

Supporting Information

Multiferroic Decorated Fe₂O₃ Monolayer Predicted from First Principles

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Section I: Magnetic ground state of pure Fe₂O₃ monolayer

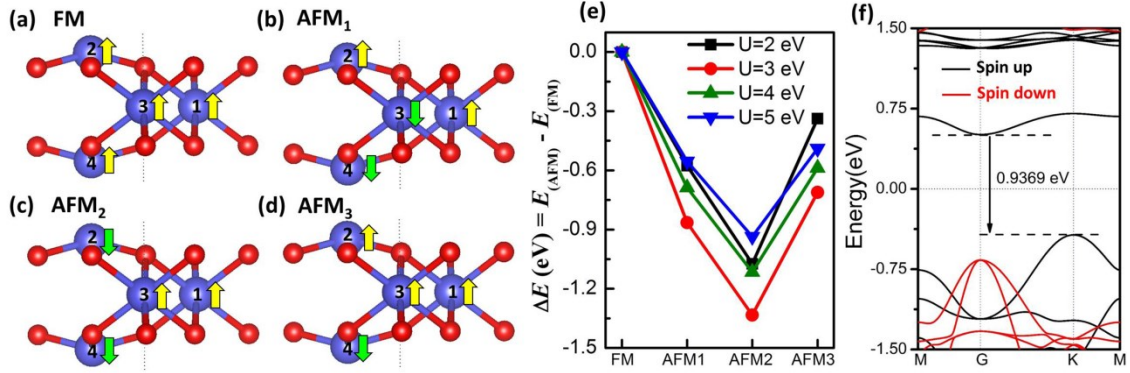


Figure S1 (a-d) Side views of the sketch for possible four FM and AFM spin orders in pure Fe₂O₃ monolayer. Yellow and green arrows represent spin up and down, respectively. Purple and red balls represent Fe and O atoms, respectively. (e) The energy difference (ΔE) with various U_{eff} (eV) values is defined as the change in energies of the various AFM spin orders based on FM configuration (the energy of the FM state is set as the reference). (f) The band structures of pure Fe₂O₃ monolayer.

The magnetic ground state is studied by comparing the energy of pure Fe₂O₃ monolayer with various possible electron spin directions on Fe atoms, including collinear ferromagnetism (FM) and three types of antiferromagnetism (AFM) due to the relatively different positions of Fe atoms, as sketched in Figure S1 (a-d). Yellow and green arrows labelled on Fe atoms represent spin up and down, respectively. The energy difference ($\Delta E = E_{\text{AFM}} - E_{\text{FM}}$) is calculated to check the relative energies of various AFM spin orders with the FM configuration as a reference.

To consider the strongly correlated electron effect of d shell, U_{eff} (Fe) values are usually adopted from previous references or test calculations. In our study, based on the values of literatures¹, we did a test by setting U_{eff} (Fe) to 2-5 eV. Although the values of electrons and spin moments are depend on the value U_{eff} (Fe), the main conclusions of multiferroic effect are not changed. The AFM₂ magnetic order is confirmed to be the most favourable as reflected by the lowest ΔE , where ions with a half-filled d shell and the super-exchange effect from Fe2-O-Fe3 usually leads to strong AFM exchanges, and this conclusion is not changed by introducing U_{eff} (Fe) (2.0 \rightarrow 5.0 eV) [see in Figure S1 (e)]. For α -Fe₂O₃, the U_{eff} (Fe) is commonly chosen to be 3.0 \rightarrow 4.3 eV. Therefore, for the discussion about the distributions of charge and magnetic moment in the main context except otherwise specified, the U_{eff} (Fe) is set to 4.0 eV.

Table S1: Calculated energy differences (ΔE) between AFM and FM spin orders, lattice parameters a and b , corresponding charge (C) (e) and magnetic moments (M) (μB) located on Fe2 and Fe4 atoms for pure Fe₂O₃ monolayer using the PBE functional with U_{eff} (Fe) = 4.0 eV.

Spin	ΔE (eV)	$a=b$ (\AA)	C (Fe2) (e)	C (Fe4) (e)	M (Fe2) (μB)	M (Fe4) (μB)
FM	0	5.20	6.87	6.87	4.16	4.16

AFM ₁	-0.687	5.18	6.942	6.942	4.043	-4.043
AFM ₂	-1.115	5.15	6.977	6.977	3.978	3.978
AFM ₃	-0.588	5.18	6.890	6.974	4.150	-3.973

