# Stabilizing OOH\* Intermediate via Pre-adsorbed Surface Oxygen of Single Ru Atom-bimetallic Alloy for Ultralow Overpotential Oxygen Generation<sup>†</sup>

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## Methods

Synthesis of CoFe<sub>2</sub> and Co<sub>2</sub>Fe metal alloys. The CoFe<sub>2</sub>/G and Co<sub>2</sub>Fe/G were synthesized via a two-step micelle incorporated sol-gel method<sup>S1</sup> followed with carbothermal reduction. <sup>S2</sup> First, 100 mg of the F124 block copolymer and 10 ml polystyrene solution (0.5 wt% in ethanol) were dissolved in 20 ml THF. Then, 1M NaOH was slowly added into the solution to tailor the pH to 9-10. Stoichiometric aqueous mixture of cobalt and iron metal ions as a metal precursor in ethanol (a molar proportion of Fe/Co = 0.5, 1, and 2) was added drop-wise into the above solution and stirred vigorously for 2 h. The metal sol was placed into a glass dish or an alumina crucible and allowed to cool naturally to room temperature for solvent vaporization. Finally, a homogenous metal-gel film was calcinated under the Ar atmosphere at 750°C for 4h to produce a fluffy porous black-shining powder after carbothermal reduction. For comparison, we also prepared CoFe<sub>2</sub>/G-H<sub>2</sub> by annealing under 30% H<sub>2</sub>/Ar for 4 h to obtain the minimum content of lattice oxygen on the metal surface.

**Synthesis of Rus**<sub>A</sub>/NP**CoFe**<sub>2</sub> **and Rus**<sub>A</sub>/NP**Co**<sub>2</sub>**Fe metal alloys.** Homogeneously anchored Ru atoms on CoFe<sub>2</sub>/G or Co<sub>2</sub>Fe/G alloys with abundant surface oxygen were produced with an additional step in the synthesis procedure of CoFe<sub>2</sub>/G or Co<sub>2</sub>Fe/G metal alloys. The varied amounts of Ru precursor (2, 4, and 8 mg) were added drop-wise into Co-Fe sol, followed by self-assembly overnight at room temperature and calcination in the Ar atmosphere at 750°C for 4h by carbothermal reduction. The isolated Ru atoms or Ru nanoparticles homogeneously anchored on CoFe alloys were obtained according to different concentrations of the Ru precursor. For comparison, we also prepared Ru<sub>SA</sub>CoFe<sub>2</sub>/G-2h by varying the calcination time to 2 h and Ru<sub>SA</sub>CoFe<sub>2</sub>/G-H<sub>2</sub> by annealing under 30% H<sub>2</sub>/Ar for 4 h to obtain higher and lower content of lattice oxygen on the metal surface, respectively. Additionally, we synthesized

Ru<sub>SA</sub>CoFe<sub>2</sub>/HG (with high graphitic carbon) and Ru<sub>SA</sub>CoFe<sub>2</sub>/LG (with low graphitic carbon) by varying the ratio between polymer amount and metal precursors.

Synthesis of Rus<sub>A</sub>CoFe<sub>2</sub>-LDHs nanosheets.  $Co(NO_3)_2$ ·6H<sub>2</sub>O and Fe(NO<sub>3</sub>)<sub>2</sub>·9H<sub>2</sub>O (Co:Fe = 1:2) were dissolved in DI water (40 mL). An aqueous solution (40 mL) of Na<sub>2</sub>CO<sub>3</sub> (3 mmol) and NaOH (21 mmol) was prepared. Both solutions were added drop-wise to a RuCl<sub>3</sub>·H<sub>2</sub>O (4 mg) precursor in a beaker containing 80 ml of DI water until the pH was 8.5. After stirring for a day, the solid dark brown precipitants settled down and were then washed several times with water and ethanol in filtration. The collected sample was dried under vacuum in an oven at 70°C overnight.<sup>83</sup> For comparison, we also prepared Ru<sub>SA</sub>CoFe<sub>2</sub> without graphitic carbon substrate by calcining the Ru<sub>SA</sub>CoFe<sub>2</sub>-LDHs under 30% H<sub>2</sub>/Ar for 3 h at 650°C.

**Synthesis of Ni4Mo cuboid arrays.** First, NiMoO<sub>4</sub> cuboid arrays were synthesized using Ni foam as support via a hydrothermal reaction. We prepared a solution consisting of Ni(NO<sub>3</sub>)<sub>2</sub>·H<sub>2</sub>O (0.04 M) and (NH<sub>4</sub>)<sub>6</sub>Mo<sub>7</sub>O<sub>24</sub>•4H<sub>2</sub>O (0.01 M) in 60 ml DI water and transferred it to a Teflon autoclave. The autoclave was placed in a hydrothermal oven and heated to 150°C for 6 h. After the reaction, the NiMoO<sub>4</sub> cuboid arrays were obtained by water purification and were dried in air overnight. The as-prepared NiMoO<sub>4</sub> cuboid arrays were calcinated at 500°C in an Ar/H<sub>2</sub> (90 sccm Ar/10 sccm H<sub>2</sub>) atmosphere. After cooling, the Ni<sub>4</sub>Mo cuboid arrays were obtained.<sup>S4</sup>

