Electronic Supplementary Information

RuO_x-decorated Multimetallic Hetero-nanocage as Highly Efficient Electrocatalyst toward the Methanol Oxidation Reaction.

Jongsik Park,[a,†] Hee Jin Kim,[b,†] Aram Oh,[c] Taehyun Kwon,[a] Hionsuck Baik,[c] Sang-Il Choi,*[b] and Kwangyeol Lee*[a]

[a]Department of Chemistry, Korea University, Seoul 02841, Korea

[b]Department of Chemistry and Green-Nano Materials Research Center, Kyungpook National University, Daegu 41566, Korea

[c]Korea Basic Science Institute (KBSI), Seoul 02841, Korea

[†]These authors contributed equally to this work.

Experimental Section

Chemical and Materials

Ruthenium(III) acetylacetonate ($Ru(acac)_3$, 99%), platinum(II) acetylacetonate ($Pt(acac)_2$, 98%), copper (II) acetylacetonate ($Cu(acac)_2$, 98%), and L-ascorbic acid (AA, 99%) were purchased from STREM. Hexadecyltrimethylammonium chloride (CTAC, 98%), 1,2-hexadecanediol (1,2-HDD, 90%), and oleylamine (technical grade, 70%) were purchased from Sigma-Aldrich. Acetic acid (99.5%) was purchased from Daejung Chemicals & Metals. All reagents were used as received without further purification.

Synthesis of PtCu nanoparticles (PC)

A slurry containing $Pt(acac)_2$ (0.02 mmol), $Cu(acac)_2$ (0.06 mmol), AA (0.2 mmol), CTAC (0.05 mmol), and oleylamine (5 mL) was placed in a Schlenk tube with a magnetic stirring. The Schlenk tube was evacuated for 10 min and purged with Ar gas, then it was directly placed in a hot oil bath for 1 h, which was preheated at 250 °C. After cooling down, toluene and ethanol were added in the reaction mixture to precipitate the product, which was then separated by centrifugation.

Synthesis of Ru-doped PtCu nanoparticles (RPC)

Synthetic protocol and work-up process are very similar to those of PC except adding $Ru(acac)_3$ (0.02 mmol) in a slurry at the initial stage.

Synthesis of hierarchical Ru branched RuPtCu nanoparticles (HRPC)

After heating and cooling down the reaction mixture of RPC, additional $Ru(acac)_3$ (0.04 mmol) was injected in a Schlenk tube, which was then purged with Ar gas. The mixture was placed in a hot oil bath for 1 h, which was preheated at 270 ^{o}C. After cooling down, toluene and ethanol were added in the reaction mixture to precipitate the product, which was then separated by centrifugation.

Chemical etching process

The resulting products of PC, RPC, and HRPC were dispersed in a mixture containing toluene (2 mL), ethanol (2 mL), and 3 M HCl (3 mL). The mixture was placed at 60 °C for 1 h. Finally, etched products of PC-, RPC-, HRPC-etched nanocages (PCE, RPCE, and HRPCE, respectively) were obtained by centrifugation, and then washed with ethanol (10 mL) for two times and dried under vacuum.

Material Characterization

Transmission electron microscopy (TEM) images, high-resolution TEM (HRTEM) images, high-angle annular dark-field scanning TEM (HAADF-STEM) images, energy dispersive X-ray spectroscopy (EDS) spectra and elemental mapping images were obtained using a Tecnai G2 20 S-Twin microscope operated at 200 kV, a Tecnai G2 F30ST microscope operated at 300 kV, and a Titan Themis 3 Double Cs & Mono, TEM with Chemi-STEM technology. X-ray diffraction (XRD) patterns were collected to understand the crystal structures with a Rigaku Ultima III diffractometer system using graphite-monochromatized Cu-Kα radiation at 40 kV and 30 mA. The fast Fourier transformation (FFT) patterns were obtained and analyzed from HRTEM images using a Gatan Digital Micrograph and TEM Imaging & Analysis software.

Preparation of nanocages supported on carbon

Suspension of 20 mg of HRPCE (or RPCE or PCE) and 80 mg of Vulcan XC-72 were dispersed in 30 mL of chloroform, and the mixture was then magnetically stirred and ultrasonicated for 5 min. After centrifugation, the resulting HRPCE/C (or RPCE/C or PCE/C) catalyst was dispersed in 30 mL of acetic acid and then heated at 60 °C for 1 h to clean the residual surfactants. HRPCE/C (or RPCE/C or PCE/C) catalyst was washed with ethanol 3 times and dried under vacuum.

Electrochemical characterization

Electrochemical measurements were performed using a three-electrode electrochemical cell connected to potentiostats (CHI 600E from CH Instruments and PGSTAT204 from Metrohm Autolab). A Ag/AgCl electrode was used as a reference electrode and potentials of as-received data were converted to the reversible hydrogen electrode (RHE). Pt mesh (1 × 1 cm^2) was used as a counter electrode and a glassy carbon disk (GC with a diameter of 5 mm from Pine Instruments) as a working electrode.

Catalyst ink was prepared by adding a catalyst powder to a solution containing 5 wt% Nafion (5 µL, Aldrich), deionized water (1.0 mL), and isopropyl alcohol (0.25 mL, >99.5%, Duksan), and further ultrasonic agitation for 30 min. Total Pt loadings on GC electrode were 2.46 µg cm^{-2} for HRPCE/C, RPCE/C, HRPC/C, and the state-of-the-art PtRu/C and 10.2 µg cm^{-2} for PCE/C and the state-of-the-art Pt/C catalysts, respectively.

Working electrodes were pre-cycled in an Ar-saturated 0.1 M $HClO_4$ solution for 100 cycles between 0.08 and 1.20 V at a scan rate of 100 mV s^{-1}. Cyclic voltammograms (CVs) were recorded on the working electrode by cycling between 0.08 and 1.20 V in a fresh Ar-saturated 0.1 M $HClO_4$ solution at 50 mV s^{-1}. In the case of HRPCE/C, the electrode was also pre-cycled in different potential ranges from 0.08 to 0.80 or 1.00 V, respectively. Then, the corresponding CVs were recorded at the same potential ranges in fresh Ar-saturated 0.1 M $HClO_4$ solutions at 50 mV s^{-1}.

For CO stripping experiments, CO was adsorbed on the pre-cleaned electrode by holding the potential at 0.05 V for 10 min in a CO-saturated 0.1 M $HClO_4$ solution. The CO stripping curve was then recorded after the extra CO in the solution had been removed by purging Ar for 10 min. From CO stripping peak, measured charge (Q_{CO}) was normalized with a reference value of 420 μC cm^{-2} and then divided by the mass of Pt loaded on GC electrode to calculate the CO stripping-based electrochemically active surface area (ECSA).

