Supplementary Information (SI) for Environmental Science: Nano.

SUPPLEMENTARY INFOMRATION

Photochemically Facilitated Todorokite Nanoparticle Formation in Circumneutral pH Environments

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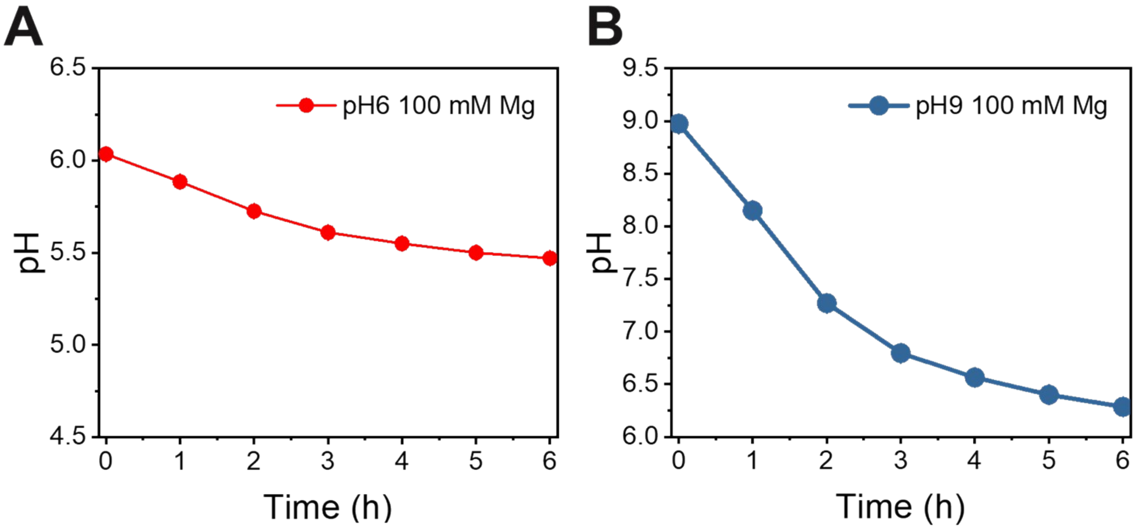

Fig. S1. pH variation from initial pH 6 and 9 over elapsed reaction time. pH drops from initial pH 6 and pH 9 were monitored during the photochemical oxidation and formation of Mn oxide in the presence of 100 mM Mg^{2+}.