#### Characterization.

**Material Characterization.** The structure and crystallinity of all catalysts (including their crystal orientations) were investigated using X-ray diffraction (XRD) (Rigaku Ultima  $|V\rangle$ ). The elemental analysis and the valence band edge of the catalysts were characterized using X-ray photoelectron spectroscopy (XPS) measurements on an AESXPS instrument (ESCA2000 from VG Microtech in England) equipped with an aluminum anode (Al K $\alpha$  = 1486.6 eV, C1s

284.6eV). Argon ion etching was done for 90 sec. The acquired data were background corrected using the Shirley method to find the valence states, and the peaks were fitted using Fityk software, with Voigt peaks containing 80% Gaussian and 20% Lorentzian components. XANES and EXAFS analyses were conducted at the BL10C beamline of the Pohang Light Source (PLS-II, Korea) under 3.0 GeV operation with a ring current of 250 mA. FESEM images were obtained using a JEOL 7500F FESEM. The EDS spectra were recorded in an Oxford Instruments X-Max with the INCA software coupled to the FESEM. The BET method was used to quantify the specific surface area by liquid nitrogen cryosorption (Micrometrics ASAP2020, USA). Sub-Å-resolution aberrated-corrected HAADF-STEM measurements and aberration-corrected TEM (JEM-ARM200CF, JEOL) equipped with a cold field emission source operating at an accelerating voltage of 200 kV were used to acquire the high-resolution transmission electron microscopy (HRTEM) and selected area electron diffraction (SAED, JEOL JEM-2100F) data to characterize the morphology and microstructure of the catalysts. The ICP-AES measurements were carried using OPTIMA 4300 DV. ICP-OES was performed on an Agilent 730.

**Electrochemical measurements.** All electrochemical tests were carried out using a VMP3 electrochemical workstation (Bio-logic Science Instruments, France) in a conventional threeelectrode system, and the overall water splitting test was carried out in a two-electrode configuration under 1 M KOH. Commercially available Ni foam coated with catalyst ink was used as a working electrode, whereas Pt mesh served as a counter electrode and Ag/AgCl (3 M KCl) was the reference electrode. First, commercial Ni foams were dipped in concentrated HCl to completely remove surface oxide and impurities for 2 min, followed by washing in ethanol under ultrasonication and drying in oven at 60°C. The catalyst ink was prepared by dispersing 5 mg of catalyst in 400 µL of ethanol containing 20 µL 5% Nafion, which was sonicated for 60 min. Then, 25  $\mu$ L of the ink was uniformly drop-casted on 0.3 cm<sup>2</sup> of washed Ni foam with a final loading of 1 mg cm<sup>-2</sup>, followed by overnight drying in the oven at 80°C. Before performing the measurements, all the working electrodes were saturated via cyclic voltammetry (CV) scans at a scan rate of 100 mV s<sup>-1</sup>. The LSV polarization curve was measured at a scan rate of 2 mV s<sup>-1</sup> to minimize the contributions from the capacitive current. The catalyst durability test was conducted by chronopotentiometry measurement at a fixed current density. Electrochemical impedance spectroscopy (EIS) studies were carried out in the faradaic region to compare the R<sub>CT</sub>. C<sub>dl</sub> was obtained by collecting CVs at different scan rates in the nonfaradaic region (-0.1 to 0 V vs. RHE). Faradaic efficiency was measured using the eudiometry method.<sup>85</sup> All the potentials referred to the Ag/AgCl were converted to the reversible hydrogen electrode using the Nernst equation.

$$E_{(\text{RHE})} = E_{(\text{Ag/AgCl})} + E^{0}_{(\text{Ag/AgCl})} + 0.059 \text{ x pH}$$
(1)

All the potentials in the three-electrode configuration were 85% iR-corrected with respect to the ohmic resistance of the solution unless specified and calibrated to the RHE using the following equation.<sup>S6</sup>

$$E_{(\text{RHE})} = E_{(\text{Ag/AgCl})} + E^{0}_{(\text{Ag/AgCl})} + 0.059 \text{ x pH} - 85\% \text{ iRs pH}$$
(2)

### **Electrical conductivity measurements**

The electrical conductivity of the  $Ru_{SA}CoFe_2$ -LDHs and  $Ru_{SA}CoFe_2/G$  were measured using a two-point probe method. To make a uniform film, the samples were grounded by a mortar pestle for 5 mins and coated on SiO<sub>2</sub> substrate (5 mm x 5 mm) and apply the silver paste on four edge points as the contact electrode. The measurement was carried out at room temperature. The corresponding conductivity (s) was calculated according to the following equation:

$$\sigma = L/RA \tag{3}$$

where L is the length of the film, R is the resistance of the film and A is the cross-sectional area of the film. The conductivity was averaged from the data of three measurements.

