Parallel Array Structured Cobalt Sulfide/Nitrogen Doped Carbon Nanocage /Carbon Fiber Composite Based on Microfluidic Spinning Technology: A Novel Design to Boost Overall Water Splitting

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Experimental methods

Materials

Co(CH₃COO)₂·4H₂O (99.5%), 2-methylimidazole (2-MeIM, 98%, Macklin), polyvinyl pyrrolidone (PVP, $M_w = 1,300,000 \text{ g} \cdot \text{mol}^{-1}$, Macklin), N,Ndimethylformamide (DMF, AR, Reagent), anhydrous methanol (AR, Reagent), anhydrous ethanol (AR, Reagent), potassium hydroxide (85%, AR, Aladdin), Nafion solution (5% by weight, DuPont).

Experimental section

Synthesis of the p-ZIF-67/PVP precursor: Firstly, 1.992 g Co(CH₃COO)₂·4H₂O and 2.624 g 2-MeIM were dissolved in 200 mL anhydrous methanol by magnetic stirring at room temperature to form a clear purple solution. After the solution was heated to 85 °C under continuous magnetic stirring for 5 h, the ZIF-67 nanocrystal was harvested via centrifugation. Subsequently, 0.2 g PVP and 2.4 g ZIF-67 nanocrystal were dissolved in 5 mL DMF solution ultrasonically stirred for 2 h. Then, 0.8 g PVP was added to the above solution and stirred for 12 h to obtain the uniformly dispersed ZIF-67 spinning solution to increase viscosity for spinning. Afterwards, microfluidic spinning technology was employed to obtain the p-ZIF-67/PVP fiber precursor on the receiver wrapped in aluminum foil under environmental conditions at 20 °C and 20 % humidity. In the microfluidic spinning process, the needle speed was set to 0.03 mL/h, while the receiver motor speed and the Needle-to-Receiver distance were set to 200 r/min and 2 mm, respectively.

Synthesis of the p-Co/NC/CF catalyst: The as-prepared p-ZIF-67/PVP fibers precursor was first pre-oxidized in air at 150 °C for 1 h and 250 °C for 1 h to improve the fiber strength and stability. Afterwards, p-ZIF-67/PVP was carbonized at 800 °C for 2 h under the protection of N_2 atmosphere to obtain the p-Co/NC/CF catalyst.

Synthesis of the p-Co₉S₈/NC/CF catalyst: To obtain the final p-Co₉S₈/NC/CF catalyst, the above p-Co/NC/CF catalyst was first oxidized in air at 300 °C for 1 h and then sulfurized in Ar&H₂ (5% H₂) atmosphere at 400 °C for 3 h. In the sulfurization step, the composite catalyst and sulfur were separately loaded in a crucible with a mass

ratio of 1:10. For comparison, the disordered Co₉S₈/NC/CF catalyst was fabricated by using electrostatic spinning technology while the other steps were the same as those of the p-Co₉S₈/NC/CF catalyst. Notably, the Co₉S₈/NC composite have the same size in p-Co₉S₈/NC/CF and Co₉S₈/NC/CF, while the diameter of carbon fibers in p-Co₉S₈/NC/CF are wider than that in Co₉S₈/NC/CF due to the difference between microfluidic spinning technology and electrostatic spinning technology.

In the fabricating process of p-Co₉S₈/NC/CF, by precisely adjusting the additive amount of the cobalt salt (Co (CH₃COO)₂·4H₂O), we can achieve a systematic variation in the Co₉S₈ content. In the preparation process of p-Co₉S₈/NC/CF, the addition of PVP and DMF keep the same due to the viscosity limitations of microfluidic spinning technology. Based on the previous exploration of optimal experimental conditions, the addition of PVP and DMF are 1.0 g and 5 mL, respectively, while the variant of the mole number of Co (CH₃COO)₂·4H₂O are 4 mmol, 6 mmol, 8 mmol and 10 mmol. Accordingly, the catalysts are named as p-Co₉S₈/NC/CF-4, p-Co₉S₈/NC/CF-6, p-Co₉S₈/NC/CF (Best), and p-Co₉S₈/NC/CF-10, respectively.

