Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supporting Information

Experimentally revealed and theoretically certified synergistic electronic interaction of V-doped CoS for facilitating oxygen evolution reaction

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Electrochemical measurements

At room temperature, using electrochemical workstation 1.0 M potassium hydroxide solution (CHI 660E) and electrochemical performance of three electrode system test materials. The working electrode was fabricated by deposition of the catalyst on a glass carbon (GC) electrode with a diameter of 5.0 mm. The reference electrode and the counter electrode were Ag/AgCl electrode and Pt sheet electrode, respectively. Polarization curve is acquired from linear sweep voltammetry (LSV) under the sweep rate is 5 mV s^{-1}. The Tafel diagram is obtained by plotting the LSV curve as the logarithm of standard potential and current density. The electrochemical double layer capacitance (C_{dl}) is performed by cyclic voltammetry (CV), and the potential scan rate is set at 100, 80, 60, 40 and 20 mV s^{-1}. From 100 kHz to 1 Hz testing electrochemical impedance spectroscopy (EIS).

As for catalyst preparation, firstly, 4 mg of electrocatalyst and 30 μL of 5% nafion solution were ultrasonically dispersed in a mixture of 1 mL water and ethanol (3:1) for 15 min to form a mixed ink. Then spread the mixture of 10 μL ink on the 5 mm diameter glass carbon electrode, and natural drying for use. Therefore, the loading capacity of the sample is 0.197 mg cm^{-2}.

Density Functional Theory

DFT calculations:

In the framework of density functional theory of first principles calculations, were performed based on the Cambridge Sequential Total Energy Package (CASTEP)[1]. The electron-electron interaction was described by exchange correlation functional under generalized gradient approximation (GGA) and Perdew–Burke–Ernzerhof (PBE) functional. A cut off energy of 650 eV was used and the convergence test of 4×4×1 K-point sampling set is carried out. 0.01 eV for tolerance force, energy tolerance for each atom is 5.0×10^{-7} eV. Storage model of each atom can be in the absence of any constraint relaxation to the minimum enthalpy. Along the direction of the vacuum of space is set to 16 Å, which is sufficient to avoid interactions between two adjacent images. CoS, MoCoS and VCoS surface was established, and their surfaces absorbed O_2, OH, O, OOH groups.

The Volmer reaction:

$$H_2O+M+e^- \rightarrow M\text{-}H^*+OH^-$$

Through calculating every step of the reaction free energy to evaluate performance of OER (**equation S1**):

$$\Delta G = \Delta E + \Delta E_{\mathrm{ZPE}} - T\Delta S - eU$$

where ΔE *is* the adsorption energy, ΔE_{ZPE} and ΔS are zero point energy (ZPE) change and entropy change (T = 300 K)[2]. U is under standard conditions for normal hydrogen electrode (NHE) measurement of potential, *e* is transferred charge for one-electron reactions.

Four steps as adsorption free energy change of ΔE_{ads} is shown below:

$$\Delta E_{OH*} = E_{OH*} - E_* - (E_{H2O} - 1/2\ E_{H2})$$

$$\Delta E_{O*} = E_{O*} - E_* - (E_{H2O} - E_{H2})$$

$$\Delta E_{OOH*} = E_{OOH*} - E_* - (2E_{H2O} - 3/2\ E_{H2})$$

Where E_*, E_{OH*}, E_{O*} and E_{OOH*} are the clean surface and three kinds of intermediates respectively adsorption on the surface of the total energy. E_{H2O}, E_{H2}, and E_{O2} are the computed energies for the individual H_2O, H_2 and O_2 molecules, respectively.

In alkaline environment, anode OER the whole process can use the following four steps combination mechanism to describe formula (**equation S2**):

$$OH^{-}+* \rightarrow OH^{*}+e^{-}$$

$$OH^{*}+OH^{-} \rightarrow O^{*}+H_2O+e^{-}$$

$$OOH^{*}+OH^{-} \rightarrow OOH^{*}+e^{-}$$

$$OOH^{*}+OH^{-} \rightarrow O_2+H_2O+e^{-}$$

Among them, * and M* represent the active site and the surface adsorption of intermediates.

