Supporting Information

Highly Selective CO_2 Electroreduction to CO by Synergy between Ni-N-C and Encapsulated Ni Nanoparticles

Yidan Sun,[a] Fang Liu,[a] Xuerong Wang,[a] Kangkang Lu,[a] Xiaojing Liu,[a] Yan Huang,[a] Fengjiao Yu,*[a] and Yuhui Chen*[a]

[a] State Key Laboratory of Materials-oriented Chemical Engineering, Nanjing Tech University, Nanjing, Jiangsu, 211816, China

* Corresponding Authors. E-mail: fjyu@njtech.edu.cn, cheny@njtech.edu.cn.

Supplementary Figure

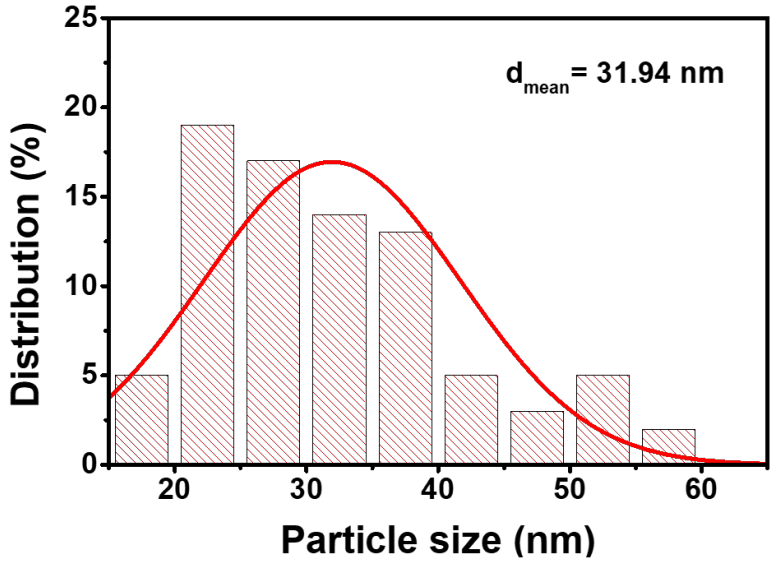

Fig. S1. Particle size distribution of Ni NPs for Ni@Ni-N-C.

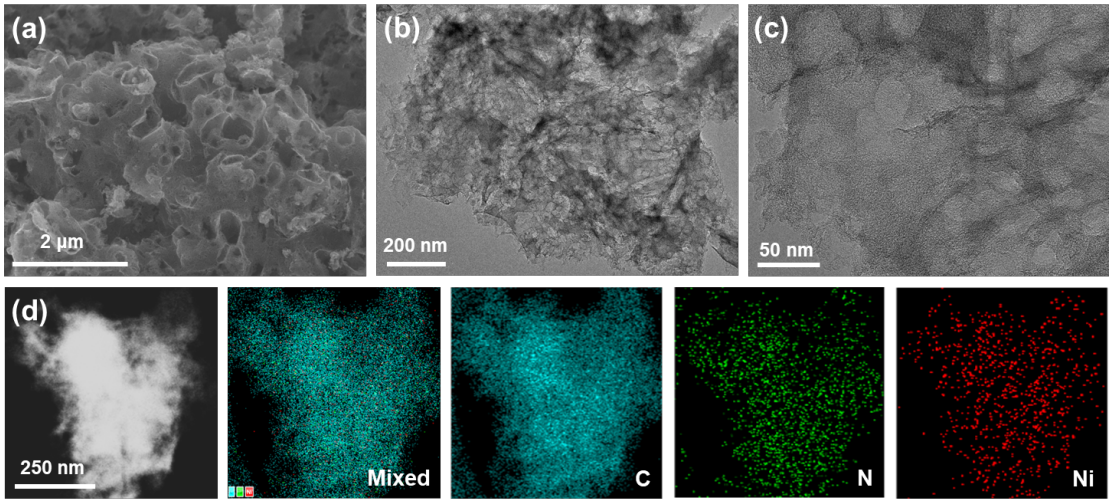

Fig. S2. Characterization of Ni-N-C. (a) SEM mages, (b, c) TEM images, (d) HADDF image and EDX element mapping images of Ni, C, N.

