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Optically Transparent, Single-Crystal-Like Oriented Mesoporous Silica Films and Plates

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Optically transparent mesoporous silica plates, which are crack-free up to centimeters in size and 0.5 mm in thickness, have been synthesized using a sol−gel process based on the self-organization between surfactant and silicate through the van der Waals-type, weak, multiple, nonbonded interaction in nonaqueous solvents. The synthesis was controlled so that mesoporous channels with uniform diameter were either hexagonally packed, parallel to the flat external surface, or randomly oriented. The ordered silica plate exhibited uniform birefringence throughout the entire plate like a single crystal. The mesoporous silica shows possibilities of the application for advanced materials, direct measurement of transport properties through channels, investigation of the order−disorder effects, and spectroscopic investigation of adsorbed species without using the diffuse reflectance.

Zeolite is a crystalline microporous aluminosilicate material that can, in principle, accommodate various guest species of nanometer-size, such as semiconductor particles, conducting wires, photosensitizers, etc., to an ordered array within the periodic array of the uniform micropores. The capability of hosting the nanometer-size objects shows many possibilities of the zeolite and other similar molecular sieves for advanced applications such as optoelectronics, sensors, laser sources, and second harmonic generators of laser. Recently, the possibilities were highlighted by the discovery of mesoporous molecular sieves[1,2] of which the pore diameter could be controlled precisely in the range of 2−10 nm by the synthesis conditions or postsynthesis treatments.[2−4] However, the applications were still hindered by the availability of the zeolite or zeolite-type materials limited mostly to the powder forms.

In the present Letter, we report our successful synthesis of optically transparent, crack-free, mesoporous silica materials in the form of thin films, fibers, and plates as large as centimeters in size and 0.5 mm in thickness. We show that the structure of the silica materials can be controlled to either the hexagonal packing of uniform mesoporous channels parallel to the flat external surface or random disorder, depending on details of the synthesis conditions. We also seek possibilities of the mesoporous silica for advanced applications.

Figure 1 shows the photograph, scanning electron micrographs, and transmission electron micrograph (TEM) obtained for the mesoporous silica materials that we synthesized as follows. Typically, 8.7 g of tetraethyl orthosilicate (TEOS, Acros, 98%) was dissolved with 3.0 g of cetylpyridinium chloride (Aldrich, 98%), 2.2 g of water, and a small amount of hydrochloric acid in an azeotropic mixture of 25.9 g of ethanol (Merck, 99.8%) and 27.7 g of *n*-heptane (99%, Aldrich), giving a clear solution with the typical molar ratios of 5 TEOS:1 surfactant:15 H_2O:0.027 HCl:67 ethanol:33 *n*-heptane. The TEOS in the solution was partially hydrolyzed by a substoichiometric amount of water (H_2O/TEOS < 4), and the resulting silicate species was oligomerized while the solution was refluxed in the presence of the HCl catalyst for 1 h. The reaction mixture after the silicate oligomerization was concentrated by evaporation of the solvent using a rotary evaporator with vacuum at 333 K, which was accomplished within 10 min. The resulting liquid with high viscosity was coated into thin films on slide glass, cast on a Petri Dish, or pulled to a fiber through a nozzle equipped with drying air flow. Solid films, plates, and fibers were obtained upon complete evaporation of the solvent in a drying oven at 313 K. The solvent evaporation for thin films and slender fibers could be carried out rapidly (<1 h) without cover in the drying oven, while the solvent evaporation for plates had to be accomplished slowly (over ~ 4 h) by covering the Petri dish partially in order to prevent curling, cracking, and discrepancy in the X-ray diffraction (XRD) pattern between the top and bottom surfaces. The obtained material was reinforced with additional silica by alternating the adsorption of TEOS vapor (i.e., contact with 1.6 kPa vapor for <5 min) and evacuation (for <5 min) repeatedly (three times or more) at 423 K. The material was then calcined in air flow while increasing the temperature linearly to 823 K over 10 h. The calcined material is optically transparent and crack-free over a centimeter size range.

