Electronic Supplementary Information (ESI) for

Microwave-assisted synthesis of mutually embedded Rh concave nanocubes with enhanced electrocatalytic activity

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Experimental Details

***Materials*:** $Rh(acac)_3$ (Kunming Institute of Precious Metals), tetraethylene glycol (TEG, Acros chemicals), benzyldimethylhexadecylammonium (HDBAC), polyvinylpyrrolidone (PVP, average molecular weight, M_w=30000) 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, 0.8 mL of 1 M PVP, 0.6 mL of 1M KI and 1.5 mL of 0.2 M HDBAC solution were added into a 50-mL round-bottle flask in turn. Then, 0.8 mL 0f 0.05 $Rh(acac)_3$ solution was added and the final volume of the reaction mixture was maintained at 10 mL by adding 6.3 mL TEG. The molar ratio of $Rh(acac)_3$/PVP/KI/HDBAC was 1/20/15/7.5 in the reaction system. After 40 min of

rigorous stirring, the resulting bright yellow solution was put into a modified domestic microwave oven (Galanz, 900W) and irradiated for 120 s with 80% of the full output power, and then a brownish black colloid solution was obtained. After cooling to room temperature, the product was collected by centrifugal separation with 10000 rpm and further washed five times with mixed ethanol/acetone solvent. The final product was redispersed in ethanol for characterization.

Characterization: Transmission electron microscopy (TEM) and HRTEM measurements were conducted on a FEI Tecnai G^2 20 and Tecnai G2 F30 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 samples followed by natural drying. A saturated calomel electrode (SCE) and a platinum wire were 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 0.1 M $HClO_4$ + 0.5 M HCOOH aqueous solution, and the stability of the as-prepared Rh nanocrystals was tested by chronoamperometry (CA) at the maximum oxidation voltage in the same solution. All CV tests were carried out in a potential range of -0.2 to 1.0 V at a sweep rate of 50 $mV \cdot s^{-1}$. Before cyclic voltammetry measurements, six cycles of potential sweeps between -0.2V and 1.0V at a sweep rate of 50 $mV \cdot s^{-1}$ were applied in order to clean the Rh surface in-situ. 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 experiment was conducted for commercial Rh black.

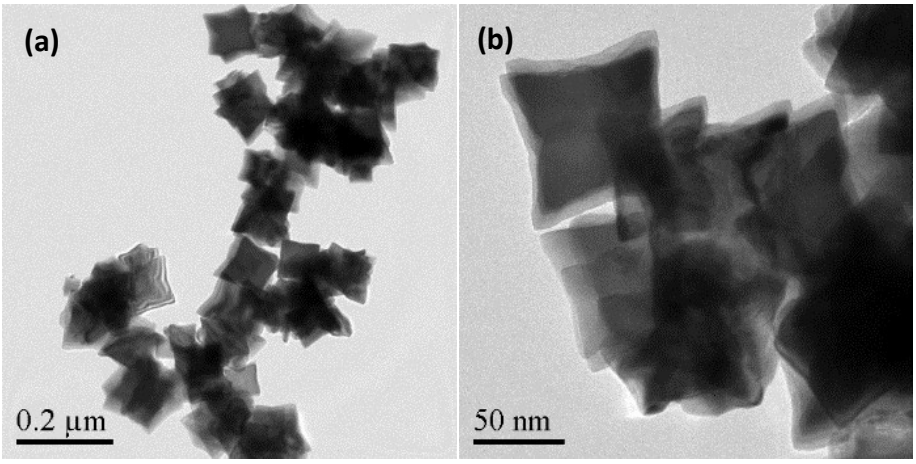

Fig. S1. (a) and (b) TEM images of the as-prepared mutually embedded Rh concave nanocubes under different scales.

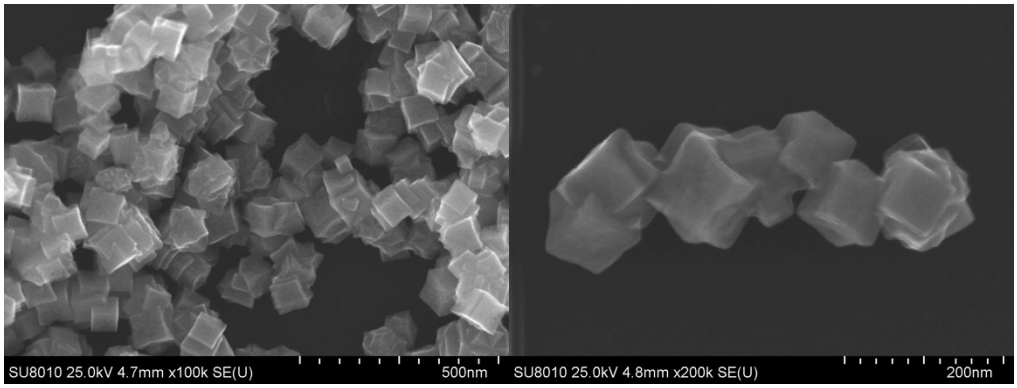

Fig. S2. SEM images of the as-prepared mutually embedded Rh concave nanocubes.

