Supporting Information

Fe-doped Co-Mo-S microtube: A highly efficient bifunctional electrocatalyst for overall water splitting in alkaline solution

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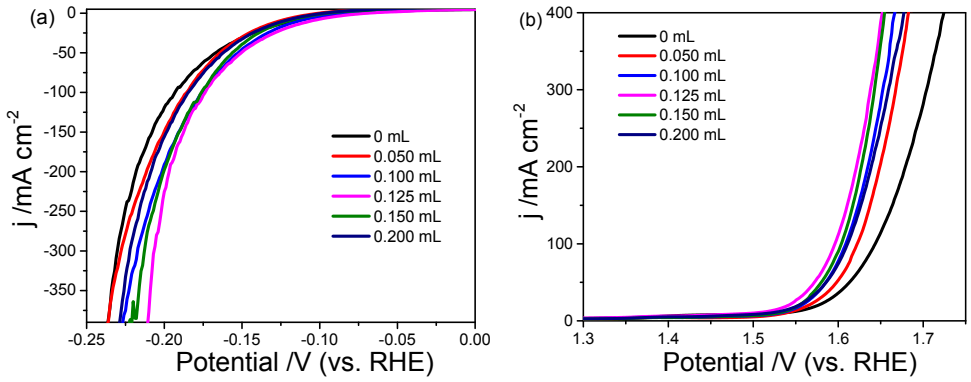


Fig.S1 The LSV curves of the Fe-doped Co-Mo-S microtubes prepared from the systems with different volumes of 0.011 g mL^{-1} $FeSO_4 \cdot 7H_2O$ methanol solution for (a) HER and (b) OER.

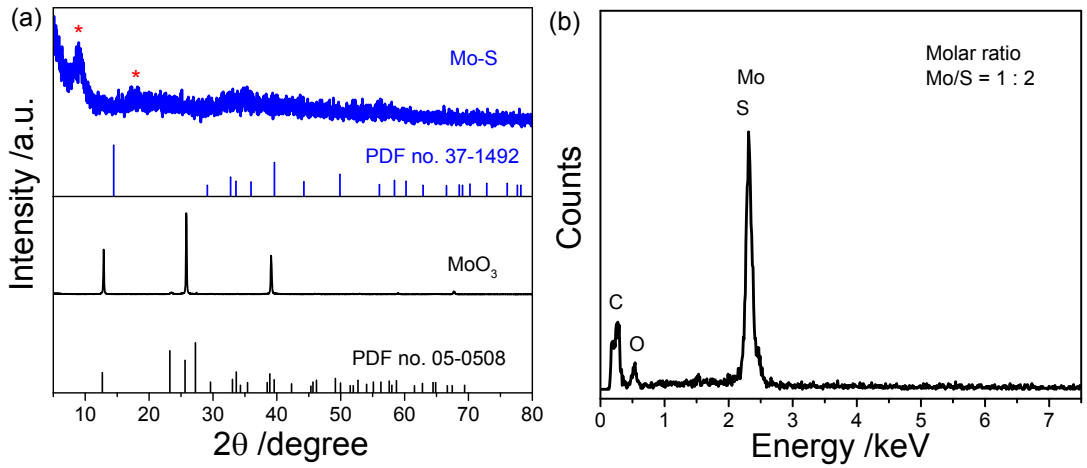


Fig.S2 (a) XRD patterns of as-prepared MoO_3 and Mo-S, and (b) EDS analysis of Mo-S.

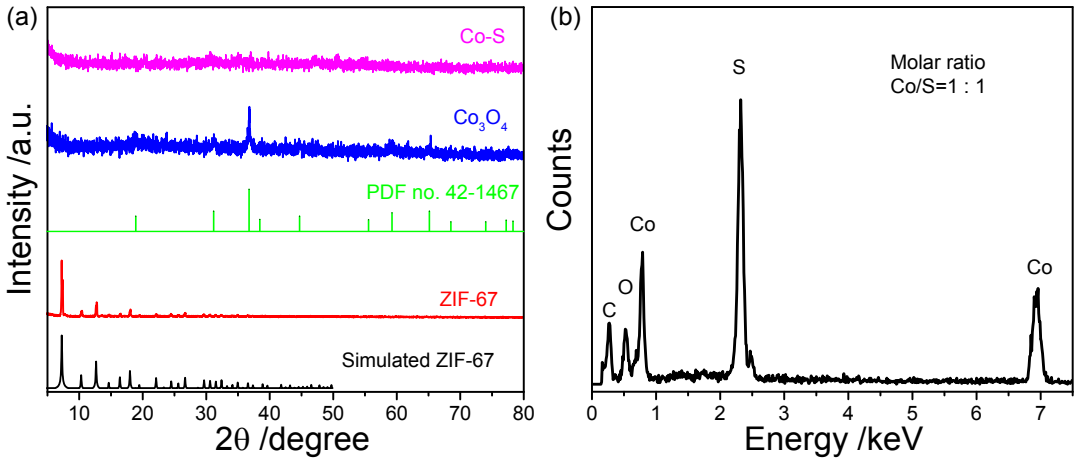


Fig.S3 (a) XRD patterns of as-prepared ZIF-67, Co_3O_4 and Co-S, and (b) EDS analysis of Co-S.

