

Supporting Information

Surface Characterization and Chemical Speciation of Adsorbed Iron(III) on Oxidized Carbon Nanoparticles

Ajith Pattammattel,^{1*} Valerie J. Leppert,² Henry Jay Forman,³ Peggy A. O'Day^{1*}

1. School of Natural Sciences and Sierra Nevada Research Institute, University of California, Merced, California, USA
2. School of Engineering, University of California, Merced, California, USA
3. Davis School of Gerontology, University of Southern California, Los Angeles, California, USA

**Corresponding authors email: apattammattel@ucmerced.edu, poday@ucmerced.edu*

Methods

Dynamic Light Scattering (DLS): Particle size distributions of aqueous dispersions of carbon nanoparticles (CNP) were estimated by homodyne dynamic laser scattering (DLS) measurements. CNP (20 to 50 $\mu\text{g/mL}$) were dispersed in ultrapure water and examined using a Brookhaven laser spectrometer (Brookhaven Instruments, NY, USA). The autocorrelation function of the scattering intensity was accumulated over a 3-minute interval to estimate the size distribution, which was calculated by the COTIN program.

Surface Area Measurements: Nitrogen gas sorption isotherms were used to measure surface area and pore size of the CNP by BET (Brunauer–Emmett–Teller) and BJH (Barrett–Joyner–Halenda) isotherms, respectively.¹ Specific surface area and pore size analysis of the samples were done at 77 K on a Micrometrics Tristar 3000 surface area analyzer. About 50-100 mg of air-dried CNP were analyzed for N_2 sorption at relative pressure ranges from 0.05 to 1, and about 45 equilibrium points were collected for BET and BJH isotherm fits. The surface area of reference materials (carbon black and silica-alumina from Micrometrics) was measured before each sample cycle.

Table S1. Surface properties of carbon nanoparticles determined from analysis of adsorption isotherms.

Type of CNP	BET Surface Area (m^2/g)	BJH Cumulative Adsorption Pore Surface Area (m^2/g)*	BJH Average Adsorption Pore Width (nm)	BJH Cumulative Adsorption Pore Volume (cm^3/g)*
M120	31.0 ± 0.2	30.5 ± 0.2	16 ± 2	0.12 ± 0.01
Oxd.M120	51.9 ± 0.4	40.1 ± 0.3	40 ± 3	0.40 ± 0.03
P90	301.0 ± 2.4	206.4 ± 1.6	17 ± 2	0.87 ± 0.03
Oxd.P90	265.1 ± 2.9	158.2 ± 1.7	11 ± 3	0.42 ± 0.04
VXC72	232.4 ± 1.9	144.0 ± 1.4	12 ± 2	0.43 ± 0.03
Oxd.VXC72	171.0 ± 2.0	103.2 ± 1.3	36 ± 4	0.42 ± 0.05
CB	31.9 ± 0.2	26.2 ± 0.2	13 ± 2	0.15 ± 0.03
Oxd.CB	74.9 ± 1.4	40.8 ± 1.1	49 ± 4	0.49 ± 0.04

*pores between 1.7 and 300 nm

Table S2. ICP-OES measurement of [Fe] coated onto CNP.

