

Nanonecklaces of Platinum and Gold with High Aspect Ratios Synthesized in Mesoporous Organosilica Templates by Wet Hydrogen Reduction

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Nanowires of platinum and gold with high aspect ratios are synthesized in one-dimensional channels of ordered mesoporous organosilica HMM. Water-saturated hydrogen reduction (wet H₂-reduction) is significantly effective for large-scale synthesis of long nanowires, while dry H₂-reduction gives monodispersed metal nanoparticles. The nanowires are characterized by TEM, XRD, UV–vis, STM, and XAFS. The Pt and Au wires are 3 nm in diameter and several hundred nanometers to micrometers in length. The metal wires extracted from HMM with HF have a nanonecklace structure, while the wires from siliceous FSM-16 have a nanorod structure. The results indicate that the hydrophobicity or hydrophilicity of the internal pore gives a significant influence on the morphology of nanowires. The nanonecklace structure is also affected by the organic groups in HMM. The mechanism for formation of Pt nanowires in wet H₂-reduction was studied. In the impregnation process, the [PtCl₆]²⁻ ion is physically adsorbed on HMM, and the Pt(IV) ion is reduced to Pt(0) via Pt(II). Tiny Pt nanoparticles are formed in the mesoporous channels, and the water vapor in the H₂ flow enhances the migration of Pt ions, leading to the growth of long nanowires.

Introduction

Nanoparticles and nanowires are a class of key precursors to ordered nanomaterials in the bottom-up approach in nanotechnology.^{1–3} Metal nanoparticles less than 10 nm in size are expected to show a quantum-size effect, and they have potential applications in magnetism, optics, electronics, separation, and catalysis.^{4–6} For the preparation of metal nanoparticles, a variety of methods has been used such as thermal hydrogen reduction, photoreduction, and electrochemical reduction of metal compounds in solutions or on the surfaces of metal oxides and polymers. However, precise control of the size and morphology of the nanoparticles has been a challenging topic of numerous works.⁴ A nanowire, or nanorod, is defined to have a rodlike structure with a diameter in the nanometer-scale, and the chemistry of the nanowire is a new research area.³ Nanowires have attracted

great attention with increased interest in the nanotechnology because they have unique physical and chemical properties based on the low-dimensionality.

Among various preparation techniques of noble metal nanowires and nanoparticles, the template synthesis is one of the promising methods, in which uniform void spaces of porous materials are used as a host to confine wires and particles as a guest. In addition to microporous zeolites,⁷ ordered mesoporous materials⁸ have been used as a host of template synthesis in recent years. Mesoporous silicas such as siliceous FSM-16,^{9,10} MCM-41,¹¹ SBA-15,¹² and organosilica HMM-1^{13,14} have a two-dimensional (2-D) hexagonal structure (*p6mm* symmetry) of 1-D channels less than 10 nm in diameter and a high surface area of up to 1000 m² g⁻¹, thus giving great opportunity for use as a template of the synthesis of nanostructured materials.

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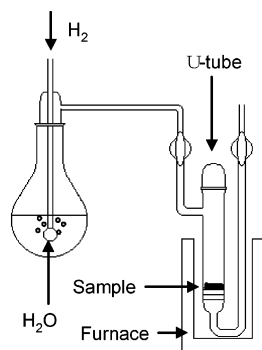


Figure 1. Reaction setup for wet H_2 -reduction.

We reported the synthesis of noble metal nanowires and nanoparticles in FSM-16 and HMM-1 and their magnetic and catalytic properties.^{15–19} For example, photoreduction of H_2PtCl_6 on FSM-16 or HMM-1 produces Pt nanowires, while thermal H_2 -reduction yields Pt nanoparticles. Other research groups also reported the formation of noble metal nanowires by H_2 -reduction.^{20–24} However, H_2 -reduction often gives a mixture of nanowire and nanoparticles, and we need careful control of reaction conditions (e.g., ramping rate of temperature, flow rate of H_2 , and amount of residual water). In our study of the synthetic conditions of nanowires, we have found that H_2 flow saturated with water vapor (wet H_2 -reduction) is highly effective for the reproducible synthesis of Pt and Au nanowires in HMM-1. Here, we report the synthesis and characterization of Pt and Au nanowires by wet H_2 -reduction. The formation mechanism of the nanowires is also discussed.

Experimental Procedures

Synthesis. Two kinds of mesoporous organosilica HMM-1 were prepared and used as templates: Et-HMM with a bridging CH_2CH_2 group and Ph-HMM with a C_6H_4 group.^{13,14} BET surface areas were 812 and 818 $m^2 g^{-1}$, and channel diameters (DFT) were 3.1 and 3.8 nm for Et-HMM and Ph-HMM, respectively. $H_2PtCl_6 \cdot 6H_2O$, $HAuCl_4 \cdot 4H_2O$, hydrofluoric acid, 1-dodecanethiol, and ethanol were used as received.