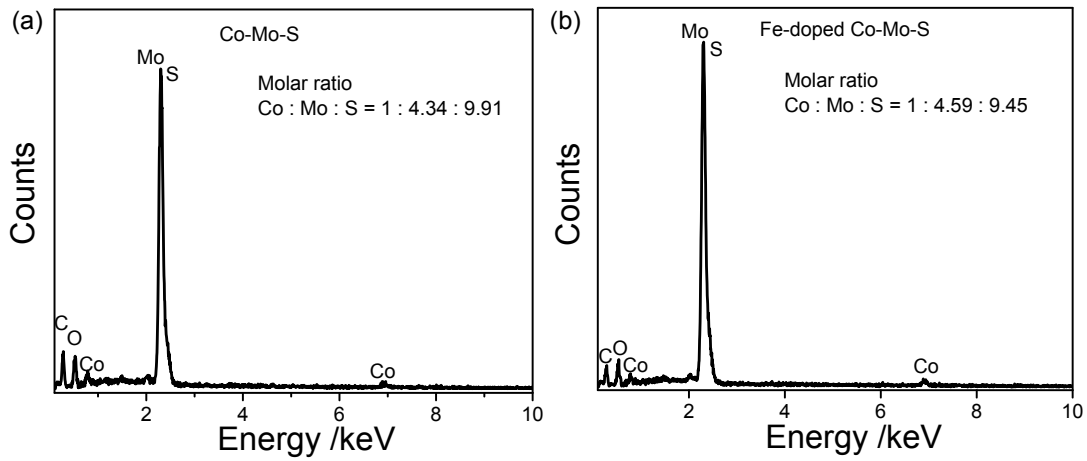


Fig.S4 The EDX analyses of Co-Mo-S (a) and Fe-doped Co-Mo-S (b).

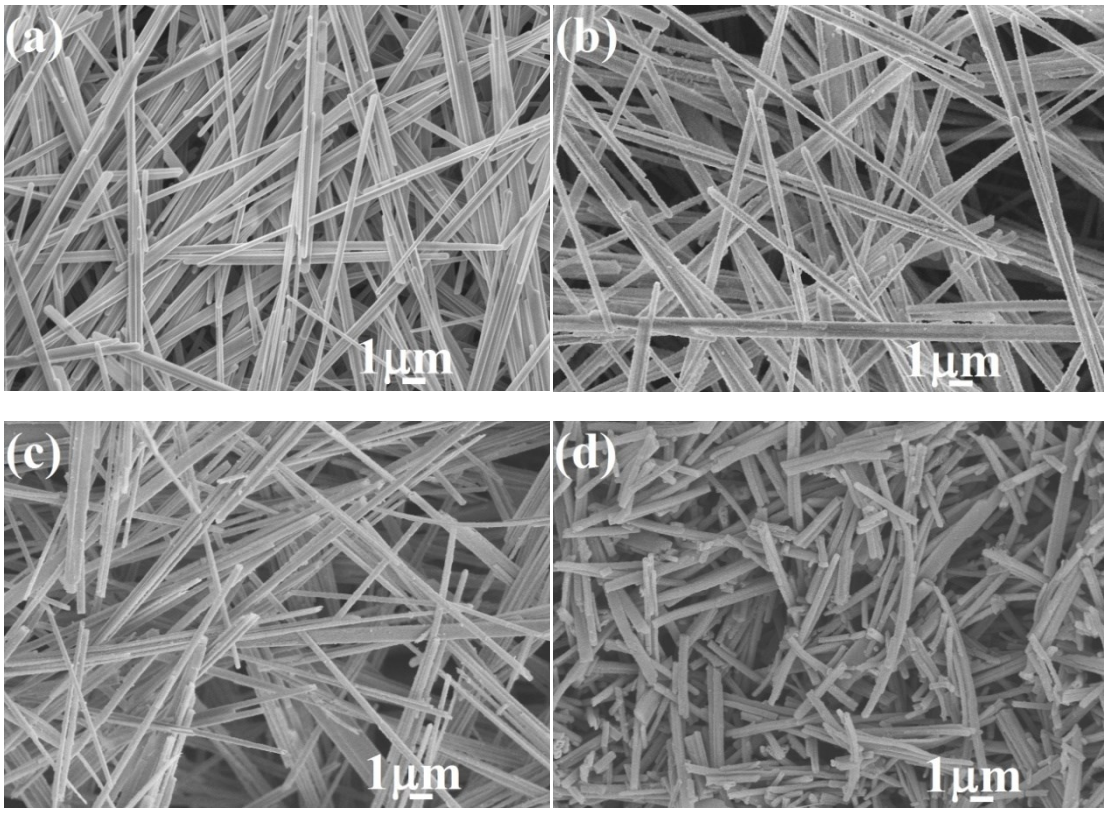


Fig.S5 Low-magnification FESEM images of the products prepared at various reaction stages: (a) MoO_3 microrods, (b) Fe-doped MoO_3@ZIF-67 microrods, (c) Fe-doped MoO_3@Co_3O_4 microrods, (d) Fe-doped Co-Mo-S.

