

# Synthesis of platinum networks with nanoscopic periodicity using mesoporous silica as template

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Received 31st August 2000, Accepted 5th December 2000  
 First published as an Advance Article on the web 2nd January 2001

**Nanoporous platinum sponges, which exhibit characteristic X-ray diffraction patterns due to structural order on the mesoscale, have been obtained after removing the silica template with HF following synthesis within the pores of MCM-48 and SBA-15 with  $\text{Pt}(\text{NH}_3)_4(\text{NO}_3)_2$ .**

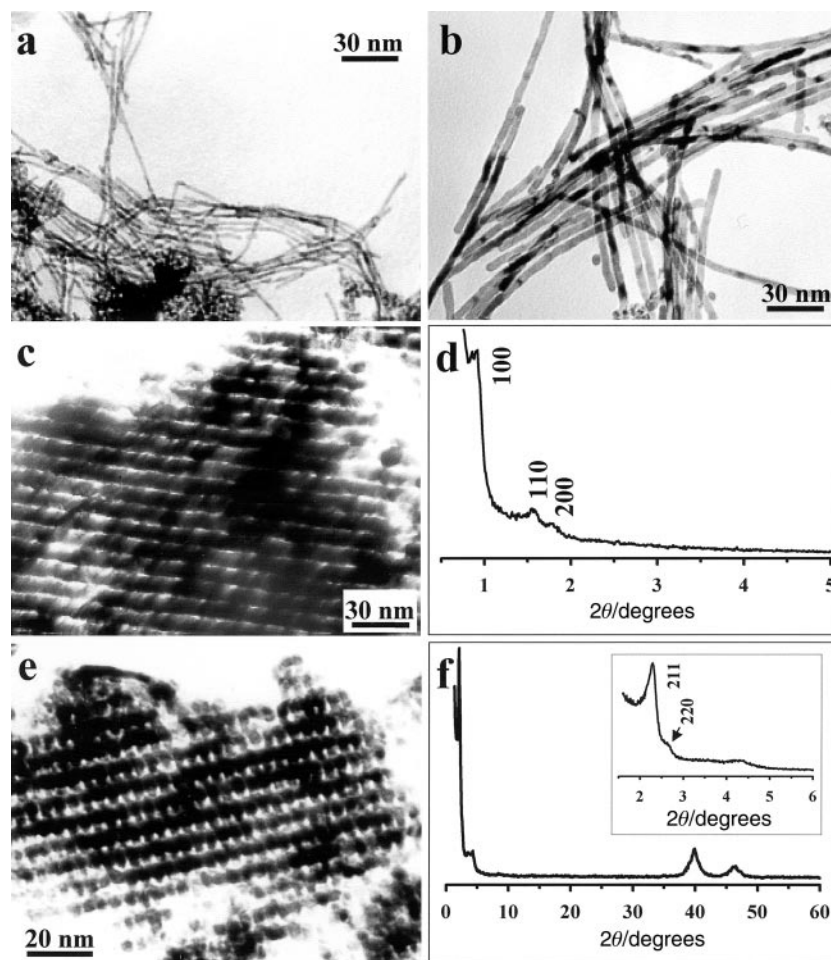
Metal nanowires and nanoparticles are of great importance in nanotechnology due to their possible uses as components of advanced electronic devices.<sup>1,2</sup> For such nanotechnologies, it is necessary to develop synthesis routes suitable for mass production of the nanomaterials with controlled sizes and dimensions. A synthesis route to nanoscale metals is the formation of a cooperative assembly between metal precursors and surfactant micelles. Recently, Attard *et al.* showed that a hexagonally ordered nanoporous (or mesoporous) Pt sponge could be obtained by the extraction of the surfactant after converting metal precursors to the metal using chemical or electrochemical reduction techniques.<sup>3,4</sup> This assembly route is suitable for the synthesis of metal sponges with mainly cylindrical pores, the pore diameter being controllable by the size of the surfactant.

Recently, we reported the synthesis of one-dimensional Pt nanowires using MCM-41 silica and SBA-15 silica as templates.<sup>5,6</sup> Later Han *et al.* carried out similar work with SBA-15 by adopting the same synthesis procedure.<sup>7</sup> The nanowires were synthesized by the reduction of  $\text{Pt}(\text{NH}_3)_4(\text{NO}_3)_2$  to the Pt(0) state, inside the mesoporous channels of the silica materials. The silica templates were subsequently removed with hydrofluoric acid. The structures of the nanowires were retained after the HF treatment. Here, we show that the template synthesis technique can be extended to the production of Pt nanowires in the form of three-dimensionally ordered networks, using MCM-48 or SBA-15 mesoporous silica as the template. The silica-free Pt networks, obtained after the removal of the template with HF, exhibit X-ray powder diffraction (XRD) patterns similar to those of the mesoporous silicas used as templates. In comparison to the previous synthesis works on Pt using mesoporous silica templates, the present work reports the characteristic XRD patterns of the highly ordered Pt nanostructures for the first time. Therefore, it is shown here that the synthesis using the mesoporous silica templates is a versatile route to three-dimensional Pt nanomaterials with excellent structural order. The template synthesis produces Pt metals in the form of single nanowires or ordered wire networks, while synthesis using surfactants is suitable for the formation of porous metals with mainly one-dimensional cylindrical channels.

