Supplementary Material (ESI) for Chemical Communications

Electronic Supplementary Information

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

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Preparation of silica nanoparticle assembly

Silica nanoparticles *ca*. 12 nm in size were basically prepared according to the literature (T. Yokoi *et al.*, *J. Am. Chem. Soc.*, 2006, **128**, 13664.) and the growth of the nanoparticles into those *ca*. 30 nm in size was based on the literature (K. D. Hartlen *et al.*, *Langmuir*, 2008, **24**, 1714.). Octane was not used for the ease of handling. We confirmed that the silica nanoparticles synthesized without octane were almost similar to those reported by Yokoi *et al.* and Hartlen *et al.*

TEOS and L-lysine were dissolved in deionized water (H_2O:TEOS:L-lysine = 154.4:1:0.02). The mixture was stirred vigorously for 20 h at 60 ˚C to obtain monodispersed silica nanoparticles *ca*. 12 nm in diameter (seed solution). Then, the silica nanoparticles were grown in the mixture with the same composition under the same condition. The volume of the mixture was 14 times larger than that of the seed solution to obtain monodispersed silica nanoparticles *ca*. 30 nm in diameter. A silica nanoparticle assembly was obtained by drying up the solution and the following calcination at 550 ˚C for 6 h.

Characterization techniques

High-resolution scanning electron microscopy (HRSEM) images were recorded by a Hitachi S-5500 microscope at an accelerating voltage of 30 kV. The samples were observed without any metal coating. High-resolution transmission electron microscopy (HRTEM) images and selective area electron diffraction (SAED) patterns were recorded by a JEOL JEM-2010 microscope at an accelerating voltage of 200kV. Samples were dispersed in ethanol and mounted on a STEM microgrid for the HRSEM and HRTEM operation. Small-angle X-ray scattering (SAXS) measurement was performed with a Rigaku Nano-Viewer using CuKα radiation under the operating conditions of 40 kV and 30 mA. N_2 adsorption-desorption isotherms were measured by a Quantachrome Autosorb-1 instrument at 77 K. The samples were outgassed under vacuum at room temperature for 24 h. The Brunauer-Emmett-Teller (BET) surface area was calculated from adsorption branch in the relative pressure range from 0.05 to 0.10. The Barrett-Joyner-Halenda (BJH) pore size distribution was calculated from adsorption branch in the relative pressure range from 0.20 to 1.0. Wide angle X-ray diffraction (WAXD) measurement was performed with a Rigaku Ultima-III diffractometer using CuKα radiation under the operating conditions of 40 kV and 40 mA.

