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Synthesis of Porous Platinum Nanoballs in Soft Templates

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Morphology-controlled synthesis of nanostructures is a great challenge in materials chemistry because the physical and chemical properties are both size and shape dependent. Therefore, a lot of research is being carried out to develop synthetic approaches to achieve control over the composition, structure, size, and shape of the nanostructures. Pt nanoparticles in particular are known for their catalytic, electrocatalytic, and fuel cell applications,[1,2] and it has been shown that the catalytic activity of platinum nanostructures highly depends on the morphology of the nanoparticles,[3,4] as it was demonstrated by the high catalytic activity of Pt nanowires toward water−gas shift reactions.[4] One important issue related to the application of platinum and its alloys in catalysis is to reduce the Pt amount while keeping a good catalytic performance. This challenge can be achieved by the synthesis of porous Pt with high surface area and interconnected structure. The interconnected structures can have another advantage: they can enhance the catalytic activities for the reactions involving two or more reactants, because they can supply different adsorption sites for different reactants in close vicinity. Herein, we describe the soft template synthesis of platinum nanoballs with hexagonal cells formed by connected nanorods.

Specific hard templates such as mesostructured silica can be used as nanomolds to obtain nanomaterials with high aspect ratio such as metal nanowires. This was first reported by Ichikawa *et al.* who synthesized platinum and palladium nanowires.[4,5] Arrays of palladium nanostructures were also obtained by using cubic and hexagonal mesoporous silica matrixes as templates.[6] In this domain, ball-shaped palladium nanocatalysts illustrate perfectly the shape effect because they exhibit remarkable selectivity for the cleavage of benzyl ethers demonstrating that nanostructured mesoporous materi-

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(1) Narayanan, R.; El-Sayed, M. A. *J. Phys. Chem. B* **2003**, *107*, 12416.
(2) Somorjai, G. A. *Proc. Natl. Acad. Sci. U.S.A.* **1985**, *82*, 2207. El-Sayed, M. A. *Acc. Chem. Res.* **2001**, *34*, 257.
(3) Narayanan, R.; El-Sayed, M. A. *Nano Lett.* **2004**, *4*, 1343.
(4) Fukuoka, A.; Higashimoto, N.; Sakamoto, Y.; Sasaki, M.; Sugimoto, N.; Inagaki, S.; Fukushima, Y.; Ichikawa, M. *Catal. Today* **2001**, *66*, 23.
(5) Fukuoka, A.; Hidenobu, A.; Sakamoto, Y.; Inagaki, S.; Fukushima, Y.; Ichikawa, M. *Inorg. Chim. Acta* **2003**, *350*, 371.
(6) Kang, H.; Jun, Y.-W.; Park, J.-I.; Lee, K.-B.; Cheon, J. *Chem. Mater.* **2000**, *12*, 3530−3532.

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als display interesting catalytic activity through cooperative properties.[7]

One drawback of using hard templates lies in the requirement to apply strong chemical treatment such as hydrofluoric acid to get rid of the silica template. Soft templates as lyotropic liquid crystals offer a good alternative because they can be dissolved very easily. Hence, mesophases resulting from surfactant self-assembly provide a class of useful and versatile templates for generating one-dimensional, two-dimensional (2D), or three-dimensional (3D) nanostructures in relatively large quantities as far as they remain stable upon addition of reagent and/or chemical reactions proceeding within. This was demonstrated first by Attard *et al.* who showed that binary liquid crystals, which are highly viscous systems, can be used as "soft" templates for the preparation of nanostructured metals because their small cell parameter (≈3 nm) provides a strong confinement in the aqueous phase: mesoporous platinum was thus synthesized by electro-reduction using lyotropic liquid-crystal templates made by a mixture of a nonionic surfactant octaethylene glycol monohexadecyl ether ($C_{16}EO_8$), hexachloroplatinic acid (H_2PtCl_6), and water.[8,9] Since then, a few examples have been reported for the preparation of 3D porous Pt nanostructures.[10−15] Platinum thin films with a highly ordered 2D-hexagonal mesoporous structure have also been obtained by contact plating in the presence of lyotropic liquid crystals.[12]