The synthesis of the Pt nanomaterials was performed with three types of mesoporous silica template: MCM-41 (hexagonal packing of one-dimensional silica nanotubes),<sup>8</sup> MCM-48

(cubic *Ia3d* packing of nanotube networks)<sup>9</sup> and SBA-15 (hexagonal packing of nanotubes, interconnected through small pores).<sup>10</sup> These silica materials were obtained following synthesis procedures reported in the literature.<sup>10–12</sup> After extraction of the surfactant with an ethanol–HCl mixture and subsequent calcination in air at 823 K, the silica templates were impregnated with aqueous tetraammineplatinum(II) nitrate [ $\text{Pt}(\text{NH}_3)_4(\text{NO}_3)_2$ ]. The Pt precursor was reacted with  $\text{H}_2$  with heating, in order to convert it to the nanomaterials. The impregnation and the reaction procedures were the same as in our previous work on imaging the channels of mesoporous silica with Pt,<sup>13,14</sup> except that the loading of the Pt precursor was increased to 70 wt% Pt by repeating the impregnation treatment, and the reduction of Pt was carried out in a single step. That is, the mesoporous samples impregnated with 1.40 g of  $\text{Pt}(\text{NH}_3)_4(\text{NO}_3)_2$  per g  $\text{SiO}_2$  were put in contact with a  $\text{H}_2$  flow while the temperature was gradually increased from room temperature to 573 K over 4 h and maintained at 573 K for 2 h, in a U-tube reactor equipped with two fritted disks. The resulting Pt/silica composites were evacuated for 30 min at 573 K, in order to remove the chemisorbed hydrogen. The samples were put in contact with air after being cooled to room temperature. The samples were then washed with 10% hydrofluoric acid until energy dispersive X-ray analysis indicated only trace amounts of silica. Black powder Pt samples thus obtained were filtered, washed with distilled water and dried in a vacuum oven at room temperature.

Fig. 1 shows the representative transmission electron microscopy (TEM) images of the template-free Pt samples synthesized using the mesoporous silica molecular sieves as templates. As the TEM images in Fig. 1(a) and (b) show, one-dimensional nanowires with uniform cross-sectional diameters were obtained when MCM-41 was used as the template. The Pt nanowires ranged from several tens to several hundred nanometers in length. The diameters were almost the same as those of the mesoporous channels of the MCM-41 templates, with the variation of typically one Pt atomic layer.<sup>5</sup> The wires were randomly agglomerated in many parts of the TEM images, suggesting that such random agglomeration should have occurred after the template removal. The XRD patterns of such disordered nanowires were featureless in the range  $1^\circ < 2\theta < 10^\circ$ . In contrast, the Pt nanowires synthesized with SBA-15 were interconnected with regular spacing as shown in Fig. 1(c). The XRD pattern in Fig. 1(d) exhibits three Bragg lines in the range  $1^\circ < 2\theta < 5^\circ$ , due to the hexagonally ordered wire arrangement. Another type of ordered nanowire network was obtained when MCM-48 was used as the template. As the TEM image in Fig. 1(e) and the XRD pattern in Fig. 1(f) show, the nanowire networks were composed of a structure with the cubic space group *Ia3d*. The XRD lines in the range  $2^\circ < 2\theta < 6^\circ$  were characteristic of the



**Fig. 1** Transmission electron micrographs of the “template-free” nanostructured platinum systems: (a) nanowire fabricated with hexagonal mesoporous silica C<sub>12</sub>-MCM-41, (b) nanowire from C<sub>22</sub>-MCM-41, (c) nanowire network from SBA-15, (d) XRD pattern of the Pt network from SBA-15, (e) nanowire network from C<sub>16</sub>-MCM-48 and (f) XRD pattern of the Pt network from C<sub>16</sub>-MCM-48. The subscript numbers preceding MCM-41 and MCM-48 denote the carbon number in the surfactant tail used for the synthesis of the mesoporous silica materials. The TEM images were obtained with a Philips CM20 transmission electron microscope operating at 100 kV. The platinum samples were suspended in ethanol and supported on a carbon-film coated copper grid for the TEM image observation.

ordered wire arrangement, while the broad diffraction lines at  $2\theta = 39.83^\circ$  and  $46.32^\circ$  corresponded to the (111) and (200) diffractions of the Pt atoms in the face-centered cubic packing. Namely, the nanowires were crystalline with a unit cell dimension of 0.3920 nm, which is very similar to the value of 0.3923 nm of bulk Pt metal.

X-Ray photoelectron spectroscopy (XPS) was used in order to confirm the oxidation state of the Pt atoms within 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 $\alpha$  X-ray source. The XPS spectra showed a Pt 4f<sub>7/2</sub> peak corresponding to a binding energy of 71.2 eV, which was very close to the value of 71.0 eV for bulk Pt metal. This XPS datum indicates that the Pt nanowires were of the same zero oxidation state as the bulk Pt metal, in agreement with the above XRD result.

The Pt nanowires are suitable for the investigation of fundamental physicochemical properties of nanostructured materials. For example, we can demonstrate that the Pt nanowires begin to agglomerate at much lower temperatures than the melting point of the bulk metal because of the nanoscale dimension.<sup>5,15</sup> In fact, the Pt nanowires shown in Fig. 1(a) began to agglomerate upon heating in helium at 573 K. Further, considering the variety of the mesoporous molecular sieves discovered recently, the present method of synthesis might be suitable for the synthesis of various types of nanostructured Pt metals. The template synthesis may also be extended to other metals and their mixtures that are suitable as components for the

construction of future quantum-electronic devices such as connection wires, switches and metal–dielectric capacitors.

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