CNP	Solution [Fe] μM (Initial)	Mass digested for ICP-OES (mg)	Measured [Fe] ppb (\pm Std. Dev.)*	Measured [Fe] per CNP ($\mu\text{mol/g}$)	Surface coverage ($\mu\text{mol Fe/m}^2$)
Oxd.M120	2.5	39.1	220.2 (0.9)	8.13 (\pm 0.06)	0.15(\pm 0.09)
	5.0	37.1	425.8 (1.8)	16.39 (\pm 0.10)	0.29 (\pm 0.03)
	15	39.8	1176 (5)	46.60 (\pm 0.38)	0.91(\pm 0.13)
	30	45.4	3205 (14)	100.8 (\pm 0.5)	1.8(\pm 0.2)
	50	46.0	4885 (16)	147.2 (\pm 0.3)	2.6(\pm 0.1)
	200	49.9	6376 (16)	548.5 (\pm 1.5)	9.8(\pm 0.5)
	500	46.3	1127 (123)	1152 (\pm 104)	21(\pm 2)
Oxd.P90	2.5	37.1	240.7 (0.9)	1.50 (\pm 0.02)	0.03(\pm 0.01)
	5.0	41.7	491.7 (2.7)	3.11 (\pm 0.06)	0.06(\pm 0.01)
	15	44.4	1542 (9)	8.98 (\pm 0.01)	0.16(\pm 0)
	30	44.0	3160 (14)	19.11 (\pm 0.39)	0.34(\pm 0.03)
	50	43.6	5292 (25)	31.2 (\pm 0.1)	0.56(\pm 0.01)
	200	45.8	4381 (20)	75.4 (\pm 0.1)	1.4(\pm 0.1)
Oxd.VXC72	2.5	48.7	278.4 (1.2)	2.24 (\pm 0.00)	0.04(\pm 0)
	5.0	49.4	487.5 (2.8)	4.82 (\pm 0.21)	0.09(\pm 0.02)
	15	45.2	1261 (7)	12.1 (\pm 0.21)	0.24(\pm 0.02)
	30	51.9	2987 (15)	20.5 (\pm 0.8)	0.37(\pm 0.09)
	50	58.3	5344 (24)	38.0 (\pm 0.1)	0.68(\pm 0.01)
	200	56.1	5423 (23)	120.2 (\pm 0.0)	2.2(\pm 0.1)
Oxd.CB	2.5	36.2	279.5 (1.4)	15.99 (\pm 0.02)	0.29(\pm 0.02)
	5.0	23.4	379.1 (2.4)	32.24 (\pm 0.07)	0.58(\pm 0.03)
	15	35.3	1406 (8)	90.9 (\pm 0.00)	1.6(\pm 0.1)
	30	23.6	2377 (14)	201.9 (\pm 0.28)	3.6(\pm 0.1)
	50	31.2	5978 (35)	350.4 (\pm 3.2)	6.3(\pm 1)
	200	28.8	4547 (25)	1053.2 (\pm 2.9)	19(\pm 1)

* Not corrected for dilutions, average of three independent measurements; measured instrumental detection limit is 3 ppb.

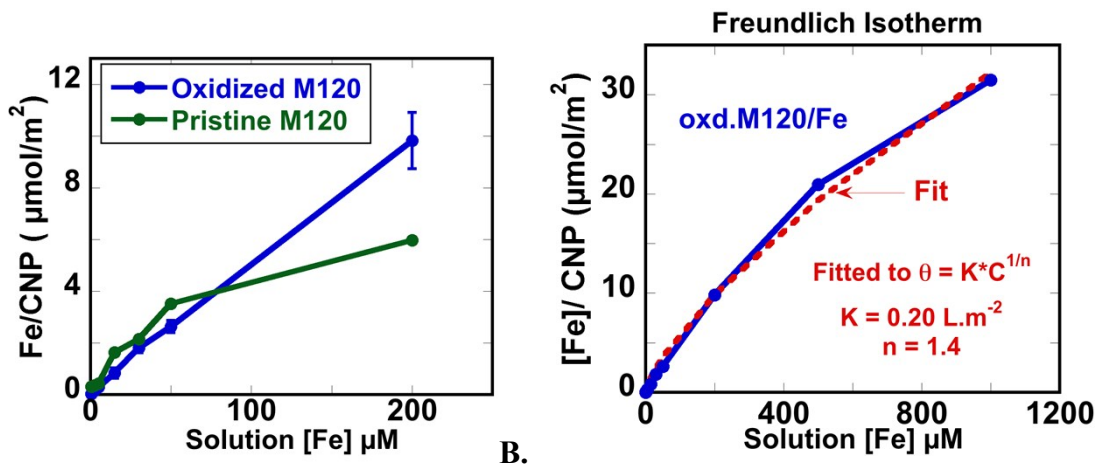


Figure S1. Adsorption of Fe(III) to CNP (normalized to BET surface area). **A.** Comparison of Fe sorption to oxidized M120 and pristine (unoxidized) M120 CNP. **B.** Adsorption of Fe on oxidized M120 fit (in red) to a Freundlich isotherm model (θ - moles of adsorbate/surface area of adsorbent, K – Freundlich adsorption constant, n – heterogeneity index).²

