

Supporting Information

CoN₄ active sites in a graphene matrix for the highly efficient electrocatalysis of CO₂ reduction

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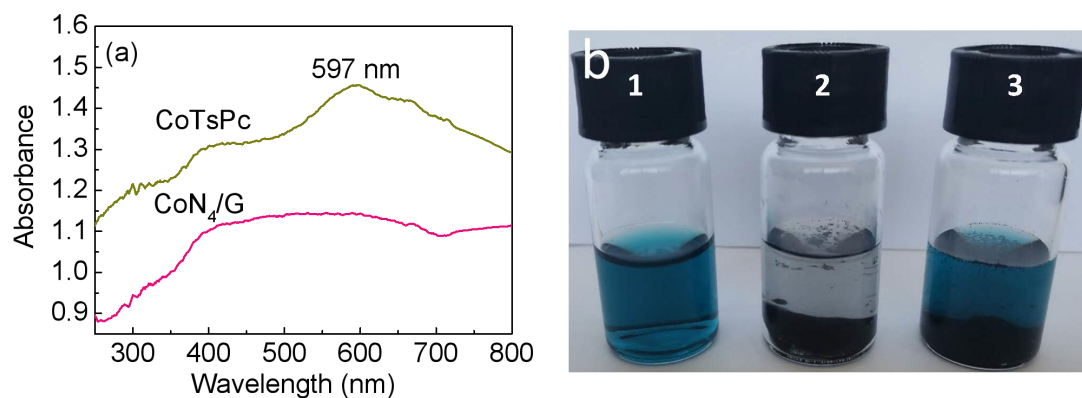


Figure S1. (a) UV-Vis absorption spectra of CoN₄/G and CoTsPc, (b) Digital photograph of various samples dispersed in water: 1. pure CoTsPc, 2. CoN₄/G, 3. the mixture of graphene and CoTsPc by hand lapping.

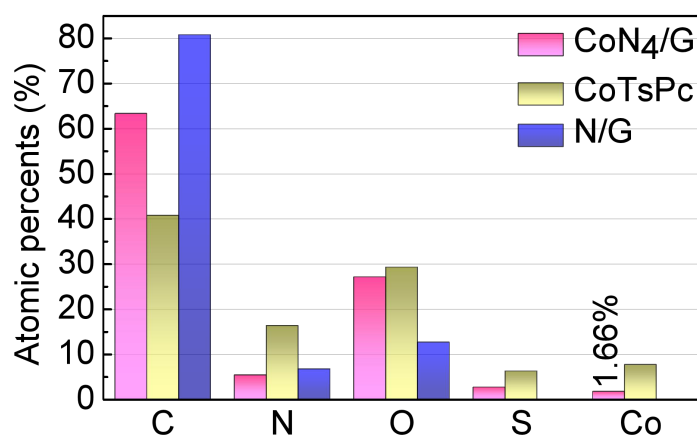


Figure S2. Atomic percentage (at %) of C, N, O, S and Co in CoN₄/G, CoTsPc and N/G.

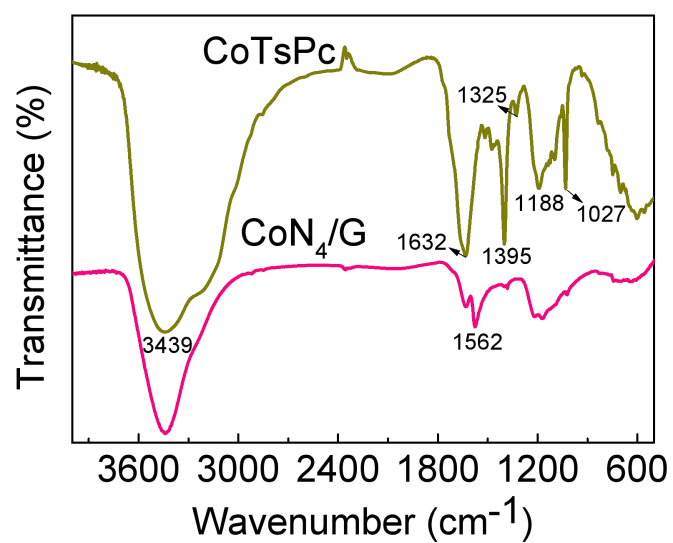


Figure S3. FT-IR spectra of CoN₄/G material in comparison with CoTsPc.

