Supplementary Information
for

Optimize the overall water splitting performance of N, S co-doped carbon-supported NiCoMnSx at high current density by the effect of sulfur defects and oxygen vacancies

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Calculation methods of electrochemical related parameters:

Electrochemically active surface area (ECSAs): The electrochemically active surface area (ECSA) of the catalysts was determined by the double-layer capacitance (C_{dl}) measurements in 1 M KOH electrolyte. The doublelayer capacitance (C_{dl}) was determined by measuring the non-Faradaic capacitive current charging from the scan-rate dependence of CVs. The potential window of CVs was 0.324 V to 0.524 vs RHE. The C_{dl} was given by the following equation:

$$C_{dl} = d(\Delta j) / (2dv_b) \qquad (1)$$

where ν is the scan rate, j is the current density.

The ECSA is calculated from the double layer capacitance according to:

$$ECSA = C_{dl} / C_s \qquad (2)$$

where C_s is the specific capacitance of the sample. We use general specific capacitances of Cs = 0.04 mF cm^{-2} based on typical reported values.

***Mass activity*:** The Mass activity (j_m, A g^{-1}) is evaluated at the overpotential of η=400 mV and the catalyst loading m (0.8 mg cm_{geo}^{-2}). The current density j_{geo} (mA cm_{geo}^{-2}) was given by the following equation:

$$j_m = j_{geo} / m \qquad (3)$$

Turnover frequency (TOF): Assuming that all Co and Mn ions in the catalysts were active and contributed to the catalytic reaction, we obtained molar number of metal atom (n) by ICP to calculate the lowest TOF. The specific calculation formula was as follows:

$$TOF = jS/(4Fn) \qquad (4)$$

Where j (A cm^{-2}) is the current density corresponding to 400 mV; S is the surface area of electrode, the number 4 is the assumption that all reactions in the paper are four-electron processes; F is Faraday constant (96485.3 C/mol), and n is the metal ions molar number.