In a typical preparation of Pt nanowires, Et-HMM was dried under vacuum (ca. 10^{-3} Torr, 1 Torr = 133 Pa) at 453 K for 2 h. To a mixture of Et-HMM (200 mg) and water (30 mL) was added an aqueous solution of $H_2PtCl_6 \cdot 6H_2O$ (26 mg in 30 mL of H_2O). The mixture was stirred for 24 h, evaporated to dryness, and dried under vacuum for 24 h. The resulting pale yellow powder, H_2PtCl_6 /Et-HMM (Pt 5 wt %), was placed in a U-shape reactor (Figure 1), and the sample was treated with H_2 flow (50 mL min^{-1}) saturated

with water vapor (ca. 20 Torr) at 293 K. The temperature was raised from 293 to 473 K in 1 h and was maintained at 473 K for 4 h. After cooling the sample to room temperature, dry N_2 gas was flowed for 20 min, and the sample was recovered.

Au nanowires were prepared by the same wet H_2 -reduction with modifications. The pH of the aqueous solution of $HAuCl_4 \cdot 4H_2O$ was adjusted to 12 with NaOH,²⁵ and the resulting $[Au(OH)_4]^-$ solution was added to a mixture of Et-HMM and water. The mixture was stirred for 3 h in the dark, and after evaporation, the impregnated sample was reduced in H_2 flow with water vapor at 393 K for 2 h. Then, the sample was washed with water to remove residual NaOH and dried in air.

To extract nanowires from HMM, aqueous HF (46 wt %) was diluted to 2.5 wt % with ethanol, and to this solution was added the powder sample. After a few minutes without stirring, the solution turned pale gray, and black Pt wires were precipitated. The unsupported Pt wires were separated on a filter paper, washed with ethanol, and dried in air. For Au nanowires, 1-dodecanethiol was added to the HF solution as a ligand in some cases.

In this paper, Pt(w)/Et-HMM is an abbreviation for Pt nanowires in Et-HMM and Pt(p)/Et-HMM for Pt nanoparticles in Et-HMM. H_2PtCl_6 /Et-HMM represents Et-HMM impregnated with H_2PtCl_6 .

Characterization. Transmission electron microscopy (TEM) and energy-dispersive X-ray spectroscopy (EDX) were performed with a Hitachi H-800 and a JEOL 2000ES. Powder X-ray diffraction (XRD) patterns were recorded on a Rigaku Miniflex using Cu $K\alpha$ radiation ($\lambda = 0.15418$ nm) at 30 kV and 15 mV. Diffuse-reflectance ultraviolet–visible (UV–vis) spectra were measured on a JASCO V-570. For scanning tunneling microscopy (STM) observation, the ethanol solution of extracted nanowire was deposited on a freshly cleaved highly oriented pyrolytic graphite (HOPG, 8×8 mm), and the sample was dried in air. STM images were acquired in air at room temperature on a JEOL JSPM-5200 with a Pt–Ir alloy tip. Topographic images were obtained in the constant current mode with a positive bias voltage applied to the tip. ^{195}Pt magic angle spinning nuclear magnetic resonance (MAS NMR) spectra were recorded on a Bruker MSL-400 spectrometer at 85.9 MHz. X-ray absorption fine structure (XAFS) spectra at the Pt L_{III} -edge (11562 eV) were measured at the BL-10B station in the Photon Factory of the High Energy Accelerator Research Organization (KEK-PF, Tsukuba), and the data were analyzed by a REX2000 program (Rigaku). In the temperature programmed reduction (TPR) of H_2PtCl_6 /Et-HMM, the offgas was analyzed by quadrupole mass spectroscopy (Pfeiffer Vacuum, Prisma).

Results and Discussion

Synthesis and Characterization of Pt and Au Nanowires. We have found that Pt nanowires and nanoparticles are selectively synthesized in Et-HMM and Ph-HMM by H_2 -reduction with or without water vapor. For the synthesis of nanowires, Et-HMM was impregnated with H_2PtCl_6 , and the impregnated sample H_2PtCl_6 /Et-HMM was dried under vacuum for 24 h. The sample was reduced in H_2 flow with water vapor at 473 K for 4 h (Figure 1), and this wet H_2 -reduction led to the formation of Pt nanowires. On the other hand, Pt nanoparticles were obtained by dry H_2 -reduction without water vapor at 473 K for 2–4 h. In the TEM images of Pt/Et-HMM (Figure 2), Pt wires and particles are clearly seen as dark stripes and dots. The Pt wires were 3 nm in diameter reflecting the pore diameter of

