Electronic Supplementary Material (ESI) for Dalton Transactions.

Maximizing Metal Utilization by Coupling Cross-linked PtRu Multi-atom on Atomically Dispersed ZnFeNC Support

Qiuqun Zhou[a, 1], Jia Li [a, 1], Mufei Yue [a,1], Meng Wang [a*], Lin Guo[b*], Yan Li[c], Siguo Chen[a*], Zidong Wei[a]

a The State Key Laboratory of Power Transmission Equipment & System Security and New Technology, Chongqing Key Laboratory of Chemical Process for Clean Energy and Resource Utilization, School of Chemistry and Chemical Engineering, Chongqing University, Chongqing 400044, China.

b Key Laboratory of Photochemical Conversion and Optoelectronic Materials, Technical Institute of Physics and Chemistry, Chinese Academy of Sciences, Beijing 100190, China

c Chongqing Medical and Pharmaceutical College, Chongqing 401331, China

1 These authors contributed equally.

Corresponding Author: *csg810519@126.com; * wmeng@cqu.edu.cn; *glynn@mail.ipc.ac.cn

Experiment section

Chemicals and materials

Chloroplatinic acid (Shanghai Jiuyue Chemical Co., Ltd., 99.9%), Zinc chloride (Adamas, 99%), Potassium chloride (Adamas, 99%), Iron(III) chloride hexahydrate (Sigma-Aldrich), *o*-phenylenediamine (Adamas, 99%), Ethanol (Chengdu Kelong Chemical Reagent Factory, 99.8%), Ammonium persulfate (Adamas, 99%), Hydrochloric acid (Chongqing Chuandong Chemical Group Co., Ltd., 36.0-38.0%), Ethylene glycol (Chengdu Kelong Chemical Reagent Factory, 99.5%), Sodium hydroxide (Chengdu Kelong Chemical Reagent Factory, 98.0%), Perchloric acid (Tianjin Xinyuan Chemical Co., Ltd., 70.0-72.0%), Methanol(Chengdu Kelong Chemical Reagent Factory, 98.0%), Antimony trichloride (Adamas,99%), Commerical PtRu/C (Johnson-Matthey Corp., 20 wt. % Pt, 60 wt.% Pt), N_2 gas (99.99%),CO gas (99.99%).

Preparation of Samples

The ZnFe-N-C carrier was synthesized via the modified polymerization-pyrolysis method we previously developed []. Firstly, $ZnCl_2$ (8 g), KCl (8 g) and $FeCl_3\cdot 6H_2O$ (2.5 g) were dissolved into 50 mL deionized water. The obtained salt solution was frozen via direct injection into liquid nitrogen, and then immediately transferred into a freeze dryer. After 60h freeze-drying, the resulting salt (named as $ZnCl_2/KCl/FeCl_3$) was transferred into a mortar. 1g of *o*-phenylenediamine (*o*PD,) dissolved into 12 mL ethanol was dropwise added into the $ZnCl_2/KCl/FeCl_3$ salt with continuous grinding for 1 h, and then $NH_4S_2O_8$ (2.5 g) dissolved HCl (1M, 4 mL) solution was dropwise added into the obtained product with continuous grinding for another 1 h. After 24 h quiet placing, the resulting mixture was transferred into a furnace, and heated at 150 ºC for 2 h. The sample was cooled to room temperature, and then heated to 800 ºC at a heating rate of 5 ºC min^{-1} and held at 800 ºC for 2 hours under flowing N_2. The obtained black powder was washed with 1M HCl solution at 80 ºC for 8 h followed by centrifugation, washing and freeze-drying. Before achieving the final products, the precursors were carbonized for the second time at 900 ºC for 2 h with a heating rate of 5 ºC min^{-1} under flowing N_2.

The MA-PtRu/ZnFeNC catalysts were synthesized via an ethylene glycol reduction strategy. 100 mg of ZnFeNC was dispersed in 12mL of ethylene glycol. The mixture was stirred ultrasonically at room temperature for 30 minutes, and then 0.0269 mmol of H_2PtCl_6·and 0.0179 mmol $RuCl_3$ dissolved in deionized water were added into the ZnFeNC solution. The mixture was stirred at room temperature for 12 h. After filtering and collecting the precipitate, the product was re-dispersed in 12 mL ethylene glycol under slightly stirring and the pH was adjusted to 11 with 0.1M NaOH solution. The resultant solution was heated at 100 ºC for 1 h and then heated at 160 ºC for 4 h with a heating rate of 10 ºC min^{-1} under slightly stirring. After cooling, the resulting product was washed three times with an ethanol/water mixture. Finally, the product was collected after dried at 70 ºC for overnight.

