Support information

Ru doped CoP Nanosheets for Efficient Hydrogen Evolution in Microbial Electrolysis Cells

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Contents

1. MECs assembly and operation

1.1 Assembly of MECs

The MECs device in this experiment was modified from a successfully domesticated MFCs (Fig S1). Keep the anode of MFCs, change the potassium ferricyanide into 0.1 M PBS solution as the catholyte, make the catalyst into working electrode and access the circuit. The gas collecting device was connected in the cathode. A DC regulated voltage power supply was used to provide voltage connecting a 7.5 Ω resistor in series to form a closed loop. The two ends of the resistance were connected to a data collector for voltage acquisition. The assembled MECs reactor is shown in Fig S3 (a-b).

1.2 Preparation of cathode working electrode

The synthesized catalysts were made into MECs cathode working electrode as follows: Weigh 20 mg of sample and dissolve it in a mixed solution of 250 μL deionized water, 200 μL absolute ethanol and 50 μL Nafion. Then place it in the ultrasonic cleaning machine ultrasonic for 30 min to make the slurry evenly dispersed. The whole slurry was evenly spread on both sides of the treated carbon cloth (1 × 2 cm) in a small amount and several times, so that the catalyst loading was 10 mg cm^{-2}. The cathode working electrode of MECs was obtained after natural air-drying at room temperature. As a comparison, working electrodes loaded with Pt/C, CoP and CC were prepared by the same method as above.

1.3 Operation of MECs

The above-prepared working electrode and gas collector were installed in the cathode reaction chamber of MECs, and electrolyte (0.1 M PBS) was injected into the cathode chamber and gas collector respectively. Note that the electrolyte in the cathode reaction chamber should not be too full. The gas collector should be filled as much as possible, but the liquid level should be within the readable scale. The newly configured anolyte was injected into the anode reaction chamber. The voltage was set to 0.80-1.20 V with an external regulated DC power supply, in which the positive and negative electrodes of the regulated DC voltage were respectively connected to the anode and cathode of the MECs reactor. At the same time, a 7.5 Ω resistor is connected in series with the external circuit,

and the voltage across the resistor is collected by a data collector. The data acquisition frequency is 200 seconds. After the above assembly is completed, the MECs can start to operate after connecting to the regulated DC power supply.

1.4 Gas collection and measurement

During the operation of the MECs reactor, hydrogen was collected by the drainage method, and the volume of hydrogen was recorded by the scale reading of the gas collecting pipe. It is generally recorded every 12 hours. When the hydrogen production rate is fast enough, the electrolyte in the gas collector needs to be added in time. Furthermore, the electrolyte in the cathode reactor also needs to be withdrawn in time to avoid damage to the device due to excessive pressure, resulting in incomplete hydrogen collection.
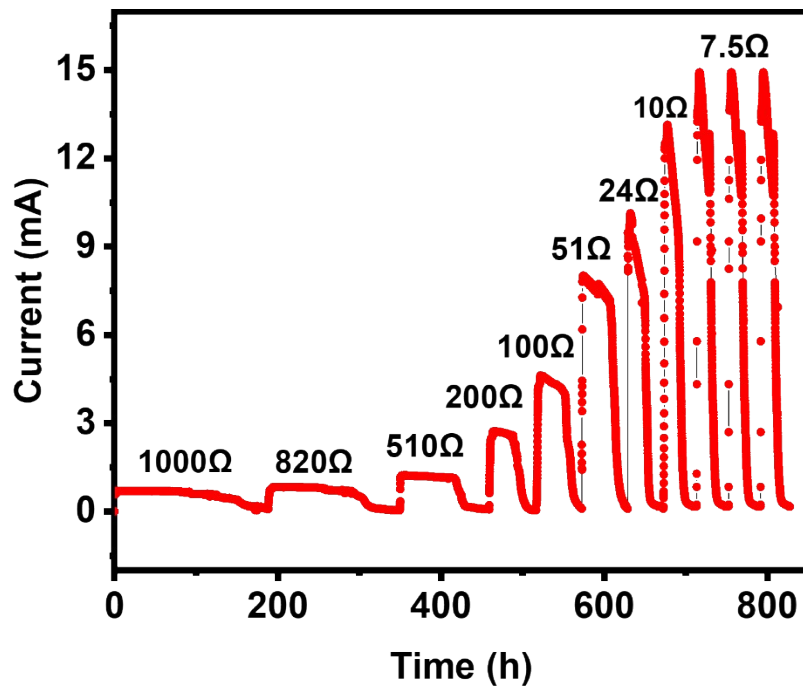
2.Figures