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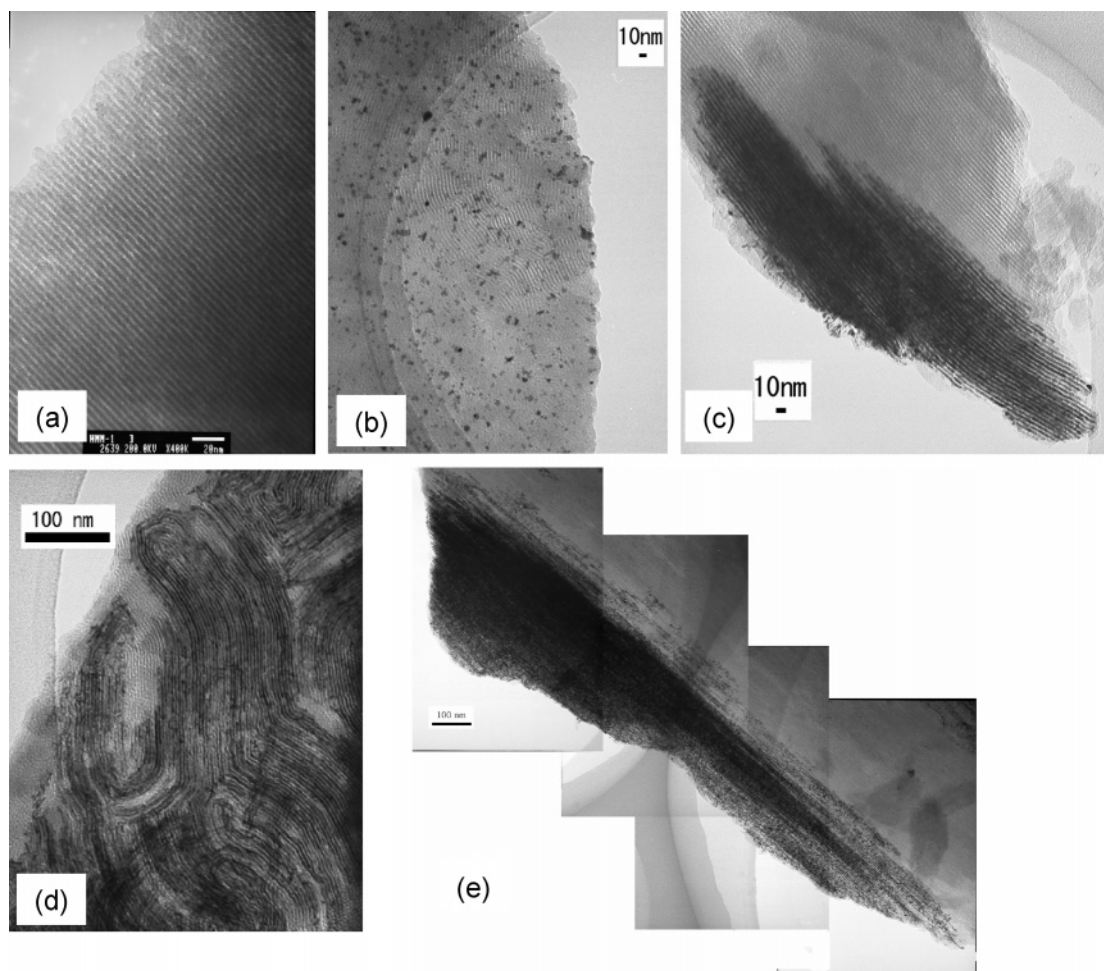


Figure 2. TEM images of (a) Et-HMM (scale bar 20 nm), (b) Pt(p)/Et-HMM (Pt 5 wt %), (c) Pt(w)/Et-HMM (5 wt %), (d) Pt(w)/Et-HMM (36 wt %), and (e) Pt(w)/Ph-HMM (33 wt %).

Et-HMM, and the length ranged from several hundred nanometers to micrometers in the 1-D channels (Figure 2c). The result clearly indicates the formation of nanowires inside the channels. The wet H_2 -reduction is simple but significantly effective in the large-scale synthesis of Pt nanowires with high reproducibility. Up to 36 wt % loading, the wet H_2 -reduction produces Pt nanowires without the formation of nanoparticles on the external surface (Figure 2d). On the other hand, dry H_2 -reduction without adding water vapor gives Pt nanoparticles with a diameter of 3 nm (Figure 2b). For Ph-HMM as a support, long Pt nanowires are formed reflecting a straight 1-D channel structure (Figure 2e), which is due to the robust crystal-like pore walls with molecular-scale periodicity.¹⁴ We attempted to synthesize Pt nanowires in siliceous FSM-16 by the wet H_2 -reduction. Pt wires were formed in the channels, but actually, large Pt particles were also formed on the external surface of FSM-16. Similar results were obtained for MCM-41 and SBA-15 as supports. Presumably, the hydrophilicity of the pore walls of siliceous mesoporous silicas enhances the migration of Pt ions from the internal pores to the external surface in the presence of water vapor.

