

Electronic Supporting Information

for

Understanding the roles of amorphous domains and oxygen-containing groups of nitrogen-doped carbon in oxygen reduction catalysis: toward superior activity

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1. Experimental

1.1 Synthesis of the N-doped carbon

All the chemicals were of analytical grade and supplied by Alfa Aesar, Strem Chemical Inc. and Sigma Aldrich. The N-doped carbon was synthesized as reported previously.¹ In short, nitrilotriacetic acid (22.937 g, 120 mmol, 1 equiv.) and magnesium carbonate ((MgCO₃)₄Mg(OH)₂, 11.657 g, 120 mmol Mg, 1 equiv.) were dissolved in water (300 mL) at 85 °C. The resulting yellow solution was stirred for an additional 15 minutes, after which ethanol (1500 mL) was added slowly ($\pm$ 5 min). The resulting white suspension was cooled in an ice bath for 3 hours, to increase the perception of the magnesium nitrilotriacetic acid (MgNTA). The liquid phase was decanted, producing an off-white gel like product. The product was dried for 3 days under vacuum at 40 °C, yielding a white solid (22-26 grams). Subsequently, the solid was grinded to a powder and pyrolyzed at 900 °C with a rate of 10 °C/min in a nitrogen (99.999% N₂, 150 mL/min) atmosphere. The resulting coarse carbon powder was washed with a 0.5 M citric acid solution (500 mL) for 24 hours, vacuum filtered, washed with water (3000 mL) and dried at 80 °C for 24 hours. A subsequent thermal treatment at 1000 °C with a ramp of 5 °C/min in a nitrogen atmosphere (99.999% N₂, 150 mL/min) yields the N-doped carbon.

1.2 Oxidation and Pyrolysis of the N-doped carbon

The N-doped carbon was oxidized in a 1:3 air:N₂ (99.999% N₂, giving 5% O₂, 150 mL/min) atmosphere. Starting with a 5 °C/min ramp up to the desired temperature of either 350, 450 or 500 °C at which it stayed for 1 hour. Afterwards, the reactor was allowed to naturally cool down. A second thermal treatment was performed, ramping the temperature with 5 °C/min to 900 °C in a nitrogen atmosphere (99.999% N₂, 150 mL/min) for 1 hour.

1.3 Material Characterization

Temperature-programmed oxidation was performed on a Thermo Fischer TPDRO 1100 series with 25 mg sample sandwiched between two quartz wool layers in a quartz tube reactor (4 mm inner diameter). The system was purged with He and a flow of 5% O₂/He was used during the temperature program. The system was heated with 2 °C/min to 900 °C and the gas output was measured using TCD. Nitrogen adsorption isotherms were measured with a Thermo Scientific Surfer instrument at 77K. Before analysis, the sample was dried in vacuum (10⁻³ mbar) at 200 °C for 3-6 h. For X-ray photoelectron spectroscopy (XPS) a Kratos AXIS equipped with monochromatic Al K α X-ray source was used and the base pressure in the analytical chamber was 10⁻⁹ mbar. Raman spectra were measured using a Renishaw InVia system (532 nm and 632.8nm) and a Kaisar Optical Systems RXN-4 system (785 nm) coupled with fiber optics to an immersion probe with a short focal length. Scanning electron microscopy (SEM, FEI Verios 460 with ETD detector) was used to study the morphology of the materials.

1.4 Electrochemical procedures

Catalyst inks were prepared by suspending 1 mg carbon sample in 1 mL ethanol and 10 μ L Nafion[®] (D-521 dispersion 5 wt.% in water/isopropanol), and sonicated overnight. The Rotating Disk Electrode (RDE) working electrode tip (glassy carbon disk 0.196 cm²) was polished with diamond polishing film containing 0.1 μ m particles and rinsed with water afterwards. The working electrode was prepared by drop casting 6 $\times$ 5 μ L ink, while air drying between casts. 20 wt.% Pt on Vulcan XC-72 was used for the Pt/C standard.

