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Ferroelectric Control of Magnetocrystalline Anisotropy at Cobalt/Poly(vinylidene fluoride) Interfaces

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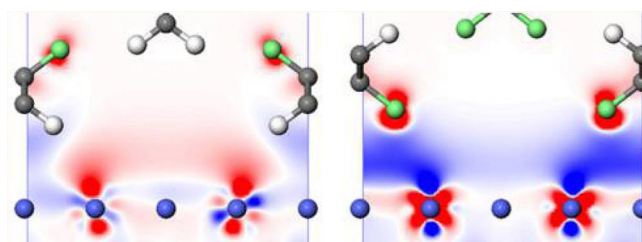
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Abstract

Electric field control of magnetization is one of the promising avenues for achieving high-density energy-efficient magnetic data storage. Ferroelectric materials can be especially useful for that purpose as a source of very large switchable electric fields when interfaced with a ferromagnet. Organic ferroelectrics, such as poly(vinylidene fluoride) (PVDF), have an additional advantage of being weakly bonded to the ferromagnet, thus minimizing undesirable effects such as interface chemical modification and/or strain coupling. In this work we use first-principles density functional calculations of Co/PVDF heterostructures to demonstrate the effect of ferroelectric polarization of PVDF on the interface magnetocrystalline anisotropy that controls the magnetization orientation. We show that switching of the polarization direction alters the magnetocrystalline anisotropy energy of the adjacent Co layer by about 50%, driven by the modification of the screening charge induced by ferroelectric polarization. The effect is reduced with Co oxidation at the interface due to quenching the interface magnetization. Our results provide a new insight into the mechanism of the magnetoelectric coupling at organic ferroelectric/ferromagnet interfaces and suggest ways to achieve the desired functionality in practice.

Keywords: electric control of magnetization, ferromagnet/ferroelectric interface, magnetocrystalline anisotropy, magnetoelectric effect, organic ferroelectric



Spintronics has revolutionized magnetic data storage with applications such as high-sensitivity magnetic field sensors for hard disk read heads and nonvolatile magnetic random access memories.⁽¹⁾ The existing technology requires, however, high currents to write the information and thus suffers from significant energy dissipation. It would be beneficial to control the magnetization orientation purely by electric fields through an applied voltage.^{2–5}

One approach to address this problem is to exploit composites of piezoelectric (ferroelectric) and magnetostrictive (ferro- or ferrimagnetic) compounds, where the coupling is mediated by elastic properties. In these composites an applied electric field induces strain in the piezoelectric constituent, which is mechanically transferred to the magnetostrictive constituent.^{6–8} Another approach is to realize a purely electronic mechanism, where the response of a ferromagnet to an applied electric field is driven by spin-dependent screening.⁹

Mediated by this mechanism the electric field was predicted to induce a net magnetic moment at the interface and to alter the magnetocrystalline anisotropy (MCA) of thin magnetic films.¹⁰ The possibility to modify the MCA is of particular interest, because the MCA determines stable orientations of magnetization, and hence its electric modulation would allow for switching of the magnetic moment direction. Experimentally, it was shown that the MCA of FePt and FePd films immersed in an electrolyte can be modified by a few percent in an applied electric field.¹¹ A strong effect of applied electric field on the interface MCA was demonstrated for the Fe/MgO (001) interfaces.¹² Magnetic easy axis manipulation by electric field was also achieved in the (Ga,Mn)As magnetic semiconductor.¹³ Theoretically, the electric field effect on the MCA was investigated for various free-standing magnetic metal films^{10,14–17} and Fe/MgO interfaces.^{18,19} Very recently, electrically induced bistable magnetization switching was realized

in MgO-based magnetic tunnel junctions at room temperature,^{20,21} demonstrating the capabilities of this approach for magnetic data storage applications.²²

Alternatively, the interface magnetic anisotropy (and hence the magnetization orientation) may be tailored electronically by the ferroelectric polarization of an adjacent ferroelectric film.^{23,24} This approach has a number of advantages. First, the effective electric field induced by the polarization charge at the interface may reach 1 GV/m, *i.e.*, be much higher than the electric field produced in laboratory conditions. Second, due to bistable polarization of the ferroelectric, the effect is nonvolatile and thus offers an additional degree of freedom in magnetoelectric devices. Finally, ferroelectric switching may be achieved at relatively low voltages, which goes a long way toward achieving energy efficiency.