The synthesis of Au nanowire and nanoparticles in mesoporous silicas had been difficult because $HAuCl_4$ easily decomposes in the light, resulting in the formation of Au particles on the external surface. However, we have found

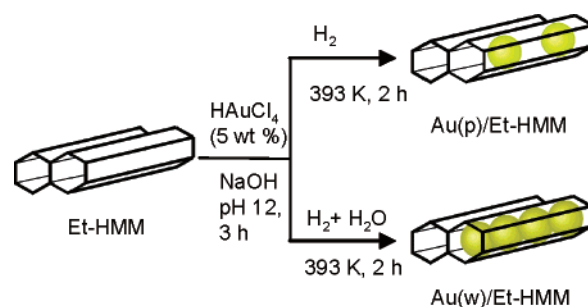


Figure 3. Selective synthesis of Au nanowire and nanoparticles by wet and dry H_2 -reduction.

optimal conditions of the selective synthesis of Au wires and particles in Et-HMM. The pH of the aqueous $HAuCl_4$ solution is adjusted to 12 with NaOH, and the reduction temperature is 393 K. Under these conditions, Au nanowires and nanoparticles are selectively formed by wet and dry H_2 -reduction (Figure 3).

In the TEM images of Au/Et-HMM (Figure 4), 3 nm Au nanoparticles are observed for the dry H_2 -reduced sample, but Au nanowires are clearly seen for the wet H_2 -reduced sample. The length is several tens of nanometers to micrometers, and the Au wires and particles are located in Et-HMM. In the XRD patterns for Au/Et-HMM (Figure 5), no significant change was observed at a low 2θ angle, indicating that the mesoporous structure remains unchanged

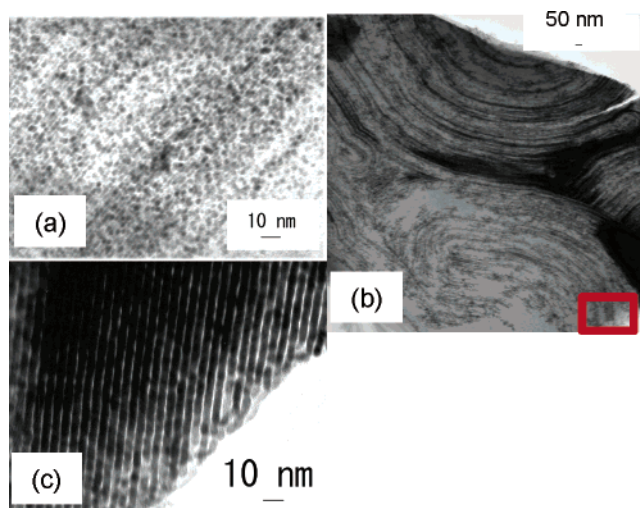


Figure 4. TEM images of (a) Au(p)/Et-HMM by dry H₂-reduction (Au 5 wt %), (b) Au(w)/Et-HMM by wet H₂-reduction (Au 5 wt %), and (c) enlarged image of the rectangular part in panel b.

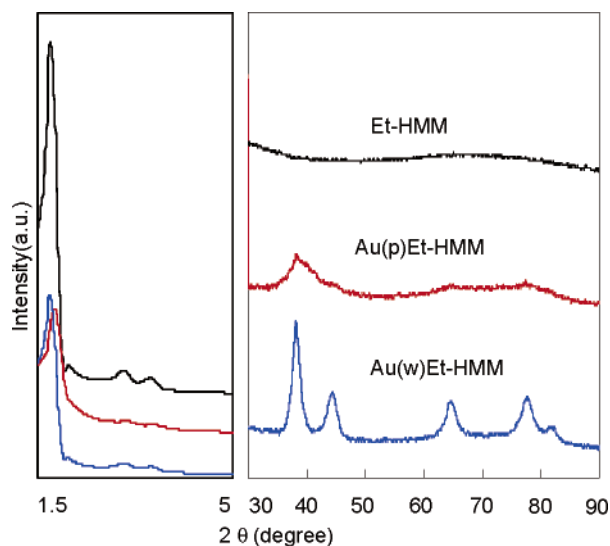


Figure 5. XRD patterns of Et-HMM, Au(p)/Et-HMM, and Au(w)/Et-HMM.

after incorporation of Au wires and particles. The peak intensity was decreased by the occlusion of metal, which results from the pore filling of mesoporous channels.²⁴ Typical peaks of fcc Au were observed at a high 2θ angle for Au(w)/Et-HMM, but the peaks were lowered and broadened for Au(p)/Et-HMM due to the formation of small nanoparticles. Similar XRD patterns were obtained for Pt/Et-HMM (Supporting Information, Figure S1).

Figure 6 shows diffuse-reflectance UV–vis spectra of Au/Et-HMM (Au 5 wt %). An orange–red powder of Au(p)/Et-HMM gave a surface plasmon resonance at 500 nm. On the other hand, the black powder of Au(w)/Et-HMM had a band of transverse resonance at 500 nm and a broad band of longitudinal resonance at 800–1300 nm.

