Fabrication of mesoporous Pt nanotubes utilizing dual templates under a reduced pressure condition†

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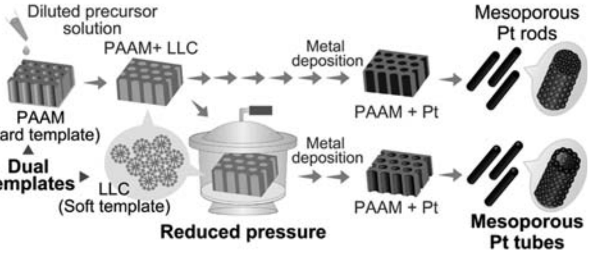
Pt nanotubes with mesoporous walls have been successfully prepared for the first time by the combination of hard templates (porous anodic alumina membranes, PAAM) and soft templates (lyotropic liquid crystals, LLC).

Various nanoarchitectured metals, such as particles,[1] rods,[2] tubes,[3] wires,[4] and necklaces,[5] have attracted much attention due to their electrochemical and catalytic activities. Among them, one dimensional (1D) metal nanostructures, such as nanorods and nanotubes, have potential applications for sensors, electronic wirings, and electrodes at nanoscale.[6] The properties of 1D metal nanorods are strongly dependent on their aspect ratios, metal compositions, and surface morphologies.[7–9] Metal nanotubes possess more advantages, such as high specific surface area and high accessibility of guest species, derived from their inherent hollow space. Furthermore, the incorporation of mesoporous structures into the walls of metal nanotubes should contribute to more efficient diffusion of guest species, which may lead to great acceleration of various reactions. Also, such a hierarchical pore system, consisting of both a hollow space and wall mesoporosity should provide more efficient relaxation for volume changes caused by incorporation of guest species into walls, in comparison with the nanorods without porosities.[10]

In order to incorporate mesoporous structures into various morphologically controlled metals, a soft template method utilizing lyotropic liquid crystals (LLC) composed of self-assembled surfactants at high concentration is a useful strategy. Many mesoporous metals can be prepared by this method, and the main process is reduction of metal ions dissolved in aqueous phases in LLC and subsequent removal of LLC.[11,12] From the viewpoint of the wide applicability of this method, it is more versatile than other methods such as a dealloying process.[13] Recently, we have proposed a new approach for the formation of metal-containing LLC through solvent evaporation.[14] Our approach can allow LLC to be successfully introduced into confined spaces due to the capillary force. After the formation of LLC, mesoporous metals are deposited in the confined spaces. Very recently, mesoporous nanorods have been prepared by using LLC filled inside the channels of a porous anodic alumina membrane (PAAM).[15] In these systems, the LLC are formed in confined spaces after solvent evaporation and used as templates without any further treatment. However, mesoporous nanotubes are not attainable by such a simple penetration of LLC followed by metal deposition.

In this communication, mesoporous Pt nanotubes were successfully prepared from the same precursor solution for mesoporous Pt nanorods[15] by applying a reduced pressure process before metal deposition. The formation of mesoporous nanotubes has been realized through the uniform coating of LLC on the channel surface. To the best of our knowledge, the morphological change of liquid crystals under reduced pressure has not been reported. The morphological control of LLC by external forces before metal deposition plays a key role for the morphological manipulation of final products. This finding is important for further development of rational design of novel mesoporous metals.

Mesoporous Pt nanorods and nanotubes were prepared as follows (Scheme 1). Nonionic surfactant ($C_{16}EO_8$, 0.21 g), 0.145 g H_2O, 0.145 g $H_2PtCl_6 \cdot 6H_2O$, and 0.26 ml ethanol as a volatile solvent were mixed for the preparation of a diluted precursor solution. This solution, stirred at room temperature, became homogeneous and showed orange in color. The precursor solution was dropped onto a PAAM (Whatman, Anodisc 25, pore diameter *ca.* 200 nm, thickness 60 μm) for the introduction into the channels of PAAM by capillary force. Subsequently, ethanol was preferentially evaporated to form LLC in the channels. After the formation of the LLC, the color of the composite (PAAM + LLC) changed from white to orange even after wiping out the LLC on the outer surface of PAAM, indicating the successful infiltration of the precursor into the channels. For the



Scheme 1 Schematic view of the preparative procedure for mesoporous Pt nanorods and nanotubes.

