Nanotubular Materials

Noble-Metal Nanotubes (Pt, Pd, Ag) from Lyotropic Mixed-Surfactant Liquid-Crystal Templates**

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A lot of attention is currently focused on nanosized tubular materials because of their unique physical properties and potential applications as gas and fluid paths or reservoirs in catalysis, fuel cells, sensors, and separation systems.[1] Since the discovery of carbon nanotubes,[2] there have been reports on a variety of inorganic nanotubes based on boron nitride,[3] metal sulfides,[4] metal borates[5] and metal oxides.[6] Besides high-temperature processes,[2–5] another approach that makes use of solid or molecular templates[6] has been developed for the synthesis of such nanotubular materials. For metals important in catalysis and other nanotechnological fields, synthesis by using nanoporous polymer and anodic aluminum films as templates led to gold,[7a] nickel,[7b] and palladium[7c] nanotubes, but with inner diameters as large as 10–100 nm. Furthermore, no report has appeared on the fabrication of metal nanotubes by using a surfactant or other molecular templates, although mesoporous platinum was obtained by using the lyotropic liquid crystals (LCs) of nonionic surfactants.[8] In brief, the previous templating approaches to metals yielded only nanoporous materials or thick-walled tubular structures. This fact seems to suggest that thin-walled metal nanotubes with diameters below 10 nm might be unobtainable because of their extremely high surface energies, in spite of their potentially attractive functionalities, as expected by analogy with the magnetically and catalytically unique properties of platinum nanowires.[9] The previous surfactant templating process that was first applied to the synthesis of mesoporous silica MCM-4,[10] used almost exclusively a single ionic or nonionic surfactant. In contrast, our recent study revealed that the lyotropic nematic media of nonionic–cationic mixed surfactant are effective for the preparation of tin oxide microwires.[11] This motivated us to apply such a mixed surfactant template to the fabrication of nanostructured metals. Herein we demonstrate the first synthesis of platinum, palladium, and silver nanotubes, with inner diameters of

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3–4 nm and outer diameters of 6–7 nm, by the reduction of metal salts confined to lyotropic mixed LCs of two different sized surfactants. The mechanism of formation of such metal nantubes is also proposed.

In the typical fabrication process, the liquid crystalline phase of hexachloroplatinic acid (H_2PtCl_6), nonaethylene glycol monododecyl ether ($C_{12}EO_9$), polyoxyethylene (20) sorbitan monostearate (Tween 60) and water at a molar ratio of 1:1:1:60 was treated with hydrazine. The transmission electron-microscope (TEM) image of the resulting black powders showed an aggregate of nanotubular materials (Figure 1 A). Energy-dispersive X-ray (EDX) analysis of the reduced powders confirmed the existence of platinum as the major component and the complete removal of chloride ions librated during the reduction of platinum ions into platinum metal. Hence, the tubular materials thus obtained can be identified as platinum nanotubes with inner and outer diameters of 3 and 6 nm, respectively. Some round spots with a diameter of about 6 nm are observed in the same image because some of the folded nanotubes are oriented parallel to the electron beam. The length of nanotubes is estimated to be much greater than 100 nm, but it is impossible to determine the total length of an isolated nanotube because the nanotubular materials are highly cohered into a dense aggregate. The X-ray-diffraction (XRD) pattern of the reduced solid also exhibited a broad shoulder at $2\theta = 0.5$–2° that is presumably due to the nanotubular structure (Figure 2). The two broad peaks at $2\theta = 39.73°$ and 46.19° are assigned to the (111) and (200) reflections, respectively, of the fcc structure with a unit cell parameter of 0.3929 nm, which is very close to that of the bulk metal (0.3923 nm). Thermogravimetric analysis (TGA) and FTIR spectroscopy revealed that the solid contains ≈ 36 wt% of remaining surfactant species, which suggests that the nanotubular platinum particles are stabilized by the remaining organic species. An additional experiment showed that the organic content is further decreased to ≈ 13 wt% by treatment with an ethanol solution of sodium acetate. The catalytic activities of platinum nanotubes would not always be lowered by surfactant or other molecular protection, as various noble metal colloids stabilized by surfactants and solvents were demonstrated to be effective for hydrogenation[12] and use in the Heck reaction.[13]