Surface Morphology of Extracted Pt and Au Nanowires. Extraction of nanowires from mesoporous supports is important in the application of nanowires as a building block of nanodevices. In addition, detailed characterization of nanowires is possible by the extraction. The Pt and Au nanowires are successfully separated by dissolving HMM with diluted HF. Pt nanowires were isolated as a black solid

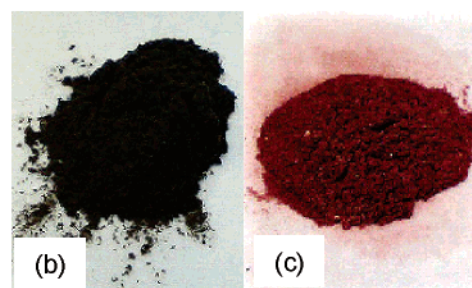
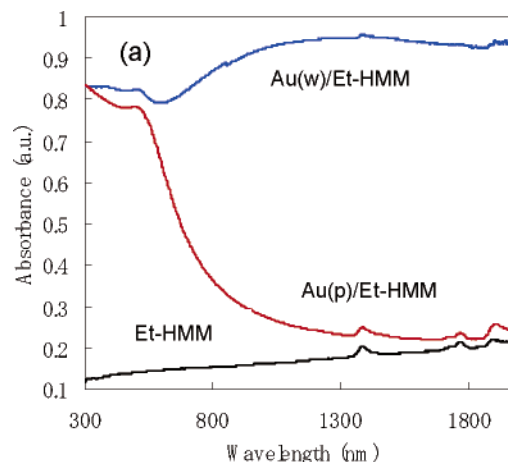


Figure 6. (a) Diffuse-reflectance UV–vis spectra for Au/HMM, (b) photo of Au(w)/Et-HMM, and (c) photo of Au(p)/Et-HMM.

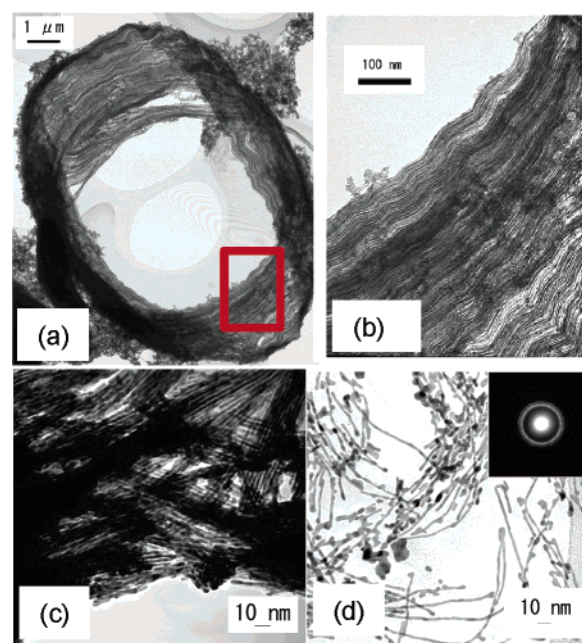


Figure 7. TEM images of extracted nanowires. (a) Ligand-free Pt nanowire extracted from Pt(w)/Et-HMM (5 wt %), (b) enlarged image of the rectangular part in panel a, (c) ligand-free Au nanowires extracted from Au(w)/Et-HMM (5 wt %), and (d) Au nanowires stabilized by 1-dodecanethiol (inset: SAED).

in 60–70% yield, and the EDX analysis confirmed the removal of Si. Figure 7 shows the TEM images of Pt wires extracted from Pt(w)/Et-HMM (Pt 5 wt). The Pt wires aggregate (Figure 7a), but each wire keeps their original structure without fusion (Figure 7b). In Figure 7a, the Pt wire forms a coil-like structure, and one circle is 25 μm. Hence, the length of the wire is at least 25 μm, and the aspect ratio is as high as 8300. The results indicate that long

