Supporting information

Oxygen and sulfur dual vacancies engineering on 3D Co_3O_4/Co_3S_4 heterostructure to improve overall water splitting activity

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Table S1. Peak area ratios and Co atomic ratios of Co_3O_4/Co_3S_4@NF and DV-Co_3O_4/Co_3S_4@NF in the XPS spectra.

Amounts		**$2p_{1/2}$ Co^{2+}**	**$2p_{1/2}$ Co^{3+}**	**$2p_{3/2}$ Co^{2+}**	**$2p_{3/2}$ Co^{3+}**	**Co^{2+}/Co^{3+}**
Co_3O_4/Co_3S_4@NF	Co_3O_4	0.13	0.87	0.38	0.62	0.34
	Co_3S_4	0.60	0.40	0.62	0.38	1.56
DV-Co_3O_4/Co_3S_4@NF	Co_3O_4	0.31	0.69	0.59	0.41	0.81
	Co_3S_4	0.64	0.36	0.92	0.08	3.55

Table S2. Peak area ratios and O atomic ratios of Co_3O_4@NF, Co_3O_4/Co_3S_4@NF, and DV-Co_3O_4/Co_3S_4@NF in the XPS spectra.

Amounts	**O_I**	**O_{II}**	**O_{III}**	**O_{II}/O_I**	**O_{II}/O_{III}**
Co_3O_4 @NF	0.27	0.18	0.55	0.67	0.33
Co_3O_4/Co_3S_4@NF	0.19	0.51	0.30	2.68	1.70
DV-Co_3O_4/Co_3S_4@NF	0.14	0.80	0.06	5.71	13.33

Table S3. Peak area ratios and S atomic ratios of Co_3O_4/Co_3S_4@NF and DV-Co_3O_4/Co_3S_4@NF in the XPS spectra.

Amounts	**S $2p_{1/2}$**	**S $2p_{3/2}$**	**$2p_{1/2}/2p_{3/2}$**
Co_3O_4/Co_3S_4@NF	0.57	0.43	1.33
DV-Co_3O_4/Co_3S_4@NF	0.75	0.25	3

Table S4. Comparison of OER performance with other Co-based electrocatalysts.

Catalyst	**OER** η_{100} (mV)	**Tafel**	**Ref.**
DV- Co_3O_4/Co_3S_4@NF	**233**	**75**	**This work**
Co_3O_4/Co_3S_4@NF	**288**	**102**	**This work**
$NiCo_2S_4$/CoNi-LDH@CC	337	111	[1]
$NiCo_2S_4$@CC	370	96	[2]
$CoMo_2S_4$@NF	370	66	[3]
$CuCo_2S_4$@NF	245	68	[4]
$FeCo_2S_4$/CoFe-LDH@NF	259	69	[5]
$NiCo_2O_4/NiMo_2S_4$@NF	420	95	[6]
Ru-$NiCo_2O_4$@NF	260	83	[7]
MgO/$NiCo_2S_4$@CC	310	115	[8]
$CuCo_2S_4$/CuCo@CF	300	70	[9]
NW-$MnCo_2O_4$/CC	482	111	[10]
NiCo-LDH/$NiCo_2S_4$/CC	280	48	[11]
$MnCo_2O_4/Ni_2P$@NF	350	114	[12]
Ru-NiCoP@NF	285	85	[13]
CoS/NiS@NF	420	78	[14]

*η_{100}: The required overpotential at the current density of 100 $mA{\cdot}cm^{-2}$.

Table S5. Comparison of HER performance with other Co-based electrocatalysts.