For the methanol electro-oxidation, CVs were recorded in an Ar-saturated solution containing 0.1 M $HClO_4$ and 1.0 M CH_3OH between 0.08 and 1.29 V at a scan rate of 50 mV s^{-1}. Long-term durability of the catalysts was performed by applying cyclic potential sweeps between 0.4 and 0.9 V at a scan rate of 100 mV s^{-1} for 1000 cycles in an Ar-saturated solution containing 0.1 M $HClO_4$ and 1.0 M CH_3OH at room temperature and then was recorded in a fresh Ar-saturated 0.1 M $HClO_4$ and 1.0 M CH_3OH solution between 0.08 and 1.29 V at a scan rate of 50 mV s^{-1}. In the case of HRPCE/C and RPCE/C, long-term durability test was measured under the same conditions for 2000 cycles. Chrono-amperometry curves of PC/C, PtRu/C, and Pt/C were recorded for 1000 s, and HRPCE/C and RPCE/C for 4000s in an Ar-saturated solution containing 0.1 M $HClO_4$ and 1.0 M CH_3OH at a certain potential.

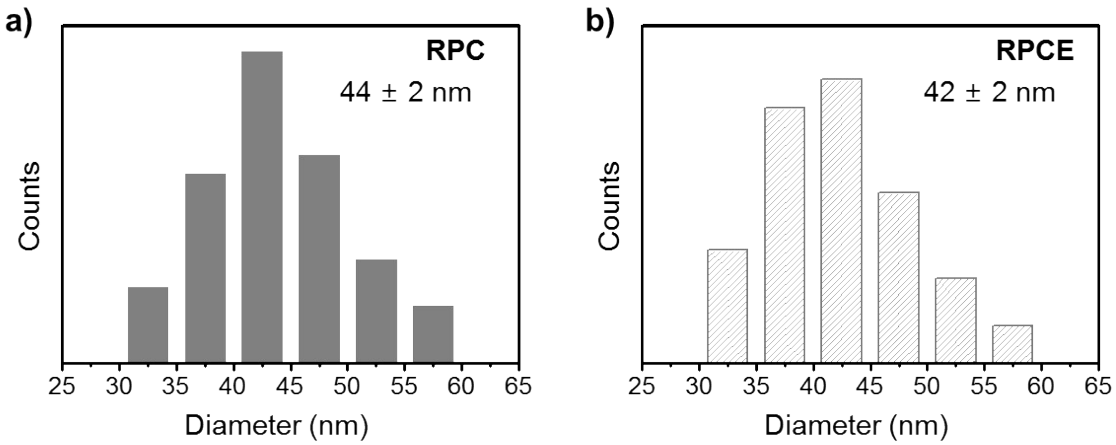


Fig. S1 Histograms for size distributions of a) Ru-doped PtCu nanoparticles (RPC) and b) nanocages (RPCE).

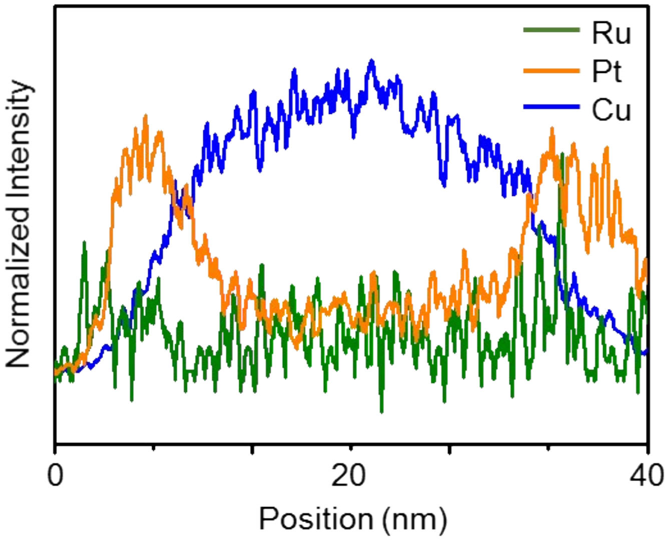


Fig. S2 EDS line profile analysis of RPC.

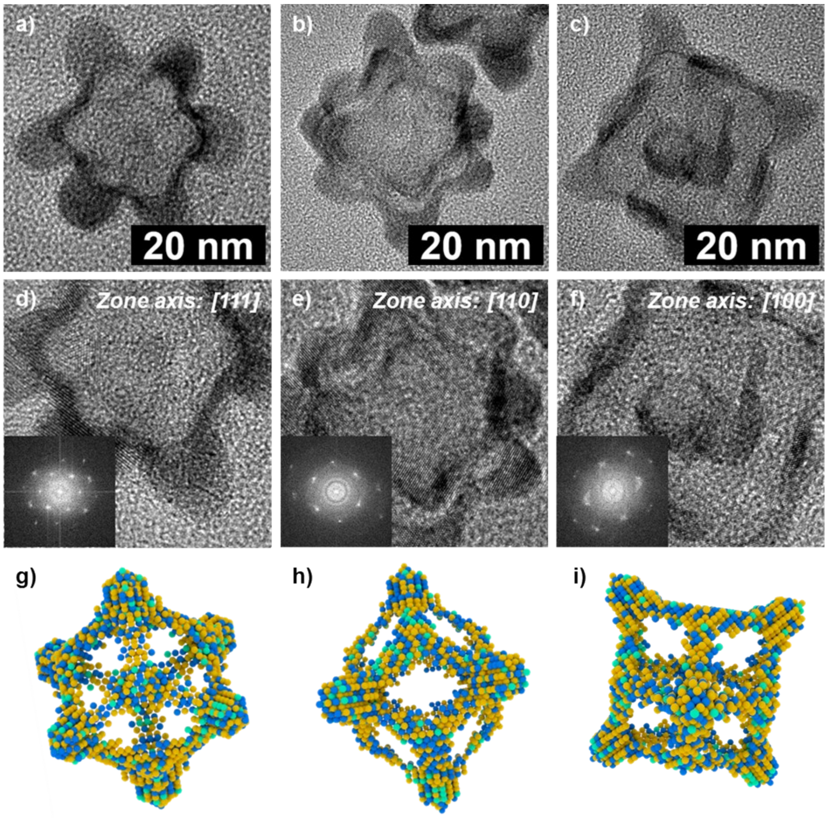
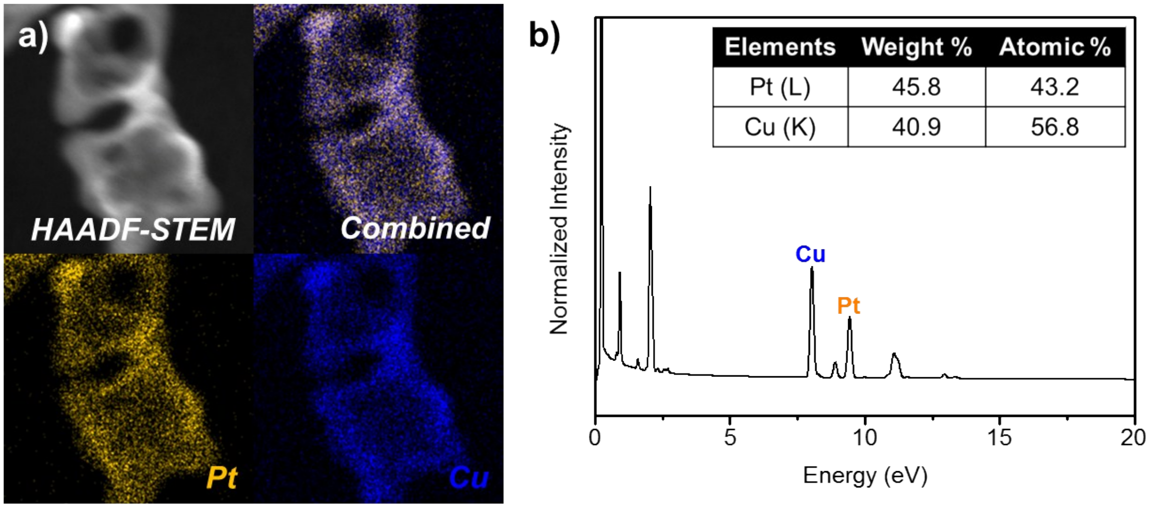


