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$\pi-\pi$ Interaction-Induced Vertical Alignment of Silica Mesochannels Templated by a Discotic Lyotropic Liquid Crystal

Mitsuo Hara,[†] Shusaku Nagano,[†,‡] and Takahiro Seki*,[†]

Department of Molecular Design and Engineering, Graduate School of Engineering, Nagoya University, Chikusa, Nagoya 464-8603, Japan, and PRESTO, Japan Science and Technology Agency (JST), Japan

Received July 13, 2010; E-mail: tseki@apchem.nagoya-u.ac.jp

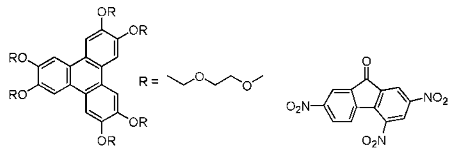
Abstract: The development of vertically aligned mesochannels in organic/inorganic hybrid films is in high demand and a challenging issue. However, there are no clear guiding principles to attain the surface-mediated vertical alignment. This work proposes the first clear versatile strategy to achieve the vertical alignment by utilizing the $\pi-\pi$ interaction between the organic template molecule of a planar discotic liquid crystalline and 2D π-plane of graphite. The crucial role of the $\pi-\pi$ interaction can be verified by the exploration with other substrates such as silicon wafer surfaces with varied surface energy (water contact angle: 5°−105°), quartz plates, and polymer films, which provided common parallel alignment with respect to the substrate plane.

Mesostructured organic/inorganic hybrids and their calcinated porous materials (mesoporous materials) synthesized via templating a liquid crystalline (LC) surfactant aggregate have been the subject of widespread research in materials chemistry.[1] The hybrids and resulting mesoporous materials have great potential for use in applications such as catalyst supports, adsorbents, and materials for optical elements.[2]

In films of such mesomaterials, the mesochannels spontaneously align parallel to the substrate surface when no artificial modifications are made.[3] On the other hand, the development of methods for vertical alignment of mesochannels in organic/inorganic hybrid films is in much higher demand and a more challenging issue. Hybrids with vertically aligned mesochannel structures have great potential in future applications to solar cells, fuel cells, separation technology, catalyst support films, high-density memory storage, etc. In spite of extensive efforts, successful examples in this direction are much less than expected. One of the strategies utilizes confined spaces of vertically aligned pores such as anodized porous alumina films,[4] lithographically topopatterned surfaces,[5] and block copolymers.[6] However, in these cases, the channels are essentially aligned parallel to the microscaled template walls. 'True' vertical alignment with respect to the substrate plane has been realized mostly using amphiphilic block copolymers via alignment inductions on specially designed surfaces,[7] and strong external magnetic fields.[8] From the view of versatility and simplification of the process, the surface-mediated alignment is more attractive. Although some successful examples have been reported,[7] there are, to date, no clear guiding principles on what type of surface interaction and factor(s) are effective to exert vertical alignment.

We propose herein a new and clear description of the substrate−molecule interaction that definitely regulates the orientation of mesochannels. Here, another templating system consisting of a π-plane discotic lyotropic LC is employed. The discotic molecules having an LC nature such as triphenylene, coronene, and porphyrin derivatives can spontaneously self-assemble to form functional columnar structures via the $\pi-\pi$ interaction.[9] In this communication, we show that the further $\pi-\pi$ interaction with the 2D π-electron surface of highly oriented pyrolytic graphite (HOPG)[10] readily induces vertical alignment of the columnar arrays in the organic/inorganic coassembly systems. The vertically aligned hybrid can be then derived to the skeletonized mesoporous arrays by calcination. Other flat surfaces without the π-conjugated plane such as a silicon wafer, a quartz plate, polymer films, etc., in contrast, always provide the parallel alignment.

Scheme 1. Chemical Structures of the Template Compounds Used in This Work



TP6EO2M **TNF**

The chemical structure of a discotic molecule used in this study, 2,3,6,7,10,11-hexa-(1,4,7-trioxaoctyl)triphenylene (TP6EO2M), is shown in Scheme 1. The columnar structure of TP6EO2M in the aggregate was reinforced by charge transfer (CT) complexation[11] with 2,4,7-trinitro-9-fluorenone (TNF) at a molar mixing ratio of 1.5:1. The molar ratio of the components to perform the silica network fixation of the column structure was tetraethoxysilane (TEOS) (1)/TP6EO2M (0.6)/TNF (0.4)/water (862)/ethanol (4)/36.5% hydrochloric acid (162). The details of the characterization procedures were described in the Supporting Information. The CT-complex/sol mixture was stirred at room temperature for 1 min. The mesostructured organic−silica hybrid films on a substrate (mostly a silicon wafer or HOPG (GE Advanced Ceramics, STM-1 grade) surface) were prepared by the hydrothermal deposition method. Fresh thin sheets of the HOPG substrate were obtained by peeling a uniform section from a graphite block with an adhesive tape. The substrate was held horizontally in the sol solution in a polypropylene flat container with a deposition surface facing down using 1 mm thick Teflon spacers. The siloxane condensation was achieved at 40 °C for 12 h. The resulting films with a ca. 2 μm thickness were washed with pure water to remove solid precipitates and subjected to structural characterizations.