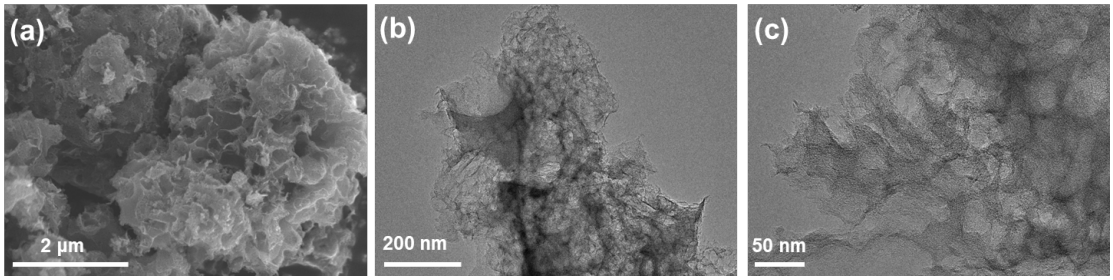

Fig. S3. Characterization of N-C. (a) SEM mages, (b, c) TEM images.

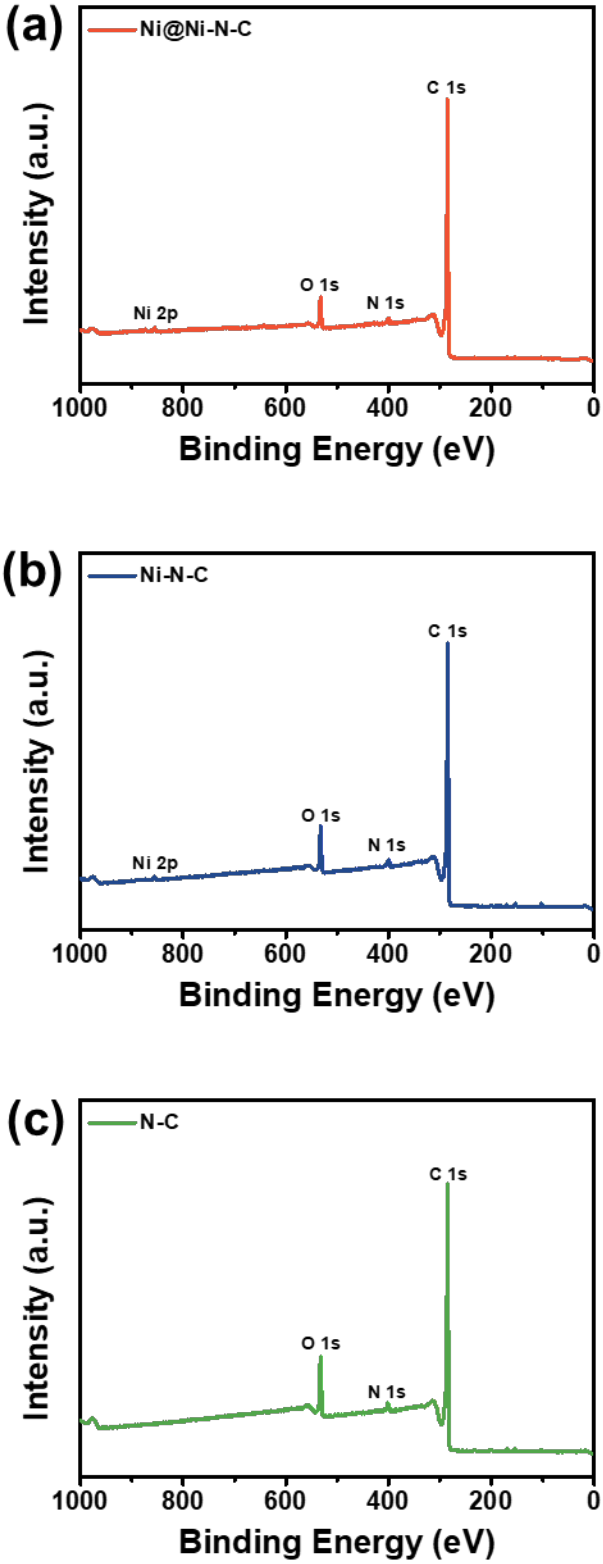

Fig. S4. XPS survey spectra of (a) Ni@Ni-N-C, (b) Ni-N-C and (c) N-C.