### **Computational methods.**

We employed the Vienna Ab Initio Package (VASP) to perform all the spin-polarized density functional theory (DFT) calculations within the generalized gradient approximation (GGA) using the PBE formulation.<sup>S7-S9</sup> We chose the projected augmented wave (PAW) potentials to describe the ionic cores and took valence electrons into account using a plane wave basis set with a kinetic energy cutoff of 400 eV.<sup>S10,S11</sup> Partial occupancies of the Kohn–Sham orbitals were allowed using the Gaussian smearing method and a width of 0.05 eV. The electronic energy was considered self-consistent when the energy change was smaller than  $10^{-7}$  eV. Geometry optimization was considered converged when the energy change was smaller than  $10^{-6}$  eV. Grimme's DFT-D3 methodology was used to describe the dispersion interactions among all the atoms in the polyimide unit cell and adsorption models of interest.<sup>S12</sup>

The equilibrium lattice constant of body-centered cubic (BCC) iron (Fe) unit cell was optimized (when using a  $15 \times 15 \times 15$  Monkhorst-Pack k-point grid for Brillouin zone sampling) to be a=2.806 Å. This lattice constant was used to build the p(3x3) Fe (110) surface slab with 4 atomic Fe layers, which contained 36 Fe atoms in total. This slab was separated by a 15 Å vacuum layer in the z-direction between the slab and its periodic images. Since the Fe:Co ratio of FeCo alloy samples in our experiments was 2:1, we replaced 12 Fe atoms in the Fe (110) surface slab by 12 Co atoms. First, the 12 Co atoms were spread evenly among the 4 atomic Fe layers, which means that each layer will have 3 Co atoms. Then, the positions of these Co atoms were determined by the following procedure. (1) Dope 3 Co atoms into the first Fe layer of the Fe(110) surface model and identify the most stable spatial arrangement by trying all the possible locational arrangements. (2) Use the surface slab with the most stable spatial

arrangement in the first layer and dope 3 Co atoms in the second Fe layer and do it the same way as in the first layer. (3) Follow similar steps for the third and fourth layers. During structural optimizations of the surface models, a  $2\times2\times1$  gamma-point centered k-point grid for Brillouin zone was used, and the top two layers were allowed to fully relax while the bottom two were fixed. The Ru<sub>SA</sub>CoFe<sub>2</sub> (110) model was constructed by replacing a surface Fe atom with a Ru single atom.



**Figure S1.** The morphology of Ru<sub>X</sub>CoFe/G samples. Scanning Electron Microscopy (SEM) images of as-prepared (a) CoFe<sub>2</sub>/G, (b) Ru<sub>SA</sub>CoFe<sub>2</sub>/G, (c) Ru<sub>NP</sub>CoFe<sub>2</sub>/G, (d) Co<sub>2</sub>Fe/G, (e) Ru<sub>SA</sub>Co<sub>2</sub>Fe/G, (f) Ru<sub>NP</sub>Co<sub>2</sub>Fe/G.



**Figure S2.** The elemental analysis of  $Ru_XCoFe/G$  samples. SEM-EDX spectrum of as-prepared (a)  $CoFe_2/G$ , (b)  $Ru_{SA}CoFe_2/G$ , (c)  $Ru_{NP}CoFe_2/G$ , (d)  $Co_2Fe/G$  and (e)  $Ru_{NP}Co_2Fe/G$ . Most of these peaks are X-rays given off as electrons return to the K electron shell. One peak is from the L shell of ruthenium.

	C	Co:Fe					
Sample	C (at. %)	Co (at. %)	Fe (at. %)	0 (at. %)	Ru (at. %)	Expt.	Obser.
Ru <sub>SA</sub> CoFe <sub>2</sub> /G	68.81	8.63	17.55	3.70	0.41	1:2	1:2
Ru <sub>SA</sub> CoFe/G	75.53	9.52	10.29	4.19	0.47	1:1	1:1.1
Ru <sub>SA</sub> Co <sub>2</sub> Fe/G	70.23	16.24	8.88	4.4	0.44	2:1	1.8:1
Ru <sub>NP</sub> CoFe <sub>2</sub> /G	73.06	6.68	12.88	6.55	0.83	1:2	1:1.9
CoFe <sub>2</sub> /G	64.51	7.13	12.18	16.18	-	1:2	1:1.7
Ru <sub>NP</sub> Co <sub>2</sub> Fe/G	69.82	16.82	8.52	3.95	0.89	2:1	1.97:1
Co <sub>2</sub> Fe/G	64.41	15.07	7.28	13.24	-	2:1	2.07:1

Table S1. EDX analysis of RuxCoFe/G samples.

Table S2. Inductively coupled plasma atomic emission spectroscopy (ICP-AES) analysis of RuxCoFe/G samples.

Sample	Ru (wt.%)
Ru <sub>1wt.%</sub> CoFe <sub>2</sub> /G (2 mg Ru precusor)	1.09
Ru <sub>SA</sub> CoFe <sub>2</sub> /G (4 mg Ru precusor)	2.01
Ru <sub>NP</sub> CoFe <sub>2</sub> /G (8 mg Ru precusor)	4.37
Ru <sub>NP</sub> Co <sub>2</sub> Fe/G (8 mg Ru precusor)	4.39



**Figure S3.** The morphologies of  $Ru_{SA}CoFe_2/G$ . (**a**,**b**) Low magnification Transmission Electron Microscopy (TEM) images of as-prepared  $Ru_{SA}CoFe_2/G$ . (**c**) Representative HAADF-STEM image and (**d**) its corresponding EDS line-scan analysis and elemental mapping of a representative  $Ru_{SA}CoFe_2/G$  (110).

