

Electronic Supplementary Information

Surface Functionalized Nanoscale Metal Oxides for Arsenic (V), Chromium (VI), and Uranium (VI) Sorption: Considering Single- and Multi- Sorbate Dynamics

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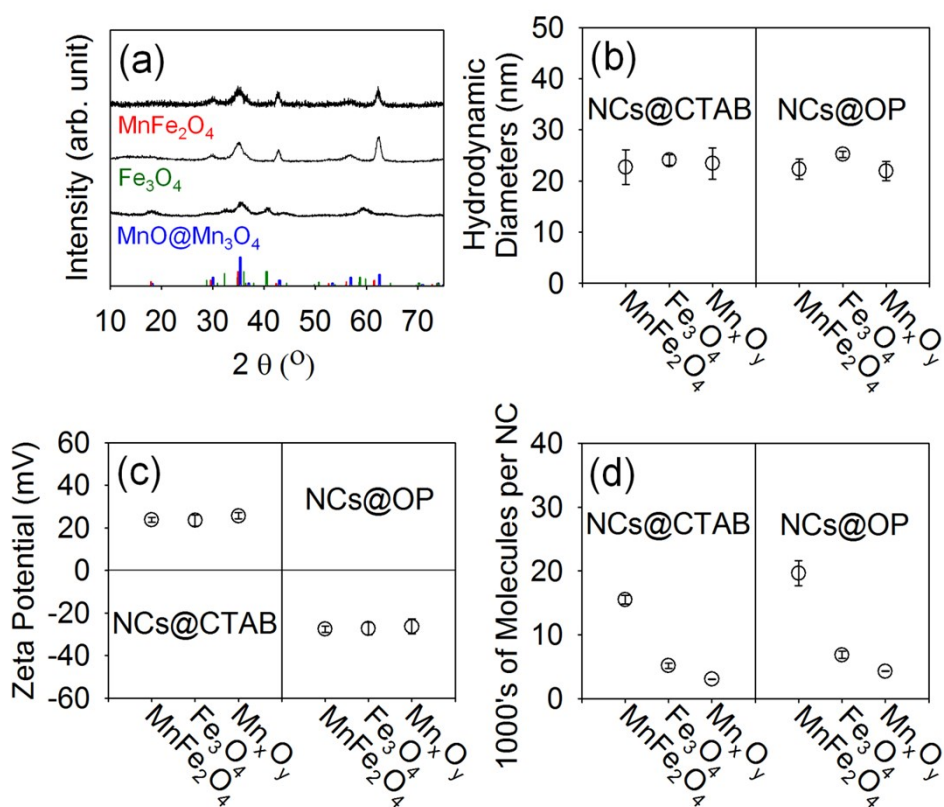


Fig. S1. (a) XRD of manganese iron oxide, iron oxide, and manganese oxide NCs. Diffraction patterns matched with MnFe_2O_4 (JCPDS Card # 380430), Fe_3O_4 (JCPDS Card # 190629), and MnO core (JCPDS Card # 070230) with Mn_3O_4 shell structure (JCPDS Card # 240734), respectively. Water disperse synthesized NCs coated with cetyltrimethylammonium bromide (CTAB) and oleyl phosphate (OP) were characterized; (b) hydrodynamic diameters at pH 7, (c) zeta potential at pH 7, and (d) number of organic molecules loaded on the NC surface.