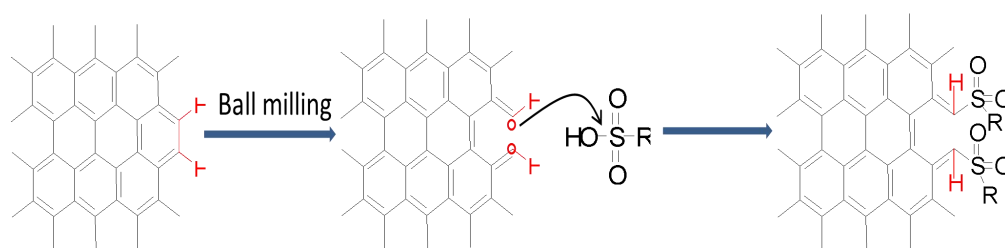


Figure S4. Proposed mechanism for the formation of $\text{-C-SO}_x\text{-C-}$. The graphene structure is simplified for clarity.

FT-IR spectra of the CoN_4/G material was measured to further analyze the chemical changes upon ball milling (Figure S3). The FT-IR spectrum of CoTsPc shows phthalocyanine skeletal vibrations in the range of $600\text{--}1650\text{ cm}^{-1}$. The band at 1027 cm^{-1} in CoTsPc was characteristic for aromatic sulfonic acid ($\text{-SO}_3\text{H}$). The characteristic peak at 1632 cm^{-1} was specific to the C=N groups present in the CoTsPc ^[1]. Compared with that of CoTsPc , the $\text{-SO}_3\text{H}$ group were absent in the CoN_4/G material. This also clearly indicated the $\text{-SO}_3\text{H}$ and the outside macrocyclic structure of CoTsPc has been broken during ball milling.

According to mechano-chemical process by ball milling, graphitic C-C bonds at the edge in graphene could be homolytic and reacted with $\text{-SO}_x\text{-C-}$ during ball milling (Figure S4)^[2]. Meanwhile, $\text{-C-SO}_x\text{-C-}$ groups are predominately located at the edge of the graphene. FT-IR spectrum of CoN_4/G shows a unique sharp peak at 1562 cm^{-1} , which was associated with S-O stretching exclusively from $\text{-C-SO}_x\text{-C-}$.

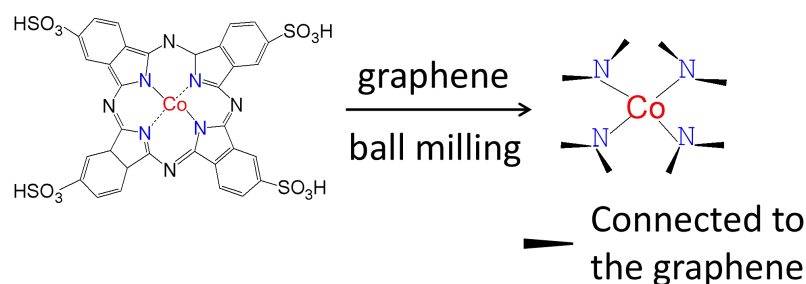


Figure S5. Proposed mechanism for preparation of CoN₄/G via ball milling.

Under the high energy of ball milling, the macrocyclic structure located on the outside of CoTsPc could be easily destroyed, and the residual isolated CoN₄ located on the centers of CoTsPc could interact with graphene lattice at the defected site, followed by reconstruct the adjacent carbon atoms of CoN₄ with graphene, thus leading to the formation of graphene-embedded CoN₄ centers^[3].