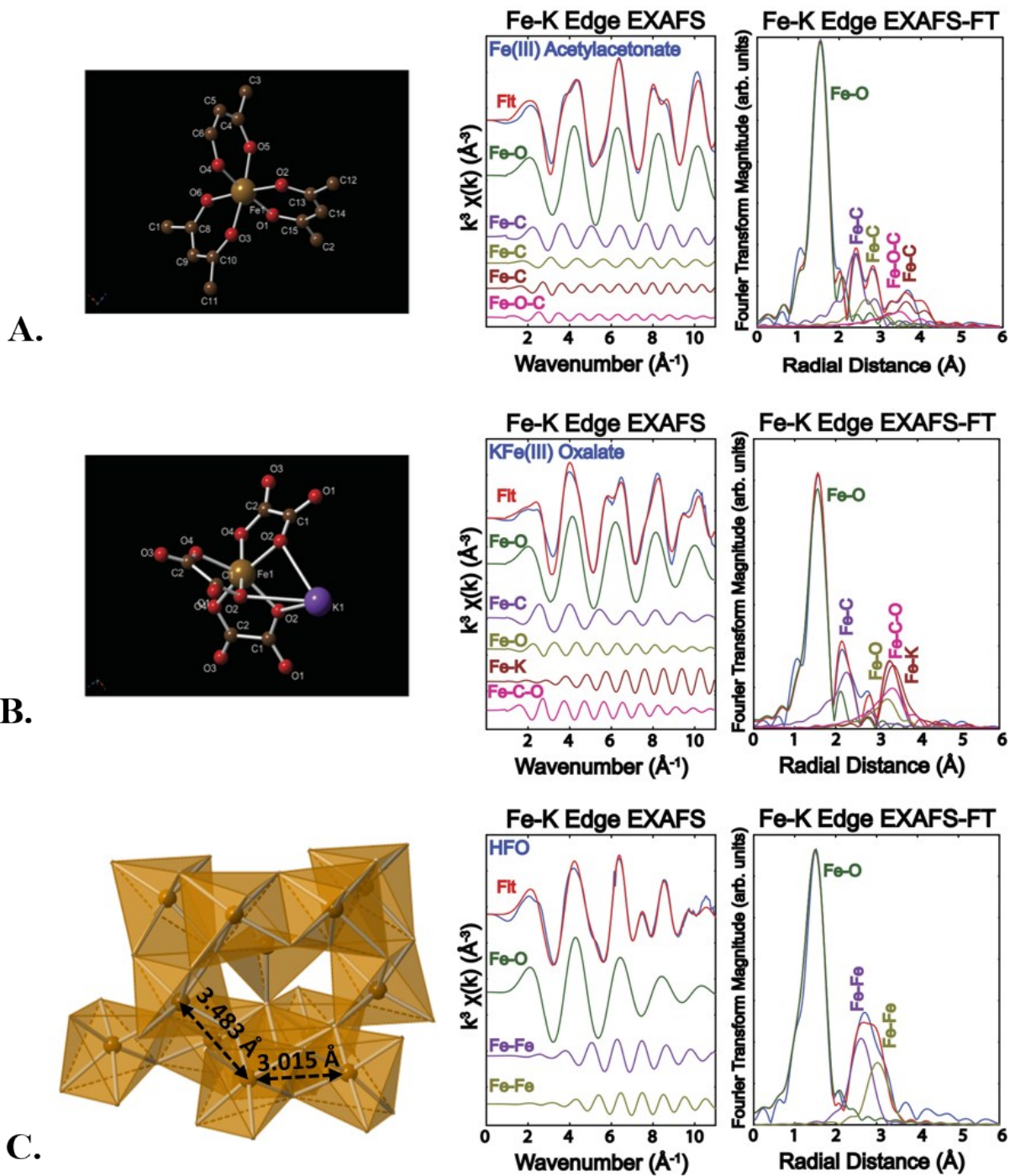


Figure S2. Molecular structure, k^3 -weighed experimental and best fit (in red) EXAFS, and Fourier transforms of **A.** Fe(III) acetylacetonate, **B.** Potassium Fe(III) oxalate, and **C.** Hydrous ferric oxide (HFO) (theoretical EXAFS absorber-backscatterer paths derived from the crystal structure of goethite). HFO structure was re-drawn from molecular structure reported by Michel *et al*³