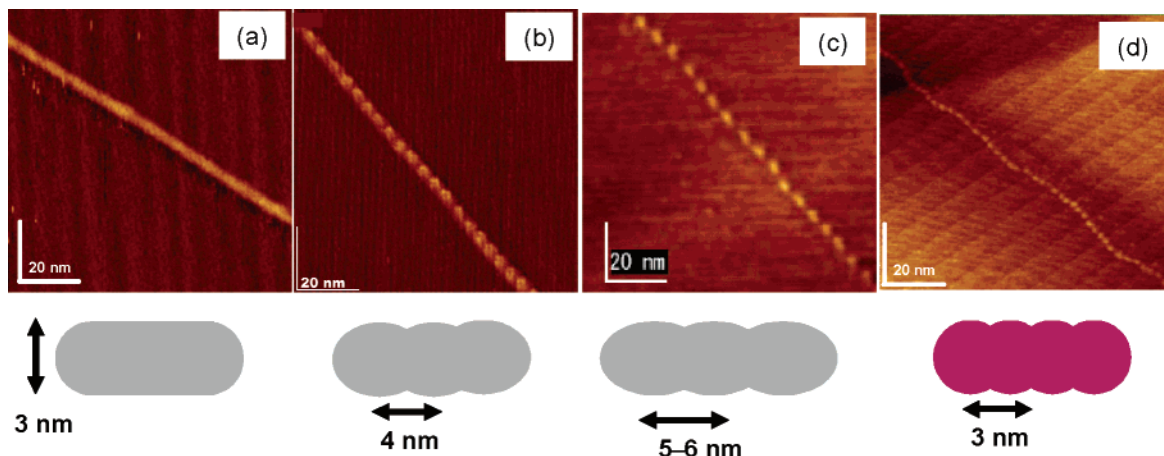


Figure 8. STM images of Pt and Au nanowires on HOPG. (a) Pt nanorod extracted from Pt(w)/FSM-16, (b) Pt nanonecklace extracted from Pt(w)/Et-HMM, (c) Pt nanonecklace extracted from Pt(w)/Ph-HMM, and (d) Au nanonecklace extracted from Au(w)/Et-HMM.

nanowires are formed even at 5 wt % loading by the wet H_2 -reduction. Similarly, extracted Au wires aggregate as seen in Figure 7c, but the wires are dispersed by the addition of 1-dodecanethiol as a ligand (Figure 7d). In the selected area diffraction (SAED) pattern (Figure 7d inset), diffraction rings of (111), (200), (220), and (311)/(222) planes are observed, showing that the wires are fcc crystalline of Au.

Ligand-free Pt and Au nanowires were deposited on HOPG, and the surface morphology was studied by STM (Figure 8). The Pt wires extracted from Et-HMM and Ph-HMM have necklace-like structures with an uneven surface, while the Pt wire extracted from FSM-16 has a rodlike structure with a smooth surface.¹⁹ The Pt nanonecklace is 3 nm in diameter, and the distance between antinodes is 4 nm for Et-HMM (Figure 8b) and 5–6 nm for Ph-HMM (Figure 8c), thus giving an oval structure for a necklace unit. The necklace periodicity is larger than the molecular periodicity of organic groups, and we propose that the surface energy of Pt is influenced by the pore walls with different organic groups (C_2H_4 and C_6H_4).²⁶ In contrast, the Au nanonecklace from Et-HMM has a spherical necklace unit because both the diameter and the antinode distance are 3 nm. The origin of the difference in the morphology of the Pt and Au necklace is under investigation.

Mechanism for Formation of Pt Nanowire in Wet H_2 -Reduction. The mechanism for the formation of Pt nanowires by wet H_2 -reduction was studied by TPR, ^{195}Pt MAS NMR, UV-vis, and EXAFS. A ligand-to-metal charge transfer (LMCT) band and two d-d bands are observed in the UV-vis of $\text{H}_2\text{PtCl}_6/\text{Et-HMM}$ (Figure 9), indicating that $[\text{PtCl}_6]^{2-}$ is physically adsorbed on Et-HMM after impregnation.²⁷ The $\text{H}_2\text{PtCl}_6/\text{Et-HMM}$ sample was heated under the conditions of wet or dry H_2 -reduction, and the offgas was analyzed by mass spectrometry (Figure 10). HCl ($m/e = 36$) was observed as a main product with a slight amount of Cl_2 ($m/e = 71$), and both wet and dry H_2 -reduction gave similar desorption curves with a peak of HCl at 373 K. The results indicate that the water vapor has no effect on the reduction of Pt ions. In ^{195}Pt MAS NMR, only $[\text{Pt}^{\text{IV}}\text{Cl}_6]^{2-}$ was observed

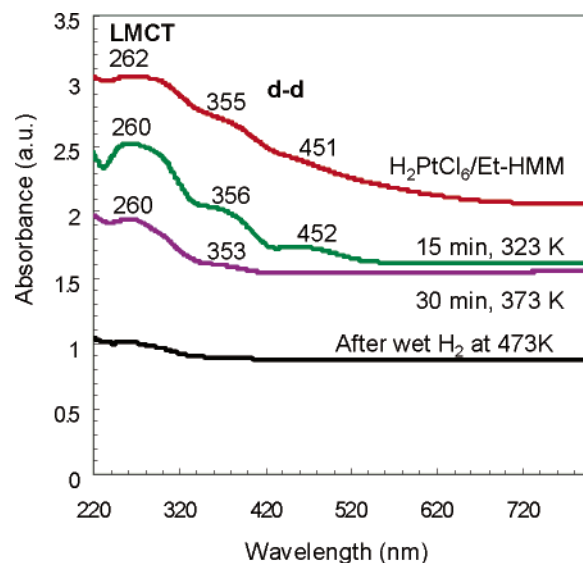


Figure 9. Diffuse-reflectance UV-vis spectra of $\text{H}_2\text{PtCl}_6/\text{Et-HMM}$ before and after wet H_2 -reduction.