Structural Characterization

Transmission electron microscopy (TEM) and high-resolution transmission electron microscopy (HRTEM) were conducted on a Tecnai G2F20S-TWIN instrument operating at 200 kV. High-angle annular dark-field scanning transmission electron microscope (HAADF-STEM) and corresponding energy-dispersive X-ray spectroscopy (EDS) characterizations were carried out on FEI Themis Z instrument operated at 200 kV with cold filed-emission gun and aberration corrector. The content of Pt and Ru was determined by the inductively coupled plasma mass spectrometry (ICP-MS) measurements (Thermo Fisher Scientific, iCAP 6000 ICP-MS). X-ray photoelectron spectroscopy (XPS) measurements were run on an ESCALAB250Xi spectrometer using standard

Al radiation (1486.6 eV). The spectrometer was calibrated by assuming the binding energy of C 1s peak to be 284.6 eV. X-ray diffraction (XRD) patterns were collected on a Shimadzu X-ray diffractometer, model 6000 at a low scanning speed of 1° per min.

XAFS measurement

XAFS spectra data (Ru K-edge, Pt L_3-edge) were collected at the 1W1B station in the Beijing Synchrotron Radiation Facility (BSRF, operated at 2.5 GeV with a maximum current of 250 mA). The data were collected at room temperature (25 ℃) (Ru K-edge in fluorescence excitation mode using a seven-element Ge detector, Pt L_3-edge in fluorescence excitation mode using a Lytle detector). All samples were pelletized as disks of 13 mm diameter and 1 mm thickness using graphite powder as a binder. The X-ray was monochromatized by a double-crystal Si(111) monochromator, and the energy was calibrated using a reference ruthenium metal foil and standard Pt metal foil. The obtained XAFS data were processed in Athena (version 0.9.25) for background, pre-edge line and post-edge line calibrations. Then, Fourier transform fitting was carried out in Artemis (version 0.9.25). The k_2 weight, k-range of ~3-12 $Å^{-1}$ and R range of 1-3 $Å^{-1}$ were used for fitting. The coordination numbers of model samples (Ru foil, Pt foil) were fixed as nominal values. The obtained S_0^2 was fixed in the subsequent fitting of the Ru K-edge, Pt L_3-edge of the samples. The internal atomic distances R, Debye–Waller factor σ_2 and the edge-energy shift ΔE0 were allowed to run freely.

Density functional theory calculation

Self-consistent periodic DFT calculations were performed using the Vienna ab initio simulation package (VASP). The interaction between ionic cores and electrons was described by projector augmented wave (PAW) pseudopotentials. The 5d and 6s electrons of Pt, the 4d and 5s electrons of Ru, the 3s and 3p electrons of Cl, the 4s and 3d of Fe and Zn, and the 2s and 2p electrons of C and N were used as the valence electrons. The exchange-correlation functional was described within the generalized gradient approximation (GGA) proposed by Perdew, Burke, and Ernzerhof (PBE). The vdW correction proposed by Grimme (DFT+D3) was employed to improve the description of the PBE function, in which a correction was added to the selected exchange-correlation functional. The Kohn-Sham equations were solved using a plane-wave basis set with a kinetic energy cutoff of 400 eV. Brillouin zone integrations were performed using Monkhorst-Pack grids of 5×5 ×1 for the slab calculations. For all kinds of energy calculations, the k-point mesh was set to 7×7×1 because increasing the k-point mesh to higher values did not produce observable energy differences, suggesting that the 7×7×1 mesh was sufficient to achieve high calculation accuracy. Spin polarization was considered in the calculations, and the Gaussian smearing method was employed to determine the electron occupancies, with a smearing parameter σ of 0.2 eV. The equilibrium geometries were obtained when the atomic forces were less than 0.01 eV/Å on each atom based on a total energy convergence of 10^{-6} eV. The isolated adsorbates (RuCl3, RuCl3/M (M=Fe, Zn)) and $Pt_{21}Ru_{22}$ closed-pack cluster were optimized in a cubic supercell (20×20×20 $Å^3$), in which the Brillouin zone integration was carried out for the Gamma point only. A supercell of 24.6×24.6×6.8 $Å^3$ with periodic boundary conditions was used for the other system. The vacuum space for the systems is larger than 15 Å. The adsorption energy (Eads) is calculated as follows:

$$E_{ads} = E_{adsorbates + graphene} - E_{adsorbates} - E_{graphene} \tag{1}$$

where $E_{adsorbates+graphene}$, $E_{adsorbates}$, $E_{graphene}$ are the energy of the whole system, adsorbates, and support, respectively.

