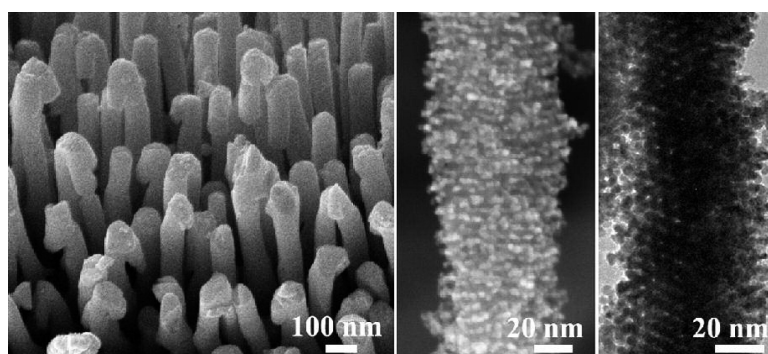


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*J. Am. Chem. Soc.*, **2008**, 130 (16), 5426-5427 • DOI: 10.1021/ja800269c • Publication Date (Web): 28 March 2008

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## Pt Fibers with Stacked Donut-Like Mesospace by Assembling Pt Nanoparticles: Guided Deposition in Physically Confined Self-Assembly of Surfactants

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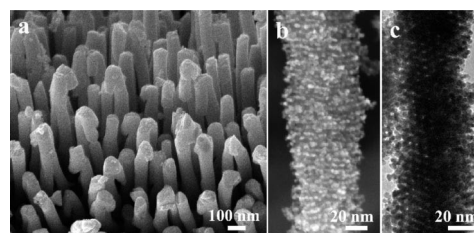
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Metal nanoparticles are currently attracting considerable research interest in several fields, including the biomedical, electrochemical, optical, and electronic fields, because they show not only a high surface area but also unique size-dependent properties (e.g., quantum confinement, plasmon resonance, and superparamagnetism). Great efforts are being focused on assembling nanoparticles as building blocks to form macroscopic structures. Various strategies have been developed to make several advanced functional materials (e.g., superlattices,<sup>1</sup> one-dimensional connections,<sup>2</sup> two-dimensional periodic arrays,<sup>3</sup> spatial assemblies<sup>4</sup>). Moreover, the introduction of periodic mesospaces into nanoparticle assemblies is important for further enhancement of the nanoparticle properties.<sup>5</sup> For instance, the presence of open mesopores in the nanoparticle assemblies is essential for high accessibility of guest species, which is useful in biomedical and electrochemical fields. If the periodic mesostructures could be oriented in a preferential manner, remarkable properties, such as anisotropic plasmon resonance and anisotropic conductivity, would be obtained. Therefore, the rational architecture of mesospaces in nanoparticle assemblies is the next challenge to overcome.

To this end, we have focused on the metal deposition behavior from lyotropic liquid crystals (LLCs) made of highly concentrated surfactants. LLCs possess long-range periodic nanostructures with lattice parameters in the mesoscale range, and they have been utilized as templates for the preparation of mesoporous materials.<sup>6</sup> The main advantage of LLC is that it enables the continuous deposition of nanoparticles with uniform sizes.<sup>7</sup> When metal nanoparticles were deposited in the 2D hexagonal LLC, in which the rod-like self-assemblies (rods) consisting of surfactants were closely packed, the nanoparticle growth was strictly hindered by the rods. Another advantage is the facile orientation control of the rods in a preferential way. Various techniques, including the electrically and magnetically induced orientations, the shear flow technique, and the physically confined self-assembly of surfactants, have been developed so far.<sup>8</sup>

LLCs are powerful templates for the facile simultaneous manipulation of both controls of nanoparticle size (i.e., at microscopic-scale length) and the orientation of mesostructures (i.e., at mesoscopic-scale length). In this communication, we demonstrate that a stacked donut-like mesospace (circularly packed 1D mesochannels) is successfully introduced into the Pt fibers by assembling nanoparticles with uniform particle sizes utilizing the guided deposition of Pt nanoparticles in the LLC with preferentially



**Figure 1.** (a and b) SEM and (c) TEM images of the Pt fibers prepared from the PAAMs with a pore diameter of 70–100 nm.

oriented rods. The used LLCs were prepared by the physically confined self-assembly of surfactants inside the channels of porous anodic alumina membranes (PAAMs).

