Supporting Information for

Ru Nanoframes with an *fcc* Structure and Enhanced Catalytic Properties

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Experimental Section

Chemicals and Materials

Ruthenium (III) chloride hydrate ($RuCl_3 \cdot xH_2O$, MW=207.4), sodium tetrachloropalladate(II) (Na_2PdCl_4, 98%), potassium bromide (KBr, ≥99%), L-ascorbic acid (AA, ≥99%), poly(vinyl pyrrolidone) (PVP, MW≈55,000), hydrochloric acid (HCl, 37%), iron(III) chloride ($FeCl_3$, 97%), *p*-nitrophenol, borane-ammonia complex ($H_3N\text{-}BH_3$, 90%), and sodium borohydride ($NaBH_4$, ≥99%) were all obtained from Sigma-Aldrich. Ethylene glycol (EG) was obtained from J. T. Baker. All aqueous solutions were prepared using deionized (DI) water with a resistivity of 18.0 MΩ·cm.

Preparation of Pd nanocrystals to be used as seeds

1) 5.6 nm Pd truncated octahedra. In a typical synthesis, 2 mL of an EG solution containing 40 mg of PVP was hosted in a vial and preheated to 160 ^{o}C in an oil bath under magnetic stirring for 10 min. 1 mL of an EG solution containing 16 mg of Na_2PdCl_4 was then quickly injected into the reaction solution using a pipette. The reaction was allowed to continue at 160 ^{o}C for 3 h. After being washed with acetone once and ethanol twice *via* centrifugation, the final product was re-dispersed in 1 mL of EG for future use.

2) 18 nm Pd nanocubes. 8.0 mL of an aqueous solution containing 105 mg of PVP, 60 mg of AA, and 600 mg of KBr was hosted in a vial and pre-heated to 80 ^{o}C in an oil bath under magnetic stirring. Subsequently, 3.0 mL of an aqueous solution containing 57 mg of Na_2PdCl_4 was added with a pipette. The reaction was allowed to continue at 80 ^{o}C for 3 h. After being washed with DI water twice *via* centrifugation, the final product was re-dispersed in 2 mL of EG for future use.

Standard procedure for the overgrowth of Ru on Pd truncated octahedral seeds

In a standard procedure, 8 mL of an EG solution containing 100 mg of PVP and 50 mg of AA was hosted in a 50-mL three-neck flask and preheated to 200 ^{o}C in an oil bath under magnetic stirring for 5 min. Then, 0.5 mL of the 5.6 nm truncated octahedral Pd seeds was added to the flask using a pipette. After 5 min, 8.0 mL of $RuCl_3 \cdot xH_2O$ solution (0.5 mg/mL, in EG) was injected to the flask at a rate of 2.0 mL/h using a syringe pump. The reaction was allowed to proceed for an additional 10 min after the $RuCl_3 \cdot xH_2O$ precursor had been completed injected. The products (*i.e.*, Pd-Ru core-frame octahedra) were collected by centrifugation, washed once with acetone, two times with water, and finally redispersed in 0.5 mL of DI water. The procedure for the overgrowth of Ru on 18 nm Pd cubic seeds was the same as the procedure above except for the substitution of 0.5 mL truncated octahedral seeds with 0.5 mL cubic seeds.

Synthesis of Ru nanowires

The Ru nanowires shown in Figure 3a were synthesized through a one-pot method. In a typical synthesis, 8 mL EG containing 100 mg of PVP was hosted in a 20-mL glass vial and preheated to 200 ^{o}C in an oil bath under magnetic stirring for 10 min. Then, 3 mL of an EG solution containing 45 mg of $RuCl_3 \cdot xH_2O$ was quickly added to the reaction solution using a pipette. The reaction was allowed to continue at 200 ^{o}C for 3 h. After being washed with acetone once and ethanol twice *via* centrifugation, the final product was re-dispersed in 5 mL of DI water for future use.

Removal of Pd cores from Pd-Ru core-frame octahedra by chemical etching

KBr (150 mg), PVP (25 mg), $FeCl_3$ (25 mg), HCl (0.15 mL, 37%), DI water (2.85 mL), and an aqueous suspension of the as-prepared Pd-Ru core-frame octahedra (0.5 mL) were mixed together in a 20-mL glass vial under magnetic stirring at room temperature for 10 min. Then, the solution was heated to 80 ^{o}C in an oil bath under magnetic stirring. After 3 h, the solution was cooled down with a water bath to room temperature and the product was collected by centrifugation, washed once with ethanol, twice with water, and finally re-dispersed in 0.5 mL of DI water for future use.

