Two-dimensional (2D) multiferroics exhibit cross-control capacity between magnetic and electric responses in reduced spatial domain, making them well suited for next-generation nanoscale devices; however, progress has been slow in developing materials with required characteristic properties. Here we identify by first-principles calculations robust 2D multiferroic behaviors in decorated Fe$_2$O$_3$ monolayer, showcasing N@Fe$_2$O$_3$ as a prototypical case, where ferroelectricity and ferromagnetism stem from the same origin, namely Fe d-orbit splitting induced by the Jahn-Teller distortion and associated crystal field changes. The resulting ferromagnetic and ferroelectric polarization can be effectively reversed and regulated by applied electric field or strain, offering efficient functionality. These findings establish strong materials phenomena and elucidate underlying physics mechanism in a family of truly 2D multiferroics that are highly promising for advanced device applications.

Ferromagnetism (FM) and ferroelectricity (FE) are fundamental physics phenomena underlying designs and working principles in many advanced nanoscale devices. Multiferroic materials that exhibit simultaneous presence and effective cross control of magnetic and electric polarization hold great promise for many applications. Of particular interest are atomically thin two-dimensional (2D) multiferroic materials [1-6] that are ideally suited for device miniaturization. Depending on the coupling between FE and FM orders, multiferroics can be classified into two types. For type I, FE polarization generally originates from either spontaneous atomic displacements [6] or synergistic effects of charge and orbital orders [7-10], while FM stems from partially filled d shells of transition metals. These materials usually possess weak magnetoelectric coupling and ineffective cross control between FM and FE, thus limiting their functional capacity. For type-II multiferroics, FE polarization is derived from local magnetic order (AFM order) [1-12] with much stronger magnetoelectric coupling. One example is Hf$_2$VC$_2$F$_2$ monolayer that exhibits FE due to broken inversion symmetry originating from an antiferromagnetic (AFM) order [1]. Another example is VOX$_2$ (X = Cl, Br, and I) monolayer [11] that possesses both FM and FE derived from the $d_{xy}$ orbital splitting of the V cation. There have been hitherto only a few type-II multiferroics discovered, and more are urgently needed for diverse material platforms.

Iron oxides, such as Fe$_3$O$_4$ [12] and Fe$_2$O$_3$ [13], show multiple magnetic states, and recent works have revealed the presence of multiferroicity in Fe-O systems [14-17]. 2D Fe$_3$O$_4$ and $\varepsilon$-Fe$_2$O$_3$ magnetic films display ferroelectric switching [17,18], but the origin of FE polarization is unclear while the magnetoelectric coupling has not been fully explored. Very recently, $\alpha$-Fe$_2$O$_3$ monolayer has been exfoliated from its bulk matrix and demonstrated to be a magnetic semiconductor [14], but this material is non-ferroelectric due to its centrosymmetric structure. Multiferroicity has been induced in $\alpha$-Fe$_2$O$_3$ monolayer by building $\alpha$-Fe$_2$O$_3$/BaTiO$_3$ ferromagnetic/ferroelectric heterostructures, and magnetism in 2D $\alpha$-Fe$_2$O$_3$ is tunable by the interaction with BaTiO$_3$ [15], but the magnetoelectric coupling is weak because the FM and FE order are driven by different sources and mechanisms.

In this Letter, we present results from first-principles studies that show robust multiferroicity in nitrogen-decorated $\alpha$-Fe$_2$O$_3$ (N@$\alpha$-Fe$_2$O$_3$) monolayer. The symmetry breaking by the decorating N atoms between the iron atoms induces a Jahn-Teller distortion that produces FE and FM order, both stemming from the $d_{xy}$-orbit splitting due to changes in the crystal field. The common origin of the FE and FM order yields strong magnetoelectric coupling, allowing an effective tuning and control of the ferroelectric switch and magnetoelectric coupling by applied electric field or mechanical strain. Similar behaviors also have been found in $\alpha$-Fe$_2$O$_3$ monolayer decorated by oxygen and lithium atoms, introducing a new family of 2D multiferroic materials. These findings provide insights into fundamental physics processes and mechanisms underlying the coexisting FE and FM order in atomically thin multiferroics and expand the material offerings for practical implementation.

