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Mesoporous Metal

Mesoporous Platinum with Giant Mesocages Templated from Lyotropic Liquid Crystals Consisting of Diblock Copolymers**

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Templated synthesis of nanostructured metals with tunable composition, structure, and morphology allows us to finely control the metals' properties, which is a typical example of materials nanoarchitectonics that emphasizes the importance of novel size- and shape-dependent properties.[1] Traditionally, various nanostructured metals (for example, nanowire arrays,[2] bicontinuous nanowire networks,[3] nanoparticle arrays[4]) have been prepared by utilizing hard templates including mesoporous silica. Currently, lyotropic liquid crystals (LLCs), formed by assembling $C_n(EO)_m$-type surfactants (EO = ethylene oxide), have been utilized as soft templates to directly prepare mesoporous metals with hexagonally packed cylindrical mesospace.[5,6] In such LLCs, metal nanoparticles with almost uniform size are continuously deposited to form unique frameworks consisting of connected nanoparticles,[7] which contribute to the development of novel metal-based nanomaterials that are not achievable by hard templating.[8]

Surprisingly, all the mesoporous metals prepared by the soft templating technique have been limited to 2D hexagonal mesostructures with mesopores less than 4 nm in diameter. Both the limits of mesostructures and pore size seriously devalue the advantages of mesoporous metals, because a small mesospace suppresses effective movement of guest species within the mesopores. Giant mesopores can incorporate large biological molecules, and also volume changes caused by incorporation of guest species into host matrices are effectively relaxed.[9] Cage-type mesostructures should enhance the accessibility of various species. Therefore, to further explore the potential properties of nanoarchitectured metals, the versatile control of mesostructures and pore size is vital.

Herein, we report the preparation of a new type of mesoporous Pt particle with giant mesocages connected closely in three dimensions, templated from LLCs consisting of diblock copolymers. The size of the mesocages is the largest (about 15 nm) reported in mesoporous metals. The advantage of diblock copolymers is that their high molecular weight and composition are well designed.[10] By utilizing LLCs made of such designed block copolymers, new nanoarchitectured metals with various mesostructures and pore sizes should be realized.

First, a precursor solution was prepared by mixing distilled water (0.75 g), hydrogen hexachloroplatinate(IV) hexahydrate ($H_2PtCl_6{\cdot}6\,H_2O$; 0.75 g), poly(styrene-*b*-ethylene oxide) block copolymer (PS_{3800}-*b*-PEO_{4800}, polydispersity index: 1.05; 0.25 g), and tetrahydrofuran (THF; 12.5 g) as volatile solvent (Figure 1 a). Then, the precursor solution was drop-coated onto an indium tin oxide (ITO; surface resistivity $10\,\Omega\,cm^{-2}$) substrate. After the preferential evaporation of THF, a yellow LLC film was formed over the entire area of the substrate (Figure 1 b). This LLC mesostructure before Pt deposition was proved by XRD measurement in the low-angle range (see the Supporting Information, Figure S2). An intense single peak ($d \approx 16$ nm) was observable, which indicates that at least a periodic mesostructure was formed, although the dimensionality was not identified. For the

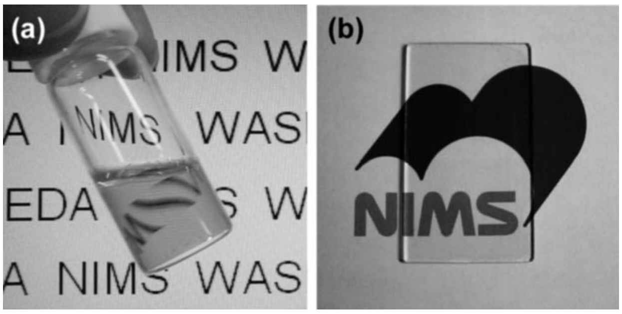

Figure 1. a) Precursor solution for the formation of the LLC film. b) LLC film prepared through solvent evaporation. See the Supporting Information (Figure S1) for the colored presentation.

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observation of the liquid crystals between crossed polarizers under an optical microscope, the film formed on the substrate was scratched, aggregated, and placed on a glass substrate. The sample showed a clear birefringence, which indicates liquid crystallinity although specific textures were not observed.