The XRD patterns of the as-synthesized and calcined mesoporous silica samples are shown in Figure 2. The XRD patterns indicate a contraction in the *d* spacing corresponding to about 15%, and line broadening is observed upon the removal of the surfactant by calcination. The XRD patterns can be indexed to the hexagonal structure, consistent with the TEM image. The XRD patterns for the single free-standing plates (0.5 mm thick) and the thin films coated on slide glass display (100) and (200) reflections even after calcination, while the powder XRD pattern shows (100), (110), (200), and (210). The absence of the (110) and (210) reflections for the calcined plate and film samples indicates that the mesoporous channel axis is oriented parallel to the flat external surface of the material. The mesoporous silica plate has a BET (Brunauer−Emmett−Teller) surface area of 1250 m^2 g^{-1} and a narrow pore-size distribution around 1.6 nm. The pore size distribution curve shown in Figure 3 has been obtained using the BJH (Barrett−Joyner−Halenda) method with argon adsorption isotherm at 87 K. The mesoporous silica material can be incorporated with $AlCl_3$, using a postsynthetic incorporation technique[5] with an ethanol solution at room temperature. After calcination, the resulting aluminosilicate plate contains framework aluminum and consequently exhibits a cation exchange capacity similar to that of the mesoporous

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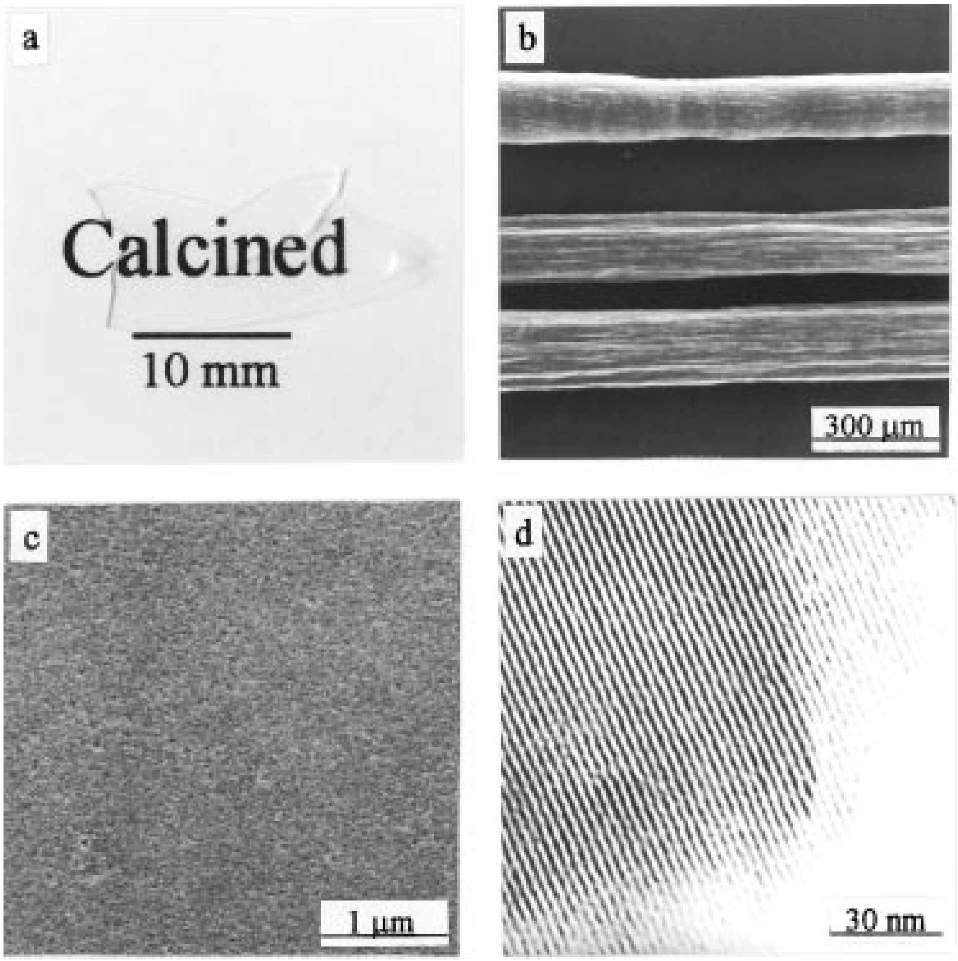

Figure 1. Photograph (a), scanning electron micrographs (b, c), and transmission electron micrograph (d) for ordered mesoporous silica after calcination at 823 K. The scanning electron micrographs were recorded on a Philips 535M apparatus operating at 20 kV. The transmission electron micrograph was obtained with JEM 200EX (JEOL) apparatus operating at 100 kV from thin edges of microparticles, which were obtained by grinding the sample shown in (a) using an agate mortar.

