Supporting Information for
Selective Synthesis of Rhodium-based Nanoframe Catalysts by Chemical Etching of 3d Metals

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Experimental Section

Synthesis

**Chemicals.** Oleylamine (OAm, J&K), RhCl₃·3H₂O (A.R., Sinopharm Chemical Reagent Co. Ltd, China), CuCl₂·2H₂O (A.R., Beijing Hongxing Chemical Factory, China), NiCl₂·6H₂O (A.R., Beijing Yili Fine Chemical Reagent Corp., China), PdCl₂ (A.R., Shenyang Institute of Nonferrous Metal, China), HCl solution (A.R., Beijing Chemical Works, China), NaBH₄ (A.R., Tianjin Xuanang Trading Co. Ltd. of Science and Industry, China), carbon black (Vulcan XC-72), N₂H₄·H₂O (98%, J&K), ethanol (A.R.), cyclohexane (A.R.) were used as received. The water used in all experiments was ultrapure.

**Synthesis of Rh-Cu Nanoctahedrons.** The precursors, 0.066 mmol of RhCl₃·3H₂O (s), 0.100 mmol of CuCl₂·2H₂O (s), and 12 mL of OAm were put in a 100 mL three-neck flask. And only one neck was equipped with a thermometer. Then the reaction container was heated to 180 °C upon stirring continually in air. During the heating-up process, the color of the reaction mixture turned from blue to green, then to yellow. In order to ensure that the solid RhCl₃ and CuCl₂ could be completely dissolved into the oleylamine, the reaction mixture was held at 180 °C for 60 min with stirring. After 60 min, the brown reaction mixture was transferred into a 25 mL Teflon-lined stainless steel autoclave, which had been preheated to 70 °C, to reduce the effect of oxygen inside the Teflon bottle on the reducing capability of OAm. The autoclave was then heated at 180 °C for 24 h before it was cooled to room temperature. The mixture was centrifuged at 9600 rpm for 12 min with importing 20 mL of ethanol, followed by washing with some cyclohexane/ethanol. Finally, the precipitated Rh-Cu nanoparticles were redispersed in cyclohexane.

If 0.066 mmol of RhCl₃·3H₂O (s), 0.100 mmol of CuCl₂·2H₂O (s), and 12 mL of OAm was kept in the three-neck flask at 180 °C for 24 h, no nanoparticles were produced because the metal precursors could not be reduced by OAm in air.

**Synthesis of Rh-Cu Nanoctahedrons/C.** Rh-Cu nanoctahedrons (0.019 mmol of Rh) and 12.5 mg of carbon black was ultrasonically dispersed in a mix of 15 mL of cyclohexane and 5 mL of acetone for 2 h. The mixture was centrifuged at 9000 rpm for 10 min, and washed with cyclohexane for two times. The precipitate was
dispersed with 17 mL of acetic acid, then transferred to a 25 mL Teflon-lined stainless steel autoclave, and heated at 70 °C for 12 h. The mixture was centrifuged at 9000 rpm for 10 min with importing 20 mL of ethanol, then washed with ethanol for three times. Finally, the precipitated Rh-Cu nanoctahedrons/C (the loaded content of Rh was 14.6 wt%) were dried under vacuum or redispersed in 8 mL of ethanol.

**Synthesis of Rh-Cu Nanoctahedral frames/C.** Rh-Cu nanoctahedrons/C (0.007 mmol of Rh) was dispersed in 5 mL of H2O, then mixed with 7.5 mL of dilute HCl solution (0.80 mol/L). The mixture was heated to 80 °C in air, and kept for 9 h. Finally, the precipitated Rh-Cu nanoctahedral frames/C (the loaded content of Rh was 9.4 wt%) were centrifuged and washed with ethanol for three times, then dried under vacuum.

**Synthesis of Rh-Pd-Cu Nanopolyhedrons.** The synthesis of Rh-Pd-Cu nanopolyhedrons was the same as that of Rh-Cu nanoctahedrons except that the precursors were 0.066 mmol of RhCl3∙3H2O (s), 0.025 mmol of PdCl2 (s), 0.175 mmol of CuCl2∙2H2O (s) and 14 mL of OAm.