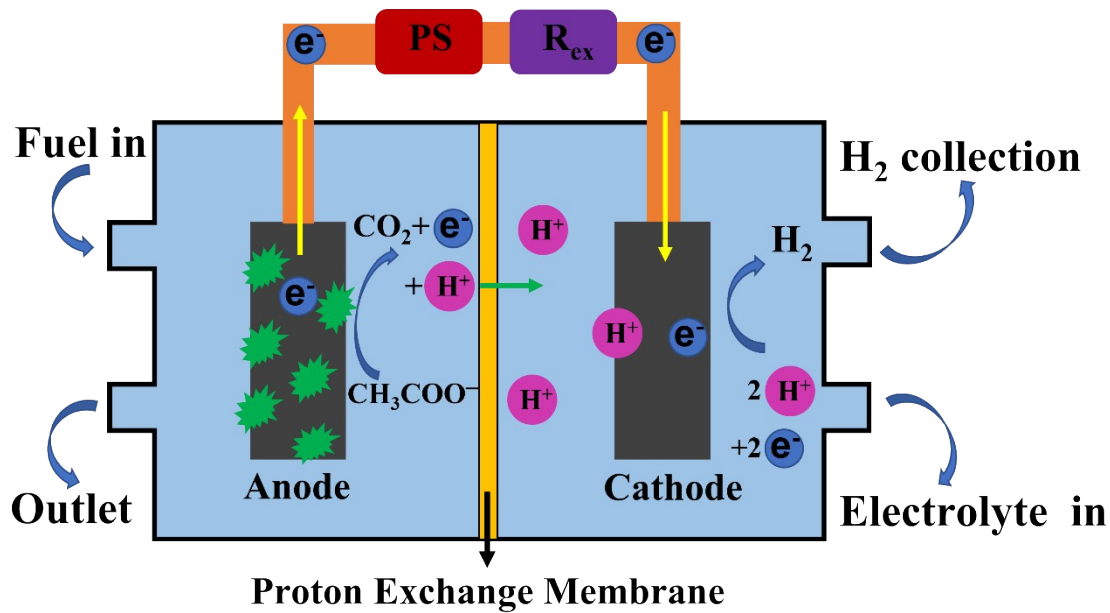**Figure.S1** MFCs domestication cycle diagram.

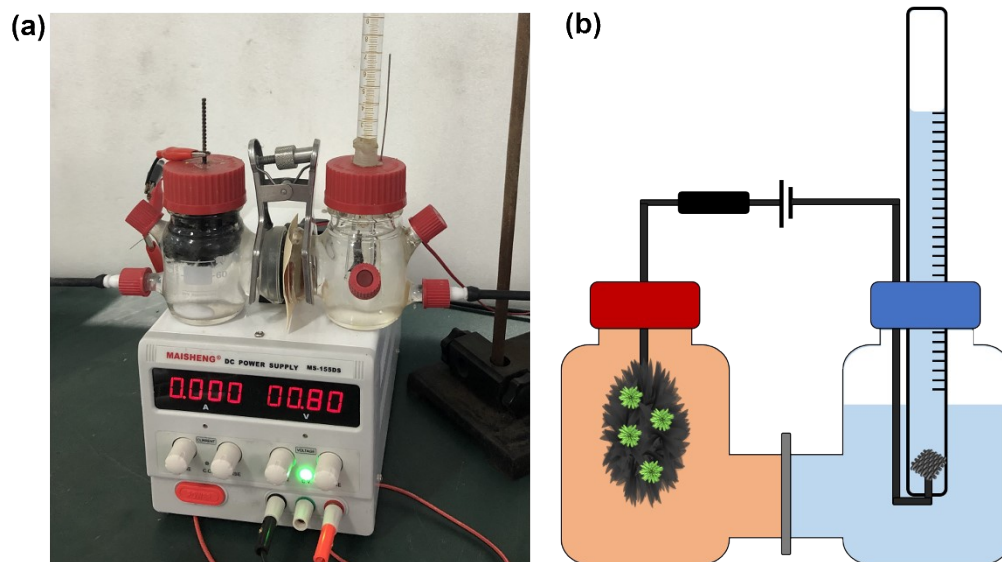**Figure S2** Schematic diagram of Microbial Electrolysis Cells.

