

Photo-orientation of Mesostuctured Silica via Hierarchical Multiple Transfer

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Received January 20, 2002

Revised Manuscript Received April 15, 2002

Photoinduced optical anisotropy has become an important and versatile tool in alignment of materials. When polymer films or Langmuir–Blodgett (LB) films possessing a photochromic unit (mostly azobenzene (Az)) are exposed to linearly polarized light (LPL), the excited chromophore undergoes a reorientation in a nonexcitable direction, namely, in the orthogonal direction.^{1–3} This photoinduced anisotropy can be transferred to the orientation of liquid crystals,^{1,4,5} dye aggregates,⁶ and polymer chains.⁷

The above photo-orienting processes are so far applicable only to soft materials and not to stiff inorganic substances. Here, we report successful photo-orientation of mesostructured silica. The surfactant-templated silicate^{8–11} is an intriguing candidate for photo-orientation because such hybrid mesophases are synthesized via sol–gel polymerization starting from a fluid lyotropic liquid-crystalline precursor. Mesoporous materials such as MCM-41^{8,9} and FSM-16^{10,11} possess large surface area and uniformly sized pores, which are more effective than crystalline zeolite molecular sieves as catalysts for larger molecules. Such compartmentalized materials also have attracted attention in optical materials,^{12,13} separations, chemical sensing of molecules,¹⁴ molds of

polymers,¹⁵ and noble metal wires.^{16,17} The mesochannels may be highly directional at local levels; however, they are randomized at larger scale levels, which can be a drawback for effective technological applications. The macroscopically aligned mesostructured silica are available by application of strong magnetic fields,¹⁸ reactant flows,¹⁹ and capillary flow with an elastic micromold for microcontact printing in electric fields.²⁰ For thin films, the spin-casting method²¹ or nucleation at interfaces^{22,23} are applicable. In such cases, a macroscale orientation of mesochannels can be attained by deposition on a rubbed surface²⁴ or a LB film²⁵ of polyimide. Nevertheless, all the above mechanical procedures are not beneficial for micropatterned orientation. This work proposes a new procedure for photo-orientation of mesostructured silica via hierarchical multiple transfers starting from a photo-oriented azobenzene monolayer.

The system adopted here is indicated in Scheme 1. The Az-containing monolayer of 6Az10–PVA was prepared by the LB method.⁷ Irradiation of LPL (436 nm) to this Az monolayer resulted in the orthogonal in-plane orientation of the Az chromophore. Onto this molecular layer, a spin-cast film of poly(di-*n*-hexylsilane) (PDHS; $M_w = 4.5 \times 10^4$, $M_w/M_n = 1.7$, thickness = 60 nm) was prepared as described previously.⁷ After sufficient crystallization of the PDHS spin-cast film, this film became highly optically anisotropic giving S (orientational order parameter) = 0.47. The Si backbone is aligned perpendicular to the polarization plane of the light, which is in accordance with the direction of the photoaligned Az layer.⁷ The mesostructured silica on the photoaligned PDHS was prepared according to a modified method described by Yang and co-workers²² using tetraethoxysilane (TEOS, $(C_2H_5O)_4Si$), and cetyltrimethylammonium chloride (CTACl, $CH_3(CH_2)_{15}N(CH_3)_3Cl$, surfactant template). Attempts at direct deposition of the surfactant-templated silica onto the Az monolayer were unsuccessful because the conditions adopted for the siloxane condensation crucially damaged the orientation of the Az layer.

Figure 1a shows the optical microscopic image of the deposited surfactant/silica hybrid on the photoaligned PDHS film. Uniaxially aligned elongated particles with widths in the micrometer range were observed. The

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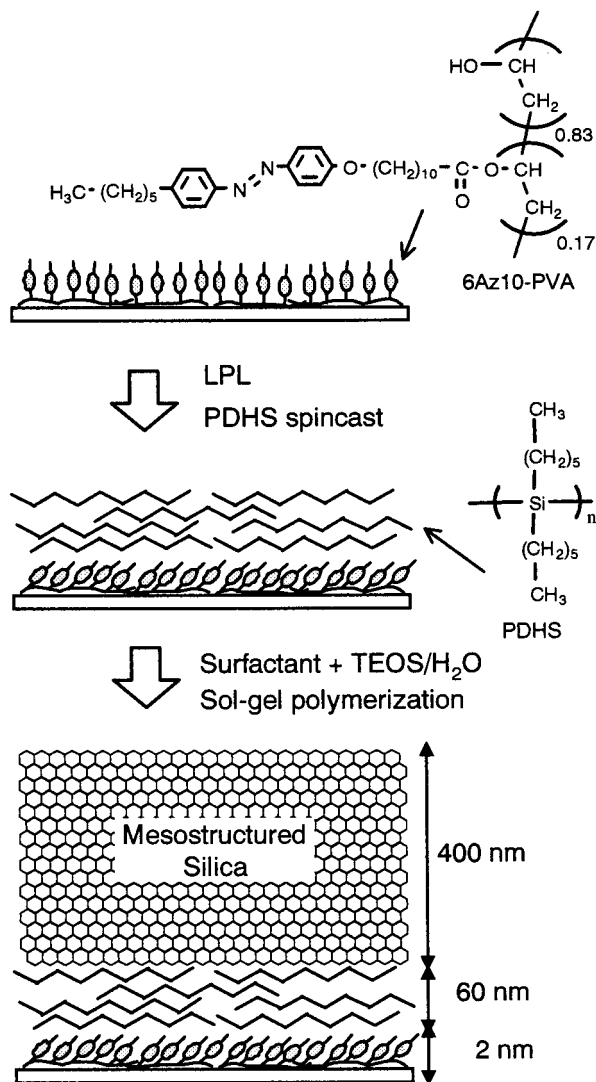
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Scheme 1. Chemical Structure of Materials and Schematic Illustration of the Layer Structure Constructed in This Work