We have recently shown that giant direct hexagonal mesophases made by a quaternary system (water, surfactant, cosurfactant, and oil)[16−18] can be used as nanoreactors to synthesize structured nanomaterials both in the aqueous and in the oil phases.[19−21] The mesophases are composed of oil-swollen cylinders hexagonally packed in a continuous water domain. The oil−water interface is covered by either anionic or cationic surfactants with pentanol as co-surfactant, and the swelling oil is cyclohexane. By adjusting the ionic strength of the aqueous medium one can tune continuously the size of the nonpolar cylinders, whose diameter ranges from 3 to 30 nm.[16] However, in all cases, the distance between the adjacent cylinders is nearly constant (∼3 nm). These soft materials are much less viscous than conventional binary hexagonal phases.[18] In this work, we have used this new class of mesophases, with water containing Pt salt to synthesize porous platinum nanoballs made of connected nanowires.

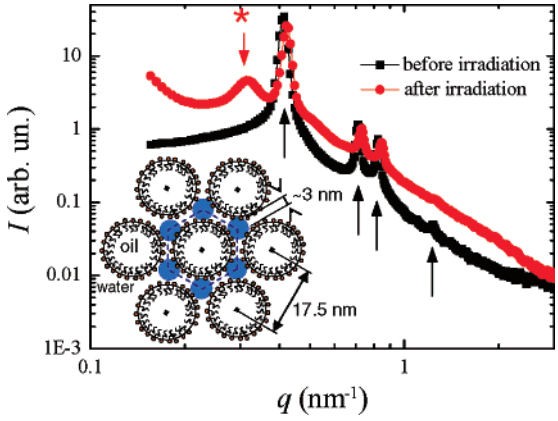

Figure 1. SAXS pattern of a Pt-doped SLC (swollen liquid crystal), before (black squares) and after (red circles) γ-irradiation. Before irradiation the diffraction pattern is characteristic of a hexagonal phase as demonstrated by four Bragg peaks (black arrows) whose positions are in the ratio $1:3^{1/2}:2:7^{1/2}$. After irradiation, the hexagonal structure is preserved, but a broad peak (marked by ∗) superimposes to the characteristic peaks of the host phase. Scheme: cross section of an oil-swollen hexagonal phase with the cylinder center-to-center distance of 17.5 nm and the water thickness between cylinders of 3 nm. Blue dots mark the preferential region for the Pt particle growth.

We used a mesophase with cetyltrimethylammonium bromide (CTAB), as surfactant, and tetraamineplatinum(II), $Pt(NH_3)_4Cl_2$, as salt. The resulting phase is translucent and birefringent, which reveals an anisotropic structure. Small-angle X-ray scattering (SAXS) experiments show that the *p6mm* hexagonal symmetry is preserved even at high Pt concentrations (0.05−0.2 M). The SAXS spectrum for a sample with a Pt concentration of 0.1 M (Figure 1) exhibits the characteristic features of a direct hexagonal phases with four Bragg peaks whose position are in the ratio $1:3^{1/2}:2:7^{1/2}$ with a lattice parameter $a = 17.5$ nm and cylinders with 14 nm diameter (see scheme in Figure 1).

This liquid crystal was used as a nanoreactor to synthesize platinum nanomaterials. The samples were exposed to γ-rays for a slow radiolytic reduction where the hydrated electrons and the reducing radicals produced during the radiolysis of the solvent are used to reduce the metal ions.[22] The pentanol also contributed to the slow reduction of Pt^{II} on the seeds induced by γ-rays. Compared to chemical reducing processes that follow a diffusion front, radiolysis induces a homogeneous nucleation and growth in the whole volume. Besides, this process does not destroy the liquid crystal as proved by the hexagonal characteristic SAXS pattern after irradiation (Figure 1). After 16 h of irradiation at a dose rate of 3 kGy h^{-1}, a homogeneous black gel was obtained.

