

## Supporting Information

### Revealing the Enhanced Activity of Nitrogen-doped Carbon Nanotubes for Oxidative Dehydrogenation of Propane

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#### 1. Preparation of NCNTs and CNTs

With aniline and/or toluene as nitrogen and carbon resource, NCNTs and CNTs were grown on the supported FeMo/Al<sub>2</sub>O<sub>3</sub> catalyst using an atmospheric pressure CVD method reported before.<sup>[S1]</sup> The pristine collected products were immersed into concentrated nitric acid with a ratio of 10 g/L by ultrasonic dispersion for 30 min and then refluxed in flask at 120 °C for 2 h. These mixtures were then filtered and washed to pH≈7 with deionized water and alcohol. After drying in an oven at 120 °C for 24 h, purified samples were

obtained. The obtained samples noted as NCNT-1, NCNT-2, NCNT-3 and CNT for 100%, 80%, 20% and 0% v/v of aniline in the CVD feeding, respectively.

## 2. Characterization

The morphology of carbon nanotubes was characterized by a JEOL 2100 transmission electron microscopy (TEM) with an accelerating voltage of 200 kV. The electron energy loss spectroscopy spectra and energy-filtered images were obtained on an FEI microscope (F20). The textural properties of samples were performed by nitrogen physisorption tests on a Micromeritics ASAP 3020 instrument at 77 K. The surface area and pore volume were calculated using BET and BJH methods, respectively. The oxidation stability was tested by a thermogravimetric analyzer (Netzsch 449 F3). The elemental composition of FeMo/Al<sub>2</sub>O<sub>3</sub> and ash in nanocarbons was analyzed on a Zeiss Supra 40 microscope. Surface chemistry of samples was investigated using an ESCALAB 250 instrument with Al K $\alpha$  X-rays (1489.6 eV). Raman spectroscopy was conducted with a LabRam HR 800 spectrometer using a 632.8 nm excitation at 25 mW laser power with a 2.5 cm<sup>-1</sup> resolution. The C<sub>3</sub>H<sub>6</sub> adsorption and oxygen TPD experiments were carried out using a Micromeritics AutoChem II 2920. The catalysts were heated in argon atmosphere to 400 °C and hold for 1h to clean the surface, then cooled to 27.0±0.5 °C to adsorb oxygen or C<sub>3</sub>H<sub>6</sub>. The amounts of samples were 0.116 g for NCNT-1 and 0.114 g for CNT, respectively.

Electrochemical measurements were performed at room temperature in a three-electrode cell connected to an electrochemical analyzer (CH Instruments 630E). Platinum wire and Ag/AgCl electrode with saturated KCl were served as counter electrode and reference electrode. Cyclic voltammetry (CV) was carried out on a glassy carbon (GC) electrode (4 mm in diameter) coated catalyst. During CV, the potential was swept from -1.25 to 0.25V vs. Ag/AgCl at the scan rate of 100 mV s<sup>-1</sup> in 0.1M KOH.

## 3. Catalytic reaction and kinetic measurements of ODH of propane

The catalytic measurements were carried out in an immobilized bed quartz reactor (8 mm i.d.) in a tri-heating system at atmospheric pressure. Carbon catalysts were fixed between two

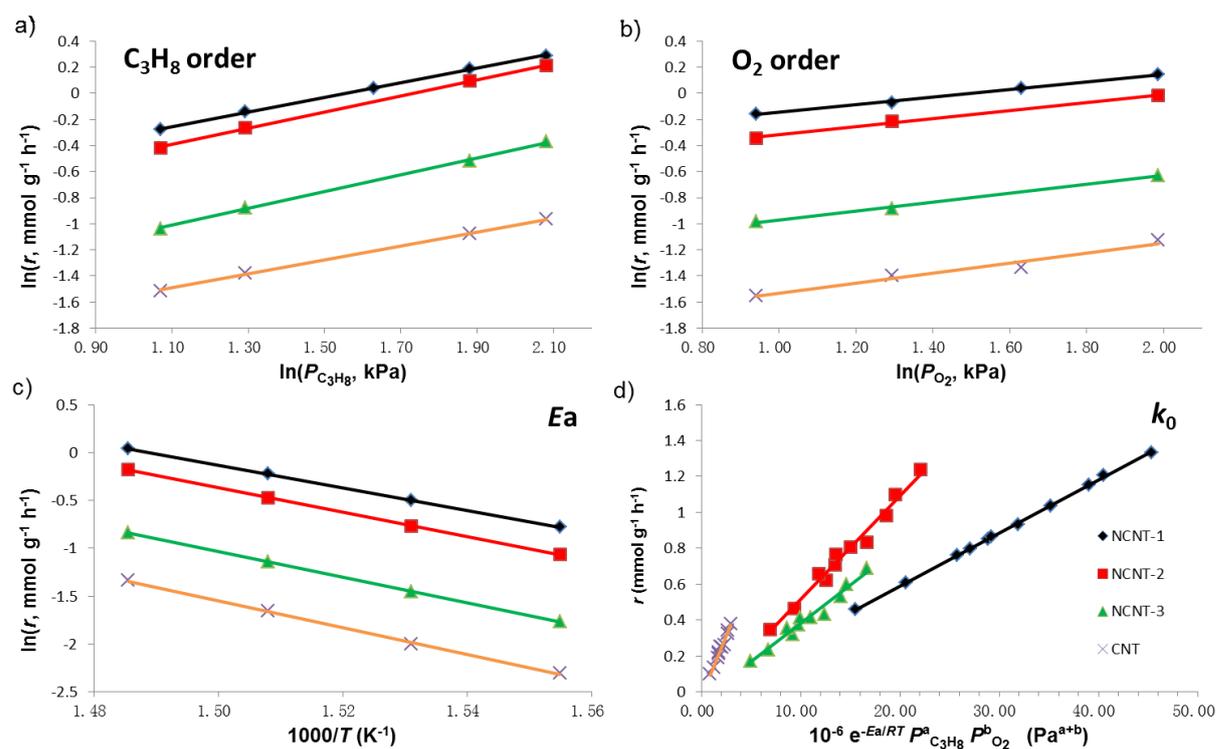
layers of quartz wool. The feed gas consisted of C<sub>3</sub>H<sub>8</sub>, O<sub>2</sub> and He as balance were controlled by MFC (Brooks, USA) to varied the total flows and partial pressures of the reactants. The product components leaving the reactor were monitored by an on-line gas chromatograph (Agilent 7890A, USA) with FID and TCD detectors. Blank experiments showed that reaction rates were negligible without carbon catalyst. For all catalytic tests, the products of propene, CO<sub>2</sub> and CO. After 24 h integral reaction, the weight losses were 12.0, 6.9, 5.3 and 2.0 mg for NCNT-1, NCNT-2, NCNT-3 and CNT, respectively. The weight of catalysts were mainly possible lost in the introduction period due to the in-situ rearrangements of functionalities and carbon debris. The carbon balance determined by GC analysis was 100.0±0.9% at the stable period during 15-22 h.

