

Electronic Supplementary Material

**Controllable growth of PtCuRh rhombic dodecahedral
nanoframes as efficient catalysts for alcohol electrochemical
oxidation**

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Contents:

1. Experimental section
2. Supplemental experiment results: Figures S1-S18
3. Supplementary data: Tables S1, S2

Experimental section

Reagents: Chloroplatinic acid hexahydrate ($\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$), Rhodium chloride (RhCl_3), Copper (II) acetylacetonate ($\text{Cu}(\text{acac})_2$, 97%), oleylamine (OAM, 80-90%), and cetyltrimethyl ammonium bromide (CTAB, 99%), cetyltrimethyl ammonium chloride (CTAC, 97%), potassium bromide (KBr, 99%), potassium iodide (KI, 99%), acetic acid (CH_3COOH , 99.5%) were purchased from Aladdin. All chemicals were used directly in the experiments without additional purification. The deionized water in all experiments was ultrapure (18.2 M Ω). The solvents such as ethanol, n-hexane and n-butylamine were analytical reagent (AR) and used directly without further purification.

Preparation of PtCuRh rhombic dodecahedron with nanodendrites (RDD): In a typical synthesis, 65 mg $\text{Cu}(\text{acac})_2$ and 720 mg CTAB were added into the 25 mL Teflon-lined autoclave containing 10 mL oleylamine. The mixture was magnetically stirred at room temperature for 10 min. During the stirring process, 0.56 mL $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$ (17.8 mgPt mL⁻¹) and 25 μL RhCl_3 solution were injected into the mixture, respectively and continued stirring for 10min. Afterwards, the Teflon-lined was transferred into a stainless-steel autoclave and sealed tightly. And then, the autoclave was placed in the oil bath which was preheated at 180 °C and heated for 24 h with magnetic stirring. After cooling to ambient temperature naturally, the black precipitates were collected and washed three times with ethanol by centrifugation at 4,000 rpm for 5 min.

Preparation of PtCuRh rhombic dodecahedron nanoframe with nanodendrites

(RDND): The PtCuRh RDND was prepared from PtCuRh RDD by etching out the Cu

atoms with acetic acid. Generally, the slurry of PtCuRh RDD was dispersed in ethanol (5ml), then 20ml acetic acid was added into the vial, which was heated for 6h at 80°C. The product was washed several times with ethanol and centrifuged at 4,000 rpm for 5 min to collect the catalyst.

Preparation of PtCuRh rhombic dodecahedron nanoframe (RDN): All the steps and chemicals are the same as synthesizing PtCuRh RDND, except to change the reaction temperature from 180°C to 170 °C.

Preparation of PtCu Nanocage (NC): PtCu nanocage was synthesized by typical process without adding Rh precursor.

Preparation and activation of carbon supported PtCuRh RDND catalysts: In a typical process, Vulcant-72 carbon and PtCuRh RDND catalysts were dispersed in 25ml n-butylamine respectively by sonicating 30min. Then the slurry containing PtCuRh RDND catalysts mixed with the carbon-containing slurry was sonicated further for 30 min. The mixture was stirred moderately at room temperature for three days. The black product was washed with methanol once to remove the excess n-butylamine and used ethanol to further wash for three times. The precipitates were dried in vacuum drying chamber for 12 hours at 80°C. Before conducting electrochemical tests, the catalyst was heated in tube furnace at 200°C for an hour to keep the surface of catalyst clean.

Materials characterizations: The X-ray powder diffraction (XRD) patterns were collected with a SmartLab3 X-ray diffractometer (Rigaku Co., Japan), using Cu K α radiation ($\lambda = 1.5405 \text{ \AA}$) at 40 kV and 30 mA. Transmission electron microscopy (TEM)

images were performed on a TITAN G2 microscope (FEI, USA) at 300 kV. High resolution-TEM, high angle annular dark field scanning transmission electron microscope (HAADF-STEM) and elemental mapping were measured on Titan G2 60-300 equipped with image corrector and highly sensitive energy dispersive X-Ray spectroscopy (EDX) system. X-ray photoelectron spectroscopy (XPS) analysis was conducted with an ESCALAB 250 Xi (Thermo Fisher Scientific, USA) and monochromatic Al K sources were used to analyze the chemical composition of the catalyst, which reference line was the carbon (C 1s) line at 284.5 eV. The Pt loadings of catalysts were measured by the inductively coupled plasma emission spectroscopy (Perkin Elmer Optima 8000DV ICP-OES, USA).

Electrochemical Measurements: The electrochemical measurements were carried out by using a three-electrode electrochemical cell with a PINE rotational disk electrode (RDE) equipped with a biopotentiostat (AFCBP1E, Pine Instrument Co., U.S.A.). Glassy carbon (GC) coated with catalyst ink served as a working electrode, carbon rod acted as a counter electrode, and saturated calomel electrode (SCE) served as a reference electrode. Typically, the electrode catalyst ink was produced by mixing 3 mg carbon-supported PtCuRh RDND catalysts, 1.8 mL of anhydrous ethanol and 0.2 mL of 0.5 wt% Nafion solution (DuPont, USA) together, and sonicated for 15 min to obtain the uniform suspension liquid. A certain amount of catalyst ink was dropped onto the glassy carbon disk electrode (0.196cm^2) and dried at room temperature. The catalytic performance of PtCuRh RDND catalysts for the methanol oxidation reaction (MOR) was measured by cyclic voltammetry (CV). The activation of electrodes was swept

from -0.2 V to 1.0 V *vs.* SCE in N₂-saturated 0.5 M H₂SO₄ solution at a scan rate of 100 mV s⁻¹. After 100 cycles' activation, the cyclic voltammetry (CV) curves were recorded at a sweep rate of 50 mV s⁻¹. The electrochemical surface area (ECSA) was determined by integrating the hydrogen adsorption charge on the cyclic voltammetry (CV) in N₂-saturated 0.5 M H₂SO₄ aqueous solution. The methanol oxidation reaction measurements were conducted in a 0.5 M H₂SO₄ + 1.0 M CH₃OH aqueous solution, and then CV curves were obtained by sweeping a potential between -0.2 and 1.0 V *vs.* SCE at a rate of 50 mV s⁻¹. Accelerated durability test (ADT) was performed in N₂-saturated 0.5 M H₂SO₄ + 1.0 M CH₃OH solution in a potential range from -0.2 to 1.0 V *vs.* SCE at a scan rate of 100 mV s⁻¹ for 1,000 cycles. CO-stripping measurements was carried out at -0.14 V *vs.* SCE in CO- saturated 0.5 M H₂SO₄ to adsorb CO, then N₂ was pumped into the solution to drain the CO gas, the CV curves was recorded at a sweep rate of 50 mV s⁻¹. In addition, chronoamperometry (CA) curves also was conducted to test the stability of catalysts, whose curves was obtained at 0.5 V *vs.* SCE in 0.5 M H₂SO₄ + 1.0 M CH₃OH solution lasting 3,600 s. For testing ethanol oxidation reaction, the process was same to MOR, except to replace 0.5 M H₂SO₄ + 1.0 M CH₃OH solution by 0.1 M HClO₄ + 0.5 M C₂H₅OH solution. Current density through the working electrode geometric area (0.196 cm²) normalized. The entire electrochemical measurements were carried out at 30 °C.