Organic ferroelectric materials are especially promising for this purpose. Organic ferroelectric polymers, such as poly(vinylidene fluoride) (PVDF) and related copolymers, form high-quality ordered layers²⁵ and exhibit robust ferroelectricity down to monolayer thickness.²⁶ The electric polarization of PVDF is comparable to that of perovskite oxide ferroelectrics,²⁷ making them favorable for use as barriers in multiferroic tunnel junctions.^{28,29} Moreover, the organic weakly binds to the metal ferromagnets, which prevents unintended chemical interface modification and/or strain coupling.

Recently Mardana *et al.*³⁰ have demonstrated experimentally that PVDF copolymers can be efficiently used to tailor the interface MCA of an adjacent ferromagnetic Co layer. Using a wedge-shaped Co film of varying thickness interfaced with a PVDF copolymer they showed that the magnetic anisotropy of the Co films changes by as much as 50% when the ferroelectric polarization of PVDF is switched from up to down. For small Co thickness they were able to rotate the magnetization through a large angle at a constant magnetic field. The large mismatch in stiffness coefficients between the soft ferroelectric and the much stiffer metallic Co film allowed minimizing strain-mediated effects.

In this paper we employ first-principles density functional calculations to demonstrate the effect of ferroelectric polarization of PVDF on the magnetocrystalline anisotropy energy (MAE) at the Co/PVDF interface. We show that switching of the polarization direction alters the interface MAE by about 50%, driven by the modification of the screening charge induced by ferroelectric polarization. Our results offer new insights into the mechanism of the magnetoelectric coupling at organic ferroelectric/ferromagnet interfaces and provide theoretical grounds for the earlier reported experimental findings.³⁰

Results and Discussion

In order to calculate the dependence of MAE on the ferroelectric polarization, we use two structural models: the pure Co/PVDF interface and the oxidized Co/O/PVDF interface. The second accounts for the fact that PVDF is deposited using the Langmuir–Blodgett technique, which entails

depositing the PVDF on the Co surface from solution. During this process the Co surface may become oxidized due to the contact with air and water from the solution. Because the calculation employs periodic boundary conditions, we introduce a nonmagnetic Cu layer at the second PVDF interface. The MAE of the PVDF/Cu interface is zero; therefore the change in MAE with ferroelectric polarization reversal may be assigned entirely to the Co/PVDF interface. The MAE contribution of the additional Co/Cu interface does not depend on the PVDF polarization. It can be obtained from a separate calculation of a Co/Cu supercell and subtracted.

Figure 1a and b show the Co/PVDF/Cu and Co/O/PVDF/Cu supercells, respectively, with PVDF polarization pointing toward (\downarrow , left panels) and away from (\uparrow , right panels) the interface. The details of the Co/PVDF and Co/O/PVDF interfaces were elaborated in previous works (refs 28, 29). Within both structural models we consider an hcp Co(0001) surface ($a = 2.507 \text{ \AA}$, $c = 4.069 \text{ \AA}$). Four monolayers of Co are used to represent the magnetic slab. The PVDF on top has the body-centered orthorhombic structure with lattice parameters $a = 8.58 \text{ \AA}$, $b = 5.12 \text{ \AA}$, and $c = 4.91 \text{ \AA}$. The polarization of PVDF is aligned along the [001] direction. The supercell has three monolayers of PVDF. This unit cell matches very well on the $\text{Co } 4 \times 1$ cubic supercell with lattice parameters of $a = 8.685 \text{ \AA}$, $b = 2.507 \text{ \AA}$, and $c = 4.069 \text{ \AA}$. As follows from our previous results (refs 28, 29), PVDF is physisorbed on the surface of Co. This is consistent with the experimental evidence that pure PVDF has a very low interfacial binding energy when deposited on a metal surface.⁽³¹⁾ The interface configuration and interface distances were obtained from minimization of the PVDF adsorption energy using dispersion-corrected density functional theory (DFT-D) (see the Methods section and ref 28 for details). The oxidized Co interface is modeled by adding a monolayer of O on top of the Co. The O atoms occupy the hcp hollow sites about 1.04 \AA above the Co surface. Four monolayers of fcc Cu(111) are added to isolate the PVDF from the second Co surface.