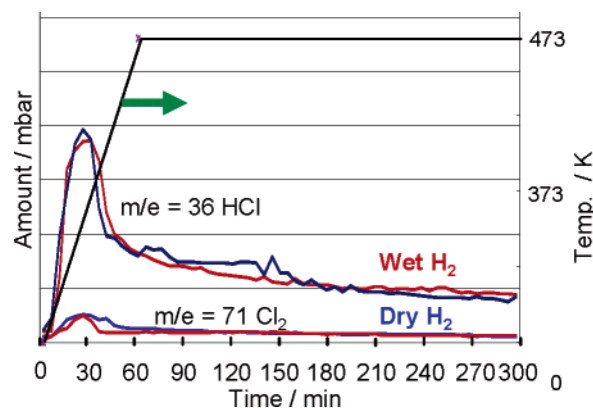


Figure 10. TPR profiles of wet and dry H_2 -reduction of $\text{H}_2\text{PtCl}_6/\text{EtHMM}$.

after impregnation in accord with the UV-vis result (Figure 11a). After the wet H_2 -reduction at 323 K, the NMR spectrum gave four small peaks of Pt(II) complexes besides a main peak of $[\text{Pt}^{\text{IV}}\text{Cl}_6]^{2-}$ (Figure 11b). It is therefore conceivable that the $[\text{Pt}^{\text{II}}\text{Cl}_x(\text{H}_2\text{O})_{4-x}]^{2-x}$ complexes work as intermediates in the wet H_2 -reduction.

The time evolution of wet H_2 -reduction was also studied by Pt L_{III}-edge EXAFS. Figure 12 shows Fourier transforms

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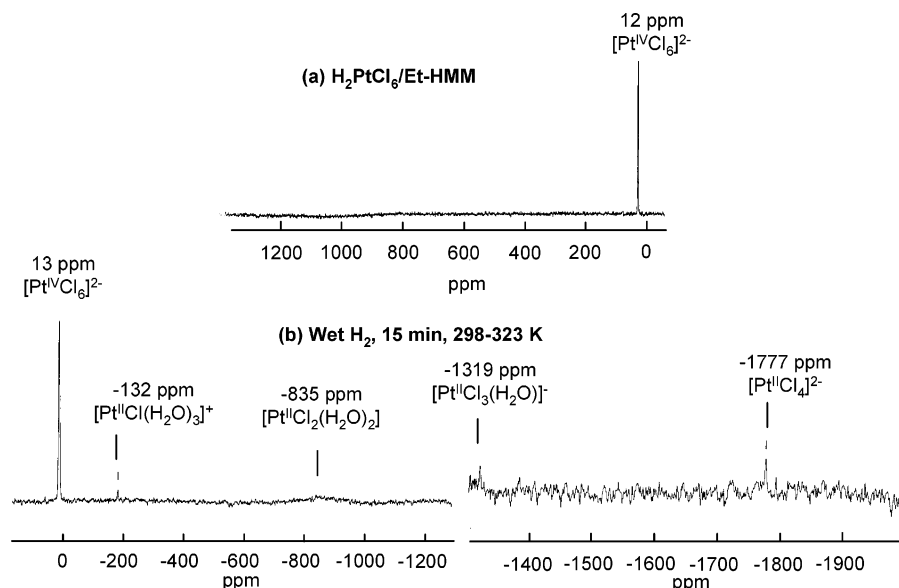


Figure 11. ^{195}Pt MAS NMR of $\text{H}_2\text{PtCl}_6/\text{Et-HMM}$. (a) After impregnation and (b) after wet H_2 -reduction for 15 min at 298–323 K. Aqueous H_2PtCl_6 solution (8 wt %) was used as a reference of chemical shift (0 ppm).

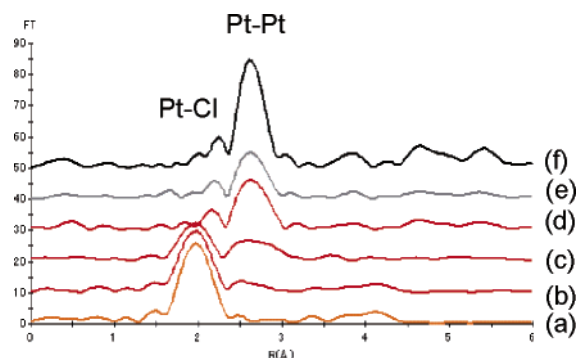


Figure 12. Fourier transforms of $k^3\chi(k)$ for Pt/Et-HMM. (a) $\text{H}_2\text{PtCl}_6/\text{Et-HMM}$; (b) wet H_2 , 15 min, 323 K; (c) wet H_2 , 30 min, 373 K; (d) wet H_2 , 300 min, 473 K; (e) dry H_2 ; and (f) Pt foil.

