

Single-spin manipulation by electric fields and adsorption of molecules

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Performing *ab initio* calculations, we reveal that the magnetic anisotropy (MA) and the spin direction of a single adatom can be manipulated with a combination of electric fields and adsorption of molecules. Choosing the Fe adatom on the Cu₂N/Cu(001) surface as a typical model system, we show that the MA of the pristine Fe adatom and the Fe adatom with an additional H or F atom adsorption remarkably changes by applying an external electric field. Moreover, we show that the F adsorption leads to the spin-reorientation transition of the Fe adatom from in plane to out of plane. Controlling the magnetization dynamics of a single magnetic adatom by molecule adsorption is demonstrated.

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Magnetic anisotropy (MA), one of the most important parameters toward the ultimate limit of future data-storage systems single-atom memory, defines the thermal stability of the spin and the energy needed to switch it from one orientation to another one [1–4]. Large MA is highly desirable for a stable and robust data storage against thermal fluctuation, but at the same time it makes the reversal of magnetization difficult. Therefore, systems with a large MA and easily controlled magnetization switching are in great demand. Since MA stems from the spin-orbital coupling (SOC), diverse strategies to scale up the MA by increasing the SOC have been proposed, such as alloying with heavy elements [5,6], increasing orbital localization by depositing on the anisotropic substrate [1,7], changing the local environment [8,9], or introducing a strong ligand field [10,11]. The MA in these systems can't be tuned continuously, however. The manipulation of magnetic properties of nanostructures with electric fields has attracted great attention in both fundamental science and innovative spintronics applications [12]. The MA of layered structures can be tuned continuously with the electric field via magnetoelectric effect [13–16] and the surface charging [17,18]. Furthermore, as the dimension of magnetic structures scales down to the atomic level, their magnetic properties can also be tuned by the electric field [19,20], for example the magnetic ordering of a Mn dimer and the spin orientation of a magnetic molecule were changed under the electric field [21,22].

Recently, it was demonstrated that spin states of antiferromagnetic atomic chains can be manipulated by a local electric field from a scanning tunneling microscopy (STM) tip or by exchange interactions between the STM tip and the atomic chains [23,24]. Since magnetic properties of nanostructures can be tailored with local perturbations, changing chemical environment of nanostructures with ligand fields, such as molecule adsorption, can also be used to tune their magnetic properties. The spin reorientation transitions in thin films induced by H or CO adsorption have been reported in experiments nearly two decades ago [25–27]. Very recently, it was reported in STM experiments that for a Co atom on the Pt or on the h-BN/Ru surfaces, spin states and the MA of the Co atom can be tailored by the adsorption of H atoms [28,29]. Moreover, the magnetism of a Hund's impurity and the chiral

magnetic interaction between two individual atoms can also be tuned by the H adsorption [30,31].

In this paper, we present the state of the art *ab initio* calculations which give clear evidence that molecule adsorption on a single magnetic adatom and external electric fields can be used to tune their MA and magnetization switching. We concentrate on the single Fe atom and the Fe atom with additional H/F atom adsorption on the Cu₂N/Cu(001) surface. The fluorine adsorption is shown to cause the spin reorientation transition in the Fe adatom. The remarkable changes in MA are found by applying an external electric field for all adsorbates. We demonstrate that the fluorine adsorption on the Fe adatom can significantly decrease magnetic fields for spin switching.

Our calculations are based on projector augmented wave (PAW) methods as implemented in the Vienna *ab initio* simulation package (VASP) [32,33] and the generalized gradient approximation (GGA). The basis set contained plane waves with a kinetic energy cutoff of 500 eV, and the total energy was converged to 10⁻⁷ eV. All geometries were optimized until all residual forces on each atom were less than 0.01 eV/Å. Spin-orbit coupling (SOC) with relativistic effects was included in all calculations. The planar dipole layer method is employed to mimic the electric field [34].

The 3×3 supercell in all calculations consists of 5 Cu(001) layers with a c(2×2)N – Cu(001) molecular network on one side, which has a larger than 10 Å distance to neighboring supercells. The Fe adatom resides on the top of the Cu site of Cu₂N, and it forms bonds with the neighboring two N atoms [7]. A hydrogen (fluorine) atom adsorbs on the top of the Fe adatom. The magnetic anisotropy energy (MAE) is defined as the total energy difference of the system as its spin orientation rotates from out of plane to in plane, i.e., MAE = E[001]–E[100].