Evaluation of catalytic activities

1) Reduction of p-nitrophenol by $NaBH_4$. The reaction was conducted in aqueous suspension and under room temperature. In a typical process, both aqueous suspensions of Ru nanocatalysts (*i.e.*, Ru nanoframes and Ru nanowires) were first diluted to 0.218 mM in terms of Ru element (based on the result of inductively coupled plasma-optical emission spectroscopy, ICP-OES). Meanwhile, aqueous solutions of *p*-nitrophenol (0.5 mM) and $NaBH_4$ (2 M) were freshly prepared. Then, 0.690 mL of DI water was mixed with 0.295 mL *p*-nitrophenol solution in a cuvette. The color of the solution changed from colorless to yellow immediately after the addition of 0.005 mL of the $NaBH_4$ solution. Finally, 0.010 mL Ru nanocatalysts was injected into the system and quickly mixed well using a pipette. The reaction time (*t*) was recorded immediately thereafter and the intensity of the absorption at 400 nm for the reaction solution was monitored from $t = 20$ s to $t = 60$ min. The final concentrations of *p*-nitrophenol, $NaBH_4$, and Ru catalysts in the reaction solution were about 0.15 mM, 10 mM, and 2.2 μM (in Ru element), respectively.

2) Dehydrogenation of ammonia borane. The reaction was conducted in aqueous suspension, at room temperature, and under one atmosphere of pressure. In a typical process, 9.8 mL of ammonia borane aqueous solution (50 mM) and 0.2 mL of an aqueous suspension of Ru catalyst (nanoframes or nanowires, 0.375 mM in Ru element) or deionized water (blank) were sequentially added into a 50 mL three-neck flask kept at room temperature (~ 22 °C) under magnetic stirring, with one of the openings connected to a gas burette. The volume of hydrogen produced from the flask at different reaction time was recorded using the gas burette. The number of moles of hydrogen (n) could be calculated from the volume of hydrogen (V) according to the ideal gas law $PV = \mathrm{nRT}$ (P: absolute pressure of gas; R: ideal gas constant; T: absolute temperature). n will then be used to calculate the turnover frequency (mol H_2 sec^{-1} $(\mathrm{mol\ Ru})^{-1}$).

Characterizations

The transmission electron microscope (TEM) images were taken using a JEOL JEM-2010 microscope operated at 200 kV. High-angle annular dark-field scanning TEM (HAADF-STEM) and the energy dispersive X-ray (EDX) analyses were performed using a JEOL ARM200F with STEM Cs corrector operated at 200 kV. The UV-vis spectra of the catalytic reaction solution were recorded using an Agilent Cary 60 UV-vis spectrophotometer. XRD patterns were taken using a Scintag XDS2000 powder diffractometer. The concentrations of Pd and Ru ions were determined using an inductively coupled plasma-optical emission spectroscopy (ICP-OES, Perkin Elmer Optima 7000DV).

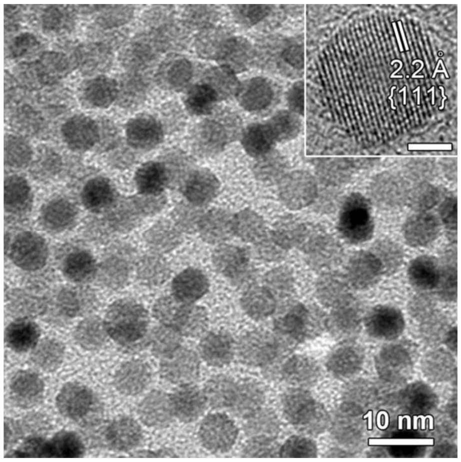

Figure S1. TEM image of Pd truncated octahedra with an overall spherical shape and an average size of 5.6 nm that served as seeds for the preparation of Pd-Ru core-frame octahedra and subsequent Ru NFs. The inset shows a HRTEM image recorded from an individual particle orientated along <110> direction.

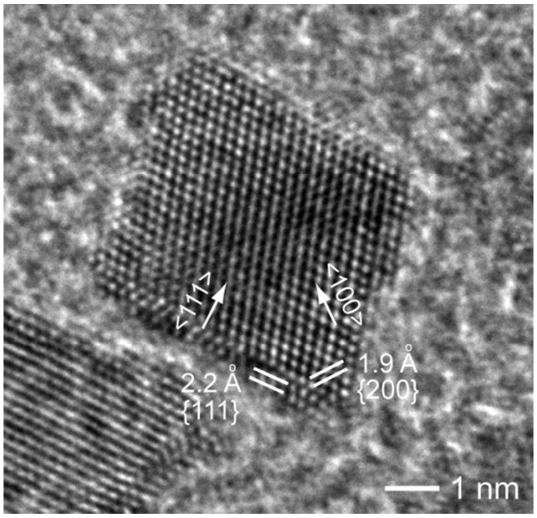

Figure S2. HRTEM image of an individual Pd-Ru core-frame octahedron orientated along <110> direction.

