Electronic Supplementary Information (ESI) for Inorganic Chemistry Frontiers

Boosting CO_2 electroreduction to CO with abundant nickel single atom active sites

Wei-juan Wang[a], Changsheng Cao[b], Kaiwen Wang[c*] and Tianhua Zhou[b]

[a] College of Chemistry, Fuzhou University, Fuzhou, Fujian 350108, P. R. China.

[b] State Key Laboratory of Structural Chemistry, Fujian Institute of Research on the Structure of Matter, Chinese Academy of Sciences (CAS), Fuzhou 350002, China.

[c] Beijing Key Lab of Microstructure and Properties of Advanced Materials, Beijing University of Technology, Beijing 100124, P. R. China.

*Corresponding authors at:

Beijing Key Lab of Microstructure and Properties of Advanced Materials

Beijing University of Technology, Beijing 100124, P. R. China

Tel: +86 18811419320

E-mail address: 56wkw@emails.bjut.edu.cn

Contents

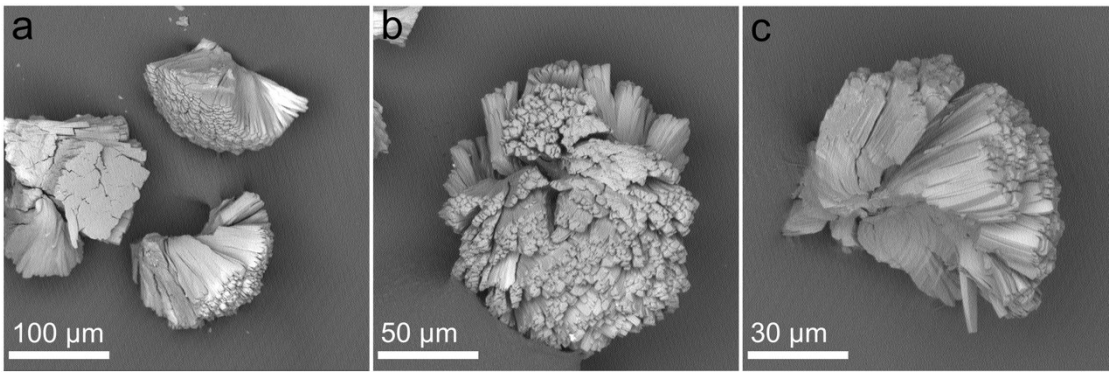

Figure S1. SEM images of Ni-TIPA.

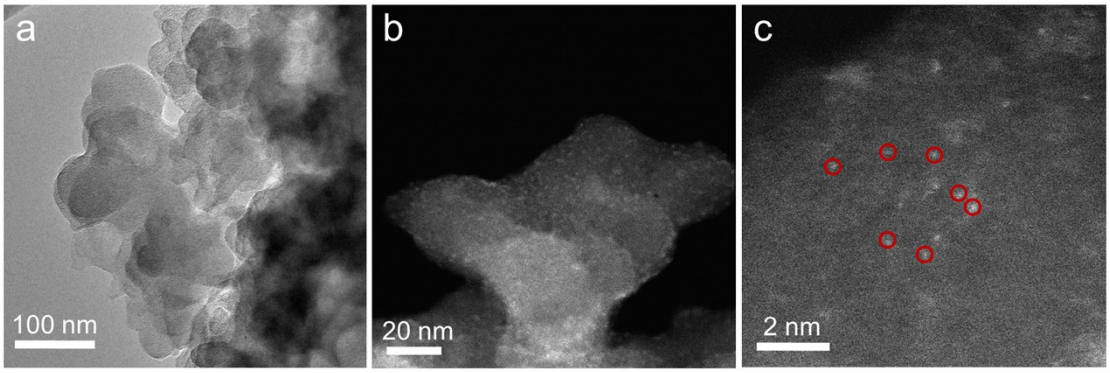

Figure S2. (a) TEM image of Ni-SAs-NC. (b, c) Magnified HAAD-STEM images of Ni-SAs-NC.

