

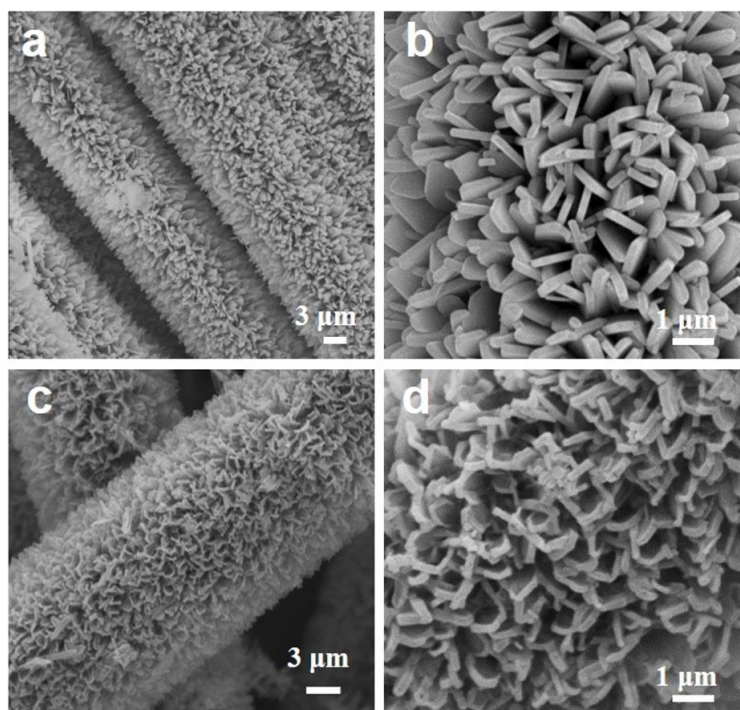
## Electronic Supplemental Information

### Surface Oxidation Protection Strategy of $\text{CoS}_2$ by $\text{V}_2\text{O}_5$ for Electrocatalytic Hydrogen Evolution Reaction

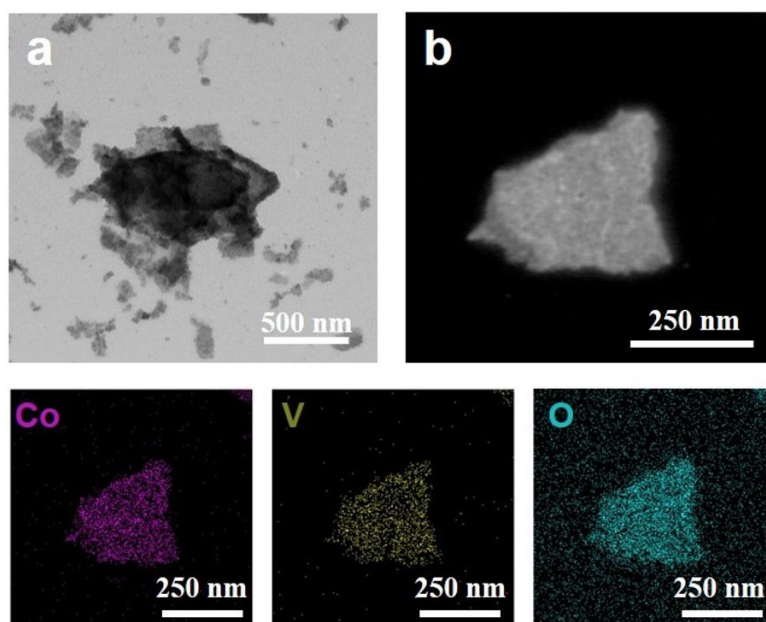
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Dedicated to the 120th anniversary of Southeast University

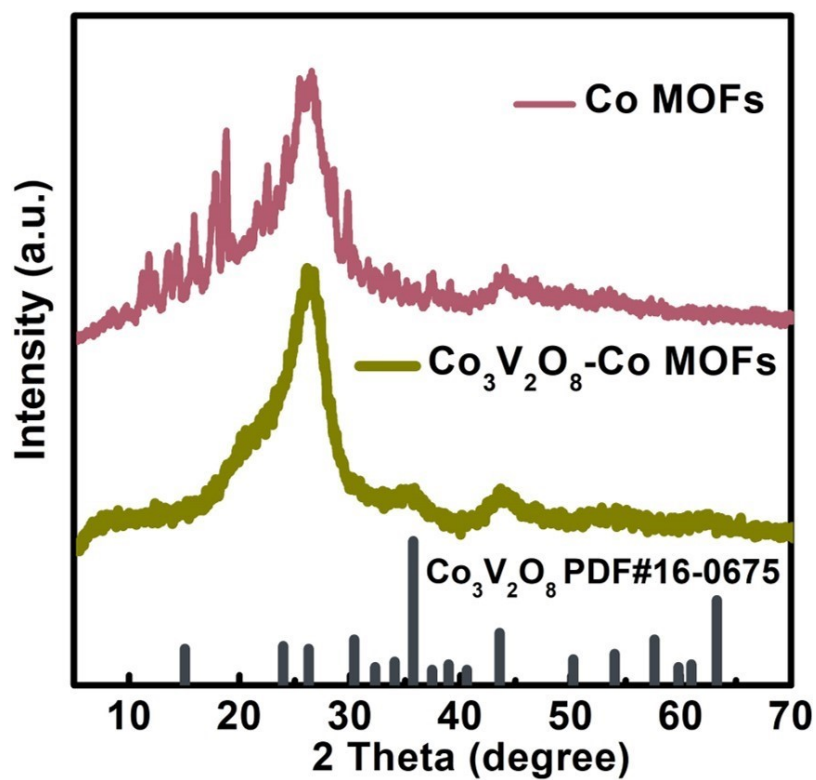
### Additional Figures



**Fig. S1** SEM images of a, b) Co MOFs, and c, d)  $\text{Co}_3\text{V}_2\text{O}_8$ -Co MOFs.



**Fig. S2** a) TEM image of  $\text{Co}_3\text{V}_2\text{O}_8\text{-Co}$  MOFs, b) STEM image of  $\text{Co}_3\text{V}_2\text{O}_8\text{-Co}$  MOFs and the corresponding elemental mappings of Co, V and O.



