Electronic Supplementary information (ESI) for

Facilitating the C–C Bond Cleavage on Sub-10-nm Concavity-Tunable Rh@Pt Core-Shell Nanocubes for Efficient Ethanol Electrooxidation

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Experimental

Chemicals

Sodium hexachlororhodate (III) dodecahydrate ($Na_3RhCl_6 \cdot 12H_2O$) was purchased from Alfa Aesar. Sodium hexachloroplatinate(IV) hexahydrate ($Na_2PtCl_6 \cdot 6H_2O$, Pt⩾37.5%), chloroplatinic acid hexahydrate ($H_2PtCl_6 \cdot 6H_2O$, Pt⩾37.5%), and perchloric acid ($HClO_4$, 70%) were purchased from Aladdin. Platinum(II) acetylacetonate ($Pt(acac)_2$) was purchased from Kunming Institute of Precious Metals. Polyvinylpyrrolidone (PVP, MW≈55000) was purchased from Sigma-Aldrich. L(+)-ascorbic Acid ($C_6H_8O_6$, ⩾99.7%), potassium bromide (KBr, ⩾99.0%), formaldehyde aqueous solution (40%), benzyl alcohol (C_7H_8O, ⩾99.0%), sodium iodide dihydrate ($NaI \cdot 2H_2O$, ⩾99.0%), and ethanol (C_2H_5OH, ⩾99.7%) were purchased from Xilong Chemical Co. Ltd. Acetone (C_3H_6O, ⩾99.5%). Ethylene glycol (EG, ⩾99.0%) was purchased from Sinopharm Chemical Reagent Co. Ltd. Ultrapure water (18.2 MΩ) was used in all experiments. All reagents were used as received without further purification.

Synthesis of Rh@Pt d-CNCs and Rh@Pt s-CNCs

In a typical synthesis of the Rh@Pt d-CNCs, 52.8 mg AA and 107.1 mg KBr were co-dissolved in 7.0 mL EG in a 50-mL three-neck flask. The solution was preheated at 110 ^{o}C for 2 h in an oil bath with a magnetic stirring (320 rpm), and then ramped up to 140 ^{o}C. After that, 0.10 mmol $Na_3RhCl_6 \cdot 12H_2O$ and 1.0 mmol PVP were separately dissolved in 5.0 mL EG at room temperature, and then injected simultaneously into the preheated reaction solution through a two-channel syringe pump at a rate of 4.0 mL/h. Subsequently, 2.0 mL EG solution containing 0.04 mmol $Na_2PtCl_6 \cdot 6H_2O$ and 2.0 mL EG solution containing 0.4 mmol PVP were simultaneously injected into the flask at a rate of 4 mL/h. After the injection, the reaction lasted for another 15 min before cooled down to room temperature. The products were collected by centrifugation and washed with acetone and ethanol several times.

For the synthesis of the Rh@Pt s-CNCs, the reaction temperature was ramped from 140 ^{o}C up to 180 ^{o}C before the injection of the $Na_2PtCl_6 \cdot 6H_2O$ EG solution, while other conditions were kept unchanged.

Synthesis of Rh@Pt FNCs

Typically, 52.8 mg AA, 108 mg KBr and 133 mg PVP were co-dissolved in 13 mL EG hosted in a 50-mL three-neck flask. The solution was then preheated at 110 ^{o}C for 2 h in an oil bath with a magnetic stirring (320 rpm), and then ramped up to 140 ^{o}C. 5.0 mL EG solution containing 0.10 mmol $Na_3RhCl_6 \cdot 12H_2O$ was then injected into the flask through a syringe pump with a rate mode as follow: 1.1 mL with a rate of 60 mL/h and the rest 3.9 mL solution with a rate of 4 mL/h. After that, the temperature was ramped up to 180 ^{o}C, and then 2.0 mL EG solution containing 0.04 mmol $Na_2PtCl_6 \cdot 6H_2O$ was injected into the flask through a syringe pump at a rate of 2.0 mL/h. After the injection, the reaction lasted for another 15 min before cooled down to room temperature. The products were collected by centrifugation and washed with acetone and ethanol several times.

Synthesis of Pt FNCs

The Pt FNCs were synthesized according to a previous report.[1] Typically, 10 mg Pt(acac)$_2$, 200 mg PVP, 2.5 mL formaldehyde solution and 10 mL benzyl alcohol were mixed together in a 20-mL Teflon-lined stainless-steel autoclave, sealed and then heated at 150 ^{o}C for 10 h before naturally cooled down to room temperature. The products were collected by centrifugation and washed with acetone and ethanol for several times.

Synthesis of alloyed RhPt FNCs

Typically, 160 mg PVP, 36 mg AA, 93 mg $NaI \cdot H_2O$, and 1.0 mL H_2O were mixed together as **solution A**. Meanwhile, 11 mg $Na_3RhCl_6 \cdot 12H_2O$ and 4 mg $H_2PtCl_6 \cdot 6H_2O$ were dissolved together in 5.0 mL EG to form **solution B**. After that, the **solution B** was quickly added into **solution A** with a pipette. The mixture solution was ultrasonicated for 7 min and then magnetically stirred at 320 rpm for another 7 min. The obtained mixture was heated at 170℃ in an oil bath under magnetic stirring for 2 h. The products were collected by centrifugation and washed with acetone and ethanol several times.

