

Supporting Information

Surface Oxygen-Mediated Ultrathin PtRuM (Ni, Fe and Co) Nanowires Boosting Methanol Oxidation Reaction

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Experimental Section

Chemicals

Platinum (II) acetylacetonate ($\text{Pt}(\text{acac})_2$, 97%), nickel (II) acetylacetonate ($\text{Ni}(\text{acac})_2$, 95%), Molybdenumhexacarbonyl ($\text{Mo}(\text{CO})_6$, 98%), glucose and oleylamine (OAm, >70%) were purchased from Sigma-Aldrich. Ruthenium (III) 2,4-pentanedionate ($\text{Ru}(\text{acac})_3$), Tris(2,4-pentanediaonato) Cobalt (III) ($\text{Co}(\text{acac})_3$, 98%), Iron (III) 2,4-pentanedionate ($\text{Fe}(\text{acac})_3$), (1-Hexadecyl) trimethylammonium chloride (CTAC, 96%), Nafion solution (5 wt.%) were bought from Alfa Aesar. Potassium hydroxide (KOH, 90%) was bought from Aladdin. Isopropanol, methanol, ethanol, and cyclohexane were supplied by Beijing Tongguang Fine Chemicals Company. All reagents were used without further purification, and all solutions were freshly prepared with ultrapure water ($18.2 \text{ M}\Omega \text{ cm}^{-1}$).

Preparation of ultrathin tri-metallic PtRuM nanowires (NWs)

In a typical preparation of ultrathin tri-metallic PtRuNi NWs, $\text{Pt}(\text{acac})_2$ (10 mg), $\text{Ru}(\text{acac})_3$ (9.96 mg), $\text{Ni}(\text{acac})_2$ (6.4 mg), CTAC (50 mg), glucose (27 mg) and $\text{Mo}(\text{CO})_6$ (19.8 mg) were added into oleylamine (5 mL) in a vial. After the vial has been capped, the mixture was sonicated for 1 h to get a homogeneous solution. The vial was heated to 180°C and then kept at this temperature for 2 h under magnetic stirring. The black colloidal products were collected by centrifugation and washed two or three times with an ethanol/cyclohexane mixture before they were naturally cooled to room temperature. The synthesis of ultrathin Pt and PtRu NWs were similar to that of PtRuNi NWs, just $\text{Pt}(\text{acac})_2$ (10 mg) or $\text{Pt}(\text{acac})_2$ (10 mg), $\text{Ru}(\text{acac})_3$ (9.96 mg) as metal precursors. The synthesis of ultrathin PtRuFe and PtRuCo NWs were also similar to that of ultrathin PtRuNi NWs, except that $\text{Ni}(\text{acac})_2$ was replaced with absence of $\text{Ni}(\text{acac})_2$, $\text{Fe}(\text{acac})_3$ (8.8 mg) or $\text{Co}(\text{acac})_3$ (8.9 mg), respectively.

Preparation of PtRuM/C catalyst

The obtained 1 mg NWs were dispersed in 10 mL of cyclohexane and 4 mg carbon (Ketjen Black-300) in 10 mL of ethanol under sonication for 1 h and collected via centrifugation with ethanol. The PtRuM/C catalysts were obtained by cleaning the surface with acetic acid solvent at 60°C for 2 h under N_2 atmosphere. Then the products were washed with ethanol two times and dried under 60°C in a vacuum.

Preparation of PtRuM-O/C catalyst

The prepared PtRuM/C was subject to thermal annealing at 220°C for 1 h in air with a heating rate of 2°C min^{-1} , obtained PtRuM-O/C nanowires catalysts.

Characterization

The PtRuM-O/C samples were ultrasonicated for a long time, some nanowires were ultrasonically removed from the carbon, further characterizing nanowires by TEM, HRTEM, etc. The morphologies of the samples were characterized by transmission electron microscopy (TEM) and high-resolution TEM (HRTEM) on an FEI Tecnai-G2 F30 at an accelerating voltage of 300 KV. Powder X-ray diffraction (XRD) spectra were recorded on X'Pert-PRO MPD diffractometer operating at 40 KV and 40 mA with Cu K α radiation. The concentrations of catalysts were determined by the inductively coupled plasma atomic emission spectrometer (Varian 710-ES). The catalysts after the durability tests were scratched off the glassy carbon electrode with the aid of sonication in ethanol and then collected for further TEM, TEM-EDX and XRD characterization. X-ray photoelectron spectra (XPS) of the samples were collected with a VG ESCALABMK II spectrometer.

Electrochemical measurements

The different catalysts were dispersed in a mixture of ultrapure water, isopropanol, and Nafion solution (v:v:v = 1:1:0.01) to reach a homogeneous catalyst ink with a concentration of 1 mg mL⁻¹ (PtRuM-O/C and PtRuM/C) by sonication for 1 h.

Electrochemical measurements were conducted on a CHI 760E Electrochemical Workstation (Shanghai Chenhua Instrument Corporation, China) in a conventional three-electrode cell by using a graphite rod electrode as the counter electrode and a saturated Ag/AgCl or calomel electrode as the reference electrode. The working electrode was a glassy carbon electrode (GCE, diameter: 3 mm, area: 0.07065 cm²). 10 μ L catalyst was dropped onto the GCE surface for further electrochemical tests. All the potentials reported in this work were converted to the reversible hydrogen electrode (RHE). Cyclic voltammograms (CVs) were performed in N₂-saturated 0.5 M H₂SO₄ solution (or 1 M KOH solution) from 0 to 1.2 V vs. RHE at a scan rate of 20 mV s⁻¹, and the electrochemical active surface areas (ECSAs) were determined by the charge of the hydrogen absorption/desorption process in the CVs. The CVs for MOR were conducted in N₂-saturated 0.5 M H₂SO₄ + 0.5 M CH₃OH solution between 0.2-1.2 V vs. RHE (or 1 M KOH + 1M CH₃OH solution between 0-1.2 V vs. RHE) at a scan rate of 20 mV s⁻¹. For the MOR stability tests, chronoamperometric (CA) tests were performed at a fixed potential of 0.7 V vs. RHE. 1000 CV cycles were measured in 0.5 M H₂SO₄ + 0.5 M CH₃OH solution (or 1 M KOH + 1M CH₃OH solution) between 0-1.2 V vs. RHE with a scan rate of 200 mV s⁻¹.

CO stripping curves were conducted in 0.5 M H₂SO₄ solution (or 1 M KOH solution). Before the tests, 0.5 M H₂SO₄ (or 1 M KOH solution) was first deaerated with high-purity N₂. Then, CO was bubbled into

the cell for 15 min while the potential of the working electrode was held at a constant potential of 0.1 V vs. RHE. Then N₂ was bubbled into the system for 15 min to remove CO gas. After that, CO stripping curves were recorded between 0-1.2 V vs. RHE at a scan rate of 20 mV s⁻¹.

Calculation Setup

Through the density functional theory (DFT) within the CASTEP codes, we have conducted all calculations to investigate the electronic and energetic behaviors.¹ The generalized gradient approximation (GGA) in the parametrization of Perdew-Burke-Ernzerhof (PBE) is chosen to reveal the exchange-correlation energy.²⁻⁴ We selected the 380 eV cutoff energy within the ultrasoft pseudopotential scheme for all the geometry optimizations.⁵ For the k-point mesh to achieve the energy minimization, the Broyden-Fletcher-Goldfarb-Shannon (BFGS) algorithm is applied.^{6, 7} The convergence criteria for the geometry optimizations have been set as that the Hellmann-Feynman forces will be less than 0.001 eV Å⁻¹ meanwhile the total energy should not exceed 5×10⁻⁵ eV per atom.

Supplementary Figures and Tables

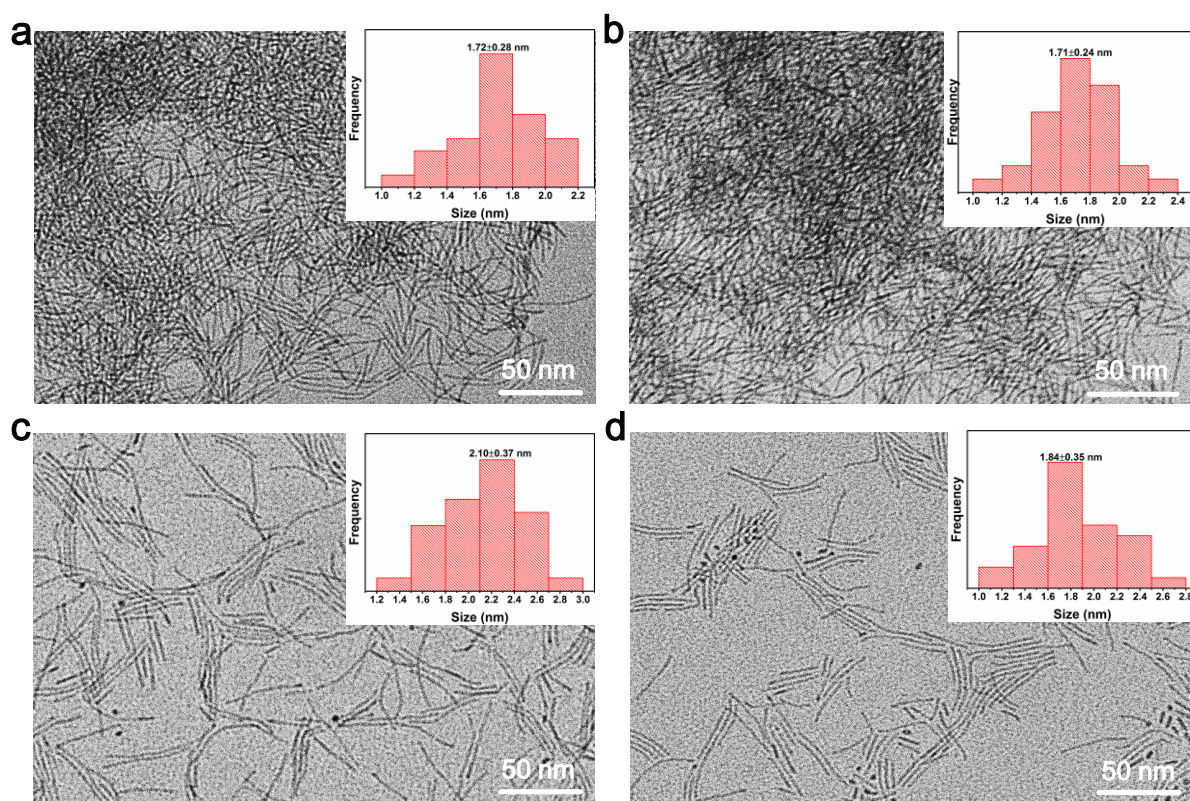


Figure S1. TEM images and histogram of the diameter. (a) $\text{Pt}_{61}\text{Ru}_{25}\text{Ni}_{14}\text{-O}$ NWs, (b) $\text{Pt}_{58}\text{Ru}_{14}\text{Ni}_{28}\text{-O}$ NWs, (c) $\text{Pt}_{65}\text{Ru}_{35}$ NWs and (d) Pt NWs.

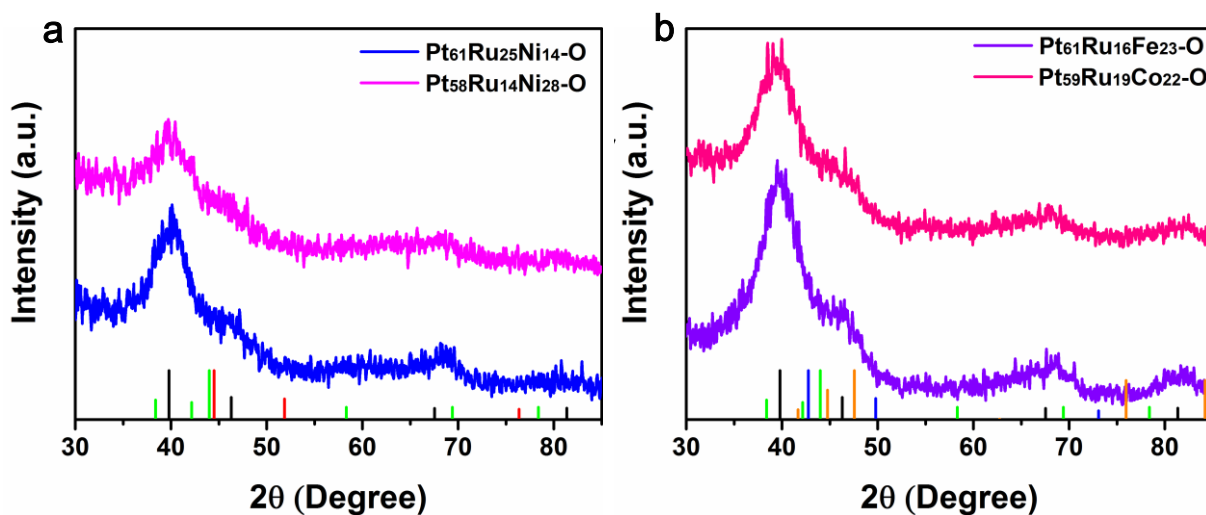


Figure S2. (a) XRD patterns of (a) $\text{Pt}_{61}\text{Ru}_{25}\text{Ni}_{14}\text{-O}$ NWs and $\text{Pt}_{58}\text{Ru}_{14}\text{Ni}_{28}\text{-O}$ NWs, (b) $\text{Pt}_{61}\text{Ru}_{16}\text{Fe}_{23}\text{-O}$ NWs and $\text{Pt}_{59}\text{Ru}_{19}\text{Co}_{22}\text{-O}$ NWs. Black: Pt PDF#04-0802, Green: Ru PDF#06-0663, Red: Ni PDF#04-0850, Blue: Fe PDF#52-0513, Orange: Co PDF#05-0727.