Electrochemical experiments were performed in a 3-electrode glass cell, with a 0.1 M KOH electrolyte. All electrochemical experiments were performed under 25 °C. A saturated calomel electrode (SCE) was used as a reference electrode, separated from the solution with a luggin capillary. Potentials were reported vs RHE by adding 1.006 V (pH = 13) to the measured SCE potential. A graphite rod was used as a counter electrode, presoaked with the electrolyte 24 hours prior to the measurements. Oxygen was bubbled through the solution for a minimum of 30 min, where after the gas was flown over the solution (gas blanket). Prior to the experiments the solution resistance was measured and 95% of this value was used as a positive correction factor in an automatic iR drop correction. Before measurements, cyclic voltammograms were recorded from 0.3 to 1.0 V vs RHE till no change in current was observed.

2. Additional Figures

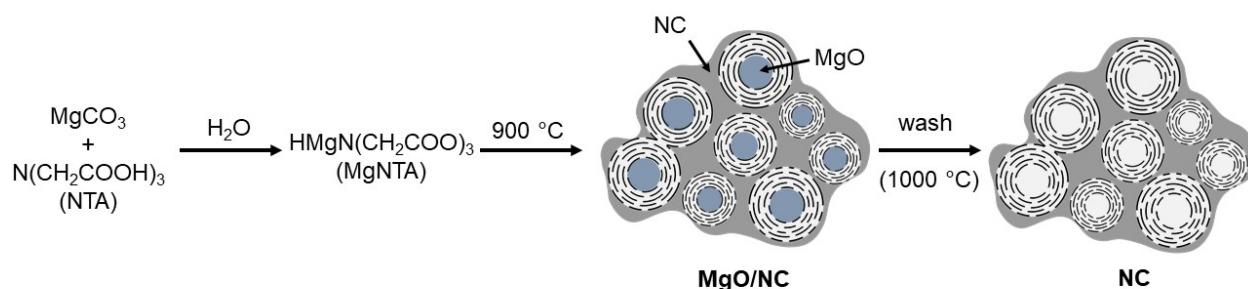


Figure S1. Typical procedure for gram-scale synthesis of nitrogen-doped carbon starting from nitrilotriacetic acid and magnesium carbonate.

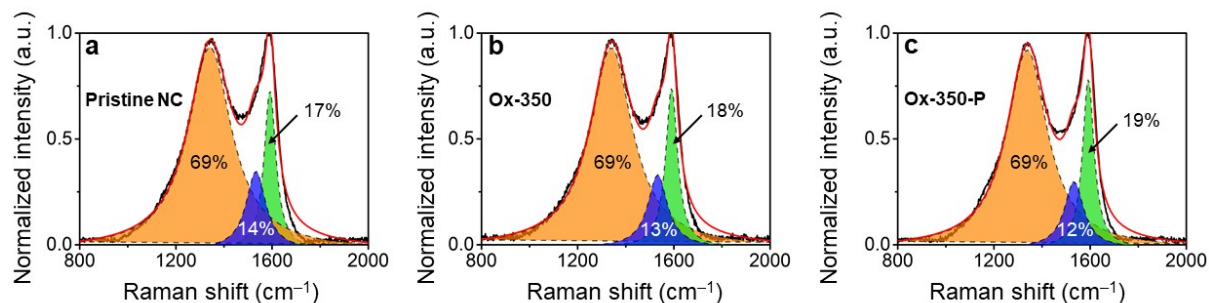


Figure S2. The deconvolution of the Raman spectra of a) Pristine NC, b) Ox-350 and c) Ox-350-P using the D1, D2 and G bands. The numbers of the peaks represent the relative areas of the peaks.