Characterizations

Transmission electron microscopy (TEM), High-angle annular dark field-scanning TEM (HAADF-STEM) images, EDS elemental mappings and line scanning profiles were recorded on a Hitachi H-7650 TEM operated at 100 kV and an FEITM Talos F20S TEM at 200 kV. Scanning electron microscope-energy dispersive X-ray spectroscopy (SEM-EDS) elemental analysis was analysed with a Hitachi S4800 equipped with an energy dispersive X-ray spectroscopy. An Agilent 7800 ICP-MS (inductively coupled plasma mass spectrometry) apparatus was used for analysing the elements. X-ray diffraction (XRD) patterns was performed on a Rigaku Smar/SmartLa operating at 30 mA and 40 kV for Cu Kα radiation ($\lambda = 1.541$ Å).

Electrocatalysis Measurements

Before the electrocatalytic tests, the as-prepared metal catalysts were loaded on Vulcan-72 carbon with 20 wt% of total metals (determined by ICP-MS). The loaded electrocatalysts were re-dispersed in 10 mL acetic acid, heated at 70 °C for 10 h with a magnetic stirring to clean the surface. The cleaned catalysts were washed with ethanol for three times, and dried under vacuum condition at 60 ^{o}C for 9 h. To prepare the homogeneous ink, 10 mg of the carbon-loaded electrocatalysts (8 mg for Pt/C) was ultrasonically dispersed in a solvent containing 2.0 mL ethanol and 10 μL of 5% Nafion ($V_{enthol}:V_{Nafion} = 1:0.005$) for 20 min. Then, 6 μL of the ink was dropped on a glassy-carbon electrode (GCE, diameter: 5 mm, area: 0.196 cm^2) and then dried in room temperature naturally.

A CHI 660E electrochemical workstation with a three-electrode system was used to estimate the EOR performance of the electrocatalysts. The saturated calomel electrode (SCE), Pt mesh (1×1 cm^2), and a catalyst-loaded glassy carbon electrode are respectively used for reference electrodes, counter electrodes and working electrodes. The electrochemical active surface areas (ECSAs) were calculated by integrating the H_{upd} desorption domains on the cyclic voltammograms (CVs), which was recorded in N_2-saturated 0.1 M $HClO_4$ solution at room temperature with a sweep rate of 50 mV/s between -0.25 and 0.95 V (vs. SCE). Electrocatalytic EOR were recorded in N_2-saturated 0.1 M $HClO_4$ solution and 0.2 M ethanol solution at room temperature with a sweep rate of 50 mV/s between -0.25 and 1.20 V (vs. SCE).

Electrochemical in situ FTIR studies

In situ FTIR reflection spectroscopy was carried out on a Nexus 8700 FTIR spectrometer (Nicolet) which equipped with a liquid nitrogen-cooled MCT-A detector and an EverGlo IR source. In this configuration, IR radiation sequentially passed through a CaF_2 window and a ~10 μm thin solution layer, and then it was reflected by the electrode surface at a spectrum resolution of 8 cm^{-1}. The resulting spectra were reported as the relative change in reflectivity and calculated as follows

$$\frac{\Delta R}{R}=\frac{R(E_S)-R(E_R)}{R(E_R)}$$

Where $R(E_S)$ and $R(E_R)$ are the single-beam spectra collected at sample potential E_S and reference potential E_R ($E_R = -0.20$ V, vs SCE), respectively.

