

Electronic Supplementary Information (ESI) for

Microwave-assisted synthesis of octahedral Rh nanocrystals and their performance for electrocatalytic oxidation of formic acid

Xiaomeng Liu, Junxuan Xu, Haoyue Zhang, Yitian Zhong, Haosheng Feng, Yanxi

Zhao, Qin Li, Xianghong Li, Tao Huang*

Key Laboratory of Catalysis and Energy Materials Chemistry of Ministry of Education & Hubei Key Laboratory of Catalysis and Materials Science, South-Central Minzu University, Wuhan 430074, China

E-mail: huangt208@163.com

Experimental Details

Materials: Rh(acac)₃ (Kunming Institute of Precious Metals), tetraethylene glycol (TEG, Acros chemicals), polyvinylpyrrolidone (PVP, average molecular weight, M_w=30000), didecyl dimethyl ammonium chloride (DDAC), didoetyl dimethyl ammonium bromide (DDAB), cetyltrimethylammonium chloride (CTAC), KI, KCl, KBr, ethylene diamine (EDA) and other reagents were of analytical grade and used without further purification.

Synthesis of mutually embedded Rh concave nanocubes: In a representative synthetic process, all reactants were dissolved in TEG to make up the corresponding solution with a certain concentration. Together with TEG acting as both a solvent and a reductant, 1 mL of 1.0 mol·L⁻¹ PVP, 0.8 mL of 1.0 mol·L⁻¹ KI, 2.0 mL of 0.2 mol·L⁻¹ DDAC solution and 1.0 mL of EDA were added into a 50-mL round-bottle flask in turn. Then, 0.8 mL of 0.05 mol·L⁻¹ Rh(acac)₃ solution was added and the final volume of the reaction mixture was maintained at 10 mL by adding 4.4 mL of TEG. The molar ratio of Rh(acac)₃/DDAC/KI/PVP was 1/10/20/25, the concentration of Rh(acac)₃ was

4 mmol·L⁻¹ and the volume of EDA/TEG was 1/9 in the reaction system. After mixing uniformly at room temperature, the resulting bright yellow solution was put into a modified domestic microwave oven (Galanz, 900W) and irradiated for 140 s with 80% of the full output power, and then a black green colloid solution was obtained. After cooling to room temperature, the product was collected by centrifugal separation with 9000 rpm, and further washed alternately with ethanol and water for 30 times. The final product was dispersed in ethanol for characterization.

Characterization: Transmission electron microscopy (TEM) and HRTEM measurements were conducted on a FEI Talos F200X field emission transmission electron microscopy operated at 200 kV, respectively. The sample for TEM observation was prepared by placing a drop of the colloidal dispersion onto a copper grid coated with a perforated carbon film, followed by evaporating the solvent at ambient temperature. SEM images were taken on a SU8010 field-emission scanning electron microscope operated at 200 kV. X-ray powder diffraction (XRD) patterns were recorded on a Bruker D8 advance X-ray diffractometer employing Cu K α radiation with 40 kV and 50 mA. X-ray photoelectron spectroscopy (XPS) was performed on a VG Multilab 2000 X-ray photoelectron spectrometer using Mg K α radiation under a vacuum of 8×10^{-7} Pa. All binding energy values were determined with reference to carbon, C_{1s} = 284.6 eV.

Electrochemical Measurements: Electrochemical tests were carried out on a CHI660E electrochemical workstation at room temperature. The working electrodes were made by modifying a glassy carbon electrode with octahedral Rh nanocrystals or Rh black followed by natural drying. A saturated calomel electrode (SCE) and a platinum wire was employed as the reference and the counter electrode, respectively. The catalytic activity for the electro-oxidation of formic acid was measured by cyclic voltammetry (CV) in 0.5 M HClO₄ + 0.5 M HCOOH aqueous solution, and the stability of the as-prepared octahedral Rh nanocrystals was tested by chronoamperometry (CA) at the maximum oxidation voltage in the same solution. Before cyclic voltammetry measurements, six cycles of potential sweeps between -0.2V and 1.2V at a sweep rate of 50 mV·s⁻¹ were applied in 0.5 M HClO₄ solution to clean the Rh surface in-situ. All

CV tests were carried out in a potential range of -0.2 to 1.2 V at a sweep rate of 50 $\text{mV}\cdot\text{s}^{-1}$. Both positive and negative CV scans were performed on each sample. The arrows in the CV curves indicate the direction of the scan. The same electrochemical experiments were conducted for commercial Rh black.

