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Supporting information

Manipulating the Concavity of Rhodium Nanocubes Enclosed with High-index Facets via Site-selective Etching

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(Ⅰ) Experimental details

Chemicals and Materials

Rhodium (Ⅲ) Chloride Hydrate ($RhCl_3 \cdot 3H_2O$, Rh 38.5-42.5%) was purchased from Aladdin. Polyvinyl pyrrolidone (PVP, K30) was purchased from BASF. Potassium bromide (KBr, AR.) and hydrochloric acid (37%, AR.) were purchased from Sinopharm Chemical Reagent Co., Ltd. The water used in all experiment was ultra-pure water which resistivity is 18 MΩ. All reagents were used as received without further purification. Rhodium Chloride precursor solution (0.05 mol/L) were prepared at room temperature by dissolving $RhCl_3 \cdot 3H_2O$ in the ultra-pure water. Hydrochloric acid was diluted to 1 mol/L before the reactions.

Synthesis of Rh concave nanocubes

$RhCl_3$ (0.05 mol/L, 200 μL), PVP (100 mg), KBr (333 mg) and hydrochloric acid (0-10 mL, 1 mol/L) were mixed together with the ultra-pure water. The dosage of hydrochloric acid was varied in the different cases, while the total volume of the reaction solution was maintained as 10 mL by controlled the amount of the ultra-pure water. The resulting brick red solution was transferred to a Teflon-lined stainless-steel autoclave with a capacity of 20 mL. The sealed vessel was heated from room temperature to 200 ℃ in 30 min and kept at this temperature for 12 h before it was cooled down to room temperature. The resultant nanocrystals suspension were precipitated by acetone, separated via centrifugation and further purified by a water-acetone mixture for several times.

Characterization

The morphology, structure and composition of the Rh nanocrystals were analyzed by transmission electron microscope (TEM), scanning electron microscope (SEM) and X-ray diffraction (XRD). TEM studies were performed on a FEI F20 transmission electron microscopy with a field emission electron gun. Important structural information was provided through high-resolution TEM (HRTEM) images and selective area electron diffraction (SAED) patterns. Furthermore, F20 is equipped with energy dispersive spectroscopy (EDS) and scanning transmission electron microscope (STEM), providing the

complementary composition and morphology information. SEM (JSM6700) was used to examine the concave surface morphology of Rh nanocrystals. In addition, XRD (MiniFlex) was used to characterize the composition and crystalline phase of Rh naonocrystals.

(Ⅱ) Supporting figures

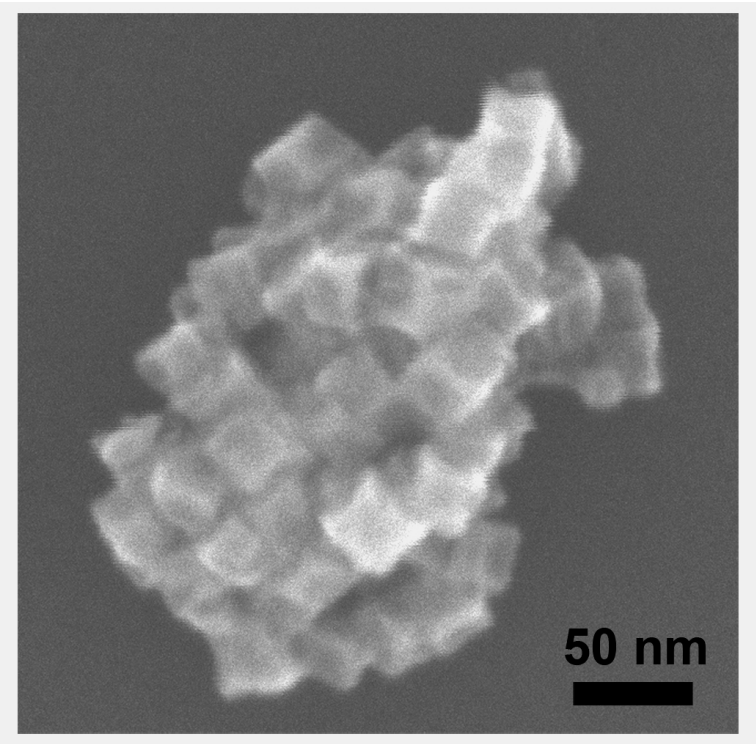

Fig. S1. Scanning electron microscope (SEM) image of concave Rh nanocubes.

