

Supporting Information

Stability of Iron Single Atoms in Graphene Structures From X-Ray Absorption Spectroscopy Data

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I. Experimental details

A PerkinElmer SCIEX ELAN DRC II (PerkinElmer SCIEX, CT, USA) inductively coupled plasma mass spectrometer with axial field technology for trace elements was used to measure iron in GNFs_pristine sample with 95% confidence interval.

XAS spectra were recorded in 200 mA mode at ESRF in RCH1 experimental hutch of ROBL beamline at ESRF. The spectral signal was of high intensity that stress the presence of the iron in all the samples under investigation. Spectra were collected at room temperature in the fluorescence mode using 18-element Ge detector and Falcon-X (XIA) electronics. For energy calibration, Fe foil was measured simultaneously in the transmission mode. To improve signal-to-noise ratio, 2 scans were recorded for each sample. The beam size during the Fe K-edge XAS experiment was 0.5·4 mm.

Analysis of the spectra was performed using ATHENA and ARTEMIS programs of IFFEFIT package.¹ Pre-processing of raw experimental data was performed in ATHENA program. Two scans for each sample were calibrated and merged. Extended X-ray Absorption Fine Structure (EXAFS) spectra were fitted following standard procedures using ARTEMIS software. Theoretical paths for Fe-C, Fe-O and Fe-Fe single scattering were generated from the structure of Fe terephthalate² with FEFF 6.0 code.³ Fitting was carried out in R space, Fourier transform (FT) was done in range 3-12 Å⁻¹ in k and 1-4.2 Å in R. During fitting, S₀² was fixed at 0.9, ΔE₀ was equal for every path and was allowed to vary, but did not exceed the range of ±10 eV. Wavelet transform of k²-weighted EXAFS spectra of reference Fe foil and GNFs_pristine was performed based on the Morlet wavelet function as described in.⁴

II. Figures and Tables

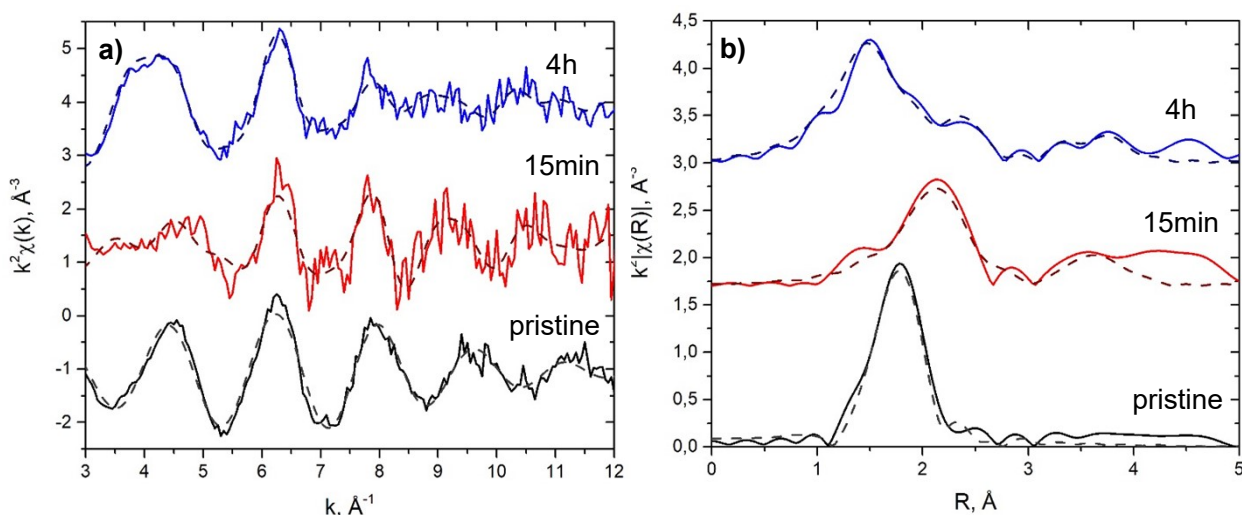


Figure S1. a) Fe K-edge k²-weighted EXAFS spectra; b) their Fourier transforms.

