Supporting Information

for

Single-Molecule Determinations of the Phase- and Facet-Dependent Adsorption of Alginate on Iron Oxide

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Table S1. Values of f_{eq} and ΔG_B extracted from fitting the Friddle-Noy-DeYoreo model to the DFS data. Values are present as mean ± standard deviation (n = 3).

pH	*IS* (mM)	Electrolyte	Phase/Face	f_{eq} (pN)	ΔG_B (kJ/mol)
5.0	10	NaCl	Fe_xO_y	276.56 ± 11.75	112.38 ± 4.78
5.0	10	NaCl	$(10\bar{1}0)$	248.72 ± 18.33	101.07 ± 7.45
5.0	10	NaCl	$(11\bar{2}0)$	216.17 ± 11.44	87.84 ± 4.65
5.0	10	NaCl	(0001)	171.32 ± 9.53	69.62 ± 3.87
7.0	10	NaCl	Fe_xO_y	256.41 ± 7.28	104.19 ± 2.96
7.0	10	NaCl	$(10\bar{1}0)$	204.84 ± 7.86	83.24 ± 3.20
7.0	10	NaCl	$(11\bar{2}0)$	173.28 ± 17.81	70.41 ± 7.23
7.0	10	NaCl	(0001)	145.96 ± 13.71	59.31 ± 5.57
9.0	10	NaCl	Fe_xO_y	202.56 ± 9.64	82.31 ± 3.92
9.0	10	NaCl	$(10\bar{1}0)$	158.96 ± 10.22	64.59 ± 4.15
9.0	10	NaCl	$(11\bar{2}0)$	164.43 ± 10.51	66.82 ± 4.27
9.0	10	NaCl	(0001)	142.58 ± 8.95	57.94 ± 3.63
7.0	1000	NaCl	Fe_xO_y	182.31 ± 5.70	74.08 ± 2.31
7.0	1000	NaCl	$(10\bar{1}0)$	143.79 ± 11.19	58.43 ± 4.55
7.0	1000	NaCl	$(11\bar{2}0)$	153.44 ± 12.43	62.35 ± 5.05
7.0	1000	NaCl	(0001)	142.02 ± 13.46	57.71 ± 5.47
7.0	100	NaCl	Fe_xO_y	204.74 ± 19.63	83.20 ± 7.98
7.0	100	NaCl	$(10\bar{1}0)$	163.01 ± 3.99	66.24 ± 1.62
7.0	100	NaCl	$(11\bar{2}0)$	173.28 ± 17.80	72.54 ± 4.41
7.0	100	NaCl	(0001)	145.96 ± 13.71	61.26 ± 3.44
7.0	1	NaCl	Fe_xO_y	267.32 ± 9.10	108.63 ± 3.70
7.0	1	NaCl	$(10\bar{1}0)$	210.98 ± 11.21	85.74 ± 4.56
7.0	1	NaCl	$(11\bar{2}0)$	209.41 ± 12.77	85.09 ± 5.19
7.0	1	NaCl	(0001)	167.95 ± 5.93	68.25 ± 2.41
7.0	10	$CaCl_2$	$(10\bar{1}0)$	224.07 ± 9.94	91.05 ± 4.04
7.0	10	$CdCl_2$	$(10\bar{1}0)$	251.53 ± 10.01	102.21 ± 4.16
7.0	10	Na_2HAsO_4	$(10\bar{1}0)$	137.18 ± 12.09	55.74 ± 5.01

Table S2. Chemical formulae and its corresponding Raman bands for hematite and amorphous Fe_xO_y. The wavenumbers of the most prominent bands in Raman signals of individual minerals are in bold.