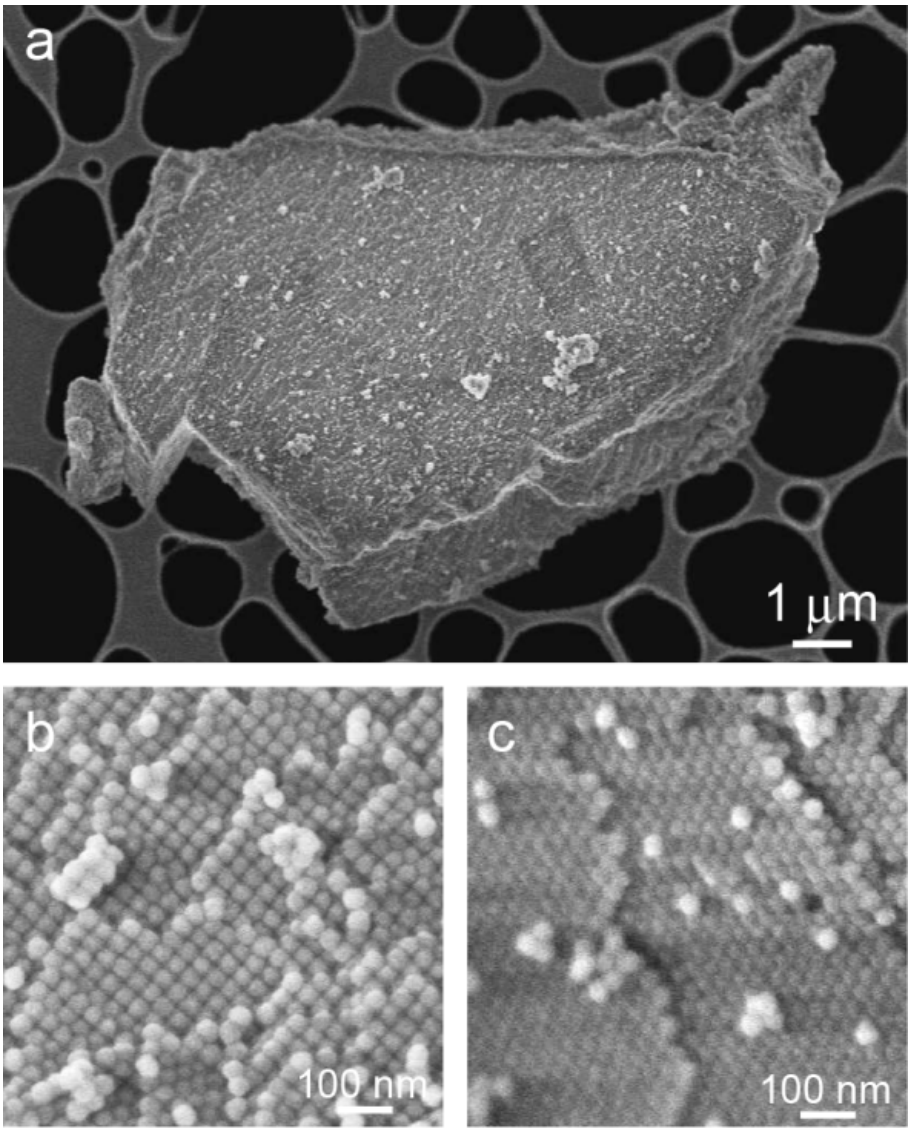

Fig. S1 HRSEM images of (a) silica nanoparticle assembly and (b, c) high-magnification images recorded along [100] and [111] axes.

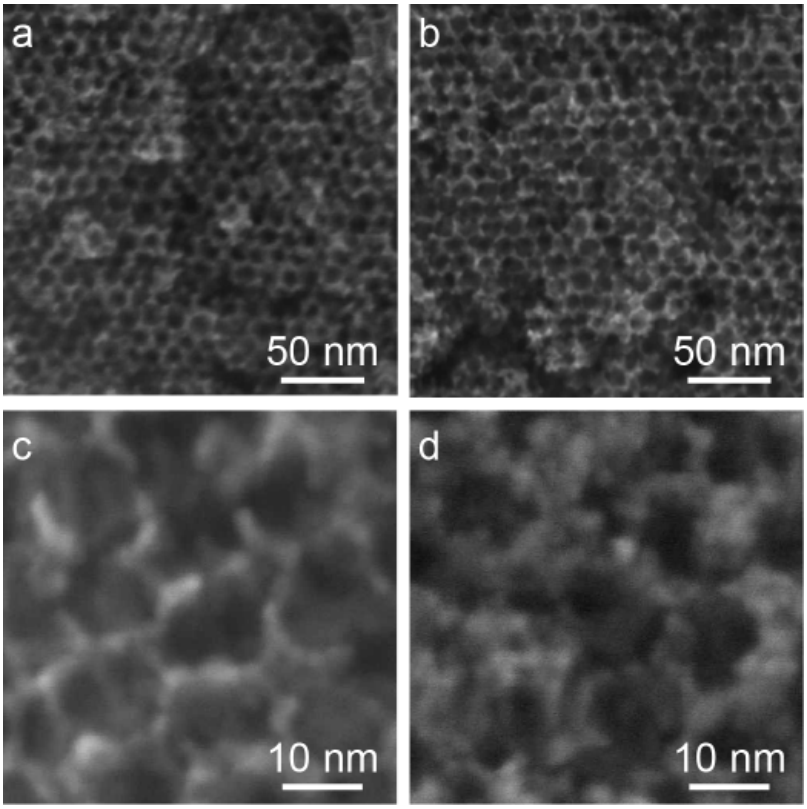

Fig. S2 HRSEM images of (a, c) Pt replica by single-template system and (b, d) dual-template system using silica nanoparticles 15 nm in size.

