## Integrated structural control of cage-type mesoporous platinum possessing both tunable large mesopores and variable surface structures by block copolymer-assisted Pt deposition in a hard-template<sup>†</sup>

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Cage-type mesoporous Pt with tunable large mesopores possessing smooth and rough pore surfaces were prepared selectively by the deposition of Pt in the absence and presence of a block copolymer in a hard-template, respectively.

Microstructural design of metals is important to provide useful properties, such as catalytic, electronic, magnetic, and optical properties, which leads to the applications including electrodes, sensors, and electrooptical devices.<sup>1</sup> Metal nanoparticles generally show size-dependent properties. High surface area resulting from a large amount of outer surfaces of nanoparticles is essential for the applications to sensors and catalysts. However, because most metal nanoparticles are randomly aggregated, guest diffusion is not controllable.

In contrast, the formation of uniform mesopores in metals is advantageous to the control of surface area, size selectivity, and guest diffusion.<sup>2</sup> The structure of mesoporous metals can be varied by using different templates and deposition processes. However, the integrated control of both pore size and surface structure is still an important issue. The expansion of pore size is certainly essential for efficient diffusion of large guest species, and the control of surface structure is quite influential to the increase in the surface area and also catalytic activities.

Recently, the syntheses of mesoporous Pt with large mesopores ca. 15 nm in size have been achieved by using block copolymer templates.<sup>3</sup> However, the pore size control in a wider range has not yet been established. Silica nanoparticle assembly is one of the ideal hard-templates because the pore size is easily controllable depending on the size of nanoparticles.

Although this method is based on the well-known colloidal templating to form macroporous metals,<sup>4</sup> the size control in mesopore range has recently been achieved for mesoporous carbon,<sup>5</sup> though the application to the preparation of mesoporous metals has not yet been reported.

To control the surface structure of mesoporous metals replicated with silica nanoparticles, we have focused on the use of a block copolymer Pluronic P123 ( $EO_{20}PO_{70}EO_{20}$ ) as a secondary template because it is effective to control the Pt deposition process. Pluronic block copolymers have been utilized for the syntheses of various metal nanoparticles (*e.g.* Au,<sup>6</sup> Pt,<sup>7</sup> and Pd<sup>8</sup>) by a surface capping mechanism. Therefore, the formation of pore walls consisting of roughly aggregated Pt nanoparticles is expected by the Pt deposition with the block copolymer. We have already revealed that some mesoporous Pt and alloys prepared by a soft-templating method have pore walls consisting of interconnected metal nanoparticles,<sup>9</sup> whereas the surface structures have not been controlled.

In this study, a dual-template consisting of silica nanoparticle assembly and Pluronic P123 was used for the structural control of mesoporous Pt (Scheme 1). The pore size was controlled by the size of the silica nanoparticles. Mesoporus Pt with smooth and rough pore surfaces were independently prepared by silica nanoparticle assembly only (single-template system) and the dual-template system, respectively.

Silica nanoparticles *ca.* 30 nm in size were prepared and assembled according to literatures<sup>5a,c</sup> with a slight modification and the details are described in the ESI.<sup>†</sup> The high-resolution scanning electron microscopy (HRSEM) images of the silica nanoparticle assembly is shown in Fig. S1 in the ESI.<sup>†</sup>



Scheme 1 Formation of mesoporous Pt with smooth and rough pore surfaces by single- and dual-template systems, respectively.

