Electronic Supplementary Information

Self-supported S-doped Fe-based organic framework platform enhances electrocatalysis toward highly efficient oxygen evolution in alkaline media

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Supporting date

Figure S1. Photograph of (a) NF, (b) Fe-BTB/NF, (c) $S_{0.05}$-Fe-BTB/NF.

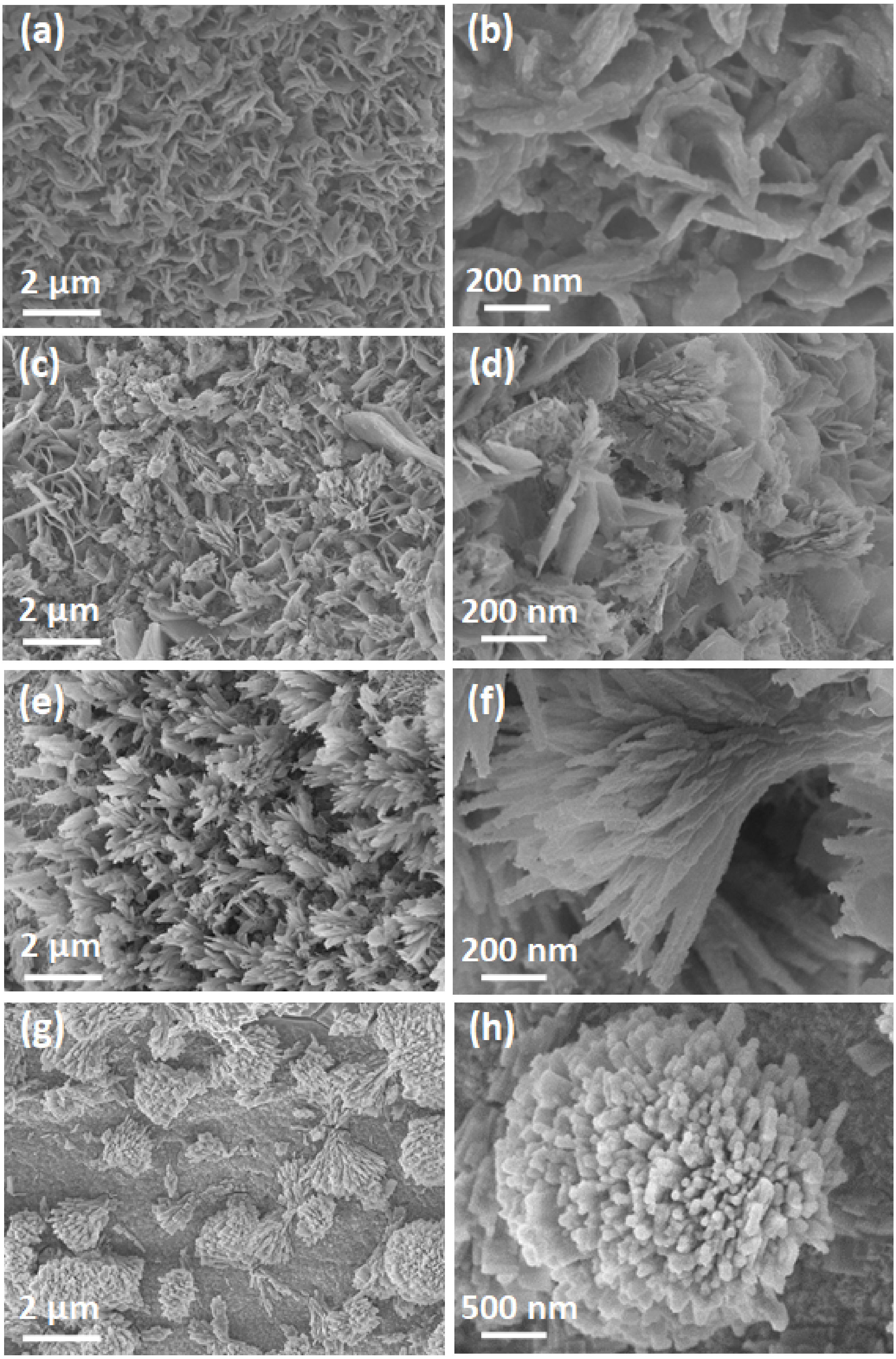

Figure S2. The low- and high-magnification FE-SEM images of (a) Fe-BTB/NF, (b) $S_{0.025}$-Fe-BTB/NF, (c) $S_{0.05}$-Fe-BTB/NF and (d) $S_{0.075}$-Fe-BTB/NF.