Figure S3 (a) Physical drawing of a double-chamber MECs; (b) Schematic diagram of a double-chamber MECs.
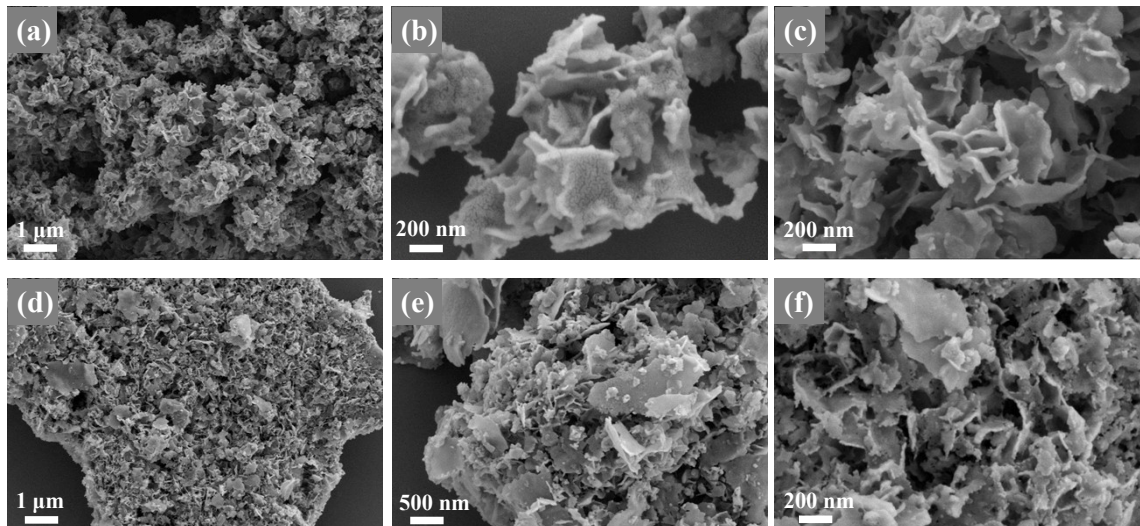
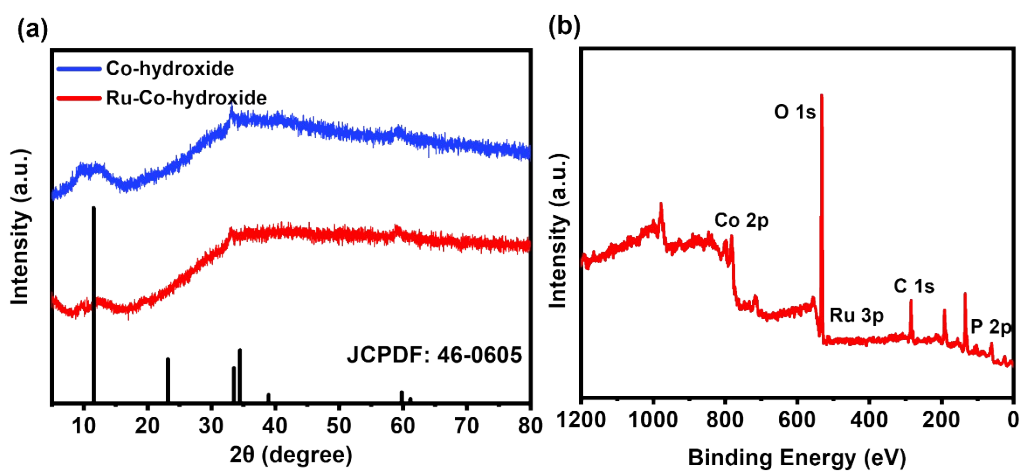**Figure S4** (a-c) SEM images of Ru/CoP NSs; (d-f) SEM images of CoP NSs.

