Electronic Supplementary Material (ESI) for ChemComm.
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Electronic Supplementary Information

One-step synthesis of cobalt-doped MoS_2 nanosheets as bifunctional electrocatalysts for overall water splitting under both acidic and alkaline conditions

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Experimental section

Preparation of Co-doped MoS_2 nanosheets (Co-MoS_2): All the chemicals were purchased from Sinopharm and used without further purification. For the synthesis of Co-MoS_2 samples, hexaammonium heptamolybdate tetrahydrate (1.0 mmol, $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$), thiourea (33 mmol, $CS(NH_2)_2$) and cobalt nitrate hexahydrate (0.05 mmol, 0.5 mmol, 1.0 mmol and 3.0 mmol $Co(NO_3)_2\cdot 6H_2O$, respectively) were dissolved in 30 mL of deionized water under vigorous stirring to form a homogeneous solution. Then, the solution was transferred into a 100 mL Teflon-lined stainless steel autoclave, maintained at 220 °C for 18 h, and allowed to cool to room temperature naturally. The final product was washed with water and absolute ethanol for several times and dried at 60 °C under vacuum. The prepared MoS_2 with different Co contents was indicated as Co-MoS_2-x (x represents the addition amount of $Co(NO_3)_2 \cdot 6H_2O$ in reaction precursors, x=0.05, 0.5, 1.0 and 3.0, respectively).

Preparation of pure MoS_2 nanosheets (MoS_2): Typically, hexaammonium heptamolybdate tetrahydrate (1.0 mmol, $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$) and thiourea (30 mmol, $CS(NH_2)_2$) were dissolved in 30 mL of deionized water under vigorous stirring to form a homogeneous solution. Then, the solution was transferred into a 100 mL Teflon-lined stainless steel autoclave and maintained at 220 °C for 18 h. The reaction system was allowed to cool to room temperature. The final product was washed with water and absolute ethanol for several times, and then dried at 60 °C under vacuum to collect for further use.

Characterizations

The crystalline structures of samples were identified by X-ray diffraction analysis (XRD, Philips X'pert PRO) using Nifiltered monochromatic CuKa radiation ($\lambda K\alpha 1$ = 1.5418 Å) at 40 kV and 40 mA. Raman spectra were carried out on a confocal microscope Raman system (LabRAMHR800, Horiba Jobin Yvon, Japan) using an Ar ion laser operating at 532 nm. The morphology and structure of samples were characterized by field emission scanning electron microscopy (FESEM, Hitachi SU8020) and transmission electron microscopy (TEM, JEOL 2010) with an energy dispersive X-ray spectrometer (EDS Oxford, Link ISIS). X-ray photoelectron spectroscopy (XPS) analysis was performed on an ESCALAB 250 X-ray photoelectron spectrometer (Thermo, America) equipped with Al Kα1, 2 monochromatized radiation at 1486.6 eV X-ray source. The extended X-ray absorption fine structure (EXAFS) spectra of samples were measured at the 1W1B beamline of Beijing Synchrotron Radiation Facility (BSRF). The Co and Mo contents in samples were determined using inductively coupled plasma atomic emission spectrometer (ICP-AES, ICP-6300, Thermo Fisher Scientific).

Electrochemical measurements

Electrochemical measurements were performed on an electrochemical workstation (CHI 760D, CH Instruments, Inc., Shanghai, China). A standard three-electrode electrochemical cell equipped with gas flow system was employed during measurements. The Co-MoS_2 catalyst inks were prepared by dispersing catalyst powder (4.0 mg) into a mixture including 10 μL of Nafion solution (0.5 wt. %) and 490 μL of ethanol, followed by ultrasonic treatment for 10 min to form a homogeneous ink. After that, 250 μL of catalyst ink was dropped on carbon fiber paper (1.0×1.0 cm^2) surface and completely dried at room temperature. For comparison, commercial Pt/C, RuO_2 and pure MoS_2 catalyst inks were also made as the same procedure as Co-MoS_2 catalyst ink. Linear sweep voltammetry and chronoamperometry with a scan rate of 5.0 mV s^{-1} were conducted in 0.5 M H_2SO_4 and 1.0 M KOH (purged with pure N_2) using Ag/AgCl (3 M KCl) and Hg/HgO as the reference electrode, respectively, carbon cloth as the counter electrode, and the carbon fiber paper with various catalysts as the working electrode. The electrochemical impedance spectroscopy (EIS) measurements were performed by applying an AC voltage with 5.0 mV amplitude in a frequency range from 10^6 to 0.1 Hz and recorded at -0.3 V (*vs*. Ag/AgCl) in 0.5 M H_2SO_4 and -0.35 V (*vs*. Hg/HgO) in 1.0 M KOH. All the potentials were calibrated to a reversible hydrogen electrode (RHE) based on following equations:

$$\boldsymbol{E}\ (vs.\ \mathrm{RHE}) = \boldsymbol{E}\ (vs.\ \mathrm{Ag/AgCl}) + 0.059\times\mathrm{pH} + 0.1976\ \mathrm{V} \qquad (1)$$

$$\boldsymbol{E}\ (vs.\ \mathrm{RHE}) = \boldsymbol{E}\ (vs.\ \mathrm{Hg/HgO}) + 0.059\times\mathrm{pH} + 0.0977\ \mathrm{V} \qquad (2)$$

Theoretical calculations

All density functional theory (DFT) computations were performed using the Vienna *ab initio* simulation package (VASP) based on the projector augmented wave (PAW) method.[1,2] Electron-ion interactions were described using standard PAW potentials, with valence configurations of $4s^24p^65s^24d^4$ for Mo (Mo_sv_GW), $3s^23p^4$ for S (S_GW), and $2s^22p^4$ for O (O_GW_new), and $1s^1$ for H (H_new) and $2s^22p^2$ for C (C_GW_new). A plane-wave basis set was employed to expand the smooth part of wave functions with a cut-off kinetic energy of 520 eV. For the electron-electron exchange and correlation interactions, the functional parameterized by Perdew-Burke-Ernzerhhof (PBE),[3] a form of the general gradient approximation (GGA), was used throughout. 2H-MoS_2 crystal was modelled with the primary unit cell including 2 Mo atoms and 4 S atoms. Before the analysis of electronic properties, the geometry was optimized. All the atoms were allowed to relax until the Hellmann-Feynman forces were smaller than 0.01eV/Å. The convergence criterion for the electronic self-consistent loop was set to 1×10^{-5} eV. The Co-doped MoS_2 slab was modelled using a (3×3) surface using one Co atom to replace one Mo atom. As such, the molar ratio of Co to Mo here is 1:8. The Gibbs free energy ($\Delta G_{\mathrm{H}*}$) was calculated by the formula:

$$\Delta G_{H*} = \Delta E_{H*} + \Delta ZPE - T\Delta S$$

where ΔE_{H*}, ΔZPE and ΔS are the binding energy, zero point energy change and entropy change of H adsorption, respectively. Herein, the $T\Delta S$ and ΔZPE are obtained by following the scheme proposed by Nørskov *et al.*[4]

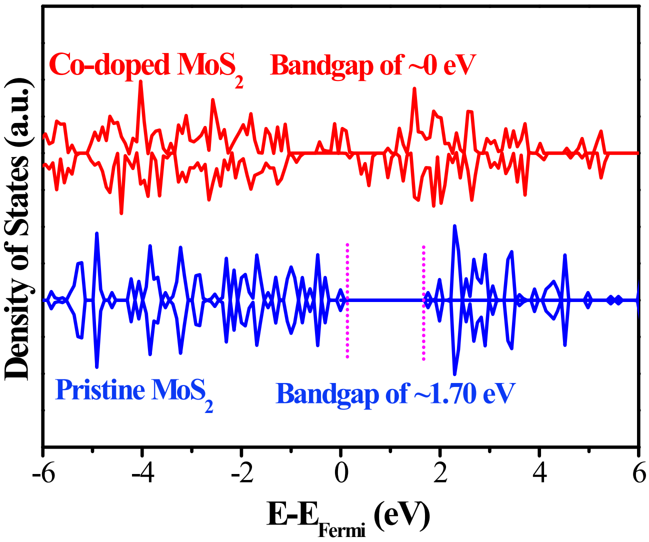

Fig. S1 The calculated density of states (DOS) of the pristine MoS_2 and Co covalently doped MoS_2.