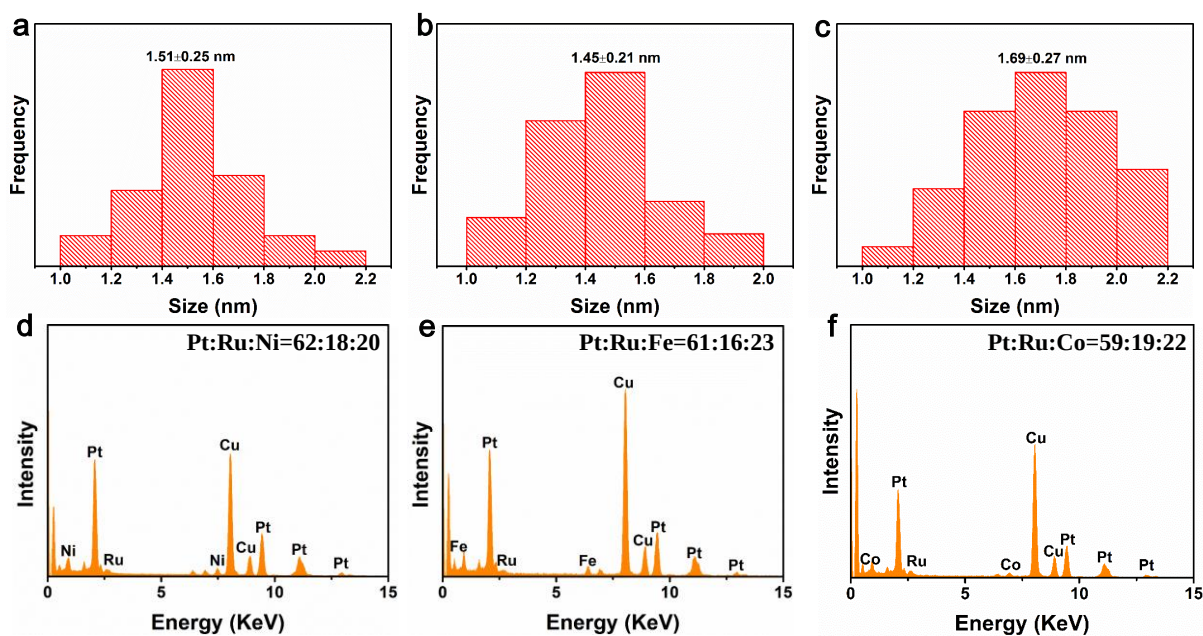


Figure S3. Histogram of the diameter (a) $\text{Pt}_{62}\text{Ru}_{18}\text{Ni}_{20}\text{-O}$ NWs, (b) $\text{Pt}_{61}\text{Ru}_{16}\text{Fe}_{23}\text{-O}$ NWs, (c) $\text{Pt}_{59}\text{Ru}_{19}\text{Co}_{22}\text{-O}$ NWs; TEM-EDX images of (d) $\text{Pt}_{62}\text{Ru}_{18}\text{Ni}_{20}\text{-O}$ NWs, (e) $\text{Pt}_{61}\text{Ru}_{16}\text{Fe}_{23}\text{-O}$ NWs, (f) $\text{Pt}_{59}\text{Ru}_{19}\text{Co}_{22}\text{-O}$ NWs.

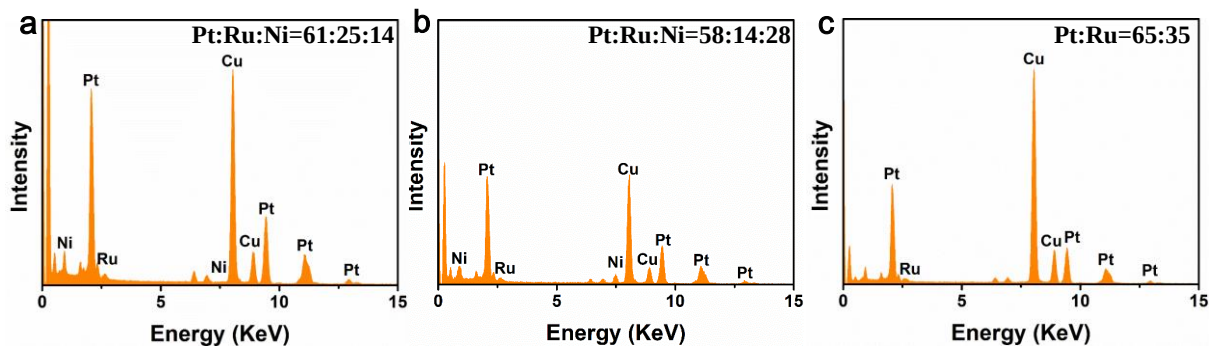


Figure S4. TEM-EDX images of (a) $\text{Pt}_{61}\text{Ru}_{25}\text{Ni}_{14}\text{-O}$ NWs, (b) $\text{Pt}_{58}\text{Ru}_{14}\text{Ni}_{28}\text{-O}$ NWs, (c) $\text{Pt}_{65}\text{Ru}_{35}$ NWs.

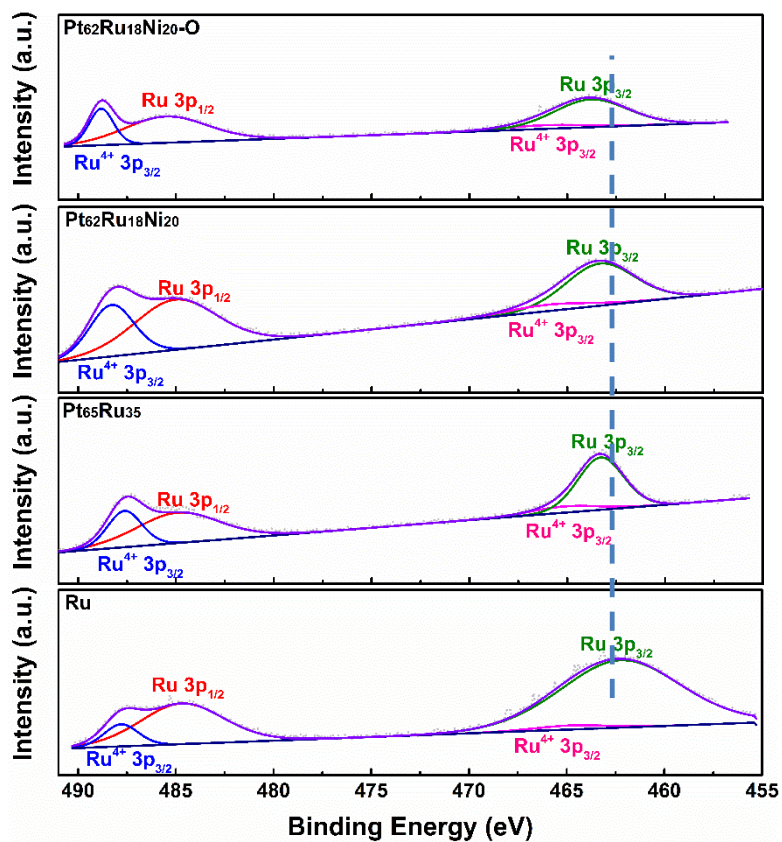


Figure S5. Ru 3p XPS spectra of different samples.

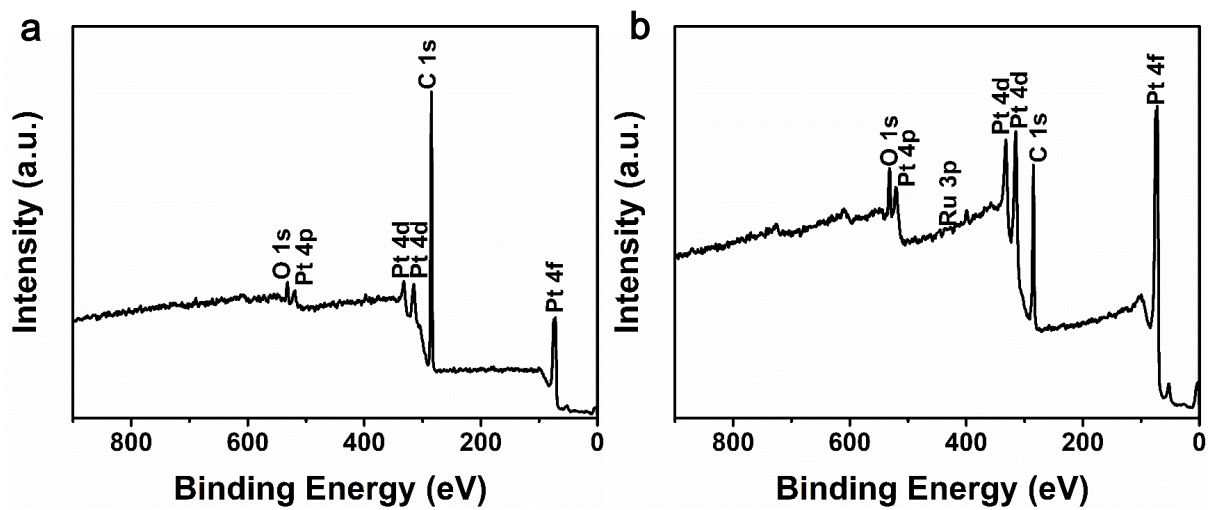


Figure S6. XPS survey spectrum of (a) Pt NWs and (b) Pt₆₅Ru₃₅ NWs.

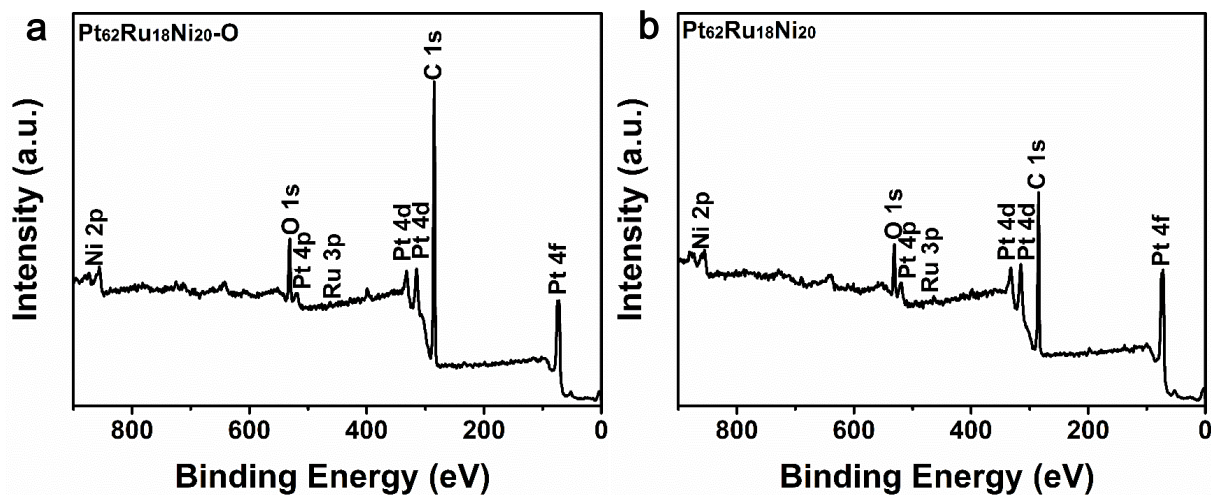


Figure S7. XPS survey spectrum of (a) Pt₆₂Ru₁₈Ni₂₀-O NWs and (b) Pt₆₂Ru₁₈Ni₂₀ NWs.

