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Electron Microscopy Study of Novel Pt Nanowires Synthesized in the Spaces of Silica Mesoporous Materials

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Abstract: Structures of Pt-nanowires, synthesized in channels of silica mesoporous materials MCM-41, SBA-15 and MCM-48, were investigated by transmission electron microscopy. One dimensional (1D) Pt-nanowires were formed inside the channels of the MCM-41, and were single crystals with a length of several tens to several hundreds nanometers and a diameter of ca. 3 nm Pt-nanowires synthesized in SBA-15 formed a new 3D-network following 3D-pore geometry of SBA-15; that is, the main 1D-channels are interconnected to each other through randomly distributed tunnels. These Pt-nanowires showed a well single crystalline. MCM-48 has two non-intersecting chiral channels, and Pt-networks were mostly formed in one of the two channels. Therefore the networks were also chiral; however, the chirality of Pt-networks remained to be determined. It was shown that all Pt-nanowires were formed following the channel geometries of silica mesoporous materials used.

Key words: Pt nanowires, mesoporous materials, HREM, 1D-nanowires, 3D-nanowires, MCM-41, MCM-48, SBA-15

Mesoporous materials have large cavities or channels (hereafter referred to as spaces) ranging from 20 to 500 Å in size. They have attracted attention as containers to synthesize new materials that are too big to be incorporated into the spaces of zeolites. The sizes of the spaces can be controlled uniformly over the wide range by selecting the proper size of amphiphilic molecules for synthesis of mesoporous materials. Recently we have developed a method to determine three-dimensional (3D) structures of silica mesoporous materials through Fourier analysis of high resolution transmission electron microscope (HRTEM) images. The 3D structures of MCM-48, SBA-1, -6, and -16 have been solved by this method (Carlsson et al., 1999; Sakamoto et al., 2000). It was accepted that MCM-41, FSM-16, and SBA-15 have one-dimensional channels arranged in two-dimensional hexagonal lattice with p6mm symmetry. However, recently we have observed in SBA-15 randomly distributed tunnels, interconnecting the 1D channels (Kruk et al., 2000; Z. Liu, O. Terasaki, T. Ohsuna, K. Hiraga, H. J. Shin and R. Ryoo, in press). Once we know the mesopore structures, we will be able to tailor new materials in their spaces and to optimize their functions. Such efforts are successful; for example, Ryoo and coworkers have developed a method to infiltrate the pores of SBA-15, MCM-41, and MCM-48 with C or Pt to synthesize novel nanowires as the negative replicas of the mesoporous systems (Ko and Ryoo, 1996; Liu et al., 2000; Shin et al., 2001a, 2001b). Theoretical discussions based on the fundamental quantum me-

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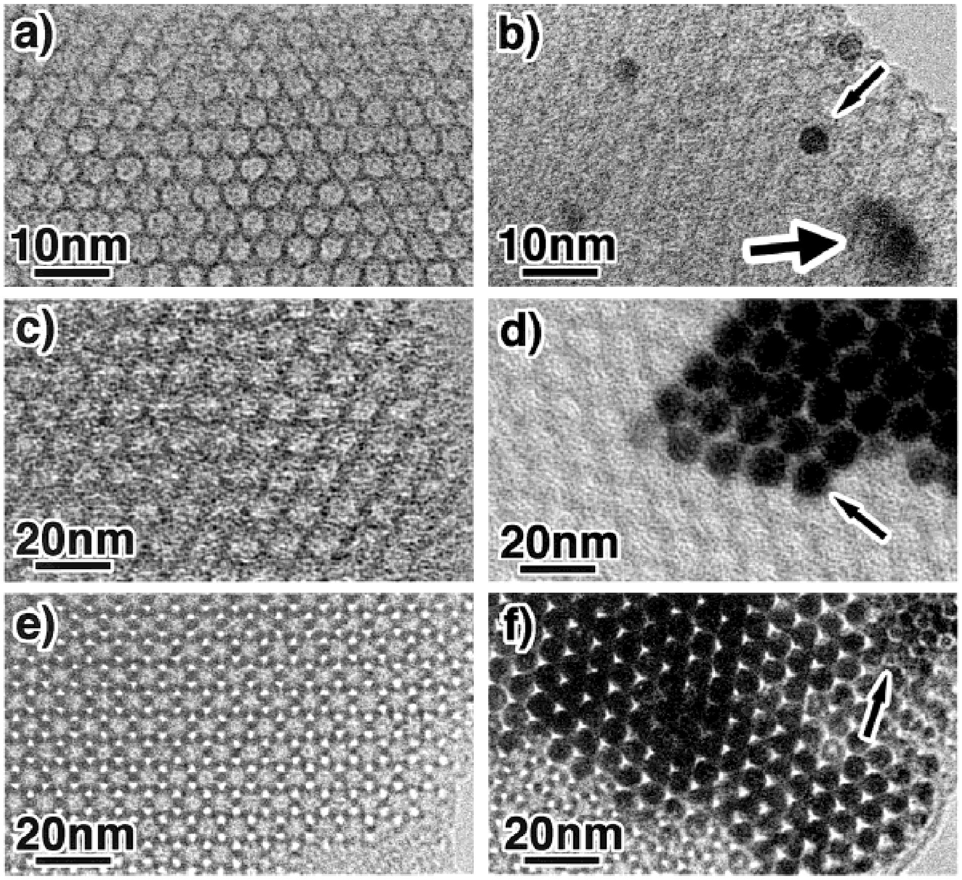

