

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 valence electrons.⁴ A $(3 \times 3 \times 1)$ Monkhorst–Pack k -point mesh was used to sample the Brillouin zone in structural optimizations.⁵ The Fe surfaces were modelled as 4-layer, (3×3) , (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 $(1 \times 1 \times 1)$ 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.*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.^{9,11,12} Briefly, NZVI particles were synthesized by dropwise addition ($\sim 7 \text{ mL min}^{-1}$) of 200 mL of $34 \text{ g L}^{-1} \text{ NaBH}_4$ solution into a continuously stirred (600 rpm) 200 mL vessel containing $10 \text{ g L}^{-1} \text{ Fe}^{2+}$ solution under N_2 purging, followed by 10 min of stirring. SNZVI particles were synthesized by dropwise addition of 200 mL of $34 \text{ g L}^{-1} \text{ NaBH}_4$ and $2.2 \text{ g L}^{-1} \text{ Na}_2\text{S}_2\text{O}_4$ solution into 200 mL of a $10 \text{ g L}^{-1} \text{ Fe}^{2+}$ 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 $60 \text{ }^\circ\text{C}$ 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.^{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

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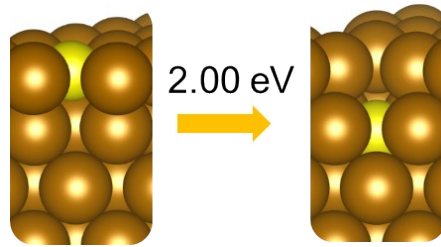


Figure S1. The process of a S atom at S-in-Fe(110) surface swapping with a subsurface Fe atom. Brown and yellow spheres represent Fe and S atoms, respectively.