Electronic Supplementary Information

for

Nano-scale investigation of organic C sequestration and distribution on Fe oxides during ferrihydrite transformation: effect of Al-substitution

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S1. Details of experimental procedures

(1) XRD analysis

We calibrated ferrihydrite as the hkl phase using the partial or no known crystal structure (PONKCS) method.[1] We prepared ferrihydrite and then freeze-dried it to obtain the pure ferrihydrite powder sample, which was mixed with 33 wt% crystalline Al_2O_3 as the internal standard. Firstly, we fitted the pure ferrihydrite as the hkl-phase with fixed cell parameters (space group Pm-3m, a = 25 Å) and the peak intensities were free. Then, the powder XRD pattern of ferrihydrite with 33 wt% Al_2O_3 was fitted using the previously fitted pure ferrihydrite (now with fixed relative peak intensities) and a structure file for Al_2O_3 (space group R-3c). Based on the fitting results, the hkl-phase from ferrihydrite was determined to obtain a mass-calibrated hkl-phase (namely 'PONKCS phase') to be used in subsequent Rietveld fitting of the experimental samples. To verify the accuracy of the Rietveld quantitative analysis, the mixtures of known mass ratios of ferrihydrite, hematite and goethite, with 0, 30, 50, 70, or 100 wt% ferrihydrite, were analyzed. The results demonstrate that ferrihydrite can be well quantified in the mixtures with goethite or hematite (Fig. S9†).

(2) Surface charge density

Acid-base titration was performanced to determined the surface charges of pure ferrihydrite and Al-substituted ferrihydrite samples at different aging time. The pre-washed Fh and Al-Fh samples were analyzed at 25 °C using a circulating water bath to keep the temperature constant. The total volume was 50 mL. The concentrations of Fh and Al-Fh were 3 g L^{-1} and the background electrolyte was 10 mM $NaNO_3$. The glass vessel was purged with high-purity N_2 to eliminate the effect of CO_2. The 0.1 M NaOH was used as the titrant. The pH of Fh and Al-Fh suspensions were adjusted to pH 3.5 using 1 M HNO_3 before the titration, which was followed with 0.1 M NaOH titration until the pH reached 10.5 using an automated titration setup (Metrohm, 836 Titrando). The surface charge density (Q, coul g^{-1}) was calculated as follows,[2]

$$H_{ads} = C_a - C_b - [H^+] + [OH^-]$$

$$Q = F * H_{ads}/a$$

in which C_a (mol L^{-1}) and C_b (mol L^{-1}) are the total concentration of the acid and base added to the suspensions, respectively, and [H^+] and [OH^-] are the concentrations of H^+ and OH^-, respectively, H_{ads} (mol L^{-1}) is the amount of adsorbed protons, F is the Faraday constant (96490 Coul mol^{-1}), and a (g L^{-1}) is the solid concentration.

(3) Specific surface area (SSA)

The obtained wet pastes were washed and then freeze-dried for SSA measurement using the N_2 adsorption/desorption technique (Quantachrome, Autosorb^{-1}, USA) with the samples dried and degassed at 30 ℃ for 24 h.

S2. Additional figures

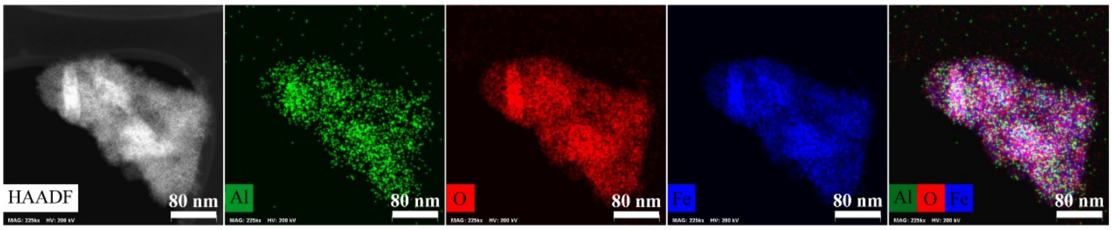


Fig. S1 STEM-HAADF images and EDS mapping for Al (green), O (red), Fe (blue), and the overlay of Al, O, and Fe for the Al-Fh treatment at 15 d.

