Supplementary Information

Origin of the hydrophobicity of sulfur-containing iron surfaces

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1 COMPUTATIONAL METHODS

Spin-polarized density functional theory (DFT) calculations were carried out using the Vienna *Ab initio* Simulation Package (VASP).\(^1\) Generalized gradient approximation (GGA) method with the functional by Perdew, Burke, and Ernzerhof was used to describe electronic exchange and correlation.\(^2\) Projector augmented wave method was employed to describe core electrons.\(^3\) Wave functions by Kohn and Sham were expanded in a plane wave basis set to describe valance electrons.\(^4\) A \((3\times3\times1)\) Monkhorst–Pack \(k\)-point mesh was used to sample the Brillouin zone in structural optimizations.\(^5\) The Fe surfaces were modelled as 4-layer, \((3\times3)\), \((110)\) surfaces, based on the characterizations shown in previous studies.\(^6–9\) The bottom two layers were fixed in bulk position, while the topmost two layers were allowed to relax. The N- and P-doped Fe\((110)\) structures were modelled by the same way as the S-doped Fe\((110)\) surfaces. The X-in-Fe\((110)\) (X=S, N, and P) surfaces were modelled by replacing the X atoms with the dopant, while the X-on-Fe\((110)\) surfaces were modelled by directly placing the dopant on the Fe\((110)\) surface. The lattice constant was set as 286.65 pm. In the *ab initio* molecular dynamics simulations, the Gamma version of VASP with \((1\times1\times1)\) Monkhorst–Pack \(k\)-point mesh was applied to speed up the calculations. In detail, the canonical ensemble was used to simulate the dynamic behavior of water molecules at 300 K. A relatively long time of 12000 ps with a step of 1 fs was applied. To obtain more accurate results, DFT-D3
corrections by Grimme et al.\textsuperscript{10} were included in the calculations. The average water-surface distance in the AIMD results is defined as the average distance between the oxygen atoms and the Fe(110) surface.

2 EXPERIMENTAL METHODS

Synthesis of NZVI and SNZVI materials: NZVI and SNZVI particles were synthesized according to previously reported methods.\textsuperscript{9,11,12} Briefly, NZVI particles were synthesized by dropwise addition (~7 mL min\textsuperscript{−1}) of 200 mL of 34 g L\textsuperscript{−1} NaBH\textsubscript{4} solution into a continuously stirred (600 rpm) 200 mL vessel containing 10 g L\textsuperscript{−1} Fe\textsuperscript{2+} solution under N\textsubscript{2} purging, followed by 10 min of stirring. SNZVI particles were synthesized by dropwise addition of 200 mL of 34 g L\textsuperscript{−1} NaBH\textsubscript{4} and 2.2 g L\textsuperscript{−1} Na\textsubscript{2}S\textsubscript{2}O\textsubscript{4} solution into 200 mL of a 10 g L\textsuperscript{−1} Fe\textsuperscript{2+} solution while mixing under nitrogen purging, providing a 0.14 S/Fe molar ratio (dose). The resulting NZVI or SNZVI suspensions were washed three times with deoxygenated DI water, and then dried in a vacuum oven at 60 °C for 8 hours. The vacuum was slowly released by air over 3 hours to stabilize the particles, which were subsequently ground and stored in sealed vials in an anaerobic glovebox prior to use.

Determination of NZVI and SNZVI hydrophobicity: the hydrophobicity of the materials was assessed by measuring the water contact angle according to the method that previously reported.\textsuperscript{6,13} 7 mm (diameter) by 1 mm (thick) pellets of each material were created using a Quick-press (PerkinElmer) in the anaerobic glovebox.
Then the pellets were dried in the vacuum oven at 60 °C for 8 hours, and gradually released the pressure with air within 1 hour. The water contact angles of NZVI and SNZVI pellets in the air were measured by a contact angle goniometer (Rame-Hart).

3 REFERENCES


12 E. J. Kim, J. H. Kim, A. M. Azad and Y. S. Chang, Facile synthesis and characterization of Fe/FeS nanoparticles for environmental applications, *ACS
Figure S1. The process of a S atom at S-in-Fe(110) surface swapping with a subsurface Fe atom. Brown and yellow spheres represent Fe and S atoms, respectively.