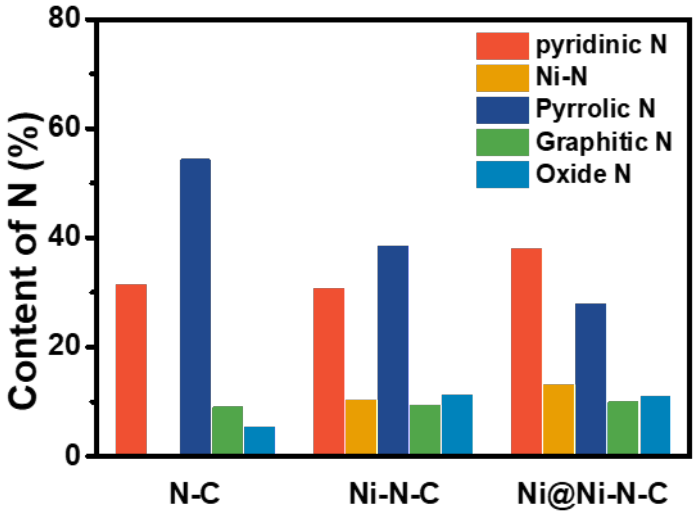

Fig. S5. N contents calculated from XPS results.

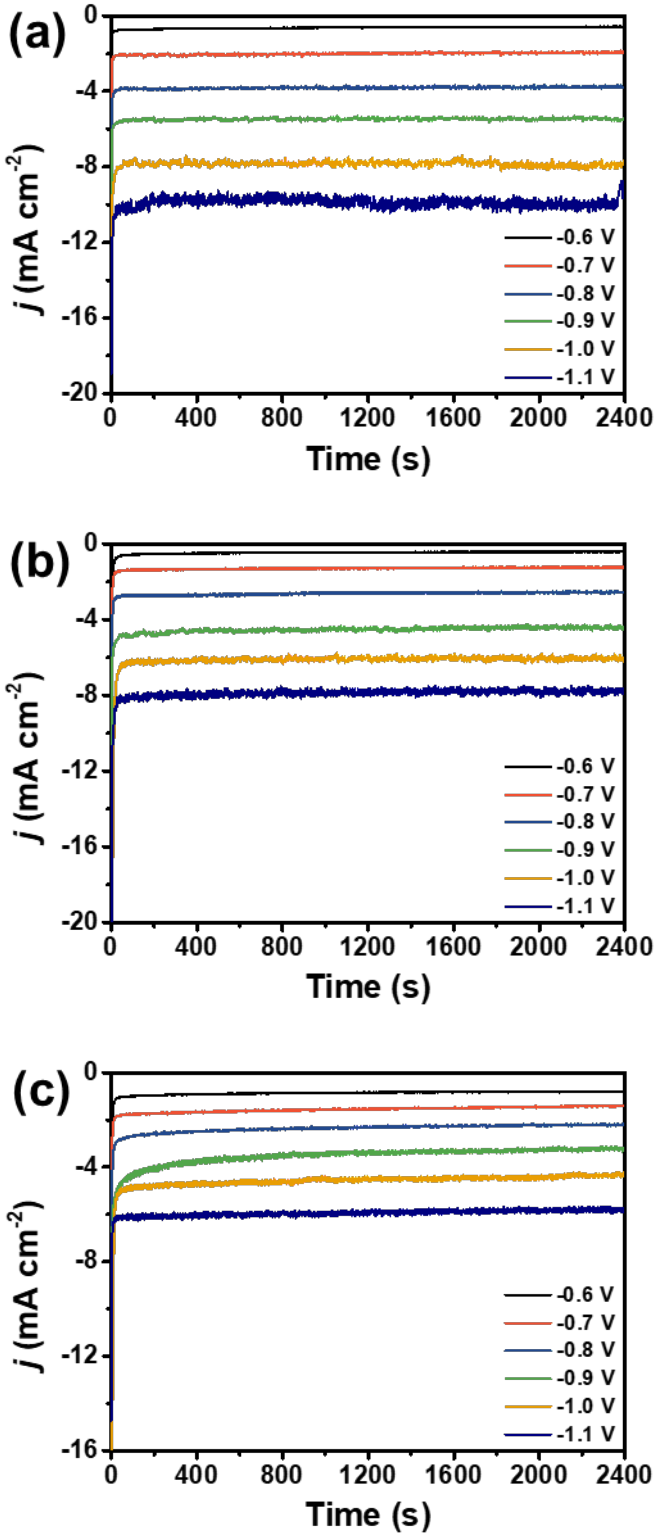

Fig. S6. Chrono-amperometry results at the corresponding potentials in CO_2-staturated 