The Gibbs free energy change for steps 1–4 can be expressed as follows:

$$\Delta G_1=\Delta G_{OH}-eU$$
$$\Delta G_2=\Delta G_{O}-\Delta G_{OH}-eU$$
$$\Delta G_3=\Delta G_{OOH}-\Delta G_{O}-eU$$
$$\Delta G_4=4.92[eV]-\Delta G_{OOH}-eU$$

Here, U is the potential measured on a normal hydrogen electrode under standard conditions. Theory of electric potential can be defined as **equation S3**:

$$\eta_{OER}=\max[\Delta G_1,\Delta G_2,\Delta G_3,\Delta G_4]/e-1.23[V]$$

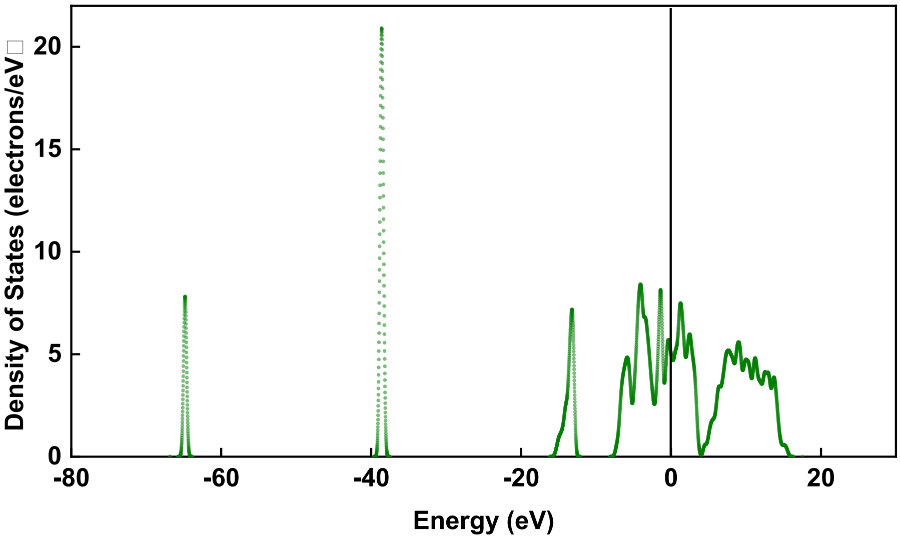

Figure S1. Calculated density of states (DOS) for CoS.

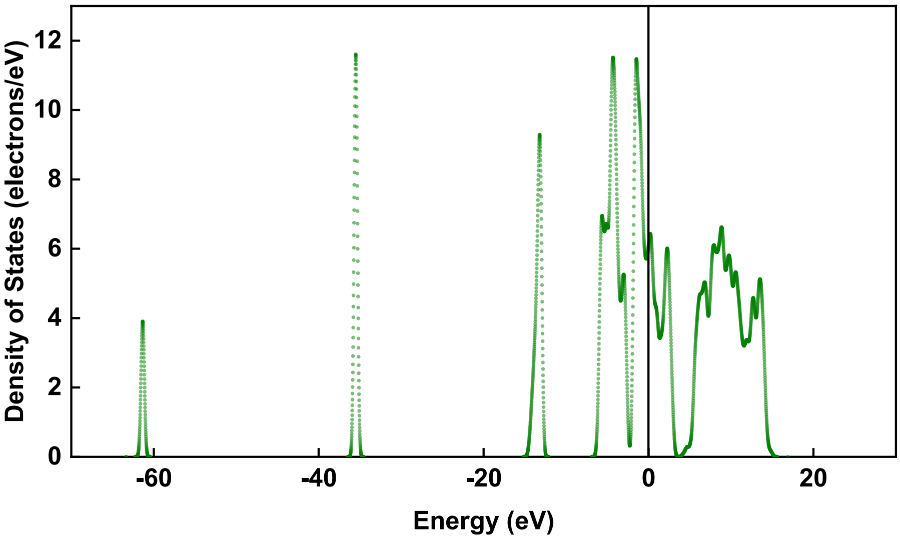

Figure S2. Calculated density of states (DOS) for MoCoS.