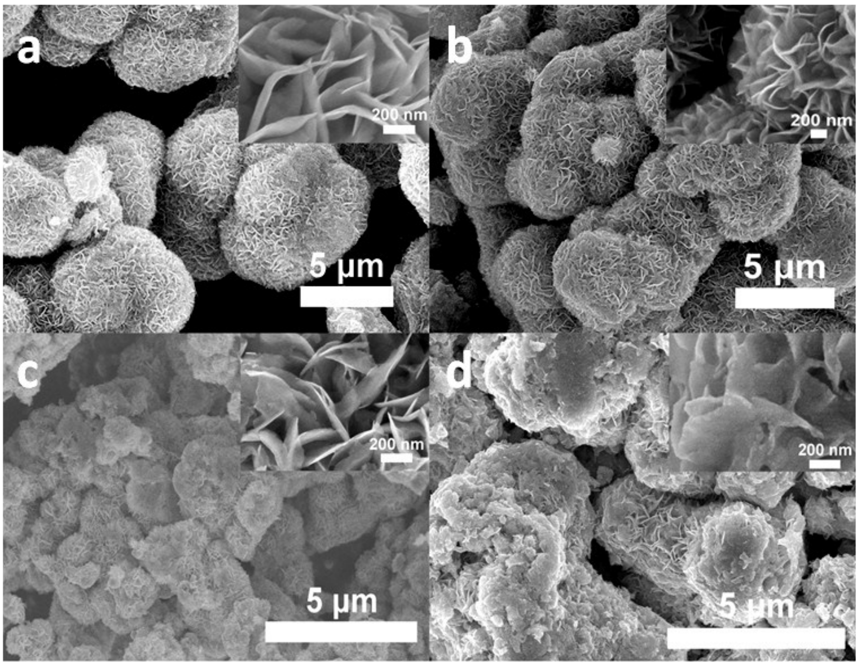

Fig. S2 SEM images of (a) MoS_2, (b) Co-MoS_2-0.05, (c) Co-MoS_2-1.0 and (d) Co-MoS_2-3.0 samples.