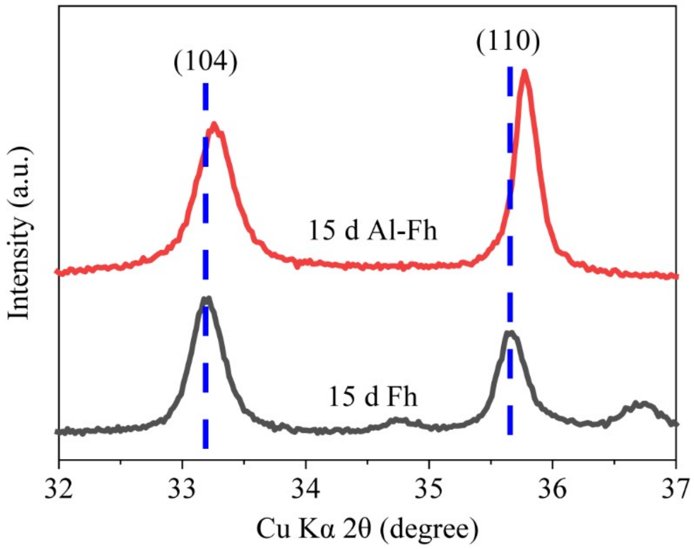
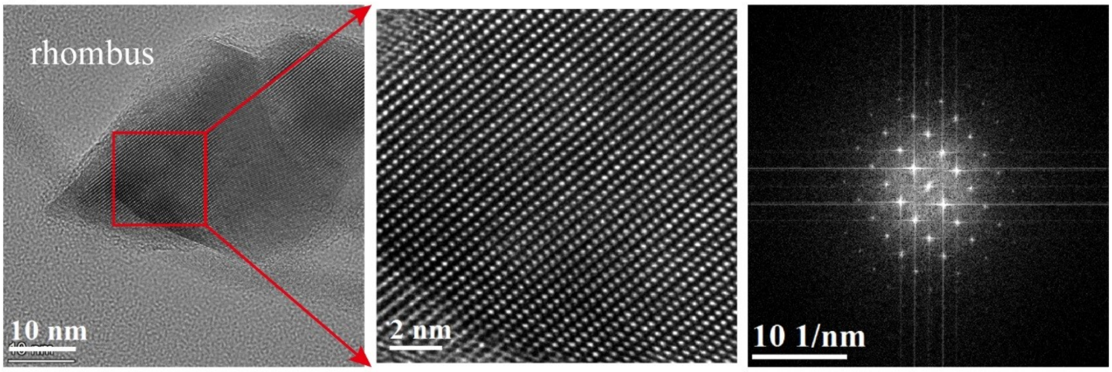
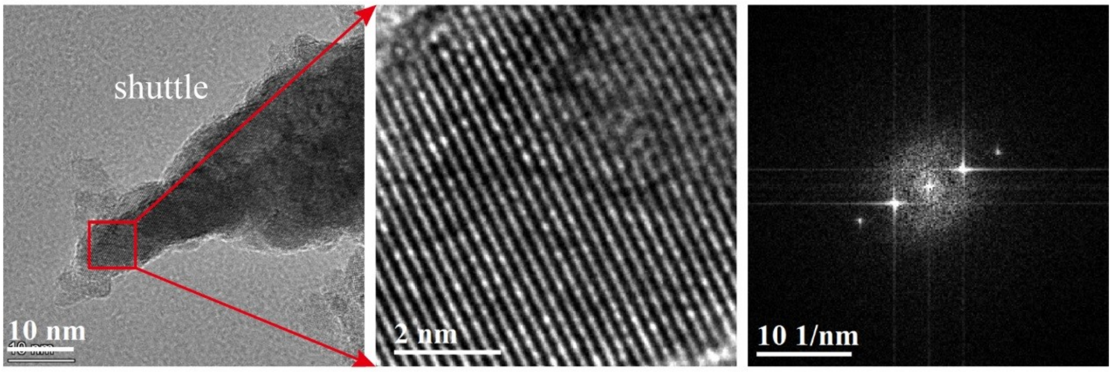


Fig. S2 The magnified XRD patterns of both Fh and Al-Fh treatments at 15 d in a 2θ range of 32-37°. The blue dotted lines are the positions of XRD peaks of the Fh treatment, showing the shifts of diffraction peaks for the Al-Fh treatment after 15 d.

