Electronic Supplementary Information

For

Low Temperature Synthesized Ultrathin $\gamma$-Fe$_2$O$_3$ Nanosheets Show Similar Adsorption Behavior for As(III) and As(V)

Rui Liu, a Jing-Fu Liu, a,b Li-Qiang Zhang, c Jie-Fang Sun, a and Gui-Bin Jiang a

a State Key Laboratory of Environmental Chemistry and Ecotoxicology, Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences, Beijing 100085, China.

b Institute of Environment and Health, Jianghan University, Hubei Province, Wuhan 430056, China

c State Key Laboratory of Heavy Oil Processing and Department of Materials Science and Engineering, China University of Petroleum, Beijing 102249, China

E-mail: jfliu@rcees.ac.cn
S1. Experiment Section

S 1.1 Materials and Chemicals.

Triton X-114 (TX-114) was purchased from Acros Organics (Geel, Belgium). NaAsO₂, Na₂HAsO₄·7H₂O, FeCl₃, Na₃PO₄, NaCl, HNO₃, and KOH were supplied by Sinopharm Chemical Reagent Co. (Beijing, China). KBH₄ was purchased from Jinke Chemical Research Institute (Tianjin, China). All the chemicals were of at least analytic grade. Ultrapure water (Millipore, Bedford, MA) was used throughout this study.

S 1.2 Characterizations

The crystal structure was determined by X-ray diffraction (XRD) analysis, which was performed with an X’ pert PRO instrument (PANalytical) using Cu Kα radiation (λ = 0.15418 nm). The chemical state was probed by X-ray photoelectron spectroscopy (XPS) analysis on AXIS ULTRADLD. For XRD analysis, samples were freeze-dried at -55 °C in high vacuum, the resulting blank/brown powder was place on Si wafers with high index facet to form a thin layer. The XPS samples were prepared by the same method for XRD analysis, but the separated black slurry was dipped on Si wafer directly, freeze-dried at -55 °C and stored at high vacuum, and the total air exposure time was less than 1 hour to suppress O₂ induced oxidation. The morphology of NSs was observed by high resolution transmission electron microscopy (HRTEM) and field emission scanning electron microscopy (FESEM). HRTEM analysis was fulfilled on a Tecnai G2 F-20(_FEI) HRTEM, the species were prepared by loading 3 μL aliquots of the aqueous sample onto ultra-thin amorphous carbon film-coated copper grid sample holders, and excess water was removed quickly with filter paper. FESEM was conducted on SU-8020 (Hitachi), the species were prepared by loading 10.0 μL aliquots of the aqueous sample onto Si wafer, after stored in 4oC for 30 min, excess water was removed quickly with filter paper. Besides HRTEM and XRD, Raman spectra was also utilized to determine the crystal structure of synthesized nanosheets, and for the enhancing the weak Raman signal, Ag nanoporous film was utilized as Raman enhancement substrate. The sample was prepared by dip 10 uL wet precipitate on Ag nanoporous film (Figure S4). ¹ 532 nm laser was employed as the excitation source, the laser

S2/24
power was maintained at about 50 uW at sample to suppress the photo damage/photo induced crystal structure change, the total accumulation time was 30s ×10. The FTIR measurements were performed using a Thermo-Nicolet Nexus 6700 FTIR spectrometer, samples for FTIR determination were ground with special grade KBr in an agate mortar.

S 1.3 X-ray Adsorption Spectra

The As K-edge EXAFS spectra were collected at beamline 14W1 of the Shanghai Synchrotron Radiation Facility (SSRF). The spectra were taken under standard SSRF operation conditions (2.8 GeV and 150-280 mA) with a double-crystal Si(111) monochromator. The spectra were collected in fluorescence mode using a Lytle fluorescence ion chamber detector positioned at a 90° angle to the incident beam at room temperature. Spectra from −200 to 1000 eV relative to the As K edge were acquired. Standard reference chemicals, Na2HAsO4·7H2O, NaAsO2 were also analyzed. Elemental arsenic (As0) was used to calibrate the energy at 11 868 eV.