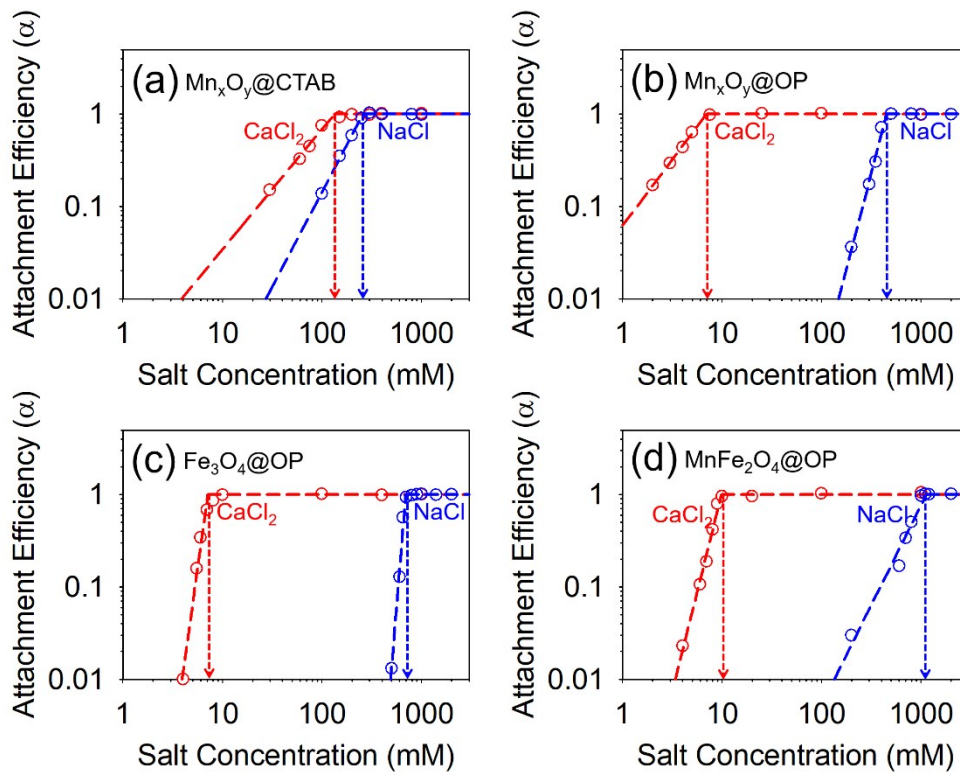


Fig. S2. Critical coagulation concentration (CCC) of water dispersed metal oxide NCs was determined by measuring attachment efficiency as a function of salt concentration (NaCl (blue) and CaCl_2 (red)); (a) $\text{Mn}_x\text{O}_y@CTAB$, (b) $\text{Mn}_x\text{O}_y@OP$, (c) $\text{Fe}_3\text{O}_4@OP$, and (d) $\text{MnFe}_2\text{O}_4@OP$.

All CCC measurements were tested at pH 7.0.