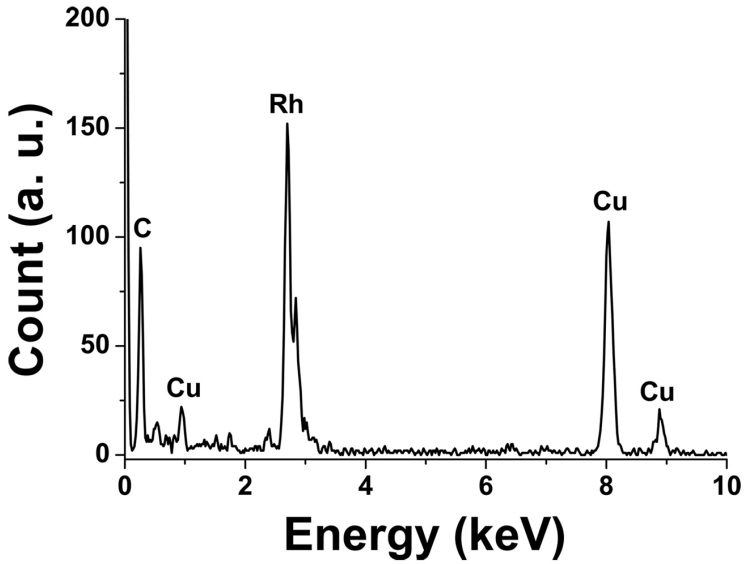

Fig. S2. Energy dispersive spectroscopy (EDS) of concave Rh nanocubes.

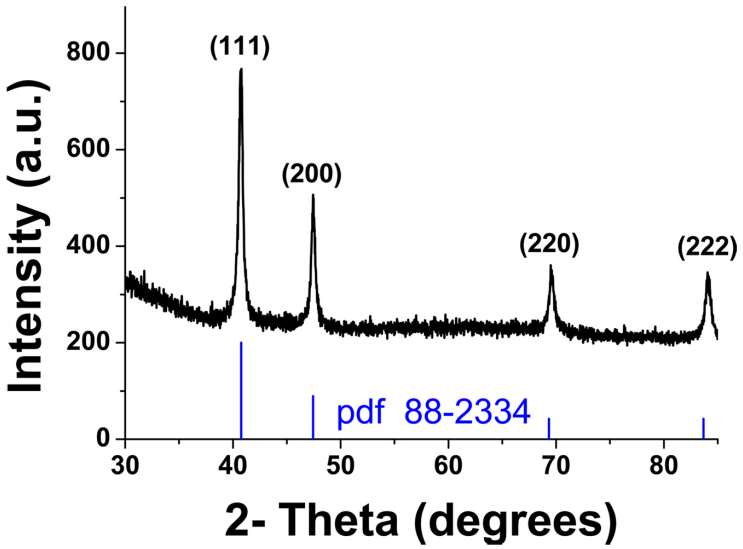

Fig. S3. X-ray diffraction (XRD) of concave Rh nanocubes.

