Supporting Information for

Synthesis and Crystal-Phase Engineering of Mesoporous Palladium-Boron Alloy Nanoparticles

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Movie S1. Mesoscopic 3D tomography of \textit{hcp}-mesoPd$_2$B-o nanoparticles.
1. Chemicals and Materials
Sodium palladium(II) chloride (Na$_2$PdCl$_4$), palladium(II) chloride (PdCl$_2$, 99.9 wt%), commercial palladium nanoparticles (Pd NPs), and L-ascorbic acid (AA) were obtained from Sigma-Aldrich. Pluronic P123 (PEO$_{20}$-PPO$_{70}$-PEO$_{20}$, Purity 99 %), borane dimethylamine complex (DMAB) were obtained from Alfa Aesar. p-nitrophenol, Hydrofluoric acid (HF), hydrochloric acid (HCl), sodium hydroxide (NaOH), ammonia monohydrate (NH$_3$•H$_2$O, 50%), 1-butanol, tetraethoxysilane (TEOS), tetrahydrofuran (THF), ethanol, phenylmethane, hexane, and ether were purchased from Sinopharm Chemical Reagent Co. Ltd. (Shanghai). Deionized H$_2$O with the resistivity of 18.25 mΩ was used in all experiments.

2. Synthesis of mesoporous silica (KIT-6 and SBA-15) templates
Mesoporous KIT-6 was synthesized according to previously reported procedures (Chem. Commun. 2003, 2136; J. Am. Chem. Soc. 2005, 127, 7601). Typically, 4.0 g of Pluronic P123 and 7.9 g of concentrated HCl solution (37 wt. %) were dissolved in 144 mL of distilled water under vigorous stirring. After the complete dissolution, 4.0 g of 1-butanol was added under stirring at 35 °C for 1 h. After the addition of 8.6 g of TEOS, the mixture was first stirred at 35 °C for 24 h and then hydrothermally heated at 75 °C for 24 h under static conditions. The solid product was collected by washed with water and ethanol and dried at 80 °C. Lastly, as-synthesized mesoporous KIT-6 was calcined at 550 °C for 6 h to remove the surfactant and release the mesoporous nanochannels.

Mesoporous SBA-15 was synthesized according to previously reported procedures (Science 1998, 279, 548; Angew. Chem. Int. Ed. 2015, 54, 7060). Typically, 20.0 g of Pluronic P123 and 100 mL of concentrated HCl (37 wt. %) were dissolved in 650 mL of H$_2$O under vigorous stirring. After complete dissolution, 41.6 g of TEOS was added dropwise and further stirred at 35 °C for 24 h. Then, the white milky suspension was hydrothermally treated at 75 °C for 24 h under static conditions. The solid product was collected by washed with water/ethanol and further dried at 80 °C. Lastly, as-synthesized mesoporous SBA-15 was calcined at 550 °C for 6 h to remove the surfactant and release the mesoporous nanochannels.

3. Synthesis of fcc-mesoPd, fcc-mesoPd$_3$B, hcp-mesoPd$_3$B-r and hcp-mesoPd$_3$B-o
fcc-mesoPd was synthesized by a classic hard-templating method. Typically, 0.2 g of KIT-6 and predominant amounts of Na$_2$PdCl$_4$ were thoroughly dispersed in 2.0 mL of water. Then, the solvent was gradually removed under reduced vacuum condition to fill the metal precursors into mesoporous channels. To crystallize Pd (mesoPd/KIT-6), 2.0 mL of 1.0 M AA aqueous solution was carefully dropped on the Na$_2$PdCl$_4$/KIT-6 powder. Then, KIT-6 template was removed with 30 mL of HF solution (double dilution) for 3 times at room temperature. fcc-mesoPd was finally obtained by freeze-dried at 60 °C before use.
fcc-mesoPd$_5$B, hcp-mesoPd$_2$B-r and hcp-mesoPd$_2$B-o were synthesized by a synergistic templating method with mesoPd/KIT-6 hybrid as the template that solvothermally treated with DMAB under different conditions. Typically, 20 mg of mesoPd/KIT-6 and 600 mg of DMAB were mixed in 10 mL of THF, and further sonicated for 30 min. Then, the mixture was transferred to a 20 mL of reaction kettle, and further solvothermally treated at 100 °C for 4.5 h (fcc-mesoPd$_5$B), at 140 °C for 5 h (hcp-mesoPd$_2$B-r), and at 160 °C for 5 h (hcp-mesoPd$_2$B-o). Lastly, fcc-mesoPd$_5$B, hcp-mesoPd$_2$B-r and hcp-mesoPd$_2$B-o were collected by etched with 30 mL of HF solution for 3 times at room temperature and freeze-dried at 60 °C (see Synthetic Scheme in Figure S1). Besides, fcc-mesoPd$_5$B and hcp-mesoPd$_2$B-o were also synthesized by using phenylmethane, hexane, and ether as the solvents. As controls, fcc-mesoPd after the removal of KIT-6 was also studied for the crystal-phase evolution (from fcc-mesoPd to hcp-mesoPd$_2$B-o) with the same procedures. Moreover, hcp-mesoPd$_2$B-o nanobundles and hcp-Pd$_2$B-o nanorods were synthesized with the same procedures but using SBA-15 as the initial hard template.

