Supplementary Information

Operando X-ray Spectroscopically Visualizing a Chameleon-Like Structural Reconstruction on Oxygen Evolution Electrocatalyst

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1. Experimental Section



Figure S1. Raman spectra of the Co₉S₈-SWCNT.



Figure S2. TEM image of the Co₉S₈-SWCNT.



Figure S3. XPS survey spectra of the Co₉S₈-SWCNT.



Figure S4. Co 2p spectra of the Co₉S₈-SWCNT.



Figure S5. S 2p XPS spectra of the Co₉S₈-SWCNT.



Figure S6. C K-edge XANES spectra of pure SWCNT and the Co_9S_8 -SWCNT.



Figure S7. X-ray absorption spectroscopy of Co $L_{2,3}$ -edge in Co_9S_8 -SWCNT and Co_9S_8 powder.



Figure S8. (a) Zoom on the absorption edge for easy observation (b) Normalized XANES spectra of Co K-edge for Co_9S_8 -SWCNT.



Figure S9. CVs of Co_9S_8 powder (A), CoOOH-SWCNT (B) and Co_9S_8 -SWCNT (C) measured in non-Faradaic region at different scan rate in 1M KOH. (D,E,F) The cathodic (red) and anodic (black) charging currents against different scan rates for the estimation of double-layer capacitance and the C_{dl} of the system is taken as the average of the absolute value of the slope of the linear fits to the data.



Figure S10. Comparison of the OER activity of Co_9S_8 -SWCNT with the recently reported electrocatalysts in alkaline media.¹⁻¹⁴



Figure S11. Electrochemical impedance spectra of Co_9S_8 powder, Co_9S_8 -SWCNT and SWCNT in 1M KOH. R_S refers to the equivalent series resistance. CPE is the constant phase element, R_{ct} determine the overall charge-transfer resistance.



Figure S12. The ring current of Co_9S_8 -SWCNT on a RRDE with a constant potential of 0.5 V (vs. RHE) in N₂-saturated 1 M KOH.



Figure S13. Faradaic efficiency of the Co_9S_8 -SWCNT in 1M KOH electrolyte by a gas chromatograph.



Figure S14. Comparison of the OER activity of Co_9S_8 -SWCNT with the recently reported electrocatalysts in neutral media.¹⁵⁻²⁵



Figure S15. CVs of Co_9S_8 powder (A) and Co_9S_8 -SWCNT (B) measured in non-Faradaic region at different scan rate in 1M PBS. (C,D) Current against different scan rates for the estimation of double-layer capacitance.



Figure S16. Electrochemical impedance spectra of Co_9S_8 powder, Co_9S_8 -SWCNT and SWCNT in 1M PBS.



Figure S17. The ring current of Co_9S_8 -SWCNT on a RRDE with a constant potential of 0.5 V (vs. RHE) in N₂-saturated 1 M PBS.



Figure S18. XRD pattern of Co_9S_8 powder after OER at pH=14.



Figure S19. Raman spectra of Co_9S_8 -SWCNT after OER at pH=14.



Figure S20. SEM (a) and TEM (b) images of the CSST-14.



Figure S21. The HAADF-STEM and EDS-mapping of Co₉S₈-SWCNT after OER at pH=14.



Figure S22. Quasi-in situ FT-IR spectra of Co₉S₈-SWCNT during OER at pH=14.



Figure S23. High-resolution Co 2p XPS spectra of CSST-14.



Figure. S24. The S 2p XPS of Co9S8-SWCNT after OER under alkaline conditions (CSST-14) and neutral conditions (CSST-7).



Figure S25. OER activity of Co_9S_8 -SWCNT in 1 M KOH before and after soaking in 0.1 mM ZnCl₂ solution and H₂O for 120 s.



Figure S26. XRD pattern of Co₉S₈ powder after OER at pH=7.



Figure S27. TEM (a) and SEM(b) images of CSST-7.



Figure S28. The HAADF-STEM and EDS-mapping of CSST-7.