**Fig. S3** XRD patterns of Co MOFs and  $\text{Co}_3\text{V}_2\text{O}_8\text{-Co}$  MOFs.

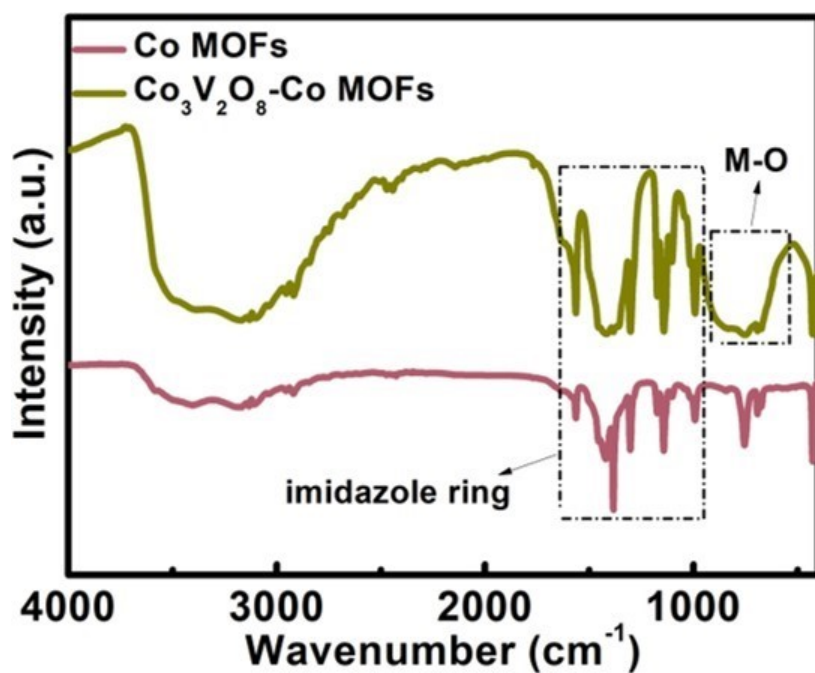


Fig. S4 FT-IR spectra of Co MOFs and  $\text{Co}_3\text{V}_2\text{O}_8$ -Co MOFs.

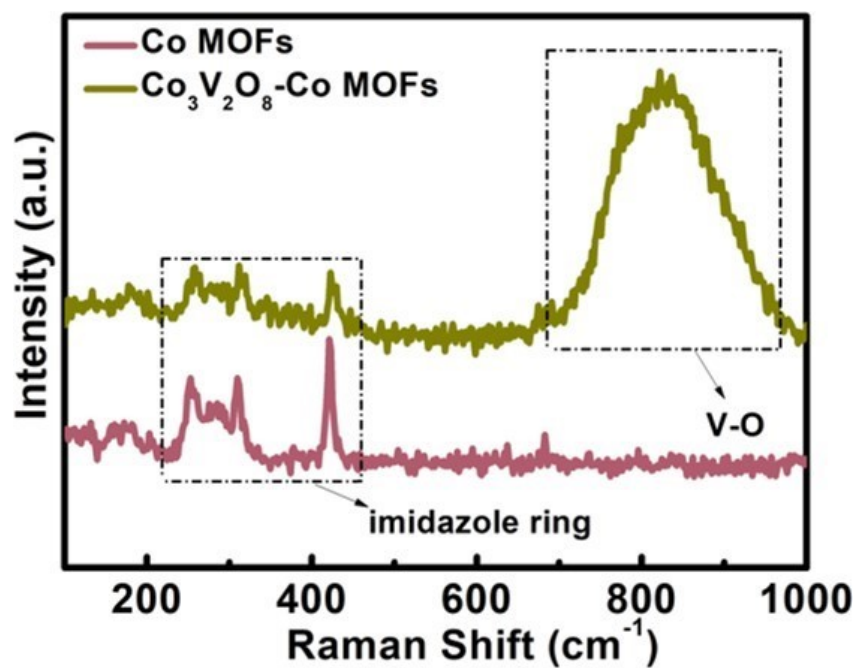


Fig. S5 Raman spectra of Co MOFs and  $\text{Co}_3\text{V}_2\text{O}_8$ -Co MOFs.

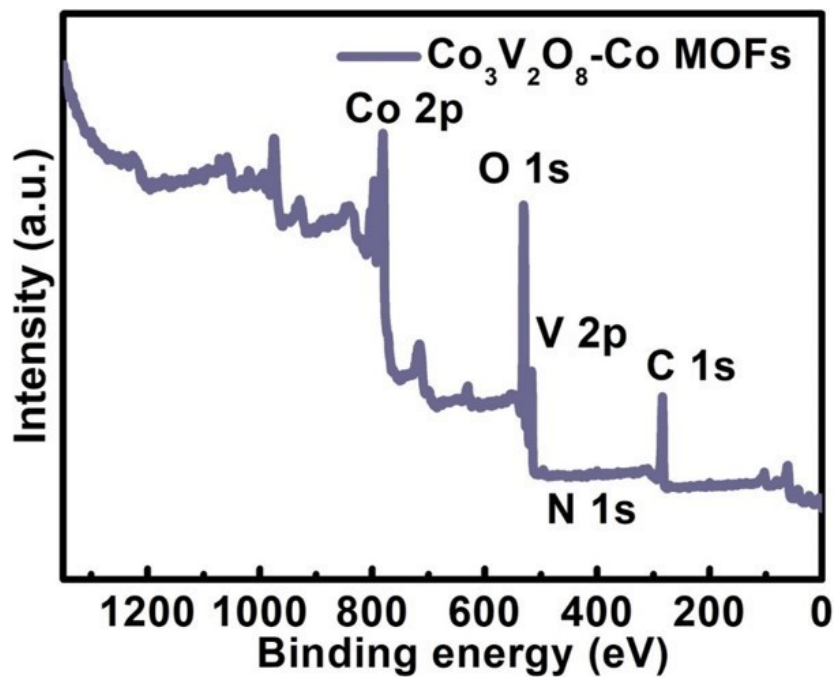


Fig. S6 Survey XPS spectrum of  $\text{Co}_3\text{V}_2\text{O}_8\text{-Co MOFs}$ .