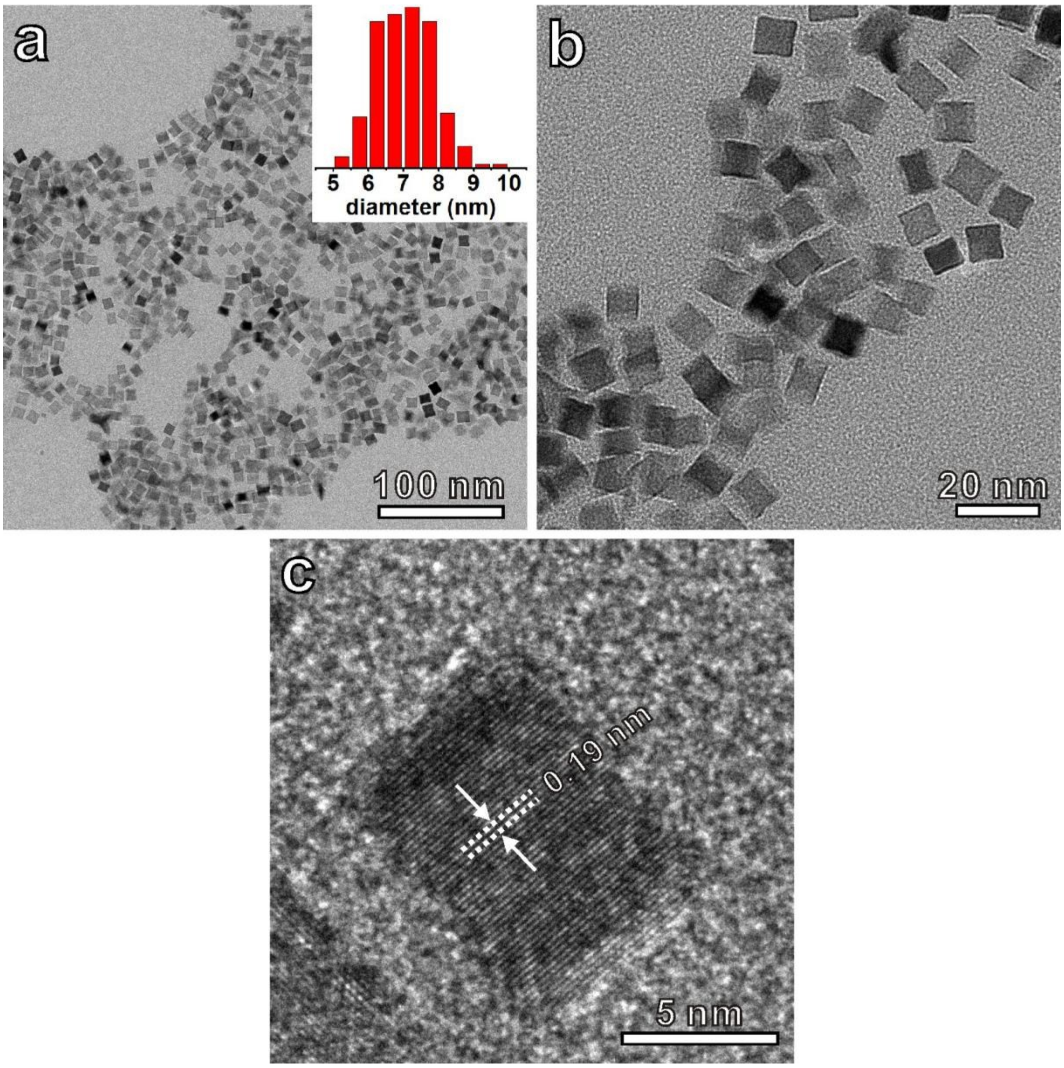


Figure. S1. (a,b) TEM images and corresponding diameter distributions of the preformed Rh CNCs. (c) HRTEM of a single Rh CNCs, the 0.19 nm interplanar spacing correspond to the Rh(200) distance.

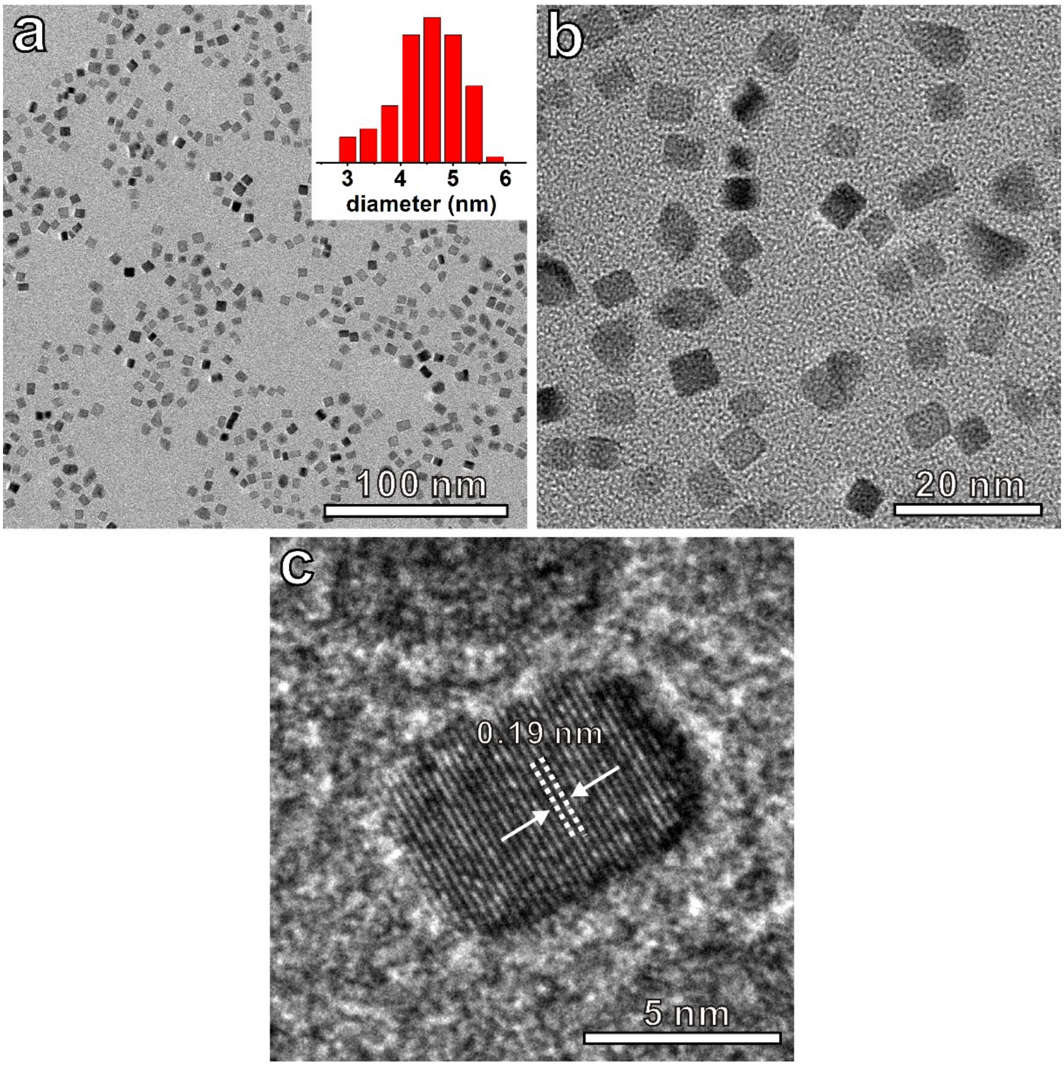
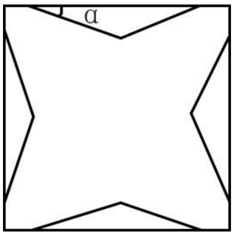
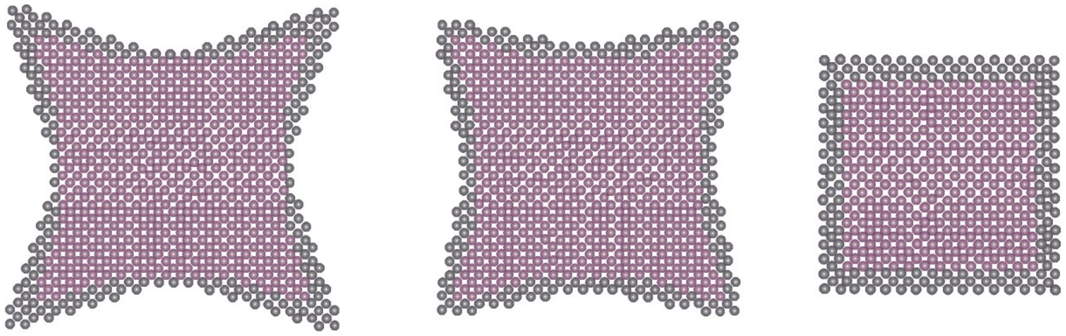