To describe the one Pt atom dissolution from all the all the adsorbates-graphene system and Pt21Ru22-cluster, Pt vacancies are introduced. Pt vacancy formation energy (Evac) is calculated as follows:

$$E_{vac} = E_{per} - E_{def} - E_{Pt} \tag{2}$$

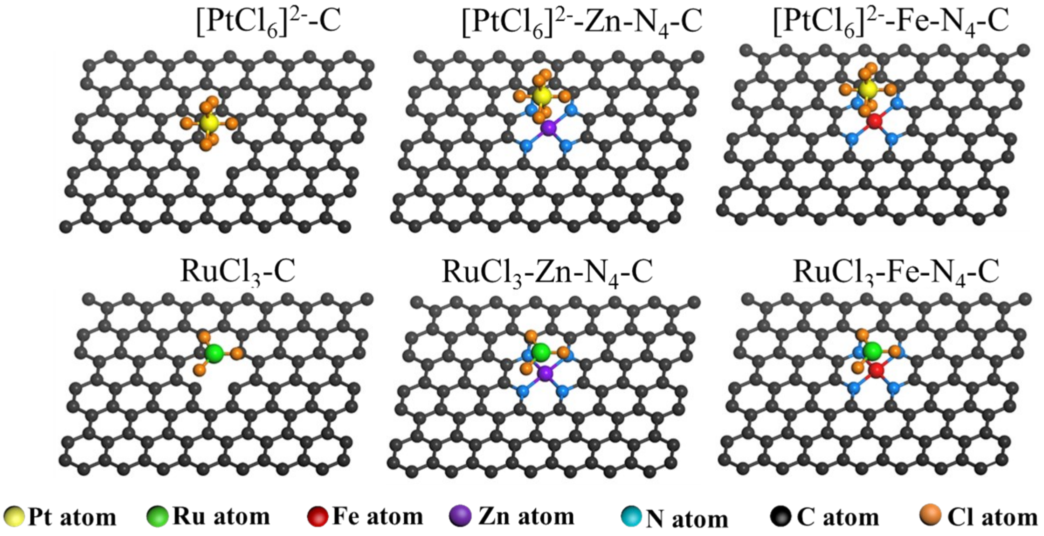
where E_{per}, E_{def}, and E_{Pt} are the formation energy of a perfect system or cluster, defective system or cluster, and the metallic Pt, respectively.

Electrochemical measurements

All electrochemical experiments were carried out in a standard three-electrode cell at room temperature. The cell consisted of a 5 mm glassy carbon working electrode, an Ag/AgCl (3 M KCl) reference electrode, and a graphite rod counter electrode. The reference electrode was calibrated to a reversible hydrogen electrode (RHE) in the same electrolyte before each measurement. A thin film of the catalyst was deposited on glassy carbon (GC) disk electrodes to form the working electrode. Disperse 2 mg of catalyst in a mixed solution of 5 μL of Nafion (5 wt%) solution and 400 μL of ethanol, and sonicate for 30 minutes to prepare a uniform catalyst ink, then 19 μL of ink (a theoretical designed Pt loading of 2 μg_{Pt}) was dropped on a pre-polished GC disk. After drying at room temperature, a thin film was formed on the working electrode. Commercial 20 wt.% PtRu/C was measured for comparison. Disperse 2 mg of 20 wt.% PtRu/C in a mixed solution of 20 μL of Nafion (5 wt%) solution and 1600 μL of ethanol, and sonicate for 30 minutes to prepare a uniform catalyst ink, then 8 μL of ink (a theoretical designed Pt loading of 2 μg_{Pt}) was dropped on a pre-polished GC disk. Each time the film was dried at room temperature, a drop of 0.05 wt% Nafion solution was applied onto the surface of the catalyst layer to form a thin protective film. Before electrochemical measurements, The catalyst-coated disk working electrode were pretreated by cyclic voltammetry (CV) at potential between 0.025 V to 1.2 V at a sweep rate of 25 mv/s for 5-10 cycles to activate the catalysts in N_2-saturated 0.1 M $HClO_4$. The methanol oxidation reaction (MOR) was conducted in N_2-saturated 0.1 M $HClO_4$ solution containing 0.5 M methanol. The accelerated durability tests (ADTs) were conducted in N2-saturated 0.1M HClO4 containing 0.5 M methanol by cyclic voltammetry (CV) at potential between 0 V to 0.6 V at a sweep rate of 100 mv/s for 2000 cycles. The CO Stripping measurements was tested in N_2-saturated 0.1 M $HClO_4$ solution which was maintained by chronoamperometry for 15 minutes to make the catalyst saturated with CO. The scan rate for measurement was 25 mV/s. The electrochemical surface area (ECSA) of Pt in the catalysts using the following equation:

$$ECSA = \frac{Q_{CO}}{0.42 * [Pt]} \tag{3}$$

where QCO (mC) is the charge due to CO adsorption/desorption in the CO stripping region of the CV, 0.42 (mC cm-2) is the electrical charge associated with CO monolayer adsorption on Pt, and [Pt] is the loading of Pt on the working electrode.