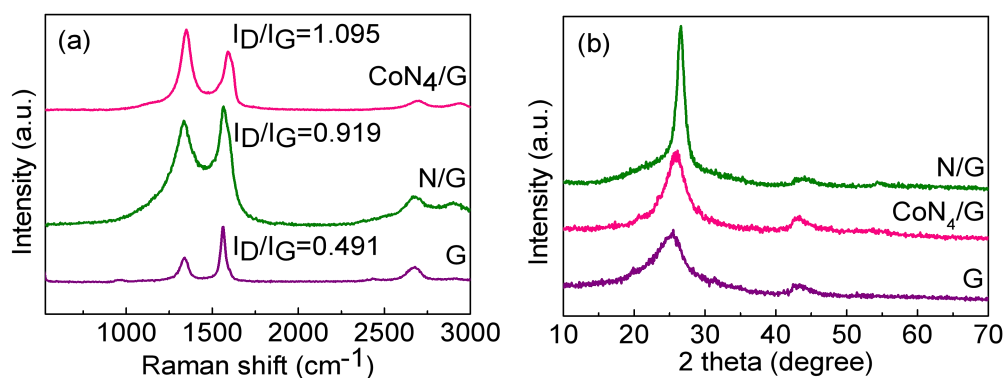


Figure S6. (a) Raman spectra and (b) XRD patterns of CoN₄/G, N/G and G.

Raman spectroscopy was employed to measure the edge/defect ratio. The ratio of D band (1360 cm⁻¹) to G band (1590 cm⁻¹) (I_D/I_G) reflects the degree of edge/defect. G shows much smaller I_D/I_G value than that of the CoN₄/G catalyst (Figure S6a). The I_D/I_G ratio for the CoN₄/G and N/G materials are quite similar. This result indicates that the edge/defect ratio could be improved upon the introduction of CoN₄ and ball milling. X-ray diffraction (XRD) patterns (Figure S6b) showed the peaks at 2θ~26.6 in both CoN₄/G and G are weaker and broader than N/G, which attributed to the thermal aggregation of graphene into graphite state during annealing in the N/G sample.

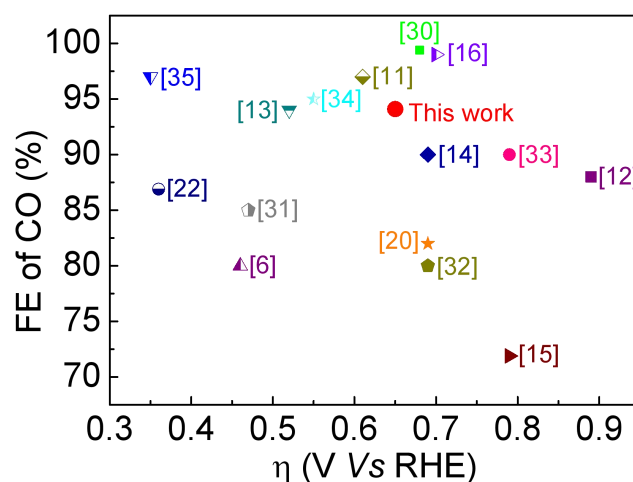


Figure S7. CO₂RR performances of CoN₄/G catalyst in comparison with other catalysts in Table S1.

Table S1. CO₂RR performances comparison of CoN₄/G catalyst with some typical catalysts for CO₂RR as reported recently.