0.1 M $KHCO_3$ solution on (a) Ni@Ni-N-C, (b) Ni-N-C and (c) N-C.

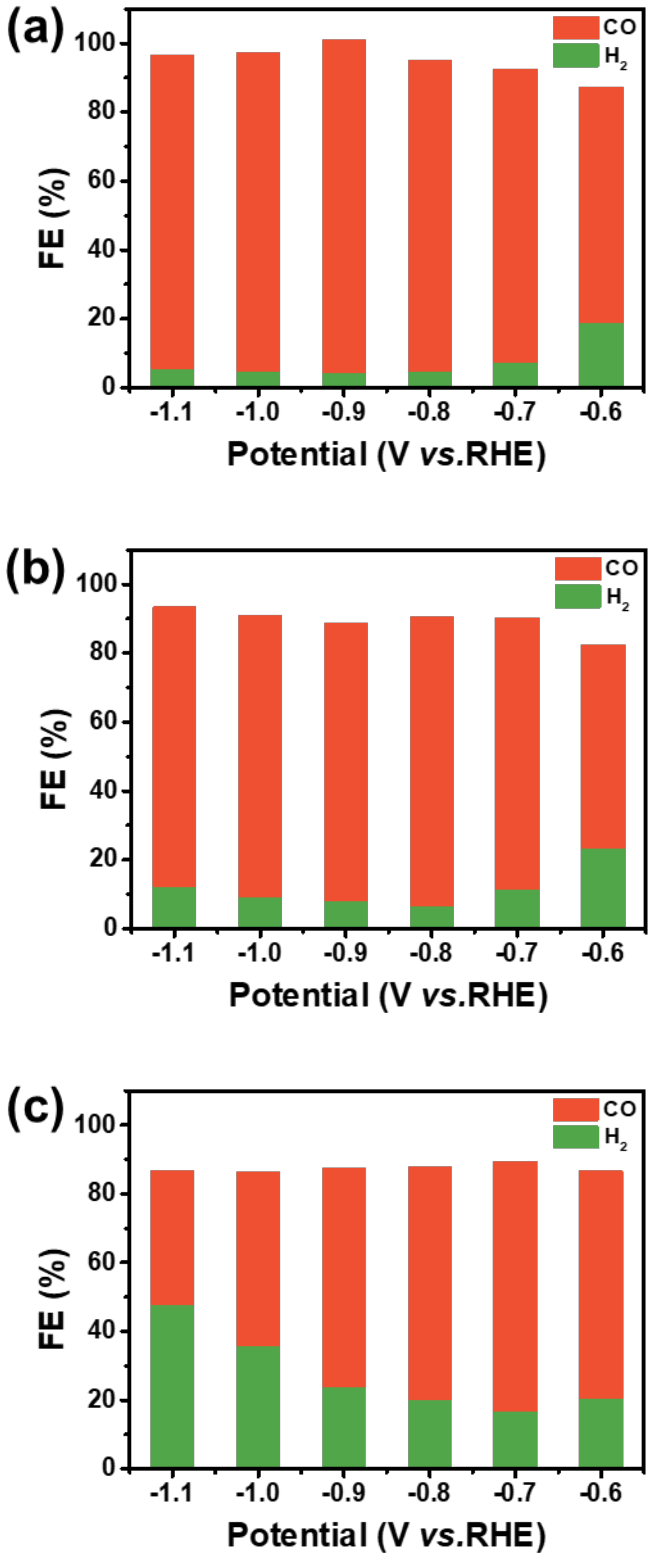

Fig. S7. Potential dependence of faradaic efficiencies for CO_2RR on (a) Ni@Ni-N-C, (b) Ni-N-C and (c) N-C.