Figure. S2. (a,b) TEM images and diameter distributions of the preformed Rh FNCs. (c) HRTEM of a single Rh FNC.

Table S1. The calculated values for the angle α when the concave nanocube is bound by different high-index crystallographic facets.[2,3]



{hkl}	Angle α°
210	26.56
950	29.05
530	30.96
850	32
320	33.69
750	35.53
430	36.85
540	38.65



(i) Rh@Pt d-CNCs **(ii) Rh@Pt s-CNCs** **(iii) Rh@Pt FNCs**

Figure. S3. Atomic profile 2D models of the three-type concavity-tuned Rh@Pt core-shell nanocubes.

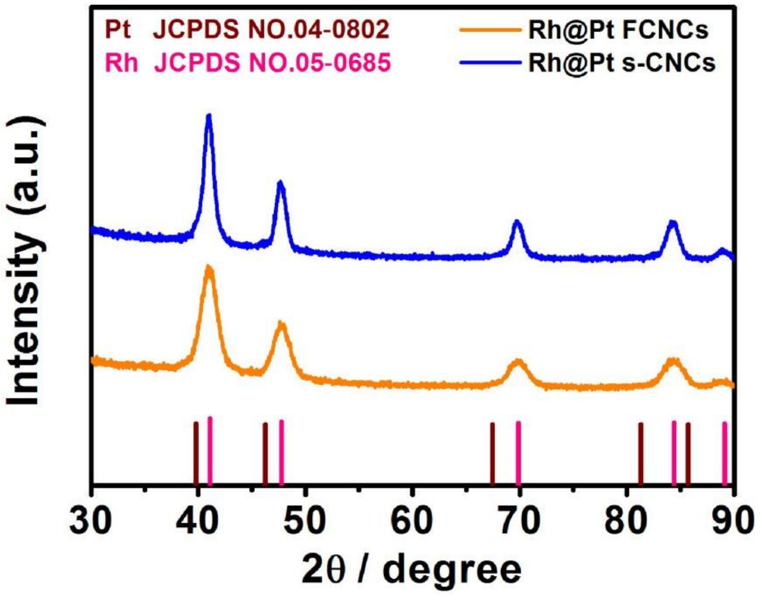


Figure. S4. XRD of the as-prepared Rh@Pt core-shell s-CNCs and FNCs.

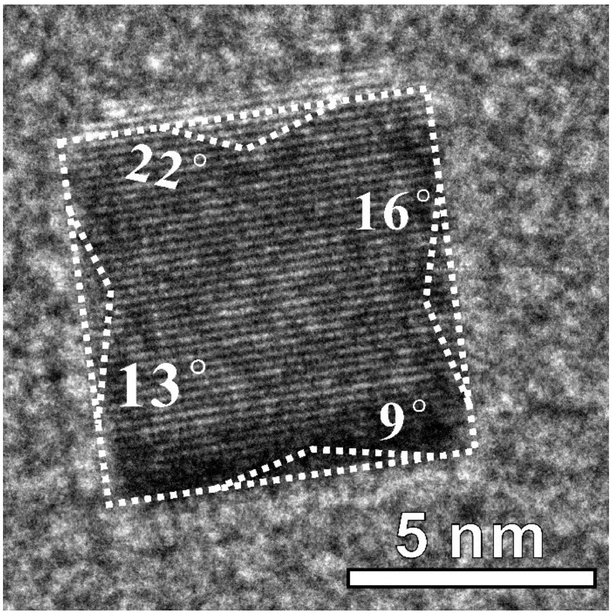


Figure S5. HRTEM of an individual Rh@Pt s-CNC showing the smaller dihedral angles (α).

Table S2. Synthesis condition and the Rh/Pt atomic ratio of the samples.

Sample	**Seed**	**Pt deposition temperature**	**Na_2PtCl_6 injection rate**	**Rh/Pt Atomic ratio***
Rh@Pt d-CNCs	Rh CNCs	140 °C	4 mL/h	69.2:30.8
Rh@Pt FNCs	Rh CNCs	180 °C	4 mL/h	67.4:32.6
Rh@Pt s-CNCs	Rh FNCs	180 °C	2 mL/h	70.5:29.5

*Determined by ICP-MS.