The octahedral Rh nanocrystals-modified glassy carbon electrode was also used to test CO stripping voltammetry. Firstly, the CO stripping voltammetry was recorded for the freshly-prepared octahedral Rh nanocrystals in 0.5 M HClO_4 at a sweep rate of 2 mV/s . After that, CO gas (99.999%) was bubbled for 15 minutes through the 0.5 M HClO_4 solution in which the above modified electrode was kept immersed. Then the modified electrode was quickly transferred into a fresh 0.5 M HClO_4 solution and the CO stripping voltammetry was recorded. Subsequently, a second potential scanning was followed at the same sweep rate.

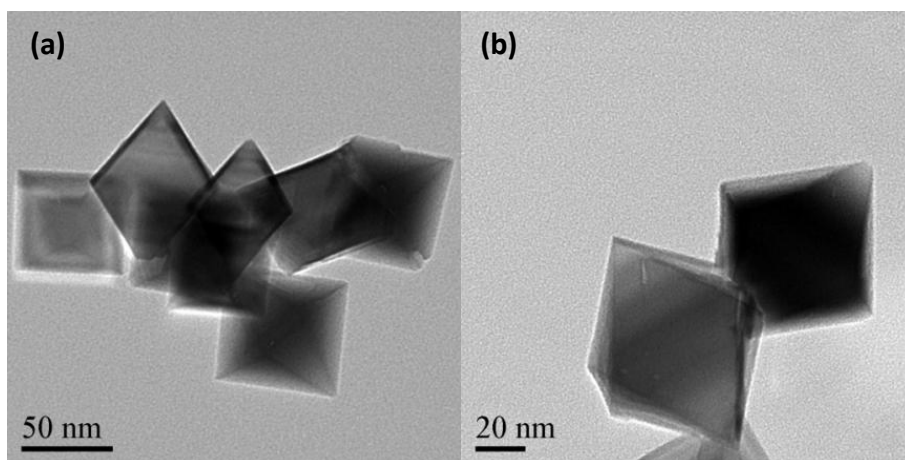


Figure S1 (a) and (b) TEM images of the as-prepared octahedral Rh nanocrystals under different scales.

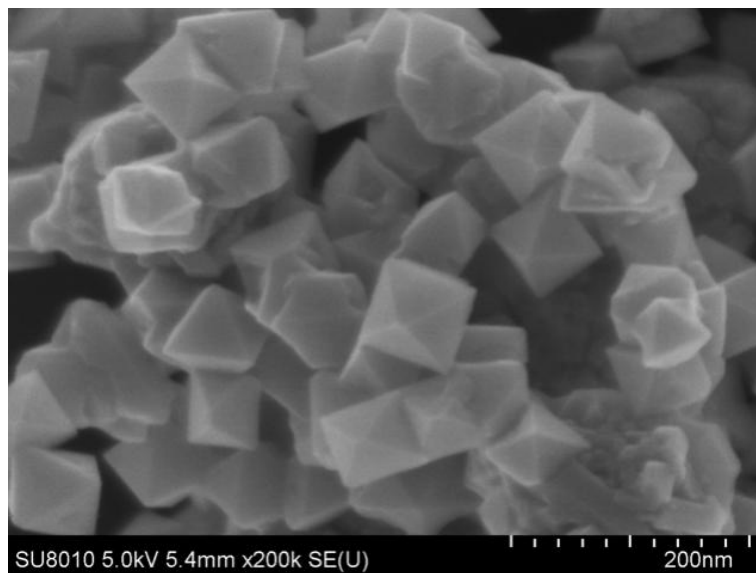


Figure S2 SEM images of the as-prepared octahedral Rh nanocrystals.