Catalyst	HER η_{10} (mV)	Tafel	Ref.
DV- Co_3O_4/Co_3S_4@NF	**26**	**58**	**This work**
Co_3O_4/Co_3S_4@NF	**134**	**99**	**This work**
$CoMo_2S_4$@NF	162	116	[3]
$CuCo_2S_4$@NF	61	53	[4]
$FeCo_2S_4$/CoFe-LDH@NF	115	3	[5]
$NiCo_2O_4/NiMo_2S_4$@NF	159	53	[6]
NiCo-LDH/$NiCo_2S_4$@CC	150	41	[11]
P-Co_3S_4@CC	65	125	[15]
$NiCo_2S_{4-x}$@CC	150	83	[16]
$MnCo_2O_4/Ni_2P$@NF	57	89	[12]
Ru-NiCoP@NF	44	45	[13]
$Co_3S_4/NiMoO_4$/rGO@NF	40	47	[17]
$NiCo_2S_4$/NiFe-LDH@NF	200	101	[18]
Fe-Co-S@NF	143	80	[19]
$Co(OH)_2$/Ni-Co-S@NF	148	88	[20]

*η_{10}: The required overpotential at the current density of 10 $mA\cdot cm^{-2}$.

Table S6. Comparison of overall water splitting (OWS) performance with other bifunctional electrocatalysts.

Catalyst	**OWS** P_{10} (V)	**Ref.**
DV- Co_3O_4/Co_3S_4@NF	**1.44**	**This work**
Co_3O_4/Co_3S_4@NF	**1.54**	**This work**
$CoMo_2S_4$@NF	1.65	[3]
$CuCo_2S_4$@NF	1.54	[4]
$FeCo_2S_4$/CoFe-LDH@NF	1.60	[5]
Ru-$NiCo_2O_4$@NF	1.45	[7]
NW-$MnCo_2O_4$/CC	1.47	[10]
$MnCo_2O_4/Ni_2P$@NF	1.63	[12]
Ru-NiCoP@NF	1.52	[13]
Co_3S_4@FNC	1.58	[21]
CoMoP/Co_3O_{4-x}@NF	1.61	[22]
CoNi/$CoFe_2O_4$@NF	1.57	[23]
Co_3O_4/Mo-Co_3S_4-Ni_3S_2@NF	1.62	[24]
Ni_3S_2/Co_3S_4/FeOOH@NF	1.58	[25]
V_oB-Co_3O_4@NF	1.67	[26]
v-NiS_2/CeO_2 HSs@NF	1.64	[27]

*P_{10}: The required a cell voltage to drive a current density of 10 mA·cm^{-2}.

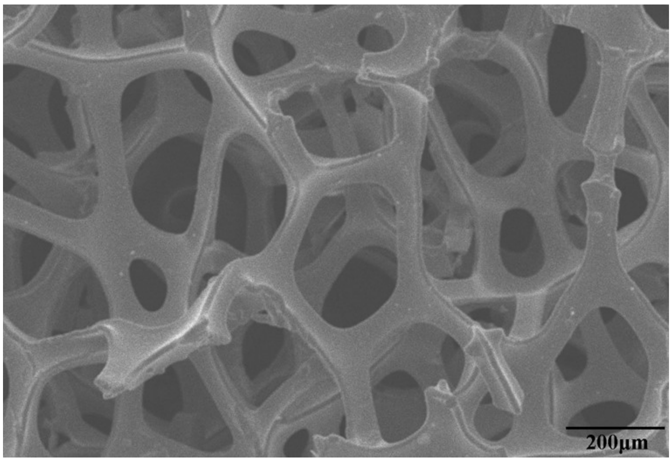

Fig. S1. SEM images of NF.