The calculated lattice parameters for various spin configurations and energies difference (ΔE) between AFM and FM, corresponding charge (e) and magnetic moments (μ_B) located on Fe2 and Fe4 atoms using the PBE functional have been listed in Table S1 with U_{eff} (Fe) set to 4.0 eV. The fully optimized lattice parameter for Fe₂O₃ monolayer with magnetic ground state configuration is $a = b = 5.15 \text{ \AA}$, which is larger than that of bulk hematite since the distance between Fe2 and Fe4 atoms decreases from 3.98 to 3.06 \AA . Besides, from Table S1, it is seen that the lattice parameters, the distribution of charge and magnetic moments on Fe2 and Fe4 atoms are strongly dependent on spin orders. Nevertheless, the charges and magnetic moments located on Fe2 and Fe4 atoms are equivalent in FM, AFM₁, and AFM₂ spin configurations, but charge distributions are inequivalent in Fe2 and Fe4 for AFM₃. Although there is an electric polarization pointing from Fe4 to Fe2, which is perpendicular to the monolayer plane in AFM₃ spin order, it is not the magnetic ground state (0.518 eV/unit higher than AFM₂). The centrosymmetric structure of the most stable magnetic ground state provides not only symmetric bond lengths but also spin population and charge distributions. Besides, the band gap shown in Figure S1 (f) indicates that pure Fe₂O₃ monolayer is a magnetic semiconductor.

Section II: The projected band of d orbitals for Fe2 and Fe4 atom in asymmetric Li@Fe₂O₃ monolayer.

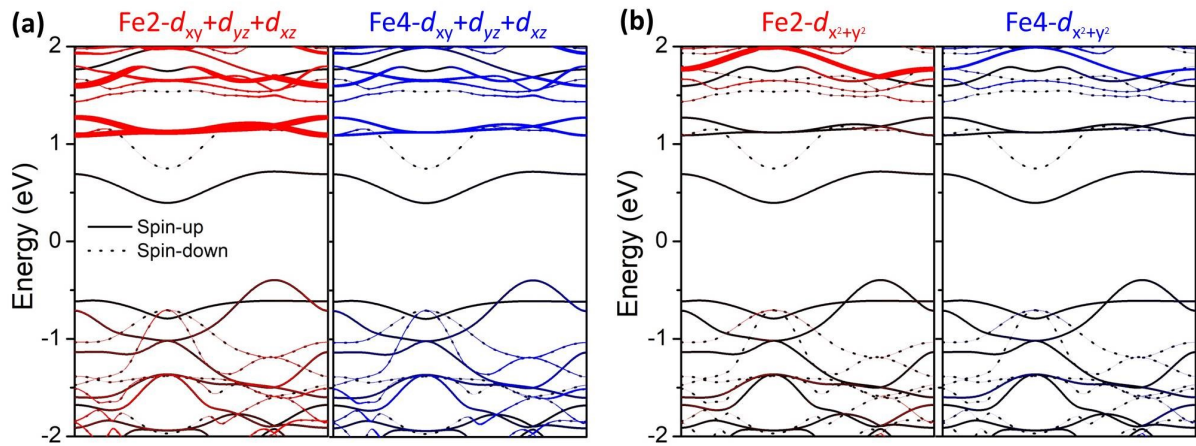


Figure S2. The projected band of the d_{xy} , d_{yz} , d_{xz} and $d_{x^2+y^2}$ orbitals for Fe2 and Fe4 atoms in the asymmetric Li@Fe₂O₃ monolayer. The red and blue lines indicate the projected states from the orbitals of Fe2 and Fe4 atoms, respectively.

Section III: The multiferrocity in X(X = Mg, Al, Cu, B, P and Na)@Fe₂O₃ monolayer

Table S2. The bond lengths of Fe-O and Fe-X (X = Mg, Al, Cu, B, P and Na)

Bond-length (Å)	Mg@Fe ₂ O ₃	Al@Fe ₂ O ₃	Cu@Fe ₂ O ₃	B@Fe ₂ O ₃	P@Fe ₂ O ₃	Na@Fe ₂ O ₃
Fe2-O	1.985	1.957	1.991	1.945	1.999	1.846
Fe4-O	1.985	1.957	1.991	1.945	2.067	1.938
Fe2-X	2.227	2.314	2.221	2.272	2.484	2.347
Fe4-X	2.227	2.314	2.221	2.272	2.484	1.317

We actually checked different atom insertions, including C, N, O, B, P, Li, Na, Mg, Al and Cu. It was found that only N, O, Li and Na can effectively induce Jahn-Teller (JT) effects and multiferroic phenomena. However, the formation energy of N insertion is positive while the JT distortion with O insertion is not obvious. Although Na@Fe₂O₃ monolayer can produce the obvious JT distortion, the extremely large difference between Fe2-Na and Fe4-Na (see Table S2) renders the ferroelectric switch very hard.

