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# Control of magnetic transitions via interlayer engineering in ferroelectric H<sub>2</sub>O–OH systems

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Jingyan Chen<sup>1,5</sup>, Qiaoxiao Zhao  $^{2,3,5}$ , Meiling Xu  $^{1,4}$ , Zijia Liu<sup>2,3</sup>, Xuegao Hu<sup>2,3</sup>, Jiaqi Feng<sup>1</sup>, Xiaodong Zhou  $^{1}$ , Hong Jian Zhao  $^{4}$ , Baojie Feng  $^{2,3}$ , Lan Chen  $^{2,3}$ , Yinwei Li  $^{1}$  & Yanchao Wang  $^{4}$ 

Controlling magnetic phase transitions in two-dimensional (2D) multiferroics is crucial for both fundamental scientific knowledge and practical applications. Here, we present a general strategy for inducing magnetic transitions in 2D ferroelectrics based on the electron pairing principle. First-principles calculations revealed the coupled ferroelectric and ferromagnetic behavior in water-hydroxyl (H<sub>2</sub>O-OH) monolayer, with ferromagnetism arising from unpaired electrons in 2p bonding orbitals of the OH groups. A ferromagneticto-nonmagnetic phase transition occurs via interlayer coupling, forming  $H_2O_2$ molecules where electrons pair up. Conversely, the nonmagnetic-toferromagnetic transition can be triggered by stacking rearrangements that prevent H<sub>2</sub>O<sub>2</sub> formation and restore unpaired electrons. Importantly, such magnetic transitions can be efficiently controlled by external electric fields. Notably, low-energy-electron-assisted synthesis method and high-resolution scanning tunneling microscopy confirm the successful creation of H<sub>2</sub>O–OH overlayer on Ag(111). These findings provide an approach for magnetism control in 2D ferroelectrics and offer insights for future spintronic and multiferroic devices.

Two-dimensional (2D) multiferroics, which integrate multiple ferroic orders–such as ferroelectricity and ferromagnetism–within a single material<sup>1-6</sup>, hold great promise for the development of high-performance, nonvolatile information storage and processing nanodevices. Controlling magnetic phase transitions in 2D multiferroics is essential for achieving higher-density data storage solutions, as it significantly enhances information capacity within a given physical space. Theoretical studies have demonstrated electric field-induced phase transitions from ferromagnetic to antiferromagnetic in ReWCl<sub>6</sub><sup>7</sup> and NbVS4<sup>8</sup> monolayers, both exhibiting strong magnetoelectric coupling. However, magnetic phase transitions in 2D multiferroics remain largely underexplored.

Given the significance of interlayer interactions in layered materials, strategies such as interlayer stacking, sliding, and twisting have become effective in tailoring the properties of materials<sup>9–21</sup>, including magnetism<sup>22–32</sup> and ferroelectricity<sup>33–46</sup>. For example, layer-dependent ferromagnetism has been observed in CrI<sub>3</sub><sup>23</sup>, Cr<sub>2</sub>Ge<sub>2</sub>Te<sub>6</sub><sup>24</sup> and CrPS<sub>4</sub><sup>25</sup> films at low temperatures. Furthermore, thickness-tunable ferromagnetism has been reported in non-van-der-Waals materials like Cr<sub>5</sub>Te<sub>8</sub><sup>26</sup> and CrCuSe<sub>2</sub><sup>27,28</sup>. Theoretical studies have also indicated that altermagnetism can be achieved in 2D antiferromagnetic van der Waals bilayers through twisting<sup>29,30</sup> and symmetrically restricted direct stacking<sup>31,32</sup>. Moreover, interlayer engineering has enabled slidinginduced 2D ferroelectricity in the topological semimetal WTe<sub>2</sub><sup>43</sup>,

<sup>&</sup>lt;sup>1</sup>Laboratory of Quantum Functional Materials Design and Application, School of Physics and Electronic Engineering, Jiangsu Normal University, Xuzhou 221116, China. <sup>2</sup>Institute of Physics, Chinese Academy of Sciences, Beijing 100190, China. <sup>3</sup>School of Physical Sciences, University of Chinese Academy of Sciences, Beijing 100049, China. <sup>4</sup>Key Laboratory of Material Simulation Methods & Software of Ministry of Education, College of Physics, Jilin University, Changchun 130012, China. <sup>5</sup>These authors contributed equally: Jingyan Chen, Qiaoxiao Zhao. e-mail: xml@calypso.cn; bjfeng@iphy.ac.cn; yinwei\_li@jsnu.edu.cn; wyc@calypso.cn

semiconducting 1T'-ReS<sub>2</sub> multilayers<sup>44</sup>, twisted bilayer graphene<sup>45</sup>, and AB-stacking bilayer *h*-BN<sup>46</sup>.

Although layer-dependent magnetism and ferroelectricity in 2D materials have been extensively explored and partially validated experimentally, reports on layer-dependent multiferroicity or slidinginduced magnetic transitions remain scarce. Advancing this field requires a comprehensive investigation into how interlayer interactions influence multiple ferroic orders. A particularly promising class of systems is 2D molecular ferroelectric-ferromagnetic materials, in which intrinsic magnetism arises from unpaired electrons in radical components. In such systems, interlayer engineering can potentially control spin-order transitions via a simple yet fundamental mechanism–electron pairing.