Conditions for integral catalytic testing: 400 °C, 150 mg catalyst, 9.0% C<sub>3</sub>H<sub>8</sub>, 9.0% O<sub>2</sub>, GHSV=13 L g<sup>-1</sup> h<sup>-1</sup>, He as a balance gas. Conditions for variaton of propene selectivity with propane conversion: 400 °C, 100 mg catalyst, 9.0% C<sub>3</sub>H<sub>8</sub>, 4.5% O<sub>2</sub>, He as a balance gas. Conditions for kinetic measurements: 370-400 °C, 5 mg catalyst, 2.9-8.1 kPa C<sub>3</sub>H<sub>8</sub>, 2.5-7.3 kPa O<sub>2</sub>, He as a balance gas.

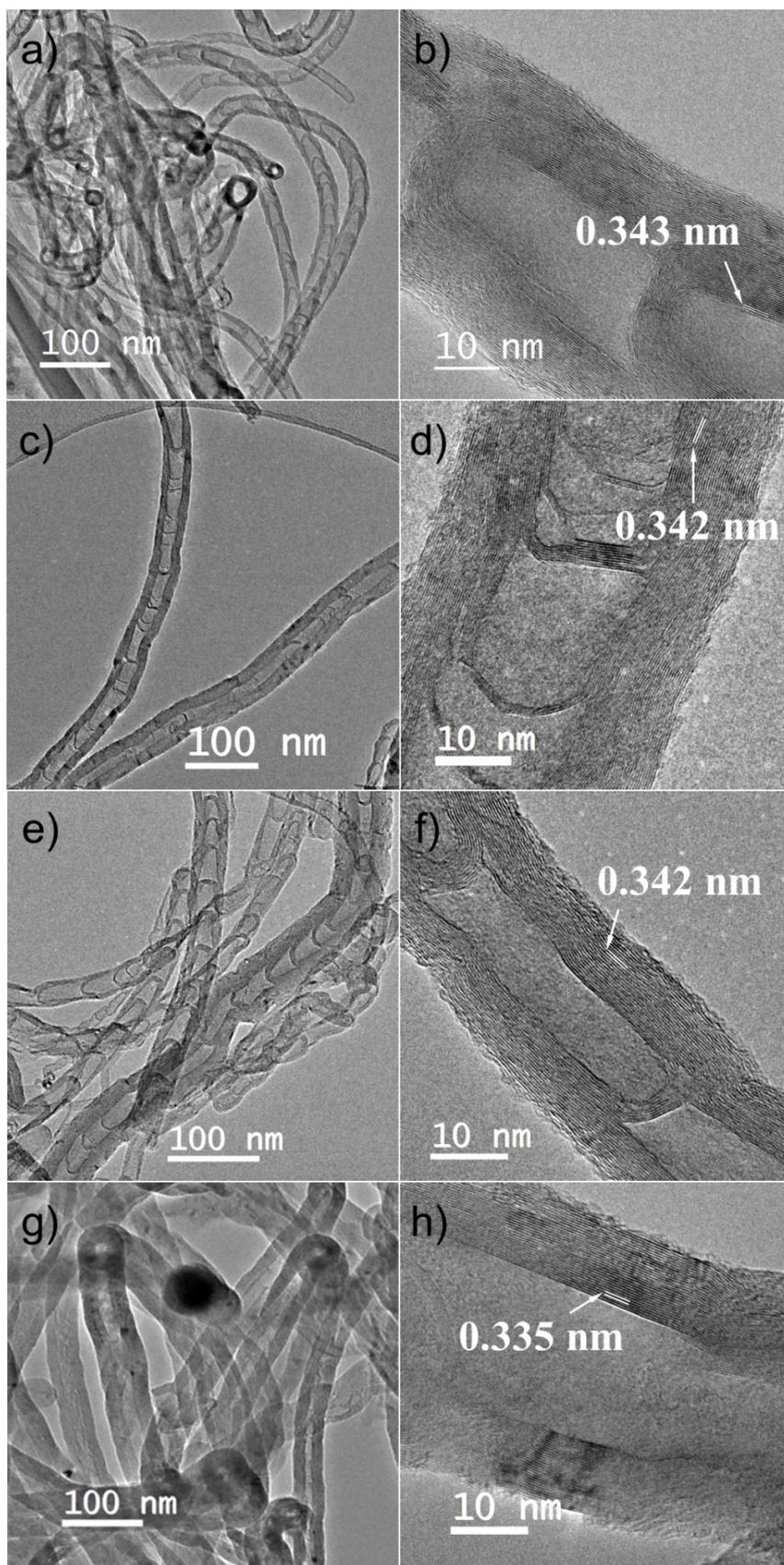
**Table S1** Textural properties of all fresh and used carbon catalysts .

