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Electronic Supplementary Information

Synthesis of metal sulfide-coated iron nanoparticles with enhanced surface reactivity and biocompatibility

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1. Experimental details

1) Materials and chemicals. All chemical solutions were prepared by dissolving chemicals ($FeCl_3 \cdot 6H_2O$, $NaBH_4$, $CuCl_2 \cdot 2H_2O$, $CoCl_2 \cdot 6H_2O$, $ZnCl_2$, $CdCl_2 \cdot 2H_2O$, NaOH, and HCl) in deoxygenated deionized (DO/DI) water. The chemical reagents were of analytical grade and used as received.

In order to synthesize metal sulfide-coated iron nanoparticles (Fe/MeS), iron nanoparticles (FeNPs) were first prepared by reducing 0.5 M $FeCl_3$ with 0.8 M $NaBH_4$. Then, the FeNPs were immersed in a 10^{-3} M sodium sulfide (Na_2S) solution containing the metal salts (10^{-3} M). After 24 h, the resulting suspension was centrifuged and washed with degassed, deionized water.

2) Characterization. The obtained particles were characterized by high-resolution transmission electron microscopy (HRTEM) and energy-filtered transmission electron microscopy (EFTEM) using a JEM-2200FS microscope with Cs correction. X-ray photoelectron spectra (XPS) was also performed, using a VG ESCALAB 220iXL using monochromatic Mg Kα (1253.6 eV) excitation source. The electrostatic force microscopy (EFM) imaging was conducted on a Digital instrument Nanoscope V (Veeco). For this, the dried samples were pressed into pellets using a hydraulic press. The hydrodynamic diameters and ζ-potentials of the NPs were measured by an electrophoretic light scattering spectrophotometer (ELS-8000) at room temperature.

3) TCE dechlorination experiments and analysis. Batch experiments were performed in 40 mL amber colored glass vials capped with Teflon Mininert valves. The vials were filled with 0.08 g of the particles and 40 mL of 0.11 mM TCE solutions. The bottle was capped with a Teflon Mininert valve and then placed on a rolling mixer (15 rpm) at room temperature. All experiments were done in triplicate. The aqueous concentrations of TCE and its chlorinated products were measured using headspace gas chromatograph equipped with an electron capture detector (GC-ECD, HP Agilent 6890).

4) Cell viability and reactive oxygen species (ROS) assay. In this study, *Escherichia coli* was used to test the antibacterial activity of Fe/MeS NPs. *E. coli* was grown aerobically in Luria-Bertani (LB) medium (Merck) at 37 °C.

The viability of control (without NPs) and NPs-treated bacteria was measured by counting colony forming units (CFU/mL). *E. coli* stock suspension was diluted in water in 20 mL culture tubes to reach final concentration of 10^6 CFU/mL. The cells were incubated with NPs (200 mg/L) at 37 °C under gentle stirring. After 10 h incubation, samples were taken, and serially diluted. The cells were plated in triplicate on LB agar plates and incubated for 12 h at 37 °C, and the colonies were counted.

The intracelullar level of reactive oxygen species (ROS) was monitored by following the fluorescence of 2,7-dichlorodihydrofluorescein diacetate acetyl ester (H2DCF-DA, Invitrogen). The cells were exposed for 3 h to 200 mg/L of NPs, and then further incubated in water containing 10 μM of H2DCF-DA for 30 min in a dark. The fluorescence intensity of cell/NP suspensions was measured with excitation at 480 nm and emission at 530 nm using a spectrofluorometer (Shimadzu RF-5301).

5) Transmission Electron Microscopy (TEM) analaysis of *E. coli* cells. After exposure to the NPs (200 mg/L), the bacterial cells were fixed with 1% formaldehyde and 1% glutaraldehyde, dehydrated in ethanol, and embedded in EMBed 812 and propylene oxide before being sectioned by an ultra-tome. The bacterial sections were analyzed with a Hitachi H-7600 TEM.