Figure 1. TEM images taken with the incident beam parallel to the channels of calcined MCM-41 (**a**), SBA-15 (**c**), [111] direction of MCM-48 (**e**), and Pt nanowires synthesized in the spaces of MCM-41 (**b**), SBA-15 (**d**), and MCM-48 (**f**). JEM-4000EX, 400 kV.

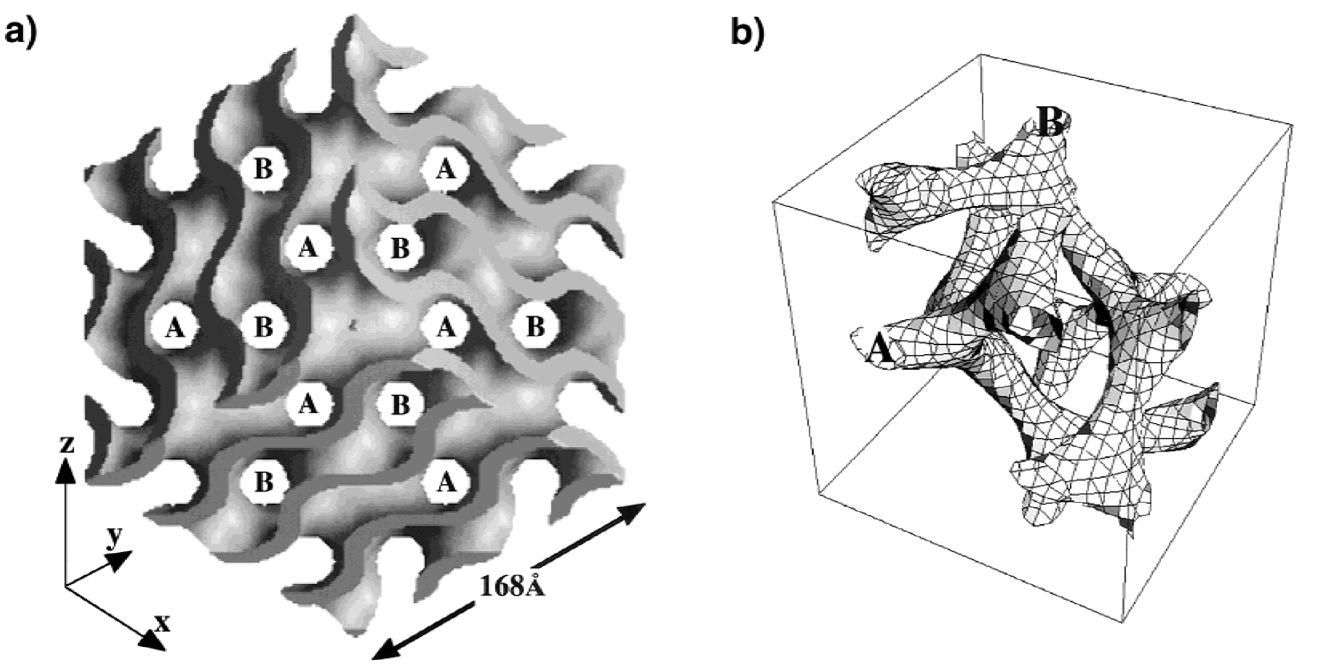

Figure 2. Structure solution of MCM-48 from HRTEM images viewed along [111] (**a**), and channels A and B are separated by the silica wall (**b**).