Samples	BET area $\text{m}^2 \text{g}^{-1}$	Pore size nm	Pore volume $\text{cm}^3 \text{g}^{-1}$
NCNT-1	87.5	8.1	0.236
NCNT-2	73.2	10.9	0.228
NCNT-3	66.8	11.0	0.181
CNT	49.1	22.5	0.144
used NCNT-1	125.3	9.7	0.285
used NCNT-2	123.8	8.8	0.277
used NCNT-3	112.0	8.6	0.228
used CNT	108.9	9.4	0.248

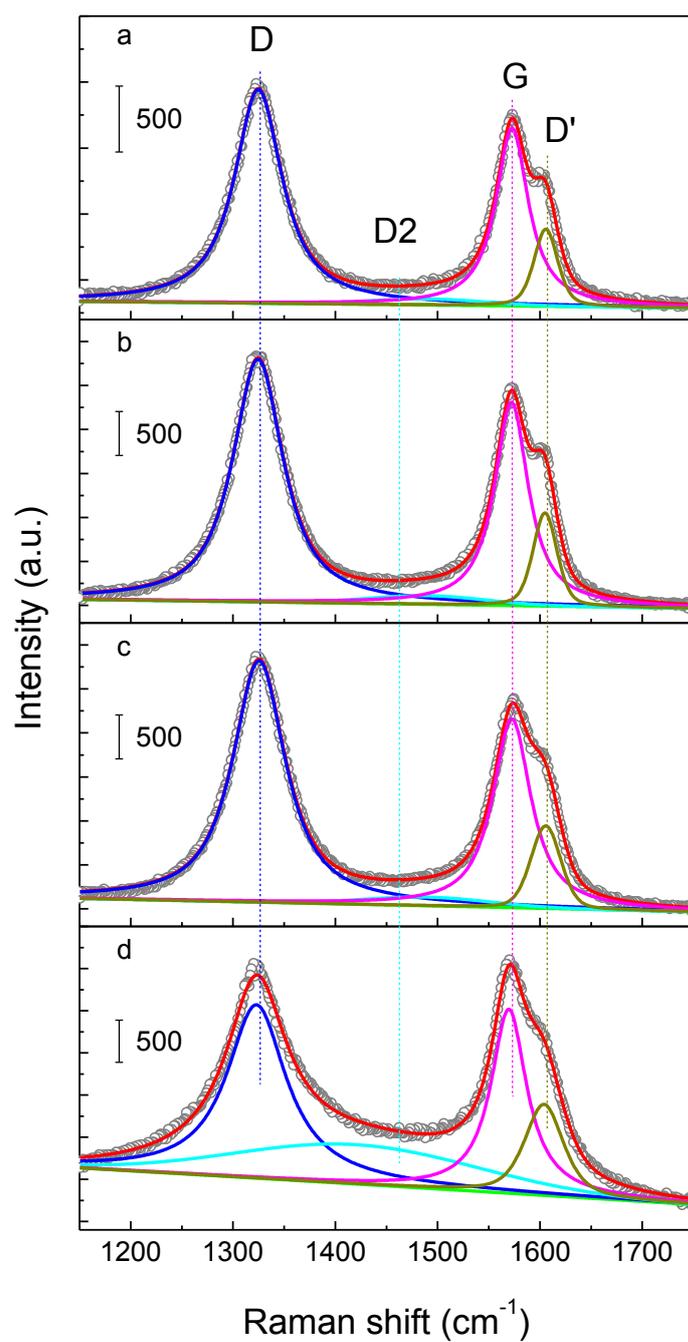
After reaction, the increments of BET area and pore volume may origin from the opening of the closed ends and graphitic arches of NCNT samples and CNT by gas-phase oxygen during the ODH reaction. The mean pore size of catalysts trended to the similar values observed in HRTEM images after reaction.



**Fig. S1** Kinetic measurements of a) C<sub>3</sub>H<sub>8</sub> and b) O<sub>2</sub> reaction orders, c) apparent activation energies of C<sub>3</sub>H<sub>6</sub> formation, as well as d) pre-exponential factors over all the selected carbon catalysts.



**Fig. S2** TEM and HRTEM images of the selected samples: a, b) NCNT-1, c,d) NCNT-2, e,f) NCNT-3 and g,h) CNT.



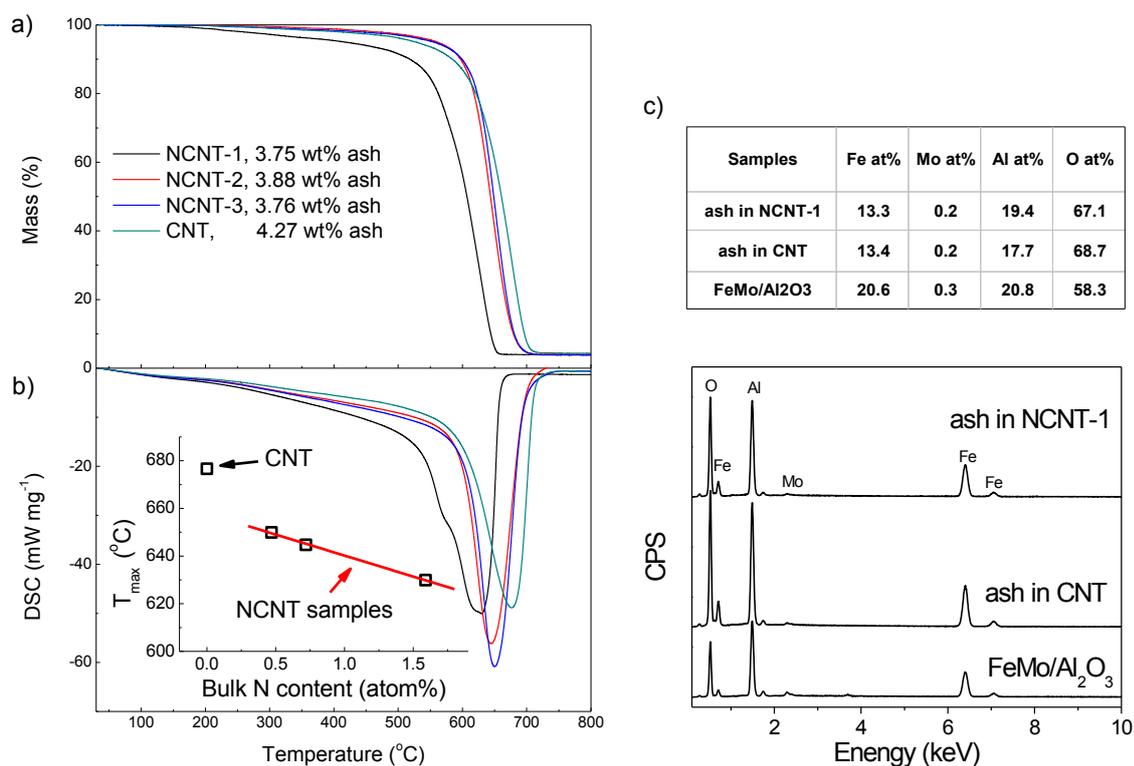
**Fig. S3** Deconvolution of Raman spectra of 1) NCNT-1, b) NCNT-2, c) NCNT-3 and d) CNT.