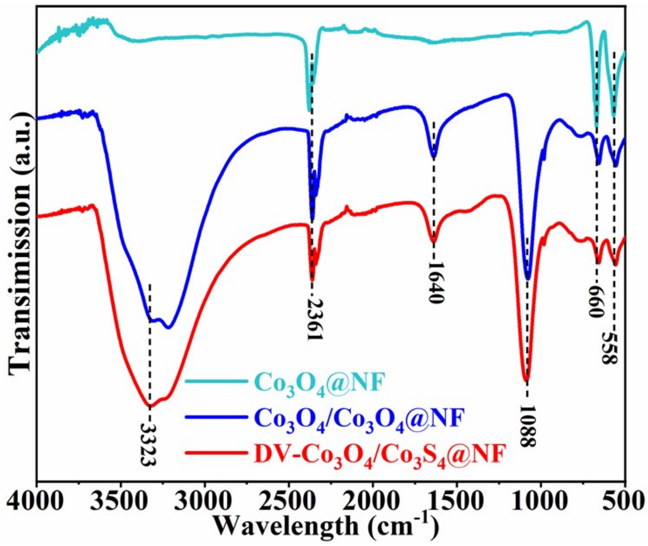

Fig. S2. FT-IR spectra of Co_3O_4 @NF, Co_3O_4/Co_3S_4@NF, and DV-Co_3O_4/Co_3S_4@NF.

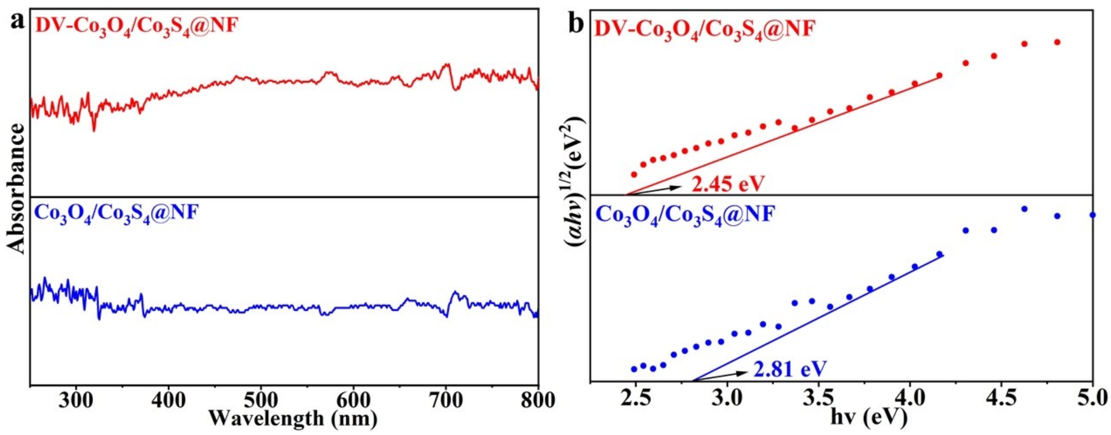

Fig. S3. (a) UV-vis absorption spectra and (b) the band gap energy of Co_3O_4/Co_3S_4@NF and DV-Co_3O_4/Co_3S_4@NF.

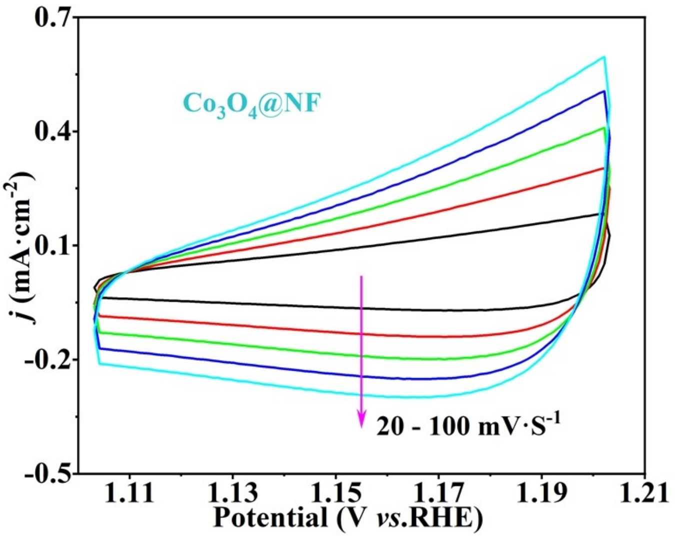

Fig. S4. CV curves at different scan rates for Co_3O_4@NF.