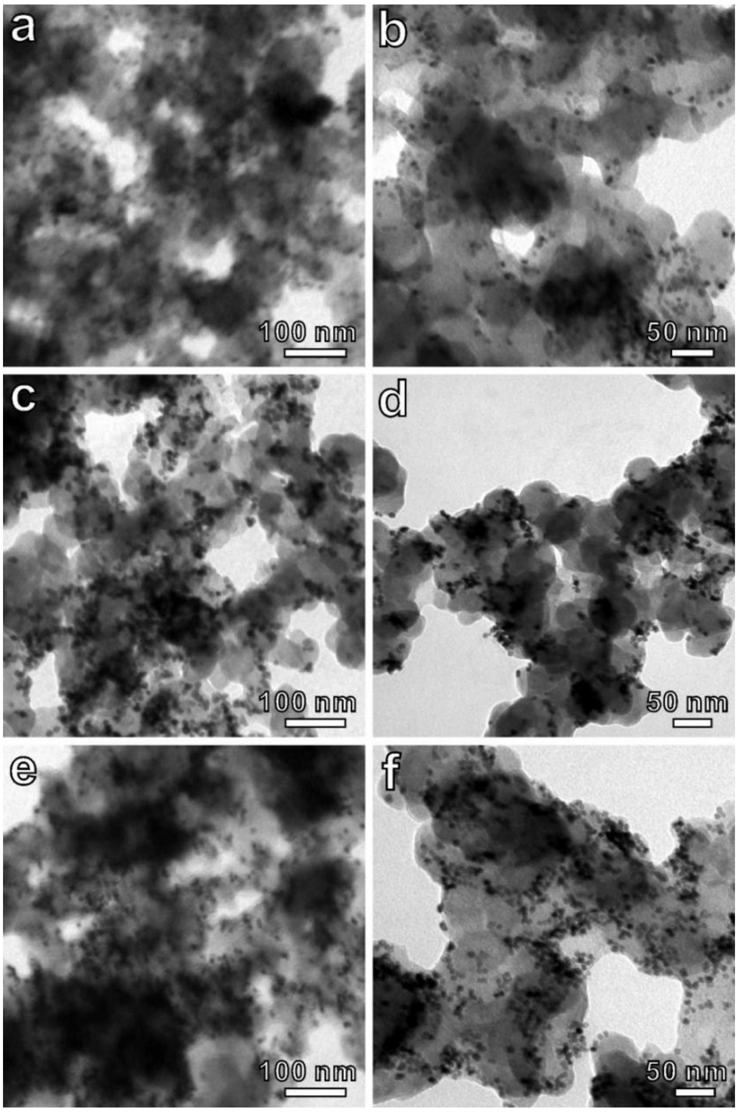


Figure. S6. TEM images of the carbon-loaded catalysts: (a,b) Rh@Pt d-CNCs/C, (c,d) Rh@Pt s-CNCs/C, (e,f) Rh@Pt FNCs/C.

