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

Supplementary materials

As(III) adsorption-oxidation behavior and mechanisms on Cr(VI)-incorporated schwertmannite

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Supplementary materials include 3 tables and 8 figures.

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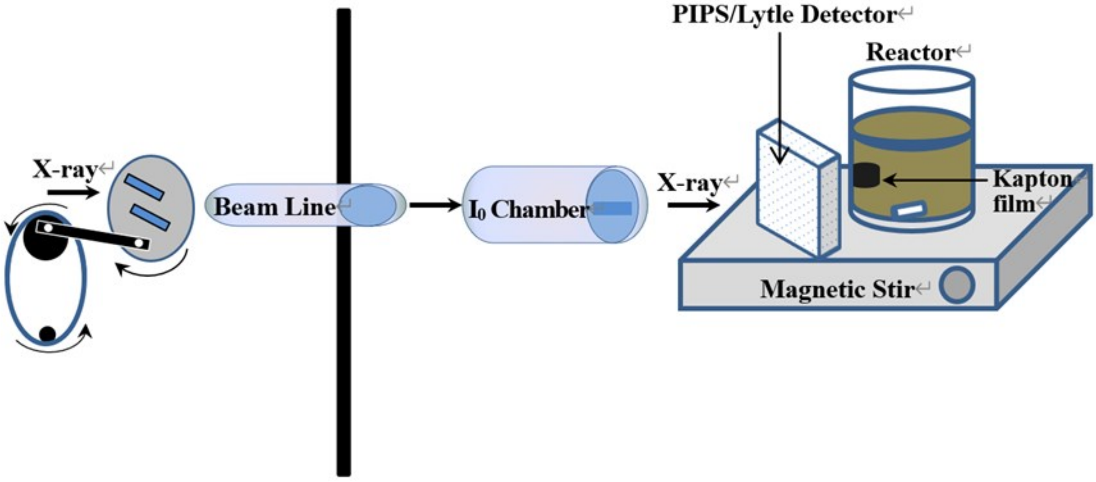
SI-1: The in-situ Q-XAS experimental settings



SI-2: Sample characterization

The synthesized samples were identified by XRD using a Bruker D8 Advance X-ray Diffractometer equipped with a LynxEye detector using Ni-filtered Cu Kα radiation (λ = 0.15418 nm) (Bruker AXS Gmbh, Karlsruhe, Germany). All XRD patterns were collected at a scan speed of 2°·min^{-1} from 10 to 70° operated at a tube voltage of 40 kV and a tube current of 40 mA. The FTIR spectra of products, making pellets with dried KBr (~1.25% sample weight), were measured over the 4000 - 400 cm^{-1} wavenumber range with a resolution of 4 cm^{-1} against the air background (Bruker VERTEX 70). 128 scans were collected for each sample, and the spectral data were acquired, processed, and analyzed using the OPUS program. The specific surface areas (SSA) of the samples were measured using N_2 adsorption-desorption at 77 K (ASAP 2460, micromeritics) after degassing 0.1 - 0.2 g samples at 80 °C for 3 h under vacuum. In addition, a small amount of synthesized samples was deposited on a conductive plastic, then plated using a sputtering apparatus and observed by scanning electron microscopy (SU8000) at an accelerating voltage of 10 or 20 kV. Furthermore, the different As and Cr valence proportion of some selected kinetic samples were determined using the LCF analysis of As and Cr K-edge XAS. The spectra were collected between 11.67 and 12.46 keV for As and between 5.796 and 6.588 keV for Cr, respectively, using a double crystal monochromator Si(111) in fluorescence mode at the beamline 1W2B of the BSRF. All spectra were processed using the Athena program.

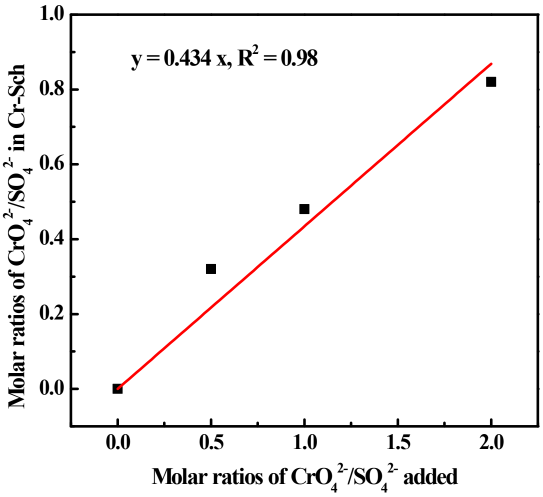


Fig. S1. The correlation analysis between the initial molar ratios of CrO_4^{2-}/SO_4^{2-} and the final molar ratios of CrO_4^{2-}/SO_4^{2-} in Cr(VI)-incorporated schwertmannite samples.

