Electronic Supplementary Information

for

Hollow porous rhodium nanoballs

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Experimental section

Chemicals. Rhodium(III) chloride hydrate ($RhCl_3 \cdot xH_2O$, 38-41% Rh) was purchased from J&K Scientific Ltd., Pt black was purchased from Alfa Aesar, 1-octanol (99%) was purchased from Xilong Scientific (Guangdong, China), and tetrabutylammonium bromide (TBAB, 99.0%) was purchased from Sinopharm Chemical Reagent Co. Ltd. (Shanghai, China). Nitrogen (N_2, 99.99%) and mixed gas (4% CO+96% N_2) were purchased from Linde Industrial Gases. The water used in all experiments were ultrapure (> 18.0 MΩ•cm). All reagents were used as received without further purification.

Synthesis of the hollow porous Rh nanoballs. $RhCl_3 \cdot xH_2O$ (5.0 mg) and TBAB (10.0 mg) were mixed with 8 mL 1-octanol in a 10 mL glass vial, which was then transferred to a 25 mL Teflon-lined stainless-steel autoclave. The steel was then heated to 200 ºC in 30 min and kept for 1 h before it was cooled to room temperature. The black products were separated via centrifugation (9000rpm, 3min) and washed with ethanol for three-four times to remove residual TBAB.

Characterization. The morphology of the as-prepared hollow Rh nanoballs was gained by TEM (JEOL 2100). The HAADF-STEM image was recorded with FEI TECNAI F30 microscope operated at 300 kV. All TEM samples were prepared by depositing a few drops of sample suspension dealt with fully ultrasonic dispersion in ethanol solvent on a copper coated with carbon film. The XRD patterns were obtained from Rigaku Ultima IV diffractometer (Cu Kα, λ = 1.54056 Å). FT-IR was conducted on a Nicolet 380 spectrometer by depositing the ethanol suspensions of hollow Rh nanoballs on dried KBr powders followed by solvent evaporation. N_2 physisorption was carried out at 77 K with a Micromeritics Tristar 3000 surface area analyzer, and the specific surface area was evaluated by the Brunauer−Emmett−Teller (BET) method.

Electrochemical measurements. The measurements were operated on an electrochemical workstation (CHI 760b, Shanghai Chenhua Co. China). The glassy carbon electrodes (with 5 mm in diameter) were polished by polished powder (particle size: 300 nm and 50 nm) then washed by water and alcohol for three times respectively before each electrochemical measurement. The sample ink was prepared by dispersing electro-catalysts in ethanol, and final concentration is 1.0 $mg\cdot mL^{-1}$. Then 5.0 μL of the suspensions was deposited and dried on the working glassy carbon electrode. A Pt sheet was served as the counter electrode. The EOR was performed in N_2-saturated 1.0 M NaOH and 1.0 M ethanol solution at 50 $mV\cdot s^{-1}$ (reference electrode: Hg/HgO).

CO oxidation was conducted in N_2-saturated 1.0 M NaOH solution. Before measurements, CO gas was first bubbled for 15 min, then N_2 was subsequently purged into solution for additional 5 min to get rid of the additional CO in the solution. The CV curve was recorded from -1.0 to 0.0 V with a scan rate of 50 $mV\cdot s^{-1}$.

The electrochemically active surface area (ECSA) of the catalysts was calculated by the equation $ECSA=Q/q_0$, in which q_0 was 420 $\mu C/cm^2$ for commercial Pt black and 380 $\mu C/cm^2$ for hollow Rh nanoballs, respectively, Q was decided by the area of the CO absorption peaks in the CV curves.