Figure S5 (a) XRD patterns of Ru/Co-hydroxide and Co-hydroxide; (b) XPS spectrum of Ru/CoP NSs.

3. Tables

Table.S1 Hydrogen evolution efficiency of MECs modified by Ru-CoP NSs series materials in 0.1 M PBS catholyte

catalyst	$^a E_{ap}$ [V]	$^b C_{total}$ [C]	$^c CE$ [%]	$^d R_{cat}$ [%]	$^e R_{H2}$ [%]	$^f Q_{H2}$ [m³ m⁻² d⁻¹]
CC	0.8	266.43±1.04	37.75±0.15	24.85±0.22	9.38±0.01	0.0171±0.0002
Pt/C	0.8	694.43±6.02	98.40±0.85	85.80±0.07	84.42±0.06	0.1397±0.0107
Ru/CoP NSs	0.8	723.77±0.57	102.56±0.08	90.99±0.05	93.33±0.01	0.1434±0.0082
CoP NSs	0.8	682.15±2.99	96.66±0.42	74.56±0.02	72.07±0.01	0.0923±0.0029

Table.S2 Hydrogen evolution efficiency of MECs modified with different catalysts in 0.1 M PBS cathode solution at different applied voltages

catalyst	$^a E_{ap}$ [V]	$^b C_{total}$ [C]	$^c CE$ [%]	$^d R_{cat}$ [%]	$^e R_{H2}$ [%]	$^f Q_{H2}$ [m³ m⁻² d⁻¹]
CC	0.8	266.43	37.75	24.85	9.38	0.0171
	1.0	418.37	47.43	58.35	27.67	0.0539
	1.2	536.36	60.80	77.61	47.19	0.1133
Pt/C	0.8	694.43	96.98	87.05	84.42	0.1397
	1.0	683.16	96.80	92.67	89.70	0.1929
	1.2	691.29	97.95	93.08	91.17	0.2179
Ru/CoP NSs	0.8	723.77	102.56	90.99	93.33	0.1434
	1.0	716.88	101.58	92.69	94.16	0.1947
	1.2	725.89	102.85	95.97	98.71	0.2359

4. A brief introduction of the computational hydrogen electrode (CHE) method.

Generally speaking, when studying about the electrocatalytic reaction through first principle, there are two difficulties, one is to calculate the reaction barrier of the proton coupled electron transfer (PCET) reaction, the other is the Gibbs free energy of the solvated H^+. The CHE method[1] proposed by Norskov et al is aiming at settling or bypassing these two difficulties. In the framework of CHE method, for the reaction
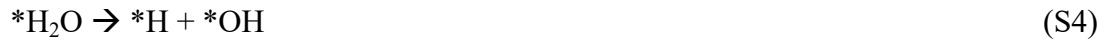
$$H^+ + e \rightarrow 1/2H_2 \tag{S1}$$

reaches equilibrium on U_{SHE}=0 V, one can replace the energy of H^+ with that of $1/2H_2$:

$$G_{H+} = 1/2G_{H2} \tag{S2}$$

The energy of electron can be expressed by $-Ue$, where U is the electrode potential vs SHE. As for the reaction barrier of PCET, the CHE method assumes the overpotential of the electrocatalytic reaction is the overpotential least to make standard reaction Gibbs free energies of all the elementary step to be exothermic. And such potential is called the reaction limiting potential, which is denoted as U_l. Usually, U_l is an activity descriptor, as for HER, U_l can be used to judge the exact reaction pathway.