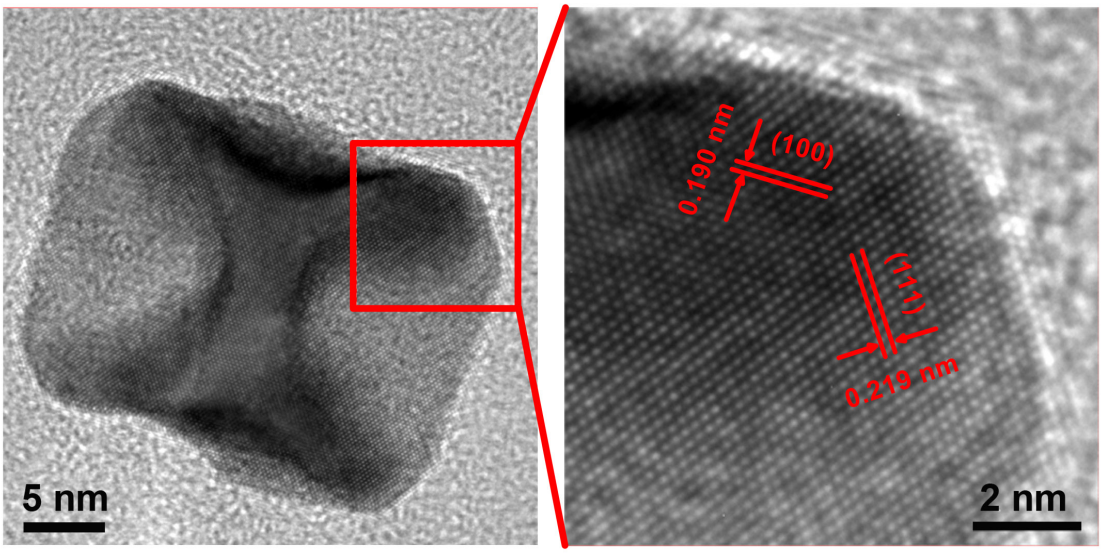

Fig. S4. (Left) HRTEM image of an individual truncated concave Rh nanocubes. (Right) Zoom-in HRTEM image of the region indicated by the box.

Control experiments:

After successfully obtaining the concave nanocubes with high-index facets, the premise for further tuning the concavity is to find out the critical factors for yielding the concave surface. To confirm the role of regents in the reaction, a series of control experiments have been carried out. The effects of hydrochloric acid, Br^-/Cl^- ions and PVP on the formation of concave Rh nanocubs were discussed below.

To investigate the effect of hydrochloric acid, the 1st control experiment was carried out without using hydrochloric acid. The reaction was conducted in a Teflon-line stainless-steel autoclave containing $RhCl_3$ (0.05 mol/L, 200 μL), KBr (333 mg) and PVP (100 mg) at 200 ℃ for 12 h. Without adding hydrochloric acid, spherical nanoparticles with an average diameter of 4.22 nm were obtained (Fig. 3a and Fig. 3b). No pits or concave facets emerge on the surface of Rh nanocrystals in absence of hydrochloric acid, even if Br^- and Cl^- ions coexist in the reactants. In a word, hydrochloric acid has a critical role in the formation of the concave nanostructure.

To further clarify whether H^+ or Cl^- ions play a decisive role in the formation of concave structure, control experiments have been executed. In the 2nd control experiment, hydrochloric acid was replaced by sulfuric acid and $RhCl_3$ was replace by $Rh_2(SO_4)_3$. The reaction was conducted in a Teflon-line stainless-steel autoclave containing $Rh_2(SO_4)_3$ (0.05 mol/L, 200 μL), sulfuric acid (10 ml, 1 mol/L), KBr (333 mg) and PVP (100 mg) at 200 ℃ for 12 h. Concave Rh nanocubes (Fig. S5a) were obtained in absence of Cl^- ions, indicating Cl^- ions are not indispensable to yield concave Rh nanocubes.