Calculation Mode	$[PtCl_6]^{2-}$-C	$[PtCl_6]^{2-}$-Zn-N_4-C	$[PtCl_6]^{2-}$-Fe-N_4-C	$RuCl_3$-C	$RuCl_3$-Zn-N_4-C	$RuCl_3$-Fe-N_4-C
Adsorption energy/eV	1.68	3.86	4.13	2.03	4.09	4.37

Figure S1. The top view model structure of $[PtCl_6]^{2-}$ and $RuCl_3$ on non-doped carbon, Fe-N_4-C, and Fe-N_4-C supports and corresponding calculated adsorption energies.

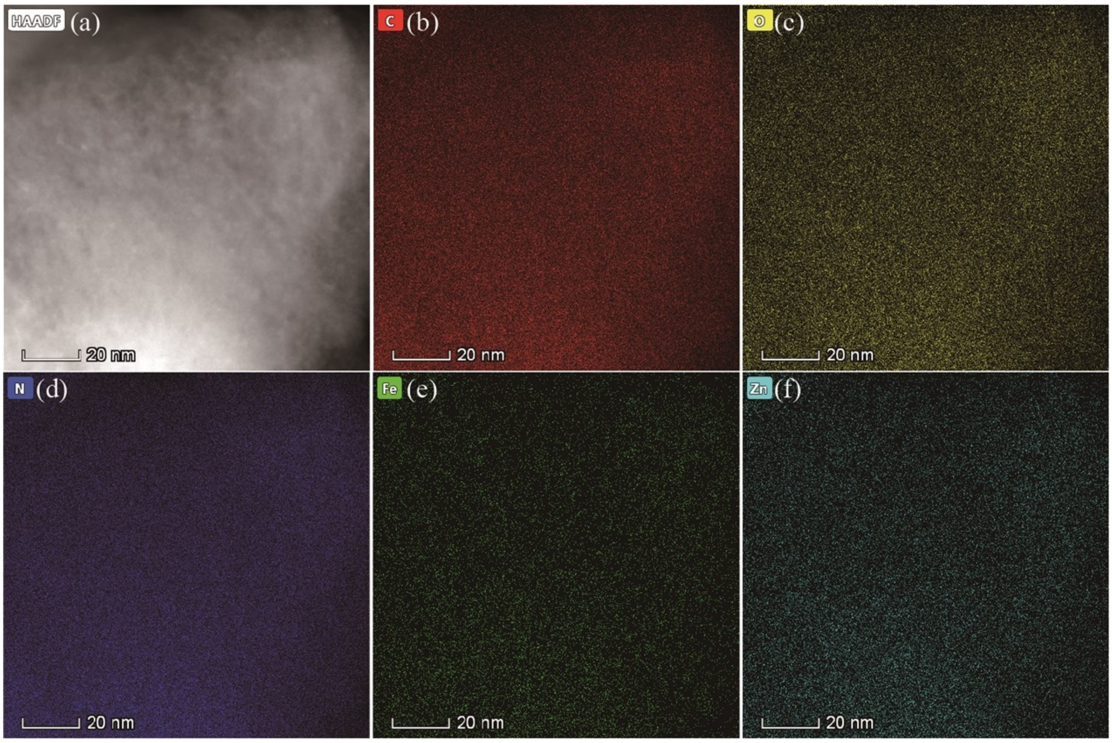


Figure S2. (a) HAADF-STEM image of ZnFeNC catalyst and the corresponding elemental mapping of all elements C (b), O (c), N (d), Fe (e), Zn (f).