After reaction, the mesophase was destabilized by 2-propanol addition and Pt nanomaterials were extracted by centrifugation and washed several times with 2-propanol. The transmission electron microscopy (TEM) pictures (Figure 2)

(7) Lee, H.-Y.; Ryu, S.; Kang, H.; Jun, Y.-W.; Cheaon, J. *Chem. Commun.* **2006**, 1325.
(8) Attard, G. S.; Göltner, C. G.; Corker, J. M.; Henke, S.; Templer, R. H. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 1315.
(9) Attard, G. S.; Barlett, P. N.; Colemen, N. R. B.; Elliott, J. M.; Owen, J. R.; Wang, J. H. *Science* **1997**, *278*, 838.
(10) Wakayama, H.; Fukushima, Y. *Chem. Commun.* **1999**, 391.
(11) Song, Y.; Yang, Y.; Medforth, C. J.; Pereira, E.; Singh, A. K.; Xu, H.; Jiang, Y.; Brinker, C. J.; van Swol, F.; Shelnutt, J. A. *J. Am. Chem. Soc.* **2004**, *126*, 635.
(12) Yamauchi, Y.; Yokoshima, T.; Momma, T.; Osaka, T.; Kuroda, K. *Chem. Lett.* **2004**, *33*, 1576.
(13) Teng, X.; Liang, X.; Maksimuk, S.; Yang, H. *Small* **2006**, *2*, 249.
(14) Ullah, M. H.; Chung, W.-S.; Kim, I.; Ha, C.-S. *Small* **2006**, *2*, 870.
(15) Ding, Y.; Mathur, M.; Chen, M.; Erlebacher, J. *Angew. Chem., Int. Ed.* **2005**, *44*, 4003.
(16) Ramos, L.; Fabre, P. *Langmuir* **1997**, *13*, 682.
(17) Ramos, L.; Fabre, P.; Ober, R. *Eur. Phys. J. B* **1998**, *1*, 319.
(18) Ramos, L.; Molino, F. *Europhys. Lett.* **2000**, *1*, 320.
(19) Pena dos Santos, E.; Tokumoto, M. S.; Surendran, G.; Remita, H.; Bourgaux, C.; Dieudonné, P.; Prouzet, E.; Ramos, L. *Langmuir* **2005**, *21*, 4362.
(20) Surendran, G.; Pena dos Santos, E.; Tokumoto, M. S.; Remita, H.; Ramos, L.; Kooyman, P. J.; Santilly, C. S.; Bourgaux, C.; Dieudonné, P.; Prouzet, E. *Chem. Mater.* **2005**, *17*, 1505.
(21) Surendran, G.; Apostelescu, G.; Tokumoto, M.; Prouzet, E.; Ramos, L.; Beaunier, P.; Kooyman, P. J.; Etcheberry, A.; Remita, H. *Small* **2005**, *1*, 964.
(22) Belloni, J.; Mostafavi, M.; Remita, H.; Marignier, J. L.; Delcourt, M. O. *New J. Chem.* **1998**, *22*, 1239.

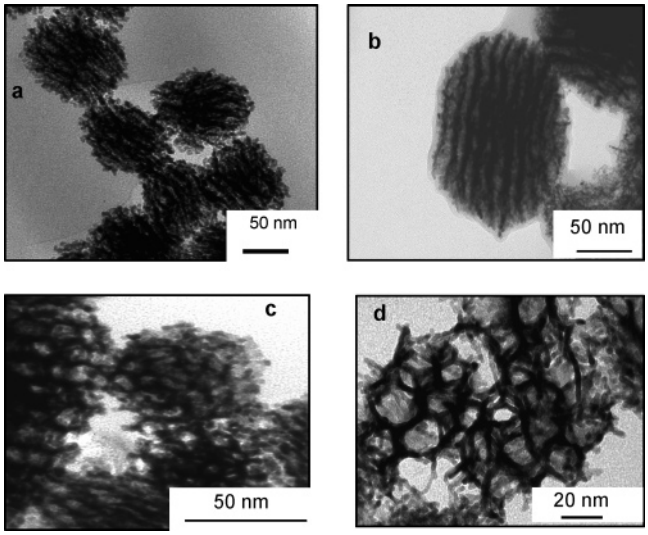

Figure 2. TEM images of porous platinum nanoballs made by connected nanowires and formed after complete reduction (16 h γ-irradiation). Dose rate 3 kGy/h.

