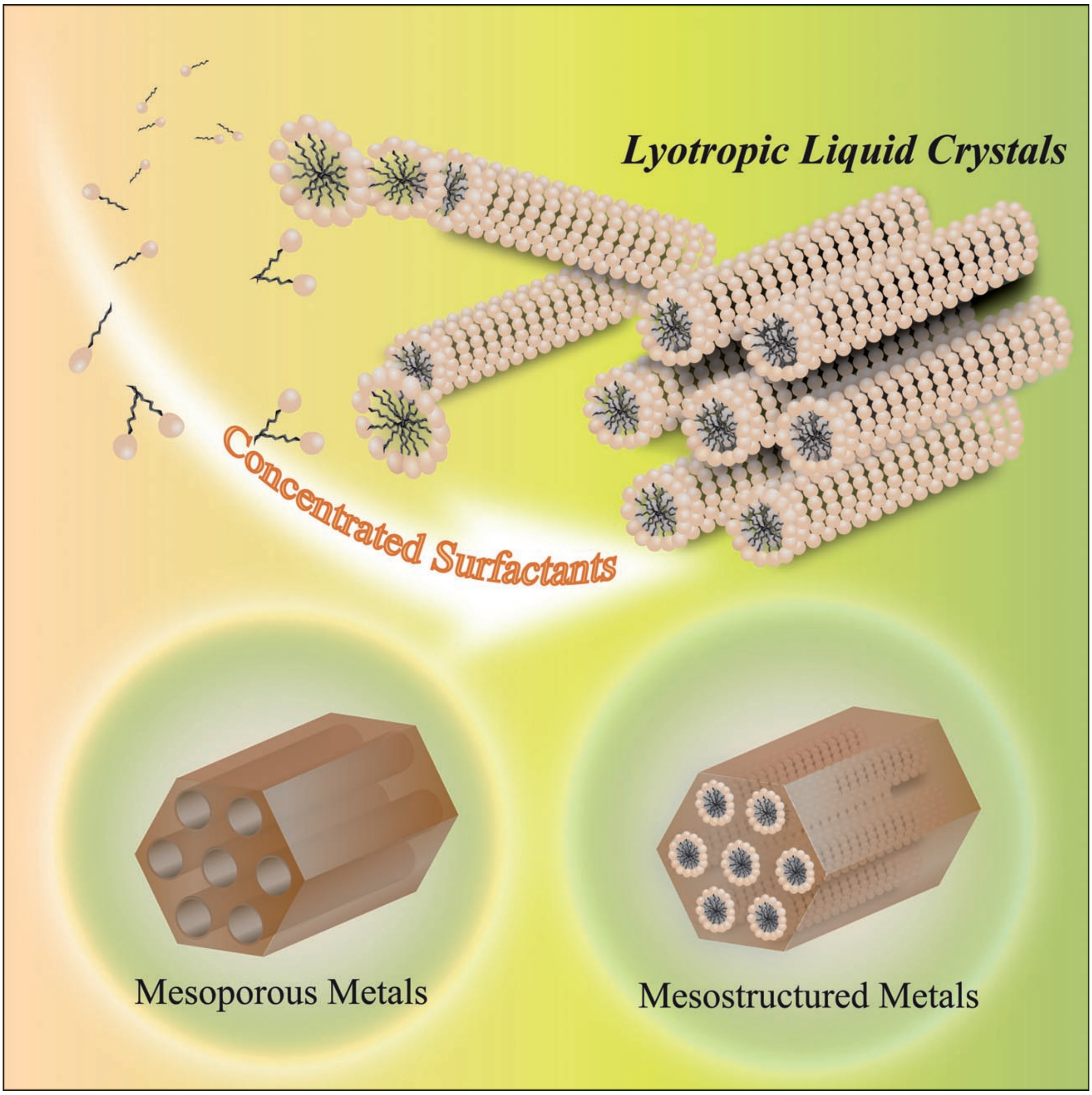
DOI: 10.1002/asia.200700350

Rational Design of Mesoporous Metals and Related Nanomaterials by a Soft-Template Approach

Yusuke Yamauchi*[a] and Kazuyuki Kuroda*[b, c]



Abstract: We review recent developments in the preparation of mesoporous metals and related metal-based nanomaterials. Among the many types of mesoporous materials, mesoporous metals hold promise for a wide range of potential applications, such as in electronic devices, magnetic recording media, and metal catalysts, owing to their metallic frameworks. Mesoporous metals with highly ordered networks and narrow pore-size distributions have traditionally been produced by using mesoporous silica as a hard template. This method involves the formation of an original template followed by deposition of metals within the mesopores and subsequent removal of the template. Another synthetic method is the direct-template approach from lyotropic liquid crystals (LLCs) made of nonionic surfactants at high concentrations. Direct-template synthesis creates a novel avenue for the production of mesoporous metals as well as related metal-based nanomaterials. Many mesoporous metals have been prepared by the chemical or electrochemical reduction of metal salts dissolved in aqueous LLC domains. As a soft template, LLCs are more versatile and therefore more advantageous than hard templates. It is possible to produce various nanostructures (e.g., lamellar, 2D hexagonal (*p*6*mm*), and 3D cubic ($Ia\bar{3}d$)), nanoparticles, and nanotubes simply by controlling the composition of the reaction bath.

Keywords: electrochemistry • liquid crystals • mesophases • mesoporous materials • thin films

1. Introduction

Ordered mesoporous materials have attracted much attention for years because of their excellent physical properties, such as a very large specific surface area, nanometer-scale fine pores, and high stability, which are beneficial for their use as catalysts, catalysis supports, inclusion vessels, and adsorbents. Many papers on mesoporous materials have been published. In 1992, researchers from Mobil Research and Development Corp. reported ordered mesoporous silicas with hexagonal (MCM-41), cubic (MCM-48), and lamellar structures (MCM-50), designated as M41S, prepared by using alkyltrimethylammonium ($C_nH_{2n+1}(CH_3)_3N^+$, C_n-TMA) surfactants.[1a,b] In 1990, our group discovered mesoporous silicas (later denoted KSW-1 for kanemite sheet Waseda) by the reaction of a layered polysilicate kanemite with C_n-TMA surfactants.[1c,d] We showed that mesopore size can be controlled by simply changing the length of the surfactants. The surfactant assembly plays a key role in controlling mesopore size. Prior to these reports in the early 1990s, a US patent by Chiola et al. had already been filed in 1971, and the synthetic procedure and structure of the obtained material was the same as that of MCM-41 reported in 1997.[2]

Since these discoveries of ordered mesoporous silicas,[1] many types of mesoporous materials have been synthesized by using the supramolecular assembly of surfactants.[3] This research area covers the synthesis, structural characterization, morphological control (e.g., film, fiber, and monolith), and alignment control of mesochannels.[3] The framework composition that governs the properties of mesoporous materials has been studied most extensively. Mesoporous materials now include a variety of inorganic-based materials, for example, transition-metal oxides, carbon compounds, inorganic–organic hybrid materials, polymers, and even metals.[4] These nonsiliceous ordered mesoporous materials, with the exception of metals, have been described in several excellent reviews.[5]

Among the many types of mesoporous materials, mesoporous metals with highly ordered networks and narrow pore-size distributions hold promise for a wide range of potential applications, such as electronic devices, magnetic recording media, and metal catalysts, owing to their metallic frame-

---

[a] Dr. Y. Yamauchi
World Premier International (WPI) Research Center
International Center for Materials Nanoarchitectonics (MANA)
National Institute for Materials Science (NIMS)
Ibaraki 305-0047 (Japan)
Fax: (+81) 29-860-4706
E-mail: Yamauchi.Yusuke@nims.go.jp

[b] Prof. Dr. K. Kuroda
Department of Applied Chemistry
Faculty of Science & Engineering
Waseda University
Tokyo 169-8555 (Japan)
E-mail: kuroda@waseda.jp

[c] Prof. Dr. K. Kuroda
CREST, Japan Science and Technology Agency (JST)
Saitama 332-0021 (Japan)

works. Traditionally, mesoporous metals have been produced by using mesoporous silica as a hard template (i.e., the replication method; Figure 1 a).[6] In 1997, Attard et al. proposed a direct-template approach from lyotropic liquid crystals (LLCs) made of nonionic surfactants at high concentrations (Figure 1 b).[7] This approach created a novel avenue for the production of mesoporous metals as well as related nanomaterials. As a soft template, LLCs are more versatile and therefore more advantageous than hard templates. In principle, the direct-template technique is applicable to a wide variety of metals that are generally known to be deposited by using electrochemical processes in the absence of LLCs, because the approach involves a simple replication of well-ordered LLCs by electrochemical processes. Therefore, many mesoporous metals have been prepared by the chemical or electrochemical reduction of metal salts dissolved in aqueous solutions of LLCs. Besides the controllability of various nanostructures (e.g., lamellar, 2D hexagonal ($p6mm$), and 3D cubic ($Ia\bar{3}d$) structures) under chosen reaction-bath compositions, it is possible to produce nanoparticles and nanotubes simply by changing the composition. Moreover, mesoporous alloys of various compositions can also be designed by controlling the composition. The most important advantage is that this method allows us to realize the microfabrication of mesoporous metals and alloys through the solvent-evaporation process, which is not achievable by the hard-template approach. The fabrication of mesoporous metals on the micrometer scale should lead to the production of more-advanced functional nanoscale devices and miniaturized sensors, as well as microelectronic devices. To the best of our knowledge, in-depth research on mesoporous metals from the soft-template approach has not been reviewed, although mesoporous metals have wide-ranging potential applications. This Focus Review addresses the synthesis and microstructure of mesoporous metals. We describe several advantages of the soft-template approach by comparing it with the hard-template approach.

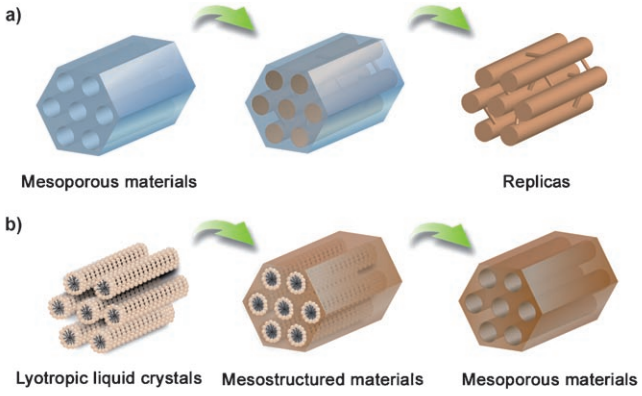


Figure 1. Synthetic procedure for the a) hard-template and b) soft-template process for the preparation of metal-based nanomaterials.