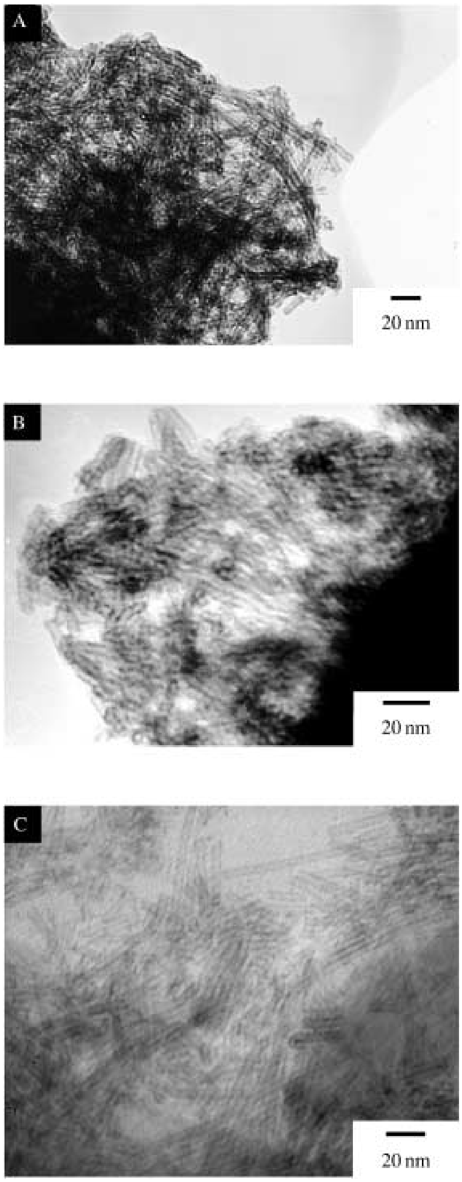


Figure 1. TEM images showing A) platinum, B) palladium, and C) silver nanotubes obtained by reducing their precursory mixed surfactant LC phases with hydrazine.

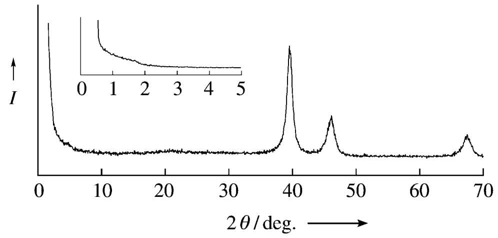


Figure 2. XRD pattern of the as-grown platinum nanotube obtained by the hydrazine treatment.

A similar reaction by using $Pd(NO_3)_2$ in place of H_2PtCl_6 also yielded palladium nanotubes with inner and outer diameters of 3 and 6 nm, respectively (Figure 1 B). Another fabrication process that uses sodium dodecylsulfate (SDS) and Tween 60 as a mixed template with $AgNO_3$ resulted in the formation of an aggregate of silver nanotubes with inner and outer diameters 4 and 7 nm, respectively (Figure 1 C). It is noted throughout the above three systems that the metal nanotubes are highly cohered into a dense aggregate. This aggregation, together with the stability of electron-beam system, which was affected by the organic species evaporated from the metal samples placed in the vacuum chamber of TEM, led to difficulties in observing a higher resolution image of an isolated metal nanotube. According to TGA, palladium nanotubes washed with ethanol were three times less contaminated with remaining organic materials than the platinum nanotubes, and hence the former metal particles tended to form more dense aggregates. This may be the reason why the TEM image of palladium is a little less clear than that of platinum as observed in Figure 1.

In marked contrast to the above observations, no nanotubular metals were obtained when the reaction was performed by using any one of $C_{12}EO_9$, SDS, and Tween 60 as the sole templating agent. These facts clearly indicate that mixed-surfactant LCs based on Tween 60 are essential to the preparation of noble-metal nanotubes. It is therefore particularly intriguing to elucidate the pathway from the precursory mixture to the formation of nanotubes and the factor that determines their dimensions. For this report, we focused our attention on the characterization of the precursory LC in the $H_2PtCl_6/C_{12}EO_9$/Tween 60/H_2O system.

