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

Supplementary Information for

Engineered Manganese Oxide Nanocrystals for Enhanced Uranyl Sorption and Separation

Seung Soo Lee, [a] Wenlu Li,[a] Changwoo Kim,[a] Minjung Cho,[b] Jeffrey G. Catalano,[c] Brandon J. Lafferty, [d] Paolo Decuzzi, [b] and John D. Fortner[a,*]

[a] Department of Energy, Environmental, and Chemical Engineering, Washington University, St. Louis, MO63130

[b] Department of Translational Imaging and Department of Nanomedicine, Houston Methodist Research Institute, Houston, TX77030

[c] Department of Earth and Planetary Sciences, Washington University, St. Louis, MO63130

[d] U.S. Army Corps of Engineers, Engineer Research and Development Center, Vicksburg, MS39180

*Corresponding author: jfortner@wustl.edu

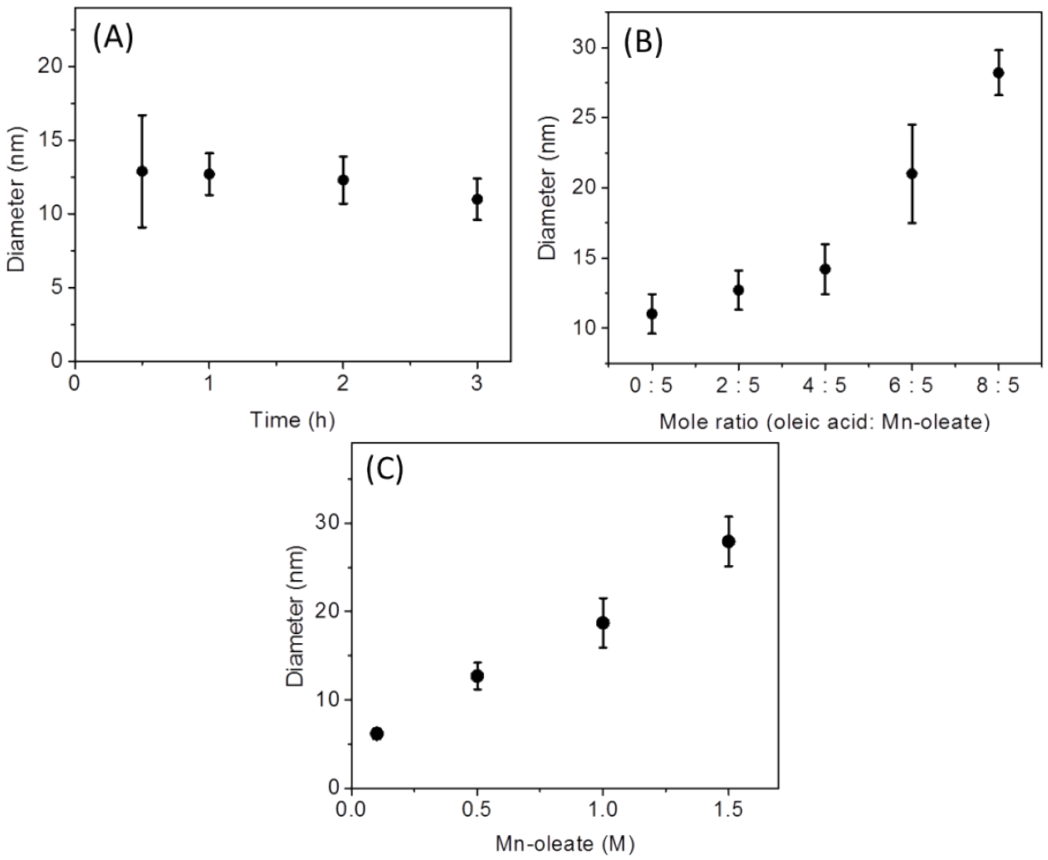

Figure S1. Control over the diameter of manganese oxide nanocrystals. Nanocrystal growth as a function of reaction time (A), the ratio of oleic acid to manganese oleate (Mn-oleate) (B), and monomer concentration (Mn-oleate in 1-octadecene) (C).