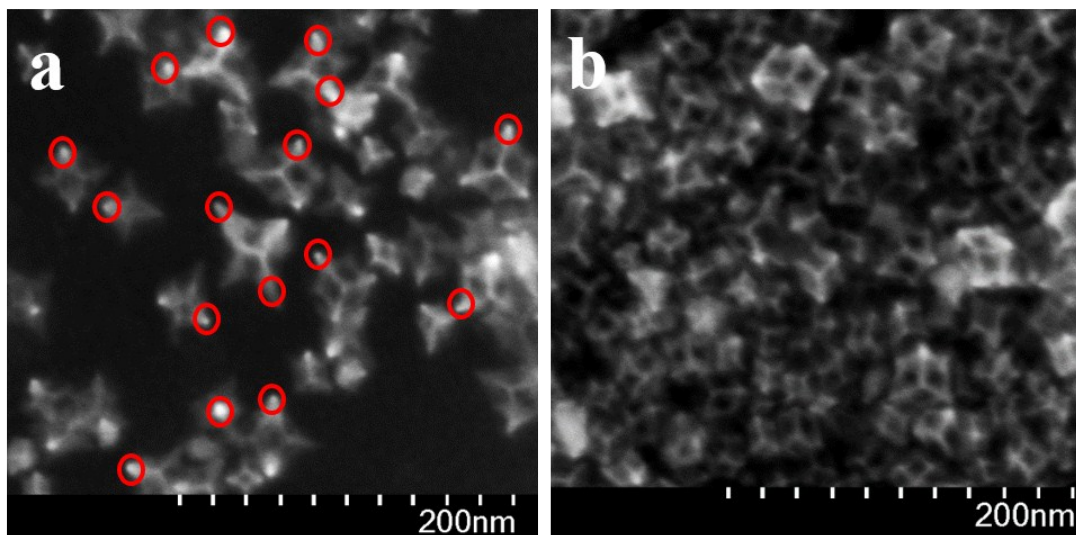


Figure S1. The typical SEM images of (a) PtCuRh rhombic dodecahedron nanoframe with nanodendrites (RDND), nanodendrites circled in red, (b) PtCuRh rhombic dodecahedron nanoframe (RDN).

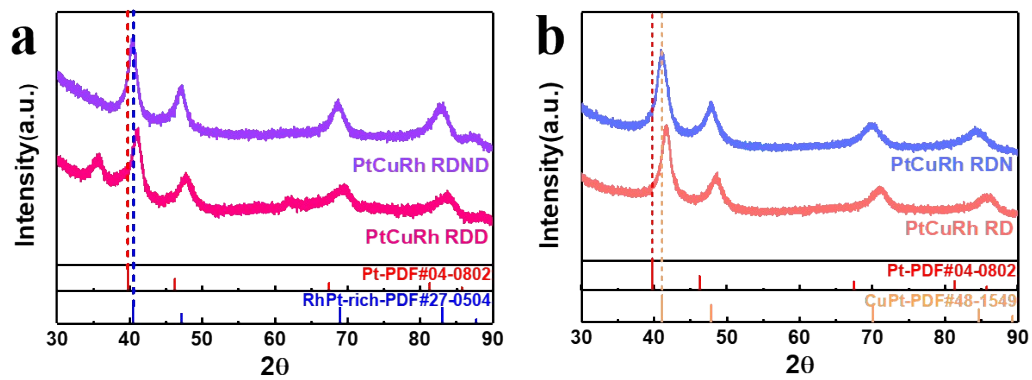


Figure S2. XRD patterns of (a) PtCuRh RDND and PtCuRh RDD, (b) PtCuRh RDN and PtCuRh RD.

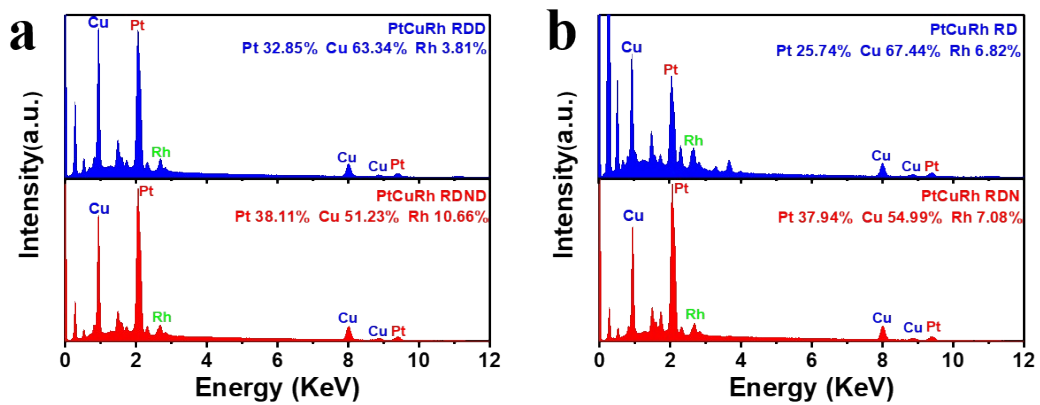


Figure S3. EDS spectrum of (a) PtCuRh RDD and PtCuRh RDND, (b) PtCuRh RD and PtCuRh RDN.