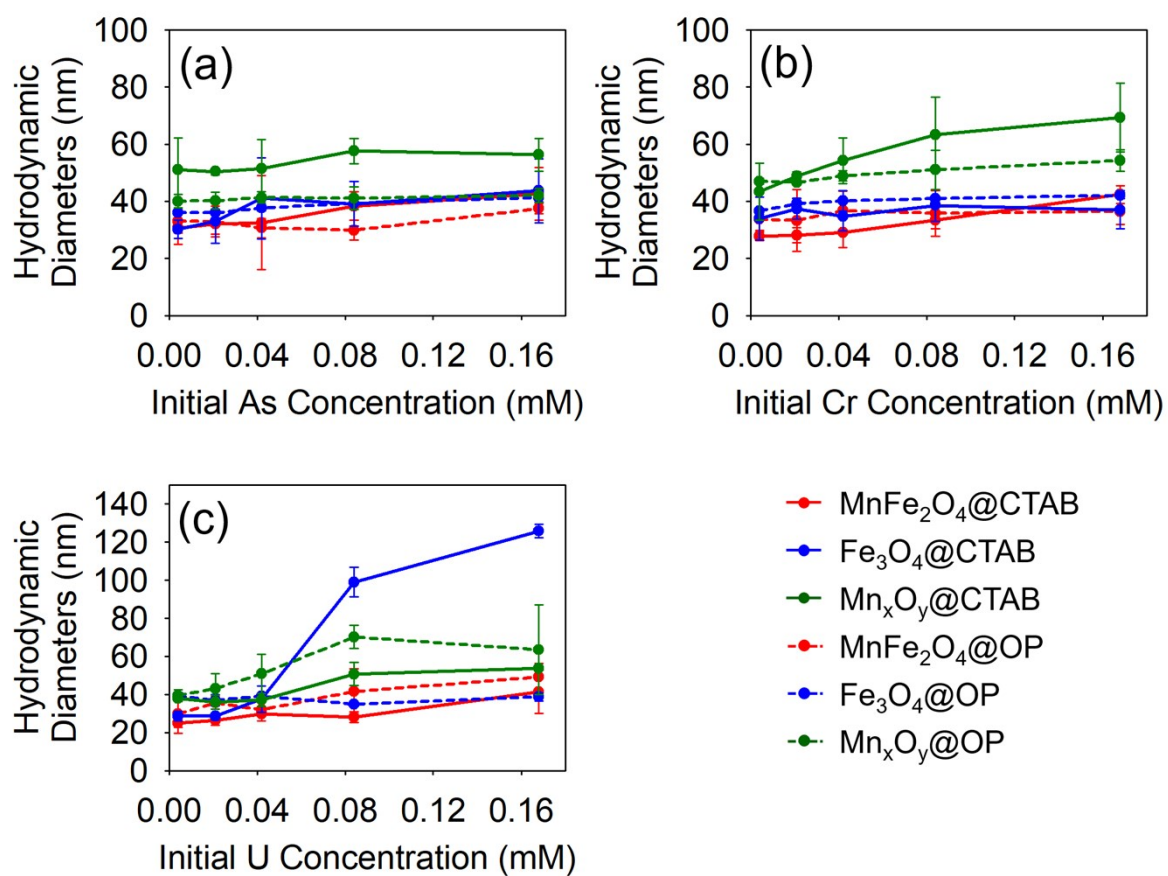


Fig. S3. Hydrodynamic diameter of CTAB (solid line) and OP (dotted line) functionalized metal oxide (MnFe₂O₄ (red), Fe₃O₄ (blue), and Mn_xO_y (red)) NCs after (a) As(V), (b) Cr(VI), and (c) U(VI) sorption experiments.

