Electronic Supplementary Information (ESI)

Experimental details

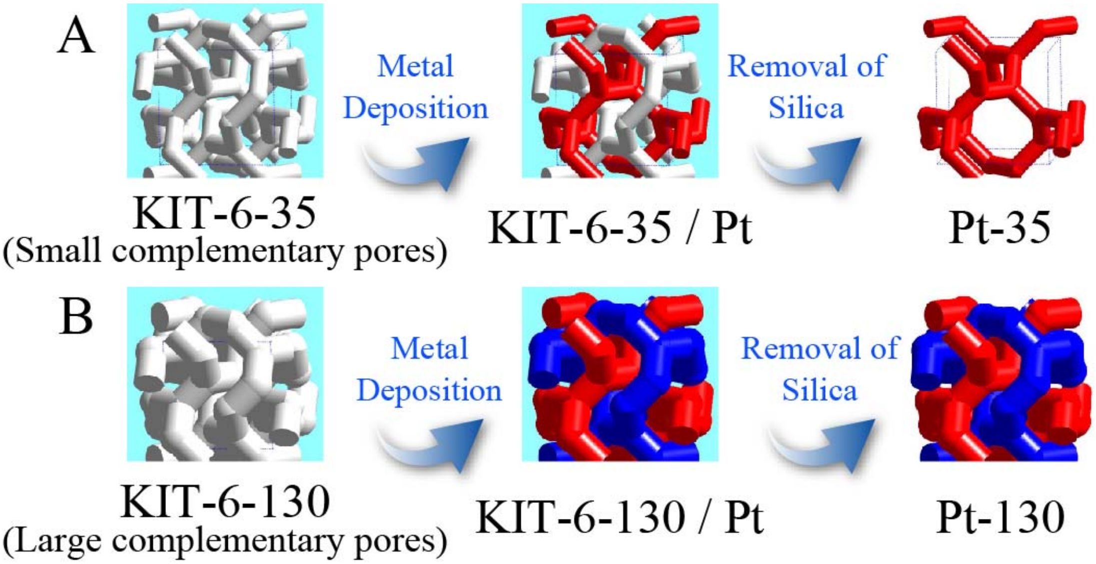
1. Preparation of KIT-6 mesoporous silica:

Conc. HCl solution (37 wt%) and Pluronic P123 were dissolved in water. After the dissolution, n-butanol was added and stirred at 35°C for 1 h. Then, 12.9 g tetraethoxysilane (TEOS) was dropped into the homogeneous clear solution and stirred at 35°C for 24 h. After that, the solution was placed at 35, 100, and 130°C for 24 h (hydrothermal treatment). Finally, KIT-6-‘x’ was obtained after washing with ethanol/HCl solution and calcined at 823 K in air (‘x’ indicates the temperature of the hydrothermal treatment).

2. Preparation of mesoporous Pt:

In the Pt deposition process, KIT-6-‘x’ (1.2 g) was immersed into 3.6 ml aqueous H_2PtCl_6 solution (30 wt%, pH < 1). Then, the composite was dried under reduced vacuum condition at room temperature. After complete drying, yellow powders were obtained and placed in a closed vessel (380 mL) at 40°C with 1.0 g dimethylamineborane (DMAB). The powders were reacted with DMAB vapor for 5 days. When DMAB vapor molecules reach the Pt species located inside the mesopores, they release considerable amounts of electrons, and eventually the Pt species are reduced. After 5 days, the color was changed to black, indicating the successful deposition of Pt. The obtained black powders were washed twice with H_2O to remove the un-reacted Pt species. Finally, after removing the silica with an 20 ml HF solution (10 wt%), mesoporous Pt-‘*x*’ was obtained as a final product.

Figure S1



5 **Figure S1** Enlarged image of Figure 1. Schematic presentation of the synthesis of Pt replicas from KIT-6 with different pore diameters. The white region indicates the mesopores in the KIT-6, while the highlighted region indicates the Pt deposition inside the mesopores. The blue and read regions in Pt-130 indicate the Pt deposition within the different sides of the KIT-6 mesopores.