The gray circle is experimental data and the red line is fitted curve.

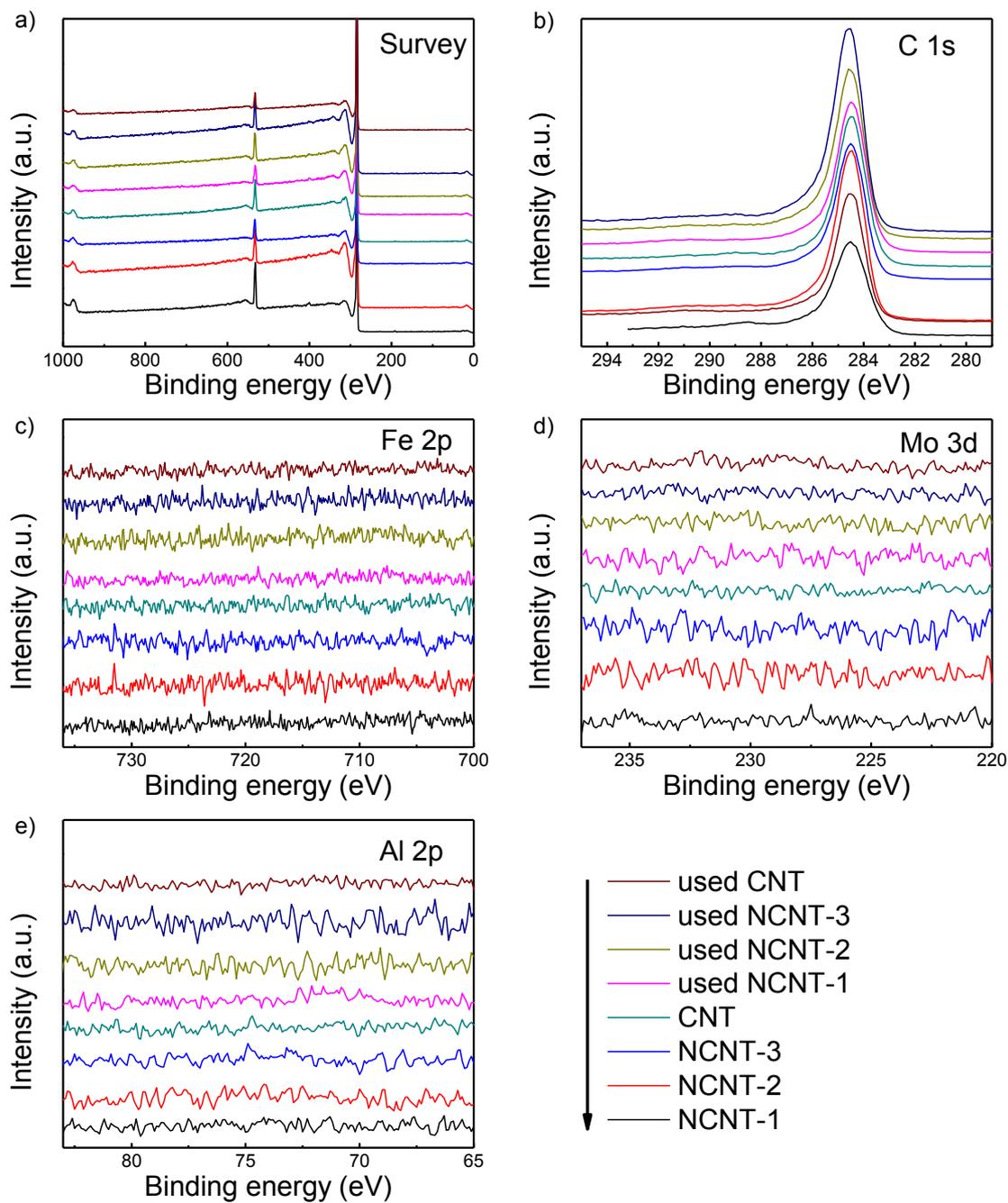
**Table S2** Fitting parameters from the peaks fitted in the Raman spectra of all samples.

Samples	Position cm <sup>-1</sup>	FWHM cm <sup>-1</sup>	Gauss ratio	Area a.u.	Intensity a.u.	D/G ratio calculated by area	D/G ratio calculated by intensity
NCNT-1	1324.8	56.0	94	139570	1601.0	1.724	1.188
	1490	133.1	0	6506			
	1572.8	38.5	98	80943	1347.3		
	1605.8	27.4	40	20300			
NCNT-2	1324.4	59.1	88	246143	2752.6	1.728	1.191
	1490	133.5	0	13956			
	1572.2	39.8	96	142460	2310.4		
	1605	27.7	34	36237			
NCNT-3	1325.4	61.6	89	256374	2746.0	1.731	1.280
	1490	143.8	0	15016			
	1572.5	45	93	148067	2144.9		
	1605.7	34.3	22	37843			
CNT	1322.9	70.3	100	227100	2055.3	1.568	0.942
	1420	278.2	0	138035			
	1569.6	42.2	100	144844	2182.9		
	1604	44.9	56	65333			