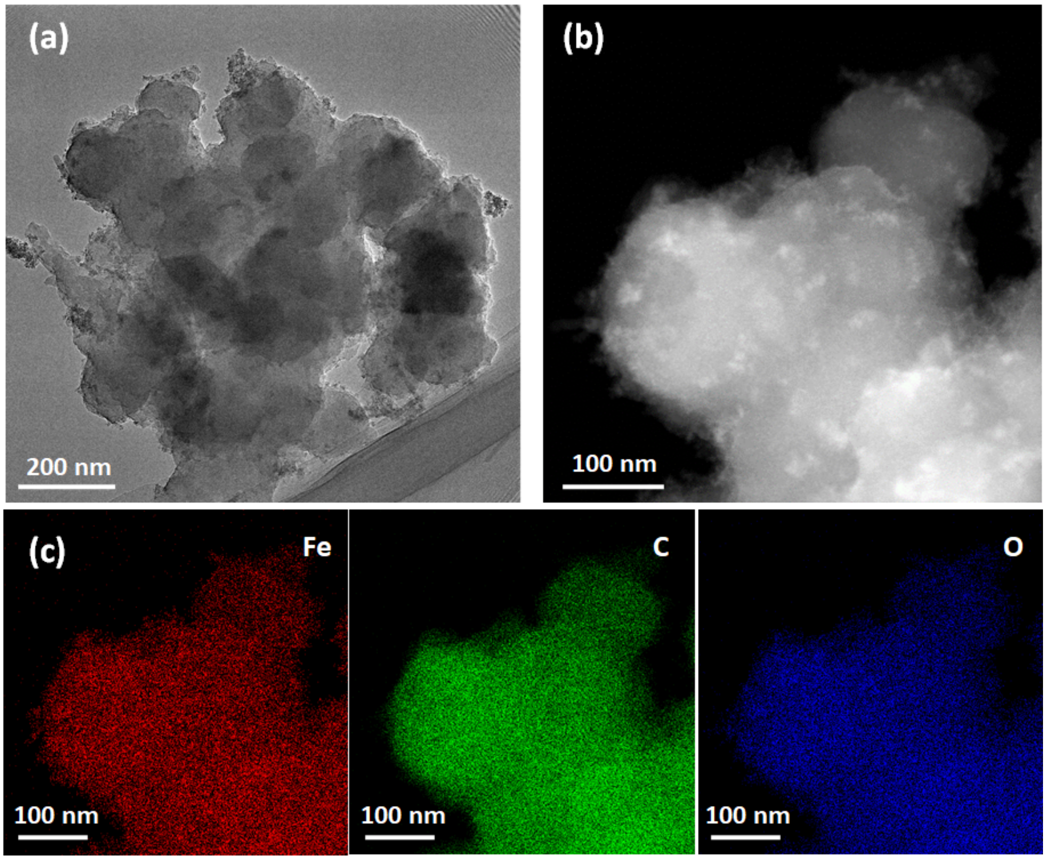

Figure S3. (a) TEM, (b) HAADF-STEM image and (c) corresponding element mapping images of Fe-BTB/NF.

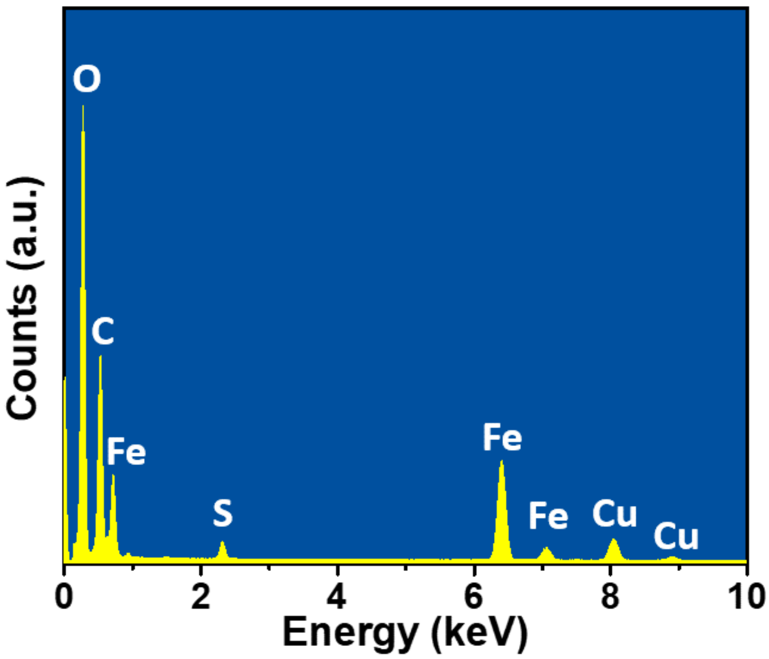

Figure S4. EDS spectrum of as-prepared $S_{0.05}$-Fe-BTB/NF.