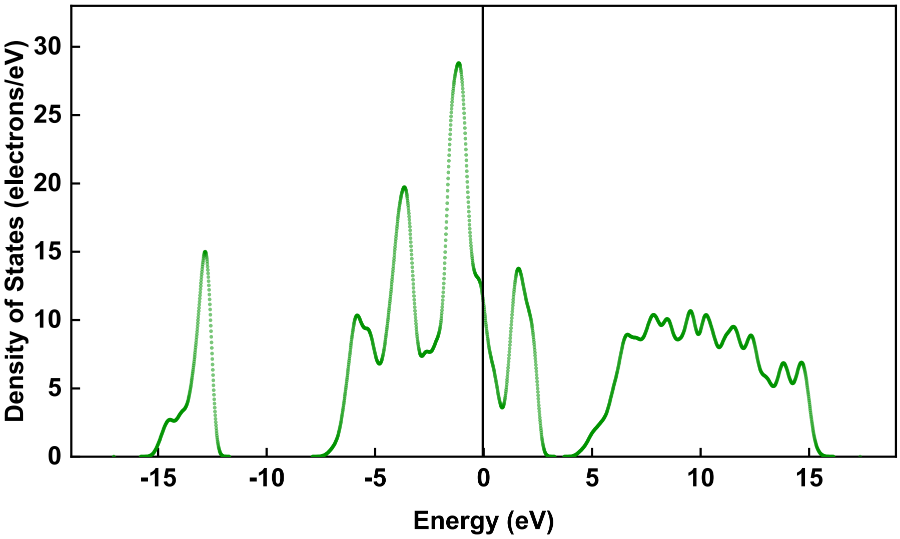

Figure S3. Calculated density of states (DOS) for VCoS.

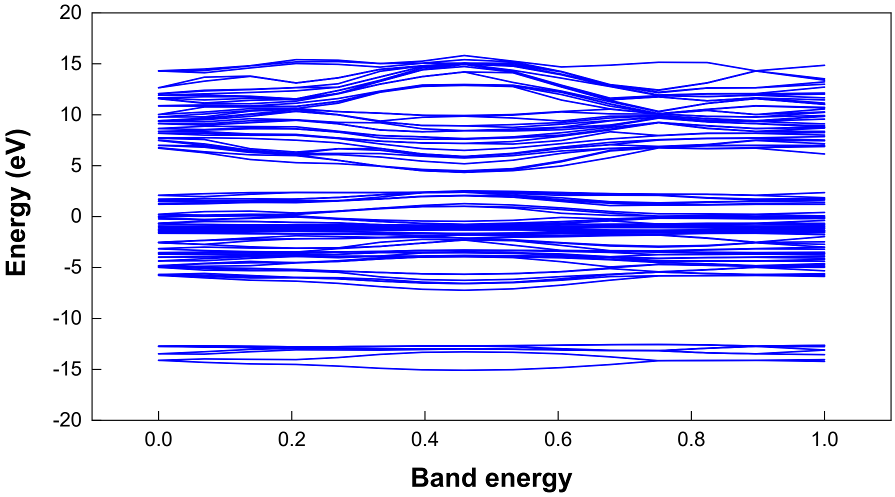

Figure S4. Calculated band structure of CoS.

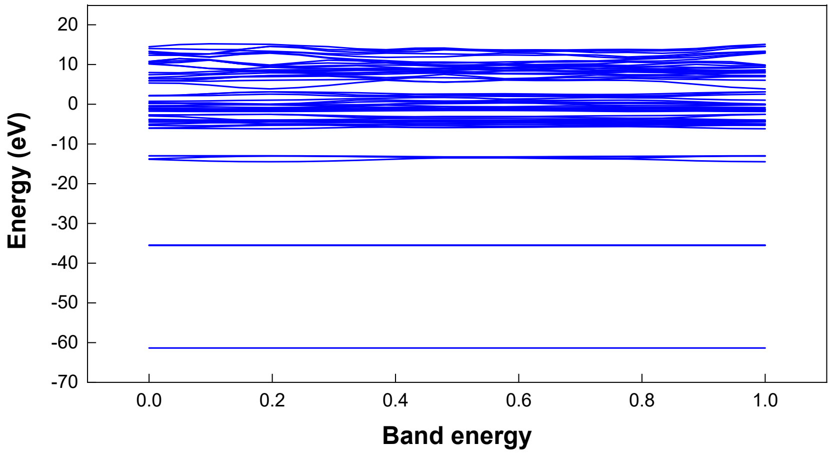

Figure S5. Calculated band structure of MoCoS.

