Field-Induced alignment controls of one-dimensional mesochannels in mesoporous materials

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Mesoporous materials prepared through the self-assembly of surfactants have attracted wide attention because of their many potential applications. The mesostructural, compositional, and morphological controls of mesoporous materials have been extensively studied thus far. In particular, the macroscopic alignments of one-dimensional (1D) mesochannels and their controls are quite important for the creation of advanced functional materials. In most cases, the direction of mesochannels in mesoporous films lies parallel to the substrate. Vertical orientation of the mesochannels can realize high diffusion and accessibility of guest species from the outside. Here, I review the recent progress on this emerging research field. Various methods have been proposed for the preparation of vertically oriented mesoporous thin films using high magnetic field, shear flow, modification of the substrate, and other methods. I also briefly introduce their applications and a perspective for the future.

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1. Mesoporous materials by self-assembly of surfactants

Ordered mesoporous materials prepared through ‘self-assembly of surfactants’ have attracted growing interest due to their special properties, including uniform mesopores (2–50 nm) and high specific surface areas.11),12) According to the International Union of Pure and Applied Chemistry (IUPAC), porous materials are classified according to their pore sizes: microporous materials with pore sizes below 2 nm, mesoporous materials with pore sizes between 2 and 50 nm, and macroporous materials with pore sizes exceeding 50 nm.3),4) Zeolites are traditional microporous materials that have been utilized for practical applications in catalysts and adsorbents. Although the microporous materials have high surface areas, due to their small-sized pores, their applications are limited to reactions only for relatively small molecules. Recently, metal–organic frameworks (MOFs) or porous coordination polymers (PCPs) consisting of metal ions coordinated with organic molecules have been extensively studied and used for the storage of gases such as hydrogen and carbon dioxide.5),6) However, their pore size is still small. In contrast, several types of macroporous materials, such as inverse opal films, track-etched polycarbonate membranes, and porous anodic alumina membranes, have been reported thus far. However, such pore expansion seriously decreases surface area.

Unlike other porous materials, mesoporous materials can be easily prepared under a wide range of synthetic conditions. Mesoporous materials exhibit several defined mesostructures, such as lamellar, two-dimensional (2D) hexagonal, three-dimensional (3D) hexagonal, and bicontinuous cubic mesostructures. Furthermore, many framework compositions (e.g., silica, organo-silica, metal, and non-siliceous oxides) and various morphologies (e.g., nanoparticle, monolith, and film) have been synthesized under various synthetic conditions. Compositional diversity, which is not achievable by other porous materials, is the most advantageous point. These unique special features and their properties have opened the gateway for many researchers and have led to innovations in many novel materials. My group also has fabricated many types of functional mesoporous/nanoporous materials under various synthetic conditions (Fig. 1).

In current ceramic research fields, several efforts have been made toward practical applications using mesoporous materials. The unique features, such as high surface area and large pore volume, make mesoporous silica an excellent candidate to be an immobilizing carrier for immunoassays.7) Mesoporous silica is a potential material for the adsorption of antibodies. Endo et al. reported formation of a thick coating of mesoporous silica powder on stainless steel by an electrosporic deposition method. The obtained material has the advantages of lightweight property and high thermal conductivity.8) Evaporation of ethanol from an ethanol/water mixture solution is also realized by using surface-modified mesoporous silica membranes.9) Mesoporous metal oxides can be synthesized by a sol–gel technique with surfactant. Matsuda et al. reported preparing mesoporous ZrO2 with P123 surfactant. The mesoporous structure can be tailored by altering several key processing factors, including calcination temperature and heating rate.10) I also investigated the photocatalytic activity of mesoporous Nb2O5 materials and the decomposition reaction of methylene blue (MB) molecules. Reaction rates depended on crystallinities in the frameworks, surface areas, and average mesopore sizes.11),12) Many other mesoporous materials with different compositions have been reported thus far.13)–17)

2. Mesoporous films with oriented mesochannels

Continuous films of mesoporous material prepared on a flat substrate have been prepared through the self-assembly of surfactants. Laboratory-made special block copolymers, as well as
commercially available block copolymers and surfactants, can be used as templates. When transparent substrates are used, the obtained films have high transparency. The mesoporous/mesos-structured films have been mostly prepared by utilizing a solvent evaporation method proposed by Ogawa. The precursor solutions, including ethanol, inorganic species, and surfactants, are coated on substrates. Various mesostructures, such as lamellar, 2D hexagonal, and bicontinuous cubic mesostructures, can be prepared by changing the precursor compositions.