Minerals	Distinguishing Raman shift (cm^{-1})	Reference
Hematite	222, 230, **290**, 408, 490, 607	1
Amorphous Fe_xO_y	361, 508, **707**, 1045	2

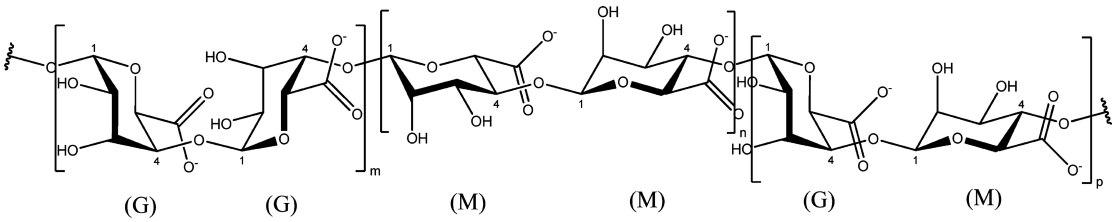

Figure S1. The structure of alginate showing that alginate is a linear polysaccharide of (1→4) linked α -L-guluronate(G) and β-D-mannuronate (M).[3] Copyright 2011 American Chemical Society.

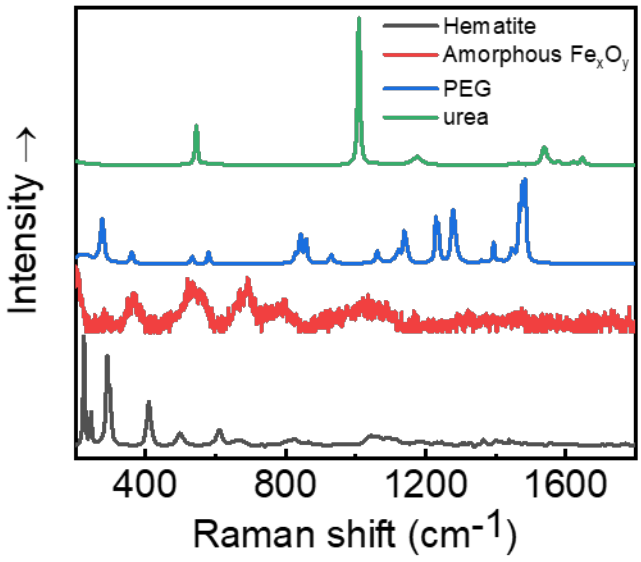

Figure S2. Raman spectra collected from hematite (black), amorphous Fe_xO_y (red), polyethylene glycol (PEG, blue), and urea (green), showing that no PEG and urea

residues were present.

