Electronic Supplementary Information

Excavated RhNi Alloy Nanobranches Enable Superior COtolerance and CO₂ Selectivity at Low Potentials toward Ethanol Electro-oxidation

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Supplemental Experimental Procedures

Chemicals and Materials

Rhodium (III) 2, 4-pentanedionate (Rh(acac)₃) was purchased from Kunming institute of precious metals. Nickel(II) 2,4-pentanedionate (Ni(acac)₂), dibenzyl ether (Bn₂O, 98+%), oleic acid (C₁₈H₃₄O₂, tech 90%) and commercial Rh black were purchased from Alfa Aesar. Formaldehyde solution (40%) was purchased from Sinopharm Chemical Reagent Co. Ltd. (Shanghai, China). Oleylamine (C₁₈H₃₇N) were purchased from J&K Chemicals. Sodium hydroxide (NaOH, AR), Sulfuric acid (H₂SO₄, AR) and ethanol (AR) were purchased from Sinopharm Chemical Reagent Co. Ltd. (Shanghai, China). Mixed gas (4% CO+96% N₂) and nitrogen (N₂, 99.99%) were purchased from Linde Industrial Gases. All chemicals were analytical graded and used without further purification. The ultrapure water (18 MΩ/cm) used in all experiments was prepared by passing through an ultra-pure purification system (Aqua Solutions).

Characterization

The morphology and the surface structure of the as-prepared products were observed by scanning electron microscopy (SEM, Hitachi S4800) and transmission electron microscopy (TEM, JEOL 2100F) with an accelerating voltage of 200 kV. All TEM samples were prepared by depositing a drop of the diluted suspension in ethanol on carbon film coated copper grid. The HAADF-STEM and EDS were performed with a FEI TECNAI F30 microscope operated at 300 kV. The crystal phase of the as-prepared product was determined by powder X-ray diffraction (XRD) using a Rigaku Ultima IV X-ray diffractometer with Cu K α radiation (λ =1.54056 Å). The precise content of every element in samples was determined by the ICP-AES (Baird PS-4). The X-ray photoelectron spectroscopy was performed on PHI Quantum-

2000 XPS system with a monochromatic aluminum anode X-ray source of K α radiation (1486.6 eV), and all the spectra were calibrated with the C1s peak at 284.6 eV as an internal standard. Electrochemical *in situ* Fourier transform IR (FTIR) spectroscopy were performed on a Nexus 870 FTIR spectrometer (Nicolet) equipped with a liquid-nitrogen-cooled MCT-A detector, an EverGlo IR source, at a spectral resolution of 8 cm⁻¹. *Ex situ* FTIR was conducted on a Nicolet iS50 spectrometer by depositing the ethanol suspensions of excavated RhNi nanobranches on dried KBr powders followed by solvent evaporation.

EXPERIMENTAL SECTION

Synthesis of excavated RhNi alloy nanobranches: In a typical experiment of preparation of excavated RhNi nanobranches, 8.2 mg of Ni(acac)₂, 4.2 mL of oleic acid and 1.8 mL of oleylamine were first added into a glass vial with capacity of 12 mL. The reaction mixture was ultrasonicated for 20 minutes. Then Rh(acac)₃ (12.8 mg) dissolved in Bn₂O (2 mL) was added and kept ultrasonic stirring for around 5 minutes. After that, 600 μ L of formaldehyde solution was injected, and the clear solution was obtained after magnetic stirring for 15 min. The glass vial was put into a Teflon-lined stainless-steel autoclave with a capacity of 25 mL. The sealed vessel was heated from 30 °C to 170 °C in around 70 min and kept at this temperature for 8 h, then allowed to cool to room temperature naturally. The products were collected by centrifugation (9500 rpm for 3 min) and washed several times with hexane and ethanol to remove impurities, then re-dispersed in 5 mL *n*-butylamine under sonication for 2h and stirred for 1 day. After that, the products were collected through centrifugation and washed several times with ethanol to remove impurities and then dried in the vacuum drying oven (80 °C).

Synthesis of excavated Rh nanobranches: The synthesis procedure of excavated Rh nanobranches was the same as that of excavated RhNi nanobarnches except that Ni(acac)₂ was absent.¹

Electrochemical measurements: Cyclic voltammogram (CV) curves were recorded using an electrochemical workstation (CHI 1030b, Shanghai Chenhua Co., China). A glassy carbon electrode (diameter = 5 mm) was carefully polished and washed before each measurement. The commercial Rh black, excavated Rh nanobarnches, and excavated RhNi nanobranches were dispersed in ethanol and 5% nation (volume ratio: 0.02%). The concentrations of the three catalysts were all 2.0 mg/mL. In a typical experiment, the suspensions of samples (2 μ L) were deposited on a glassy carbon electrode, which was used as the working electrode after the solvent was dried under room temperature. A Pt slice and Hg/HgO (1 M KOH) were served as the counter electrode and the reference electrode, respectively. Before the electrocatalytic experiments were performed, the glassy carbon electrode loaded with the sample was electrochemically cleaned by continuous potential cycling between -0.9 V and 0.10 V at 50 mV·s⁻¹ in N₂-saturated 1 M NaOH solution until a stable cyclic CV curve was obtained. The catalytic activity was measured by cyclic voltammetry method in a solution containing 1.0 M $CH_3CH_2OH + 1.0 \text{ M NaOH with a scan rate of 50 mV} \cdot \text{s}^{-1}$.