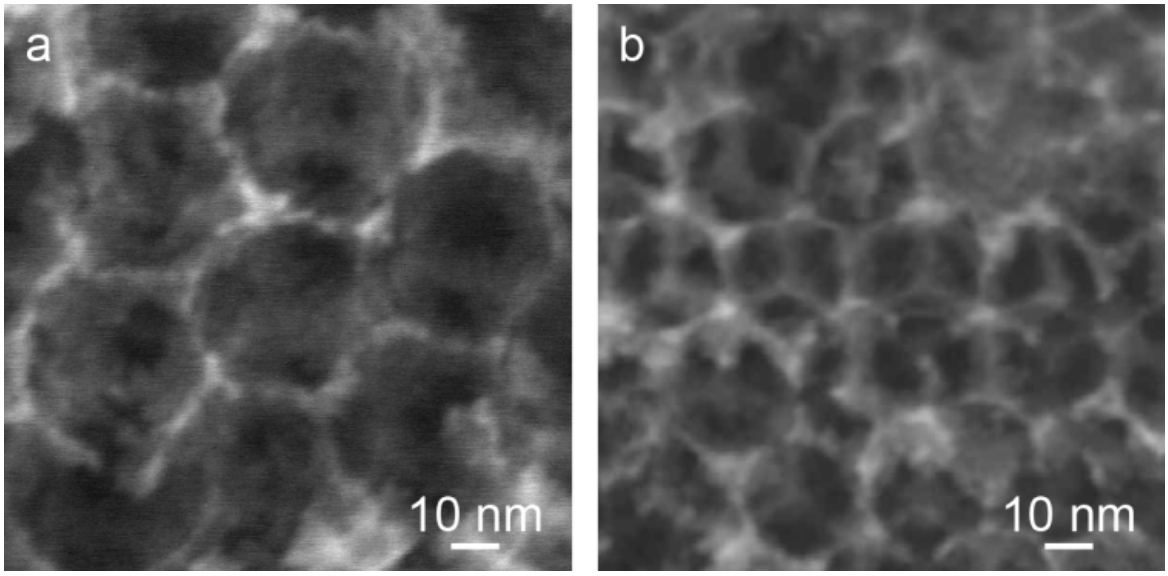

Fig. S3 HRSEM images of mesoporous Pt prepared by the single-template system using silica nanoparticles (a) *ca.* 40 nm and (b) *ca.* 25 nm in size. Both images show spherical mesopores with smooth pore surfaces.