We calculate the MAE in the structures described above using first-principles calculations based on density functional theory (DFT) (see the Methods section for details). First, we consider the pure Co/PVDF interface. It is evident from Figure 1a that most of the induced charge density is localized at the interface with PVDF. This suggests that changes in the magnetic properties of Co should largely be determined by the interface contribution. The calculated layer-resolved and ferroelectric polarization-dependent spin and orbital moments of Co confirm this expectation. As seen from the upper part of Table 1, Co spin moments range between 1.66 and $1.76 \mu_{\text{B}}$, increasing from inside of the Co slab toward the interface. Reversal of polarization direction in PVDF alters the interface Co_0 spin moments by $\Delta\mu \approx 0.02 \mu_{\text{B}}$. Spin moments of other Co monolayers are not sensitive to the polarization orientation in PVDF, indicating that the dominant contribution to the magnetoelectric effect comes from the interfacial Co atoms. The orbital moments on Co atoms vary between 0.08 and $0.11 \mu_{\text{B}}$. The largest change in the orbital moment,

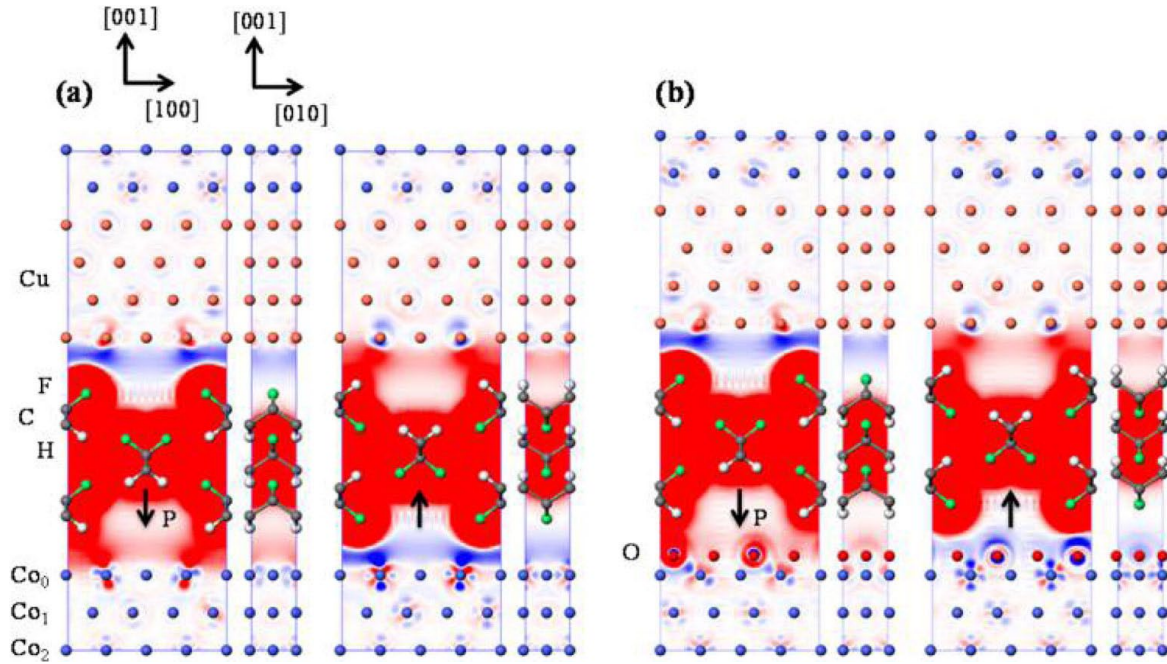


Figure 1. Atomic structure of the Co/PVDF/Cu (a) and Co/O/PVDF/Cu (b) supercells for ferroelectric polarization pointing toward the Co interface (left panels) and away from the interface (right panels). The total charge density in the PVDF and the polarization-induced charge density in the Co are indicated by a background color. Red corresponds to electron depletion and blue to electron accumulation.

when magnetization orientation is switched from the [100] to [001] direction, occurs at the interface of Co_0 atoms. This fact again indicates that MAE is dominated by the interface contribution.

For the Co/PVDF/Cu supercell, the MAE values are 0.72 (0.90) meV for the polarization of PVDF pointing toward (away from) the interface. The contribution to MAE comes both from the Co/PVDF and Co/Cu interfaces. The MAE of the Co/Cu interface was calculated separately, for the supercell of four Co and six Cu monolayers with four atoms per monolayer. We found that the MAE is 0.66 meV per volume unit cell, which corresponds to 0.24 mJ/m^2 per Co/Cu interface. After subtracting the contribution of the Co/Cu interface, we