In a typical experiment, the precursor solution (0.145 g of distilled water, 0.21 g of nonionic surfactant C<sub>16</sub>EO<sub>8</sub>, 0.145 g of H<sub>2</sub>PtCl<sub>6</sub>·6H<sub>2</sub>O, and 0.23 mL of ethanol) was drop-cast onto PAAM and introduced into the channels of PAAM with a capillary force. The LLCs were gradually formed within the channels through the evaporation of ethanol. The PAAMs were then placed in a closed vessel with a small amount of dimethylamine borane (DMAB) in a dish, and the vessel was kept at 25 °C for 15 h. During the process, the Pt species in the presence of LLCs were gradually reduced by vapor infiltration.<sup>7</sup> The color of the PAAM changed uniformly from orange to black (see Supporting Information Figures S1 and S2). After the Pt deposition, the PAAMs were washed by ethanol to remove surfactants and subsequently soaked in an aqueous solution of phosphoric acid to be dissolved.

The LLC mesophase within the PAAM before the Pt deposition was characterized by 2D XRD measurements (Figure S3). Out-of-plane and in-plane structural information can be simultaneously obtained from the measurement. The 2D XRD showed well-resolved diffraction spots from both out-of-plane and in-plane reflections, which are assignable to (10), (01), and (1–1). The 2D XRD geometry and the proposed LLC mesophase structure are shown in Figure S3-c. It is indicated that the hexagonally arranged rods orient with the (10) lattice plane parallel to the curved PAAM channel surface. The formation of the unique LLC mesophase is due to the confined growth of hexagonal rods within the cylindrical pore channels. When the same precursor solution was cast onto a flat substrate, a 2D hexagonal LLC mesophase with the long axes of the rods oriented parallel to the substrate surface was formed (Figure S3-b). Therefore, the effect of the confinement can be thought to be equivalent to rolling up a flat substrate surface into a scroll.

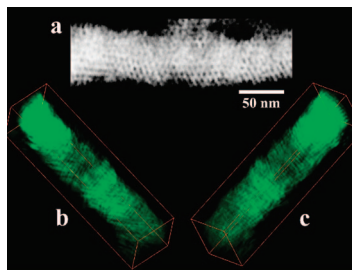
Figure 1a shows a low-magnified SEM image after the Pt deposition followed by removal of the PAAM and the surfactants.

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**Figure 2.** (a) BF-STEM image of the Pt fibers prepared from the PAAMs with a pore diameter of 50–60 nm; (b and c) 3D tomography.

PAAMs (Whatman Anodisc 25) with a pore diameter of 70–100 nm and a thickness of 60  $\mu\text{m}$  were used. The fibrous morphology was observable over the entire area. The diameter of the obtained fibers ranged from 70 to 100 nm, which coincided with the pore size of the channels of the original PAAM. The average length of the obtained rods was about 15  $\mu\text{m}$ . A simple infiltration of precursor solutions followed by a reduction process led to the successful formation of the Pt fibers (Figures S1 and S2).

The arrangements of the Pt nanoparticles in the fibers were further investigated by HR-SEM observation. On the top surface of the fibers, stripes ran perpendicular to the long axis of the fibers (Figure 1b). The 1D mesochannels were circularly packed around the curved PAAM channel surface. Consequently, the ordered mesospace was definitely templated from those of the original LLC. More importantly, the framework of the mesopores was well constructed by a connection of nanoparticles with a size of 3 nm (Figures 1c and S4-a). The distance between neighboring mesopores was measured to be about 6 nm, in agreement with the lattice constant by the 2D XRD measurement of the original LLCs, indicating the direct templating without contraction. The selected-area ED pattern from a 50 nm region shows ring-like patterns with intense spots assignable to *fcc* Pt (Figure S4-b). The presence of intense spots indicates that the lattice fringes coherently run across several nanoparticles to some extent. The formation of an ordered mesostructure is attributed to the excellent organization of the Pt nanoparticles.

