

Template Synthesis of Asymmetrically Mesostructured Platinum Networks

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Recently there has been a growing attention to mesoporous molecular sieves, due to the possibilities as a template for the synthesis of nanostructured new materials. For example, a new type of ordered mesoporous carbon molecular sieves designated CMK-1 was obtained by using MCM-48 silica as a template and sucrose as a carbon source.^{1,2} Platinum nanowires were synthesized using MCM-41 or SBA-15 silica as templates.^{3–5} The investigation with high-resolution transmission electron microscopy (TEM) and the energy-dispersive X-ray (EDX) spectroscopy revealed that the Pt nanowires obtained after the removal of the template were composed of Pt atoms with the face-centered cubic structure.⁴

Here we report that the template synthesis technique can be extended to the composition of Pt nanowires 3 nm in diameter in a form of three-dimensionally ordered asymmetric networks, using MCM-48 silica as the template. The asymmetrically nanostructured Pt material has been obtained by templating the Pt metal with one of the enantiomeric pair of the chiral channel systems, which are three-dimensionally interwoven, in the structure of MCM-48.^{6,7} The Pt networks, obtained after complete removal of the template with HF, exhibited the characteristic X-ray powder diffraction (XRD) pattern and TEM images, indicating the highly ordered nanostructure.

High-quality MCM-48 silica was obtained via a synthesis method using cationic–nonionic surfactants mixture.^{8,9} The silica source was a sodium silicate solution with Na/Si = 0.5 (2.3 wt % Na₂O, 9.0 wt % SiO₂, 88.7 wt % H₂O), which was prepared with the colloidal silica Ludox (40 wt % SiO₂, Aldrich) and NaOH.¹⁰ Octadecyltrimethylammonium chloride (C₁₈H₃₇N(CH₃)₃Cl, 97%, TCI) and Triton X-100 (C₈H₁₇C₆H₄O(C₂H₄O)₁₀H, Aldrich) were dissolved in doubly distilled water. The surfactant solution and the silica source were rapidly mixed using a high-speed blender for 5 min at room temperature. The mixture was transferred to a polypropylene bottle and continuously stirred for 1 h with a magnetic stirrer. The molar composition of the mixture was 5.0 SiO₂:1.25 Na₂O:0.92 C₁₈H₃₇N(CH₃)₃Cl:0.08 Triton X-100:

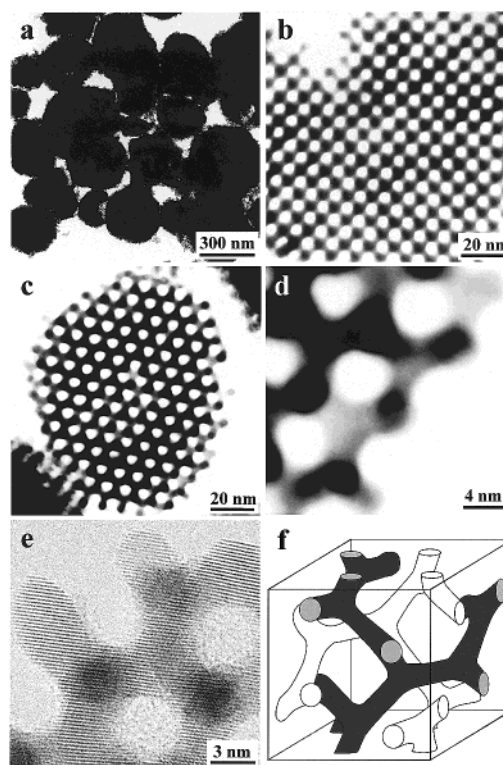


Figure 1. (a–e) TEM images of nanostructured Pt networks obtained using MCM-48 silica as a template. (f) A structure model proposed by Luzzati and Speg¹² for cubic *Ia3d* lipid mesophase. Note that the TEM images in (d) and (e), taken at an extremely thin edge of Pt network, shows a remarkable similarity with the dark-shaded chiral network in the structure model shown in (f).