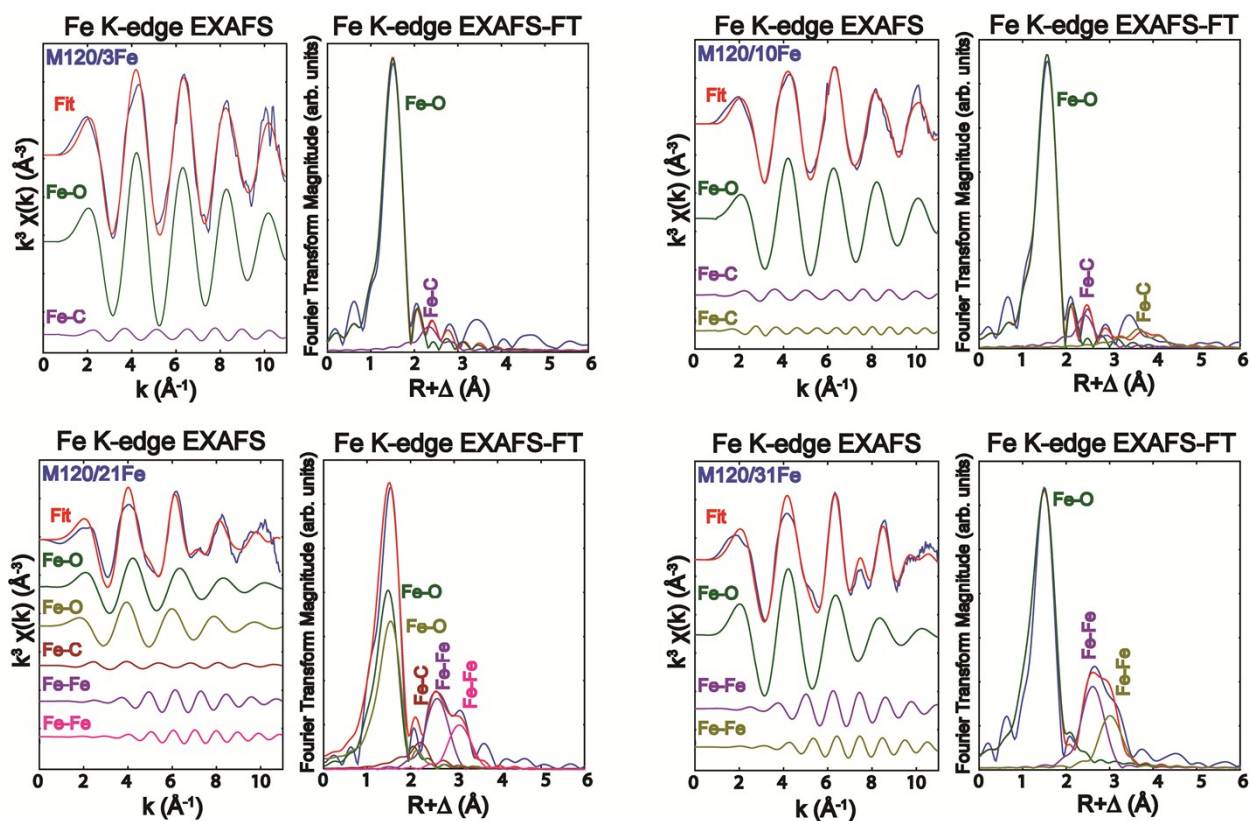


Figure S3. k^3 -weighted experimental and best fit (in red) EXAFS and Fourier transforms with resolved backscattering paths for **A.** M120/3Fe **B.** M120/10Fe, **C.** M120/21Fe, and **D.** M120/31Fe. Numerical results reported in manuscript Table 2.

