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## **Supporting Information**

# Cu-doped Fe@Fe<sub>2</sub>O<sub>3</sub> Core-Shell Nanoparticles Shifted Oxygen Reduction Pathway for

# High-Efficiency Arsenic Removal in Smelting Wastewater

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# This file includes 8 additional sections, 16 figures and 8 tables.

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### Text S1 Synthesis of Fe@Fe<sub>2</sub>O<sub>3</sub>.

0.4 M of NaBH<sub>4</sub> was dropwise added into 0.01 M of FeCl<sub>3</sub>·6H<sub>2</sub>O solution, and the synthetic process was agitated by a revolving propeller. The formed black fine particles were aged in water for 2 h. The whole process of synthesis is simple without any protection gas. Finally, the fabricated materials were washed with deionized water or ethanol and then dried vacuum freeze.<sup>1</sup>

## Text S2 Synthesis of Fe/Cu bimetallic.

The Fe/Cu was prepared by dissolving CuSO<sub>4</sub> and FeCl<sub>3</sub>·6H<sub>2</sub>O in 800 ml deionized water, stirring constantly for 40 min in nitrogen atmosphere. After being uniformly mixed, 50 ml NaBH<sub>4</sub> aqueous solution was dropwise added into the mixture solution and stirred vigorously under the protection of nitrogen. The obtained black solid particles washed with deionized water and dried vacuum freeze.<sup>2</sup> For comparison, Fe/Cu bimetallic with different Fe/Cu mass of ratio were prepared (Fe:Cu=1:1, 1:2, 3:10, 1:5, 1:10, 1:20).

## Text S3 Synthesis of NFF.

Briefly, 0.188 g NiCl<sub>2</sub>·6H<sub>2</sub>O was dissolved in 800 ml deionized water containing 12.8 mmol sodium citrate and then purged with N<sub>2</sub> into solution at least 40 min for the sake of oxygen exclusion. Then 2.1 M NaBH<sub>4</sub> was added dropwise into the aqueous solution until uniform black particles appeared. The synthetic process was stirred by a revolving propeller under N<sub>2</sub> conditions. 30 ml of 0.45 M FeSO<sub>4</sub>·7H<sub>2</sub>O and 16 ml of 2.1 M NaBH<sub>4</sub> aqueous solution were successively added dropwise into the solution without N<sub>2</sub> protection. After the addition, the nanoparticles were aged in water for 2 h and then collected and washed with deionized water three times. Finally, nanoparticles were dried by vacuum freeze drying. For comparison, NFF nanoparticles with different Fe/Ni mass of ratio were prepared (Fe:Ni=1:1, 1:2, 3:10, 1:5, 1:10, 1:20).

### Text S4 Synthesis of Fe/Ni bimetallic.

The Fe/Ni was prepared by dissolving NiCl<sub>2</sub>·6H<sub>2</sub>O and FeCl<sub>3</sub>·6H<sub>2</sub>O in 800 ml deionized water, stirring constantly for 40 min in nitrogen atmosphere. After being uniformly mixed, 50 ml NaBH<sub>4</sub> aqueous solution was dropwise added into the mixture solution and stirred vigorously under the protection of nitrogen. The obtained black solid particles washed with deionized water and dried vacuum freeze drying.<sup>3</sup> For comparison, Fe/Ni bimetallic with different Fe/Ni mass of ratio were prepared (Fe:Ni=1:1, 1:2, 3:10, 1:5, 1:10, 1:20).

#### **Text S5 Characterizations.**

The synthesized samples were characterized by transmission electron microscopy (TEM) and TEM images were taken by a JEOL-2100F electron microscope operated at 200 kV. Scanning electron microscopy (SEM) image was obtained on a LEO 1450VP scanning electron microscope. Energy-dispersive spectroscopy (EDS) system was attached to the TEM system. The crystalline structure analysis of the synthesized materials was performed using an Empyrean diffractometer (PANalytical) equipped with monochromated Cu K $\alpha$  radiation ( $\lambda = 1.54178$  Å). Zeta potential measurements versus pH were performed on a Malvern ZEN3600 Zetasizer Nano. X-ray diffraction (XRD) patterns were collected with a Bruker D8 Advance X-ray diffractometer (Cu Ka radiation,  $\lambda = 1.54178$  Å). X-ray photo-electron spectroscopy (XPS) was recorded by a Kratos ASIS-HS X-ray photoelectron spectroscope (15 kV, 10 mA). Furthermore, Cu@Fe@Fe<sub>2</sub>O<sub>3</sub> before and after treatment were also characterized by XPS to compare the difference in surface compositions.

