

Supporting Information

Towards N-doped graphene via solvothermal synthesis

Dehui Deng¹, Xiulian Pan^{1*}, Liang Yu¹, Yi Cui¹, Yeping Jiang², Jing Qi³, Wei-Xue Li¹, Qiang Fu¹, Xucun Ma², Qikun Xue², Gongquan Sun³ and Xinhe Bao^{1*}

¹*State Key Laboratory of Catalysis, Dalian Institute of Chemical Physics, Chinese Academy of Sciences, Zhongshan Road 457, Dalian 116023, China.*

²*Institute of Physics, The Chinese Academy of Sciences, Beijing 100190, China*

³*Direct Alcohol Fuel Cell Laboratory, Dalian Institute of Chemical Physics, Chinese Academy of Science, Zhongshan Road 457, Dalian 116023, China*

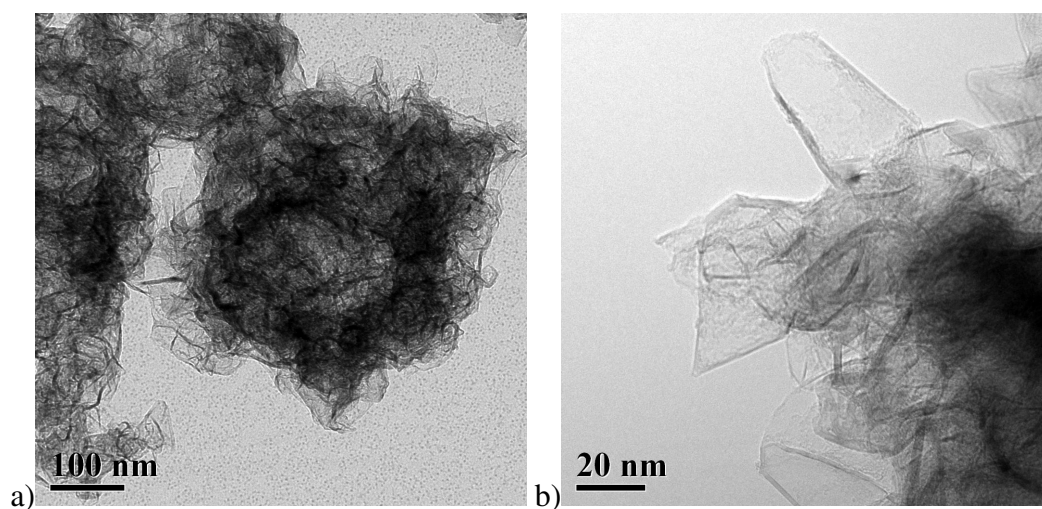


Figure S1. TEM images of NG-1 at different magnifications.