For the CO stripping experiments in 1 M NaOH solution, N_2 was first purged to the solution for 10 min. Then, the electrode was put in the solution followed by CO purging into the solution for 15 minutes to allow the complete adsorption of CO onto the catalyst. Then the electrode was taken out and transferred to the electrochemical cell with 1 M NaOH solution bubbled with N_2 for 15 min for CO stripping measurement. The CO-stripping voltammogram was recorded -0.8 V to 0 V with a scan rate of 10 mV·s⁻¹. Besides, for the CO stripping experiments in 0.5 M H_2SO_4 electrolyte, the procedure is the same as that of in 1 M NaOH solution, except that the recorded potentials is from -0.21 V to 0.8 V with a standard calomel electrode as the counter electrode and the solution is 0.5 M H_2SO_4 solution. The electrochemically active surface area (ECSA) of the catalysts were calculated by the equation ECSA = Q/q^0 , in which Q is determined by the area of the CO absorption peaks in the cyclic voltammetry measurement performed in 0.5 M H_2SO_4 electrolyte with a scan rate of 50 mV·s⁻¹ (298 K), and q^0 is 380 μ C·cm⁻².

Electrochemical *in situ* FTIR Spectroscopy: Electrochemical *in situ* FTIR spectroscopic studies were carried out on a Nexus 870 FTIR spectrometer (Nicolet), which is equipped with a liquid-nitrogen-cooled MCT-A detector, an EverGlo IR source and at a spectral resolution of 8 cm⁻¹. In this configuration, infrared radiation sequentially passed through a CaF₂ window and a thin-layer solution (about 10 μ m), and then it was reflected by the electrode surface. The resulting spectra were reported as relative change in reflectivity:

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

where $R(E_S)$ and $R(E_R)$ are the single-beam spectra collected at sample potential E_S and reference potential E_R , respectively. And, for ethanol oxidation reaction, 1.0 M CH₃CH₂OH + 1.0 M NaOH was used as electrolyte. The counter electrodes and the reference electrodes were a Pt slice and Hg / HgO (1 M KOH) electrode, respectively. The E_R was fixed at -0.9 V (vs. Hg/HgO). In addition, the oxidation of CO was taken in 1 M NaOH, and the E_R was fixed at 0 V (vs. Hg/HgO), at which CO has been removed completely by electrooxidation.

The evaluation of the selectivity for ethanol to CO_2 is based on the following equation:

$$\eta(\text{CO}_2) = \frac{\frac{1}{2} [\text{CO}_3^{2-}]}{[\text{CH}_3\text{COO}^-] + \frac{1}{2} [\text{CO}_3^{2-}]}$$

in which [CH₃COO⁻] and [CO₃²⁻] are respectively relative concentration (C_R) of CH₃COO⁻ and

CO32- obtained by using quantitative analytical IR method.2-4

Results and Discussion



Scheme S1. Dual-pathway mechanism of the ethanol oxidation



Fig. S1. TEM images of RhNi nanocrystals collected at different reaction time, (a) 1 h, (b) 3 h, (c) 5 h and (d) 8 h.



Fig. S2. XRD patterns of RhNi nanocrystals collected at different reaction time, (a) 1 h, (b) 3 h, (c) 5 h and (d) 8 h.



Fig. S3 (a) XRD patterns and (b) the measured Ni contents of the as prepared products by varying the molar ratio of Rh/Ni precursors.



Fig. S4 TEM images of the obtained products by varying the molar ratios of Rh/Ni precursors (a) 9:1, (b) 3:1, (c) 1:2.



Fig. S5 Positive scan curves of the commercial Rh black, the excavated Rh nanobranches, the as-prepared excavated Rh₉₄Ni₆ nanobranches (molar ratio Rh/Ni precursor, 9:1), excavated

 $Rh_{90}Ni_{10}$ nanobranches (molar ratio Rh/Ni precursor, 3:1) and excavated $Rh_{85}Ni_{15}$ nanobranches (molar ratio Rh/Ni precursor, 1:1) in 1.0 M ethanol + 1.0 M NaOH solution (scan rate: 50 mV·s⁻¹).