In this work, we realize the layer- and sliding-dependent multiferroicity in the 2D water-hydroxyl (H<sub>2</sub>O-OH) systems, identified through first-principles calculations and subsequently synthesized using low-energy-electron-assisted (LEEA) synthesis method. Our calculations reveal coupled ferroelectric and ferromagnetic orders in the freestanding H<sub>2</sub>O-OH monolayer: the asymmetric hydrogen-bonding network gives rise to in-plane polarization, while unpaired electrons in the OH group's 2p orbitals contribute to ferromagnetism. By strategically stacking two monolayers into a bilayer, interlayer OH-OH interactions lead to the formation of hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>) molecules, resulting in complete electron pairing and a transition to a nonmagnetic state. Conversely, interlayer sliding prevents H2O2 formation, restores unpaired electrons, and induces a transition from nonmagnetism back to ferromagnetism. Furthermore, STM measurements confirm the successful synthesis of H<sub>2</sub>O-OH multilayers on the Ag(111) surface.

#### Results

**Ferromagnetism and ferroelectricity in the H<sub>2</sub>O–OH monolayer** The freestanding H<sub>2</sub>O–OH monolayer adopts an orthorhombic structure with the space group *Amm*2. This structure comprises alternating H<sub>2</sub>O molecules and OH groups interconnected through hydrogen bonds, as illustrated in Fig. 1a. Various computational methods, including the HSEO6 functional, DFT+U method, meta-GGA with the modified Becke-Johnson potential, and the Perdew-Burke-Ernzerhof hybrid functional (PBEO), were used to calculate the spin-polarized band structures and projected density of states (PDOS). The results indicate that the H<sub>2</sub>O-OH monolayer is a ferromagnetic semiconductor (Fig. 1b and Supplementary Fig. 1).

The total magnetic moment for the H<sub>2</sub>O-OH monolayer is found to be -0.79  $\mu_B$ . A major portion of this moment (-0.70  $\mu_B$ ) is primarily localized on the O atoms within the OH groups (Fig. 1c), whereas the O atoms in H<sub>2</sub>O molecules contribute only a minor amount (-0.09  $\mu_B$ ). H atoms in the OH groups exhibit an almost negligible magnetic moment of -0.003  $\mu_B$ . To further investigate the magnetic properties, three spin configurations were considered on the honeycomb lattice: one ferromagnetic and two antiferromagnetic arrangements. Total energy calculations show that the ferromagnetic configuration is the most stable, with the lowest energy (Supplementary Fig. 2a-c). Furthermore, Monte Carlo simulations estimate a Curie temperature of approximately 11 K for the H<sub>2</sub>O-OH monolayer (Supplementary Fig. 2d).

The alternating arrangement of H<sub>2</sub>O molecules and OH groups forms an asymmetric hydrogen-bonding network, resulting in the absence of spatial inversion symmetry of the H<sub>2</sub>O-OH monolayer. Consequently, a spontaneous electric polarization emerges<sup>47</sup>. The configuration of H<sub>2</sub>O and OH groups stabilizes the electric dipoles along in-plane direction, thereby enhancing the polarization effect. Berry phase calculations yield an in-plane polarization of  $0.28 \times 10^{-9}$  C/m along the [110] direction (Supplementary Fig. 3), comparable to other well-studied 2D materials<sup>6,48-54</sup>, such as SnS ( $0.26 \times 10^{-9}$  C/m)<sup>48</sup>, VOI<sub>2</sub> ( $0.23 \times 10^{-9}$  C/m)

m)<sup>49</sup>, Bi<sub>2</sub>O<sub>2</sub>Se ( $0.28 \times 10^{-9}$  C/m)<sup>50</sup>,  $\gamma$ -AlOOH ( $0.85 \times 10^{-10}$  C/m)<sup>51</sup> and 1T' CrCoS<sub>4</sub> ( $0.86 \times 10^{-10}$  C/m)<sup>6</sup>. This polarization exceeds that of materials exhibiting out-of-plane polarization<sup>33,46,55-58</sup>.

The kinetics pathways for polarization reversal processes were constructed, and the corresponding energy profiles were estimated to determine the energy barrier for ferroelectric switching in the H<sub>2</sub>O-OH monolayer. As a brute-force check, 180° ferroelectric switching involves the displacement of three hydrogen atoms along the directions of their respective hydrogen bonds (highlighted by the black arrows in the insets of Fig. 1d). This leads to an energy barrier between the ferroelectric and intermediate nonpolar states of 0.23 eV for the ferromagnetic state and 0.19 eV for the antiferromagnetic state during the 180° ferroelectric switching (Fig. 1d). During the hydrogen atom shifting process, the intermediate nonpolar state-comprising O<sup>-</sup> anions and hydronium ions (H<sub>3</sub>O<sup>+</sup>)-is identified as a metastable phase with an antiferromagnetic ground state (Supplementary Fig. 4). This finding suggests that during ferroelectric switching, a transition from ferromagnetic to antiferromagnetic order may occur, providing a pathway for the magnetic control of intrinsic polarization.

More importantly, the polarization of the H<sub>2</sub>O-OH monolayer can be switched by 60°, 120°, 240°, or 300° by directly shifting a single H atom along the hydrogen bond direction (highlighted by the black arrows in the insets of Fig. 1e), which efficiently reduces the energy barrier to 70 meV for the ferromagnetic state (Fig. 1e and Supplementary Fig. 5). It is of particular interest to explore how the magnetization responds to changes in the polarization direction. The magnetic anisotropic energy as a function of the magnetization angle were calculated and presented in Fig. 1f. One can see that the easy axis of magnetization for the H<sub>2</sub>O-OH monolayer lies in the plane, with the lowest energy corresponding to in-plane magnetization (Fig. 1f). Interestingly, the easy axis direction can be switched within the xy plane as the polarization direction rotates (Fig. 1g-i). This demonstrates the potential for electric-field control of magnetization direction through ferroelectric switching.