Materials characterization

The morphologies and microstructures of these samples were characterized by scanning electron microscope (SEM, ZEISS SIGMA 500) and transmission electron microscopy (TEM, FEI Talos-F200S). Raman spectra were obtained by Horiba LabRAM HR Evolution spectrometer. X-ray photoelectron spectroscopy (XPS) was used to analyze the chemical state of materials by AXIS Supra facility, and 284.8 eV was used for C 1s calibration. X-ray diffraction (XRD) using Rigaku Ultima IV system with Cu Kα radiation was used to determine the composition and structure of materials. Fourier transform infrared spectrometer (FT-IR) spectra were recorded on the Thermo Scientific Nicolet iS50. The specific surface area and pore structure were determined on ASAP 2020 by the Brunauer-Emmett-Teller (BET) method. X-ray absorption spectroscopy (XAS) measurements at the Co K-edge were performed on the 1W1B-XAFS beamline of Beijing Synchrotron Radiation Facility (BSRF), China.

Electrochemical measurements

Electrochemical tests were characterized using a three-electrode system on a CHI 760E electrochemical workstation at room temperature. The saturated calomel electrode (SCE) and graphite electrode were used as the reference electrode and the counter electrode, respectively. To prepare the working electrode, the catalyst ink was dropped onto the L-type glassy carbon electrode (diameter of 3 mm) with a mass loading of 0.35 mg·cm⁻². The catalyst ink was prepared by ultrasonically dispersing 5 mg catalysts into 740 μ L of ethanol, 200 μ L of deionized water, and 60 μ L of Nafion solution. All potentials shown in this work were calibrated to the reversible hydrogen electrode (RHE) by equation (1).

$$E_{RHE} = E_{SCE} + 0.059 \times pH + 0.24 V$$
 (1)

The linear sweep voltammetry (LSV) was conducted at a rate of 5 mV·s⁻¹ with 80% iR compensation to evaluate OER ($1.0 \sim 2.0$ V vs. RHE) and HER ($0 \sim -1.0$ V vs. RHE) performances in the 1 M O₂-saturated KOH solution. The Cyclic voltammetry (CV) curves were performed in the 1 M N₂-saturated KOH solution between 0.16 V to 0.26 V at different scan rates to obtain the double-layer capacitance (C_{dl}), which could further determine the electrochemical active surface areas (ECSA). Electrochemical impedance spectroscopy (EIS) was carried out from 0.1 to 10⁶ Hz with an amplitude of 5 mV. The long-term performance of the catalysts was evaluated by chronopotentiometry at a current density of 10 mA cm⁻². For comparison, the commercial Pt/C (20 wt%) and RuO₂ catalyst was measured in the same way.

Calculation of the turnover frequency (TOF)

The turnover frequency (TOF) is estimated by the following equation¹:

$$TOF = \frac{j \times N_A}{n \times F \times \Gamma}$$

where j is the current density, N_A is the Avogadro number, n is the number of electron transferred for the evolution of a single O₂ molecule, F is the Faraday constant, and Γ is the surface concentration or the number of active sites.

DFT calculation

According to the first principles, all spin-polarization density functional theory (DFT) calculations were performed within the generalized gradient approximation (GGA) by means of the Perdew-Burke-Ernzerhof (PBE) formulation^{2, 3}. The DFT-D3 empirical correction method was employed to describe van der Waals interactions. Geometry optimizations were performed with the force convergency smaller than 0.05 eV/Å. Monkhorst-Pack k-points of $2 \times 2 \times 1$ were applied for all the calculations. The free energy changes (Δ G) of each elementary reaction step during OER were calculated using the computational hydrogen electrode (CHE) model. In this model, the chemical potential is equal to the energy of half of the gas-phase H₂ at 0 V vs RHE.