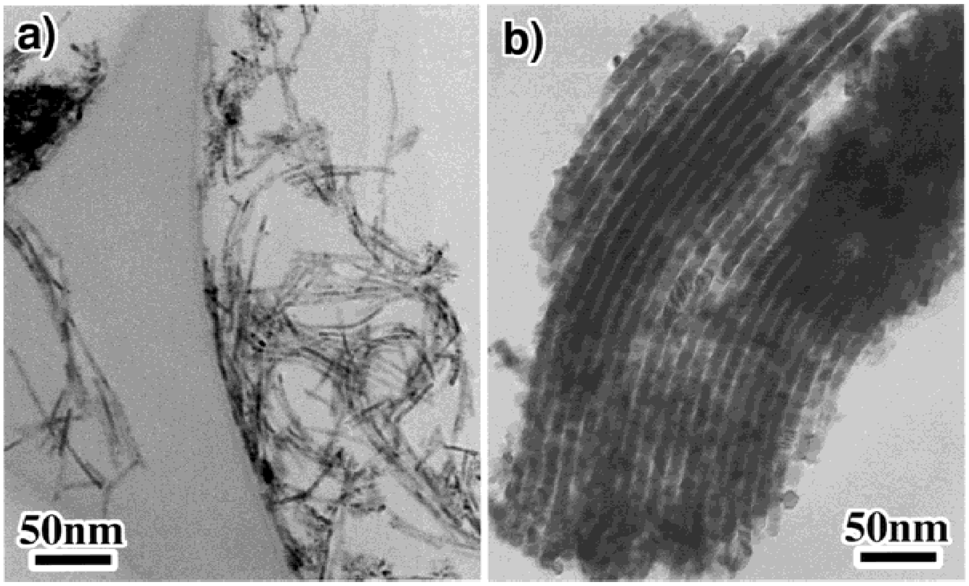

Figure 3. TEM images of Pt nanowires extracted from the channels of MCM-41 (**a**) and SBA-15 (**b**). JEM-4000EX, 400 kV.

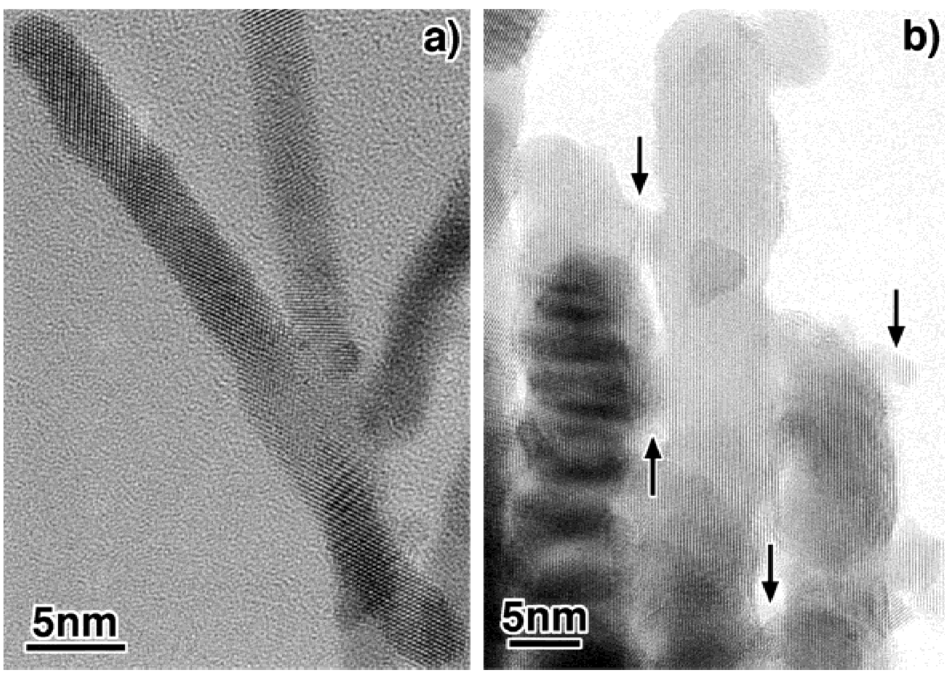

Figure 4. HREM images of the Pt nanowires extracted from the channels of MCM-41 (**a**) and SBA-15 (**b**). JEM-4000EX, 400 kV.

chanics have been reported indicating that the motion of electrons confined in curved geometry is different to that in 3D bulk crystals (Jensen and Koppe, 1971; da Costa, 1981; Ikegami and Nagaoka, 1991). It is pure theoretical discussion. However, we have now real systems where the electrons are confined in well-defined geometry and diameters of rods are much smaller than the characteristic length for physical properties of the materials such as a mean-free-path for electron conductivity.

In this report, we show the structural study of the Pt nanowires synthesized in the spaces of MCM-41, SBA-15, and MCM-48 by TEM.