(a) 15 d Fh



(b) 15 d Al-Fh



(c) 15 d Al-Fh

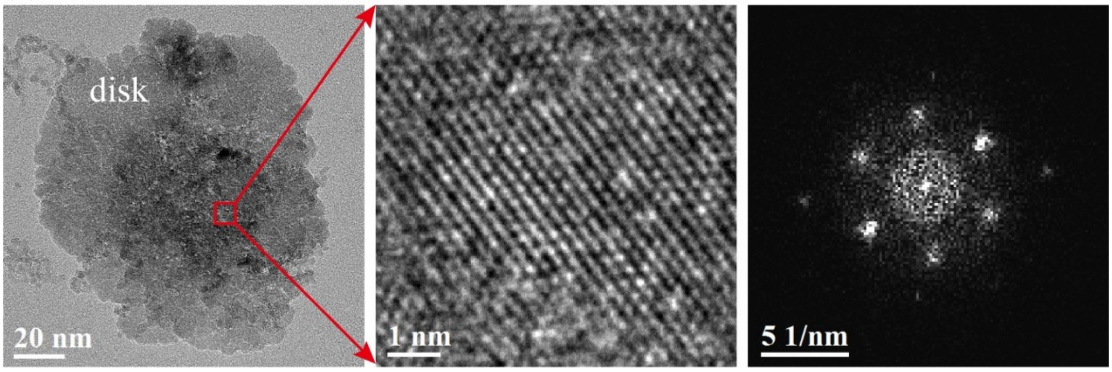
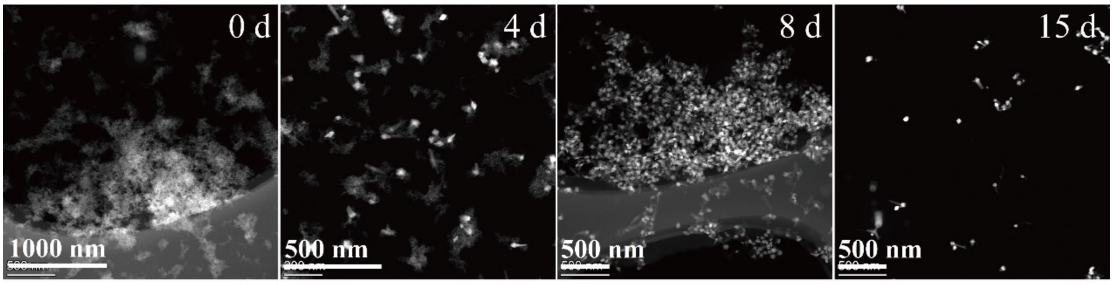


Fig. S3 The HRTEM images and fast Fourier transform (FFT) of the Fh and Al-Fh treatments after aging 15 d. (a) Fh treatment, (b) Al-Fh treatment with shuttle like particles, (c) Al-Fh treatment with disk like particles.

(a) Fh



(b) Al-Fh

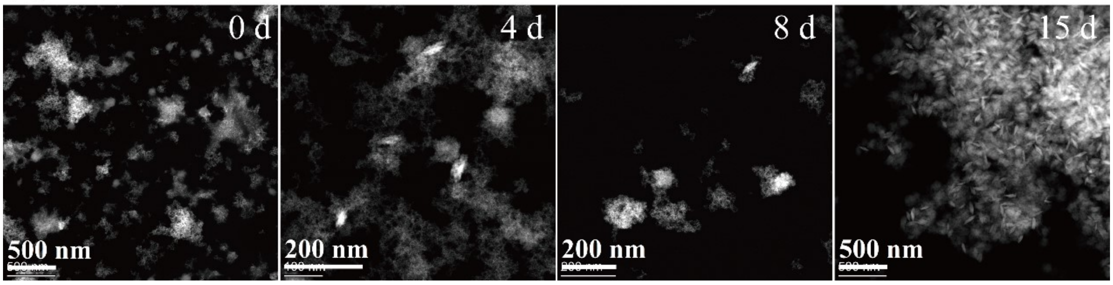


Fig. S4 Additional HAADF-STEM images of (a) Fh and (b) Al-Fh treatments at different transformation times with different magnifications.