Abstract in Japanese:

高比表面積を有し、かつ細孔が数nmで規則性を有するメソポーラス材料は、これまでにない新たな化学反応の場をもつ材料として期待され、触媒材料及び吸着材料等への研究・開発が活発に行われている。その中でもメソポーラス金属は、その材料自体の持つ金属としての触媒特性や高い電気伝導性を利用して、新たな電極材料・触媒材料として期待できる。メソポーラス金属の合成は、1) メソポーラスシリカを鋳型として用いそのレプリカを合成する手法と、2) リオトロピック液晶を直接鋳型として用い電気化学的手法により金属を析出する手法に大別される。後者の手法では、用いた液晶構造が直接生成物に反映されるので、この液晶の構造を制御することで様々なメソ構造が得られている。最近では、この手法は他の金属系へと展開され、種々の金属・合金組成のメソポーラス金属の合成が報告されている。本論文では、これらメソポーラス金属に関する一連の報告をまとめ、両者の合成法を比較し各々の特徴等を紹介する。

2. Hard-Template Process

The hard-template process is a powerful method of creating mesoporous materials that are difficult to synthesize by conventional processes by utilizing a cooperative assembly between the surfactant and inorganic species. The concept, first proposed by Ryoo et al. and Hyeon and co-workers,[6] is very simple (Figure 1 a). The synthetic pathway involves three main steps: 1) choosing and forming the original template (mesoporous silica or carbon is usually used as the

Yusuke Yamauchi *was born in 1980 and received his BSc (2003), MSc (2004), and PhD (2007) from Waseda Univ. As a PhD student, he was also a Research Associate of the 21st COE program "Practical Nanochemistry" at Waseda Univ. (April 2005–March 2006) and a JSPS Research Fellow (April 2006–March 2007). After his PhD, he joined the National Institute for Materials Science (NIMS). Currently, he is also a visiting researcher at the Kagami Memorial Laboratory for Materials Science and Technology, Waseda Univ. His present research interest is the rational synthesis of novel mesoporous materials, in particular, mesoporous metals and films.*

Kazuyuki Kuroda *received his BSc (1974), MSc (1976), and PhD in applied chemistry (1979) from Waseda Univ. A Professor in the Department of Applied Chemistry, Waseda Univ. since 1989, he was also a principal investigator for the CREST program (JST; 2002–2007). He is currently President of the International Mesostructured Materials Association. His primary research interest is in materials chemistry, including materials synthesis based on inorganic–organic interactions, porous and layered materials, intercalation compounds, silicate chemistry, inorganic polymers, and related topics.*

original template), 2) filling the target precursors into the mesopores and then converting the precursor into an inorganic solid (i.e., formation of a composite consisting of the original template and a target inorganic solid), and 3) removing the original template (Figure 1 a). The mesoporous structures obtained are negative replicas if the casting process is performed only once. To date, various mesoporous materials have been produced by a hard-template pathway.

When choosing the original template, two important points must be considered.[5g] One is whether the template can maintain its ordered mesostructure during the conversion process in the second step. The other is whether the template can be easily removed without disrupting the mesoporous structure in the resulting replica. Although mesoporous silicas have been used mainly as templates, various composite mesoporous materials, including carbon, can also be applied.

Various types of nanostructured metals, including 3D networks, nanoparticles, nanowires, and nanonecklaces, have been created by using mesoporous silicas (e.g., FSM-16, MCM-41, MCM-48, and SBA-15) as hard templates. Ryoo and co-workers reported nanoporous Pt with 3D networks by the impregnation of a Pt precursor followed by H_2 reduction within the mesopores of the MCM-48 ($Ia\bar{3}d$) template (Figure 2 a and b).[8] By using SBA-15 as a hard template, 2D hexagonally packed nanowires interconnected by small bridges were prepared owing to the small tunnels between the main 1D mesochannels.[9] Furthermore, isolated Pt-based nanowires were synthesized by the replication method with MCM-41 as a hard template.[10] Optical irradiation is another efficient method for the reduction of metal precursors in situ. Fukuoka et al. selectively prepared nanoparticles and nanowires (e.g., Pt and Pt/Rh) by UV/Vis irradiation.[11] Uniformly dispersed metallic nanoparticles were successfully formed by inducing simultaneous nucleation in mesoporous silica matrices (FSM-16).

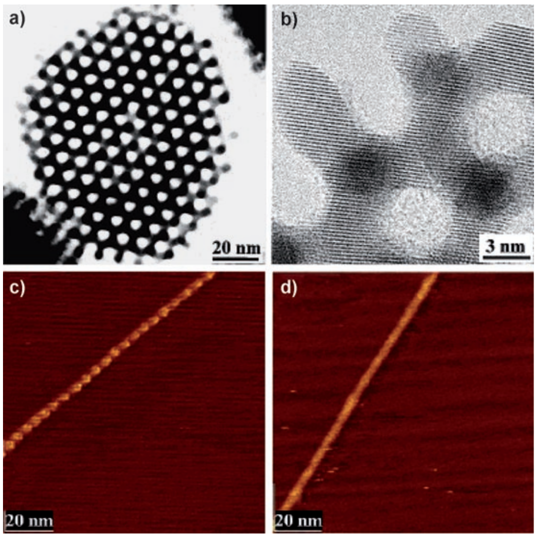


Figure 2. a) and b) TEM images of nanostructured Pt networks obtained with MCM-48 silica as a template. Reprinted with permission from reference [8]. (Copyright American Chemical Society, 2001.) c) and d) Scanning tunneling microscopy (STM) images of isolated Pt nanowires: c) Pt nanonecklace separated from HMM-1; d) Pt nanorod separated from FSM-16. Reprinted with permission from reference [12b]. (Copyright American Chemical Society, 2004.)

Organic–inorganic hybrid mesoporous materials (HMM), synthesized by Inagaki et al.,[4a] have been used as a new hard template to change the interactions between the deposited metal and the internal surface inside the mesochannels.[12] Owing to the interactions, novel necklacelike Pt, Pt/Ru, and Pt/Pd nanowires, which show unusual physical properties, including magnetic susceptibility, due to the low dimensionality of the metal topology (Figure 2 c and d), have been successfully prepared.

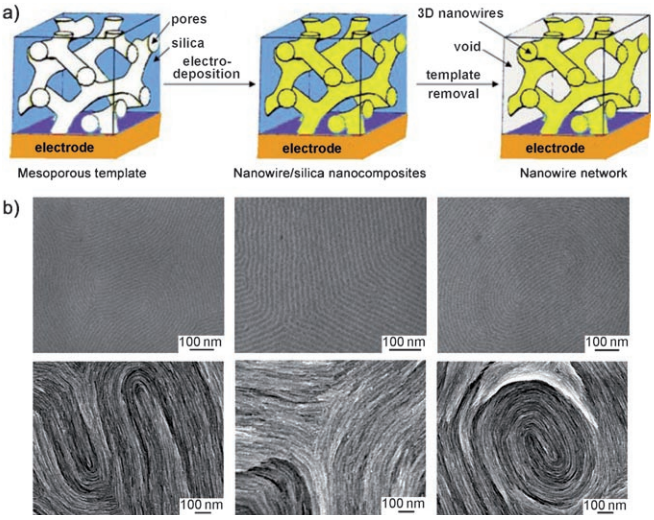


Figure 3. a) Schematic representation of the formation of 3D continuous macroscopic metal nanowire networks by a template-electrodeposition technique. Reprinted with permission from reference [13b]. (Copyright John Wiley & Sons, Inc., 2004.) b) HRSEM images of the top surface of a 2D hexagonal mesoporous silica film (top) and its replicated Pt nanowires (bottom), showing the S (left), Y (middle), and swirl shapes (right). Reprinted with permission from reference [13d]. (Copyright Royal Society of Chemistry, 2006.)

Moreover, the hard-template method has been widely applied to the creation of metal nanowire films by utilizing electrochemical processes (Figure 3 a).[13] The electrodeposition method, which uses an external power source, is an efficient technique for depositing metals in mesoporous silica films. Brinker and co-workers fabricated Pd nanowire thin films through the reduction of Pd ions within the mesochannels of 2D hexagonally ordered mesoporous silica films.[13a] After the removal of the mesoporous silica template, Pd nanowire thin films were successfully prepared. Several 3D nanowire networks can be prepared by using mesoporous silica films with 3D mesoporous structures (Figure 3 a).[13b] With the above system, mesoporous silica films used as templates have been prepared by the evaporation-induced self-assembly process first developed by Ogawa.[14] Au-coated glass or ITO (indium tin oxide) with high electroconductivity is generally used as substrate. The metal nanowires gradually grow from the bottom surface of the conductive substrate by electrodeposition. Because the metal nanowires can expand to the thickness of the mesoporous silica film, the electrodeposition process can easily prevent metal deposition in the outer part of the silica template by controlling the electrodeposition time. Recently, Wu et al. and our group reported the synthesis of Pt nanowire thin films by using SBA-15-type (*p6mm*) thin films (Figure 3b).[13d] From HRSEM (high-resolution scanning electron microscopy) observations, the original mesoporous silica film contained several types of morphologies, such as S, Y, and swirl shapes, on the top surface (Figure 3b). After Pt deposition and extraction of the silica matrix, the corresponding Pt nanowires were prepared with the S, Y, and swirl shapes; these unique shapes cannot be attained by the replication method with SBA-15 powder as a hard template.

Another method is electroless deposition by using a reducing agent.[15] In this system, it is required that the nucleation sites for metal deposition are located inside the mesoporous silica matrices. Otherwise, metal deposition would start from the outer surface of the matrices. Zhang et al. fabricated high-density ordered Ni nanowire arrays by immersing Pd-loaded mesoporous silica films in a conventional Ni-plating bath.[15a] The Pd nanoparticles acted as nucleation sites for the deposition of Ni.

The nanocasting pathway with hard templates opens the door to the design of highly mesoporous materials with multifunctional compositions that are more difficult to synthesize by conventional processes that utilize cooperative assembly between the surfactant and the inorganic species. However, the hard-template strategy is a complex, high-cost, and industrially unfeasible method because the synthetic pathway involves several steps.