**Synthesis of Rh-Pd-Cu Nanopolyhedrons/C.** The synthesis of Rh-Pd-Cu nanopolyhedrons/C was the same as that of Rh-Cu nanoctahedrons/C except using Rh-Pd-Cu nanopolyhedrons (0.021 mmol of Rh) rather than Rh-Cu nanoctahedrons (0.019 mmol of Rh).

**Synthesis of Rh-Pd-Cu Nanopolyhedral Frames/C.** The synthesis of Rh-Pd-Cu nanopolyhedral frames/C was similar to that of Rh-Cu nanoctahedral frames/C. Rh-Pd-Cu nanopolyhedral frames/C (0.009 mmol of Rh) were dispersed in 5 mL of H2O, then mixed with 7.5 mL of dilute HCl solution (0.80 mol/L). The mixture was heated to 60 °C in air, and kept for 25 min.

**Synthesis of Rh-Ni Nanopolyhedrons.** The synthesis of Rh-Ni nanopolyhedrons was the same as that of Rh-Cu nanoctahedrons except that the precursors were 0.023 mmol of RhCl3∙3H2O (s) and 0.080 mmol of NiCl2∙6H2O (s), and the solvothermal temperature was lifted to 210 °C.

**Synthesis of Rh-Ni Nanopolyhedrons/C.** The synthesis of Rh-Ni nanopolyhedrons/C was the same as that of Rh-Cu nanoctahedrons/C except using Rh-Ni nanopolyhedrons (0.015 mmol of Rh) rather than Rh-Cu nanoctahedrons (0.019 mmol of Rh).

**Synthesis of Rh-Ni Porous Nanoparticles/C.** The synthesis of Rh-Ni porous nanoparticles/C was similar to that of Rh-Cu nanoctahedral frames/C. Rh-Ni nanopolyhedrons/C (0.005 mmol of Rh) were dispersed in 5 mL of H2O, then mixed with 5.3 mL of dilute HCl solution (0.68 mol/L). The mixture was heated to 80 °C in air, and kept for 6 h.

**Synthesis of Rh/C.** The synthesis of Rh/C was followed by a modified process as described in Ref. S1. 0.078 mmol of RhCl3 was ultrasonically dissolved in 2 mL of H2O, then 40 mg of carbon black was added to the aqueous solution with sonication and stirring for 5 min. Then, 2 mL of solution NaBH4 (0.075 M) was rapidly added to the mixture, followed by stirring for 1 h. Finally, the precipitated Rh/C (the loaded content of Rh was 9.4 wt%) was centrifuged and washed with ethanol for three times, then dried under vacuum.
**Synthesis of Cu/C.** The synthesis of Cu/C was followed by a modified process as described in Ref. S1. 0.100 mmol of CuCl$_2$ was ultrasonic dissolved in 2.5 mL of H$_2$O, then 30 mg of carbon black was added to the aqueous solution with sonication and stirring for 5 min. Then 1.5 mL of NaBH$_4$ solution (0.352 M) was rapidly added to the mixture, followed by stirring for 1h. Finally, the precipitated Cu/C (the loaded content of Cu was 15.1 wt%) was centrifuged and washed with ethanol for three times, then dried under vacuum.

**Synthesis of Rh$_{1.7}$Cu/C.** The synthesis of Rh$_{1.7}$Cu/C was followed by a modified process as described in Refs. S1 and S2. The synthesis of Rh-Cu/C was the same as that of Cu/C except that the precursors were 0.096 mmol of RhCl$_3$ and 0.050 mmol of CuCl$_2$. Finally, the precipitated Rh$_{1.7}$Cu/C (the loaded content of Rh was 13.3 wt%) was centrifuged and washed with ethanol for three times, then dried under vacuum.