The XRD patterns of the $C_{12}EO_9$/Tween 60/H_2O mixtures at a molar ratio of 1:y:60 exhibited one major peak around $2\theta = 1.5°$ and a very weak broad band near $2\theta = 2.5°$ (Figure 3A). These two peaks are attributed to the 100 and 110 reflections for a hexagonal structure with $a \approx 7$ nm. Similarly to the $C_{12}EO_8/H_2O$[14] and $C_{16}EO_8/H_2O$[8a,14b] LCs, the $C_{12}EO_9/H_2O$ ($y = 0$) mixture also forms a hexagonal phase with $a = 6.82$ nm. No layered-phase characteristic of the binary Tween 60/H_2O system is observed for the $y = 0$–2 compositions. It is also remarked that even upon addition of much larger surfactant molecules, the hexagonal structure is maintained over a wide range of $y = 0$–1.6 while keeping the parameter a in the narrow range of 6.8–7.2 nm. More interestingly, the parameter a, which corresponds to the rod-to-rod distance in an array of cylindrical rodlike micelles, varies in a sine-wave with the Tween 60 content y and has a minimum of $a = 6.9$ nm at $y \approx 1$ (Figure 3C). These findings suggest that $C_{12}EO_9$ and Tween 60 surfactant molecules, which are very different in size, mix at the molecular level to form a hexagonal array of cylindrical micelles and that their equimolar composition may afford the most dense or stabilized phase. When H_2PtCl_6 was added to the $y = 1$ hexagonal composition, the XRD peaks of the resulting phases showed a marked tendency to decrease in intensity with increasing platinum content x (Figure 3B). Thus, the precursory 1:1:1:60 phase that contained the $PtCl_6^{2-}$ ion could be identified as an LC with a hexagonal but disordered array of mixed surfactant cylindrical micelles corresponding to $a = 6.9$ nm.

On the basis of the above X-ray observations along with the structural parameters of surfactant molecules (Table 1), we proposed a structure model for the precursory 1:1:1:60 LC (Figure 4A). This model is based on a structural calculation done by assuming that equimolar amounts of $C_{12}EO_9$ and Tween 60 molecules are arranged side by side with their hydrophobic tail groups fully extended and tilted at the same angle to form a cylindrical rodlike micelle; their hydrophilic heads are assumed to be directed to the outside and the rodlike micelles further assembled into a hexagonal array with a rod-to-rod distance equal to the observed value of 6.9 nm.[15] Additionally, the hydrophilic head groups of both surfactant molecules were assumed to adopt a spherical conformation with the same packing coefficient of 0.681 as observed for a number of amorphous or poorly crystalline polymers.[16] The structural calculations also indicated that the surfactant molecules in the mixed surfactant LC are much less tilted with respect to the rod axis than those in the hexagonal LC of $C_{12}EO_9$ (Fig-

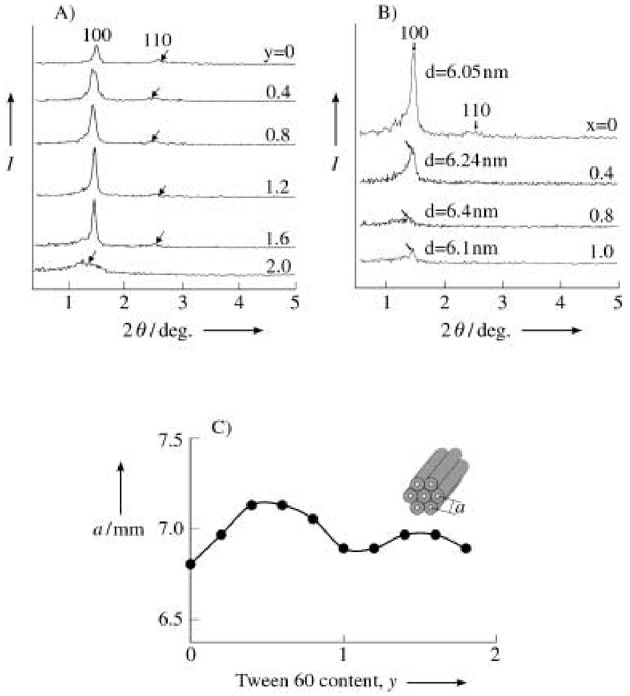
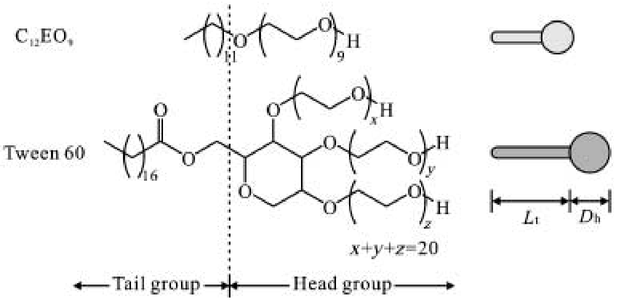