Pt nanowires were produced by hydrogen (H_2) gas reduction of Pt compound at a moderate temperature such as 573 K after the mesoporous materials were impregnated with aqueous tetraammineplatinum(II)nitrate $[Pt(NH_3)_4(NO_3)_2]$. The silica mesoporous materials were dissolved by HF solution, and Pt nanowires were filtered and washed with distilled water. An ethanol dispersion of the samples was dropped onto a microgrid and the solvent was dried at room temperature.

Figures 1a, 1c, and 1e are TEM images taken from calcined mesoporous materials of MCM-41, SBA-15, and MCM-48 and Figures 1b, 1d, and 1f are those from Pt nanowires synthesized in their spaces. The incident beam is parallel to the channels, [001], for MCM-41 and SBA-15, and to the [111] direction for MCM-48. It can be seen from Figures 1a and 1c that the channels of MCM-41 and "average structure" SBA-15 appear as a well-ordered hexagonal structure with p6mm symmetry, and the channel diameters of MCM-41 and SBA-15 are about 3 nm and 8 nm, respectively. The more detailed mesostructure of SBA-15 will be shown later. The black dots shown by the arrows in Figures 1b and 1d are the projections of Pt nanowires. In Figure 1b, there are two different types of dark contrast from the Pt particles. The smaller and darker ones, indicated by a small arrow, correspond to Pt nanowires located inside the honeycomb channels. The other, as shown by a bigger arrow, is smeared contrast over the channels, which corresponds to a Pt particle on the external surface. Figure 2a shows structure solution of MCM-48 along the [111] direction. It is clear that the silica wall of MCM-48 follows the Gyroid minimal surface, which has $Ia\bar{3}d$ space group symmetry. The silica wall separates two nonintersecting channels, A and B, part of which are imaged as white dots in Figure 1e. Two nonintersecting 3D channels, A and B, are schematically shown in Figure 2b. The characteristic feature of the channel is a three-connected network, which may be an interesting system for detecting interference effects of electrons under high magnetic fields. From Figure 1f, it can be seen that the Pt clusters almost exist in one set of the nonintersecting compartments, although in some areas they exist in both compartments as shown by the arrow. It can be seen that the Pt nanowires reside inside the channels of MCM-41, SBA-15, and MCM-48 without destroying the channel geometries.

After the complete dissolution of the silica walls by HF solution, Pt nanowires can be extracted from channels. Low magnification EM images of Pt nanowires extracted from the channels of MCM-41 and SBA-15 are shown in Figure 3 and high resolution EM (HREM) images of those are shown in Figure 4, respectively. From many TEM images, the length of Pt nanowires extracted from both MCM-41 and SBA-15 ranged from several tens to several hundreds of nanometers.

It can be seen that the Pt nanowires extracted from MCM-41 have good crystallinity and that each of them can be regarded as a single crystal. The wires have fairly smooth surfaces. In contrast, although the Pt nanowires manufactured in the channels of calcined SBA-15 are close to single crystals, two aspects, different from those synthesized in MCM-41, are clearly observed in the image. Those are: (1) the outer-surfaces projections of the Pt rods are not straight but smoothly curved, and (2) there are bridges between adjacent rods and small protrusions on the surfaces of the rods (e.g., the arrows in Figure 4b). It can be

