Alignment control of a cyanine dye using a mesoporous silica film with uniaxially aligned mesochannels

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The feasibility of alignment control of low-molecular-weight guest species by controlling the orientation of mesochannels in a mesoporous silica host has been shown for the first time; spectroscopically anisotropic absorption behaviour of a cyanine dye was observed upon its incorporation into the mesochannels of a mesoporous silica film with uniaxially aligned porous structure, proving that the preferred alignment of the dye molecules was achieved on a macroscopic scale.

Transparent mesostructured silica films with ordered mesopores[1–4] are applicable to optical materials such as lasers and photochromic materials[5–7] by incorporating various guest species into the mesopores. However, precise control of the pore orientation in the films and the consequent alignment control of the guest species[8] are required for the development of optical materials of the next generation using these films. Since conventional mesoporous silica films prepared by solvent evaporation using spin-coating[1] and dip-coating[2] have randomly oriented mesochannels, these films are not applied as host materials for guest orientation. Recently, we have succeeded in preparing continuous mesoporous silica films with uniaxially aligned mesochannels on a glass substrate through heterogeneous nucleation and growth at a solid–liquid interface using a rubbing-treated polyimide coating.[9,10] The mesoporous silica film with highly aligned mesochannels provides nanospaces that causes a preferred orientation of guest molecules.

Here, we report the alignment control of a cyanine dye using a mesoporous silica film with highly aligned channel structure. The dye-incorporated film with aligned mesochannels showed anisotropic absorption behavior in which the maximum absorption was obtained when polarization was parallel to the mesochannel orientation, whereas that with a random porous structure provided isotropic absorption. This is the first report that proves a preferred alignment of low-molecular-weight guest species using aligned mesopores. These results indicate that the anisotropic nano-spaces can bring preferred alignment of guest species even though the size of the guest is much smaller than the pore diameter. The alignment control through such a facile strategy will lead to development of novel optical and electronic materials.

A silica glass substrate with a rubbing-treated polyimide coating was used for the alignment control of mesochannels in a mesoporous silica film.[10,11] The same polyimide that was used in the previous report was employed.[11] The mesoporous silica film was also prepared according to the procedure in the previous report[11] using a non-ionic surfactant $C_{16}H_{33}(OC_2H_5)_{10}OH$ [$C_{16}EO_{10}$] as the templating agent.† The incorporation of a cyanine dye (1,1′-diethyl-2,2′-cyanine (NK-1046), Nippon Kanko-Sikiso Kenkyusho Co., Ltd., Japan) into the mesochannels was performed by immersing the mesoporous silica film into a 1.0% aqueous solution of the cyanine dye at

room temperature. After the adsorption, the film was washed thoroughly with ethanol.

The porous structure of the film was elucidated by X-ray diffraction (XRD). Two types of XRD measurements, conventional θ–2θ scanning and in-plane diffraction, were employed for determining the horizontal and vertical structures, respectively.‡ The polarized absorption spectra were recorded with changing the angle of the polarization by rotating the polarizer which was placed in front of the sample.§ A depolarizer was placed between the incident monochromator and the polarizer to counter the incident polarization caused by the monochromator.

The mesoporous silica film was continuous and optically transparent. The θ–2θ scanning XRD profiles proved the formation of a 2D-hexagonal porous structure with a d_{100} value of 4.4 nm. The in-plane ϕ scanning XRD profile of the ($1\bar{2}0$) diffraction peak intensity proves that the mesochannels are uniaxially aligned perpendicularly to the rubbing direction.[11] The distribution of the alignment direction was estimated to be ~ 19° from the full-width-at-half-maximum of the ϕ scanning peaks.

The film after the introduction of the dye was transparent and homogeneously red colored and the retention of the porous structure was confirmed by the XRD measurements. The in-plane ϕ scanning XRD profile of the ($1\bar{2}0$) diffraction peak intensity recorded for the dye-incorporated film is shown in Fig. 1. This showed that the alignment of the mesochannels was unchanged upon dye incorporation.

The visible absorption spectrum of the dye-incorporated mesoporous silica film is shown in Fig. 2 (trace A).§ The spectrum which showed an absorption maximum at 525 nm suggests that the cyanine dyes are adsorbed in the monomeric state[12] in the mesochannels. The visible absorption spectrum of a simply cast film of the same dye prepared on a glass substrate showed an absorption maximum at 573 nm (Fig. 2 (trace B)), which is characteristic of J-aggregates.[12] The monomeric nature of the adsorbed dye in the mesoporous silica film excludes the
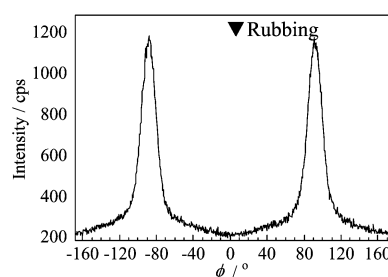

Fig. 1 In-plane ϕ scanning XRD profile of the ($1\bar{2}0$) diffraction peak intensity recorded for the mesoporous silica film with aligned mesochannels after the incorporation of the cyanine dye.

possibility that the dye was adsorbed exclusively onto the outer surface.