The macroscopic-scale control of 1D mesochannels in the films is important for application in molecular-scale devices. After incorporating the guest species, the films can show macroscopically anisotropic properties, due to the aligned guest species in the mesopores. For example, Miyata and Tolbert et al. reported alignment control of semiconducting polymers using uniaxially aligned mesoporous silica films. The semiconducting polymer was well aligned along the uniaxial mesochannels. The polymer/silica composite film showed the polarized absorption and fluorescence caused by aligned polymers. Seki et al. reported in-situ photopolymerization of liquid crystalline monomers inside oriented mesochannels prepared by the photo-induced orientation method. Bundles of nanofibers, containing polymer chains with a narrow molecular weight distribution, were obtained.

Vertical porosity is also attractive and can provide new applications. I reported formation of uniform mesoporosity oriented vertically to the substrate through thermal conversion from a cage-type Im-3m mesostructure. Highly stable γ-alumina films with vertical mesoporosity are useful in a wide range of applications, such as highly sensitive sensors and highly reactive catalyst supports. By utilizing these films, vertically aligned fluorescent polymer arrays with poly(9,9-di-n-octylfluorenyl-2,7-diyl) (PFO) could be formed by simple drop-casting onto mesoporous alumina film (Fig. 2). The oriented PFO arrays exhibited anisotropic photoluminescence (PL) along the orientation of the main chains. As another example, the vertical pores effectively prevent drifting of colored dye molecules, leading to a clear image at high driving speeds (Fig. 3). With full-color features, this kind of electrochromic display (ECD) promises to be a competitive candidate for a reflective electric display. A high-speed and high-quality passive-matrix ECD is realized by using the vertical porosity. Walcarius et al. also utilized vertically oriented mesoporous silica film coated on an ITO substrate as electrode material for deposition of Prussian Blue. They nicely demonstrated the electrocatalytic behavior towards H$_2$O$_2$ reduction. Mou et al. demonstrated the synthesis of well-ordered mesoporous carbon film with vertical channels and its application to the direct methanol fuel cell. Actually, this carbon material forms free-standing thin sheets, which is desirable for some possible applications in catalysis, masking, and separation. This carbon material with short channels vertical to the film was synthesized by replicating the mesoporous silica SBA-15 template. After deposition of Pt-Ru nanocatalyst, this carbon material showed greatly enhanced methanol electrochemical oxidation activity. Osaka et al. also reported creating a perpendicular mesoporous Pt electrode with a flat surface by electrodeposition using titania nanopillars as hard-template. Electrochemical studies have demonstrated that this Pt electrode shows promise as a catalytic electrode for fuel cells. To realize precise orientation controls of mesochannels, many techniques for alignment control have been reported, including the use of anisotropic surfaces, modified surfaces, photo-induced polymer orientation, shear flows, and the ternary surfactant system.

3. Use of a strong magnetic field

3.1 Principle of high magnetic field processing

Recently, a high magnetic field generated from a superconducting magnet has been widely utilized for orientation control of paramagnetic or diamagnetic materials with extremely small susceptibility. High magnetic processing is widely applicable to various ceramics with asymmetric unit cells (i.e., anisotropic susceptibility), such as Al$_2$O$_3$, TiO$_2$, AlN, and ZnO. When the high magnetic field is applied to particles in stable suspensions,
the particles are gradually rotated to an angle minimizing the system energy by magnetic torque generated from the interaction between the magnetic anisotropy and the applied magnetic field.