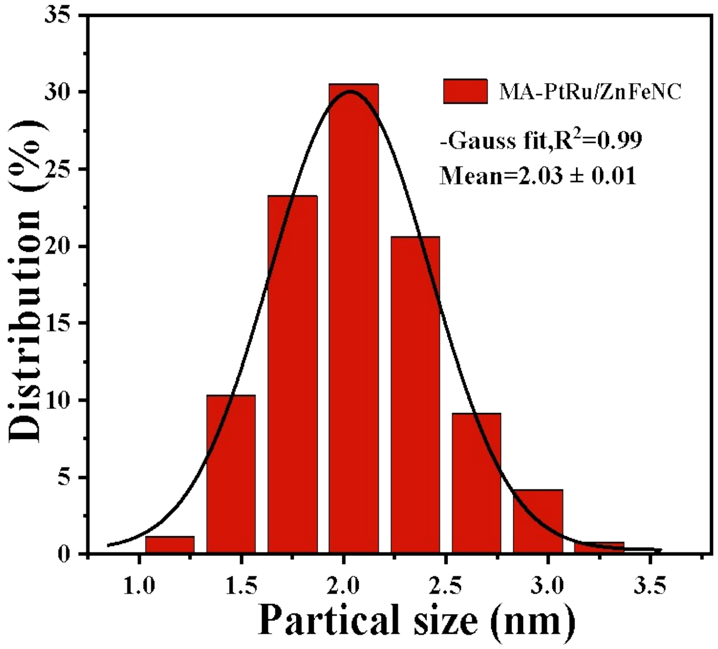


Figure S3. The particle-distribution histogram of MA-PtRu/ZnFeNC catalyst.

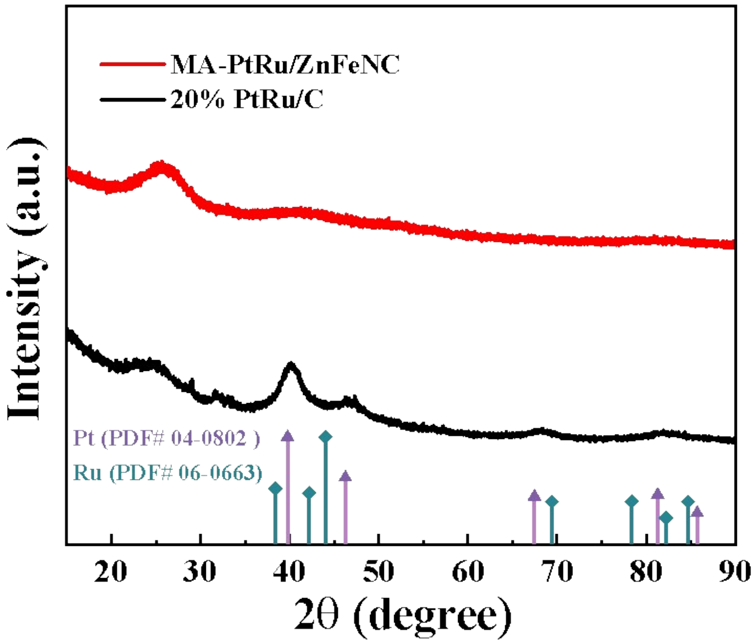
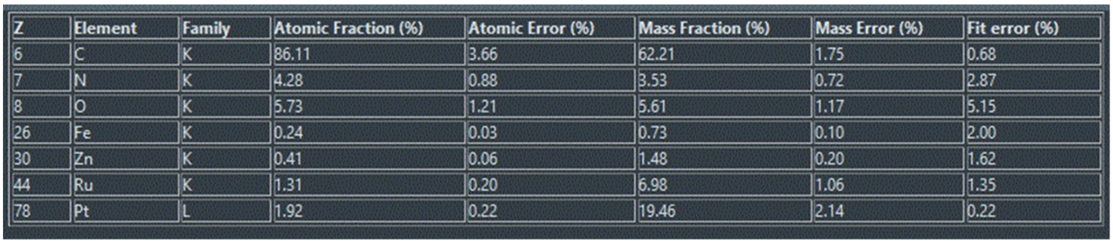
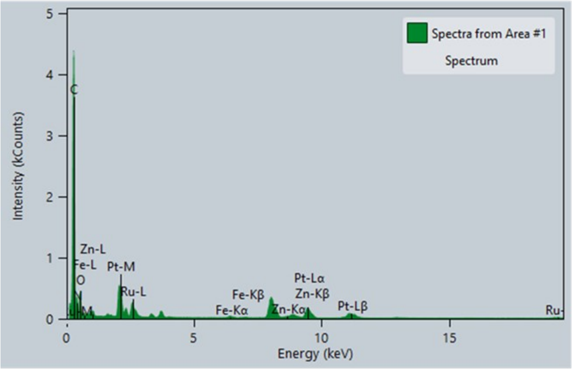


Figure S4. XRD patterns of MA-PtRu/ZnFeNC and 20 % Pt/C catalysts.