Our process through solvent evaporation allows the direct formation of LLCs from a precursor solution without general heating–aging processes.[5a,b] Even after a few hours, the XRD pattern of the LLC film did not change, and showed good stability. Any phase transformations or phase separation were not observed by optical microscopy. The water molecules are hard to evaporate once the LLC mesophase is formed after the preferential evaporation of THF. In the hydrophilic PEO domains of the LLC mesophase under low pH conditions, $H_2PtCl_6{\cdot}6\,H_2O$ salts are dissolved as $[PtCl_6]^{2-}$ ions with water.[11]

For Pt deposition, a Pt plate as a counter electrode was placed on the LLC-modified ITO substrate to sandwich the LLCs. An Ag/AgCl electrode was used as a reference electrode and connected to the LLCs by using a salt bridge. Electrochemical deposition was carried out at room temperature at a constant potential (−0.10 V vs. Ag/AgCl) by using a potentiostat. The deposited Pt was washed with THF, ethanol, and water to extract the undeposited Pt species and the diblock copolymer. Energy-dispersive X-ray (EDX) analysis of the extracted sample showed the presence of less than 2 wt % of carbon and the absence of chlorides, which indicates that almost all the undeposited Pt species and the diblock copolymer were removed by careful washing.

Figure 2 shows high-resolution scanning electron microscopy (HRSEM) images of the extracted samples. Spherical particles were observed over the entire area. The particle size ranged from 100 to 1000 nm (Figure 2a). The mesostructure was further investigated by highly magnified SEM and transmission electron microscopy (TEM) observations. Open, large mesopores are present on the top surface of each particle (Figure 2b and c); the framework is constructed by connected Pt nanoparticles (Figure 2d). The TEM image also shows the formation of spongelike mesoporous structures (see the Supporting Information, Figure S3). The selected-area electron diffraction from a 50-nm region shows ringlike patterns with intense spots assignable to face-centered cubic Pt. The presence of the intense spots indicates that the lattice fringes run coherently across several nanoparticles to some extent. Therefore, one nanoparticle of diameter 3–4 nm can be regarded as being the "single-crystalline state".

Bright-field scanning transmission electron microscopy (BF-STEM) was carried out by tilting the sample over an angular range of ±70° for 3D tomographic imaging (Figure 3). In the 3D imaging, the inside as well as the outside mesostructure of the particles can be successfully visualized (Movie S1 in the Supporting Information). Furthermore, slice images at any cross section of the sample can be obtained from the constructed 3D tomographic images. Here, we show the slice images as if the particles were virtually cut from top to bottom (Movie S2 in the Supporting Information). It is clearly visualized that large, spherical mesopores (mesocages) with uniform size (about 15 nm) were indeed formed and closely connected at the inner part of the particle (Movie S3 in the Supporting Information). Figure 3c shows the slice image at the central height of Figure 3b. It is shown that the large mesopores are interconnected by small windows. The distance between neighboring mesocages was