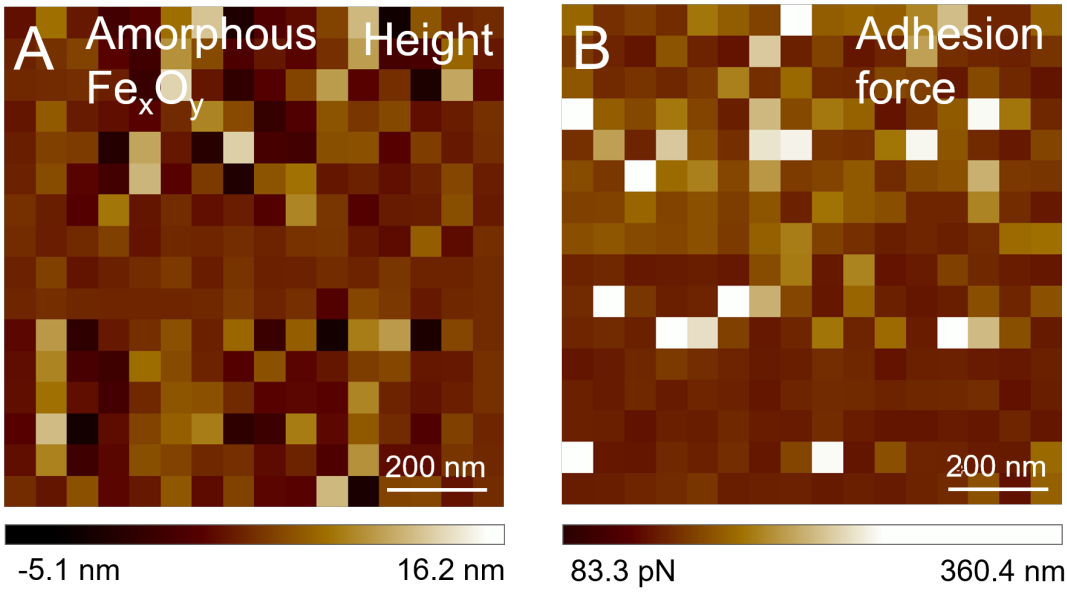

Figure S3. (A) The height and (B) the corresponding adhesion force of amorphous Fe_xO_y measured with alginate-decorated tip in the force-volume mode showing the adhesion force is independent of the height.

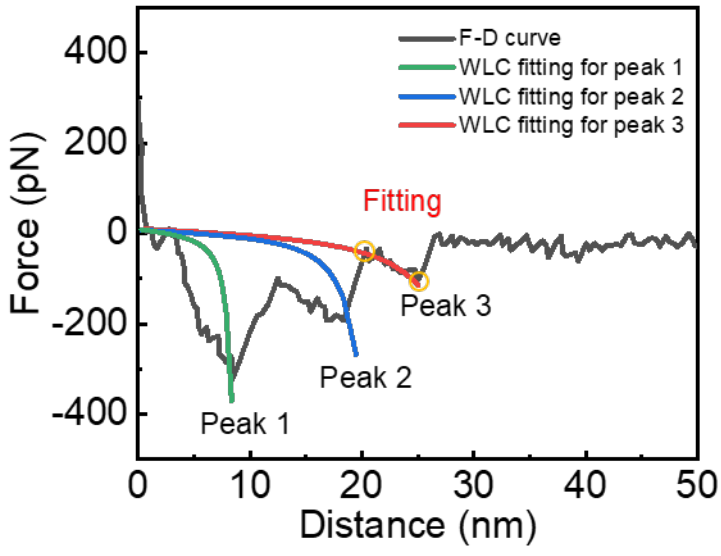

Figure S4. A representative force-distance curve showing only the last rupture event (Peak 3) fitted into the WLC model.

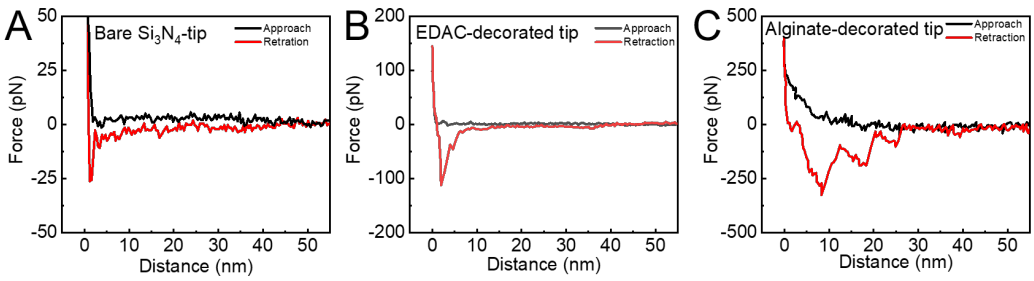

Figure S5. Representative force curves obtained with the (A) bare Si_3N_4 tip, (B) linker (1-(3-dimethylaminopropyl)-3-ethylcarbodiimide hydrochloride, EDAC)-coating tip and (C) alginate-decorated tip on the hematite ($10\bar{1}0$) surface.