## Text S6 Tafel Scan Experiments.

To prepare the CFF film working electrode, 5 mg CFF was dispersed in 1ml of diluted nafion solution and sonicated for 2 min to form uniform slurry. A 2.5  $\mu$ L aliquot of uniform slurry was then dropped onto the glassy carbon surface to form a thin slurry layer. After drying with nitrogen, CFF was uniformly coated on the glassy carbon disk electrode. Tafel diagrams were recorded on a CHI-760E electrochemical workstation employing a three electrode system of saturated calomel electrode as the reference electrode, and platinum electrode as the counter. All the Tafel diagrams were obtained by polarizing the work electrodes ±200 mV with respect to their open circuit potentials. All the potentials in the Tafel diagrams were with respect to the standard hydrogen electrode (SHE).

Tafel scans were used for determining the free corrosion potentials of CFF nanoparticles. The calomel reference electrode, the work electrode, and the Pt counter electrode were placed in 20 ml of  $Na_2SO_4$  aqueous solution (50 mM) in a 50 ml beaker. To obtain the initial corrosion potential of CFF nanoparticles, Tafel scans were performed immediately after the work electrode was immersed into the electrolyte solution. For comparison, nZVI, Fe/Cu bimetal and Fe@Fe\_2O\_3 have also been tested.

### **Text S7 Chemical Analysis.**

An AF9700 atomic fluorescence spectrophotometer (Beijing Haiguang Instrument Company, China) was used to determine the arsenic concentration. The concentration of  $H_2O_2$  and iron speciation (Fe<sup>2+</sup> and Fe<sup>3+</sup>) was all determined by UV–vis spectroscopy (SHIMADZU 2550). An UV-visible spectrophotometer (Cary 300, USA) was used to monitor the concentration of tetracycline in water at its maximum absorption wavelength of 554 nm.

## Text S8 Models for Adsorption Kinetic and Isotherm Experiments.

The adsorption behavior is explained by the pseudo-first-order model and pseudo-second-order model. The models are described as follows<sup>4</sup>:

$$\ln(q_e - q_t) = \ln q_e - \frac{k_1}{2.303}t$$
(1)

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e}$$
(2)

where  $q_e$  and  $q_t$  (mg g<sup>-1</sup>) are the values of amount of As(III) adsorbed onto adsorbents at equilibrium time t (min),  $k_1$  is the pseudo-first-order adsorption equilibrium rate constant (min<sup>-1</sup>),  $k_2$  ( $k_{As}$ ) is the pseudo-second-order adsorption rate constant (g/(mg·min)).

Two typical isotherm models, such as Langmuir and Freundlich isotherm are served to explain the equilibrium data, and the non-linear forms are described as follows<sup>4</sup>:

where  $q_{max}$  is the maximum adsorption capacity (mg g<sup>-1</sup>);  $k_L$  is the Langmuir constant related to the maximum monolayer ability(L mol<sup>-1</sup>);  $k_f$  is the Freundlich constant (L mg<sup>-1</sup>)<sup>1/n</sup>, 1/n is a measure of adsorption strength.

Langmuir model: 
$$q_e = \frac{q_{max}K_LC_e}{1 + K_LC_e}$$
 (3)  
Freundlich model:  $q_e = k_f C_e^{1/n}$  (4)

where  $C_1$  is the initial As(III) concentration (mg L<sup>-1</sup>). The values of  $R_L$  is the irreversible equilibrium ( $R_L \equiv 0$ ), favorable equilibrium ( $0 < R_L < 1$ ), linear case ( $R_L \equiv 1$ ) or unfavorable equilibrium ( $R_L > 1$ )<sup>4</sup>



Fig. S1. Distribution histograms of the diameters of CFF.



Fig. S2. XRD patterns of the CFF and nZVI.