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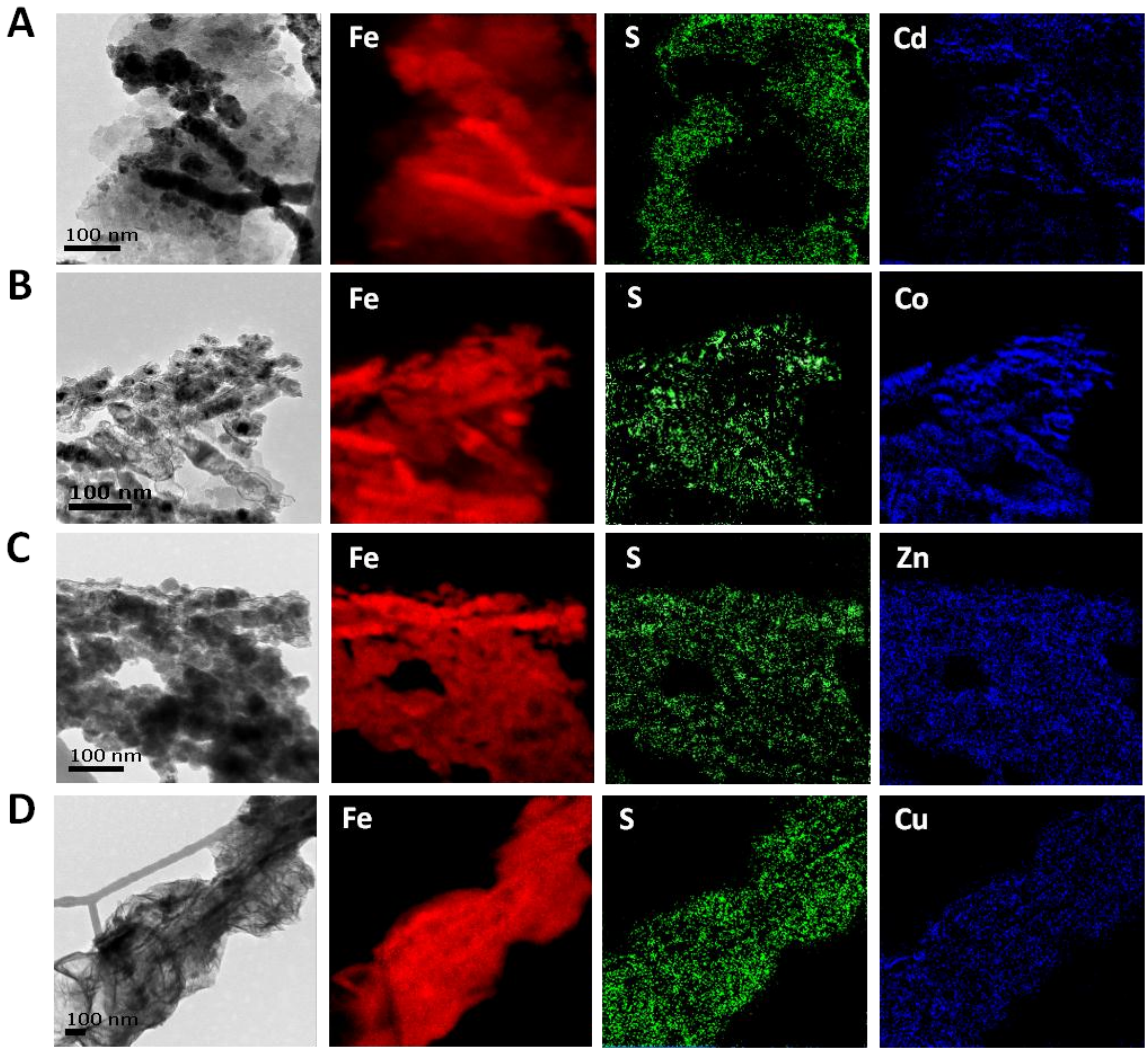

Fig. S1 Energy filtered transmission electron microscopy (EFTEM) images of (A) Fe/CdS, (B) Fe/CoS, (C) Fe/ZnS, and (D) Fe/Cu_2S NPs.

