<div align="center">Supplemental Material for</div>

The Fe-N bonding in a carbon nanotube-graphene complex for oxygen reduction: an XAS study

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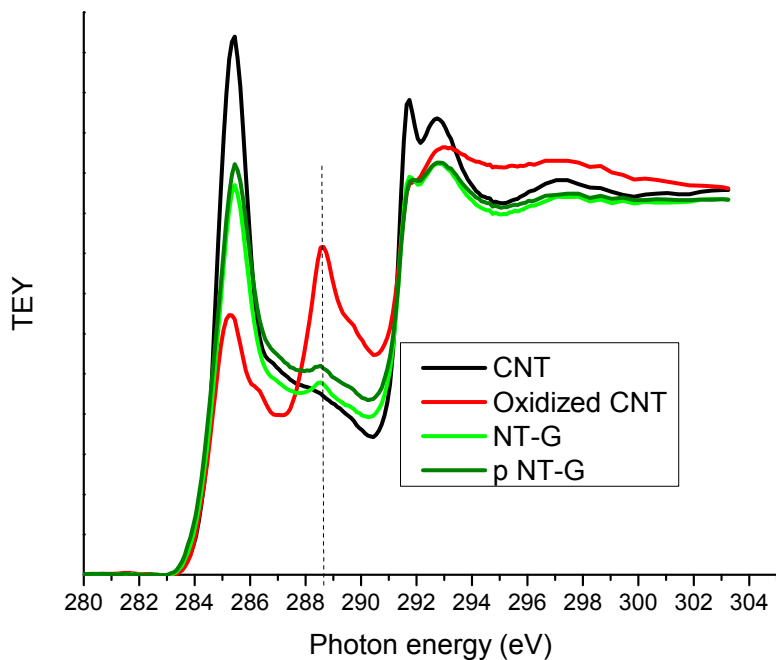
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1. XANES

Support Fig.1: C K-edge XANES of NT-G, p NT-G and CNT are compared with oxidized CNT before annealing. The same position of C-O feature in NT-G and p NT-G relative to carboxyl C-O feature in oxidized CNT highlights the similarity between them.
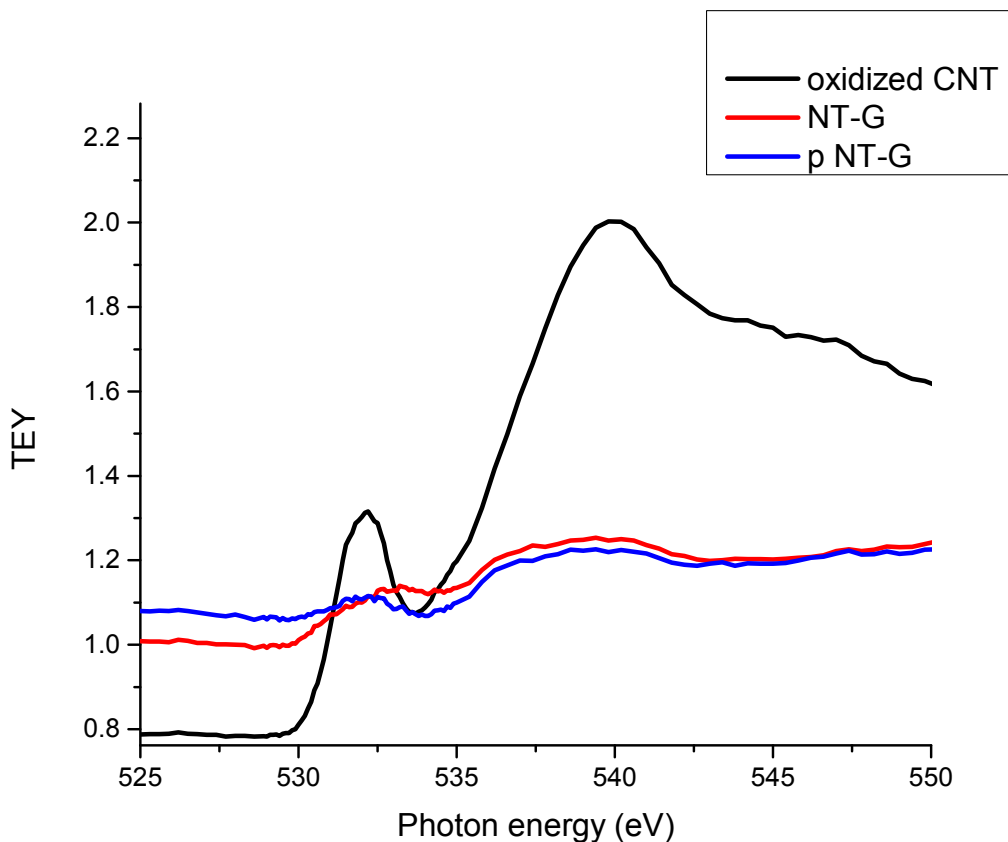
Support Fig.2 : O K-edge XANES of NT-G, p NT-G and oxidized CNT. O conetration is much lower in NT-G and p NT-G. the peak at ~532 eV in NT-G and p NT-G then can be assigned to carboxylic feature as that in oxidized CNT.