#### Nonmagnetism and ferroelectricity in the H<sub>2</sub>O-OH bilayer

The AB-stacked H<sub>2</sub>O-OH bilayer represents the global energy minimum, as identified using the CALYPSO method<sup>59-62</sup>. This structure is formed by shifting the H<sub>2</sub>O-OH monolayer along the c-axis and rotating it by 60° before assembling it with the original monolayer (Fig. 2a). At this configuration, interlayer OH-OH interactions drive the formation of H<sub>2</sub>O<sub>2</sub> molecules (Fig. 2b). The O-O bond length in the resulting  $H_2O_2$  is 1.47 Å, consistent with that in  $H_2O_2$  molecular crystals<sup>63</sup>. The dynamical stability of the H<sub>2</sub>O–OH bilayer has been confirmed by the absence of imaginary frequency modes in the phonon spectra (Supplementary Fig. 6a). Ab initio molecular dynamics (AIMD) simulations support the thermal stability of the H<sub>2</sub>O-OH bilayer at room temperature (Supplementary Fig. 6b). Band structures and spin-polarized PDOS calculations (Fig. 2c) reveal that the H<sub>2</sub>O-OH bilayer is a nonmagnetic insulator with a wide band gap of 6.58 eV. No spin polarization is observed within the H<sub>2</sub>O<sub>2</sub> molecules, in agreement with our calculations, which yield a total magnetic moment of 0  $\mu_B$ . These results confirm that the formation of H<sub>2</sub>O<sub>2</sub> molecules effectively quenches spin polarization in the bilayer configuration.

The AB-stacked phase belongs to the *C*2 space group and exhibits a *C*<sub>2</sub> point group symmetry. Berry phase calculations indicate that the net in-plane polarization for the H<sub>2</sub>O-OH bilayer is identical to that of the monolayer, with a value of  $0.28 \times 10^{-9}$  C/m along the [110] direction (Supplementary Fig. 7). The switching process proceeds via the displacement of four hydrogen atoms-two in the upper layer and two in the lower layer–along the respective directions of the hydrogen bonds, as indicated by the black arrows in the insets of Fig. 2d. Energy



Fig. 1 | Crystal structure, ferromagnetism and ferroelectricity of the H<sub>2</sub>O-OH monolayer. a Top and side views of the crystal structure. Orange spheres represent O atoms in OH groups, and pink spheres represent O atoms in H<sub>2</sub>O molecules. White spheres represent H atoms. b Spin-polarized band structure and PDOS calculated using the HSE06 functional. Gray and red curves denote the spin-up and spin-down channels, respectively. c Spin density distribution plotted with an iso-surface value of 0.027 e/bohr<sup>3</sup>. d, e Energy profile along the ferroelectric switching pathway, showing the relative energy with respect to the initial

ferroelectric phase. Insets depict the atomic configurations of the initial, transition, and final states during polarization reversal. FM and AFM refer to ferromagnetic and antiferromagnetic states, respectively. Hollow cyan arrows indicate the possible polarization directions, and black arrows indicate atomic displacement during the switching process. **f**-**i** Angular dependence of the magnetic anisotropic energy (MAE) for polarization orientations of 0°, 60°, 120°, and 180°. Orange and cyan lines indicate the magnetization directions in the *xy* and *yz* planes, respectively.

difference calculations between the ferroelectric and intermediate nonpolar states suggest that the energy barrier for 180° ferroelectric switching in the  $H_2O$ –OH bilayer is 0.26 eV (Fig. 2d), slightly higher than that of the monolayer.

In addition to 180° switching, the polarization of the bilayer can also be reversed by 60°, 120°, 240°, or 300°, through the direct displacement of two hydrogen atoms along hydrogen bond directions (highlighted in Fig. 2e), reducing the energy barrier to 0.14 eV (Fig. 2e and Supplementary Fig. 8). However, for six-state polarization switching, the energy barrier in the bilayer is approximately twice that of the monolayer due to the involvement of two hydrogen atoms in the process.

# Layer- and stacking-dependent magnetic transitions in the ferroelectric $\rm H_2O\text{-}OH$ multilayers and the electron pairing mechanism

To better understand the structural and ferroic evolution of  $H_2O-OH$  multilayers, we first constructed trilayer and tetralayer configurations with various stack configurations. Our calculations indicate that the ABA-stacked  $H_2O-OH$  trilayer possesses the lowest energy (Supplementary Table 1), consisting of an AB-stacked bilayer and an additional monolayer on top (Supplementary Fig. 9a and Fig. 3a). Owing to the weak van der Waals (vdW) interactions between the bilayer and the third layer, the OH groups in the outermost layer retain their magnetic behavior. For the tetralayer  $H_2O-OH$  structure, the ABAB-stacked



**Fig. 2** | **Crystal structure, nonmagnetism and ferroelectricity of the H<sub>2</sub>O-OH bilayer. a** Top and side views of the crystal structure. Orange and blue spheres represent O atoms in H<sub>2</sub>O<sub>2</sub> molecules; pink and yellow spheres represent O atoms in H<sub>2</sub>O molecules; white spheres represent H atoms. **b** 2D electron localization function maps. **c** Band structure and spin-polarized PDOS calculated using the

HSE06 functional. **d**, **e** Relative energy with respect to the initial ferroelectric phase along the polarization switching pathway of the  $H_2$ O-OH bilayer. Insets show atomic configurations of the initial, transition, and final states. Hollow cyan arrows indicate the possible polarization directions, while black arrows attached to atoms depict atomic displacements during the polarization reversal process.

configuration is the most energetically favorable (Supplementary Fig. 9b and Fig. 3a), comprising two AB-stacked bilayers with weak vdW interactions. Phonon spectrum calculations support the dynamical stability of both trilayer and tetralayer structures (Supplementary Fig. 9c, d).

Based on these insights, we further explored multilayer configurations ranging from pentalayer to octalayer (Supplementary Table 2). These structures preserve the asymmetric hydrogen-bonding network, thereby sustaining in-plane polarization across multilayers (Supplementary Fig. 10a–d).