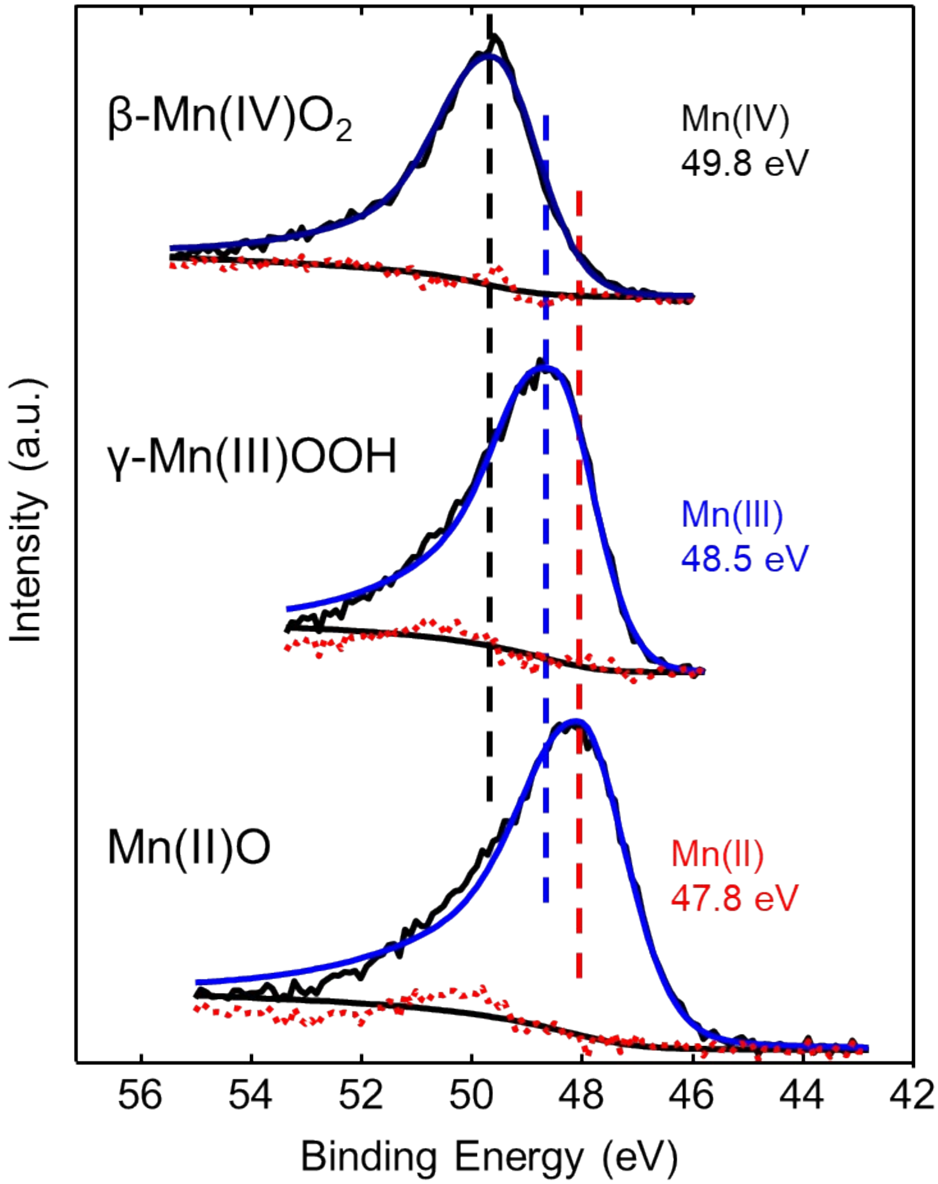

Fig. S2. Mn 3p XPS spectra of reference Mn oxides measured in this study. Black solid lines are raw data. Blue solid lines are fitting curves. Red dots are the intensity differences between raw data and fitting data at each binding energy point.