Table S1. Element percentage of $S_{0.05}$-Fe-BTB/NF obtained from EDS, and XPS.

Elements	Weight% (EDS)	Atom% (EDS)	Weight% (XPS)	Atom% (XPS)
Fe	18.08	4.78	15.2	4.0
S	1.47	0.68	1.5	0.6
O	14.00	12.90	20.6	20.9
C	66.45	81.64	62.7	74.5
Total	100	100	100	100
Fe:S	12.3:1	7.0:1	10.1:1	6.7:1

Table S2. The Fe and S contents of synthesized S_x-Fe-BTB/NF catalysts measured by ICP-OES.

Catalyst	Fe (weight%)	S (weight%)	Fe:S (weight)	Fe:S (atom)
Fe-BTB/NF	12.53	-	-	-
$S_{0.025}$-Fe-BTB/NF	12.19	0.51	24.0:1	13.7:1
$S_{0.05}$-Fe-BTB/NF	11.34	0.95	11.9:1	6.9:1
$S_{0.075}$-Fe-BTB/NF	10.71	1.39	7.7:1	4.4:1

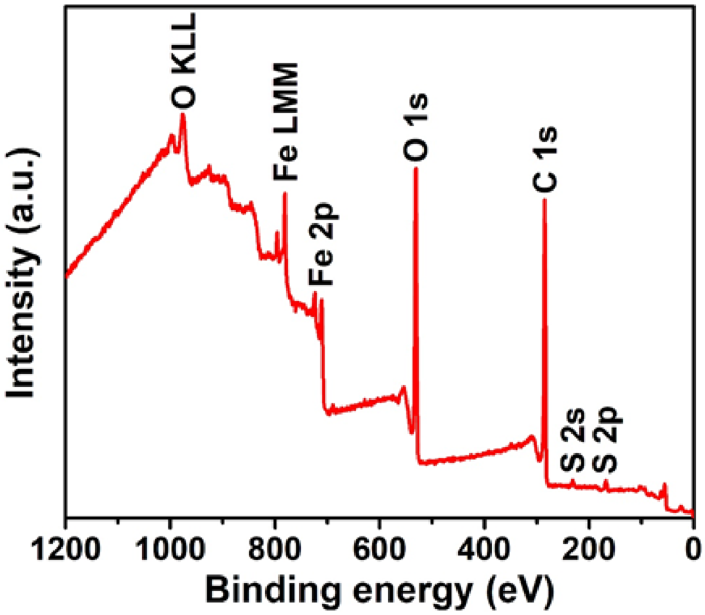

Figure S5. XPS survey spectrum of $S_{0.05}$-Fe-BTB/NF sample.