We have performed calculations using the Vienna Ab-initio Simulation Package (VASP) [19], and computational details are given in Supplemental Material [20]. The Fe$_2$O$_3$ monolayer is modeled based on the structure exfoliated from iron ore hematite ($\alpha$-Fe$_2$O$_3$), which exhibits ferromagnetic order [14]. We first establish benchmarks for pure Fe$_2$O$_3$ monolayer, whose unit cell [Fig. 1(a)] contains 4 Fe atoms with 4 possible magnetic configurations depending on the spin orientations,
where $E_f = (E_{N+Fe2O3} - E_{pure-Fe2O3} - E_N)/n$  

Here, we again compare the symmetric Fe$_2$O$_3$ monolayer, pure Fe$_2$O$_3$ monolayer, and a single isolated nitrogen atom, respectively, and $n$ is the number of atoms in the system. The calculated $E_f$ is -0.186 eV/atom, indicating an exothermic reaction when N atoms are embedded into the Fe$_2$O$_3$ monolayer. This result shows that fabrication of N@Fe$_2$O$_3$ monolayer is energetically feasible.

The fully relaxed structure with a N atom embedded between Fe2 and Fe4 is shown in Fig. 1(c), and the original symmetry is obviously broken. To understand the structural and electronic evolutions, we first built a symmetric structure by placing a N atom in the middle of the Fe2-Fe4 positions to preserve the inversion symmetry, as shown in Fig. 1(b). The uniform initial Fe-O and Fe-N bond lengths ensure a centrosymmetric structural configuration with equivalent charge and magnetic moment distributions on Fe2 and Fe4, resulting in no net out-of-plane polarization. As shown in Fig. 1(a) and (b), N-atom incorporation stretches the Fe-O bond length from 1.82 Å to 1.93 Å, leading to redistributions of electron and spin polarization. However, this symmetric structure is only metastable. When the initially imposed symmetry constraint is removed, structural relaxation produces a deformed monolayer with an energy that is 0.84 meV/unit-cell (14.68 meV/unit-cell at $U=3.0$ eV) lower than the symmetric structure. For the distorted N@Fe$_2$O$_3$, the bond lengths of the upper surface Fe2-O become longer (1.942 Å) while those at the under surface become shorter (1.914 Å), comparing to the value of 1.926 Å in non-polar N@Fe$_2$O$_3$ monolayer. The N atom is significantly shifted along the z direction, and the Fe-N bond lengths are 1.667 and 1.752 Å, respectively, compared with 1.709 Å for the symmetric case, as shown in Fig. 1(c). The Jahn-Teller (JT) distortion occurring spontaneously in this system helps to lower the total energy and break structural symmetry. As a result, charge distributions on Fe2 and Fe4 atoms (7.19e and 7.08e, respectively) are unequal, resulting in the misalignment of the centers of positive and negative charges. The polarization is estimated to be 0.05 eÅ from the berry phase calculation at $U=4.0$ eV. To check the effect of the N atom on the magnetic ground state, we calculated the total energy of all the magnetic arrangements, and the results show that the AFM spin configuration remains the ground state (see Fig. S3). However, the distribution of spin charges is affected by the structural symmetry breaking and becomes unequal as seen in Fig. 1(c). The coexisting ferroelectricity and ferrimagnetism makes N-doped Fe$_2$O$_3$ monolayer a truly 2D multiferroic.

To explore the mechanism underlying the distortion-induced out-of-plane FE polarization of N@Fe$_2$O$_3$ monolayer, we examine changes of the crystal field and energy reduction from the associated electronic band splitting. Here, we again compare the symmetric Fe$_2$O$_3$, symmetric N@Fe$_2$O$_3$, and asymmetric N@Fe$_2$O$_3$ monolayers and assess the Fe-$d$ orbital splitting in the distinct Fe-O and Fe-N bonding environments (Fe1 is bonded with 6 surrounding O atoms while Fe2 is bonded with 3 O atoms), the spin polarization on these Fe atoms are different (4.17 µB on Fe1 and Fe3 [see Fig. 1(a)]. Due to different bonding environments (Fe1 is bonded with 6 surrounding O atoms while Fe2 and Fe4 have the same spin direction, opposite to that on Fe1 and Fe3 [see Fig. 1(a)]. Due to different bonding environments (Fe1 is bonded with 6 surrounding O atoms while Fe2 and Fe4 have the same spin direction, opposite to that on Fe1 and Fe3 [see Fig. 1(a)]. Due to different bonding environments (Fe1 is bonded with 6 surrounding O atoms while Fe2 and Fe4 have the same spin direction, opposite to that on Fe1 and Fe3 [see Fig. 1(a)]. Due to different bonding environments (Fe1 is bonded with 6 surrounding O atoms while Fe2 and Fe4 have the same spin direction, opposite to that on Fe1 and Fe3 [see Fig. 1(a)].
FIG. 2: (a,b) Tetrahedron and hexahedron structural units. The projected partial DOS for Fe2 and Fe4 atoms in (c) pure Fe2O3 monolayer, (d) symmetric N@Fe2O3 monolayer, and (e) asymmetric N@Fe2O3 monolayer with JT distortion. Transverse red and green lines indicate the peaks of Fe d_{xy} orbitals, and red and green arrows show the tendency of energy splits for Fe d_{xy} orbitals.