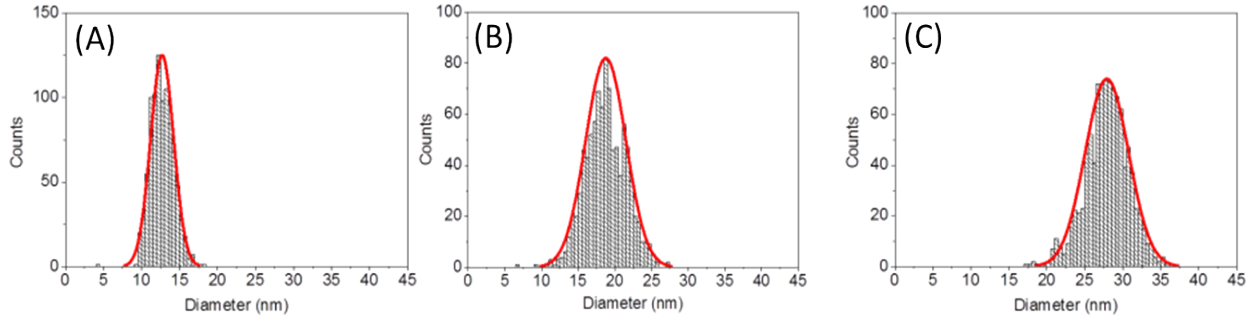

Figure S2. The histograms of the diameter distribution of manganese oxide nanocrystals. The average diameter and its standard deviation is 12.2 ± 1.2, 18.7 ± 2.2, 27.9 ± 2.8 nm from (A) to (C), respectively. The x and y axes are the size of the nanoparticles (nm) and their counts, respectively.

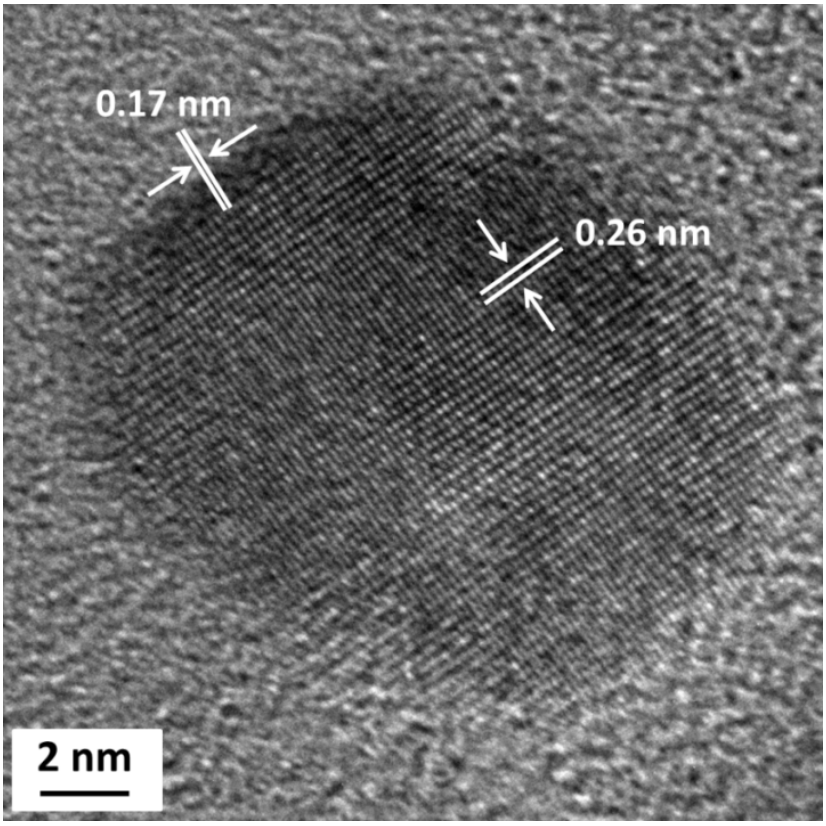

Figure S3. High resolution TEM image of manganese oxide nanocrystal.