Each CoFe<sub>2</sub> alloy was encapsulated by graphitic carbon which facilitated the electron transfer from an alloy to other alloys (Fig. S3b). The homogeneously isolated Ru atoms (brighter atoms) were identified by representative HAADF-STEM images (Fig. S3c).



**Figure S4.** (a) XRD pattern of graphitic carbon. Inset in a Raman spectra showed defects in graphitic carbon substrate. (b) EDX pattern and (c) O 1s XPS spectra of graphitic carbon showing the surface oxygen (G-O<sub>substrate</sub>). (d) Nitrogen adsorption-desorption isotherms and (e) corresponding pore size distribution profiles for  $Ru_{SA}CoFe_2/G$ .

XRD pattern and Raman spectra showed the successful synthesis of graphitic carbon with high defects after the carbothermal treatment (Fig. S4a). The EDX pattern confirmed the existence of C and O in the G (Fig. S4b). The O 1s XPS spectra of G revealed the presence of only one type of oxygen attached to the graphitic substrate (G-O<sub>substrate</sub>) whereas no peak corresponding to M-O<sub>lattice</sub> around 529 eV was detected (Fig. S4c). The nitrogen adsorption-desorption isotherms with corresponding pore size distribution profiles for Ru<sub>SA</sub>CoFe<sub>2</sub>/G also corroborated to their porous nature along with high pore volume (Ru<sub>SA</sub>CoFe<sub>2</sub>/G: 0.54 cm<sup>3</sup>/g) and larger pore diameter (Ru<sub>SA</sub>CoFe<sub>2</sub>/G: 39 nm) necessary for smooth mass diffusion of reactants and products during the catalysis process to and from the active metal sites (Fig. S4d,e).



**Figure S5.** TEM image of Ru<sub>SA</sub>CoFe<sub>2</sub>/G showing the partially covered porous defective graphitic carbon layers with abundantly exposed active metal sites.



**Figure S6.** The morphologies of CoFe<sub>2</sub>/G. (**a**,**b**) Transmission Electron Microscopy (TEM) images of as-prepared CoFe<sub>2</sub>/G. (**c**) TEM-EDS elemental mapping of CoFe<sub>2</sub>/G catalyst.



**Figure S7.** The morphologies of Co<sub>2</sub>Fe/G. (**a**,**b**) Transmission Electron Microscopy (TEM) images of as-prepared Co<sub>2</sub>Fe/G. (**c**) TEM-EDS elemental mapping of Co<sub>2</sub>Fe/G catalyst.



Figure S8. The morphologies of  $Ru_{NP}Co_2Fe/G$ . (a) Low magnification and (b) High magnification of TEM images of as-prepared  $Ru_{NP}Co_2Fe/G$ . (c) TEM-EDS elemental mapping of  $Ru_{NP}Co_2Fe/G$  catalyst.

			XPS			Co	o:Fe
Sample	C (at. %)	Co (at. %)	Fe (at. %)	O (at. %)	Ru (at. %)	Expt.	Obser.
Ru <sub>SA</sub> CoFe <sub>2</sub> /G	73.86	2.95	5.83	16.65	0.1	1:2	1:1.93
Ru <sub>NP</sub> CoFe <sub>2</sub> /G	80.10	2.61	4.66	12.43	0.2	1:2	1:1.78
CoFe <sub>2</sub> /G	71.54	2.62	4.57	21.27	-	1:2	1:1.74
Ru <sub>NP</sub> Co <sub>2</sub> Fe/G	74.68	4.39	2.52	18.22	0.2	2:1	1.74:1
Co <sub>2</sub> Fe/G	73.70	6.07	3.10	17.73	-	2:1	1.95:1

Table S3. XPS Quantitative analysis of RuxCoFe/G samples.

Table S4. XPS Quantitative analysis of RuxCoFe/G samples before and after Ar etching for 90s.

Sample	r etching							
Sample	C (at.%)	Co (at. %)	Fe (at. %)	O <sub>Total</sub> (at. %)	O <sub>Lattice</sub> (at. %)	Ru (at. %)		
CoFe <sub>2</sub> /G	71.54	2.62	4.57	21.27	3.44	-		
Ru <sub>SA</sub> CoFe <sub>2</sub> /G	73.86	2.95	5.83	16.65	1.86	0.1		
Ru <sub>NP</sub> Co <sub>2</sub> Fe/G	74.68	4.39	2.52	18.22	-	0.2		
Correcto	After Ar etching							
Sample	C (at. %)	Co (at. %)	Fe (at. %)	O <sub>Total</sub> (at. %)	OLattice (at. %)	Ru (at. %)		
CoFe <sub>2</sub> /G	74.46	3.96	7.75	13.82	7.11	-		
Ru <sub>SA</sub> CoFe <sub>2</sub> /G	69.98	10.03	5.56	14.28	6.62	0.14		
Ru <sub>NP</sub> Co <sub>2</sub> Fe/G	71.52	11.1	5.19	10.91	-	0.38		



**Figure S9.** X-ray photoelectron spectroscopy characterization. XPS spectra of Co<sub>2</sub>Fe/G and Ru<sub>NP</sub>Co<sub>2</sub>Fe/G samples: (a) Co 2p, (b) Fe 2p, (c) C 1s of Co<sub>2</sub>Fe/G and (d) Co 2p, (e) Fe 2p, (f) Ru 3p of Ru<sub>NP</sub>Co<sub>2</sub>Fe/G samples.



