Electronic Supplementary Information (ESI) for Inorganic Chemistry Frontiers

Poly-phenylenediamine-derived Atomically Dispersed Ni Sites for Electroreduction of CO_2 to CO

Yonglong Zheng, [a,b] Jianyu Han, [a] Leta Takele, [a,b] Feng Xie, [a,c] Yin Zhang, [a,b] Jiqing Sun, [a,b] Bing Han, [a] Jing Chen, [a] Yan Gao, *[a,b] and Zhiyong Tang [a,b]

[a]CAS Key Laboratory of Nanosystem and Hierarchical Fabrication, CAS Center for Excellence in Nanoscience, National Center for Nanoscience and Technology, Beijing 100190, China.

[b]University of Chinese Academy of Sciences, Beijing 100049, China.

[c]Advanced Membranes and Porous Materials Center, Physical Science and Engineering Division, King Abdullah University of Science and Technology, Thuwal 23955-6900, Saudi Arabia.

Corresponding authors at: National Center for Nanoscience and Technology. No. 11 Beiyitiao, Zhongguancun, Beijing, P.R.China. Tel: +86 01082545659 E-mail address: gaoyan@nanoctr.cn

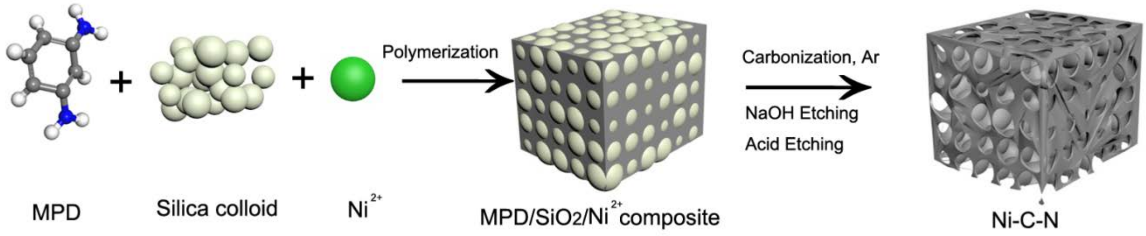

Figure S1. Schematic illustration of the synthesis of Ni-C-N catalyst.