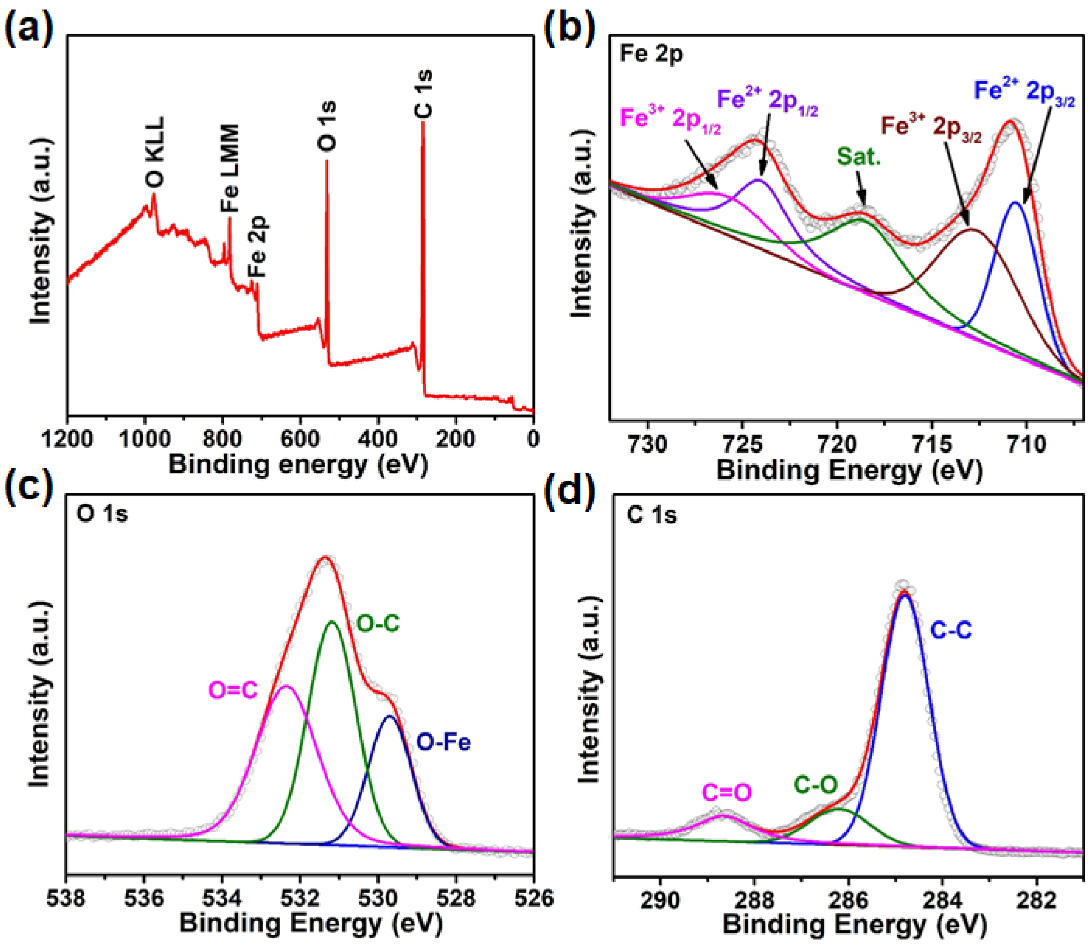

Figure S6. (a) XPS survey spectrum, (b) High-resolution XPS spectrum of Fe 2p, (c) O 1s, and (d) C 1s of as-prepared Fe-BTB/NF sample.

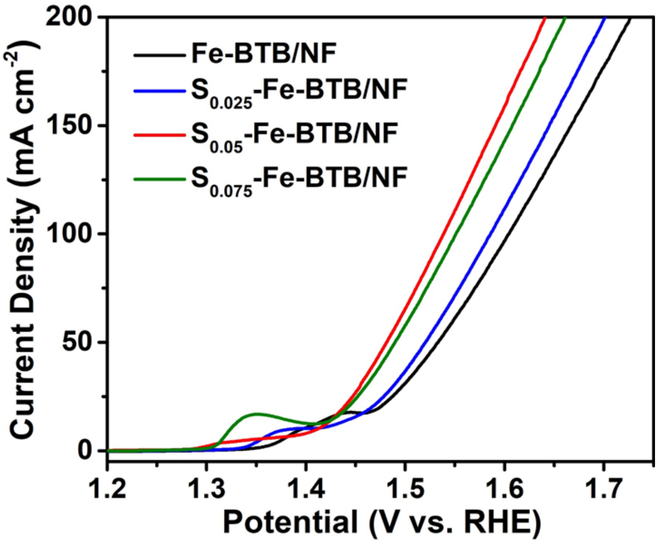

Figure S7. The linear sweep voltammetry (LSV) curves of Fe-BTB/NF doped with different sulfur content in 1.0 M KOH.

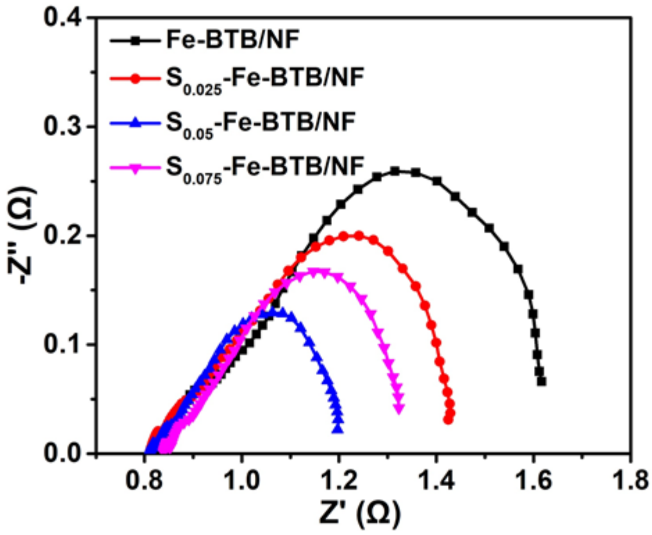

Figure S8. Electrochemical impedance spectroscopy for S_x-Fe-BTB/NF various thiourea added amount at an applied potential of 1.5 V (vs. RHE).