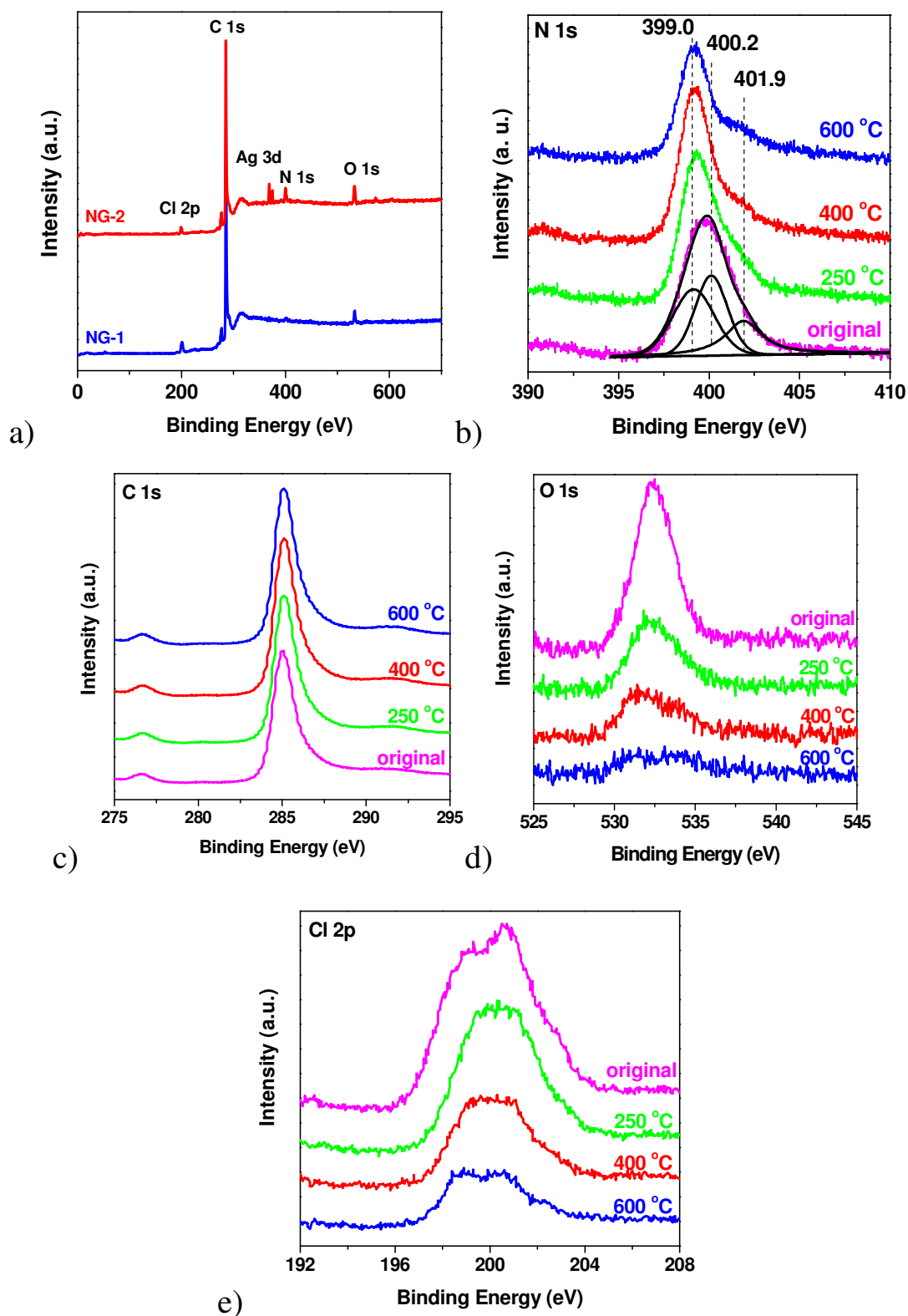


Figure S2. XPS spectra: (a) wide spectra of NG-1 and NG-2. The Ag 3d signals come from the Ag substrate. (b) N1s spectra of NG-2 upon in situ heat-treatment, fitting this signal indicating the presence of three types of nitrogen species: graphitic, pyridinic and pyrrolic N. (c) C1s, (d) O1s and (e) Cl2p of NG-1 upon in situ heat-treatment. The O bonds with C is

mainly in the type of C-OH, C=O and C-O-C¹⁻², while the Cl bonds with C is in the type of C-Cl³.

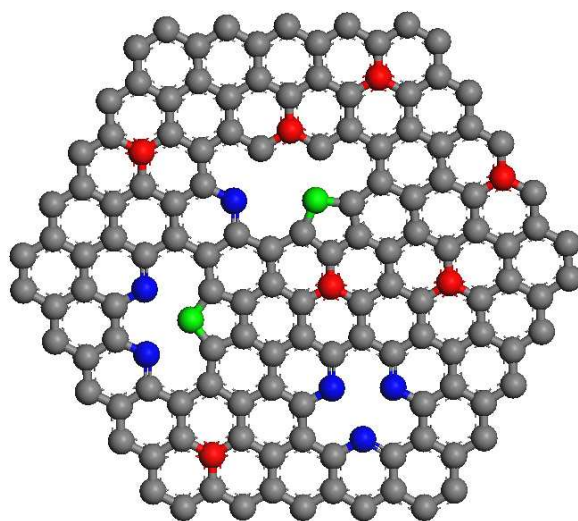


Figure S3. An atomic model for N-doped graphene. The grey balls represent C atoms, while the red, blue, and green ones present graphitic, pyridinic and pyrrolic N atoms, respectively.

Table S1. Compositions of NG-1 after in situ treatment at different temperatures estimated from XPS measurements.

Temperature (°C)	C (at. %)	Graphitic\Pyridinic\ Pyrrolic N (at. %)	O (at. %)	Cl (at. %)	N/C (%)
RT	89.6	2.82\0.39\0.79	3.7	2.7	4.5
250	92.6	2.33\0.68\0.19	1.8	2.4	3.5
400	94.0	2.37\0.77\0.06	1.4	1.4	3.4
600	96.0	2.38\0.47\0.05	0.2	0.9	3.0

Table S2. Compositions of NG-2 after in situ treatment at different temperatures estimated from XPS measurements.