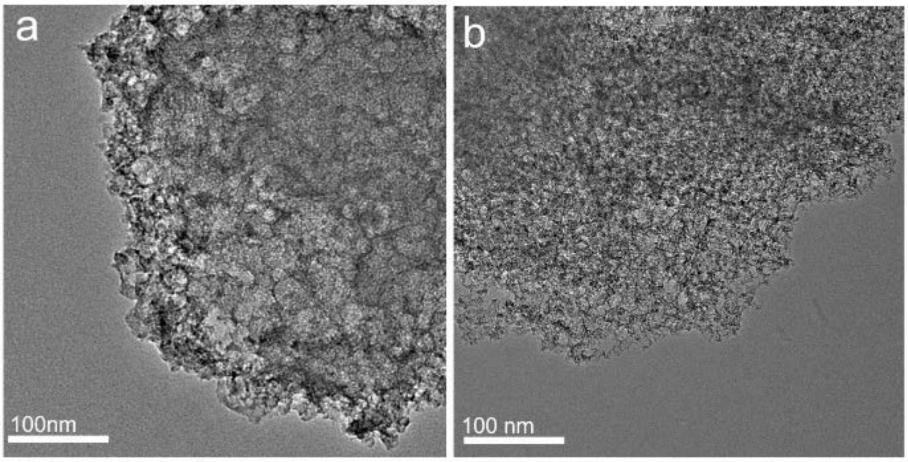

Figure S2 TEM images for the catalyst (a) Ni-C-N (b) N-C

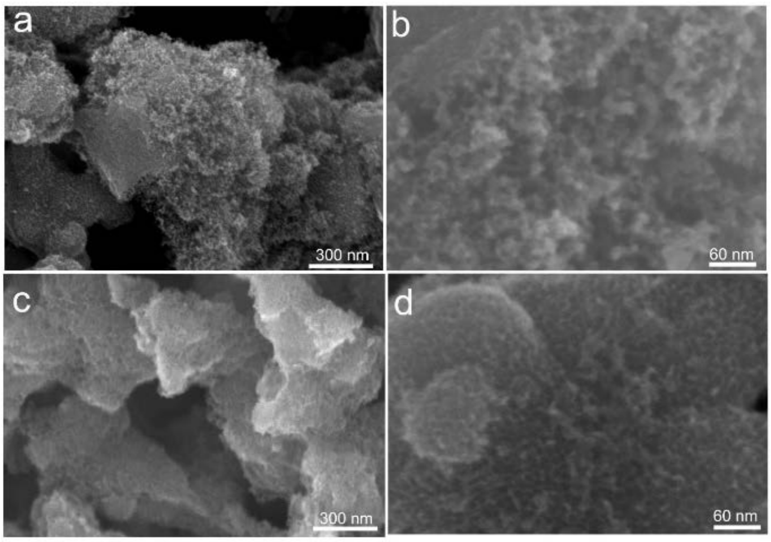

Figure S3. SEM images with different resolution for the catalyst (a) (b) Ni-C-N (b) (d)

N-C

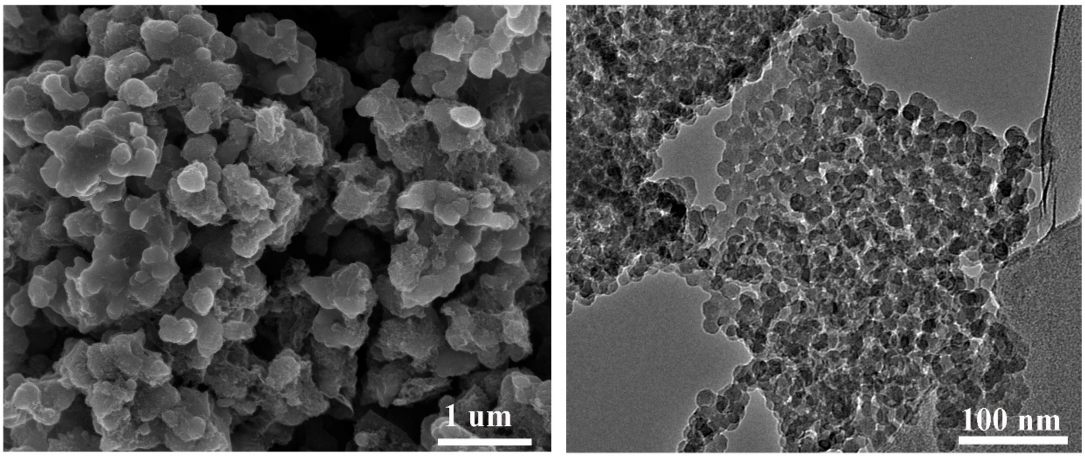

Figure S4 (a) SEM images for Ni-C-N in micrometre size (b) TEM image of SiO_2 template.