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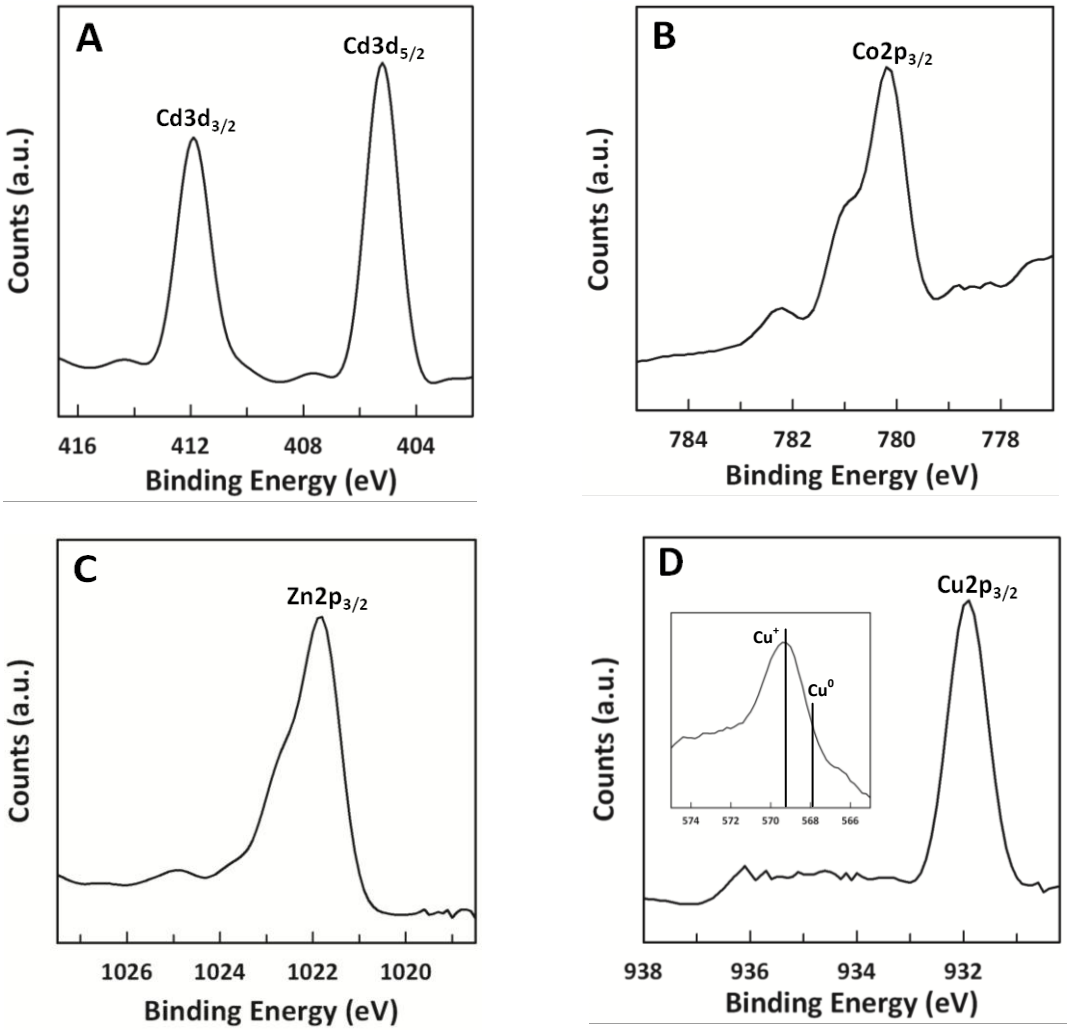

Fig. S2 X-ray photoelectron spectroscopy (XPS) spectra obtained from (A) Fe/CdS, (B) Fe/CoS, (C) Fe/ZnS, and (D) Fe/Cu_2S NPs (inset : Auger Cu LMM spectrum).