To investigate the evolution of magnetism with increasing layer number, we calculated total energies, structural features, polarization, and magnetic ordering across multilayers, as summarized in Fig. 3a. Spin-polarized electronic structure calculations reveal a striking oddeven oscillation: odd-layer systems exhibit ferromagnetism, whereas even-layer systems are nonmagnetic. The magnetic moments in odd layers mainly originate from O atoms in the OH groups and are comparable to those in the monolayer (Supplementary Fig. 11). Spin density calculations further confirm this trend (Supplementary Fig. 12).

This behavior is well explained by molecular orbital theory. As shown in Fig. 3b, magnetism of the OH groups arises from unpaired electron in the 2*p* bonding orbitals. Upon formation of  $H_2O_2$ molecules-via interlayer coupling between OH groups-ten electrons (2*p*<sup>5</sup> for a pseudoatom of OH) become fully paired, quenching magnetic moments and rendering the structure nonmagnetic. Thus, unpaired electrons in OH groups account for ferromagnetism in odd layers, whereas electron pairing in  $H_2O_2$  molecules leads to nonmagnetism in even layers. This establishes  $H_2O$ -OH multilayers as oddeven-dependent multiferroics, emphasizing the central role of electron pairing in determining magnetic order. Building on this mechanism, we explored the possibility for restoring ferromagnetism in even-layer systems via stacking rearrangement to suppress  $H_2O_2$  formation and retain unpaired electrons. We chose the bilayer as a representative system for detailed study.

As shown in Fig. 3c-f, we constructed four additional stacking configurations–AA, AC, AD, and AE. After full structural relaxation,  $H_2O_2$  formation was found only in the AA-stacked phase, which consequently exhibits nonmagnetism. In contrast, the other three phases, stabilized via vdW interactions, do not form  $H_2O_2$  and thus retain ferromagnetic ground states. The AA-stacked phase is energetically close to the AB-stacked one, with a small energy difference of 6.4 meV/atom, whereas the AC, AD, and AE phases have higher in energy ( -200 meV/atom). These energy differences are consistently reproduced across different vdW correction methods (Supplementary Table 3). Phonon spectra validate the dynamical stability of all four stacking configurations (Supplementary Fig. 13). Although the AC-, AD-, and AE-stacked configurations are energetically less favorable, they may still be experimentally accessible via precise stacking control or interlayer sliding techniques.

Symmetry analysis shows that the AA- and AD-stacked bilayers exhibit spontaneous polarization along the  $[1\overline{10}]$  direction, while the AB-, AC-, and AE-stacked phases exhibit spontaneous polarization along the [110] direction. A 90° rotation of the electric polarization can be achieved by applying an electric field, which simultaneously induces structural transformations and modifies the magnetic phases. This is confirmed by transitions between the AA- and AC-stacked phases by applying perpendicular electric field (Supplementary Fig. 14a).

Starting from AB- and AA-stacked phases, we slide the upper layer by a distance d = ma + nb, where *a* and *b* are the lattice vectors, to investigate the sliding-induced transitions. As shown in Fig. 3g, the AC-



Fig. 3 | Layer- and stacking-dependent magnetic transitions and their mechanism. a Total energy of H<sub>2</sub>O-OH as a function of layer number from monolayer to octalayer. Insets show the crystal structures of H<sub>2</sub>O-OH multilayers, along with their space groups and point groups, and molecular units. **b** The molecular orbital scheme of the OH group and H<sub>2</sub>O<sub>2</sub> molecule. The OH group is treated as a pseudoatom with five electrons to construct the molecular orbital diagram of H<sub>2</sub>O<sub>2</sub> molecule. **c**-**f** Crystal structures of the H<sub>2</sub>O-OH bilayers with

different stacking configurations. Relative energies (with respect to the AB-stacked phase) and corresponding space and point groups are indicated. FM and NM refer to ferromagnetic and nonmagnetic states, respectively. **g** Sliding energy profiles of the H<sub>2</sub>O-OH bilayer with AB and AA stacking along various directions. Interlayer distances were optimized throughout the sliding process. After identifying low-energy configurations, full structural optimization was performed. Hollow squares indicate the energies of the fully optimized H<sub>2</sub>O-OH bilayer structures.

and AE-stacked phases can be obtained by shifting the upper layer of the AB-stacked phase by (m = 1/3, n = 1/3) and (m = 2/3, n = 2/3), respectively. Similarly, the AD-stacked phases emerge from the AA-stacked phase with sliding distances of (m = 1/2, n = 0).

Theoretical calculations further predict that an external electric field of -0.43 V/Å along the [110] direction can induce a transition from the AB to AC structure, while a field of -0.25 V/Å along the [1 $\overline{10}$ ] direction can drive the AA-to-AC transformation (Supplementary Fig. 14b, c). These findings demonstrate that magnetic transitions in the H<sub>2</sub>O-OH bilayer can be effectively controlled via interlayer sliding, mediated by externally applied electric fields.

#### Synthesis of the H<sub>2</sub>O-OH multilayers on Ag(111)

Our calculations demonstrated that the  $(\sqrt{7} \times \sqrt{7})$ -(H<sub>2</sub>O–OH) supercell has a small lattice mismatch of 3.1% with the (4×4)-Ag(111) surface. This minor mismatch reduces the interfacial strain, making the formation of the overlayer energetically favorable. Based on this result, we selected Ag(111) as the substrate for synthesizing the H<sub>2</sub>O–OH multilayers using the LEEA method. In this process, low-energy electrons dissociate H<sub>2</sub>O at low temperatures, facilitating the formation of H<sub>2</sub>O–OH overlayers on the Ag(111) surface. When a small amount of H<sub>2</sub>O is deposited on the Ag surface, the combined effects of electron injection and thermal activation result in the formation of a wellordered H<sub>2</sub>O–OH monolayer, as illustrated in Fig. 4a. Increasing the  $\rm H_2O$  coverage leads to the development of multilayer  $\rm H_2O$ -OH structures (Supplementary Fig. 15 and Fig. 4b). STM images of these structures on Ag(111) consistently reveal a hexagonal pattern characterized by six bright protrusions. Height profile analyzes confirm that these structures correspond to bilayer, trilayer, and multilayer  $\rm H_2O$ -OH formations (Fig. 4b,c).