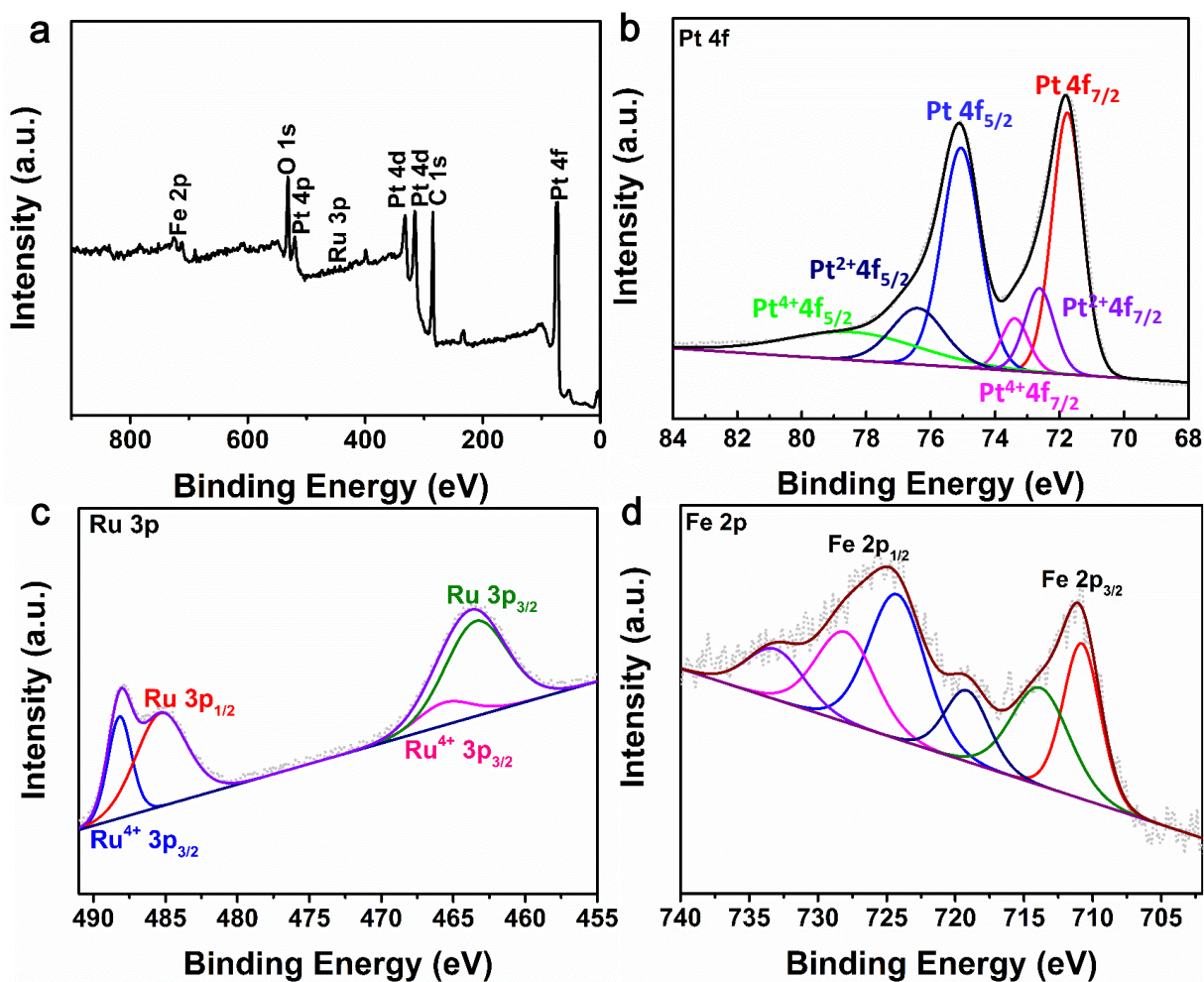


Figure S8. (a) XPS survey spectrum. XPS spectra (b) Pt 4f, (c) Ru 3p and (d) Fe 2p of Pt₆₁Ru₁₆Fe₂₃-O NWs.

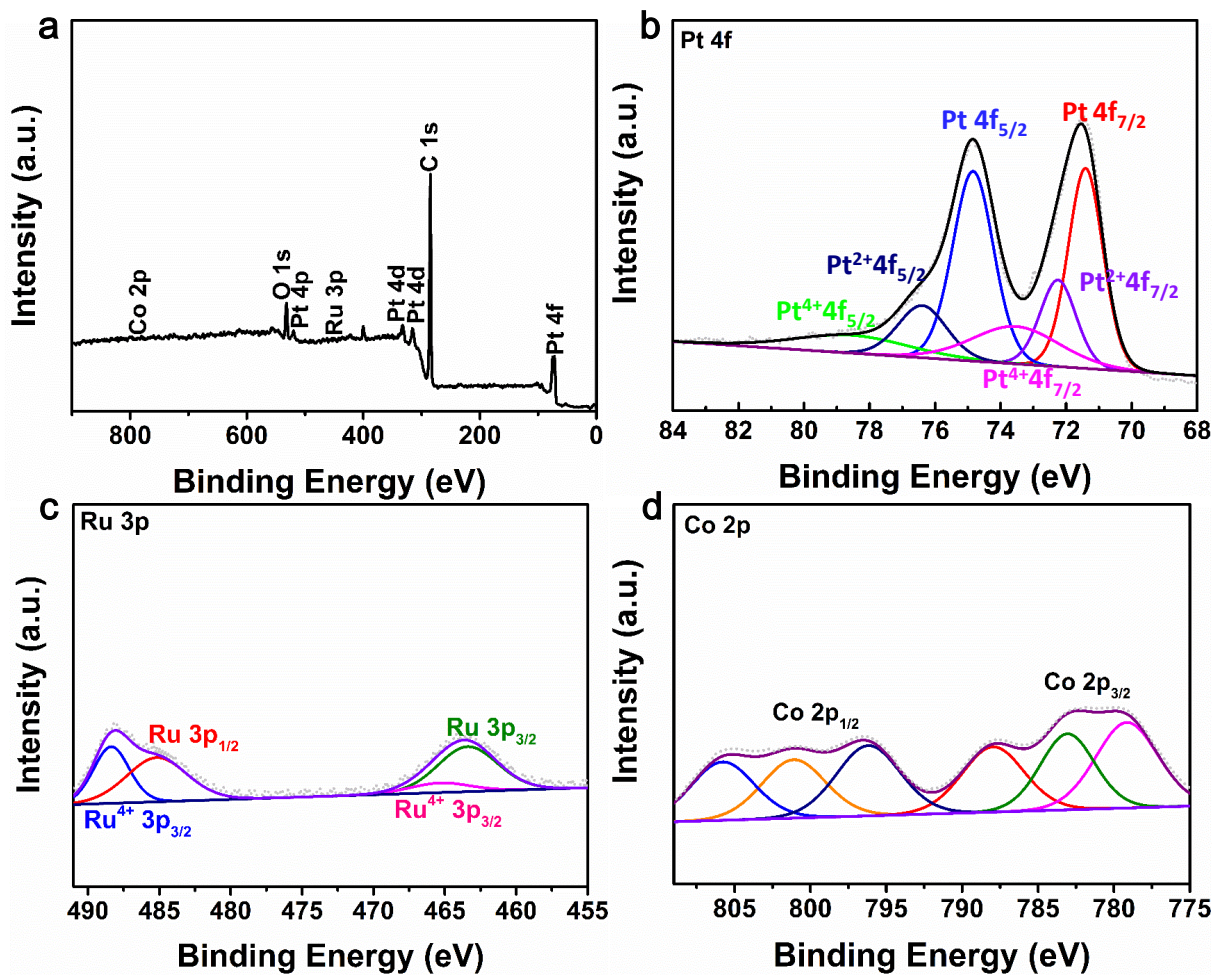


Figure S9. (a) XPS survey spectrum. XPS spectra (b) Pt 4f, (c) Ru 3p and (d) Co 2p of Pt₅₉Ru₁₉Co₂₂-O NWs.

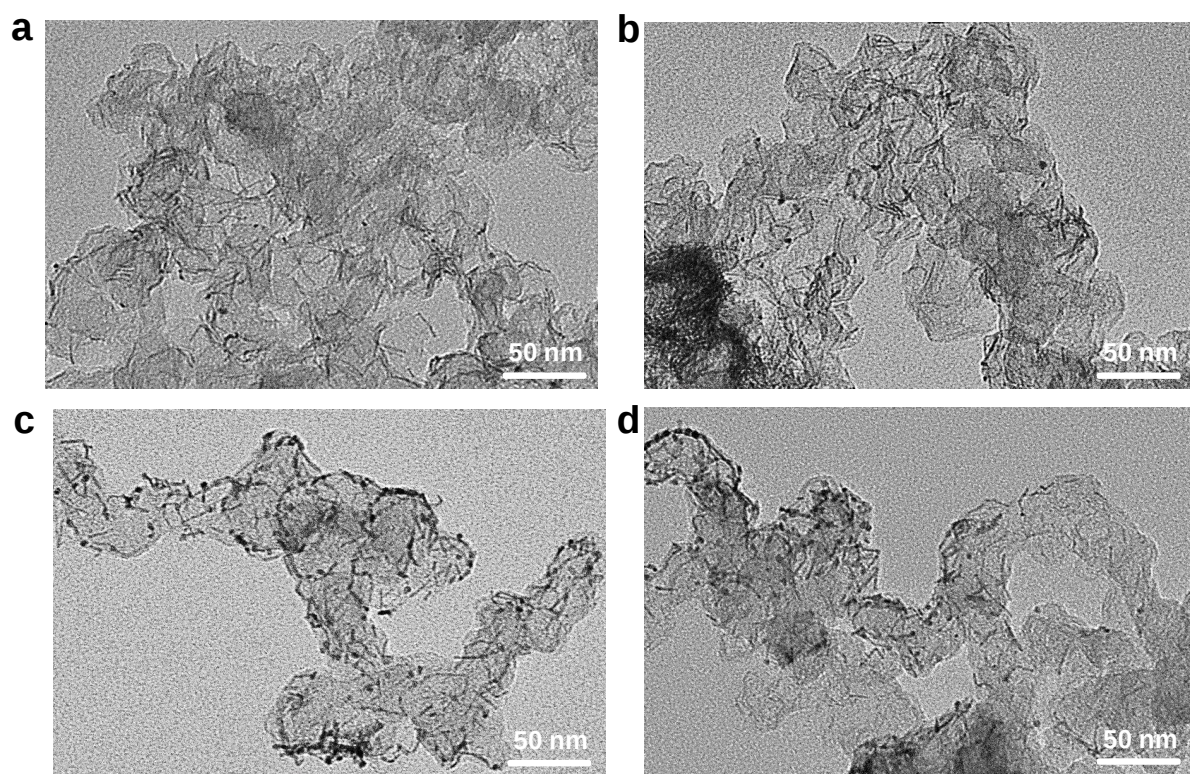


Figure S10. Representative TEM images of (a) Pt₆₂Ru₁₈Ni₂₀-O/C before and (b) after MOR stability measurement. (c) Pt₅₈Ru₁₄Ni₂₈-O/C before and (d) after MOR stability measurement.