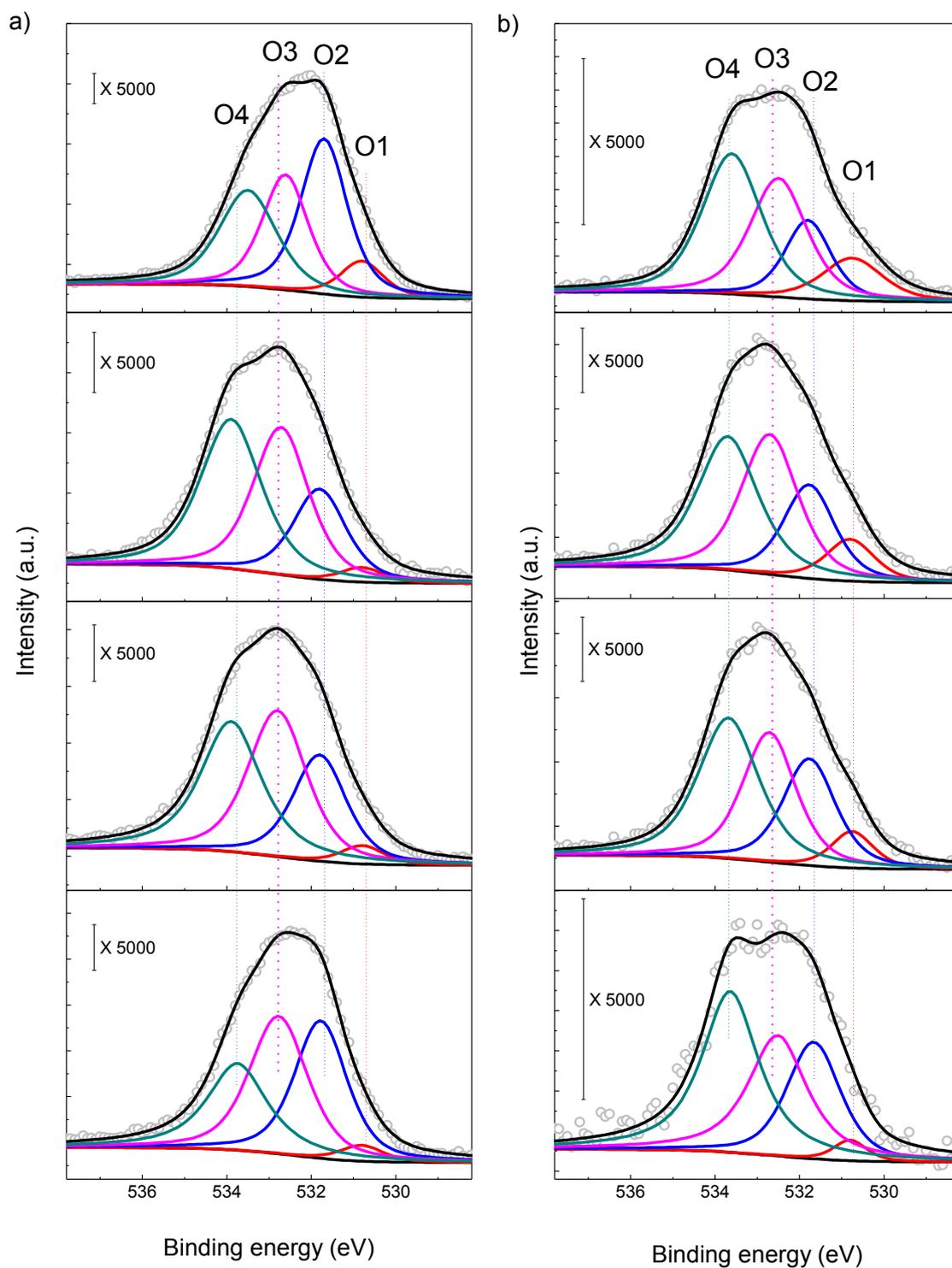
The D band of carbon materials centered at ca. 1320 cm<sup>-1</sup> is usually attributed to lattice defects and amorphous carbon impurities, and the G band at ca. 1580 cm<sup>-1</sup> is due to graphitic structure of the sample. Lattice defects caused by N dopant largely determined the disorder degree of carbon nanotubes, i.e. D/G ratio, as evidence with sharp increase of interlayers spacing after nitrogen doping. However, the surface disorder carbon also played an important role in raising the D/G ratio.<sup>[S2]</sup> As shown in HRTEM images in ESI, Fig. S2, the amount of amorphous impurities decreased slightly with the increasing doping level, leading to the minimum D/G value of 1.724 for NCNT-1. In fact, the D/G ratios of the four catalysts were very close.



**Fig. S4** a) TG and b) DSC profiles of TPO experiments, as well as c) EDS results of the selected FeMo/Al<sub>2</sub>O<sub>3</sub> and ashes in nanocarbons. Inset in b the  $T_{max}$  as a function of bulk nitrogen content over nanocarbons.