Table 1. Curve-Fitting Analysis of the First Coordination Shells of Pt–Cl and Pt–Pt for Pt/Et-HMM

sample	bond	CN ^a	R^b (Å)	ΔE^c (eV)	σ^d (Å)	R^e (%)
Pt foil	Pt–Pt	12.0	2.76	6.4	0.06	4.7
dry H_2	Pt–Pt	7.8	2.76	7.6	0.07	0.9
wet H_2 , 300 min, 473 K	Pt–Pt	8.9	2.76	7.5	0.07	1.2
wet H_2 , 30 min, 373 K	Pt–Pt	4.5	2.78	15	0.06	3.7
	Pt–Cl	3.5	2.30			
wet H_2 , 15 min, 323 K	Pt–Pt	1.0	2.78	17	0.05	2.0
	Pt–Cl	5.4	2.31			
$\text{H}_2\text{PtCl}_6/\text{Et-HMM}$	Pt–Cl	6.0	2.32	15	0.02	3.0

^a Coordination number. ^b Interatomic distance. ^c Correction of threshold energy. ^d Debye–Waller factor. ^e Residual factor.

of $k^3\chi(k)$, and Table 1 summarizes the curve-fitting results. In the curve-fitting analysis, the observed peaks were ascribed to the first coordination shells of Pt–Cl and Pt–Pt, and the contribution of Pt–O was not observed. The coordination number (CN) of Pt–Cl declines from 6.0 to 3.5 after 30 min at 373 K, and the CN of Pt–Pt increases from 0 to 4.5. The result corresponds to the desorption of HCl as described in the TPR study (vide supra). Even after 15 min at 323 K, the contribution of Pt–Pt is detected, which shows the clustering of Pt(0). By combining the data of EXAFS and ^{195}Pt NMR, small amounts of Pt(II) and Pt(0) are generated after 15 min, and Pt(0) forms tiny Pt particles as shown in Figure 12.

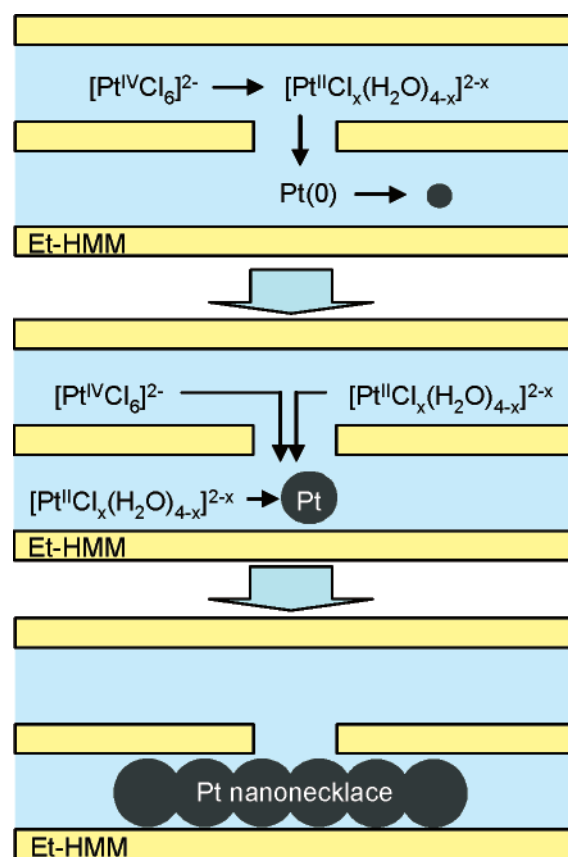


Figure 13. Proposed mechanism for formation of Pt nanonecklaces in mesoporous organosilica Et-HMM.

From the previously mentioned experimental results, we propose that the role of water vapor in the wet H_2 -reduction is to enhance the migration of Pt(IV) and Pt(II) species to the surface of Pt particles in the mesoporous channels (Figure 13). The Pt ions are catalytically reduced on the particle surface to grow nanowires. Under the conditions of dry H_2 -reduction, the migration of the Pt ion is inhibited to result in the formation of nanoparticles. If the impregnated sample is not sufficiently dried, or if the H_2 gas contains small amount of

water vapor, Pt nanowires can be formed even under the condition of dry H₂-reduction.

Conclusion

It is demonstrated in this paper that nanowires and nanoparticles of Pt and Au are selectively synthesized by wet and dry H₂-reduction in mesoporous organosilicas Et-HMM and Ph-HMM. The wet H₂-reduction is simple but highly effective for the synthesis of metal nanowires with high aspect ratios in HMM. Water vapor added to H₂ flow facilitates the migration of Pt ions in the 1-D channels of HMM, leading to the growth of nanowires. The Pt and Au nanowires have a necklace-like structure, and the surface morphology of the nanonecklaces can be controlled by the

organic groups of HMM. Nanonecklaces with a variety of morphologies would provide new physical and chemical properties that are not given by nanorods.

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Supporting Information Available: Figure of XRD patterns of Pt/Et-HMM. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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