Fig. S3. Plots of  $ln(C/C_0)$  versus time over CFF (a) and Fe/Cu bimetallic (b) with different Cu contents.



Fig. S4. (a) Concentration of ferrous ion as a function of time and (b) plots of  $\ln(C/C_0)$  versus time over CFF under anoxic conditions.



Fig. S5. (a) The removal rate constants (k) of As(III) in the absence of oxygen with and without 1,10phenanthroline, with nonlinear fitting curve of inhibition rate of anoxic As(III) removal over CFF with 1,10phenanthroline (blue line). (b) Plots of  $\ln(C/C_0)$  versus time over nZVI, Fe/Cu bimetallic, and CFF with and without 1,10-phenanthroline.



Fig. S6. (a) The concentration of Fe(II) in solution released by CFF, Fe@Fe<sub>2</sub>O<sub>3</sub>, nZVI, CFF under aerobic condition, respectively. (b) The concentration of  $H_2O_2$  in solution produced by CFF, Fe@Fe<sub>2</sub>O<sub>3</sub>, nZVI, CFF under aerobic condition, respectively. (pH 7.0±0.2)



Fig. S7. The concentration of dissolved oxygen in solution during the arsenic removal by CFF under aerobic condition.



Fig. S8. Aerobic removal of As(III) in the presence of TBA or p-Benzoquinone.



Fig. S9. (a) Changes of the concentrations of As(V) generated during As(III) oxidation and (b) plots of  $ln(C/C_0)$  versus time by CFF/air system in the absence and presence of TBA or p-Benzoquinone under aerobic conditions. Digital image of the after reaction solution, (c) in the absence of p-Benzoquinone and TBA, (d) in the presence of p-Benzoquinone and TBA. (These four glass bottles, from left to right: nZVI, Fe/Cu bimetallic, CFF, and Fe@Fe<sub>2</sub>O<sub>3</sub>)



Fig. S10. (a) TEM image of CFF and (b-f) corresponding EDS elemental mapping for Fe, O, Cu and As atoms .



Fig. S11. Snapshots from LAMMPS simulation display the formation process of CFF. CFF molecular dynamic model (a) changed with different time, (b) 0 ps, (c) 10 ps, (d) 20 ps, (e) 50 ps, (f) 100 ps. (green atom: Fe; reddish brown atom: Cu)



Fig. S12. The temporal concentration change of As(III) as a function of reaction time during the aerobic removal of As(III) over NFF (a) and Fe/Ni bimetallic (b) with different Ni contents. (Insets are the plots of  $ln(C/C_0)$  versus time) (c) SEM and (d) TEM image of NFF. Initial CFF was 100 mg/L, As(III) was 3.5 mg/L, and the pH values were 7.0±0.2.



Fig. S13. (a) Comparison of the As(III) removal by CFF with low and high concentrations of As(III) under aerobic conditions. (b) Adsorption capacity change with low and high concentrations of As(III) under aerobic conditions fitted by (c) pseudo-first-order and (d) pseudo-second-order models. (Note: conc represents concentration. low conc: 3.7 mg/L; and high conc: 6.7 mg/L; initial CFF conc: 50 mg/L; pH 7.0±0.2)

Acid water elements	Concentration	Water Quality standard (mg/L)	Exceeding standard rate (%)		
	(mg/L)	water Quanty standard (ing/L)			
As	4.35×10 <sup>2</sup>	1.0×10 <sup>-2</sup>	43350		
Cd	4.1	5.0×10 <sup>-3</sup>	799		
Cr	4.1×10 <sup>-2</sup>	5.0×10 <sup>-2</sup>	-0.2		
Cu	2.1×10 <sup>-2</sup>	2.0	-0.98		
Hg	2.2	1.0×10 <sup>-3</sup>	2299		
Mn	1.1×10 <sup>-1</sup>	1.0×10 <sup>-1</sup>	0		
Zn	3.15×10	1.0	31.5		
Р	3.3				
S	$1.4 \times 10^{4}$				

Table S1. The contents of main metal and inorganic elements in waste acid wastewater.

