Supporting Information for

Abiotic photomineralization and transformation of iron oxide nanominerals in aqueous systems

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13 Figures, 2 Tables and 16 Pages

Supporting tables

Table S1 Chemical compositions of the schwertmannite formed in the mixed solution of $FeSO_4$ (5.0 mmol L⁻¹) and NaNO₃ (100 mmol L⁻¹) with the initial pH of 6.0 under UV irradiation for different time periods in nitrogen atmosphere.

| Reaction time (h) | Final pH | Chemical formula | Fe (wt.%) | S (wt.%) | Fe/S (molar) |
|-------------------|----------|--|-----------|----------|--------------|
| 6 | 2.74 | Fe ₈ O ₈ (OH) _{5.59} (SO ₄) _{1.20} ·3.95H ₂ O | 44.46 | 3.82 | 6.64 |
| 12 | 2.68 | $Fe_8O_8(OH)_{5.47}(SO_4)_{1.27} \cdot 4.07H_2O$ | 51.84 | 4.70 | 6.30 |
| 24 | 2.60 | Fe ₈ O ₈ (OH) _{5.34} (SO ₄) _{1.33} ·4.70H ₂ O | 50.96 | 4.84 | 6.01 |
| 48 | 2.46 | $Fe_8O_8(OH)_{5.18}(SO_4)_{1.41}$ · 5.20H ₂ O | 50.17 | 5.05 | 5.67 |

Table S2 Chemical compositions of the schwertmannites formed in the mixed solution of $FeSO_4$ (5.0 mmol L⁻¹) and NaNO₃ (100 mmol L⁻¹) with different initial pHs under solar irradiation for 12 h in nitrogen atmosphere.

| Initial pH | Final pH | Chemical formula | Fe (wt.%) | S (wt.%) | Fe/S (molar) |
|------------|----------|--|-----------|----------|--------------|
| 3.0 | 2.45 | Fe ₈ O ₈ (OH) _{5.72} (SO ₄) _{1.14} ·4.33H ₂ O | 52.06 | 4.24 | 7.02 |
| 4.5 | 2.46 | Fe ₈ O ₈ (OH) _{5.88} (SO ₄) _{1.06} ·3.62H ₂ O | 53.15 | 4.02 | 7.55 |
| 6.0 | 2.43 | Fe ₈ O ₈ (OH) _{5.94} (SO ₄) _{1.03} ·3.14H ₂ O | 53.82 | 3.96 | 7.77 |

Supporting figures



Fig. S1 TEM images of the iron oxides formed in the mixed solutions of $FeSO_4$ (a)/FeCl₂ (b) (0.1 mmol L⁻¹) and NaNO₃ (0.2 mmol L⁻¹) with the initial pH of 6.0 under solar irradiation for 12 h in nitrogen atmosphere.



Fig. S2 Photos of the aqueous reaction systems of $FeSO_4$ (a)/ $FeCl_2$ (b) (5.0 mmol L⁻¹) and NaNO₃ (100 mmol L⁻¹) with the initial pH of 6.0 under UV, vis light and dark conditions for 6 h in nitrogen atmosphere.



Fig. S3 UV-vis absorption spectra of the solutions of FeSO₄, NaNO₃ and the mixed solution of FeSO₄ and NaNO₃.



Fig. S4 FTIR and Raman spectra of the iron oxides formed in the mixed solution of $FeSO_4$ (a, b)/FeCl₂ (c, d) (5.0 mmol L⁻¹) and NaNO₃ (100 mmol L⁻¹) with the initial pH of 6.0 under UV irradiation for different time periods.

As shown in Fig. S4b, the Raman bands at 715 and 420 cm⁻¹ are assigned to the v_4 and v_2 of SO₄^{2–}, respectively. The Raman bands at 550, 350 and 302 cm⁻¹ are assigned to the v_2 , v_4 and v_5 of Fe–O in schwertmannite, respectively.¹ As shown in Fig. S4d, Raman bands at 246 and 373 cm⁻¹ can be assigned to the characteristic peaks of lepidocrocite.²



Fig. S5 XPS broad scan of the schwertmannite formed in the mixed solution of $FeSO_4$ (5.0 mmol L^{-1}) and NaNO₃ (100 mmol L^{-1}) with the initial pH of 6.0 under UV irradiation for 48 h in nitrogen atmosphere.