The lattice constants for the H<sub>2</sub>O–OH systems on Ag were determined to be  $a = b \approx 11.56$  Å and  $\theta \approx 120^\circ$ , which corresponds to a 4 × 4 superstructure of the Ag(111) surface, which is consistent with our structural model for  $(\sqrt{7} \times \sqrt{7})$ -(H<sub>2</sub>O-OH)/(4 × 4)-Ag(111), as shown in Supplementary Fig. 16a–c. After structural optimization, the calculated step heights closely align with the experimental data (Supplementary Fig. 17). The atomic structures of the topmost layers in the H<sub>2</sub>O-OH multilayer exhibit strong similarity to those of the monolayer, resulting in consistent STM images across all formations. The topmost H<sub>2</sub>O–OH layer in the trilayer, when superimposed on STM images, aligns precisely with experimental observations (Fig. 4d). Furthermore, the simulated STM image (Supplementary Fig. 18) accurately reproduces the experimental results, displaying the characteristic hexagonal pattern of six bright protrusions and thereby supporting the proposed structural model.

To reveal the electronic structures, we performed scanning tunneling spectroscopy (STS) measurements on monolayer  $H_2O$ -OH. As shown in Supplementary Fig. 19, the dI/dV spectrum obtained at the



Fig. 4 | STM images showing the evolution of the Ag(111) surface with increasing H<sub>2</sub>O coverage exposed to an electron beam of energy 120 eV for 45 s at 70 K, followed by annealing at 275 K. a STM image of monolayer H<sub>2</sub>O-OH on Ag(111) (V = 2 V). b STM image showing the coexistence of monolayer, bilayer,

trilayer, and multilayer H<sub>2</sub>O–OH on Ag(111) (V = –0.5 V). **c** Height profiles corresponding to the purple line in (**b**). **d** A zoomed-in STM image of H<sub>2</sub>O–OH trilayer overlaid with a structural model (V = 0.1 V). The blue parallelogram in (**d**) denotes the  $(\sqrt{7} \times \sqrt{7})$  lattice cell.

bright protrusion (marked with a '+' symbol) of the hexagonal ring reveals a characteristic gap of ~0.60 eV. The STS shows two shoulders in the DOS, located at 0.4 eV above and 0.95 eV below the Fermi level, corresponding to the conduction band minimum and valence band maximum, respectively. The band edges are notably broadened, making the precise determination of the band gap challenging. Nevertheless, the semiconducting nature of the material is clearly demonstrated.

In summary, we propose a general strategy for achieving transitions between ferromagnetic and nonmagnetic states based on electron pairing principles through interlayer engineering. Using firstprinciples calculations, we demonstrate that the H<sub>2</sub>O-OH monolayer is a 2D multiferroic material, with ferromagnetism arising from unpaired electrons in the bonding orbitals of OH groups. In AB- and AA-stacked bilayer structures, interlayer interactions between OH groups lead to the formation of H<sub>2</sub>O<sub>2</sub> molecules, resulting in complete electron pairing and the suppression of magnetism. Consequently, the multiferroicity of H<sub>2</sub>O-OH multilayers exhibits an odd-even layer-dependent behavior. By tailoring the stacking configuration to prevent H<sub>2</sub>O<sub>2</sub> formation and preserve unpaired electrons, a transition from a nonmagnetic to a ferromagnetic state can be induced. Importantly, such magnetic transitions in even-layer bilayers can potentially be controlled by externally applied electric fields, offering a promising route for the realization of multifunctional device applications. Furthermore, we have successfully synthesized  $H_2O-OH$  multilayers on the Ag(111) surface, providing experimental validation of the proposed structure. By introducing a route for electric-field-controlled magnetic switching based on the fundamental principle of electron pairing, this work

opens avenues for exploring coupling mechanisms in 2D multiferroics and offers valuable insights for the development of voltage-controlled magnetic switches and non-volatile memory storage devices.

#### Methods

#### **First-principles calculations**

Our first-principles calculations were performed using density functional theory (DFT)<sup>64</sup> with the projector-augmented wave method (PAW)<sup>65</sup>, as implemented in the Vienna ab initio Simulation Pack (VASP)<sup>66,67</sup>. The exchange-correlation functional was described by the generalized gradient approximation (GGA) in the form of the Perdew-Burke-Ernzerhof (PBE). The kinetic energy cutoff of the plane wave basis was set to be 650 eV. The first Brillouin zone was sampled using a  $\Gamma$ -centered 7 × 7 × 1 Monkhorst-Pack grid<sup>68</sup>. All structures were relaxed until the convergence criteria for energy and force were 10<sup>-6</sup> eV and 0.01 eV<sup>-1</sup>, respectively. We employed several alternative functionals, including DFT+U method, meta-GGA with the modified Becke-Johnson potential, and the Perdew-Burke-Ernzerhof hybrid functional (PBEO), and HSEO6 hybrid functional<sup>69</sup> to estimate the band gap. The optB88vdW, optB86b-vdW, optPBE-vdW, and vdW-DF methods were used exclusively to describe vdW interactions between layers to identify the optimal stacking order. Electric polarization was calculated using the Berry phase method<sup>70</sup>. A ferroelectric switching pathway was obtained using the climbing-image nudged elastic band method<sup>71,72</sup>. Phonon spectrum calculations were performed using the finite displacement method, as implemented in the PHONOPY code<sup>73</sup>. The temperaturedependent effective potential method was used to determine the influence of thermal effects on the phonon dispersion relations<sup>74</sup>. The

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external in-plane electric field was applied by imposing a finite homogeneous electric field using the perturbation expression after discretization (PEAD) approach<sup>75,76</sup>. AIMD simulations were performed using a Nosé–Hoover chain thermostat with a total simulation time of 10 ps (time step of 1 fs).