4. Catalytic activity evaluations
Catalytic activities of as-synthesized fcc-mesoPd, fcc-mesoPd$_5$B and hcp-mesoPd$_2$B-o with different crystal-phase structures were evaluated through the reduction of p-nitrophenol to p-aminophenol with NaBH$_4$ as the reducing agent. Typically, 1 mL of 0.1 mM p-nitrophenol and 1 mL of 30 mM NaBH$_4$ were successively mixed in a quartz cuvette. Then, 0.05 mL of 0.2 mg mL$^{-1}$ fcc-mesoPd, fcc-mesoPd$_5$B and hcp-mesoPd$_2$B-o were injected the above solution to start the reduction reaction. The reaction kinetics and stability were collected by in situ Ultraviolet-visible (UV-vis) spectroscopy (Cary 60 UV-Vis spectrophotometer) at different time intervals.

5. Characterizations
Transmission electron microscopy (TEM) observations were performed with a JEOL JEM-2100 microscope operated at 200 kV (Cs 0.5 mm, point resolution 1.9 Å). High-angle annular dark-field (HAADF) STEM images were taken on an aberration-corrected Thermo Scientific Themis Z electron microscope operating at 300 kV, as well as on a JEOL JEM-2100F microscope that are equipped with STEM and EDS detectors for elemental mapping analysis. Samples for TEM and STEM observations were prepared by casting a suspension of the samples on a carbon coated copper grid (300 mesh). X-ray diffraction (XRD) patterns were recorded on powder samples using a D/max 2500 VL/PC diffractometer (Japan) equipped with graphite-monochromatized Cu Kα radiation (λ = 1.5406 Å). Small Angle X-Ray Scattering (SAXS) was studied using Anton Paar SAXSpoint 2.0. X-ray photoelectron spectra (XPS) were performed on a scanning X-ray microprobe (Thermo ESCALAB 250Xi) that uses Al Kα radiation. Binding energy of the C 1s peak (284.8 eV) was employed as a standard to calibrate binding energies of other elements. Inductively coupled plasma mass spectrometry (ICP-MS) was performed on a NexION 350D.
6. Figures and Table

**Figure S1.** A Scheme illustrating the crystal-phase-controlled formation of *fcc*-mesoPd, *fcc*-mesoPd$_5$B, *hcp*-mesoPd$_2$B-r and *hcp*-mesoPd$_2$B-o nanoparticles with the highlighting of the double gyroid mesoporous channels.

Notes for **Figure S1:** Nanoconfinement effect of mesoPd/KIT-6 hybrids as the synergistic template is critically important for preserving mesoporous morphology and simultaneously engineering crystal-phase structures of mesoPd-B, including *fcc*-mesoPd, *fcc*-mesoPd$_5$B, *hcp*-mesoPd$_2$B-r and *hcp*-mesoPd$_2$B-o. In contrast, when *fcc*-mesoPd after the removal of KIT-6 was used as the initial source, mesoporous framework of mesoPd was gradually destroyed during the crystal-phase evolution. Only nanoparticles with a larger size distribution were obtained accordingly.
Figure S2. TEM images of (a,b) mesoporous KIT-6 and (c,d) SBA-15. KIT-6 has a random morphology with bicontinuous double gyroid mesostructure ($Ia-3d$), while the morphology of SBA-15 is rod-like with a hexagonal mesoporous structure ($p6mm$).
**Figure S3.** Pawley fit of the experimental XRD pattern ($\lambda = 1.5406$ Å) of $fcc$-mesoPd. Red curve, simulated data; black curve, observed data; blue curve, difference profiles; black bars, peak positions.