Fig. S6. EIS of RhNi nanobranches and Rh nanobranches carried out at the open-circuit potential in N₂-saturated aqueous solution containing 1.0 M NaOH and 1.0 M ethanol.



Fig. S7. Current-time curves for ethanol oxidation at -0.40 V (vs. Hg/HgO, at 298 K).

Catalyst	Electrolyte	Mass Activity (mA mg⁻¹)	Reference
Hollow porous Rh	1M NaOH +	78.6	Chem. Commun.
nanoballs	1M C₂H₅OH		2019, 55, 4989-4992
Rh tetrahedra	1M NaOH + 1M C₂H₅OH	31. 0	J. Am. Chem. Soc. 2018, 140, 11232-11240
Rh-on-Pd	1M KOH +	30. 1-102. 8	J. Mater. Chem. A
nanodendrites	1M C₂H₅OH		2013, 1, 906-912
Rh tetrahedra	1M NaOH + 1M C₂H₃OH	42. 0	<i>Nano Res.</i> 2018, 11, 656-664
PtRh alloy nanodendrites	1М КОН + 1М С₂Н₅ОН	462.1	ACS Appl. Mater. Interfaces 2018, 10, 19755-19763
Cyclic Penta-Twinned	1M NaOH +	185. 3	J. Am. Chem. Soc.
Rh nanobranches	1M C₂H₅OH		2018, 140, 11232-11240
Rh icosahedra	1M NaOH + 1M C₂H₅OH	50.4	Nano Res. 2018, 11, 656-664
PtRhNi	1M KOH +	456.6-1388.4	Nano Res.
nanoassemblies	1M C₂H₅OH		2017, 10, 3324-3332
Hyprebranched	1M NaOH +	41. 9-146. 6	Sci. China Mater.
Rh nanoplates	1M C₂H₅OH		2017, 60, 685-696
Pt₅₀Rh₅₀	1M KOH +	~10	<i>Electrocatal.</i>
nanoparticles/C	1M C₂H₅OH		2016, 1, 297-304
octahedral PtNiRh	0.1M KOH +	N/A	Angew. Chem. Int. Ed.
nanoparticles	0.5M C₂H₅OH		2017, 56, 6533-6538
Excavated RhNi Nanobranches	1M NaOH + 1M C₂H₅OH	159.0	This work

Table S1 Summary of the electrocatalytic activities of the reported Rh-based eletrocatalyts toward EOR in alkaline solution.



Fig. S8. TEM images of (a) the excavated RhNi nanobranches, (b) excavated Rh nanobranches and (c) commercial Rh black after current-times tests for EOR.



Fig. S9. (a) EDS and (b) STEM image and cross-sectional compositional line profile of excavated RhNi nanobranches after current-times tests for EOR.



Fig. S10. *Ex situ* FTIR spectra of pure oleyalmine, pure oleic acid and the RhNi nanobranches after washing procedure.

Fig. S10 shows the *ex situ* FTIR spectrum of the RhNi naonobranches after the cleaning procedure in Experimental Section, and with the spectra of pure oleic acid and oleyalmie for comparison. The removal of oleic acid and oleylamine is confirmed by the disappearance of the bands at 2850 and 2922 cm⁻¹, corresponding to their CH_2 symmetric and asymmetric stretching modes, respectively. Strikingly, singles for these stretching modes of oleic acid and oleylamine are absent in the FTIR spectrum of RhNi nanobranches, indicating that oleic acid and oleylamine on the products can be removed effectively through the above procedure.



Fig. S11. *In situ* FTIR spectra of ethanol electro-oxidation of (a) excavated Rh nanobranches and (b) commercial Rh black at different potential in 1.0 M ethanol + 1.0 M NaOH solution at 298 K, E_S was varied from -0.80 to -0.1 V, E_R =-0.80 V, 200 scans, 8 cm⁻¹.

It should be noted that the main soluble products of completely oxidation of ethanol in the high pH enviroment (1M NaOH + 1M C₂H₅OH) exist in the form of carbonate (CO₃²⁻) instead of CO₂. The carbonate band (1390 cm⁻¹) overlaps with the acetate band at 1415 cm⁻¹, which would result in higher intensity and more asymmetrical shape of the band 1415 cm⁻¹ than that of 1550 cm⁻¹.² And substract method was used to rule out the contribution of acetate to the peak near 1415 cm⁻¹, meanwhile, the band near 1550 cm⁻¹ disappeared and a band near 1390 cm⁻¹ can be clearly obsereved, which belongs to the C-O strentching peak of CO₃²⁻, as described in **Fig. 4**c.³⁻⁵ Thus, the relative concentrations (*C*_R) of CH₃COO⁻ at -0.1 V is 0.96*0.1 M= 0.096M. Similarly, the *C*_R of CO₃²⁻ at 1390 cm⁻¹ can be evaluated by further subtracting (c₀) with the transmission spectrum of (d₀). The product distributions obtained from the *in situ* spectra are shown in **Fig. S12**.



