



Supporting Information

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Ligand-Free Platinum Nanoparticle Encapsulated in a Hollow Porous Carbon Shell as a Highly Active Heterogeneous Catalyst in Hydrogenation Reactions

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Experimental details for characterization and analytical procedures

The structures of the synthesized materials were confirmed by TEM using a Hitachi H-9000 transmission electron microscope operating at an accelerating voltage of 300 kV. Histograms of particle size distribution of Pt nanoparticles were obtained from the TEM images by measuring more than 200 particles in each sample. The powder XRD pattern of Pt@*hmC* was recorded on a Rigaku MiniFlex X-ray diffractometer (CuK α , Ni filter). The N₂ adsorption-desorption isotherm of Pt@*hmC* was measured at 77 K by using a Quantachrome AUTOSORB-1 automated gas sorption system after drying samples at 573 K for 2 h. Corresponding pore size distribution and an α_s -plot were calculated from the adsorption branch of the isotherm by using the Barrett-Joyner-Halenda (BJH) model and the standard N₂-adsorption isotherm of a nonporous carbon black (Wako Pure Chemical, 86 m² g⁻¹), respectively. The XP spectra of Pt@*hmC* were recorded on a Shimadzu ESCA-1000 X-ray photoelectron spectrometer. Quantitative analysis of the amount of Pt in Pt@*hmC* was carried out by using a Perkin-Elmer OPTIMA 3000-XL inductively coupled plasma emission spectrometer (ICP). For this measurement, the Pt component was dissolved by dispersing the Pt@*hmC* samples in an aqua regia for 3 h. After dilution of the suspension with distilled water to an appropriate concentration, the solution part was collected by centrifugal removal of

remaining solid parts.

Supporting data for structural characteristics of Pt@hmC

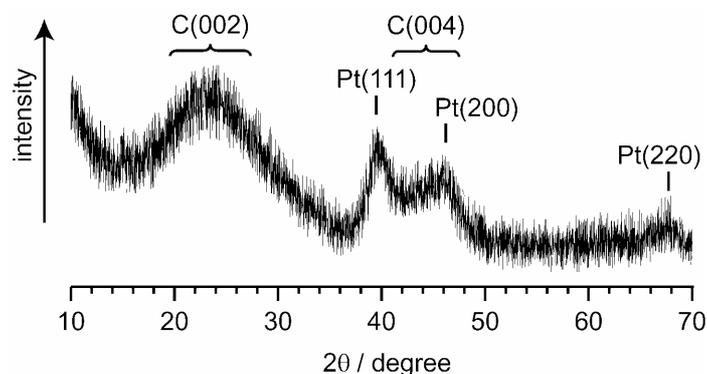


Figure S1. Powder XRD pattern of Pt@hmC. The powder XRD pattern exhibits typical (111), (200), and (220) reflections corresponding to Pt metal of a face-centered cubic structure. The crystallite size of the Pt nanoparticle, determined by the Scherrer equation and the half-height width of the Pt(111) reflection was 2.5 nm. This value is consistent with the average particle size of Pt nanoparticles determined by TEM observation shown in Figure 1c. Thus, each Pt nanoparticle in Pt@hmC is likely to be a single crystal. In addition to these reflections, two broad reflections ($2\theta = 10\text{-}30^\circ$, $35\text{-}50^\circ$) are also observed in the XRD pattern. These are attributed to C(002) and C(004) reflections of amorphous carbon composed of polycyclic aromatic carbon sheets oriented in a random manner.^[a]

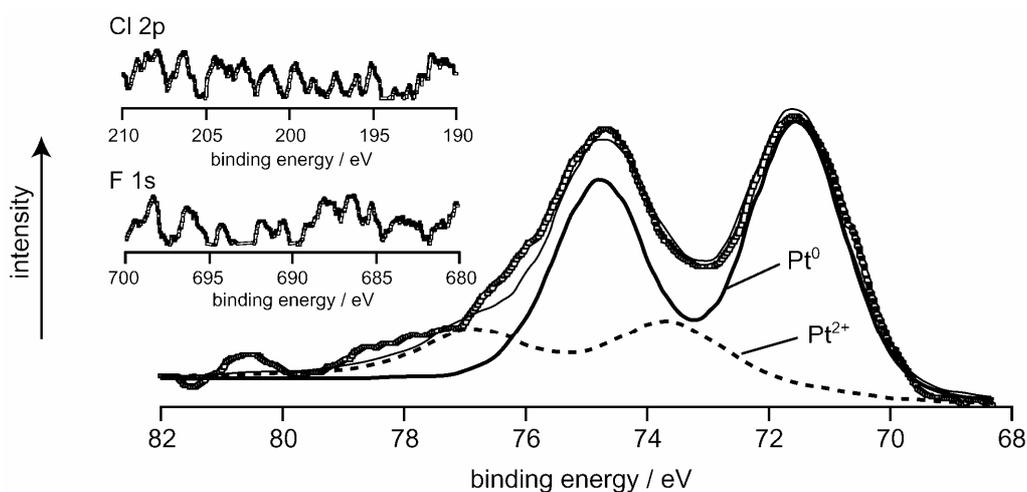


Figure S2. Pt 4f core-level XP spectrum of Pt@hmC. The spectrum predominantly showed Pt⁰ peaks at binding energies (BEs) of 71.5 eV ($4f_{7/2}$) and 74.7 eV ($4f_{5/2}$) with appreciable

contributions of Pt^{2+} components at BEs of 73.6 eV ($4f_{7/2}$) and 76.8 eV ($4f_{5/2}$),^[b] indicating that the surface of the Pt nanoparticle was partially oxidized, probably due to exposure of the sample to atmospheric conditions. On the other hand, no Pt^{4+} component was included in the spectrum and there is no peak of expected impurities such as chlorine (Cl 2p) and fluorine (F 1s) originated from the Pt precursor (H_2PtCl_6) and HF solution (insets of the figure). Thus, the surface of Pt nanoparticle core was free from any ligand.