Figure S2

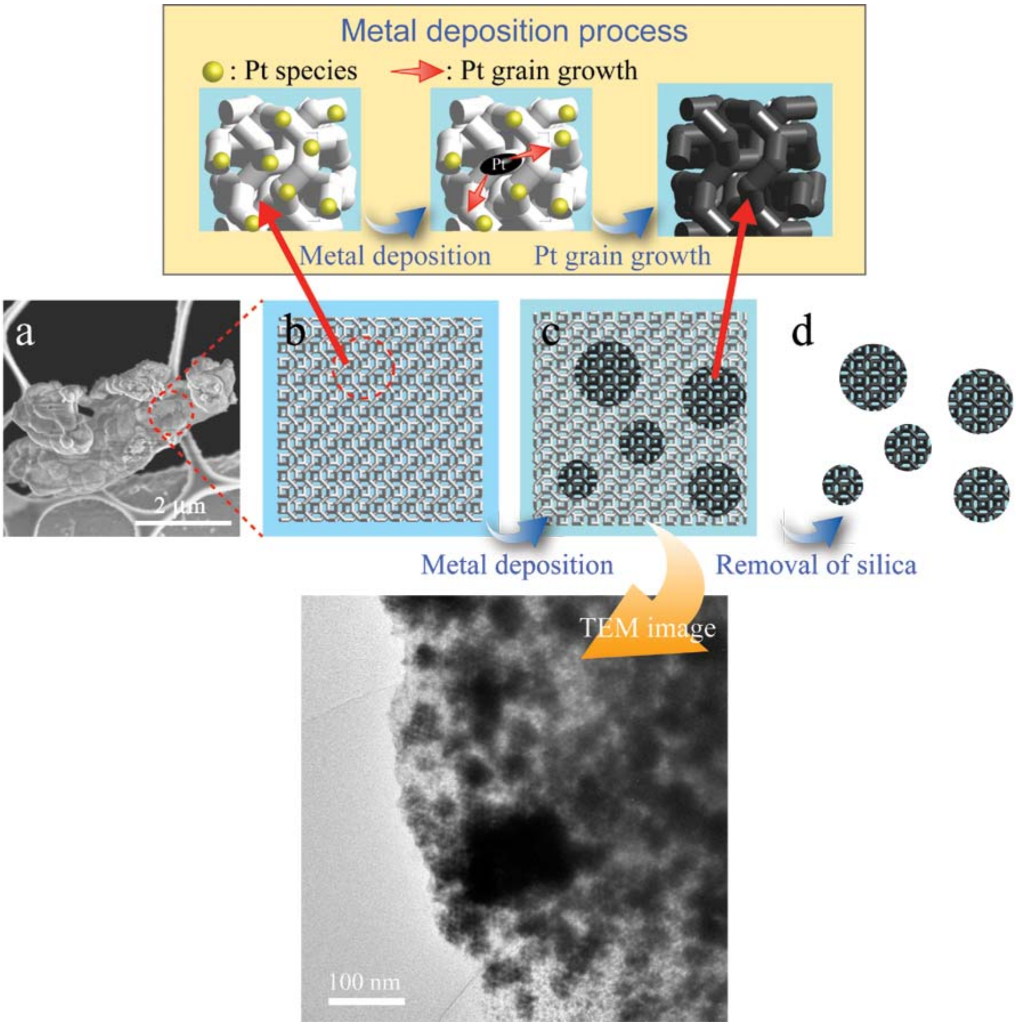


Figure S2 Schematic presentation of the Pt deposition behavior inside the KIT-6. (a) Low magnified SEM image of the orignal KIT-6. (b) Infiltration step of the Pt precursor solution. The used precursor solution is very acidic (pH < 1). Therefore, the silica surface is positively charged after the infiltration of the precursor solution. The Si-OH groups on the surface exist as a protonated state ($Si(OH_2^+)$). It is natural that the negative Pt species ($[PtCl_6]^{-2}$) dissolved in the precursor solution are interacted with the protonated $Si(OH_2^+)$ sites. (c) Pt deposition step inside the mesoporous silica matrix. From the TEM observation of mesoporous silica/Pt composites after the Pt deposition (The black parts in the TEM image indicated the deposited Pt), it is proved that the Pt was not deposited over the entire area, but located in some parts. No Pt deposition was observed outside the mesoporous silica and all the Pt deposition was carried out inside the mesoporous silica matrix. (d) Removal of silica.