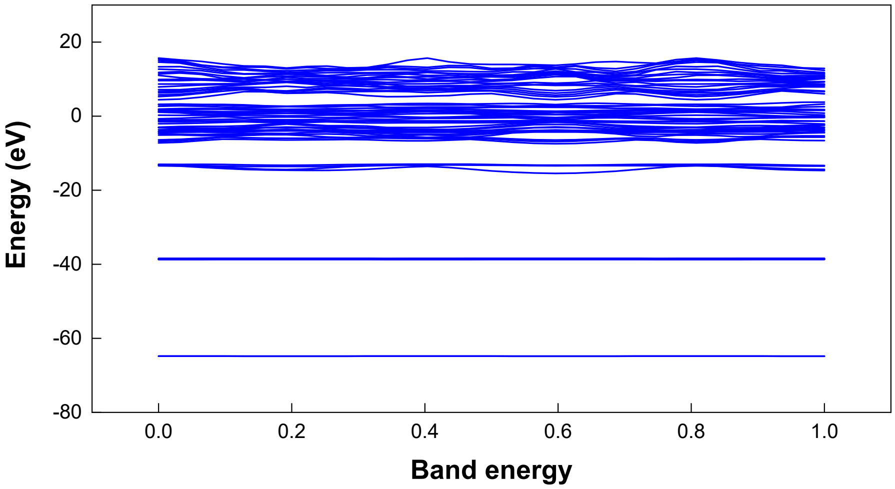

Figure S6. Calculated band structure of VCoS.

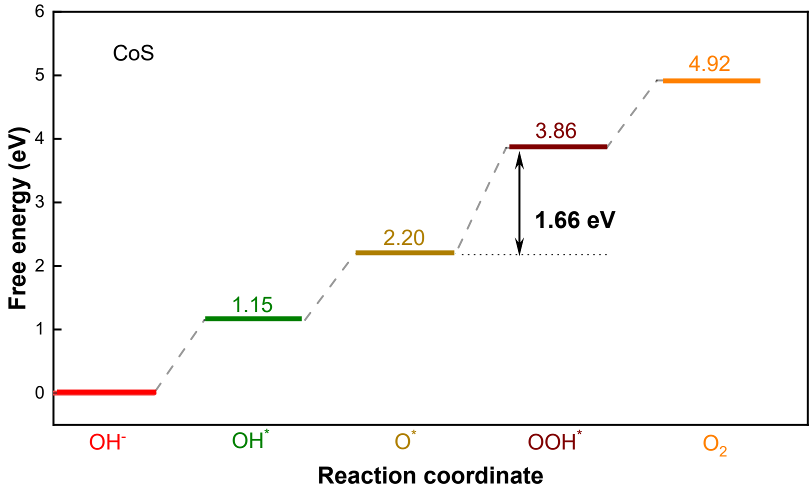

Figure S7. Free energy diagrams of CoS for OER.