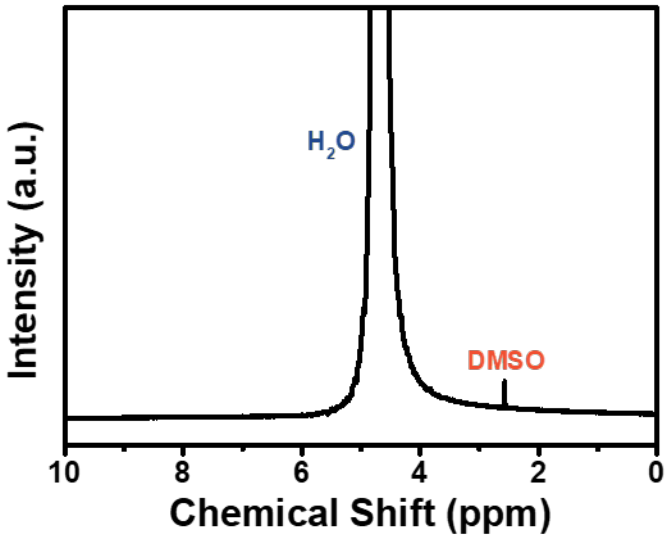

Fig. S8. ^{1}H NMR spectrum of Ni@Ni-N-C for the electrolyte after CO_2RR in CO_2-saturated 0.1 M $KHCO_3$.