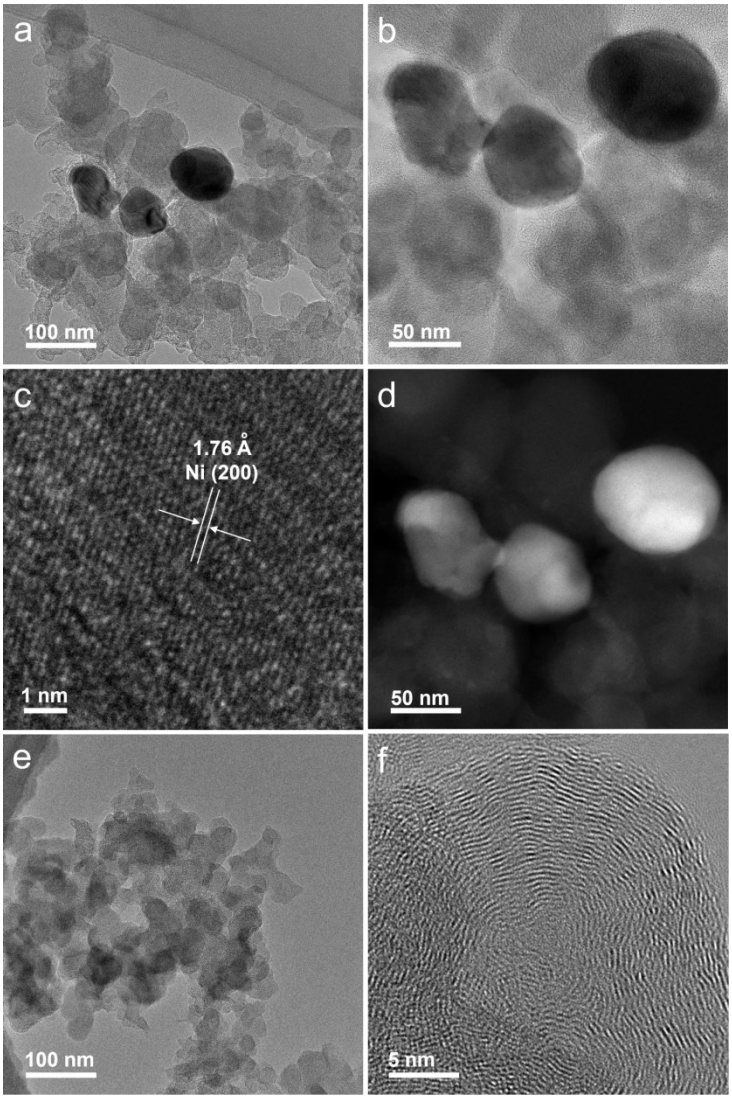

Figure S3. (a-c) TEM images of Ni-NPs-NC. (d) STEM image of Ni-NPs-NC. (e, f) TEM images of NC.

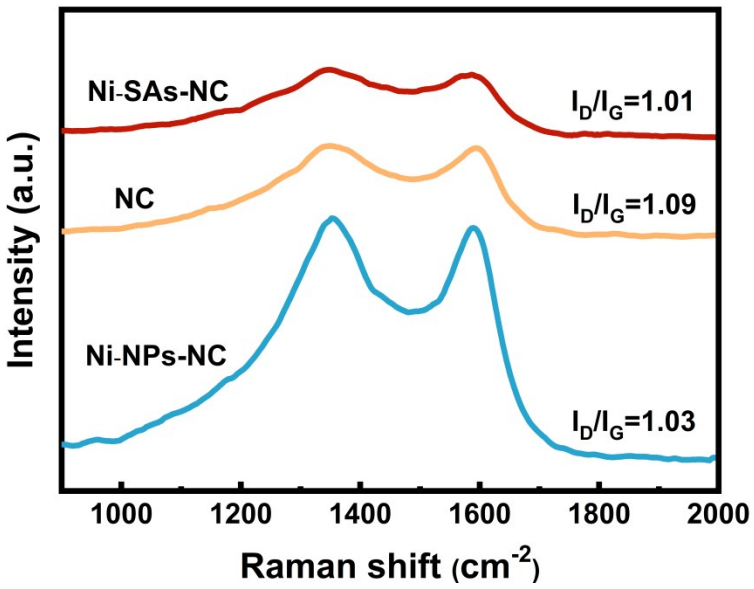

Figure S4. Raman spectra of Ni-SAs-NC, NC and Ni-NPs-NC.

