Supporting Information

Cr(III)-Incorporated Fe(III) Hydroxides for Enhanced Redox Conversion of As(III) and Cr(VI) in Acidic Solution

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Section S1 Measurement of As species in solution by IC-HG-AFS

In this experiment, the total concentration of arsenic in an aqueous solution was analyzed using a hydride generation atomic fluorescence photometer (HG-AFS, RGF-6300, Bohui, China) with a determination limit of 0.01 μ g/L¹. The determining condition for the instrument was used to maintain the argon (Ar) gas flow rate at 400 mL·min⁻¹ as carrier gas and 800 mL·min⁻¹ as the shielded gas, with 280 V negative pressure. For total As analysis, the mobile phase was a mixture of 5% dilute hydrochloric acid, and pumped for hydride generation of volatile arsines. When detecting the concentration of total As, 2% thiourea and 5% concentrated hydrochloride were added into solutions as sample pretreatment.

The As(III) and As(V) species in an aqueous solution were detected using ion chromatography-hydride generation-atomic fluorescence spectrometry (IC-HG-AFS, ICS2100, Thermo Fisher, USA). Here, As(III) and As(V) were separated and quantified using PRP-X100 chromatographic column (250 mm \times 4.1 mm, 10 µm, Hamilton, Switzerland) by maintaining 1.0 mL·min⁻¹ flow rate of mixed 5 mM Na₂HPO₄ and 30 mM NaH₂PO₄ (pH = 6.0), and 25 µL injection volume was used. The column temperature was maintained at 25°C during the IC measurement. The mobile phase was a mixture of 5% dilute hydrochloric acid as carrier solution and the reducing agent (2% thiourea and 0.5% sodium hydroxide), and pumped for hydride generation of volatile arsines. Finally, the speciation of As(III) and As(V) was analyzed through Bohui Co., LTD software.

Section S2 Calculation of coupled As(III)-Cr(VI) redox conversion ratio

To evaluate the dominate mechanism for redox conversion of As(III) and Cr(VI) by Crincorporated Fe hydroxides, As and Cr species in aqueous solution and solid phase were analyzed after Fe8Cr2 reaction with 150 μ M As(III)+150 μ M Cr(VI) for 24 h. As shown in Eq. (1) of the main paper, the rate of As(III) oxidized to As(V) over Cr(VI) reduced to Cr(III) could be described by Eq. (S1). The surface adsorbed As(V) could be calculated by Eq. (S2), based on XPS measurements for solids and IC-HG-AFS measurements for aqueous As removal.

Redox ratio =
$$\frac{As(V)_{produced}}{Cr(III)_{produced}} = \frac{As(V)_{aq} + As(V)_{ad}}{Cr(III)_{aq} + Cr(III)_{ad}}$$
 (S1)

$$As(V)_{ad} = As_{ad} \times \alpha_{As(V)} = (As_{init} - As_{aq}) \times \alpha_{As(V)}$$
(S2)

As(V)_{aq} — the As(V) mass detected in aqueous solution after reaction (1.74 µmol); As(V)_{ad} — the As(V) mass adsorbed on Fe8Cr2 surface (3.55 µmol). Cr(III)_{aq} — the Cr(III) mass in aqueous solution (2.02 µmol); As_{ad} — the total As mass adsorbed on Fe8Cr2 surface (4.12 µmol); $\alpha_{As(V)}$ — the percentage of As as As(V) detected by XPS (86.2%); As_{init} — the initial mass of As(III) in aqueous solution (6 µmol); As_{aq} — the total As mass (As(III)+As(V)) in aqueous solution (1.88 µmol).

The adsorption of $Cr(III)_{ad}$ produced by Cr(VI) reduction on solid phase should equal to the amounts of total surface Cr(III) calculated by XPS results $(Cr(III)_{sur})$ minus the initial Cr(III)incorporated on Fe8Cr2 surface $(Cr(III)_{sur-incorp})$, as shown in Eq. (S3). To calculate $Cr(III)_{sur$ $incorp}$, we assume that Fe8Cr2 is a spherical nanoparticle (with the radius of *R*, being 2-4 nm considering the standard deviation, Fig. S5 and Table 2) and that Cr(III) is uniformly distributed in the coprecipitation. The XPS detected depth may affect the percentage of Cr(III) on solid phase, with the penetration depth of XPS considered (*d*, being 1-2 nm considering the energy used, Fig. S5 and Table 2), the structurally incorporated Cr(III) detected by XPS (Cr(III)_{sur-incorp}) in the surface layer is calculated according to Eq. (S4). Finally, the total Cr(III) in the surface layer (Cr(III)_{sur}) was calculated using the surface adsorbed total Cr (Cr_{ad}, calculated as the aqueous Cr concentration change before and after reaction), the structurally incorporated Cr(III) detected by XPS (Cr(III)_{sur-incorp}), and the percentage of As detected as As(III) by XPS, as shown in Eq. (S5).