Z	Element	Family	Atomic Fraction (%)	Atomic Error (%)	Mass Fraction (%)	Mass Error (%)	Fit error (%)
6	C	K	86.11	3.66	62.21	1.75	0.68
7	N	K	4.28	0.88	3.53	0.72	2.87
8	O	K	5.73	1.21	5.61	1.17	5.15
26	Fe	K	0.24	0.03	0.73	0.10	2.00
30	Zn	K	0.41	0.06	1.48	0.20	1.62
44	Ru	K	1.31	0.20	6.98	1.06	1.35
78	Pt	L	1.92	0.22	19.46	2.14	0.22



Element	at./%	mt./%
C	86.11	62.21
N	4.28	3.53
O	5.73	5.61
Fe	0.24	0.73
Zn	0.41	1.48
Pt	1.92	19.46
Ru	1.31	6.98

Figure S5. EDS analysis of MA-PtRu/ZnFeNC and corresponding elements content.

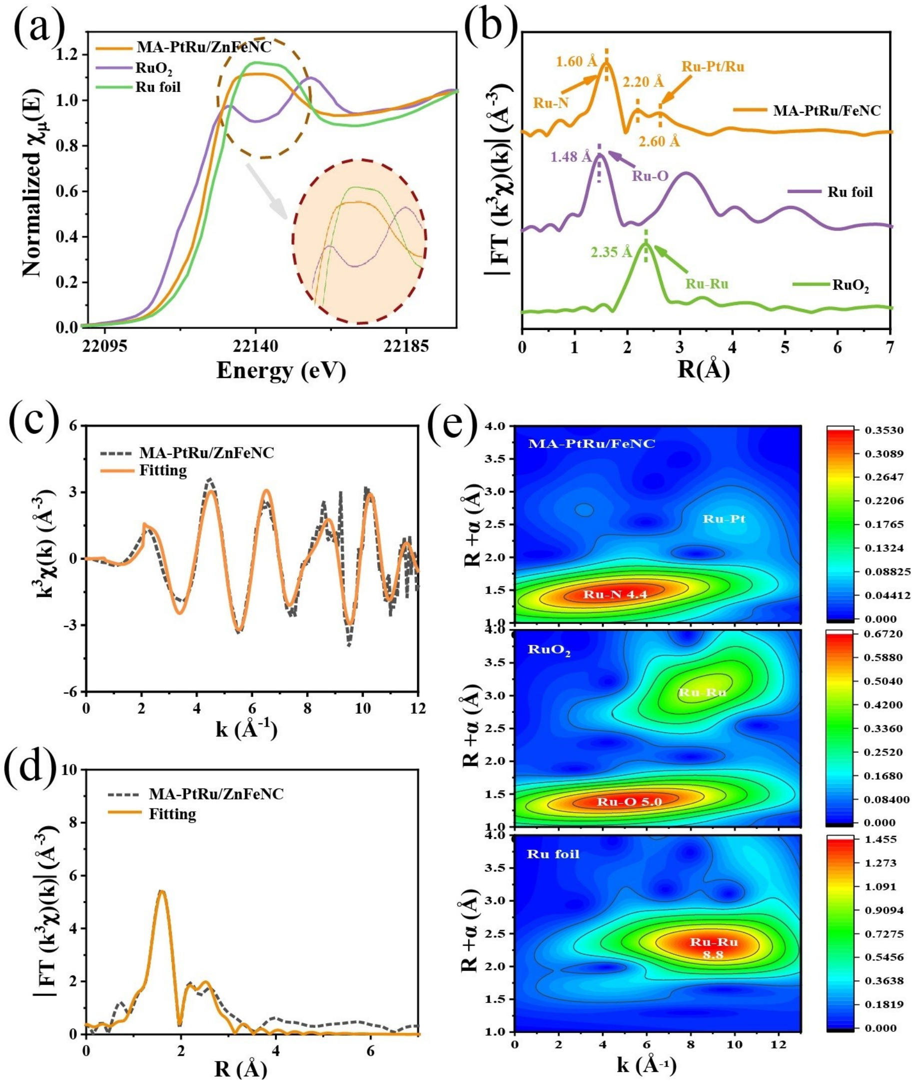


Figure S6. (a) Ru L_3-edge XANES spectra of MA-PtRu/ZnFeNC, RuO_2 and Ru foil. (b) k^2-weighted χ(k)-functions of the EXAFS spectra. Corresponding EXAFS fitting for MAC-MA-PtRu/ZnFeNC in the k (c) and R (d) spaces. (e) WT for k^2-weighted Pt L_3-edge EXAFS signals in the MA-PtRu/ZnFeNC and reference samples (RuO_2 and Ru foil).