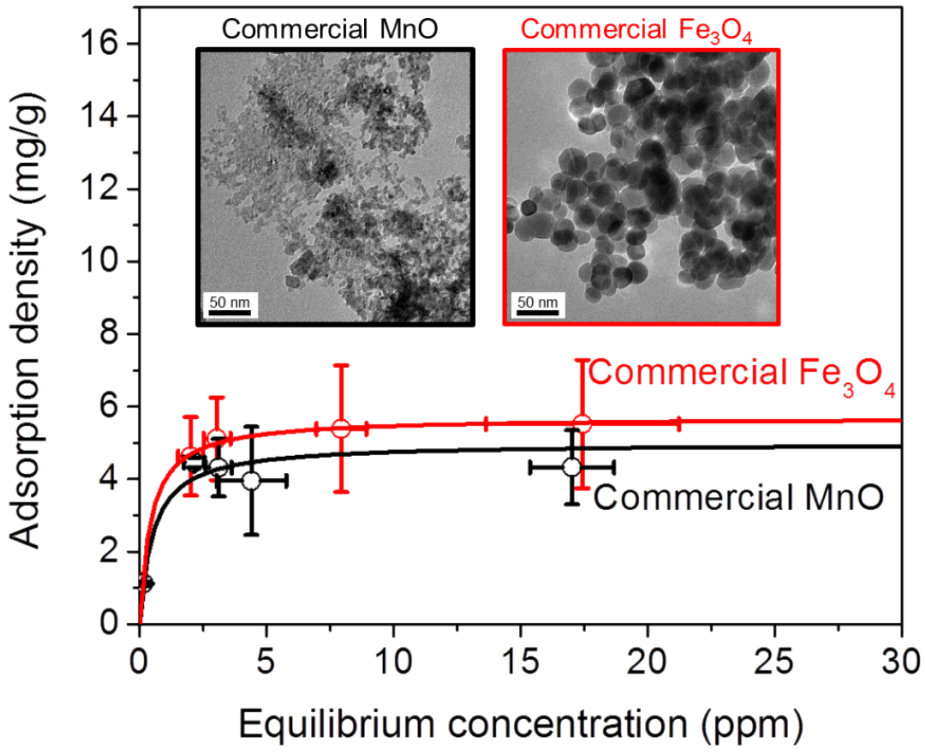

Figure S4. Uranium sorption isotherm on commercial samples (Fe_3O_4 and MnO). Commercial MnO (black, 6.7 mg of manganese (II)) and Fe_3O_4 (red, 5.5 mg of iron (III)) at pH 5.6. All solid lines were plotted by Langmuir isotherm equation using the experimental data.