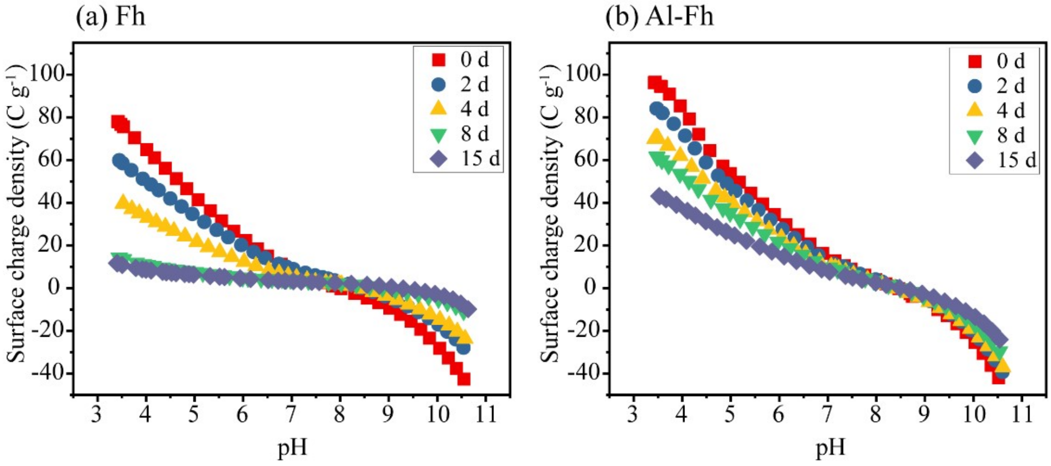


Fig. S5 Surface charge density (C g^{-1}) of (a) Fh and (b) Al-Fh treatments at different aging times as a function of titration pH.