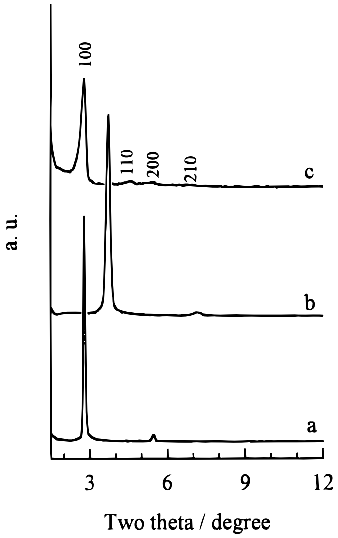

Figure 2. X-ray diffraction patterns for ordered mesoporous silica samples: (a) single free-standing plate (0.5 mm thick) as synthesized, (b) after calcination of the plate, and (c) after grinding the as-synthesized plate in an agate mortar. The patterns were obtained from a Rigaku D/MAX-III instrument at room temperature using Cu Kα radiation. Diffractograms (a) and (b) were obtained with the reflecting plane of X-rays parallel to the flat surface of the plate. XRD patterns for the as-synthesized and calcined thin film coated on slide glass were very similar to the XRD patterns for the free-standing plate.

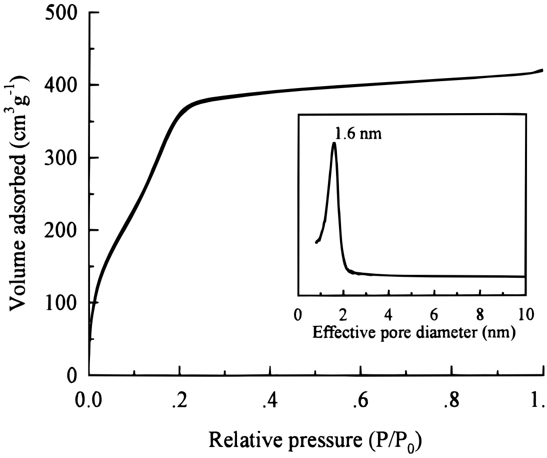

Figure 3. Argon adsorption−desorption isotherms for the ordered mesoporous silica plate after calcination, obtained at liquid argon temperature. The isotherm was obtained on a Micromeritics ASAP 2010 apparatus with volumetric method. Relative pressure is P/P_0, where P is the equilibrium pressure of the adsorbate at temperature and P_0 is the saturation pressure of the adsorbate at the temperature. Volume adsorbed is at STP. Inset: the corresponding pore size distribution curve obtained by the BJH (Barrett−Joyner−Halenda) analysis.

aluminosilicate MCM-41 reported recently.[6] The presence of silanol groups and the ion exchange capacity on the pore wall is a promising property for hosting various chemical species into arrays inside the pores.

The use of surfactant micelles[1−2,7−11] is a currently wide-spreading route to template nanostructured materials. Ordered mesoporous silica can be synthesized in micrometer-size powder forms[1−2] and thin films[8,9] by templating silicates with surfactant micelles in aqueous solutions. The templating mechanism is based on the ionic interaction[1−2,7−10] and the hydrogen bonding[11] between surfactant micelles and silicates, which lead to self-organization into an ordered array of mesostructures. The self-organization of the surfactant−silicate mesostructures in the aqueous solution is a thermodynamic process that occurs due to strong enthalpy-driven effects of the ionic interaction between surfactant micelles and silicates.