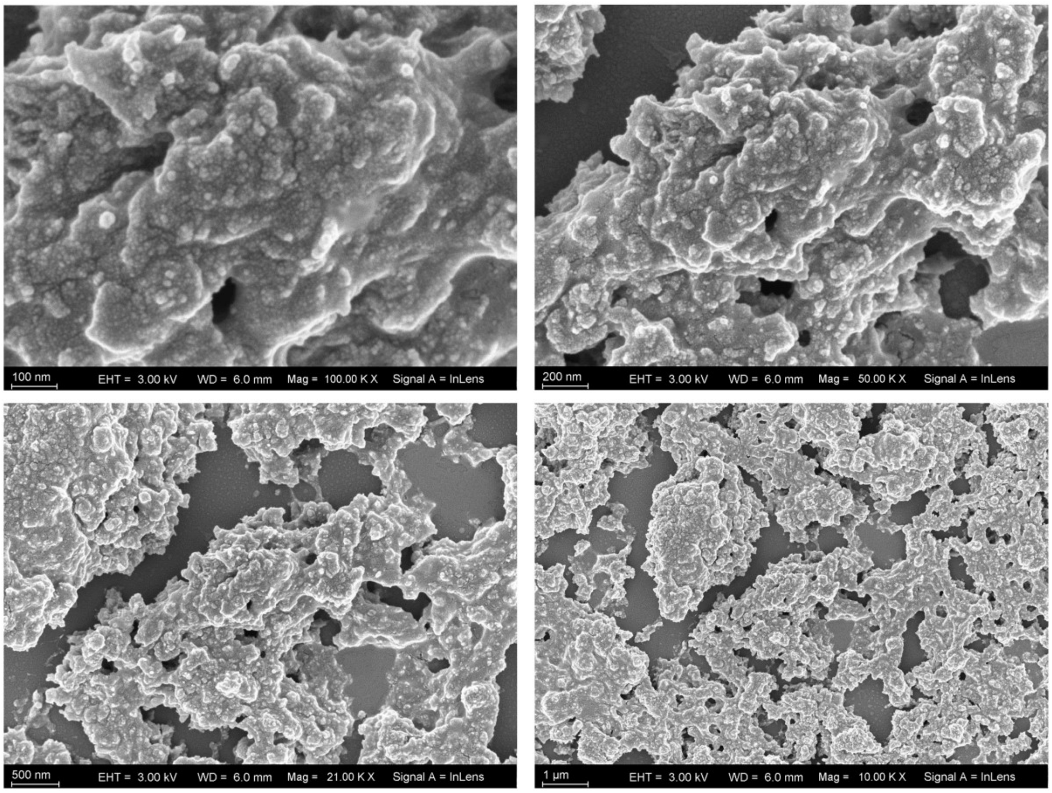

Figure S8. SEM images at different scales for MoCoS.

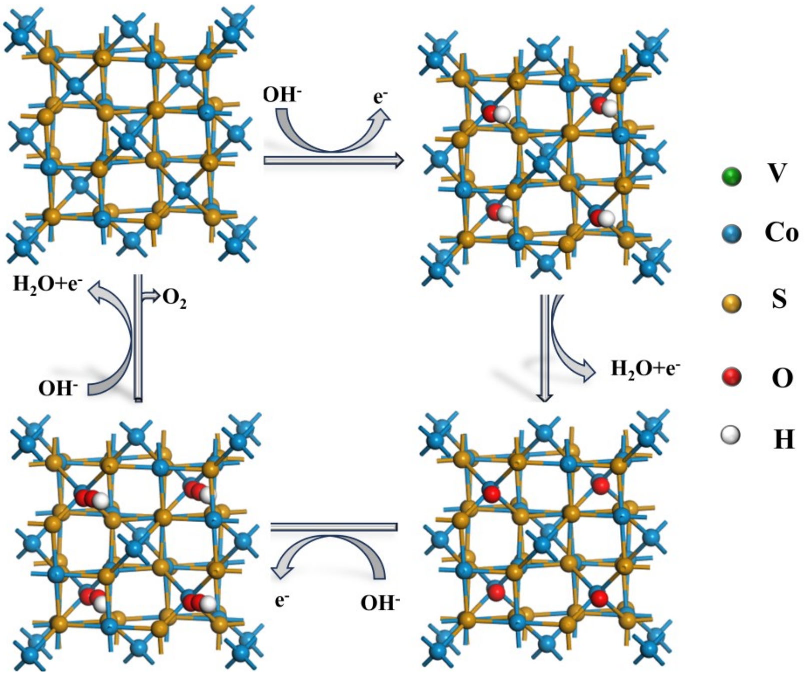

Figure S9. The schematics of mechanism of the OER on CoS.

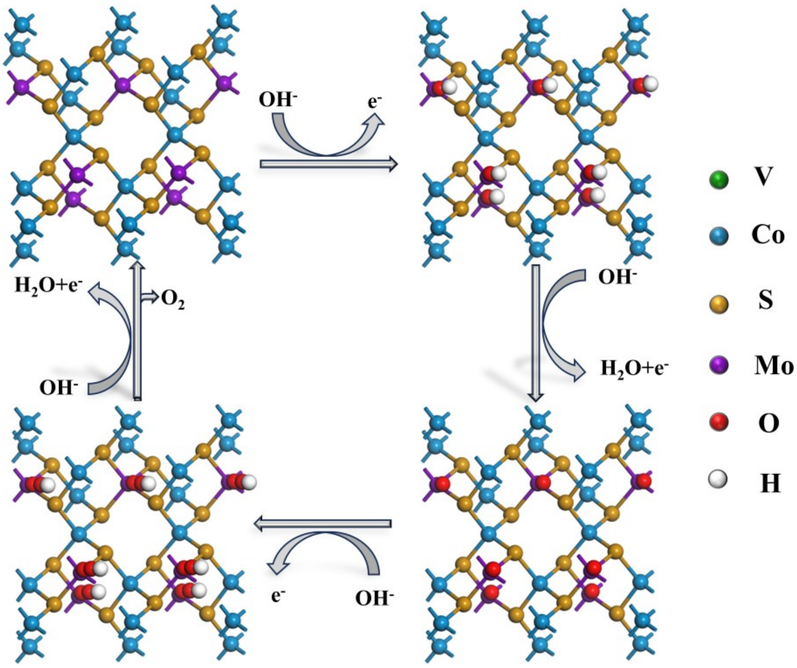

Figure S10. The schematics of mechanism of the OER on MoCoS.