Temperature (°C)	C (at. %)	Graphitic\Pyridinic\ Pyrrolic N (at. %)	O (at. %)	Cl (at. %)	N/C (%)
RT	79.2	3.29\5.00\4.71	6.0	1.8	16.4
250	81.4	3.07\5.60\3.53	5.3	1.1	15.0
400	85.2	2.98\6.21\2.61	2.0	0.9	13.8
600	89.1	3.00\4.78\1.62	1.0	0.5	10.5

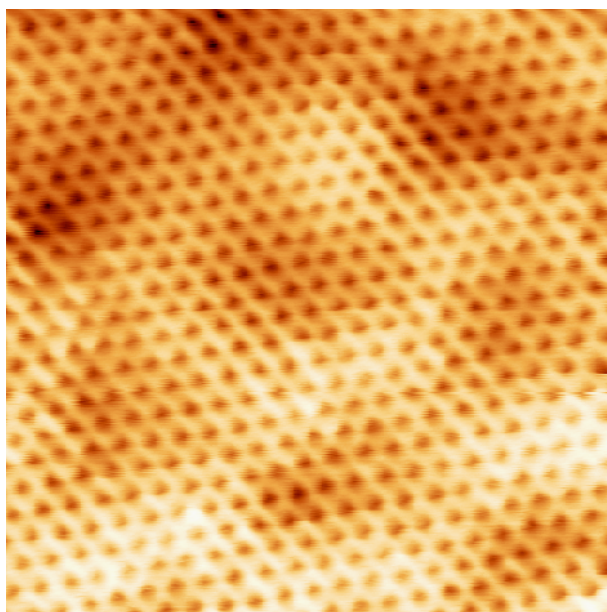


Figure S4. STM image of the SiC (0001) substrate covered with a perfect monolayer graphene derived from epitaxial growth. The size of the image is 5 nm× 5 nm.

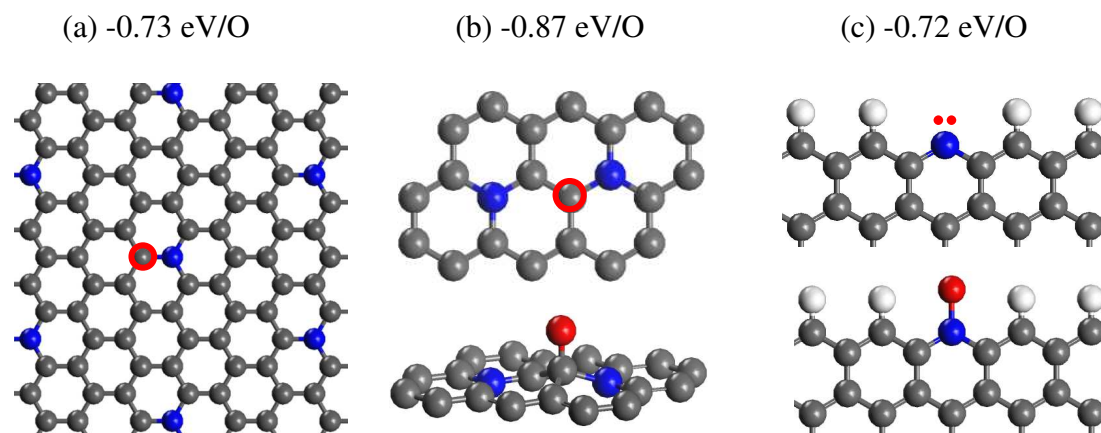


Figure S5. DFT calculation of oxygen activation by N-doped graphene. (a) and (b) Adjacent carbon atoms being the active sites for top oxygen on the graphitic-N-doped graphene: (a) 5.6 at.% N species distributed homogeneously and (b) 2 at.% N species distributed inhomogeneously in the graphene structure; (c) pyridinic N atoms being the active sites for oxygen by bonding through the lone pair electrons. The grey, blue, red and white balls represent C, N, O and H atoms, respectively.

The Vienna Ab-initio Simulation Package (VASP) was used in the calculation with the spin-polarized projector augmented wave method and a cutoff energy of 400 eV⁴⁻⁷. The PW91 functional with generalized gradient approximation method was adopted for the exchange-

correlation term⁸, and the Monkhorst-Pack scheme was used to sample the Brillouin zone. A periodically repeating hexagonal (3×3) supercell was taken for the graphitic N-doped graphene model with lattice vectors *a* and *b* parallel, *c* vertical to the plane. The lattice constant *a* and *b* were taken from pure graphene after being optimized. *c* was set as 14 Å which was large enough to avoid interplanar interactions. Various adsorption sites for dissociative atomic oxygen were considered, and energetically most favorable site was found to be the top site of C atoms adjacent to graphitic N with a value of -0.73 eV/O atom (Figure S5a) in the supercell containing 5.6at.% N species. When the graphitic N species were not evenly distributed in the case of low N content e.g. two N atoms in a (7×7) supercell, the adjacent C atoms were more active if the distance between the two N was less than three C atoms. The dissociative energy was -0.87 eV/O atom (Figure S5b).

