Electronic Supplementary Material (ESI) for Environmental Science: Nano.

Supporting Information

Probing biotransformation of hematite nanoparticles and magnetite formation mediated by *Shewanella oneidensis* MR-1 at molecular scale

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This supporting information contains 8-page document, including 3 tables, 4 figures and this cover page.

Table S1 STXM describing Fe(III) surface density on the surface of hematite NPs as a function of incubation time with *Shewanella oneidensis* MR-1.

Incubation time (h)	Min surface density (μg/cm^2)	Max surface density (μg/cm^2)
24	1.57837e-005	1.25190e-004
48	1.56226e-005	1.18898e-004
72	1.04495e-005	3.13369e-005
144	9.88261e-006	2.63732e-005

Table S2 Raman shifts and assignments of Fe(III) and Fe(II) minerals.

Raman shift (cm^{-1})	Assignment	Fe minerals
218	Fe-O sym. str	hematite
289	Fe-O sym. bend	hematite
403	Fe-O sym. bend	hematite
491	Fe-O sym. str	hematite
516	Fe-O asym. bend	magnetite
600	Fe-O sym. bend	hematite
658	Fe-O sym. str	magnetite
968	PO_4 sym. str	vivianite

Table S3 Calculated free energy change (ΔG) on the crystal surface of hematite upon microbial reduction.

Redox reaction equations	ΔG (kJ/mol)
$[Fe(OH)(H_2O)_5]^{2+} + H_2PO_4^- + e^- \rightarrow Fe(HPO_4)(H_2O)_5 + H_2O$	-356.352
$[Fe(OH)_2(H_2O)_4]^+ + 2H_2PO_4^- + e^- \rightarrow [Fe(HPO_4)_2(H_2O)_4]^{2-} + 2H_2O$	-124.220
$Fe(OH)_3(H_2O)_3 + 3H_2PO_4^- + e^- \rightarrow [Fe(HPO_4)_3(H_2O)_3]^{4-} + 3H_2O$	258.200
$[Fe_2(OH)_4(H_2O)_6]^{2+} + H_2PO_4^- + e^- \rightarrow Fe_2(HPO_4)(OH)_3(H_2O)_6 + H_2O$	-340.164
$[Fe_2(OH)_4(H_2O)_6]^{2+} + H_2PO_4^- + e^- \rightarrow Fe_2(PO_4)(OH)_2(H_2O)_6 + 2H_2O$	47611.193