4.1 The reaction models and pathways

In alkaline medium, the reaction mechanisms for HER written as follows:

$$H_2O + * \rightarrow *H_2O \tag{S3}$$

$$*H_2O \rightarrow *H + *OH \tag{S4}$$

$$*H + *OH + e^- \rightarrow *H + OH^- \tag{S5}$$

$$2H_2O + 2e^- \rightarrow H_2 + 2OH^- \tag{S6}$$

The asterisk stands for the sites on the surface of the catalysts.

4.2 The DFT details

The spin-polarized DFT calculations were performed using PWSCF codes contained in the Quantum ESPRESSO to get the geometry and the total energy.[2] The perdew-Burke-Ernzerhof (PBE) exchange correlation functional in the generalized gradient approximation (GGA) was used to describe the exchange correlation effect. The Kohn-Sham orbitals were expanded in a plane-wave basis set with a kinetic energy cutoff of 30 Ry and the charge-density cutoff of 300 Ry. The Fermi-surface effects has been treated by the smearing technique of Methfessel and Paxton, using a smearing parameter of 0.02 Ry. For bulk structures optimizations, the Gamma-centered Monkhorst-Pack k-points grids were set to 9×6×5 for primitive cell of CoP (orthorhombic, space group: Pnma). For surface structures optimizations, k-points samplings were reset to 3×3×1 for 2×2 supercell of CoP (111) (the bottom two of four atomic layers were fixed). To discuss the influence of doping

Ru atoms, we use one Ru atom to replace one surface Co atom which directly interacts with Co atoms of the active sites (Figure S6). All atoms including the adsorbates are allowed to relax during the geometric optimization until the Cartesian force components acting on each atom were below 10^{-3} Ry/Bohr and the total energy converged to within 10^{-5} Ry. The vacuum space along the Z-direction is set to 15 Å.

In calculating the Gibbs free energy differences from R1 to R6, the associated adsorption free energy of the adsorbates are calculated by the following expression:

$$G_A = E_A + ZPE - TS + \int C_p dT \tag{S7}$$

Where E_A is the total energy of a certain molecule or adsorbate A*. When A is representing a certain molecule, the total energies can be calculated directly. When A is representing a certain adsorbate, it is calculated by the difference between the DFT based substrate with (E_{A*}^{DFT}) and without adsorbate A (E_*^{DFT}):

$$E_A = E_{A*}^{DFT} - E_*^{DFT} \tag{S8}$$

ZPE, TS and $\int C_p dT$ are the correction from zero point energy, entropy and heat capacity.. Other than that, H^+ is calculated by the Gibbs free energy of $1/2H_2$, the energy of electron is calculated by $-Ue$. As for the calculation of H*, we take the calculation of Pt as the standard and eliminate the error through the following calculation method(S3). The difference between the H adsorption results calculated by Pt and those calculated by J. K. Nørskov et al is the error of calculation.[3] When calculating the H adsorption results of other catalysts, the obtained results should subtract the error previously calculated (Figure S8). The intermediate stable configuration calculated by simulation is shown in figure (Figure S8~Figure S10).
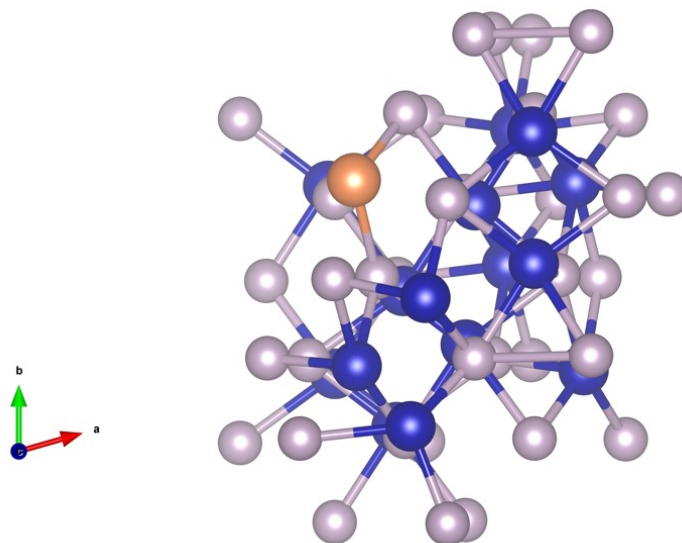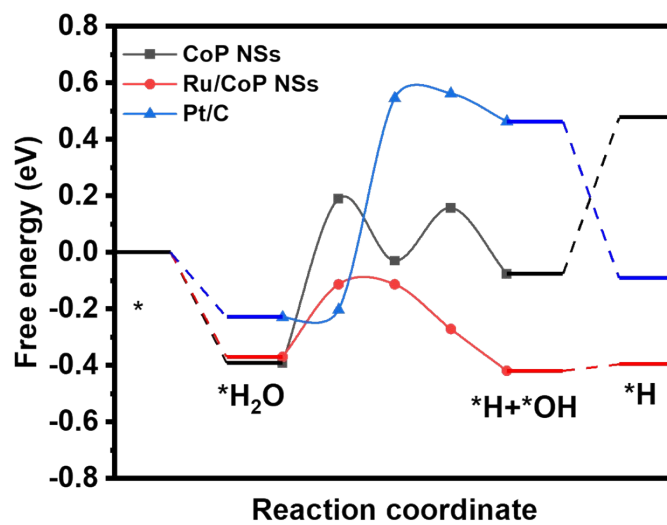
Figure.S6 Stable configures of Ru/CoP NSs.