First, we show that MAE of a single atom can be manipulated by an additional ligand field, such as molecule adsorption. Among all molecules, hydrogen and fluorine are of particular interest. The high reactivity and the relatively small desorption barrier make the reversible manipulation of adsorbed H atoms easy [35–38]. Fluorine has the largest electronegativity and can provide a strong ligand field, which has been used to tune spin states of magnetic molecules [39,40]. Under zero

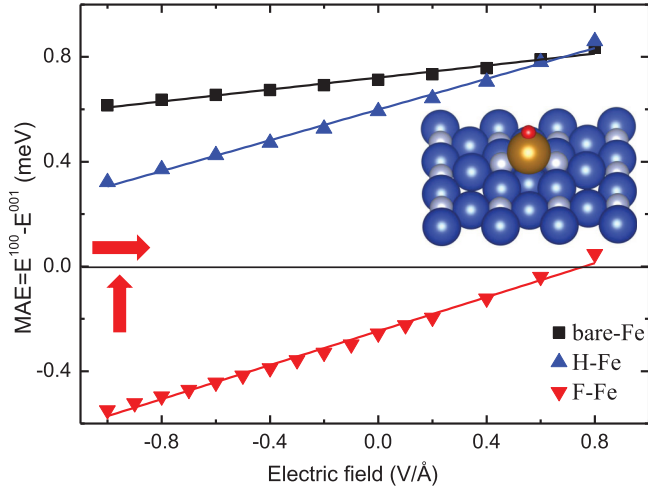


FIG. 1. Magnetic anisotropy energy as a function of the electric field for an Fe adatom on the $\text{Cu}_2\text{N}/\text{Cu}(001)$ surface (denotes bare-Fe) with an additional hydrogen (denotes H-Fe) or fluorine (denotes F-Fe) atom adsorption. Horizontal (vertical) arrow stands for an in-plane (out-of-plane) magnetization. The lines are obtained by the linear fit to the set of data.

electric field, the calculated spin moment of the Fe atom for bare-Fe, H-Fe, and F-Fe systems are $3.05 \mu_B$, $2.79 \mu_B$, and $3.11 \mu_B$, respectively. Variation of spin moments is due to the hybridization between the Fe atom and the H/F atom. The MAE of a single Fe adatom on the Cu_2N surface (denotes as bare Fe) is 0.71 meV, as shown in Fig. 1, and its easy axis is in plane and along with the bonds with the two neighboring N atoms, coinciding with experimental results [7,23,24] and our previous calculations [41]. With an additional H atom adsorbed on the Fe adatom (H-Fe), the MAE decreases to 0.59 meV and the in-plane magnetization is preserved. When substituting the H atom with a F atom (F-Fe), the MAE further decreases to -0.26 meV. Remarkably, in this case, the magnetization axis of the Fe adatom is rotated from in plane to out of plane.

The electric field dependence of MAE is presented in Fig. 1. Here, a positive electric field is defined to be pointed to the surface. Our calculations show that the electric field induced changes in the bond length between Fe and H(F) only result in less than 5% variation in MAE. The MAE of the bare-Fe system changes linearly with the electric field. The increase rate of MAE with respect to the electric field is estimated to be 0.12 meV per Fe atom per $\text{V}/\text{\AA}$, which is slightly larger than that of previous theoretical estimations for the pure Fe surface [14]. This is due to the pd hybridization between N atoms and the Fe atom in the Cu_2N molecular network. A similar linear behavior can also be found in the H-Fe system. An increase of 46% to 0.86 meV in MAE is found with a positive field of $0.8 \text{ V}/\text{\AA}$, which is higher than that of the bare-Fe system. With a negative field of $-1.0 \text{ V}/\text{\AA}$, the MAE of the F-Fe system strongly enhances by 110% from -0.26 meV (zero field) to -0.55 meV. The slope for H-Fe and F-Fe is about 0.3 meV and 0.33 meV per Fe atom per $\text{V}/\text{\AA}$, respectively, which is nearly the same as that for the Pt/Fe/Pt(001) system, about 0.39 meV per Fe atom per $\text{V}/\text{\AA}$ [15]. Interestingly, with a positive field of $0.8 \text{ V}/\text{\AA}$, the MAE of the F-Fe system decreases to 0.05 meV. However, its easy axis changes from out of plane to in plane.