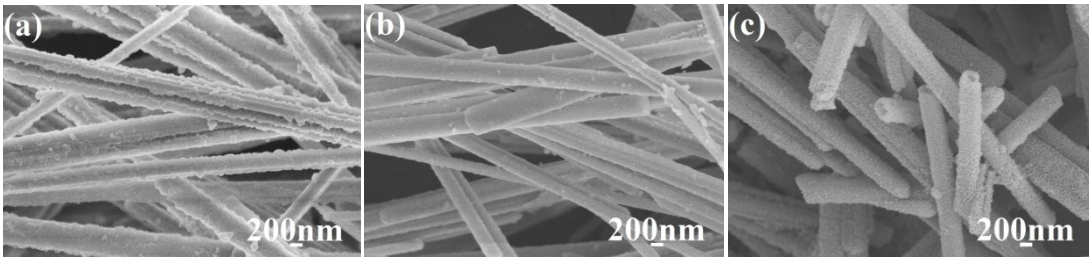
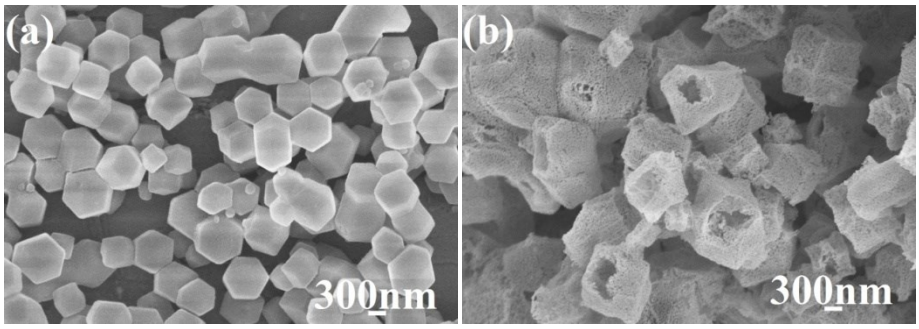


Fig.S6 Representative FESEM images of the undoped products obtained at various stages: (a) MoO_3@ZIF-67, (b) MoO_3@Co_3O_4, and (c) Co-Mo-S microtubes.



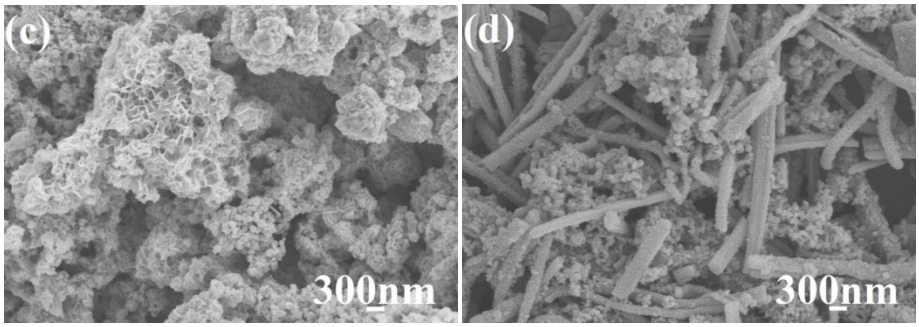


Fig.S7 Representative FESEM images of single component obtained at different stages: (a) ZIF-67, (b) Co_3O_4, (c) Co-S and (d) Mo-S.

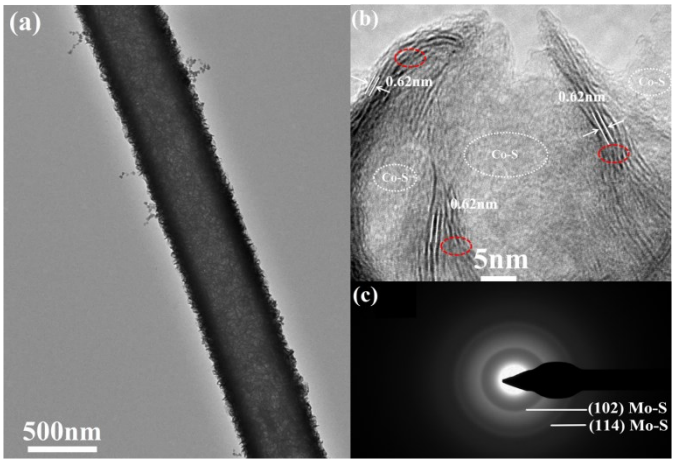
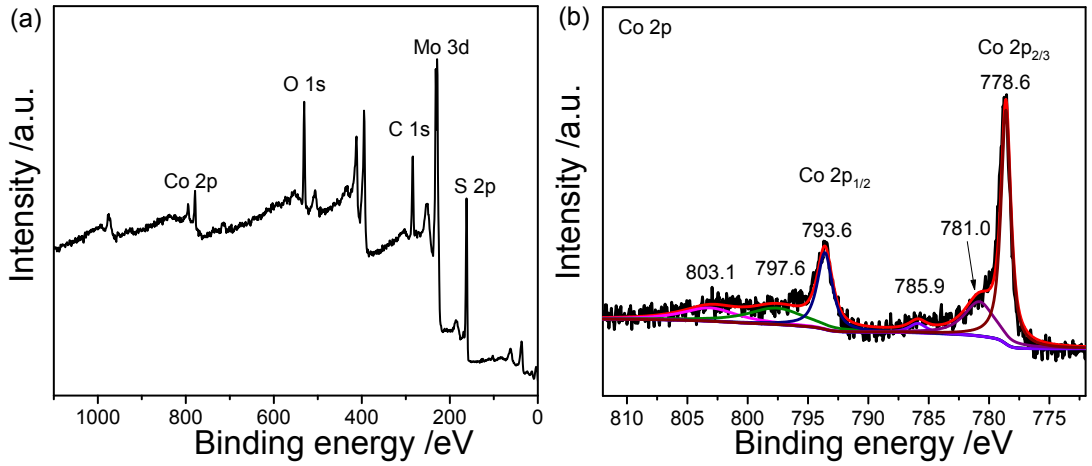