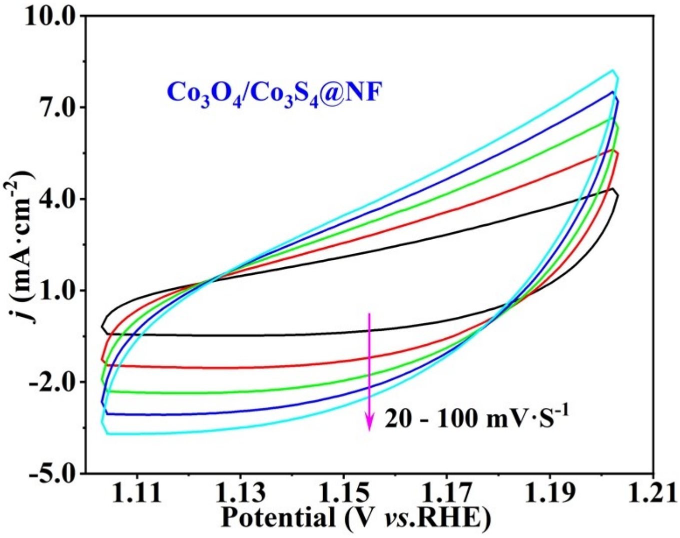

Fig. S5. CV curves at different scan rates for Co_3O_4/Co_3S_4@NF.

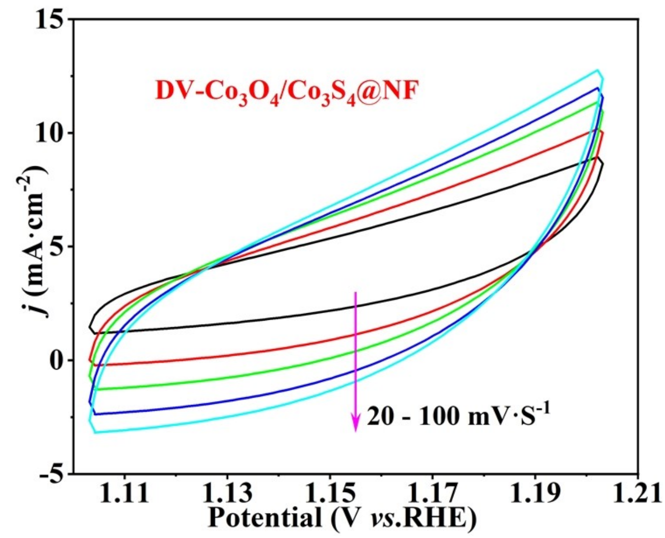

Fig. S6. CV curves at different scan rates for DV-Co_3O_4/Co_3S_4@NF.

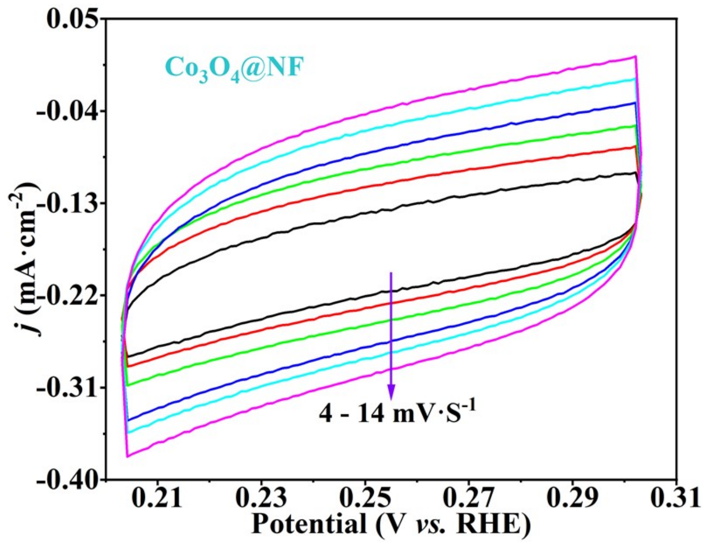

Fig. S7. CV curves at different scan rates for Co_3O_4 @NF.