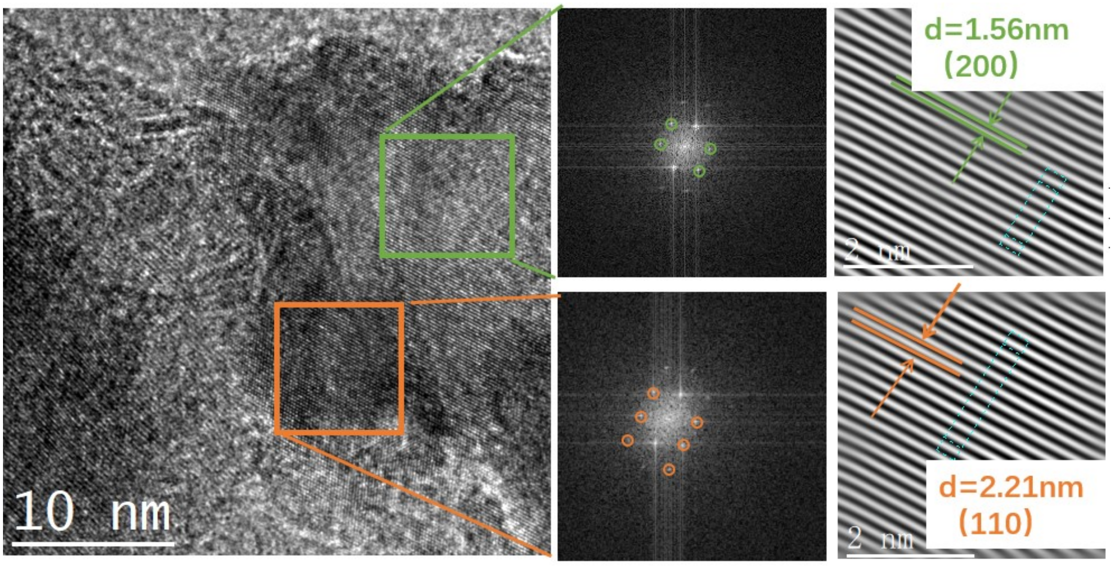

Figure S11. TEM images and IFFT pattern of MoCoS.

Supplementary Note1. For the work function, it was calculated according to the method reported by Liu et al.[3].Through the excitation energy ($h\nu$=21.22 eV) subtracting He I UPS spectrum to estimate the width of ionization potential (the equivalent of valence band energy E_{VB})

$$\Phi = h\nu-(E_{cutoff}-E_{fermi})$$

Supplementary Table 1. Comparison of the reported metal-based electrocatalysts on alkaline HER activity.

Catalyst	Electrolyte	Overpotential at 10 mA cm geo^{-2} / mV	Reference
VCoS	1 M KOH	255	This work
Au@NiCo$_2$S$_4$	1 M KOH	299	4
Mn-doped-NiMoO$_4$/NF	1 M KOH	237	5
N-MoS$_2$/COF-C$_4$N	1 M KOH	239	6
Ni$_{0.5}$Co$_{2.5}$O$_4$	1 M KOH	363	7
M-Co$_3$O$_4$/NPC	1 M KOH	264	8
SSFF@ NiFe LDH	1 M KOH	198	9
PNGF	1 M KOH	278	10
LaNiO$_3$ (LNO)	1 M KOH	288	11
PAN-N/3% Co	1 M KOH	460	12
Hf$_2$B$_2$Ir$_5$	0.1 M H$_2$SO$_4$	287	13
InSnO$_2$N	1 M KOH	450	14