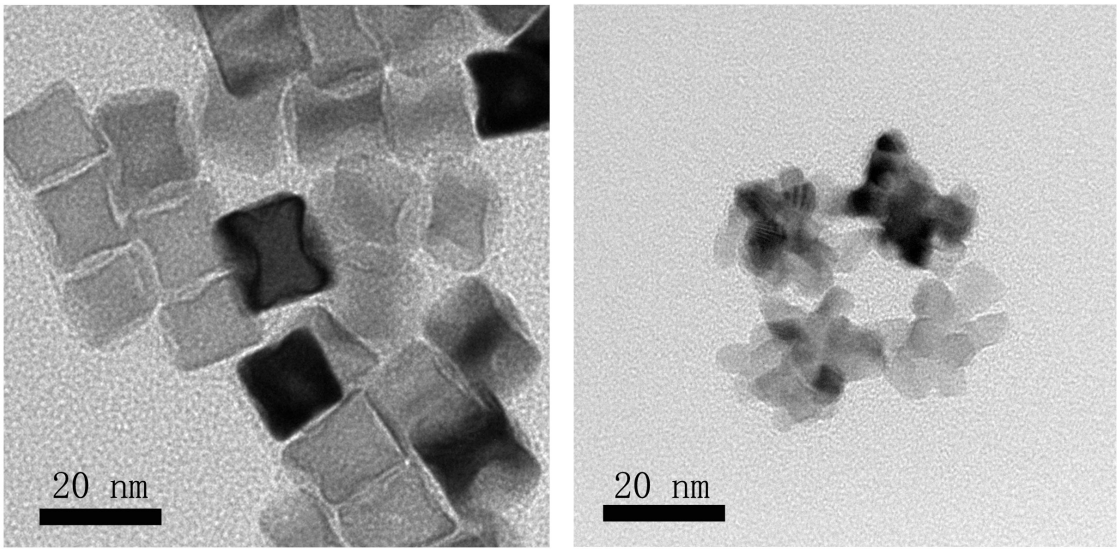

Fig. S5 (a) TEM image of Rh nanocrystals obtained in the 2nd control experiment. **(b)** TEM image of Rh nanocrystals obtained in the 3rd control experiment.

Our 3rd control experiment was carried out without using any Cl^- ions or Br^- ions. The reaction was conducted in a Teflon-line stainless-steel autoclave containing $Rh_2(SO_4)_3$ (0.05 mol/L, 200 μL), sulfuric acid (10 ml, 1 mol/L) and PVP (100 mg) at 200 ℃ for 12 h. The Control experiment showed that multi-pod nanostructure was obtained in absence of Cl^- ions and Br^- ions. Cl^- ions and Br^- ions are important capping agents (shape-directing agents), which prefer to adsorb on {100} in stead of {111} facets, causing the formation of Rh nanocubes mainly enclosed by {100} facets.[1] Therefore, the cubic profile of

Rh nanocrystals is difficult to be maintained without using any Cl^- ions or Br^- ions. The corrosion of Rh becomes serious indicates that it is not Br^- ions or Cl^- ions but H^+ ions play a role of etchant.