Figure S3

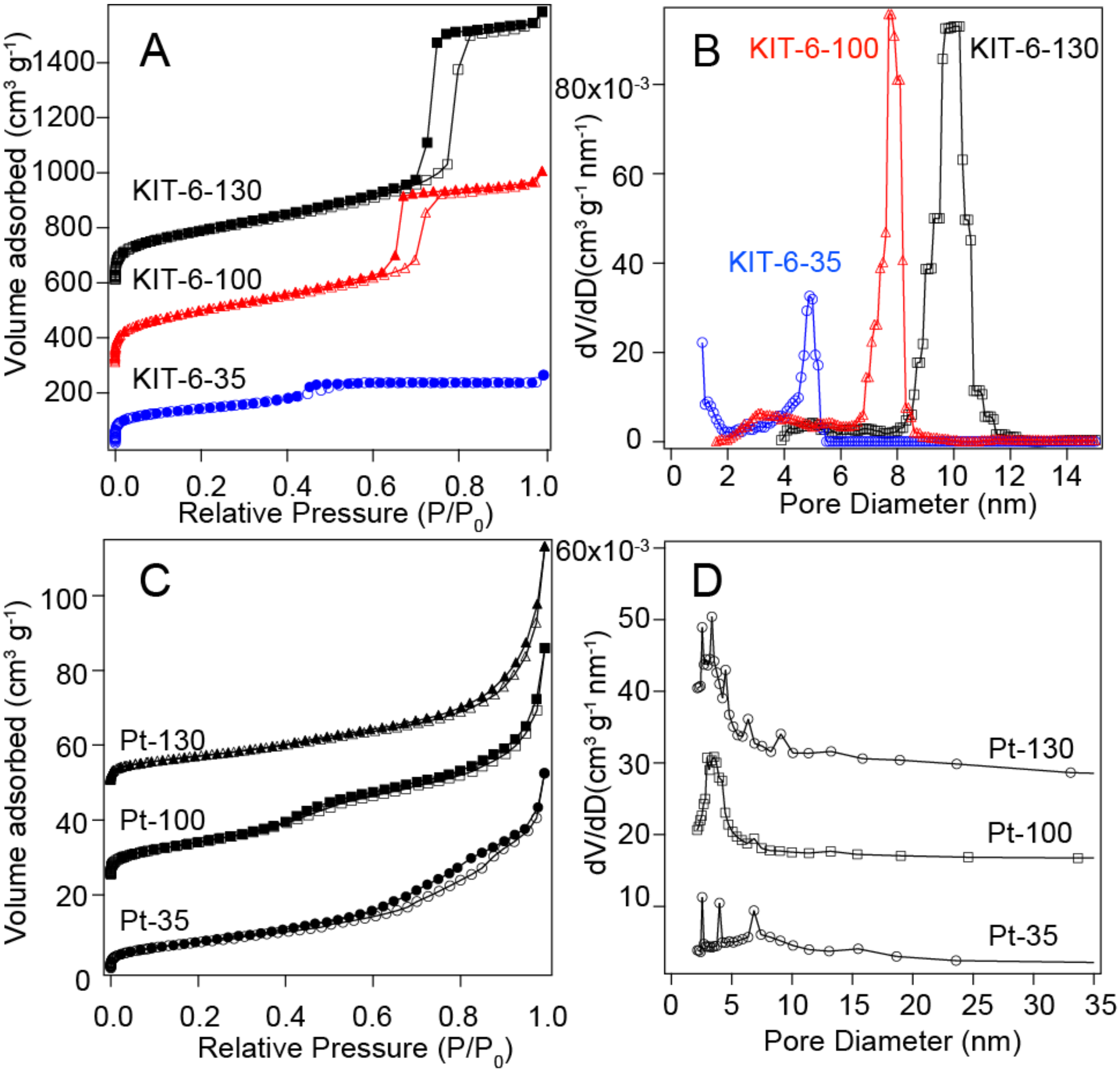


Figure S3 N_2 adsorption-desorption isotherms and pore-size distribution curves of KIT-6 mesoporous silica (A and B) and their Pt replicas (C and D). The BET surface areas are calculated to be 490 $m^2•g^{-1}$ (for KIT-6-35), 720 $m^2•g^{-1}$ (for KIT-6-100), 690 $m^2•g^{-1}$ (for KIT-6-130), 30 $m^2•g^{-1}$ (for Pt-35), 35 $m^2•g^{-1}$ (for Pt-100), and 38 $m^2•g^{-1}$ (for Pt-130). To calculate the average pore sizes of KIT-6-‘x’ and Pt-‘x’, we utilized a NLDFT (Non-Localized Density Functional Theory) method and a BJH method, respectively. Here we used a BJH method traditionally regarded as a high-integrity method for the Pt-‘x’, because the NLDFT is established based on the adsorption modeling onto silica or carbon surfaces.