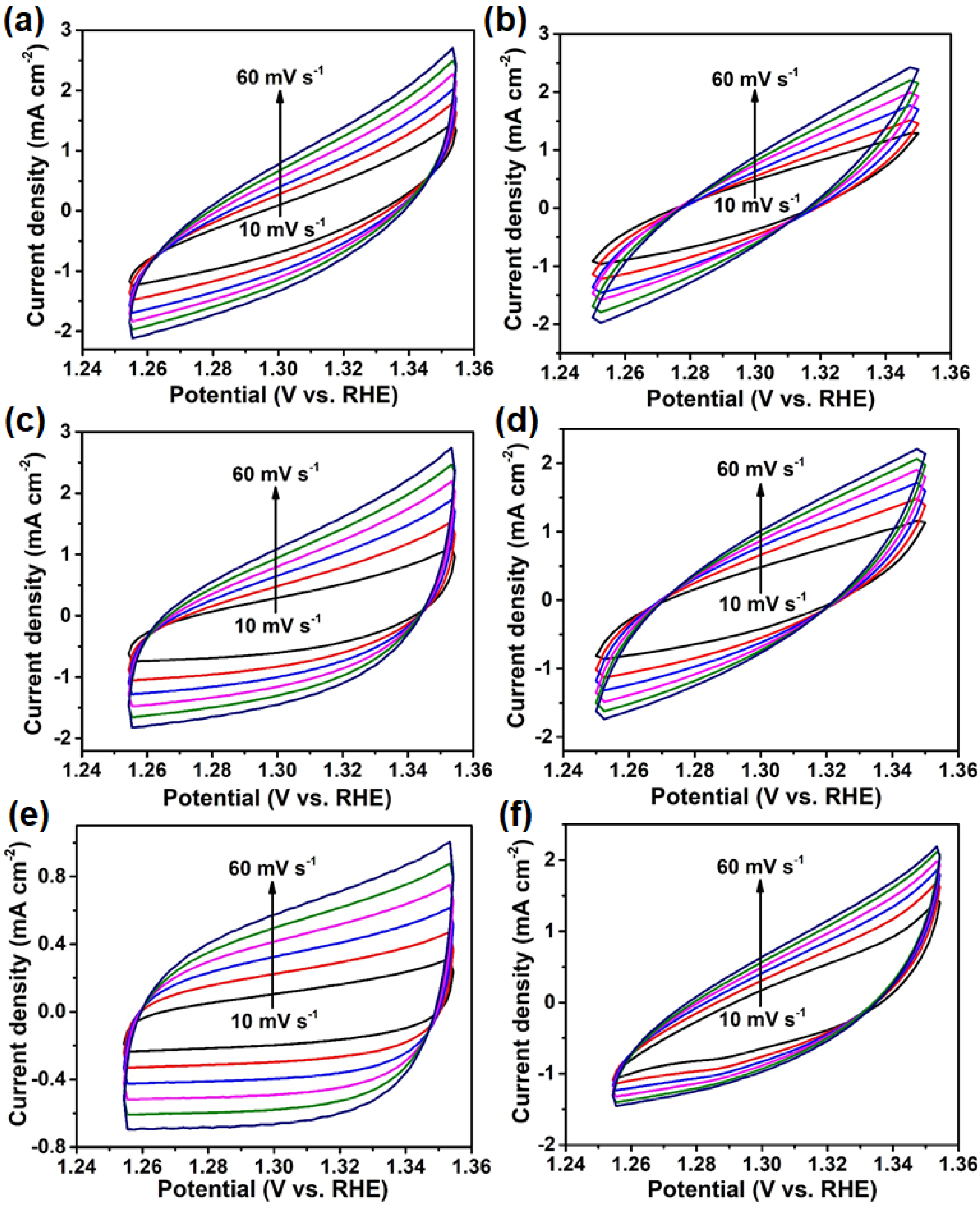

Figure S9. CV curves of as-prepared catalysts at different scan rates in 1.0 M KOH. (a) Fe-BTB/NF, (b) $S_{0.025}$-Fe-BTB/NF, (c) $S_{0.05}$-Fe-BTB/NF, (d) $S_{0.075}$-Fe-BTB/NF, (e) bare NF, (f) RuO_2/NF.