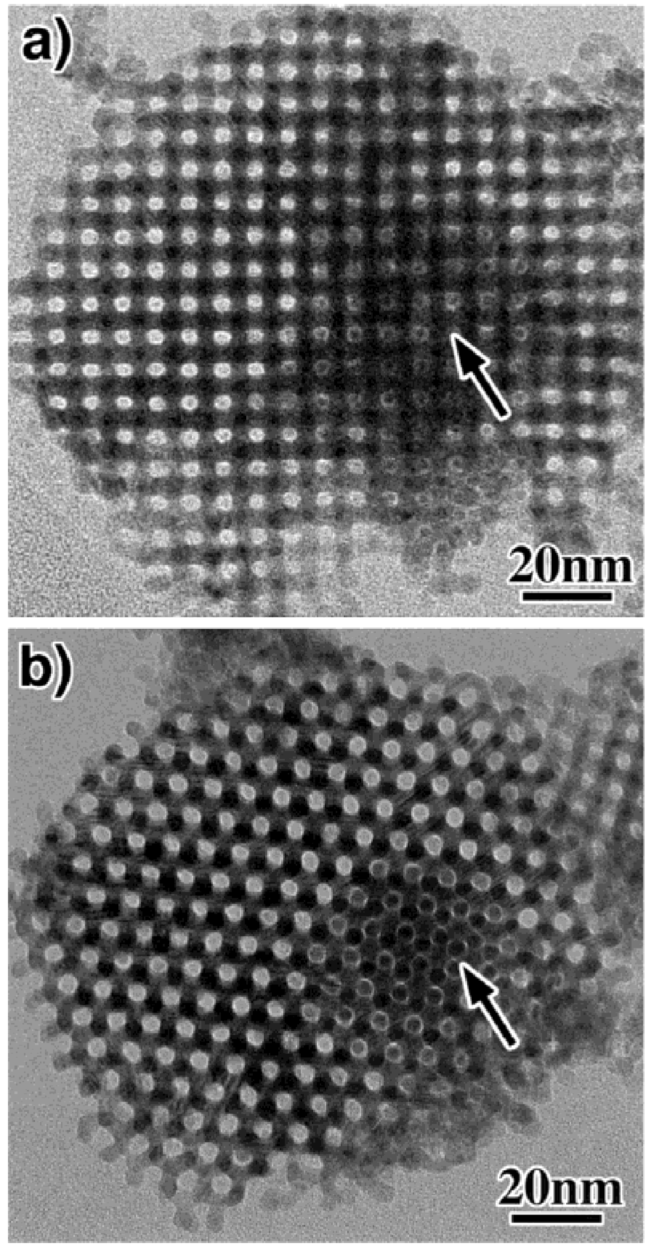

Figure 5. HREM images of Pt network extracted from MCM-48 taken with the [100] (**a**) and the [111] (**b**) incidences, respectively. JEM-1250, 1250 kV.

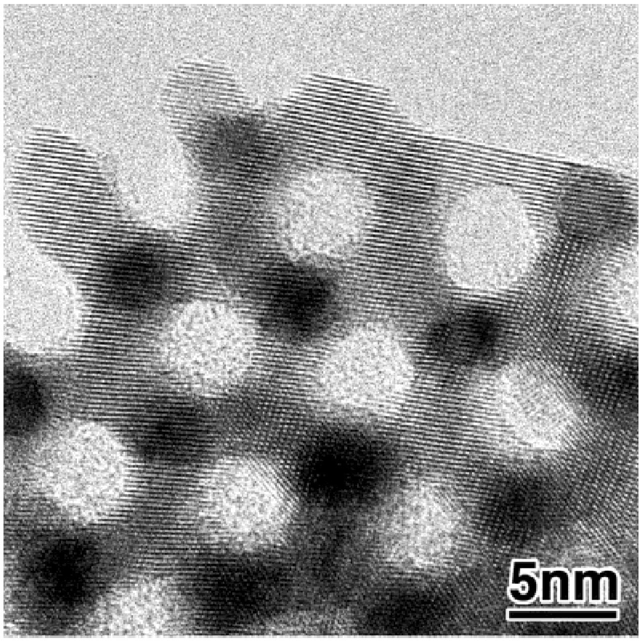

Figure 6. An HREM image of Pt network extracted from MCM-48 taken with the [111] incidence. JEM-4000EX, 400 kV.

clearly seen that the crystal orientations of the two adjacent Pt rods and the small Pt bridge that connects those two rods are the same, that is, the two adjacent Pt rods with the small Pt bridge between them tend to form single crystals. It elucidates the evidence for the existence of small pores, interconnecting the main channels of SBA-15. It can be concluded from the observations that there are small catenoid-shaped Pt domains interconnecting the main channels in calcined SBA-15. However, the small bridges are arranged in a random way with an average diameter of about 3.5 nm, and "as an average" we can observe the p6mm symmetry (Z. Liu et al., 2001).

Figures 5a and 5b are the TEM images taken from the same Pt nanowire network (Pt network), after the dissolution of MCM-48 by tilting, so that the incident beam is parallel to the [100] and [111] directions of the network, respectively. It is clear that the Pt network remains a 3D structure. This also proves that when the Pt compound was introduced into MCM-48 and reduced, the Pt network was formed inside the channels of MCM-48 without destroying the channel geometry. Since the MCM-48 has a chiral channel structure, the Pt networks formed inside such channels are also chiral. It also can be seen from Figures 5a and 5b that a majority of the Pt networks were formed in one set of the nonintersecting compartment, despite the formation of Pt chiral networks in both compartments of MCM-48, as shown by arrows. Figure 6 is an HREM image of a Pt network taken with the same incidence as Figure 5b and shows the Pt network is well single crystalline. Further discussion on chirality of the Pt network will be reported separately.

Acknowledgments

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