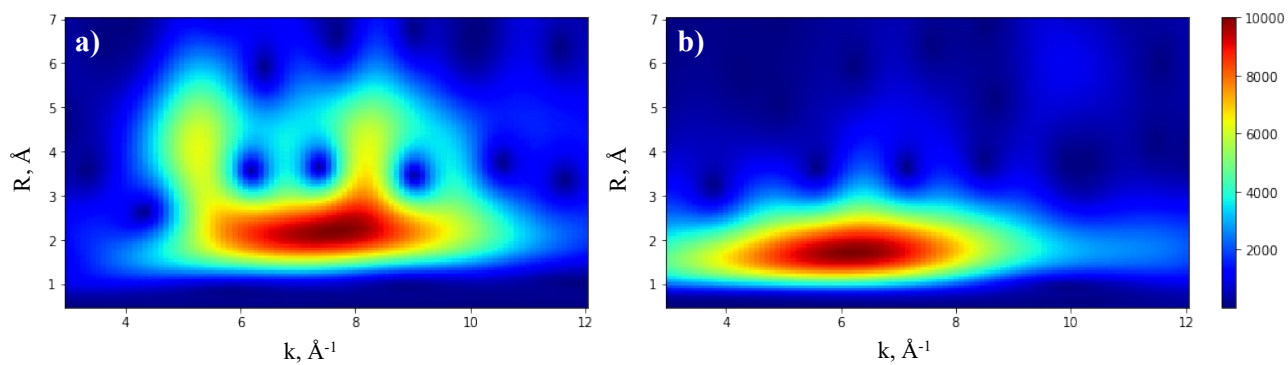


Figure S2. Wavelet transform of k^2 -weighted EXAFS spectra: a) Fe foil; b) GNFs_pristine.

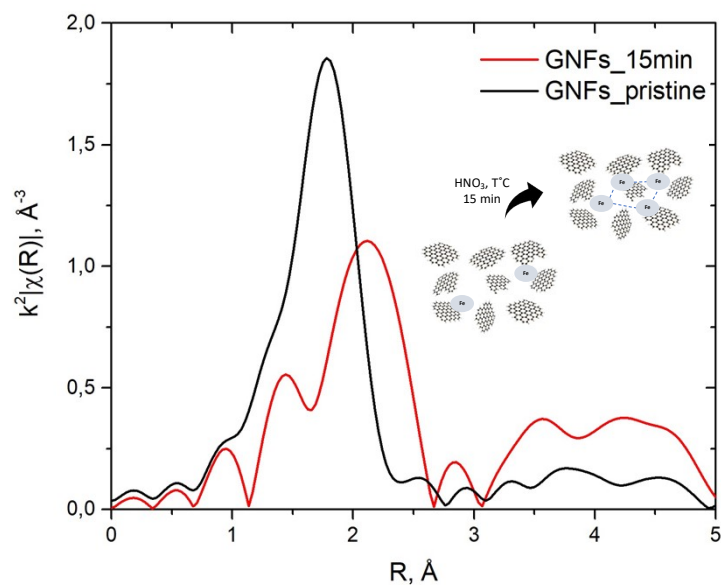


Figure S3. FT of GNFs_pristine and GNFs_15min.

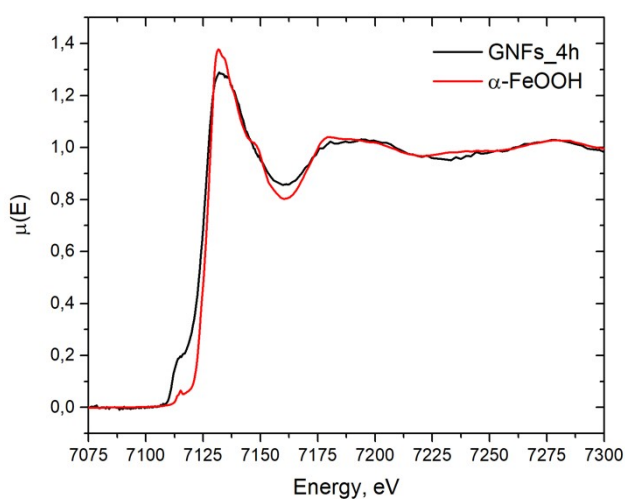


Figure S4. XANES region of GNFs_4h and α -FeOOH.