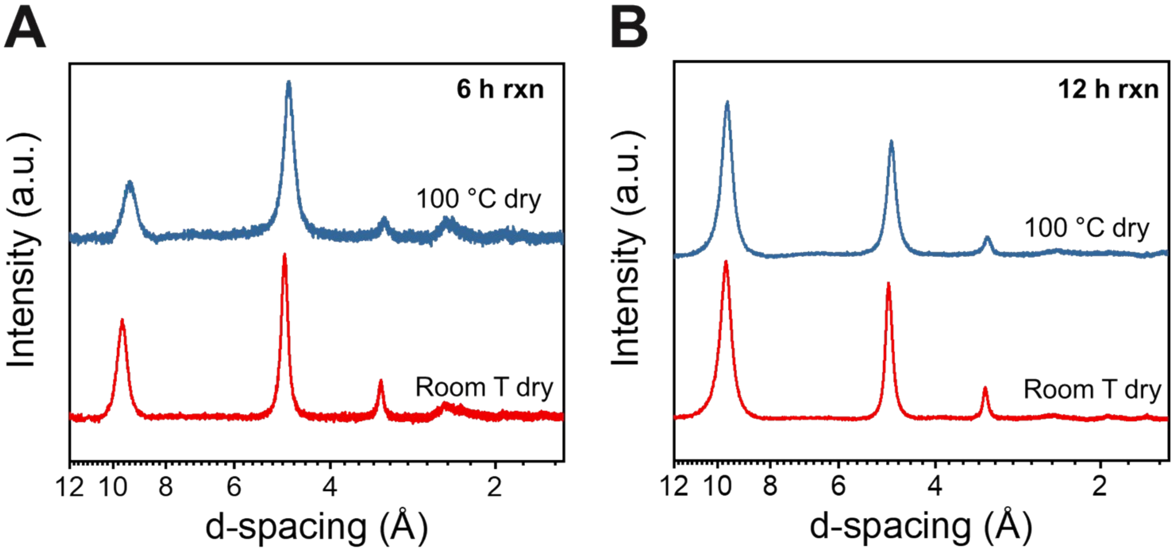

Fig. S3. Confirmation of todorokite formation in a sample prepared at pH 7–8 with 100 mM Mg^{2+}. The diffraction patterns of todorokite after (A) 6 hr reaction and (B) 12 hr reaction observed in both room temperature dried and 100 °C dried samples, providing evidence for the formation of todorokite.

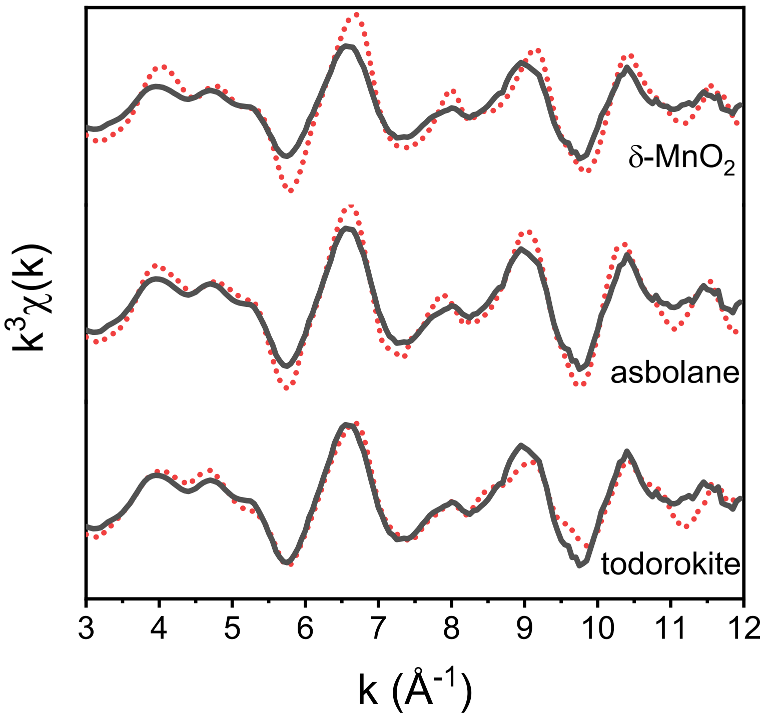

Fig. S4. Comparisons of extended X-ray absorption fine structure (EXAFS) of the synthesized todorokite with Mn oxides. The dotted lines represent the EXAFS spectra of reference Mn oxides, and the solid line represents the EXAFS spectrum of the synthesized todorokite.

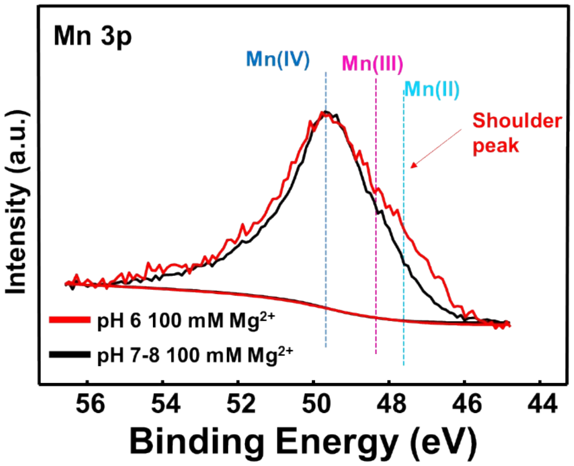

Fig. S5. Inclusion of Mn(II) in Mn oxides formed at pH 6. Overlapped high resolution X-ray photoelectron spectroscopy (XPS) of Mn 3p shows a shoulder peak at ~47.8 eV resulting from Mn(II) in the structure of Mn oxides.