For pyridinic N species located at the graphene edge oxygen, it interacts directly with nitrogen via the lone-pair electrons of nitrogen (Figure S5c, using graphene nanobelt with (6 × 4sqrt(3)) as a model) The dissociative energy is -0.72 eV/O.

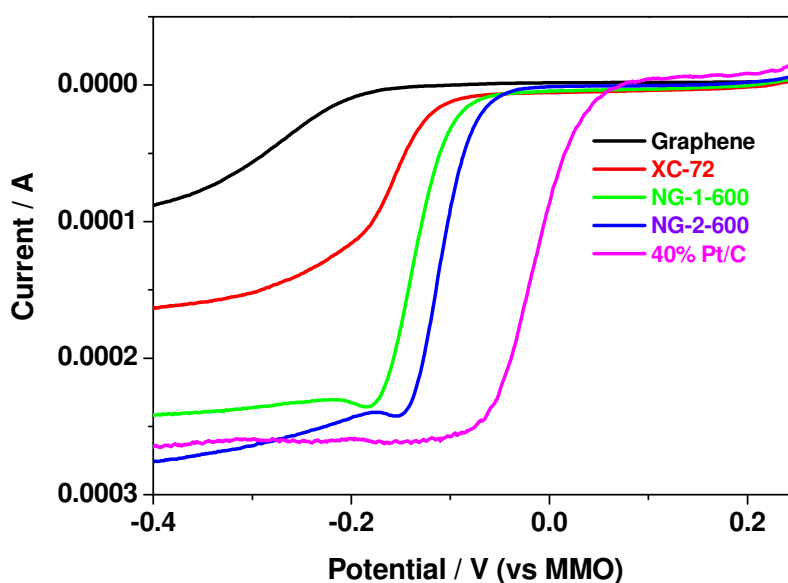


Figure S6. Oxygen reduction voltammogram of pure graphene (obtained by thermal splitting of silicon carbide granules⁹), XC-72, NG-1-600 (NG-1 sample subjected to treatment at 600 °C in Ar), NG-2-600 (NG-2 treated at 600 °C in Ar) and 40% Pt-C/GC in O₂-saturated 1.0 M NaOH at the scan rate of 5 mV·s⁻¹. Before measurements, the samples were repeatedly swept from +0.3 to -0.8 V in an N₂-protected 1.0 M NaOH until a steady voltammogram curve had been obtained.

The ORR activity was evaluated using a CHI 760B potentiostat/galvanostat equipped with a three-electrode electrochemical cell and gas flow controlling systems. A mercury/mercuric oxide electrode (1 M NaOH-filled) was used as the reference electrode, and a Pt-foil as the

counter electrode. A glassy carbon rotating ring disk electrode with a diameter of 5 mm covered by a thin film of the catalyst was used as the working electrode. Typically 5 mg catalyst was ultrasonically suspended in 1 mL ethanol and 50 μL of Nafion solution (5wt. %, Du Pont) to form a homogeneous ink. Then 25 μL of the ink was spread onto the surface of the glassy carbon with a micropipette followed by drying under an infrared lamp. All experiments were conducted in a 1 M NaOH solution saturated with oxygen at 25 $^{\circ}\text{C}$, a rotation rate of 2500 rpm and a sweep rate of 5 $\text{mV}\cdot\text{s}^{-1}$. All potentials were referred to the normal hydrogen electrode (NHE).

References

1. X. B. Fan, W. C. Peng, Y. Li, X. Y. Li, S. L. Wang, G. L. Zhang, and F. B. Zhang, *Adv. Mater.* **20**, 4490 (2008).
2. H. P. Boehm, *Carbon* **40**, 145 (2002).
3. John F. Moulder, William F. Stickle, Peter E. Sobol and Kenneth D. Bomben (editor: Jill Chastain), *Handbook of X-ray Photoelectron Spectroscopy* (1992).
4. P. E. Blochl, *Phys. Rev. B* **50**, 17953 (1994).
5. G. Kresse, and D. Joubert, *Phys. Rev. B* **59**, 1758 (1999).
6. G. Kresse, and J. Hafner, *Phys. Rev. B* **48**, 13115 (1993).
7. G. Kresse, and J. Furthmuller, *Phys. Rev. B* **54**, 11169 (1996).
8. J. P. Perdew, J. A. Chevary, S. H. Vosko, K. A. Jackson, M. R. Pederson, D. J. Singh, and C. Fiolhais, *Phys. Rev. B* **46**, 6671 (1992).
9. D. H. Deng, X. L. Pan, H. Zhang, Q. Fu, D. L. Tan, and X. H. Bao, *Adv. Mater.* **22**, 2168 (2010).