Catalyst	Electrolyte	Maximum FE _{CO}	Potential (RHE)	Overpotential	Reference
CoN ₄ /G	0.1 M KHCO ₃	94.1%	-0.76 V	0.65 V	This work
Co-N ₂	0.5 M NaHCO ₃	94%	-0.63 V	0.52 V	[Ref. 13] Angew. Chem. Int. Ed., 2018,57,1944-1948
Co-N ₂ /HNPCs	0.2 M NaHCO ₃	99.4%	-0.79 V	0.68 V	[Ref. 30] J. Am. Chem. Soc., 2018, 140, 4218-4221
Co ₁ -N ₄	0.1 M KHCO ₃	82%	-0.80 V	0.69	[Ref.20] Appl. Catal. B: Environ., 2019, 240, 234-240
NCNT	0.1 M KHCO ₃	80%	-0.80 V	0.69 V	[Ref. 32] ACS Nano, 2015, 9, 5364-5371
NCNT-3-700	0.5 M NaHCO ₃	90%	-0.90 V	0.79 V	[Ref. 33] ChemSusChem, 2016, 9, 1085-1089
NG	0.1 M KHCO ₃	85%	-0.58 V	0.47 V	[Ref. 31] Nano Lett., 2016, 16, 466-470
A-Ni-NSG	0.5 M NaHCO ₃	97%	-0.72 V	0.61 V	[Ref. 11] Nature Energy, 2018, 3, 140-147
Ni SAs/N-C	0.5 M KHCO ₃	71.9%	-0.90 V	0.79 V	[Ref.15] J. Am. Chem. Soc., 2017, 139, 8078-8081
Ni-NG	0.5 M KHCO ₃	95%	-0.66 V	0.55 V	[Ref. 34] Energy Environ. Sci., 2018, 11, 893-903
Ni-N ₄	0.5 M KHCO ₃	99%	-0.81 V	0.70 V	[Ref.16] J. Am. Chem. Soc., 2017, 139, 14889-14892
SE-Ni SAs@PNC	0.1 M KHCO ₃	88%	-1.0 V	0.89 V	[Ref. 12] Angew. Chem. Int. Ed., 2018, 57, 14095-14100
NC-CNTs (Ni)	0.1 M KHCO ₃	90%	-0.80 V	0.69 V	[Ref.14] Adv. Energy Mater., 2019, 10, 1903068
FeN ₃	0.1 M KHCO ₃	97%	-0.46 V	0.35 V	[Ref.35] Angew. Chem. Int. Ed., 2019, 58, 14871-14876
FeSAs/CNF-900	0.5 M KHCO ₃	86.9%	-0.47 V	0.36 V	[Ref.22] Applied Catalysis B: Environmental, 2020, 267, 118720
Fe/NG-750	0.1 M KHCO ₃	80%	-0.57 V	0.46 V	[Ref. 6] Adv. Energy Mater., 2018, 1703487

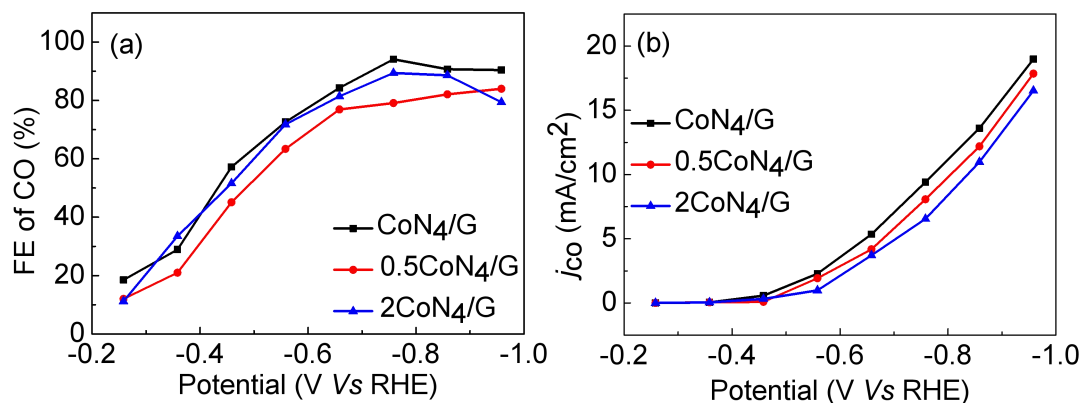


Figure S8. Comparison of the (a) FE of CO and (b) j_{CO} obtained with the different CoN₄/G composites.

Compared with CoN₄/G, 0.5CoN₄/G and 2CoN₄/G were prepared by halving or doubling the amount of cobalt source added into the graphene precursor, respectively. We found that CoN₄/G (1.61 wt% Co) was optimized (Figure S8). This is likely due to the fact that 0.5CoN₄/G with a lower Co content cannot provide surface active sites enough, while 2CoN₄/G with a larger Co content may reduce the electronic conductivity of the catalyst, consequently reducing the performance for CO₂RR.