**Figure S4.** Pawley fit of the experimental XRD pattern ($\lambda = 1.5406$ Å) of $fcc$-mesoPd$_5$B. Red curve, simulated data; black curve, observed data; blue curve, difference profiles; black bars, peak positions.
**Figure S5.** Zoom-in XRD patterns of observed hcp-mesoPd$_2$B-o nanoparticles and simulated hcp-Pd$_2$B-o in the range of 32-44°.

**Figure S6.** Pawley fit of the experimental XRD pattern (λ = 1.5406 Å) of hcp-mesoPd$_2$B-o. Red curve, simulated data; black curve, observed data; blue curve, difference profiles; black bars, peak positions.
Figure S7. (a,b) Low-magnification SEM and (c,d) TEM images of hcp-mesoPd$_2$B-o nanoparticles, indicating a uniform structure/morphology. (e-h) TEM images of hcp-mesoPd$_2$B-o nanoparticles observed from different directions, confirming the geometry of the double gyroid mesoporous channels (Ia-3d).

Figure S8. TEM images of (a) fcc-mesoPd and (b) fcc-mesoPd$_5$B. It is clearly seen that both of them replicated from two sets of mesoporous channels of KIT-6 (Ia-3d).
**Figure S9.** TEM images of \textit{hcp}-mesoPd\textsubscript{2}B synthesized with and without KIT-6. The result indicated the key nanoconfinement effect of mesoPd/KIT-6 hybrids for preserving mesoporous structure/morphology.

**Figure S10.** STEM images of \textit{hcp}-mesoPd\textsubscript{2}B-o nanoparticles observed from different angles, indicating a double gyroid \textit{la}-3\textit{d} mesostructure.
Figure S11. SAXS profiles of KIT-6 and hcp-mesoPd$_2$B-o nanoparticles. Mesoporous KIT-6 has double gyroid $la$-$3d$ mesostructure, while hcp-mesoPd$_2$B-o ($la$-$3d$) perfectly replicated the mesoporous structure of KIT-6.

Notes for Figure S11: The mesoscopic directions are defined in a similar way as those of the crystal structure at the atomic scale. We first define a unit cell in the mesoscopic scale. In this case, the mesostructures are replicated from KIT-6. Combined with the structural information from SAXS data, hcp-mesoPd$_2$B-o has a unit cell in mesoscopic scale of $a = 21.5$ nm, with a space group of $la$-$3d$. The mesoscopic direction can be deduced from the mesoscopic unit cell.
(a₁ and a₂) Atomic crystal-phase structural models of $\text{hcp}$-mesoPd₂B-o viewing perpendicular and parallel to the packing direction, respectively. (b₁ and b₂) Atomic crystal-phase structural models of $\text{hcp}$-mesoPd₂B-r viewing along the same direction as in a₁ and a₂, respectively. The B atoms have an ordered sequence in $\text{hcp}$-mesoPd₂B-o while they are randomly distributed in $\text{hcp}$-mesoPd₂B-r.

Figure S13. Pawley fit of the experimental XRD pattern ($\lambda = 1.5406$ Å) of $\text{hcp}$-mesoPd₂B-r. Red curve, simulated data; black curve, observed data; blue curve, difference profiles; black bars, peak positions of $\text{hcp}$-mesoPd₂B-r phase; green bars, peak positions of $\text{fcc}$-mesoPd phase.
Figure S14. (a) XRD, (b) TEM, and (c) high-resolution STEM images of hcp-mesoPd$_2$B-r with randomly distributed B atoms in Pd-Pd interatomic lattices.

Figure S15. TEM images of (a,b) Pd-B synthesized with the soft-templating method and (c,d) Pd$_3$B-o obtained using Pd-B MSs as the initial template.
Figure S16. XRD patterns and TEM images of hcp-mesoPd$_2$B-o nanoparticles synthesized with phenylmethane, hexane, and ether as the solvents.