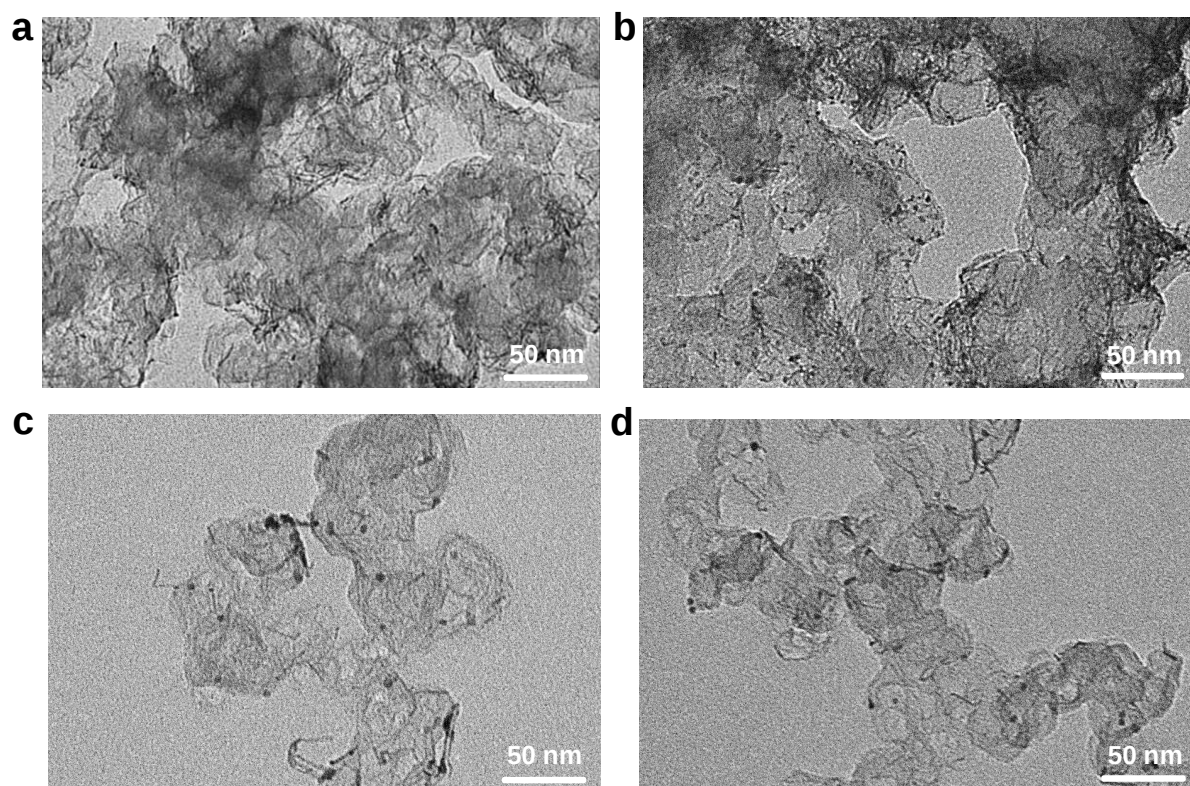


Figure S11. Representative TEM images of (a) Pt₆₁Ru₂₅Ni₁₄-O/C before and (b) after MOR stability measurement. (c) Pt₆₅Ru₃₅/C before and (d) after MOR stability measurement.

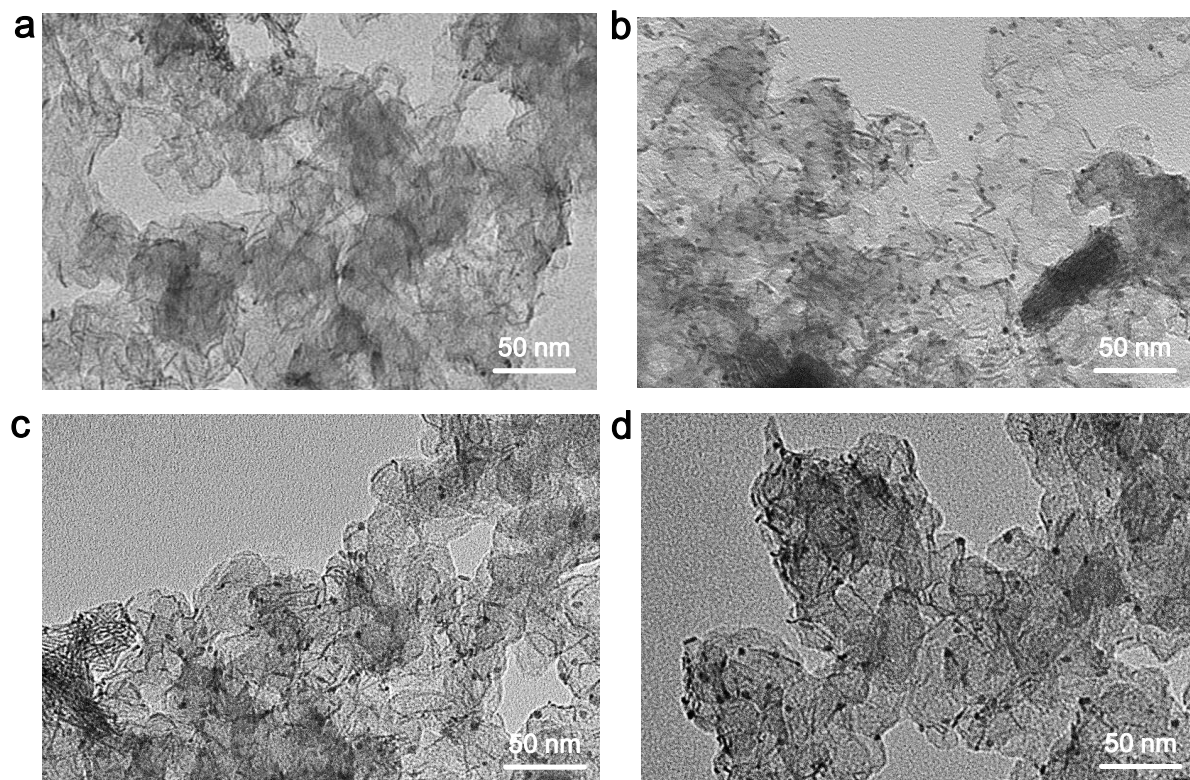


Figure S12. Representative TEM images of (a) Pt₆₁Ru₁₆Fe₂₃-O/C before and (b) after MOR stability measurement. (c) Pt₅₉Ru₁₉Co₂₂-O/C before and (d) after MOR stability measurement.

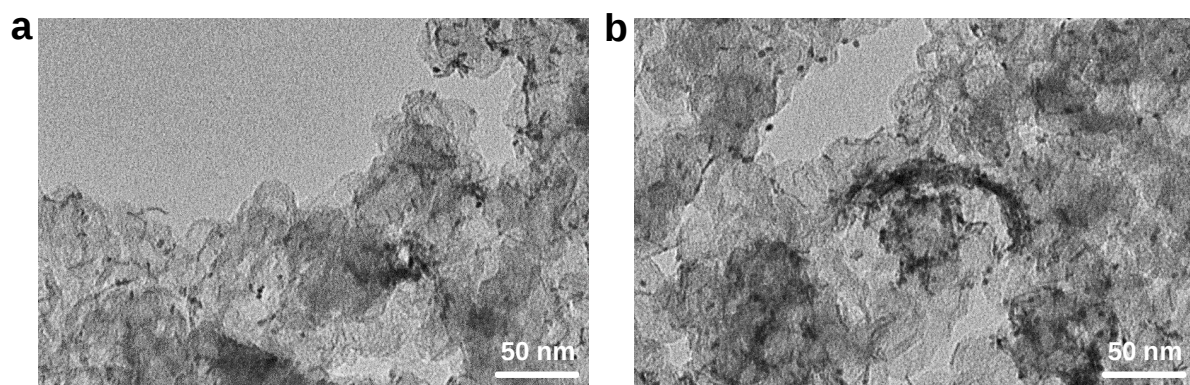


Figure S13. Representative TEM images of (a) Pt/C NWs before and (b) after MOR stability measurement.

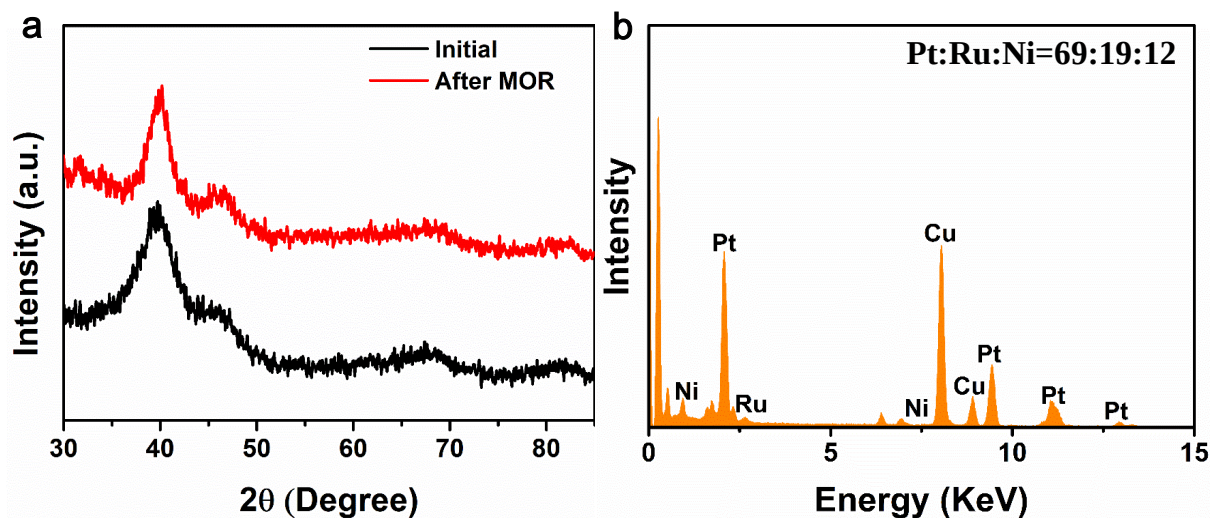


Figure S14. (a) XRD patterns of the $\text{Pt}_{62}\text{Ru}_{18}\text{Ni}_{20}\text{-O/C}$ before and after MOR stability measurement. (b) TEM-EDX images after MOR stability measurement.

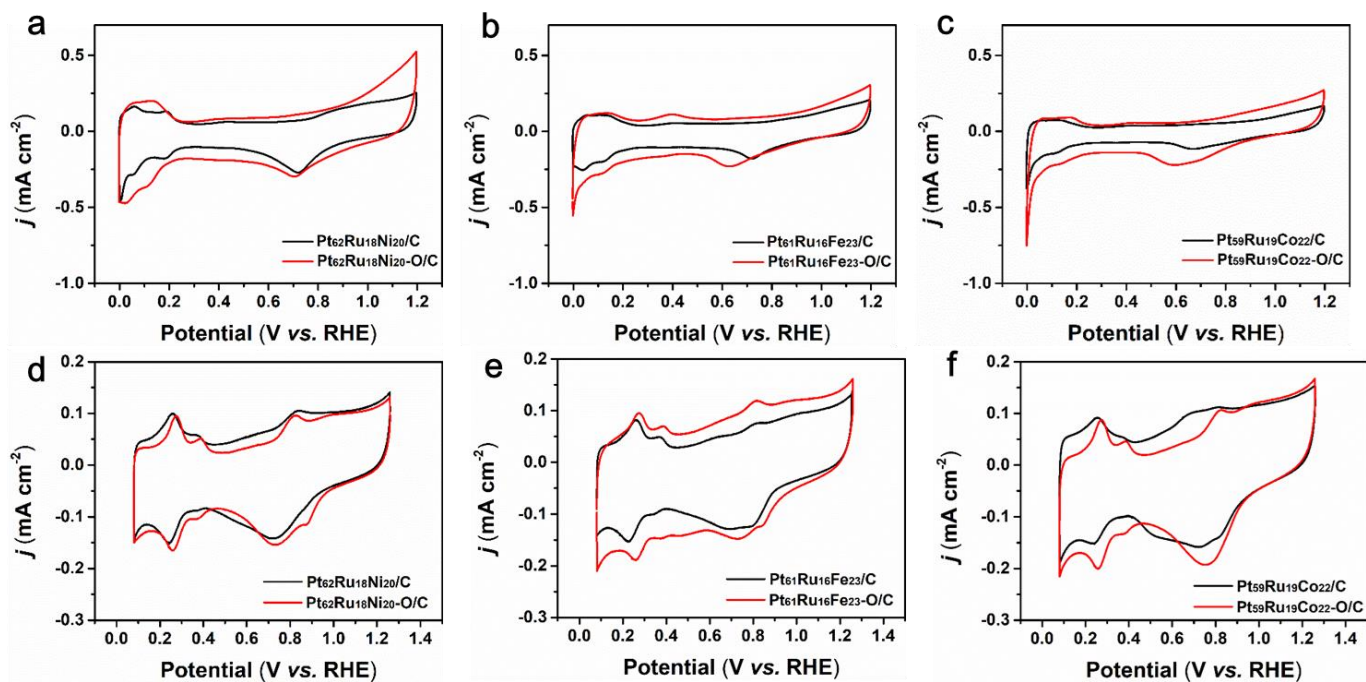


Figure S15. CVs recorded at room temperature in an N_2 -saturated (a), (b) and (c) 0.5 M H_2SO_4 solution. (d), (e) and (f) 1 M KOH solution at a sweep rate of 20 mV s^{-1} .