Table 1 peak position at Fe L-edge XANES

	1	3	4
FePc	~706.9	708	709.3
FePC ref 11	~707	~708	~709.2
FePc ref12	~707	~708	~709.2

2. EXAFS

Experimental EXAFS plots were obtained using WinXAS software (Ressler, T. *J. Synchrotron Radiat.* **1998**, *5*, 118−122) by applying a Fourier Transform to the data between 2.5 and 12.5 Å^{-1} for each absorption spectrum. Fitting was performed based on FEFF modeling within a specific region of interest for each sample (Fe_2O_3: 1.0 – 2.75 Å, FePc: 1.0 – 3.0 Å, CNT: 1.3 – 2.6 Å, and NT-G: 1.4 – 2.55 Å). Uncertainties were determined by weighting the off-diagonal elements of the correlation matrix by the reduced $\chi 2$ value of the fit, as recommended by Newville *et al.* (Newville, M.; Boyanov, B. I.; Sayers, D. E. *J. Synchrotron Radiat*. **1999**, *6*, 264−265). Details specific to the fitting of each particular sample are presented below.

Fe_2O_3: This (bulk) material was selected for determination of the S_0^2 parameter value used in all subsequent fits because of its relatively simple and well-known structure ; in addition to the use of a single E_0 shift value , by correlating the Debye-Waller (σ^2) parameter values of the Fe–O scattering paths and constraining the sum of their total coordination numbers (CNs) to 5 atoms (based on crystallographic data), an S_0^2 value of 0.9 ± 0.1 was obtained. The remaining parameter values were then determined by fixing this value and removing the previous CN constraints.

FePc: Due to the purity of the FePc material, CNs for the nearest-neighbour Fe–N and Fe–C paths could be fixed to known values. It was also necessary to fix σ^2 values for the Fe–N and Fe–O scattering paths in order to obtain a good fit to the experimental data.

CNT: A single E0 shift value was used during fitting, and the σ² value for the Fe–N/O path was fixed to match that determined from fitting of the NT-G sample.

NT-G: No additional constraints or correlations were used in fitting the NT-G sample data.

Sample	Path	CN	R / Å	σ^2 / Å^2	ΔE_0 / eV
CNT	Fe-C	1.4(5)	1.97(7)	0.007**	-2(2)
	Fe-Fe	5(1)	2.52(1)	0.010(3)	
NT-G	Fe-N/O	3.3(3)	1.994(9)	0.007(1)	4(1)
	Fe-Fe	2.5(3)	2.514(7)	0.006(1)	-2(1)
FePc	Fe-N	4	1.92(2)	0.001	4(5)
	Fe-O	1.8(7)	2.11(4)	0.001	14(6)
	Fe-C	8	2.89(5)	0.005(4)	-4(5)

* CN = Coordination number, R = Bond length, σ^2 = Debye-Waller factor, ΔE_0 = E_0 shift.

** This value was fixed based on the Fe-N/O scattering path in the NT-G sample in order to obtain the best possible fit to the experimental data.

Support table 2: EXAFS fitting results