orientation of each particle was parallel to each other and the direction of the long axis of the particles was perpendicular to the Si backbone direction. This indicates that the orientation of elongated particles are parallel to the polarization direction of pre-irradiated actinic polarized light. A nonoriented surface yielded round and spherical surfactant/silica particles. Thus, the elongation of the particle strongly suggests the alignment of the mesochannels.

Removal of organic surfactant molecules from the composite was subsequently attempted. The surfactant molecules are generally removed by calcination by heating to high temperatures exceeding 573 K. We adopted here a recently developed "photocalcination" achievable at room temperature according to a modified method of Hozumi and co-workers.²⁶ The mesostructured silica films on the photoaligned PDHS film were irradiated for 1 h with vacuum ultraviolet light (185 and 254 nm) at room temperature under an O₂ atmosphere. The complete removal of the organic template surfactant

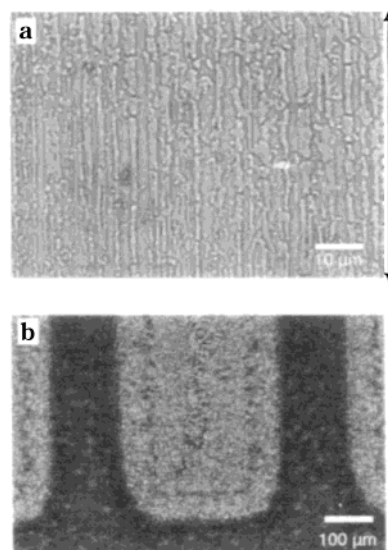


Figure 1. (a) Optical microscopic image of the mesostructured silica films on the photoaligned PDHS film. The arrow shows the polarization direction of actinic polarized light. (b) Optical microscopic image of the mesoporous silica films, which was prepared on the locally photoaligned PDHS film after irradiation of UV light (365 nm) through a micropatterned photo-mask.

was confirmed by infrared spectroscopy (Biorad FTS6000) for a photoaligned composite film synthesized on a silicon wafer. The complete disappearance of C–H stretching bands (2840–2970 cm^{−1}) also indicates the removal of the "alignment template" of the PDHS film lying underneath. The Si–O stretching band around 1070 cm^{−1} was essentially unchanged, indicative of the retention of the siloxane network structure.

Figure 2a shows X-ray diffraction (XRD) patterns of the as-synthesized composite and photocalcinated mesoporous silica films obtained with a Philips X'Pert-MPD diffractometer. In as-synthesized surfactant/silica composite films, two diffraction peaks were observed at $2\theta = 2.63$ and 5.20 corresponding to (100) and (200) of the hexagonal packing of the mesochannels ($d_{100} = 3.33$ nm). The absence of the (110) and (210) diffraction peaks in this XRD pattern indicates that the mesochannels are oriented parallel to the PDHS surface.²² For the mesoporous silica films after photocalcination, the XRD peaks shifted to a slightly higher 2θ angle ($d_{100} = 3.27$ nm). From these results, the hexagonal structure of the mesoporous silica films was maintained. The retention of the spacing period and anisotropy clearly indicates the formation of mesochannels and excludes a possibility of layer structure formation.

The in-plane orientation of mesochannels was further evaluated by the XRD measurement. A scan of in-plane rotation (ϕ) was conducted, fixing the detector position ($2\theta = 2.10^\circ$) at the ($1/2, 1/2, 0$) diffraction peak maximum as shown in Figure 2b. The starting angle ($\phi = 0^\circ$) coincided with the orthogonal direction of the actinic polarized light. Two peaks were observed at every 180° (Figure 2c), indicating that the photo-oriented mesochannels have a preferential orientation parallel to the direction of the pre-irradiated actinic polarized light.