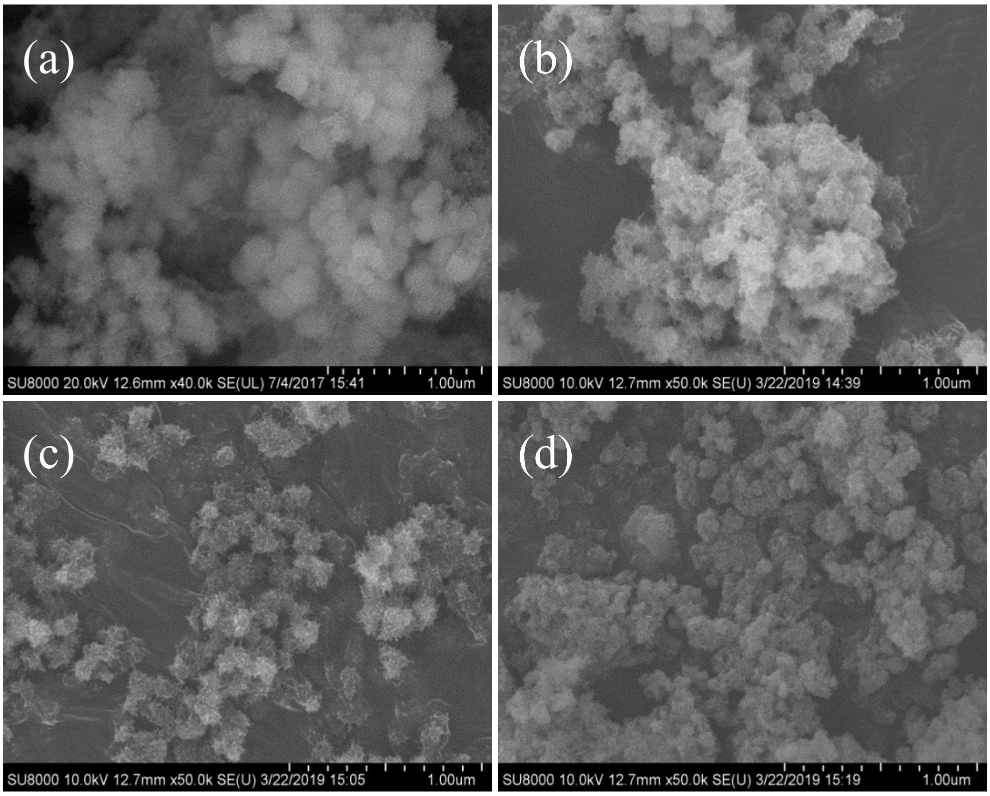


Fig. S2. The SEM images of Cr(VI)-incorporated schwertmannite samples obtained from Fe^{3+} hydrolysis in the presence of different molar ratios of CrO_4^{2-}/SO_4^{2-} (a: $CrO_4^{2-}/SO_4^{2-} = 0$; b: $CrO_4^{2-}/SO_4^{2-} = 0.5$; c: $CrO_4^{2-}/SO_4^{2-} = 1$; d: $CrO_4^{2-}/SO_4^{2-} = 2$).

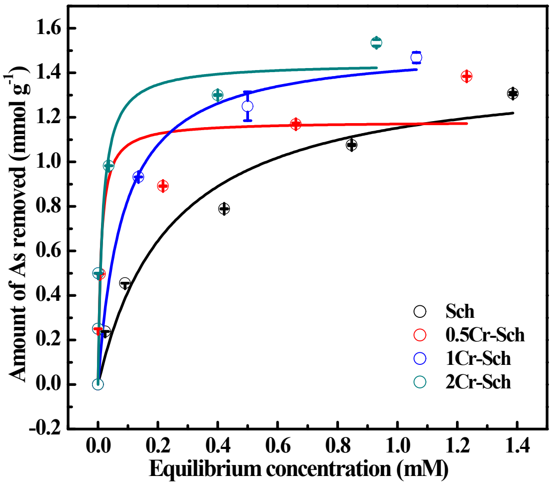


Fig. S3. As(III) adsorption-oxidation isotherms on Cr(VI)-incorporated schwertmannite samples at pH 5 and 0.05 M $NaNO_3$ fitted with the Langmuir equation.