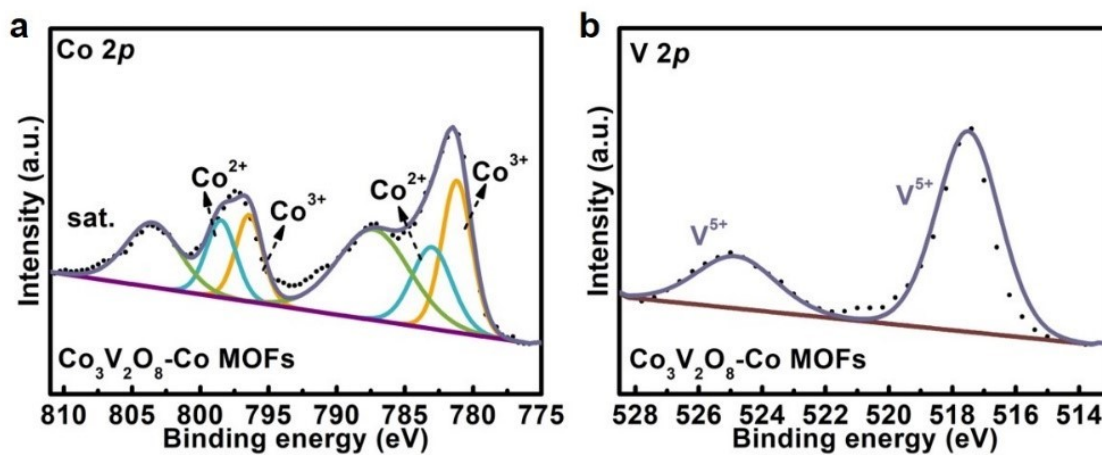


Fig. S7 a)  $\text{Co } 2p$  XPS spectrum, b)  $\text{V } 2p$  XPS spectrum of  $\text{Co}_3\text{V}_2\text{O}_8\text{-Co MOFs}$ .

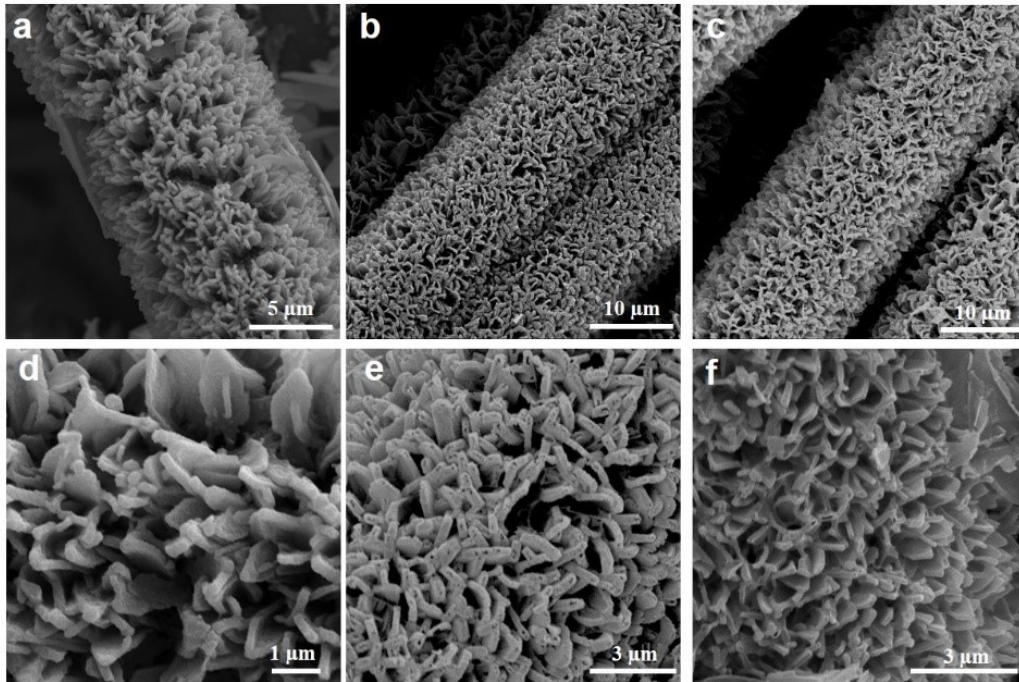


Fig. S8 SEM images of a, d)  $\text{CoS}_2$ , b, e)  $\text{CoS}_2\text{-V}_2\text{O}_5\text{-Ox-1h}$ , c, f)  $\text{CoS}_2\text{-V}_2\text{O}_5\text{-Ox-3h}$ .