reveal that platinum forms nanorods that aggregate into ball-shaped domains of typical size 50−80 nm (Figure 2a; a few aggregates were bigger than 100 nm). The average diameter of the nanorods is about 2.8 nm. These nanorods were built as a 3D interconnected network templated by the specific morphology of the soft template (anisotropy and hexagonal structure; Figure 2 b−d). In several balls, parallel nanowires spaced by 10 nm are observed (Figure 2a,b). In a few balls, hexagonal cells of 15−20 nm diameter were clearly observed as shown in Figure 2c,d. These observations correspond to a same structure viewed in two different planes, parallel or perpendicular to the rods. Remarkably, the diameter of the nanorods is comparable to the thickness of the water channels in between the cylinders (3 nm), and the characteristic distance of the cells is similar to the spacing between the oil-swollen cylinders in the host hexagonal phase (see scheme in Figure 1). The electron diffraction pattern and high-resolution TEM (HRTEM) images (see Supporting Information) show that the nanostructures are well crystallized. The actual confinement effect of this giant liquid crystal in spite of its lower viscosity, compared to conventional binary mesophases, is preserved upon irradiation as confirmed by SAXS analysis (Figure 1): the SAXS pattern of the irradiated sample displays the characteristic Bragg peaks of the host hexagonal phase. In addition a broad peak emerges at a smaller wave-vector, $q^* = 0.32$ nm^{-1}. This peak is due to the presence of the Pt nanostructures. The characteristic size associated to this peak, $2\pi/q^* \approx 20$ nm, corresponds to the typical distances between cells (Figure 2c,d and scheme in Figure 1). Moreover, the increase in the intensity scattered at very small wave vectors ($q < 0.2$ nm^{-1}), as compared to the signal before irradiation, indicates the presence of large objects, in accordance with the presence of nanoballs.

If we keep the mesophase at rest a few days after total reduction, we observe that the platinum particles settle, leaving the mesophase transparent. TEM observations confirm that the shape of the Pt nanoballs has been preserved (see Supporting Information).

The pore volume of the platinum nanoballs determined from the N_2 adsorption isotherm at a relative pressure of 0.95 is 0.055 cm^3·g^{-1} with a BET specific surface area of about 23 m^2·g^{-1}.[23] This value is close to that reported for mesoporous Pt synthesized by electro-reduction, 17−23 m^2·g^{-1}.[8,9] The BJH (Barrett−Joyner−Halenda) pore size distribution model[20] applied to the adsorption branch led to a pore diameter ranging from 6.6 to 9.6 nm.[24] Compared with silica on a molar ratio basis (SiO_2, 60 g, and Pt, 195.1 g), this value would correspond to a specific surface area of 74 m^2.

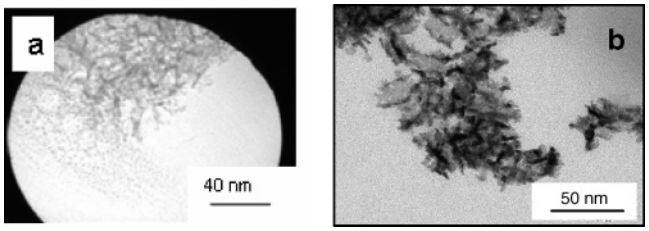

Figure 3. TEM images of (a) aggregated nanoparticles and fractal aggregates (b) obtained after partial reduction (6 h irradiation). Dose rate 3 kGy/h.