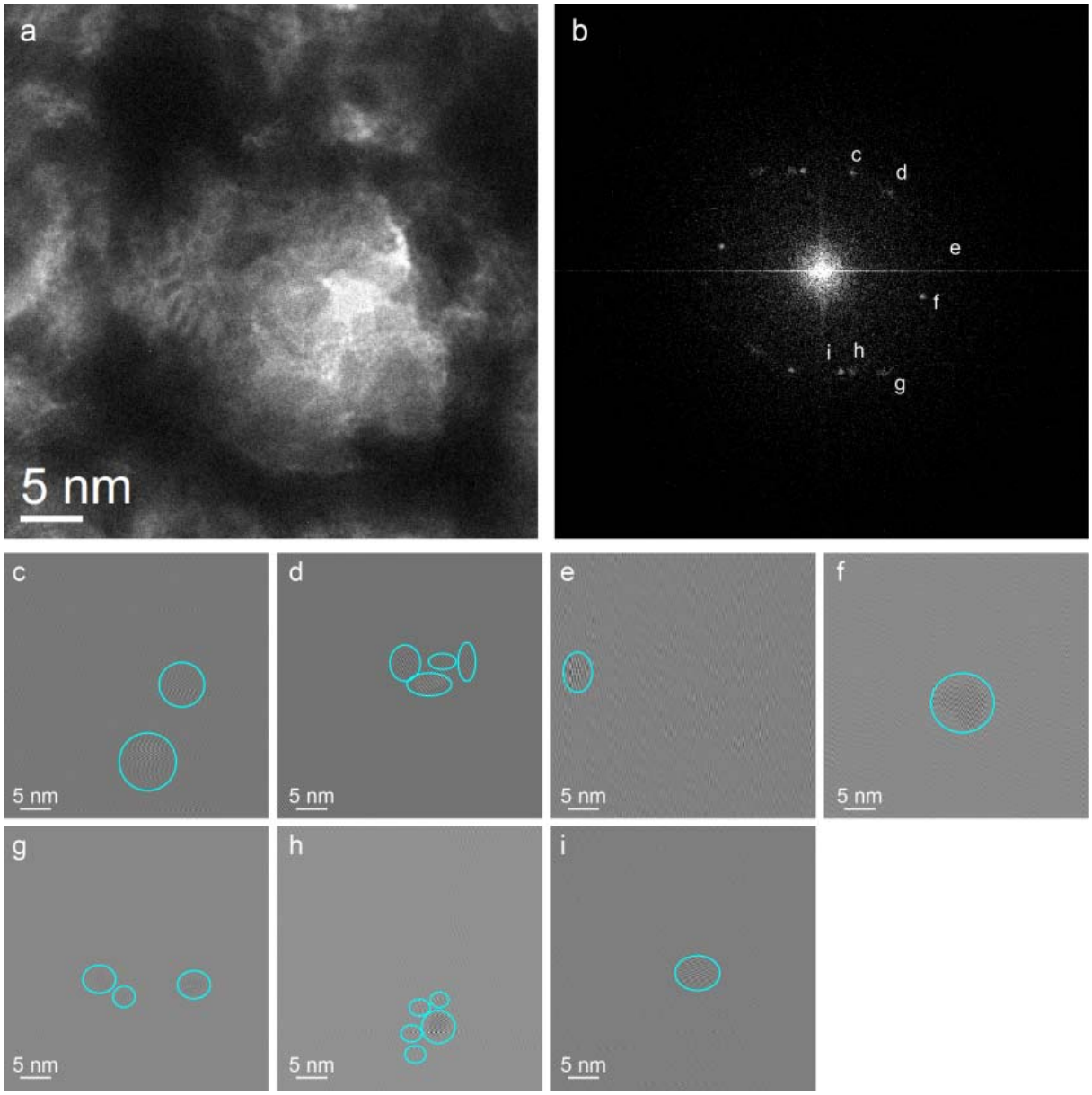

Fig. S4 (a) HRTEM image of MP-S and (b) the corresponding FFT pattern. The spots correspond to the lattice fringes of fcc Pt observed in the image (a). Images (c-i) are inverse fast Fourier transforms of the FFT pattern (b) extracting each spot. The size of the images was reduced in half. The fringes (shown in the blue ellipses) observed in the images (c-i) correspond to Pt crystal, showing that each crystal domain is typically 5-10 nm in size.

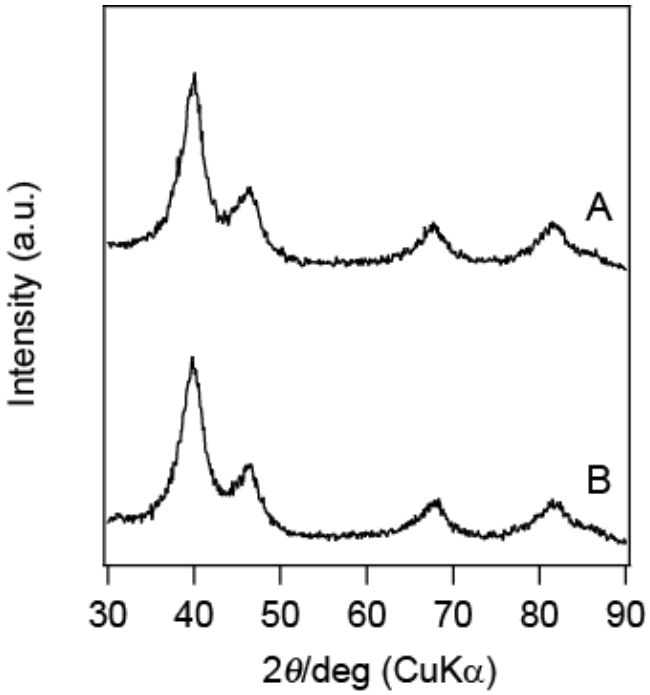

Fig. S5 WAXD patterns of (A) MP-S and (B) MP-D.