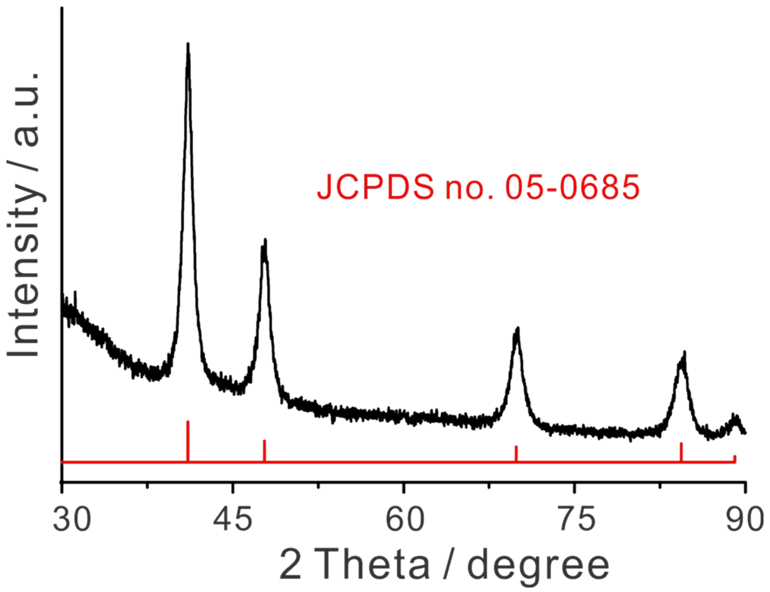

Figure S1. XRD pattern of the as-prepared hollow porous Rh nanoballs.

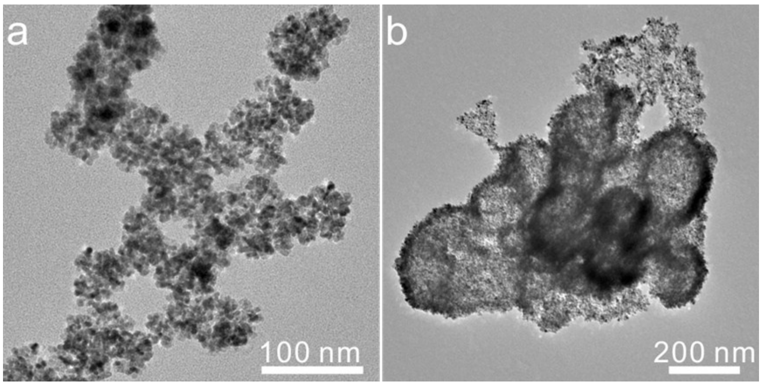

Figure S2. TEM images of products that were produced by replacing TBAB with equimolar (a) NaBr, (b) TBAC.