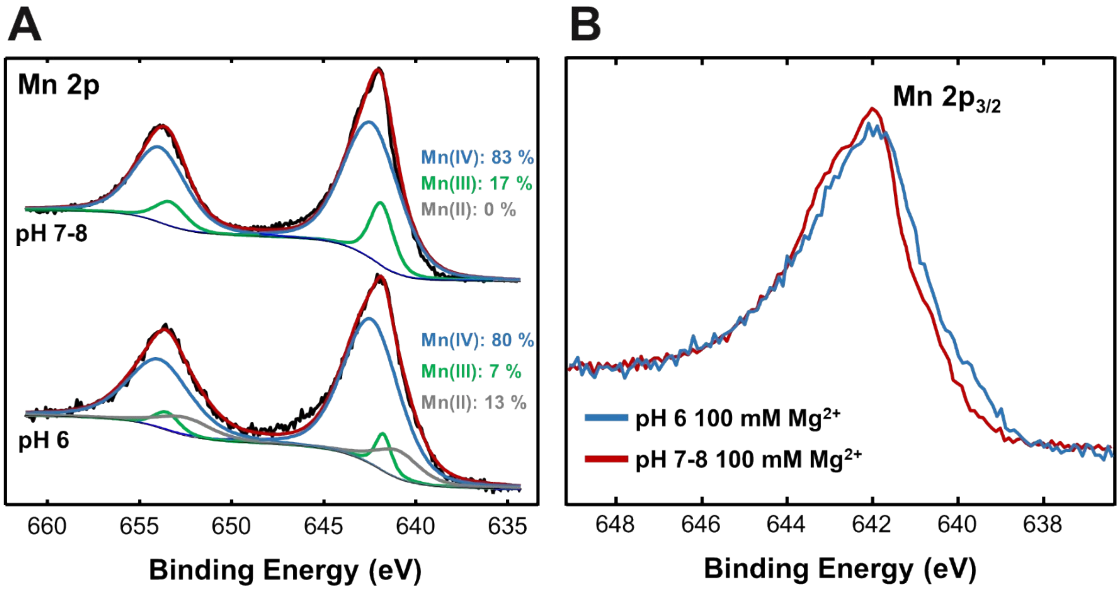

Fig. S6. Mn $2p_{3/2}$ spectra of Mn oxides prepared in the presence of Mg^{2+}. (A) The deconvolution of Mn $2p_{3/2}$ spectra of Mn oxides show the predominance of Mn(III) over Mn(II) in Mn oxides prepared at pH 7–8. (B) Overlapped high resolution X-ray photoelectron spectroscopy (XPS) of Mn $2p_{3/2}$ shows a shoulder peak at ~641.0 eV, resulting from Mn(II) in the structure of Mn oxides.