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The powdery nanoparticle assembly was dried under vacuum at room temperature. For the preparation of mesoporous Pt with smooth pore surfaces by a single-template system (denoted as MP-S), 0.1 g mL<sup>-1</sup> of H<sub>2</sub>PtCl<sub>6</sub>·6H<sub>2</sub>O in ethanol was used as a precursor solution. For the preparation of mesoporous Pt with rough pore surfaces by a dual-template system (denoted as MP-D), Pluronic P123 block copolymer was dissolved (3 mg mL $^{-1}$ ) in the same precursor solution as that of MP-S. The following procedure is common for both MP-S and MP-D. One gram of silica nanoparticle assembly was infiltrated with 0.2 mL of the precursor solution. The mixtures were placed in a closed vessel which contained dimethylamineborane (DMAB).<sup>10</sup> The reaction temperature was optimized to be at 40 °C where DMAB became liquid. The reaction was performed for three days. Unreacted H<sub>2</sub>PtCl<sub>6</sub> and excess DMAB were washed with water and ethanol after the reaction. The silica nanoparticles and P123 were removed by a HF treatment and washing twice with water, respectively. The EDX data of the products did not show the remaining of Si. The characterization techniques are described in the ESI.<sup>†</sup>

The small angle X-ray scattering (SAXS) pattern of the template (silica nanoparticle assembly only) shows several peaks which can be interpreted as the overlapping of peaks corresponding to a face-centered cubic arrangement of the nanoparticles (Fig. 1A).<sup>5a,b</sup> The SAXS profiles of MP-S and MP-D are similar to that observed for the template though the resolution is lowered (Fig. 1B and C). Direct observation of both MP-S and MP-D by HRSEM shows the highly ordered pore arrangements, which are attributable to the formation of the inverse structure of the template (Fig. 1a and b). The broadening of the SAXS peaks (Fig. 1B and C) after the replication is probably due to the short coherent length of the ordered mesostructures, which is similar to that reported previously using a soft-template.<sup>9</sup> The better structural ordering of MP-D than MP-S is possibly due to the flexible framework consisting of roughly aggregated Pt nanoparticles. When silica nanoparticles ca. 15 nm in size were used as templates, such a replication was also confirmed (Fig. S2, ESI<sup>+</sup>).



Fig. 1 (left) SAXS patterns of (A) the template, (B) MP-S, and (C) MP-D. (right) HRSEM images of (a) MP-S and (b) MP-D recorded along [111].

Highly magnified HRSEM images of both MP-S and MP-D (Fig. 2a and b) show spherical mesopores. The details of the images display the outlines of the pore surfaces indicated by blue lines, showing that MP-S and MP-D possess smooth and rough pore surfaces, respectively. The wall thicknesses of MP-S and MP-D are 2-4 and 3-8 nm, respectively, the variation of which corresponds to their surface roughness. Fig. S3 in the ESI<sup>†</sup> also shows smooth pore walls of mesoporous Pt prepared by the single-template system with different size of silica nanoparticles. The high-resolution transmission electron microscopy (HRTEM) image of MP-S does not show any specific features on the pore walls, though it seems that the pore walls consist of irregular Pt nanoparticles (Fig. 2c). The domain size of Pt crystallites observed in the high magnification image of MP-S is typically 5-10 nm in size (Fig. S4, ESI<sup>+</sup>), suggesting that the pore walls consist of many small Pt crystallites. The selective area electron diffraction (SAED) pattern of MP-S shows a ring-like pattern with many intense spots, which corresponds to the presence of many small Pt domains in the pore walls (Fig. 2e). Such pore walls can be formed by continuous grain growth of Pt with a small amount of Pt nuclei.9 In contrast, the pore walls of MP-D consist of roughly aggregated spherical Pt nanoparticles 3-4 nm in size (Fig. 2d). Each nanoparticle is a single crystal and the size and shape of the Pt nanoparticles are uniform probably due to the surface stabilization with P123. The SAED pattern of MP-D is attributable to random crystal orientation of the Pt nanoparticles in the pore walls (Fig. 2f). Because both samples consist of small Pt nanoparticles in the pore walls, little difference was observed in the wide-angle X-ray diffraction (WAXD) patterns (Fig. S5, ESI<sup>+</sup>). Low magnification TEM images (Fig. S6, ESI<sup>†</sup>) show that similar features are present in a wide range of samples.