Cetylpyridinium chloride used in the present synthesis is an ionic surfactant that can template mesoporous silica following the ionic templating route in the aqueous solution. The direct interaction between surfactant cation (S^+) and silicate anion (I^-) contributes to the formation of surfactant−silicate mesostructures in basic aqueous solutions, following a S^+I^--type ionic mechanism.[12] On the other hand, the silicate surface can be positively charged in strongly acidic aqueous media with a pH lower than the isoelectric point, due to a high concentration of H^+. The formation of the mesostructures in the acidic solution is known to occur via a $S^+X^-I^+$-type ionic mechanism,[12] where X^- is a counteranion of S^+. However, the ordered mesostructures were obtained in the present study even when the HCl/TEOS molar ratio was decreased to 1×10^{-4}. Under the present synthesis conditions, the concentration of the positively charged silicate species was too low to follow the ionic templating route. The smaller the amount of the HCl used as a catalyst, the longer the reaction time required for the TEOS hydrolysis and oligomerzation. It is evident that the molecular weight of the silicate is an important factor to control the self-organization. Ordered structures are not obtained at low degrees of silicate polymerization. This result leads us to conclude that the formation of the surfactant−silica mesostructure in the present case occurs due to weak multiple nonbonded interactions between surfactants and silicates such as ion−dipole, dipole−dipole, etc., as well as weak hydrogen bonding between Cl^- ions and HO−Si groups. It is also reasonable that an ordered mesostructure is difficult to form if the size of the silicate species increases beyond the preferred silicate wall thickness.

Recently, a disordered mesostructure has been reported to form between nonionic surfactants and silicates, following a hydrogen-bonding route (i.e., the S^0I^0 route).[11] Although the nonbonded interaction between silicates and surfactant micelles is not strong enough for the formation of the ordered mesostructures in solutions, due to the naturally disordering effects of entropy, we have found that the formation of the mesostructures can be performed by using the weak interaction if the solvent is removed. In situ XRD indicates that ordered mesostructures are not formed in the viscous liquid that was used to cast plates and coat films but obtained during complete evaporation of the solvent in the oven.

Other surfactants such as hexadecyltrimethylammonium bromide and tetradecyltrimethylammonium bromide can be used for the synthesis of the ordered mesoporous silica. The solvent may be substituted by the ethanol−acetonitrile azeotrope. Details of the synthesis conditions including the refluxing time for the silicate oligomerization, drying time, and the TEOS/surfactant, H_2O/TEOS, and HCl/TEOS ratios should be adjusted depending on the surfactants and solvents. The degree of the silicate hydrolysis and polymerization prior to the solvent evaporation affects the surfactant−silicate organization very critically. The details will be reported elsewhere.[13] Disordered mesoporous silica films, plates, and fibers are obtained instead of the ordered materials if the refluxing time in the azeotropic solvent is increased or the amount of H_2O is increased. The disordered materials show only a broad XRD peak in the 2θ region between 2.0° and 3.5°. The local structure of the channel connectivity of the disordered silica has been investigated using the TEM imaging technique[14] after incorporating nanosize Pt wires within the mesoporous channels. The mesoporous channels have the same diameter as the ordered material, but the channels in the disordered material are interconnected in a three-dimensional disordered way, similar to a mesoporous silica reported recently in the powder form.[15]

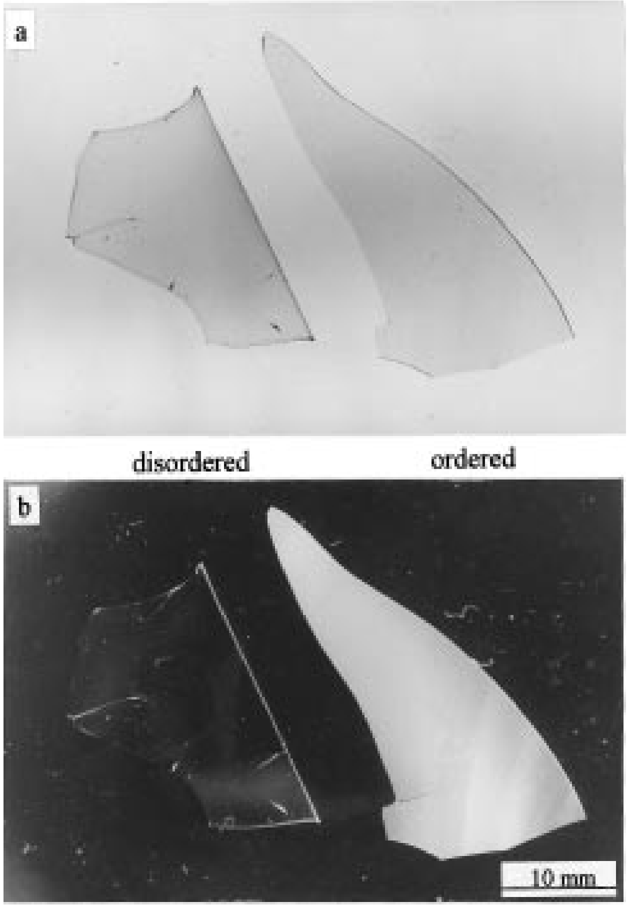

Figure 4. Photographs of calcined mesoporous silica plates with ordered and disordered channel structures placed between two Polaroid plates: (a) with polarization of the Polaroid plates oriented to the same direction and (b) perpendicular.