400 H₂O. The mixture was heated for 40 h in an oven at 373 K and subsequently cooled to room temperature. Acetic acid equivalent to 57% of the total Na content was added to the mixture, drop by drop, with vigorous magnetic stirring. After subsequent heating for 48 h at 373 K, product was filtered, washed with distilled water, and dried at 393 K. The product was calcined in air at 823 K after extraction of the surfactant with an ethanol–HCl mixture.¹¹

The template synthesis of the nanostructured Pt was carried out as follows: aqueous solution of tetraammineplatinum(II) nitrate (Pt(NH₃)₄(NO₃)₂, Aldrich) was impregnated into the calcined MCM-48 silica powder, so that the Pt content corresponded to 30–60 wt % of the SiO₂ weight. If necessary, the impregnation was repeated after evaporation of the solvent. After being completely dried at 373 K, the MCM-48 sample impregnated with Pt(NH₃)₄(NO₃)₂ was mounted inside a Pyrex U-tube reactor equipped with two fritted disks. The Pt compound was reduced to Pt(0) with H₂ flow through the reactor while the temperature was changed from room temperature to 383 K over 1 h, maintained at 383 K for 1 h, increased from 383 to 573 K over 2 h, and finally maintained at 573 K for 2 h. The resultant Pt/MCM-48 composite sample was exposed to air after the reactor was cooled to room temperature. The Pt/MCM-48 sample was washed with 10 wt % hydrofluoric acid until the EDX analysis indicated trace amounts of silica. The black-colored powder Pt sample thus obtained was filtered, washed with distilled water, and dried in a vacuum oven at room temperature. Centrifugation was preferred to the filtration in the case of small amounts of sample.

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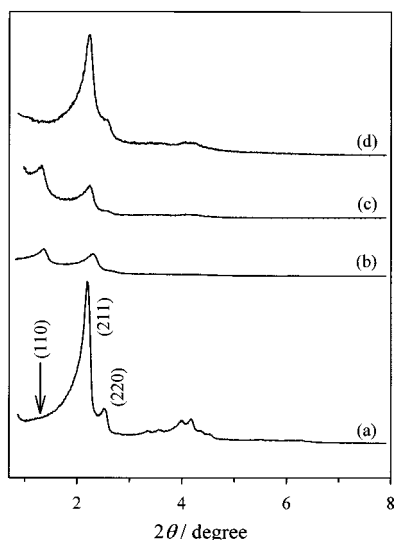


Figure 2. XRD patterns of (a) MCM-48 silica, (b) Pt/MCM-48 composite, (c) template-free Pt obtained after removing silica from Pt/MCM-48 with HF, and (d) MCM-48 silica recovered from Pt/MCM-48 after removing Pt with aqua regia.

The template-free Pt sample was characterized by TEM. The TEM images were taken with a Philips CM20 transmission electron microscope operated at 100 kV and JEOL JEM-4000EX operated at 400 kV. Samples for the TEM measurement were suspended in ethanol and supported on a carbon-coated copper grid. Figure 1a–e shows representative TEM images for the template-free Pt material. The TEM investigation revealed that the Pt material consisted mainly of particles 50–400 nm in diameter, which were composed of three-dimensional regular networks of Pt wire 3 nm in diameter. The Pt material contained very little impurities other than the ordered mesoporous networks. Many of the Pt networks exhibited edges and corners characteristic of typical crystal morphologies. The TEM images shown in Figure 1d and e were taken from an extremely thin edge, so that images of single nanowires could be obtained. The images show a remarkable resemblance to the dark-shaded portion in Figure 1f, which corresponds to a helical micelle in the structure model proposed for the cubic $Ia3d$ lipid mesophase.¹² This is the first direct observation of TEM image corresponding to the micelle network system of the cubic $Ia3d$ mesophase since the structure model was proposed in 1967.¹²