The porosity of the mesoporous Pt reflects the difference of the surface structures. The Brunauer-Emmett-Teller (BET)equivalent surface areas of MP-S and MP-D were 40 and 70 m<sup>2</sup> g<sup>-1</sup>, respectively.<sup>11</sup> The calculated surface area of a hypothetical Pt nanoparticle 3 nm in size is *ca.* 93 m<sup>2</sup> g<sup>-1</sup>, therefore, many surfaces, where N2 molecules can access, should be exposed inside the pore walls of MP-D. The N<sub>2</sub> adsorption-desorption isotherm and Barrett-Joyner-Halenda (BJH) pore size distribution of MP-S (Fig. S7A and C, ESI<sup>†</sup>) show the presence of only large mesopores (ca. 30 nm). In contrast, those of MP-D (Fig. S7B, D, and E, ESI<sup>+</sup>) show the presence of large mesopores (ca. 30 nm) and possibly small mesopores among Pt nanoparticles (ca. 5 nm).<sup>12</sup> An uptake in the low pressure region  $(P/P_0 < 0.1)$ , observed for the isotherm of MP-D, is also attributable to the cavities. The reason for the large hysteresis in the isotherm of MP-D is unclear, which might be due to slow diffusion of N2 in the cavities.

In the single-template system, a relatively highly crystalline framework was formed by continuous grain growth of Pt.<sup>9,10</sup> In the dual-template system, the adsorption of P123 on the surface of Pt suppresses the continuous growth of Pt nanoparticles. Additionally, the spatial occupancy of polymer chain among Pt nanoparticles causes the formation of the cavities. We think that the possibility of micelle formation of P123 on Pt nanocrystals in the voids of the silica nanoparticle assembly





**Fig. 2** HRSEM images of the pore walls of (a) MP-S and (b) MP-D. Blue lines indicate the outlines of the surfaces. HRTEM images of (c) MP-S and (d) MP-D. SAED patterns of (e) MP-S and (f) MP-D in circular areas 160 nm in diameter.

is low, though further studies on micelle formation within confined spaces, depending on the space size, is necessary.

In conclusion, we have demonstrated the control of pore size and surface structure of cage-type mesoporous Pt by using single- and dual-templates consisting of a silica nanoparticle assembly and a block copolymer. High surface area of *ca*. 70 m<sup>2</sup> g<sup>-1</sup> was observed in spite of large mesopores *ca*. 30 nm in size. The varied crystallinity and pore surfaces are essential to the development of catalytic activity and optical property. The concept, the block copolymer-assisted metal deposition in a confined space of hard-templates, should be effective for further control of crystal surfaces (*e.g.* formation of catalytically active facets on the surface) by using proper capping agents.