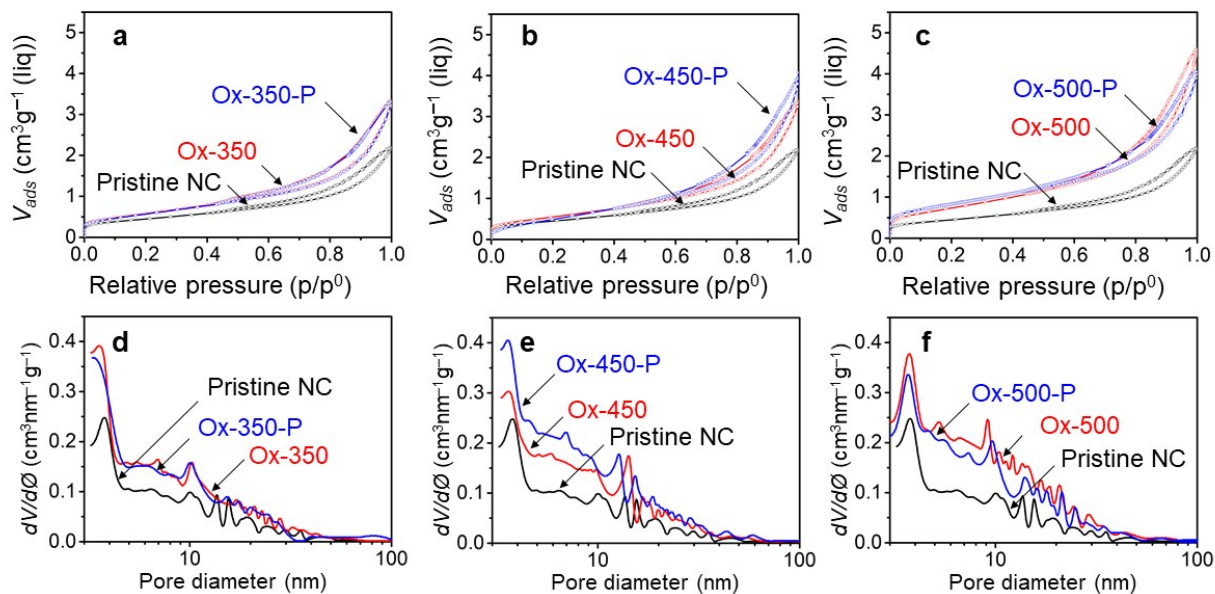


Figure S3. The N_2 adsorption derived BJH mesopore size distribution for of a) 350 °C oxidized samples, b) 450 °C oxidized samples, c) 500 °C oxidized samples.