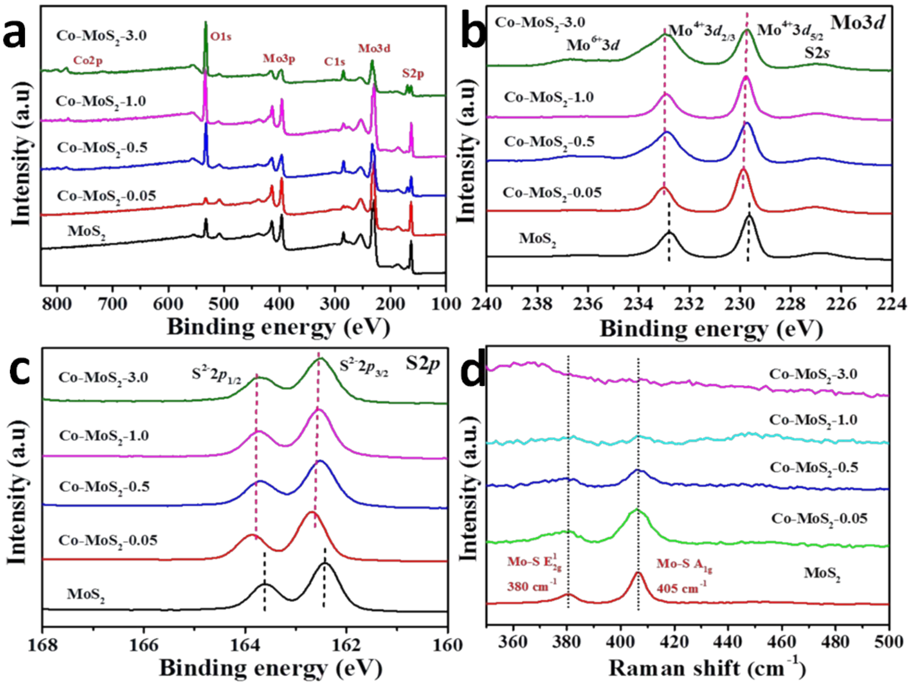

Fig. S3 (a) XPS survey spectra, (b) High resolution Mo 3*d* XPS spectrum, (c) High resolution S 2*p* XPS spectrum and (d) Raman spectra of MoS_2, Co-MoS_2-0.05, Co-MoS_2-0.5, Co-MoS_2-1.0 and Co-MoS_2-3.0 samples.

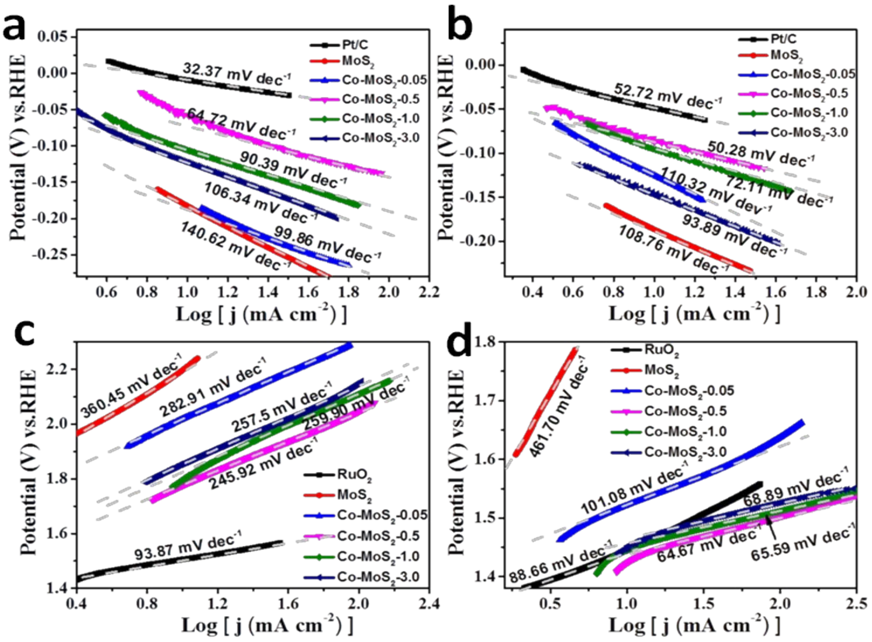

Fig. S4 (a) Tafel plots in 0.5 M H_2SO_4 solution. (b) Tafel plots in 1.0 M KOH solution. The samples of Pt/C, MoS_2, Co-MoS_2-0.05, Co-MoS_2-0.5, Co-MoS_2-1.0 and Co-MoS_2-3.0 for HER. (c) Tafel plots in 0.5 M H_2SO_4 solution. (d) Tafel plots in 1.0 M KOH solution. The samples of RuO_2, MoS_2, Co-MoS_2-0.05, Co-MoS_2-0.5, Co-MoS_2-1.0 and Co-MoS_2-3.0 for OER.