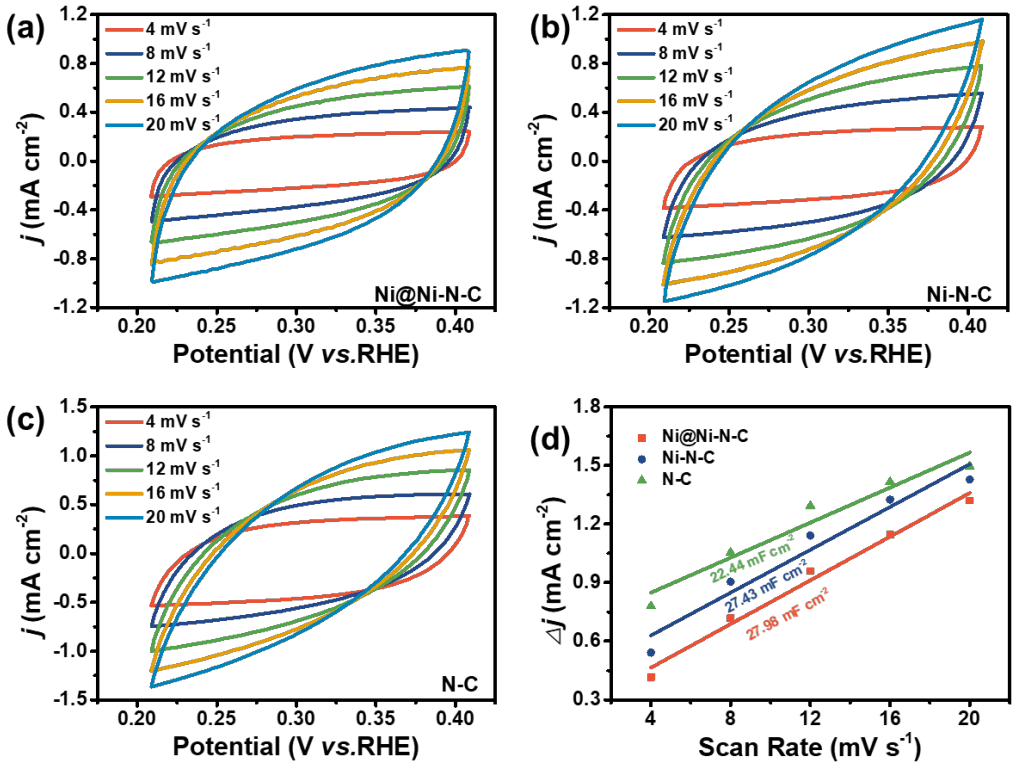

Fig. S9. CV curves of (a) Ni@Ni-N-C, (b) Ni-N-C and (c) N-C performed in CO_2-saturated 0.1 M $KHCO_3$ at different scan rates. (d) A plot of changing current density against scan rates for electrochemical active surface area (ECSA).

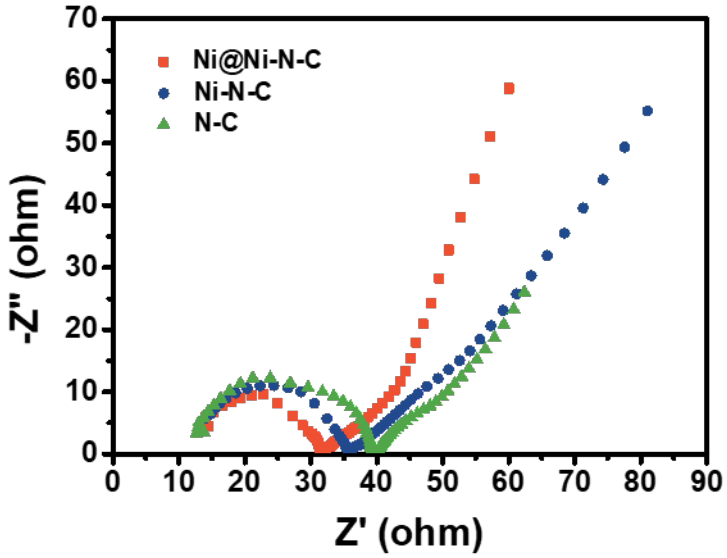

Fig. S10. Nyquist plots of Ni@Ni-N-C, Ni-N-C and N-C.

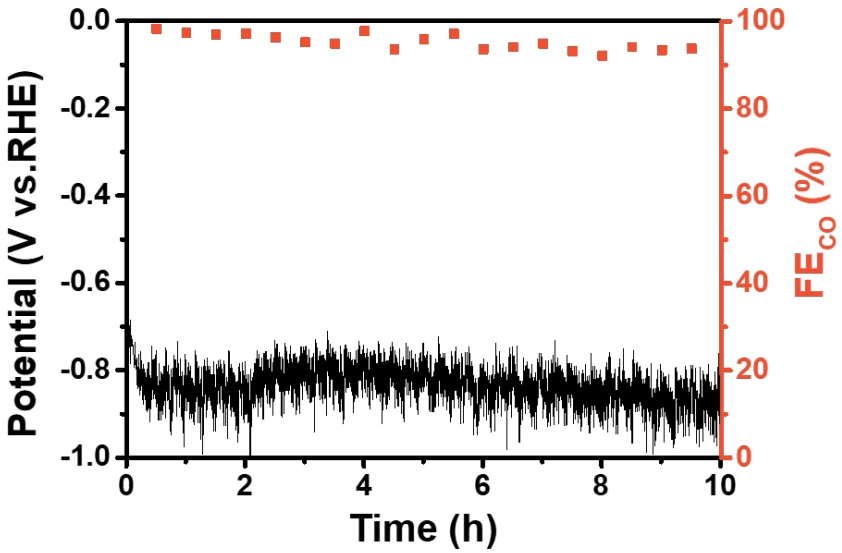

Fig. S11. Long-term stability test at-100 mA cm^{-2} of Ni@Ni-N-C catalyst in 1M KOH.