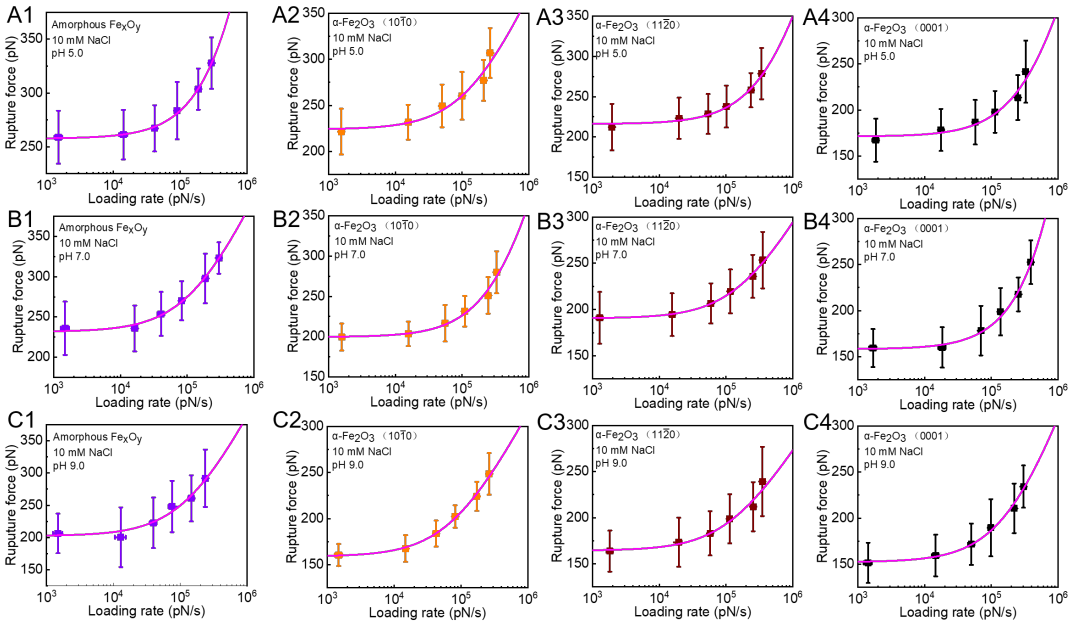

Figure S6. Dynamic force spectra (DFS) of alginate binding to amorphous Fe_xO_y or hematite (α-Fe_2O_3) with the ($10\bar{1}0$), ($11\bar{2}0$), and (0001) faces in 10 mM NaCl solutions at (A1-A4) pH 5.0, (B1-B4) pH 7.0 and (C1-C4) pH 9.0.

