Supplementary Information for

Reactive halogen radicals in saline water promote photochemically-assisted formation of manganese oxide nanosheets

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Summary:

11 pages, including 8 figures and 1 table.

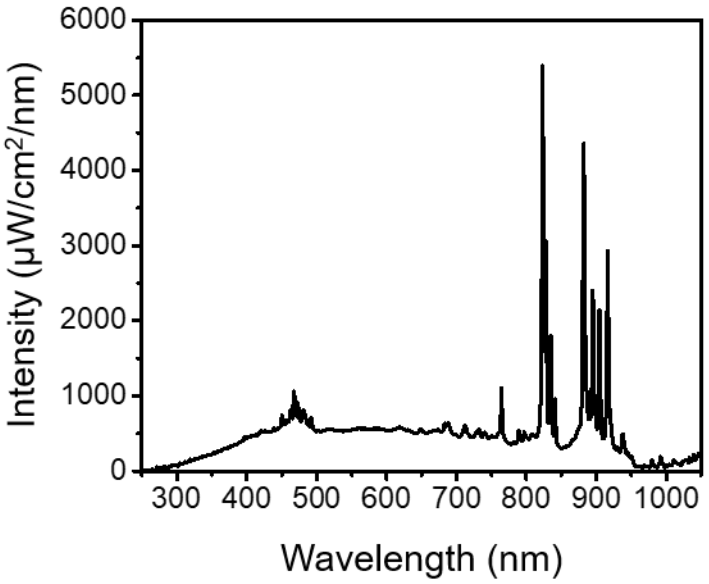

Figure S1. Light spectrum of xenon arc lamp over 250–1050 nm wavelengths.

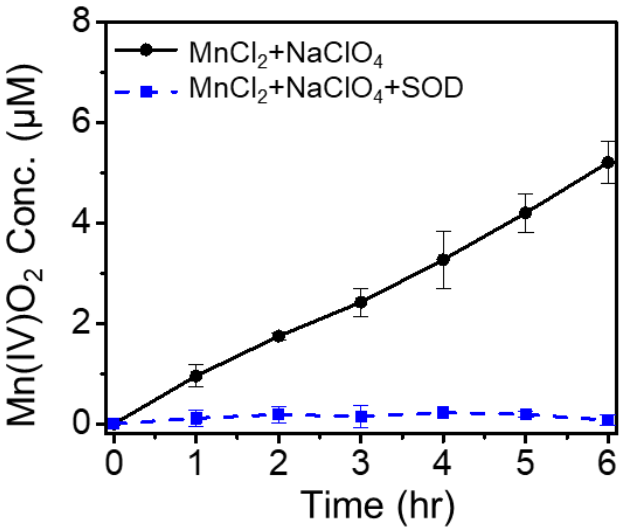

Figure S2. $Mn(IV)O_2$ concentrations during 6 hr of photolysis of two solutions, one containing 0.1 mM $MnCl_2$ and 500 mM $NaClO_4$ at an initial pH of 9, and another containing 0.1 mM $MnCl_2$, 500 mM $NaClO_4$, and 0.5 μM SOD at initial pH 9. Error bars represent standard errors of the data obtained from duplicate experiments. No Mn oxidation was observed in the presence of SOD, indicating that $O_2^{\bullet-}$ generated from photolysis of $NaClO_4$ can $Mn^{2+}(aq)$.