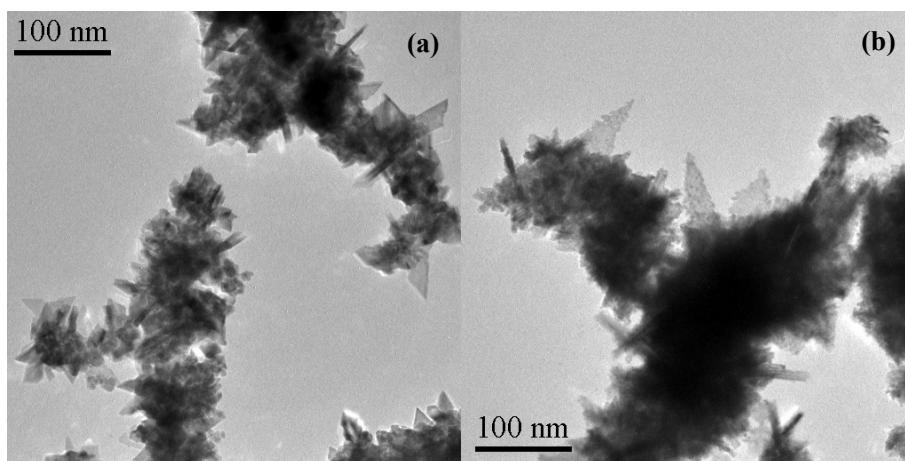


Figure S3 TEM images of the products prepared with KCl or KBr instead of KI.

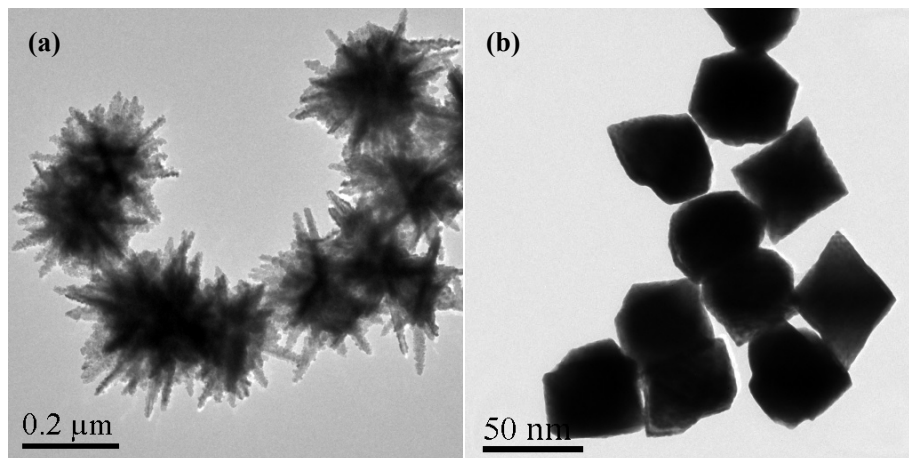


Figure S4 TEM images of the products prepared with CTAC (a) or DDAB (b) instead of DDAC.