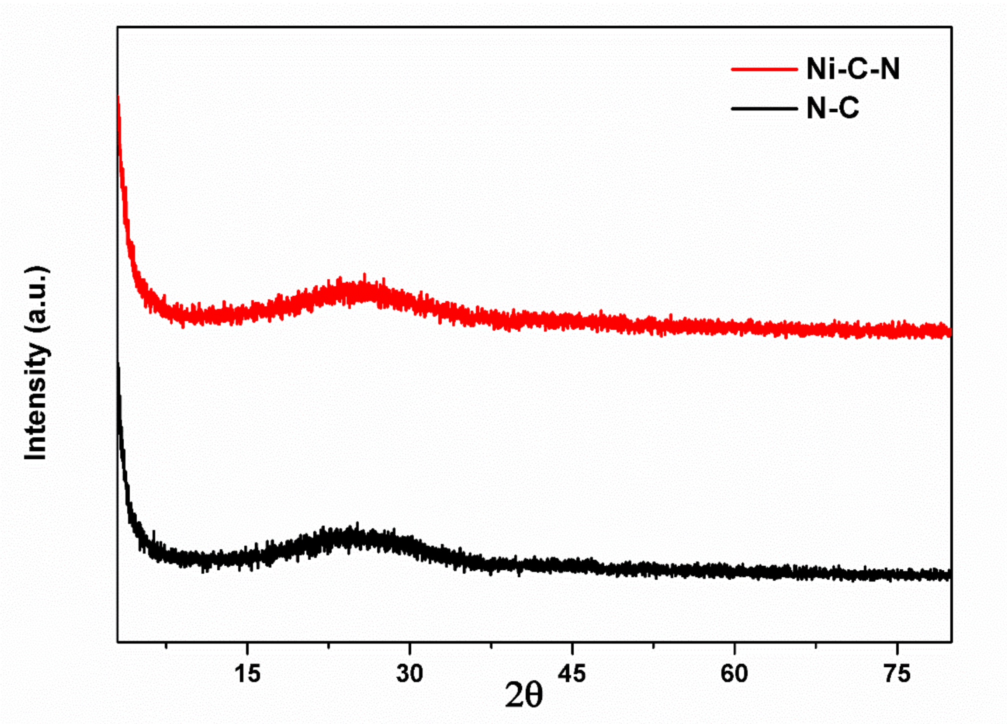

Figure S5. XRD patterns of Ni-C-N and N-C.

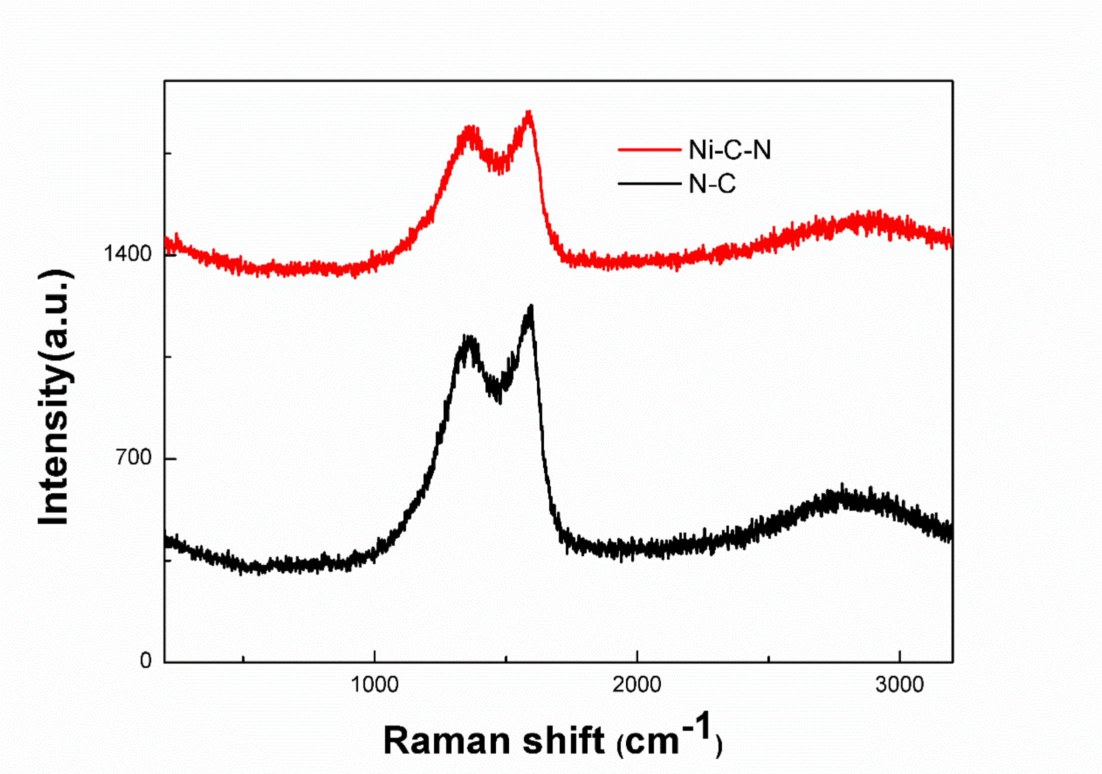

Figure S6. Raman spectra of Ni-C-N and N-C.