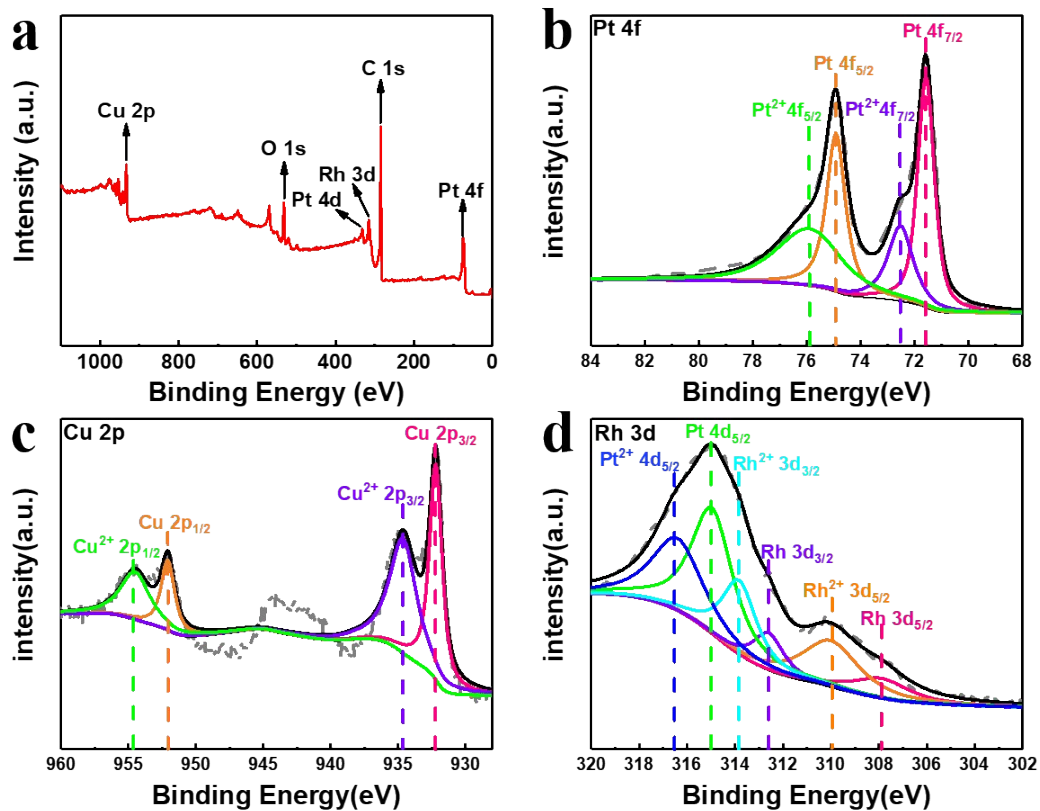


Figure S4. (a) XPS survey spectrum of the PtCuRh RDND, XPS spectrum of (b) Pt 4f, (c) Cu 2p, and (d) Rh 3d of the PtCuRh RDND.

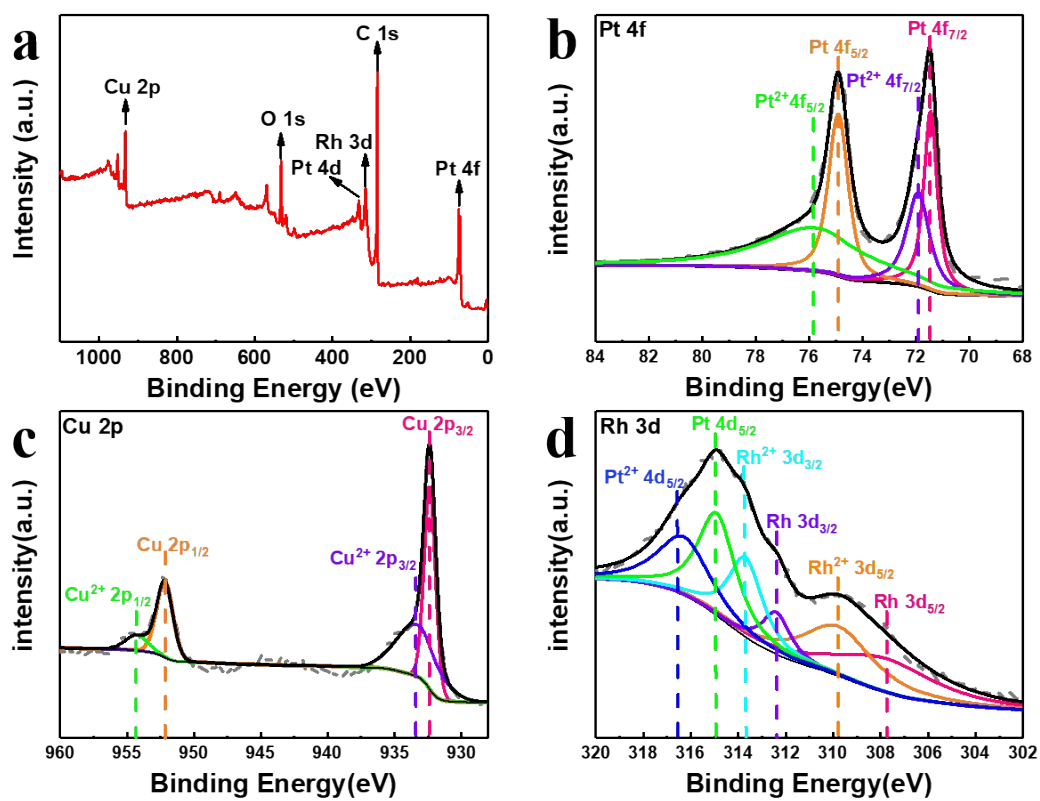


Figure S5. (a) XPS survey spectrum of the PtCuRh RDN, XPS spectrum of (b) Pt 4f, (c) Cu 2p, and (d) Rh 3d of the PtCuRh RDN.

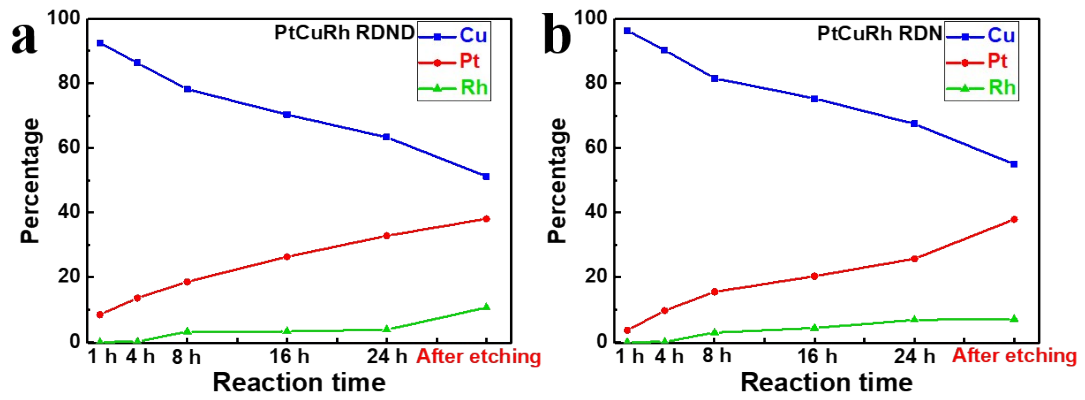


Figure S6. The change curves of elements composition with different reaction time: (a) PtCuRh RDND and (b) PtCuRh RDN, determined by EDS.