Explanation of Figure S3:

The N_2 adsorption-desorption isotherms of mesoporous silica KIT-6 showed type IV isotherms with hysteresis loops (Fig. S3). The pore-size distribution curves of KIT-6-100 and KIT-6-130 showed both the main mesopores and the complementary pores. The additional peaks, observed as smaller than the main peaks, indicated the complementary pores. Both sizes increased gradually with the increase of the temperature during the hydrothermal treatment. At temperatures higher than the clouding point (*e.g.*, clouding point of Pluronic P123 is 85 °C), micelles consisting of P123 molecules become larger in the solutions and strongly interact with each other to form bridges connecting themselves to one another. The acceleration of such a phenomenon makes the sizes of complementary pores larger, which coincides with the following previous report.

[Reference] A. Galarneau, H. Cambon, F. D. Renzo, R. Ryoo, M. Choi and F. Fajula, *New J. Chem.*, 2003, **27**, 73.

Figure S4

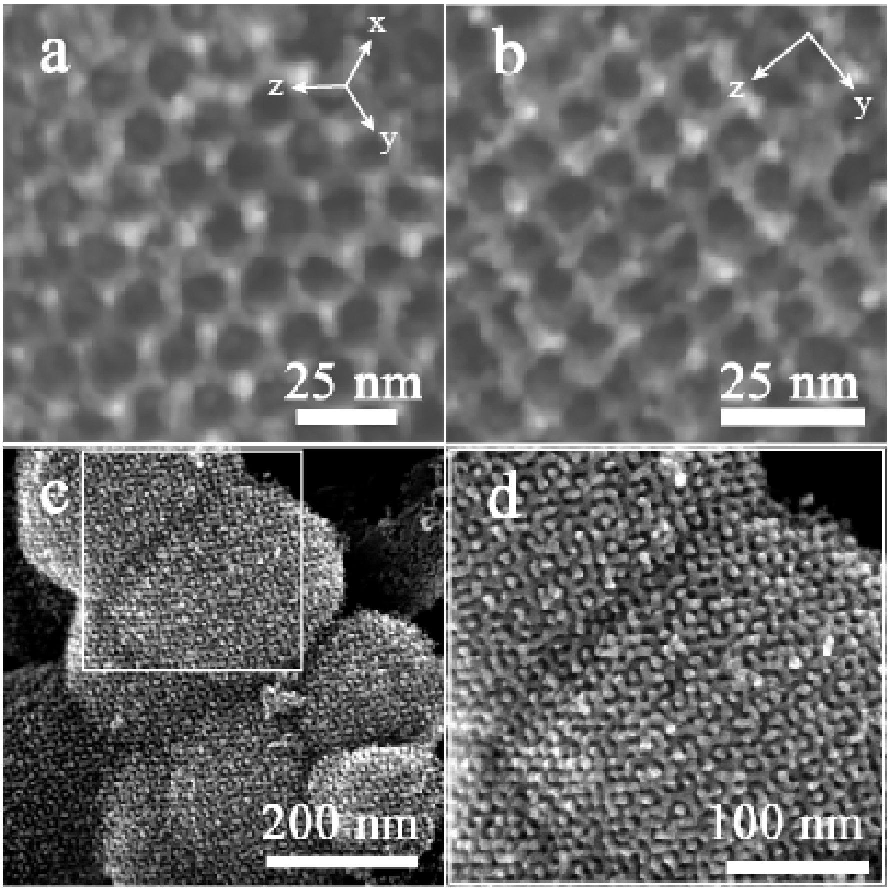


Figure S4 High resolution SEM images of (a, b) Pt-35 taken with [111] and [100] and (c, d) Pt-100.
5 Figure (d) is an enlarged image of the square area of Figure (c).