3. Soft-Template Process

3.1. Evolution of Mesoporous Metals from Lyotropic Liquid Crystals

Amphiphilic molecules, such as surfactants or amphiphilic block copolymers, are compounds in which the hydrophilic and hydrophobic parts are covalently linked. When the amphiphilic molecules are dissolved in water and the mixed solution is above the critical micelle concentration, spherical micellar structures are formed through self-organization. When the surfactant concentration increases, the LLC phases appear. The LLC phases contain long-range spatially periodic nanostructures with lattice parameters in the range of 2–15 nm. The mesostructures of the LLCs formed strongly depend on the molecular structure, concentration, and temperature.[16] Generally, with an increase in surfactant concentration, the LLC mesostructures are dramatically changed from a micellar solution (L_I) through micellar cubic (I_I), hexagonal (H_I), bicontinuous cubic (V_I), lamellar (L_α), to inverse micellar (L_2) phases. The mesostructures have been characterized by polarized optical microscopy and low-angle XRD. In 1995, Attard et al. reported the formation of mesoporous silicas from LLCs with direct templates.[17] This approach[17,18] is quite different from the template mechanism that takes place by a cooperative process that utilizes the interaction between inorganic ions and surfactants in the surfactant solution at low concentrations.[1a,b] In the direct-template approach from LLCs, the hydrolysis and polycondensation of silica precursors (e.g., 2-trimethylsilylethoxycarbonyl, TEOS) are conducted in a confined aqueous LLC domain. The resulting mesostructure is truly the cast of the original architecture of the LLC used. The phase diagram of the surfactant+silica+water system at high surfactant concentration is similar to the known phase diagram of surfactant+water.[16–17] Therefore, this direct-template approach brings an element of predictability to the synthesis of mesoporous materials

The most significant advantage of the LLC direct-template method is that it can be used to produce mesoporous/mesostructured metals and alloys. In 1997, Attard et al. reported mesoporous Pt microparticles from LLCs: the first true formation of a mesoporous metal.[7a] The LLC mixtures were prepared by dissolving hydrogen hexachloroplatinate(IV) hydrate (H_2PtCl_6) in water and mixing it with the nonionic surfactant $C_{16}(EO)_8$ (EO = ethylene oxide). For Pt deposition, reducing agents were added to the LLCs. After the removal of the templates, mesoporous Pt microparticles with high surface areas were obtained.

A greater discovery, also reported in 1997, was that mesoporous Pt films could be produced by electrodeposition from LLCs.[7b] The resulting mesoporous Pt films are mechanically robust, remarkably flat, and shiny in appearance. Furthermore, they have large surface areas relative to those of commercial Pt black deposited from conventional electroplating baths. Moreover, the mesochannels stand out, on average, at an angle of 20° with respect to the normal plane of the electrode surface. In some domains, the mesochannels are completely perpendicular. (For comparison, in mesoporous silica films prepared by the evaporation-induced self-assembly process,[14] all mesochannels run parallel to the substrates.) The driving force of this alignment may be the electric field created during the electrodeposition process, but further clarification is needed. The presence of perpendicular mesoporosity in mesoporous Pt films is desirable because such a pore configuration should increase the accessibility and enhance the efficiency of mass transport.

Both chemical and electrochemical methods can be applied to the LLC direct-template approach. In the electrochemical method, the thickness of the films can be directly controlled through the amount of charge passed to carry out the deposition.

3.2. Developments in Mesoporous Metals

Since the discovery of mesoporous Pt particles and films in 1997 (see Section 3.1),[7] many researchers have been working to extend this concept to other metals.[19–29] The LLC direct-template approach is widely applicable to the production of a range of metals (Figures 4 and 5). We believe that LLCs made of surfactants are more versatile and therefore more advantageous as a soft template than as a hard template such as mesoporous silica. It is possible to produce mesoporous metals with lamellar (Figure 4e),[30] 2D hexagonal (*p6mm*), 3D cubic ($Ia\bar{3}d$), and other mesostructures by simply controlling the composition of the reaction baths. For example, if an LLC mesophase used as the template has a 2D hexagonal structure, the deposited material would have a mesoporous structure with 2D hexagonal symmetry. The same concept can also be applied to other phases, such as the cubic ($Ia\bar{3}d$) and lamellar phases. The mesopore diameters can be easily controlled by the choice of surfactant and the addition of lipophilic substances. Other metal-based nanostructures, such as nanotubes,[31] nanorods,[32] nanosheets/plates,[33] and nanoparticles,[34] have been designed by modifying the LLCs. Kijima et al. reported the unique synthesis of Pt, Pd, and Ag nanotubes, with inner diameters of 3–4 nm and outer diameters of 6–7 nm, by chemical reduction of the corresponding metal salts in the presence of mixed LLCs made of differently sized surfactants of $C_{12}(EO)_9$ and tween 60 (polyethylene glycol sorbitan monostearate).[31]

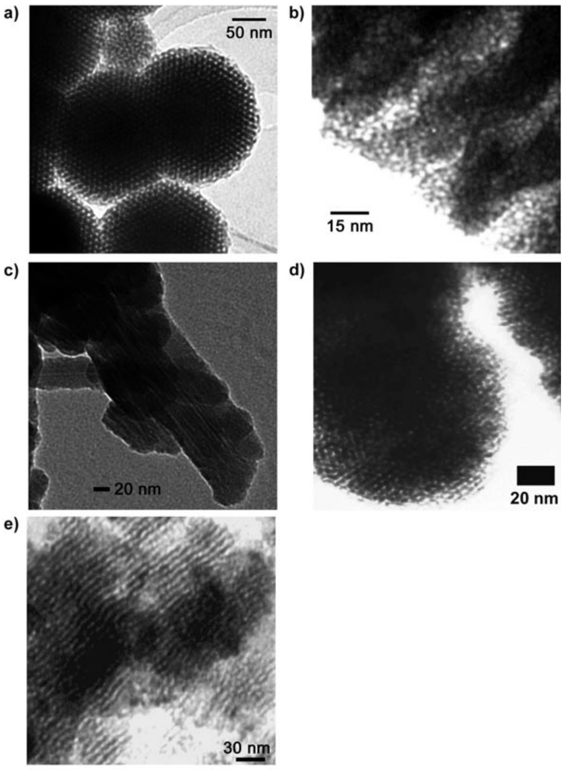


Figure 4. TEM images of mesoporous metals and lamellar Pt nanostructures. a) Mesoporous Ni particles. Reprinted with permission from reference [36a]. (Copyright The Chemical Society of Japan, 2004.) b) Mesoporous Sn film. Reprinted with permission from reference [28a]. (Copyright Royal Society of Chemistry, 1999.) c) Mesoporous Ni film. Reprinted with permission from reference [20]. (Copyright American Chemical Society, 2004.) d) Mesoporous Pd film. Reprinted with permission from reference [24a]. (Copyright Royal Society of Chemistry, 2002.) e) Lamellar Pt nanostructures. Reprinted with permission from reference [30]. (Copyright The Chemical Society of Japan, 2004.) Mesoporous metal films except the mesoporous Ni particles in a) were electrodeposited from LLC, including the corresponding metal ions. The particles in a) were synthesized by an electroless deposition method with reducing agents.

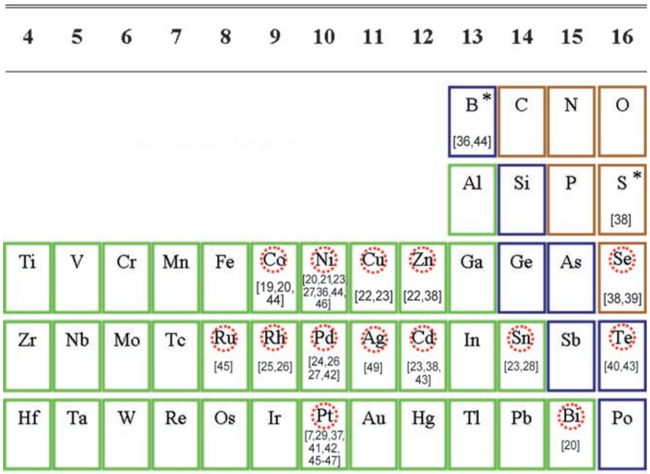


Figure 5. Part of the periodic table showing the mesoporous metals and alloys prepared in the presence of LLCs, as indicated by the circles. The nonmetal Se is included in the table. Se can be readily obtained from LLC template by an electrodeposition method. Reference numbers are given in square brackets. Green = metals, blue = semimetals, brown = nonmetals, * = codeposition with other metals such as Ni and Cd.

Figure 5 shows part of the periodic table highlighting the elements known (or claimed) to be deposited by an electrodeposition method with an external power source in the absence of LLCs. The LLC template method is basically applicable to a wide range of metals that are generally known to be deposited. However, from previous reports, it can be seen that metals from some groups (e.g., Group 10; indicated by circles in Figure 5) can be readily formed from a template, whereas no successful attempts have been reported for several metals of other groups. Moreover, there have been few reports of successful work on mesoporous metals with a high degree of order.

The following important points should be noted for the production of highly ordered mesoporous metals: 1) the stability of the mesophases in the presence of metal ions confined in the aqueous LLC domain (i.e., the formation of highly ordered LLCs), and 2) the reduction process of metal salts in the aqueous domain.

3.2.1. Stability of LLC Mesophases

In LLC mesophases, dissolved metal ions are coordinated by water molecules to form metal aqua complexes.[35] Hydrogen bonds between the EO groups of surfactants and coordinated water molecules are formed, which results in the stabilization of the metal aqua complexes in the LLC.[35a] The interactions between the EO groups of the surfactants and the solvated metal ions vary with the nature of the metal ions and the counteranions in the aqueous domain, which has an influence on the stability and structure of various LLC mesophases.[35a] For example, Dag et al. investigated the stability of LLCs consisting of transition-metal aqua complexes and $C_n(EO)_m$-type nonionic surfactants.[35c] In this system, the transition-metal aqua complexes of chlorides and sulfates were insoluble and did not form LLCs. On the other hand, the transition-metal aqua complexes of nitrates and perchlorates were soluble and formed 2D and 3D hexagonal and cubic mesophases. Phase transformations were carried out by changing the mole ratios of the surfactants and transition-metal aqua complexes. Therefore, the appropriate selection and concentration of metal salts play a key role in the preparation of highly ordered LLCs.