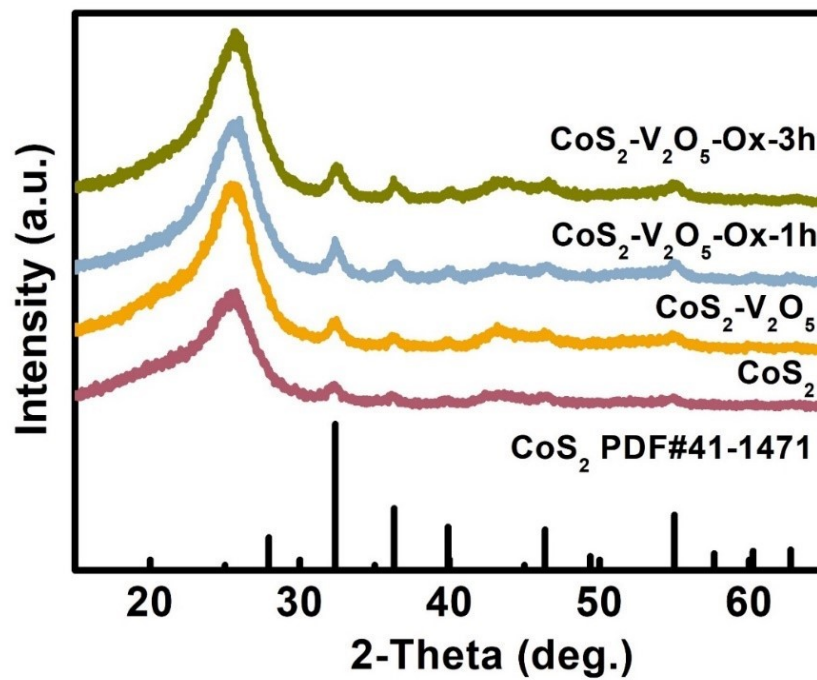
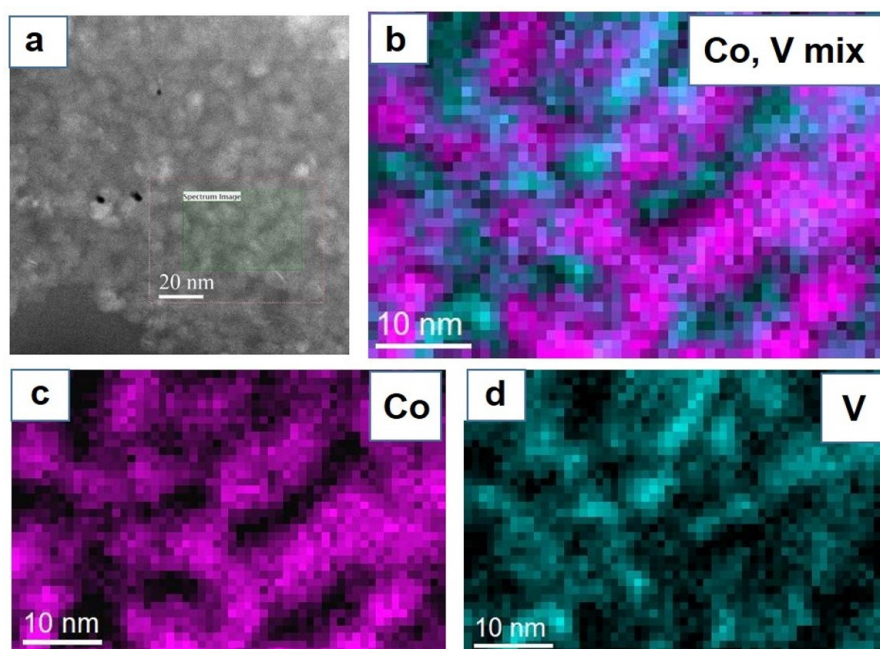
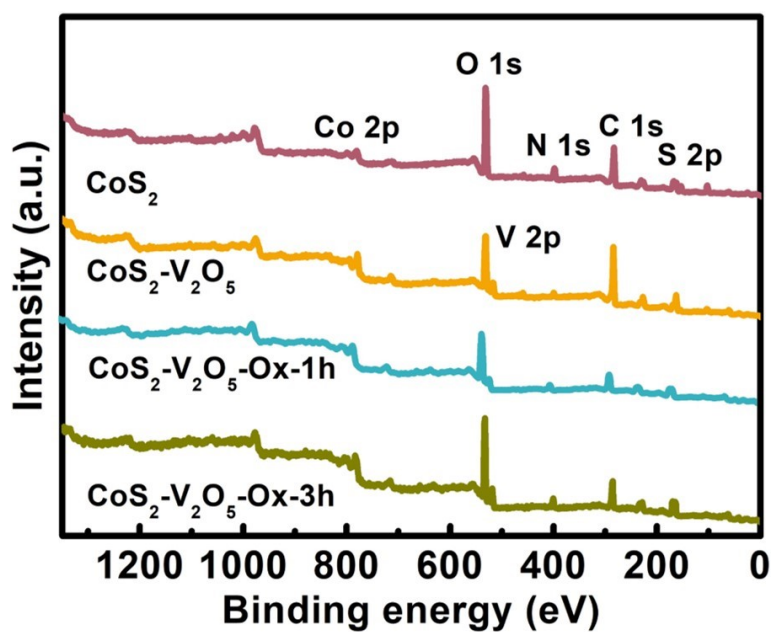


Fig. S9 XRD patterns of  $\text{CoS}_2$ ,  $\text{CoS}_2\text{-V}_2\text{O}_5$ ,  $\text{CoS}_2\text{-V}_2\text{O}_5\text{-Ox-1h}$  and  $\text{CoS}_2\text{-V}_2\text{O}_5\text{-Ox-3h}$ .





**Fig. S10** a) the low magnification STEM image of  $\text{CoS}_2\text{-V}_2\text{O}_5$ , b) cobalt and vanadium colormix mapping, c) cobalt mapping and d) vanadium mapping.



**Fig. S11** Survey XPS spectra of  $\text{CoS}_2$ ,  $\text{CoS}_2\text{-V}_2\text{O}_5$ ,  $\text{CoS}_2\text{-V}_2\text{O}_5\text{-Ox-1h}$  and  $\text{CoS}_2\text{-V}_2\text{O}_5\text{-Ox-3h}$ .

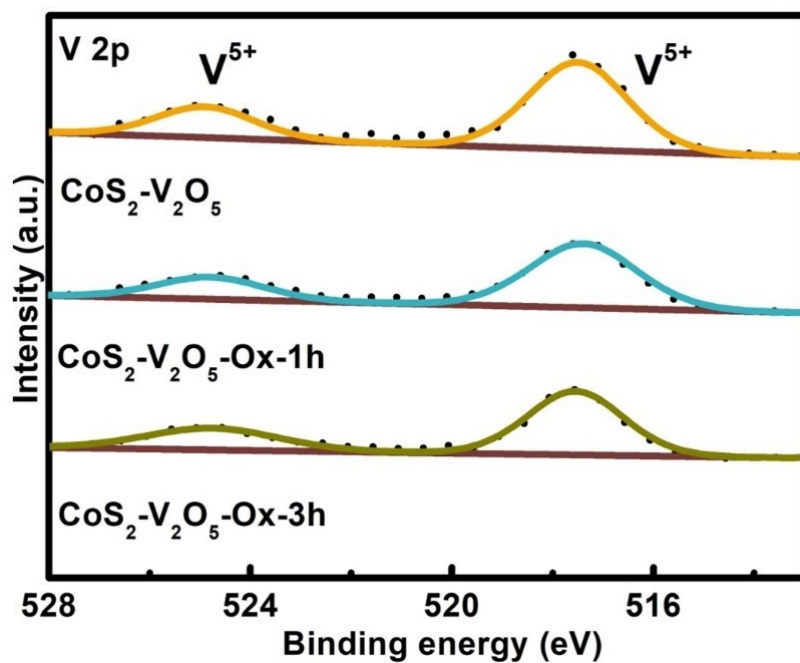


Fig. S12 V 2p XPS spectra of  $\text{CoS}_2\text{-V}_2\text{O}_5$ ,  $\text{CoS}_2\text{-V}_2\text{O}_5\text{-Ox-1h}$  and  $\text{CoS}_2\text{-V}_2\text{O}_5\text{-Ox-3h}$ .