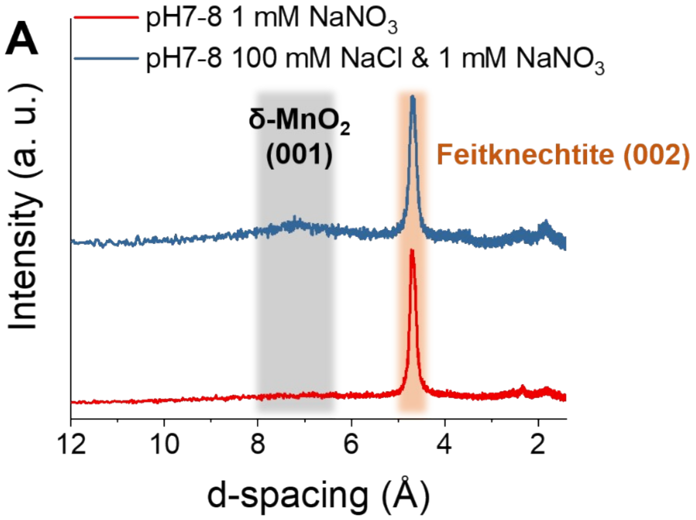

Fig. S7. The role of Mg^{2+} in the formation of todorokite. Without Mg^{2+} in solution, feitknechtite occurred instead of todorokite. (A) XRD spectra of Mn oxides samples obtained from photochemical oxidation of 100 μM Mn^{2+}(aq) by nitrate photolysis in the presence of 100 mM NaCl and 1 mM NaNO$_3$, and only 1 mM NaNO$_3$. (B) Crystalline structure of feitknechtite.

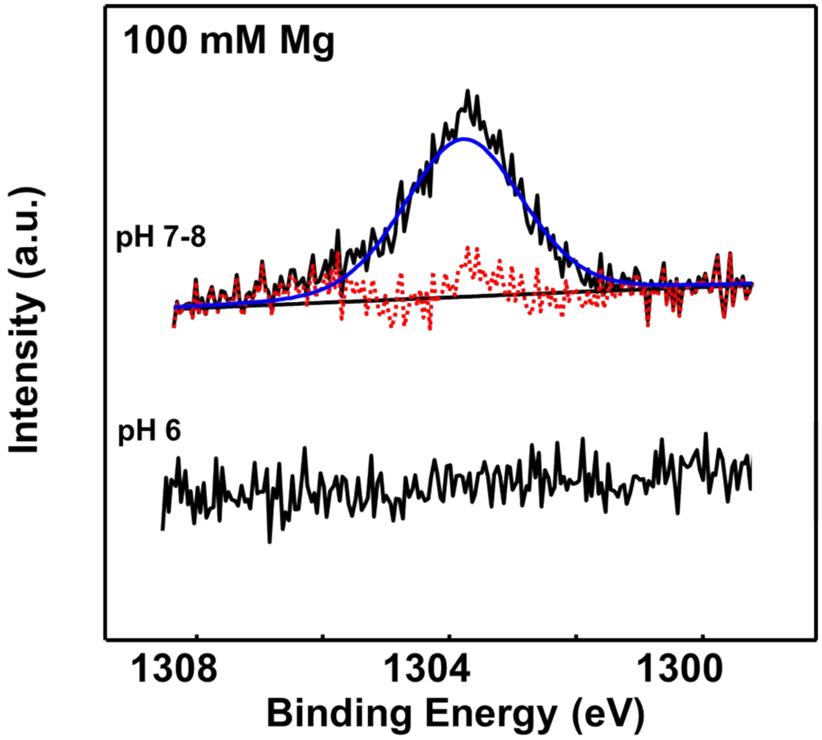

Fig. S8. High resolution XPS of Mg 1s. XPS spectra of samples from the photochemical oxidation of 100 μM Mn^{2+}(aq) in the presence of 100 mM Mg^{2+} and controlled pH conditions of pH 6 or pH 7–8. Mg^{2+} was observed in Mn oxides prepared at pH 7–8, but not at pH 6. Black lines are from raw data. Blue line is fitting curve. Red dots are from the intensity differences between raw data and fitting data at each binding energy value.