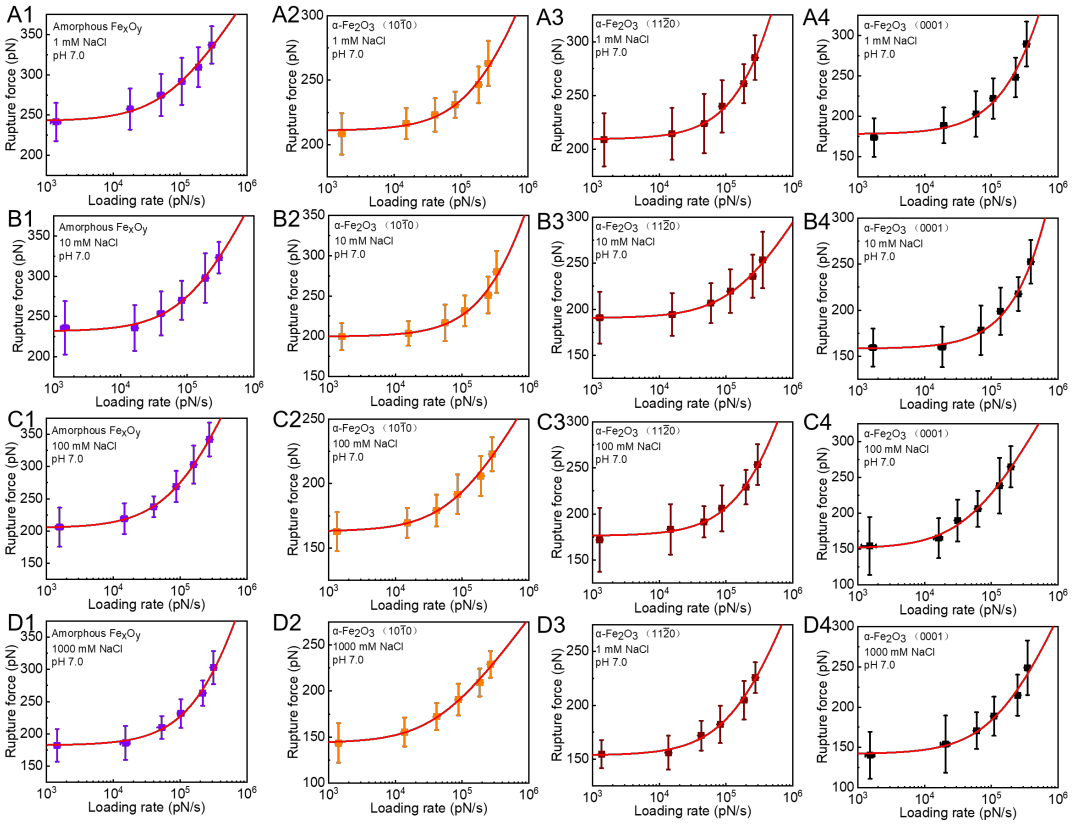

Figure S7. Dynamic force spectra (DFS) of alginate binding to amorphous Fe_xO_y or hematite (α-Fe_2O_3) with the (10$\bar{1}$0), (11$\bar{2}$0), and (0001) faces in solutions at (A1-A4) 1, (B1-B4) 10, (C1-C4) 100, and (D1-D4) 1000 mM at pH 7.0.

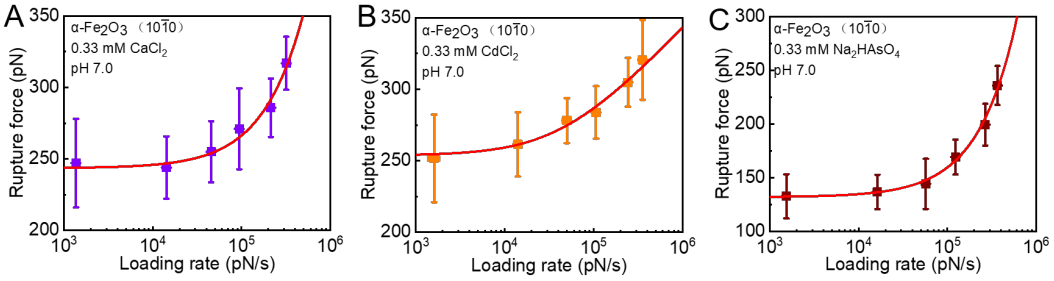

Figure S8. Dynamic force spectra (DFS) of alginate binding to the (10$\bar{1}$0) face of hematite (α-Fe_2O_3) in solutions (total *IS* = 10 mM and pH 7.0) containing (A) 0.33 mM $CaCl_2$, (B) 0.33 mM $CdCl_2$, or (C) 0.33 mM Na_2HAsO_4.

SI References.

1. M. A. Legodi, D. de Waal, The preparation of magnetite, goethite, hematite and maghemite of pigment quality from mill scale iron waste. *Dyes Pigments*, 2007, **74**, 161–168.
2. S. Das, and M. J. Hendry, Application of Raman spectroscopy to identify iron minerals commonly found in mine wastes. *Chem*. *Geol*., 2011, **290**, 101-108.
3. P. Agulhon, M. Robitzer, L. David, and F. Quignard, Structural regime identification in ionotropic alginate gels: influence of the cation nature and alginate structure. *Biomacromolecules*, 2011, **13**, 215-220.