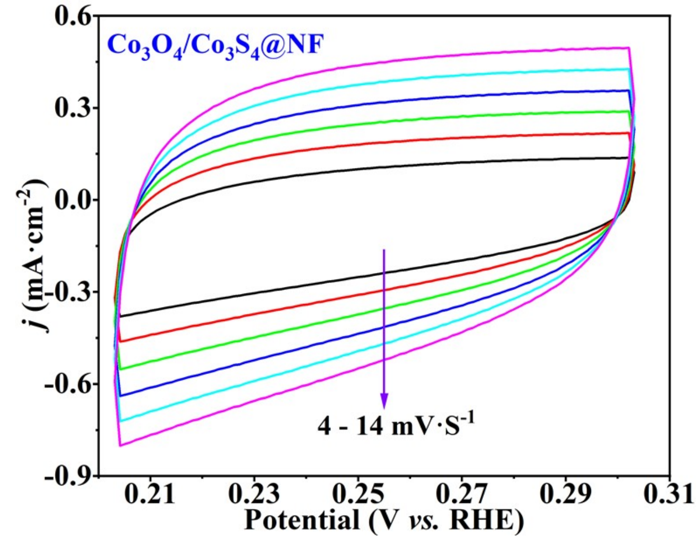

Fig. S8. CV curves at different scan rates for Co_3O_4/Co_3S_4@NF.

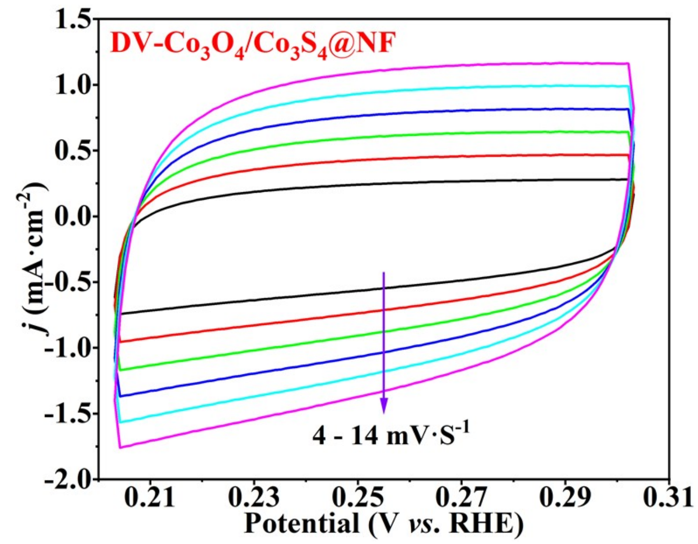

Fig. S9. CV curves at different scan rates for DV-Co_3O_4/Co_3S_4@NF.