Liquid crystals composed of diamagnetic materials also can be aligned in a high magnetic field. For instance, when surfactant concentration is increased over around 30 wt%, lyotropic liquid crystals (LLCs) are formed. These LLCs consist of lots of self-assembled surfactants that are diamagnetic materials. The alignment of the LLCs is induced by the interaction between the magnetic field and the anisotropic diamagnetic susceptibility \( \Delta \chi \) of constituent surfactants. Aliphatic hydrocarbon and PEO chains have negative \( \Delta \chi (\chi_\| - \chi_\perp) \), where \( \chi_\| \) and \( \chi_\perp \) are

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Fig. 2. (a) Measurement of photoluminescence of vertically oriented conjugated polymers. (b) High resolution SEM image of mesoporous alumina film with vertical mesoporosity. (c) Polarized photoluminescence spectra of vertically oriented conjugated polymers. (Reprinted with permission from30 ©2012 RSC Publishing)

Fig. 3. (a) Electrochromic display (ECD) with mesoporous film with vertical mesoporosity. (b) Imaging tests using mesoporous electrode at various scan rates. (c) Imaging tests using normal electrode at various scan rates. (Reprinted with permission from32 ©2010 John Wiley and Sons Inc.)
are magnetic susceptibilities along the directions parallel and perpendicular to the molecular axis, respectively. Consequently, the molecular axis is expected to orient perpendicularly to the direction of the magnetic field. However, an individual surfactant cannot be affected by a magnetic force because the magnetic interaction energy related to $\Delta \chi$ of an individual surfactant is very small (less than thermal energy ($kT$) in a 12 T field at room temperature). When the surfactants are assembled to form LLCs, the total magnetic energy can overcome the thermal disordering energy. The total magnetic energy of all constituent surfactants in LLCs contributes to the alignment of the LLCs, resulting in the formation of rod-like micelles that align along the direction of the magnetic field. The magnetic energy ($\Delta E$) of diamagnetic domains in liquid crystals is generally given by the following equation.\(^{50}\) Once the $\Delta E$ exceeds the thermal energy ($kT$), the liquid crystals can be simply aligned.

$$\Delta E = -(1/2) \cdot V \cdot \Delta \chi \cdot \mu_0^{-1} \cdot B^2,$$

where $V$ is the volume of a rod-like micelle in a 2D-hexagonal mesophase, $\mu_0$ is the magnetic permeability of a vacuum, and $B$ is the applied magnetic field. Tolbert et al. demonstrated the alignment control of 1D mesochannels in mesoporous silica monolith by applying a high magnetic field (11.7 T).\(^{51-53}\) Unpolymerized hexagonal silicate-surfactant LLCs are first prepared under alkaline conditions, and the silicate-surfactant LLC is subsequently oriented in a high magnetic field.\(^{53}\) This alignment can be preserved after polymerization of the silicate species by acid treatment. The 1D mesochannels are perfectly aligned parallel to the magnetic direction. However, this system cannot be extended to prepare mesoporous thin films with oriented mesochannels.

### 3.2 Magnetically controlled mesochannels in films

To prepare continuous mesoporous films with oriented mesochannels, I and my colleague proposed new high magnetic processing combined with the commercially available EISA method. As structure-directing agents, two typical types of surfactants, Pluronic P123 (polyethylene oxide-$b$-polypropylene oxide-$b$-polyethylene oxide triblock copolymer) and CTAB (hexadecyltrimethylammonium bromide), were selected.\(^{54}\) The ethanol-based precursor solution was cast onto a substrate and then dried up completely under a high magnetic field (12.0 T) in a superconducting magnet. In both cases, when the magnetic direction was applied parallel to the substrate, the mesochannels were uniaxially aligned over the entire film [Fig. 5(a)]. From the in-plane XRD measurements, it was proved that the alignment degree in the P123 system was higher than that in the CTAB system. This is caused by the significant difference in the molecular sizes of P123 and CTAB. With the increase in the $V$ of a diamagnetic domain, the $\Delta E$ is thought to increase, even though the values of $\chi$ may change slightly with the types of constitutive bonds. Therefore, using large molecules is very effective for successful magnetically induced orientation. From cross-sectional TEM images of the obtained films, it is confirmed that mesochannels run parallel to the substrate over the entire thicknesses of the film along the magnetic direction.