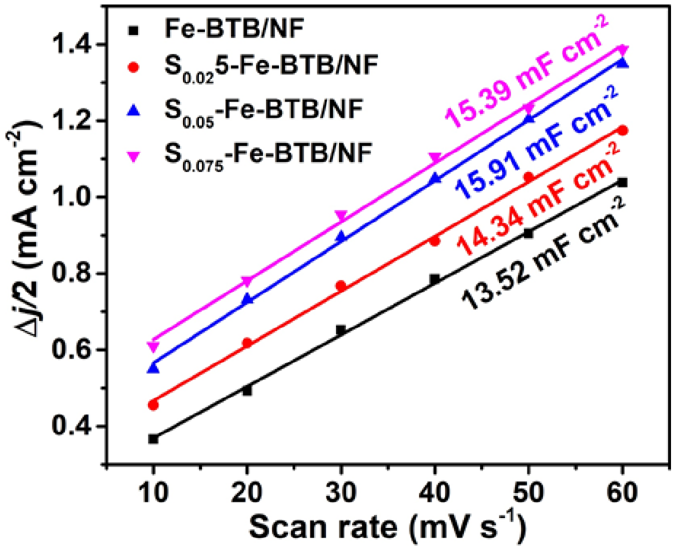

Figure S10. The Plots showing the extraction of the C_{dl} for the estimation of the ECSA for S_x-Fe-BTB/NF various thiourea added amount acquired at an applied potential of 1.3 V vs. RHE.

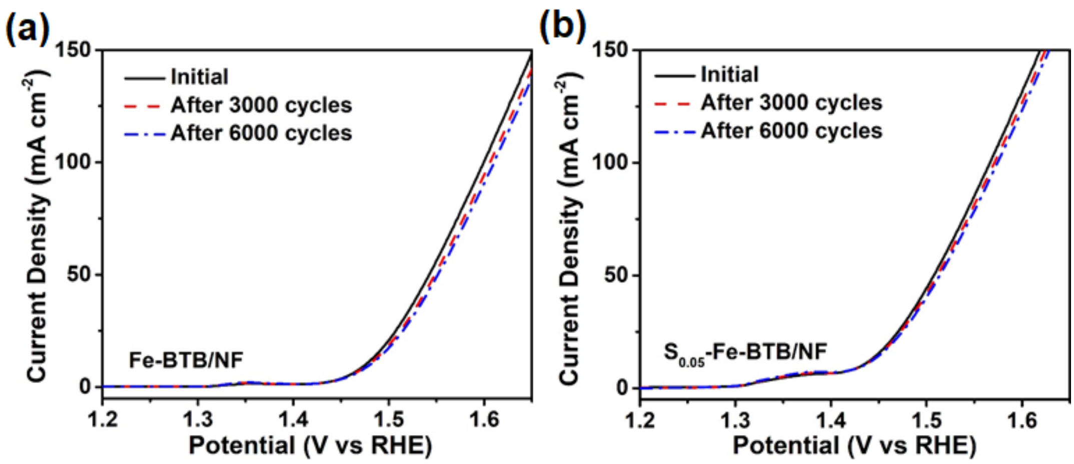

Figure S11. LSV curves of (a) Fe-BTB/NF and (b) $S_{0.05}$-Fe-BTB/NF before and after 6000 potential cycling tests in 1.0 M KOH between 1.2 and 1.5 V vs. RHE at a scan rate of 50 mV s^{-1}.