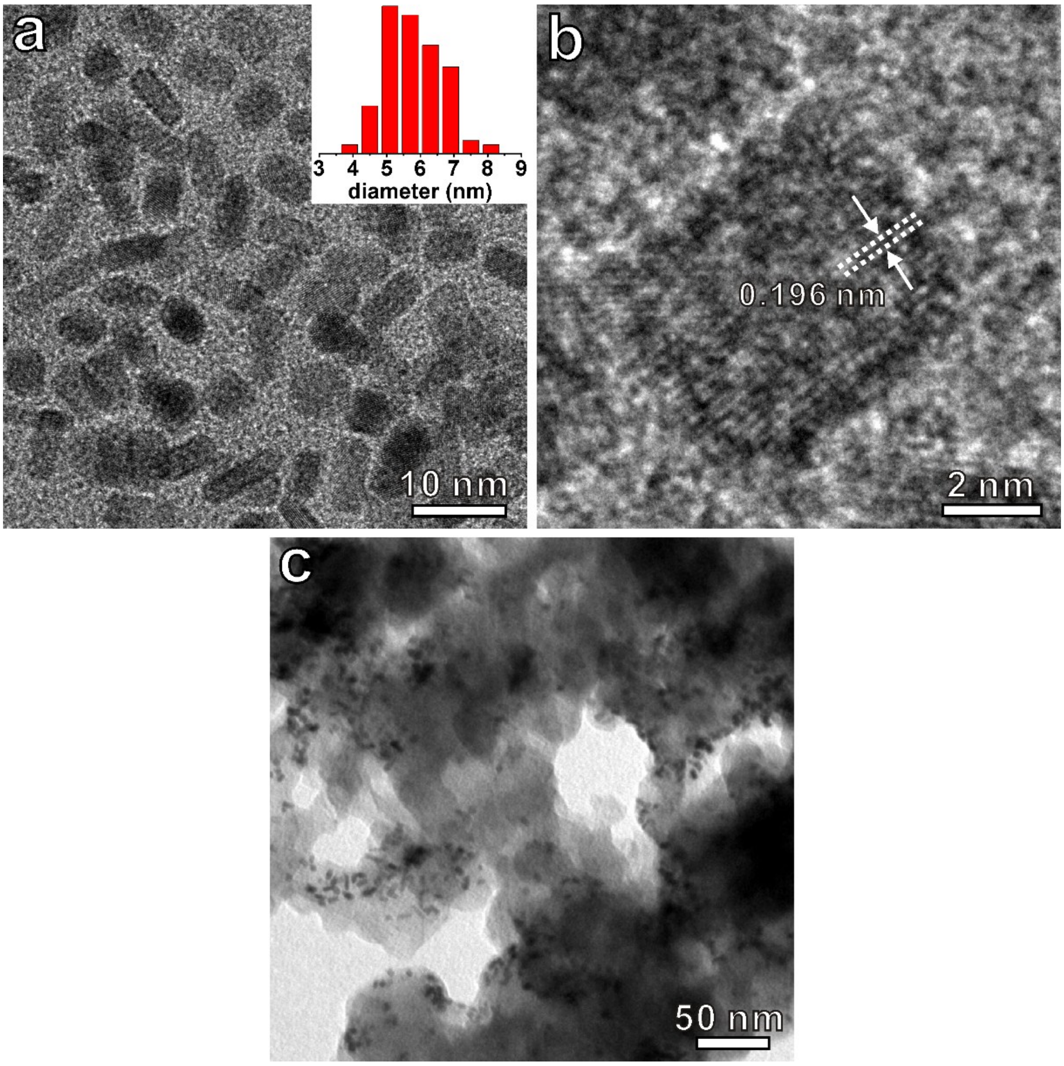


Figure. S7. (a) TEM images of the as-prepared Pt FNCs, (b) HRTEM of a single Pt FNC and (c) TEM image of the carbon-loaded Pt FNCs/C catalysts.

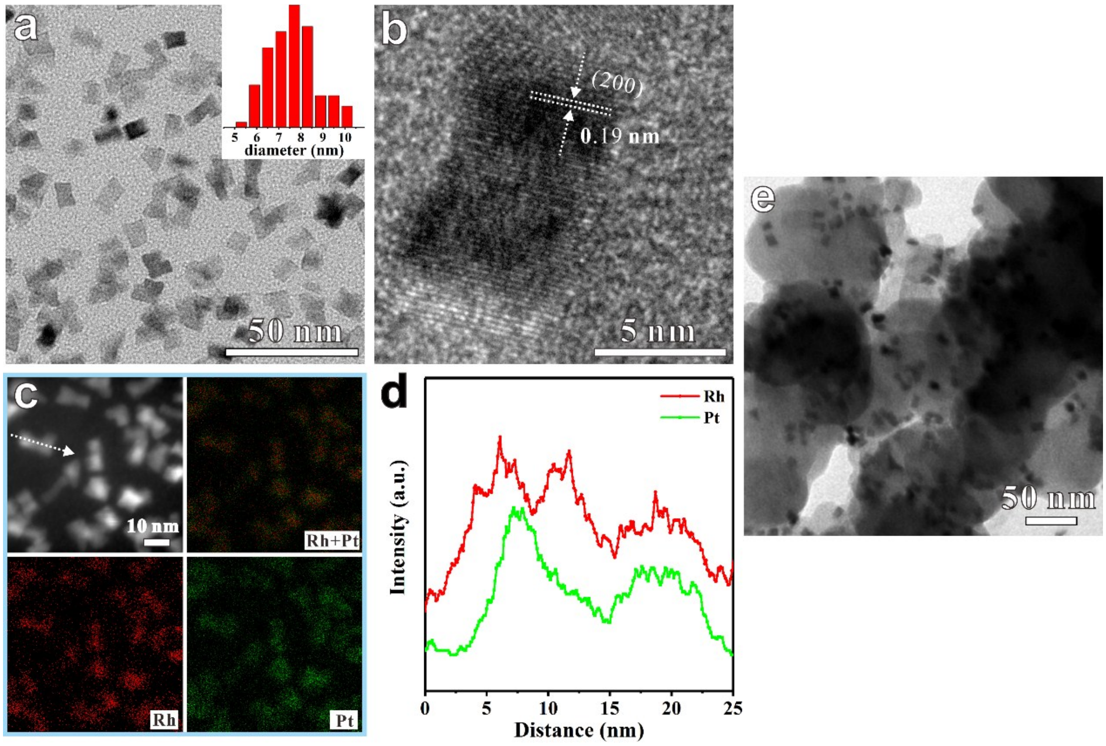


Figure S8. Characterization of the alloyed RhPt FNCs: (a) TEM and size distribution, (b) HRTEM, (c) STEM and EDS mapping, (d) EDS line scanning, and (e) TEM image after loading on carbon. The Rh/Pt mole ratio of the RhPt FNCs is determined to be 62.8/37.2 by ICP-MS.