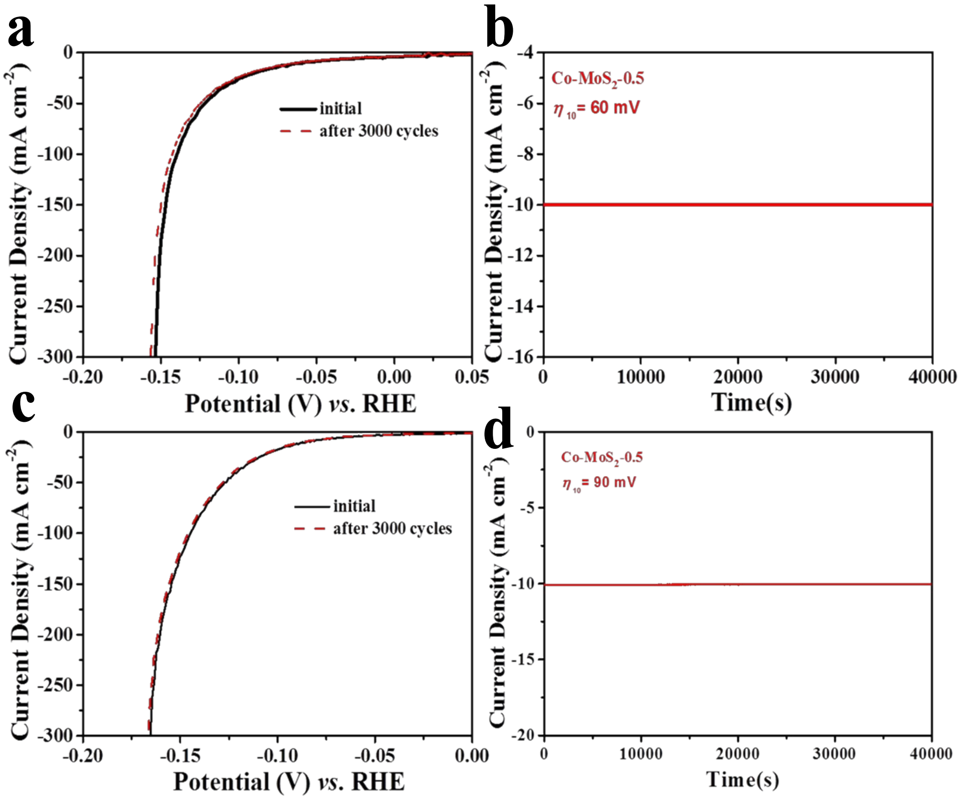

Fig. S5 (a) LSV curves of Co-MoS_2-0.5 before and after 3000 CV cycles at 10 mV s^{-1} and (b) Durability test of Co-MoS_2-0.5 at an overpotential of 60 mV for HER in 0.5 M H_2SO_4 solution. (c) LSV curves of Co-MoS_2-0.5 before and after 3000 CV cycles at 10 mV s^{-1} and (d) Durability test of Co-MoS_2-0.5 at an overpotential of 90 mV for HER in 1.0 M KOH solution.