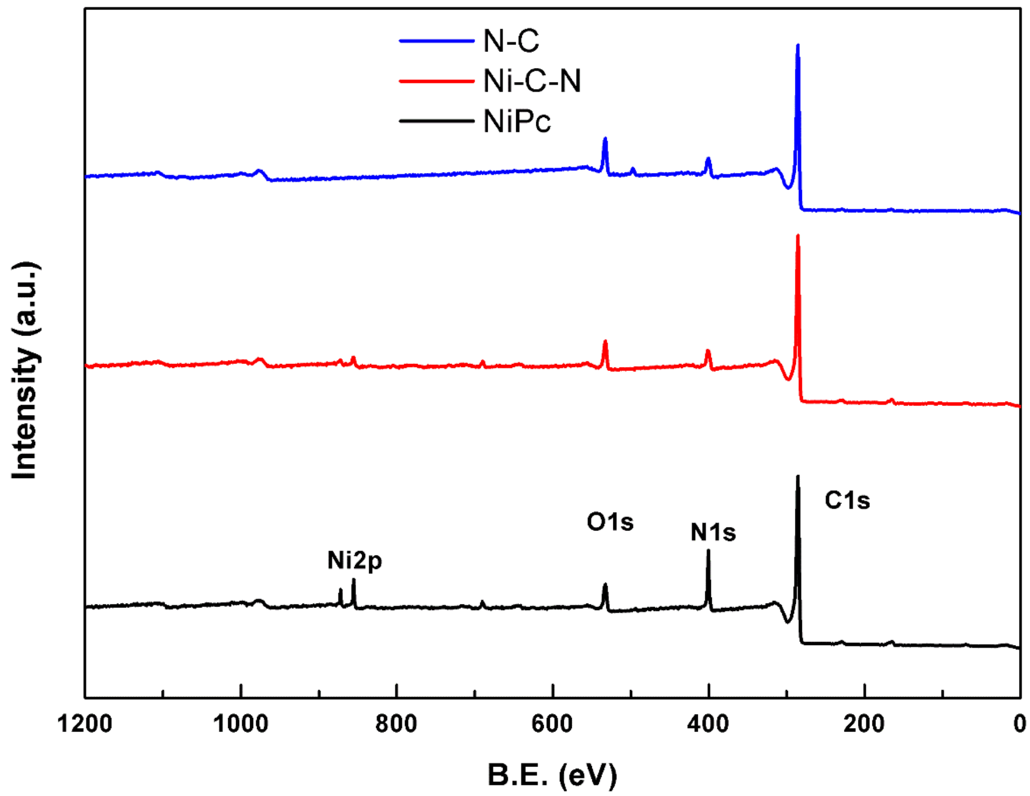

Figure S7. XPS survey spectra of N-C, Ni-C-N, and NiPc.