obtained the MAE of the pure Co/PVDF interface to be 0.28 (0.42) mJ/m^2 for the polarization of PVDF pointing toward (away from) the interface. The positive sign of the MAE indicates that the easy axis is oriented perpendicular to the plane of the multilayer. We define the relative change of MAE with polarization reversal as $\Delta\text{MAE} = (\text{MAE}_\uparrow - \text{MAE}_\downarrow) / \text{MAE}_\downarrow$. Using the results of calculations we obtain that reversal of ferroelectric polarization direction in PVDF leads to a MAE change of about 50%, which is a clear manifestation of the large magnetoelectric coupling.

We note that, in addition to the surface (interface) magnetocrystalline anisotropy, significant contribution to magnetic anisotropy in thin films comes from the magnetostatic energy (the so-called shape anisotropy). The total anisotropy energy per unit volume K is given by $K = (K_s + K_{S0})/d + K_M$, where K_s is the switchable MAE of the interface with ferroelectric layer, K_{S0} is the MAE of the other interface, K_M

$= -(1/2)\mu_0 M^2$ is the shape anisotropy energy (M is the saturation magnetization), and d is the film thickness.³² In the thin-film geometry the shape anisotropy is negative and thus favors the in-plane easy axis. Thus, for a given value of K_M a judicious choice of the film thickness d , such that $K_{S0} + 0.28(\text{mJ/m}^2) < -K_M d < K_{S0} + 0.42(\text{mJ/m}^2)$, would result in the magnetic easy axis switching from in-plane to out-of-plane and *vice versa* in a small applied electric field, which reverses the PVDF polarization.

Table 1. Calculated Interface MAE Values for the Co/PVDF and Co/O/PVDF Interfaces and Spin and Orbital Moments (in units of μ_B) of Co Atoms in the Respective Supercell Structures.*

	P					
	↓			↑		
	Co₂	Co₁	Co₀	Co₂	Co₁	Co₀
Co/PVDFMAE = 0.28 mJ/m ² MAE = 0.42 mJ/m ²						
M_s	1.659	1.689	1.763	1.661	1.696	1.783
$L[100]$	0.081	0.083	0.107	0.080	0.083	0.108
$L[001]$	0.085	0.087	0.092	0.085	0.087	0.095
ΔL	-0.004	-0.004	0.015	-0.005	-0.004	0.013
Co/O/PVDFMAE = -1.16 mJ/m ² MAE = -1.12 mJ/m ²						
M_s	1.662	1.740	0.286	1.666	1.740	0.282
$L[100]$	0.083	0.101	0.003	0.084	0.101	0.003
$L[001]$	0.082	0.090	0.009	0.083	0.090	0.009
ΔL	0.001	0.011	-0.006	0.001	0.011	-0.006

* The values of Co spin and orbital moments are averaged over the plane.