From the above results, a 12-Tesla magnetic field utilizing a superconducting magnet is not enough for low-molecular-weight surfactants (e.g., cationic surfactants and nonionic surfactants).\(^{55}\) As discussed above, the diamagnetic domain ($V$) made of low-
molecular-weight surfactants cannot provide sufficient magnetic energy ($\Delta E$) for a smooth magnetic orientation. To overcome this issue, mesoporous films were synthesized under an extremely high magnetic field of 30 Tesla generated by a hybrid magnet.\textsuperscript{56} Magnetic energy ($\Delta E$) is proportional to the square of the applied magnetic field. Compared to 12 Tesla, 30 Tesla can provide around 6.25 times more magnetic energy into the system. Therefore, this approach is applicable to any kind of surfactant with various molecular weights. When the magnetic field is applied perpendicular to the substrate, the mesochannels are oriented completely perpendicular to the substrate [Fig. 5(b)], as is confirmed by XRD measurement and TEM observation (Inset TEM image in Fig. 4). The magnetic field technique is able to control the applied direction easily. Therefore, it becomes possible to prepare mesoporous films with designed alignments of mesochannels.

3.3 Several attempts at high magnetic field processing

As described above, a high magnetic field works as a driving force for the alignment of mesochannels in the preparation of film by solvent evaporation. Initially, the precursor solutions contain a large amount of ethanol and have low viscosity; therefore, the liquid crystalline state of the surfactants does not form at all. At this stage, the magnetic energy cannot overcome the thermal energy because many surfactants are not aggregated. During the solvent evaporation process, the domain made of self-assembled surfactants gradually grows. For example, in the case of LLCs in a binary system (water and surfactant), the domain sizes are increased to at least micrometer scale, although it depends on several factors such as surfactant type and temperature. Then, magnetic torque acts on the large-sized domains due to their anisotropic structure. If the total magnetically induced energy ($\Delta E$) overcomes the thermal energy ($kT$), the rod-like assembly tends to orient parallel to the direction of the applied field.

In another approach to preparing mesoporous films, a hydrothermal deposition process is based on heterogeneous nucleation and growth of mesostructured silica.\textsuperscript{57} Substrates are immersed in the reaction solution and aged for several hours in a closed vessel. Although this approach is not influenced by ambient factors such as humidity, the possible compositions are limited to only a few, such as silica. During the mesostructured silica growth, I applied a high magnetic field perpendicular to the substrate. However, the (10) peak intensity derived from 2D-hexagonal structure was not changed at all, as compared with the film prepared without a magnetic field.\textsuperscript{58} In this case, the high magnetic force cannot work well. In the hydrothermal deposition process, small-sized mesostructured seeds approach the substrates. This size cannot generate enough magnetically induced energy to induce the seeds to rotate. Further assembly of the seeds occurs near the substrate surface, and then 1D mesochannels are formed. However, the siloxane network simultaneously develops, and the mesostructured silica in the growth layer is fixed in a short time. This is why the high magnetic field is not effective for the hydrothermal deposition process.

In a previous work, the alignment of LLCs formed by CTAB with D$_2$O was studied by time-resolved $^1$H NMR. At CTAB/D$_2$O concentrations between 1.01 and 1.29 mol kg$^{-1}$, it takes a few hours to complete the magnetic alignment of liquid crystalline domains.\textsuperscript{59} The time until the LLCs are fixed by the silica polymerization reaction is critical for determining the degree of alignment. To extend the effective magnetic time, I prepared a mesostructured silica monolith (Fig. 6).\textsuperscript{60} The precursor solution was prepared by mixing nonionic surfactant F127, water, a silica source, and an acid solution in plastic bottle. As the solvent evaporated, the surfactant concentration increased. Then, the birefringent hexagonal liquid crystal phase was observed using a polarized optical microscope. Because the precursor solution was acidic, the silica polymerization occurred simultaneously during the magnetic transition of the LLCs. The silicate condensation reaction immediately started from the top-surface of the monolith (the liquid/air interface). Therefore, the alignment distribution of mesochannels in the top-surface of the film was very wide. However, the mesochannel orientation in the inner part of the monolith was totally vertical along the applied magnetic direction. The obtained monolithic surfactant-silica composites were highly transparent without any cracks and voids, which will be useful for optical applications.