**Figure S10.** X-ray photoelectron spectroscopy characterization. Ru 3p XPS spectra of Ru<sub>SA</sub>CoFe<sub>2</sub>/G and Ru<sub>NP</sub>Co<sub>2</sub>Fe/G.



**Figure S11.** (a) Ru oxidation state analysis in different samples by corresponding XANES edge energy. (b) Bader charge analyses of  $Ru_{SA}CoFe_2$  (O-8) (110).

Table S5. EXAFS fitting parameters at the	Ru K-edge for various samples	$(S_0^2=0.829)$
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Sample	Shell	Na	$R(\text{\AA})^b$	$\sigma^2(\text{\AA}^2)^c$	$\Delta E_0(\mathrm{eV})^d$	R factor
Ru foil	Ru-Ru	12	2.68	0.0037	0.3	0.0094
	Ru-O	0.2	1.95	0.0037		
Ru <sub>SA</sub> CoFe <sub>2</sub> /G	Ru-Co	6.5	2.49	0.0051	-9.2	0.0005
	Ru-Fe	6.4	2.81	0.0061		

<sup>*a*</sup>N: coordination numbers; <sup>*b*</sup>R: bond distance; <sup>*c*</sup> $\sigma^2$ : Debye-Waller factors; <sup>*d*</sup>  $\Delta E_0$ : the inner potential correction. *R* factor: goodness of fit.  $S_0^2$  was set to 0.829 (Ru), according to the experimental EXAFS fit of Ru foil reference by fixing CN as the known crystallographic value.



**Figure S12.** Potential calibration of the Ag/AgCl reference electrode in H<sub>2</sub> saturated 1 M KOH solution and conversion to RHE before and after electrocatalytic durability measurement.

The Ag/AgCl reference electrode was calibrated in H<sub>2</sub> saturated 1 M KOH electrolyte with Pt mesh as both the working and counter electrode. The LSV polarization curves were recorded at a scan rate 5 mV s<sup>-1</sup>. The potential at which current becomes zero is the reversible potential for H<sub>2</sub> evolution/oxidation. Initially, the zero-point current at -1.011 V corresponds to  $E_{RHE} \sim 0$  ( $E_{RHE} = E_{Ag/AgCl} + 1$ ). After the measurement, the zero-point current remains at -1.007 V, suggesting that the reference electrode potential remains unaltered in alkaline media.



**Figure S13.** The electrocatalytic OER performance of  $Ru_{SA}$  with different composition of CoFe alloy. (a) The OER LSV polarization curves for  $Ru_{SA}$  with different composition of CoFe alloy and (b) the required overpotential to reach 10 mA cm<sup>-2</sup>.



**Figure S14.** The comparison of electrocatalytic OER performance in 1 M KOH electrolyte. The polarization curves of (a) different ratios of Co and Fe with Ru loading of around 4 wt.% and (b) Ru amount (0, 1.09, 2.01 and 4.37 wt.%, respectively) on  $CoFe_2/G$ .



**Figure S15.** (a) Comparison of electrocatalytic OER performance of Ru<sub>SA</sub> on different metal alloys covered by graphitic carbon layer. (b-d) OER performance comparison of Ru<sub>SA</sub>NiFe<sub>2</sub>/G with NiFe<sub>2</sub>/G, Ru<sub>SA</sub>MgAl<sub>2</sub>/G with MgAl<sub>2</sub>/G, and Ru<sub>SA</sub>NiCo<sub>2</sub>/G with NiCo<sub>2</sub>/G, respectively.



**Figure S16.** (a) Low magnification SEM images and (b) high magnification SEM images and SEM elemental mapping of Ru, Fe, Co, and O in Ru<sub>SA</sub>CoFe<sub>2</sub>-LDH sample. Most of these peaks are X-rays given off as electrons return to the K electron shell. One peak is from the L shell of ruthenium.



**Figure S17.** (a) The comparison of electrocatalytic OER performance of  $Ru_{SA}CoFe_2$ -LDH and  $Ru_{SA}CoFe_2/G$  in 1 M KOH electrolyte and (b) corresponding Nyquist plots at 606 mV overpotential. (c) Valence band maximum (VBM) of the  $Ru_{SA}CoFe_2$ -LDH,  $Ru_{SA}CoFe_2$ , and  $Ru_{SA}CoFe_2/G$ . (d) Current-Voltage (I-V) characteristic curves of  $Ru_{SA}CoFe_2/G$  and  $Ru_{SA}CoFe_2$ -LDH.



**Figure S18.** The mass activity plots of the Ru<sub>SA</sub>CoFe<sub>2</sub>/G, 5% Ru/C, and RuO<sub>2</sub> in 1 M KOH. S22



**Figure S19.** (a) XRD pattern, (b) O1s XPS spectra, and (c) LSV polarization curve for OER of Ru<sub>SA</sub>CoFe<sub>2</sub>/G-2h and Ru<sub>SA</sub>CoFe<sub>2</sub>/G.