3.2.2. Reduction of Metal Salts

The deposition rate is also an important parameter in achieving mesoporous metals of the highest quality. We previously reported the formation of highly ordered mesoporous Ni particles by applying autocatalytic deposition under controlled bath conditions.[36] When only SBH (sodium borohydride) was used as a reducing agent, a large number of metallic nuclei immediately formed, and a disordered mesoporous structure was obtained. The grain growth was probably insufficient to coat the rodlike self-assemblies in the LLCs. On the other hand, when DMAB (dimethylaminoborane) was used as a reducing agent, the deposition speed was lower than that with SBH. The isotropic metal deposition due to the autocatalytic reaction led to the formation of spherical Ni particles, which also led to the formation of the ordered mesostructure. Thus, in the electroless deposition system, the deposition rate can be controlled by reducing agents. Through direct TEM observations of highly ordered mesoporous Ni metals, it was clarified that the arrangements of rodlike self-assemblies in LLCs indeed work as a scaffold to direct the grain growth of Ni (Figure 4a).[36c] The Ni mesostructures have macroscopic alignments derived from those of the LLCs.[36c] Similarly, in the electrodeposition method, a slow deposition controlled by the potential was appropriate. Attard and co-workers also demonstrated the effect of the deposition rate on the ordering of a mesoporous structure.[37] Mesoporous Pt films were deposited over the potential range +0.1 to −0.3 V (vs. saturated calomel electrode, SCE) by using the electrodeposition method. When films were deposited at −0.1 V versus SCE and above, their XRD patterns exhibited a sharp diffraction peak corresponding to a repeat distance of 5.3 nm. However, as the deposition potentials were decreased (i.e., as the deposition speeds were increased), the order of the mesoporous structures was gradually lowered.

3.2.3. Additional Points

All mesoporous metals except noble metals (e.g., Pt, Ru, and Au) are easily oxidized in air. For example, the metal surfaces of mesoporous Ni (Figure 4a) by electroless deposition are easily oxidized in air, which causes the ordered mesostructures to collapse. Therefore, dehydrated solvents such as ethanol should be used during the removal of the templates. It is desirable that all experimental procedures be carried out under inert atmosphere for the retention of highly ordered mesoporous structures. Moreover, the thermal stability of mesoporous metals is quite low relative to that of mesoporous silica. In the case of Pt particles, when samples were irradiated by electron beams for more than 10 min, the metal crystals gradually grew, thus resulting in ordered mesoporous structures being destroyed to form bulk metal with a single-crystalline state. Therefore, during TEM observations, the above points should be carefully considered.

Even non-oxide semiconductors (e.g., CdS)[38] and nonmetals (e.g., Se,[39] Te[40]) have been prepared by the direct-template approach with oligomeric nonionic surfactants. Stupp and co-workers prepared mesostructured sulfides for the first time by using hydrogen sulfide or hydrogen selenide gas.[38] The LLCs were prepared with the addition of appropriate metal ions such as Cd^{2+}. The reaction gas (hydrogen sulfide or hydrogen selenide) was then passed into the LLCs to form mesostructured organic–inorganic composites. A family of mesostructured solids, including CdS, ZnS, and CdSe, was successfully prepared. On the other hand, for Ag_2S, CuS, HgS, and PbS, mesoscopic periodicity could not be formed due to unmatched interactions between the metal ions or corresponding sulfide nanoparticles and the surfactants, which demonstrates the importance of choosing appropriate inorganic precursors.

3.3. Microstructures of Mesoporous Metals

LLCs with high viscosity form the confined reaction medium for metal deposition. The LLC template is a soft template, and the environment for nanoscale metal deposition is very different from that inside the 1D mesochannels of mesoporous silica. This metal deposition has a positive–negative relation with 1D metal deposition along the mesochannels of mesoporous silica (Figure 1).

We previously clarified that the frameworks of mesoporous metals are composed of nanoparticles, and that the morphology does not show a smooth surface.[41] For example, 2D hexagonally ordered mesoporous Pt particles were prepared by Pt deposition in the aqueous domains of LLC by chemical reduction with Zn powder. Interestingly, the framework is composed of connected nanoparticles about 3 nm in size (Figure 6a and b). Moreover, the lattice fringes on the atomic crystallinity are coherently extended over several nanoparticles in the framework. The formation of such a unique framework can be reasonably explained by the following suggested mechanism (Figure 6c).[41] In the first step, a primary cluster of metal atoms is formed by the first reduction. The aqueous domain among the rodlike self-assemblies is the nanoscale reaction medium for the metal deposition. In the second step, in the aqueous domain, the primary Pt cluster grows isotropically into a sphere to minimize the surface energy of the Pt grain. After that, the isotropic grain growth is hindered by the 2D hexagonally ordered rods to

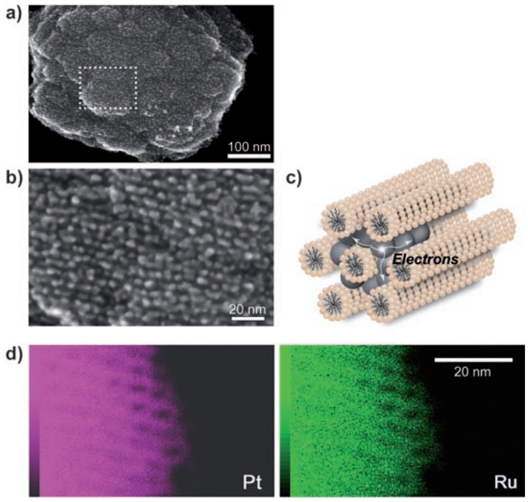


Figure 6. a–c) SEM images of mesoporous Pt particles. b) High-magnification image of the square area in a). c) Suggested mechanism of formation of the nanoparticles connected like a necklace. Reprinted with permission from reference [41]. (Copyright American Chemical Society, 2005.) d) EDX map of mesoporous Pt/Ru alloy particles. Reprinted with permission from reference [45e]. (Copyright American Chemical Society, 2007.)

produce stress against the rods, which are slightly distorted and undergo a plastic deformation. The nanoparticles grown would fit and be stabilized among the rods. As the Pt deposition proceeds, the isotropic growth of the second nanoparticle starts from the next primary nucleus formed by the transferred electrons. Consequently, the continuous deposition of Pt nanoparticles from one nanoparticle makes a unique framework composed of connected nanoparticles with extended crystallinity (Figure 6c), which is not attainable by the traditional approach of using mesoporous silica as a hard template.

Accurate structural information on mesoporous metals contributes to the development of mesoporous metals with superior physical and chemical properties. Recently, Saramat et al. reported that a mesoporous Pt/Al_2O_3 catalyst showed an ignition profile for CO oxidation at lower temperatures than Pt black or wet-impregnated Pt.[29g] This may be related to the differences in the surface curvature of Pt.[29g]

Alloying in frameworks is another key element for the further development of novel mesoporous metals with tunable functions. There have been a few reports on the formation of mesoporous alloys[42–46] such as Pt/Pd,[42] Te/Cd,[43] Ni/Co,[44] Pt/Ru,[45] and Pt/Ni[46] by the co-reduction of two metal species in the presence of LLCs. By simply controlling the bath conditions, the composition of the metal framework can be varied. The excellent control of the composition of the framework is of considerable importance in terms of the functional design of mesoporous alloys.

In the cases of mesoporous Pt/Pd,[42] Te/Cd,[43] and Ni/Co,[44] it has been considered that nanoscale phase separation of the constituent metals occurs in the pore wall. In contrast, the pore walls of mesoporous Pt/Ru[45] and Pt/Ni[46] are in a binary intermetallic state; that is, there is a uniform dispersion of the constituent metals. In the case of mesoporous Pt/Ru, the intermetallic state was proven through high-angle XRD and extended X-ray absorption fine structure (EXAFS) analysis by Attard et al.[45a,b] Recently, we characterized directly the intermetallic state of mesoporous Pt/Ru[45e] and Pt/Ni[46] by TEM, selected-area electron diffraction (SAED), energy-dispersive X-ray (EDX) spectroscopy, and X-ray photoelectron spectroscopy (XPS). Figure 6d shows the EDX map of the mesoporous Pt/Ru alloy particles. The dark-field (DF) STEM image completely corresponds to the EDX maps of Pt and Ru. The Pt and Ru atoms are well-dispersed within the pore walls, and no phase separations on the nanometer scale are observed. The EDX map shown here is the first direct evidence that the pore wall is in a binary intermetallic state with a uniform dispersion of the constituent metals. In particular, Pt-based intermetallic alloys such as Pt/Ni and Pt/Ru have recently attracted great interest as candidates for electrode materials for oxygen-reduction reactions (ORRs). The improvement in the ORR can be explained by several factors, including surface structural and electronic states. The electronic states of the surface of the mesoporous alloys are very important for a detailed investigation of ORR. In the case of mesoporous Pt/Ni alloys, the Pt $4f_{7/2}$ and $4f_{5/2}$ signals were observed at 71.0 and 74.5 eV, respectively.[46] These values are very close to those for bulk Pt metal, which suggests that Pt is present in the zero-valent state. On the other hand, the top of the Ni 2p peak is located at a binding energy of 852 eV, which corresponds to Ni^0. Importantly, in mesoporous Pt/Ni alloys, Ni is thought to be in the zero-valent metallic state, even though it is well-known that bulk Ni is easily oxidized in the atmosphere. Similarly, Ru on the surface of mesoporous Pt/Ru alloy is basically present in the zero-valent state, although nanosized Ru is also easily oxidized in air.[45e] Further studies on this point are required to understand the electronic states more deeply. Mesoporous Pt-based alloys with both high specific surface areas and a uniform distribution of metals will have an impact in a wide range of fields.

A deeper understanding of the alloy state in the pore wall is of considerable importance for the application of mesoporous alloys. It will also provide new insight into the bath conditions governing the grain growth of alloy deposition within the limited spaces of LLCs.

3.4. Newly Designed Electrode Materials

The successful fabrication of mesoporous metals on the micrometer scale should lead to the production of more-advanced functional nanoscale devices (e.g., highly sensitive microchip reactors, miniaturized sensors, and microelectronic devices) on the miniature scale. However, the use of general LLCs has been limited to the production of planar films and particles because LLCs cannot be uniformly introduced into a confined space on the micrometer scale owing to their very high viscosities, which makes the application of this method in a nanomaterials system impossible.