Fig. S3 a-c) TEM, d-f) HRTEM images, and g-i) geometrical models of RPCE taken at different zone axes.



Elements	Weight %	Atomic %
Pt (L)	45.8	43.2
Cu (K)	40.9	56.8

Fig. S4 a) Elemental mapping analysis and b) EDS spectrum of PCE.

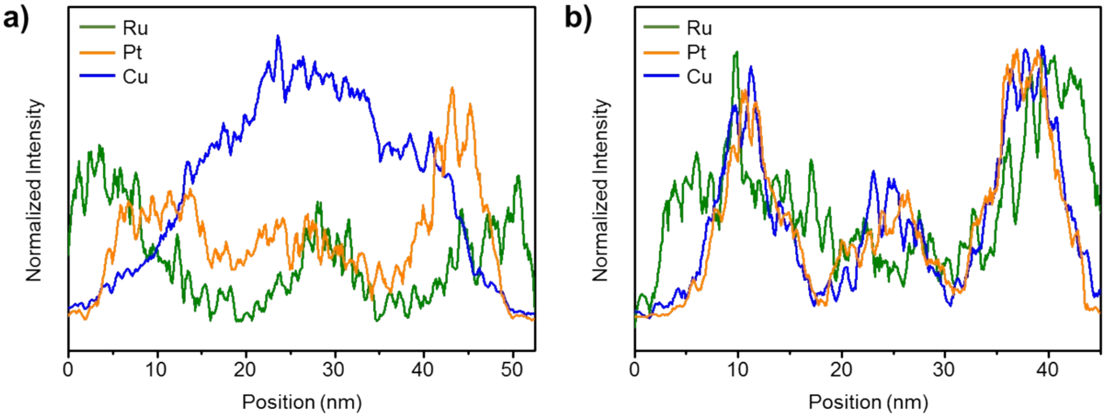


Fig. S5 EDS line profile data of a) HRPC and b) HRPCE.

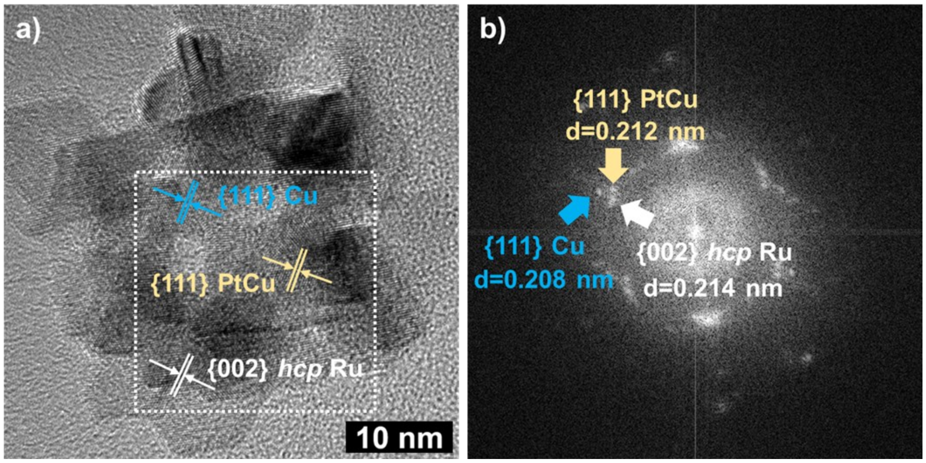


Fig. S6 a) HRTEM image of HRPC and b) the corresponding FFT pattern.