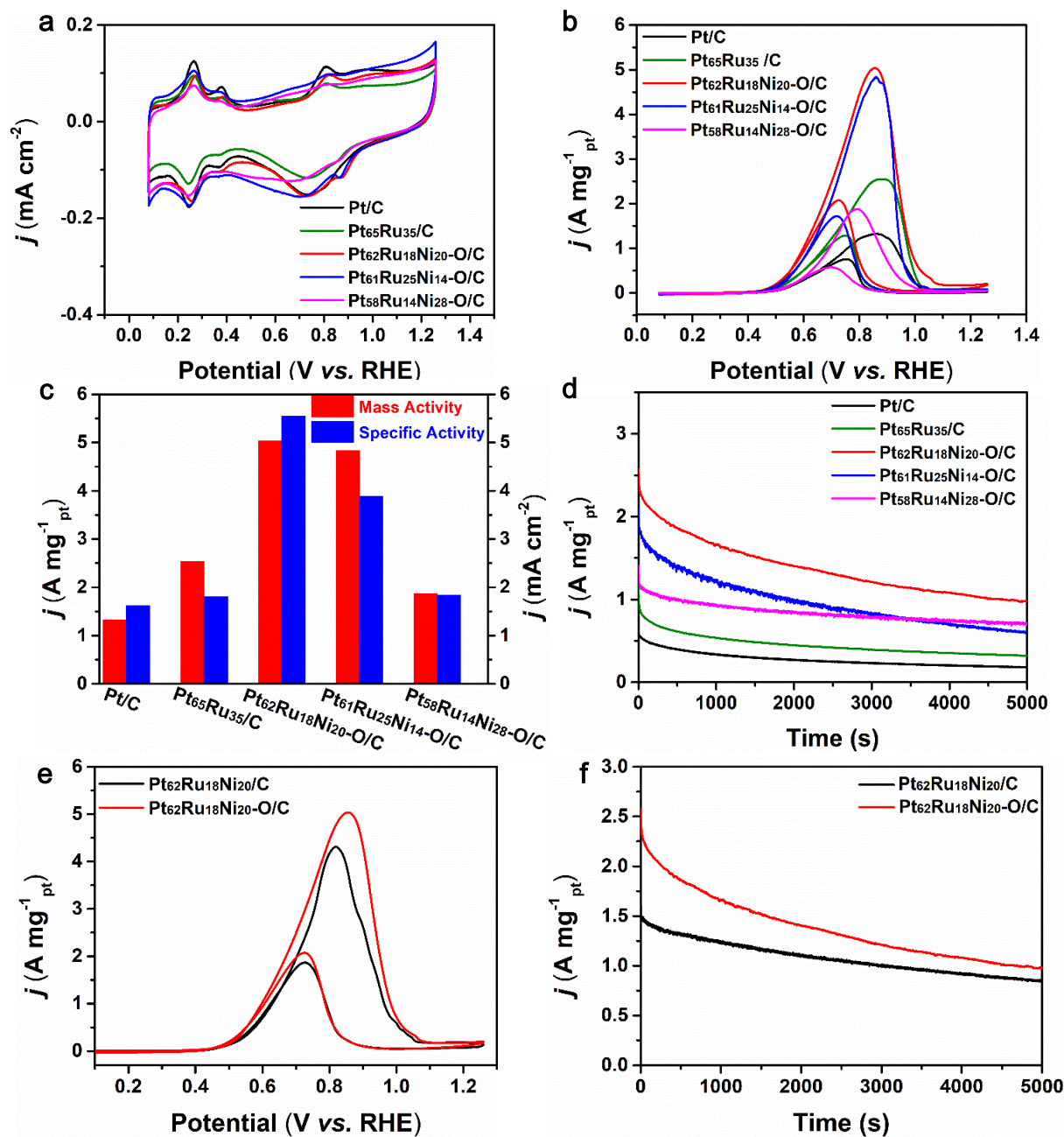


Figure S16. Methanol electro-oxidation performance of different electrocatalysts. (a) CVs in 1 M KOH, (b) CVs, (c) Corresponding histogram of specific and mass activities, and (d) chronoamperometric tests for MOR in 1 M KOH + 1 M CH₃OH solution at 0.7 V vs. RHE. (e) CVs, and (f) chronoamperometric tests of Pt₆₂Ru₁₈Ni₂₀-O/C and Pt₆₂Ru₁₈Ni₂₀/C in 1 M KOH + 1 M CH₃OH solution.

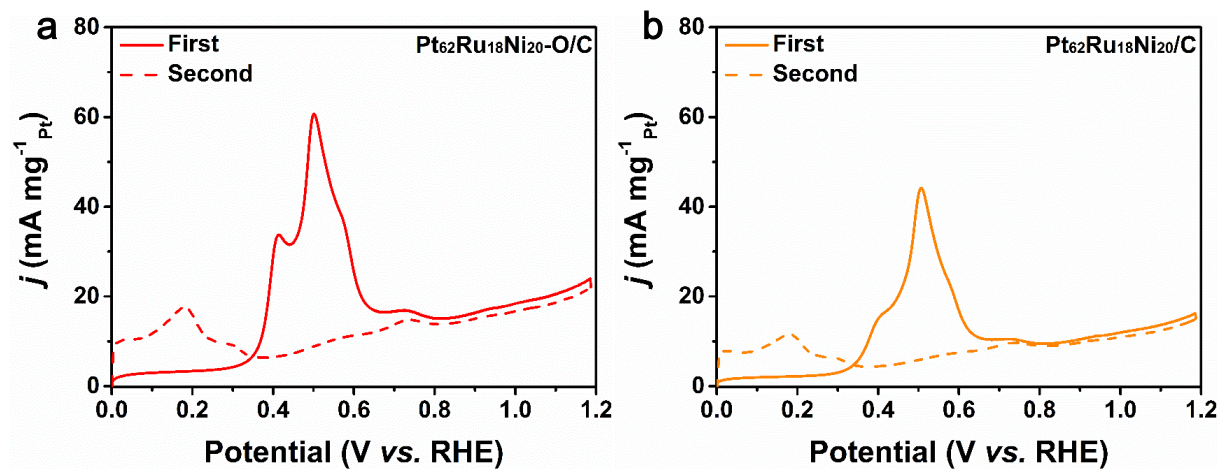


Figure S17. CO stripping curves of (a) Pt₆₂Ru₁₈Ni₂₀-O/C and (b) Pt₆₂Ru₁₈Ni₂₀/C in 1 M KOH solution.

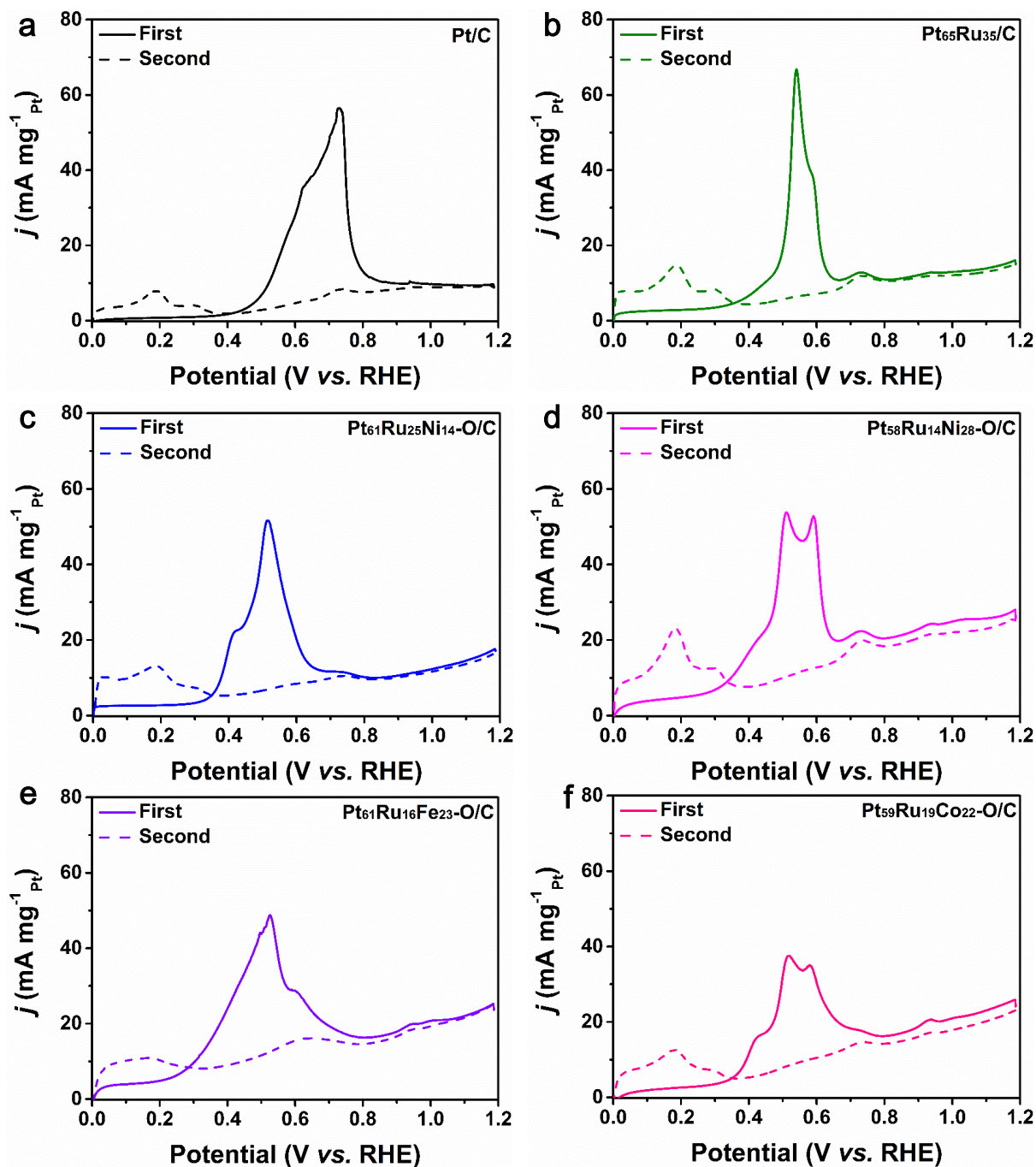


Figure S18. CO stripping curves of different electrocatalysts in 1 M KOH solution.

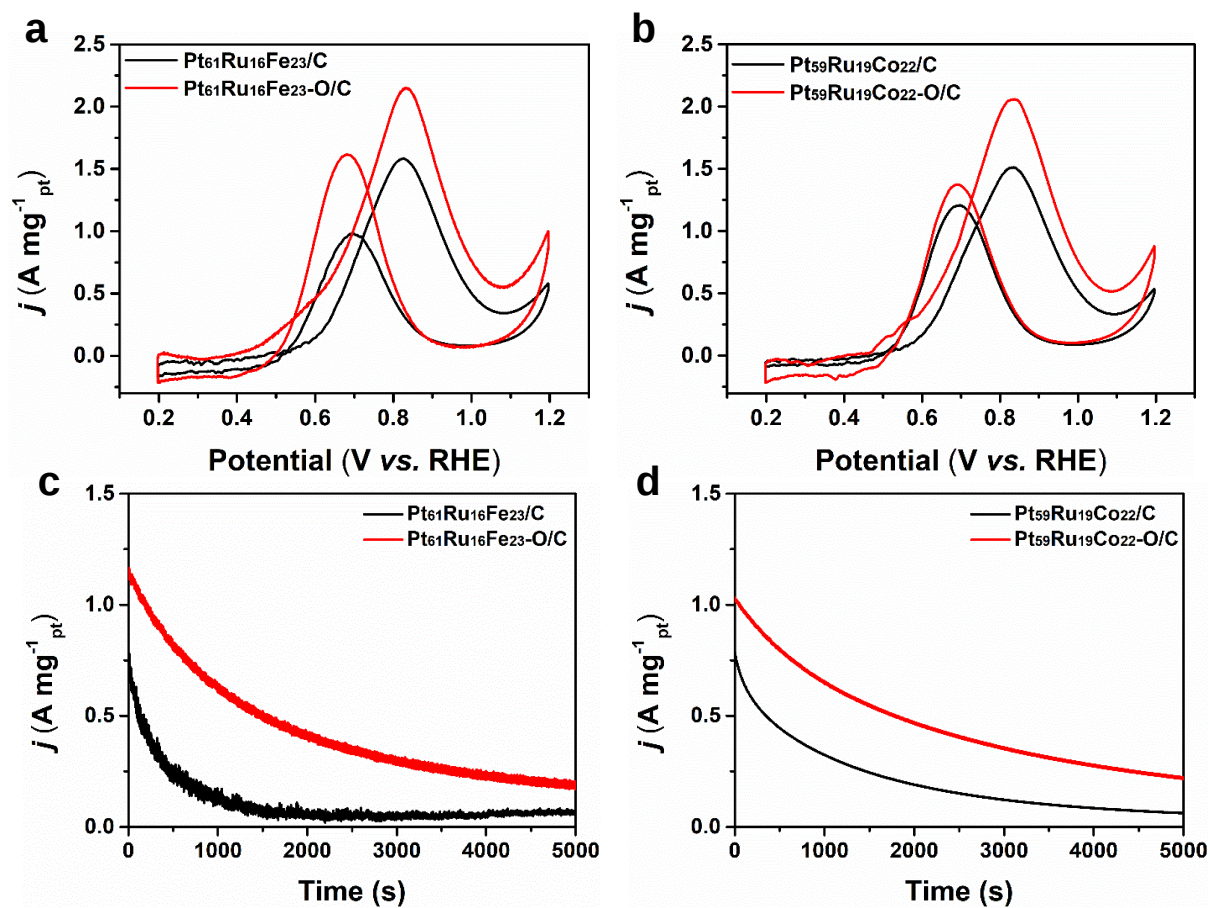


Figure S19. (a) and (b) CVs. (c) and (d) chronoamperometric tests for MOR in 0.5 M H₂SO₄ and 0.5 M CH₃OH solution.