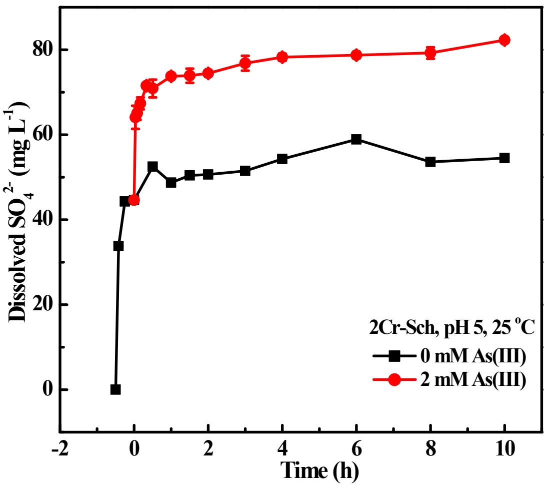


Fig. S4. The concentration of dissolved SO_4^{2-} during the reaction of 2 g·L^{-1} Cr(VI)-incorporated schwertmannite samples with 0 mM or 2 mM As(III) at pH 5 and 25 ºC. The addition of As(III) solution was set as the start point of reaction (*i.e.*, 0 h).

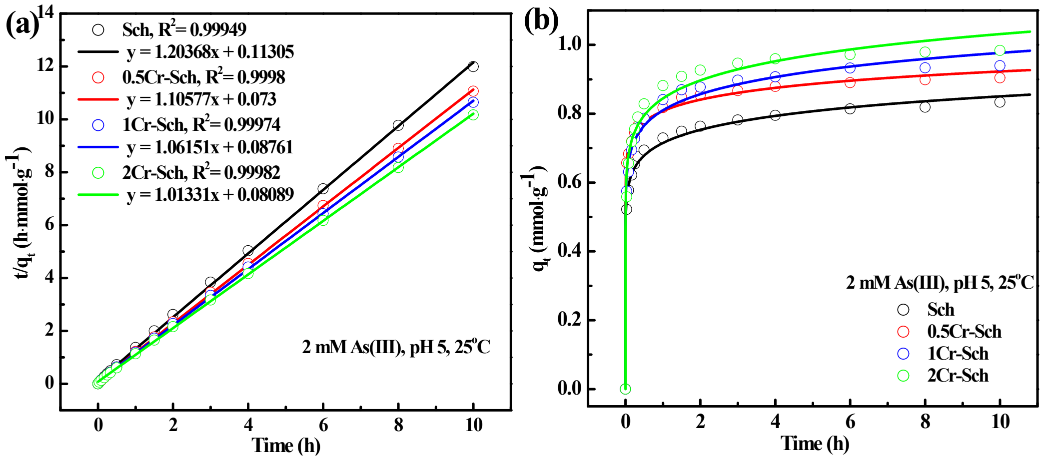


Fig. S5. Kinetics of 2 mM As(III) adsorption on Cr(VI)-incorporated schwertmannite at pH 5 and 25 ºC fitted using the second-order kinetic equation (a) and the power function (b) (solid line). The fitted results are summarized in Table S2.