Fig. S5 illustrates the XPS broad scan of the schwertmannite formed in the aqueous solution system of FeSO₄ (5.0 mmol L^{-1}) and NaNO₃ (100 mmol L^{-1}) with the initial pH of 6.0 under UV irradiation for 48 h in nitrogen atmosphere. The Fe/S molar ratio was calculated to be 6.4 from the XPS spectrum, and this ratio is in good agreement with that obtained by chemical analysis method.



Fig. S6 Photos of the aqueous reaction systems of $FeSO_4$ (5.0 mmol L⁻¹) and NaNO₃ at different concentrations under solar light irradiation for 6 h in nitrogen atmosphere.



Fig. S7 FTIR spectra of the iron oxides formed in the mixed solution of $FeSO_4$ (a)/FeCl₂ (b) (5.0 mmol L⁻¹) and NaNO₃ (100 mmol L⁻¹) with different initial pHs under solar irradiation for 12 h in nitrogen atmosphere.

Fig. S7a shows the FTIR spectra of the iron oxides formed in the mixed solution of FeSO₄ (5.0 mmol L⁻¹) and NaNO₃ (100 mmol L⁻¹) with different initial pHs. The absorption bands at 1118, 970 and 610 cm⁻¹ are due to the stretching vibrations of S–O, and the absorption bands at 690 and 466 cm⁻¹ are owing to the stretching vibrations of Fe–O.³ The absorption bands at 3420 and 1639 cm⁻¹ are attributed to the stretching and bending vibrations of crystal water and adsorbed water, respectively.⁴ Fig. S7b shows the FTIR spectra of the iron oxides formed in the mixed solution of FeCl₂ (5.0 mmol L⁻¹) and NaNO₃ (100 mmol L⁻¹) with different initial pHs. The absorption bands at 1150 and 1020 cm⁻¹, 750 and 470 cm⁻¹ are caused by the in-plane and out-plane bending vibrations of Fe–O–H in lepidocrocite, respectively.⁴ The absorption bands at 890 and 790 cm⁻¹ are attributed to the in-plane bending vibrations of Fe–OH–Fe in goethite.⁴ The absorption bands at 3423 and 1640 cm⁻¹ are assigned to the stretching and bending vibrations of crystal water and adsorbed water and adsorbed water, respectively.⁴



Fig. S8 Photos of the aqueous reaction systems of $FeSO_4$ (a)/FeCl₂ (b) (5.0 mmol L⁻¹) and NaNO₃ (100 mmol L⁻¹) with constant pH of 6.0 under solar light and dark conditions for 6 h in nitrogen atmosphere.



Fig. S9 XRD patterns (a) and the corresponding SEM images of the iron oxides formed in the mixed solution of $FeSO_4$ (b)/ $FeCl_2$ (c) (5.0 mmol L⁻¹) and $NaNO_3$ (100 mmol L⁻¹) with constant pH of 6.0 under solar irradiation for 12 h in nitrogen atmosphere.



Fig. S10 SEM images of the tranformation products of schwertmannite reacted with initial Fe^{2+} concentration of 1.00 mmol L⁻¹ for 0.5 h (a), 4 h (b) and 8 h (c), 2.33 mmol L⁻¹ for 0.5 h (d), 4 h (e) and 8 h (f) and 4.66 mmol L⁻¹ for 0.5 h (g), 4 h (h) and 8 h (i) at constant pH of 6.0.



Fig. S11 Concentration of NO_2^- in the mixed solution of $FeSO_4$ (0.1 mmol L⁻¹) and $NaNO_3$ (0.2 mmol L⁻¹) with the initial pH of 6.0 under UV irradiation for different time periods in nitrogen atmosphere.



Fig. S12 XRD patterns (a) and the corresponding TEM images of the schwertmannite formed in the mixed solution of FeSO₄ (0.1 mmol L^{-1}), NaNO₃ (0.2 mmol L^{-1}) and Na₂SO₄ (0.9 mmol L^{-1}) with the initial pH of 6.0 under UV (b) and solar (c) irradiation for 6 h.



Fig. S13 pH at different time points in the reaction system of $FeSO_4$ (5.0 mmol L⁻¹) and NaNO₃ (100 mmol L⁻¹) with initial pH of 6.0 under solar light in nitrogen atmosphere.

Supporting references

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