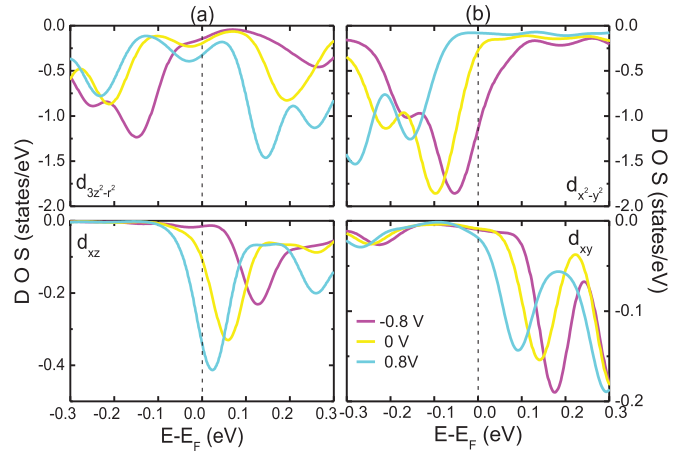


FIG. 2. Evolution of projected density of states (PDOS) for minority d orbitals of the Fe adatom under electric fields (a) for the bare-Fe system and (b) for the F-Fe system.

These results suggest that not only the value of the MAE but also the spin orientation of a single atom with molecule adsorption can be further tailored by the electric field.

In all three systems, interactions between the Fe and the Cu substrate are screened by the Cu_2N insulating monolayer. Moreover, light elements in these systems, such as N, H, and F, have very small contributions to MAE. Thus, MAE in these systems solely stems from the Fe atom. The variation of the MAE can be related with changes of electronic structure under the electric field modulation, which can be qualitatively analyzed with the second-order perturbation formula [42]

$$MAE \sim \xi^2 \sum_{o,u} \left(\frac{|\langle \psi_u | l_z | \psi_o \rangle|^2}{\epsilon_u - \epsilon_o} - \frac{|\langle \psi_u | l_y | \psi_o \rangle|^2}{\epsilon_u - \epsilon_o} \right), \quad (1)$$

where the ξ parameter is an average of the spin orbital coupling coefficients, $\{\psi_u, \psi_o\}$ stand for the unoccupied (occupied) states, and $\{l_y, l_z\}$ are the angular momentum operators, respectively. In the following parts, we will concentrate on the minority density of states of the Fe atom near the Fermi level because they have dominant contributions to the MAE determined by Eq. (1).

For the bare-Fe system, the population of $d_{3z^2-r^2}$ and d_{xz} orbitals at the Fermi level increases with the increasing electric field, as shown in Fig. 2(a). The coupling between them through l_y operator $\langle d_{3z^2-r^2} | l_y | d_{xz} \rangle$ enhances, thus, resulting in a gradual raising in-plane MAE through the second term in Eq. (1). Due to the hybridization between the F atom and the Fe atom, $d_{x^2-y^2}$ orbitals in Fig. 2(b) move to the Fermi level with *negative* electric fields. The increased $d_{x^2-y^2}$ population leads to a partial cancellation of the slightly decreased d_{xy} , and the coupling between them through l_z operator $\langle d_{x^2-y^2} | l_z | d_{xy} \rangle$ enhances leading to an increased out-of-plane MAE. Under *positive* fields, however, the intensity of $d_{3z^2-r^2}$ orbital at the Fermi level decreases and thus the intensity of the coupling $\langle d_{x^2-y^2} | l_z | d_{xy} \rangle$ also reduces, which becomes comparable with that of $\langle d_{3z^2-r^2} | l_y | d_{xz} \rangle$ (not shown), leading to a small MA, and the magnetization axis of the system also rotates from out of plane to in plane.

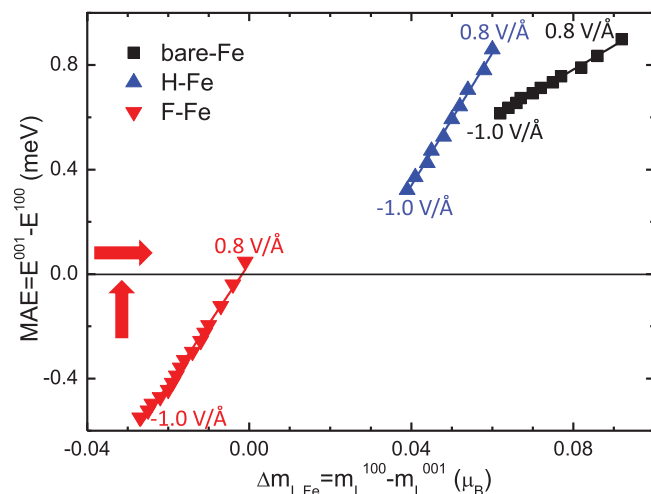


FIG. 3. Relationship between MAE and OMA of the Fe adatom for a bare-Fe, H-Fe, and F-Fe system, respectively. Horizontal (vertical) arrow indicates an in-plane (out-of-plane) magnetization. The lines are obtained by the linear fit to the set of data.