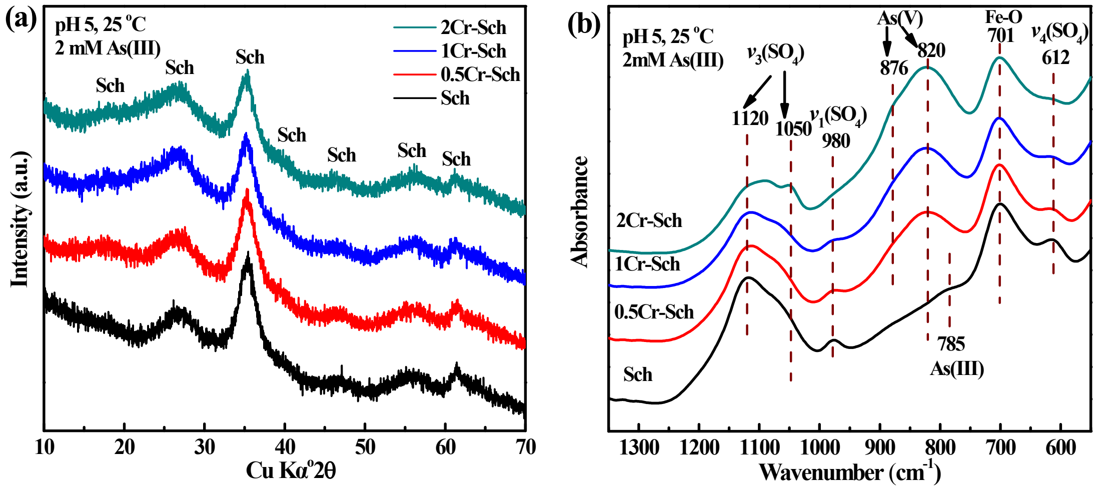


Fig. S6. The XRD patterns (a) and FTIR spectra (b) of finial solid products after the reaction of 2 mM As(III) with 2 g·L^{-1} Cr(VI)-incorporated schwertmannite at pH 5 and 25 ºC.

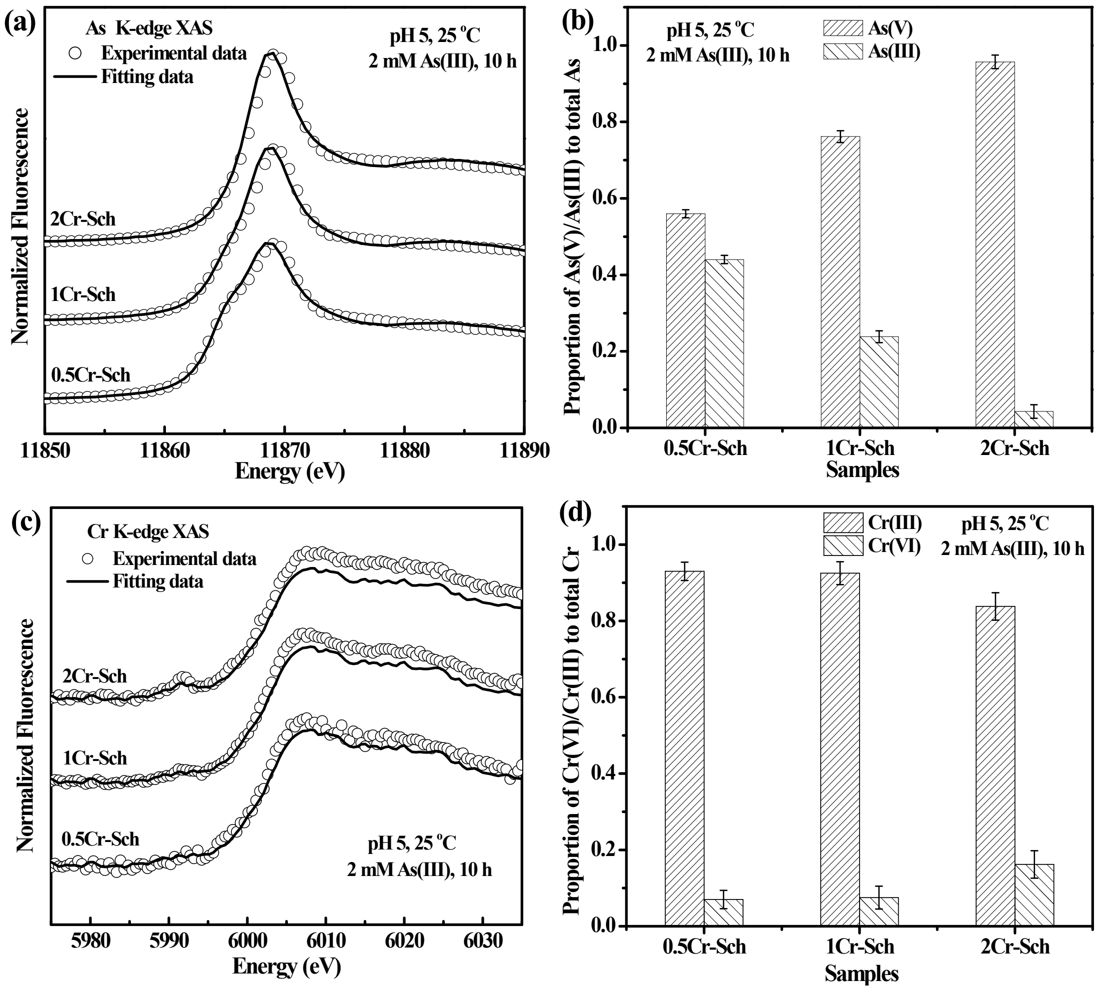


Fig. S7. The selected As or Cr K-edge XAS spectra of finial products (a and c) and the obtained proportion of As(III) and As(V) or Cr(VI) and Cr(III) by the linear combination fitting (LCF) analysis (b and d) from 2 g·L^{-1} Cr(VI)-incorporated schwertmannite with 2 mM As(III) at pH 5 and 25 ºC.