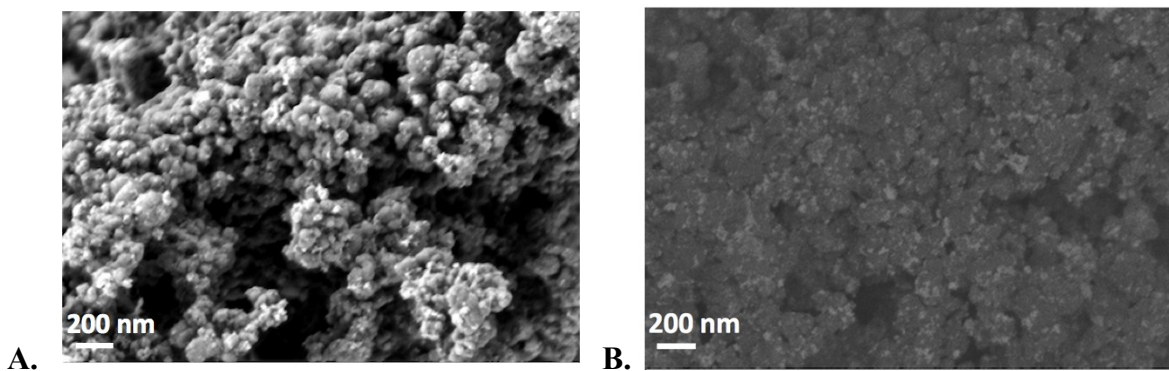


Figure S4. SEM images of M120/31Fe show putative iron clusters present on CNP **A.** in scanning mode and **B.** in backscattering mode (bright spots).

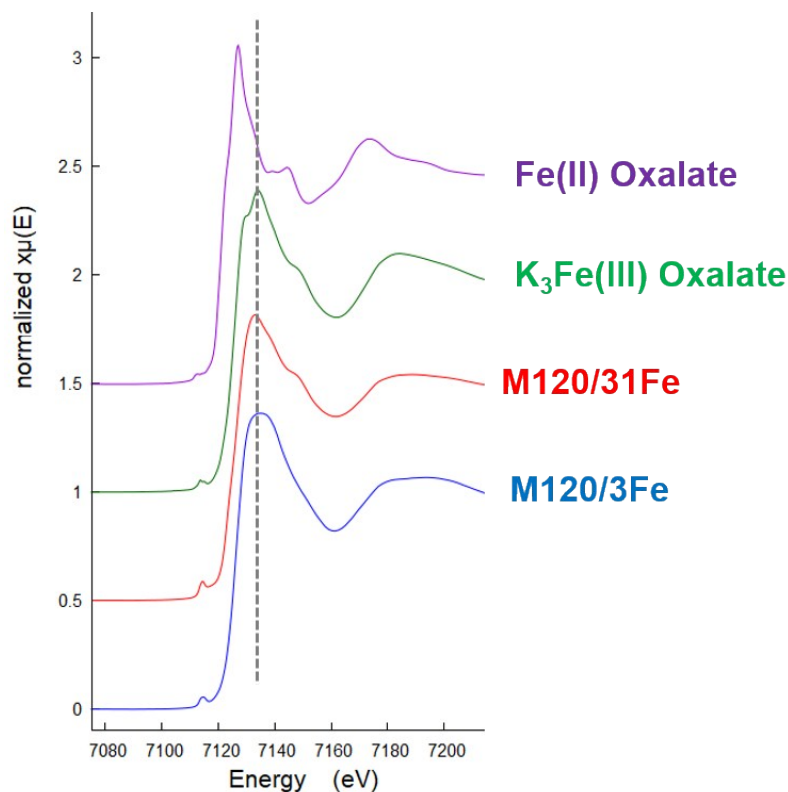


Figure S5. Fe K-edge XANES of M120/3Fe (low surface coverage) and M120/31Fe (high surface coverage) in comparison with Fe(II) and Fe(III) organic complexes.

¹ M. Kruk, M. Jaroniec and Y. Berezniński, Adsorption study of porous structure development in carbon blacks, *J. Colloid Interface Sci.*, 1996, **182**, 282-288.

² Van der Bruggen, Bart 2015: 'Freundlich Isotherm'. In Enrico Drioli and Lidietta Giorno *Encyclopedia of Membranes*; Berlin, Heidelberg: Springer Berlin Heidelberg, pp. 1-2.

³ F. M. Michel, L. Ehm, S. M. Antao, P. L. Lee, P. J. Chupas, G. Liu, D. R. Strongin, M. A. Schoonen, B. L. Phillips and J. B. Parise, *Science*, 2007, **316**, 1726-1729.