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† Electronic supplementary information (ESI) available: Experimental section: Synthetic procedure for mesoporous silica. Fig. S1: Schematic view of 2D-XRD geometry and the proposed mesophase structure. Fig. S2 and S3: SEM images. Fig. S4: TEM image and ED patterns. Fig. S5: SEM images of nanotubes after the heat treatment. Fig. S6: Suggested formation mechanism. Fig. S7: SEM image of mesoporous silica nanorods. Fig. S8: SEM images of the products prepared by changing the amount of ethanol/surfactant weight ratios. See DOI: 10.1039/b804072a

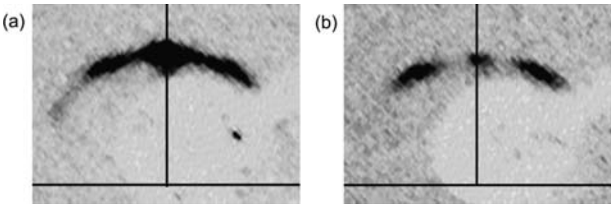

Fig. 1 2D-XRD patterns of the LLC in channels of PAAM by (a) before and (b) after reduced pressure process. The arc patterns are not observable in a small angle region by a beam stopper.

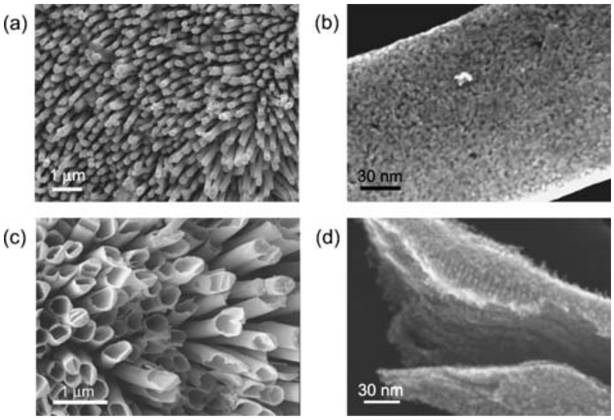

Fig. 2 SEM images of (a, b) mesoporous Pt nanorods and (c, d) mesoporous Pt nanotubes. Fig. (b) and (d) are highly magnified images of (a) and (c), respectively.

preparation of nanotubes, PAAM was placed in a vacuum desiccator for 10 min. Nanorods were also prepared without the treatment of reduced pressure for comparison. Both of the PAAM were placed in a closed vessel with a small amount of dimethylamine borane (DMAB) powders at 25 °C. The color of LLC in PAAM was changed from orange to black, indicating the Pt deposition in LLC. After the Pt deposition, PAAM was dissolved with an aqueous solution about 10 wt% phosphoric acid. Then, Pt nanorods or nanotubes were washed with ethanol and water to remove phosphoric acid and surfactants.

The 2D-XRD pattern of the LLC before the reduced pressure process shows one main spot with an arc in the out-of-plane direction (Fig. 1a). The arc is attributed to both the random orientation of mesochannels within the PAAM channels and the formation of a mesostructure with a low ordering. After the process, the 2D-XRD pattern of the LLC was changed, showing three spots (Fig. 1b). One spot was observable in the out-of-plane direction, which is located at the same position as that of the LLC before the application of reduced pressure. On the other hand, the intense right and left spots appeared at ±30° to the out-of-plane direction. These two spots suggest that hexagonally arranged mesochannels are partially oriented along with the (10) lattice plane parallel to the curved PAAM channel surface (*i.e.*, formation of donut-like mesochannels, see Fig. S1†).[16] Probably the LLC mesophases are slightly rearranged during the reduced pressure process, which will be discussed later.

After the reduction of Pt species and the following removal of PAAM, the SEM images of the mesoporous nanorods and nanotubes are shown in Fig. 2. By applying the reduced pressure process, the morphologies are dramatically changed from nanorods (Fig. 2a) into nanotubes (Fig. 2c). The unidirectional arrays of the nanotubes are derived from the channel arrangement of the original PAAM. The nanotubes are observed over the entire area. The wall thickness of the nanotubes was *ca.* 10 nm roughly estimated from the HR-SEM image (Fig. S2).† Here we successfully introduced 1D hollow spaces into nanorods just under reduced pressure conditions before the Pt deposition. The nanotubes were connected to each other and retained the array formation even after ultrasonic treatment, because the original PAAM has branched and combined channels to each other.