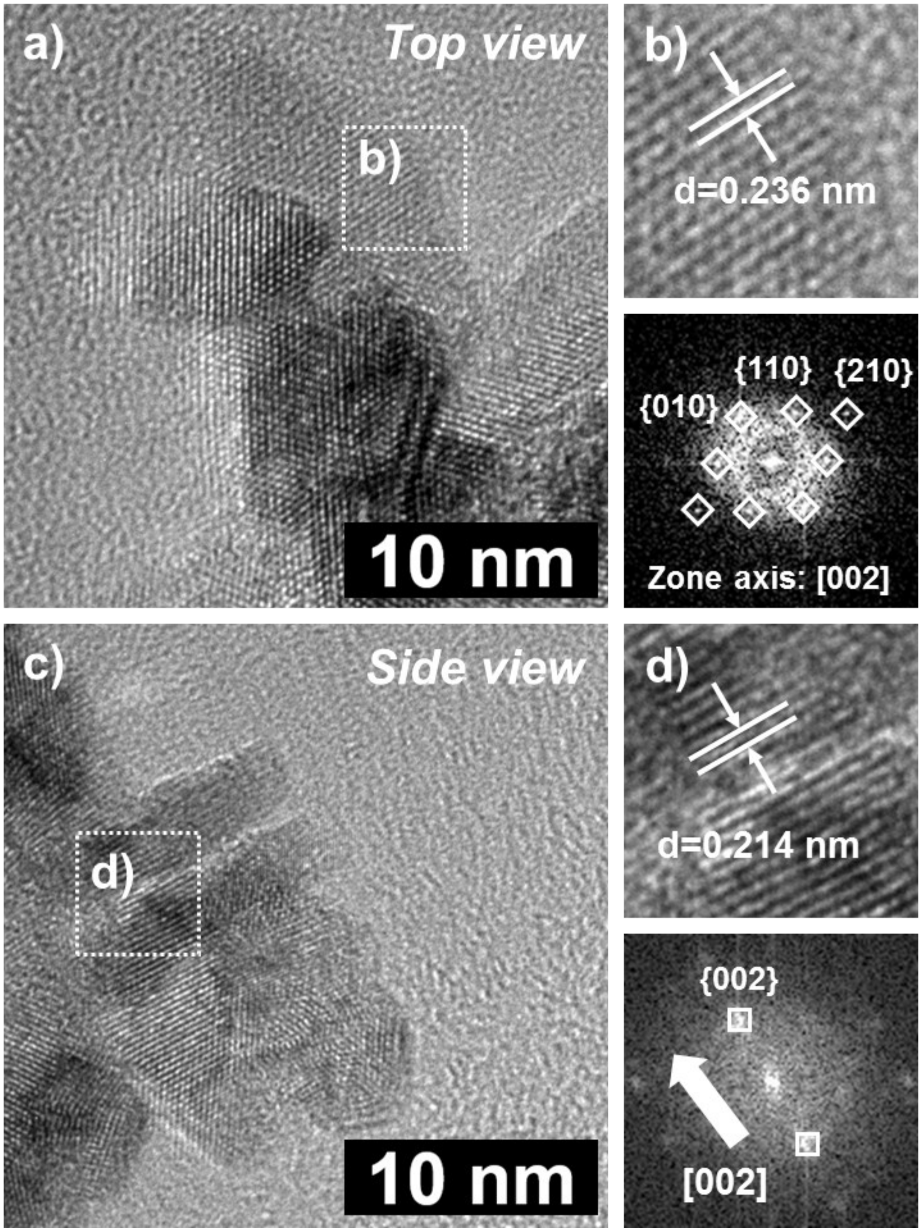


Fig. S7 HRTEM images and corresponding FFT patterns of hierarchical Ru branches on HRPCE.

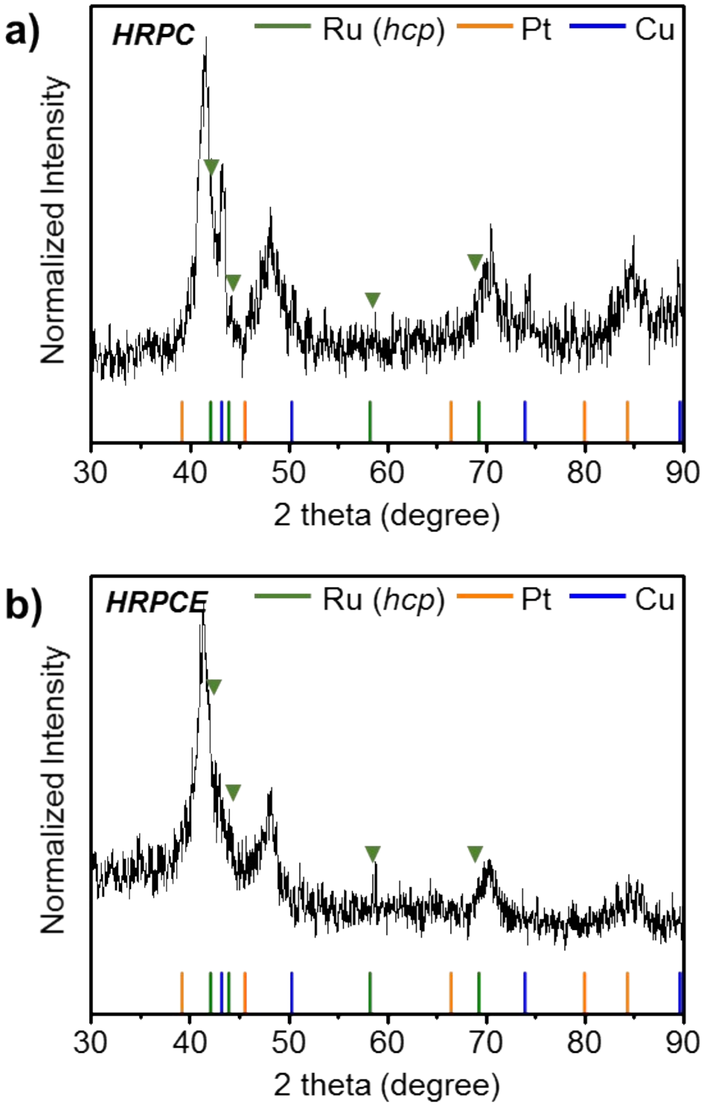


Fig. S8 PXRD patterns of a) HRPC and b) HRPCE.