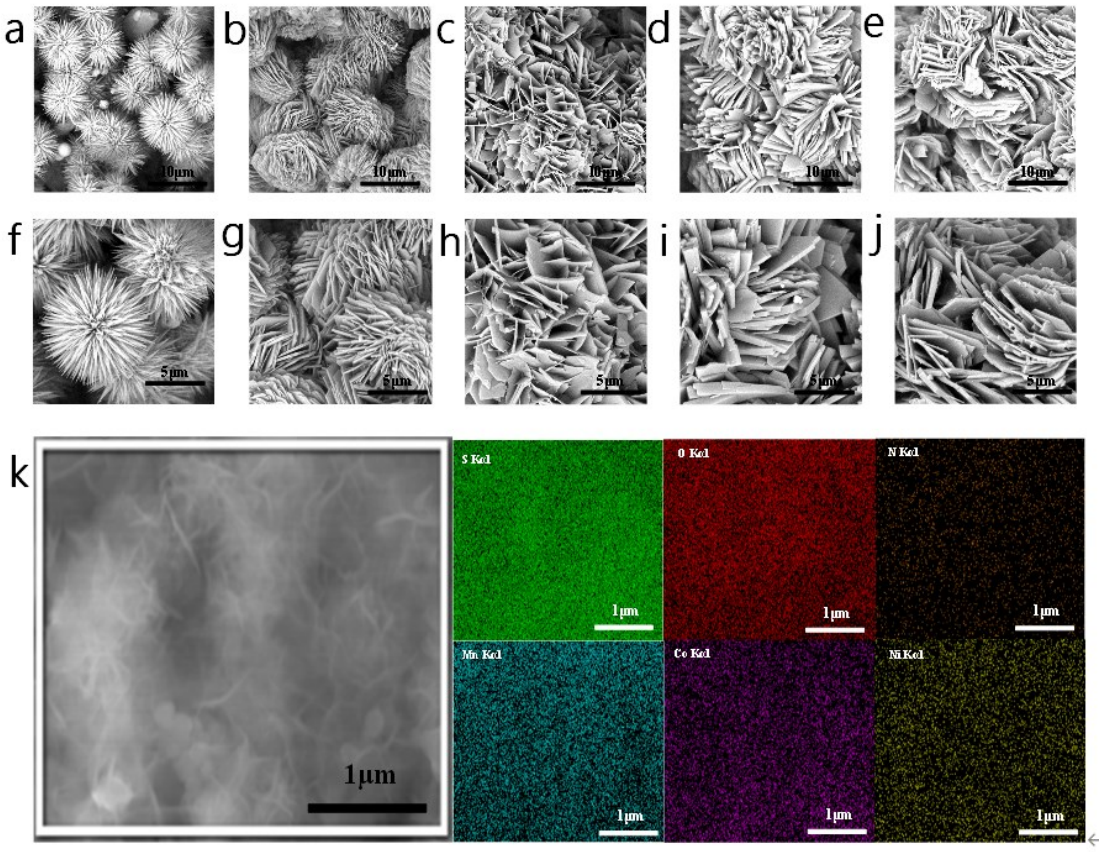

Figure S1 (a,f) FESEM images of NCM(OH)x; (b,g) FESEM images of NCM(BDC)x-5;(c,h) FESEM images of NCM(BDC)x-10; (d,i) FESEM images of NCM(BDC)x-15; (e,j) FESEM images of NCM(BDC)x-20;(k) EDS element distribution map of NCMSx-10.

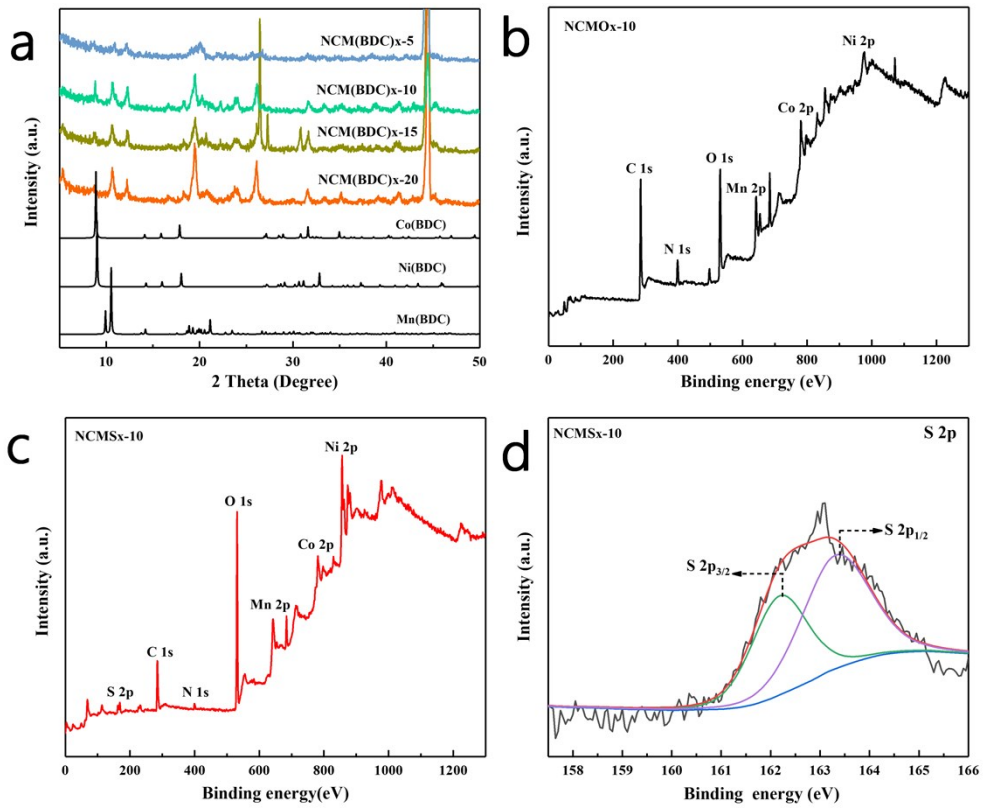

Figure S2 (a) XRD patterns of NCM(BDC)x; (b) XPS survey spectra of NCMOx-10 ;(c) XPS survey spectra of NCMSx-10; (d) S 2p spectra of NCMSx-10.

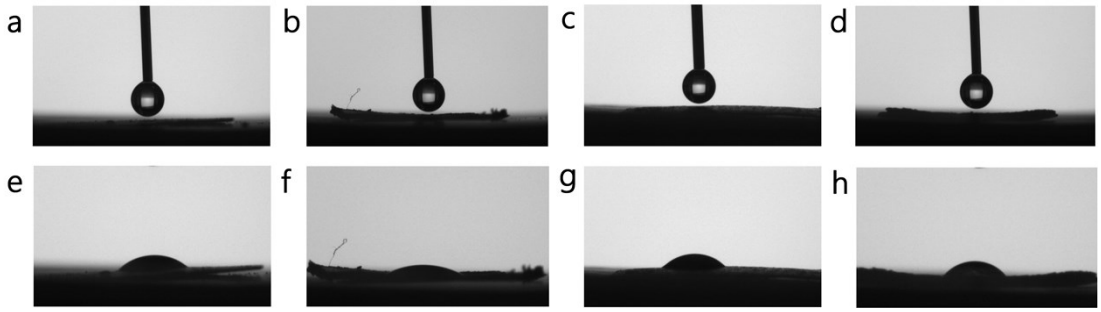

Figure S3 (a,e) Water contact angle of NCMSx-5;(b,f) Water contact angle of NCMSx-10;(c,g) Water contact angle of NCMSx-15;(d,h) Water contact angle of NCMSx-20.