#### Sample preparation and STM/STS measurements

Single-crystal Ag(111) was prepared by repeated cycles of Ar ion sputtering and annealing. Ultrapure H<sub>2</sub>O (2 ppm; Alfa Aesar) was used and further purified under vacuum by freeze-pump-thaw cycles to eliminate residual impurities. H<sub>2</sub>O molecules were dosed in situ onto the pristine Ag(111) surface held at 70 K using a dosing tube. Electron injection was performed over the entire sample surface to ensure homogeneity. The sample was then heated to 275 K, resulting in the appearance of a well-ordered overlayer. Subsequently, the sample was cooled back to 70 K for further measurements. The successful growth of the ordered H<sub>2</sub>O-OH monolayer was verified STM. STM measurements were performed in a home-built system at -5 K. The sample was kept at low temperature during the transfer process. The STS spectra were measured by using lock-in technology with an AC voltage of 20 mV and a superimposed frequency of 667 Hz on the bias voltage. The STM/STS data were processed using the free WSxM software<sup>77</sup>.

# Data availability

All data generated in this study are provided in the Supplementary Information.

# References

- 1. Wang, Z. & Dong, S. Alterferroicity with seesaw-type magnetoelectricity. *Proc. Natl. Acad. Sci.* **120**, e2305197120 (2023).
- Huang, C. et al. Toward room-temperature electrical control of magnetic order in multiferroic van der Waals materials. *Nano Lett.* 22, 5191–5197 (2022).
- Huang, C. et al. Prediction of intrinsic ferromagnetic ferroelectricity in a transition-metal halide monolayer. *Phys. Rev. Lett.* **120**, 147601 (2018).
- 4. Zhao, Y. et al. Surface vacancy-induced switchable electric polarization and enhanced ferromagnetism in monolayer metal trihalides. *Nano Lett.* **18**, 2943–2949 (2018).
- Zhang, J.-J. et al. Type-II multiferroic Hf<sub>2</sub>VC<sub>2</sub>F<sub>2</sub> MXene monolayer with high transition temperature. J. Am. Chem. Soc. 140, 9768–9773 (2018).
- Tang, C., Zhang, L., Sanvito, S. & Du, A. Enabling room-temperature triferroic coupling in dual transition-metal dichalcogenide monolayers via electronic asymmetry. J. Am. Chem. Soc. 145, 2485–2491 (2023).
- Xu, M. et al. Electrical control of magnetic phase transition in a type-I multiferroic double-metal trihalide monolayer. *Phys. Rev. Lett.* **124**, 067602 (2020).
- 8. Qu, Z. et al. Strong magnetoelectric coupling in a double transition metal dichalcogenide monolayer. *Phys. Rev. B* **110**, L161408 (2024).
- Qiao, J., Kong, X., Hu, Z.-X., Yang, F. & Ji, W. High-mobility transport anisotropy and linear dichroism in few-layer black phosphorus. *Nat. Commun.* 5, 4475 (2014).
- Yan, J. et al. Stacking-dependent interlayer coupling in trilayer MoS<sub>2</sub> with broken inversion symmetry. *Nano Lett.* **15**, 8155–8161 (2015).
- Çakır, D., Sevik, C. & Peeters, F. M. Significant effect of stacking on the electronic and optical properties of few-layer black phosphorus. *Phys. Rev. B* **92**, 165406 (2015).
- Olsen, R., van Gelderen, R. & Smith, C. M. Ferromagnetism in ABCstacked trilayer graphene. *Phys. Rev. B* 87, 115414 (2013).
- Zhang, F., Sahu, B., Min, H. & MacDonald, A. H. Band structure of ABC-stacked graphene trilayers. *Phys. Rev. B* 82, 035409 (2010).
- Cao, Y. et al. Correlated insulator behaviour at half-filling in magicangle graphene superlattices. *Nature* 556, 80–84 (2018).