Figure S17. TEM images of hcp-mesoPd$_2$B-o nanoparticles with different sizes of (a,b) ~65 nm and (c,d) ~170 nm. The samples were obtained using the same procedures but with different AA amounts added in the initial stage (for the formation of fcc-mesoPd/KIT-6).
Figure S18. A Scheme illustrating the crystal-phase-controlled formation of \(\text{fcc-mesoPd, fcc-mesoPd}_5\text{B}\) and \(\text{hcp-mesoPd}_2\text{B-o}\) nanoparticles with the highlighting of the single gyroid channel.

Notes for Figure S18: There are two sets of interconnected mesopores in \(\text{l}a\text{-}3\text{d}\)-structured KIT-6. Generally, the hard-templating growth resulted in the infiltration of the materials within two sets of channels of KIT-6 (Figure S1). However, when carefully controlling the infiltration process, the resulting materials can be also filled into one set of KIT-6 channel, forming mesoporous materials with a chiral single-gyroid structure (Figure S18) \((\text{J. Am. Chem. Soc. 2008, 130, 5262})\).

Figure S19. A Scheme illustrating the crystal-phase-controlled formation of \(\text{fcc-mesoPd, fcc-mesoPd}_5\text{B}\) and \(\text{hcp-mesoPd}_2\text{B-o}\) nanobundles with the highlighting of the columnar channels. The samples were synthesized with mesoPd/SBA-15 hybrids as the synergistic template.
Figure S20. A Scheme illustrating the crystal-phase-controlled formation of fcc-Pd, fcc-Pd$_5$B and hcp-Pd$_3$B-o nanorods. The samples were synthesized with mesoPd/SBA-15 hybrids as the synergistic template (Chem. Commun. 2003, 2136; ACS Nano 2008, 2, 1205).

Figure S21. UV-vis spectra for the reduction of $p$-nitrophenol catalyzed by (a) fcc-mesoPd$_5$B, (b) fcc-mesoPd, and commercial Pd black.
Figure S22. Catalytic stability of hcp-mesoPd$_2$B-o. UV-vis spectra for the reduction of $p$-nitrophenol over hcp-mesoPd$_2$B-o for (a) second and (b) third time. (c) The relationship between $\ln(A/A_0)$ and time, and (d) kinetic rate constants over hcp-mesoPd$_2$B-o for three times.
Table S1. Crystallographic data and Pawley fit results of *fcc-mesoPd, fcc-mesoPd$_5$B, hcp-mesoPd$_2$B-o, and hcp-mesoPd$_2$B-r*.

| Crystal system | *fcc-mesoPd* | *fcc-mesoPd$_5$B* | *hcp-mesoPd$_2$B-o* | *hcp-mesoPd$_2$B-r* |
|----------------|--------------|-------------------|---------------------|---------------------|
| Space group    | *Fm-3m* (No. 225) | *Fm-3m* (No. 225) | *Pnnm* (No. 58)    | *P6$_3$/mmc* (No. 194) |
| $a$/Å          | 3.8890(1)    | 4.0233(2)         | 4.735(1)            | 2.816(1)            |
| $b$/Å          | = $a$        | = $a$             | 5.091(2)            | = $a$              |
| $c$/Å          | = $a$        | = $a$             | 3.1047(8)           | 4.747(3)           |
| Temperature/K  | 298(2)       | 298(2)            | 298(2)              | 298(2)             |
| Wavelength/Å    | 1.5406       | 1.5406            | 1.5406              | 1.5406             |
| 2θ range/°     | 30.00-90.00  | 33.00-90.00       | 33.00-90.00         | 35.00-90.00        |
| $R_p$          | 0.0429       | 0.0495            | 0.2300*             | 0.0451             |
| $R_{wp}$       | 0.0552       | 0.0628            | 0.3618*             | 0.0572             |
| $R_{exp}$      | 0.1084       | 0.0896            | 0.1032*             | 0.0609             |
| GOOF           | 0.509        | 0.700             | 3.507*              | 0.939              |

* The high R values are caused by the strong peak overlap.