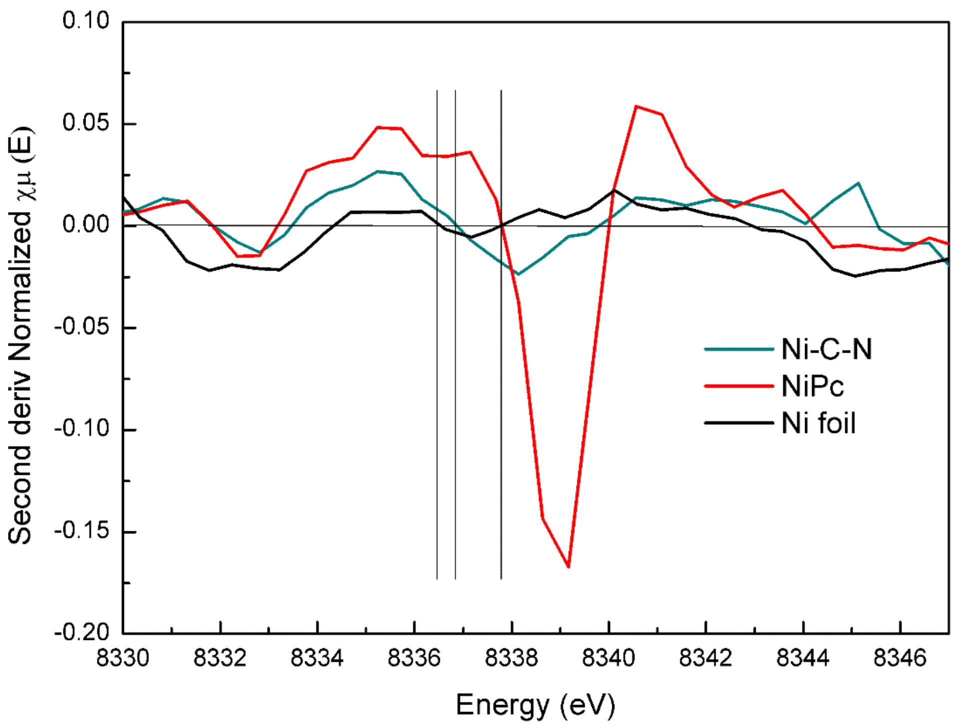

Figure S8. The second derivative spectra obtained from Ni K-edge XANES spectra.

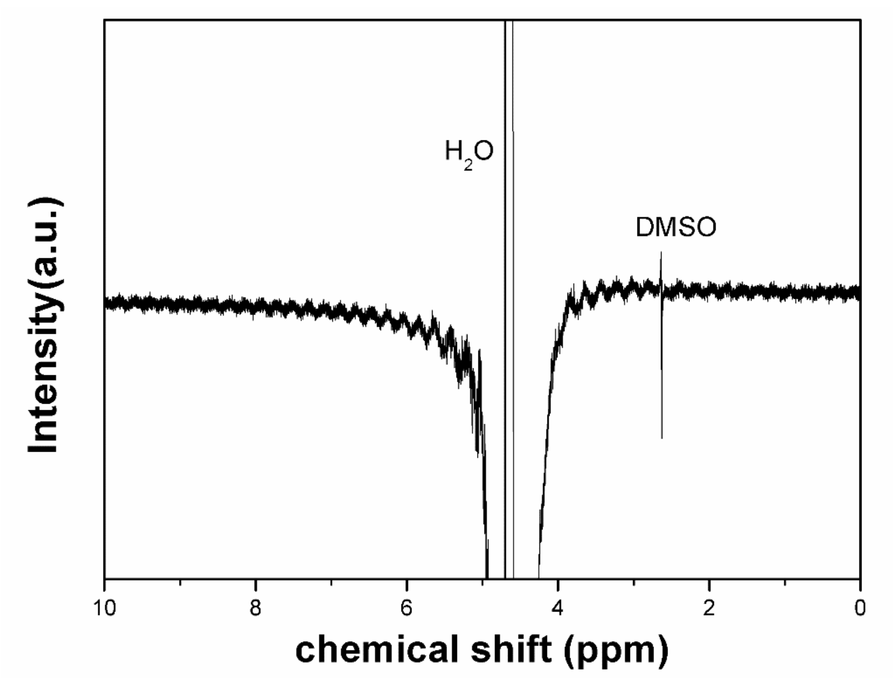

Figure S9. ^{1}H NMR spectra of the liquid products after 4 h CO_2 reduction electrolysis at −0.85 V *vs.* RHE for Ni-C-N