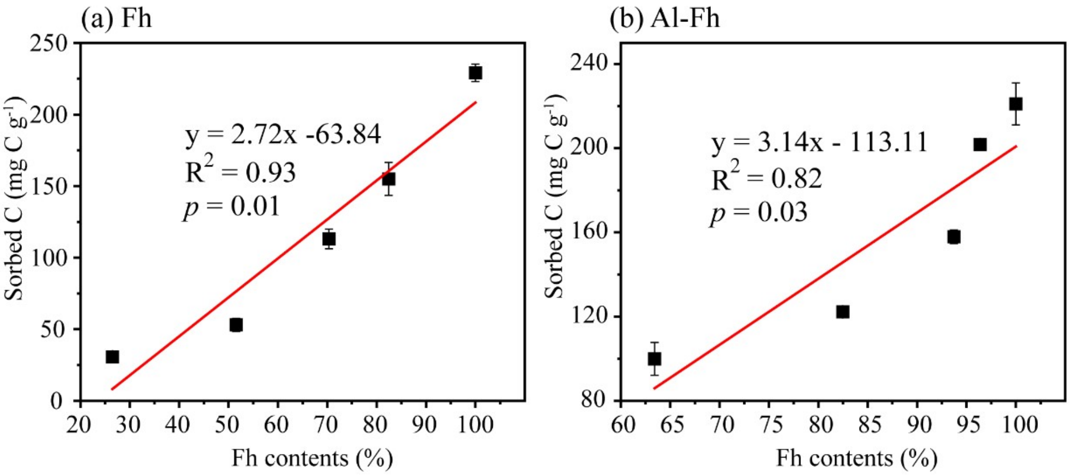
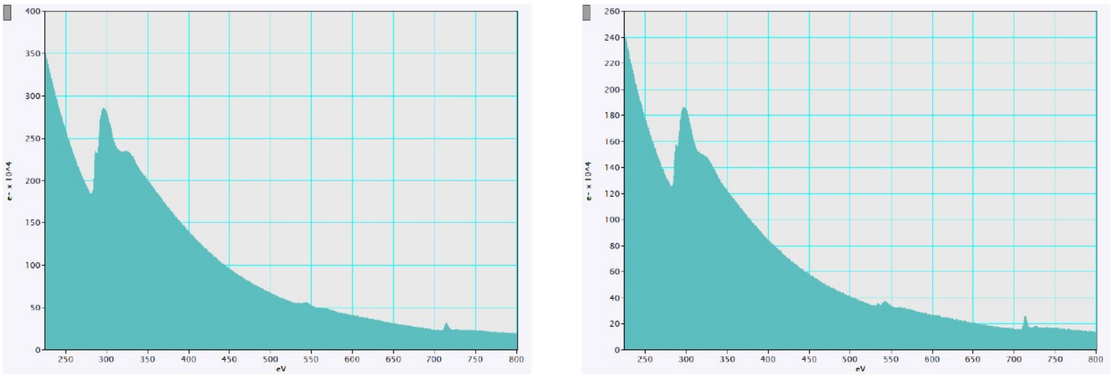
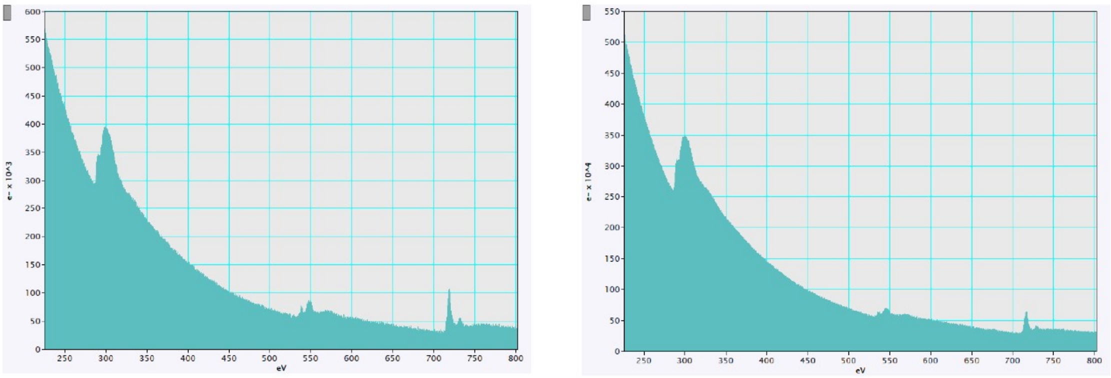


Fig. S6 The linear correlations between the maximum SRFA sorption capacity and the ferrihydrite contents of (a) Fh and (b) Al-Fh treatments at different aging times. The filled black squares are the experimental data and the red lines represent linear fits to the data.



(a) 8 d Fh

(b) 8 d Al-Fh



(c) 15 d Fh

(d) 15 d Al-Fh

Fig. S7 Original EELS spectra extracted from the raw data. (a) Fh treatment at 8 d, (b) Al-Fh treatment at 8 d, (c) Fh treatment at 15 d, and (d) Al-Fh treatment at 15 d.