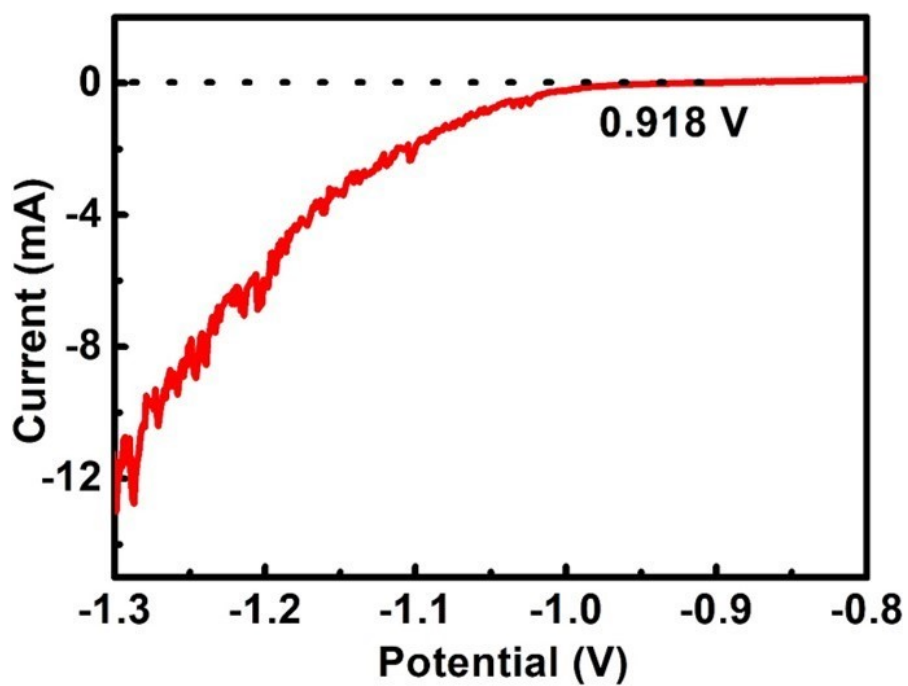


Fig. S13 Calibration LSV curve of the reference electrode (Hg/HgO) in 1 M KOH solution under room temperature.

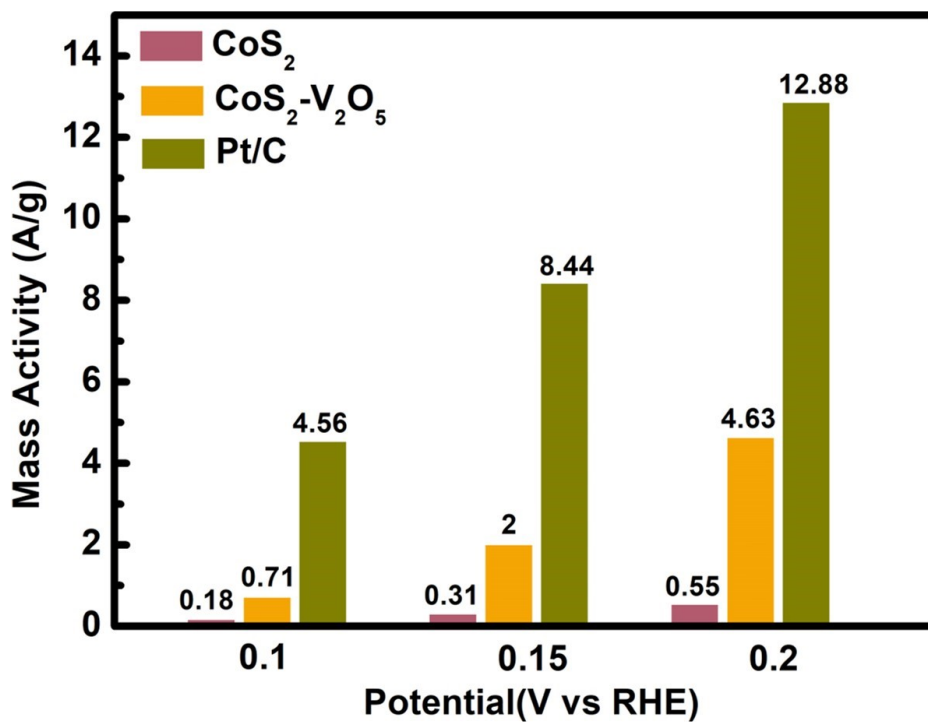


Fig. S14 Mass activity of CoS<sub>2</sub>, CoS<sub>2</sub>-V<sub>2</sub>O<sub>5</sub> and Pt/C.