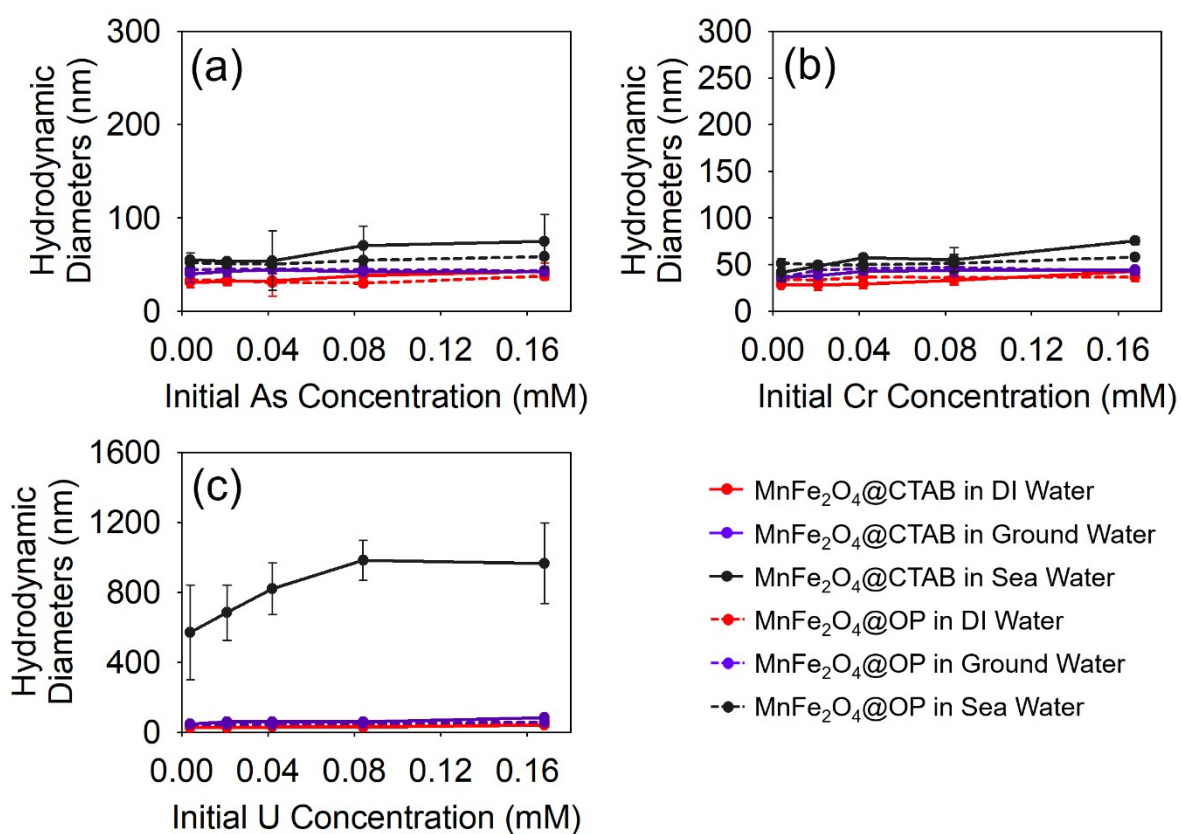


Fig. S4. Hydrodynamic diameter of CTAB (solid line) and OP (dotted line) functionalized MnFe₂O₄ NCs after (a) As(V), (b) Cr(VI), and (c) U(VI) sorption experiments in DI water (red), ground water (purple), and sea water (black); MnFe₂O₄@OP precipitated after uranyl sorption in sea water conditions.

