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Supporting Information for

Tunable ferroelectricity and antiferromagnetism via ferroelastic switching in FeOOH monolayer

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SI. Plausibility and stability of FeOOH monolayer

The stability of FeOOH monolayer was verified from the phonon spectrum, ab initio molecular dynamic (AIMD) simulations and elastic constants. No imaginary frequency mode was found in the phonon spectrum. Neither broken bond nor structure reconstruction is observed after the AIMD process at 300K. In addition, we find the configuration in this article is energetically more stable than another configuration, namely δ-FeOOH, which was also synthesized,[4-5] as shown in Fig. S5. The energy difference of above two configurations is about 0.1 eV/atom. Hence, we consider the FeOOH monolayer is equipped with thermal stability at room temperature, albeit possible thermal dehydroxylation phenomenon at higher temperatures.[6] The elastic constants listed in Table 1 meet the Born criteria: $C_{11}C_{22} - C_{12}^2 > 0$ and $C_{66} > 0$,[7] demonstrating the mechanical stability of FeOOH monolayer. The aqueous stability of FeOOH monolayer has also been confirmed,[8] suggesting the feasibility of producing FeOOH monolayer via liquid exfoliation techniques.

SII. AFM configurations and the Heisenberg model for FeOOH monolayer

Starting from different initial spin configurations, our self-consistent DFT calculations converged to four collinear AFM orderings (Fig. S6) besides the FM ordering. The bubbles in different colors represent the spin-resolved differential charged density ($\Delta\rho=\rho_{\uparrow}-\rho_{\downarrow}$) of the systems. Obviously, electron spin-polarization occurs mainly at the Fe ions. Furthermore, we constructed two possible non-collinear AFM magnetic orders, AFM4 and AFM5, for considering the spin frustration effect. It

is found that this AFM state (AFM3) is energetically most favorable among these magnetic orderings. It is more stable than the FM, AFM1, AFM2, AFM4 and AFM5 by about 1.115, 0.050, 0.741, 0.011 and 0.025 eV/supercell, respectively.

The effective Hamiltonian based on the Heisenberg model reads as:

$$H = -J_1\sum_{<ij>} S_i \cdot S_j - J_2\sum_{<ik>} S_k \cdot S_l - J_3\sum_{<il>} S_m \cdot S_n - A\sum_i (S_i^e)^2 ,$$

where J_1, J_2 and J_3 represent the nearest exchange coupling along [100], [010] and [110] directions, as indicated in the inset of Fig.3(e), $S = 5/2$ is the spin vector of the corresponding Fe ions. S_i^e is the component of spin along the easy magnetic axis. Only the nearest exchange couplings along these three directions are included in this Hamiltonian. The single-ion magnetic anisotropy energy parameter A is given as:

$$A = \frac{E(001) - E(100)}{S^2} .$$

which is 0.018 meV/Fe.

The total energies of the four magnetic orders are given as:

$$E_{FM} = E_0 - 16J_1S^2 - 8J_2S^2 - 8J_3S^2 - AS^2$$
$$E_{AFM1} = E_0 - 8J_2S^2 + 8J_3S^2 - AS^2$$
$$E_{AFM2} = E_0 + 16J_1S^2 - 8J_2S^2 - 8J_3S^2 - AS^2$$
$$E_{AFM3} = E_0 + 8J_2S^2 + 8J_3S^2 - AS^2$$

The nearest exchange coupling strengths obtained by fitting the energies of the FM and AFM states are J_1 = -8.776 meV, J_2 = -0.500 meV and J_3 = -1.872 meV, respectively. The orders of these exchange coupling strengths are consistent with above analysis using the Goodenough–Kanamori–Anderson rules.

References

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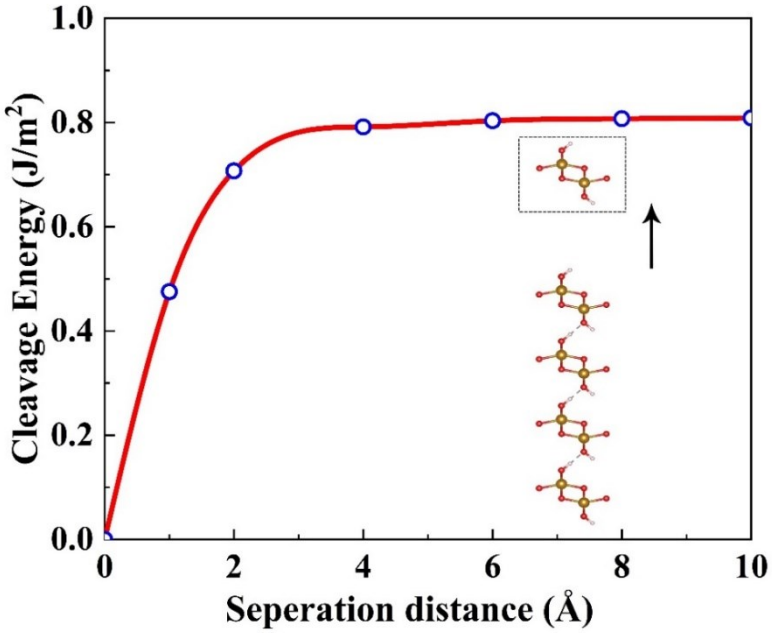