The XRD pattern of Ru<sub>SA</sub>CoFe<sub>2</sub>/G-2h was similar to that of Ru<sub>SA</sub>CoFe<sub>2</sub>/G, confirming the formation of CoFe<sub>2</sub> alloy with the absence of any Ru<sub>NPs</sub>/Cluster formation (Fig. S19a). The O1s XPS spectra of Ru<sub>SA</sub>CoFe<sub>2</sub>/G-2h showed that lower calcination time for 2h yielded a higher amount of surface oxygen bonded to the metals (M-O<sub>lattice</sub>) compared to Ru<sub>SA</sub>CoFe<sub>2</sub>/G (Fig. S19b and Table S5).

Table	e S6. XPS	5 analysis o	of RusaCoFe2/	G and Rusa	CoFe <sub>2</sub> /G-2h sample	es.
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Samula		Co:Fe						
Sample	C (at. %)	Co (at. %)	Fe (at. %)	O <sub>Total</sub> (at. %)	Olattice (at. %)	Ru (at. %)	Expt.	Obser.
Ru <sub>SA</sub> CoFe <sub>2</sub> /G	73.86	2.95	5.83	16.65	1.86	0.1	1:2	1:1.93
Ru <sub>SA</sub> CoFe <sub>2</sub> /G -2h	53.83	2.54	4.15	39.35	3.9	0.13	1:2	1:1.16



**Figure S20.** (a) XRD, (b) EDX and (c) O 1s XPS spectra for  $Ru_{SA}CoFe_2/G-H_2$ ,  $CoFe_2/G-H_2$  and  $Ru_{SA}CoFe_2$ . (d) TEM image and (e) STEM-EDX elemental mapping of  $Ru_{SA}CoFe_2$ . Inset in **d** showed the corresponding HRTEM images.

The XRD patterns in Fig. S20a confirmed the synthesis of Ru<sub>SA</sub>CoFe<sub>2</sub>/G-H<sub>2</sub>, CoFe<sub>2</sub>/G-H<sub>2</sub>, and Ru<sub>SA</sub>CoFe<sub>2</sub> without any diffraction from Ru-based nanoparticles suggesting the incorporation of Ru<sub>SA</sub> in CoFe alloys. The EDX patterns confirmed the presence of Ru, Co, Fe, O, and C in Ru<sub>SA</sub>CoFe<sub>2</sub>/G-H<sub>2</sub> and CoFe<sub>2</sub>/G-H<sub>2</sub>, and Ru, Co, Fe, and O in Ru<sub>SA</sub>CoFe<sub>2</sub> (Fig. S20b). The O 1s XPS spectra for Ru<sub>SA</sub>CoFe<sub>2</sub>/G-H<sub>2</sub> and CoFe<sub>2</sub>/G-H<sub>2</sub> and CoFe<sub>2</sub>/G-H<sub>2</sub> showed the existence of M-O<sub>lattice</sub> and G-O<sub>substrate</sub>, but only M-O<sub>lattice</sub> with adsorbed water for Ru<sub>SA</sub>CoFe<sub>2</sub> (Fig. S20c). The TEM image confirmed the severe agglomeration of Ru<sub>SA</sub>CoFe<sub>2</sub> (without G substrate) but the uniform elemental distribution of Co, Fe, Ru, and O was shown in the STEM-EDX elemental mapping (Fig. S20d,e).

	EDX						Co:Fe	
Sample	C (at. %)	Co (at. %)	Fe (at. %)	0 (at. %)	Ru (at. %)	Expt.	Obser.	
Ru <sub>SA</sub> CoFe <sub>2</sub> /G-H <sub>2</sub>	74.15	7.41	16.64	1.37	0.44	1:2	1:2.24	
CoFe <sub>2</sub> /G- H <sub>2</sub>	78.56	4.34	9.15	7.95	-	1:2	1:2.1	

Table S7. EDX analysis of RuxCoFe/G-H<sub>2</sub> samples.

Table S8. XPS Quantitative analysis of Ru<sub>x</sub>CoFe<sub>2</sub>/G-H<sub>2</sub> and Ru<sub>sA</sub>CoFe<sub>2</sub> samples.

Comula		XPS							
Sample	C (at.%)	Co (at. %)	Fe (at. %)	O <sub>Total</sub> (at. %)	O <sub>Lattice</sub> (at. %)	Ru (at. %)			
CoFe <sub>2</sub> /G-H <sub>2</sub>	74.29	2.44	4.48	18.79	1.71	-			
RusACoFe2/G-H2	78.93	3.26	5.55	12.15	0.45	0.11			
Ru <sub>SA</sub> CoFe <sub>2</sub>	-	24.78	48.16	26.20	6.90	0.86			



**Figure S21.** (a) Comparison of OER activity of  $Ru_{SA}CoFe_2/G$  with  $Ru_{SA}CoFe_2/G-2h$ , and  $Ru_{SA}CoFe_2/G-H_2$ . (b) Comparison of overpotential at -10 mA/cm<sup>2</sup> with varying amount of O<sub>lattice</sub> content among  $Ru_{SA}CoFe_2/G$ ,  $Ru_{SA}CoFe_2/G-2h$ , and  $Ru_{SA}CoFe_2/G-H_2$ . (c) Comparison of OER activity of  $Ru_{SA}CoFe_2/G$  with  $Ru_{SA}CoFe_2-LDH$  and  $Ru_{SA}CoFe_2/G-H_2$  in 1 M KOH electrolyte.