Fig.S8 (a) TEM image, (b) HRTEM image and (c) SAED pattern of a Co-Mo-S microtube.



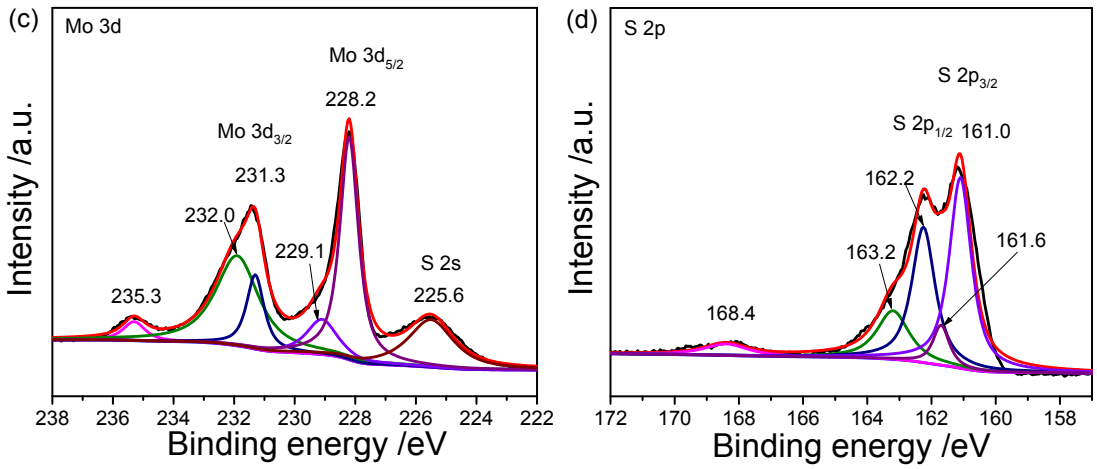


Fig.S9 XPS analyses of the Co-Mo-S microtubes: (a) survey, (b) Co 2p, (c) Mo 3d, and (d) S 2p.

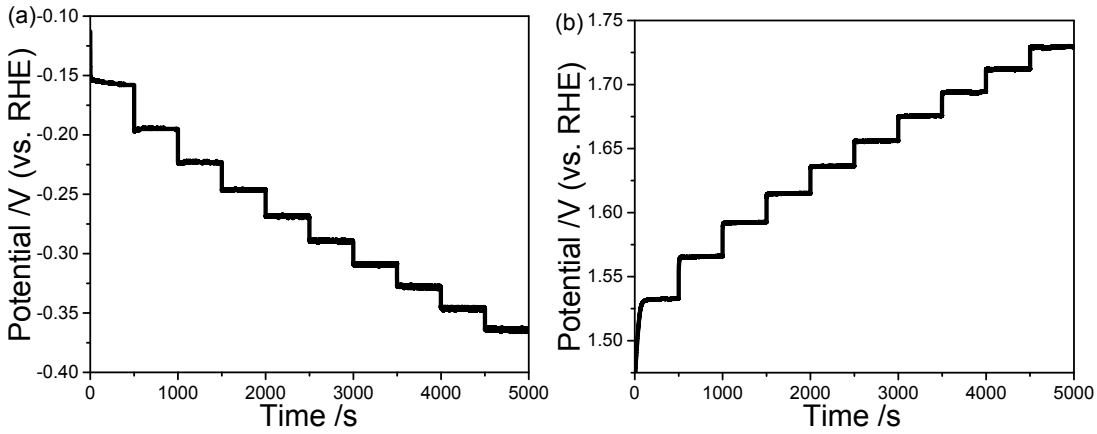


Fig.S10 Multi-step chronopotentiometric curves of the Fe-doped Co-Mo-S/NF electrode in the HER (a) and OER (b) tests without iR compensation.