Fig. S1. The cleavage energy of FeOOH bulk as a function of separate distance *d* during the process of exfoliating monolayer.

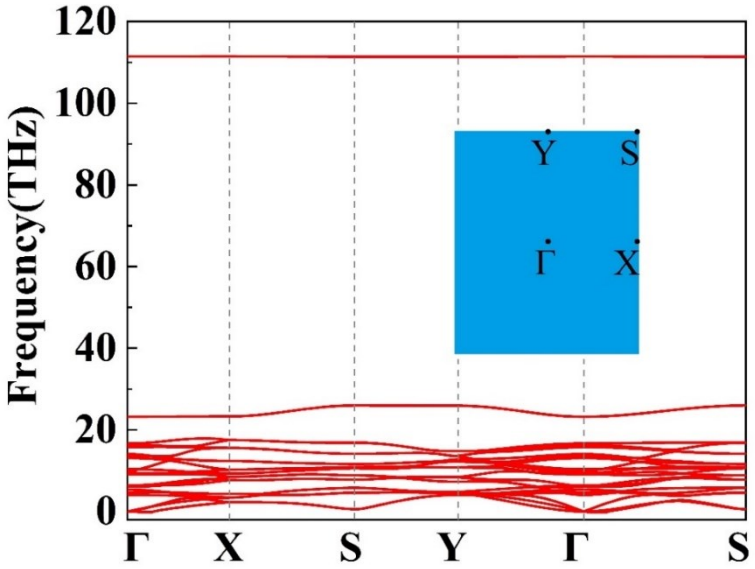

Fig. S2 The phonon spectra of FeOOH monolayer. The inset of this figure shows the Brillouin zone

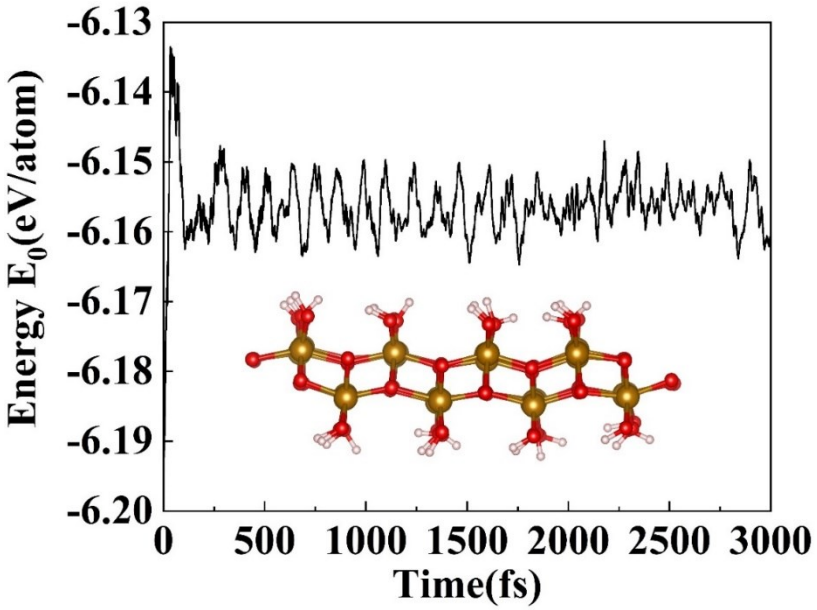

Fig. S3 Fluctuation of total energy per atom with time in the AIMD simulation of FeOOH monolayer at 300 K and its corresponding snapshot taken from the end of the simulation.