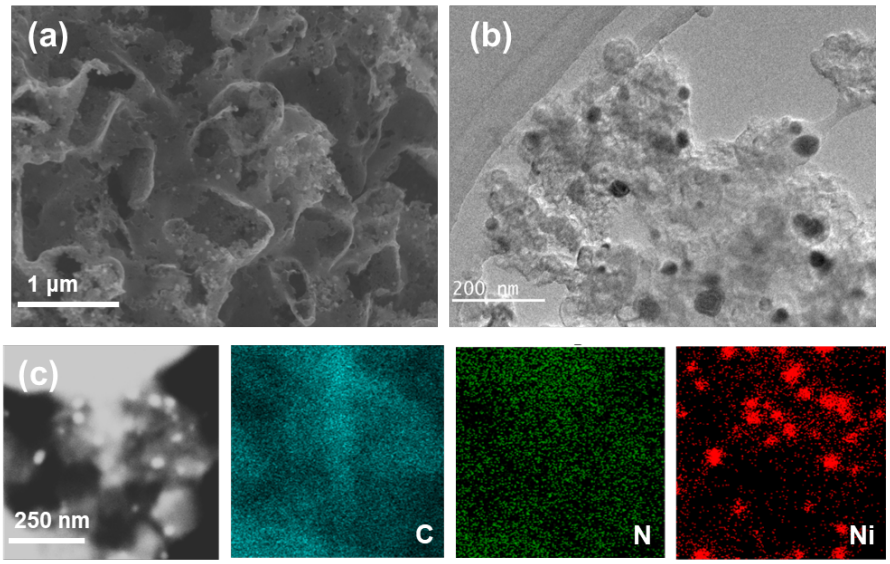

Fig. S12. (a) SEM, (b) TEM image and (c) HAADF image and EDX elemental maps of Ni@Ni-N-C after long-time stability test.

Supplementary Tables

Table S1. Summary of the atomic ratio of C, N, Ni and O based on the XPS survey spectra.

Sample	Contents (at.%)			
	C	N	Ni	O
Ni@Ni-N-C	90.42	3.1	0.42	6.06
Ni-N-C	89.18	2.89	0.27	7.66
N-C	87.6	2.55	0	9.86

Table S2. Comparison with other Ni-based electrocatalysts for CO_2 electrochemical reduction in the literatures.

Catalysts	Electrolyte	Operating potential (V vs RHE)	Faradaic efficiency of CO	CO partial current density (mA/cm^2)	Reference
NC-CNTs (Ni)	0.1 M $KHCO_3$	-0.8	90%	~ 7	[1]
Ni-N-C	0.5 M $KHCO_3$	-0.67	93%	3.63	[2]
SA-NiNG-NV	0.5 M $KHCO_3$	-0.7	96.4%	~ 10	[3]
NiSA-NGA-900	0.5M $KHCO_3$	-0.8	90.2%	~ 6	[4]
Ni SAs/N-C	0.5 M $KHCO_3$	-0.9	71.9%	~ 5.68	[5]
Ni-NC@Ni	0.5 M $KHCO_3$	-0.78	87.4%	14.77	[6]
Ni_3N/C	0.5M NaCl	-0.9	85.7%	~ 6.2	[7]
NiSA-N-CNTs	0.5 M $KHCO_3$	-0.7	91.3%	23.5	[8]
Ni-N-C-rGO	0.5 M $KHCO_3$	-0.87	85%	8.5	[9]
N^{i2+}@NG	0.5 M $KHCO_3$	-0.68	92%	9.38	[10]
ACP/S-N-Ni	0.5 M $KHCO_3$	-0.77	91%	3.4	[11]
Ni-N-C	0.5 M $KHCO_3$	-0.9	91.2%	11.63	[12]
CNS-NiSA	0.5 M $KHCO_3$	-0.8	95%	7.8	[13]
Ni@Ni-N-C	0.1 M $KHCO_3$	-0.9	96.4%	5.26	***This work***

Table S3. ICP result of as-prepared catalysts.

Sample	Ni Contents (wt %)
Ni@Ni-N-C	6.29
Ni-N-C	1.337

References

1. Q. Fan, P. F. Hou, C. H. Choi, T. S. Wu, S. Hong, F. Li, Y. L. Soo, P. Kang, Y. S. Jung and Z. Y. Sun, Activation of Ni particles into single Ni-N atoms for efficient electrochemical reduction of CO_2, *Adv. Energy Mater.*, 2020, **10,** 1903068.