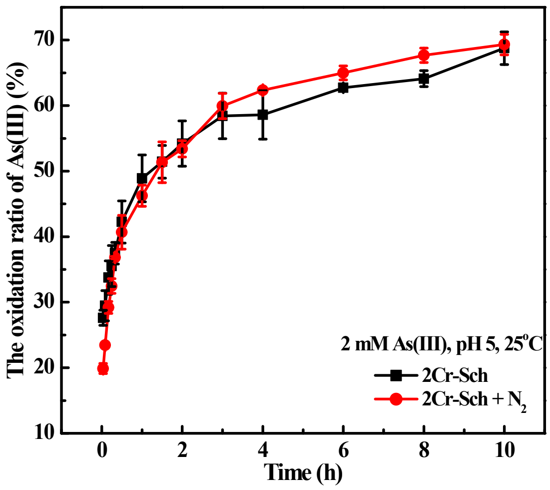


Fig. S8. The oxidation ratio of As(III) during the reaction of 2 g·L^{-1} Cr(VI)-incorporated schwertmannite samples with 2 mM As(III) at pH 5 and 25 °C in air or N$_2$ atmosphere.

Table S1. The fitted parameters for As(III) adsorption-oxidation isotherms with Langmuir equation at pH 5 and 0.05 M $NaNO_3$. Langmuir equation is described as $Q_e = q_m K C_e/(1 + K C_e)$, where Q_e (mmol/g) is the amount of As adsorbed on per unit mass, C_e ($mmol \cdot L^{-1}$) is As equilibrium concentrations, q_m (mmol/g) is As adsorption capacity, and K (L/mg) is a Langmuir constant[1].

Samples	Langmiur		
	q_{max} ($mmol \cdot g^{-1}$)	K ($L \cdot mg^{-1}$)	R^2
Sch	1.43	4.09	0.9681
0.5Cr-Sch	1.18	101.15	0.8890
1Cr-Sch	1.53	11.95	0.8210
2Cr-Sch	1.44	68.91	0.8354

Table S2. The fitted results of As(III) adsorption kinetics on Cr(VI)-incorporated schwertmannite at pH 5 and 25 ºC with the pseudo-second-order kinetic equation and the power function.

Sample	pseudo-second-order kinetic[A]			power function[B]			
	K_2	q_e ($mmol\cdot g^{-1}$)	R^2	a	b	K	R^2
Sch	12.82	0.83	0.9995	0.715	0.075	0.054	0.9732
0.5Cr-Sch	16.75	0.90	0.9998	0.808	0.058	0.047	0.9781
1Cr-Sch	12.86	0.94	0.9997	0.900	0.081	0.066	0.9528
2Cr-Sch	12.69	0.99	0.9998	0.844	0.087	0.073	0.9325

[A] The pseudo-second-order kinetic equation: $t/q_t=1/(K_2q_e^2)+(1/q_e)*t$, where q_t is the As adsorption amount at a given time ($mmol\cdot g^{-1}$), K_2 is the rate constant of adsorption ($g\cdot mmol^{-1}\cdot h^{-1}$); q_e is the As adsorption amount at equilibrium ($mmol\cdot g^{-1}$)[2]; [B] the power function: $q_t = a*t^b$, where q_t is the As adsorption amount at a given time ($mmol\cdot g^{-1}$), a and b are constants with b <1. a*b (K) is also a constant, being the specific adsorption rate at unit time, that is, when t =1[3].

References

1. Y. Liao, J. Liang and L. Zhou, Adsorptive removal of As(III) by biogenic schwertmannite from simulated As-contaminated groundwater, *Chemosphere*, 2011, **83**, 295-301.
2. S. Liao, X. M. Wang, H. Yin, J. E. Post, Y. P. Yan, W. F. Tan, Q. Y. Huang, F. Liu and X. H. Feng, Effects of Al substitution on local structure and morphology of lepidocrocite and its phosphate adsorption kinetics, *Geochim. Cosmochim. Acta*, 2020, **276**, 109-121.
3. X. M. Wang, Z. M. Wang, D. Peak, Y. D. Tang, X. H. Feng and M. Q. Zhu, Quantification of coexisting inner- and outer-sphere complexation of sulfate on hematite surfaces, *ACS Earth Space Chem.*, 2018, **2**, 387-398.