**Figure S22.** Nyquist plots at (**a**) 606 mV overpotential for OER catalysts and (**b**) 464 mV overpotential for HER catalysts in 1 M KOH (iR uncorrected).



**Figure S23.** Non-Faradaic scan for double-layer capacitance. (**a**,**c**) Electric double-layer capacitance ( $C_{dl}$ ) measurement at the non-Faradic region (0.936 V to 1.036 vs. RHE) with various scan rates (10 mV s<sup>-1</sup> to 30 mV s<sup>-1</sup>) and (**b**,**d**) Corresponding  $C_{dl}$  calculations of CoFe<sub>2</sub>/G and Ru<sub>SA</sub>CoFe<sub>2</sub>/G in 1 M KOH, respectively. The slopes ( $C_{dl}$ ) were used to represent the electrochemical active surface area (ECSA).



**Figure S24.** (a) The comparison of electrocatalytic OER performance of  $Ru_{SA}CoFe_2/G$  and  $Ru_{SA}CoFe_2$  (without G) catalysts in 1 M KOH electrolyte and (b) corresponding Nyquist plot at 606 mV overpotential. (c) CV plots of  $Ru_{SA}CoFe_2$  (without G) at the non-Faradic region (0.936 V to 1.036 vs. RHE) with various scan rates (10 mV s<sup>-1</sup> to 30 mV s<sup>-1</sup>) and (d) corresponding C<sub>dl</sub> calculations in 1 M KOH. The slopes (C<sub>dl</sub>) were used to represent the electrochemical active surface area (ECSA).

Comple			XPS		
Sample	C (at.%)	Co (at. %)	Fe (at. %)	O <sub>Total</sub> (at. %)	Ru (at. %)
Ru <sub>SA</sub> CoFe <sub>2</sub> /LG (Low G)	43.34	9.30	18.02	29.03	0.31
Ru <sub>SA</sub> CoFe <sub>2</sub> /G	73.86	2.95	5.83	16.65	0.11
Ru <sub>SA</sub> CoFe <sub>2</sub> /HG (High G)	86.73	0.47	0.80	11.98	0.02

Table S9. XPS Quantitative analysis of Ru<sub>SA</sub>CoFe<sub>2</sub> with different amounts of graphitic carbon (G).



**Figure S25.** (a) The comparison of the OER activity of  $Ru_{SA}CoFe_2/G$  with  $Ru_{SA}CoFe_2$  (without G),  $Ru_{SA}CoFe_2/LG$  (Low G), and  $Ru_{SA}CoFe_2/HG$  (High G). (b) The comparison of overpotential at -10 mA/cm<sup>2</sup> with varying amounts of G.

Table S10. ICP-OES analysis of the electrolyte before and after long term stability test of RusACoFe<sub>2</sub>/G for OER.

	Со	Fe	Ru
Electrolyte	(ppm, mg/kg)	(ppm, mg/kg)	(ppm, mg/kg)
Before stability	-0.0010	0.0318	0.0062
After stability	-0.0035	0.0317	0.0057



**Figure S26.** The structural analysis and oxidation states of catalysts after the OER stability test. (a) XRD pattern and (b) HRTEM image of  $Ru_{SA}CoFe_2/G$  following stability test. (c) STEM-EDX elemental mapping of  $Ru_{SA}CoFe_2/G$  after the OER stability test. High-resolution X-ray photoelectron spectroscopy (XPS) of (d) C 1s, (e) Co 2p, (f) Fe 2p and (g) O 1s in the  $Ru_{SA}CoFe_2/G$  after long term stability test.



Figure S27. Reproducibility tests of the OER performance with different batches of  $Ru_{SA}CoFe_2/G$  in 1 M KOH electrolyte.



**Figure S28.** Top and side view of the (a)  $CoFe_2$  (O-1) (110), (b)  $CoFe_2$  (O-6) (110), (c)  $CoFe_2$  (O-7) (110), and (d)  $CoFe_2$  (O-9) (110) model with OOH\* molecule before and after optimization.

Table S11. Adsorption energy  $(E_{ads})$  of OOH\* intermediate on models with different preadsorbed O<sub>lattice</sub>.

Model	OOH* $E_{ads}$ (eV)		
CoFe <sub>2</sub> (O-7) (110)	-0.87		
CoFe <sub>2</sub> (O-8) (110)	-0.90		
CoFe <sub>2</sub> (O-9) (110)	-0.37		

Model		Bader charge (e)			
	Ru	Со	Fe	0	
CoFe <sub>2</sub> (O-8) (110)	-	-0.012	+0.237	-0.688	
Ru <sub>SA</sub> CoFe <sub>2</sub> (O-8) (110)	+0.728	-0.008	+0.262	-0.833	

Table S12. The Bader charge of CoFe<sub>2</sub> (O-8) (110) and RusACoFe<sub>2</sub> (O-8) (110) models.