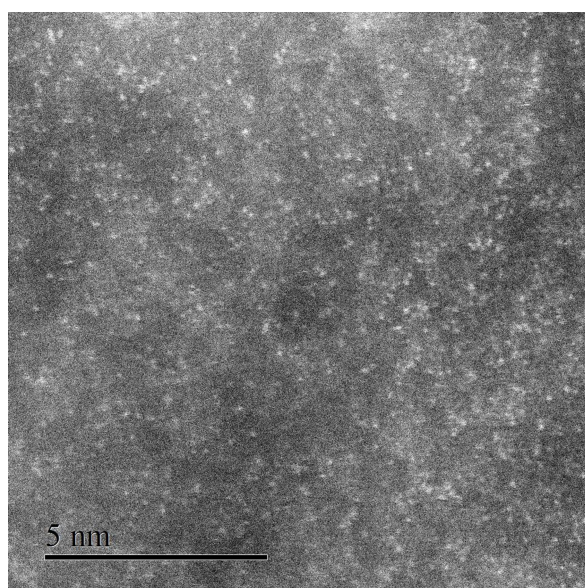


Figure S9. The STEM images of CoN₄/G catalyst after durability test for 15 h: single Co atoms remain atomically dispersed on graphene matrix.

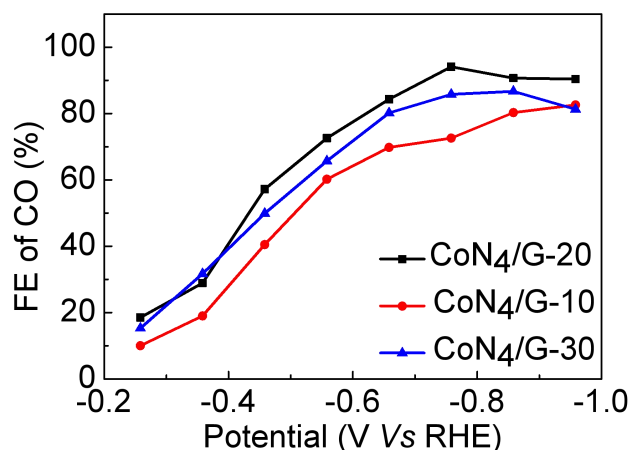


Figure S10. Comparison of the FE of CO of CoN₄/G composites obtained by different ball milling time.

The CO₂RR performance of CoN₄/G sample prepared by different ball milling time (10 h, 20 h and 30 h) were tested. The samples are named as CoN₄/G-10, CoN₄/G-20 and CoN₄/G-30, respectively. The Co contents from ICP analysis in CoN₄/G-10, CoN₄/G-20 and CoN₄/G-30 were determined to be 0.78%, 1.61% and 2.43%, respectively. The CoN₄/G-20 sample could reach a maximum FE of ~95%, which comparable to the best single Co atom electrocatalyst reported to date (*Angew. Chem. Int. Ed.*, 2018, 57, 1944; *Appl. Catal. B: Environ.*, 2019, 240, 234; *J. Am. Chem. Soc.*, 2018, 140, 4218). The worst CO₂RR performance was found in CoN₄/G-10, which should be attributed to the shortest ball milling time, leading to the inadequate Co content that cannot provide surface active site enough. While larger Co content of CoN₄/G-30 may reduce the electronic conductivity of the catalyst, consequently reducing the performance for CO₂RR.

References

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- 2 Jeon I Y, Shin Y R, Sohn G J, et al. Edge-carboxylated graphene nanosheets via ball milling[J]. PNAS, 2012, 15(109): 5588-5593.
- 3 Cui X J, Xiao J P, Wu Y H, et al. A graphene composite material with single cobalt active sites: a highly efficient counter electrode for dye-sensitized solar cells[J]. Angewandte Chemie International Edition, 2016, 23(55): 6708-6712.