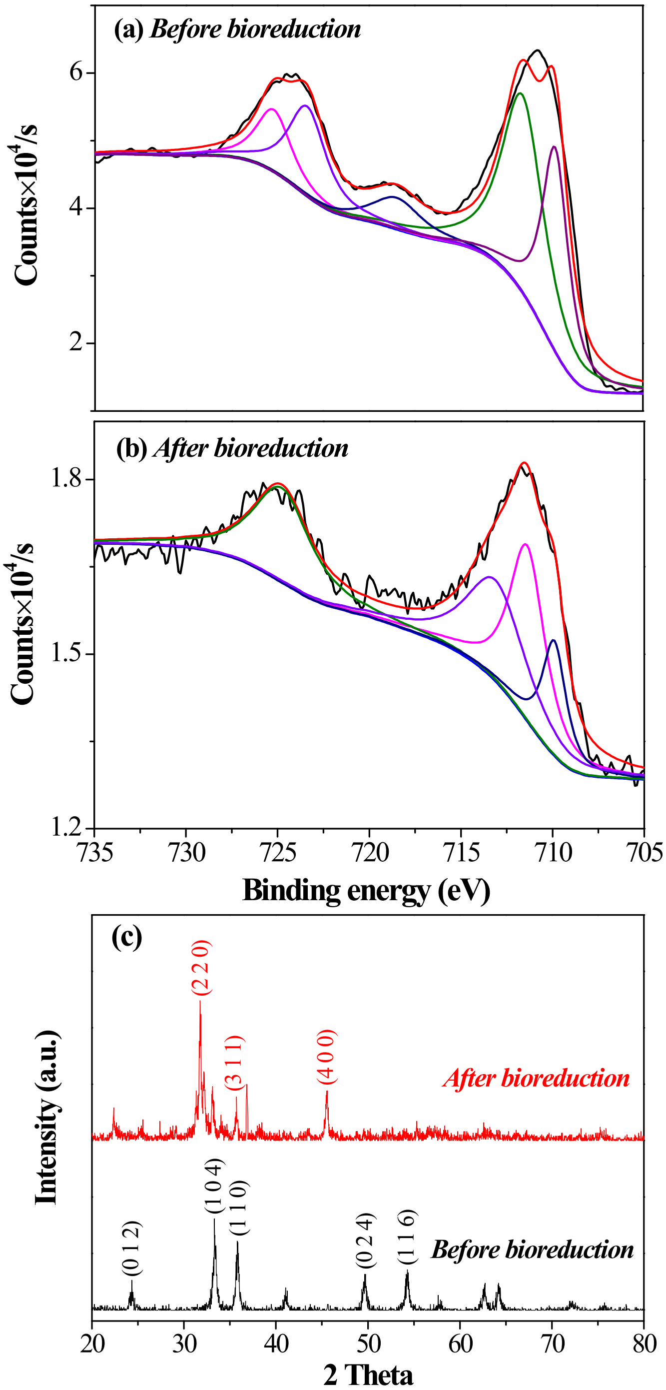


Figure S1. High-resolution XPS spectra showing the Fe2p region (a, b); and XRD patterns (c) before and after bioreduction of hematite NPs (50 ppm) for 48 h.

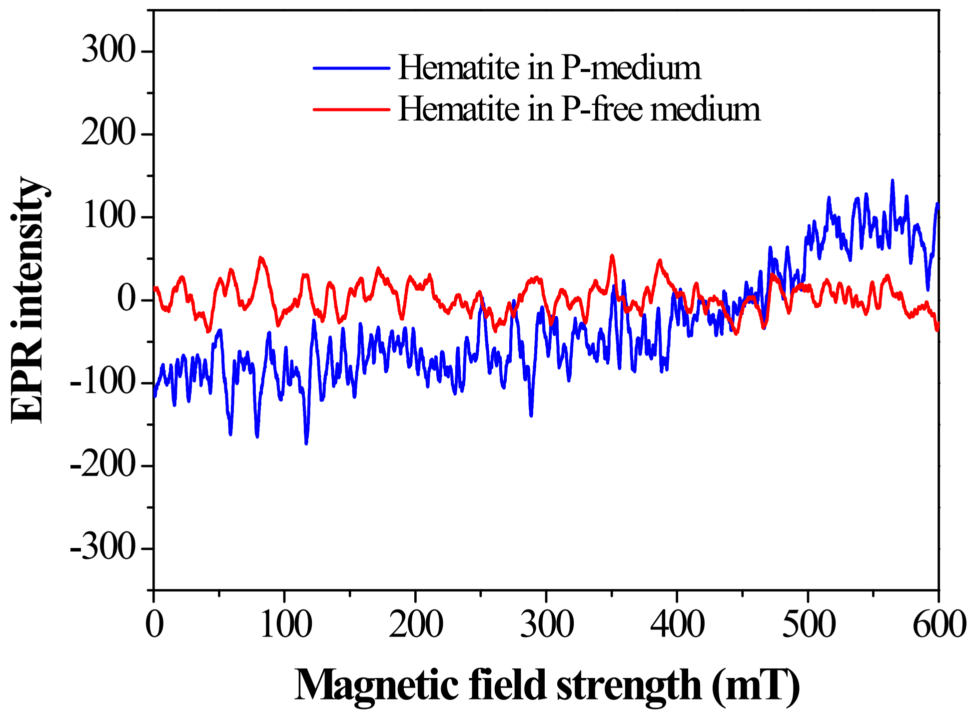
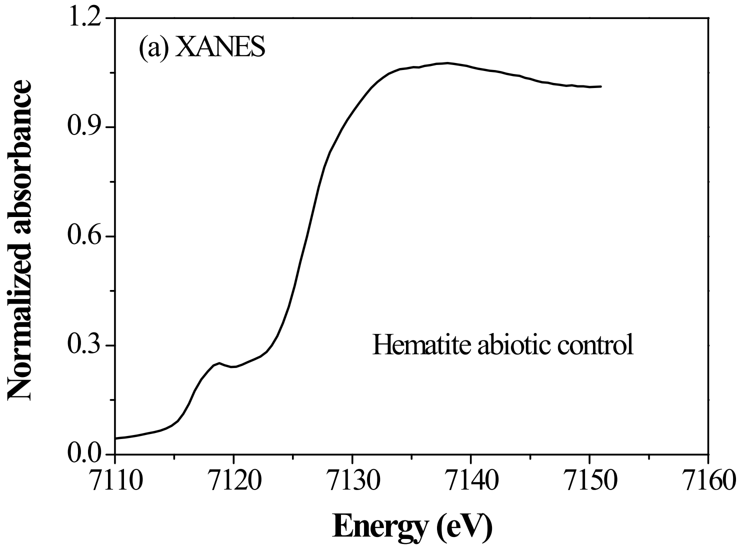