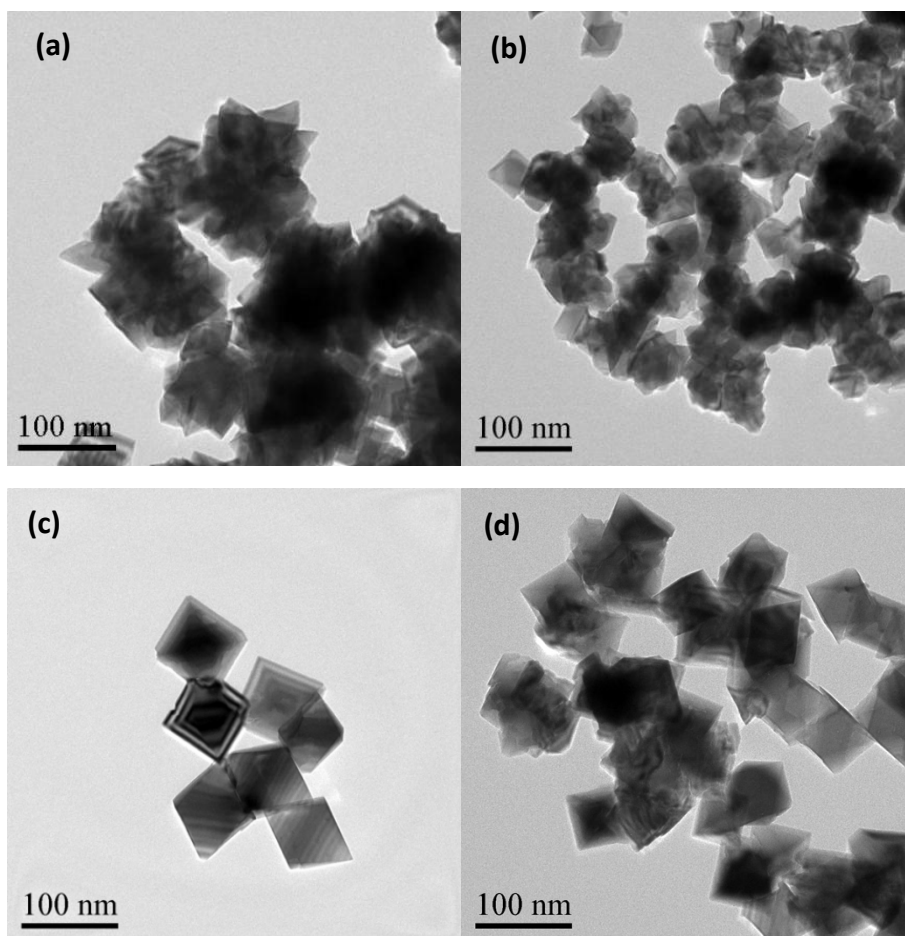


Figure S5 TEM images of the products prepared with different amount of EDA while keeping the same other conditions. (a) 0 mL; (b) 0.5 mL; (c) 1.0 mL;(d) 2.0 mL.

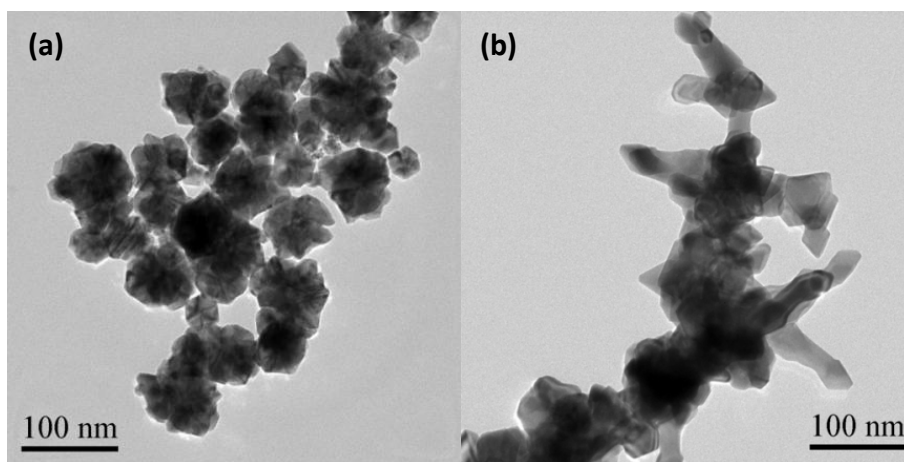


Figure S6 TEM images of the products prepared with different other amines. (a) n-butylamine; (b) n-octylamine.