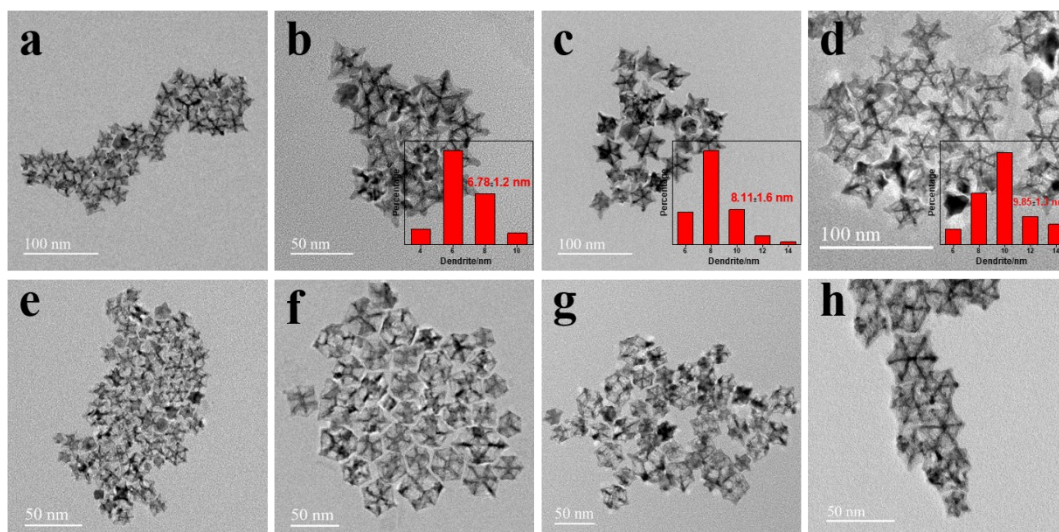


Figure S7. TEM images of catalysts prepared from the standard synthesis procedure of PtCuRh RDD and PtCuRh RD by using different reaction time: (a, e) 16 h, (b, f) 24 h, (c, g) 30 h and (d, h) 36 h.

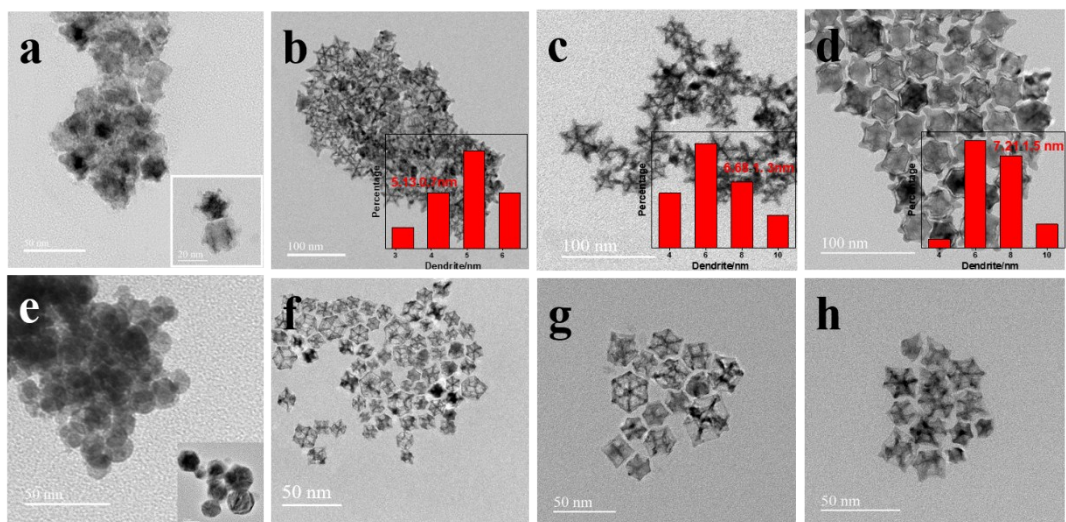


Figure S8. TEM images of catalysts prepared from the standard synthesis procedure of PtCuRh RDD and PtCuRh RD by using different amount of surfactants: (a, e) 0 mg, (b, f) 360 mg, (c, g) 720 mg and (d, h) 900mg.

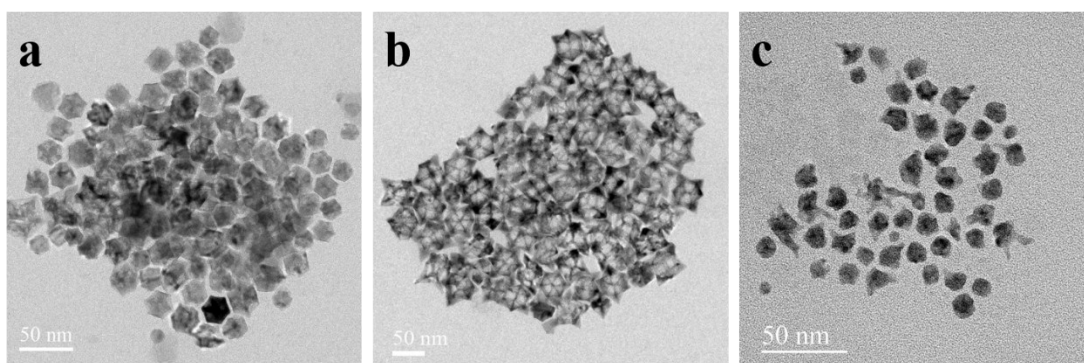


Figure S9. TEM images of catalysts prepared from the standard synthesis procedure of PtCuRh RDD by replacing CTAB with: (a) CTAC, (b) KBr, (c) KI.