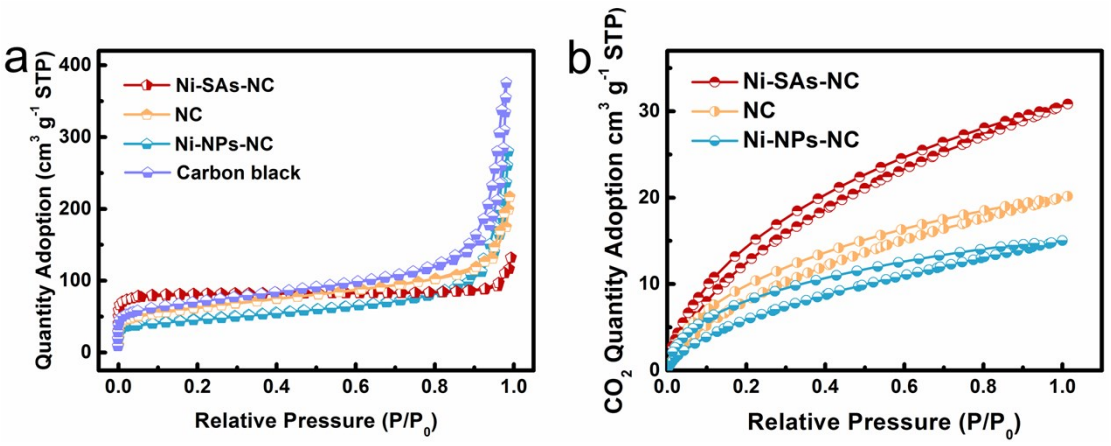

Figure S5. (a) Nitrogen adsorption-desorption isotherms for Ni-SAs-NC, NC, Ni-NPs-NC and carbon black. (b) CO_2 adsorption-desorption isotherms of Ni-SAs-NC, NC and Ni-NPs-NC at 298K.

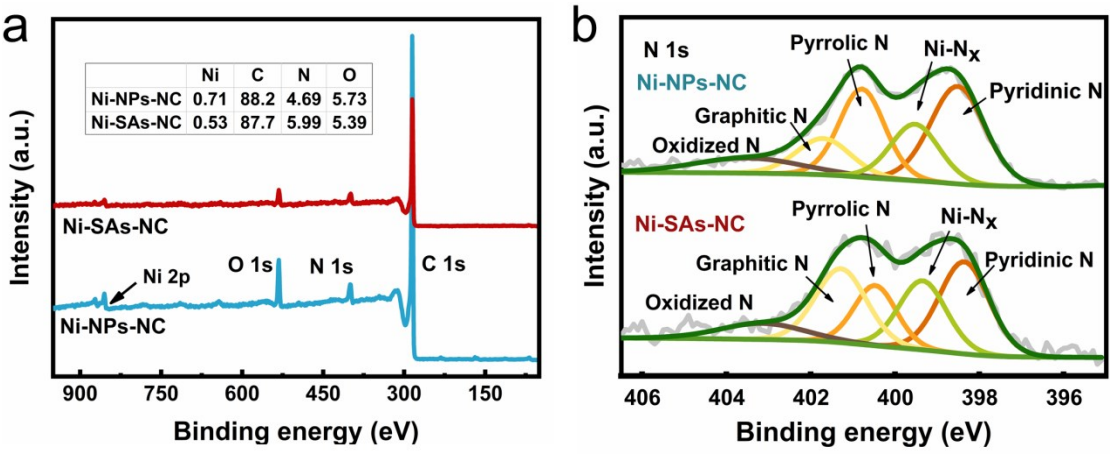

Figure S6. (a) XPS survey spectra of Ni-SAs-NC and Ni-NPs-NC. (b) N 1s XPS spectra of Ni-NPs-NC and Ni-SAs-NC.