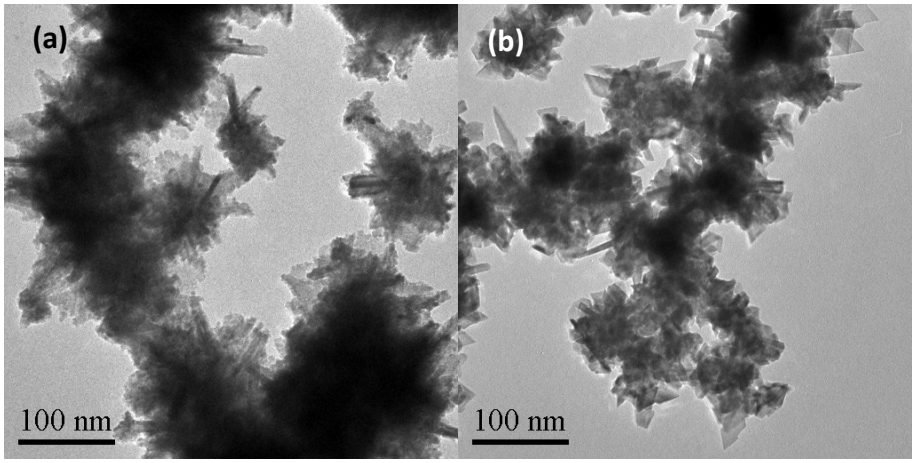

Fig. S3. TEM images of the products prepared with using KBr (a) or KCl (b) instead of KI while keeping the same other conditions.

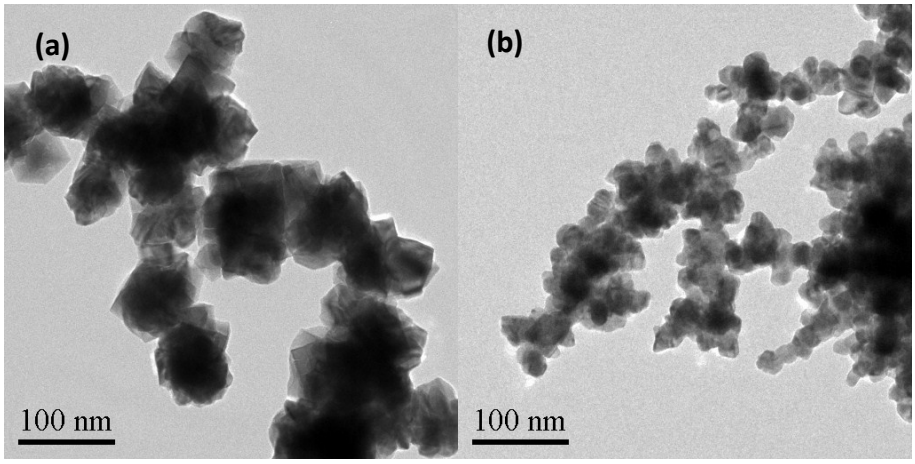

Fig. S4. TEM images of the products prepared with using CTAB (a) or CTAC (b) instead of HDBAC while keeping the same other conditions.

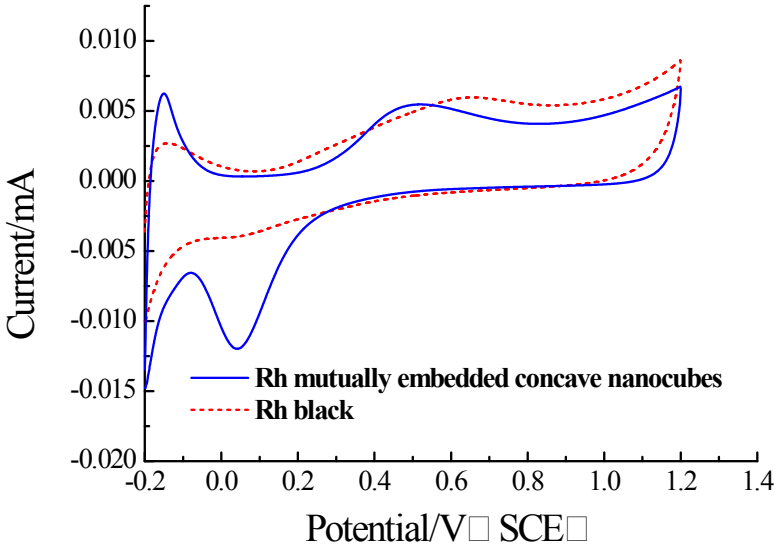

Fig. S5. Cyclic voltamogramms of different Rh catalysts in 0.1 M $HClO_4$ at a scan rate of 50 $mV \cdot s^{-1}$ between -0.2 and 1.2 V.