We proposed a convenient, novel pathway, EDIT (evaporation-mediated direct template), for the fabrication of mesoporous metals in a very confined area (Figure 7a).[47] The EDIT process involves two basic steps: 1) the formation of the LLC template by solvent evaporation, and 2) the reduction of the metal species in the presence of the LLC. For example, the successful deposition of highly ordered mesoporous Pt inside a micrometer channel is shown in Figure 7b. A precursor solution as an LLC former was prepared by mixing distilled water, surfactant, Pt species, and ethanol as a volatile solvent. The precursor solution was a homogeneous yellow solution with low viscosity. At this stage, the viscosity of the precursor solution became low relative to those of general LLC template mixtures used in the previous system. Therefore, the precursor solution can be introduced efficiently into the channels due to capillary force. After the volatile solvent was preferentially evaporated, the LLCs, including the Pt complexes, were formed entirely inside the channel. By the Pt-electrodeposition process in the presence of LLCs, mesostructured Pt can be deposited only inside the channels. The use of a lithography technique enables mesoporous Pt to be selectively deposited only in a particular channel. Moreover, well-ordered Pt thin films with a macro–meso bimodal pore system were prepared by combining the EDIT method with a colloidal crystal-template process.[47c]

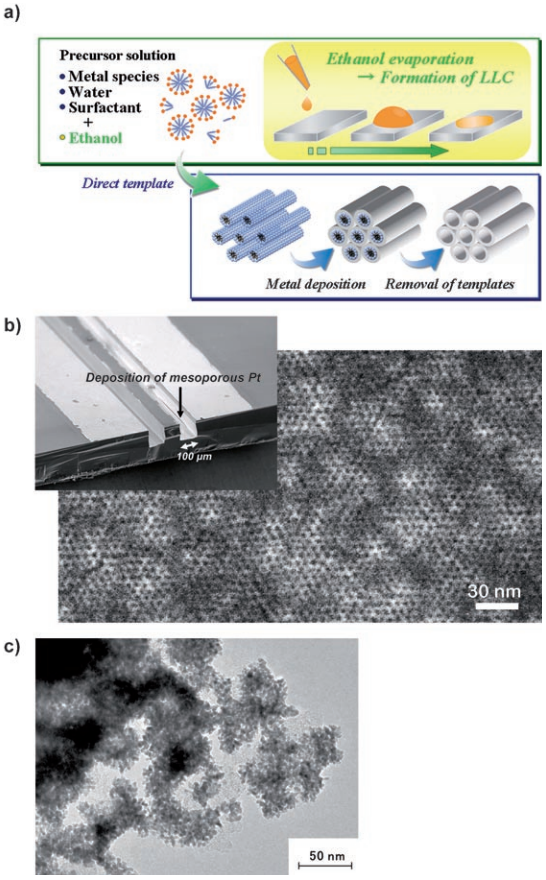


Figure 7. a) Synthesis of mesoporous metals by the EDIT method. b) SEM images of mesoporous Pt film inside the microchannels. The highly magnified SEM image is of the mesoporous Pt layer inside the microchannels. c) TEM image of nanogroove-networked Pt nanosheets on carbon support. Reprinted with permission from reference [50]. (Copyright John Wiley & Sons, Inc., 2007.)

The EDIT process is fundamentally different from the conventional evaporation-induced self-assembly (EISA) method utilized for the formation of mesoporous films (e.g., silica).[14,48] In the EDIT system, a homogeneous precursor solution is initially prepared, and then preferential evaporation of ethanol accelerates to form LLC mesophases. During LLC formation, no reactions among metal species are carried out; that is, these species are stabilized in the aqueous LLC domain. In contrast, in the EISA system, the polymerization of inorganic species occurs simultaneously during solvent evaporation, in which various interactions between the inorganic species and surfactants are inevitable. Therefore, several types of phase transformations of mesoporous structures have often been observed in the films, depending on the experimental conditions.[48] In the EDIT system, the final LLC mesophases after preferential evaporation of ethanol can be directly predicted by a phase diagram of ternary composition (surfactant + water + metal species) independent of the amount of ethanol solvent, which does not strongly influence the final structure of the LLC mesophase. In the direct-template approach from LLCs, it is possible to predict the final structures after metal deposition from the original LLC mesophases. The LLC mesophases act as true templates; that is, the final materials are formed through the direct-template process by the LLC formed through solvent evaporation. Consequently, the EDIT system is quite different from the conventional EISA system. This concept has also been applied in the explanation of the synthesis of mesoporous carbon materials from soluble phenolic resin and triblock copolymers.[4i,j] The self-assembly of triblock copolymers is induced by solvent evaporation. At this stage, the triblock copolymers are assembled together with phenolic resin, and condensation of the latter does not occur. The polymerization is only carried out in the subsequent thermopolymerization process.

Recently, two research groups reported the application of the EDIT system. Edler and co-workers applied the method to a mixed nonionic–anionic surfactant system to make mesoporous silver film.[49] As described above, this system was developed by Kijima et al.[31] The used precursor solution consists of a nonionic surfactant (polyethylene glycol octadecyl ether, Brij76), an anionic surfactant (sodium dodecyl sulfate, SDS), ethanol, water, and silver nitrate. This precursor solution was dip-coated onto glass slides. As the ethanol was preferentially evaporated, the concentration of the mixed surfactants was increased to form an LLC film on the substrate. After that, the silver ions in the film were photochemically reduced by exposure to ambient light or chemically reduced by formaldehyde gas. In the case of photochemical reduction, ordered 2D hexagonal mesoporous silver films were obtained. This unique photochemical-reduction method of synthesizing mesoporous metal films allows the low-cost and rapid fabrication of novel catalysts, sensors, and surface coatings for nonconductive substrates, electrodes for fuel cells, and so on. However, the XRD patterns and TEM images are not well-resolved. More and more intensive structural characterization with electron microscopic techniques is required to detect the formation of 2D hexagonal mesostructures. The surface area of the films obtained should also be investigated by using gas adsorption–desorption measurements or electrochemical analysis.

Recently, Sakai, Kijima, and co-workers reported the formation of nanogroove-network Pt nanosheets on a carbon support through a solvent-evaporation process (Figure 7c).[50] Carbon powder was added to a precursor solution of Pt salts, surfactants, and water. Excess water was then evaporated to make LLCs. The concept is very similar to that of the EDIT method, although ethanol was not included in the precursor solution. An aqueous solution of SBH was added to the resulting LLCs to deposit Pt, and the nanogrooved Pt nanostructures were successfully loaded onto carbon particles (Figure 7c). The carbon-supported nanogroove-network-structured Pt exhibited fairly high electrocatalytic activity for the ORR. The new material is promising as a high-performance cathode catalyst for polymer electrolyte fuel cells (PEFCs).

We strongly believe that this convenient, novel pathway through solvent evaporation is very important for the rapid production of functional nanoscale devices and novel nanomaterials that utilize mesoporous metals. Another advantage of this method is that the LLC template mixture can be formed directly from a precursor solution without the heating–aging processes commonly used in the general synthesis of mesoporous metals. The entire synthetic procedure is simple and can be extended to various mesoporous alloys by using precursor solutions, including mixed metal ions.

4. Other Processes

In this section, other approaches to highly nanoporous metals are briefly summarized. Stucky and co-workers prepared mesoporous ZnO[51a] and Pt[51b] thin films by an electrodeposition method by utilizing potential-controlled surfactant assemblies. The Pt thin film obtained had a 2D hexagonal ordered mesostructure, although the mesoscopic periodicity was relatively low. The TEM image shows that the estimated pore size and wall thickness were both about 4 nm, which coincide with the diameters of the cylinder assemblies of the surfactants used.

Several nanostructured matrices have been utilized as hard templates. Ordered macroporous materials have been prepared by colloidal crystal templates, as first demonstrated by Velev et al. in 1997.[52a] Such colloidal crystals are constructed by the well-ordered assembly of spherical particles, and spherical particles from 50 nm to microns in size are generally used.[52] By utilizing electrochemical processes, metal-based macroporous materials can be obtained, and arrays of interconnected spherical voids with uniform diameters are formed.[53] The diameters of the voids can be controlled by choosing the diameters of the spherical particles used to make the colloidal crystal templates; however, as the spherical particles decrease in size, it becomes more difficult to make ordered colloidal crystal templates, which leads to a decrease in the order of the arrays of the voids in the final materials.

Anodic porous alumina[54] has also been used as a hard template. Masuda and co-workers reported that highly ordered metal nanohole arrays (e.g., Pt, Au) were fabricated by the two-step replication of the honeycomb structure of anodic porous alumina.[55] Preparation of the negative porous structure of porous alumina followed by formation of the positive structure with metal resulted in a metallic honeycomb structure. The metal nanohole arrays of the film had a uniform, closely packed honeycomb structure approximately 70 nm in diameter and 1–3 μm thick. Because of its textured surface, the metal nanohole arrays of gold showed a notable color change relative to bulk gold.

Wakayama and Fukushima synthesized nanoporous Pt and Pt/Ru fibers replicated from activated carbon through the nanoscale-casting process with supercritical fluids.[56] This process easily allows the impregnation of the precursor molecules into micropores of less than 1 nm without condensation into the liquid phase. The morphology of the fibers obtained is exactly the same as that of the activated carbon and can be easily controlled by the choice of the shape of activated carbon. The Brunauer–Emmett–Teller (BET) surface area of the Pt obtained is 47 $m^2 g,^{-1}$ which is larger than that found for platinum black (20–30 $m^2 g^{-1}$) by N_2-adsorption measurements.

Hanada et al. developed a new way of making nanopores in bulk metals and alloys.[57] First, numerous thermal vacancies are frozen into ordered bulk alloys (e.g., FeAl) by a conventional rapid-solidification process. Through controlled heat treatment at high temperatures, the clustering of the supersaturated vacancies generates a large number of nanopores (10–100 nm) near the surfaces. Nanoporous surfaces can be clearly visualized by SEM and AFM. Interestingly, these generated nanopores have pore surfaces aligned along the {100} crystallographic plane.

Dealloying is another method of making nanopores. First, an Au/Ag phase is chemically driven to aggregate into 2D clusters by a phase-separation process (i.e., spinodal decomposition).[58] Then, nanoporous Au film can be prepared by the selective dissolution of the electrochemically active element (Ag).

5. Potential Applications and Outlook

The synthesis of metal-based nanoarchitectured materials is currently an active research area owing to potential applications in such diverse areas as electrochemistry, electronics, magnetics, optics, photonics, and catalysis. Many types of metal-based nanomaterials, including mesoporous metals, nanoparticles, nanowires, and nanosheets, can now be rationally designed, and further applications for mesoporous metals and alloys can be expected.