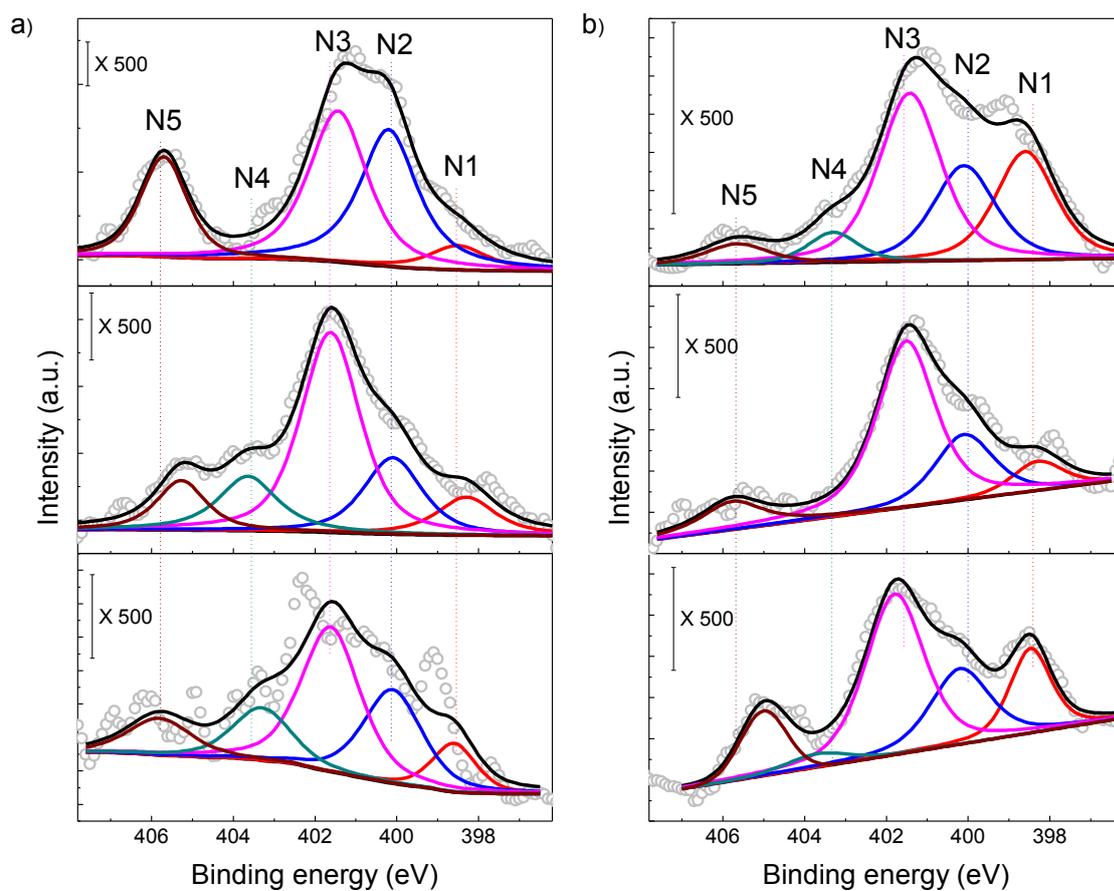
**Fig. S5** a) XPS survey and core level profiles of b) *C 1s*, c) *Fe 2p*, d) *Mo 3d* and e) *Al 2p* of all the samples before and after ODH reaction .



**Fig. S6** *O*1s core level spectra of a) fresh and b) used samples: NCNT-1, NCNT-2, NCNT-3 and CNT from top down. The gray circle is experimental data and the black line is fitted curve.

**Table S3** Fitting parameters of O1s deconvolution.<sup>[S3]</sup>

Samples	Total O atom%	Assignment	Shift eV	FWHM eV	G/L %	Area a.u.	Content atom%
fresh NCNT-1	6.92	O1	530.8	1.20	50	9527	0.55
		O2	531.7	1.31	50	44441	2.55
		O3	532.6	1.29	50	32680	1.88
		O4	533.5	1.60	50	33764	1.94
fresh NCNT-2	4.91	O1	530.8	1.20	50	1570	0.11
		O2	531.8	1.48	50	14696	1.00
		O3	532.7	1.56	50	24348	1.66
		O4	533.9	1.70	76	31414	2.14
fresh NCNT-3	6.00	O1	530.7	1.20	50	1615	0.13
		O2	531.8	1.50	50	19778	1.54
		O3	532.8	1.64	50	27667	2.15
		O4	533.9	1.70	73	28042	2.18
fresh CNT	6.31	O1	530.8	1.20	50	2242	0.16
		O2	531.8	1.47	50	29483	2.12
		O3	532.8	1.62	50	32081	2.31
		O4	533.8	1.68	85	23866	1.72
used NCNT-1	4.75	O1	530.8	1.70	50	2874	0.58
		O2	531.8	1.29	50	4030	0.81
		O3	532.5	1.59	50	7489	1.51
		O4	533.6	1.65	50	9215	1.85
used NCNT-2	4.85	O1	530.8	1.36	50	5844	0.42
		O2	531.8	1.43	50	13782	1.00
		O3	532.7	1.59	50	22890	1.65
		O4	533.7	1.70	64	24592	1.78
used NCNT-3	4.84	O1	530.8	1.17	50	4389	0.32
		O2	531.8	1.48	50	16213	1.17
		O3	532.7	1.49	52	19987	1.46
		O4	533.7	1.70	61	25576	1.87
used CNT	4.24	O1	530.8	1.20	50	953	0.17
		O2	531.7	1.47	50	6499	1.17
		O3	532.8	1.70	80	8517	1.53
		O4	533.8	1.65	80	7559	1.36

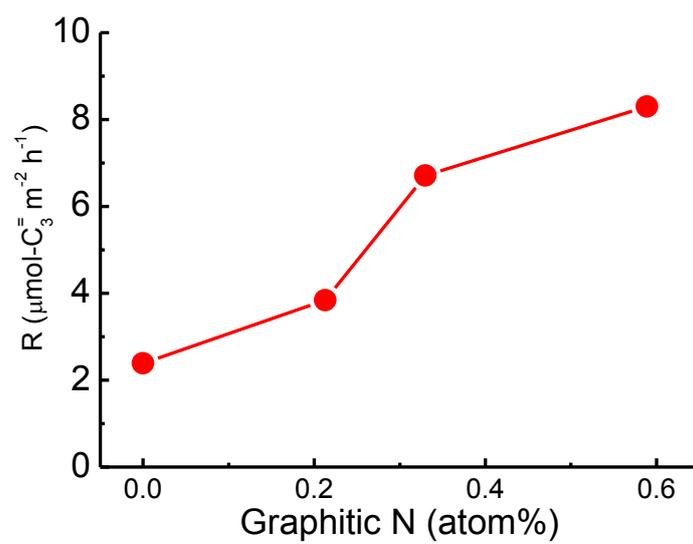


**Fig. S7** N1s core level spectra of a) fresh and b) used samples: NCNT-1, NCNT-2 and NCNT-3 from top down. The gray circle is experimental data and the black line is fitted curve.