- 15. Cao, Y. et al. Unconventional superconductivity in magic-angle graphene superlattices. *Nature* **556**, 43–50 (2018).
- Kumar, K., Sharma, M. & Pandey, R. Tunability in electronic and optical properties of GaS/PbS vdW heterostructure. *J. Phys. Chem. Solids* 196, 112348 (2025).
- Sharma, M., Kumar, A., Ahluwalia, P. & Pandey, R. Strain and electric field induced electronic properties of two-dimensional hybrid bilayers of transition-metal dichalcogenides. J. Appl. Phys. **116**, 063711 (2014).
- Sharma, M., Jamdagni, P., Kumar, A. & Ahluwalia, P. Electronic, dielectric and mechanical properties of MoS<sub>2</sub>/SiC hybrid bilayer: A first principle study. *Phys. E: Low.-dimensional Syst. Nanostruct.* **71**, 49–55 (2015).
- Rani, R., Sharma, M., Bharti, A. & Sharma, R. Giant quantum capacitance and Rashba splitting in tellurene bilayer derivatives. *Phys. E: Low.-dimensional Syst. Nanostruct.* **152**, 115757 (2023).
- Thakur, R., Ahluwalia, P., Kumar, A., Sharma, M. & Sharma, R. Twisted helical armchair graphene nanoribbons: mechanical and electronic properties. *Eur. Phys. J. B* 94, 99 (2021).
- Sharma, M., Jamdagni, P., Kumar, A. & Ahluwalia, P. K. Electronic and dielectric properties of MoS<sub>2</sub>-MoX<sub>2</sub> heterostructures. *AIP Conf. Proc.* **1661**, 080028 (2015).
- 22. Jiang, P. et al. Stacking tunable interlayer magnetism in bilayer CrI<sub>3</sub>. *Phys. Rev. B* **99**, 144401 (2019).
- 23. Huang, B. et al. Layer-dependent ferromagnetism in a van der Waals crystal down to the monolayer limit. *Nature* **546**, 270–273 (2017).
- 24. Gong, C. et al. Discovery of intrinsic ferromagnetism in twodimensional van der Waals crystals. *Nature* **546**, 265–269 (2017).
- 25. Son, J. et al. Air-stable and layer-dependent ferromagnetism in atomically thin van der Waals CrPS<sub>4</sub>. ACS Nano **15**, 16904–16912 (2021).
- Chen, C. et al. Air-stable 2D Cr<sub>5</sub>Te<sub>8</sub> nanosheets with thicknesstunable ferromagnetism. *Adv. Mater.* **34**, 2107512 (2022).
- 27. Peng, J. et al. Even-odd-layer-dependent ferromagnetism in 2D nonvan-der-Waals CrCuSe<sub>2</sub>. *Adv. Mater.* **35**, 2209365 (2023).
- Sun, Z. et al. Evidence for multiferroicity in single-layer CuCrSe<sub>2</sub>. Nat. Commun. 15, 4252 (2024).
- 29. He, R. et al. Nonrelativistic spin-momentum coupling in antiferromagnetic twisted bilayers. *Phys. Rev. Lett.* **130**, 046401 (2023).
- Liu, Y., Yu, J. & Liu, C.-C. Twisted magnetic van der Waals bilayers: An ideal platform for altermagnetism. *Phys. Rev. Lett.* **133**, 206702 (2024).
- Zeng, S. & Zhao, Y.-J. Bilayer stacking A-type altermagnet: a general approach to generating two-dimensional altermagnetism. *Phys. Rev. B* **110**, 174410 (2024).
- 32. Pan, B. et al. General stacking theory for altermagnetism in bilayer systems. *Phys. Rev. Lett.* **133**, 166701 (2024).
- Li, L. & Wu, M. Binary compound bilayer and multilayer with vertical polarizations: two-dimensional ferroelectrics, multiferroics, and nanogenerators. ACS Nano 11, 6382–6388 (2017).
- Xun, W. et al. Coexisting magnetism, ferroelectric, and ferrovalley multiferroic in stacking-dependent two-dimensional materials. *Nano Lett.* 24, 3541–3547 (2024).
- Yang, L., Ding, S., Gao, J. & Wu, M. Atypical sliding and moiré ferroelectricity in pure multilayer graphene. *Phys. Rev. Lett.* **131**, 096801 (2023).
- 36. Wu, M. & Li, J. Sliding ferroelectricity in 2D van der Waals materials: related physics and future opportunities. *Proc. Natl Acad. Sci.* **118**, e2115703118 (2021).
- 37. Ji, J., Yu, G., Xu, C. & Xiang, H. General theory for bilayer stacking ferroelectricity. *Phys. Rev. Lett.* **130**, 146801 (2023).
- Yang, L. & Wu, M. Across-layer sliding ferroelectricity in 2D heterolayers. Adv. Funct. Mater. 33, 2301105 (2023).
- Ding, N., Ye, H. & Dong, S. Quasi-one-dimensional sliding ferroelectricity in Nbl<sub>4</sub>. *Phys. Rev. B* **110**, 024115 (2024).

- Hou, C. et al. In-plane sliding ferroelectricity realized in penta-PdSe<sub>2</sub>/penta-PtSe<sub>2</sub> van der Waals heterostructure. ACS Nano 18, 16923–16933(2024).
- Tang, P. & Bauer, G. E. Sliding phase transition in ferroelectric van der Waals bilayers. *Phys. Rev. Lett.* **130**, 176801 (2023).
- Sivadas, N., Okamoto, S., Xu, X., Fennie, C. J. & Xiao, D. Stackingdependent magnetism in bilayer Crl<sub>3</sub>. *Nano Lett.* 18, 7658–7664 (2018).
- Fei, Z. et al. Ferroelectric switching of a two-dimensional metal. Nature 560, 336–339 (2018).
- Wan, Y. et al. Room-temperature ferroelectricity in 1T'-ReS<sub>2</sub> multilayers. *Phys. Rev. Lett.* **128**, 067601 (2022).
- Zheng, Z. et al. Unconventional ferroelectricity in moiré heterostructures. *Nature* 588, 71–76 (2020).
- Yasuda, K., Wang, X., Watanabe, K., Taniguchi, T. & Jarillo-Herrero, P. Stacking-engineered ferroelectricity in bilayer boron nitride. *Science* 372, 1458–1462 (2021).
- Shi, P.-P. et al. Symmetry breaking in molecular ferroelectrics. Chem. Soc. Rev. 45, 3811–3827 (2016).
- Wu, M. & Zeng, X. C. Intrinsic ferroelasticity and/or multiferroicity in two-dimensional phosphorene and phosphorene analogues. *Nano Lett.* 16, 3236–3241 (2016).
- Tan, H. et al. Two-dimensional ferromagnetic-ferroelectric multiferroics in violation of the d<sub>0</sub> rule. *Phys. Rev. B* 99, 195434 (2019).
- Wu, M. & Zeng, X. C. Bismuth oxychalcogenides: a new class of ferroelectric/ferroelastic materials with ultra high mobility. *Nano Lett.* 17, 6309–6314 (2017).
- Liu, C. et al. First-principles study of ferroelectricity, antiferroelectricity, and ferroelasticity in two-dimensional γ-AlOOH. *Phys. Rev. B* **107**, L121402 (2023).
- Chang, K. et al. Enhanced spontaneous polarization in ultrathin SnTe films with layered antipolar structure. *Adv. Mater.* **31**, 1804428 (2019).
- Fei, R., Kang, W. & Yang, L. Ferroelectricity and phase transitions in monolayer group-IV monochalcogenides. *Phys. Rev. Lett.* **117**, 097601 (2016).
- Guan, S., Liu, C., Lu, Y., Yao, Y. & Yang, S. A. Tunable ferroelectricity and anisotropic electric transport in monolayer β-GeSe. *Phys. Rev. B* 97, 144104 (2018).
- Yang, Q., Xiong, W., Zhu, L., Gao, G. & Wu, M. Chemically functionalized phosphorene: two-dimensional multiferroics with vertical polarization and mobile magnetism. *J. Am. Chem. Soc.* **139**, 11506–11512 (2017).
- Di Sante, D., Stroppa, A., Barone, P., Whangbo, M.-H. & Picozzi, S. Emergence of ferroelectricity and spin-valley properties in twodimensional honeycomb binary compounds. *Phys. Rev. B* **91**, 161401 (2015).
- Zhang, C. et al. First-principles study of a Mn-doped In<sub>2</sub>Se<sub>3</sub> monolayer: coexistence of ferromagnetism and ferroelectricity with robust half-metallicity and enhanced polarization. *Phys. Rev. B* 102, 134416 (2020).
- Luo, W., Xu, K. & Xiang, H. Two-dimensional hyperferroelectric metals: A different route to ferromagnetic-ferroelectric multiferroics. *Phys. Rev. B* 96, 235415 (2017).
- 59. Wang, Y. et al. An effective structure prediction method for layered materials based on 2D particle swarm optimization algorithm. *J. Chem. Phys.* **137**, 224108 (2012).
- 60. Wang, Y., Lv, J., Zhu, L. & Ma, Y. Crystal structure prediction via particle-swarm optimization. *Phys. Rev. B* **82**, 094116 (2010).
- Gao, B. et al. Interface structure prediction via CALYPSO method. Sci. Bull. 64, 301–309 (2019).
- Shao, X. et al. A symmetry-orientated divide-and-conquer method for crystal structure prediction. J. Chem. Phys. 156, 014105 (2022).