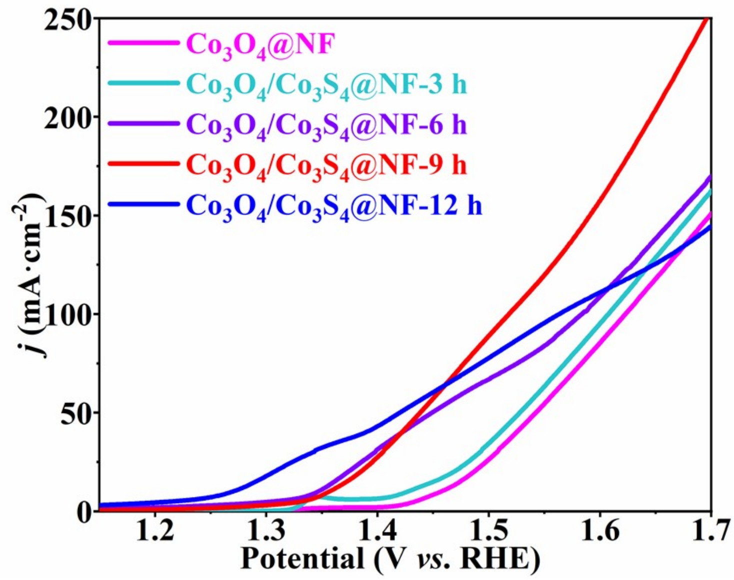

Fig. 10. OER polarization curves of Co_3O_4/Co_3S_4@NF by different sulphuration time

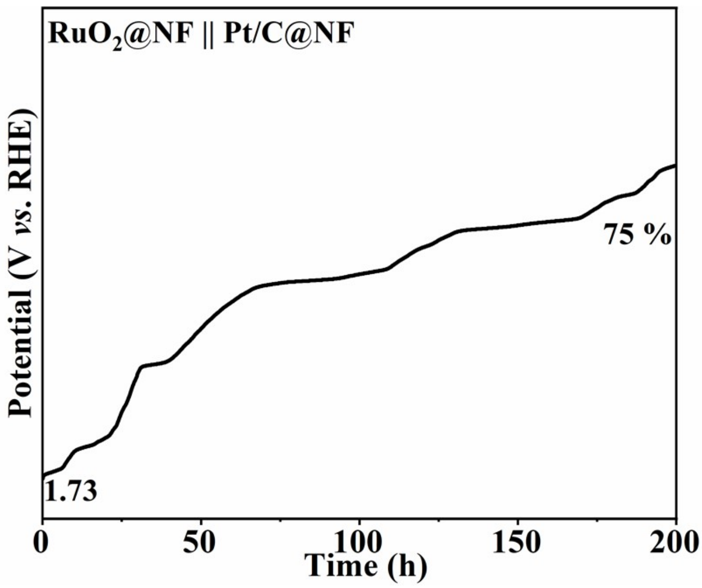

Fig. S11. The chrono-potentiometric curve of RuO_2@NF || Pt/C@NF.

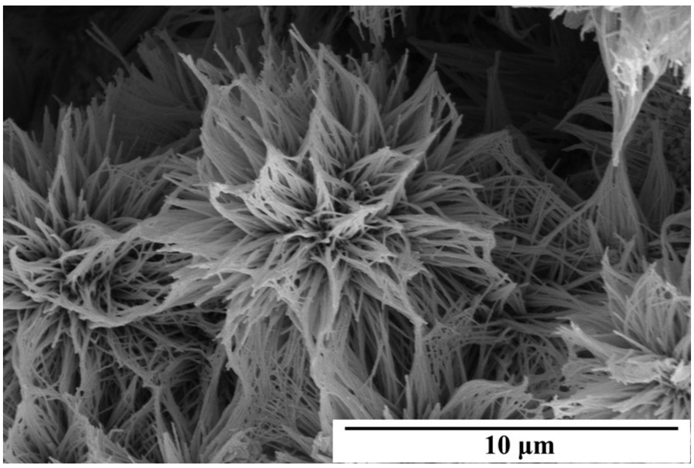

Fig. S12. SEM image of DV-Co_3O_4/Co_3S_4@NF after OER test.