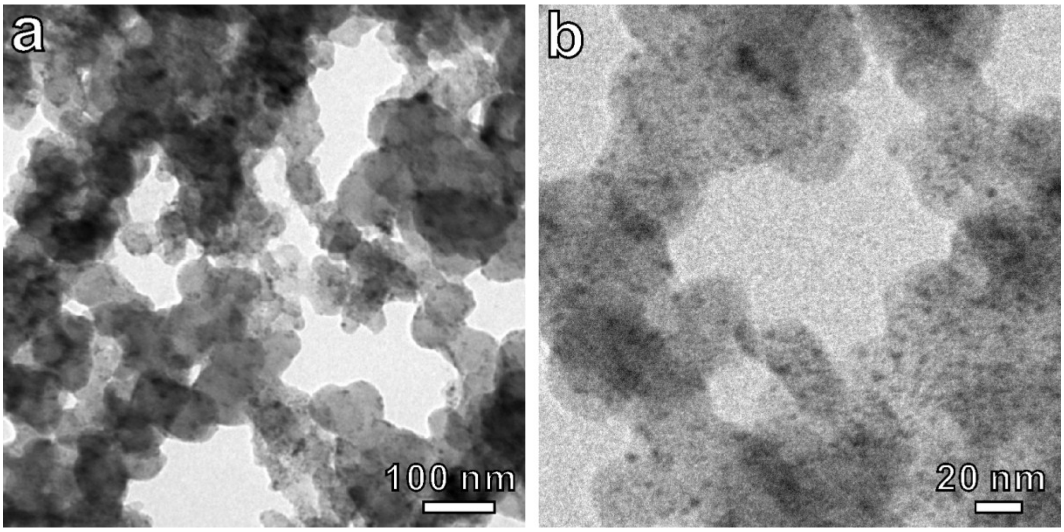


Figure. S9. (a,b) TEM images of the commercial Pt/C.

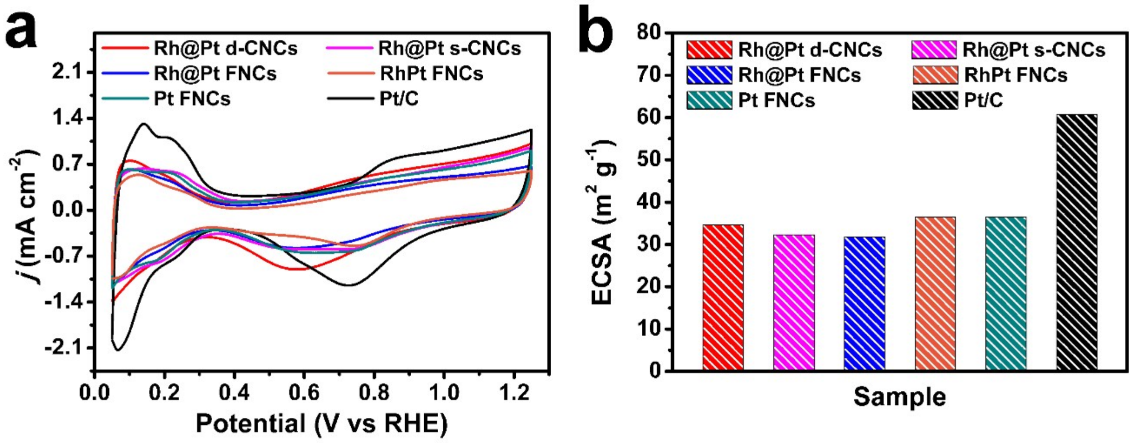


Figure. S10. (a) CVs of the carbon loaded electrocatalysts and commercial Pt/C recorded at room temperature in a N_2-saturated 0.1 M $HClO_4$ solution with a sweep rate of 50 mV s^{-1}, (b) histogram of the corresponding ECSAs calculated from the H_{upd} desorption region.

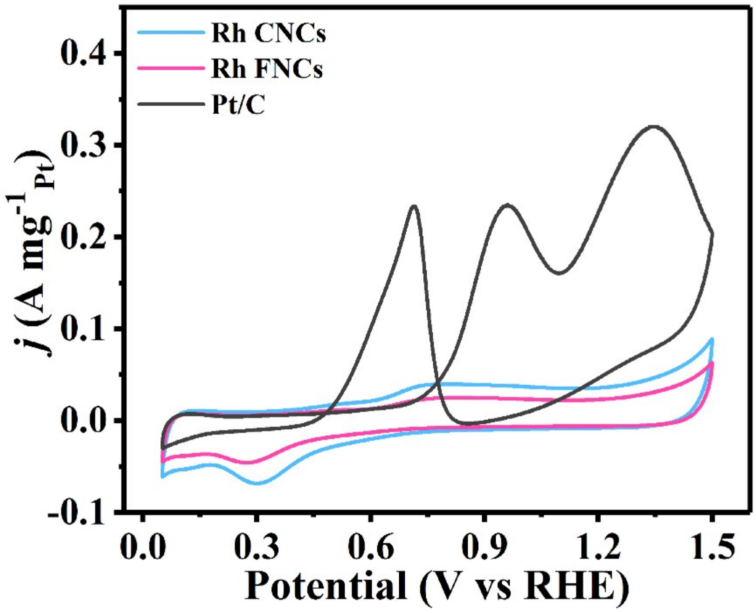


Figure S11. CV curves normalized by the metal mass showing the inactive EOR catalysis on the Rh CNCs and Rh FNCs.