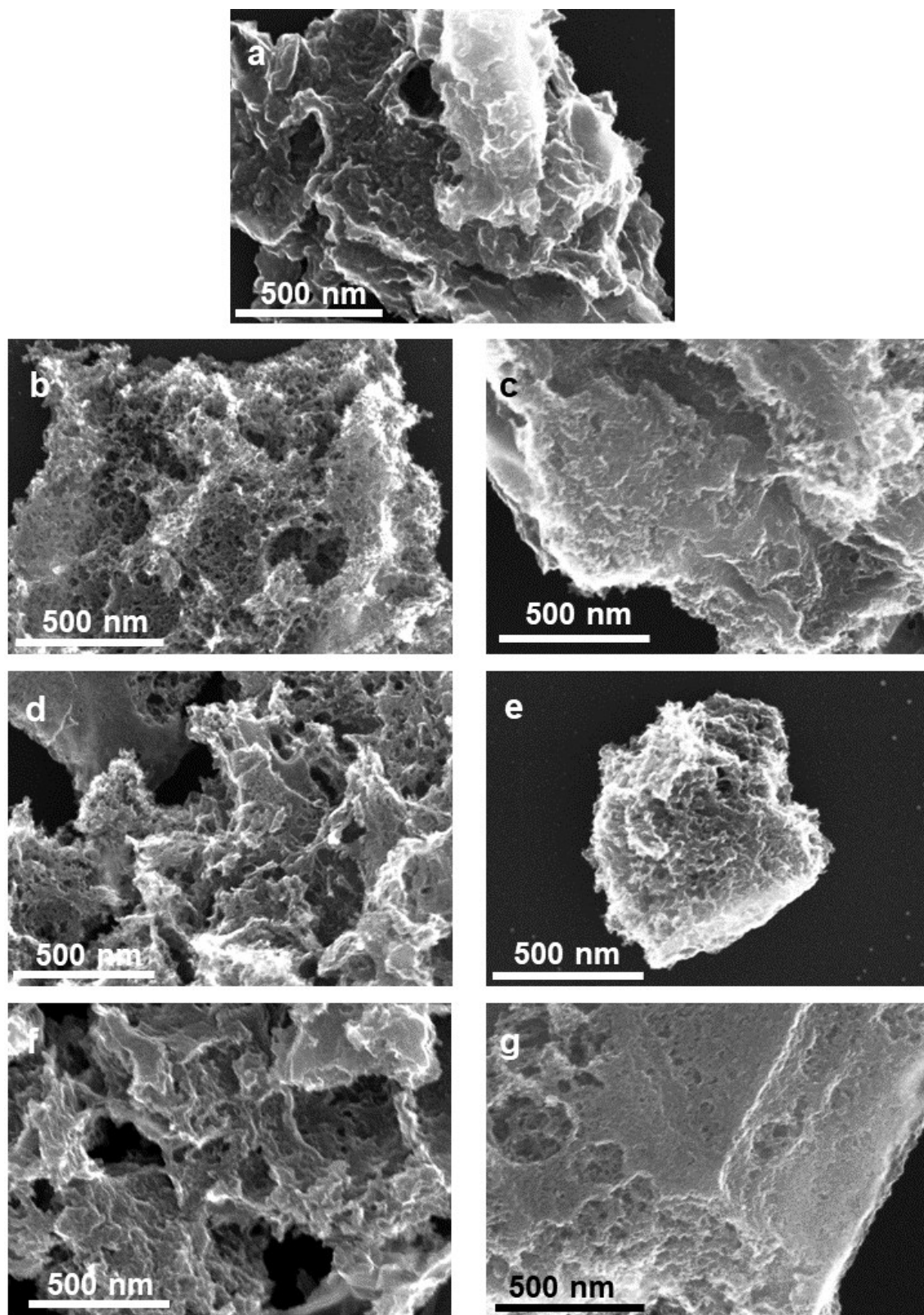


Figure S4. The SEM micrographs of a) pristine NC, b) Ox-350, c) Ox-350-P, d) Ox-450, e) Ox-450-P, f) Ox-500 and g) Ox-500-P.