Spatial modulations by micropatterning were further performed. In this experiment, the photoalignment of PDHS was first performed all over the area, and

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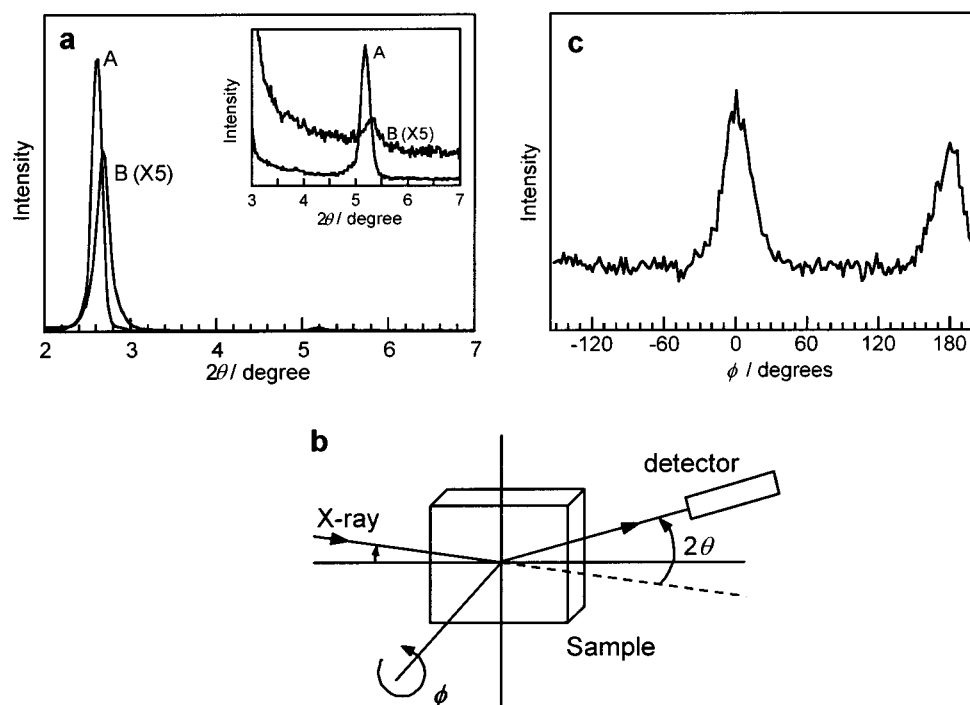


Figure 2. (a) XRD patterns for the mesostructured silica films on the photoaligned PDHS film (A, as-synthesized; B, photocalcinated). The inset shows magnified XRD reflection profiles at $2\theta = 3^\circ$ – 7° . (b) Illustration of the in-plane XRD measurement. (c) The ϕ scan profile of in-plane XRD for the as-synthesized mesostructured silica film on the photoaligned PDHS film. $\phi = 0^\circ$ was set in the orthogonal direction of the actinic polarized light. The position of the detector is adjusted as the $(1/2, 0)$ diffraction peak (2.10°).

successively local photoscission of PDHS backbone through a photomask was carried out by 365-nm light illumination. The local photocleaved parts could be washed out with methanol. Figure 1b shows the optical microscopic image of the mesostructured silica films synthesized on the PDHS film prepared above. As seen, the orientational modulation could be readily visualized. The bright area corresponds to the UV exposed parts where PDHS was decomposed. In these areas, the deposited mesostructured silica particles had no preferential orientation. On the other hand, the dark area corresponds to unexposed areas with retention of the photo-orientated PDHS film, where elongated and oriented mesostructured silica films were formed. The contrast is due to the difference in the light-scattering intensity. It is stressed here that the photo-orientation method readily allows for such microscopic architectures, which would be intricate in mechanical procedures such as rubbing or the LB method. Thus, the photoprocess can provide new ways for utilization of mesostructured materials directing downsized and directional device fabrications. Optical patterning of photosensitive silica mesophases can be performed by incorporating a photoacid generator which promotes

localized acid-catalyzed siloxane condensation in the organic template.²⁷ This process, however, does not provide controlled orientations of the mesochannels. The present work combines the photoaligning technology and fabrication of mesostructured materials. It is anticipated that rapid recent developments in both research fields could lead to new aspects in mesostructured materials with a wide range of applicability.

Acknowledgment. We thank Prof. M. Ogawa of Waseda University for technical assistance and helpful discussions. We also thank Dr. A. Saiki of Center for Advanced Materials Analysis of the Tokyo Institute of Technology for the in-plane XRD measurements. This work was supported by a Grant-in-Aid for Scientific Research (No. 13875188 to T.S.) from The Ministry of Education, Culture, Sports, Science and Technology, Japan.

CM025515Z

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