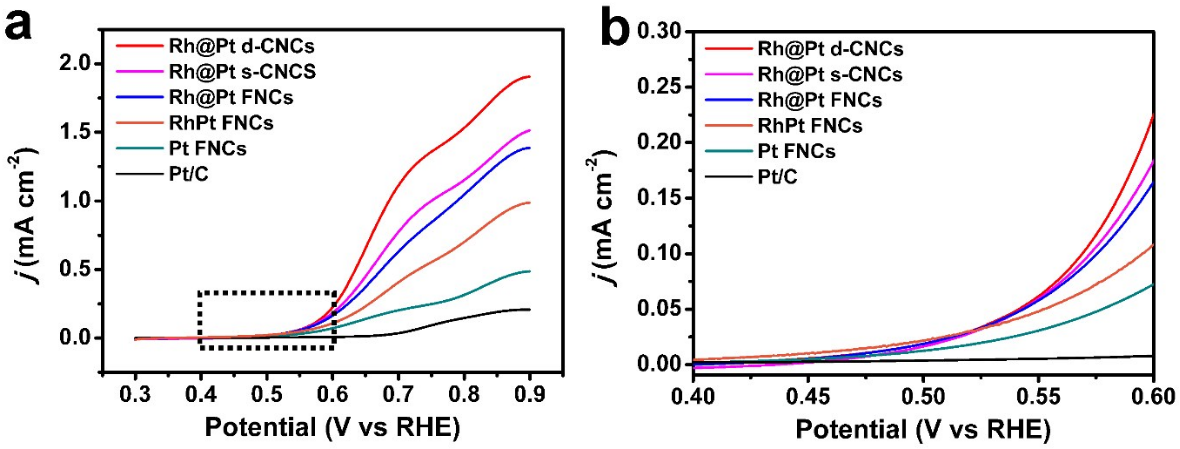


Figure. S12. Linear scan voltammetric (LSV) curves for the as-prepared catalysts in N_2-purged 0.2 M ethanol + 0.1 M $HClO_4$ aqueous solution at room temperature at 10 mV s^{-1}.

Table. S3. Assignment of the absorption bands in the in situ FTIR spectra for EOR.[4-7]

Wavenumber/cm^{-1}	Assignment
2342	CO_2 asymmetric stretching
2050	CO_L (linearly adsorbed CO)
1900	CO_B (bridge adsorbed CO)
1718	C=O stretching of acetaldehyde/acetic acid
1390	CH_3 asymmetric bending vibration in CH_3COOH
1280	C–O stretching deformation in CH_3COOH

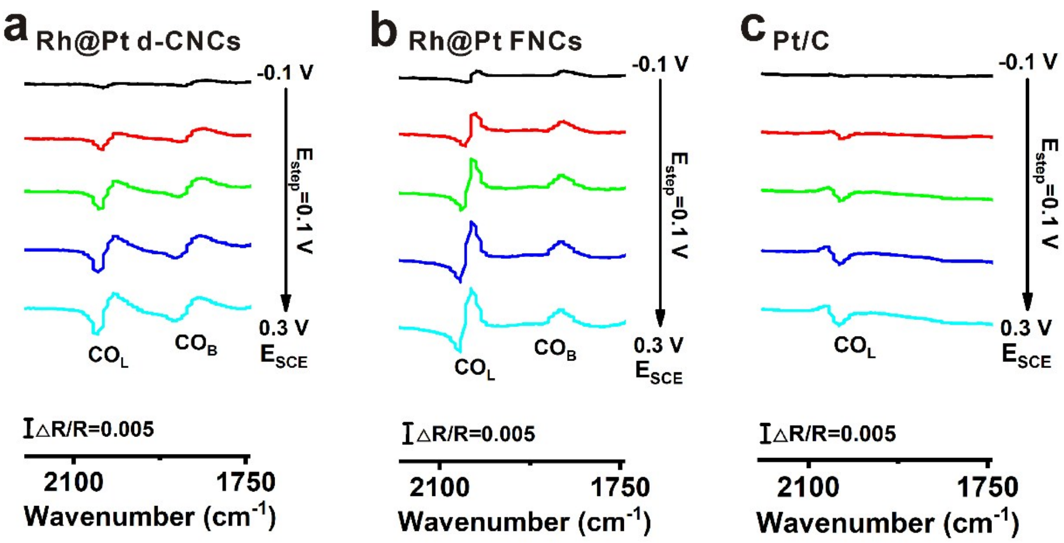


Figure S13. (a-c) Extracted in situ FTIR spectra showing the adsorption of CO_{ads} species at the low potential range from -0.1 V to 0.3 V (vs SCE).

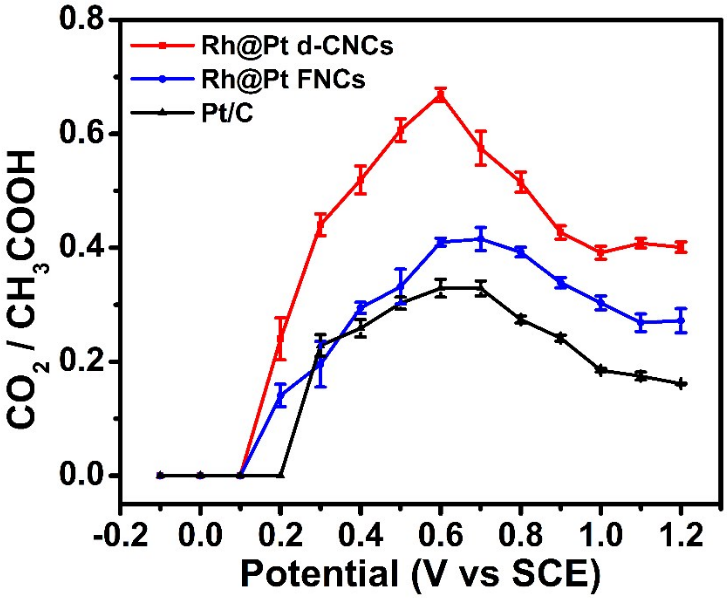


Figure S14. Relative intensity of CO_2/CH_3COOH as a function of the electrode potential.

Reference

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