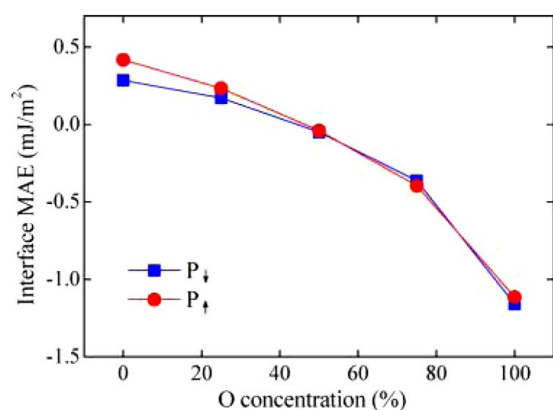


Figure 2. Interface MAE as a function of the O concentration at the Co/O/PVDF interface for polarization direction toward the interface (P_{\downarrow} , blue squares) and away from the interface (P_{\uparrow} , red circles).

Next, we consider a fully oxidized Co/O/PVDF interface (Figure 1b). It is evident from the lower part of Table 1 that the presence of oxygen at the interface suppresses Co spin moments at the interface layer (Co_0). The quenching of the Co_0 spin moment is due to the chemical bonding of the O monolayer with the Co surface, as explained in refs 29 and 33. Since the polarization-induced charge is largely localized on the O layer and the first Co layers (Figure 1b), the effect of ferroelectric polarization on the interface magnetic moment is significantly reduced, $\Delta\mu \approx 0.005 \mu_B$. In addition, the orbital moment is quenched at the interface leading to the reduced ΔMAE . We find that the interface MAE values are -1.16 (-1.12) mJ/m^2 for polarization pointing toward (away from) the Co/O/PVDF interface. (Here the quoted values have been adjusted for the contribution of the Co/Cu interface.) The presence of the O monolayer at the PVDF/Co interface results in the MAE sign change, consistent with the earlier reported results of the oxygen-induced spin reorientation transition.³⁴ The effect produced by polarization switching is significantly reduced ($\Delta\text{MAE} = 4\%$) as compared to the non-oxidized interface.

We can obtain a qualitative understanding of the behavior under partial O coverage gradually removing the O atoms from the interface (no additional structural optimization is performed). Figure 2 shows the dependence of the calculated interface MAE on the O coverage for the two polarization directions. There is a relatively smooth transition involving the MCA change from out-of-plane for pure Co surface to in-plane for fully oxidized surface. A crossover occurs at about 50% coverage. Respectively, ΔMAE decreases from approximately 47% to 4% as O concentration increases from 0% to 100%.

Finally, we discuss the mechanism responsible for the effect of ferroelectric polarization on MAE at the Co/PVDF interface. Since the chemical bonding at the PVDF/Co interface is weak, we do not expect considerable change in the interfacial electronic structure of Co upon polarization reversal of the PVDF. Indeed, the density of states of the interfacial Co

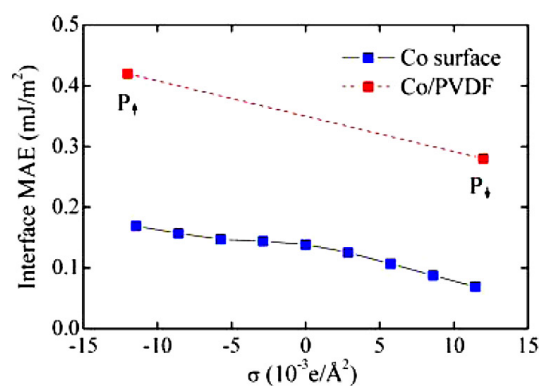


Figure 3. Change in the interface MAE as a function of added surface charge for a four-monolayer hcp Co(0001) slab (blue squares) and polarization screening charge for the Co/PVDF interface (red squares).