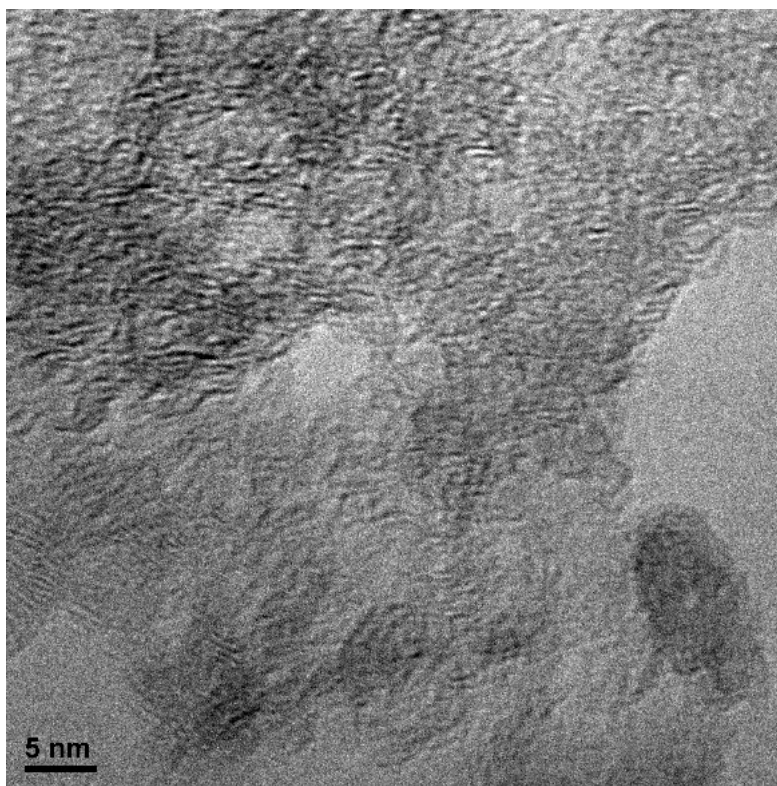


Figure S5. The HRTEM image of Ox-500-P.

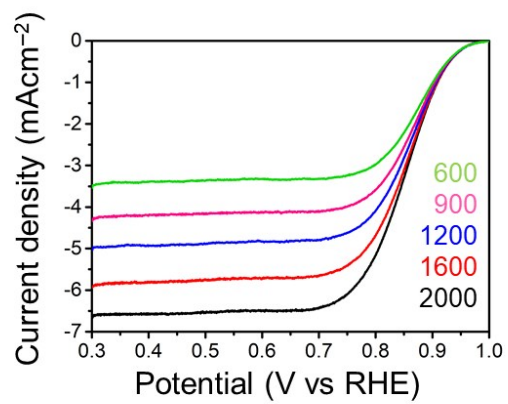


Figure S6. The LSV curves of Ox-500-P at different rotation speeds (rpm).