With current environmental issues and the demand for more-efficient power supplies, the development of fuel cells is accelerating. Direct methanol fuel cells (DMFCs) can generate electricity directly from methanol and water at low temperatures without reforming the fuel into hydrogen.[59] The activity of the catalyst increases with increasing specific surface area because the chemical reaction of the fuel cell takes place on the surface of the catalyst layer. Mesoporous Pt with a high surface area shows high activity in O_2 reduction, which points toward the evolution of a novel class of efficient fuel-cell electrocatalysts.[29e] Mesoporous Pt/Ru alloys are more active than mesoporous Pt in CH_3OH oxidation.[45d] Evans et al. reported that mesoporous Pt showed excellent amperometric sensing for the detection of hydrogen peroxides over a wide range of concentrations.[29b] Imokawa et al. used mesoporous Pd for pH sensing. The mesoporous Pd exhibited a stable and reproducible response over a wide pH range owing to the highly active surface area.[24c]

The above systems, however, utilize only high surface area. Other structural characteristics (e.g., uniformly sized mesopores and their periodic arrangement) are not efficiently utilized. Therefore, researchers should reconsider whether highly ordered mesoporous metals are truly necessary and whether disordered mesoporous metals with high surface areas can be used as substitutes. To make this point clear, reference samples (e.g., Pt black and Raney Ni) should be compared with mesoporous metals, and highly ordered mesoporous metals should be compared with disordered mesoporous metals. Nie and Elliott reported that well-ordered mesoporous Pt microelectrodes showed improved electrocatalytic properties for oxygen reduction relative to disordered mesoporous Pt microelectrodes.[29f] However, the relationship between the order of the mesostructures and their electrocatalytic behavior is still unclear.[29f] Further research in this area is required. Moreover, researchers should find new applications in which all the structural characteristics of the mesoporous metals are required.

Recently, new-concept μ-DMFCs have come into demand for cellular phones, laptop computers, and portable cameras. Miniature fuel cells are also sought after as implantable micropower sources for medical devices such as shunt pumps for cerebrospinal fluid and microinsulin pumps.[60] For these applications, it is desirable to prepare mesoporous metals in the form of thin films in a very confined area. Recently, an innovative EDIT method (see Section 3.4) was developed for the fabrication of highly ordered mesoporous metals in a very confined area. This approach allows easy control over the location, composition, thickness, and mesoporous structure of a particular device, thus making it possible to design and fabricate new μ-DMFCs. The microscale design of mesoporous metals should contribute greatly to future applications such as microsensors, microbioactive materials, and miniaturized devices.

The development of new LLCs is vital for the evolution of new mesostructures. The LLCs generally used consist of short oligomeric $C_n(EO)_m$-type surfactants. If large block copolymers are used to make LLC mesophases, mesoporous metals with large mesopores could be designed. The sizes of the mesopores would be easily controlled over a wide range, from a few nanometers to 50 nm, by simply choosing the appropriate template. Applications for energy storage would benefit from optimized nanostructures, compositions, and conduction pathways. With great progress being made in mesostructured materials, there are fascinating new opportunities for inorganic and materials chemists, who should remain very active in this field.

Acknowledgements

We acknowledge Prof. T. Osaka, Dr. T. Momma (Applied Physical Chemistry Laboratory, Department of Applied Chemistry, Waseda University), and Dr. T. Yokoshima (Department of Applied Chemistry, Waseda University; present address: National Institute of Advanced Industrial Science and Technology, AIST) for valuable discussions and continuous encouragement. We also acknowledge Prof. O. Terasaki (Stockholm University) and Dr. T. Ohsuna (Waseda University) for their collaboration and useful discussions on the structural study of mesoporous metals. We are grateful to our co-workers whose names appear in the references for their contributions to this work. This work was supported by the Global COE Program "Practical Chemical Wisdom" and by the Encouraging Development Strategic Research Centers Program "Establishment of Consolidated Research Institute for Advanced Science and Medical Care" from MEXT. This work was also supported by the A3 Foresight Program "Synthesis and Structural Resolution of Novel Mesoporous Materials" from the Japan Society for the Promotion of Science (JSPS). Partial support came from a Grant-in-Aid for Scientific Research (No. 19850031).

---

[1] a) C. T. Kresge, M. E. Leonowicz, W. J. Roth, J. C. Vartuli, J. S. Beck, *Nature* **1992**, *359*, 710–712; b) J. S. Beck, J. C. Vartuli, W. J. Roth, M. E. Leonowicz, C. T. Kresge, K. D. Schmitt, C. T. W. Chu, D. H. Olson, E. W. Sheppard, S. B. Mccullen, J. B. Higgins, J. L. Schlenker, *J. Am. Chem. Soc.* **1992**, *114*, 10834–10843; c) T. Yanagisawa, T. Shimizu, K. Kuroda, C. Kato, *Bull. Chem. Soc. Jpn.* **1990**, *63*, 988–992; d) T. Yanagisawa, T. Shimizu, K. Kuroda, C. Kato, *Bull. Chem. Soc. Jpn.* **1990**, *63*, 1535–1537.

[2] a) V. Chiola, J. E. Ritsko, C. D. Vanderpool (Sylvania Electric Products, Inc.), US patent No. 3556725, **1971**; b) F. DiRenzo, H. Cambon, R. Dutartre, *Microporous Mater.* **1997**, *10*, 283–286.

[3] a) A. Shimojima, K. Kuroda, *Chem. Rec.* **2006**, *6*, 53–63; b) A. Vinu, T. Mori, K. Ariga, *Sci. Technol. Adv. Mater.* **2006**, *7*, 753–771; c) Y. Huang, H. Cai, T. Yu, X. Sun, B. Tu, D. Zhao, *Chem. Asian J.* **2007**, *2*, 1282–1289; d) J. H. Xu, T. T. Zhuang, Y. Cao, J. Yang, J. J. Wen, Z. Y. Wu, C. F. Zhou, L. Huang, Y. Wang, M. B. Yue, J. H. Zhu, *Chem. Asian J.* **2007**, *2*, 996–1006; e) Y. Wan, D. Zhang, Y. Zhai, C. Feng, J. Chen, H. Li, *Chem. Asian J.* **2007**, *2*, 875–881; f) Y. Wan, D. Zhao, *Chem. Rev.* **2007**, *107*, 2821–2860; g) S. W. Boettcher, J. Fan, C. K. Tsung, Q. H. Shi, G. D. Stucky, *Acc. Chem. Res.* **2007**, *40*, 784–792; h) J. D. Bass, D. Grosso, C. Boissiere, E. Belamie, T. Coradin, C. Sanchez, *Chem. Mater.* **2007**, *19*, 4349–4356; i) C. M. Yang, H. A. Lin, B. Zibrowius, B. Spliethoff, F. Schueth, S. C. Liou, M. W. Chu, C. H. Chen, *Chem. Mater.* **2007**, *19*, 3205–3211; j) S. Y. Choi, B. Lee, D. B. Carew, M. Mamak, F. C. Peiris, S. Speakman, N. Chopra, G. A. Ozin, *Adv. Funct. Mater.* **2006**, *16*, 1731–1738; k) Y. Yamauchi, M. Sawada, M. Komatsu, A. Sugiyama, T. Osaka, N. Hirota, Y. Sakka, K. Kuroda, *Chem. Asian J.* **2007**, *2*, 1505–1512.

[4] a) S. Inagaki, S. Guan, Y. Fukushima, T. Ohsuna, O. Terasaki, *J. Am. Chem. Soc.* **1999**, *121*, 9611–9614; b) S. Inagaki, S. Guan, T. Ohsuna, O. Terasaki, *Nature* **2002**, *416*, 304–307; c) Y. Goto, K. Okamoto, S.

Inagaki, *Bull. Chem. Soc. Jpn.* **2005**, *78*, 932–936; d) O. Ohtani, Y. Goto, K. Okamoto, S. Inagaki, *Chem. Lett.* **2005**, *34*, 1342–1343; e) Y. Meng, D. Gu, F. Q. Zhang, Y. F. Shi, H. F. Yang, Z. Li, C. Z. Yu, B. Tu, D. Y. Zhao, *Angew. Chem.* **2005**, *117*, 7215–7221; *Angew. Chem. Int. Ed.* **2005**, *44*, 7053–7059; f) K. Nakajima, M. Hara, K. Domen, J. N. Kondo, *Chem. Lett.* **2005**, *34*, 394–395; g) H. F. Yang, D. Y. Zhao, *J. Mater. Chem.* **2005**, *15*, 1217–1231; h) Y. Wan, Y. F. Shi, D. Y. Zhao, *Chem. Commun.* **2007**, 897–926; i) Y. Meng, D. Gu, F. Q. Zhang, Y. F. Shi, L. Cheng L, D. Feng, Z. X. Wu, Z. X. Chen, Y. Wan, A. Stein, D. Y. Zhao, *Chem. Mater.* **2006**, *18*, 4447–4464; j) Y. Wan, H. F. Yang, D. Y. Zhao, *Acc. Chem. Res.* **2006**, *39*, 423–432.

[5] a) A. Sayari, P. Liu, *Microporous Mater.* **1997**, *12*, 149–177; b) A. Stein, *Microporous Mesoporous Mater.* **2001**, *44–45*, 227–239; c) F. Schüth, *Chem. Mater.* **2001**, *13*, 3184–3195; d) G. J. D. A. Soler-Illia, E. L. Crepaldi, D. Grosso, C. Sanchez, *Curr. Opin. Colloid Interface Sci.* **2003**, *8*, 109–126; e) J. L. Shi, Z. L. Hua, L. X. Zhang, *J. Mater. Chem.* **2004**, *14*, 795–806; f) B. Sakintuna, Y. Yurum, *Ind. Eng. Chem. Res.* **2005**, *44*, 2893–2902; g) A. H. Lu, F. Schüth, *Adv. Mater.* **2006**, *18*, 1793–1805; h) T. Valdes-Solis, A. B. Fuertes, *Mater. Res. Bull.* **2006**, *41*, 2187–2197; i) M. P. Kapoor, S. Inagaki, *Bull. Chem. Soc. Jpn.* **2006**, *79*, 1463–1475; j) B. Smarsly, M. Antonietti, *Eur. J. Inorg. Chem.* **2006**, 1111–1119; k) M. G. Kanatzidis, *Adv. Mater.* **2007**, *19*, 1165–1181.

[6] a) R. Ryoo, S. H. Joo, S. Jun, *J. Phys. Chem. B* **1999**, *103*, 7743–7746; b) J. Lee, S. Yoon, T. Hyeon, S. M. Oh, K. B. Kim, *Chem. Commun.* **1999**, 2177–2178.

[7] a) G. S. Attard, C. G. Goltner, J. M. Corker, S. Henke, R. H. Templer, *Angew. Chem.* **1997**, *109*, 1372–1374; *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 1315–1317; b) G. S. Attard, P. N. Bartlett, N. R. B. Coleman, J. M. Elliott, J. R. Owen, J. H. Wang, *Science* **1997**, *278*, 838–840.

[8] H. J. Shin, R. Ryoo, Z. Liu, O. Terasaki, *J. Am. Chem. Soc.* **2001**, *123*, 1246–1247.