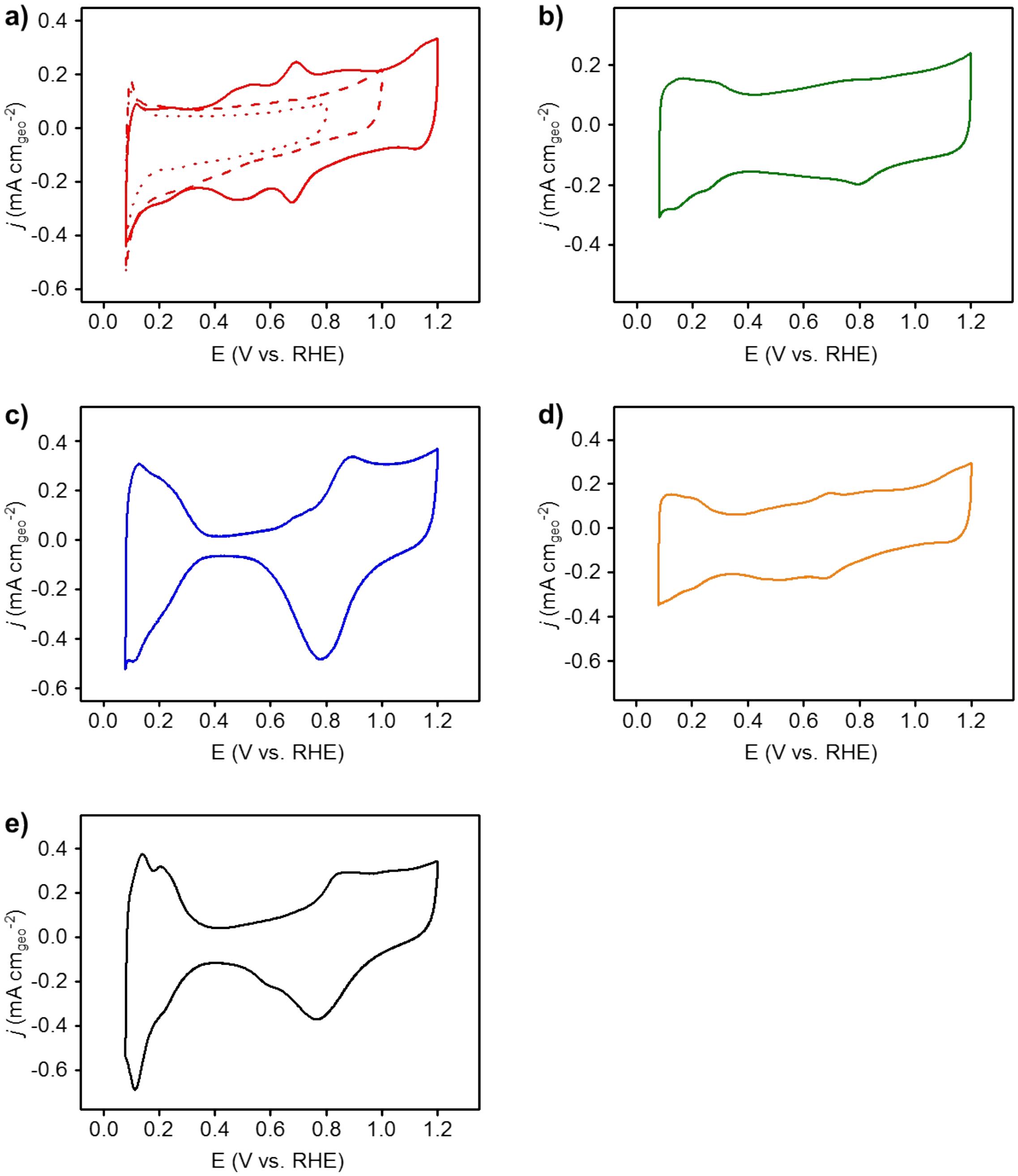


Fig. S9 CVs of a) HRPCE/C, b) RPCE/C, c) PCE/C, and d) the state-of-the-art PtRu/C and e) Pt/C. CVs were recorded in solutions containing 0.1 M $HClO_4$ with a scan rate of 50 mV s^{-1} at room temperature and normalized to the geometric area of a glassy carbon electrode (0.196 cm^2). Before CV measurements of HRPCE/C, working electrodes were pre-cycled for 100 cycles at 100 mV s^{-1} in potential ranges from 0.08 to 0.80 (dotted line) or 1.00 (dashed line) or 1.20 V (solid line), respectively.

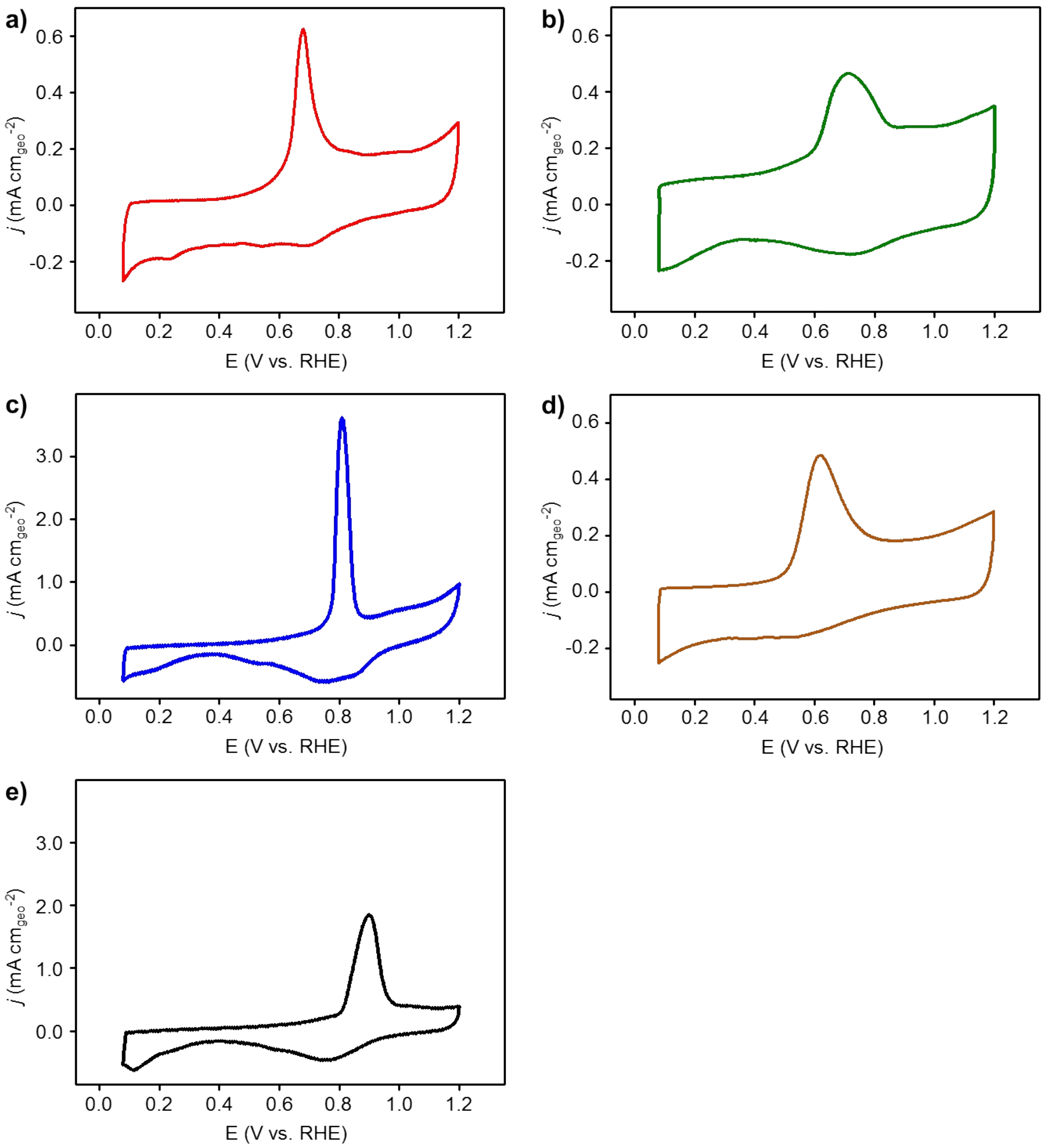


Fig. S10 CO stripping of a) HRPCE/C, b) RPCE/C, c) PCE/C, and d) the state-of-the-art PtRu/C and e) Pt/C recorded in solutions containing 0.1 M $HClO_4$ with a scan rate of 50 mV s^{-1} at room temperature. CO was adsorbed by holding the potential at 0.05 V for 10 min in a CO-saturated 0.1 M $HClO_4$ solution.