The amount of the adsorbed dye was determined using a mesoporous silica powder sample that is concomitantly obtained during the film formation since direct estimation of the small amount of the adsorbed dye for the film sample is difficult. After the powder sample was calcined under the same conditions,† the dye was introduced from the aqueous solution with the same concentration as that used for the film samples. From the specific surface area and the results of CHN analyses of the powder sample, the amount of the adsorbed dye was estimated to be 0.05 molecule nm^{-1}.^{2}¶ This value is much lower than that expected by a simple geometrical calculation assuming the full occupation of the dye in the mesopores.

The absorption spectra of the film samples were recorded with changing the polarization to investigate the preferred alignment of the dye molecules in the mesochannels. The solid line in Fig. 3 shows the polarization dependences of the absorbance at the absorption maximum. The absorbance values are normalized using the values at $\phi = 0°$. For the film with aligned mesochannels, it was demonstrated that the maximum absorption was obtained when the electric field was parallel to the alignment direction of the mesochannels ($\phi = -90°$ and $90°$) and that the minimum absorption was obtained for the perpendicular polarization ($\phi = 0°$). The dichroic ratio of the absorbance was estimated to be ~ 1.5, and this result clearly shows the preferential adsorption of the cyanine dye along the mesochannel direction. It is considered that host–guest interactions can lead to preferential adsorption of guest species on the pore walls, even though the size of the guest is much smaller than the pore diameter. In other words, the mesochannels can provide an optimum adsorptive direction even for small molecules.

To prove that the observed absorption anisotropy is caused by the anisotropy of the porous structure, the same experiment was performed using a mesoporous silica film prepared through spin-coating.[1] In-plane XRD measurements revealed the iso-tropic porous structure in the spin-coated film (not shown). The spin-coated mesoporous silica film provided a similar incorporation of the cyanine dye, and showed substantially the same absorption spectrum as trace A in Fig. 2. Although the absorption peaks were slightly shifted, the observed spectrum shows that dye was also adsorbed as monomers in the mesochannels of the spin-coated films, and it was considered that the state of the adsorbed dye molecules was similar to that in the mesochannels of the uniaxially aligned mesoporous silica film. However, in contrast to the results for the film with the aligned mesochannels, the absorbance of the dye-doped spin-coated film was independent of the polarization of the incident light as shown in the dotted line in Fig. 3. These results indicate that the observed optical isotropy of the dye-doped spin-coated film is brought about by the random orientation of the mesochannels. Although the dye molecules are not randomly adsorbed on the channel walls, the random orientation of the mesochannels leads to the observed optical isotropy.

In conclusion, we have proved, for the first time, the feasibility of mesoporous silica films with uniaxially aligned mesochannels for the control of the alignment of relatively low-molecular-weight guest species. Optimization of the system, including pore-size control of the mesochannels and use of guest species with appropriate shapes and properties, will lead to higher alignment control. Such orientation control of molecules will be useful for applications in future molecular devices.

Notes and references

† The mesostructured silica film was grown on the rubbing-treated polyimide film by contacting the substrate with the reactant solution with the rubbed surface downward. The molar ratio of the reactant solution was 0.10 tetraethoxysilane [TEOS] : 0.11 $C_{16}EO_{10}$: 100 H_2O : 3.0 HCl. The reactant solution containing the substrate was kept at 80 °C for 5 days for the formation of the mesostructured silica film. The template of the mesostructured silica was removed by calcining the film at 540 °C for 6 h.

‡ The θ–2θ scanning profiles were recorded with a MAC Science M03XHF diffractometer using Mn-filtered Fe-Kα radiation operating at 40 kV–20 mA. The in-plane diffraction profiles were recorded with a Rigaku ATX-G diffractometer using Ni-filtered Cu-Kα radiation operating at 60 kV–300 mA.

§ Visible absorption spectra and the polarization dependence of the absorbance were measured with a Shimadzu UV-2500PC spectrophotometer.

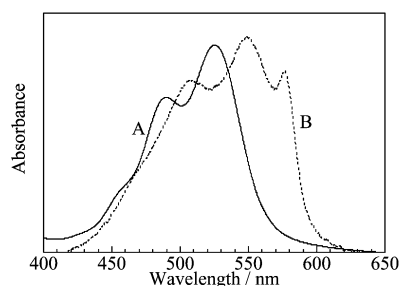¶ The specific surface area was estimated by nitrogen adsorption using a Belsorp 28SA apparatus.

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Fig. 2 Visible absorption spectra of the cyanine dye incorporated into the aligned mesochannels of the mesoporous silica film (A; solid line) and cast on a glass substrate from an aqueous solution (B; dotted line).
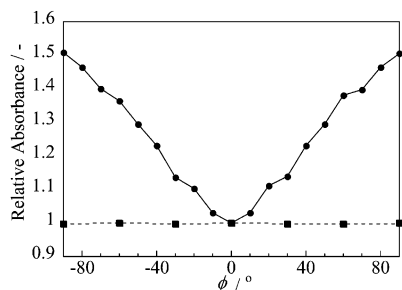

Fig. 3 Polarization dependence of the absorbance of the dye-incorporated mesoporous silica films with uniaxially aligned mesochannels (solid line) and random pore orientation (dotted line). The absorbance values are normalized using the values at $\phi = 0°$. For the uniaxially aligned porous film $\phi = 0°$ corresponds to the rubbing direction while for the spin-coated film an arbitrary direction was selected.