S 1.4 EXAFS data analysis

EXAFS data analysis was performed using the ATHENA and AETEMIS program in the Demeter computer package.23 The analysis procedure was similar to our previous studies.45 The raw data measured in intensities were converted to μ(E), and averaged spectra were used in the analysis. The EXAFS signal χ(k) was extracted from the measured data using the AUTOBK algorithm where k is the photoelectron wave number.6 The primary quantity for EXAFS is then χ(k), the oscillations as a function of photoelectron wave number. χ(k) was weighted by k2 to account for the dampening of oscillations with increasing k. The different frequencies in the oscillations in χ(k) correspond to different near neighbor coordination shells which can be described and modeled according to the EXAFS equation

$$\chi(k) = \sum_j N_j f_j(k) e^{-2k^2 \sigma_j^2} \frac{1}{kR_j^2} \sin[2kR_j + \delta_j(k)]$$

where f(k) and δ(k) represent the photoelectron backscattering amplitude and phase shift, respectively, N is the number of neighboring atoms, R is the distance to the neighboring atom, and the σ2 is the Debye-Waller factor representing the disorder in the neighbor distance. The $k^3$
weighted EXAFS in k-space (Å⁻¹) was Fourier transformed (FT) to produce the radial structure function (RSF) in R-space (Å). The experimental spectra were fitted with single-scattering theoretical phase-shift and amplitude functions calculated with the *ab initio* computer code FEFF6 using atomic clusters generated from the crystal structure of FeAsO₄.⁷ The many-body amplitude reduction factor (S₀²) was established as 0.95 by isolating and fitting the first-shell As-O of the spectrum. The spectrum was fit by first isolating and fitting the first-shell As-O to estimate ΔE₀, the difference in threshold energy between theory and experiment. Then ΔE₀ was fixed to the best fit value from first-shell fitting and kept the same for all interatomic shells in a given spectrum. In addition, the ΔE₀ value was allowed to float by no more than ±10 eV. The parameters such as interatomic distance (R), coordination number (CN), and Debye-Waller factor (σ²) were first established with reasonable guesses and were fitted in R-space. The error in the overall fits was determined using R-factor, the goodness-of-fit parameter: R-factor = Σ(χ_data − χ_fit)²/Σ(χ_data)². Good fits occur for R-factor < 0.05.

3. Reference

2. Figures and Tables

*Figure S1.* a) TEM, b) HRTEM and c), d) STEM images of $\gamma$-Fe$_2$O$_3$ NSs, all of which indicate the ultrathin characteristic of the as-synthesized nanostructure.
Figure S2. FESEM images of γ-Fe$_2$O$_3$ NSs.
**Figure S3.** High-resolution Fe$_{2p}$ XPS spectra of the $\gamma$-Fe$_2$O$_3$ NSs before and after loading As(III), the spectra of As(III) loaded Fe@Fe$_2$O$_3$ nanochains (NCs) and As(III) loaded $\alpha$-Fe$_2$O$_3$ NPs were also presented for comparison. The small peak at 707 eV which associated with Fe(0) in $\gamma$-Fe$_2$O$_3$ NSs was completely disappeared after treated with As(III) for 2 h. For the presence of protective Fe$_2$O$_3$ shell on Fe(0) in Fe@Fe$_2$O$_3$ nanochains, the reaction between As(III) and Fe(0) is not as fast as that in $\gamma$-Fe$_2$O$_3$ NSs, and Fe(0) peak is also visible after treat with As(III) for 2 h. As this time, about 9.1 % of adsorbed As(III) was reduced into As(0). All samples were kept in frozen drier at high vacuum before XPS analysis to minimize the oxidation in air.
Figure S4. FESEM image of γ-Fe$_2$O$_3$ Nanosheets on Ag nanoporous film for enhanced Raman spectra collection. To acquire high quality Raman spectra of γ-Fe$_2$O$_3$ NSs at very low Laser power (50 μW, which is very crucial for the minimized sample damage or phase transform during Raman analysis), 10 μL diluted γ-Fe$_2$O$_3$ NSs water dispersion was load on Ag nanoporous film to enhance the Raman signal.
**Figure S5.** Room temperature hysteresis loop of fresh synthesized $\gamma$-Fe$_2$O$_3$ NSs and sample aged in air for 1 and 6 month. After aged in air for 1 month and 6 month, the room temperature saturation magnetization were reduced to 64 and 61 emu g$^{-1}$, respectively, which is due to the gradually oxidation Fe(0) impurity, and supports the notion that the presence of Fe(0) enhanced the magnetic response of the $\gamma$-Fe$_2$O$_3$ NSs.
Figure S6. TEM images of synthesized nanostructure at different stage. The residue nanoclusters were highlighted by arrows. With the elongation of aging time, the amount of nanoclusters was gradually decreased, and size of NSs was kept increase with time.
Figure S7. HRTEM images of synthesized nanostructure at different stage. Lattice analysis on all discernible area showed the Fe$_3$O$_4$ or γ-Fe$_2$O$_3$ nature of these nanoparticles. However, for the chemical instability of Fe(0) nanoclusters, the possibility of oxidizing Fe(0) on TEM grid during sample preparation and storage cannot be excluded.
**Figure S8.** HRTEM images that reveals the existence of stack faults and twin boundary inside the synthesize NSs, and indirectly support the notion that the nanosheets were growth by the oriented attachment of small nanocrystal.
Figure S9. Effect of KBH₄ concentration on the morphology of synthesized nanostructures.
**Figure S10.** Effect of TX-114 concentration on the morphology of synthesized nanostructure.