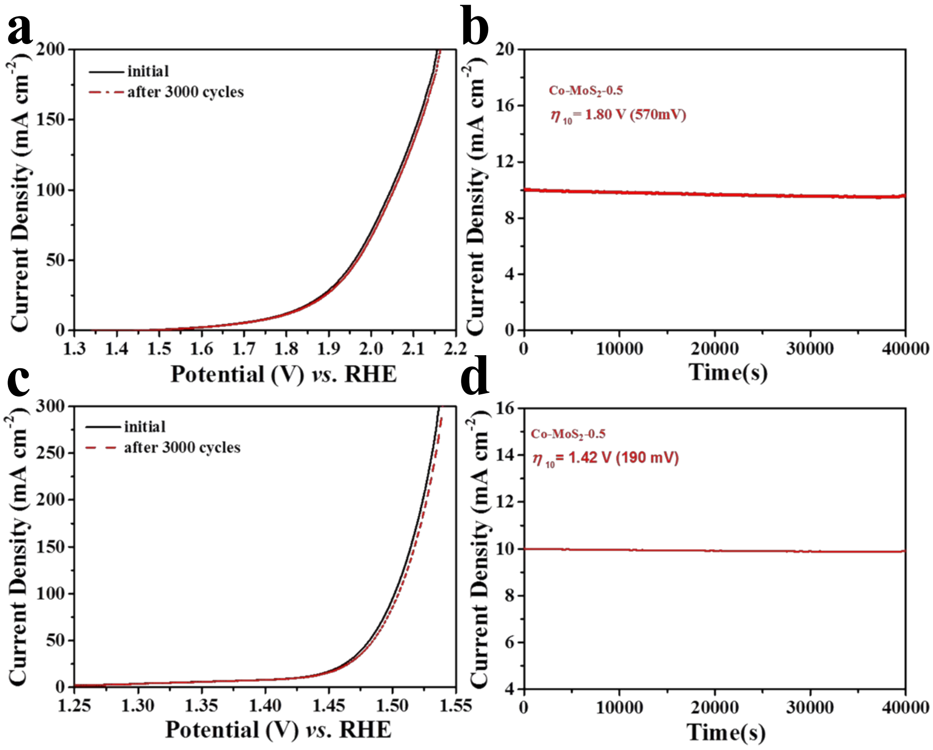

Fig. S6 (a) LSV curves of Co-MoS$_2$-0.5 before and after 3000 CV cycles at 10 mV s^{-1} and (b) Durability test of Co-MoS$_2$-0.5 at an overpotential of 570 mV for OER in 0.5 M H_2SO_4 solution. (c) LSV curves of Co-MoS$_2$-0.5 before and after 3000 CV cycles at 10 mV s^{-1} and (d) Durability test of Co-MoS$_2$-0.5 at an overpotential of 190 mV for OER in 1.0 M KOH solution.

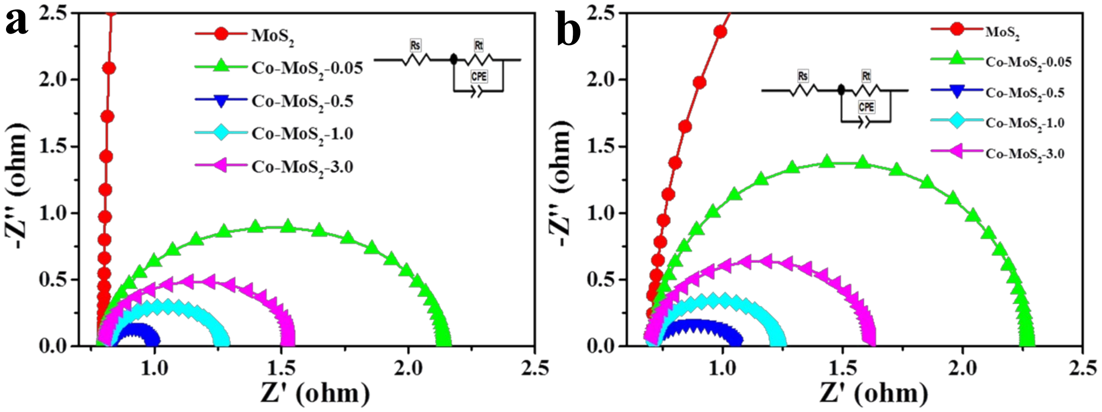

Fig. S7 The electrochemical impedance spectra (EIS) of MoS$_2$, Co-MoS$_2$-0.05, Co-MoS$_2$-0.5, Co-MoS$_2$-1.0 and Co-MoS$_2$-3.0 samples in (a) 0.5 M H_2SO_4 and (b) 1.0 M KOH solution.

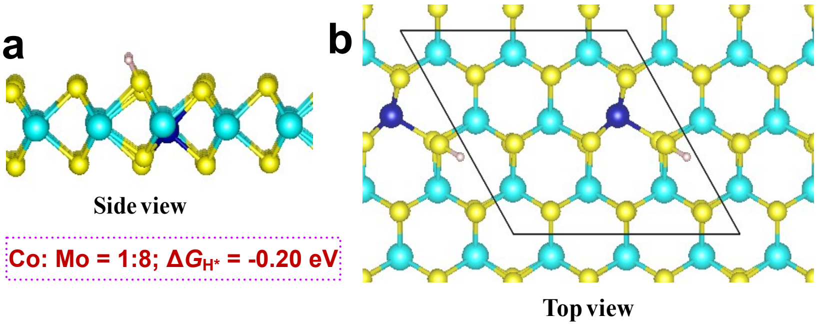

Fig. S8 The side view (a) and top view (b) of the optimized H adsorption configuration of Co-doped MoS$_2$. Green balls: Mo; yellow balls: S; blue balls: Co; pink balls: H.