4. Use of confined space

4.1 Cylindrically confined space

Mesoporous materials were prepared in a confined space of various matrixes, such as porous anodic alumina (PAA) membrane. In the synthetic approach, surfactant-based precursor solutions penetrated the matrixes due to capillary force and were subsequently dried up until the solvents were completely evaporated. According to previous reports, when cetyltrimethylammonium bromide (CTAB) is used as a structural direct agent, the long axes of the mesochannels are aligned with the long axes of the PAA membrane channels (columnar orientation).\textsuperscript{61,62} In contrast, when nonionic surfactants, such as block copolymers of P123 and Brij 56, are used as large structural direct agents, in most cases, the mesochannels are oriented perpendicular to the PAA channels and circularly packed like stacked donuts (circular orientation).\textsuperscript{63-66} Currently, the orientation direction of mesochannels can be controlled more flexibly by several factors such as surfactant concentration, reaction temperature, and humidity.\textsuperscript{67} However, how such factors affect the orientation of mesochannels is still unclear.

A high magnetic processing was applied to control the direction of mesochannels inside the PAA channels (pore diameter, 200 nm).\textsuperscript{68} In general, the mesochannels prepared from P123 block copolymer were circularly packed like stacked donuts [Fig. 7(a)]. The columnar orientation of large-sized mesochannels inside the
PAA channels is highly useful for the incorporation and separation of large-sized molecules. When a high magnetic field of 30 Tesla was applied along the PAA channels, the mesochannels were effectively induced to orient along the applied magnetic direction [Fig. 7(b)]. In some parts, the observed mesochannels were not perfectly straight but were bended inside the channels. Consequently, high magnetic processing is effective for orientation control of mesochannels in very confined areas without complex preparative conditions.

Mesoporous materials with metallic frameworks, mesoporous metals, can also be prepared in confined space. Compared to traditional compositions (e.g., silica, alumina, titania), mesoporous metals can be expected to be applied in a wide range of potential applications, such as electronic devices, magnetic recording media, and metal catalysts, due to their high electroconductivity and high surface areas. At an early stage of mesoporous metal research, LLCs have been directly utilized as templates. The used LLCs are prepared by mechanically mixing surfactants, metal sources, and water. Because the LLCs are highly sticky, it is impossible to penetrate the LLCs into confined space. I and my colleague proposed a convenient pathway, EDIT (evaporation-mediated direct templating), through solvent evaporation for the fabrication of mesoporous metals (Fig. 8). The precursor solution is prepared by adding surfactants, metal sources, water, and a volatile organic solvent. The precursor solution is a greatly diluted surfactant solution, so it can be fully introduced into the channels due to capillary force. After the volatile solvent is preferentially evaporated, the LLCs with Pt sources fill the PAA channels. By applying an electrodeposition process, the mesostructured Pt is deposited only inside the PAA channels. After removing the surfactant and the PAA membrane, mesoporous Pt rods are prepared. All the Pt rods have a circular orientation that is directly replicated from the original LLCs before the Pt deposition. Collaboration of both LLC templating by electrochemical processes and hard templating utilizing a confined effect can lead to the genesis of new nanostructured metals.