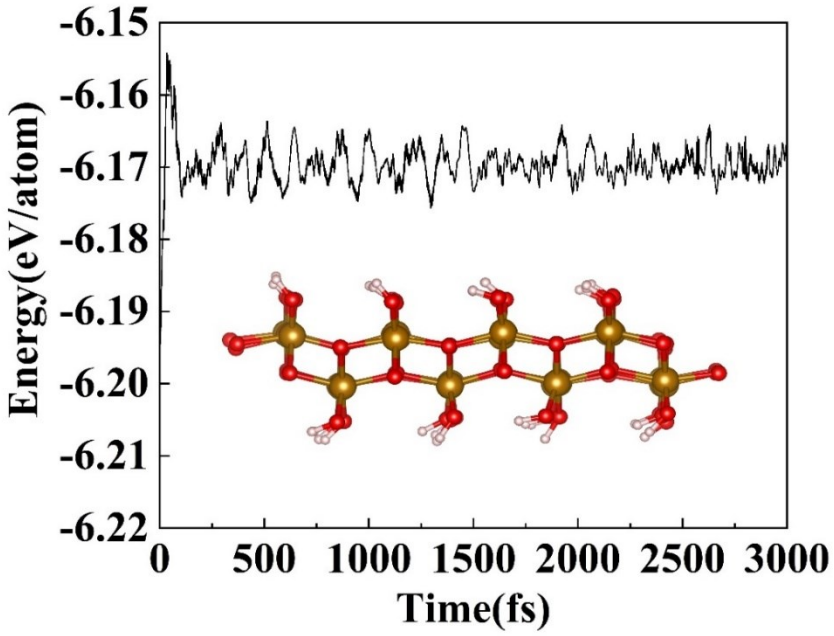

Fig. S4 Fluctuation of total energy per atom with time in the AIMD simulation of FeOOH monolayer at 200 K and its corresponding snapshot taken from the end of the simulation.

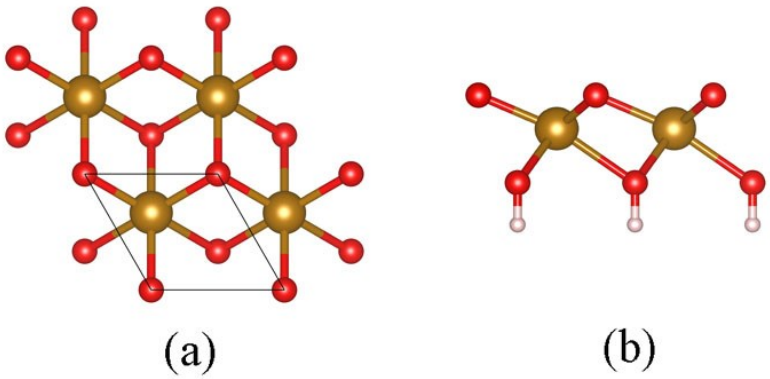

Fig. S5 Top (a) and side (b) views of δ-FeOOH monolayer

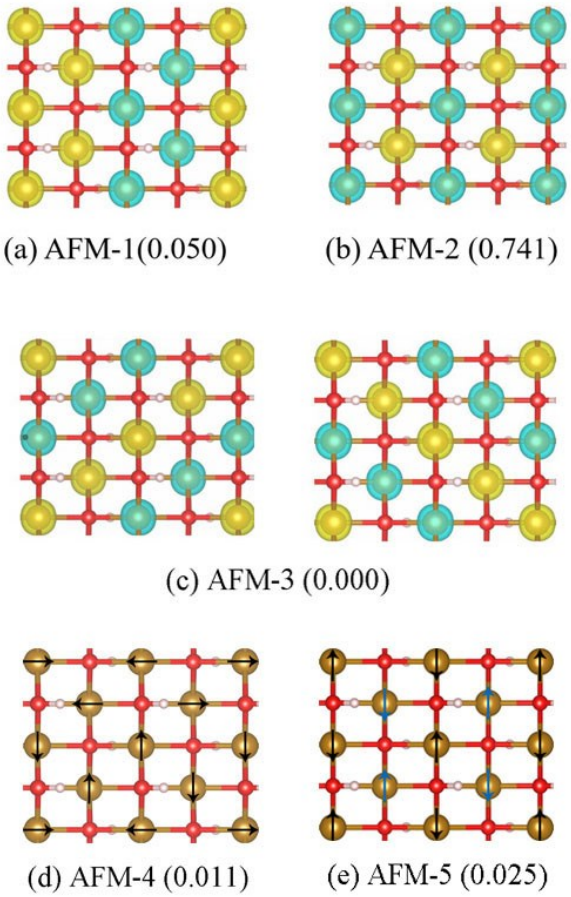

Fig. S6 (a-c) Different collinear AFM ordering of FeOOH monolayer. The two AFM states in (c) are energetically degenerate. The bubble in different colors represents the isovalue surfaces of spin-resolved differential charge density. (d-e) Two non-collinear AFM orderings of FeOOH monolayer. The black and blue arrows represent the in-planes and out-of-plane spin vectors, respectively. The number in parentheses is the energy (eV/supercell) relative to the most stable AFM ordering.