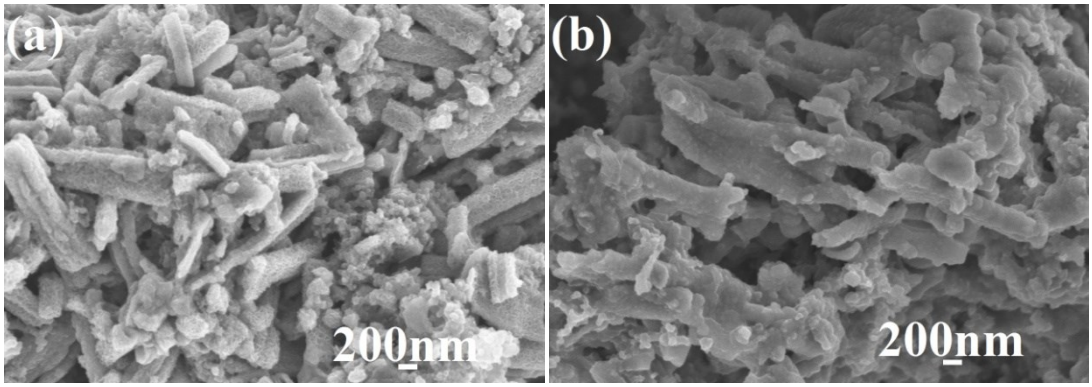


Fig.S11 Representative FESEM images of the Fe-doped Co-Mo-S microtubes catalyst after continuously catalyzing 60 h for HER (a) and OER (b).

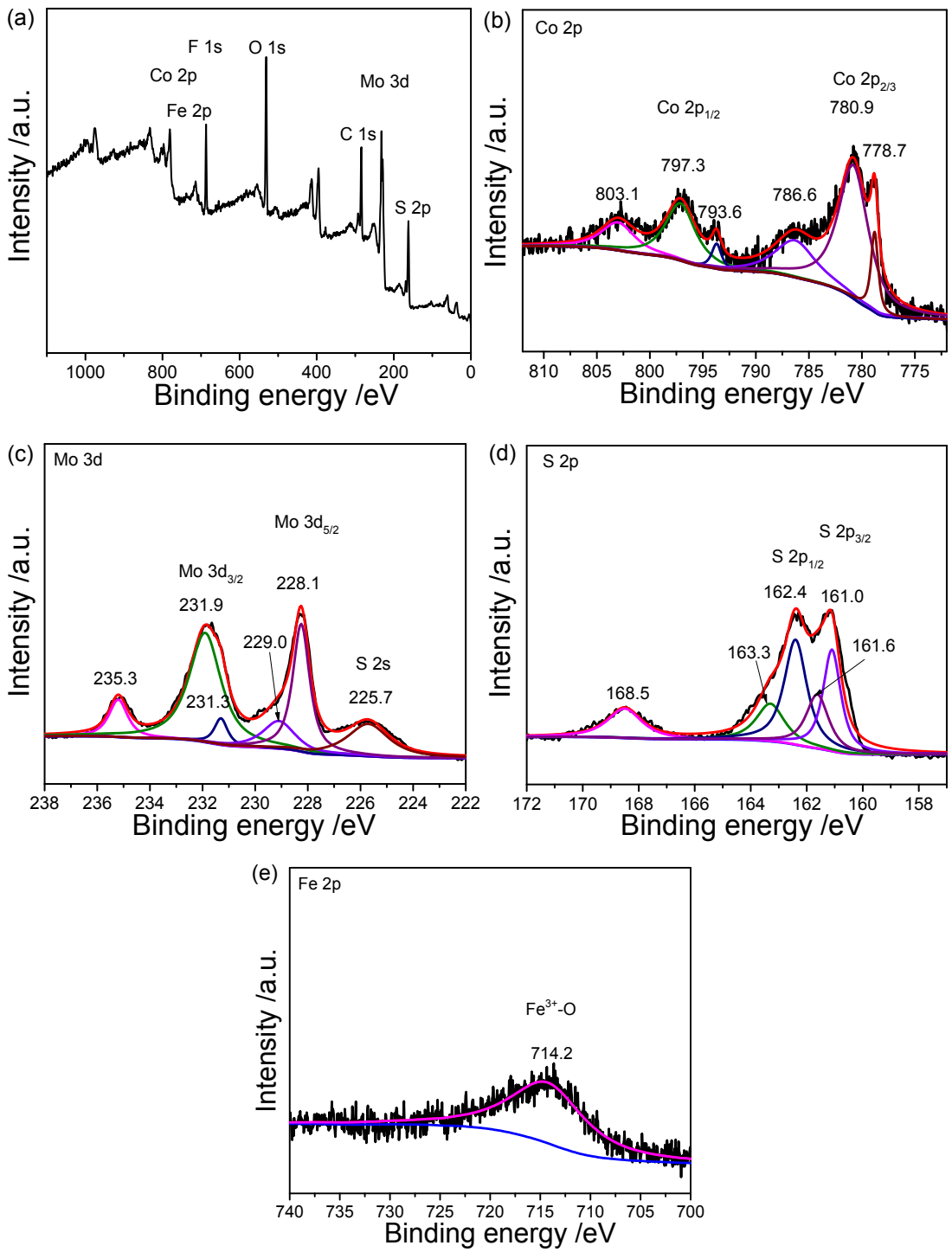


Fig.S12 XPS analyses of the Fe-doped Co-Mo-S microtubes after the HER electrochemical stability test: (a) survey, (b) Co 2p, (c) Mo 3d, (d) S 2p and (e) Fe 2p.