The formation of the Pt networks during the template synthesis was investigated with XRD. Figure 2 shows the XRD patterns obtained with a Rigaku D/MAX-RC (3 kW, Cu K α X-ray source) diffractometer at room temperature. As the XRD pattern in Figure 2a shows, the silica template prior to the incorporation of Pt gave an XRD pattern of highly ordered MCM-48 sample. The XRD pattern in Figure 2b shows that the Pt incorporation into the MCM-48 silica brought about two distinct changes in the XRD pattern. First, all of the diffraction peaks in the range of $2^\circ < 2\theta < 6^\circ$ decreased in intensity. Second, a new peak similar to the (110) diffraction of the MCM-48 silica phase appeared at $2\theta = 1.30^\circ$. However, this peak cannot be due to the (110) diffraction since the diffraction is symmetry-forbidden for the cubic $Ia3d$ structure. It is noteworthy that this diffraction was retained even

after the complete removal of the silica template using HF, as shown in Figure 2c. The XRD pattern in Figure 2d was obtained to investigate if the diffraction changes were related to changes in the silica template. The XRD pattern shows that the structure of the silica template was retained after the removal of the Pt network using aqua regia, despite the line broadening. On the basis of these results and the aforementioned TEM data, the difference between Figure 2a and b can be attributed to the formation of the Pt networks that occupy exclusively one of the two chiral channel systems in the MCM-48 structure. It is therefore possible to infer that the Pt networks have a left- or right-handed chiral structure of the cubic space group $I4_132$ or $I4_332$, depending on the individual particles. Unfortunately, these two space groups are not distinguished by normal XRD pattern.

In addition to the XRD lines observed in the small angle region, the Pt nanowire networks exhibited two broad lines at $2\theta = 39.83^\circ$ and 46.32° . These diffractions corresponded to the (111) and (200) diffractions of the face-centered cubic structure with the unit cell dimension of 0.3920 nm, which was very close to 0.3923 nm of the bulk metal. The Pt nanowires were completely crystalline as indicated by the lattice fringe in Figure 1e. X-ray photoelectron spectroscopy (XPS) was used to confirm the oxidation state of the Pt atoms consisting of the nanowires. The XPS spectra of the template-free Pt materials were taken with powder samples after evacuation at room temperature, using an ESCA Lab-200R instrument with an Mg K α X-ray source. The XPS spectra showed a Pt $4f_{7/2}$ peak corresponding to the binding energy of 71.2 eV, which was very close to 71.0 eV for the bulk Pt metal.

In obtaining the Pt network, it turned out that the most important experimental factor was the control of the reaction temperature during the conversion of $\text{Pt}(\text{NH}_3)_4(\text{NO}_3)_2$ to Pt. The present asymmetric networks were obtained when the reaction temperature was slowly increased in the aforementioned mode. On the other hand, separate Pt particles 3–5 nm diameters were obtained inside the MCM-48 when the temperature was rapidly increased. Measurement of H_2 uptake under the reaction conditions showed that the major reaction of $\text{Pt}(\text{NH}_3)_4(\text{NO}_3)_2$ occurred around 383 K. At this temperature, the MCM-48 frameworks contain moisture so that the impregnated $\text{Pt}(\text{NH}_3)_4(\text{NO}_3)_2$ is mobile inside the silica channels. On this ground, we believe that the key to the success of the template synthesis is in the reaction control so that the conversion of the Pt precursor to the metal can occur catalytically at the growing tips of the Pt agglomerates. It is reasonable that the reaction can be initiated at such catalytic active sites as the solid-state defects located on the pore walls of MCM-48 silica. Small Pt agglomerate formed at the active site should then catalyze the conversion of $\text{Pt}(\text{NH}_3)_4(\text{NO}_3)_2$, as Pt is a well-known catalyst for hydrogenation. The growth of the Pt agglomerate under this circumstance is believed to lead to the formation of the nanostructured network inside the mesoporous silica structure, similar to growth of a porous crystal. We also believe that the present synthesis methodology using MCM-48 template may open a possibility for synthesizing various nanoscale materials with chirality. Further, if it is possible to control the nucleation of Pt so that agglomeration occurs within the same kind of the chiral channels, the synthesis will be chiral-selective.

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