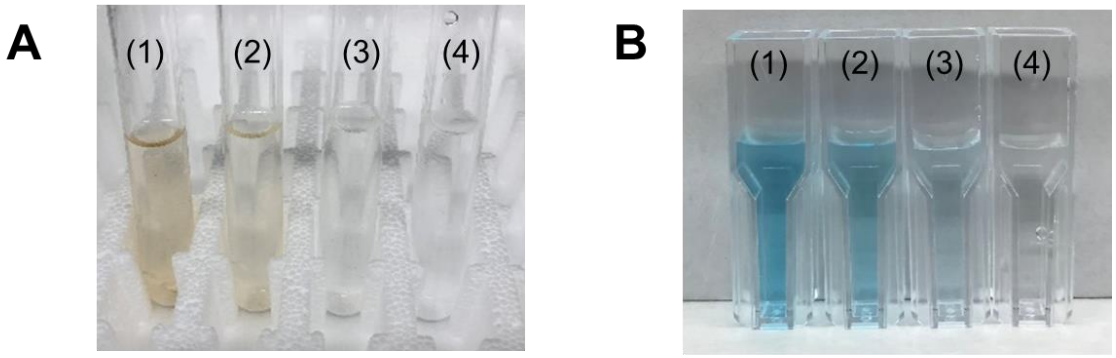

Figure S3. Mn^{2+} oxidation by $O_2^{\bullet-}$ or/and Br radicals. (A) Higher concentration of Mn oxide solids displays a darker yellowish color. (B) Mn oxide samples were mixed with LBB solution to quantify Mn oxide generation amount. Darker blue corresponds to a higher concentration of Mn oxide solids. Conditions of (1)–(5) are (1) 0.1 mM $MnCl_2$, 1 mM $NaNO_3$, and 1 mM NaBr; (2) 0.1 mM $MnCl_2$ and 1 mM $NaNO_3$; (3) 0.1 mM $MnCl_2$, 1 mM $NaNO_3$, 1 mM NaBr, and 0.5 μM SOD; (4) 0.1 mM $MnCl_2$, 1 mM $NaNO_3$, 1 mM Na_2SO_4, and 0.5 μM SOD; and (5) 0.1 mM $MnCl_2$, 1 mM $NaNO_3$, and 0.5 μM SOD. MnO_2 solution color and LBB solution color of (5) are the same as (4) because of no Mn^{2+} oxidation for (4) and (5). Error bars represent standard errors of the data obtained from duplicate experiments.

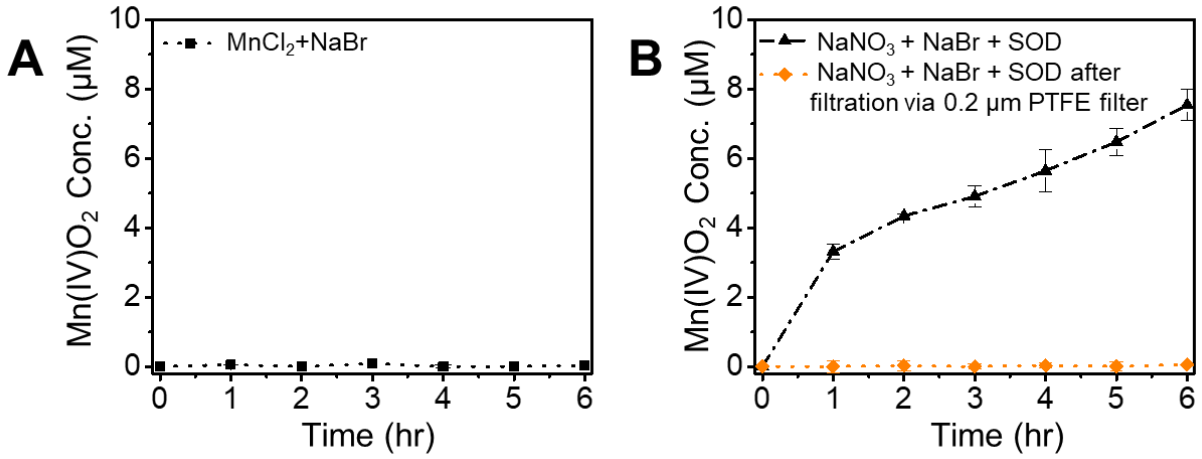

Figure S4. (A) No Mn oxide solids formed during photolysis of solution containing 0.1 mM $MnCl_2$ and 1 mM NaBr. (B) Oxidized Mn concentrations during 6 hr photolysis of a solution containing 0.1 mM $MnCl_2$, 1 mM $NaNO_3$, 1 mM NaBr, and 0.5 µM SOD, before and after filtration by a 0.2 µm PTFE membrane for three times. Error bars represent standard errors of the data obtained from duplicate experiments.