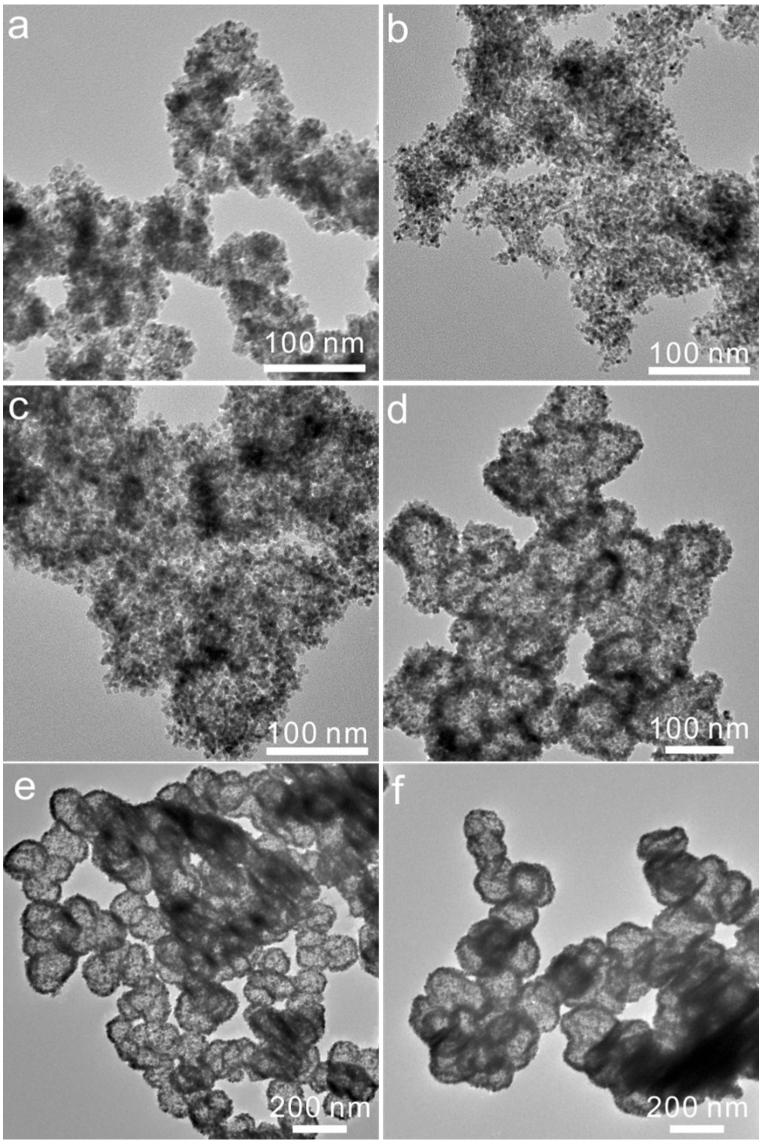

Figure S3. TEM images of products when using different amount of TBAB: (a) 0.0, (b) 0.5, (c) 1.0, (d) 5.0, (e) 10.0, and (f) 100.0 mg.

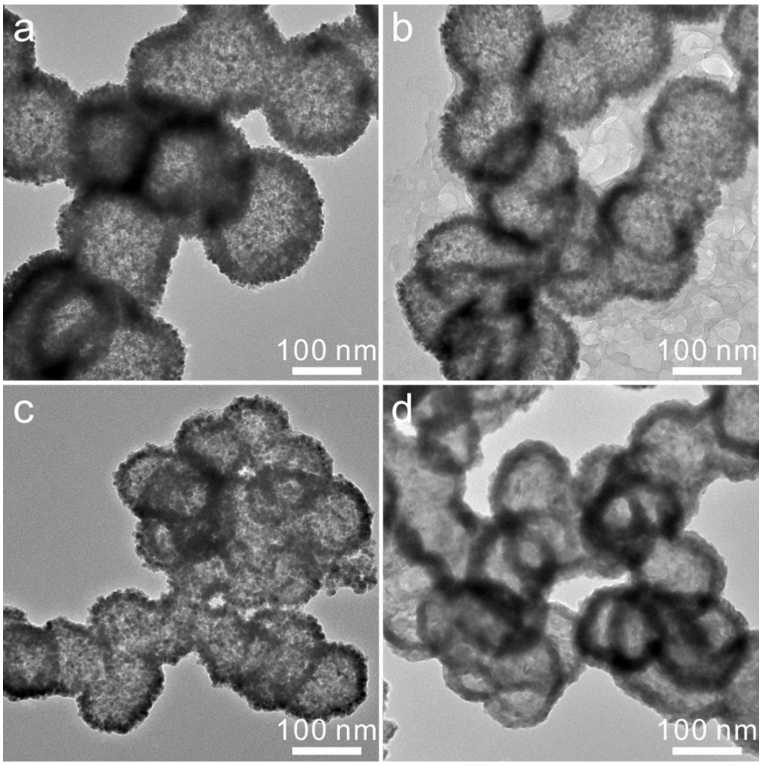

Figure S4. The thermal stability of as-prepared hollow porous Rh nanoballs under different calcination temperatures in air for 1h: (a) 200, (b) 300, (c) 400, and (d) 500 °C.