Figure 3. XRD patterns of A) the 1:y: 60 mixtures of $C_{12}EO_9$, Tween 60 and H_2O and B) the x:1:1:60 mixtures of H_2PtCl_6, $C_{12}EO_9$, Tween 60 and H_2O at ≈15 °C ($Cu_{K\alpha}$), and C) plots of the rod-to-rod distance, a, as a function of Tween 60 content, y, for the former ternary mixtures.

Table 1: Stuctural parameters of $C_{12}EO_9$ and Tween 60 molecules.[a]

Surfactant	Head group		Tail group		Molecule	
	Effect. Volume $V_{h,i}$ [nm^3][b]	Diameter $D_{h,i}$ [nm]	Volume $V_{t,i}$ [nm^3]	Length $L_{t,i}$ [nm]	Volume $V_{m,i}$ [nm^3]	Length $L_{m,i}$ [nm]
$C_{12}EO_9$	0.589	1.04	0.214	1.61	0.803	2.65
Tween 60	1.299	1.30	0.324	2.53	1.623	3.88

[a] The CO_2 group of Tween 60 molecules is assumed to be a part of the tail. [b] Effective volume is given by the van der Waals volume/0.681 according to Slonimskii et al. [16]



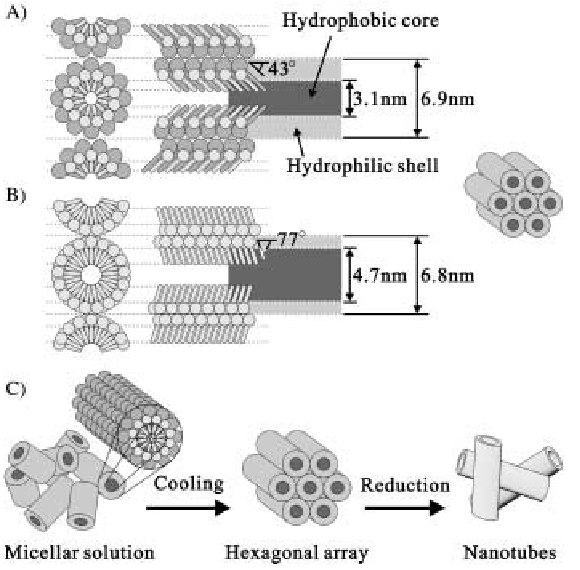
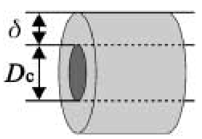


Figure 4. Schematic models for the formation of platinum nanotubes in the mixed surfactant templating system: A) Mixed ($C_{12}EO_9$/Tween 60) and B) single ($C_{12}EO_9$) surfactant cylindrical rodlike micelles. C) Pathway from micellar solution to metal nanotubes by the reduction of metals salts confined to the aqueous shell of mixed-surfactant cylindrical micelles. The metal salts and water molecules are omitted from the models.

ure 4B). Thus, we supposed that the present platinum nanotubes are formed by a mixed surfactant templating mechanism (Figure 4C). In this mechanism, the rodlike micelles of $C_{12}EO_9$ molecules in an aqueous medium are combined with much larger-sized sorbitan-based non-ionic surfactant molecules (Tween 60) to form an aqueous solution of the mixed surfactant cylindrical micelles as described above. On cooling the mixed micellar solution would be converted into a hexagonal LC with $a = 6.9$ nm. At the final stage, the platinum species confined to the aqueous region of the molecular assemblies are reduced into platinum atoms.