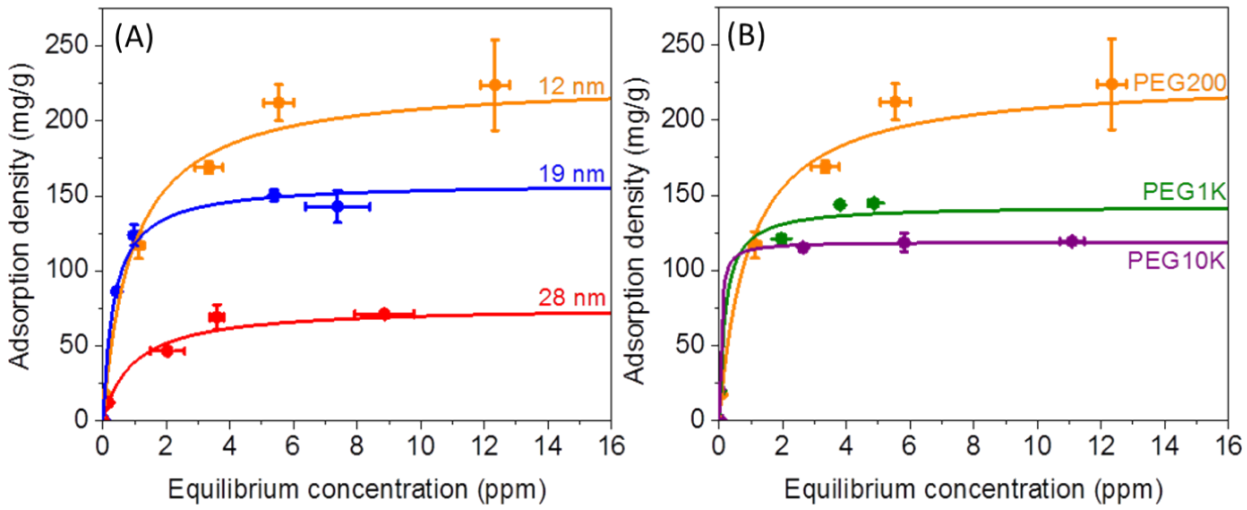

Figure S5. Size and surface coating thickness dependent uranium sorption isotherms for engineered PEGylated manganese oxide nanocrystals. (A) Sorption isotherm was performed using three different diameters of PEG 200 coated monodisperse manganese oxide nanocrystals (12, 19, and 28 nm; 0.2 mg of manganese (II)) at pH 5.6. (B) Surface coating thickness dependent uranium sorption measurement was conducted by three different surface coating samples (PEG 200 (yellow), PEG 1K (green), and PEG 10K (purple); 0.2 mg of manganese (II)) at pH 5.6. All solid lines were plotted via Langmuir isotherm equation using the experimental data.

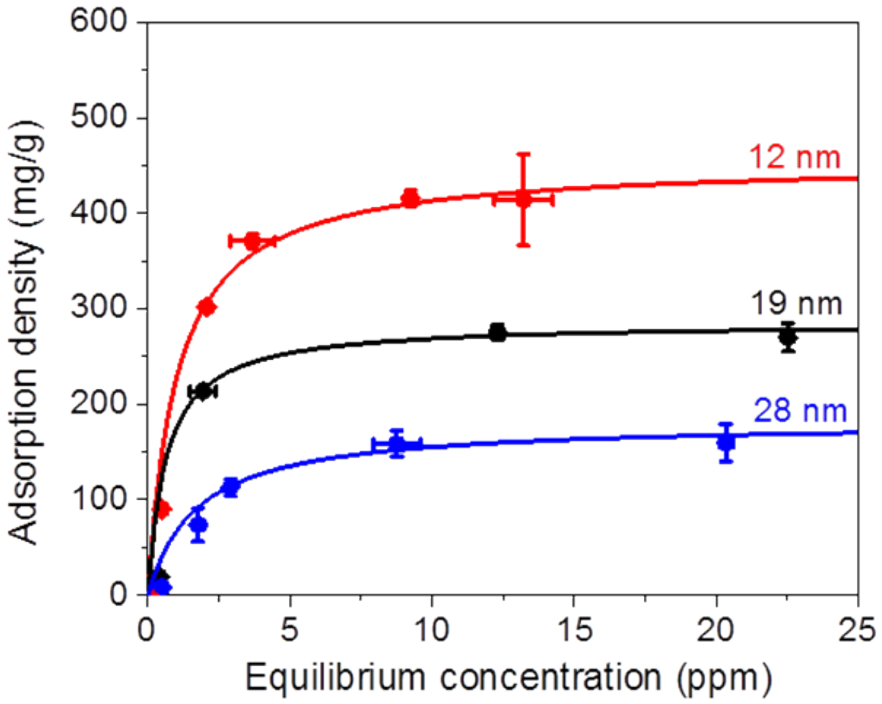

Figure S6. Size dependent uranium sorption isotherm on oleic acid bilayered manganese oxide nanocrystals. Sorption isotherm was carried out on manganese oxide nanocrystals with diameters of 12 nm (red), 19 nm (black), and 28 nm (blue); 0.2 mg of manganese(II)) at pH 5.6. All solid lines were plotted by the Langmuir isotherm equation using the experimental data.