Fig. S12. Potential dependence of $C_{\rm R}$ of CH₃COO⁻ and CO₃²⁻ generated from EOR on (a) the as-prepared excavated RhNi alloy nanobranches, (b) excavated Rh nanobranches and (c) commerical Rh black.

Table S2 Summary of the representative reports on selectivity of ethanol oxidation in alkaline solution.

Catalyst	Electrolyte	Selectivity of CO ₂ (%)	Reference
Excavated RhNi	1M NaOH +	16.0 % (-0.4V <i>vs.</i> Hg/HgO)	This work
Nanobranches	1M C₂H₅OH	15.1 % (-0.5V <i>vs.</i> Hg/HgO)	
Commercial Pt black	1M NaOH + 1M C₂H₅OH	0 % (-0.4V vs. Hg/HgO) 0 % (-0.5V vs. Hg/HgO)	This work
Cyclic Penta-Twinned	1M NaOH +	ca. 8% (-0.4V <i>vs.</i> Hg/HgO)	J. Am. Chem. Soc.
Rh Nanobranches	1M C₂H₅OH	ca. 6% (-0.5V <i>vs.</i> Hg/HgO)	2018, 140, 11232-11240
Excavated	1M NaOH +	8.1 % (-0.4V vs. Hg/HgO)	Mater. Today energy
Rh Nanobranches	1M C₂H₅OH	4.1 % (-0.5V vs. Hg/HgO)	2019, 11, 120-127
Commercial Rh black	1M NaOH + 1M C₂H₅OH	ca. 4 % (-0.4V <i>vs</i> . Hg/HgO) ca. 2 % (-0.5V <i>vs</i> . Hg/HgO)	<i>Mater. Today energy</i> 2019, 11, 120-127; This work
Pd/Ni(OH)₂/rGO	1M KOH + 1M C₂H₅OH	26 % (ca0.05V vs. Hg/HgO)	<i>Adv. Mater.</i> 2017, 29, 1703057
Pd Electrode	1M NaOH +	ca. 1 % (-0.4V <i>vs.</i> Hg/HgO)	Electrochimica Acta
	1M C₂H₅OH	ca. 0 % (-0.5V <i>vs.</i> Hg/HgO)	2010, 55, 7995-7999



Fig. S13. Potential dependence of (a) $C_{\rm R}$ of CH₃COO⁻ and CO₃²⁻ generated from EOR and (b) selectivity (η) for complete oxidation of ethanol on commercial Pt black.



Fig. S14. CV curves in N₂-saturated 1.0 M NaOH (scan rate: 50 mV s⁻¹).



Fig. S15. Linear sweep voltammograms of CO oxidation in 0.5 M H₂SO₄ solution.



Fig. S16. In situ FTIR spectra of CO oxidation on electro-catalysts in 1 M NaOH, E_S was varied from -0.75 V to -0.1 V, E_R = 0 V: (a) commercial Rh black, (b) excavated Rh nanobranches and (c) excavated RhNi nanobranches.



Fig. S17. In situ FTIR spectra of CO oxidation on electro-catalysts in 1 M NaOH, E_S was varied from -0.75 to -0.10 V, E_R = -0.80 V: (a) commercial Rh black, (b) excavated Rh nanobranches and (c) excavated RhNi nanobranches. (d) Potential dependence of CO₃²⁻ band integrated intensity (1390 cm⁻¹).

In **Fig. S**16, on Rh black and excavated Rh nanobranches, it is clearly observed that the C-O band of linearly-adsorbed CO_{ad} species (CO_L) at 1960-1998 cm⁻¹ and bridge-adsorbed CO_{ad} species (CO_B) at 1840-1885 cm⁻¹, while only weak CO_B band can be observed on the excavated RhNi nanobranches.⁶ Notably, the frequence and relative intensities from different configurations of CO_{ad} on catalysts are closely related with the different surface states (such as the facets, defects and coadsorbates on catalysts surfaces) as well as the overall CO coverage on the catalysts.⁷ The band at about 1630 cm⁻¹ can be safely assigned to the adsorbed H₂O. What's more, the CO_3^{2-} band appeares at -0.65 V on excavated RhNi nanobranches, 50 mV more negative than that of the excavated Rh nanobranches or commercial Rh black (**Fig. S**17). Importantly, the integrated intensity of CO_3^{2-} on excavated RhNi nanobranches is more than that of the excavated Rh nanobranches or Rh black ($E_S > -0.70$ V). The results revealed that the

alloying of the excavated RhNi nanobranches does facilitate the oxidation of CO_{ad} and enhance the CO_{ad} antipoisoning ability.

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