**Catalytic Reactions for Hydrous Hydrazine Decomposition.**

Catalytic reactions were carried out by following the method previously reported by Xu and coworkers with some modifications (see Ref. S1). Typically, Rh-based NP catalysts (0.01 mmol Rh) and 1 mL of ultrapure water were stirred in the glass reaction tube. The reaction temperature was kept constant at 25 °C using a water bath. 1.0 mmol of hydrazine monohydrate was injected to the reaction tube to initiate hydrazine decomposition reaction. The gas released during the reaction was passed through a hydrochloric acid solution (1.0 M) to absorb NH$_3$, and measured using a self-made gas burette. For the catalytic reactions using carbon black or Cu/C, the amount of catalysts is 20 mg or 0.01 mmol of Cu, respectively.

**Calculation of turnover frequency (TOF) and the H$_2$ selectivity.**

The hydrazine decomposition mainly includes two reactions: complete decomposition, H$_2$NNH$_2$ → N$_2$ (g) + 2H$_2$(g) (reaction 1); and incomplete decomposition, 3H$_2$NNH$_2$ → 4NH$_3$(g) + N$_2$(g) (reaction 2). TOFs are calculated on the basis of the data at 50% completion of hydrazine decomposition, measured in [mol H$_2$][mol Rh]$^{-1}$h$^{-1}$ (Rh = 0.01 mmol). And given that $\chi$ represents the selectivity toward H$_2$ generation, so the combined reaction for reaction (1) and (2) can be expressed as 3H$_2$NNH$_2$ → 4(1-$\chi$)NH$_3$(g) + (1+2$\chi$)N$_2$(g) + 6$\chi$H$_2$(g) (reaction 3), and H$_2$ selectivity can be expressed as $\chi = (3\lambda-1)/8$ [$\lambda$ = n(H$_2$+N$_2$)/n(H$_2$NNH$_2$)] (Ref. S3), and the value of n(H$_2$NNH$_2$) in this work is 1.0 mmol.

**Instrumentation.**

Samples for transmission electron microscopy (TEM) observations were prepared by drying few droplets of cyclohexane dispersion of Rh-Cu nanoctahedrons or few droplets of ethanol dispersion of Rh-Cu nanoctahedrons/C or Rh-Cu nanoctahedral frames/C on nickel grids coated with amorphous carbon membranes. For Rh-Pd-Cu systems, they were similar to those of Rh-Cu systems. For Rh-Ni systems, they were similar to those of Rh-Cu systems except using copper grids rather than nickel grids. TEM, selected area electron diffraction (SAED), high-resolution TEM (HRTEM), and energy dispersive X-ray spectroscopy (EDS) analyses were
performed on a FEG-TEM (JEM-2100F, JEOL, Japan) operated at 200 kV. X-ray diffraction (XRD) patterns were obtained on a D/MAX-2000 diffractometer (Rigaku, Japan) with Cu-Kα radiation. Inductively coupled plasma-atomic spectroscopy (ICP-AES) analysis was performed on a Profile Spec ICP-AES spectrometer (Leeman, USA). X-ray photoelectron spectroscopy (XPS) analysis was taken on an Axi Ultra imaging photoelectron spectrometer (Kratos, UK).

![XRD patterns of as-prepared Rh-Cu nanoctahedrons, Rh-Cu nanoctahedrons/C (the loaded content of Rh was 14.6 wt%) and Rh-Cu nanoctahedral frames/C (the loaded content of Rh was 9.3 wt%), with the standard data for fcc Rh (JCPDS Card No.: 05-0685) and fcc Cu (JCPDS Card No.: 04-0836) as references.](image-url)
Figure S2. HRTEM images of Rh-Cu nano-octahedrons orientated along different directions.