O-N crystal-field environments in Fig. 2(a-b). For pure Fe2O3 monolayer, Fe atoms at the surface (Fe2 and Fe4) are coordinated with three surrounding oxygen atoms, forming the tetrahedral ligand field, and the Fe-t_{2g} states of both Fe2 and Fe4 split equally into the higher $d_{xy}$ and lower doubly degenerated $d_{yz}$ and $d_{xz}$ states stemming from the symmetric structures [see Fig. 1(a) and Fig. 2(c)]. For the symmetric N@Fe2O3 case, the crystal field changes from tetrahedron to hexahedron, and consequently $d_{xy}$ orbitals of both Fe2 and Fe4 atoms are reduced significantly to lower energy levels, as indicated by the red arrow in Fig. 2(d). Once the symmetry constraint is removed, a spontaneous electronic energy split between the Fe2- and Fe4-$d_{xy}$ states [green arrows in Fig. 2(e)] with orbital-ordering occurs, which originates from the JT distortion with the elongated and shortened Fe-O and Fe-N bond lengths, respectively, thereby inducing the higher Fe2-$d_{xy}$ and lower Fe4-$d_{xy}$ energy levels. The asymmetric shift of the $d$ orbitals, especially the $d_{xy}$ states of Fe2 and Fe4 atoms not only leads to the out-of-plane electric ligand field, but also induces spin redistributions on relevant Fe atoms, as shown in Fig. 1(c), to reach the ferrimagnetic ground state. Here, both the electric polarization and magnetic states share the same origin, stemming from the $d$ orbital shift after N decoration.

Spontaneous polarization of FE materials is reversible by external electric stimuli, which is the basis for information encoding in non-volatile memory devices [23]. To verify this key functionality, we assess the response of the electric polarization along with magnetism in N@Fe2O3 monolayer to an external out-of-plane electric field. Results in Fig. 3 show that the bond length, electric polarization and magnetic moment variations can be well controlled by electric field in the range of 0 to -0.1 eV/Å (the negative value is measured relative to the positive z-axis pointing from Fe2 to Fe4). Since the asymmetric N@Fe2O3 monolayer possesses an intrinsic electric field, a positive field has an insignificant effect. The bond-length difference $|\Delta d| = d(Fe2-N) - d(Fe4-N)$ changes from negative to positive under an increasing negative electric field ($0 \rightarrow -0.1$ eV/Å), as seen in Fig. 3(a), indicating that the N atom is moving from an upper to lower position. At the electric field of -0.06 V/Å, the Jahn-Teller distortion is removed and the structure (inset of Fig. 3a) becomes symmetric as in Fig. 1(b), which not only has identical Fe-N bond length, but also the Fe-O bond length for upper and lower surfaces. This is the crossover point for the vertical polarization reversal, and the process occurs in the external field range of -0.045 to -0.065 eV/Å when the polarization is switched from pointing upward to downward as shown in Fig. 3(b). Meanwhile, the magnetic moment $|\Delta M = M(Fe2) - M(Fe4)|$ also can be reversed by the external electric field. For an intuitive understanding of the polarization reversal, we plot in Fig. 3(d) the charge transfer results, taking the symmetric structure with zero polarization at E=-0.06 eV/Å as a reference since it has the same electron distribution on both surfaces. For the structure with E=0, electron is depleted at the upper surface while accumulated at the lower surface compared with that of the symmetric monolayer at E=-0.06 eV/Å, therefore possessing a polarization pointing upward. When the electric field is increased to -0.1 eV/Å, electron is accumulated (depleted) at the upper (lower) surface, leading to a reversed polarization. The polarization reversal therefore can be attributed to the electric-field controlled electron transfer, rendering this 2D multiferroic a promising material platform for spintronics applications.

Since the electric polarization in N@Fe2O3 monolayer stems from the Jahn-Teller distortion, the asymmetric structure should be sensitive to strain engineering [24]. Hence, we have applied an in-plane biaxial strain to eval-
FIG. 4: The activation energy barrier (a) and FE polarization transition (b) of the distorted N@Fe$_2$O$_3$ monolayer along the CI-NEB simulation pathway at selected $U$ values. The inset in (a) shows an amplified view of the barrier at $U_{eff}=4.0$ eV.