**Figure S29.** The differential charge density plot of (a)  $CoFe_2$  (8-O) (110) and (b)  $Ru_{SA}CoFe_2$  (O-8) (110). The yellow and cyan regions represent negative (charge aggregation) and positive charges (charge consumption), respectively, with an isovalue of 0.0025 e-/Å<sup>-3</sup>. (c) Total density of states (DOS) plots of CoFe<sub>2</sub> (110), CoFe<sub>2</sub> (8-O) (110), and  $Ru_{SA}CoFe_2$  (O-8) (110).



**Figure S30.** The comparison of electrocatalytic HER performance in 1 M KOH electrolyte. (a) HER polarization curves and (b) comparison of the overpotentials required to reach the current density of -10 mA cm<sup>-2</sup> of Ni foam, Co<sub>2</sub>Fe/G, Ru<sub>NP</sub>Co<sub>2</sub>Fe/G, Ru<sub>SA</sub>CoFe<sub>2</sub>/G, and Pt/C. (c) The corresponding Tafel plots of Co<sub>2</sub>Fe/G, Ru<sub>NP</sub>Co<sub>2</sub>Fe/G, Ru<sub>SA</sub>CoFe<sub>2</sub>/G, and Pt/C.



**Figure S31.** Comparison of electrocatalytic HER performance in 1 M KOH electrolyte. The polarization curves of (**a**) Ru amount (around 0, 1, 2, and 4 wt.%, respectively) on Co<sub>2</sub>Fe/G and (**b**) different ratio of Co and Fe with Ru loading of 4.39 wt.%.



**Figure S32.** Non-Faradaic scan for double-layer capacitance. (**a**,**c**) Electric double-layer capacitance ( $C_{dl}$ ) measurement at the non-Faradic region (0.936 V to 1.036 vs. RHE) with various scan rates (60 mV/s to 100 mV/s) and (**b**,**d**) corresponding  $C_{dl}$  calculations of  $Co_2Fe/G$  and  $Ru_{NP}Co_2Fe/G$  in 1 M KOH, respectively. The slopes ( $C_{dl}$ ) were used to represent the electrochemical active surface area (ECSA).



**Figure S33.** Chronopotentiometric curves of  $Ru_{NP}Co_2Fe/G$ , and Pt/C in 1M KOH electrolyte with a current density of -50 mA cm<sup>-2</sup> for 24 h.



**Figure S34.** The surface structure and morphology of  $Ru_{SA}CoFe_2/G$  catalyst after HER stability. (a) XRD pattern, (b) HRTEM image, and (c) The EDX analysis of the  $Ru_{SA}CoFe_2/G$  after long term stability test.



**Figure S35.** (a) Low magnification and (b) high magnification of SEM images. (c,d) SEM elemental mapping of Ni and Mo in Ni<sub>4</sub>Mo sample. (e) The XRD pattern of Ni<sub>4</sub>Mo on Ni foam. The high-resolution XPS pattern of (f) Ni 2p and (g) Mo 3d for Ni<sub>4</sub>Mo on the nickel foam.

The high-resolution XPS pattern of Ni 2p showed the existence of Ni<sup>0</sup> state (Fig. S35f). In the high-resolution XPS pattern of Mo 3d for the Ni<sub>4</sub>Mo, the peaks checked at 230.2 eV, 232.5 eV, and 233.6 eV correlating to Mo<sup>4+</sup>  $3d_{5/2}$ , Mo<sup>4+</sup>  $3d_{3/2}$  and Mo<sup>6+</sup>  $3d_{3/2}$ , respectively. The Mo<sup>0</sup>  $3d_{5/2}$  and Mo<sup>0</sup>  $3d_{3/2}$  were located at 229.3 eV and 231.5 eV, respectively (Fig. S35g).<sup>S13</sup>



**Figure S36.** Electrocatalytic HER performance of Ni<sub>4</sub>Mo/Ni foam and Ni foam in 1 M KOH electrolyte.



**Figure S37.** (a) The digital image of  $Ru_{SA}CoFe_2/G$  and  $Ni_4Mo$  catalysts on Ni foam before overall water splitting test, (b) SEM image of  $Ru_{SA}CoFe_2/G$  loaded on Ni foam, and (c) the digital image of  $Ru_{SA}CoFe_2/G$  and  $Ni_4Mo$  catalysts on Ni foam during overall stability test at 100 mA/cm<sup>2</sup>.

Figure S37b showed the actual loading of  $Ru_{SA}CoFe_2/G$  on Ni foam substrate and Fig. S37c displayed the oxygen and hydrogen bubbles released from the respective electrodes during the overall water splitting test at a current density of 100 mA/cm<sup>2</sup>.



**Figure S38**. Durability test at a current density of 200 mA cm<sup>-2</sup> in 1M KOH for Ru<sub>SA</sub>CoFe<sub>2</sub>/G (+)  $//Ni_4$ Mo (-) electrolyzer (Inset: LSV curve before and after stability test).

The matching LSV polarization curve after the stability test confirmed the retention of the active sites even at high current density (Fig. S38 inset).

## **Supporting References**

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