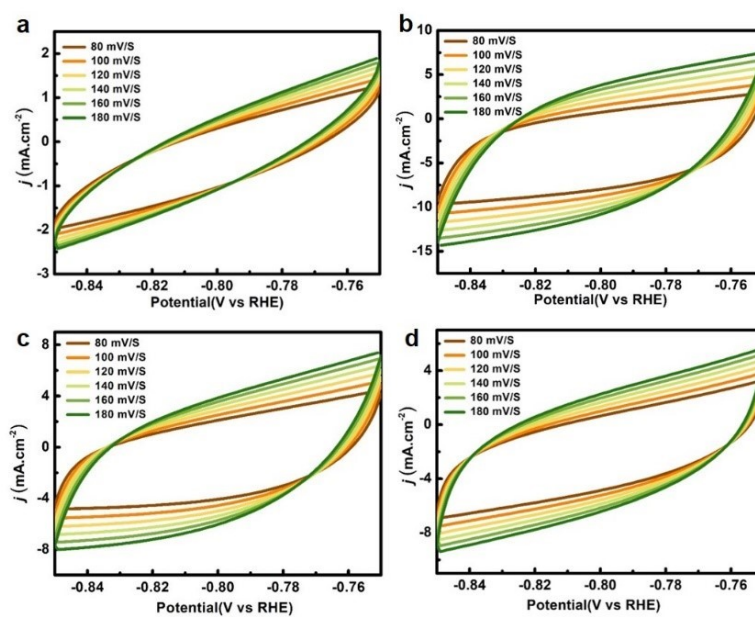


Fig. S15 CV curves of a) CoS<sub>2</sub>, b) CoS<sub>2</sub>-V<sub>2</sub>O<sub>5</sub>, c) CoS<sub>2</sub>-V<sub>2</sub>O<sub>5</sub>-Ox-1h and d) CoS<sub>2</sub>-V<sub>2</sub>O<sub>5</sub>-Ox-3h under different scan rates in the region from -0.85 V (vs. RHE) to -0.75 V (vs. RHE).



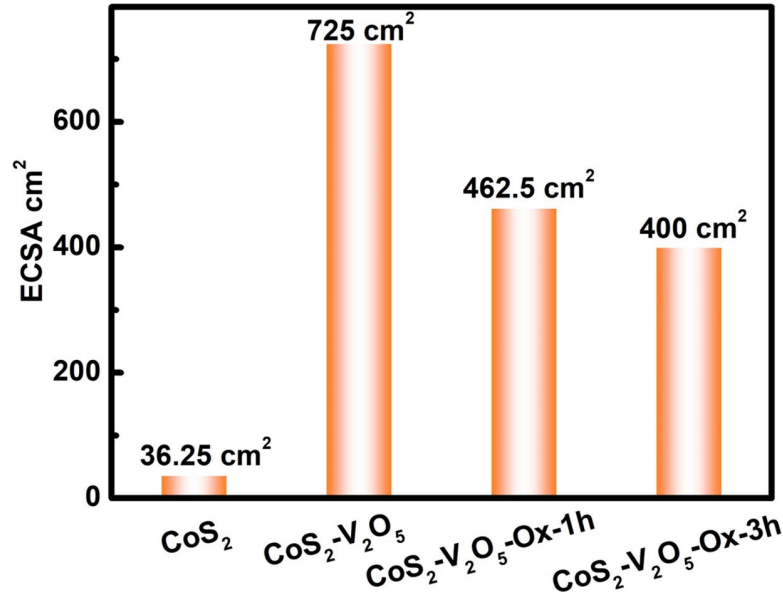


Fig. S16 Comparison of the ECSA for CoS<sub>2</sub>, CoS<sub>2</sub>-V<sub>2</sub>O<sub>5</sub>, CoS<sub>2</sub>-V<sub>2</sub>O<sub>5</sub>-Ox-1h and CoS<sub>2</sub>-V<sub>2</sub>O<sub>5</sub>-Ox-3h.

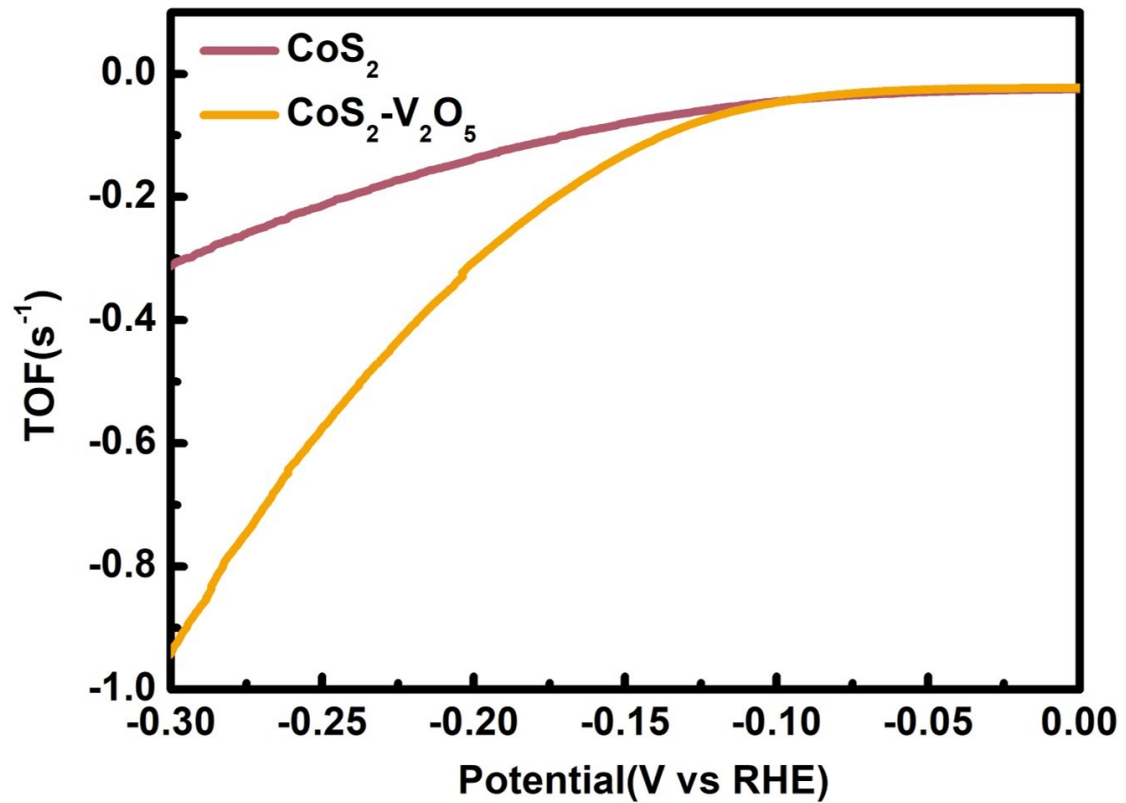
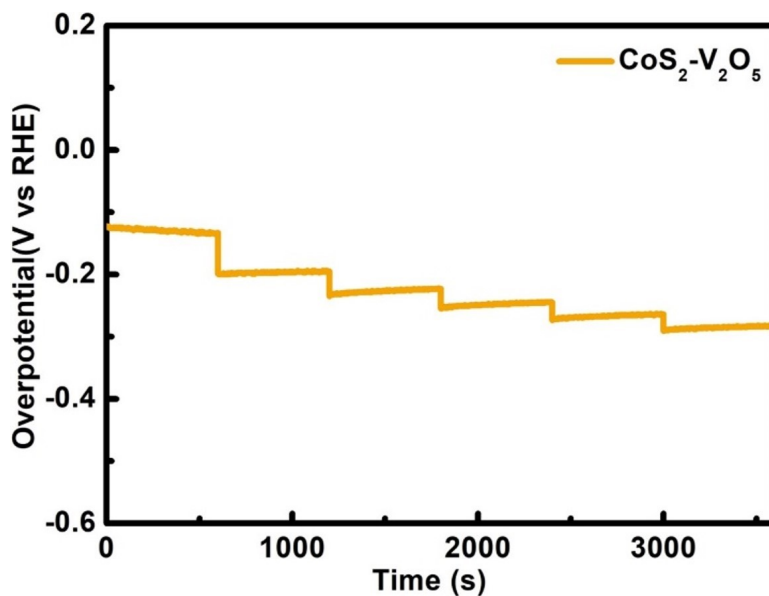
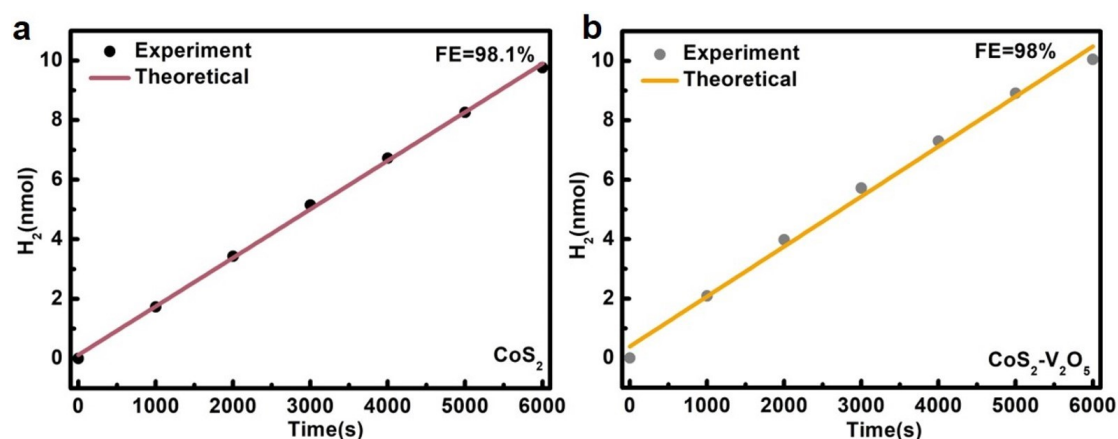