4.2 Spherically confined space

Spherical droplets can be regarded as spherically confined space, which is different from cylindrically confined space. In a spray-drying process (i.e., an aerosol-assisted process), the precursor solutions, including surfactants, inorganic species, and solvents, are sprayed through a nozzle into a hot steam of gas. Spherical droplets are continuously generated and dried immediately. The dried samples are collected with membrane filters. In my study, I established a laboratory-made apparatus useful for rapid mass production for industrial uses. Unlike previous reports, the resultant powdery samples can be collected by a cyclone separator due to strong centrifugal force, which makes long hours of operation possible without any complex processing. In spherically confined space, interesting mesostructures were observed. In the case of lamellar structure, multi-layered vesicular mesostructures formed in the spherical particles. When cage-type mesostructure formed using F123 surfactant, uniform-sized spherical mesopores were closely packed each other in the particles. This synthetic process is widely applicable to other compositions such as organosilica and metal oxides. Several spherical particles of surfactant-templated mesoporous materials have been prepared thus far. In my spray-drying system, particle size can be controlled by tuning the applied nozzle pressure and amount of solvent in the precursor solutions. As the nozzle pressure increases and the surfactant concentration decreases, the average particle size gradually decreases. Particle-size distribution shows a bell curve with a normal distribution. Spherical morphology with controlled particle sizes is very useful in high-performance liquid chromatography. Mesoporous spheres are fascinating materials for drug delivery carriers, because of their high capacity for guest molecules and high biocompatibility.

5. Use of shear flows

It has been known that orientation of collooidally dispersed anisotropic particles containing nanorods/nanowires and nanosheets can be anisotropically arranged in macroscopic scale by applying shear field because of the anisotropic interactions of...
the particles and the field.90),91) In the case of nanosheets, the anisotropic orientation is optically detected by characteristic birefringence. It is interesting that, even below the critical concentration of the isotropic-to-liquid crystalline phase transition, clear birefringence due to nanosheet orientation is observed when the nanosheets are under shear flow. Thus, the shear field is very effective for orientation controls of materials.

I have utilized this technique for orientation controls of mesochannels. At the early stage of my study, I applied the shear flow in cylindrically confined space of polycarbonate (PC) membrane filter (pore diameter, 200 nm) (Fig. 9).92),93) When 2D hexagonal mesostructure is formed in the PC pores, most of mesochannels can be oriented parallel to the long axis of the fibers by strong aspiration.92) In the experiment, the PC membrane filter was set in an ordinary membrane filtration apparatus. The P123-based precursor solution was dropped onto the PC filter and then aspirated strongly until the PC filter was dried completely. The mesochannels were aligned to the flow direction in the PC filter smoothly. Under the strong shear force, tubular micelles can be anisotropically arranged along the flow direction.

In a recent study, this concept has been utilized for preparation of mesoporous silica films using a rubbing method (Fig. 10). The mesochannels are aligned to the rubbing direction. I reported a facile process for uniaxial orientation control of mesochannels in silica films using two different kinds of surfactant, such as Pluronic and Brij 56.94) This method needs no special requirements for the supports or substrates. This method can provide strict control of the uniaxial orientation of mesochannels without any disorder in or damage to the hexagonal arrangement. Furthermore, multilayered mesoporous silica thin films with different orientations of mesochannels can be achieved. In the experimental, the precursor solutions were uniformly coated with pre-organized lyotropic liquid crystalline states by a rubbing machine. After coating, completely transparent films without any cracks were obtained. In both the cases of the Pluronic and Brij 56 systems, the conventional θ-2θ XRD of the as-prepared films showed several strong diffraction peaks. Two peaks correspond to the (10) and (20) diffractions of the 2D-hexagonal structure. From these results, both films proved an ordered 2D-hexagonal mesostructure was indeed formed on the substrate, even tough a strong rubbing process was applied during the synthetic process. This concept is applicable to many types of nonionic surfactants that have been known to have lyotropic liquid crystal behavior at high surfactant concentrations. Lu et al. reported a facile and highly effective air flow method that is able to control the unidirectional alignment of titania mesochannels in a desired direction (e.g., parallel, perpendicular, or oblique) on a large scale via manipulation of the air flow rate and incident angle.95),96) Thus, shear flow techniques will demonstrate wide applicability in tuning the mesopore size and the framework compositions in the near future.