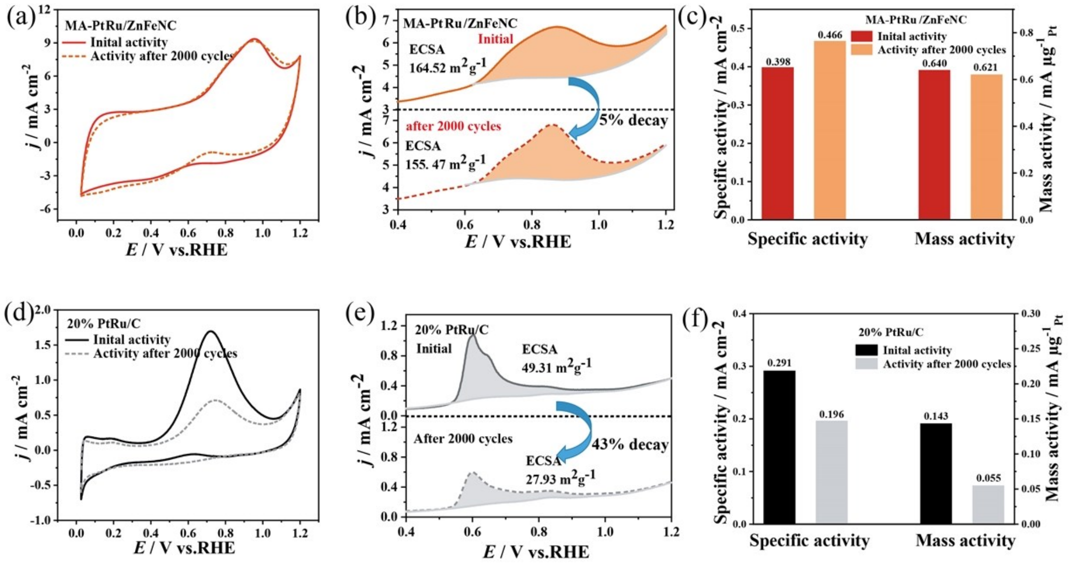


Figure S7. CV curves of MA-PtRu/ZnFeNC (a) and PtRu/C (d) catalysts in N_2-saturated 0.1M $HClO_4$ +0.5M CH_3OH solution at a scan rate of 50 mV/s before and after 2000 CV cycles in 0.1M $HClO_4$ solution. (b,e) CO stripping voltammograms of the MAC-Pt/ZnFe-N-C catalyst before and after 2000 CV cycles and the corresponding ECSA. (c,f) MA and SA of the MAC-Pt/ZnFe-N-C catalyst before and after 2000 CV cycles.