The observed inner diameter of 3 nm for both the platinum and palladium nanotubes agrees closely with 3.1 nm calculated for the diameter of the hydrophobic core of the mixed surfactant micelle (Table 2). This is because the reduced metal is stabilized at the interface between the hydrophobic and the hydrophilic domains, as Attard et al. explained the formation of H_I-platinum from a hexagonal LC of $C_{16}EO_8$.[8a] The subsequent process, however, is remarkably different between both systems. In the mixed-surfactant system, the reduced metal grows into nanotubes with a wall-thickness of 1.5 nm within the cylindrical micelle because the aqueous shell has a maximum thickness of 1.93 nm according to the calculation (Table 2). In contrast, the aqueous shells in the $C_{16}EO_8$ and the $C_{12}EO_9$ systems are as thin as 1.0 nm. The insufficient thickness for the separate growth of nanotubes would lead to mesoporous or bulk metals as a result of agglomeration and coalescence of metal clusters deposited within neighboring micelles, as observed for these single-surfactant systems. A similar mechanism would apply to the Ag-based system. A preliminary experiment showed that the 1:1:1:60 composition of $AgNO_3$/SDS/Tween 60/water is also a hexagonal LC with $a = 7.03$ nm close to that for the platinum system. The observed inner diameter of 4 nm for the silver nanotube (larger than 3 nm for the other two metals) may be due to an increase in the effective diameter of hydrophobic core by the coulomb-repulsive effect of the sulfate group bonded to the dodecyl chain.

Table 2: Structural parameters of surfactant cylindrical rodlike micelles.



Surfactant	Number of molecules per cross section *N*	Diameter of core D_c [nm]	Thickness of shell δ [nm]
$C_{12}EO_9$	17	4.73	1.04
$C_{12}EO_8$	21	5.72	1.00
$C_{12}EO_9$/Tween 60	12/12	3.12	1.93

In summary, the reduction of metal salts confined to lyotropic mixed surfactant LCs resulted in the first synthesis of platinum, palladium, and silver nanotubes of 6–7 nm outer diameter. Equimolar amounts of medium and large surfactant molecules are combined into a hexagonal array of cylindrical rodlike micelles ≈6.9 nm in diameter and the aqueous outer shell of the rodlike micelles is so thick that the reduced metal grows into nanotubes separately within the aqueous shell. This can be explained by a structure model constructed on the basis of the molecular parameters of surfactants along with X-ray observations. The uniformly sized platinum and the other two metal nanotubes are promising for potential applications as electrodes in batteries and fuel cells, environmental catalysts, and electronic nanodevices. The mixed surfactant templating method could also be extended to the synthesis of a wide range of nanotubular materials, inorganic or organic.

Experimental Section

A mixture of H_2PtCl_6, $C_{12}EO_9$, Tween 60, and H_2O in a 1:1:1:60 molar ratio was shaken at 60°C, then cooled to between 15 and 25°C and allowed to stand at that temperature for 30 min. Polarizing optical microscopy revealed that the homogeneous mixture was an isotropic solution at 60°C and transformed around 28°C into a LC phase. An excess amount of hydrazine was added to the cooled (25°C) pasty material and then kept at that temperature for 24 h. The resulting solid was separated, washed with water and then repeatedly with ethanol prior to drying in air. Similar syntheses by using $Pd(NO_3)_2$, or $AgNO_3$, SDS, and in place of H_2PtCl_6 and $C_{12}EO_9$ were carried out to obtain palladium and silver nanotubes. To characterize the precursory LC phases, pasty mixed phases of $C_{12}EO_9$, Tween 60, and H_2O with different compositions were also prepared by using the same heating and cooling processes as above. All TEM images were taken with a Hitachi H-800 MU microscope operated at 200 keV. Wide-angle XRD patterns were measured by the reflectance method using $Cu_{K\alpha}$ radiation, and small angle ones for pasty or powdered samples were measured by the transmission method on a Shimadzu XRD-7000 diffractometer equipped with a glass plate of 1 mm thick with a slit of 1 mm wide filled with specimen.

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