The detailed mesostructures of internal and external surface of the nanotubes are directly observed by HR-SEM images (Fig. 2d, S3†). In almost all the nanotubes, the ordering of mesoporous structures was relatively low and the ordered domain size was quite small (Fig. S2).† In some parts, mesochannels were oriented parallel to the curved PAAM channel surface, which reflects the original LLC mesophases measured by the 2D-XRD (Fig. 1b). The nanotubes are composed of the assembled Pt nanoparticles of 3 nm in size. The reason why the nanoparticles were formed in the LLC has already been explained previously.[14] The HR-SEM images proved that the connection of the Pt nanoparticles creates mesoporosity. The selected ED pattern shows ring patterns assignable to the *fcc* structure of Pt (Fig. S4).† The Pt crystallinity is randomly oriented over several nanoparticles. The mesostructure of the nanorods was also investigated by HR-SEM (Fig. 2b). A similar mesostructure was observed. The original size of nanoparticle was retained up to 100 °C. The nanoparticles heated in the range between 150 °C and 300 °C were aggregated and grew to be larger particles, though the nanotubular morphology was retained (Fig. S5).†

The formation mechanism of the nanotubes is discussed. Generally, it is understandable that the volume of soft materials is expanded under reduced pressure. LLC are regarded as one of soft materials and an intermediate phase between solid and liquid with fluidity. Therefore, the volume change should occur in the present system (Fig. S6).† When the LLC contained in the channels of PAAM are placed in a vacuum desiccator, the volume of the LLC is expected to be increased. The LLC were expanded along the channel direction (Step 2) and then overflowed out of the channels (Step 3). The LLC outside of the PAAM might cover the surface of the PAAM. After that, when the pressure is returned to normal pressure, the volume of the expanded LLC is immediately decreased and shrunk. We consider that the LLC overflowed onto the outer PAAM surface are unable to return to the original position due to the strong interaction between the LLC and the PAAM surface. Then, air was introduced into voids of the LLC in the channels of the PAAM, resulting that the LLC are uniformly coated on the channel surface (Step 4). At this stage, LLC mesophases should rearrange by the movement of surfactants in the coated LLC during the shrinkage. The formation of donut-like mesochannels is expected to be preferentially induced along the curved PAAM channel surface (Fig. S1),† due to a strong hydrophilic interaction between the surfactants and the PAAM surface. Such an arrangement is easily understandable, because the donut-like mesophases within straight channels of PAAM is highly stable. This reason has been well explained by using simulation by self-consistent field theory.[17]

Also, it should be noted that the *d* values in the out-of-plane diffractions do not change even after the application of the reduced pressure condition at all, as is confirmed by θ-2θ XRD (not shown) and 2D-XRD measurements (Fig. 1). This is because the dissolved metal species are coordinated with water and counter ions, and they are stabilized in the hydrophilic part of surfactants.[18]

In order to further discuss the above formation mechanism, the same experimental procedure under reduced pressure was applied to the preparation of mesoporous silica involving sol-gel reactions *via* EISA method (see ESI).† However, only rods were observed by SEM (Fig. S7†). In this case, the silica polymerization reaction simultaneously proceeded during the solvent evaporation. Therefore, after the solvent evaporation, the surfactant-silica complexes became rigid and were fixed inside the PAAM channels. In contrast, in the case of the LLC containing the metal species, the metal species before metal deposition are stable in the LLC and the LLC are mobile enough to be reformed.

To roughly estimate the active surface area of mesoporous Pt nanorods and nanotubes, cyclic voltammetry (CV) was measured in an aqueous 1.0 M H_2SO_4 solution (scan rate: 500 mV s^{-1}). The CV curves of both samples showed a typical feature of polycrystalline nature of Pt. On the basis of the assumption that a monolayer of hydrogen corresponds to an adsorption charge of 210 μC cm^{-2}, the electrochemically active surface areas of the mesoporous Pt rods and tubes were around 30–40 m^2 g^{-1}. The contribution of the inner channel surface to total surface area is not so large in these cases because the major porosities of rods and tubes arise from the internal mesostructures. These values are close to those of the mesoporous Pt particles and films reported previously.[11]

The use of a reduced pressure is essential, and the attempt to form nanotubes by diluting a precursor solution with volatile solvent was unsuccessful, which means that nanotubular LLC did not form without reduced pressure. We attempted to prepare mesoporous Pt nanotubes by just increasing the weight ratio of ethanol to surfactants in the precursor solutions. The precursor solutions were drop-cast on PAAM. After the solvent evaporation, Pt ions were reduced by the same vapor infiltration method. However, the mesoporous Pt nanotubes were not obtained. When the weight ratio of ethanol/surfactant ranged from 1 to 50, mesoporous Pt nanorods were mainly formed (Fig. S8a, b).† Even when the ratio was higher than 100, Pt nanotubes were rarely formed and by-products with no characteristic morphologies, such as aggregated nanoparticles, were mainly formed (Fig. S8c).† Probably the LLC were segregated within the PAAM channels during solvent evaporation under normal pressure. A visible example of such segregation has been reported for the fabrication of an opal film using artificial opals.[19] Varied evaporation rates, depending on the area of a film, induces the heterogeneity in the film, resulting in the formation of an uneven film on a substrate. The similar situation should occur in the LLC system because surfactant molecules can also move under a capillary force to cause a heterogeneous state. Consequently, the successful coating of LLC with uniform thickness is vital to the synthesis of mesoporous metal nanotubes, which is achievable only under the reduced pressure condition.