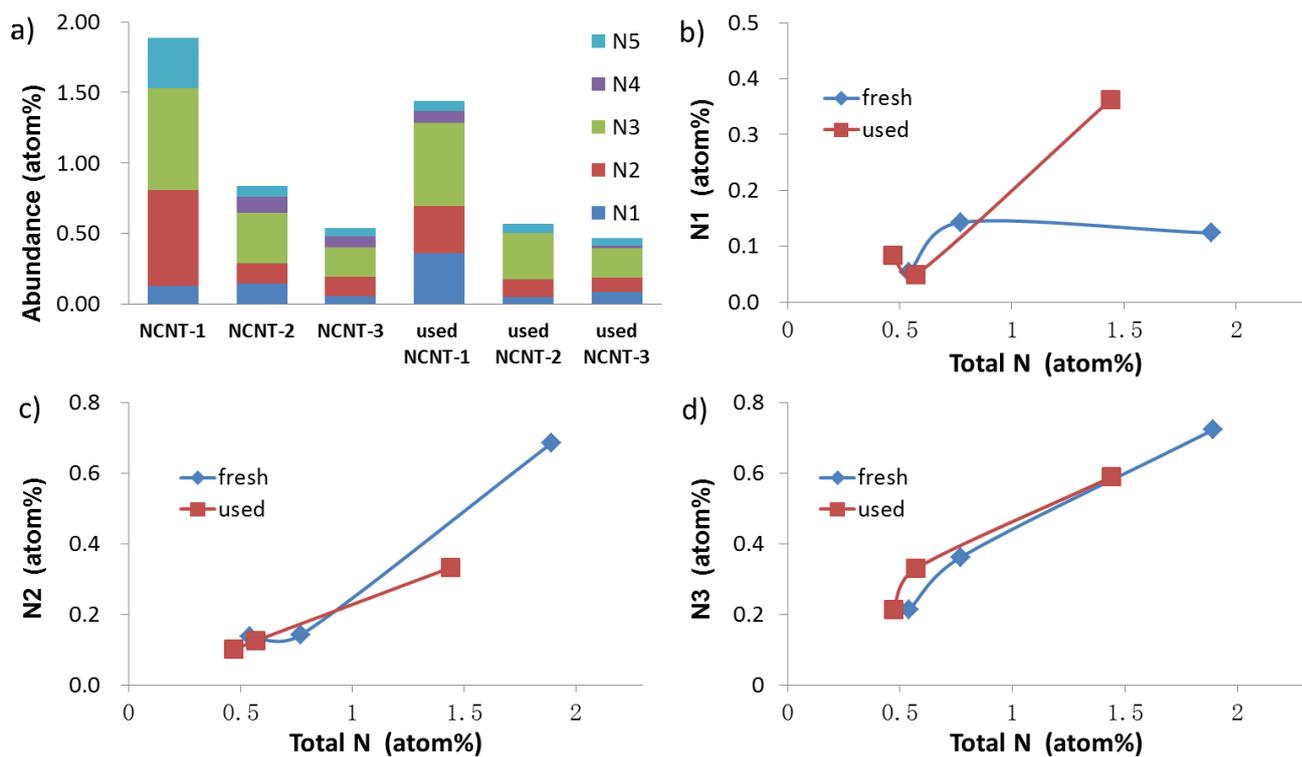
**Table S4** Fitting parameters of N1s deconvolution.<sup>[S3]</sup>

Samples	Total N atom%	Assignment	Shift eV	FWHM eV	G/L %	Area a.u.	Content atom%
fresh NCNT-1	1.89	N1	398.5	1.7	80	698	0.12
		N2	400.2	1.7	80	3853	0.69
		N3	401.4	1.7	63	4062	0.72
		N4	/	/	/	/	0
		N5	405.7	1.4	50	2024	0.36
fresh NCNT-2	0.77	N1	398.3	1.7	80	716	0.14
		N2	400.1	1.7	61	1339	0.14
		N3	401.6	1.7	53	3396	0.36
		N4	403.6	1.7	80	1022	0.11
		N5	405.3	1.4	69	745	0.08
fresh NCNT-3	0.54	N1	398.6	1.3	50	486	0.05
		N2	400.1	1.7	50	1257	0.14
		N3	401.6	1.7	50	1944	0.21
		N4	403.3	1.7	50	708	0.08
		N5	405.8	1.8	50	530	0.06
used NCNT-1	1.44	N1	398.6	1.7	50	642	0.36
		N2	400.1	1.8	50	590	0.33
		N3	401.4	1.8	50	1044	0.59
		N4	403.3	1.4	50	151	0.08
		N5	405.6	1.8	50	125	0.07
used NCNT-2	0.57	N1	398.3	1.5	50	276	0.05
		N2	400.1	1.7	50	713	0.13
		N3	401.5	1.7	59	1860	0.33
		N4	/	/	/	/	0
		N5	405.7	1.8	80	364	0.06
used NCNT-3	0.47	N1	398.5	1.3	45	677	0.08
		N2	400.3	1.7	50	822	0.10
		N3	401.8	1.8	45	1729	0.21
		N4	403.7	1.8	50	147	0.02
		N5	405.1	1.3	50	442	0.05