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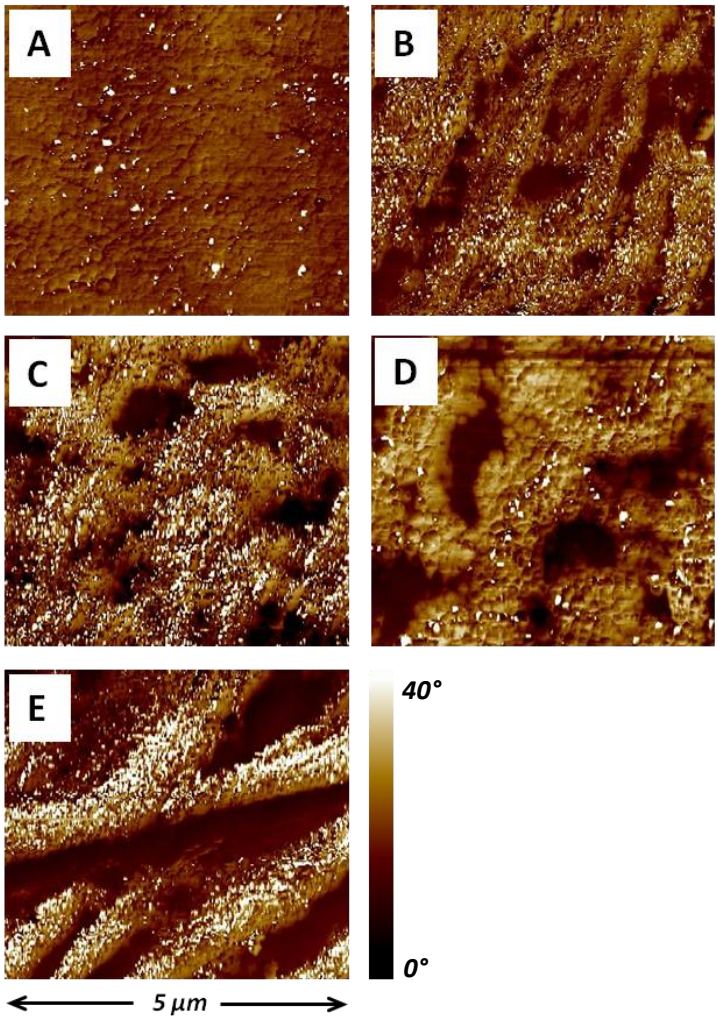

Fig. S3 Electrostatic force microscopy (EFM) images of (A) Fe, (B) Fe/CdS, (C) Fe/CoS, (D) Fe/ZnS, and (E) Fe/Cu_2S NPs.

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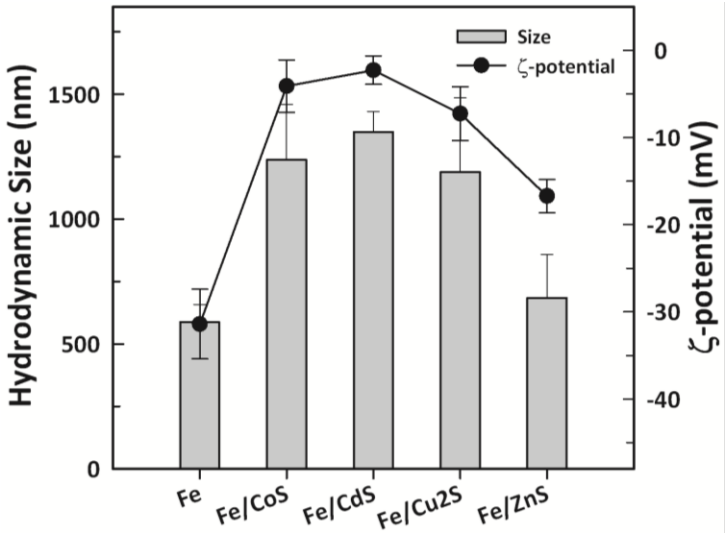

Fig. S4 Hydronamic sizes and ζ-potentials of the diluted suspension of Fe and Fe/MeS NPs (20 mg/L) at pH 7.0 ± 0.2 in the absence of background electrolyte.