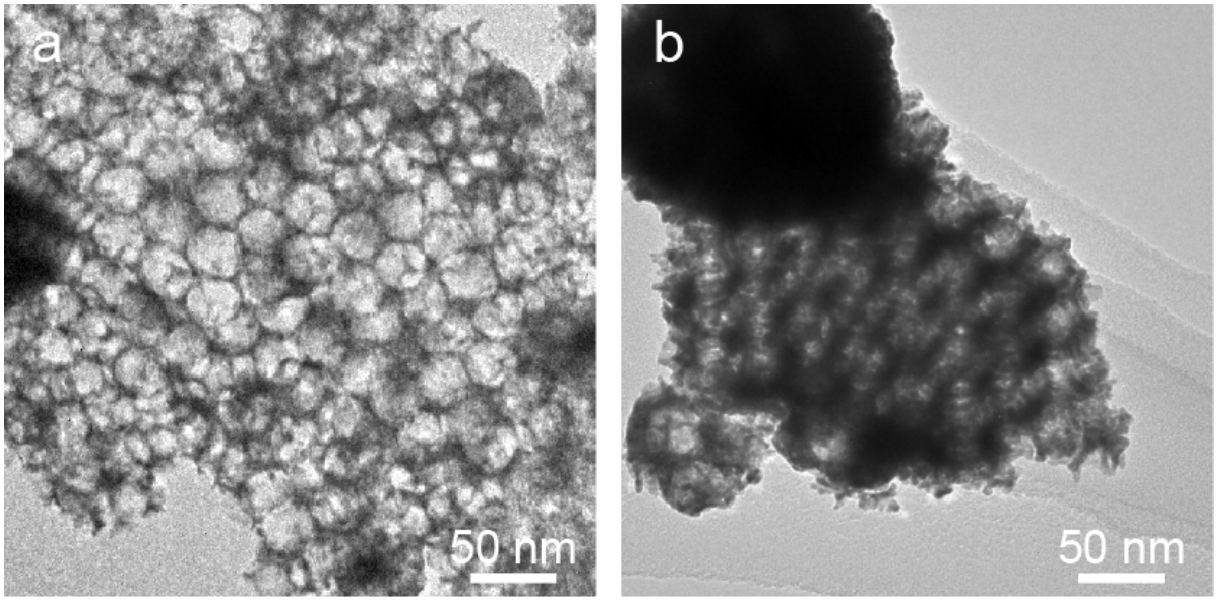

Fig. S6 Low magnification HRTEM images of (a) MP-S and (b) MP-D.

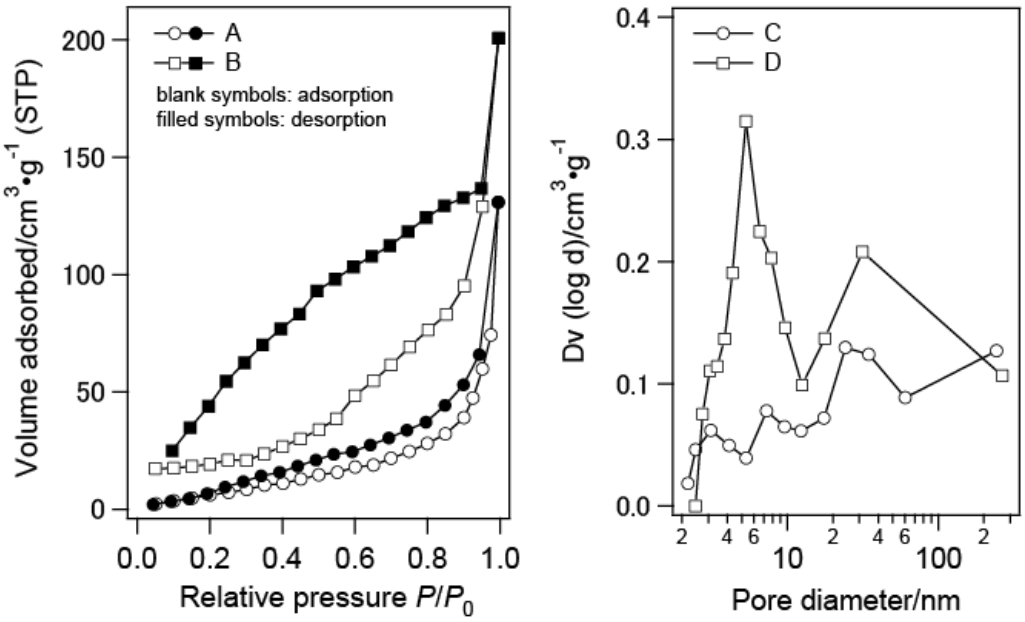

Fig. S7 N_2 adsorption-desorption isotherms of (A) MP-S and (B) MP-D. BJH pore size distributions (Dv (log d) ≡ d*V*/d(log D)) of (C) MP-S and (D) MP-D.