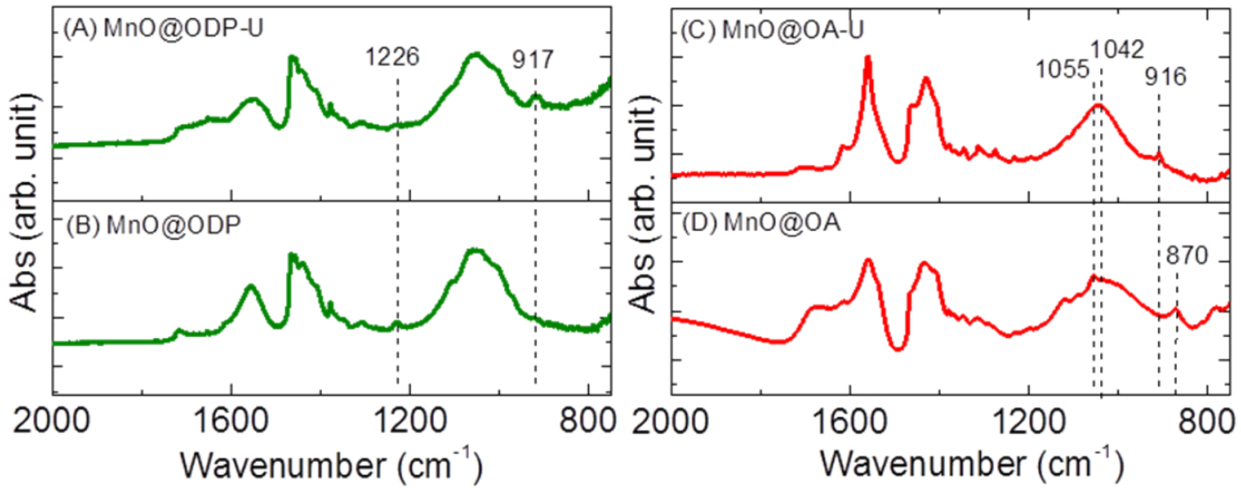

Figure S7. FT-IR measurements of engineered nanocrystals coated with octadecylphosphonic acid (A for uranium loaded sample and B for control), and oleic acid (C for uranium loaded sample and D for control). The bands at 1460 cm^{-1} and at 1550 cm^{-1} were assigned to the symmetric and asymmetric COO- vibrational stretch modes, respectively. Also the bands at 1226 cm^{-1} and at 1055 cm^{-1} are PO_2^- and CO stretching vibrations, respectively. The bands at 916 and 917 cm^{-1} are due to the existence of uranyl ions. The 876 cm^{-1} band is from vibration of the methylene group.