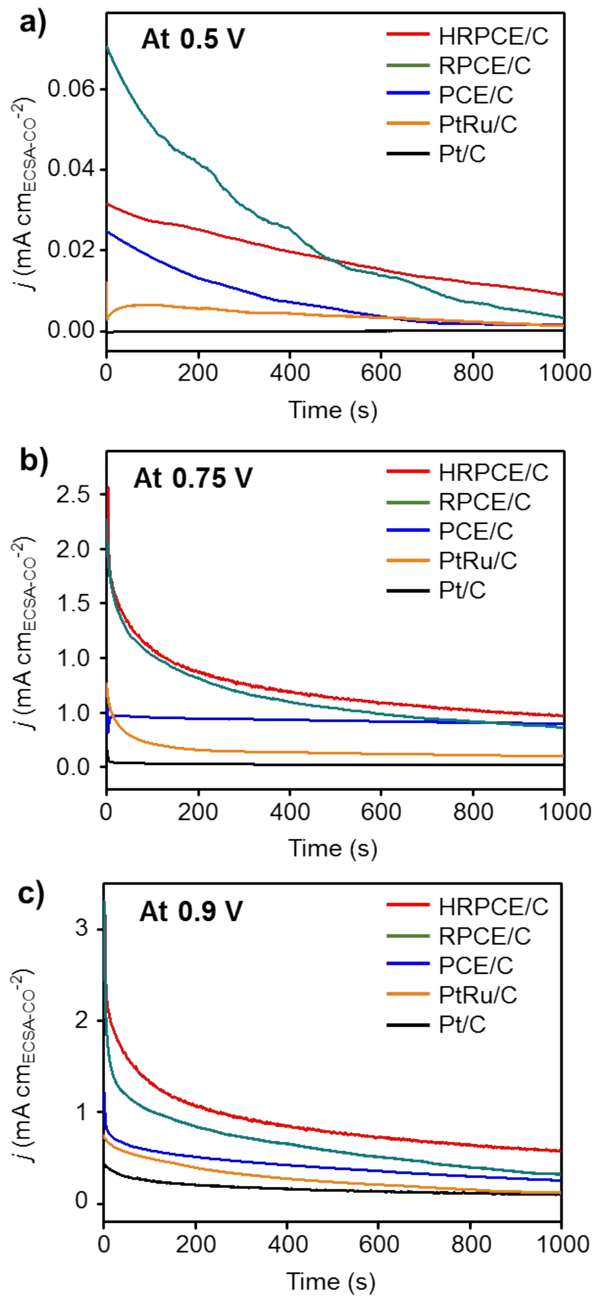


Fig. S11 Chrono-amperometry of HRPCE/C, RPCE/C, PCE/C, and the state-of-the-art PtRu/C and Pt/C measured in an Ar-saturated solution containing 0.1 M $HClO_4$ and 1.0 M CH_3OH at a) 0.5, b) 0.75, and c) 0.9 V (vs. RHE) for 1000 seconds.

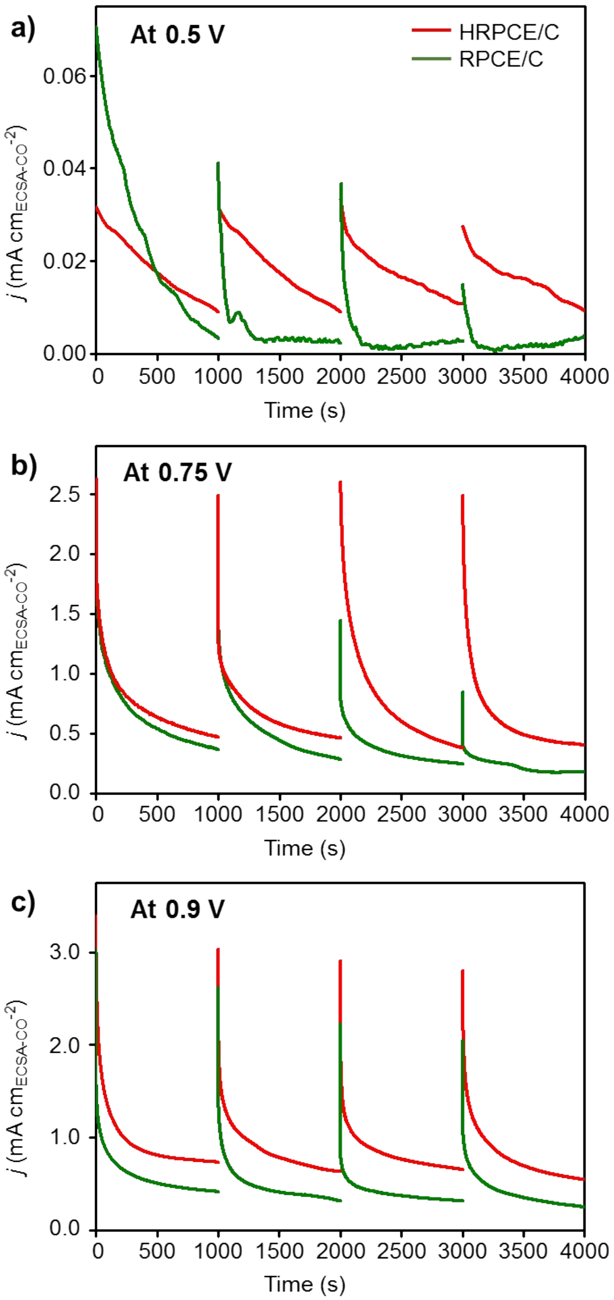


Fig. S12 Chrono-amperometry of HRPCE/C and RPCE/C measured in an Ar-saturated solution containing 0.1 M $HClO_4$ and 1.0 M CH_3OH at a) 0.5, b) 0.75, and c) 0.9 V (vs. RHE) for 4000 seconds.

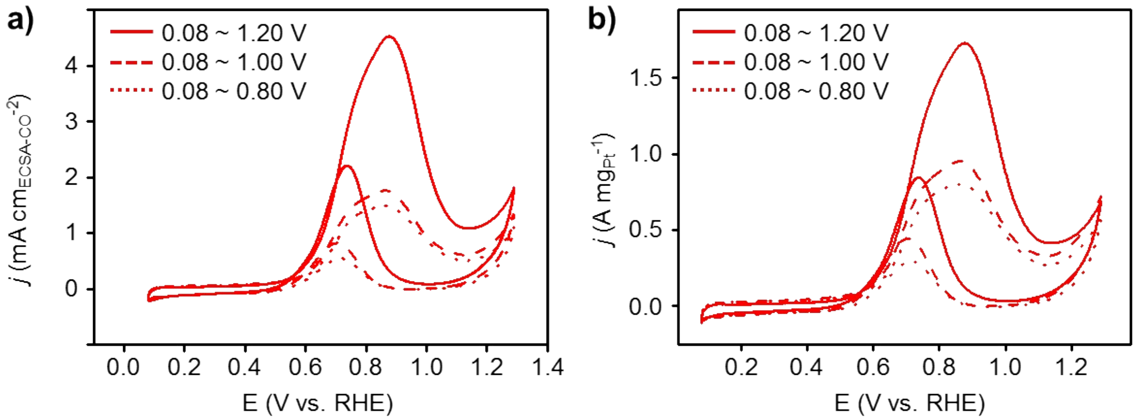


Fig. S13 CVs of HRPCE/C normalized by a) ECSA and b) Pt loading measured in solutions containing 0.1 M $HClO_4$ and 1.0 M CH_3OH with a scan rate of 50 mV s^{-1} at room temperature. Before CV measurements, working electrodes were pre-cycled for 100 cycles at 100 mV s^{-1} in potential ranges from 0.08 to 0.80 (dotted line) or 1.00 (dashed line) or 1.20 V (solid line), respectively.