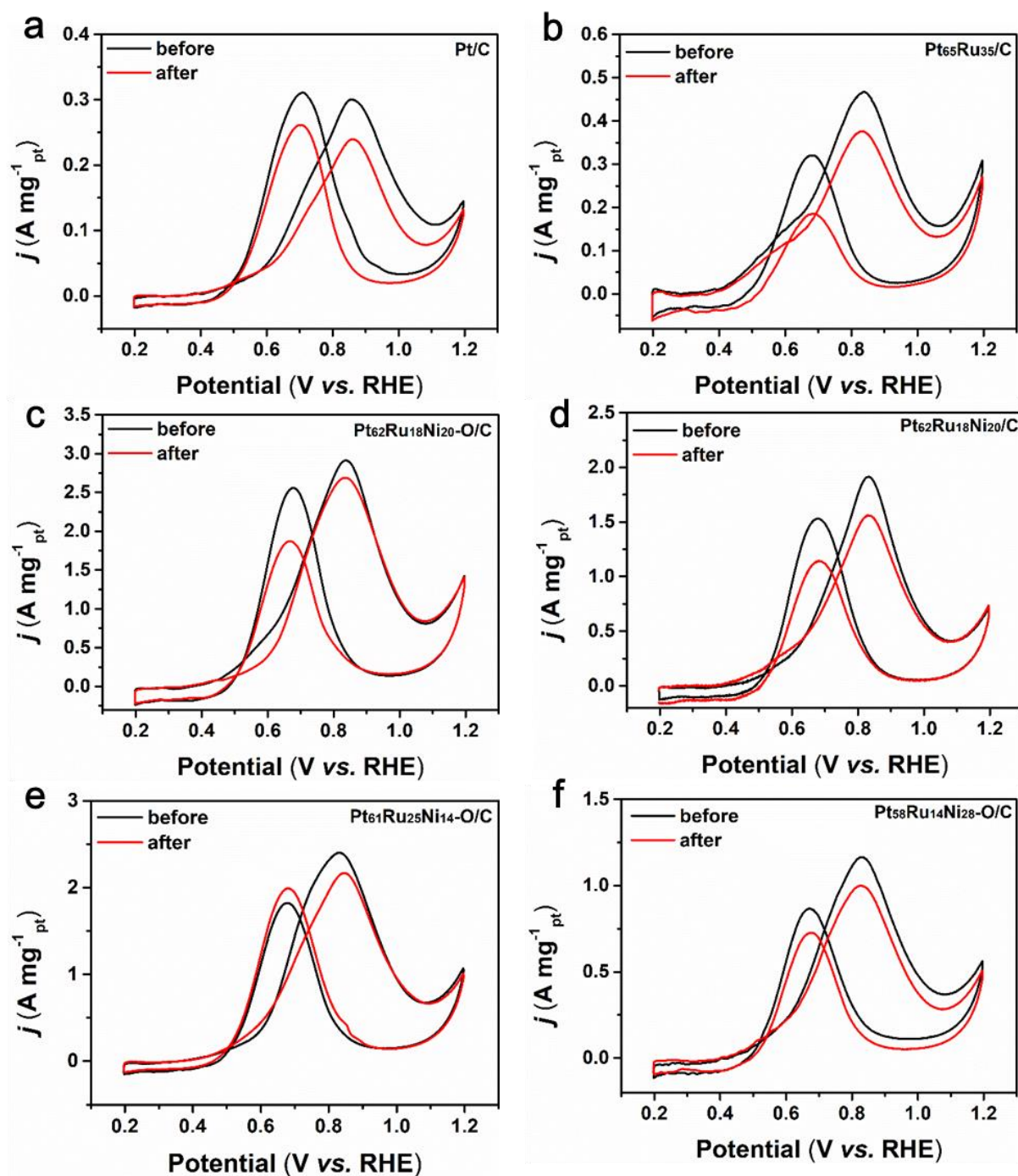


Figure S20. CV curves of different electrocatalysts before and after 1000 cycles in 0.5 M H_2SO_4 and 0.5 M CH_3OH solution.

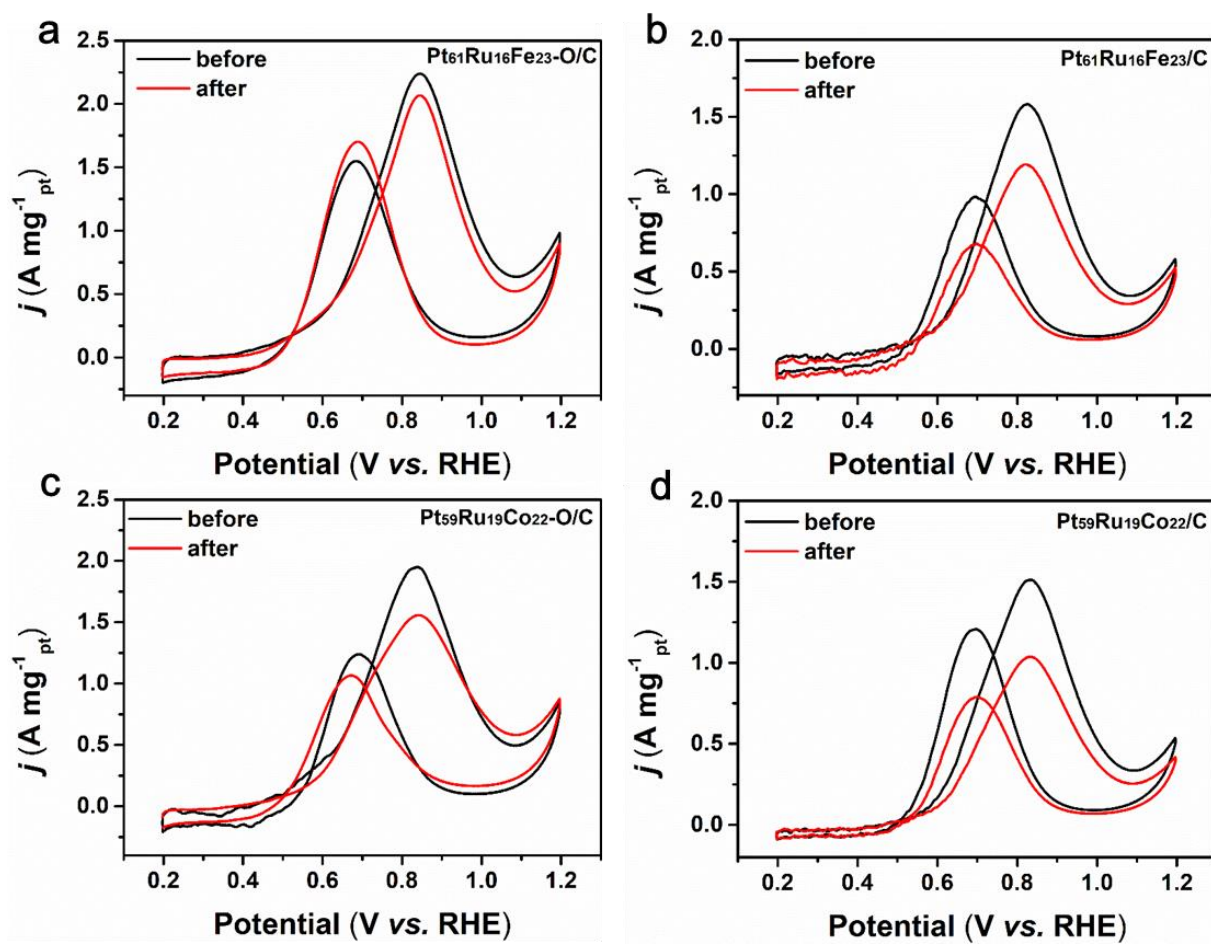


Figure S21. CV curves of different electrocatalysts before and after 1000 cycles in 0.5 M H_2SO_4 and 0.5 M CH_3OH solution.

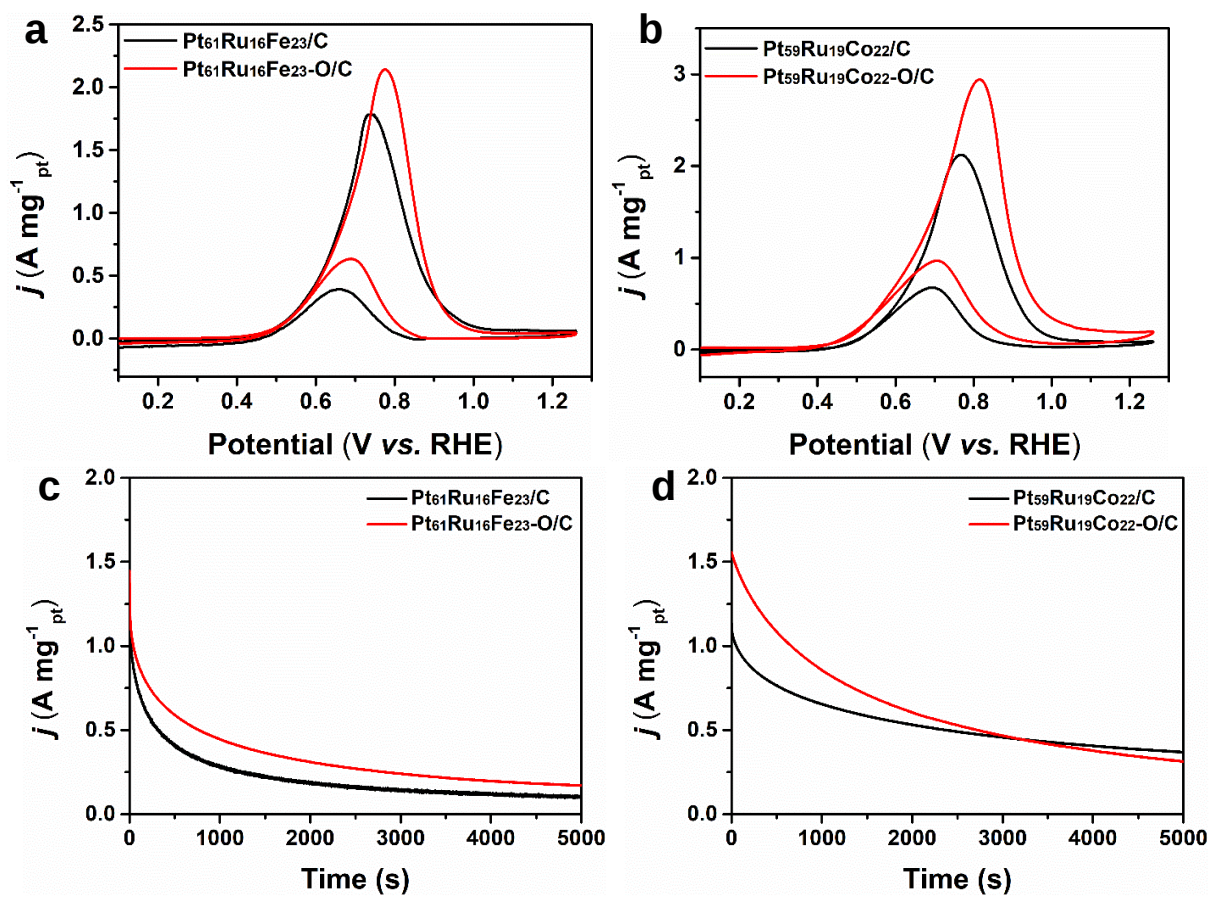


Figure S22. (a) and (b) CVs. (c) and (d) chronoamperometric tests for MOR in 1 M KOH and 1 M CH₃OH solution.