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## Notes and references

- (a) A. N. Shipway and I. Willner, Chem. Commun., 2001, 2035;
   (b) W. P. Zhou, A. Lewera, R. Larsen, R. I. Masel, P. S. Bagus and A. Wieckowski, J. Phys. Chem. B, 2006, 110, 13393;
   (c) R. Narayanan and M. A. El-Sayed, J. Phys. Chem. B, 2005, 109, 12663; (d) S. Sun, Adv. Mater., 2006, 18, 393; (e) P. V. Kamat, J. Phys. Chem. B, 2002, 106, 7729; (f) C. M. Welch and R. G. Compton, Anal. Bioanal. Chem., 2006, 384, 601;
   (g) Y. Xia, Y. Xiong, B. Lim and S. E. Skrabalak, Angew. Chem., Int. Ed., 2009, 48, 60.
- Y. Yamauchi and K. Kuroda, *Chem.-Asian J.*, 2008, **3**, 664;
   G. S. Attard, J. M. Corker, C. G. Göltner, S. Henke and R. H. Templer, *Angew. Chem.*, 1997, **109**, 1372; (c) Y. Yamauchi, T. Yokoshima, H. Mukaibo, M. Tezuka, T. Shigeno, T. Momma, T. Osaka and K. Kuroda, *Chem. Lett.*, 2004, **33**, 542;
   (d) H. J. Shin, R. Ryoo, Z. Liu and O. Terasaki, *J. Am. Chem. Soc.*, 2001, **123**, 1246.
- 3 (a) Y. Yamauchi, A. Sugiyama, R. Morimoto, A. Takai and K. Kuroda, Angew. Chem., Int. Ed., 2008, 47, 5371; (b) S. C. Warren, L. C. Messina, L. S. Slaughter, M. Kamperman, Q. Zhou, S. M. Gruner, F. J. DiSalvo and U. Wiesner, Science, 2008, 320, 1748.
- 4 (a) O. D. Velev, P. M. Tessier, A. M. Lenhoff and E. W. Kaler, *Nature*, 1999, **401**, 548; (b) Y. Yamauchi and K. Kuroda, *Electrochem. Commun.*, 2006, **8**, 1677.
- 5 (a) T. Yokoi, Y. Sakamoto, O. Terasaki, Y. Kubota, T. Okubo and T. Tatsumi, J. Am. Chem. Soc., 2006, **128**, 13664; (b) W. Fan, M. A. Snyder, S. Kumar, P.-S. Lee, W. C. Yoo, A. V. McCormick, R. L. Penn, A. Stein and M. Tsapatsis, Nat. Mater., 2008, **7**, 984; (c) K. D. Hartlen, A. P. T. Athanasopoulos and V. Kitaev, Langmuir, 2008, **24**, 1714; (d) T. Yokoi, J. Wakabayashi, Y. Otsuka, W. Fan, M. Iwama, R. Watanabe, K. Aramaki, A. Shimojima, T. Tatsumi and T. Okubo, Chem. Mater., 2009, **21**, 3719.
- 6 (a) T. Sakai and P. Alexandridis, *Langmuir*, 2004, 20, 8426;
  (b) T. Sakai and P. Alexandridis, *J. Phys. Chem. B*, 2005, 109, 7766;
  (c) X. Wang, H. Kawanami, N. M. Islam, M. Chattergee, T. Yokoyama and Y. Ikushima, *Chem. Commun.*, 2008, 4442;
  (d) K. Rahme, F. Gauffre, J.-D. Marty, B. Payré and C. Mingotaud, *J. Phys. Chem. C*, 2007, 111, 7273.
- 7 K. Niesz, M. Grass and G. A. Somorjai, Nano Lett., 2005, 5, 2238.
- 8 Y. Piao, Y. Jang, M. Shokouhimehr, I. S. Lee and T. Hyeon, Small, 2007, 3, 255.
- (a) Y. Yamauchi, T. Momma, M. Fuziwara, S. S. Nair, T. Ohsuna, O. Terasaki, T. Osaka and K. Kuroda, *Chem. Mater.*, 2005, 17, 6342; (b) Y. Yamauchi, S. S. Nair, T. Momma, T. Ohsuna, T. Osaka and K. Kuroda, *J. Mater. Chem.*, 2006, 16, 2229; (c) Y. Yamauchi, T. Ohsuna and K. Kuroda, *Chem. Mater.*, 2007, 19, 1335; (d) Y. Yamauchi, A. Takai, T. Nagaura, S. Inoue and K. Kuroda, *J. Am. Chem. Soc.*, 2008, 130, 5426.
- 10 Y. Yamauchi, A. Takai, M. Komatsu, M. Sawada, T. Ohsuna and K. Kuroda, *Chem. Mater.*, 2008, 20, 1004.
- 11 M. Asai, T. Onoe, H. Kanoh and K. Kaneko, *Colloids Surf.*, A, 2005, 253, 199.
- 12 The size of the small mesopores could be overestimated due to the shifts of  $N_2$  adsorption amount from the equilibria, which is suggested by the presence of large hysteresis.