Figure S29. Co 2p XPS spectra of Co₉S₈-SWCNT and the CSST-7.



Figure S30. LSV curve of the Co₉S₈-SWCNT in acetic acid-sodium acetate buffer solution (pH=5).

To validate our hypothesis that Co_9S_8 -SWCNT undergo a chameleon-like structural self-optimization during OER process, we performed additional OER tests in buffer solutions of pH=5 (acetic acid-sodium acetate buffer solution). As shown in Figure S30, the Co_9S_8 -SWCNT showed superb catalytic performances, and the sample after reaction was characterized using XAFS later.



Figure S31. LSV curve of the Co₉S₈-SWCNT in ammonia-ammonium chloride buffer solution (pH=10).



Figure S32. Normalized XANES spectra of Co K-edge for Co_9S_8 -SWCNT and CSST-5.



Figure S33. k^3 -weighted FT-EXAFS spectra for Co_9S_8 -SWCNT and CSST-5.



Figure S34. Normalized Co K-edge XANES spectra for Co_9S_8 -SWCNT and the reference samples, including CoO, CoS_2 , and CSST-10.



Figure S35. k³-weighted FT-EXAFS spectra for CSST-10 and c-CoS₂.



Figure S36. XRD patterns of reference sample CoOOH.



Figure S37. XRD patterns of reference sample CoS.





 Co_9S_8 -SWCNT. ① electrochemical work station.

Table S1. The fitting results of Co K-edge EXAFS spectra for Co_9S_8 - SWCNT and reference sample CoS_2 .

	Path	Ν	R(Å)	$\sigma^2 (10^{-3} \text{ Å}^2)$
Co ₉ S ₈ -	Co-S	4.0	2.20	7.4
SWCNT	Co-Co/S	1.8	2.46	5.3
CoS_2	Co-S	6*	2.31	5.1

Notes: Path means the nearest and second nearest coordination shell. N is coordination number, R is the bond length and σ^2 is Debye-Waller factor. Error bounds (accuracies) were estimated as N, ±10%; Bond length, ±1%; σ^2 , ±10%. * is fixed coordination number according to the standard crystal structure.

 Table S2. Content of active components in Co₉S₈-SWCNT.

C09S8- SWCNT	Co(µg/mL)	S(µg/mL)	Co(µmol/mL)	S(µmol/mL)
Electrolyte	3.435	1.632	0.058	0.051

Notes: The geometric area of Co_9S_8 -SWCNT is 1 cm², and the volume of the solution for ICP-AES test is 4 mL.

pH=14	Co(µg/mL)	S(µg/mL)	Co(µmol/mL)	S(µmol/mL)
Electrolyte after i-t	0	0.011	0	0.0003

Table S3. Electrolyte composition after OER at pH=14.

Notes: the volume of electrolyte is 40 mL.

pH=7	Co(µg/mL)	S(µg/mL)	Co(µmol/mL)	S(µmol/mL)
Electrolyte after i-t	0.016	0	0.0002	0

Table S4. Electrolyte composition after OER at pH=7.

Notes: the volume of electrolyte is 40 mL.

	Path	Ν	R(Å)	$\sigma^2(10^{-3} \text{ Å}^2)$
	Co-O	3.9	1.91	4.1
1.8 V	Co-S	1.0	2.30	6.0
	Co-Co	3.7	2.85	4.5
	Co-O	2.9	1.93	5.4
1.1 V	Co-S	1.7	2.31	5.0
	Co-Co	2.3	2.83	4.7
СоООН	Со-О	6*	1.90	3.3
	Co-Co	6*	2.84	4.0

Table S5. The fitting results of Co K-edge EXAFS spectra for Co_9S_8 - SWCNT working at 1.1 V and 1.8 V, and reference sample CoOOH.

Notes: Path means the nearest and other nearest coordination shells. N is coordination number, R is the bond length and σ^2 is Debye-Waller factor. Error bounds (accuracies) were estimated as N, ±10%; Bond length, ±1%; σ^2 , ±10%. * is fixed coordination number according to the standard crystal structure.

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