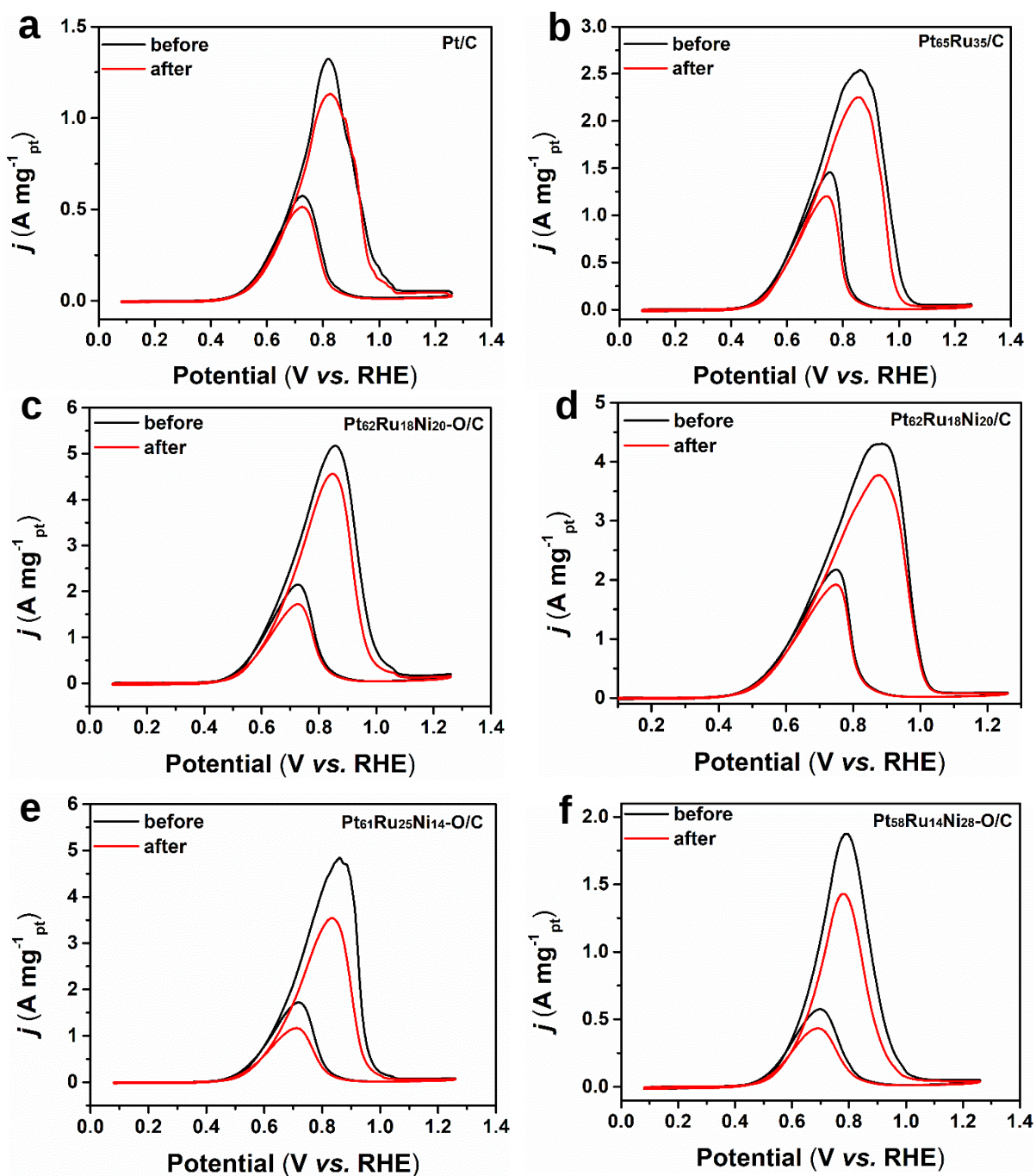


Figure S23. CV curves of different electrocatalysts before and after 1000 cycles in 1 M KOH and 1 M CH_3OH solution.

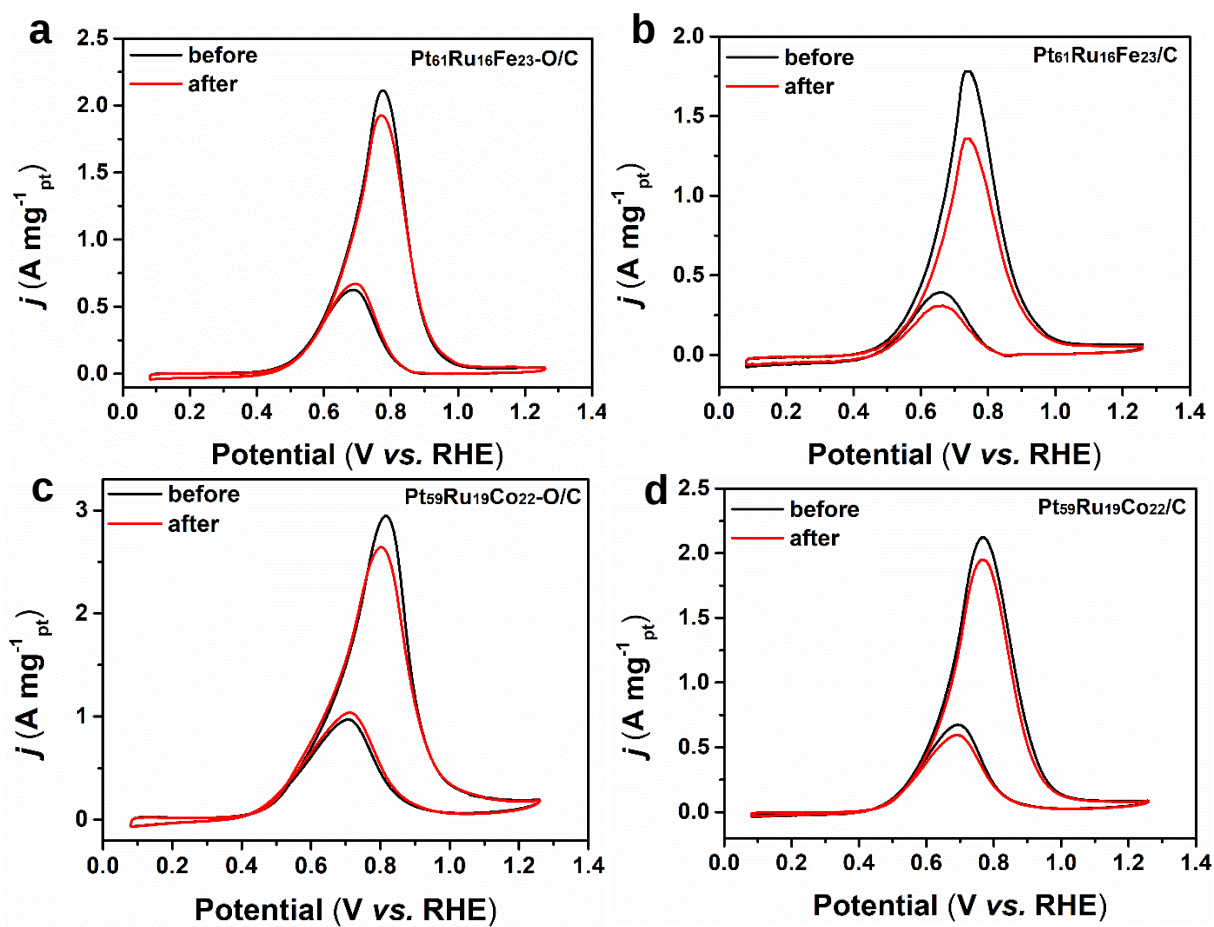


Figure S24. CV curves of different electrocatalysts before and after 1000 cycles in 1 M KOH and 1 M CH_3OH solution.

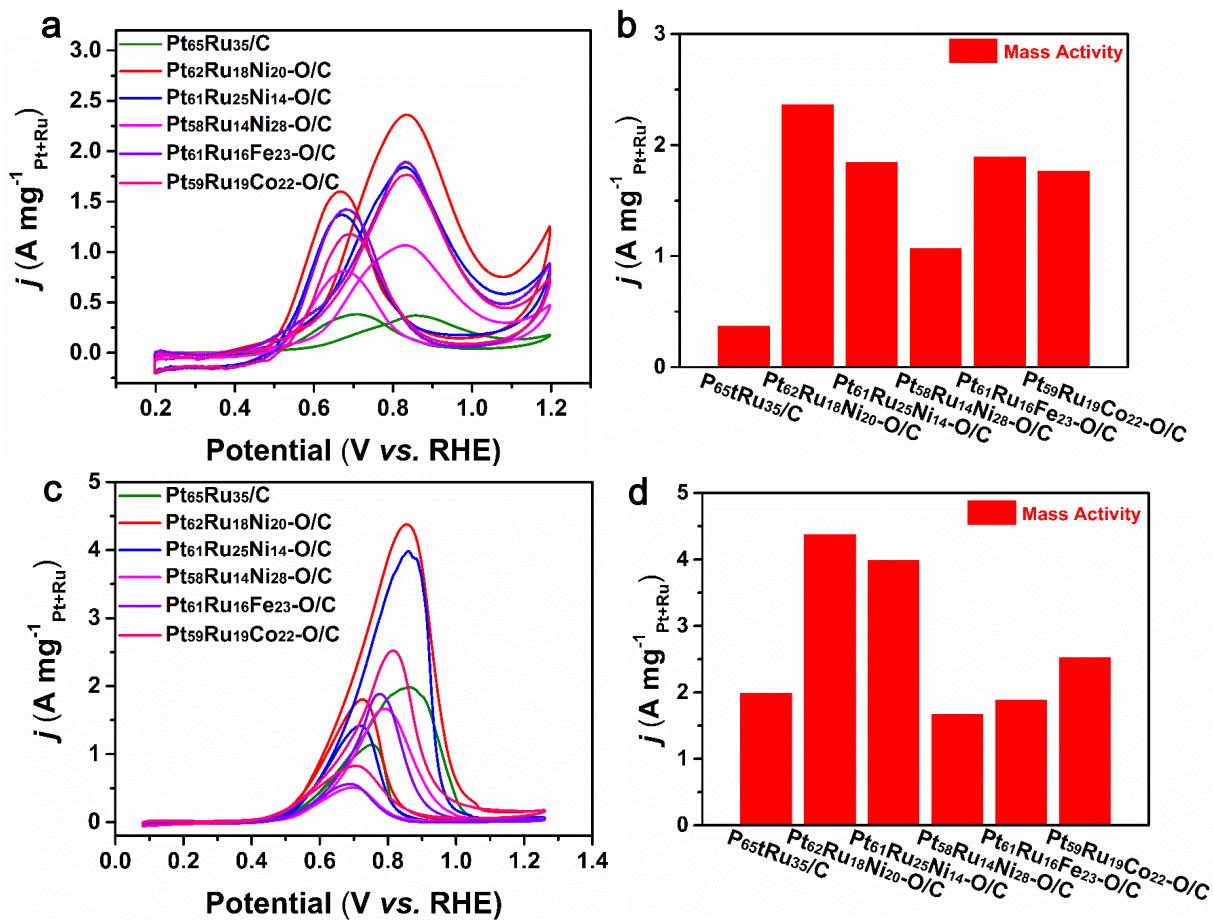


Figure S25. Mass activity (Pt+Ru) of different electrocatalysts for methanol oxidation reaction. (a) CVs and (b) Corresponding histogram of mass activities in 0.5 M H₂SO₄ + 0.5 M CH₃OH solution. (c) CVs and (d) Corresponding histogram of mass activities in 1 M KOH + 1 M CH₃OH solution.