**Figure S11** Summarization of the effect of reaction condition on the morphology of synthesized nanostructure and the proposed single-crystalline nanosheets growth mechanism.
**Figure S12.** TEM and HRTEM images of the As(III) treated NSs (the concentration of As(III) is 10 mg L\(^{-1}\)). After treated with As(III), the NS morphology of \(\gamma\)-Fe\(_2\)O\(_3\) was preserved in some extend, but some crystallized particles were also observed on the TEM grid, which may from the distroy of NS.
**Figure S13.** The FTIR spectra of the as-synthesized γ-Fe₂O₃ NSs and 10.0 mg L⁻¹ As(III)/As(V) treated NSs (upper). Apparent IR band of As-O were observed at 804, 822 and 870 cm⁻¹, in constant with reported value in literature. The detailed IR band assignment was show in the lower graph, which is the transmittance spectrum of 10 mg L⁻¹ loaded γ-Fe₂O₃ NSs. The bands of Fe-O, As-O, Fe-OH, adsorbed water, C-H, and –OH were appeared at 670, 805, 1060, 1632, 2230, 2950 and 3400 cm⁻¹, respectively.
Figure S14. The removal rate of arsenic ions by 0.1 g L$^{-1}$ γ-Fe$_2$O$_3$ NSs. For initial As(III)/As(V) with concentration no more than 2.5 mg L$^{-1}$, the removal rate were higher than 95%. Higher concentration of initial As ion result in the lowered removal rate for limited adsorption sites on γ-Fe$_2$O$_3$ NSs. In all cases, the removal rate of As(III) are larger than that of As (V), again ascribed to the superior As(III) capture capacity.
Figure S15. Deprive the adsorption capacity of NSs for As(III)/(V) by Freundlich fitting. Compared with the high linearity shown by Langmuir model, the low linearity here indicates Freundlich model is less appropriate in describing the adsorption process of Arsenic ion on γ-Fe₂O₃ NSs than Langmuir model.
**Figure S16.** XPS survey spectra of the as-synthesized $\gamma$-Fe$_2$O$_3$ NSs before and after loaded with As(III)/As(V) at defferent condition. High As signal can be seen for all As(III) loaded sample. While for As(V) treated sample, good As(V) signal was only observed at pH 3.0 or in the presence of 200 mM NaCl.
Figure S17. Different adsorption configuration of As ions on $\gamma$-Fe$_2$O$_3$ NSs surface and the alternation on surface –OH amount. Only the formation of linear monodentate complexion results in the net increase of surface –OH.
Figure S18. High-resolution O₁s XPS spectrum of the as-synthesized γ-Fe₂O₃ NSs. The surface –OH is as high as 40.58%, which is very important for the capture of As ions.
Figure S19. Regeneration the spent γ-Fe₂O₃ NSs sorbent with 10.0 mM NaOH, and the Arsenic ion adsorption performances of the regenerated NSs in the subsequent round of use.
**Figure 20.** Arsenic solid stability analysis by the Toxicity Characteristic Leaching Procedure (TCLP), the concentration of Arsenic species in the solution leach by 50 g L\(^{-1}\) \(\gamma\)-Fe\(_2\)O\(_3\) NSs that loaded with 82.06 and 44.05 mg g\(^{-1}\) As(III) and As(V) ion were monitored at the first, second, third, fifth and the tenth day.
**Table S1.** The pseudosecond-order adsorption model fitting parameters of As(III) adsorption kinetics on 0.1 g L\(^{-1}\) γ-Fe\(_2\)O\(_3\) NSs