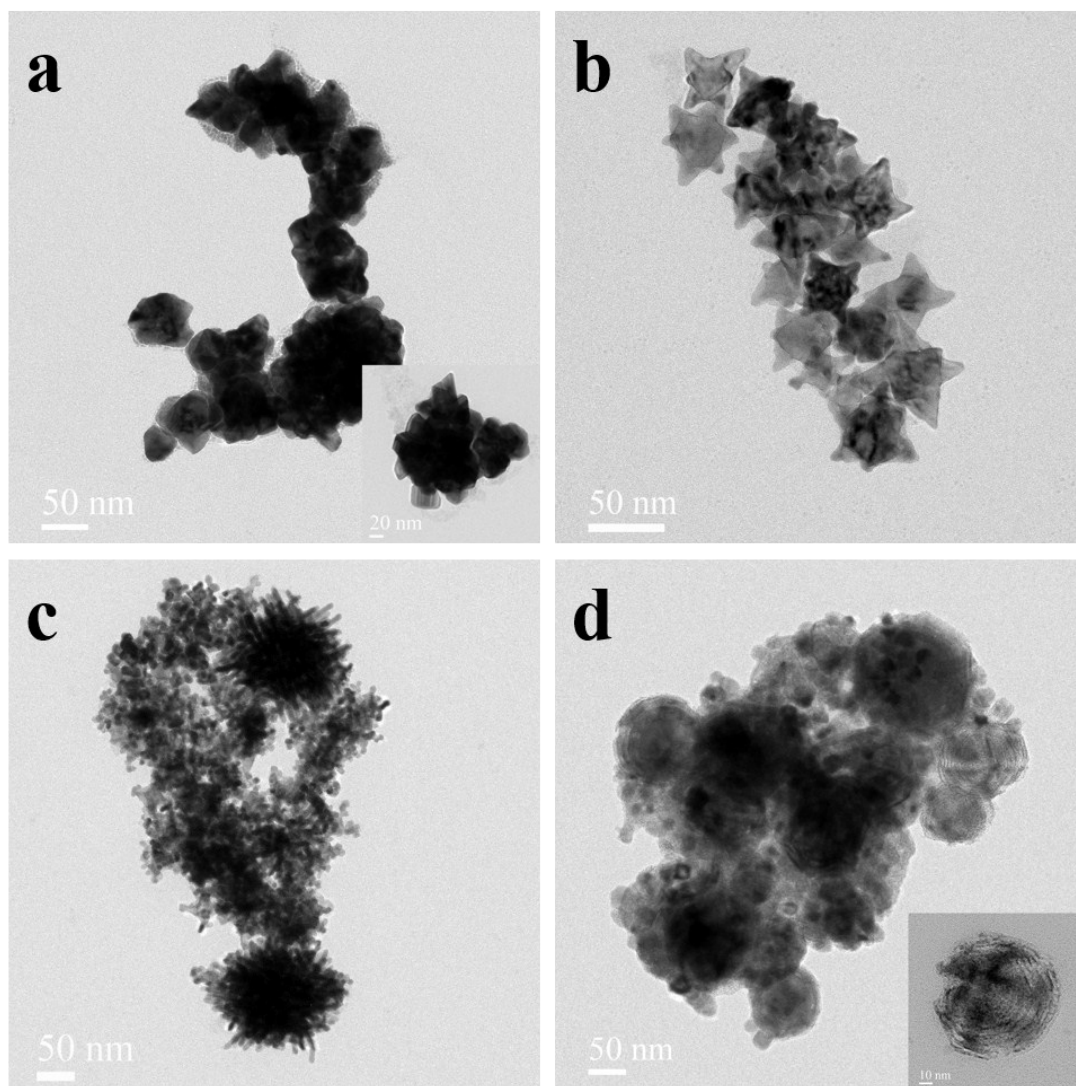


Figure S10. TEM images of samples prepared from the standard procedure of PtCuRh RDND when using different feeding ratio of Cu to Pt precursors (instead of 5:1): (a) 0:1, (b) 1:1, (c) 3:1 and (d) 5:0, the amount of Rh added remains unchanged.

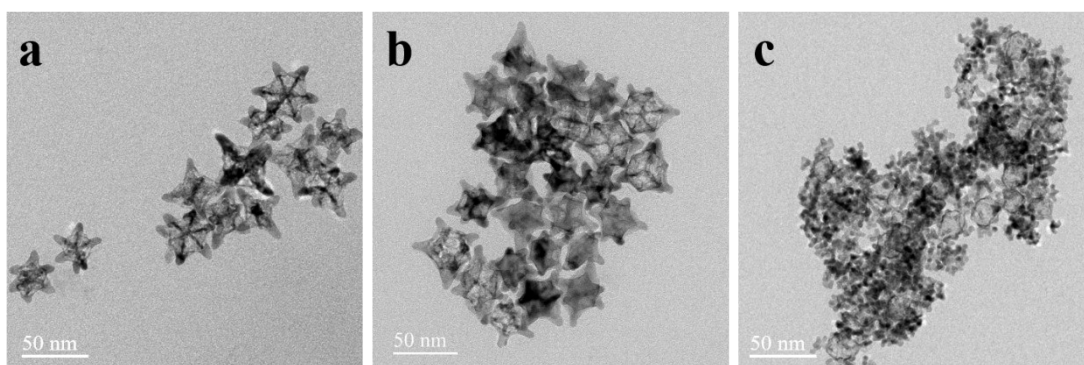


Figure S11. TEM images of catalysts prepared from the standard synthesis procedure of PtCuRh RDD by using different amount of RhCl₃: (a) 0 μ L, (b) 50 μ L, (c) 100 μ L.

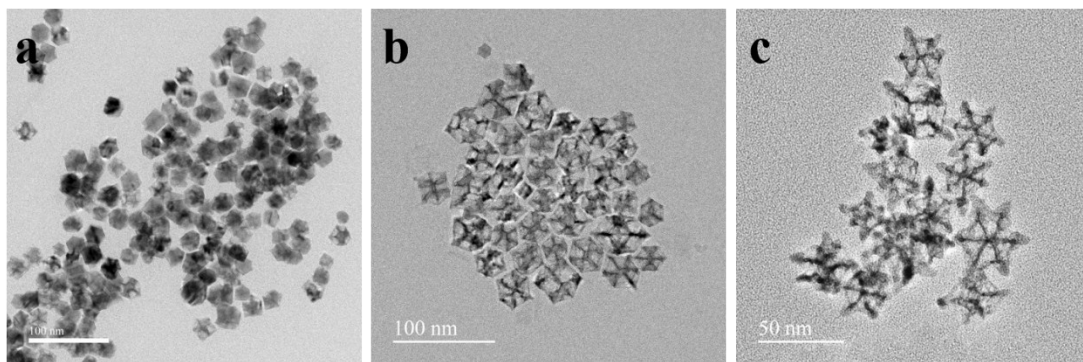


Figure S12. TEM images of the catalysts synthesized by different reaction temperature (a) 160°C, (b) 170°C and (c) 180°C.