Figure S2. EPR spectra of hematite NPs (100 ppm) exposed to sterile medium with and without phosphate.



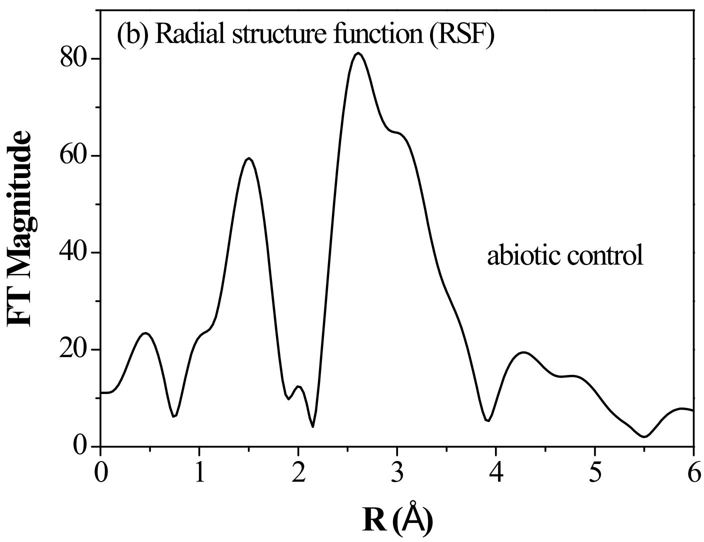


Figure S3. (a) Fe K-edge XANES spectra of hematite (100 ppm) in abiotic control; and (b) the corresponding radial structure function (RSF) derived from Fourier transformations.