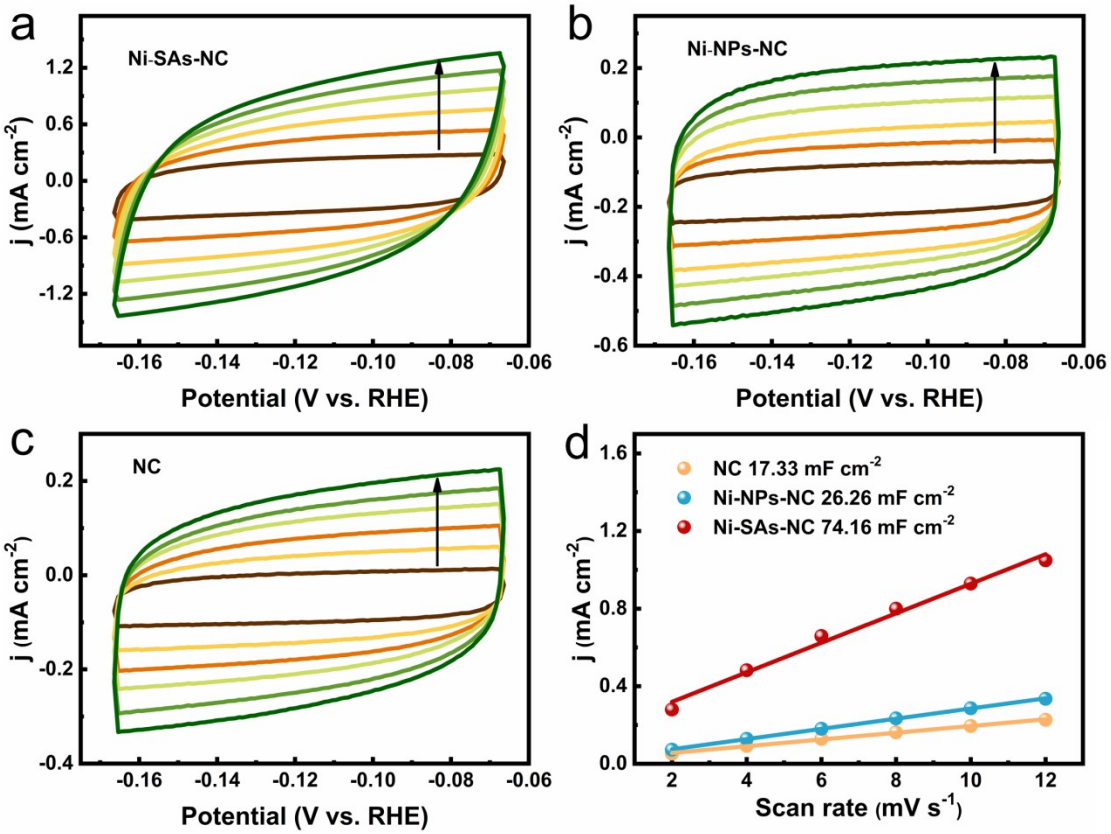

Figure S7. CV curves with different scan rates for (a) Ni-SAs-NC, (b) Ni-NPs-NC, (c) NC and (d) Capacitive Δj (= j_a-j_c) against scan rates.

The electrochemically active surface area (ECSA) of the catalysts can be evaluated from the measurements of electrochemical double layer capacitance (C_{dl}), since ECSA can be calculated from the formula of ECSA = C_{dl}/C_s, where C_{dl} corresponds to the slope of the double-layer current versus the scan rates, C_s represents a specific capacitance value (20 μF cm^{-2}).[1] Therefore, the electrochemically active surface area of Ni-SAs-NC, Ni-NPs-NC and NC can be calculated of 3708 cm^2, 1313 cm^2, 866.5 cm^2, respectively.