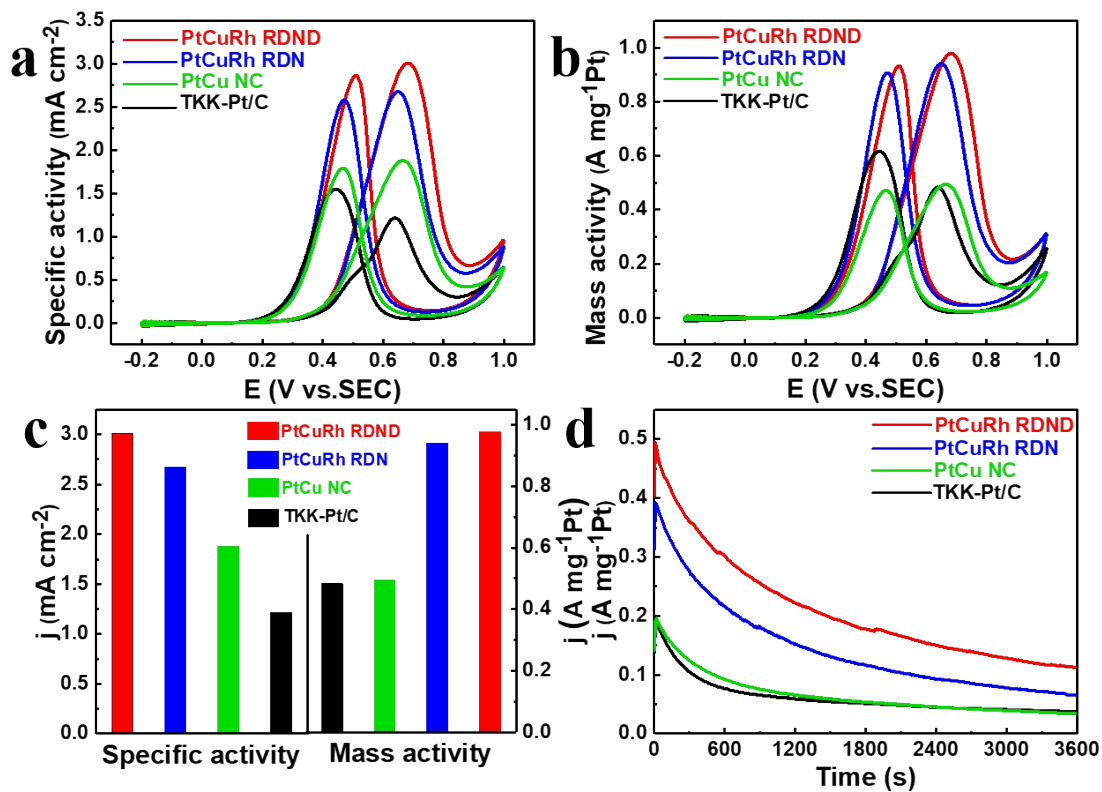


Figure S13. CV curves for (a) specific activity and (b) mass activity. Histogram of (c) specific activity and mass activity of the PtCuRh RDND, PtCuRh RDN, PtCu NC and TKK-commercial Pt/C catalysts were recorded in 0.5 M H₂SO₄ + 1 M CH₃OH aqueous solution at a sweep rate of 50 mV⁻¹. (d) Chronoamperometry curves for the catalysts in 0.5 M H₂SO₄+ 1.0 M CH₃OH aqueous solution at 30 °C with the potential held at 0.50 V.

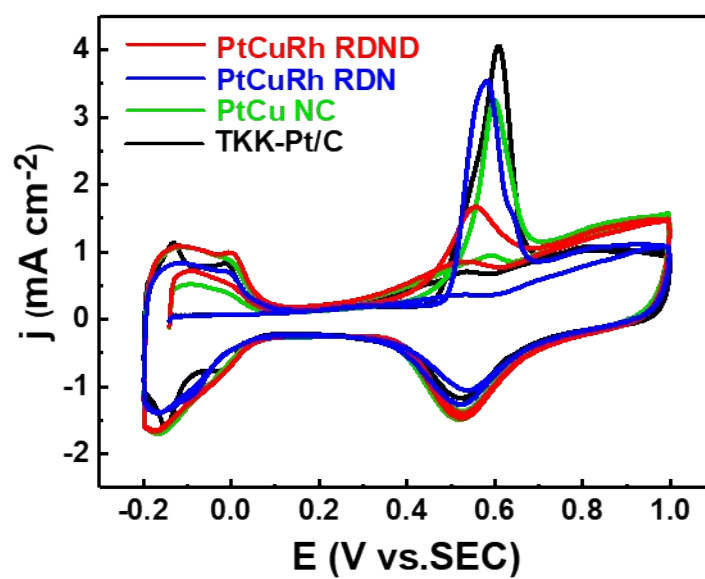


Figure S14. CO-stripping voltammograms for the PtCuRh RDND, PtCuRh RDN, PtCu NC and commercial TKK-Pt/C catalysts in 0.5 M H₂SO₄ aqueous solution at a scan rate of 50 mV s⁻¹. Pre-adsorption of CO over Pt at -0.14 V (vs SCE) for 15 min.

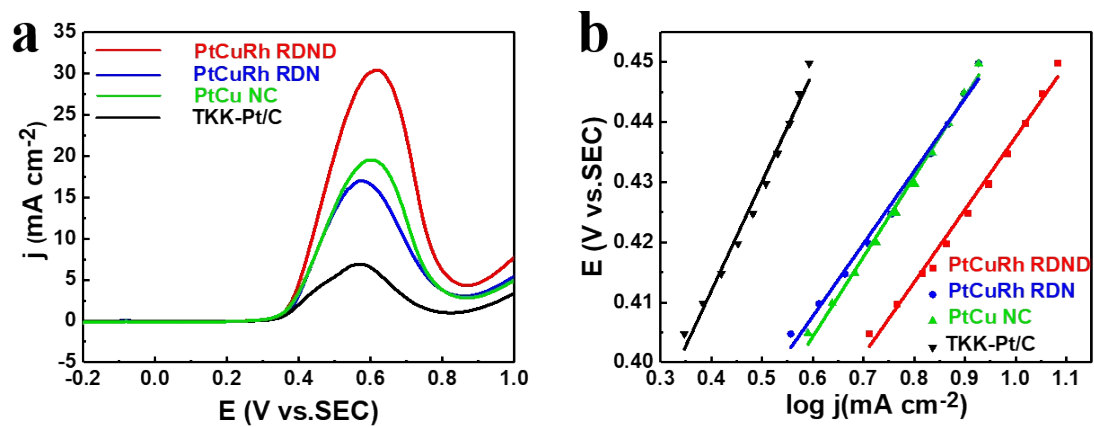


Figure S15. (a) CV curves were recorded at a sweep rate of 2 mV s^{-1} in $0.5 \text{ M H}_2\text{SO}_4 + 1.0 \text{ M CH}_3\text{OH}$ solution, (b) Tafel plots for methanol oxidation reaction.