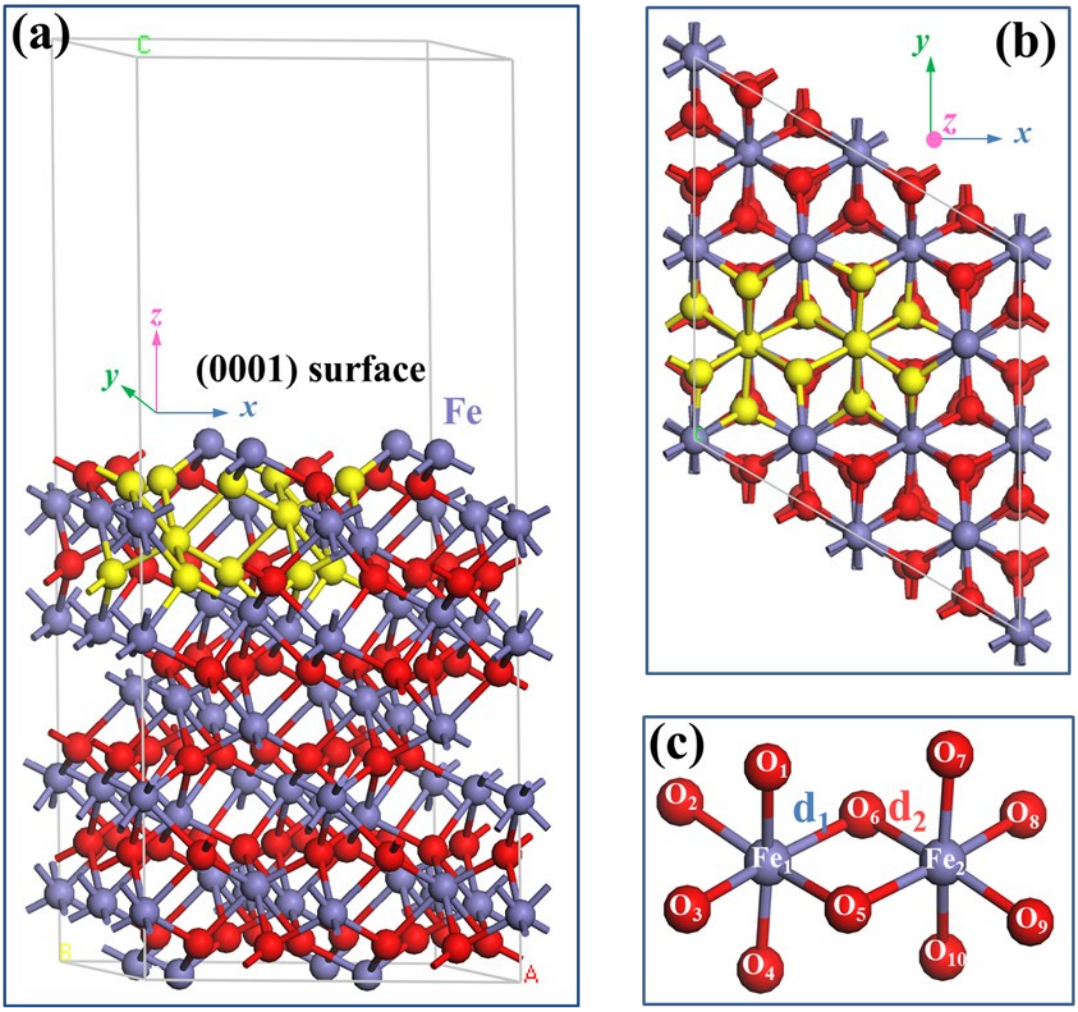


Figure S4. Structural characteristics of α-Fe_2O_3. (a) (0001) crystal surface of α-Fe_2O_3 with (2×2) supercell ($a = b = 10.076$ Å, $c = 23.167$ Å, $\alpha = \beta = 90°$, $\gamma = 120°$); (b) the top view of the (0001) crystal surface with the unit monodentate and bidentate oxygen ligands highlighted; and (c) the structure of bidentate oxygen ligands on the (0001) crystal surface of α-Fe_2O_3 with two types of Fe-O distances: $d_1 = 1.946$ Å, and $d_2 = 2.116$ Å, Fe_1-O_2, Fe_1-O_4, Fe_1-O_6, Fe_2-O_5, Fe_2-O_7, and Fe_2-O_9 equal d_1, and Fe_1-O_1, Fe_1-O_3, Fe_1-O_5, Fe_2-O_6, Fe_2-O_8, and Fe_2-O_{10} equal d_2.