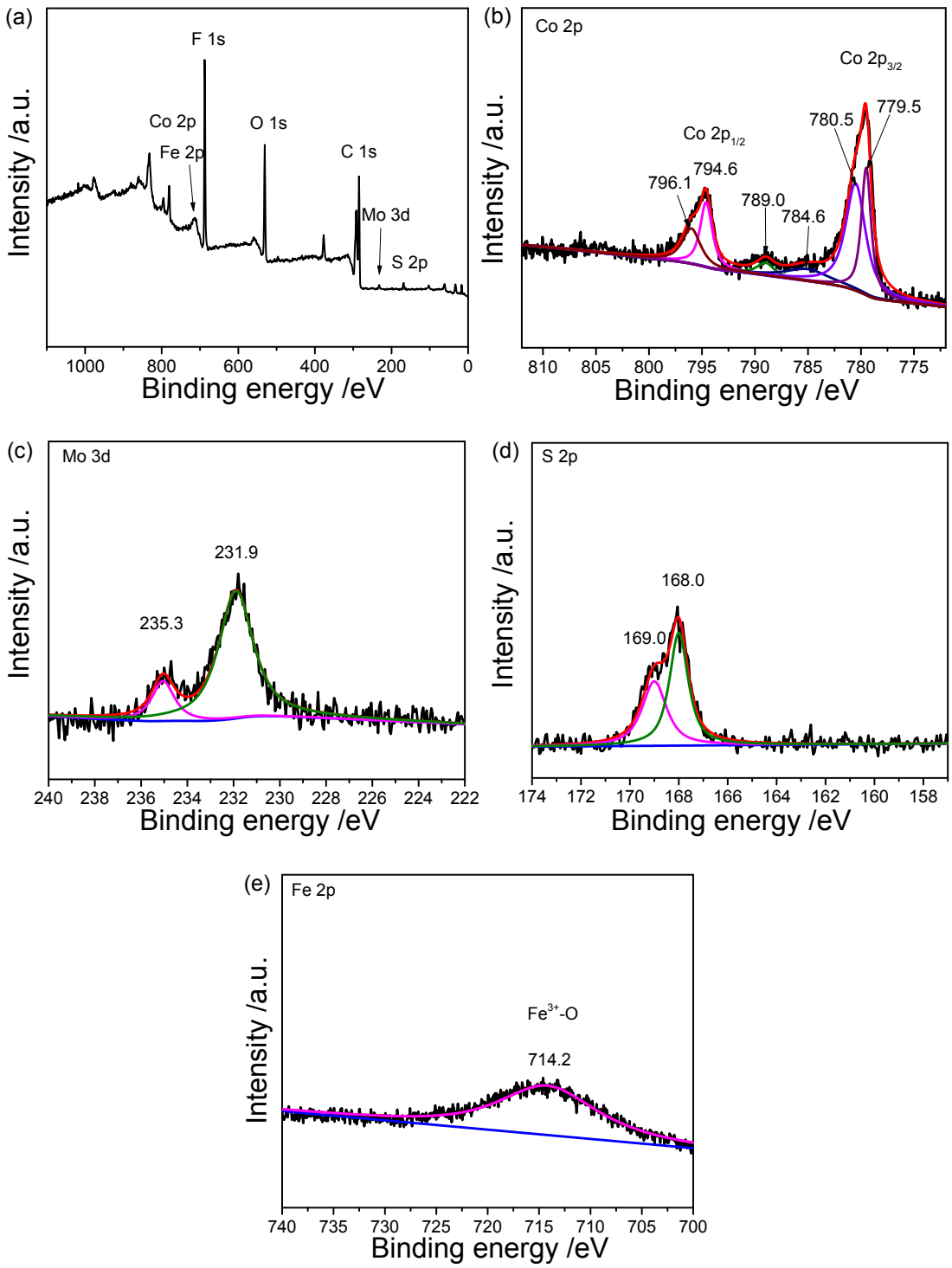


Fig.S13 XPS analyses of the Fe-doped Co-Mo-S microtubes after the OER electrochemical stability test: (a) survey, (b) Co 2p, (c) Mo 3d, (d) S 2p and (e) Fe 2p.