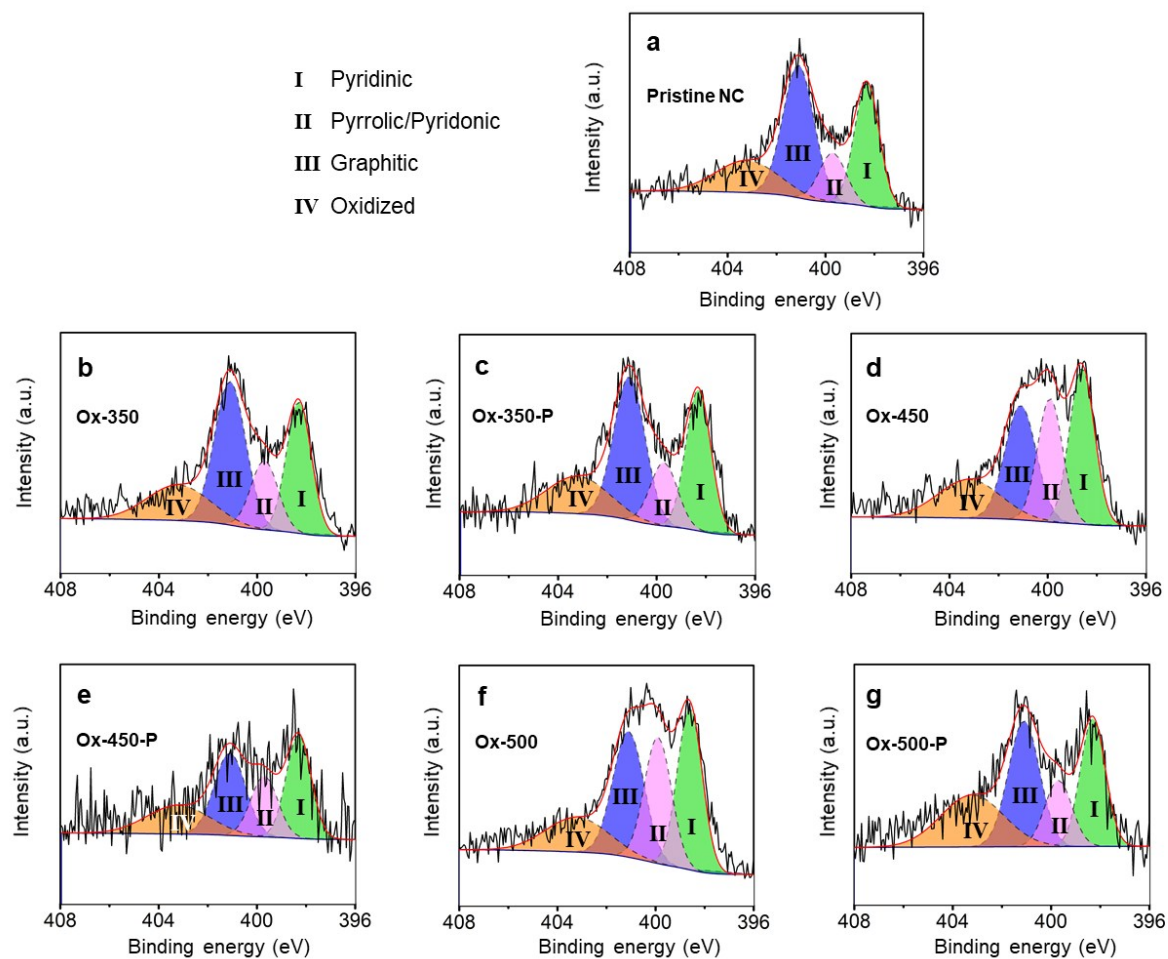


Figure S7. The deconvolution of the N1s XPS peak of (a) pristine NC, (b) Ox-350, (c) Ox-350-P, (d) Ox-450, (e) Ox-450-P, (f) Ox-500 and (g) Ox-500-P.