Figure S5

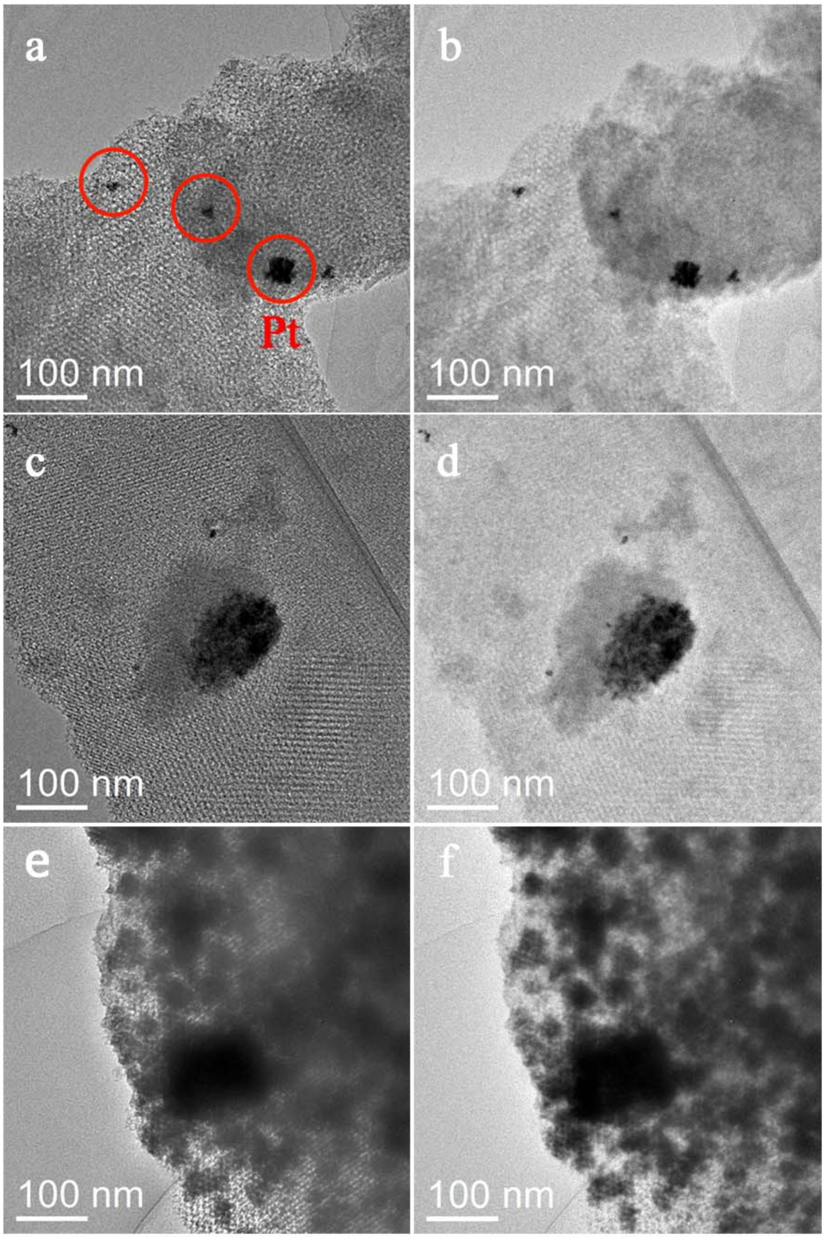


Figure S5 TEM images of mesoporous silica/Pt composites prepared by different Pt deposition periods ((a and b) 5 hours, (c and d) 1 day, and (e and f) 5 days). Two types of TEM observation were conducted. Figures a, c, and e were taken when the electron beam was focused on mesoporous silica, while Figures b, d, and f were taken when the electron beam was focused on the deposited Pt.

Explanation of Figure S5:

At the initial stage of the Pt deposition (**Figure S5a,b**), small Pt nanoparticles (a few dozens nanometer) were observed. With the increase of the deposition period, the size of the Pt nanoparticles was gradually increased (**Figure S5c,d**). During this stage, the infiltrated Pt species move to the initial nucleation sites and are reduced by vaporized DMAB, because the grain growth occurs more easily compared to the nucleation reaction. Then, the Pt particles isotropically grow inside the mesoporous silica matrix. After 5 days (**Figure S5e,f**), almost all the Pt species were reduced and the Pt growth was terminated. All the pore voids of the mesoporous silica were not completely filled with the deposited Pt, because the amount of Pt in the precursor solution is clearly insufficient. After the silica removal, the Pt particles with around a few hundred nanometers were obtained. The average size is much smaller rather than that of the original mesoporous silica particles (around a few micrometers). Concequently, it is proved that the spherical shape in the products is not derived from the original morphology of the KIT-6 templates, but is created by isotropic grain growth of the Pt.

When the Pt deposition was terminated (**Figure S5e,f**), the Pt was not deposited over the entire area and the deposited Pt was located inside the mesoporous silica matrix. No Pt deposition was observed outside the mesoporous silica. Therefore, all the deposited Pt particles can possess ordered nanostructure replicated from the original mesoporous silica without any formation of by-products.