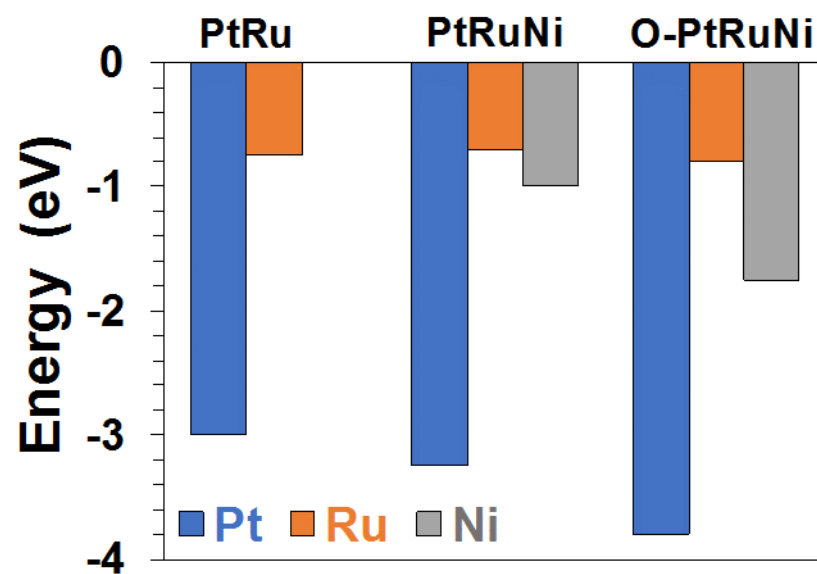


Figure S26. The band position changes of Pt, Ni and Ru in different systems.

Table S1. Comparison performance of Pt₆₂Ru₁₈Ni₂₀-O/C and Pt-based electrocatalysts for MOR in acidic solution.

No.	Catalysts	Electrolyte	Mass Activity	Specific Activity	References
1	Pt₆₂Ru₁₈Ni₂₀-O/C	0.5 M H₂SO₄ 0.5 M methanol	2.72 A mg⁻¹_{Pt} 2.36 A mg⁻¹_{Pt+Ru}	4.36 mA cm⁻²	This work
2	Pt ₆₉ Ni ₁₆ Rh ₁₅ NWs/C	0.1 M HClO ₄ 0.5 M methanol	1.72 A mg ⁻¹	2.49 mA cm ⁻²	<i>Adv. Mater.</i> 2019 , 1805833
3	High crystalline PtCu nanotubes	0.5 M H ₂ SO ₄ 1.0 M methanol	2.25 A mg ⁻¹	6.09 mA cm ⁻²	<i>Energy Environ. Sci.</i> 2017 , 10, 1751
4	Pt ₃ Zn alloy nanocrystals	0.1 M HClO ₄ 0.5 M methanol	1.25 A mg ⁻¹	1.69 mA cm ⁻²	<i>ChemCatChem</i> 2019 ,11
5	Pt-Ag octahedral alloy nanocrystals	0.1 M HClO ₄ 0.5 M methanol	0.72 A mg ⁻¹	6.61 mA cm ⁻²	<i>Nano Energy</i> 2019 , 61, 397
6	Pt NW/N-doped low-defect graphene	1.0 M HClO ₄ 2.0 M methanol	1.28 A mg ⁻¹	-	<i>Small</i> 2017 , 13, 1603013
7	Cubic Pt-Sn alloy nanocrystals	0.5 M H ₂ SO ₄ 0.5 M methanol	0.35 A mg ⁻¹	2.30 mA cm ⁻²	<i>Angew. chem. Int.</i> <i>Ed.</i> 2016 , 55, 9021
8	PtRu porous nanoalloy	0.1 M HClO ₄ 0.5 M methanol	1.70 A mg ⁻¹	10.98 mA cm ⁻²	<i>Adv. Energy Mater.</i> 2017 , 1601593
9	PtPdRuTe nanotubes	0.5 M H ₂ SO ₄ 1.0 M methanol	1.26 A mg ⁻¹	2.96 mA cm ⁻²	<i>J. Am. Chem. Soc.</i> 2017 , 139, 5890
10	PtZn intermetallic NPs	0.5 M H ₂ SO ₄ 1.0 M methanol	0.61 A mg ⁻¹	1.08 mA cm ⁻²	<i>J. Am. Chem. Soc.</i> 2017 , 139, 4762
11	PtNi Colloidal nanocrystal cluster	0.5 M H ₂ SO ₄ 0.5 M methanol	0.69 A mg ⁻¹	1.37 mA cm ⁻²	<i>Adv. Funct. Mater.</i> 2017 , 1704774
12	Porous PtCu NCs	0.1 M HClO ₄ 1.0 M methanol	1.55 A mg ⁻¹	13.01 mA cm ⁻²	<i>Nanoscale</i> 2015 , 7, 16860
13	Pt ₉₅ Co ₅ NWs	0.5 M H ₂ SO ₄ 1.0 M methanol	0.49 A mg ⁻¹	2.54 mA cm ⁻²	<i>Nano Res.</i> 2018 , 11, 2562
14	PtPb/Pt nanoplate	0.1 M HClO ₄ 0.1 M methanol	1.50 A mg ⁻¹	2.60 mA cm ⁻²	<i>Science</i> 2016 , 354, 1410
15	PtCo NWs	0.1 M HClO ₄ 0.2 M methanol	1.02 A mg ⁻¹	1.95 mA cm ⁻²	<i>Nat. Commun.</i> 2016 , 7, 11850
16	Ultrathin Pt ₃ Cu MWs	0.5 M H ₂ SO ₄ 0.5 M methanol	0.63 A mg ⁻¹	2.80 mA cm ⁻²	<i>Chem. Sci.</i> 2016 , 7, 5414
17	Screw thread-like PtCu _{2.1} MWs	0.1 M HClO ₄ 0.2 M methanol	1.56 A mg ⁻¹	3.31 mA cm ⁻²	<i>Nano Lett.</i> 2016 , 16, 5037
18	Dendrite Pt ₃ Cu nanocubes	0.5 M H ₂ SO ₄ 1.0 M methanol	0.93 A mg ⁻¹	1.70 mA cm ⁻²	<i>Chem. Sci.</i> 2015 , 6, 7122
19	Pt ₃ Cu icosahedra	0.1 M HClO ₄ 0.2 M methanol	0.74 A mg ⁻¹	2.14 mA cm ⁻²	<i>ACS nano</i> 2015 , 9, 7634
20	RDH Pt-Ni NFs/C	0.1 M HClO ₄ 0.2 M methanol	1.04 A mg ⁻¹	1.9 mA cm ⁻²	<i>Nano Lett.</i> 2016 , 16, 2762
21	PdRuPt Nanowire Networks	0.1 M HClO ₄ 0.5 M methanol	1.10 A mg ⁻¹	1.98 mA cm ⁻²	<i>Nano Res.</i> 2018 , 11, 4348

22	PtRu NWs	0.1 M HClO ₄ 0.5 M methanol	0.82 A mg ⁻¹	1.16 mA cm ⁻²	<i>J. Am. Chem. Soc.</i> 2018 , 140, 1142
23	Pt nanowires	0.1 M HClO ₄ 0.1 M methanol	1.31 A mg ⁻¹	5.84 mA cm ⁻²	<i>Nano Res.</i> 2016 , 9, 2811
24	Pt-Ni-P NTAs	0.5 M H ₂ SO ₄ 0.5 M methanol	-	3.85 mA cm ⁻²	<i>J. Am. Chem. Soc.</i> 2012 , 134, 5730
25	PtRuNi nanoframes	0.1 M HClO ₄ 0.5 M methanol	1.49 A mg ⁻¹	-	<i>J. Mater. Chem. A.</i> 2019 , 7, 2547
26	PtRu NPs	0.1 M HClO ₄ 0.5 M methanol	1.67 A mg ⁻¹	4.41 mA cm ⁻²	<i>Appl. Catal. B: Environ.</i> 2019 , 118345

Table S2. I_f/I_b ratio of different electrocatalysts for MOR in acidic solution.

Electrocatalysts	I _f /I _b
Pt ₆₂ Ru ₁₈ Ni ₂₀ -O/C	1.47
Pt ₆₂ Ru ₁₈ Ni ₂₀ /C	1.26
Pt ₆₅ Ru ₃₅ /C	1.45
Pt/C	0.96

Table S3. Comparison performance of Pt₆₂Ru₁₈Ni₂₀-O/C and Pt-based electrocatalysts for MOR in alkaline solution.

No.	Catalysts	Electrolyte	Mass Activity	Specific Activity	References
1	Pt ₆₂ Ru ₁₈ Ni ₂₀ -O/C	1 M KOH 1 M methanol	5.03 A mg ⁻¹ _{Pt} 4.38 A mg ⁻¹ _{Pt+Ru}	5.55 mA cm ⁻²	This work
2	PtCu ₃ alloy	0.5 M KOH 1M methanol	3.05 A mg ⁻¹	9.96 mA cm ⁻²	<i>Small</i> , 2019 , 15, 1804407
3	PtCuPd@Ru yolk-cage	2 M KOH 1M methanol	2.48 A mg ⁻¹ _{Pt+Pd}	-	<i>J. Am. Chem. Soc.</i> 2019 , 141, 14496
4	PtCuNi Tetrahedra	1 M KOH 1M methanol	7.0 A mg ⁻¹	14.0 mA cm ⁻²	<i>Nano Lett.</i> 2019 , 19, 5431
5	PtZn intermetallic NPs	0.1 M KOH 1 M methanol	0.58 A mg ⁻¹	1.15 mA cm ⁻²	<i>J. Am. Chem. Soc.</i> 2017 , 139, 4762
6	Pt-Ni(OH) ₂ -rGO	1 M KOH 1 M methanol	1.23 A mg ⁻¹	-	<i>Nat. Commun.</i> 2015 , 6, 10035
7	Au/Ag/Pt hetero-nanostructure	1 M KOH 1 M methanol	1.00 A mg ⁻¹	1.40 mA cm ⁻²	<i>Adv. Mater.</i> 2015 , 27, 5573
8	SANi-Pt NWs	1 M KOH 1 M methanol	7.93 A mg ⁻¹	-	<i>Nature Catalysis</i> 2019 , 2, 495
9	Pt _{0.5} Ag ₁	0.5 M KOH 2 M methanol	2.92 A mg ⁻¹	-	<i>J. Catal.</i> 2012 , 290, 18
10	PtAuRu	1 M KOH 1 M methanol	1.60 A mg ⁻¹	-	<i>J. Mater. Chem. A</i> 2013 , 1, 7255
11	PtNi/C	1 M NaOH 1 M methanol	1.20 A mg ⁻¹	-	<i>Catal. Commun.</i> 2010 , 12, 67
12	Popcorn-like PtAu	1 M KOH 1 M methanol	0.60 A mg ⁻¹	0.80 mA cm ⁻²	<i>J. Mater. Chem. A</i> 2014 , 2, 8386
13	Pt ₁ Ni ₁ /C	1 M KOH 1 M methanol	1.75 A mg ⁻¹	4.90 mA cm ⁻²	<i>Nano Res.</i> 2018 , 11, 2058
14	Pt _{3.5} Pb nerve nanowires	0.5 M KOH 1M methanol	2.84 A mg ⁻¹	2.78 mA cm ⁻²	<i>Nanoscale</i> 2017 , 9, 201
15	PtAg popcorns	1 M KOH 1 M methanol	1.65 A mg ⁻¹	116.1 mA cm ⁻²	<i>ACS Nano</i> 2012 , 6, 7397
16	PtCu nanoframes	0.5 M KOH 1M methanol	2.26 A mg ⁻¹	18.2 mA cm ⁻²	<i>Adv. Mater.</i> 2016 , 28, 8712
17	Porous Pt Nanotubes	1 M KOH 1 M methanol	2.33 A mg ⁻¹	~ 4.9 mA cm ⁻²	<i>ACS Appl. Mater. Interfaces</i> 2016 , 8, 16147.
18	PdAgRhPt nanoframes	0.5 M NaOH 2 M methanol	1.15 A mg ⁻¹ _{Pt+Pd}	-	<i>Small</i> 2016 , 12, 5261
19	Pt/rGO	0.5 M KOH 0.5 M methanol	0.55 A mg ⁻¹	-	<i>ACS Appl. Mater. Interfaces</i> 2015 , 7, 22935

Table S4. I_f/I_b ratio of different electrocatalysts for MOR in alkaline solution.

Electrocatalysts	I_f/I_b
Pt ₆₂ Ru ₁₈ Ni ₂₀ -O/C	2.43
Pt ₆₂ Ru ₁₈ Ni ₂₀ /C	2.30
Pt ₆₅ Ru ₃₅ /C	1.98
Pt/C	1.74

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