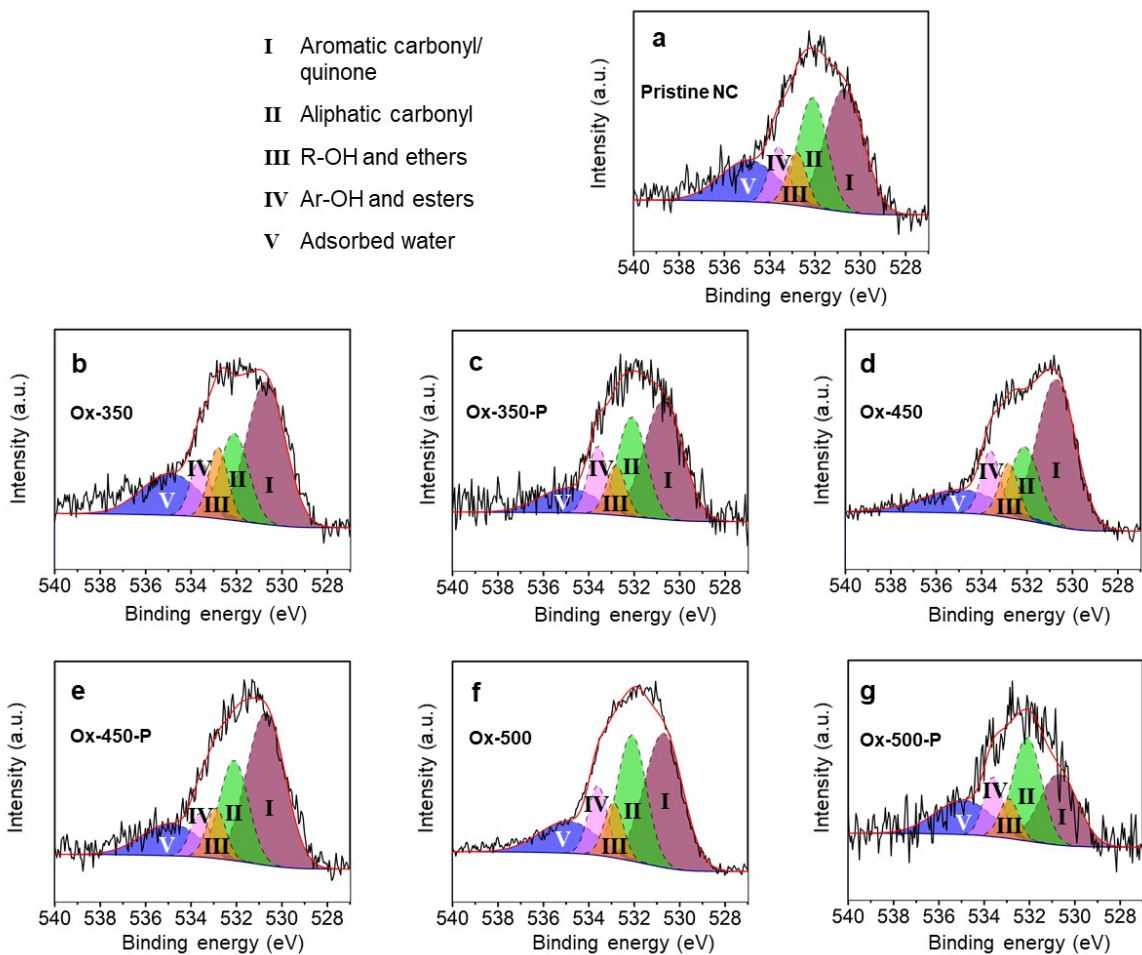


Figure S8. A modified version of the XPS peaks reported by Burg *et al* was used.² The deconvolution of the O1s XPS peak of (a) pristine NC, (b) Ox-350, (c) Ox-350-P, (d) Ox-450, (e) Ox-450-P, (f) Ox-500 and (g) Ox-500-P.

3. Additional Tables

Table S1. The specific surface area (SSA), pore volume (V_{pore}) and specific capacitance of the NC samples

Entry	Sample	SSA (m^2g^{-1})	V_{pore} (cm^3g^{-1}) ^a	Specific capacitance (Fg^{-1}) ^b
1	Pristine NC	1320	2.1	36
2	Ox-350	1380	3.4	85
3	Ox-350-P	1360	3.4	38
4	Ox-450	1320	3.4	94
5	Ox-450-P	1360	4.3	41
6	Ox-500	1760	4.5	48
7	Ox-500-P	1930	3.8	35

^a Barret, Joyner and Halenda (BJH) pore volume calculated from $p/p^0 = 0.99$. ^b Measured at 20 mV s^{-1}

Table S2. Recently reported high-performance N-doped carbons and their ORR activity

Material name	Journal	Onset (V vs RHE)	Halfwave (V vs RHE)	Ref
N-HsGDY-900 °C	Lv <i>et al.</i> , Nat. Commun., 2018	~1.0	0.85	3
ONC	Chen <i>et al.</i> , Catal. Commun., 2018	0.98	0.87	4
Ox-500-P	This work	0.97	0.85	
NCN-1000-5	Jiang <i>et al.</i> , Energy Environ. Sci., 2019	0.95	0.82	5
NPMC-1000	Zhang <i>et al.</i> , Nat. nanotechnol., 2015	0.94	0.85	6
NG-800	Liu <i>et al.</i> , Nat. Commun., 2016	0.92	n.d.	7
Pristine NC ^a	Eisenberg <i>et al.</i> , Chem. - Eur. J., 2016	0.91	0.81	1
CCa	Ferrero <i>et al.</i> , Carbon, 2016	0.9	0.75	8
N-CNS-120	Yu <i>et al.</i> , Adv. Mater., 2016	0.9	0.75	9
NGM	Tang <i>et al.</i> , Adv. Mater., 2016	0.89	0.77	10
GZ80C	Thomas <i>et al.</i> , ACS Appl. Mater. Interfaces, 2016	0.88	0.75	11

NEMC/G	Lai <i>et al.</i> , Adv. Funct. Mater., 2016	0.88	0.82	12
NMCS-3	Tang <i>et al.</i> , Angew. Chem., 2015	0.87	n.d.	13
NCNP-CNF	Panomswan <i>et al.</i> , ACS Appl. Mater. Interfaces, 2016	0.82	n.d.	14

^aThis is the base material used in this research

4. References

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