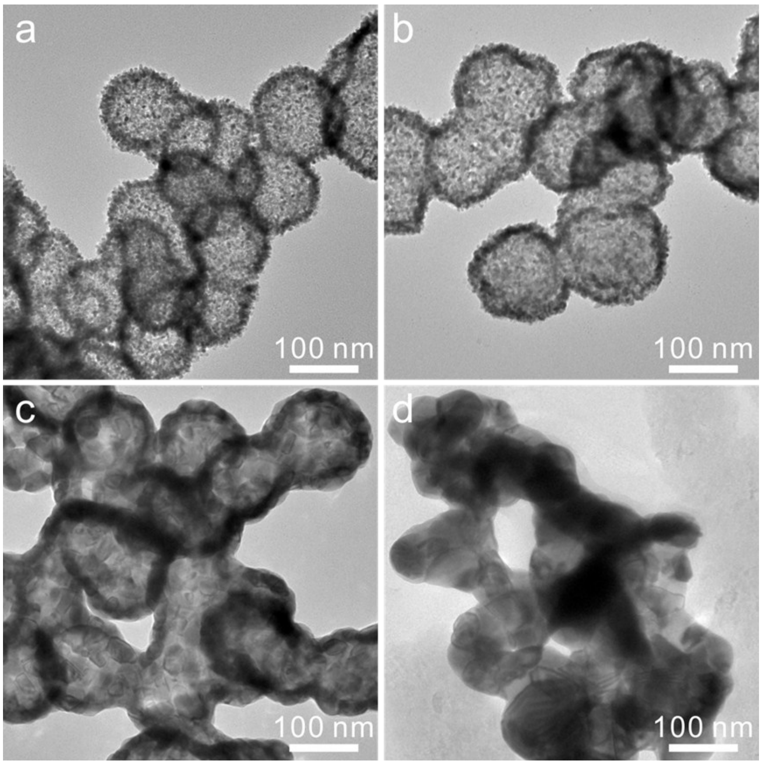

Figure S5. The thermal stability of as-prepared hollow porous Rh nanoballs under different calcination temperatures in Ar for 1h: (a) 200, (b) 300, (c) 400, and (d) 500 °C.

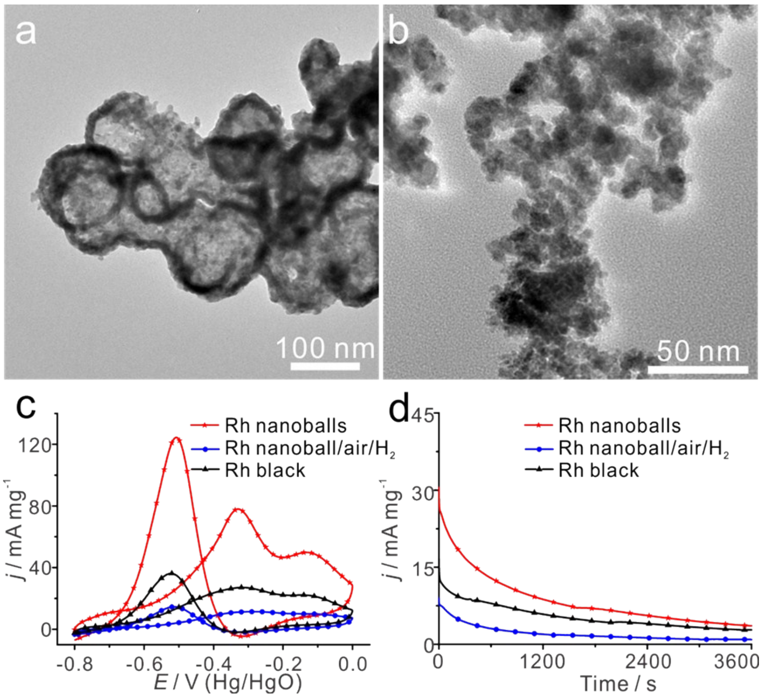

Figure S6. TEM images of (a) hollow Rh nanoballs with compact and smooth exteriors (Rh nanoball/air/H_2), and (b) commercial Rh black. (c) CV curves (scan rate: 50 mV s^{-1}), and (d) i-t curves at -0.35V of different electrocatalysts in N_2 saturated 1.0 M ethanol + 1.0 M NaOH solution. The hollow Rh nanoballs with compact and smooth exteriors were prepared by calcination of as-prepared hollow porous Rh nanoballs under 500 °C in air for 1h (Figure S4d), and subsequently under 220 °C in H_2 for additional 1.5h. The commercial Rh black (99.9%) is purchased from Alfa Aesar.