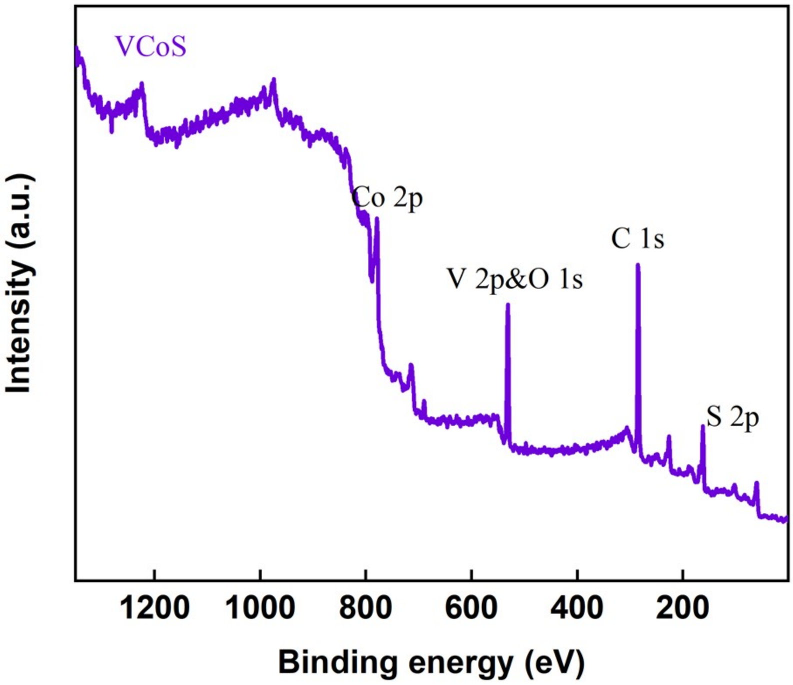

Figure S12. Survey spectra of XPS for VCoS.

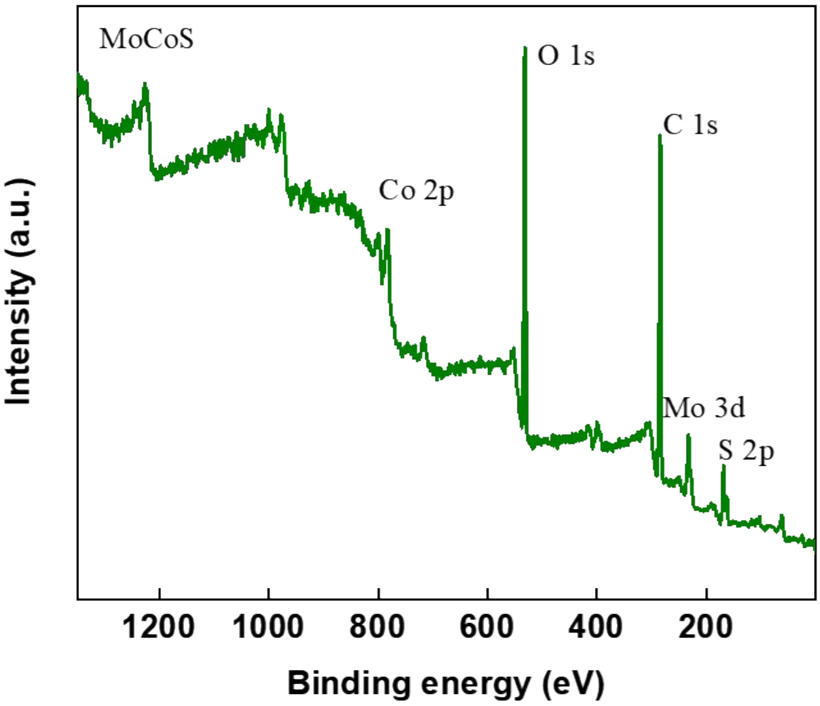

Figure S13 Survey spectra of XPS for MoCoS.

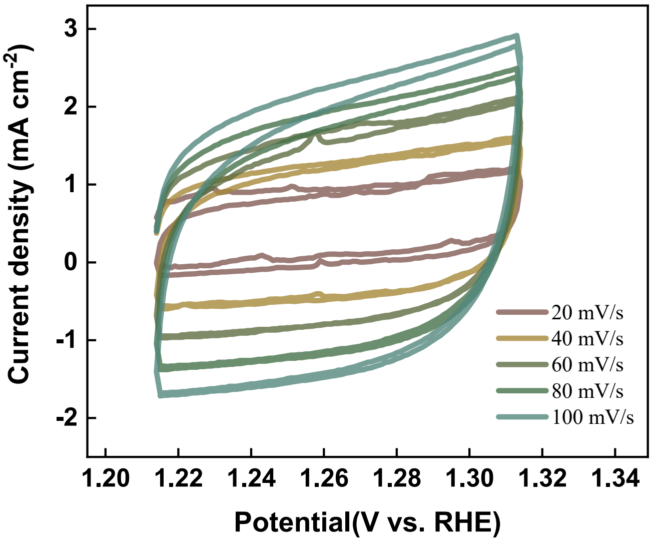

Figure S14. Double layer VCoS CV curves under different scan rate.