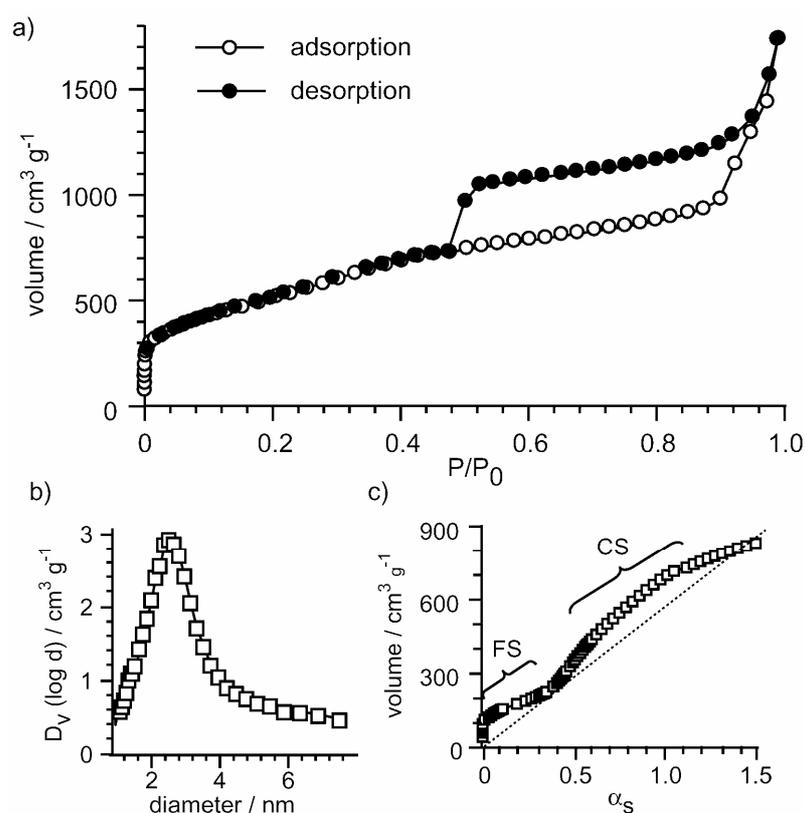


Figure S3. a) N_2 adsorption-desorption isotherm and corresponding b) pore size distribution and c) α_s -plot of Pt@*hmC*. The most characteristic feature of the isotherm is the presence of a significant hysteresis loop enclosed by a sudden drop in the volume adsorbed of the desorption isotherm at the P/P_0 range of 0.42-0.46. This phenomenon is often referred to as the tensile strength effect and is typically observed in material having a large mesopore encapsulated by a pore system of relatively small pore size (see ref. 12). Therefore, the carbon shell of Pt@*hmC* should consist of a porous wall structure. Actually, the application of the BJH model results in specification of a small mesopore system centered at 2.2 nm (Figure S1b). Moreover, construction of an α_s -plot indicates an appreciable filling swing (FS) and a broad cooperative swing (CS),^[c] as shown in Figure S1c. The former represents existence of micropore systems

of < 0.9 nm in diameter and the latter might denote the presence of relatively large micropores (> 1 nm) extending to the meso-range as confirmed by the above mesopore analysis using the BJH model. Consequently, the carbon shell has a bimodal pore structure, i.e., both micro- (< 0.9 nm) and nano- (1-4 nm) sized pore systems simultaneously present in the wall of the carbon shell.

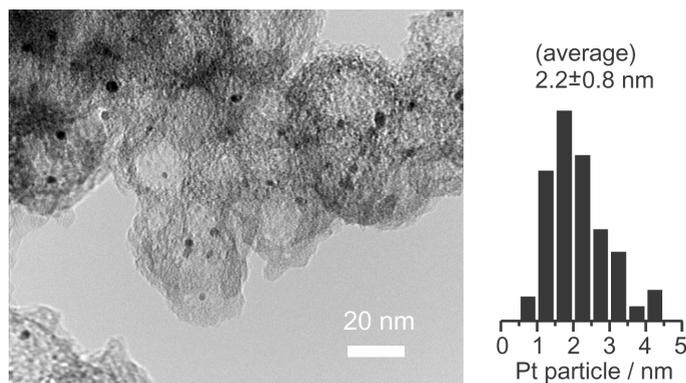


Figure S4. TEM image and Pt particle-size distributions of Pt@hmC after catalytic hydrogenation of nitrobenzene. It is clear that there is almost no change in the structure in comparison with the TEM image and corresponding Pt particle-size distribution of the Pt@hmC sample before the catalytic reaction (see Figure 1c).

- [a] 1) N. Tsubouchi, C. Xu, Y. Ohtsuka, *Energy Fuels* **2003**, 17, 1119-1125; 2) M. Hara, T. Yoshida, A. Takagaki, T. Takata, J. N. Kondo, S. Hayashi, K. Domen, *Angew. Chem. Int. Ed.* **2004**, 43, 2955-2958
- [b] K. S. Kim, N. Winograd, R. E. Davis, *J. Am. Chem. Soc.* **1971**, 93, 6296-6297
- [c] M. El-Merraoui, H. Tamai, H. Yasuda, T. Kanata, J. Mondori, K. Nadai, K. Kaneko, *Carbon* **1998**, 36, 1769-1776