Figure.S7 The reaction FED for HER on CoP NSs, Ru/CoP NSs and Pt/C, where Pt/C is set as the benchmark.
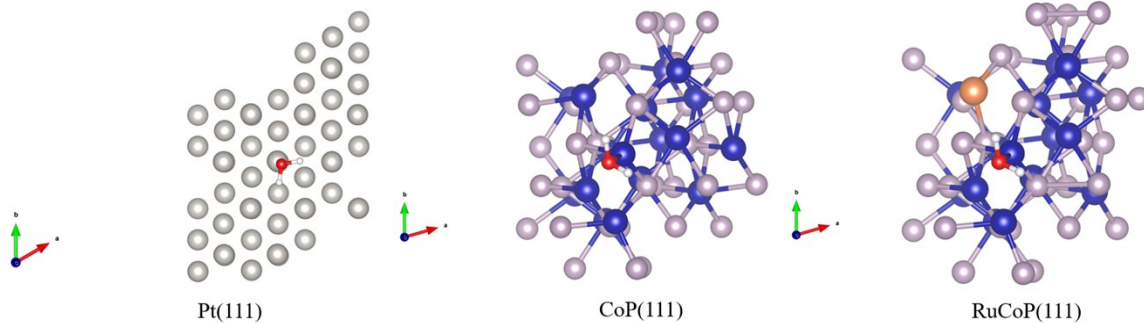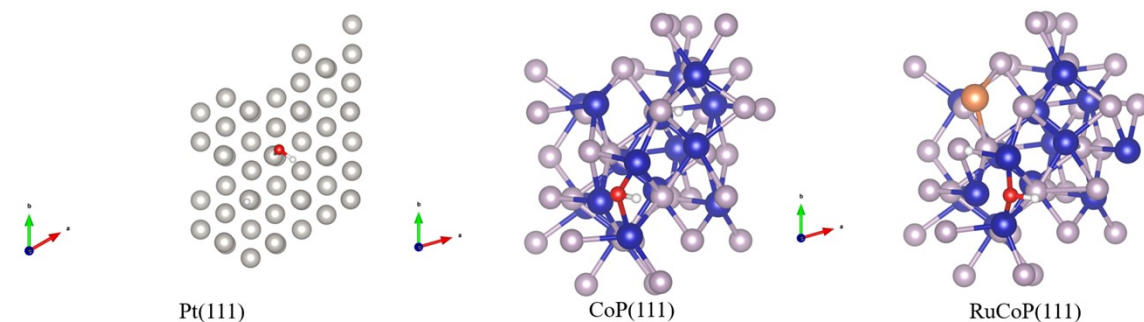
Figure.S8 Stable configures of H_2O.
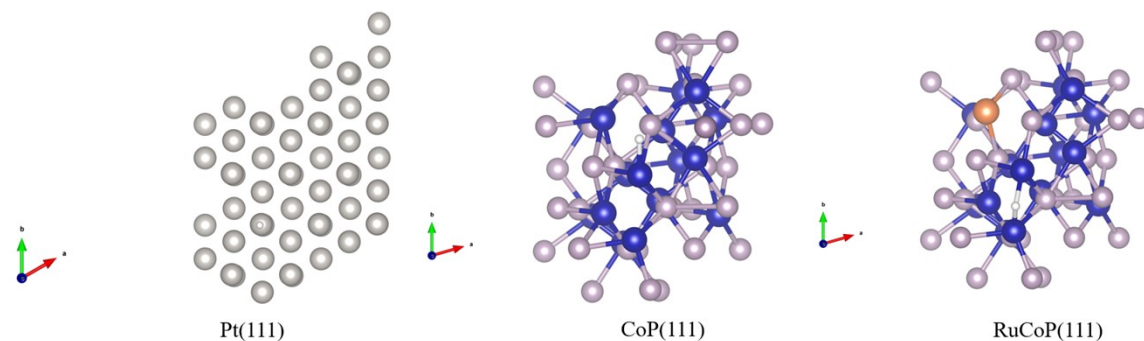