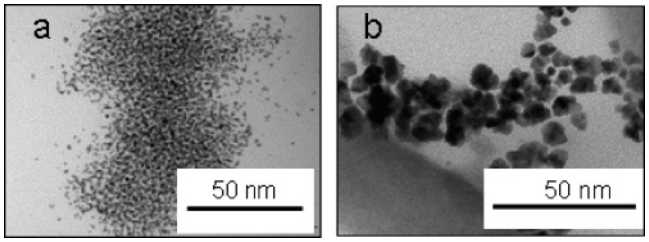

Figure 4. TEM images showing (a) individual spherical particles formed in a micellar solution containing CTAB and the platinum salt (15 h of γ-irradiation, dose rate 3 kGy·h^{-1}) and (b) large aggregates of platinum particles formed in the hexagonal mesophase when the reduction was carried using electron beams (30 kGy, dose rate 7.9 MGy·h^{-1}).

We studied the evolution of the nanoparticles shape with irradiation dose. After 6 h of irradiation (partial reduction), individual nanoparticles of 2 nm as well as nanorods and fractal aggregates are observed (Figure 3 and Supporting Information). The nanorods seem to result from the coalescence of spherical seeds (see HRTEM images in Supporting Information). This growth process has been recently observed for the formation of platinum rods synthesized by γ-irradiation of a platinum chloride/CTAB complex in the presence of hexanol.[25] Upon growth, the confinement imposed by the liquid crystal drives the nanorods connection, which leads to 3D nanostructures.

As a comparison, the reduction of platinum salt in a binary CTAB micellar solution instead of a giant hexagonal phase led only to 2 nm individual Pt nanoparticles without any aggregation (Figure 4a). Besides, a faster reduction performed with electron beams gives also spherical nanoparticles (6−8 nm; Figure 4b), which demonstrates that the slow reduction provided by γ-radiation is necessary to obtain these 3D nanostructures.

Other experiments were conducted by changing the symmetry of the liquid crystal: swollen lamellar phases

(23) Brunauer, S.; Emmet, P. H.; Teller, E. *J. Am. Chem. Soc*. **1938**, *60*, 309.
(24) Barrett, E. P.; Joyner, L. G.; Halenda, P. P. *J. Am. Chem. Soc*. **1951**, *78*, 373.
(25) Krishnaswamy, R.; Remita, H.; Imperor-Clerc, M.; Even, C.; Davidson, P.; Pansu, B. *ChemPhysChem* **2006**, *7*, 1510.

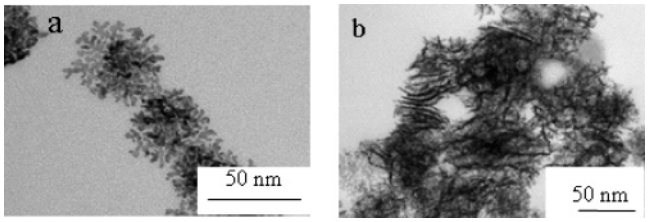

Figure 5. TEM images showing Pt fractals formed in a lamellar mesophase when the reduction was carried using γ-rays (30 kGy).

doped with platinum salt (0.1 M) were obtained by slightly increasing the ratio of cosurfactant/surfactant with respect to the one required for a hexagonal phase. Their lamellar structure was confirmed by both polarized light microscopy and SAXS. Pt nanomaterials were collected after complete reduction by γ-radiolysis and washing with 2-propanol. 2D objects are extracted, which are made either of fractal-like aggregates (Figure 5a) or of assembly of parallel nanorods (Figure 5b). This provides clear evidence that the symmetry of the liquid crystal directs the coalescence process of the spherical nanoparticles. Hence, our whole set of observations clearly demonstrates that the swollen hexagonal mesophases play an actual role of a soft template for the Pt nanoballs synthesis.

In summary, we have synthesized porous Pt nanoballs using soft templates made by a quaternary system as nanoreactors that form giant hexagonal liquid crystals. The mesophases can be doped by high concentrations of platinum (up to 0.2 M) without any disturbance which allows the quantitative synthesis of 3D Pt nanostructures made by interconnected nanorods. We have demonstrated that both confinement effect and slow reduction of the platinum salt are necessary to obtain the porous nanoballs. Catalytic and electro-catalytic activities of these nanostructures are under investigation.

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Supporting Information Available: Experimental details of the preparation of mesophase, characterization techniques, and additional TEM images (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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