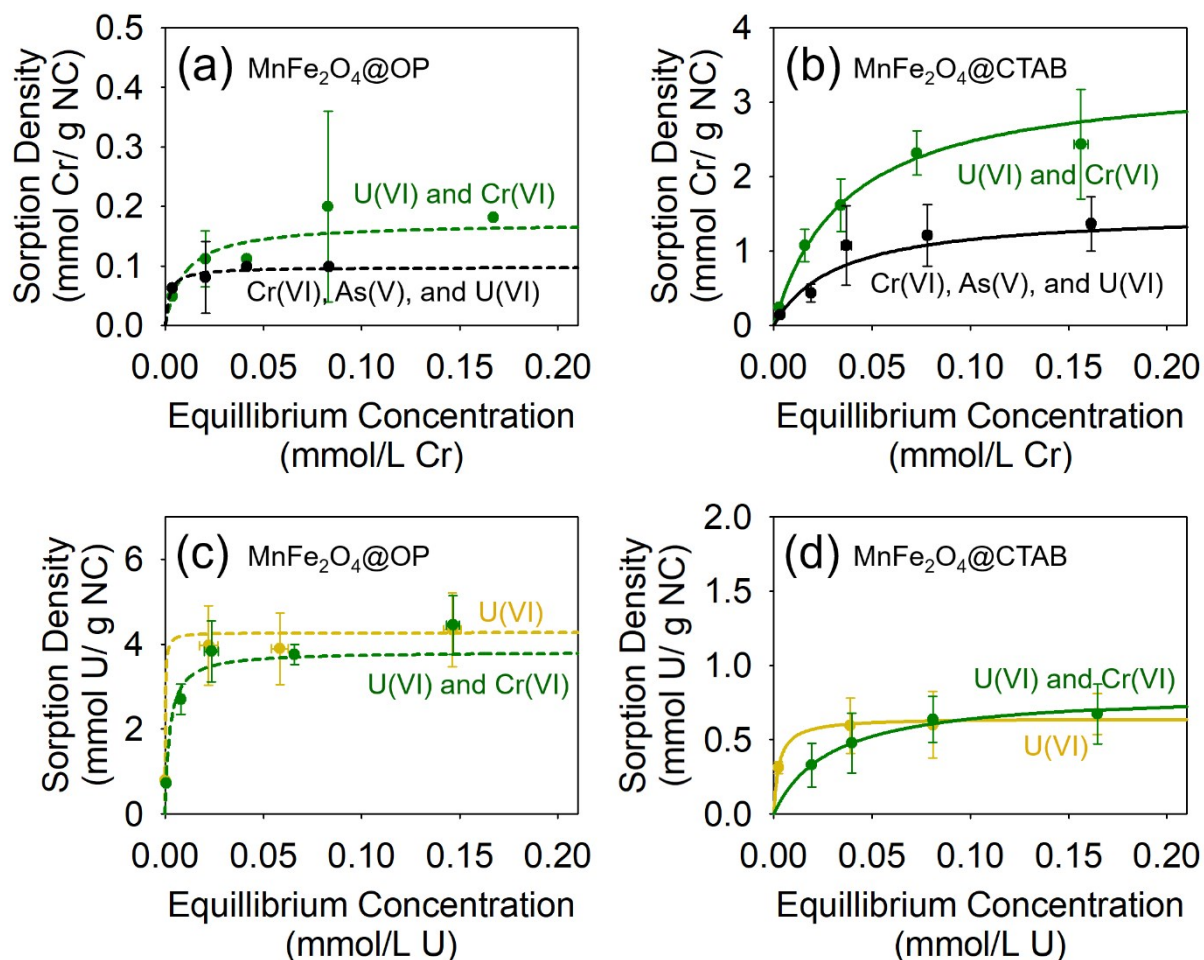


Fig. S5. Single- and multi-sorbate sorption isotherm on MnFe₂O₄ NCs coated with CTAB (solid line) or OP (dotted line); single sorbate systems (U(VI) (yellow)) and multi sorbate systems (Cr(VI) and U(VI) (green); and As(V), Cr(VI), and U(VI) (black)). Experiments were conducted in DI water at pH 7.0 ± 0.2. Dot plots with error bars and line plots present experiment measurement values with standard deviations and Langmuir isotherm fittings, respectively.

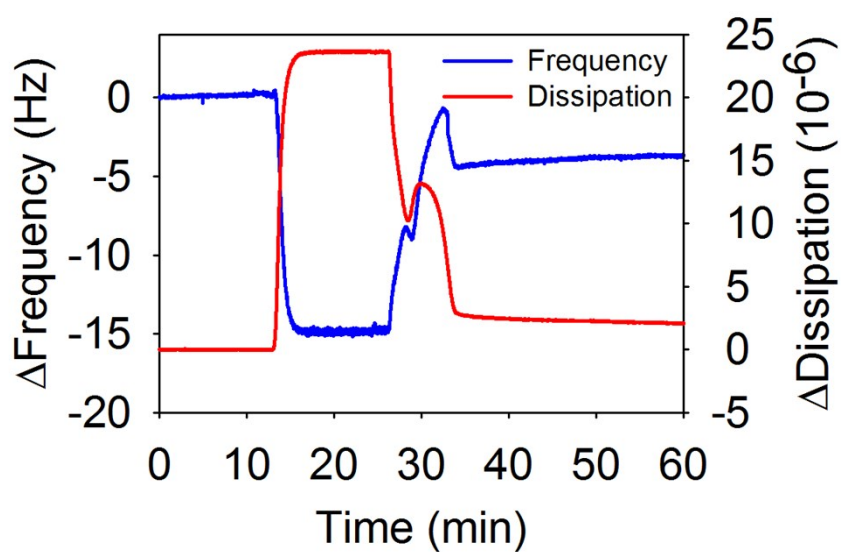


Fig. S6. Time dependent frequency (blue) and dissipation (red) shifts for Q-sensor with overtone ($n = 3$). The DI stabilized Q-sensor was coated by PDDA solution (after 12 min) and further stabilized for 15 min. Then the PDDA coated Q-sensor was restabilized with DI water at pH 7 (for 27 min to 60 min).

Table S1. Maximum sorption capacity per number of surfactant (or functional group as either amine or phosphate).