- Busing, W. R. & Levy, H. A. Crystal and molecular structure of hydrogen peroxide: a neutron-diffraction study. *J. Chem. Phys.* 42, 3054–3059 (1965).
- 64. Kohn, W. & Sham, L. J. Self-consistent equations including exchange and correlation effects. *Phys. Rev.* **140**, A1133 (1965).
- 65. Blöchl, P. E. Projector augmented-wave method. *Phys. Rev. B* **50**, 17953 (1994).
- 66. Kresse, G. & Hafner, J. Ab initio molecular dynamics for open-shell transition metals. *Phys. Rev. B* **48**, 13115 (1993).
- Kresse, G. & Furthmüller, J. Efficient iterative schemes for ab initio total-energy calculations using a plane-wave basis set. *Phys. Rev. B* 54, 11169 (1996).
- 68. Monkhorst, H. J. & Pack, J. D. Special points for Brillouin-zone integrations. *Phys. Rev. B* **13**, 5188 (1976).
- 69. Heyd, J., Scuseria, G. E. & Ernzerhof, M. Hybrid functionals based on a screened Coulomb potential. *J. Chem. Phys.* **118**, 8207–8215 (2003).
- 70. King-Smith, R. & Vanderbilt, D. Theory of polarization of crystalline solids. *Phys. Rev. B* **47**, 1651 (1993).
- 71. Henkelman, G., Uberuaga, B. P. & Jónsson, H. A climbing image nudged elastic band method for finding saddle points and minimum energy paths. J. Chem. Phys. **113**, 9901–9904 (2000).
- 72. Henkelman, G. & Jónsson, H. Improved tangent estimate in the nudged elastic band method for finding minimum energy paths and saddle points. *J. Chem. Phys.* **113**, 9978–9985 (2000).
- 73. Togo, A., Oba, F. & Tanaka, I. First-principles calculations of the ferroelastic transition between rutile-type and  $CaCl_2$ -type SiO<sub>2</sub> at high pressures. *Phys. Rev. B* **78**, 134106 (2008).
- Hellman, O., Steneteg, P., Abrikosov, I. A. & Simak, S. I. Temperature dependent effective potential method for accurate free energy calculations of solids. *Phys. Rev. B* 87, 104111 (2013).
- Ding, W. et al. Prediction of intrinsic two-dimensional ferroelectrics in In<sub>2</sub>Se<sub>3</sub> and other III<sub>2</sub>-VI<sub>3</sub> van der Waals materials. *Nat. Commun.* 8, 14956 (2017).
- Nunes, R. & Gonze, X. Berry-phase treatment of the homogeneous electric field perturbation in insulators. *Phys. Rev. B* 63, 155107 (2001).
- 77. Horcas, I. et al. Wsxm: a software for scanning probe microscopy and a tool for nanotechnology. *Rev. Sci. Instrum.* **78**, 013705 (2007).

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# **Author contributions**

M.X., B.F., Y.L. and Y.W. conceived and designed the project and directed the calculations and experiments. J.C. and M.X. performed structure prediction and first-principles calculations. Q.Z., Z.L. and X.H. performed experimental measurements. Y.L., H.J.Z., X.Z., J.F. and L.C. analyzed the data. M.X., B.F. and Y.W. wrote the manuscript with input from all other authors. This manuscript reflects the contributions of all authors.

### **Competing interests**

The authors declare no competing interests. Correspondence should be addressed to M.X., B.F., Y.L., and Y.W.

#### Additional information

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**Correspondence** and requests for materials should be addressed to Meiling Xu, Baojie Feng, Yinwei Li or Yanchao Wang.

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