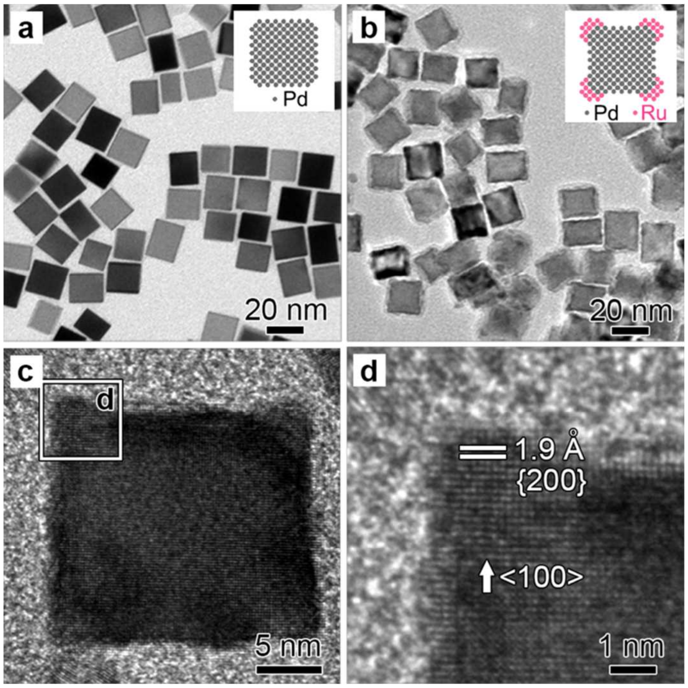

Figure S3. Overgrowth of Ru on the corners of 18 nm Pd nanocubes as the seeds. (a) TEM image of the 18 nm Pd cubic seeds; (b) TEM image of the Pd-Ru octapods that were grown from the 18 nm Pd cubic seeds; (c) HRTEM of an individual Pd-Ru octapod orientated along the <100> direction; (d) magnified HRTEM image of the region marked by a white box in (c), showing the *fcc* structure of Ru at the corners. Insets in (a, b) show corresponding atomic models of the samples.

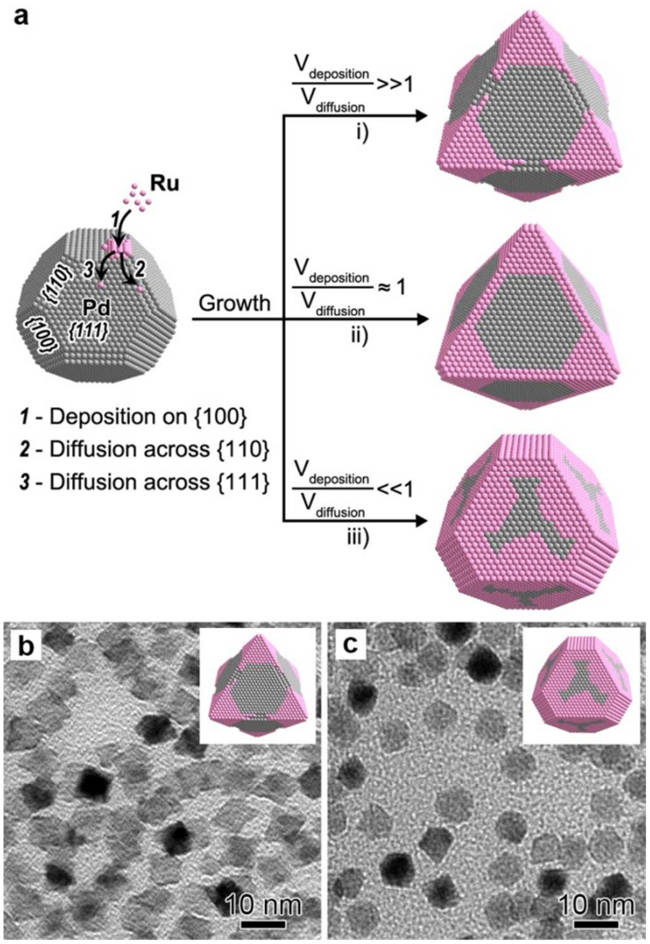

Figure S4. (a) Schematic illustrations summarizing the different pathways and the corresponding morphologies expected for the overgrowth of Ru on a Pd truncated octahedral seed under three different conditions; (b) TEM image of Pd-Ru hexapods corresponding to the case *i*) in (a), which were obtained by increasing the injection rate for $RuCl_3 \cdot xH_2O$ in a standard synthesis of Pd-Ru core-frame octahedra from 2.0 mL/h to 10 mL/h; (c) TEM image of Pd-Ru truncated octahedra corresponding to the case *iii*) in (a), which were obtained by decreasing the injection rate for $RuCl_3 \cdot xH_2O$ in a standard synthesis of Pd-Ru core-frame octahedra from 2.0 mL/h to 0.5 mL/h. Note that the TEM images of Pd-Ru core-frame octahedra corresponding to the case *ii*) in (a) are shown in Figure 2.