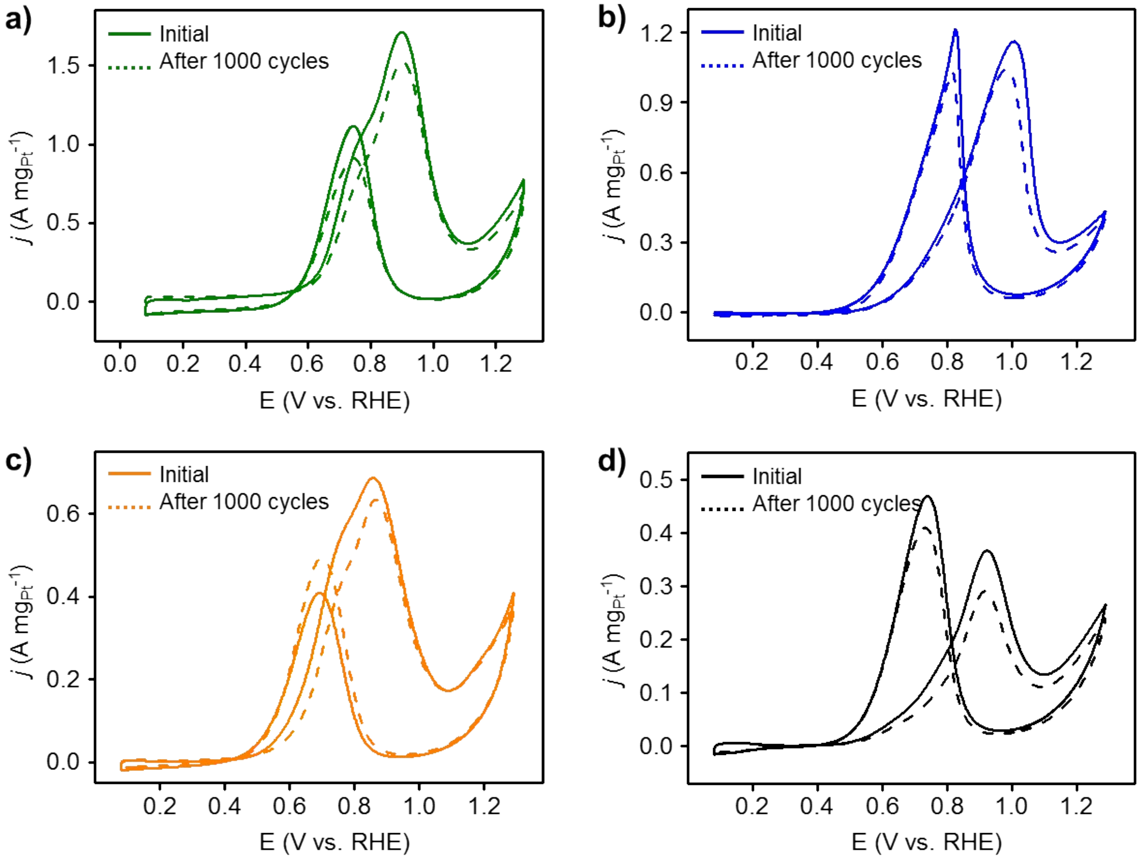
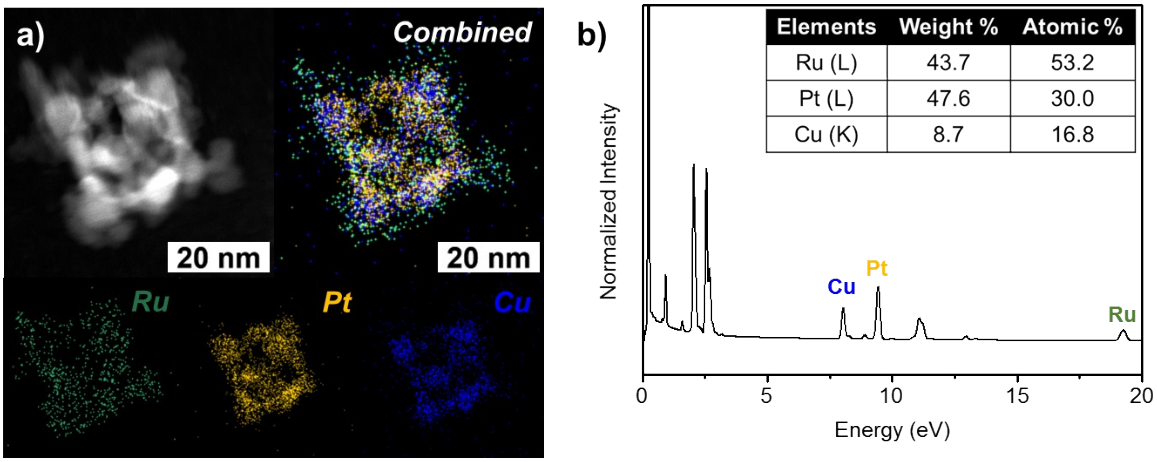


Fig. S14 CVs of a) the RPCE/C, b) PCE/C, c) PtRu/C, and d) Pt/C before and after the durability tests measured under continuous potential cycling between 0.4 and 0.9 V in solutions containing 0.1 M $HClO_4$ and 1.0 M CH_3OH with a scan rate of 100 mV s^{-1} at room temperature.



Elements	Weight %	Atomic %
Ru (L)	43.7	53.2
Pt (L)	47.6	30.0
Cu (K)	8.7	16.8

Fig. S15. a) Elemental mapping and b) EDS spectrum of HRPCE/C after long-term MOR operation.