Figure S3. FTIR spectra of oleyamine, carbon black, Rh-Cu nano-octahedrons/C, and Rh-Cu nano-octahedral frames/C. The very weak absorption peak at 3300 cm$^{-1}$ due to the N-H stretching mode (Ref. S4) indicated most of OAm was removed from the surfaces of Rh-Cu nano-octahedrons/C and Rh-Cu nano-octahedral frames/C.
Figure S4. XPS full spectra of (a) Rh-Cu nano-octahedrons/C and (b) Rh-Cu nano-octahedral frames/C.
Figure S5. (a) Rh 3d and (b) Cu 2p$_{3/2}$ XPS spectra of Rh-Cu nanooctahedrons/C and Rh-Cu nanooctahedral frames/C. For Rh-Cu nanooctahedrons/C, through the calculation by dividing the sum of corrected area of the peak ascribed to Rh$^0$ 3d$_{3/2}$ (311.9 eV, see Ref. S5) and that of Rh$^0$ 3d$_{5/2}$ (307.2 eV, see Ref. S5) by the total corrected area of Rh 3d (Ref. S5), it was noted that a high proportion of surface Rh was in oxidized state. On the other hand, through the calculation of dividing the corrected area of the peak ascribed to Cu$^0$ 2p$_{3/2}$ (932.7 eV, see Ref. S5) by the total corrected area of the Cu 2p$_{3/2}$ peak, it was known that most of Cu element was in its metallic state after HAc treatment. However, for Rh-Cu nanooctahedral frames/C, more Rh and a small fraction of Cu were in oxidized states after HCl etching.
Figure S6. EDS line scan profiles of Rh-Cu nanoctahedrons/C. The average molar ratios of Rh in (a) and (b) are 49% and 44%, respectively.

Figure S7. HRTEM images of Rh-Cu nanoctahedral frames/C orientated along different directions.
**Figure S8.** TEM image (a) and EDS line scan profiles (b) of Rh-Pd-Cu nanopolyhedrons. HAADF-STEM image (c) and EDS line scan profiles (d) of Rh-Pd-Cu nanopolyhedral frames/C. Inset in panel (a) is the size distribution histogram of Rh-Pd-Cu nanopolyhedrons.

**Figure S9.** XRD patterns of as-prepared Rh-Pd-Cu nanopolyhedrons, Rh-Pd-Cu nanopolyhedrons/C and Rh-Pd-Cu nanopolyhedral frames/C, with the standard data for fcc Pd (JCPDS Card No.: 05-0681), fcc Rh (JCPDS Card No.: 05-0685) and fcc Cu (JCPDS Card No.: 04-0836) as references.
**Figure S10.** HRTEM image of Rh-Pd-Cu nanopolyhedrons.

**Figure S11.** (a) TEM image, (b) and (c) HRTEM images of Rh-Pd-Cu nanopolyhedrons/C after treated in acetic acid.

**Figure S12.** TEM image (a), HRTEM image (b) of Rh-Pd-Cu nanopolyhedral frames/C.
**Figure S13.** TEM image (a) and EDS line scan profiles (b) of Rh-Ni multi-twinned nanocrystals synthesized via the oleylamine solvothermal method. HAADF-STEM image (c) and EDS line scan profiles (d) of Rh-Ni porous nanoframes/C via HCl/O₂ etching. Inset in panel (a) is the size distribution histogram of Rh-Ni multi-twinned nanocrystals.
Figure S14. (a) TEM image, (b) magnified TEM image, (c) and (d) HRTEM images of Rh-Ni nanopolyhedrons. The red arrows in panel (c) and (d) indicate the locations of the (111) grain boundaries in a single nanoparticle, so the as-prepared Rh-Ni nanopolyhedrons are multi-twinned nanocrystals.

Figure S15. (a) TEM image, (b) and (c) HRTEM images of Rh-Ni nanopolyhedrons/C of Rh-Ni nanopolyhedrons/C after treated in acetic acid.

Figure S16. TEM images of (a) Rh/C (the loaded content of Rh was 9.4 wt%), (b) Cu/C (the loaded content of Cu was 15.1 wt%), (c) Rh\textsubscript{1.7}Cu/C (the loaded content of Rh was 13.3 wt%) synthesized via NaBH\textsubscript{4} reduction, and (d) XRD pattern of Rh\textsubscript{1.7}Cu/C.
Figure S17. TEM images of Rh-Cu nanoctahedral frames/C after the catalytic reactions of hydrazine decomposition for the second cycle (a) and the fourth cycle (b).