Sulfur modified charge-asymmetry FeNi nanoalloy catalyst anchored on N-doped carbon nanosheets for efficient electrochemical CO₂ reduction

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1. Materials

FeCl₃, NiCl₂ dicyandiamide (DCDA), sulfur powder, sodium sulfide (Na₂S·9H2O), afion D-521 dispersion (5% w/w in water and 1-propanol) and commercial Pt/C (20 wt% metal) were purchased from Alfa Aesar. Methanol, ethanol and KOH were obtained from Sinopharm Chemical. The deionized water used in all experiments was obtained through ion-exchange and filtration. All the chemicals were analytical grade and used without further purification.

2. Synthesis of FeNi Alloy/NC, Fe/NC, and Ni/NC.

To obtain the FeNi Alloy/NC, 50 mg of FeCl₃, 100 mg of NiCl₂, 0.12 g of triacid, and 1.2 g of dicyandiamide were dissolved in 5 mL of deionized water. The solution was continuously stirred and then dried at 75 °C. After drying, the resulting mixture was transferred to a ceramic boat, which was placed in a quartz tube within a horizontal furnace. The material was annealed at 900 °C for 2 hours in a nitrogen atmosphere at a ramp rate of 5 °C/min, followed by cooling to room temperature. The samples were then thoroughly washed with ethanol and deionized water and subsequently dried under vacuum at 60 °C overnight. For comparison, Fe/NC and Ni/NC catalysts were synthesized using the same procedure.

3. Characterizations

The morphology of the samples was characterized by transmission electron microscope (TEM, FEI Tecnai G2 F20 S-Twin, an accelerating voltage of 200 kV). The crystal phases present in each sample were identified using powder X-ray diffraction (XRD) patterns were recorded on a Bruker D8 Advance powder X-ray diffractometer at a scanning rate of 5 $^{\circ}$ C min⁻¹. The Fe K-edge and Ni K-edge X-ray absorption data were collected at BL14W1 station in Shanghai Synchrotron Radiation Facility (SSRF, operated at 3.5 GeV with a maximum current of 250 mA). The radiation was monochromatized by a Si (111) double-crystal monochromator. Data were collected as fluorescence excitation spectra with a Lytle detector. All data were collected at room temperature.

4. XAFS Data Process

The acquired EXAFS data were processed according to the standard procedures using the Athena and Artemis implemented in the IFEFFIT software packages. The fitting detail is described below:

The acquired EXAFS data were processed according to the standard procedures using the ATHENA module implemented in the IFEFFIT software packages. The EXAFS spectra were obtained by subtracting the post-edge background from the overall absorption and then normalizing with respect to the edge-jump step. Subsequently, the $\chi(k)$ data of were Fourier transformed to real (R) space using a hanning windows (dk=1.0 Å⁻¹) to separate the EXAFS contributions from different coordination shells. To obtain the quantitative structural parameters around central atoms, least-squares curve parameter fitting was performed using the ARTEMIS module of IFEFFIT software packages.

The following EXAFS equation was used:

$$\chi(k) = \sum_{j} \frac{N_j S_o^2 F_j(k)}{kR_j^2} exp[-2k^2 \sigma_j^2] exp[\frac{-2R_j}{\lambda(k)}] sin[2kR_j + \phi_j(k)]$$

 S_0^2 is the amplitude reduction factor, $F_j(k)$ is the effective curved-wave backscattering amplitude, N_j is the number of neighbors in the j^{th} atomic shell, R_j is the distance between the X-ray absorbing central atom and the atoms in the j^{th} atomic shell (backscatterer), λ is the mean free path in Å, $\varphi_j(k)$ is the phase shift (including the phase shift for each shell and the total central atom phase shift), σ_j is the Debye-Waller parameter of the j^{th} atomic shell (variation of distances around the average R_j). The functions $F_j(k)$, λ and $\varphi_j(k)$ were calculated with the ab initio code FEFF8.2. The coordination numbers of model samples were fixed as the nominal values. The obtained S_0^2 was fixed in the subsequent fitting. While the internal atomic distances R, Debye-Waller factor σ^2 , and the edge-energy shift ΔE_0 were allowed to run freely.

Supporting Figures and Tables



Figure S1. TEM images of FeNi Alloy/NC.



Figure S2. TEM images of Fe/NC.



Figure S3. TEM images of Ni/NC.