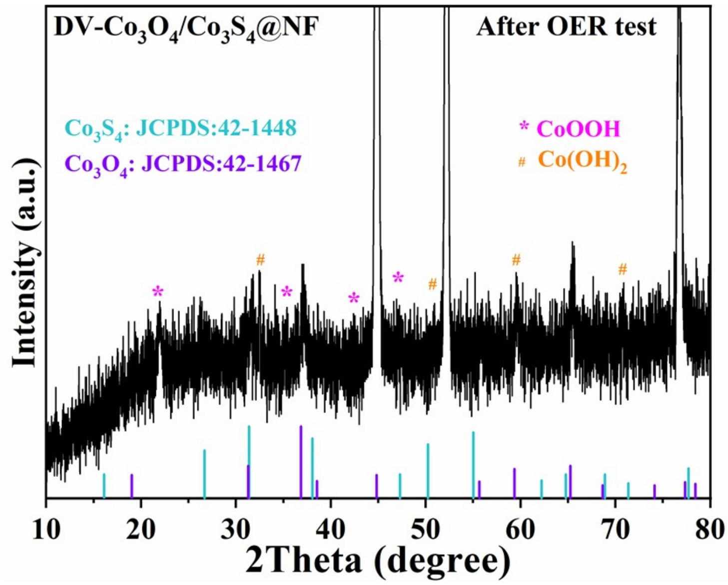

Fig. S13. XRD pattern of DV-Co_3O_4/Co_3S_4@NF after OER test.

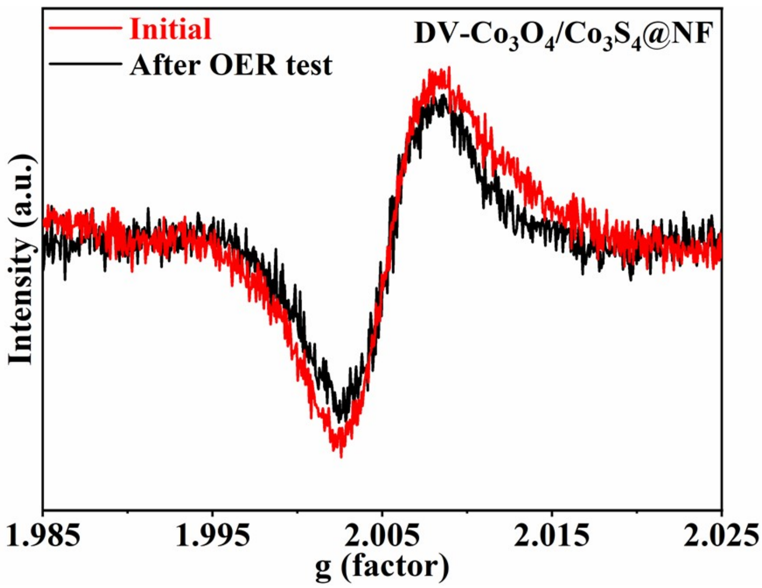

Figure S14. EPR spectra of DV- Co_3O_4/Co_3S_4@NF before and after OER test.