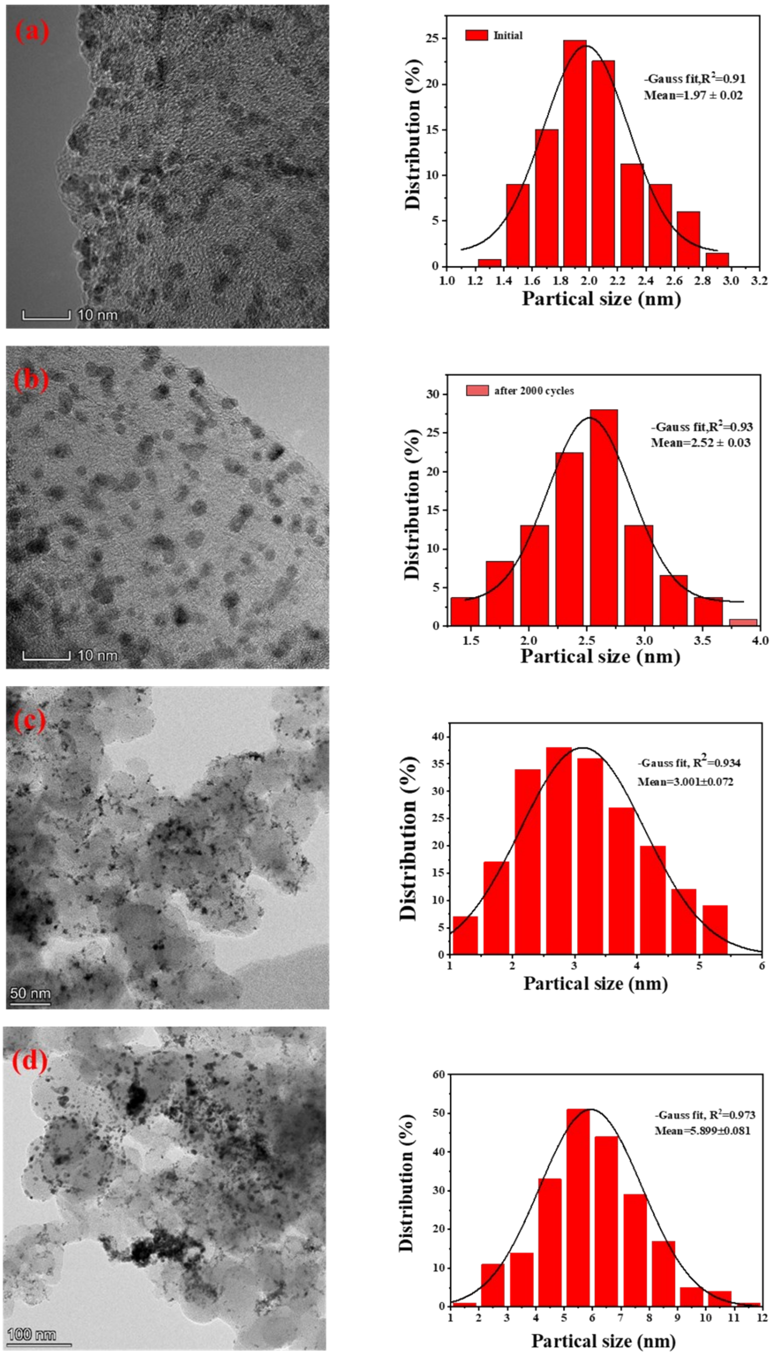


Figure S8. TEM image, particle size distribution histograms of MA-PtRu/ZnFeNC (a, b) and PtRu/C (c, d) catalysts before (a,c) and after (b,d) 2000 CV cycles in N_2-saturated 0.1M $HClO_4$.

Table S1. The elemental quantification determined by EDS analysis of ZnFeNC support.

Element	C	O	N	Fe	Zn
at.%	**86.8**	**4.03**	**7.90**	**0.39**	**0.88**
ma.%	**80.9**	**5.09**	**8.41**	**1.50**	**4.01**

Table S2. EXAFS fitting data of Pt L_3-edge and Ru K-edge in MA-PtRu/ZnFeNC, PtO_2, Pt foil, RuO_2 and Ru foil (S_0^2 = 0.86, 0.84).

Sample	Path	C.N.	R (Å)	$\sigma^2 \times 10^3$ (Å^2)	ΔE_0 (eV)	R factor
Pt foil	Pt-Pt	12*	2.77±0.002	4.7±0.2	7.8±0.5	0.002
PtO_2	Pt-O	5.3±0.5	2.02±0.01	2.8±0.8	11.3±1.3	0.005
	Pt-Pt	4.9±1.3	3.10±0.01	2.7±1.8	8.3±3.3	
	Pt-O	11.6±3.9	3.67±0.03	12.1±3.8	9.4±4.2	
MA-PtRu/ZnFeNC	Pt-N	2.7±0.3	2.03±0.01	6.6±1.2	11.0±1.5	0.005
	Pt-Ru/Pt	4.1±0.6	2.73±0.01	9.0±1.0	7.0±1.6	
Ru foil	Ru-Ru	12*	2.68±0.003	3.9±0.3	-6.2±0.8	0.003
RuO_2	Ru-O	5.8±0.8	1.98±0.01	1.9±1.1	-2.1±2.2	0.004
MA-PtRu/ZnFeNC	Ru-N	4.2±0.5	2.08±0.01	4.0±0.9	1.7±1.6	0.008
	Ru-Pt	0.8±0.3	2.51±0.02	3.2±2.2	16.4±5.2	

Table S3. The elemental quantification determined by XPS of MA-PtRu/ZnFeNC and 60% Pt/C catalysts.

Sample	**Elements content (at.%)**						
	C 1s	**O 1s**	**N 1s**	**Zn 2p**	**Fe 2p**	**Pt 4f**	**Ru 3d**
MA-PtRu/ZnFeNC	71.94	20.30	3.10	1.03	0.09	1.19	2.41
60% PtRu/C	86.70	10.22	-	-	-	1.30	1.78

Table S4. The states distribution analysis by the deconvoluted peaks of Pt 4f and Ru 3d XPS spectra of MA-PtRu/ZnFeNC.

Peak area (%)					
Pt^0	**Pt-N**	**Pt oxide**	**Ru^0**	**Ru-N**	**Ru oxide**
44.02	40.04	15.94	19.59	41.87	38.54