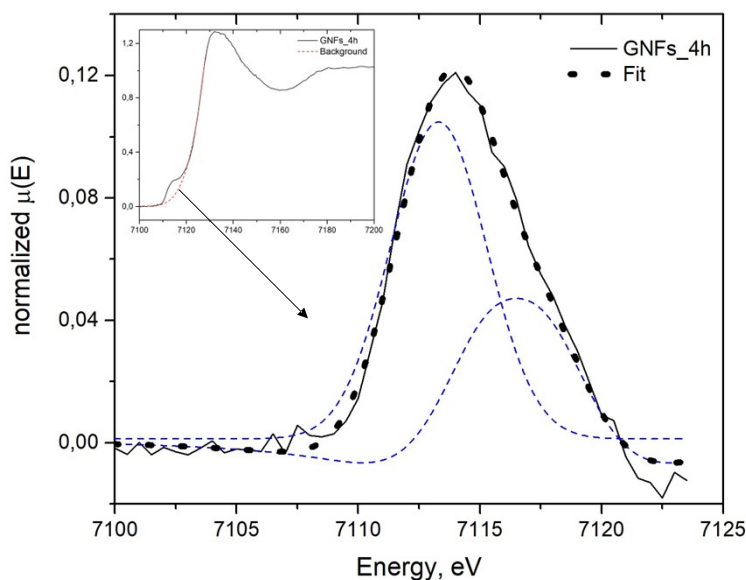


Figure S5. Normalized pre-edge feature in GNFS_4h (black solid line) fitted with PsdVoigt function (black dotted line). Blue dash lines show two contributions of $1s \rightarrow 3d/4p$ transitions in 6-coordinated Fe^{3+} . Pre-edge region was separated from the main edge by subtracting polynomial-fitted function

Table S1. EXAFS spectra fitting parameters.

Sample	Fe-O/C			Fe-Fe		
	CN	R, Å	$\sigma^2, \text{\AA}^2$	CN	R, Å	$\sigma^2, \text{\AA}^2$
GNFS_pristine	3.5	2.02	0.005			
	10.5	2.39	0.005			
GNFS_15min	8.4	2.45	0.005^{a)}	5.1	4.29	0.008
	14.3	2.85	0.005			
GNFS_4h	6 (O)	1.95	0.009	5.5	4.32	0.008
	4.3 (C/O)	2.45	0.005			
	6.2 (C/N)	2.90				

a) Bold type indicates parameters that were set during fitting.

III. References

1. Ravel B, Newville M. ATHENA, ARTEMIS, HEPHAESTUS: Data analysis for X-ray absorption spectroscopy using IFEFFIT. *J Synchrotron Radiat.* 2005;12(4):537-541. doi:10.1107/S0909049505012719

2. Bara D, Meekel EG, Pakamore I, Wilson C, Ling S, Forgan RS. Exploring and expanding the Fe-terephthalate metal-organic framework phase space by coordination and oxidation modulation. *Mater Horiz.* 2021;8(12):3377-3386. doi:10.1039/d1mh01663f
3. Rehr JJ, Albers RC, Zabinsky SI. High-order multiple-scattering calculations of x-ray-absorption fine structure. *Phys Rev Lett.* 1992;69(23):3397-3400. doi:10.1103/PhysRevLett.69.3397
4. Tagirov BR, Trigub AL, Filimonova ON, et al. Gold transport in hydrothermal chloride-bearing fluids: Insights from in situ x-ray absorption spectroscopy and ab initio molecular dynamics. *ACS Earth Space Chem.* 2019;3(2):240-261. doi:10.1021/acsearthspacechem.8b00103