Figure S4. XRD pattern of FeNi/Alloy SNC.



Figure S5. Raman spectrum of the FeNi/Alloy SNC sample.



Figure S6. XPS spectra of FeNi/Alloy SNC.



Figure S7. (a) Fe K-edge XANES spectra and (b) Fe K-edge FT-EXAFS spectra of FeNi alloy/NC and Fe/NC. (c)

Ni K-edge XANES spectra and (d) Ni K-edge FT-EXAFS spectra of FeNi/NC and Ni/NC.



Figure S8. WT-EXAFS plots of Fe Clu/SNC and Ni Clu/SNC, respectively.



Figure S9. The Fe K-edge EXAFS fitting results of FeNi Alloy/SNC.



Figure S10. The Ni K-edge EXAFS fitting results of FeNi Alloy/SNC.



Figure S11. The Fe K-edge EXAFS fitting results of Fe Clu/SNC.



Figure S12. The Ni K-edge EXAFS fitting results of Ni Clu/SNC.



Figure S13. The Ni K-edge EXAFS fitting results of Ni/NC.



Figure S14. The Fe K-edge EXAFS fitting results of Fe/NC.



Figure S15. The Fe K-edge EXAFS fitting results of Fe-FeNi alloy/NC.



Figure S16. The Ni K-edge EXAFS fitting results of Ni-FeNi alloy/NC.



Figure S17. The Fe K-edge EXAFS fitting results of Fe foil.



Figure S18. The Ni K-edge EXAFS fitting results of Ni foil.



Figure S19. (a) CO Faradaic efficiencies of FeNi Alloy/NC, (b) Fe/NC, and (c) Ni/NC. (d) Polarization curves of

the catalysts tested in a CO_2 -saturated 0.5 M KHCO₃ electrolyte.



Figure S20. The TEM images of FeNi Alloy/SNC after test.



Figure S21. The Fe K-edge EXAFS fitting results of FeNi Alloy/SNC at ex situ condition.



Figure S22. The Ni K-edge EXAFS fitting results of FeNi Alloy/SNC at ex situ condition.



Figure S23. The Fe K-edge EXAFS fitting results of FeNi Alloy/SNC at OCP.



Figure S24. The Ni K-edge EXAFS fitting results of FeNi Alloy/SNC at OCP.



Figure S25. The Fe K-edge EXAFS fitting results of FeNi Alloy/SNC at -0.4 V.



Figure S26. The Ni K-edge EXAFS fitting results of FeNi Alloy/SNC at -0.4 V.



Figure S27. The Fe K-edge EXAFS fitting results of FeNi Alloy/SNC at -0.7 V.



Figure S28. The Ni K-edge e EXAFS fitting results of FeNi Alloy/SNC at -0.7 V.

Sample	Path	CN	R(Å)	σ²(10 ⁻³ Ų)	ΔE ₀ (eV)	R factor
Fe foil	Fe-Fe	12*	2.47	4.9	2.4	0.004
Fe Clu/SNC	Fe-N	4.2	1.94	3.8	2.7	
	Fe-S	0.7	2.22	4.2	2.4	0.009
	Fe-Fe	1.7	2.48	5.5	3.1	_
FeNi Alloy/SNC	Fe-N	3.8	1.93	3.9	3.5	
	Fe-S	0.6	2.21	4.5	4.2	0.011
	Fe-Fe/Ni	1.8	2.47	5.2	4.2	_

Table S1. Structural parameters extracted from Fe K-edge EXAFS fitting. (S_0^2 =0.84)

 S_0^2 is the amplitude reduction factor; CN is the coordination number; R is interatomic distance (the bond length between Co central atoms and surrounding coordination atoms); σ^2 is Debye-Waller factor (a measure of thermal and static disorder in absorber-scatterer distances); ΔE_0 is edge-energy shift (the difference between the zero kinetic energy value of the sample and that of the theoretical model). R factor is used to value the goodness of the fitting.

* This value was fixed during EXAFS fitting, based on the known structure.

Error bounds that characterize the structural parameters obtained by EXAFS spectroscopy were estimated as N \pm 20%; R \pm 1%; $\sigma^2 \pm$ 20%; $\Delta E_0 \pm$ 20%.