Figure S6

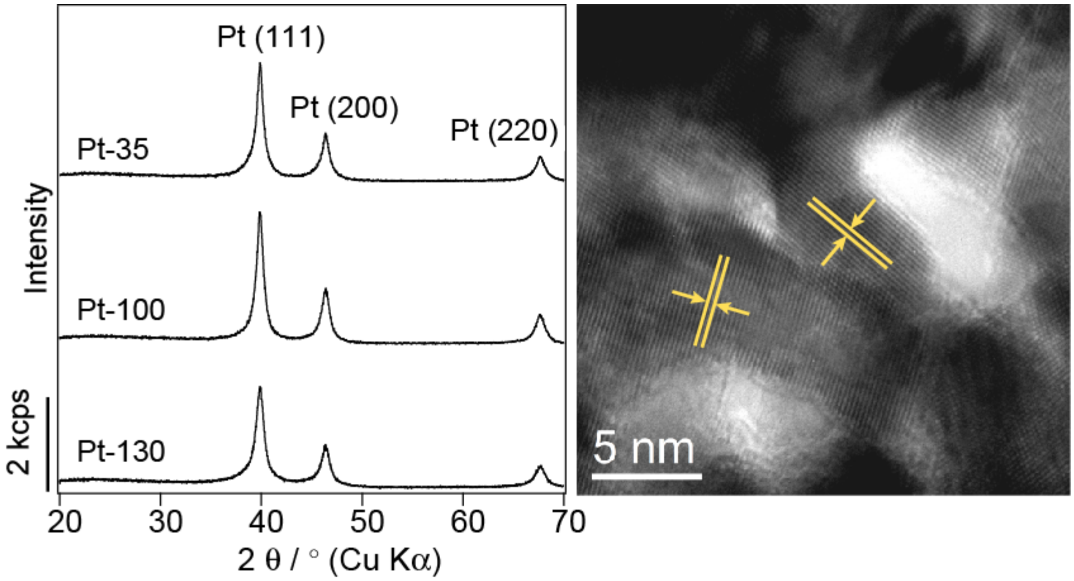


Figure S6 (Left side) Wide-angle XRD profiles of Pt-35, Pt-100, and Pt-130. (Right side) High-resolution TEM image of Pt-130. Lattice fringes corresponding to {111} planes of Pt are observed. Both *d* spacings are measured at 0.23 nm.

Figure S7

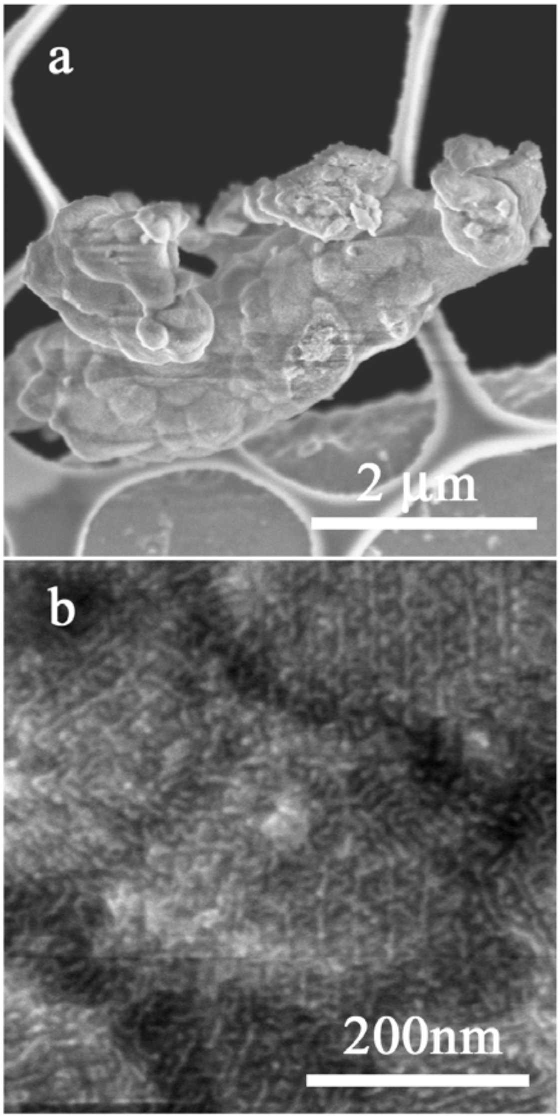


Figure S7 SEM images of KIT-6-130. Figure (b) is a highly magnified SEM image of the top surface of the KIT-6-130.

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