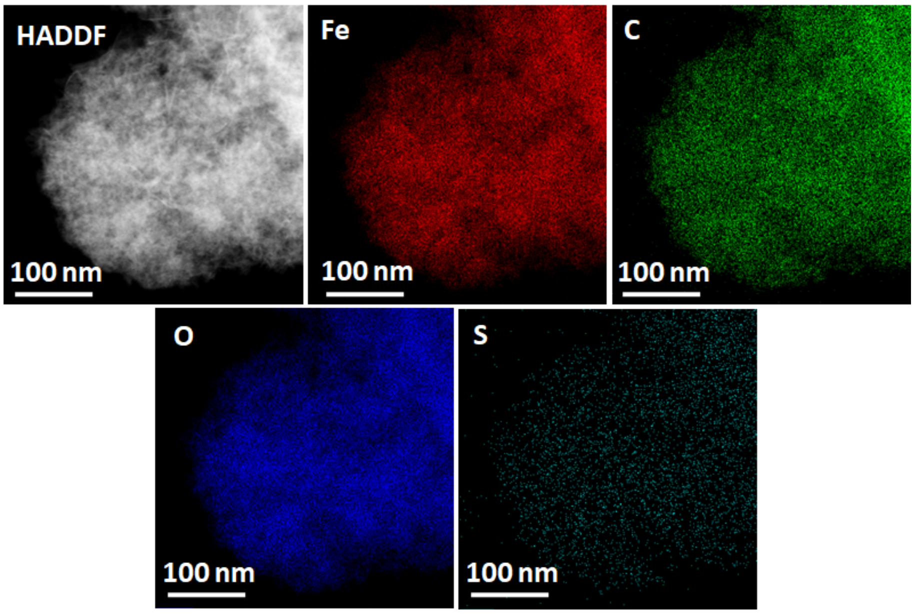

Figure S12. HAADF-STEM image and corresponding EDS element mapping images of $S_{0.05}$-Fe-BTB/NF after OER electrocatalysis.

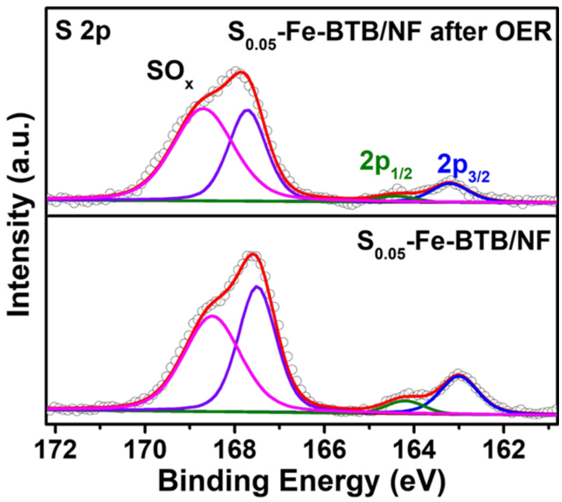

Figure S13. Comparison of high resolution S 2p XPS spectra of $S_{0.05}$-Fe-BTB/NF before and after OER stability test.

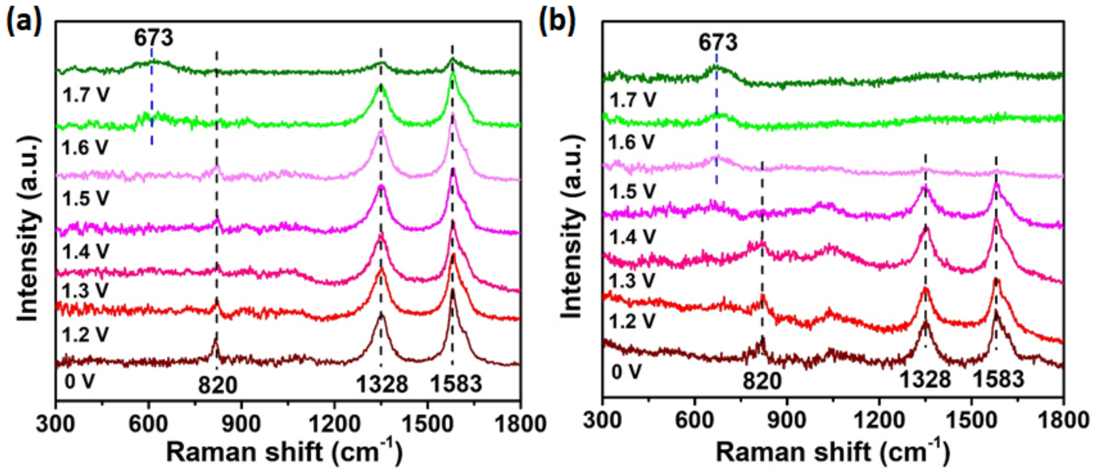

Figure S14. *Operando* Raman spectroscopy measurements of (a) Fe-BTB/NF and (b) $S_{0.05}$-Fe-BTB/NF catalysts, respectively.

Table S3. Comparison of OER performance in 1.0 M KOH for $S_{0.05}$-Fe-BTB/NF with other reported Fe-based electrocatalysts and MOFs as electrocatalysts loaded on conductive substrate (*j*: Current density; η_j: Overpotential at the corresponding current density).