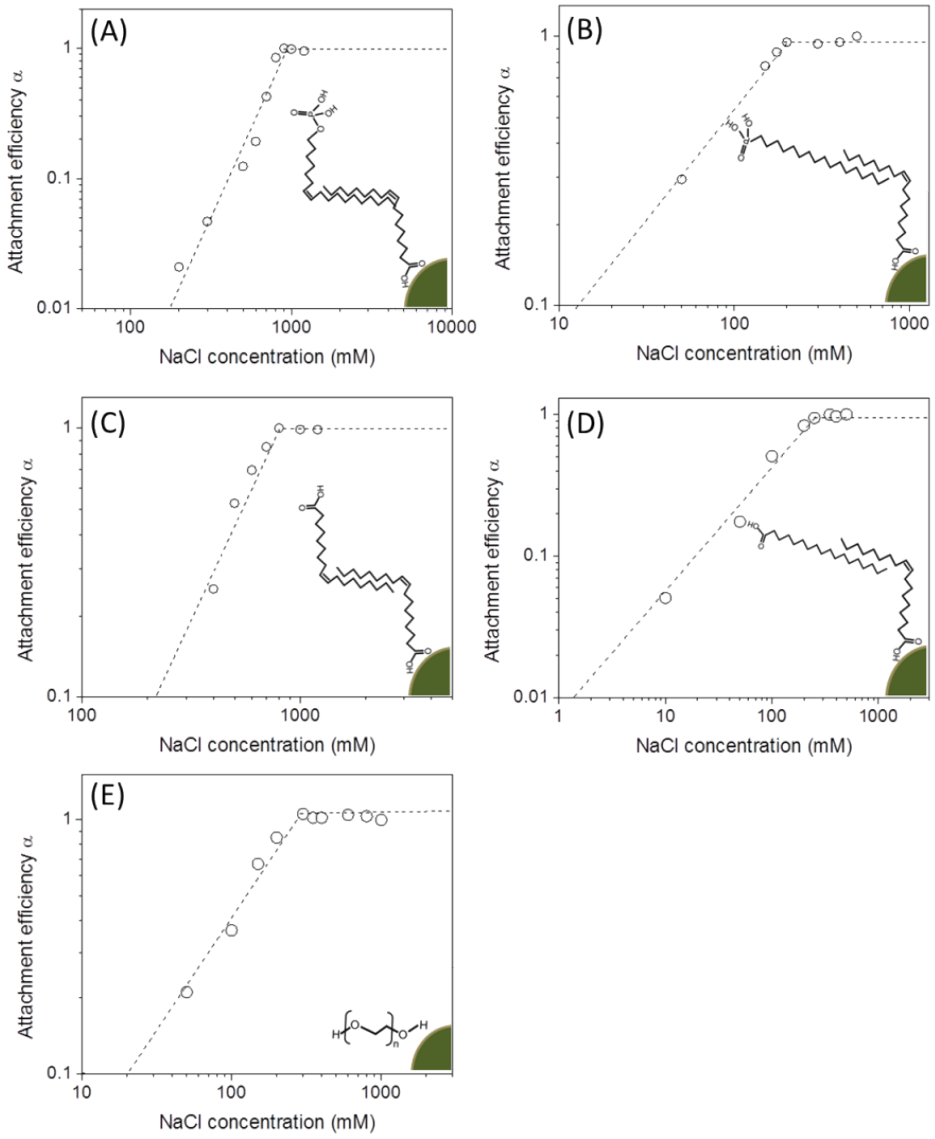

Figure S8. Attachment efficiencies of both bilayered- (A for oleyl phosphate coated-,B for octadecylphosphonic acid coated-, C for oleic acid coated-, and D for stearic acid coated-manganese oxides) and pegylated-manganese oxide nanocrystals (E) as a function of $NaCl_2$ concentrations at pH 5.6. The nanocrystal concentration employed was 2.7×10^{14} nanocrystals/L. The cartoon images showed the bilayered and single layered structure and the single layered structure. The critical coagulation concentrations (CCC) are 883.7mM of NaCl for oleyl phosphate coated-, 201.5 mM of NaCl for octadecylphosphonic acid coated-, 810.1 mM of NaCl for oleic acid coated-, and 245.8 mM of NaCl for stearic acid coated- bilayered manganese oxide nanocrystals. The critical coagulation concentrations for PEG 200 coated manganese oxide nanocrystals was 261.4 mM of NaCl.

Table S1. The maximum uranium sorption capacity (q_{max}) and the sorption constant (k) for bilayered manganese oxides and PEG 200 coated manganese oxide samples at three different pH calculated by the Langmuir isotherm equation (see the experimental details).