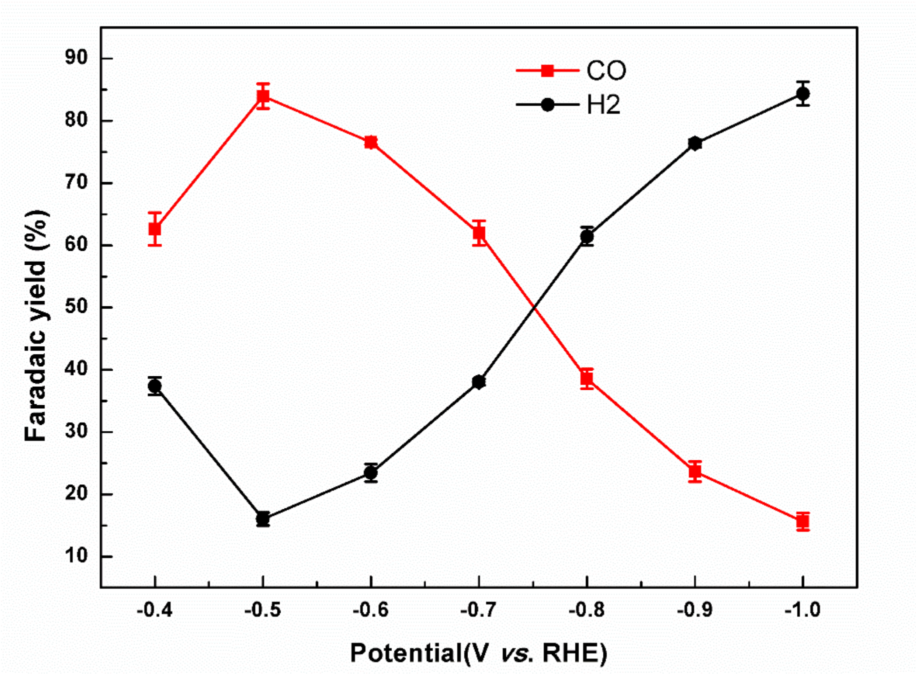

Figure S10. Dependence of FE on applied potential for N-C.

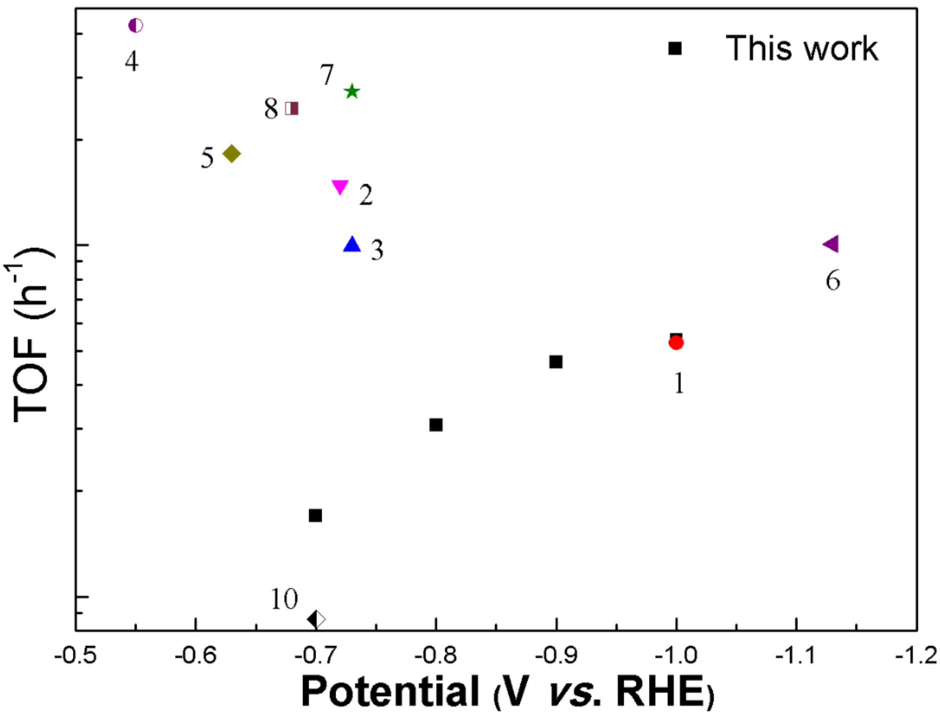

Figure S11. TOF of Ni-C-N compared with reported SACs for electroreduction of CO_2 to CO. The number in the figure represents the number of quoted references.

Table S1. EXAFS fitting result of the Ni-C-N catalyst.

The data range adopted for data fitting in k-space (Δk) and R space (ΔR) are 2-11.426 $Å^{-1}$and 1-3 Å, respectively.

Sample	Shell	N	R/Å (EXAFS)	Debye-Waller factor $\Delta\sigma^2$ ($\times 10^{-3}$ $Å^2$)	ΔE_0(eV)	R factor
Ni-C-N	Ni-N	4	1.847	7±0.59	4.47	0.00002

N, coordination number; R, interatomic distance; EXAFS, extended X-ray absorption fine structure

Table S2. Comparisons of Ni-C-N catalyst with reported SACs for electroreduction of CO_2 to CO.