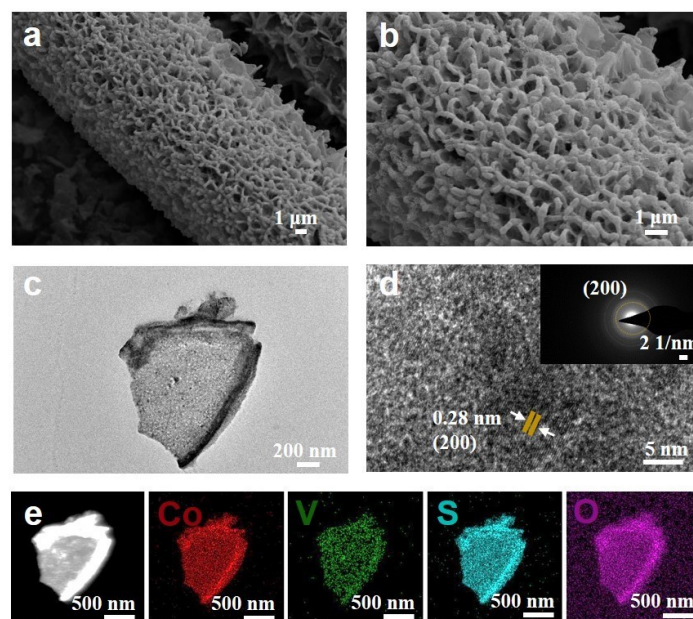
Fig. S17 TOF curves of CoS<sub>2</sub> and CoS<sub>2</sub>-V<sub>2</sub>O<sub>5</sub>.



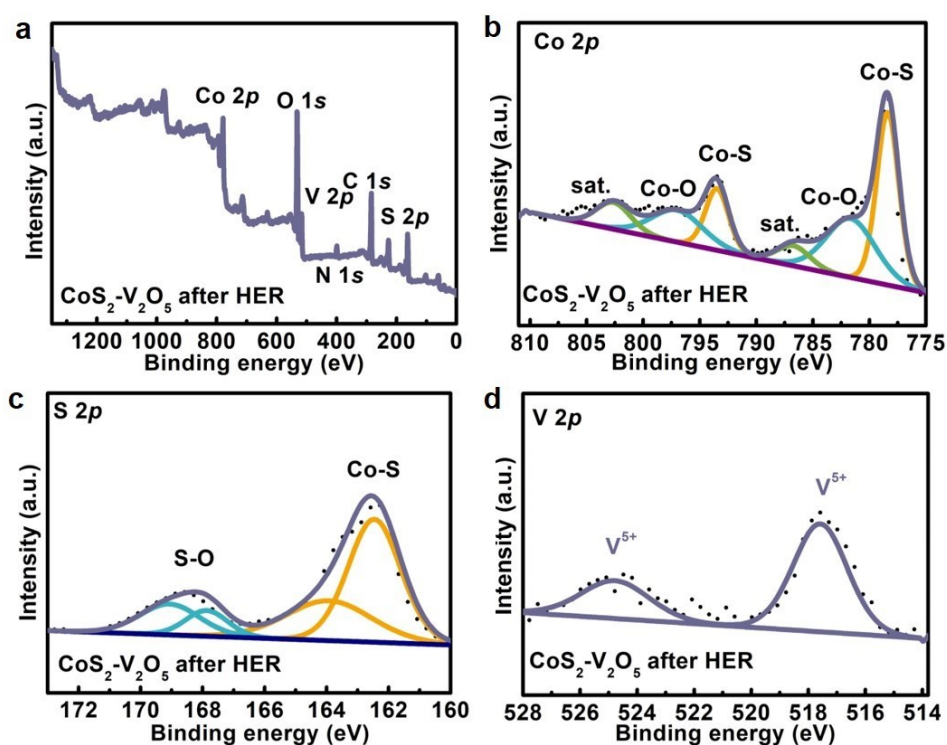
**Fig. S18** The multi-current process obtained with  $\text{CoS}_2\text{-V}_2\text{O}_5$  electrode without  $iR$ -correction. The current density started at  $10 \text{ mA cm}^{-2}$  and finished at  $60 \text{ mA cm}^{-2}$ , with an increment of  $10 \text{ mA cm}^{-2}$  after every 600 s.