Dramatically, leading to larger structural distortions [see Fig. S5(a)] [20]. As a result, larger $d$-orbital splitting is induced, and electrons are redistributed to reinforce the spontaneous electric polarization. Meanwhile, the magnetic moment difference on Fe$_2$ and Fe$_4$ atoms (∆M) also increases under the tensile strains [see Fig. S5(b)] [20]. In contrast, the JT distortion is weakened or even eliminated by compressive strains, with the bond length difference between Fe$_2$-N and Fe$_4$-N gradually reduced to zero at the strain of -0.06, leading to the non-polar centrosymmetric structure as shown in Fig. 1(b). Correspondingly, the charge and magnetic moment differences between Fe$_2$-N and Fe$_4$-N gradually reduced to zero at the strain of -0.06, leading to the non-polar centrosymmetric structure as shown in Fig. 1(b). Correspondingly, the charge and magnetic moment differences for the upper and lower surface disappear, thus turning off all the multiferroic features. Like the mechanism under electric field, the electron transfer between upper and lower surfaces is also responsible for the strain induced polarization variation [Fig. S5(d)] [21]. The sensitive dependence of the structure, charge distribution and magnetic moment on externally applied electric field and strain indicates that N@Fe$_2$O$_3$ monolayer is a robust and highly responsive multiferroic system with concurrently tuneable FE and FM behaviors.

The energy barrier for the polarization reversal gives good indications on FE stability and switchability. We have performed CI-NEB calculations [20] to assess the energy barrier of polarization reversal at selected $U$ values for N@Fe$_2$O$_3$ monolayer. Results in Fig. 4 show that the transition barrier is 0.667 meV/unit cell at $U_{eff}=4.0$ eV, indicating that the ferroelectric switch can be easily manipulated. Correspondingly, the out-of-plane polarization continuously changes from -0.05 eÅ to +0.05 eÅ, which again indicates that there is no depolarization during the FE reversal. The barrier and FE polarization strength are closely related to electron correction as measured by the $U$ term, as shown in Fig. 4(b). The FE switch barrier rises to 15.0 meV/unit cell at the polarization of 0.1 eÅ in N@Fe$_2$O$_3$ monolayer when $U_{eff}=3.0$ eV, but reduces to almost zero at $U_{eff}=5.0$ eV.

It is noted that multiferroic behaviors are not limited to the case discussed above, but a more general phenomenon in decorated Fe$_2$O$_3$ monolayer. In fact, the JT distortion and induced FE polarization are even more robust when Li atom is inserted between the iron atoms (see Fig. S6) [20]. The AFM ferrimagnetic ground state with the magnetic moment of 1.15 $\mu_B$ is still preserved regardless of the $U$ value. The inserted Li atom locates at the position that is 0.07 Å away from the middle point, while the Fe-O bond lengths are 1.95 Å and 1.84 Å at the upper and lower surfaces, respectively. Similar to the N decorated case, the JT distortion is not only helpful to reduce the total energy of the system, but also move the $d_{xy}$ orbital of Fe$_2$ into the valence band while shift the $d_{yz}$ orbital of Fe$_4$ into the conduction band (Fig. S7) [20], thereby generating strong out-of-plane FE polarization. The reversal barrier is 0.2 eV/unit cell (Fig. S8) [20], which renders the FE phase quite stable. In addition to N and Li decorations, introduction of an O atom between Fe$_2$ and Fe$_4$ also can induce similar multiferroic behaviors in Fe$_2$O$_3$ monolayer although the JT distortion and associated FE polarization are relatively weak.

In summary, we have shown by first-principles calculations that N@Fe$_2$O$_3$ monolayer is a robust 2D multiferroic with concurrent out-of-plane FM and FE orders. The electric polarization in N@Fe$_2$O$_3$ monolayer stems from the crystal-field splitting of $d_{xy}$-orbitals in Fe$_2$ and Fe$_4$ atoms, driven by a spontaneous Jahn-Teller distortion induced by the decorated N atoms. Meanwhile, a net out-of-plane magnetization on Fe$_2$ to Fe$_4$ is induced by the FE polarization, highlighting the common origin and close correlation of the FM and FE responses to external stimuli. Applied electric field or strain can act as an effective means to reverse or reinforce the FM and FE polarization, offering the crucial switchable on/off functionality. The multiferroic behavior unveiled in the present work is a general phenomenon in multiple decorated Fe$_2$O$_3$ monolayer systems, providing new material platforms for exploring intriguing physics mechanisms and innovative device applications.

We acknowledge the grants of high-performance computer time from computing facility at the Queensland University of Technology, the Pawsey Supercomputing Centre and Australian National Computational Infrastructure (NCI). L.K. gratefully acknowledges financial support by the ARC Discovery Project (DP190101607).

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