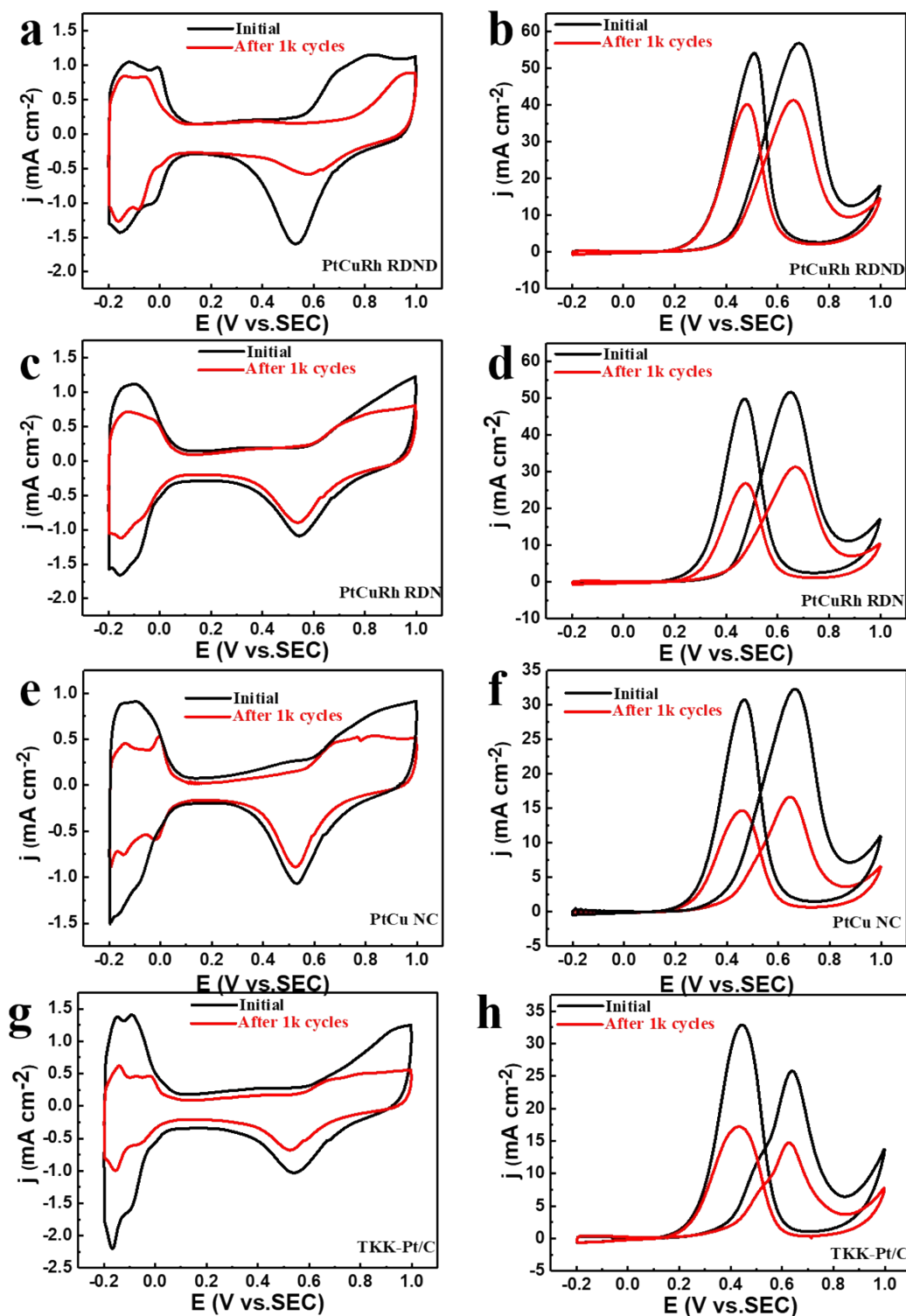


Figure S16. Stability test of the PtCuRh RDND, PtCuRh RDN, PtCu NC and TKK-commercial Pt/C before and after 1k cycles in (a, c, e, g) 0.5 M H₂SO₄ aqueous solution, and (b, d, f, h) 0.5 M H₂SO₄ + 1 M CH₃OH aqueous solution at a sweep rate of 50 mV s⁻¹.

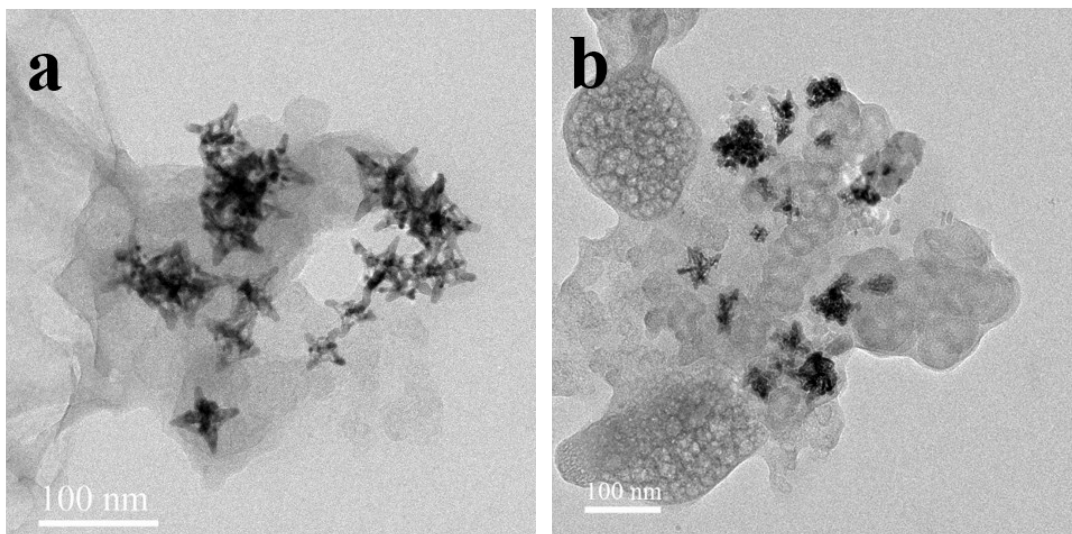


Figure S17. After durability tests, TEM images of (a) PtCuRh RDND catalysts, (b) PtCu NC catalyst.