2. X.-M. Hu, H. H. Hval, E. T. Bjerglund, K. J. Dalgaard, M. R. Madsen, M.-M. Pohl, E. Welter, P. Lamagni, K. B. Buhl, M. Bremholm, M. Beller, S. U. Pedersen, T. Skrydstrup and K. Daasbjerg, Selective CO_2 reduction to CO in water using earth-abundant metal and nitrogen-doped carbon electrocatalysts, *Acs Catal.* 2018, **8,** 6255-6264.

3. C. Jia, S. Li, Y. Zhao, R. K. Hocking, W. Ren, X. Chen, Z. Su, W. Yang, Y. Wang, S. Zheng, F. Pan and C. Zhao, Nitrogen vacancy induced coordinative reconstruction of single-atom Ni catalyst for efficient electrochemical CO_2 reduction, *Adv. Funct. Mater.*, 2021, **31,** 2107072.

4. K. Mou, Z. Chen, X. Zhang, M. Jiao, X. Zhang, X. Ge, W. Zhang and L. Liu, Highly efficient electroreduction of CO_2 on nickel single-atom catalysts: atom trapping and nitrogen anchoring, *Small*, 2019, **15,** 1903668.

5. C. Zhao, X. Dai, T. Yao, W. Chen, X. Wang, J. Wang, J. Yang, S. Wei, Y. Wu and Y. Li, Ionic exchange of metal-organic frameworks to access single nickel sites for efficient electroreduction of CO_2, *J. Am. Chem. Soc.*, 2017, **139,** 8078-8081.

6. Y. He, Y. Li, J. Zhang, S. Wang, D. Huang, G. Yang, X. Yi, H. Lin, X. Han, W. Hu, Y. Deng and J. Ye, Low-temperature strategy toward Ni-NC@Ni core-shell nanostructure with single-Ni sites for efficient CO_2 electroreduction, *Nano Energy*, 2020, **77,** 105010.

7. P. Hou, X. Wang, Z. Wang and P. Kang, Gas phase electrolysis of carbon dioxide to carbon monoxide using nickel nitride as the carbon enrichment catalyst, *ACS Appl. Mater. Interfaces*, 2018, **10,** 38024-38031.

8. 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, Atomically dispersed transition metals on carbon nanotubes with ultrahigh loading for selective electrochemical carbon dioxide reduction, *Adv. Mater.*, 2018, **30,** 1706287.

9. F. Wang, Y. Liu, Z. Song, Z. Miao and J. Zhao, Ni-N-doped carbon-modified reduced graphene oxide catalysts for electrochemical CO_2 reduction reaction, *Catalysts*, 2021, **11,** 561.

10. W. Bi, X. Li, R. You, M. Chen, R. Yuan, W. Huang, X. Wu, W. Chu, C. Wu and Y. Xie, Surface immobilization of transition metal ions on nitrogen-doped graphene realizing high-efficient and selective CO_2 Reduction, *Adv. Mater.*, 2018, **30,** 1706617.

11. S. Li, M. Ceccato, X. Lu, S. Frank, N. Lock, A. Roldan, X.-M. Hu, T. Skrydstrup and K. Daasbjerg, Incorporation of nickel single atoms into carbon paper as self-standing electrocatalyst for CO_2 reduction, *J. Mater. Chem. A*, 2021, **9,** 1583-1592.

12. C.-Z. Yuan, K. Liang, X.-M. Xia, Z. K. Yang, Y.-F. Jiang, T. Zhao, C. Lin, T.-Y. Cheang, S.-L. Zhong and A.-W. Xu, Powerful CO_2 electroreduction performance with N-carbon doped with single Ni atoms, *Catal. Sci. Technol.*, 2019, **9,** 3669-3674.

13. X. Zhao, S. Huang, Z. Chen, C. Lu, S. Han, C. Ke, J. Zhu, J. Zhang, D. Tranca and X. Zhuang, Carbon nanosheets supporting Ni-N_3S single-atom sites for efficient electrocatalytic CO_2 reduction, *Carbon*, 2021, **178,** 488-496.