6. Oriented growth

Tolbert et al. demonstrated nanometer-scale epitaxy, in which the honeycomb arrangements of mesopores on the top surface of cubic mesoporous films were utilized as patterns.97) Although this paper improved the degree of perpendicular orientations, the size...
of the mesopores obtained ranged only from 10 to 15 nm. Therefore, the oriented mesochannels with a smaller size (<10 nm) are still a challenging issue.

To this end, I proposed an oriented growth concept that utilizes a porous anodic alumina (PAA) substrate. In this case, a general PAA substrate having straight holes was used. The standing mesochannels epitaxially were generated in the continuous film, induced by the mesochannels oriented along the straight PAA holes. Orientation of small mesochannels of about 3 nm was achieved. From SEM and TEM observations, it has been proven that standing tubular mesochannels grow from the interface between holes and the continuous silica region. The CTAB chains inside the PAA holes are oriented parallel to the substrate because the mesochannels are oriented along the PAA holes. Therefore, the surfactant assemblies in the continuous region are forced into a conformation normal to the substrate. Thus, the oriented mesochannels within the PAA holes truly act as a trigger for the evolution of the standing mesochannels. Furthermore, by using this concept, perpendicularly oriented P123-based mesochannels were prepared on porous anodic alumina (PAA) substrates with conical holes (Fig. 11). The aspect ratios of the conical holes are critical for mesochannel orientations. When the aspect ratios of the conical holes are lower, sponge-like mesopores are generated within the conical holes. This formation of sponge-like mesopores is lower, sponge-like mesopores are generated within the conical holes. This formation of sponge-like mesopores truly acts as a trigger for the evolution of perpendicularly oriented and tilted mesochannels. Such a formation is thought to be based on an oriented growth mechanism induced by sponge-like structures formed within the conical holes.

7. Future perspective

The mesostructural, compositional, and morphological controls of mesoporous materials have been extensively studied so far. In this review, I summarized the researches on mesoporous materials with uniaxially oriented mesochannels. Various methods using high magnetic field, shear flow, modification of the substrate, and other methods have been reported for the mesochannel controls. By utilizing these techniques, many types of mesoporous materials with different orientations and various compositions can now be totally designed. Therefore, innovative and practical applications should be the next challenging issues. Toward this goal, collaboration with experts who are working in different research areas is quite important. With great progress being made in mesoporous materials, we will be able to encounter an impressive new opportunity for technological innovation. I strongly believe that we can find new applications in several interdisciplinary research fields.