The Gibbs free energy was calculated by the following equation (2):

$$\Delta G = \Delta E + \Delta E_{ZPE} - T\Delta S \tag{2}$$

Where the value of ΔE , $\Delta EZPE$ and ΔS denotes the changes of DFT energy, the zero-point energy and the entropy at 300K, respectively.

The OER undergoes the *OH, *O, and *OOH transition processes, where * represents adsorption points on the catalyst surface.

$$\Delta G_1 = \Delta G(*OH) \tag{3}$$

$$\Delta G_2 = \Delta G(*O) - \Delta G(*OH) \tag{4}$$

$$\Delta G_3 = \Delta G(*OOH) - \Delta G(*O) \tag{5}$$

$$\Delta G_4 = 4.92 - \Delta G(*OOH) \tag{6}$$

In addition, the overpotential of OER is calculated using the following Equation (10):

$$U_{\text{overpotential}} = 1.23 - \max \{ \Delta G_1, \Delta G_2, \Delta G_3, \Delta G_4 \}$$
(7)

In an alkaline electrolyte, the OER process follows the following reaction steps:

$$OH^- + * \rightarrow *OH^+ e^- \tag{8}$$

$$*OH+OH \rightarrow *O+H_2O+e^-$$
 (9)

$$*O+OH \rightarrow *OOH+e^{-}$$
 (10)

$$*OOH+OH^{-} \rightarrow O_2+H_2O+e^{-}$$
(11)



Figure S1. Schematic illustration of the synthesis of ZIF-67.



Figure S2. (b-c) SEM images of ZIF-67 under different magnifications.



Figure S3. XRD pattern of ZIF-67.



Figure S4. SEM image of p-ZIF-67/PVP.



Figure S5. Elemental mapping images of p-Co/NC/CF.



Figure S6. FR-IR spectrum of p-Co₉S₈/NC/CF and p-Co/NC/CF.









Figure S8. (a) XRD pattern, (b) Raman spectra of Co₉S₈/NC/CF.



Figure S9. XPS spectra of $Co_9S_8/NC/CF$ (a) XPS survey spectra, (b) Co 2p, (c) S 2p and (d) N 1s high-resolution XPS spectra.



Figure S10. (a) BET adsorption isotherm (b-c) pore size distribution of Co₉S₈/NC/CF.



Figure S11 LSV curves for (a) OER, (b) HER of $p-Co_9S_8/NC/CF$ with different proportions of Co (CH₃COO)₂·4H₂O.



Figure S12. the Enlarged image of polarization curves for OER.



Figure S13. Comparison of the overpotentials at 10 mA·cm⁻² for p-Co₉S₈/NC/CF with reported catalysts.



Figure S14. I-t chronoamperometric curves.



Figure S15. XRD spectrum of p-Co₉S₈/NC/CF after OER stability test.



Figure S16. TEM images of p-Co₉S₈/NC/CF after OER stability test.



Figure S17. XPS spectra of p-Co₉S₈/NC/CF after OER stability test (a) survey spectra, (b) Co 2p, (c) S 2p and (d) N 1s high-resolution spectra.



Figure S18. LSV curves of p-Co₉S₈/NC/CF before and after OER stability test.



Figure S19. CV curves of p-Co₉S₈/NC/CF, Co₉S₈/NC/CF, p-Co/NC/CF and RuO₂ electrocatalysts at different scan rates from 10 to 60 mV \cdot s⁻¹.



Figure S20. (a) CV curves of Pt/C electrocatalyst at different scan rates from 10 to 60 $mV \cdot s^{-1}$, (b) C_{dl} value of Pt/C electrocatalyst.



Figure S21. ECSA-normalized OER LSV curves.



Figure S22. (a) Crystal structure of Co₉S₈, (b) Co₉S₈ (440) surface model.