Sample	Path	CN	R(Å)	σ²(10 ⁻³ Ų)	ΔE₀(eV)	R factor
Ni foil	Ni-Ni	12*	2.46	4.9	2.4	0.004
	Ni-N	4.1	1.99	3.9	3.1	
Ni Clu/SNC	Ni-S	0.9	2.21	4.1	2.2	0.008
	Ni-Ni	1.5	2.55	4.4	2.5	_
FeNi Alloy/SNC	Ni-N	3.9	1.98	2.8	2.7	
	Ni-S	0.7	2.22	3.2	4.1	0.011
	Ni-Ni	1.3	2.54	3.3	2.5	_

Table S2. Structural parameters extracted from Ni K-edge EXAFS fitting. (S_0^2 =0.82)

Catalyst	J _{CO} (mA cm ⁻²)	FE _{co} (%)	Reference
FeNi Alloy/SNC	78.45	98.1	This work
Ag ₂ /graphene	44.3	93.4	Appl. Catal. B 2020, 268,
Fe-N-G-p	4.5	94	ACS Catal. 2020, 10, 19,
Ni-SA/CN	213.2	96.9	Nano energy. 2021, 82,
Ni SAs/N-C	10.48	71.9	J. Am. Chem. Soc. 2017, 139,
Ni–G	50	97	Energy Environ. Sci. 2018, 11,
C-Zn ₁ Ni ₄ ZIF-8	71.5	98	Energy Environ. Sci., 2018,11,
Ni-NC	22	97	Nat. Energy, 2018, 3, 140–147
Ni-N ₃ -V	65	90	Angew. Chem., Int. Ed. Engl.
Cu _{0.5} Zn _{0.5} /ZIF-8	11.57	88.5	Adv. Mater. 2023, 35,
M-Ni-N-C-2/CNTs	19.8	98	J. Colloid Interface Sci., 2023,
Ni–N–C	92.3	92	Energy Environ. Sci., 2022,15,
N-Fe@NC	6.68	97.5	ACS Appl. Mater. Interfaces
V-CuInSe	112	91	Adv. Mater. 2022, 34,

Table S3 Summary of various reported CO₂RR catalysts, compared with FeNi Alloy/SNC.

Sample	Path	CN	R(Å)	σ²(10 ⁻³ Ų)	ΔE₀(eV)	R factor
- Ex situ	Fe-N	3.7	1.94	4.1	2.5	
	Fe-S	0.7	2.22	4.4	2.2	0.009
	Fe-Fe/Ni	1.9	2.45	5.1	3.2	_
ОСР	Fe-N	3.9	1.92	3.6	2.5	
	Fe-S	0.7	2.22	3.8	3.2	0.011
	Fe-Fe/Ni	1.8	2.45	4.1	3.1	_
-0.4 V	Fe-N	4.0	1.91	3.3	3.1	
	Fe-S	0.8	2.23	4.2	2.1	0.012
	Fe-Fe/Ni	1.9	2.47	3.2	2.2	_
-0.7 V	Fe-N	4.1	1.91	4.9	2.3	
	Fe-S	0.9	2.24	3.5	2.3	0.011
	Fe-Fe/Ni	1.7	2.49	3.2	2.7	_

Table S4. Structural parameters extracted from the Fe K-edge EXAFS fitting. $(S_0^2=0.84)$

Sample	Path	CN	R(Å)	σ²(10 ⁻³ Ų)	ΔE₀(eV)	R factor
Ex situ	Ni-N	3.8	1.99	2.7	3.7	
	Ni-S	0.6	2.21	3.2	3.7	0.011
	Ni-Ni/Fe	1.4	2.52	3.5	3.8	
OCP	Ni-N	3.9	1.98	3.4	3.8	
	Ni-S	0.7	2.23	3.4	4.0	0.012
	Ni-Ni/Fe	1.3	2.54	3.2	4.2	
-0.4 V	Ni-N	3.9	1.96	2.7	3.5	
	Ni-S	0.8	2.24	2.9	3.8	0.009
	Ni-Ni/Fe	1.3	2.55	3.4	4.1	-
-0.7 V	Ni-N	4.1	1.95	3.1	3.8	
	Ni-S	0.8	2.26	2.8	3.7	0.009
	Ni-Ni/Fe	1.1	2.56	3.3	4.2	_

Table S5. Structural parameters extracted from Ni K-edge EXAFS fitting. $(S_0^2=0.82)$