Catalyst	*j* (mA cm^{-2})	η_j (mV)	Tafel Slope (mV dec^{-1})	References
$S_{0.05}$-Fe-BTB/NF	**20**	**231**	**41**	**This work**
Fe-BTB/NF	**20**	**268**	**44**	**This work**
NiFe-LDH/NF	20	260	50	Chem. Commun., 2014, 50, 6479
$Ni_{1.85}Fe_{0.15}P$ NSAs/NF	20	270	96	ACS Appl. Mater. Interfaces, 2017, 9, 31, 26001
$(Ni_{0.5}Fe_{0.5})_2P$/NF	20	219	57	J. Mater. Chem. A, 2017, 5, 11229
FeOOH(Se)/IF	10	287	54	J. Am. Chem. Soc., 2019, 141, 7005
FeOOH/Co/	20	250	32	Angew. Chem. Int. Ed.,

FeOOH-NF				2016, 55, 3694
$FeSe_2$/NF	10	245	-	Angew. Chem. Int. Ed., 2017, 56, 1056
Fe-Ni_3S_2/FeNi	20	~320	54	Small, 2017, 13, 1604161
S-$NiFe_2O_4$/NF	10	267	37	Nano Energy, 2017, 40, 264
FeNi/$NiFe_2O_4$@ NC-800	10	~316	60	ACS Appl. Mater. Interfaces, 2016, 8, 34396
FeNi LDH-rGO	10	210	39	Angew. Chem. Int. Ed., 2014, 53, 7584
Ru-MnFeP/NF	20	191	69	Adv. Energy Mater., 2020, 10, 2000814
Co_3O_4/$Fe_{0.33}Co_{0.66}P$ /NF	50	215	60	Adv. Mater., 2018, 30, 1803551
$(Ni_2Co_1)_{0.975}Fe_{0.075}$-MOF-NF	10	257	41	Adv. Mater., 2019, 31, 1901139
$FeNi_2S_4$/GA/NF	20	~290	66	J. Mater. Chem. A, 2018, 6, 19417
NiFe LDH @NiCoP/NF	10	220	49	Adv. Funct. Mater., 2018, 28, 1706847
7.5-1h LDH-MOF@NF	10	275	47	Adv. Funct. Mater., 2019, 29, 1903875
NiFeMn-LDH/CP	20	289	47	Chem. Commun., 2016, 52, 908
NiFe-MOF-74/NF	20	~240	76	Chem. Commun., 2018, 54, 7046
NiFe-LDH/CNT	10	~240	40	Nat. Commun., 2014, 5, 4477
$W_{0.5}Co_{0.4}Fe_{0.1}$/NF	10	250	32	Angew. Chem. Int. Ed., 2017, 56, 4502
$Fe_{17.5\%}$-Ni_3S_2/NF	20	222	42	ACS Catal., 2018, 8, 5431
FeCoP UNSAs/NF	20	260	63	Nano Energy, 2017, 41, 583

NFN-MOF/NF	20	~260	58.8	Adv. Energy Mater., 2018, 8, 1801065
NiFe-MOF/NF	10	240	34	Nat. Commun., 2017, 8, 15341
CoFePO@NF	20	~295	52	ACS Nano, 2016, 10, 8738
NiFe LDH@ NiCoP/NF	10	220	48.6	Adv. Funct. Mater., 2018, 28, 1706847
Am $FePO_4$/NF	10	218	43	Adv. Mater., 2017, 29, 1704574
FeOOH/Ni_3N/CC	20	~265	65	Appl. Catal. B, 2020, 269, 118600
NiMo-PVP/NiFe-PVP/CC	10	297	48	Adv. Energy Mater., 2017, 7, 1700220
NiO/NiFe LDH/CP	~30	205	30	Adv. Mater., 2019, 31, 1804769
NiFe-LDH@NiCu	10	218	57	Adv. Mater., 2019, 31, 1806769
NiFe LDH/CNT	10	247	31	J. Am. Chem. Soc., 2013, 135, 8452
NiFe LDHs@ FeOOH/NF	10	208	42	ACS Appl. Mater. Interfaces, 2017, 9, 464.

Table S4. The concentration of electrochemical extraction of Fe species of synthesized Fe-BTB/NF and $S_{0.05}$-Fe-BTB/NF catalysts measured by ICP-MS after 6000 CV cycles.

Catalyst	Fe content from electrochemical extraction (mg L^{-1})
Fe-BTB/NF	0.038
$S_{0.05}$-Fe-BTB/NF	0.018