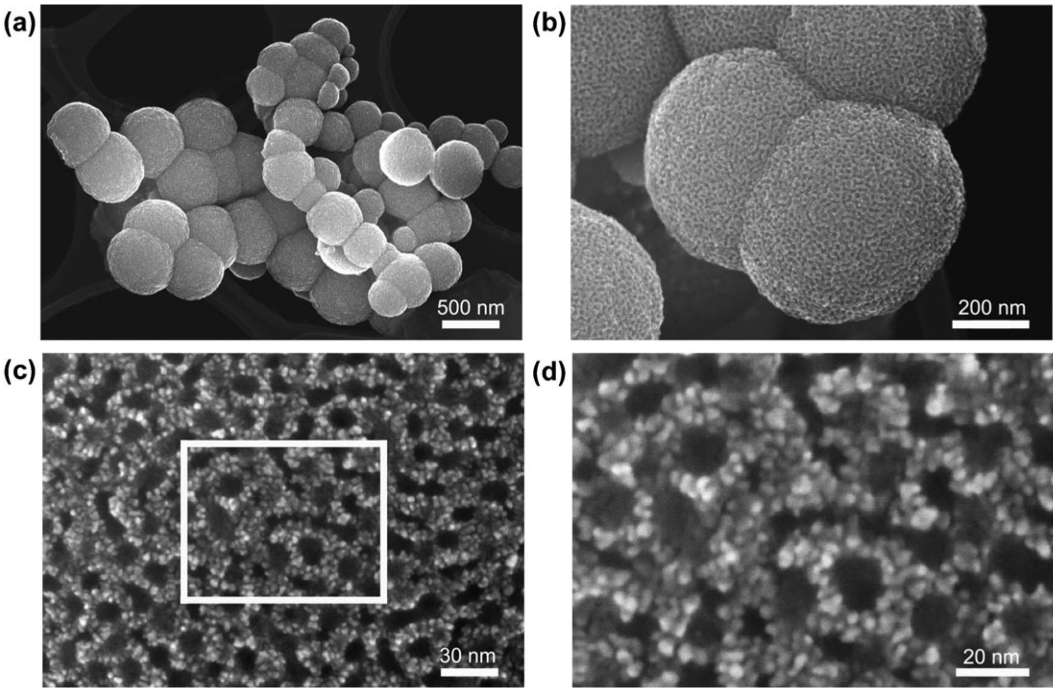

Figure 2. a, b) HRSEM images of mesoporous Pt particles with giant mesocages. c, d) Highly magnified images of the surface of the particle, with (d) showing the square area in (c). The images were obtained with a Hitachi S-5500 microscope operating at 20 kV. Samples were observed directly without any coatings.

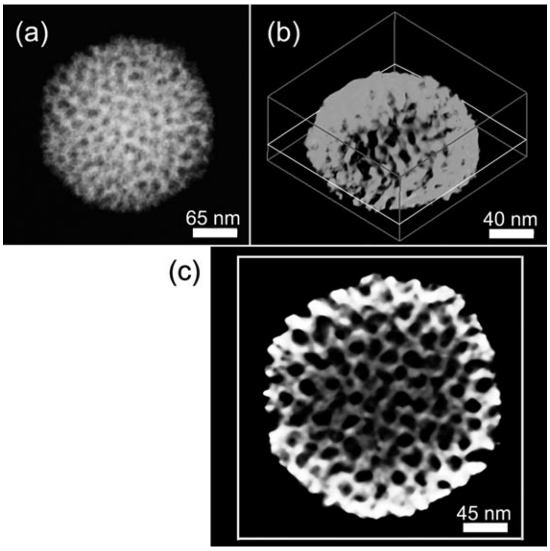

Figure 3. a) BF-STEM image and b) 3D tomographic imaging of the mesoporous Pt. Half of the spherical particle is visualized by 3D tomographic imaging. c) Slice image at the cross section in (b). See the Supporting Information (Figure S4) for the colored presentation.

measured to be about 15 nm, which is basically in agreement with that of the original LLCs measured by XRD.

According to the above TEM and SEM observations, the distance between the mesocages is slightly different depending on location. The framework is constructed by connected Pt nanoparticles (Figure 2c). Therefore, the surface of the framework shows a bumpy morphology and the thickness of the framework is not uniform, which results in the small variation of the distance between neighboring mesocages.

The cyclic voltammogram of the mesoporous Pt in aqueous H_2SO_4 solution (1.0 M) revealed a typical feature that can identify the clean Pt surface (see the Supporting Information, Figure S5). The three anodic peaks at potentials of -0.09 to 0.06 V (vs. Ag/AgCl) were consistent with those of the polycrystalline nature of Pt. On the basis of the assumption that a monolayer of hydrogen corresponds to an adsorption charge of $210\,\mu C\,cm^{-2}$, the electrochemically active surface area of the Pt can be estimated to be about $74\,m^2\,g^{-1}$ from the hydrogen desorption charge. This value is close to that of about $93\,m^2\,g^{-1}$ calculated roughly for the unconnected, well-dispersed nanoparticles of diameter 3 nm, thus indicating that the inner large mesopores are truly electrochemically active.

In conclusion, we have demonstrated the evolution of novel mesoporous Pt with closely connected giant mesocages templated from LLCs consisting of amphiphilic diblock copolymers by an electrochemical process. Our soft templating method can be extended to other metals and various mesostructures that are not accessible by hard templating methods.[2–4] Furthermore, by using appropriately architectured block copolymers, the mesopores can be controlled over a wide range of pore sizes. The presence of such accessible giant mesopores is important from the viewpoints of enhancement of accessibility of guest species and electrochemical reactions of large molecules.

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