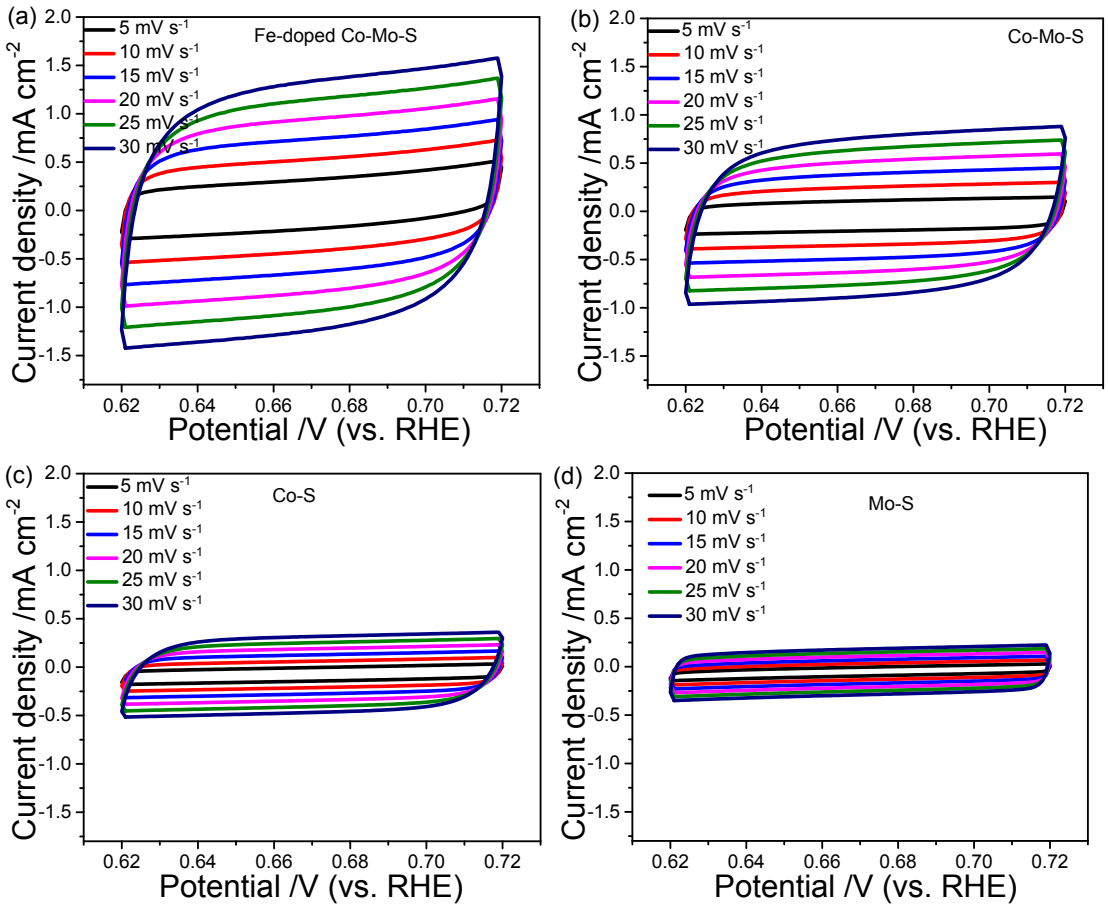


Fig.S14 CV curves of various electrodes in the potential window of 0.62 ~ 0.72 V (vs.RHE) at the scan rate of 5, 10, 15, 20, 25 and 30 mV s^{-1}: (a) Fe-doped Co-Mo-S/NF, (b) Co-Mo-S/NF, (c) Co-S/NF and (d) Mo-S/NF.

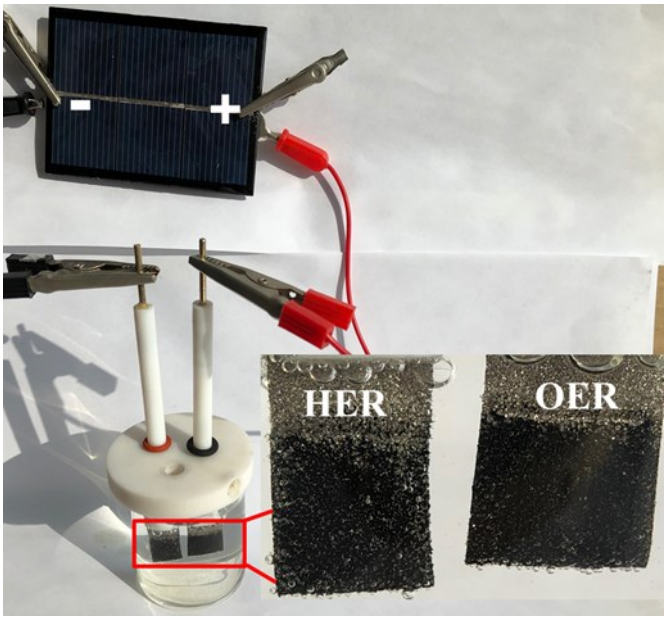


Fig.S15 Digital photograph of water electrolysis driven by a commercial solar cell panel of 1.5~1.6 V in the Fe-doped Co-Mo-S microtubes (- // +) cell system.

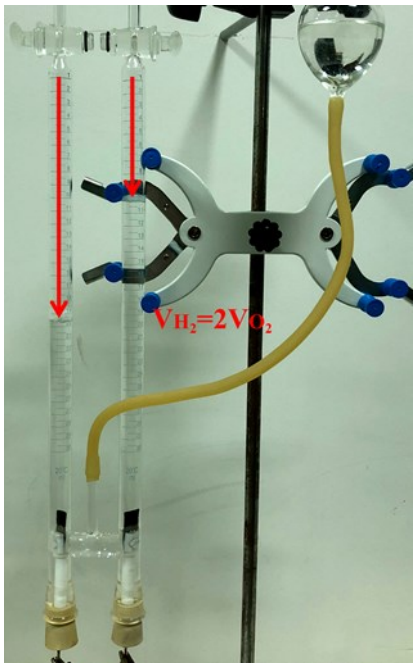


Fig.S16 The photograph of as-used Hoffman apparatus setup for overall water splitting utilizing the present Fe-doped Co-Mo-S microtubes (- // +) electrode at a current density of 100 mA cm^{-2}.