It is interesting to apply to the above results the Bruno's relation [43] $MAE \propto -\frac{\xi}{4\mu_B}(m_L^{100} - m_L^{001})$. m_L^{001} and m_L^{100} are the orbital moment for magnetization perpendicular and within the surface plane, respectively.

It can be seen from Fig. 3 that the MAE of the Fe atom in all systems increases monotonically with orbital magnetization anisotropy (OMA). One can relate the MAE to the OMA for the bare-Fe and the F-Fe systems, which are found to partially follow the Bruno's relation [43]. But, this is not the case for the H-Fe system, because the Bruno's relation is a model for bulk and surfaces. The linear relation between the MAE and the OMA, however, still can be found in the H-Fe system. For bare-Fe and H-Fe systems, the highest orbital moment of the Fe adatom lies in the easy axis along the (100) direction, leading to an in-plane anisotropy, while lies along the (001) direction for the F-Fe system which prefers an out-of-plane anisotropy. The slope of the MAE dependence on the OMA is $9.1 \text{ meV}/\mu_B$ for the bare-Fe system. It remarkably rises up to $25.3 \text{ meV}/\mu_B$ and $23.1 \text{ meV}/\mu_B$, respectively, for H-Fe and F-Fe systems because their electronic environments have been greatly changed by the electric field. It should be kept in mind that a higher slope does not necessarily mean an enhanced spin-orbital coupling parameter, because electronic structures in these systems also change under electric fields.

Finally, we perform atomic-scale magnetization dynamics simulations using the Landau-Lifshitz-Gilbert equation [44–46] with magnetic moments and the MAE obtained from our *ab initio* calculations. Calculation details can be found in our previous work [46]. To investigate spin switching of the bare-Fe and the F-Fe systems, two experimentally realizable setups are considered: (1) The system is under the action of two constant magnetic fields oriented along/perpendicular to their easy axis [denoted as H_{easy} and H , Fig. 4(a)]. (2) Only short rectangular magnetic pulses perpendicular to their easy axis [H , Fig. 4(b)] are applied. In these cases, magnetic fields/pulses

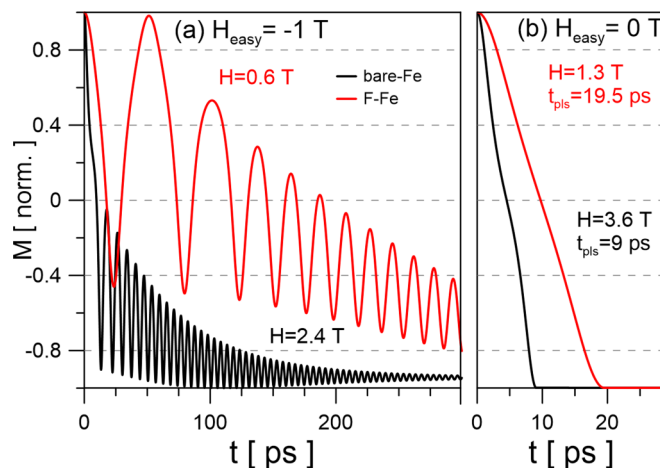


FIG. 4. Magnetization switching of the bare-Fe and the F-Fe systems with (a) two constant magnetic fields, H_{easy} and H , are applied along/perpendicular to their own easy axis and (b) only rectangular magnetic pulses H are applied perpendicular to their own easy axis.

perpendicular to the easy axis are used to trigger precessional motions of the magnetization. As an example, we show results under the zero external electric field. The minimal value of the switching magnetic field in F-Fe is decreased by four times in comparison with that of the bare-Fe [Fig. 4(a)]: from 2.4 T to 0.6 T, with the simultaneous presence of a 1 T constant magnetic field along the easy axis. The switching time is about 200 ps for the bare-Fe and 400 ps for the F-Fe. Drastic reduction of the switching time to the level of a few ps can be achieved by applying short magnetic pulses, as shown in Fig. 4(b), and the minimum magnetic field for the spin reversal decreases from 3.6 T for the bare-Fe to 1.3 T for the F-Fe.

In summary, we have demonstrated that the magnetic anisotropy and magnetization dynamics of a single spin on surfaces can be engineered by electric fields and adsorption of molecules. Linear dependence of the MAE upon the electric field is found for all systems. Moreover, due to the strong ligand field of the F atom, the spin direction of the F-Fe system is reoriented to be out of plane. With the electric field, however, its magnetization axis can be further rotated to the in-plane direction. Variations of the MAE in all systems are due to charge accumulation and changes in electronic structures. The spin orbital parameter of the Fe atom is remarkably enhanced by the H or F atom adsorption. The significant effect of the F adsorption on magnetization switching at a single atom level is also revealed.

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