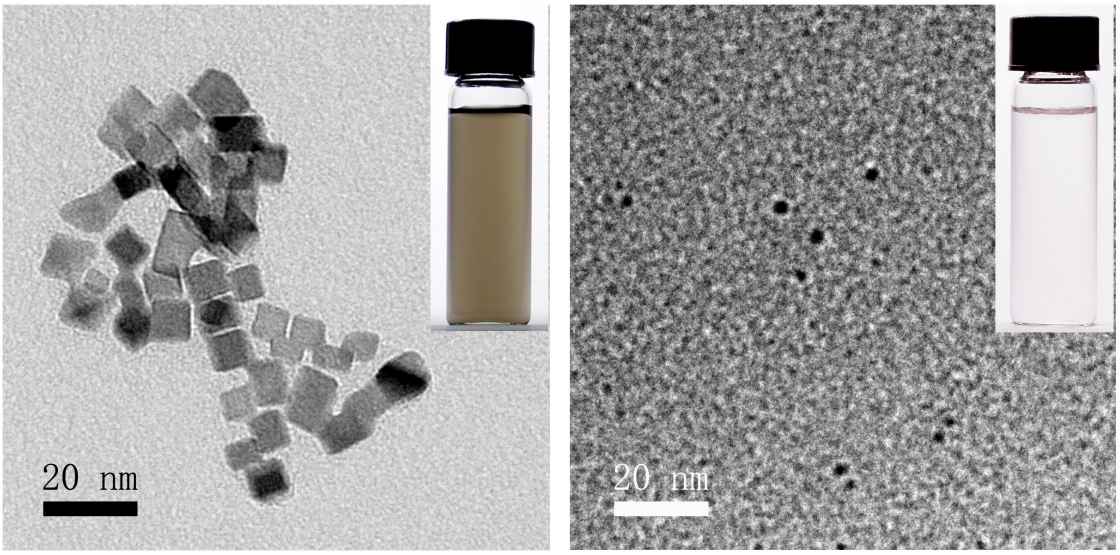

Fig. S6. TEM images of Rh nanocrystals obtained at the first step (a) and at the second step (b) in the 4th control experiment. The inserted pictures display the appearance of the products.

The 4th control experiments were designed to confirm the dissolved corrosion of Rh nanocrystals by using hydrochloric acid as an etchant at 200 ℃ under hydrothermal conditions. At the first step, Rh nanocubes have been synthesized in a Teflon-line stainless-steel autoclave containing $RhCl_3$ (0.05 mol/L, 200 μL), PVP (100 mg), KBr (333 mg) and acetic acid (0.01 mol) at 200 ℃ for 12 h. The resultant nanocrystals suspension were precipitated by acetone, separated via centrifugation and further purified by a water-acetone mixture for several times. TEM image (Fig. S6a) shows that the prepared Rh nanocubes have a diameter of 10 nm approximately. At the second step, the nanocubes were mixed with 10 mL hydrochloric acid (1 mol/L), transformed to another autoclave, and then heated at 200 ℃ for 12 h. The dark brown nanocrystals suspension becomes transparent light pink after the treatment of hydrochloric acid. The change could be intuitively observed by comparing the inserts of Figure S6a and b. The TEM image (Fig. S6b) displays that the nanocubes have been dissolved into smaller spherical nanoparticles in hydrochloric acid under hydrothermal conditions. Though Rh is inert against many kinds of acids (including aqua regia) at room temperature, the control experiment indicates that Rh will be dissolved in some acids (such as hydrochloric acid) at high temperature under hydrothermal conditions.

The 5th control experiment was designed to investigate the role of PVP. The reaction was conducted in a Teflon-line stainless-steel autoclave containing $RhCl_3$ (0.05 mol/L, 200 μL), KBr (333 mg), hydrochloric acid (1 mol/L, 10 mL) at 200 ℃ for 12 h. No precipitation (i. e. Rh nanocrystals) would be

yielded in absence of PVP, indicating that PVP is an indispensable reducing agent in our case.[2] We consider that Rh^{3+} ions are firstly reduced into Rh atom in the presence of PVP at the nucleation stage of concave Rh nanocubes. The Rh atoms at {100} facets of the generated nanocrystals seed could be selectively dissolved by hydrochloric acid with the capping of Br^- ions and Cl^- ions. At the same time, Rh^{3+} ions in the solution will be reduced into Rh atom by PVP and prefer to deposit on the nanocrystals along <111>/<100> directions. These two competitive processes coexist at the crystal growth stage and affect the ultimate morphology and structure of Rh nanocrystals.

In a word, these control experimental results not only indicate that hydrochloric acid is an effective etchant for the synthesis of Rh nanocubes with concave surfaces, but also confirm that both Br^- ions and Cl^- ions are not the most critical factors in the formation of concave nanostructure in our case.

Reference

[1] Y. Zhang, M. E. Grass, J. N. Kuhn, F. Tao, S. E. Habas, W. Huang, P. Yang, G. A. Somorjai, *J. Am. Chem. Soc.* **2008**, *130*, 5868-5869.

[2] Q. Yuan, Z. Zhou, J. Zhuang, X. Wang, *Inorganic chemistry* **2010**, *49*, 5515-5521.