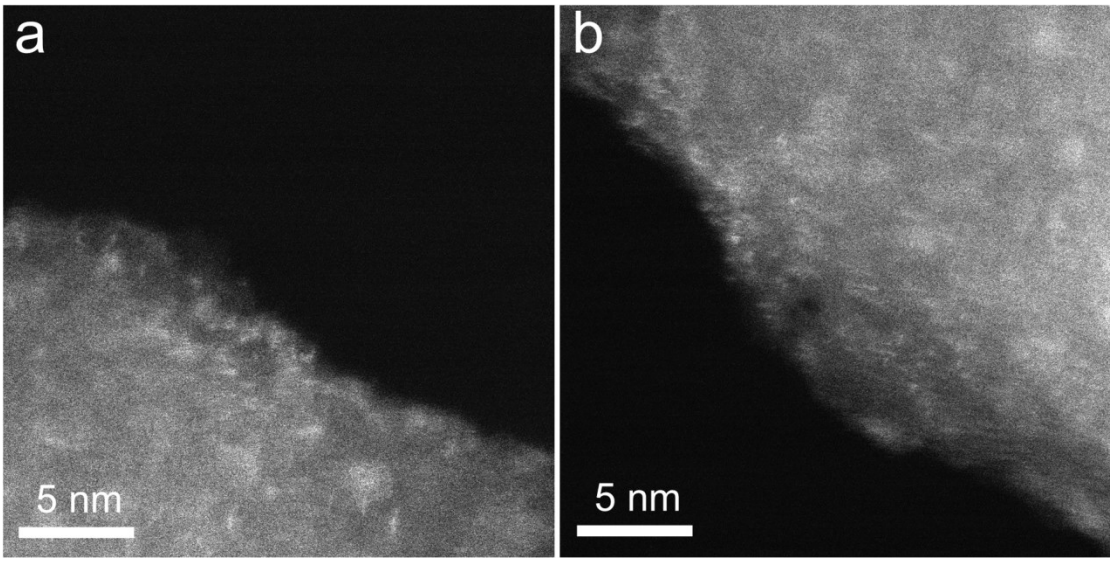

Figure S8. (a, b) Magnified HAAD-STEM images of Ni-SAs-NC after 30-hour electrocatalysis.

Table S1. The content of different-type N in Ni-SAs-NC and Ni-NPs-NC.

	Pyridinic N(%)	Ni-N_x(%)	Pyrrolic N(%)	Graphitic N(%)	Oxidized N(%)
Ni-SAs-NC	25.7	22.4	15.2	27.9	8.8
Ni-NPs-NC	33.9	12.6	25.6	17.6	10.3

Table S2. EXAFS data fitting results of Ni-SAs-NC for Ni K edge.

Sample	Scattering pair	CN	R (Å)	$\sigma^2(10^{-3}Å^2)$	ΔE0 (eV)	R factor
Ni-T@CB	Ni-N	4.0	1.97	0.00872	-4.542	0.028

Table S3. Comparisons the CO_2RR performance of Ni-SAs-NC with reported Ni-based SACs.

Catalyst	Ni content	FE_{CO} (%)	j (mA/cm^2)	Overpotential (mV)	Reference
Ni-SAs-NC	2.0 wt%	98	32	540	**This work**
C-Zn1Ni4	5.44 wt%	92	70	420	*Energy Environ. Sci.*, **2018**, *11*, 1204-1210
Ni-N-C	1.25 wt%	91.2	15	790	*Catal. Sci. Technol.*, **2019**, 9, 3669
Ni-C-Gr	2.2 wt%	95	3	590	*Small*, **2016**, *12*, 6083-6089
Ni-CNT-CC	0.27 wt%	95	95	540	*Angew. Chem., Int. Ed.*, **2020**, *59*, 798-803
Ni_{SA}-N_2-C	0.9 wt%	98	26	690	*Angew. Chem., Int. Ed.*, **2020**, *59*, 2705-2709
NiN-GS	2 at%	95	24	550	*Chem*, **2017**, *3*, 950-960
A-Ni-NSG	2.8 wt%	97	95	500	*Nat. Energy*, **2018**, *3*, 140-147
NiSA/PCFM	1.3 wt%	96	30	590	*Nat. Commun.*, **2020**, *11*, 593
Ni-Fe-N-C	0.97 wt%	98	20	590	*Angew. Chem., Int. Ed.*, **2019**, *58*, 6972-6976
Ni-NCB	0.27 wt%	99	22	571	*Joule*, **2019**, *3*, 265-278
Ni-SAC	1.8 wt%	98.9	4	1090	*Nat. Commun.*, **2019**, 1, 4585

Reference

1. H. B. Yang, S.-F. Hung, S. Liu, K. Yuan, S. Miao, L. Zhang, X. Huang, H.-Y. Wang, W. Cai, R. Chen, J. Gao, X. Yang, W. Chen, Y. Huang, H. M. Chen, C. M. Li, T. Zhang and B. Liu, *Nat. Energy*, 2018, **3**, 140-147.