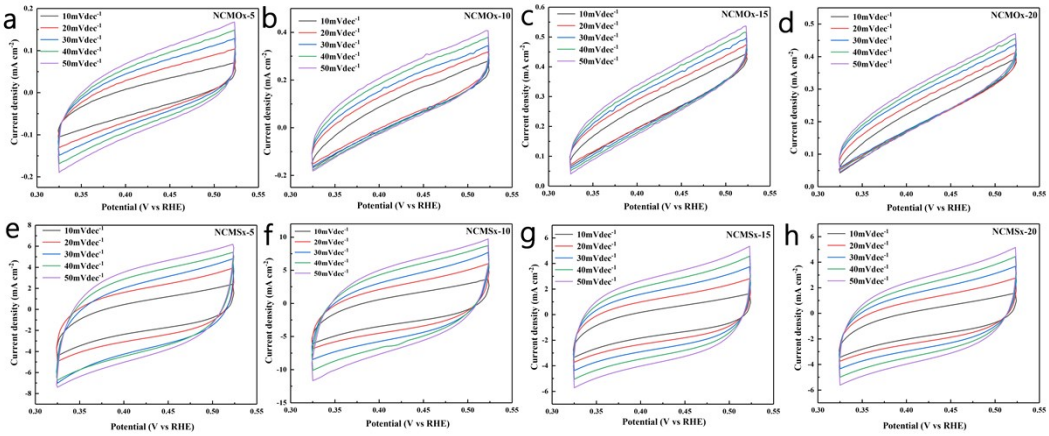

Figure S4 (a) CV curves of NCMOx-5; (b) CV curves of NCMOx-10;(c) CV curves of NCMOx-15; (d) CV curves of NCMOx-20; (e) CV curves of NCMSx-5 ; (f) CV curves of NCMSx-10; (g) CV curves of NCMSx-15;(h) CV curves of NCMSx-20.

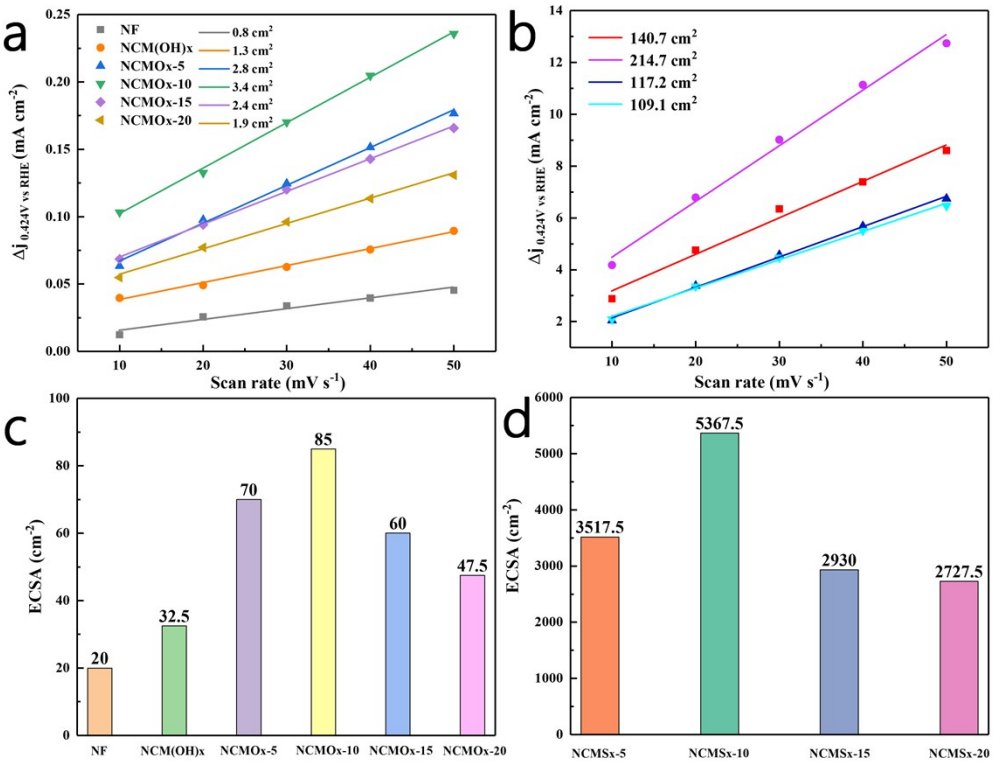

Figure S5 (a) C_{dl} of NCMOx;(b) C_{dl} of NCMSx;(c) ECSA of NCMOx;(d)ECSA of NCMSx.