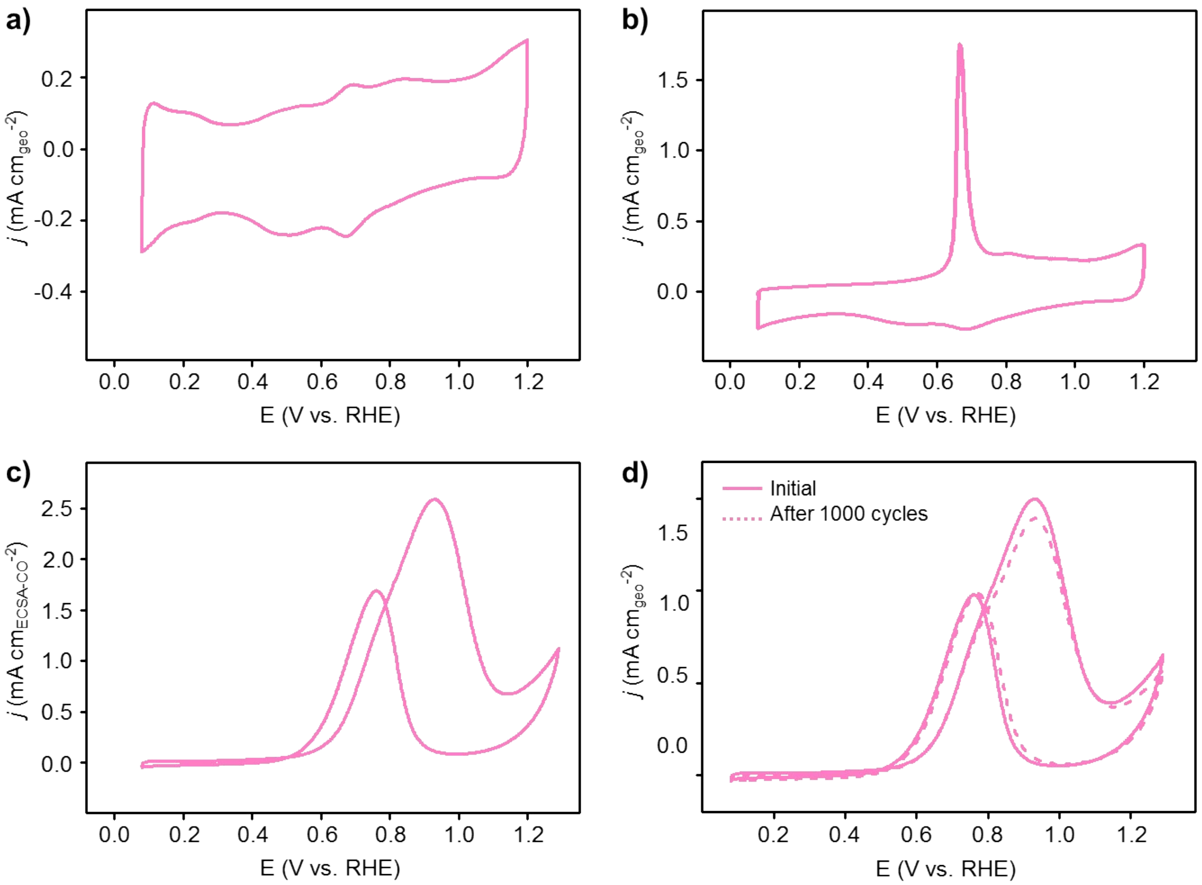


Fig. S16 a) CVs of HRPC/C were recorded in solutions containing 0.1 M $HClO_4$ with a scan rate of 50 mV s^{-1} at room temperature and normalized to the geometric area of a glassy carbon electrode (0.196 cm^2). b) CO stripping of HRPC/C recorded in solutions containing 0.1 M $HClO_4$ with a scan rate of 50 mV s^{-1}. CVs of HRPC/C normalized by c) ECSA and d) Pt loading in solutions containing 0.1 M $HClO_4$ and 1.0 M CH_3OH with a scan rate of 50 mV s^{-1} at room temperature.

Table S1. Metal contents in HRPCE/C, HRPC/C, RPCE/C, RPC/C, and PCE/C catalysts determined by ICP-AES analysis.

Sample		**Atomic Percent (%)**		
	Ru/Pt	Ru	Pt	Cu
HRPCE/C	1.61	46.5	28.9	24.6
HRPC/C	1.59	29.6	18.6	51.8
RPCE/C	0.65	24.4	37.3	38.3
RPC/C	0.58	14.1	24.4	61.5
PCE/C	-	-	49.8	50.2

Table S2. Comparison of MOR mass and specific activities, and ECSAs.

Catalyst	**Test Protocol**	**Mass Activity (mA mg^{-1})**	**Specific Activity (mA cm^{-2})**	**ECSA (m^2 g^{-1})**	**Ref.**
Hierarchical RuPtCu NCs	0.1 M $HClO_4$ + 1.0 M CH_3OH	1730	4.59	38.24	**This work**
High crystalline opened PtCu Nanotubes	0.5 M H_2SO_4 + 1.0 M CH_3OH	2252	6.09	38	S1
Pt NWs	0.1 M $HClO_4$ + 0.1 M CH_3OH	1312	5.84	21.5	S2
Pt NW/ N-doped low-defect graphene	1.0 M $HClO_4$ + 2.0 M CH_3OH	1283.1	-	24.7	S3
Pt-Ni_2P/C	0.5 M $HClO_4$ + 1.0 M CH_3OH	1431.68	4.05	69.34	S4
Pt/Mo_2C NTs	0.5 M H_2SO_4 + 0.5 M CH_3OH	-	1.52	31.52	S5
Pt_3Cu icosahedra	0.1 M $HClO_4$ + 0.2 M CH_3OH	736	2.14	34.4	S6
Dendrite Pt_3Cu nanocubes	0.5 M H_2SO_4 + 1.0 M CH_3OH	~930	~1.7	54.3	S7
Screw thread-like $PtCu_{2.1}$ NWs	0.1 M $HClO_4$ + 0.2 M CH_3OH	1560	3.31	46.9	S8
Ultrathin Pt_3Cu way NWs	0.5 M H_2SO_4 + 0.5 M CH_3OH	635	2.8	20.3	S9
PtNiCu Nanocrystals	0.5 M H_2SO_4 + 2.0 M CH_3OH	-	2.61	-	S10
Core/Shell Au/CuPt NPs	0.1 M $HClO_4$ + 0.1 M CH_3OH	411	0.755	-	S11
Ultrathin PtRuFe NWs	0.1 M $HClO_4$ + 0.5 M CH_3OH	-	2.27	-	S12
PtRu/TiWC NPs	0.1 M $HClO_4$ + 1.0 M CH_3OH	-	~1.8	68 ± 6	S13
PtCo NWs	0.1 M $HClO_4$ + 0.2 M CH_3OH	1020	1.95	52.1	S14
PtPb/Pt nanoplate	0.1 M $HClO_4$ + 0.1 M CH_3OH	1500	~2.6	55	S15
PtCu NWs	0.5 M H_2SO_4 + 1.0 M CH_3OH	-	1.26		S16
Porous Pt NTs	0.5 M H_2SO_4 + 1.0 M CH_3OH	-	1.62		S17
$PtCu_3$ nanocages	0.1 M $HClO_4$ + 1.0 M CH_3OH	-	14.1	35.7	S18
PtRu/Cu NWs	0.1 M $HClO_4$ + 1.0 M CH_3OH	-	1.6	29	S19
Ru decorated Pt icosahedra	0.5 M H_2SO_4 + 0.5 M CH_3OH	74.43	0.76	9.8	S20
Porous PtCu NCs	0.1 M $HClO_4$ + 1.0 M CH_3OH	1550	13.01	54.1	S21

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