	Mn_xO_y@OP			Mn_xO_y@ODP			Mn_xO_y@OA			Mn_xO_y@SA			Mn_xO_y@PEG200		
pH	5.6	7.0	8.5	5.6	7.0	8.5	5.6	7.0	8.5	5.6	7.0	8.5	5.6	7.0	8.5
q_{max} (mg/g)	625.0	476.2	454.5	500.0	384.6	357.1	454.6	344.8	217.4	256.4	238.1	192.3	227.3	125.0	122.0
K (L/mg)	0.7	1.5	0.9	0.5	1.3	14	1.0	1.2	1.4	4.3	5.3	1.9	1.1	2.2	3.7

Table S2. The maximum uranium sorption capacity (q_{max}) and the sorption constant (k) for size and surface coating thickness dependent uranium sorption isotherm on engineered PEGylated manganese oxide nanocrystals calculated by the Langmuir isotherm equation (see the experimental details).

	Diameter dependent			Surface coating dependent			Commercial sample	
	12 nm	19 nm	28 nm	PEG 200	PEG 1K	PEG 10K	MnO	Fe_3O_4
q_{max} (mg/g)	454.6	285.7	181.8	227.3	142.9	119.1	5.7	5.0
K (L/mg)	1.0	1.6	0.6	1.1	5.4	21.0	2.3	1.9
	*The nanocrystals were coated with PEG 200 and pH was 5.6.			*The diameter of Mn_xO_y was 12 nm and at pH 5.6				

Table S3. XPS binding energies of individual peaks of the U4f spectrum for the sample before and after uranium sorption. V_1 and V_3 are attributed to U(IV) and V_2 and V_4 are the characteristic peaks of U(VI).

Sample	V_1	V_2	V_3	V_4	%U(IV)/U(VI)
Mn_xO_y@OP-U	32.16 (380.31)	28.70 (381.35)	22.67 (391.19)	16.47 (392.47)	54.8/45.2
Uranium nitrate		55.70 (381.50)		44.30 (392.40)	0/100

Table S4. XPS binding energies of individual peaks of the Mn2P spectrum for the sample before and after uranium sorption. The concentration of each of oxidation state of Mn(II) and Mn(III) is V_a+V_c and V_b+V_d, respectively.

Sample	V_a	V_b	V_c	V_d	%Mn(II)/Mn(III)
Mn_xO_y@OP-U	30.10 (640.62)	42.64 (641.82)	12.19 (652.36)	15.07 (653.75)	42.29/57.71
MnO@OP	34.00 (640.75)	40.17 (642.28)	15.40 (652.81)	10.43 (653.83)	49.40/50.60

Table S5. Hydrodynamic diameters of manganese oxide nanocrystals designed in the research.

Sample	Number mean (nm)	Volume mean (nm)	Intensity mean (nm)
12 nm Manganese oxide @ OP	21.7 ± 2.6	27.7 ± 0.7	55.3 ± 0.5
12 nm Manganese oxide @ ODP	19.2 ± 0.6	27.3 ± 0.5	52.7 ± 1.5
12 nm Manganese oxide @ OA	20.4 ± 2.5	25.0 ± 2.7	51.3 ± 1.3
12 nm Manganese oxide @ SA	23.6 ± 0.5	35.2 ± 6.8	59.4 ± 1.0
19 nm Manganese oxide @ OA	25.7 ± 0.6	35.5 ± 0.2	56.3 ± 3.7
28 nm Manganese oxide @ OA	35.0 ± 0.8	41.2 ± 0.4	56.8 ± 1.0
12 nm Manganese oxide @ PEG 200	21.5 ± 2.0	42.7 ± 0.1	68.0 ± 0.4
19 nm Manganese oxide @ PEG 200	29.9 ± 1.1	43.4 ± 2.3	84.9 ± 7.6
28 nm Manganese oxide @ PEG200	37.5 ± 2.4	65.5 ± 6.8	167.8 ± 1.9
12 nm Manganese oxide @ PEG 1K	31.5 ± 2.0	51.3 ± 4.4	82.9 ± 9.1
12 nm Manganese oxide @ PEG 10K	46.6 ± 0.7	66.2 ± 0.7	104.9 ± 0.8