[9] Z. Liu, O. Terasaki, T. Ohsuna, K. Hiraga, H. J. Shin, R. Ryoo, *ChemPhysChem* **2001**, *2*, 229–231.

[10] Z. Liu, Y. Sakamoto, T. Ohsuna, K. Hiraga, O. Terasaki, C. H. Ko, H. J. Shin, R. Ryoo, *Angew. Chem.* **2000**, *112*, 3237–3240; *Angew. Chem. Int. Ed.* **2000**, *39*, 3107–3110.

[11] a) A. Fukuoka, N. Higashimoto, Y. Sakamoto, S. Inagaki, Y. Fukushima, M. Ichikawa, *Microporous Mesoporous Mater.* **2001**, *48*, 171–179; b) A. Fukuoka, H. Araki, Y. Sakamoto, S. Inagaki, Y. Fukushima, M. Ichikawa, *Inorg. Chim. Acta* **2003**, *350*, 371–378; c) A. Fukuoka, H. Araki, J. Kimura, Y. Sakamoto, T. Higuchi, N. Sugimoto, S. Inagaki, M. Ichikawa, *J. Mater. Chem.* **2004**, *14*, 752–756; d) J. L. Gu, J. L. Shi, Z. Hua, L. M. Xiong, L. X. Zhang, L. Li, *Chem. Lett.* **2005**, *34*, 114–115; e) A. Fukuoka, J. I. Kimura, T. Oshio, Y. Sakamoto, M. Ichikawa, *J. Am. Chem. Soc.* **2007**, *129*, 10 120–10 125.

[12] a) A. Fukuoka, Y. Sakamoto, S. Guan, S. Inagaki, N. Sugimoto, Y. Fukushima, K. Hirahara, S. Iijima, M. Ichikawa, *J. Am. Chem. Soc.* **2001**, *123*, 3373–3374; b) Y. Sakamoto, A. Fukuoka, T. Higuchi, N. Shimomura, S. Inagaki, M. Ichikawa, *J. Phys. Chem. B* **2004**, *108*, 853–858; c) A. Fukuoka, T. Higuchi, T. Ohtake, T. Oshio, J. Kimura, Y. Sakamoto, N. Shimomura, S. Inagaki, M. Ichikawa, *Chem. Mater.* **2006**, *18*, 337–343.

[13] a) D. H. Wang, W. L. Zhou, B. F. McCaughy, J. E. Hampsey, X. L. Ji, Y. B. Jiang, H. F. Xu, J. K. Tang, R. H. Schmehl, C. O'Connor, C. J. Brinker, Y. F. Lu, *Adv. Mater.* **2003**, *15*, 130–133; b) D. H. Wang, H. M. Luo, R. Kou, M. P. Gil, S. G. Xiao, V. O. Golub, Z. Z. Yang, C. J. Brinker, Y. F. Lu, *Angew. Chem.* **2004**, *116*, 6295–6299; *Angew. Chem. Int. Ed.* **2004**, *43*, 6169–6173; c) D. H. Wang, H. P. Jakobson, R. Kou, J. Tang, R. Z. Fineman, D. H. Yu, Y. F. Lu, *Chem. Mater.* **2006**, *18*, 4231–4237; d) C. W. Wu, Y. Yamauchi, T. Ohsuna, K. Kuroda, *J. Mater. Chem.* **2006**, *16*, 3091–3098; e) F. F. Gao, S. P. Naik, T. Okubo, *J. Nanosci. Nanotechnol.* **2007**, *7*, 2894–2898.

[14] a) M. Ogawa, *J. Am. Chem. Soc.* **1994**, *116*, 7941–7942; b) M. Ogawa, *Chem. Commun.* **1996**, 1149–1150.

[15] a) Z. T. Zhang, Z. W. Pan, S. M. Mahurin, S. Dai, *Chem. Commun.* **2003**, 2584–2585; b) H. Li, J. L. Shi, L. Li, J. L. Gu, L. X. Zhang, H. R. Chen, W. Shi, *Chem. Lett.* **2005**, *34*, 210–211; c) J. L. Gu, J. L. Shi, L. M. Xiong, H. R. Chen, L. Li, M. L. Ruan, *Solid State Sci.* **2004**, *6*, 747–752; d) T. Asefa, R. B. Lennox, *Chem. Mater.* **2005**, *17*, 2481–2483.

[16] N. R. B. Coleman, G. S. Attard, *Microporous Mesoporous Mater.* **2001**, *44*, 73–80.

[17] G. S. Attard, J. C. Glyde, C. G. Goltner, *Nature* **1995**, *378*, 366–368.

[18] a) S. A. El-Safty, T. Hanaoka, F. Mizukami, *Chem. Mater.* **2005**, *17*, 3137–3145; b) S. A. El-Safty, F. Mizukami, T. Hanaoka, *J. Phys. Chem. B* **2005**, *109*, 9255–9264.

[19] P. N. Bartlett, P. N. Birkin, M. A. Ghanem, P. de Groot, M. Sawicki, *J. Electrochem. Soc.* **2001**, *148*, C119–C123.

[20] H. M. Luo, L. Sun, Y. F. Lu, Y. S. Yan, *Langmuir* **2004**, *20*, 10 218–10 222.

[21] a) P. A. Nelson, J. M. Elliott, G. S. Attard, J. R. Owen, *Chem. Mater.* **2002**, *14*, 524; b) V. Ganesh, V. Lakshminarayanan, *Electrochim. Acta* **2004**, *49*, 3561–3572; c) R. Campbell, M. G. Bakker, *J. Porous Mater.* **2004**, *11*, 63–69; d) D. D. Zhao, W. J. Zhou, H. L. Li, *Chem. Mater.* **2007**, *19*, 3882–3891.

[22] H. M. Luo, J. F. Zhang, Y. S. Yan, *Chem. Mater.* **2003**, *15*, 3769–3773.

[23] F. Bender, R. K. Mankelow, D. B. Hibbert, J. J. Gooding, *Electroanalysis* **2006**, *18*, 1558–1563.

[24] a) P. N. Bartlett, B. Gollas, S. Guerin, J. Marwan, *Phys. Chem. Chem. Phys.* **2002**, *4*, 3835–3842; b) P. N. Bartlett, J. Marwan, *Phys. Chem. Chem. Phys.* **2004**, *6*, 2895–2898; c) T. Imokawa, K. J. Williams, G. Denuault, *Anal. Chem.* **2006**, *78*, 265–271.

[25] P. N. Bartlett, J. Marwan, *Microporous Mesoporous Mater.* **2003**, *62*, 73–79.

[26] P. N. Bartlett, J. Marwan, *Chem. Mater.* **2003**, *15*, 2962–2968.

[27] P. A. Nelson, J. R. Owen, *J. Electrochem. Soc.* **2003**, *150*, A1313–A1317.

[28] a) A. H. Whitehead, J. M. Elliott, J. R. Owen, G. S. Attard, *Chem. Commun.* **1999**, 331–332; b) A. H. Whitehead, J. M. Elliott, J. R. Owen, *J. Power Sources* **1999**, *81–82*, 33–38.

[29] a) J. M. Elliott, P. R. Birkin, P. N. Bartlett, G. S. Attard, *Langmuir* **1999**, *15*, 7411–7415; b) S. A. G. Evans, J. M. Elliott, L. M. Andrews, P. N. Bartlett, P. J. Doyle, G. Denuault, *Anal. Chem.* **2002**, *74*, 1322–1326; c) S. Park, T. D. Chung, H. C. Kim, *Anal. Chem.* **2003**, *75*, 3046–3049; d) H. Boo, S. Park, B. Ku, Y. Kim, J. H. Park, H. C. Kim, T. D. Chung, *J. Am. Chem. Soc.* **2004**, *126*, 4524–4525; e) J. Jiang, A. Kucernak, *Electrochem. Solid-State Lett.* **2000**, *3*, 559–562; f) M. Y. Nie, J. M. Elliott, *J. Mater. Sci. Technol.* **2005**, *21*, 863–865; g) A. Saramat, M. Andersson, S. Hant, P. Thormählen, M. Skoglundh, G. S. Attard, A. E. C. Palmqvist, *Eur. Phys. J. D* **2007**, *43*, 209–211.

[30] J. K. Zhao, X. Chen, L. Y. Jiao, Y. C. Chai, G. D. Zhang, J. Liu, *Chem. Lett.* **2004**, *33*, 842–843.

[31] T. Kijima, T. Yoshimura, M. Uota, T. Ikeda, D. Fujikawa, S. Mouri, S. Uoyama, *Angew. Chem.* **2004**, *116*, 230–234; *Angew. Chem. Int. Ed.* **2004**, *43*, 228–232.

[32] Q. Zhou, X. Y. Liu, Y. M. Zhao, N. Q. Jia, L. Liu, M. M. Yan, Z. Y. Jiang, *Chem. Commun.* **2005**, 4941–4942.

[33] a) H. Kawasaki, M. Uota, T. Yoshimura, D. Fujikawa, G. Sakai, M. Annaka, T. Kijima, *Langmuir* **2005**, *21*, 11 468–11 473; b) H. Kawasaki, G. Sakai, T. Kijima, *Appl. Surf. Sci.* **2006**, *253*, 1512–1516; c) J. K. Zhao, X. Chen, *Acta Pediatr. Esp. Acta Chim. Sinica* **2007**, *65*, 803–808; d) L. Y. Wang, X. Chen, Y. C. Chai, J. C. Hao, *Colloids Surf. A* **2007**, *293*, 95–100.

[34] a) T. M. Dellinger, P. V. Braun, *Chem. Mater.* **2004**, *16*, 2201–2207; b) H. Kawasaki, M. Uota, T. Yoshimura, D. Fujikawa, G. Sakai, T. Kijima, *J. Colloid Interface Sci.* **2006**, *300*, 149–154.

[35] a) Ö. Çelik, Ö. Dag, *Angew. Chem.* **2001**, *113*, 3815–3815; *Angew. Chem. Int. Ed.* **2001**, *40*, 3700–3803; b) Ö. Dag, O. Samarskaya, C. Tura, A. Günay, Ö. Çelik, *Langmuir* **2003**, *19*, 3671–3676; c) Ö. Dag, S. Alayoğlu, C. Tura, Ö. Çelik, *Chem. Mater.* **2003**, *15*, 2711–2717; d) Ö. Dag, S. Alayoğlu, İ. Uysal, *J. Chem. Phys. B* **2004**, *108*, 8439–8446; e) A. F. Demirörs, B. E. Eser, Ö. Dag, *Langmuir* **2005**,

21, 4156–4162; f) C. Albayrak, G. Gülten, Ö. Dag, *Langmuir* **2007**, *23*, 855–860.