References

1) C. T. Kresge, M. E. Leonowicz, W. J. Roth, J. C. Vartuli and J. S. Beck, Nature, 359, 710–712 (1992).
2) C. T. Kresge and W. J. Roth, Chem. Soc. Rev., 42, 3663–3670 (2013).
3) K. Ariga, A. Vinu, Y. Yamauchi, Q. Ji and J. P. Hill, Bull. Chem. Soc. Jpn., 85, 1–32 (2012).
4) Y. Yamauchi, N. Suzuki, L. Radhakrishnan and L. Wang, Chem. Rec., 9, 321–339 (2009).
5) H. Sakamoto, R. Kitaura, R. Matsuda, S. Kitagawa, Y. Kubota and M. Takata, Chem. Lett., 39, 218–219 (2010).
6) M. Hu, J. Reboul, S. Furukawa, N. L. Torad, Q. Ji, P. Srinivasu, K. Ariga, S. Kitagawa and Y. Yamauchi, J. Am. Chem. Soc., 134, 2864–2867 (2012).
7) T. Orita, K. Kato and M. Tomita, J. Ceram. Soc. Japan, 119, 238–245 (2011).
8) H. Negishi, A. Miyamoto, K. Sasaki and A. Endo, J. Ceram. Soc. Japan, 119, 168–172 (2011).
9) T. Jin, Y. Ma, W. Matsuda, Y. Masuda, M. Nakajima, K. Ninomiya, T. Hiraoka, Y. Daiko and T. Yazawa, J. Ceram. Soc. Japan, 119, 549–556 (2011).
10) M. T. Soo, G. Kawamura, H. Muto, K. Y. Cheong, Z. Lockman, A. F. M. Noor and A. Matsuda, J. Ceram. Soc. Japan, 119, 517–521 (2011).
11) N. Suzuki, T. Athar, Y. T. Huang, K. Shimasaki, N. Miyamoto and Y. Yamauchi, J. Ceram. Soc. Japan, 119, 405–411 (2011).
12) N. Suzuki, M. Imura, Y. Nemoto, X. Jiang and Y. Yamauchi, CrystEngComm, 13, 40–43 (2011).
13) X. Jiang, N. Suzuki, B. P. Bastakoti, K. C.-W. Wu and Y. Yamauchi, Chem. Asian J., 7, 1713–1718 (2012).
14) H.-Y. Lian, Y.-H. Liang, Y. Yamauchi and K. C.-W. Wu,
and B. Alonso, J. Mater. Chem., 18, 1368–1382 (2008).
80) Q. Hu, R. Kou, J. Pang, T. L. Ward, M. Cai, Z. Yang, Y. Lu and J. Tang, Chem. Commun., 601–603 (2007).
81) C. K. Tsung, J. Fan, N. Zheng, Q. Shi, A. J. Forman, J. Wang and G. D. Stucky, Angew. Chem., Int. Ed., 47, 8682–8686 (2008).
82) Y. Yamauchi, P. Gupta, K. Sato, N. Fukata, S. Todoroki, S. Inoue and S. Kishimoto, J. Ceram. Soc. Japan, 117, 198–202 (2009).
83) Y. Yamauchi, P. Gupta, N. Fukata and K. Sato, Chem. Lett., 38, 78–79 (2009).
84) Y. Yamauchi, F. Takeuchi, S. Todoroki, Y. Sakka and S. Inoue, Chem. Lett., 37, 72–73 (2008).
85) Y. Yamauchi and T. Kimura, Chem. Lett., 37, 892–893 (2008).
86) Y. Yamauchi, N. Suzuki, P. Gupta, K. Sato, N. Fukata, M. Murakami, T. Shimizu, S. Inoue and T. Kimura, Sci. Technol. Adv. Mater., 10, 025005 (2009).
87) Y. Yamauchi, N. Suzuki, K. Sato, N. Fukata, M. Murakami and T. Shimizu, Bull. Chem. Soc. Jpn., 82, 1039–1043 (2009).
88) T. Kimura, K. Kato and Y. Yamauchi, Chem. Commun., 4938–4940 (2009).
89) M. Sakurai, A. Shimojima, Y. Yamauchi and K. Kuroda, Langmuir, 24, 13121–13126 (2008).
90) T. Nakato and N. Miyamoto, Materials, 2, 1734–1761 (2009).
91) N. Miyamoto, M. Shintate, S. Ikeda, Y. Hoshida, Y. Yamauchi, R. Motokawa and M. Annaka, Chem. Commun., 49, 1082–1084 (2013).
92) Y. Yamauchi, N. Suzuki and T. Kimura, Chem. Commun., 5689–5691 (2009).
93) N. Suzuki, T. Kimura and Y. Yamauchi, J. Mater. Chem., 20, 5294–5300 (2010).
94) L. Radhakrishnan, H. Wang and Y. Yamauchi, Chem. Asian J., 5, 1290–1293 (2010).
95) B. Su, X. Lu and Q. Lu, J. Am. Chem. Soc., 130, 14356–14357 (2008).
96) F. Shan, X. Lu, Q. Zhang, J. Wu, Y. Wang, F. Bian, Q. Lu, Z. Fei and P. J. Dyson, J. Am. Chem. Soc., 134, 20238–20241 (2012).
97) E. K. Richman, T. Brezesinski and S. H. Tolbert, Nat. Mater., 7, 712–717 (2008).
98) Y. Yamauchi, T. Nagaura and S. Inoue, Chem. Asian J., 4, 1059–1063 (2009).
99) Y. Yamauchi, T. Nagaura, A. Ishikawa, T. Chikyow and S. Inoue, J. Am. Chem. Soc., 130, 10165–10170 (2008).

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