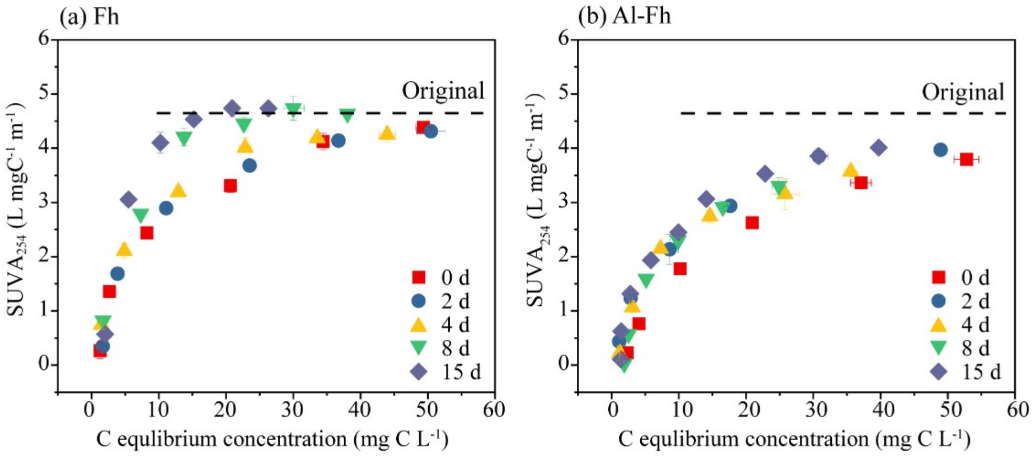


Fig. S8 SUVA_{254} values of the samples from the sorption isotherms of (a) Fh and (b) Al-Fh treatments at different aging times. "Original" denotes the SUVA_{254} value of the SRFA stock solution.

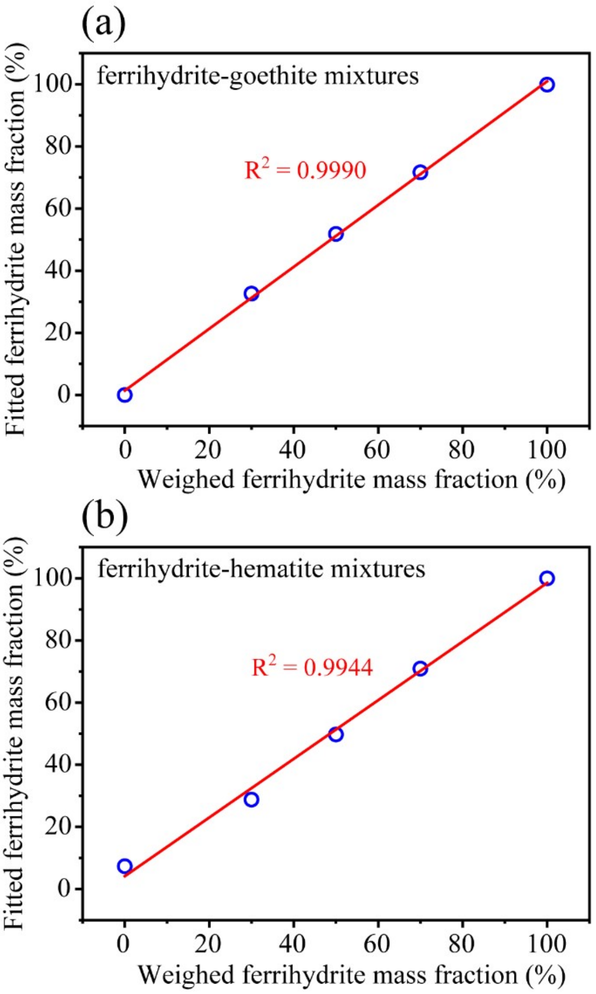


Fig. S9 Rietveld fitting of XRD results of (a) ferrihydrite-goethite and (b) ferrihydrite-hematite mixtures of known iron oxide mass fractions. The blue circles are the experimental data and the red lines represent the linear fits to the data.

S3. Supplementary tables

Table S1. The basic information of SRFA from IHSS[a].

Sample	Catgory No.	Elemental compositions (%(w/w))								Acidic functional groups (meq/g C)	
		H_2O	Ash	C	H	O	N	S	P	Carboxyl	Phenolic
SRFA	2S101F	16.9	0.58	52.34	4.36	42.98	0.67	0.46	0.004	11.17	2.84

[a]Data source: https://humic-substances.org

Table S2. The specific surface areas (SSA) of Fh and Al-Fh after aging 0, 4 and 15 d.

Samples	SSA (m^2/g)		
	0 d	4 d	15 d
Fh	199	154	50
Al-Fh	274	214	123

References

1 N. V. Y. Scarlett and I. C. Madsen, Quantification of phases with partial or no known crystal structures, *Powder Diffr.*, 2012, **21**, 278-284.

2 Y. Gao and A. Mucci, Acid base reactions, phosphate and arsenate complexation, and their competitive adsorption at the surface of goethite in 0.7 M NaCl solution, *Geochim. Cosmochim. Acta*, 2001, **65**, 2361-2378.