PS-*b*-PDMS-1 and PS-*b*-PDMS-2 films after spin-coating (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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