$$Cr(III)_{ad} = Cr(III)_{sur} - Cr(III)_{sur-incorp}$$
 (S3)

$$\operatorname{Cr}(\operatorname{III})_{\text{sur-incorp}} = \operatorname{Cr}(\operatorname{III})_{\text{incorp}} \times \beta_{\text{XPS}} = \operatorname{Cr}(\operatorname{III})_{\text{incorp}} \times (1 - \frac{(R-d)^3}{R^3})$$
(S4)

$$Cr(III)_{sur} = (Cr_{ad} + Cr(III)_{sur-incorp}) \times \alpha_{Cr(III)} = (Cr_{init} - Cr_{aq} + Cr(III)_{sur-incorp}) \times \alpha_{Cr(III)}$$
(S5)

Cr(III)_{incorp} ——initially incorporated Cr(III) mass on Fe8Cr2 (3.56 µmol in Table 1); β_{XPS} —— the percentage of Fe8Cr2 volume detected by XPS (%), shown as the brown ring in Fig. S5;

Cr_{ad} —— the total Cr mass adsorbed on Fe8Cr2 surface (2.25 µmol);

 $\alpha_{Cr(III)}$ —— the percentage of Cr as Cr(VI) detected by XPS (82.3%);

Cr_{init} —— the initial mass of Cr(VI) in aqueous solution (6 µmol);

 Cr_{aq} —— the total Cr mass (Cr(VI)+Cr(III)) in aqueous solution (3.75 µmol).

Section S3 Determination of involved free radicals

Before the experiment, Fe8Cr2 hydroxides were sonicated for 15 min to be uniformly dispersed. The preparation of reacted solution for 'OH detected by EPR was as following orders: (1) added 900 μ L 10 mM Cr(VI) stock solution; (2) 600 μ L 2.5 mM NaCl (pH = 3.0 \pm 0.2) as background electrolyte was added and mixed; (3) 600 μ L Fe8Cr2 hydroxides was added and mixed; (4) finally, 900 μ L 10 mM As(III) stock solution was added and mixed. The total concentrated volume was 3 mL. After 2 and 5 min reaction, the solution was immediately filtered using centrifugal filter units, and then detected by EPR.

To detect O_2^{-} by EPR, methanol should be captured in a concentrated system instead of ultrapure water. The preparation of reacted solution for O_2^{-} detected by EPR was as follows orders: (1) added 18 µL 500 mM Cr(VI) stock solution; (2) 6 µL 250 mM NaCl (pH = 3.0 ± 0.2) as background electrolyte was added and mixed; (3) 32 µL concentrated Fe8Cr2 hydroxides was added and mixed; (4) 18 µL 500 mM As(III) stock solution was added and mixed; (5) finally, 2926 µL methanol (pH adjusted to 3.0 ± 0.2) was added and mixed. The total concentrated volume was 3 mL. After reacting for 2 or 5 min, the solution was immediately filtered using centrifugal filter units, and then detected by EPR.

Section S4 The XPS spectra of O 1s before and after the reaction

In the O 1s spectrum, the binding energies can be deconvoluted into three peaks as follows: metal oxide (M-O) at peaks of 529.4-530.7 eV, hydroxyl bonded to metal (M-OH) at peaks of 530.6-531.4 eV, and adsorbed H₂O at peaks of 532.4-532.8 eV, respectively ². Besides, M-O and M-OH peaks were also represented as the lattice oxygen atoms (O_L) and the adsorbed oxygen atoms (O_A) from –OH, respectively ³. After reaction with the two contaminants, the percentage of M-OH increased from 42.0% to 48.0%, which indicates that the immobility of As(III) and Cr(VI) is favorable. On the other hand, the percent fractions of H₂O increased after Fe8Cr2 reacted with the two contaminants due to the complexation between M-OH and As(III), as well as between M-OH and Cr(VI). Thus, As(III) and Cr(VI) can also be immobilized through surface complexation on the Cr-incorporated Fe hydroxides surface.



Fig. S1 The kinetic experiment of total As/Cr removal by pure or Cr-incorporated Fe hydroxides. As(III): 150 μ M; Cr(VI): 150 μ M; pH = 3.0 \pm 0.2; reaction time: 0, 120, 360, and 1440 min.



Fig. S2 Band gaps of pure or Cr-incorporated Fe hydroxides at $pH = 3.0 \pm 0.2$ with duplicate measurements.



Fig. S3 XPS spectra of O 1s (a) before and (b) after reacting with Fe8Cr2. As(III): 150 μ M; Cr(VI): 150 μ M; pH = 3.0 \pm 0.2; reaction time: 24 h.



Fig. S4 XPS spectra of Fe 2p (Fe $2p_{3/2}$ at 711.2 and Fe $2p_{1/2}$ at 724.8 eV of Fe(III)) regions before and after reacting with Fe8Cr2. As(III): 150 μ M; Cr(VI): 150 μ M; pH = 3.0 \pm 0.2; reaction time: 24 h.



Fig. S5 The schematic of Fe8Cr2 surface detected depth and volume by XPS.

References

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