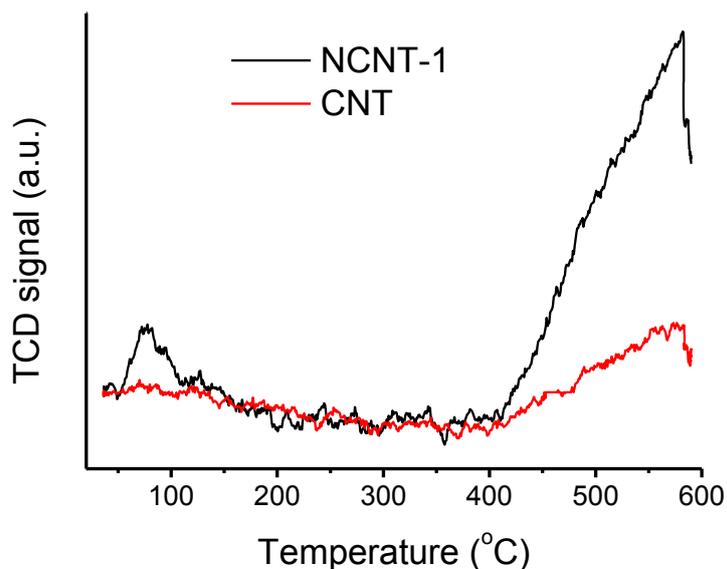
In the former study of N-doped CNT, the transition route of pyridone (lactame) and pyridinic N functionalities had been clearly proposed and evidenced by TP-XPS measurement.<sup>[S4]</sup> Pyridone (or lactame) is more unstable, which can degrade to form pyridinic N at high temperature. It is the main reason for N1 raised from 0.12% to 0.36% whereas N2 decreased from 0.69% to 0.33% for NCNT-1 after 24h ODH reaction. Another possible could be the slight degradation of graphitic N. Considering the adjacent C atom itself is liable to react with active oxygen to release CO and CO<sub>2</sub>, the graphitic N would undergo a slight degradation to yield pyridinic N (N1) and pyridine-N-oxide (N4) as intermediates.



**Fig. S8** Kinetic rate as a function of graphitic N content.

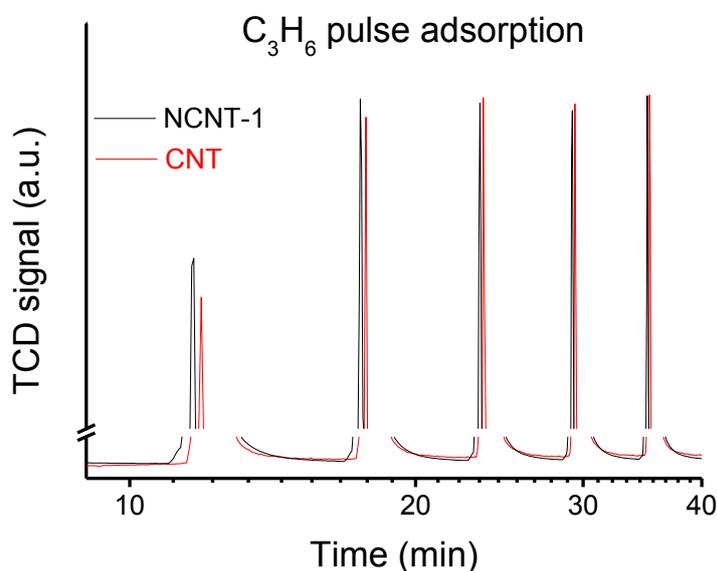


**Fig. S9** a) Abundance of N functionalities and b) N1, c) N2, as well as N3 as a function of total N contents of all the carbon catalysts before and after ODH reaction.



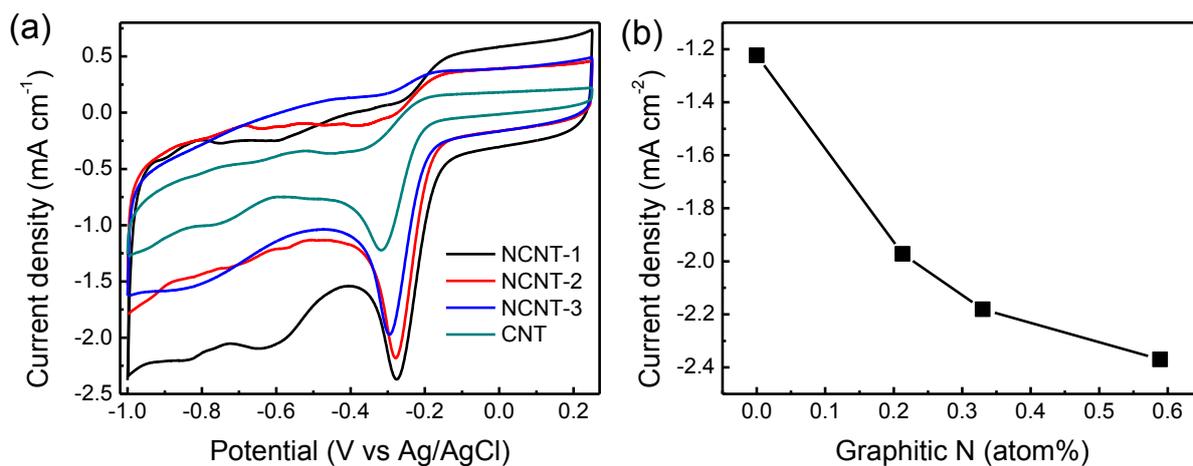
**Fig. S10** TPD of O<sub>2</sub> on CNT and NCNT-1 samples.

The result shows a small O<sub>2</sub> desorption peak during 50~110 °C on NCNT-1 whereas there is no obvious peak on CNT, evidencing the adsorption of oxygen molecules on the N-doped CNT. After 400 °C, the desorption peak is mainly attributed to the decomposition of surface functionalities.



**Fig. S11** Pulse adsorption of C<sub>3</sub>H<sub>6</sub> on CNT and NCNT-1 samples.

The calculated adsorbances of C<sub>3</sub>H<sub>6</sub> are 15 μmol g<sup>-1</sup> for NCNT-1 and 23 μmol g<sup>-1</sup> for CNT confirmed the weaker adsorption of C<sub>3</sub>H<sub>6</sub> on nitrogen doped CNT.



**Fig. S12** CV curves and ORR activity as a function of graphitic N content for CNT and NCNT catalysts

NCNT samples show an excellent catalytic performance in oxygen reduction reaction (ORR). With the nitrogen dopant increasing, the peak potential shift and the peak current density increase. The current density of ORR increases with the increasing amount of graphitic N. So, the doping with graphitic N can obviously promote activation of oxygen.

## Reference

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