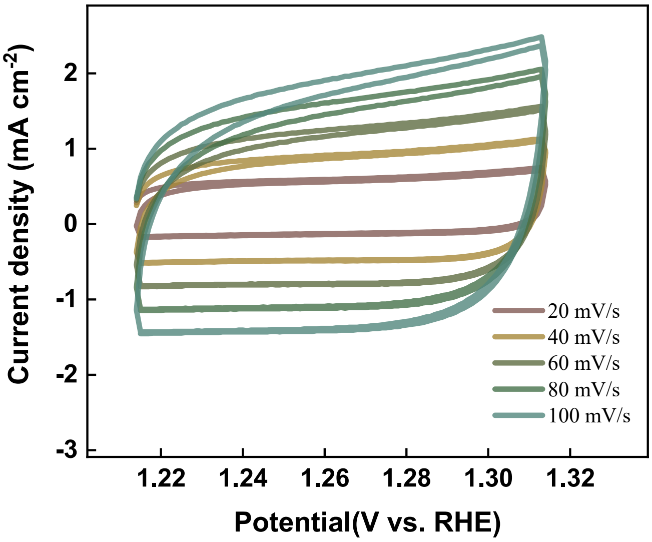

Figure S15. Double layer CoS CV curves under different scan rate.

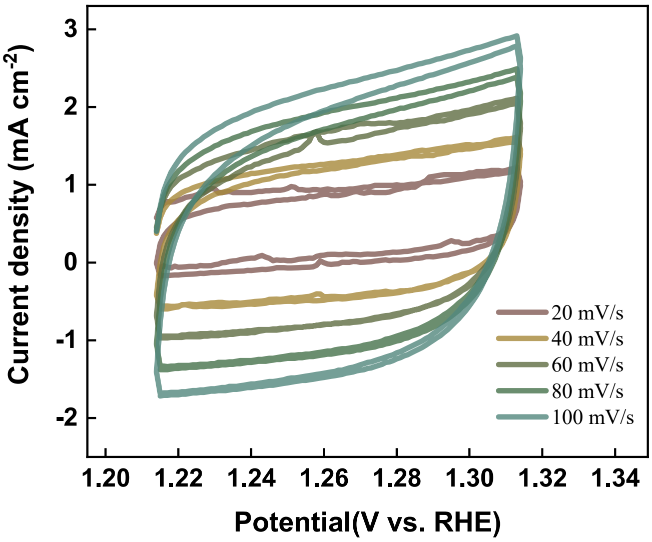

Figure S16. Double layer MoCoS CV curves under different scan rate.

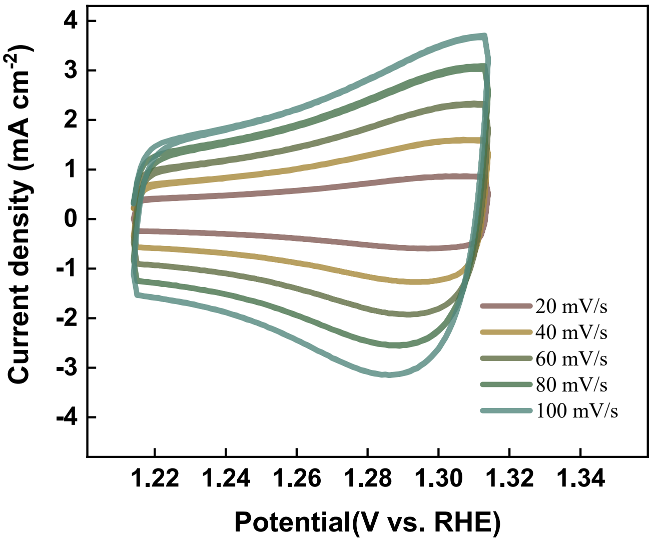

Figure S17. Double layer RuO_2 CV curves under different scan rate.

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