In the present system, the LLC mesophases after solvent evaporation act as true templates, that is, the final materials are truly the reflection of the LLC. Therefore, the formation of well-organized LLC mesophases before the Pt deposition is very important for the creation of mesostructures with high quality, in contrast to previous systems for preparation of silica-based mesoporous rods from PAAMs through a sol–gel reaction.<sup>8</sup> In the previous system, the polymerization of silica species occurs simultaneously with the self-assembly of surfactants by solvent evaporation, in which various interactions between the silica species and surfactants are inevitable. Therefore, the ordering of the mesostructures and alignment directions of mesochannels are strongly dependent on the experimental conditions, such as the humidity and temperature.<sup>8</sup> In the present system, the original LLC mesophase structures directly determine those of the finally deposited mesoporous metals.<sup>6</sup>

The diameters of the fibers are simply controlled by changing the pore size of the PAAM channels used. Pt fibers with a diameter of 200 nm were prepared using PAAMs (Whatman, Anodisc 25, pore diameter about 200 nm, thickness 60  $\mu\text{m}$ ) following the same experimental procedure. However, the mesochannels were randomly oriented, although the Pt fibers were composed by the aggregation of Pt nanoparticles with a size of 3 nm.<sup>7</sup> In this case, the physically confined effect on the self-assembly of surfactants became weaker. In fact, the 2D XRD of the original LLCs showed

a ring pattern, indicating the random orientation of the rods within the PAAMs. To enhance the physically confined effect on self-assembly of surfactants, the pore size of the PAAM channels should be further reduced.

The Pt fibers were prepared with PAAMs (pore diameter 50–60 nm) under our optimized anodization condition (Figure S5). Three-dimensional (3D) tomography of the 50 nm fibers was employed by high-angle annular dark-field (HAADF) scanning transmission electron microscopy (STEM) to obtain valuable spatial information on the mesospace at mesoscopic-scale length (Figure S6). We took 140 images by tilting the sample over an angular range of  $\pm 70^\circ$  to construct the 3D tomography. It was clearly visualized that the 1D mesochannels were stacked like a donut within the Pt fiber (Figures 2 and S6). A highly magnified SEM image provides evidence of the Pt fibers by assembling the nanoparticles (Figure S5-c). Also, the Pt fibers with a further small diameter (30–50 nm) have also similar oriented mesostructure by assembling the nanoparticles (Figure S7).

To conclude, we proposed a generic platform for the preparation of new types of Pt fibers having stacked donut-like mesostructures with an excellent arrangement of uniformly sized nanoparticles. Here, we clearly demonstrate that the collaboration of both LLC templating by electrochemical processes and hard templating utilizing a confined effect can lead to the genesis of new nanostructured metals. Such a unique metal-based nanoarchitecture enhances the surface area and enables the high-mass transportation of guest species. Preferentially oriented mesochannels should contribute significantly to the fine control and transport of electronic carriers through metal fibers.

**Acknowledgment.** We sincerely thank Prof. Ohsuna (Waseda University) for valuable advice on 3D tomography. The present study is supported by a Grant-in-Aid for Scientific Research (No. 19850031) from JSPS and by the Global COE Program “Practical Chemical Wisdom” and the Encouraging Development Strategic Research Centers Program (Super COE) “Establishment of a Consolidated Research Institute for Advanced Science and Medical Care” from MEXT. This work is also supported by the A3 Foresight Program “Synthesis and Structural Resolution of Novel Mesoporous Materials” from JSPS.

**Supporting Information Available:** Experimental procedures and structural characterizations of the Pt fibers. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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JA800269C