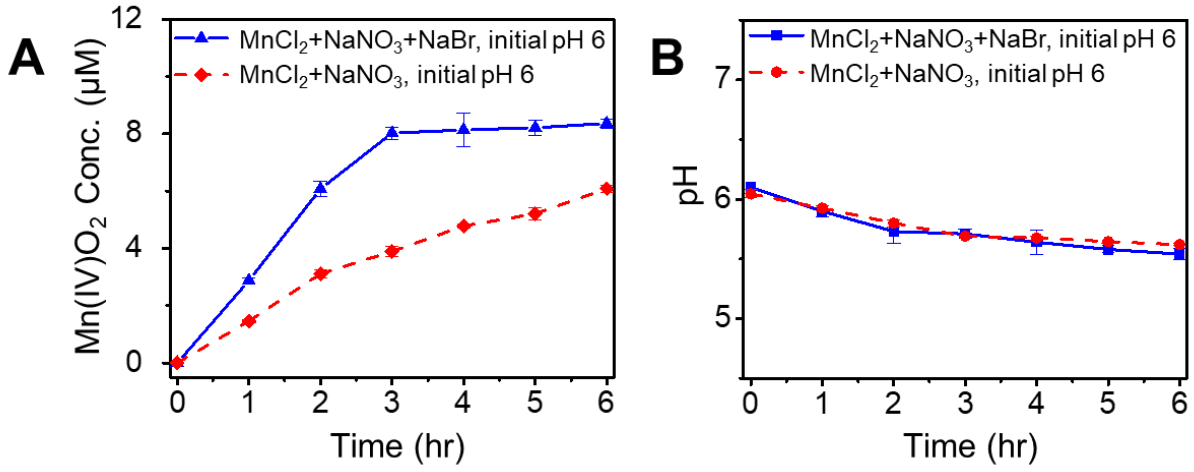

Figure S5. Mn^{2+} oxidation by $O_2^{\bullet-}$ or/and Br radicals at initial pH 6. (A) $Mn(IV)O_2$ concentrations and (B) pH values of during 6 hr of photolysis of two solutions, one containing 0.1 mM $MnCl_2$, 1 mM $NaNO_3$, and 1 mM NaBr at initial pH 6, and another containing 0.1 mM $MnCl_2$ and 1 mM $NaNO_3$ at initial pH 6. Error bars represent standard errors of the data obtained from duplicate experiments.

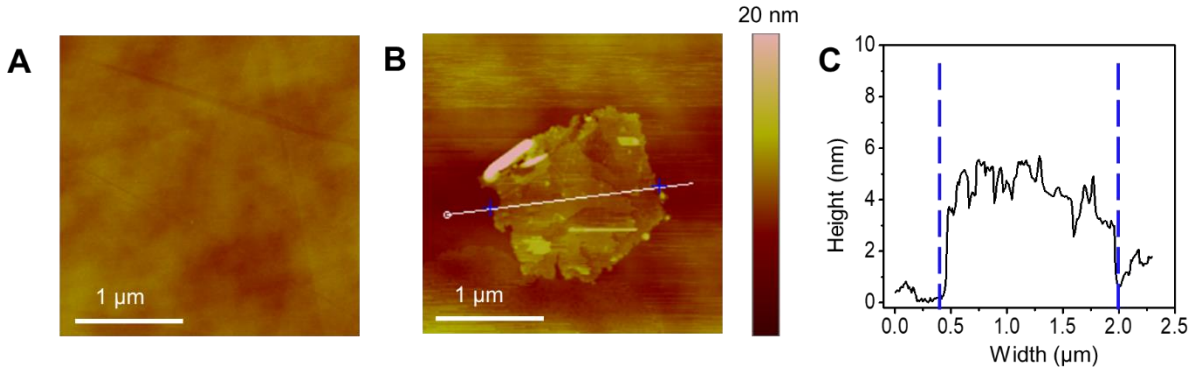

Figure S6. Thickness and lateral size of Mn oxide solids. Atomic force microscopy (AFM) images of (A) a clean Si wafer and (B) formed MnO_2 solids on a clean Si wafer. MnO_2 solids were formed after 6 hr of photolysis of a solution containing 0.1 mM $MnCl_2$, 1 mM $NaNO_3$, and 1 mM NaBr at initial pH 9. Then one droplet of the solution was dropped on a clean Si wafer and allowed to air-dry.

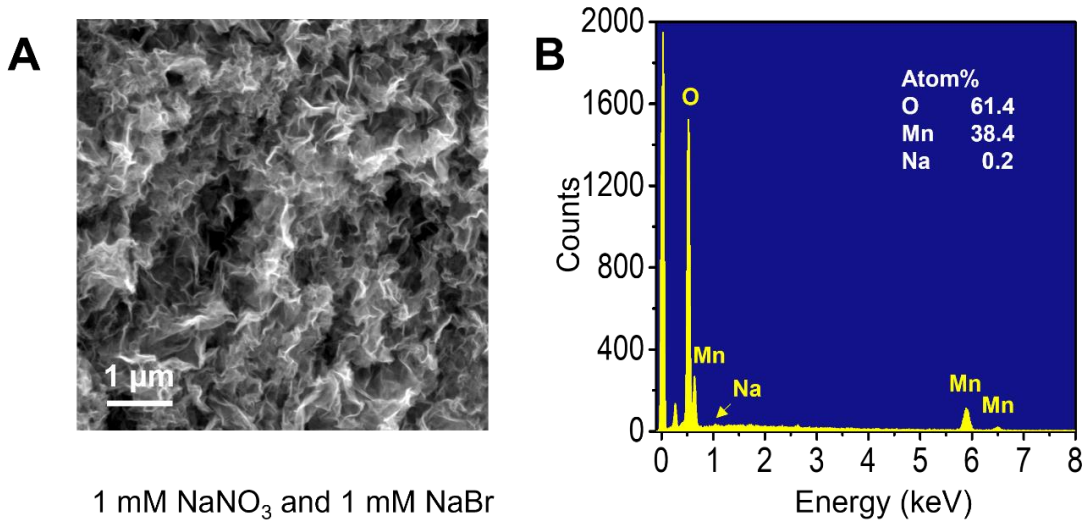

Figure S7. (A) Morphology and (B) elemental composition of Mn oxide solids formed under the condition of 0.1 mM $MnCl_2$, 1 mM $NaNO_3$, and 1 mM NaBr. Image and spectrum by ESEM-EDX.