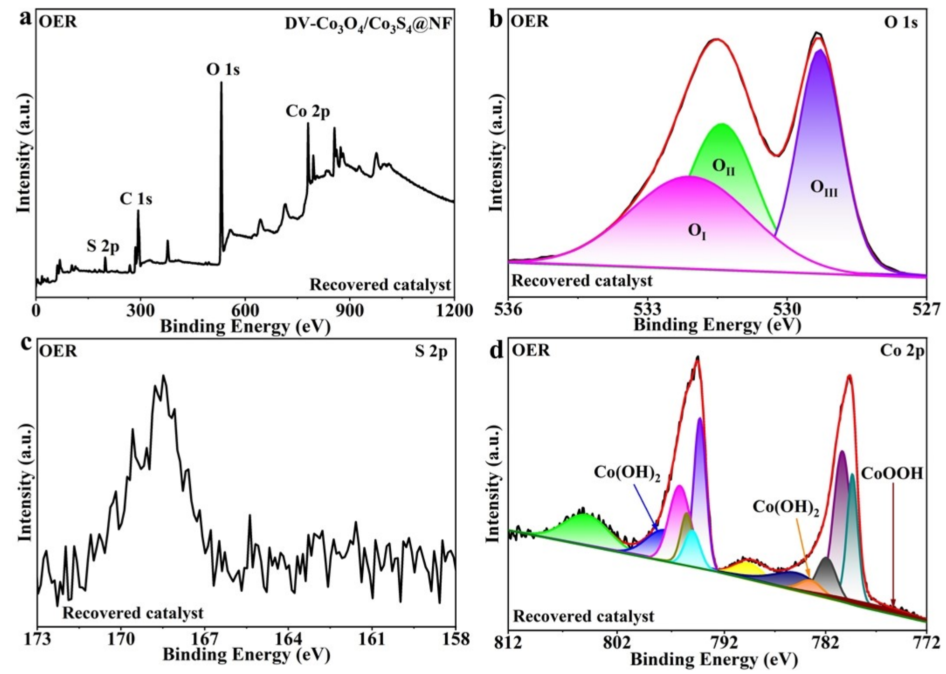

Fig. S15 (a) XPS spectra of DV-Co_3O_4/Co_3S_4@NF, high-resolution XPS of (b) O 1s, (c) S 2p, and (d) Co 2p after 100 h stability test for OER.

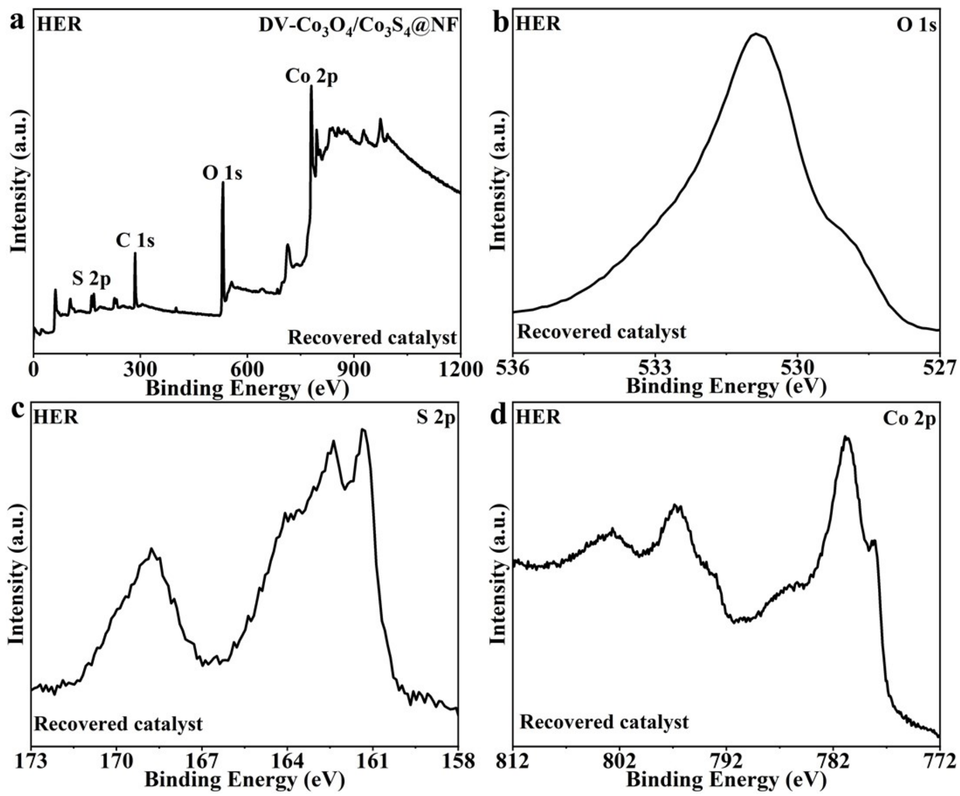

Fig. S16 (a) XPS spectra of DV-Co_3O_4/Co_3S_4@NF, high-resolution XPS of (b) O 1s, (c) S 2p, and (d) Co 2p after 100 h stability test for HER.

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