Figure.S9 Stable configures of *H+*OH.

Figure.S10 Stable configures of *H.

All the structures above are shown using VESTA software[4] , where red is oxygen, white is hydrogen, brown is ruthenium, blue is cobalt, pink is phosphorus, and grey is platinum.
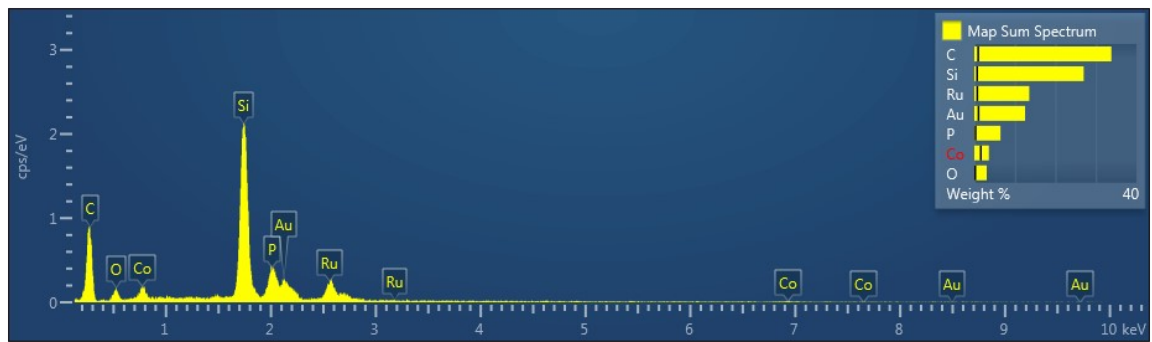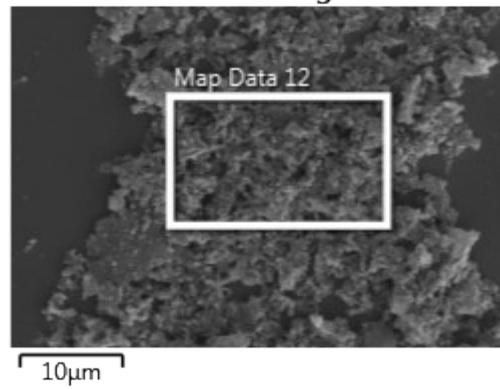
Figure.S11 Mapping of Ru/CoP NSs

Element	Wt%	Atomic %
C	33.83	63.50
O	3.05	4.30
Si	26.98	21.66
P	6.45	4.70
Co	3.61	1.38
Ru	13.57	3.03
Au	12.52	1.43
Total:	100.00	100.00

Tabal.S3 Calculation results of Ru/CoP NSs Mapping

Reference

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