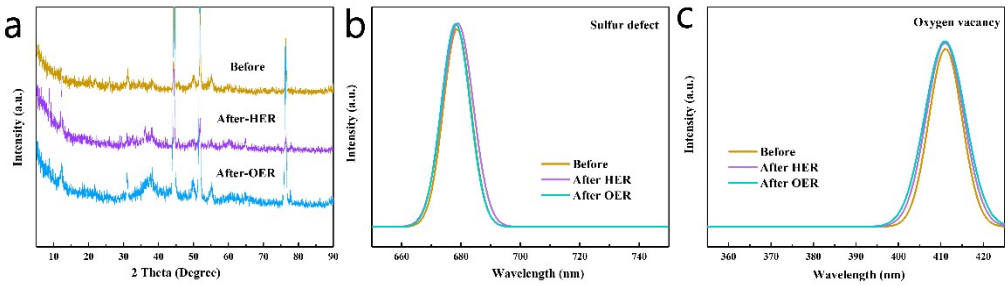

Figure S6 (a)XRD patterns of NCMSx-10 before and after the reaction; (b) When the excitation wavelength is 530nm, the comparison of the PL curve of NCMSx-10 before and after reaction;(c) When the excitation wavelength is 285nm, the comparison of the PL curve of NCMSx-10 before and after reaction.

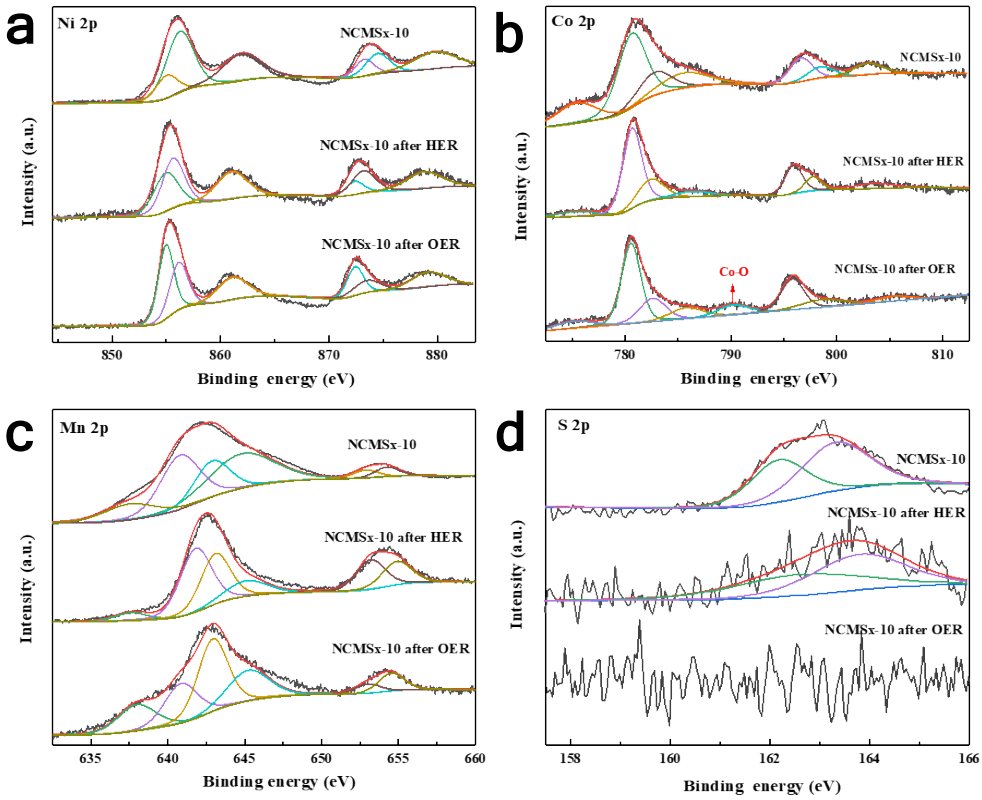

Figure S7 (a)Ni 2p patterns of NCMSx before and after the reaction;(b) Co 2p patterns of NCMSx before and after the reaction;(c) Mn 2p patterns of NCMSx before and after the reaction;(d) S 2p patterns of NCMSx before and after the reaction.