The disordered plate was also optically transparent and crack-free. However, the ordered plate and disordered plate showed a remarkable difference when they were placed between two Polaroid plates that were oriented at 90° as shown in Figure 4. The ordered plate was clearly visible and homogeneous due to the uniform birefringence property, without showing mosaic or marble-like domains, whereas the disordered plate became invisible. This result distinguishes the isotropic nature of the disordered plate and the anisotropic single-crystal-like nature of the ordered plate constructed with the uniform channel orientation.

The preparation of ordered mesoporous silica in the form of continuous films and monoliths has also been attempted in two other recent works.[16,17] In one study,[16] the concentration of surfactant was so high that the aqueous solution formed a uniform and continuous liquid crystalline phase, into which tetramethyl orthosilicate (TMOS) was added. In the other study,[17] surfactant was added to a partially hydrolyzed TMOS without solvents. The XRD patterns of the resulting materials showed the (100), (110) and (200), reflections similar to powder XRD patterns for the hexagonal phase. However, the monolith suffered from microcracks upon calcination. In previous reports, the synthesis conditions were difficult to control since the silicate polymerization and the self-organization with surfactant occurred simultaneously. We show that precise control of the degree of

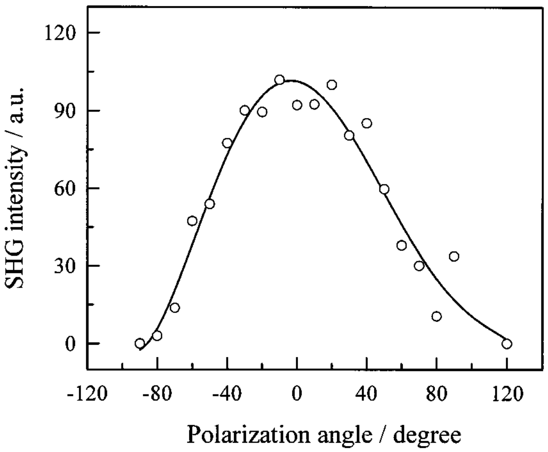

Figure 5. Second harmonic generation effects of the ordered mesoporous silica plate after the adsorption of *p*-nitroaniline, plotted against the polarization angle with respect to the channel direction.

polymerization by refluxing in solvent was very important for the self-organization. Azeotropes such as ethanol−acetonitrile and ethanol−heptane were more suitable than ethanol in preventing the microcrack formation. The resulting plates after complete evaporation of solvent were crack-free, but it was nevertheless difficult to prevent the formation of microcracks during calcination. After various attempts, we have discovered that the treatment with TEOS vapor at 423 K is useful to prevent the microcrack formation. It may be reasonable that the surfactant−silicate mesostructure in the plate before calcination is a living polymer so that TEOS vapor is added to the silicate through condensation polymerization. The resulting product ethanol and excess TEOS vapor are then removed by subsequent evacuation. The repeated treatment of the TEOS vapor adsorption and subsequent evacuation is believed to result in the addition of SiO_2 within the space between the surfactant micelle and the surrounding silicate wall structure, leading to the structure reinforcement.

Our successful synthesis of the oriented mesoporous silica in the form of continuous films, plates, and fibers, with the pore diameter controllable by surfactant size, is expected to open new possibilities of materials development as membranes, sensors, electrodes, optoelectronic devices, and so on. When *p*-nitroaniline was adsorbed within the nanotubes, the silica plate showed, indeed, the second harmonic generation of laser effect for 1064-nm Nd:YAG laser as shown in Figure 5. Furthermore, the mesoporous silica plates may be useful for direct measurement of transport properties through channels, investigation of the order−disorder effects, and spectroscopic investigation of adsorbed species without using the diffuse reflectance.

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