In conclusion, we have realized the selective preparation of mesoporous Pt nanorods and nanotubes utilizing both LLC as a soft template and PAAM as a hard template. Mesoporous Pt nanotubes have been synthesized by controlling LLC morphology under a reduced pressure. The 1D hollow space of the mesoporous Pt nanotubes should contribute to the great enhancement of the accessibility of guest species, which is an important finding for electrochemical applications with improved functionalities. The application of the reduced pressure processing into soft templates is a facile method for the creation of nanotube morphology. In future, the application of various external forces such as electric, magnetic, gravity fields[20] should lead to the evolution of new types of mesoporous metals with unique morphologies. This desirable collaboration of external forces (induced by the hard templates in the present case) and soft templates will open the door to a new methodology for design of functional nanomaterials.

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Notes and references

1 X. Teng, X. Liang, S. Maksimuk and H. Yang, *Small*, 2006, **2**, 249–253.
2 H. J. Shin, R. Ryoo, Z. Liu and O. Terasaki, *J. Am. Chem. Soc.*, 2001, **123**, 1246–1247.
3 T. Kijima, T. Yoshimura, M. Uota, T. Ikeda, D. Fujikawa, S. Mouri and S. Uoyama, *Angew. Chem., Int. Ed.*, 2003, **43**, 228–232.
4 Z. Shen, M. Yamada and M. Miyake, *Chem. Commun.*, 2007, 245–247.
5 Y. Sakamoto, A. Fukuoka, T. Higuchi, N. Shimomura, S. Inagaki and M. Ichikawa, *J. Phys. Chem. B*, 2004, **108**, 853–858.
6 M. Li, R. B. Bhiladvala, T. J. Morrow, J. A. Sioss, K.-K. Lew, J. M. Redwing, C. D. Keating and T. S. Mayer, *Nat. Nanotech.*, 2008, **3**, 88–92.
7 B. R. Martin, D. J. Dermody, B. D. Reiss, M. Fang, L. A. Lyon, M. J. Natan and T. E. Mallouk, *Adv. Mater.*, 1999, **11**, 1021–1025.
8 F. Liu, J. Y. Lee and W. J. Zhou, *Small*, 2006, **2**, 121–128.
9 C. K. Chan, H. Peng, G. Liu, K. Mcilwrath, X. F. Zhang, R. A. Huggins and Y. Cui, *Nat. Nanotech.*, 2008, **3**, 31–35.
10 H. Nara, Y. Fukuhara, A. Takai, M. Komatsu, H. Mukaibo, Y. Yamauchi, T. Momma, K. Kuroda and T. Osaka, *Chem. Lett.*, 2008, **37**, 141–142.
11 G. S. Attard, C. G. Göltner, J. M. Corker, S. Henke and R. H. Templer, *Angew. Chem., Int. Ed.*, 1997, **36**, 1315–1317.
12 Y. Yamauchi, T. Yokoshima, H. Mukaibo, M. Tezuka, T. Shigeno, T. Momma, T. Osaka and K. Kuroda, *Chem. Lett.*, 2004, **33**, 542–543.
13 Y. Sun and Y. Xia, *Science*, 2002, **298**, 2176–2179.
14 (*a*) Y. Yamauchi, A. Takai, M. Komatsu, M. Sawada, T. Ohsuna and K. Kuroda, *Chem. Mater.*, 2008, **20**, 1004–1011; (*b*) Y. Yamauchi and K. Kuroda, *Chem. Asian J.*, 2008, **3**, 664–676.
15 Y. Yamauchi, A. Takai, T. Nagaura, S. Inoue and K. Kuroda, *J. Am. Chem. Soc.*, 2008, **130**, 5426–5427.
16 B. Platschek, N. Petkov and T. Bein, *Angew. Chem., Int. Ed.*, 2006, **45**, 1134–1138.
17 Y. Wui, G. Cheng, K. Katsov, S. W. Sides, J. Wang, J. Tang, G. H. Fredrickson, M. Moskovits and G. D. Stucky, *Nat. Mater.*, 2004, **3**, 816–822.
18 Ö. Çelik and Ö. Dag, *Angew. Chem., Int. Ed.*, 2001, **40**, 3799–3803.
19 H. Fudouzi, *J. Colloid Interface Sci.*, 2004, **275**, 277–283.
20 Y. Yamauchi, M. Sawada, M. Komatsu, A. Sugiyama, T. Osaka, N. Hirota, Y. Sakka and K. Kuroda, *Chem. Asian J.*, 2007, **2**, 1505–1512.