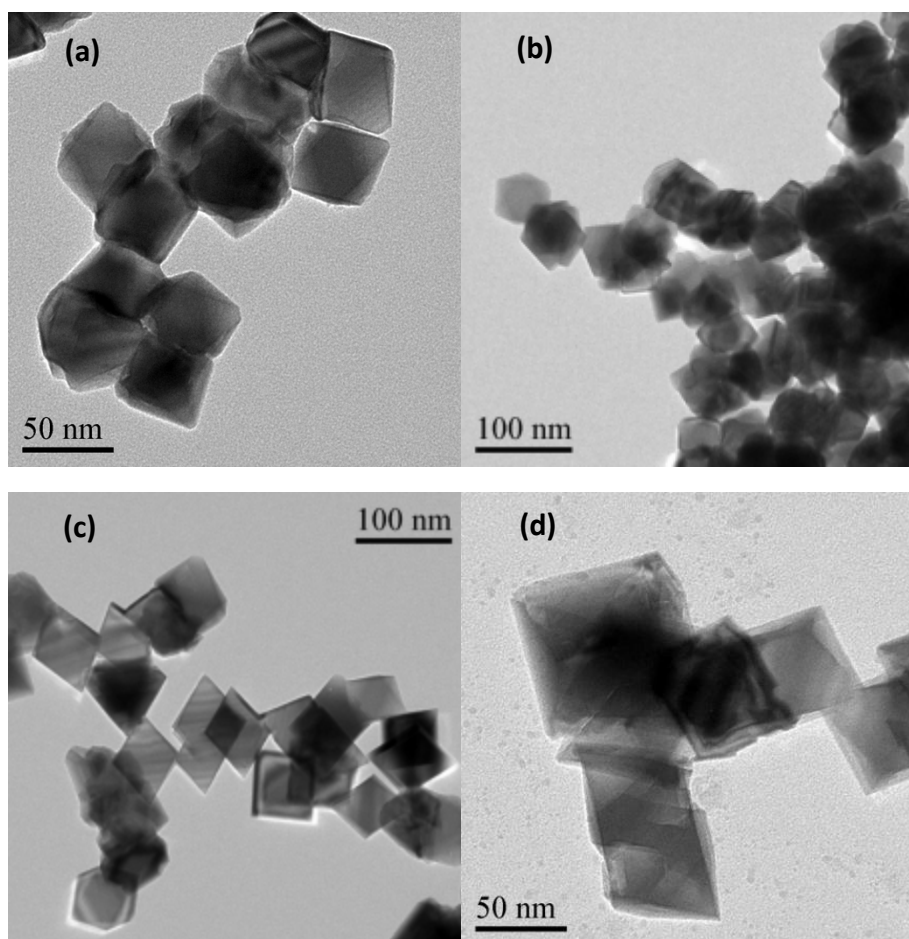


Figure S7 TEM images of the products prepared with different molar ratio of Rh(III)/PVP while keeping the same other conditions. (a) 1/0; (b) 1/10; (c) 1/20; (d) 1/40.

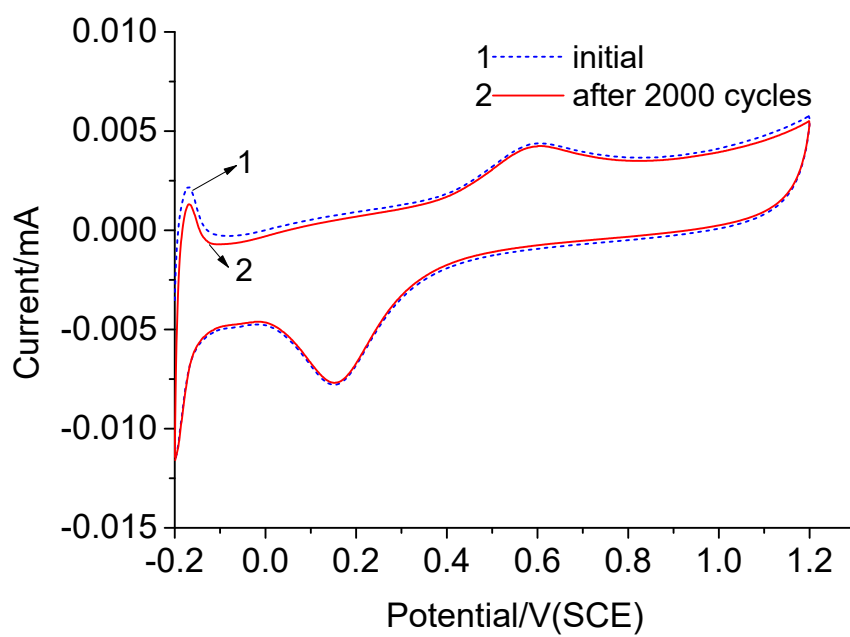


Figure S8 Cyclic voltammograms of the as-prepared octahedral Rh catalysts in 0.5 M HClO₄ at a scan rate of 50 mV·s⁻¹ between -0.2 and 1.2 V.