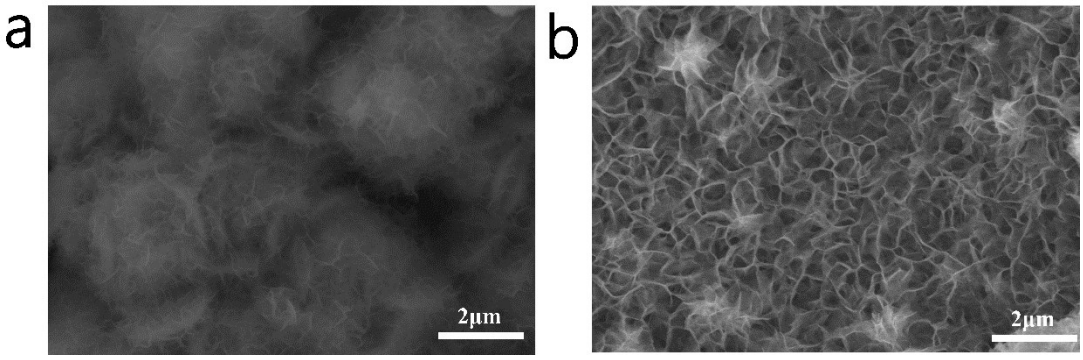

Figure S8 (a) SEM image after HER ;(b) SEM image after OER.

Table S1 Ratios of Co to Mn elements in NCM(BDC)x determined by ICP-OES analysis.

Catalysts	NCM(BDC)x-5	NCM(BDC)x-10	NCM(BDC)x-15	NCM(BDC)x-20
Co:Mn	1:0.88	1:0.99	1:1.01	1:0.82

Table S2 EIS data fitting results of NCMOx and NCMSx electrodes for HER, respectively.

Catalysts	R_s (Ω)	R_{ct} (Ω)
NCMOx-5	1.20	168.10
NCMOx-10	1.10	129.80
NCMOx-15	1.19	195.80
NCMOx-20	1.27	222.10
NCMSx-5	0.98	38.07
NCMSx-10	1.17	37.37
NCMSx-15	1.25	99.24
NCMSx-20	1.29	129.20

Table S3 EIS data fitting results of NCMOx and NCMSx electrodes for OER, respectively.

Catalysts	Rs (Ω)	R_{ct} (Ω)
NCMOx-5	0.76	179.11
NCMOx-10	0.87	142.70
NCMOx-15	0.87	199.92
NCMOx-20	0.76	243.84
NCMSx-5	0.95	123.21
NCMSx-10	0.94	74.73
NCMSx-15	0.98	124.22
NCMSx-20	0.77	127.80

Table S4 The corresponding voltages of NCMOx and NCMSx electrodes at a current density of 10 mA cm^{-2}.

Catalysts	$\eta(_{j=10\ mA\ cm^{-2}})$/mV (HER)	$\eta(_{j=10\ mA\ cm^{-2}})$/mV (OER)	$\eta(_{j=10\ mA\ cm^{-2}})$/V (Overall water spiliting)
NCMOx-5	-160	321	1.796
NCMOx-10	-152	334	1.788
NCMOx-15	-161	356	1.847
NCMOx-20	-164	375	1.878
NCMSx-5	-123	234	1.642
NCMSx-10	-105	226	1.506
NCMSx-15	-136	228	1.535
NCMSx-15	-158	245	1.660

Table S5 When the current density is 10 mA cm^{-2}, the HER and overall water splitting performance of NCMSx-10 are compared with other non-precious electrocatalysts in alkaline electrolytes.

Catalysts	HER/mV	Overall water splitting /V	Electrolyte	Ref.
NCMSx-10	105	**1.506**	**1 M KOH**	**This work**
$NiCo_2O_4$	110	1.65	1 M KOH	1
MoS_2-NiS_2/N-doped graphene	172	1.64	1 M KOH	2
NiFeOH/CoS_x	146	1.563	1 M KOH	3
NiCoSe/C	143	1.68	1 M KOH	4
CVN/CC	118	1.64	1 M KOH	5
$Co_{0.9}S_{0.58}P_{0.42}$	139	1.59	1 M KOH	6
$Co_{0.25}Fe_{0.75}S_2$	267	1.60	1 M KOH	7

References

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