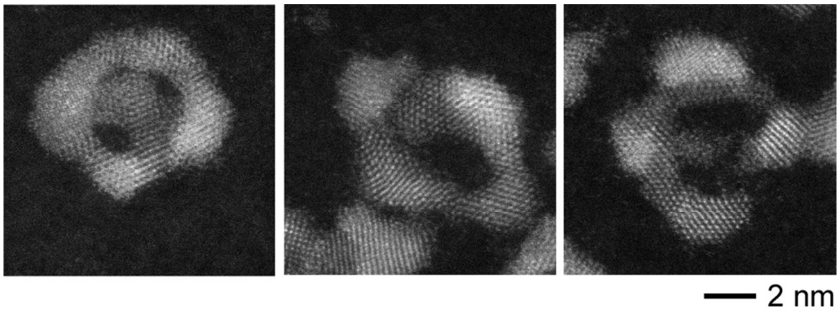

Figure S5. Representative HAADF-STEM images of individual Ru NFs showing the imperfect octahedral shape of the sample.

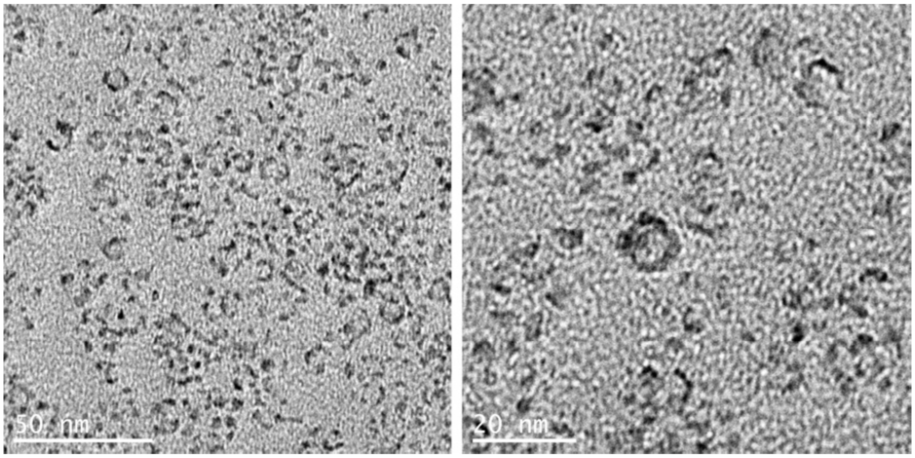

Figure S6. TEM images of the sample prepared using the same procedure for the Ru NFs shown in Figure 4 except for the reduction of Ru precursor by 50%.

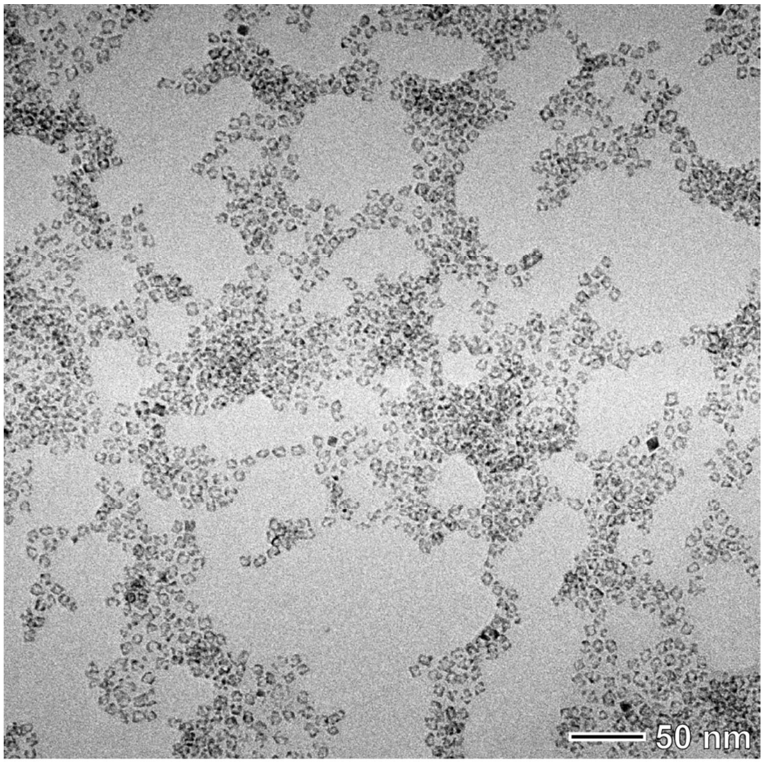

Figure S7. Additional TEM image of the Ru NFs at a lower magnification relative to the images shown in Figure 4.