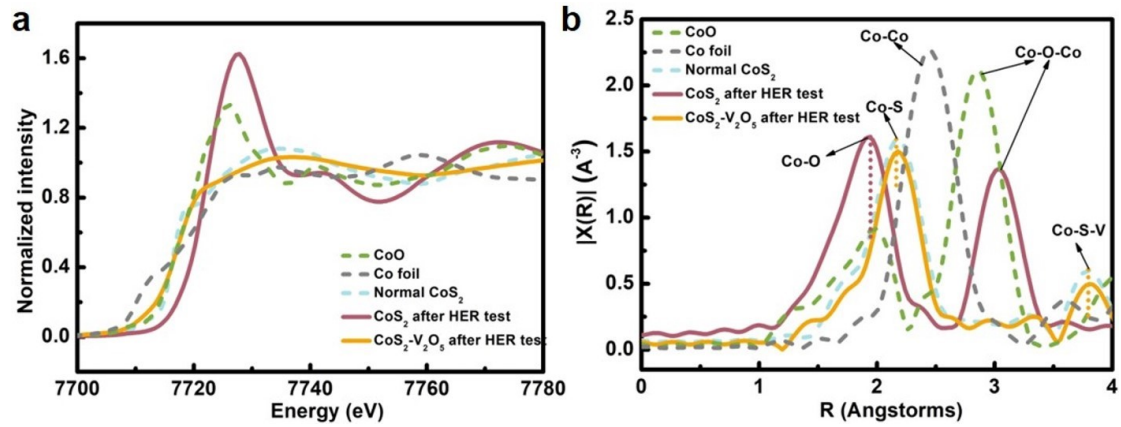
**Fig. S19** Faradaic efficiency of a)  $\text{CoS}_2$  and b)  $\text{CoS}_2\text{-V}_2\text{O}_5$ , the theoretical and experimental  $\text{H}_2$  evolution amount were obtained by electrocatalysis with  $\text{CoS}_2$  and  $\text{CoS}_2\text{-V}_2\text{O}_5$  at a cathodic current density of  $10 \text{ mA cm}^{-2}$  for 6000 s.



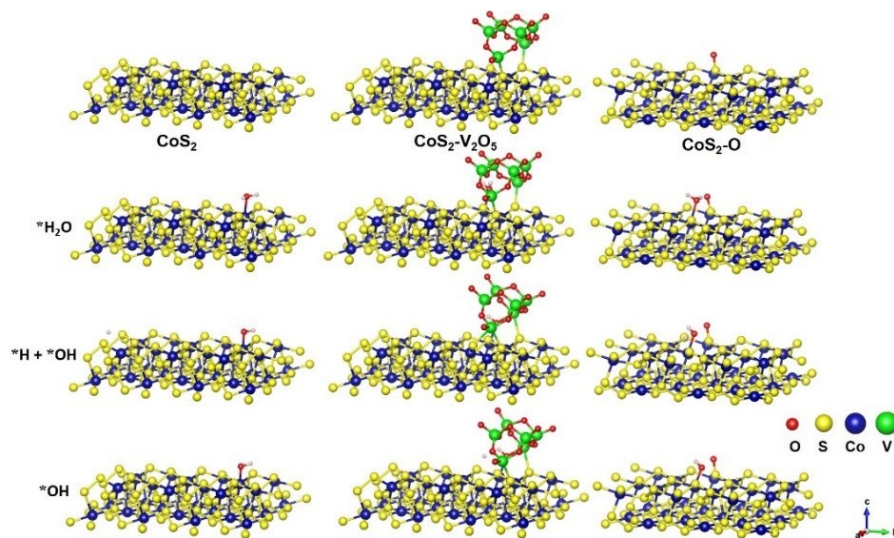
**Fig. S20** a, b) SEM images of  $\text{CoS}_2\text{-V}_2\text{O}_5$  after HER test, c) TEM image of  $\text{CoS}_2\text{-V}_2\text{O}_5$  after HER test, d) HRTEM image of  $\text{CoS}_2\text{-V}_2\text{O}_5$  after HER test (inset shows the corresponding SAED pattern), e) STEM image of  $\text{CoS}_2\text{-V}_2\text{O}_5$  after HER test and the corresponding elemental mappings of Co, V, S and O.



**Fig. S21** a) Survey XPS spectrum, b) Co  $2p$  spectrum, c) S  $2p$  spectrum, and d) V  $2p$  spectrum of  $\text{CoS}_2\text{-V}_2\text{O}_5$  after HER.



**Fig. S22** a) Co K-edge XANES of  $\text{CoS}_2$  after HER test,  $\text{CoS}_2\text{-V}_2\text{O}_5$  after HER test, normal  $\text{CoS}_2$ ,  $\text{CoO}$  and  $\text{Co}$  foil, b) Co K-edge EXAFS of  $\text{CoS}_2$  after HER test,  $\text{CoS}_2\text{-V}_2\text{O}_5$  after HER test, normal  $\text{CoS}_2$ ,  $\text{CoO}$  and  $\text{Co}$  foil.



**Fig. S23** The reaction intermediates during HER process of  $\text{CoS}_2$ ,  $\text{CoS}_2\text{-O}$  and  $\text{CoS}_2\text{-V}_2\text{O}_5$ .