Figure S23. front view of the optimized adsorption configuration of OER intermediates (*OH, *O, and *OOH) on the p-Co₉S₈/NC/CF surfaces.



Figure S24. Top view of the optimized adsorption configuration of OER intermediates (*OH, *O, and *OOH) on the p-Co₉S₈/NC/CF surfaces.



Figure S25. the Gibbs free energy changes for four steps about the OER reaction.



Figure S26. ECSA-normalized HER curves.



Figure S27. Photograph of two-electrode configuration for overall water splitting.



Figure S28. Corresponding cell voltages.

p-Co/NC/CF					
elements	atomicity	Normalized mass(%)	Atom(%)	Abs. error (%)	
С	6	73.59	86.99	28.59	
0	8	6.91	6.13	4.85	
Co	27	16.68	4.02	8.11	
Ν	7	2.82	2.86	3.80	

Table S1. Energy Dispersive X-ray spectroscopy (EDX) of p-Co/NC/CF.

Table S2. Energy Dispersive X-ray spectroscopy (EDX) of p-Co₉S₈/NC/CF.

p-Co ₉ S ₈ /NC/CF						
elemen	ts atomicity	Normalized mass(%)	Atom(%)	Abs. error (%)		
С	6	50.76	68.22	15.89		
Ο	8	16.84	16.99	5.78		
S	16	13.47	6.78	1.38		
Co	27	15.71	4.30	5.19		
Ν	7	3.21	3.70	1.77		

p-Co/NC/CF					
elements	Pos.	FWHM	Area	At%	
O 1s	531.81	3.63	1280.33	16.97	
C 1s	284.81	2.89	50900.80	80.96	
N 1s	399.81	3.94	31265.40	1.13	
Co 2p	780.81	5.48	11218.16	0.93	

Table S3. XPS element content of p-Co/NC/CF.

Table S4. XPS element content of p-Co₉S₈/NC/CF.

p-Co ₉ S ₈ /NC/CF						
elements	Pos.	FWHM	Area	At%		
O 1s	531.79	3.14	48318.31	21.35		
C 1s	284.79	2.87	53283.92	68.97		
N 1s	399.79	4.7	2573.92	1.85		
Co 2p	780.79	5.06	31928.74	2.16		
S 2p	163.79	4.14	7345.39	5.67		

Table S5. Comparative OER performance of $p-Co_9S_8/NC/CF$ and other transition-metal-based electrocatalysts.

Catalyst	j value (mA·cm ⁻²)	Overpotentials (mV)	Tafel slope (mV·dec ⁻¹)	Reference
p-Co ₉ S ₈ /NC/CF	100	398	75	This work
Ni@N-HCGHF	100	470	63	4
Fe ₃ C-Co/NC	100	450		5
Ni ₂ P-VP ₂ /NF	100	398	56	6
FeCoNi-HNTAs	100	490		7
Co-ZIF/CDs/CC	100	401	147	8
Ni-Mo-S nanowire	100	390	75	9
$Ni(S_{0.5}Se_{0.5})_2$	100	501	94	10
Cu ₂ S-Ni ₃ S ₂ /NF	10	329	44	11
$Bi_2S_3/Ni_3S_2/NF$	10	268	82	12
Ni-doped CZTS	10	214	109	13

Table S6. C_{dl} and ECSA values of electrocatalysts.

	p-Co ₉ S ₈ /NC/CF	Co ₉ S ₈ /NC/CF	p-Co/NC/CF	RuO ₂	Pt/C
$C_{dl} (mF \cdot cm^{-2})$	15.2	13.1	5.0	7.5	9.9
ECSA	253.3	218.3	83.3	125	165

 Table S7. TOF values of electrocatalysts.

	p-Co ₉ S ₈ /NC/CF	Co ₉ S ₈ /NC/CF	p-Co/NC/CF
$TOF(s^{-1})$	1.179	0.508	0.122

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