Figure 1 depicts the 2D X-ray diffraction profiles taken on an imaging plate by the grazing incidence X-ray diffraction (GI-XRD) measurements for the organic−silica hybrid films on a silicon wafer (a) and HOPG (b) surfaces. The three spots for the silicon wafer (a) indicate that the hexagonally packed mesochannels of 2.2 nm spacing were aligned parallel to the substrate as is ordinarily

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[†] Nagoya University.
[‡] PRESTO, JST.

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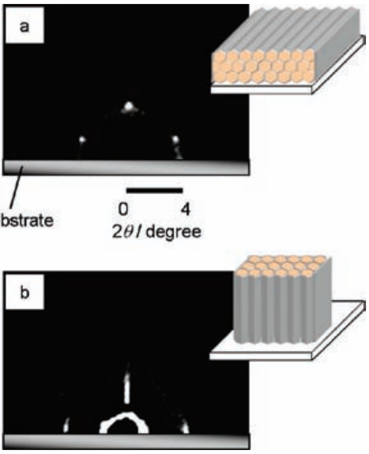

Figure 1. Diffraction patterns on the imaging plates obtained by GI-XRD measurements and structural models of the CT complex/silica hybrid films deposited onto a Si wafer (a) and an HOPG substrate (b).

observed for the hybrid films. By sharp contrast, the hybrid film deposited onto the HOPG surface exhibited the two diffraction spots symmetrical to the direct beam along the in-plane direction of the film with the spacing of 2.1 nm (Figure 1a). Because the *d* spacing agrees well with the one obtained for the sol solution in the liquid crystalline state (see Supporting Information), we assume that the lyotropic LC columnar structure of the CT complex is precisely immobilized by the silica network in the hybrid films. In the case of the HOPG surface (b), in-plane diffractions ($d = 2.1$ nm) were observed and no diffraction peak was observed in the out-of-plane direction except for the specular reflection, indicating that full vertical alignment of the mesochannels was attained on the HOPG surface at macroscopic scale. The orientations of the hexagonally packed hybrid on the silicon wafer and HOPG are schematically illustrated in each X-ray image in Figure 1. Vertical alignment was not obtained on a quartz surface or polymer films such as polyimide. Furthermore, it is worth mentioning that the parallel alignment of the column orientation was hardly affected by surface energy (contact angle of water ranging 5°−105°) of modified silicon wafer surfaces (see Supporting Information). The surface roughness of modified silicon wafers are equally at the same levels as revealed by atomic force microscopy; thus the influence of the surface topology can be ruled out. Moreover, the use of a nonaromatic template of cetyltrimethylammonium chloride (CTAC) did not lead to the vertical alignment of the micellar rods of CTAC aggregates on the HOPG substrate. The CTAC rods were randomly aligned on the substrate. These facts clearly indicate the significant role of the $\pi-\pi$ interaction between the column-forming discotic molecules and the HOPG substrate[12] to exert the vertical alignment. Supposedly, the vertical alignment is formed as follows. The $\pi-\pi$ interaction at the substrate interface regulates the molecular direction of TP6EO2M parallel to the HOPG in the vicinity of the surface, which is then reflected to the whole column arrays throughout the hybrid films via the long-range structure ordering in the fluid state before the silica network formation. The process should resemble the case of nematic LC systems.[13] Then the column orientation is firmly fixed after the silica network formation by heating.

The decisive evidence for the formation of a uniaxially aligned CT complex in the hybrid film was obtained by transmission electron microscopic (TEM) observation (Figure 2). As shown, the hybrid film deposited onto the HOPG substrate exhibited a highly oriented stripe morphology directed perpendicular to the substrate plane (a). The image contrast profile taken along the line (b) reveals that the stripe pitch is ca. 2 nm (c), which closely agrees with the spacing period evaluated by the GI-XRD measurement (Figure 1).