Catalysts	**CO FE %**	**j(mA cm^{-2})**	**Potential of highest FE**	**Electrolyte**	**Reference**
Ni-C-N	90	11.6	−0.8 (*vs*. RHE)	0.5M $NaHCO_3$	This work
Ni SAs/N-C	70.3	10.48	−1.0 (*vs*. RHE)	0.5M $NaHCO_3$	1
ZnNx/C	95	4.8	−0.43 (*vs*. RHE)	0.5M $NaHCO_3$	2
A-Ni-NSG	97	36.5	−0.72 (*vs*. RHE)	0.5M $NaHCO_3$	3
NiSA-N-CNTs	91.3	23.5	−0.7 (*vs*. RHE)	0.5M $NaHCO_3$	4
Co-N_2	94	18.1	−0.63 (*vs*. RHE)	0.5M $NaHCO_3$	5
C-Zn_1Ni_4	98	22	−0.83 (*vs*. RHE)	0.5M $NaHCO_3$	6

NiN-GS	93.2	4	−0.82 (vs. RHE)	0.5M $NaHCO_3$	7
Ni-NG	95	11	−0.73 (*vs*. RHE)	0.5M $NaHCO_3$	8
Ni-N_4-C	99	28.6	−0.81 (*vs*. RHE)	0.5M $NaHCO_3$	9
Ni-N-MEGO	92.1	26.8	−0.70 (*vs*. RHE)	0.5M $NaHCO_3$	10
Ni-NC	89%	30	−0.85 (*vs*. RHE)	0.5M $NaHCO_3$	11

3. References

1. C. Zhao, X. Dai, T. Yao, W. Chen, X. Wang, J. Wang, J. Yang, S. Wei, Y. Wu and Y. Li, *J. Am. Chem. Soc.*, 2017, **139**, 8078-8081.
2. F. Yang, P. Song, X. Liu, B. Mei, W. Xing, Z. Jiang, L. Gu and W. Xu, *Angew. Chem. Int. Ed.*, 2018, **57**, 12303-12307.
3. 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.
4. Y. Cheng, S. Zhao, B. Johannessen, J.-P. Veder, M. Saunders, M. R. Rowles, M. Cheng, C. Liu, M. F. Chisholm, R. De Marco, H.-M. Cheng, S.-Z. Yang and S. P. Jiang, *Adv. Mater.*, 2018, **30**, 1706287.

5. X. Wang, Z. Chen, X. Zhao, T. Yao, W. Chen, R. You, C. Zhao, G. Wu, J. Wang, W. Huang, J. Yang, X. Hong, S. Wei, Y. Wu and Y. Li, *Angew. Chem. Int. Ed.*, 2018, **130**, 1962-1966.
6. C. Yan, H. Li, Y. Ye, H. Wu, F. Cai, R. Si, J. Xiao, S. Miao, S. Xie, F. Yang, Y. Li, G. Wang and X. Bao, *Energy Environ. Sci.*, 2018, **11**, 1204-1210.
7. K. Jiang, S. Siahrostami, A. J. Akey, Y. Li, Z. Lu, J. Lattimer, Y. Hu, C. Stokes, M. Gangishetty, G. Chen, Y. Zhou, W. Hill, W.-B. Cai, D. Bell, K. Chan, J. K. Nørskov, Y. Cui and H. Wang, *Chem*, 2017, **3**, 950-960.
8. K. Jiang, S. Siahrostami, T. Zheng, Y. Hu, S. Hwang, E. Stavitski, Y. Peng, J. Dynes, M. Gangisetty, D. Su, K. Attenkofer and H. Wang, *Energy Environ. Sci.*, 2018, **11**, 893-903.
9. X. Li, W. Bi, M. Chen, Y. Sun, H. Ju, W. Yan, J. Zhu, X. Wu, W. Chu, C. Wu and Y. Xie, *J. Am. Chem. Soc.*, 2017, **139**, 14889-14892.
10. Y. Cheng, S. Zhao, H. Li, S. He, J.-P. Veder, B. Johannessen, J. Xiao, S. Lu, J. Pan, M. F. Chisholm, S.-Z. Yang, C. Liu, J. G. Chen and S. P. Jiang, *Appl Catal B*, 2019, **243**, 294-303.
11. L. Zhao, Y. Zhang, L.-B. Huang, X.-Z. Liu, Q.-H. Zhang, C. He, Z.-Y. Wu, L.-J. Zhang, J. Wu, W. Yang, L. Gu, J.-S. Hu and L.-J. Wan, *Nat Commun*, 2019, **10**, 1278.