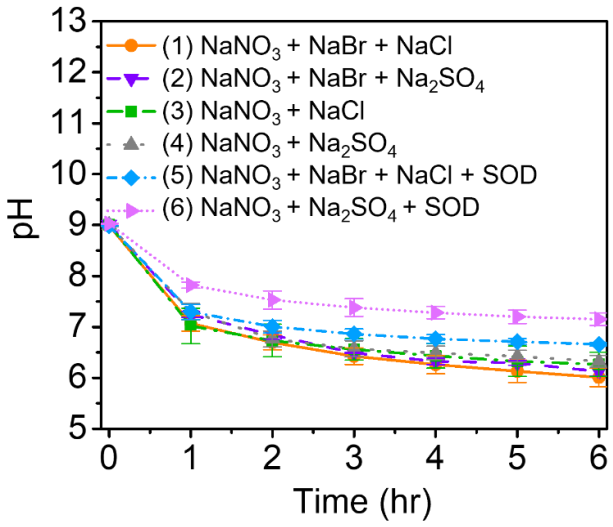

Figure S8. pH values during 6 hr photolysis of solutions containing (1) 0.1 mM $MnCl_2$, 1 mM $NaNO_3$, 1 mM NaBr, and 500 mM NaCl; (2) 0.1 mM $MnCl_2$, 1 mM $NaNO_3$, 1 mM NaBr, and 166.7 mM Na_2SO_4; (3) 0.1 mM $MnCl_2$, 1 mM $NaNO_3$, and 500 mM NaCl; (4) 0.1 mM $MnCl_2$, 1 mM $NaNO_3$, and 166.7 mM Na_2SO_4; (5) 0.1 mM $MnCl_2$, 1 mM $NaNO_3$, 1 mM NaBr, 500 mM NaCl, and 0.5 μM SOD; and (6) 0.1 mM $MnCl_2$, 1 mM $NaNO_3$, 166.7 mM Na_2SO_4, and 0.5 μM SOD. Error bars represent standard errors of the data obtained from duplicate experiments.

Table S1. Summary of XPS references for Mn(II), Mn(III), and Mn(IV).

Oxidation state	Mn oxide sample	Mn $2p_{3/2}$ Binding energy (eV)	References
Mn(II)	Mn(II) in δ-MnO_2	640.8	Jung et al. (2017) [1]
	Mn(II) in MnO	640.8	Junta and Hochella (1994) [2]
	Mn(II) in MnO	641.0	Di Castro and Polzonetti (1989) [3]
Mn(III)	Mn(III) in γ-MnOOH	641.7	Junta and Hochella (1994) [2]
	Mn(III) in γ-MnOOH	641.7	Jung and Jun (2016) [4]
	Mn(III) in Mn_2O_3	641.8	Ramesh et al. (2008) [5]
	Mn(III) in δ-MnO_2	641.8	Jung et al. (2017) [1]
	Mn(III) in Mn_2O_3	641.9	Di Castro and Polzonetti (1989) [3]
Mn(IV)	Mn(IV) in MnO_2	642.0	Junta and Hochella (1994) [2]
	Mn(IV) in MnO_2	642.2	Oku et al. (1975) [6]
	Mn(IV) in δ-MnO_2	642.2	Jung et al. (2017) [1]
	Mn(IV) in MnO_2	642.3	Ramesh et al. (2008) [5]

Supplemental References

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3. V. Di Castro and G. Polzonetti, XPS study of MnO oxidation, *J. Electron Spectrosc. Relat. Phenom.*, 1989, **48**, 117-123.
4. H. Jung and Y.-S. Jun, Ionic strength-controlled Mn (hydr)oxide nanoparticle nucleation on quartz: effect of aqueous $Mn(OH)_2$, *Environ. Sci. Technol.*, 2016, **50**, 105-113.
5. K. Ramesh, L. Chen, F. Chen, Y. Liu, Z. Wang and Y.-F. Han, Re-investigating the CO oxidation mechanism over unsupported MnO, Mn_2O_3 and MnO_2 catalysts, *Catal. Today*, 2008, **131**, 477-482.
6. M. Oku, K. Hirokawa and S. Ikeda, X-ray photoelectron spectroscopy of manganese—oxygen systems, *J. Electron Spectrosc. Relat. Phenom.*, 1975, **7**, 465-473.