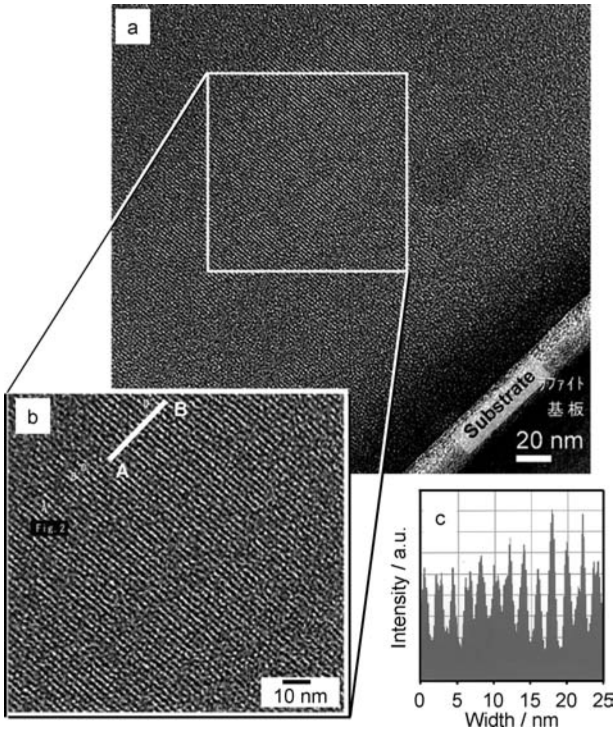

Figure 2. Wide (a) and magnified (b) cross-sectional TEM image of the CT complex/silica hybrid films deposited onto the HOPG substrate at 40 °C for 12 h. The contrast profile is taken along the lines in the image of b (c).

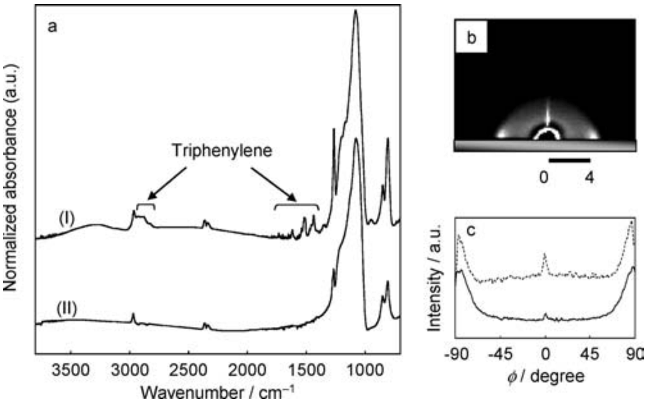

Figure 3. (a) IR spectra of the CT complex/silica hybrid films before (I) and after calcination at 400 °C for 1 h (II). (b) Diffraction pattern on the imaging plate obtained by GI-XRD measurement of the calcinated silica film on the HOPG substrate. (c) ϕ (circumference) profiles at the peaks of the imaging plate obtained by GI-XRD measurement of the hybrid (dashed line) and calcinated film (solid line) on the HOPG substrate.

The vertically aligned hybrid film was then derived to the mesoporous film by removing the organic template by thermal calcination. Before the removal of the template, further silylation with dichlorodimethylsilane was performed in 1 wt % dry toluene at 50 °C for 30 h.[14] Then, calcination of the hybrid film was performed at 400 °C for 1 h. The change in the IR spectrum of the calcinated film displayed in Figure 3a clearly indicates the complete removal of the organic triphenylene component. The thermal gravimetric analysis of the CT complex revealed that the mass significantly reduces in the range 230−400 °C, suggesting that the template is removed in the above calcination conditions. In the imaging plate of the GI-XRD measurement for the calcinated film (Figure 3b), two in-plane diffraction spots giving a spacing of 2.1 nm were detected. This value coincides with the one before calcination (see Figure 1b). This close agreement of the spacing is to be noted since it is widely recognized that, for both powder samples[15] and parallel aligned films,[3h] shrinkage of the periodicity occurs after calcination. It seems that the periodicity is unaffected by calcination in the vertically aligned system because one terminal of the channel is firmly anchored onto the surface.

The degree of orientation within a 180° range, D.O. (%) defined as $100 \times (180 - \sum W_i)/180$, can be estimated from the 1D profile shown in Figure 3c,.[16] Here, W_i (deg) is the full-width degree at half-maximum of the diffraction peak in the GI-XRD profile, with the subscript i being the number of peaks. The D.O. values obtained before and after the calcination were 90% and 82%, respectively. These values demonstrate that the channel structure is highly aligned in both cases. In this manner, the vertically aligned mesoporous silica film whose structure closely reflects that of the precursor hybrid was readily obtained.

In conclusion, the surface mediated alignment of the mesostructured organic−silica hybrid is performed via the surface $\pi-\pi$ interaction for the first time. The mechanism involved in this strategy is simple, and therefore various types of π-plane conjugated molecules are expected to be applicable. The pore size can be tuned on-demand by using different sizes of the π-plane lyotropic LC systems. We anticipate that this method will provide new opportunities in the fabrication of novel optical devices such as solar cells with defined vertical structures.

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Supporting Information Available: Synthesis of TP6EO2M, experimental procedures for the preparation of hybrids, calcination, and characterization methods. Structural characterizations of LC state of TP6EO2M-TNF charge transfer columns (Figure S1), orientation of columnar structure on modified silicon wafer surfaces (Figure S2), and supplementary IR spectra (Figure S3). This material is available free of charge via the Internet at http://pubs.acs.org.

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