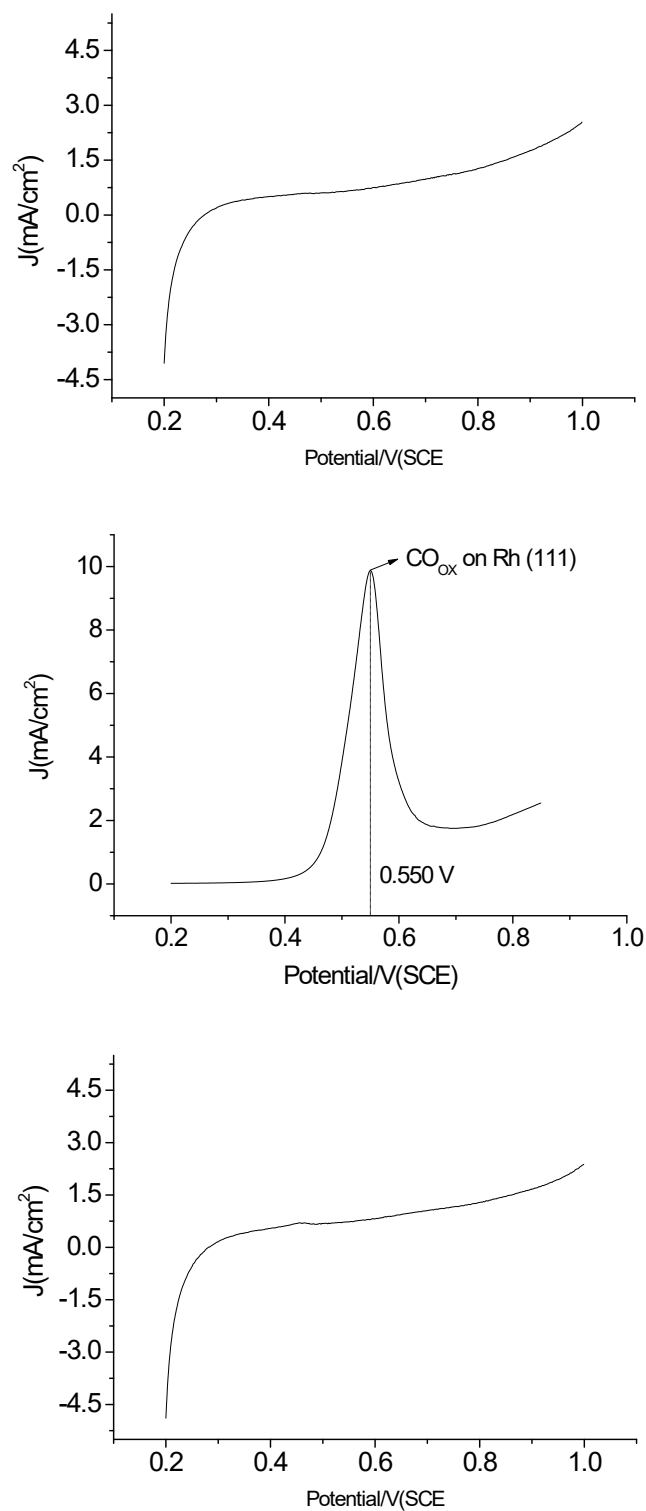


Figure S9 CO stripping voltammetry of the octahedral Rh nanocrystals in 0.5 M HClO₄ solution at a sweep rate of 2 mV/s. (a) for the freshly-prepared octahedral Rh nanocrystals; (b) after dosing CO for 15 minutes for the clean octahedral Rh nanocrystals; (c) the following second potential scanning for the octahedral Rh nanocrystals after CO stripping once.