Supporting Information

N-Doped Graphene as an Efficient Metal-Free Electrocatalyst for Indirect Nitrate Reduction Reaction

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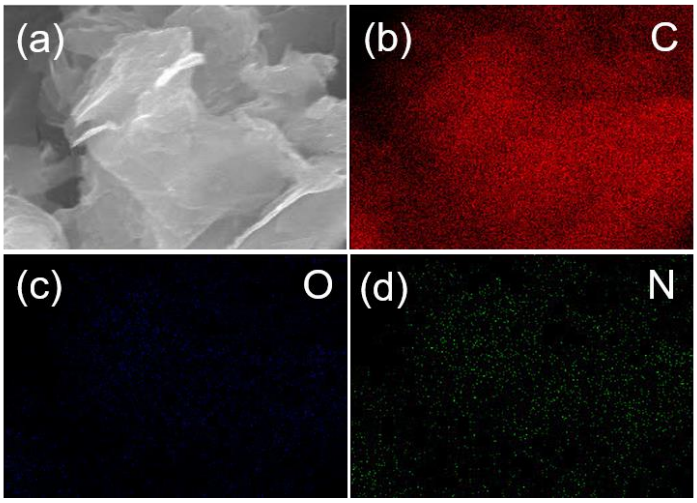

Figure S1. (a) SEM and (b-d) EDS mapping of C, O, and N in NGR1, respectively.

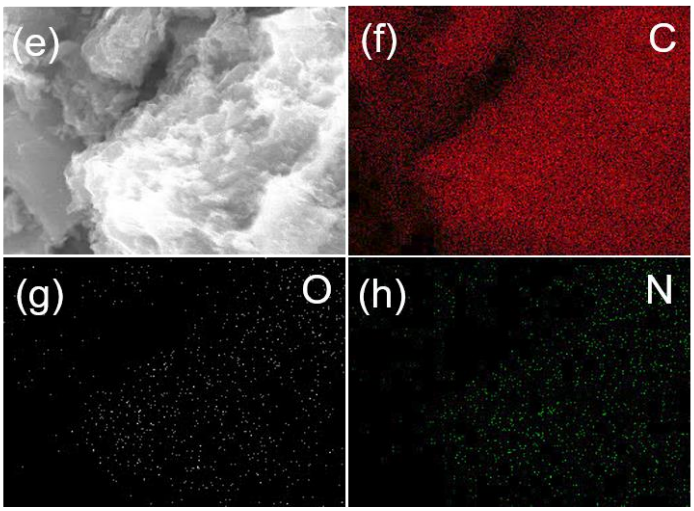

Figure S2. (a) SEM (b-d) EDS mapping of C, O, and N in NGR2, respectively.

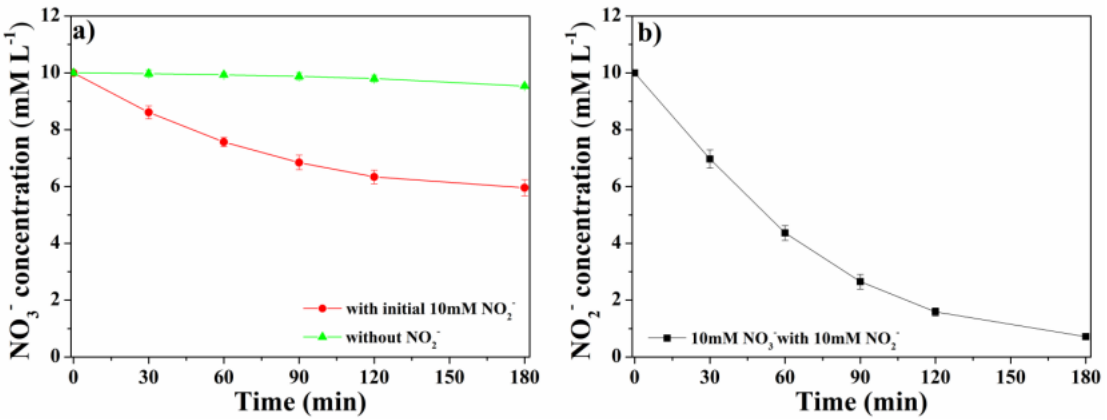

Figure S3. (a) Electrochemical reduction of NO_3^- on NGR2 at 0.6 V for 3 h, with and without initial 10 mM NO_2^- with a 5 M H_2SO_4 electrolyte; (b), amount of NO_2^- on NGR2 at 0.6 V for 3 h with the initial 10 mM NO_2^- and 10 mM NO_3^-.

Table S1 Summary of chemical composition analysis from XPS and Raman results and electrochemical properties of samples.

Sample	At% (C)	At% (O)	At % (N)	Pyridinic-N of total N (%)	Pyrrolic-N of total N (%)	Graphitic-N of total N (%)	I_D/I_G	Onset Potential (V)	Half-wave Potential (V)
GR	84.56	15.35	n/a	n/a	n/a	n/a	0.983	0.698	0.506
NGR1	86.26	8.39	5.35	23	50.9	26.1	0.989	0.85	0.732
NGR2	86.81	8	5.19	40.48	29.34	30.18	0.993	0.932	0.833

Text S1 Computational details of the DFT calculations

The calculations were performed using spin-polarized DFT as implemented in VASP. We chose the projected augmented wave (PAW) potentials [1,2] to describe the ionic cores and took valence electrons into account using a plane wave basis set with a kinetic energy cutoff of 400 eV. Partial occupancies of the Kohn−Sham orbitals were allowed using the Gaussian smearing method and a width of 0.05 eV. The electronic energy was considered self-consistent when the energy change was smaller than 10−5 eV. A geometry optimization was considered convergent when the force change was smaller than 0.02 eV/Å. Grimme's DFT-D3 methodology [3] was used to describe the dispersion interactions.

The equilibrium lattice constant of hexagonal graphene unit cell separated by a vacuum layer in the depth of 20.00 Å was optimized to be a=2.468 Å, when using a 15×15×1 Monkhorst–-Pack k-point grid for Brillouin zone sampling. We then used it to construct a graphene sheet model with (5×5) periodicity in the x and y directions and 1 atomic layer in the z direction by a vacuum layer in the depth of 15 Å in order to separate the surface slab from its periodic duplicates. This graphene sheet model contained 50 C atoms. We constructed three graphene models. In model 1, six neighboring C atoms were removed from this model in order to mimic the vacant graphene. In model 2, one C atom on the edge of model 1 was replaced by N in order to mimic pyridinic-N on graphene. In model 3, one N atom was added to the edge of model 1 in order to mimic pyrrolic-N on graphene. During structural optimizations, the gamma point in the Brillouin zone was used for k-point sampling, and all atoms in the models were allowed to relax.

References

[1] Kresse, G.; Joubert, D. From Ultrasoft Pseudopotentials to the Projector Augmented-Wave Method. Phys. Rev. B 1999, 59, 1758-1775.

[2] Blo̎chl, P. E. Projector Augmented-Wave Method. Phys. Rev. B 1994, 50, 17953−17979.

[3] Grimme, S.; Antony, J.; Ehrlich, S.; Krieg, H. J. Chem. Phys. 2010, 132, 154104.

Text S2 Detection of nitrate and nitrite

Nitrate: National Environmental Protection Standard of the People's Republic of China, Water Quality - Determination of Nitrate-nitrogen - Ultraviolet spectrophotometry, HJ/T 346-2007.
Nitrite: National Standard of the People's Republic of China, Water Quality - Determination of nitrogen (nitrite) - Spectrophotometric method, GB 7489-87.