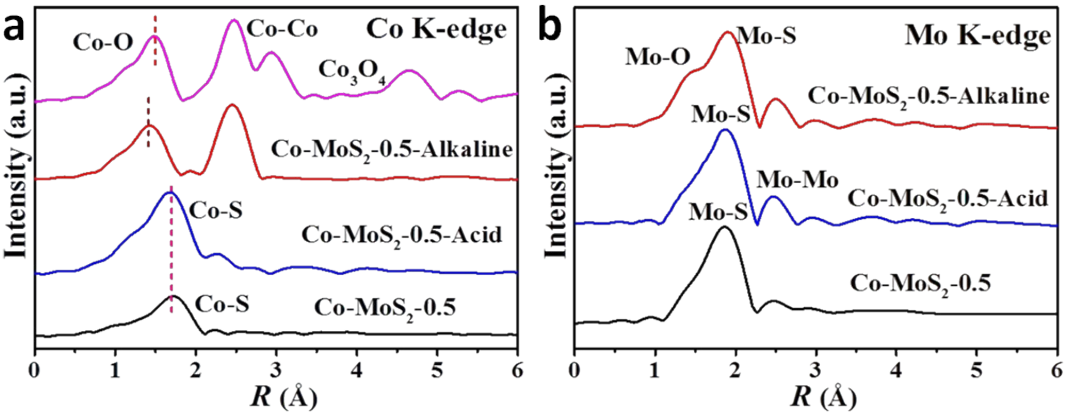

Fig. S9 (a) The Co K-edge k^2-weighted EXAFS spectra of Co_3O_4 for comparison and Co-MoS_2-0.5 before and after OER measurements in 0.5 M H_2SO_4 and 1.0 M KOH. (b) The Mo K-edge k^2-weighted EXAFS spectra of Co-MoS_2-0.5 before and after OER measurements in 0.5 M H_2SO_4 and 1.0 M KOH.

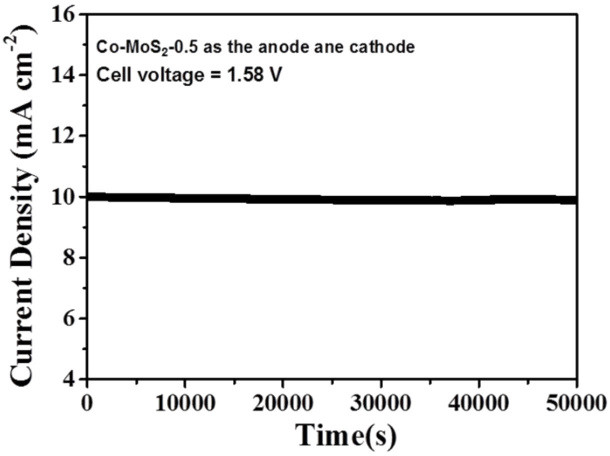

Fig. S10 Durability test of the overall water splitting in a two electrode system with Co-MoS_2-0.5 catalyst as cathode and anode.

Table S1 The Co and Mo contents and molar ratio of Mo to Co in samples obtained by ICP analysis.

Sample	Mo (at.%)	Co (at.%)	Mo/Co	$Co(NO_3)_2/(NH_4)_6Mo_7O_{24}$
MoS_2	15.29	/	/	/
Co-MoS_2-0.05	14.89	0.11	135.36	0.05
Co-MoS_2-0.5	13.59	0.97	14.01	0.50
Co-MoS_2-1.0	12.66	1.91	6.63	1.06
Co-MoS_2-3.0	12.03	4.86	2.48	2.83

Table S2 The element content (at.%) and Mo/S ratio of various electrocatalysts obtained by XPS analysis.

Sample	C	S	Mo	O	Co	Mo/S
MoS_2	26.36	35.54	19.73	17.97	/	0.55
Co-MoS_2-0.05	12.73	49.17	26.94	10.5	0.66	0.54
Co-MoS_2-0.5	25.97	24.16	13.66	35.03	1.19	0.56
Co-MoS_2-1.0	18.74	43.21	22.99	13.35	1.71	0.53
Co-MoS_2-3.0	18.84	28.1	8.99	41.7	2.37	0.32

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