[36] a) Y. Yamauchi, T. Yokoshima, H. Mukaibo, M. Tezuka, T. Shigeno, T. Momma, T. Osaka, K. Kuroda, *Chem. Lett.* **2004**, *33*, 542–543; b) Y. Yamauchi, T. Momma, T. Yokoshima, K. Kuroda, T. Osaka, *J. Mater. Chem.* **2005**, *15*, 1987–1994; c) Y. Yamauchi, T. Yokoshima, T. Momma, T. Osaka, K. Kuroda, *Electrochem. Solid-State Lett.* **2005**, *8*, C141–C144.

[37] J. M. Elliott, G. S. Attard, P. N. Bartlett, N. R. B. Coleman, D. A. S. Merckel, J. R. Owen, *Chem. Mater.* **1999**, *11*, 3602–3609.

[38] a) P. V. Braun, P. Osenar, S. I. Stupp, *Nature* **1996**, *380*, 325–328; b) P. V. Braun, P. Osenar, V. Tohver, S. B. Kennedy, S. I. Stupp, *J. Am. Chem. Soc.* **1999**, *121*, 7302–7309; c) B. M. Rabatic, M. U. Pralle, G. N. Tew, S. I. Stupp, *Chem. Mater.* **2003**, *15*, 1249–1255; d) P. V. Braun, P. Osenar, M. Twardowski, G. N. Tew, S. I. Stupp, *Adv. Funct. Mater.* **2005**, *15*, 1745–1750.

[39] I. Nandhakumar, J. M. Elliott, G. S. Attard, *Chem. Mater.* **2001**, *13*, 3840–3842.

[40] T. Gabriel, I. S. Nandhakumar, G. S. Attard, *Electrochem. Commun.* **2002**, *4*, 610–612.

[41] Y. Yamauchi, T. Momma, M. Fuziwara, S. S. Nair, T. Ohsuna, O. Terasaki, T. Osaka, K. Kuroda, *Chem. Mater.* **2005**, *17*, 6342–6348.

[42] S. Guerin, G. S. Attard, *Electrochem. Commun.* **2001**, *3*, 544–548.

[43] a) I. S. Nandhakumar, T. Gabriel, X. Li, G. S. Attard, M. Markham, D. C. Smith, J. J. Baumberg, *Chem. Commun.* **2004**, 1374–1375; b) M. L. Markham, J. J. Baumberg, D. C. Smith, X. Li, T. Gabriel, G. S. Attard, I. S. Nandhakumar, *Appl. Phys. Lett.* **2005**, *86*, 011912; c) X. H. Li, I. S. Nandhakumar, T. Gabriel, G. S. Attard, M. L. Markham, D. C. Smith, J. J. Baumberg, K. Govender, P. O'Brien, D. Smyth-Boyle, *J. Mater. Chem.* **2006**, *16*, 3207–3214.

[44] a) Y. Yamauchi, T. Yokoshima, T. Momma, T. Osaka, K. Kuroda, *J. Mater. Chem.* **2004**, *14*, 2935–2940; b) Y. Yamauchi, S. S. Nair, T. Yokoshima, T. Momma, T. Osaka, K. Kuroda, *Stud. Surf. Sci. Catal.* **2005**, *156*, 457–464.

[45] a) G. S. Attard, S. A. A. Leclerc, S. Maniquet, A. E. Russell, I. Nandhakumar, P. N. Bartlett, *Chem. Mater.* **2001**, *13*, 1444–1446; b) G. S. Attard, S. A. A. Leclerc, S. Maniguet, A. E. Russell, I. Nandhakumar, B. R. Gollas, P. N. Bartlett, *Microporous Mesoporous Mater.* **2001**, *44*, 159–163; c) J. Jiang, A. Kucernak, *J. Electroanal. Chem.* **2003**, *543*, 187–199; d) J. Jiang, A. Kucernak, *Chem. Mater.* **2004**, *16*, 1362–1367; e) Y. Yamauchi, T. Ohsuna, K. Kuroda, *Chem. Mater.* **2007**, *19*, 1335–1342.

[46] Y. Yamauchi, S. S. Nair, T. Momma, T. Ohsuna, T. Osaka, K. Kuroda, *J. Mater. Chem.* **2006**, *16*, 2229–2234.

[47] a) Y. Yamauchi, T. Momma, T. Osaka, K. Kuroda (Waseda University), Japanese Patent 233272, **2006**; b) Y. Yamauchi, T. Momma, H. Kitoh, T. Osaka, K. Kuroda, *Electrochem. Commun.* **2005**, *7*, 1364–1370; c) Y. Yamauchi, K. Kuroda, *Electrochem. Commun.* **2006**, *8*, 1677–1682; d) Y. Yamauchi, H. Kitoh, T. Momma, T. Osaka, K. Kuroda, *Sci. Technol. Adv. Mater.* **2006**, *7*, 438–445; e) Y. Yamauchi, M. Komatsu, A. Takai, R. Sebata, M. Sawada, T. Momma, M. Fuziwara, T. Osaka, K. Kuroda, *Electrochim. Acta* **2007**, *53*, 604–609.

[48] a) Y. F. Lu, R. Ganguli, C. A. Drewien, M. T. Anderson, C. J. Brinker, W. L. Gong, Y. X. Guo, H. Soyez, B. Dunn, M. B. Huang, J. I. Zink, *Nature* **1997**, *389*, 364–368; b) S. P. Naik, S. Yamakita, Y. Sasaki, M. Ogura, T. Okubo, *Chem. Lett.* **2004**, *33*, 1078–1079; c) S. P. Naik, M. Ogura, H. Sasakura, Y. Yamaguchi, Y. Sasaki, T. Okubo, *Thin Solid Films* **2006**, *495*, 11–17; d) S. P. Naik, W. Fan, M. Ogura, T. Okubo, *J. Porous Mater.* **2006**, *13*, 303–306.

[49] K. Luo, C. T. Walker, K. J. Edler, *Adv. Mater.* **2007**, *19*, 1506–1509.

[50] G. Sakai, T. Yoshimura, S. Isohata, M. Uota, H. Kawasaki, T. Kuwahara, D. Fujikawa, T. Kijima, *Adv. Mater.* **2007**, *19*, 237–240.

[51] a) K. S. Choi, H. C. Lichtenegger, G. D. Stucky, E. W. McFarland, *J. Am. Chem. Soc.* **2002**, *124*, 12402–12403; b) K. S. Choi, E. W. McFarland, G. D. Stucky, *Adv. Mater.* **2003**, *15*, 2018–2021.

[52] a) O. D. Velev, T. A. Jede, R. F. Lobo, A. M. Lenhoff, *Nature* **1997**, *389*, 447–448; b) Y. Sakka, *J. Ceram. Soc. Jpn.* **2006**, *114*, 371–376; c) J. Hamagami, Y. Ato, K. Kanamura, *J. Ceram. Soc. Jpn.* **2006**, *114*, 51–54; d) M. Sadakane, C. Takahashi, N. Kato, H. Ogihara, Y. Nodasaka, Y. Doi, Y. Hinatsu, W. Ueda, *Bull. Chem. Soc. Jpn.* **2007**, *80*, 677–685; e) K. Zhao, Y. Q. Fan, N. P. Xu, *Chem. Lett.* **2007**, *36*, 464–465; f) F. Chai, X. H. Wang, R. X. Tan, F. H. Cao, F. Y. Zhai, L. L. Xu, C. L. Shao, Y. C. Liu, *Chem. Lett.* **2007**, *36*, 260–261; g) S. Li, J. T. Zheng, W. Y. Yang, Y. C. Zhao, *Chem. Lett.* **2007**, *36*, 542–543.

[53] a) P. Jiang, J. Cizeron, J. F. Bertone, V. L. Colvin, *J. Am. Chem. Soc.* **1999**, *121*, 7957–7958; b) P. N. Bartlett, P. R. Birkin, M. A. Ghanem, *Chem. Commun.* **2000**, 1671–1672; c) P. N. Bartlett, J. J. Baumberg, P. R. Birkin, M. A. Ghanem, M. C. Netti, *Chem. Mater.* **2002**, *14*, 2199–2208; d) M. Asai, T. Onoe, H. Kanoh, K. Kaneko, *Colloid. Surface. A* **2005**, *253*, 199–202.

[54] a) H. Masuda, K. Takenaka, T. Ishii, K. Nishio, *Jpn. J. Appl. Phys.* **2006**, *45*, L1165–L1167; b) H. Masuda, M. Nagae, T. Morikawa, K. Nishio, *Jpn. J. Appl. Phys.* **2006**, *45*, L406–L408.

[55] a) H. Masuda, K. Fukuda, *Science* **1995**, *268*, 1466–1468; b) T. Yanagishita, K. Nishio, H. Masuda, *Jpn. J. Appl. Phys.* **2006**, *45*, L804–L806; c) S. Sunkari, S. Nagashima, M. Murata, H. Nishihara, Y. Matsui, K. Nishio, H. Masuda, *Chem. Lett.* **2006**, *35*, 406–407; d) T. Yanagishita, K. Nishio, H. Masuda, *Jpn. J. Appl. Phys.* **2006**, *45*, L1133–L1135.

[56] a) H. Wakayama, Y. Fukushima, *Chem. Commun.* **1999**, 391–392; b) H. Wakayama, T. Hatanaka, Y. Fukushima, *Chem. Lett.* **2004**, *33*, 658–659.

[57] S. Hanada, K. Yoshimi, A. Inoue (Tohoku University), Japanese Patent 105460, **2003**.

[58] J. Erlebacher, M. J. Aziz, A. Karma, N. Dimitrov, K. Sieradzki, *Nature* **2001**, *410*, 450–453.

[59] a) T. Osaka, T. Momma, S. Tominaka, *Chem. Lett.* **2006**, *35*, 10–11; b) T. Shimizu, M. Mohamedi, T. Momma, T. Osaka, *Electrochemistry* **2006**, *74*, 326–331.

[60] a) J. W. Long, B. Dunn, D. R. Rolison, H. S. White, *Chem. Rev.* **2004**, *104*, 4463–4492; b) M. Ishizuka, H. Houjou, S. Motokawa, J. Mizuno, T. Momma, T. Osaka, S. Shoji, *Jpn. J. Appl. Phys.* **2006**, *45*, 7944–7948; c) S. Motokawa, M. Mohamedi, T. Momma, S. Shoji, T. Osaka, *Electrochemistry* **2005**, *73*, 346–351.

Received: October 22, 2007
Revised: December 17, 2007