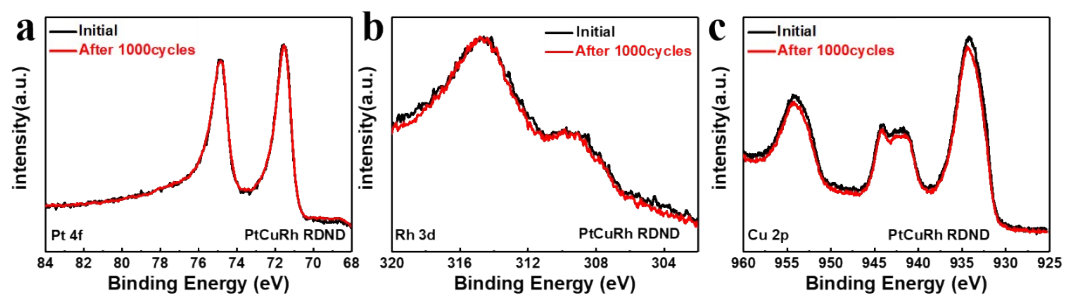


Figure S18. (a), (b) and (c) Pt, Rh and Rh XPS spectra recorded from PtCuRh RDND before and after 1,000 cycles electrocatalysis.

Table S1. Atomic ratio of the PtCuRh RDND and PtCuRh RDN determined by XPS.

	PtCuRh RDD	PtCuRh RDND (After etching)	PtCuRh RD	PtCuRh RDN (After etching)
Pt	29.91%	40.25% ↑	28.37%	39.03% ↑
Cu	51.95%	29.07% ↓	49.59%	31.58% ↓
Rh	18.14%	30.68% ↑	22.04%	29.39% ↑

Table S2. Comparison of catalytic properties for methanol oxidation reaction and ethanol oxidation reaction between PtCuRh RDND and catalysts reported recently. (NA: not available).

Methanol Oxidation Reaction (MOR)				
Catalysts	Electrolyte	Specific Activity (mA/cm²)	Mass Activity (A/mg_{Pt})	Reference
PtCuRh RDND	0.5 M H₂SO₄ + 1 M CH₃OH	3.01	0.98	This work
PtPdCo MHNPs	0.5 M H ₂ SO ₄ + 1 M CH ₃ OH	1.71	0.91	Nanoscale 2019 , 11, 4781-4787
Pt ₆₆ Ni ₂₇ Ru ₇ DNSs	0.5 M H ₂ SO ₄ + 0.5 M CH ₃ OH	4.30	0.81	Nano Res. 2019 , 12,651-657
TOh PtAu NFs	0.1 M H ₂ SO ₄ + 1 M CH ₃ OH	1.06	0.25	Nanoscale 2019 , 11, 2840-2847
Pt ₅₄ Rh ₄₆ NSs	0.5 M H ₂ SO ₄ + 1 M CH ₃ OH	1.23	0.41	Electrochim. Acta 2018 , 266, 305-311
PtPb CNCs	0.1 M HClO ₄ + 0.5 M CH ₃ OH	2.09	0.97	Chem. Mater. 2017 , 29, 4557-4562
PtPbCu NDs	0.5 M H ₂ SO ₄ + 0.5 M CH ₃ OH	1.14	0.69	Appl. Catal. B-Environ. 2017 , 211, 205-211.
PtCu nanodendrites	0.5 M H ₂ SO ₄ + 0.5 M CH ₃ OH	1.99	0.39	J. Mater. Chem. A, 2016 , 4, 13425-13430
Pt ₃ Co NWs/C	0.1 M HClO ₄ + 0.2 M CH ₃ OH	1.95	1.02	Nat. Commun. 2016 , 7, 11850
Dendrite Pt ₃ Cu nanocubes	0.1 M H ₂ SO ₄ + 1 M CH ₃ OH	1.7	0.93	Chem. Sci. 2015 , 6, 7122-7129
Ethanol Oxidation Reaction (EOR)				
Catalysts	Electrolyte	Specific Activity (mA/cm²)	Mass Activity (A/mg_{Pt})	Reference
PtCuRh RDND	0.1 M HClO₄ + 0.5 M C₂H₅OH	2.84	1.07	This work
Pt ₆₆ Ni ₂₇ Ru ₇ DNSs	0.5 M H ₂ SO ₄ + 0.5 M C ₂ H ₅ OH	4.10	0.75	Nano Res. 2019 , 12, 651-657
Rh @ Pt _{3.5} L NW/C	0.1 M HClO ₄ + 0.2 M C ₂ H ₅ OH	1.18	0.81	Adv. Funct. Mater. 2018 , 1806300
Pt ₉ RhFe ₃ /C	1.0 M HClO ₄ + 1.0 M C ₂ H ₅ OH	27.5	0.97	ACS Appl. Mater. Interfaces 2017 , 9, 9584-9591
Pt _{2.3} Ni/C	0.1 M HClO ₄ + 0.2 M C ₂ H ₅ OH	1.48	NA	ACS Catal. 2017 , 7, 5134-5141
PtRh NW/GNS	1.0 M H ₂ SO ₄ +1.0	2.8	1.0	ACS Appl. Mater.

	M C ₂ H ₅ OH			Interface 2017 , 9, 3535-3543.
PtMoNi nanowires	0.5 M H ₂ SO ₄ + 2.0 M C ₂ H ₅ OH	2.6	0.87	Sci. Adv. 2017 , 3, e1603068.
Pt ₃ Co NWs/C	0.1 M HClO ₄ + 0.2 M C ₂ H ₅ OH	1.55	0.81	Nat. Commun. 2016 , 7, 11850
PtRu/C core-shell	0.5 M H ₂ SO ₄ +1.0 M C ₂ H ₅ OH	0.81	NA	Int. J. hydrogen energy, 2016 , 41, 11359
Pt ₆₀ Rh ₄₀ -SnO ₂ /C	0.5 M H ₂ SO ₄ +1.0 M C ₂ H ₅ OH	0.028	NA	J. Power sources, 2016 , 315, 47