emoval rates constants (k <sub>As</sub> ) over various Fe/Cu mass ratios.									
	Fe/Cu mass ratio								
Sample	$(m^2 \cdot g^{-1})$	1:1	1:2	3:10	1:5	1:10	1:20		
CFF	20.53	6.0×10 <sup>-3</sup>	1.3×10 <sup>-2</sup>	3.0×10 <sup>-2</sup>	1.1×10 <sup>-1</sup>	9.0×10-2	1.5×10-2		
Fe/Cu bimetallic	18.43	4.8×10-3	1.1×10 <sup>-2</sup>	2.3×10 <sup>-2</sup>	1.4×10 <sup>-2</sup>	1.4×10 <sup>-2</sup>	1.3×10-2		

Table S2. The BET surface areas of CFF and Fe/Cu bimetallic with same Cu contents (1:5) and their removal rates constants ( $k_{As}$ ) over various Fe/Cu mass ratios.

	Anoxic			Aerobic			
Materials	Removal rate(%)	adsorption (%)	Ferrous (%)	Removal rate (%)	adsorption (%)	Ferrous (%)	
CFF	57	21	36	98	8	89	
Fe/Cu	40	16	14	50	16	34	
nZVI	30	17	13	45	10	35	

Table S3. The contributions of adsorption and the ferrous ions released with different materials on the removal of As (III).

Table S4. The content of copper with different valence states before and after reaction.

	Cu <sup>0</sup>	Cu(I)	Cu(II)
Before reaction	44.4%	26.0%	29.6%
After reaction	31.6%	33.9%	34.5%

Table S5. The removal rates of with different systems.

K (min <sup>-1</sup> )
1.1×10 <sup>-1</sup>
6.7×10 <sup>-2</sup>
5.8×10-2

Table S6. The concentration of copper and arsenic in the solution during the removal of As(III).

Time (min)	2	4	8	20	30	60	120
Cu-Concentration (mg/L)	6×10-2	6×10-2	7×10-2	8×10-2	8×10-2	9×10-2	11×10-2
Water Quality standard (mg/L)				1.0			
As- Concentration (ug/L)	3.56×10 <sup>3</sup>	2.48×10 <sup>3</sup>	1.88×10 <sup>3</sup>	9.96×10 <sup>2</sup>	78.3	24.2	0
Water Quality standard (ug/L)				10			

Concentrations (mg/L)	<i>a.</i>	Pseudo-first-order modal			Pseudo-second-order model		
	(mg/g)	q <sub>e,cal</sub> (mg/g)	k <sub>1</sub> (1/min)	R <sup>2</sup>	q <sub>e,cal</sub> (mg/g)	k₂ g/(mg∙min)	R <sup>2</sup>
3.7	37.25	28.9	2.18×10-1	0.87	39.1	4.67×10-3	0.99
6.7	67.31	64.6	1.34×10 <sup>-1</sup>	0.93	69.0	2.29×10 <sup>-3</sup>	0.99

Table S7. Parameters of the pseudo first-order and second-order kinetic models for the adsorption of As(III) on the CFF.

# **References:**

1. Tang, L.; Feng, H.; Tang, J.; Zeng, G.; Deng, Y.; Wang, J.; Liu, Y.; Zhou, Y., Treatment of arsenic in acid wastewater and river sediment by Fe@Fe<sub>2</sub>O<sub>3</sub> nanobunches: The effect of environmental conditions and reaction mechanism. *Water Res.* **2017**, *117*, 175-186.

2. Zhu, F.; Li, L.; Ma, S.; Shang, Z., Effect factors, kinetics and thermodynamics of remediation in the chromium contaminated soils by nanoscale zero valent Fe/Cu bimetallic particles. *Chem. Eng. J.* **2016**, *302*, 663-669.

3. Gao, Y.; Wang, F.; Wu, Y.; Naidu, R.; Chen, Z., Comparison of degradation mechanisms of microcystin-LR using nanoscale zero-valent iron (nZVI) and bimetallic Fe/Ni and Fe/Pd nanoparticles. *Chem. Eng. J.* **2016**, *285*, 459-466.

4. Wang, H.; Li, Z.; Mitlin, D., Tailoring Biomass–Derived Carbon Nanoarchitectures for High–Performance Supercapacitors. *Chemelectrochem* **2014**, *1* (2), 332–337.