<table>
<thead>
<tr>
<th>Ce (mg L(^{-1}))</th>
<th>Calculated qe (mg.g(^{-1}))</th>
<th>(k_2)(g.mg(^{-1}).min(^{-1}))</th>
<th>(R^2)</th>
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<td>5.22</td>
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<td>30.0</td>
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<td>0.0016</td>
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**Table S2.** The pseudosecond-order adsorption model fitting parameters of As(V) adsorption kinetics on 0.1 g L\(^{-1}\) γ-Fe\(_2\)O\(_3\) NSs.

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<th>Ce (mg L(^{-1}))</th>
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<th>(k_2)(g.mg(^{-1}).min(^{-1}))</th>
<th>(R^2)</th>
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<td>30.0</td>
<td>37.05</td>
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**Table S3.** The Languir and Freundlich model fitting parameters.

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<th>Langmuir model</th>
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<td></td>
<td>a</td>
<td>b</td>
<td>R²</td>
<td>k</td>
<td>n</td>
<td>R²</td>
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<tr>
<td>As(III)</td>
<td>109.3</td>
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<td>0.992</td>
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<td>As(V)</td>
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<td>12.15</td>
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**Table S4.** Fitted date for the high resolution O1s XPS spectra.

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<td>B.E. (eV)</td>
<td>Amount</td>
<td>B.E. (eV)</td>
<td>Amount</td>
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<td>Pristine</td>
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<td>532.1</td>
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<td>530.95</td>
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<td>pH 3.0</td>
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<td>532.13</td>
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<td></td>
<td>As(V)</td>
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<td>17.89%</td>
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<td>As(III)</td>
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<td>As(V)</td>
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<td>14.25%</td>
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**Table S5.** Structure parameters derived from As K-edge EXAFS analysis.

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<tr>
<th>shell</th>
<th>CN $^a$</th>
<th>R (Å) $^b$</th>
<th>$\sigma^2$ (Å$^2$) $^c$</th>
<th>$\Delta E_0$ (eV) $^d$</th>
<th>R-factor $^e$</th>
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<td>As-O</td>
<td>4.09</td>
<td>1.69 ± 0.01</td>
<td>0.003 ± 0.002</td>
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<td>As-Fe</td>
<td>0.74</td>
<td>3.31 ± 0.04</td>
<td>0.004± 0.006</td>
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$^a$ coordination number.

$^b$ interatomic distance.

$^c$ Debye-Waller factor.

$^d$ threshold energy shift.

$^e$ goodness-of-fit parameter: R-factor = $\Sigma(\chi_{\text{data}} - \chi_{\text{fit}})^2 / \Sigma(\chi_{\text{data}})^2$
Table S6. Inorganic arsenic ion removal performance in natural water samples (10 mL) with the as-synthesized γ-Fe$_2$O$_3$ NSs (0.15 mgL$^{-1}$)

<table>
<thead>
<tr>
<th>Sample</th>
<th>Spiked (µg/L)</th>
<th>As(V) (µg/L) in water samples</th>
<th>As(III) (µg/L) in water samples</th>
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Table S7. pH and the concentration of other ions in the tested water samples.

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<th>Sample 1</th>
<th>Sample 2</th>
<th>Sample 3</th>
<th>Sample 4</th>
<th>Sample 5</th>
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<td>7.46</td>
<td>8.31</td>
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<tr>
<td>K&lt;sup&gt;a&lt;/sup&gt;</td>
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<td>Na</td>
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<td>458.47</td>
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<sup>a</sup> all ions were determined by ICP-AES, and this technology is not sensitive to Br and Cl.