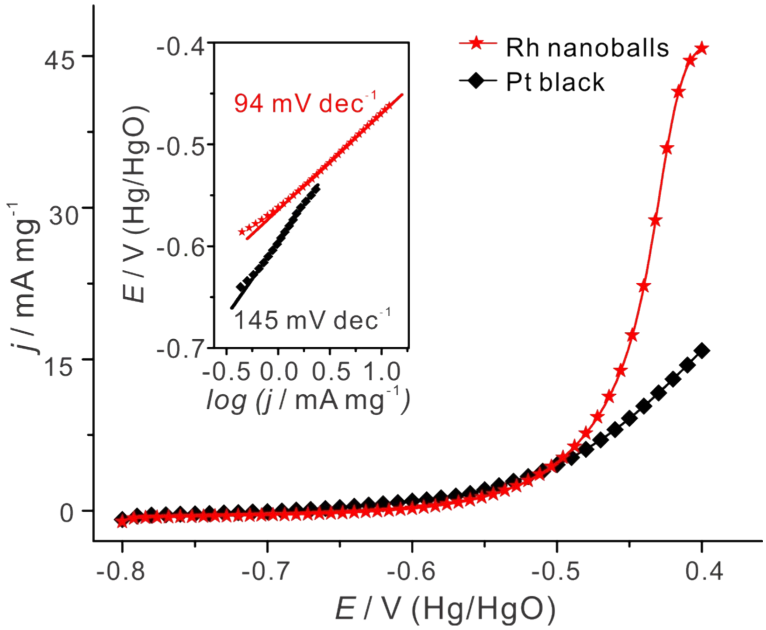

Figure S7. A steady-state linear sweep voltammetry curves of the ethanol oxidation on the hollow porous Rh nanoballs and commercial Pt black in N_2-saturated 1.0 M NaOH and 1.0 M ethanol solution at 1 mV s^{-1}. Inset is corresponding calculated Tafel plots.

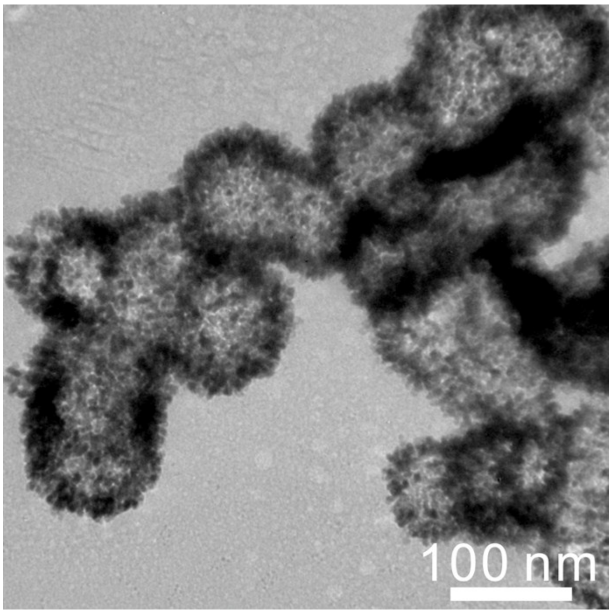

Figure S8. TEM images of hollow porous Rh nanoballs after i-t experiments recorded at -0.35 V for 3600 s in 1.0 M NaOH and 1.0 M ethanol solution.

Table S1. Summary of the electrocatalytic performance of reported Rh-based catalysts toward the electrooxidation of ethanol in alkaline media.

Catalyst	Mass Activity (mA mg^{-1})	Condition	Ref.
Rh tetrahedra	31.0	1.0 M NaOH + 1.0 M ethanol	*J. Am. Chem. Soc.*, 2018, **140**, 11232
Rh icosahedra	50.4	1.0 M NaOH + 1.0 M ethanol	*Nano Res.*, 2018, **11**, 656
Rh tetrahedra	42.0	1.0 M NaOH + 1.0 M ethanol	*Nano Res.*, 2018, **11**, 656
Hyperbranched Rh nanoplates	41.9-146.6	1.0 M NaOH + 1.0 M ethanol	*Sci. China Mater.* 2017, **60**, 685
Cyclic penta-twinned Rh nanobranches	185.3	1.0 M NaOH + 1.0 M ethanol	*J. Am. Chem. Soc.*, 2018, **140**, 11232
Excavated Rh nanobranches	79.1	1.0 M NaOH + 1.0 M ethanol	*Mater. Today Energy* 2019, **11**, 120
$Pt_{50}Rh_{50}$ nanoparticles/C	~10	1.0 M KOH + 1.0 M ethanol	*Electrocatal.*, 2016, **7**, 297
PtRh alloy nanodendrites	462.1	1.0 M KOH + 1.0 M ethanol	*ACS Appl. Mater. Interfaces* 2018**, 10**, 19755
Hollow porous Rh nanoballs	78.6	1.0 M NaOH + 1.0 M ethanol	This work