Section III: The multiferrocity in O@Fe₂O₃ monolayer

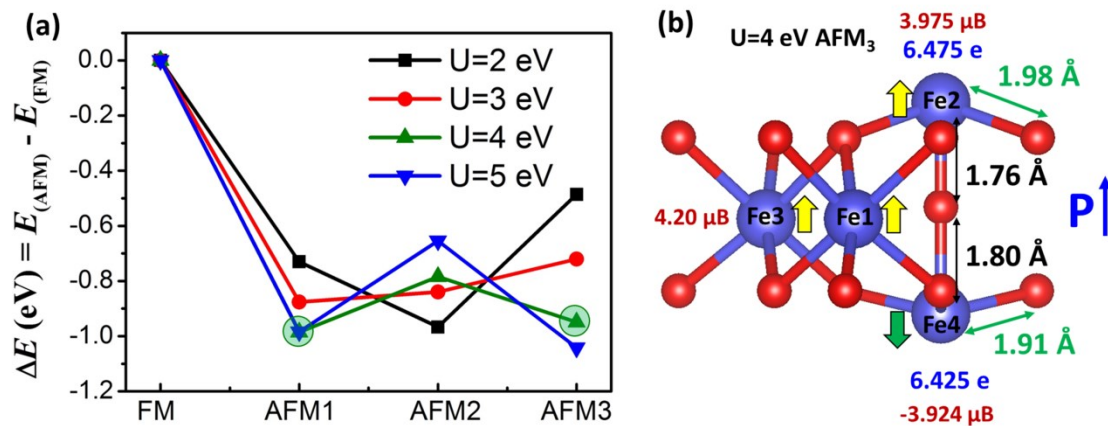


Figure S3. (a) The calculated energy differences (ΔE) between AFM and FM spin orders for different U values. The total energies of FM are set to be 0. The green circles are labelled as two ground states (AFM₁ and AFM₃ spin) with $U_{\text{eff}}(\text{Fe}) = 4.0$ eV. (b) The structures with bond lengths of Fe-O, charges and magnetic moments on Fe2 and Fe4 based on the magnetic ground states of O@Fe₂O₃ monolayer with AFM₃ spin configuration with $U_{\text{eff}}(\text{Fe}) = 4.0$ eV. The letter “P” indicates the direction of electric polarization from Fe2 to Fe4.

We also checked the case of having oxygen decorate the Fe₂O₃ monolayer without introducing any impurities and oxidation reaction. From the results shown in Figure S3 (a), the magnetic ground state is related with U_{eff} values. Compared to the pure Fe₂O₃ monolayer, when $U_{\text{eff}}(\text{Fe}) = 4.0$ eV, the magnetic ground states of O@Fe₂O₃ monolayer can be in either AFM₁ or AFM₃ spin orders, labelled by the green circles in Figure S3 (a). Therefore, we present the structures with bond lengths of Fe-O,

charges and magnetic moments on Fe2 and Fe4 of O@Fe₂O₃ monolayers with AFM₃, and found that the structural symmetry is broken and O is preferred to locate at the position where it slightly shifts away from the middle position as shown in [Figure S3 (b)]. The differences of charge between Fe2 and Fe4 lead to the electric polarization in the system, which is also reflected in the difference of Fe2-O and Fe4-O bond lengths.

Section IV: The multiferroics in multiple layers

To check possible multiferroic phenomena in multiple layers, we chose the double-layer Fe₂O₃ as an example. Results show that inserted Li atoms prefer to get close to Fe atoms near the surfaces, labelled as Fe2 and Fe6 atom in Figure S4. Similar to the case of Fe₂O₃ monolayer, an obvious Jahn-Teller distortion can be seen as evidenced by the distinct bond lengths of Fe6-Li and Fe2-Li and unequal electron transfer between Li and Fe (Fe2 and Fe6 obtained more charges from Li than that of Fe3 and Fe5). It is expected to reverse the directions of polarization and magnetism simultaneously by shifting the Li atom position and the associated electron transfer. The similar mechanism and multiferroics in bilayer structures indicate the universality of the phenomena in Li@Fe₂O₃ system.

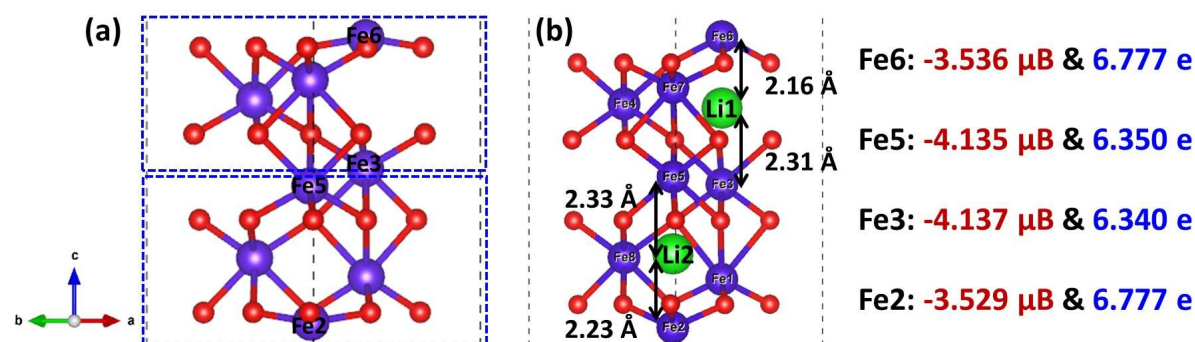


Figure S4: Schematics of the Fe₂O₃ monolayer exfoliated from bulk hematite. Here structures for a double layer are presented.

1. Padilha, A. C. M.; Soares, M.; Leite, E. R.; Fazzio, A., Theoretical and Experimental Investigation of 2d Hematite. *The Journal of Physical Chemistry C* **2019**, *123*, 16359-16365.