Table S1. Atomic percentages of Fe, Co, and Mo elements obtained by the Fe-doped Co-Mo-S microtubes based on ICP-MS technology.

Sample/element	Atomic %
Fe	0.40
Co	6.40
Mo	30.6
S	62.7

Table S2. Electrocatalytic performance comparison of some reported HER electrocatalysts in 1.0 M KOH solution.

Electrocatalysts	Substrate	Current Density /mA cm^{-2}	Overpotential /mV	Stability /h	Ref.
Fe-doped Co-Mo-S microtubes	Ni foam	10 100	105 173	60	This work

MoS_2/Co_9S_8 /Ni_3S_2/Ni	Ni foam	10	113	-	1
Ni/$CoMoS_4$ Nanosheet arrays	Ni foam	10	158	10	2
CoS_x/Ni_3S_2	Ni foam	10	204	20	3
$Co_5Mo_{1.0}P$ nanosheets	Ni foam	10 100	173 300	20	4
CoS-$Co(OH)_2$@MoS_{2+x}	Ni foam	10	143	27.8	5
NiS-$Ni(OH)_2$@MoS_{2+x}	Ni foam	10	226	-	5
Co-Mo-S	Ni foam	10	190	10	6
Co_1Mo_1S	Ni foam	10	146	18	7
Fe-Doped MoS_2 Nanocanopies	Ni foam	10	153	-	8
Fe–MoS_2/Ni_3S_2	Ni foam	10	130.6	-	9
MoO_2/MoS_2/ CoS_2	Copper foam	10	123	40	10
Mo-Co_9S_8@C nanoflakes	Carbon cloth	10 100	113 330	24	11
amorphous $CoMoS_4$	Carbon cloth	10	143	-	12
Co_xMo_y@NC	Glassy carbon	10	218	14	13
$NiCo_2O_4$@ MoS_2	Carbon paper	10	180	20	14
Co_9S_8@Co_9S_8 @MoS_2-0.5	Glassy carbon	10	173	12	15
Co_9S_8@MoS_2	Glassy carbon	10	143	10	16
Co,Fe-MoS_2	Glassy carbon	10	113	10	17

Table S3. Electrocatalytic performance comparison of some reported OER electrocatalysts in 1.0 M KOH solution.

Electrocatalysts	Substrate	Current Density /mA cm^{-2}	Overpotential /mV	Stability /h	Ref.
Fe-doped Co-Mo-S microtubes	Ni foam	10 100	268 339	60	This work
CoS-$Co(OH)_2$@MoS_{2+x}	Ni foam	10	380	27.8	5
NiS-$Ni(OH)_2$@MoS_{2+x}	Ni foam	10	417	9	5
Co-Mo-S	Ni foam	10	280	10	6
Co_1Mo_1S	Ni foam	10	276	18	7
Fe-CoS_2	Carbon cloth	10	302	20	18
Mo-Co_9S_8@C nanoflakes	Carbon cloth	10 100	200 450	72 24	11
amorphous $CoMoS_4$	Carbon cloth	10	342	-	12
Co–FeS_2/CoS_2	Carbon cloth	10	278	-	19
$NiCo_2O_4$@ MoS_2	Carbon paper	10	305	20	14
$(Ni,Fe)S_2$@ MoS_2	Carbon paper	10 100	270 330	44	20
Co_9S_8@MoS_2 /CNFs	Glassy carbon	10	430	12	21
Co_9S_8@Co_9S_8 @MoS_2-0.5	Glassy carbon	10	340	12	15

Co/CoS_x-MoS_2	Glassy carbon	10	325	16.7	22
Co_9S_8@MoS_2	Glassy carbon	10	340	10	16

Table S4. Electrocatalytic performance comparison of some reported electrocatalysts for overall water splitting in 1.0 M KOH solution.

Electrocatalysts	Substrate	Current Density /mA cm^{-2}	Cell voltage /V	Stability /h	Ref.
Fe-doped Co-Mo-S microtubes	Ni foam	10 100	1.605 1.820	60	This work
$Co_5Mo_{1.0}P$ nanosheets	Ni foam	10	1.68	30	4
Co_9S_8@MoS_2	Ni foam	10	1.67	16	16
NiS-$Ni(OH)_2$@MoS_{2+x}	Ni foam	10	1.65	-	5
$NiCo_2S_4$ nanowires	Ni foam	10	1.63	50	23
MoS_2/NiS	Ni foam	10	1.61	45	24
Co_1Mo_1S	Ni foam	10	1.668	20	7
Fe-MoS_2/Ni_3S_2	Ni foam	10	1.61	20	9
CoNC@MoS_2/CNF	Ni foam	10	1.62	55.6	25
MoO_2/MoS_2/CoS_2	Copper foam	10	1.68	24	10

amorphous $CoMoS_4$	Carbon cloth	10	1.72	12	12
MoS_2-Co_9S_8-NC	Carbon papers	10 100	1.63 1.86	25	26
$NiCo_2O_4$@ MoS_2	Carbon paper	10	1.75	20	14

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