Nanocrystals	Maximum sorption capacity per number of surfactant (dimensionless)		
	Arsenic	Chromium	Uranium
$\text{Mn}_x\text{O}_y\text{@CTAB}$	0.21	0.30	0.46
$\text{Fe}_3\text{O}_4\text{@CTAB}$	0.39	1.1	0.29
$\text{MnFe}_2\text{O}_4\text{@CTAB}$	0.25	0.33	0.064
$\text{Mn}_x\text{O}_y\text{@OP}$	0.050	0.047	0.96
$\text{Fe}_3\text{O}_4\text{@OP}$	0.045	0.065	0.81
$\text{MnFe}_2\text{O}_4\text{@OP}$	0.063	0.12	0.35

Table S2. Composition of synthesized ground water and sea water. The carbonate system including bicarbonate, carbonic acid, carbonate, and carbon dioxide, was not included in this solution chemistry. The pH of synthesized solution was adjusted using HNO₃ and NaOH.

	Ground water pH 7.0 ± 0.2	Sea water pH 7.0 ± 0.2
Ion	mM	mM
Cl ⁻	6.6	564.1
Na ⁺	7	488.9
K ⁺	-	8.7
Mg ²⁺	-	45.2
Ca ²⁺	0.8	8.6
SO ₄ ²⁻	1.0	27.9
Br ⁻	-	0.6

Table S3. Summary of the maximum sorption density (q_{max} , mmol/g) and Langmuir sorption constant (K_L , L/mmol) for single sorbate system.

Solution (pH 7.0 ± 0.2)	Sorbent	Sorbates					
		As(V)		Cr(VI)		U(VI)	
		q_{max}	K_L	q_{max}	K_L	q_{max}	K_L
DI water	Comercial MnO	0.0068	33	0.025	12	0.026	79
DI water	Comercial Fe ₃ O ₄	0.051	200	0.038	21	0.027	2100
DI water	Comercial MnFe ₂ O ₄	0.14	310	0.025	65	0.043	4500
DI water	Mn _x O _y @CTAB	0.31	120	0.45	93	0.69	160
DI water	Mn _x O _y @OP	0.10	170	0.093	210	1.9	71
DI water	Fe ₃ O ₄ @CTAB	0.86	18	2.5	20	0.64	420
DI water	Fe ₃ O ₄ @OP	0.14	81	0.20	210	2.5	510
DI water	MnFe ₂ O ₄ @CTAB	2.6	21	3.4	18	0.65	380
DI water	MnFe ₂ O ₄ @OP	0.77	56	1.4	35	4.3	5990
Ground water	MnFe ₂ O ₄ @CTAB	0.57	51	0.051	280	0.34	43
Ground water	MnFe ₂ O ₄ @OP	0.48	63	0.027	110	2.2	54
Sea water	MnFe ₂ O ₄ @CTAB	0.34	200	0	N.A.	0.099	310
Sea water	MnFe ₂ O ₄ @OP	0.039	950	0	N.A.	1.0	61

Table S4. Summary of the maximum sorption density (q_{max} , mmol/g) and Langmuir sorption constant (K_L , L/mmol) for multi sorbate system.

Solution (pH 7.0 ± 0.2)	Sorbates	Sorbent	Sorbate					
			As(V)		Cr(VI)		U(VI)	
			q_{max}	K_L	q_{max}	K_L	q_{max}	K_L
DI water	As(V), Cr(VI)	MnFe ₂ O ₄ @OP	0.83	33	0.23	66	N.A.	N.A.
	Cr(VI), U(VI)		N.A.	N.A.	0.17	100	3.8	440
	As(V), Cr(VI), U(VI)		N.A.	N.A.	0.097	490	N.A.	N.A.
	As(V), Cr(VI)	MnFe ₂ O ₄ @CTAB	2.7	22	1.6	31	N.A.	N.A.
	Cr(VI), U(VI)		N.A.	N.A.	3.4	27	0.82	34
	As(V), Cr(VI), U(VI)		N.A.	N.A.	1.5	31	N.A.	N.A.