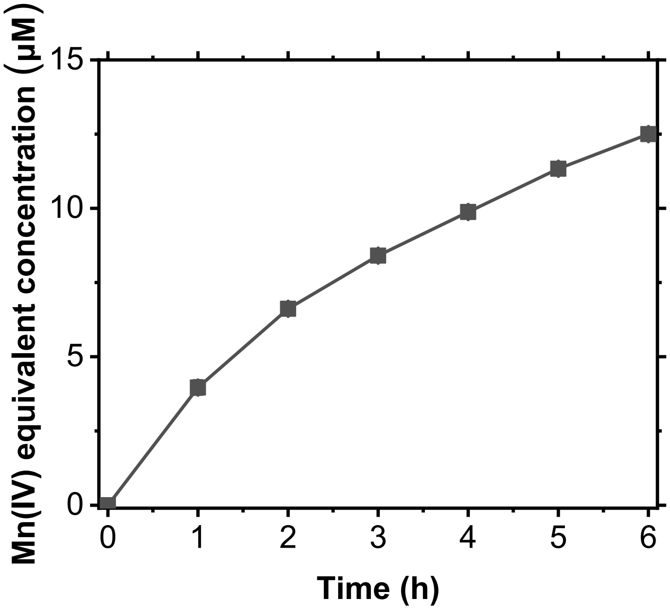

Fig. S9. Oxidation kinetics at initial pH 9 in the presence of 100 mM Mg^{2+}. Because of observed aggregates from vigorous stirring after adding 10 mM NaOH, the oxidation kinetics at pH 7–8 might be erroneous. Thus, instead of using pH 7–8, we measured the oxidation kinetics at initial pH 9, which shows homogeneously dispersed Mn oxides. We found the oxidation rate by linearizing the first 2 hrs (pH values were within 7–9 in the first 2 hrs) to represent the photochemical oxidation rates of Mn^{2+}(aq) at pH 7–8. The approximated oxidation rate of Mn^{2+}(aq) to Mn(IV) in the presence of Mg^{2+} is ~3.3 μM/h. The oxidation of Mn^{2+}(aq) is usually faster at higher pH. Thus, the approximated oxidation rate at initial pH 9 should be equal to or faster than that at pH 7–8. The data was obtained from duplicate experiments.

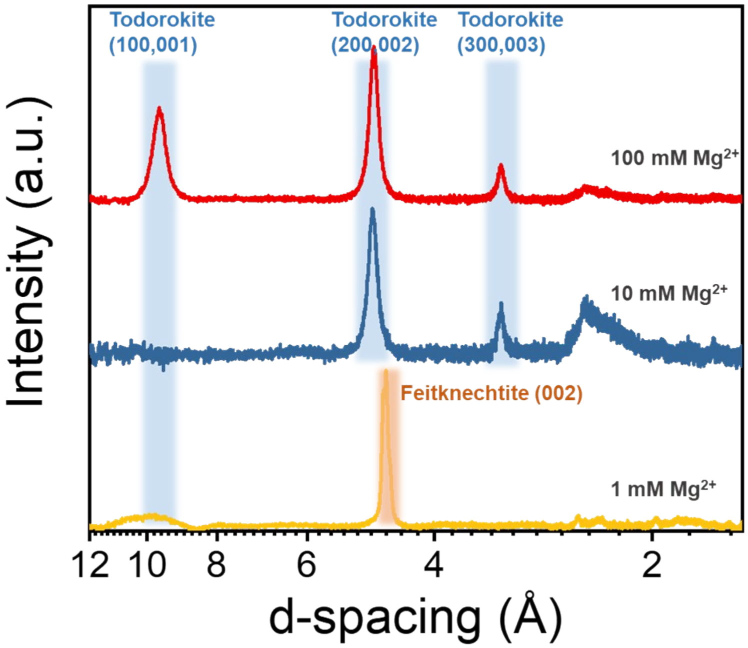

Fig. S10. The occurrence of feitknechtite under a limited concentration of $Mg(OH)^+$. When the amount of $Mg(OH)^+$ is limited in comparison to the Mn(III) generated from comproportionation, feitknechtite is formed at pH 7–8 with 1 mM Mg^{2+}. The solution containing higher concentration of Mg^{2+} has larger amount of $Mg(OH)^+$.than that in the solution containing lower concentration of Mg^{2+}. While some Mn(III) interacts with $Mg(OH)^+$ in the solution with 1 mM Mg^{2+}, the remaining Mn(III), which does not interact with $Mg(OH)^+$, might develop as feitknechtite.