layer in the Co/PVDF structure is not sizably sensitive to the polarization direction.²⁹ This is in contrast to the strongly polarization-dependent interfacial bonding^{35–37} and exchange splitting³⁸ in some inorganic ferroelectric–ferromagnetic systems. Here, we instead show that the electrostatic screening of PVDF polarization charges at the Co/PVDF interface is responsible for the large change in MAE.

Using the calculated value of the spontaneous ferroelectric polarization in PVDF, $19.3 \mu\text{C/cm}^2$ ($0.012 \text{ e}/\text{Å}^2$), we estimate the change in the bound charge at the interface associated with polarization reversal to be $\Delta\sigma_p \approx 0.024 \text{ e}/\text{Å}^2$. Assuming a complete screening, polarization reversal alters the amount of the screening charge at the Co interface by the same amount. In order to estimate the effect of this extra charge on the MAE of Co, we calculate a change in MAE of the free-standing four-monolayer hcp Co(0001) slab as a function of band filling (*i.e.*, additional valence charge). Given the fact that the MAE is fully determined by the interfacial Co layer, we analyze changes in MAE as a function of surface charge σ , which we estimate as the extra charge per Co monolayer in the slab. These results are presented in Figure 3 (blue squares) in comparison to the results for the Co/PVDF interface (red squares). We see that, although the magnitude of the interface MAE for the Co slab is different from that at the Co/PVDF interface, there is a very similar tendency in the MAE change. In both cases the interface MAE decreases with increasing electron charge with a comparable relative change. This behavior originates from the changing occupation of the Co d orbitals, which alters the spin–orbit coupling between occupied and empty states.³⁹ Thus, the electrostatic screening of ferroelectric polarization is the primary factor responsible for the change in MAE for PVDF polarization switching.

These results have direct implications for experimental studies of magnetoelectric effects at organic ferroelectric/ferromagnetic metal interfaces. Figure 2 indicates that clean, uncontaminated interfaces display larger MCA changes in Co/PVDF heterostructures. In practice, oxidation of the surface Co layer in the process of the Langmuir–Blodgett deposition

of the ferroelectric polymer likely leads to formation of a CoO insulating layer thicker than just one monolayer considered in this work. Exposure to water and further annealing procedure may result in further modifications of the interface. In spite of these interface modifications, the magnetoelectric coupling has been clearly observed,³⁰ and the magnitude of the MCA change with polarization reversal was found to be similar to those calculated here for an uncontaminated surface. Although the experimental evidence indicates the presence of an insulating layer at the interface, the exact composition and structure of this layer is not known. Thus, a possible explanation is that the insulating layer at the interface, contrary to an O monolayer, does not quench the magnetic moment of Co adjacent to the oxide. The screening in this case will produce a similar effect at the Co/insulator interface, and the effect may be comparable to that found in this work for a clean interface. In general, charge screening and other interfacial effects are very sensitive to the exact nature of the interface.⁴⁰ Therefore, better experimental characterization of the interfacial structure and further theoretical investigations would be necessary to understand this phenomenon.

Our results also have implications for spin transport properties of multiferroic tunnel junctions based on PVDF barriers.^{28,29} The effect of PVDF on the interface magnetic anisotropy in these junctions may lead to tunneling anisotropic magnetoresistance^{41,42} being controlled by ferroelectric polarization.

Conclusions

In summary, we have shown that organic ferroelectric materials can be efficiently used to modulate the magnetocrystalline anisotropy at interfaces with metallic ferromagnets and thus to control the magnetization orientation by electric fields. By considering a Co/PVDF interface, as an example, we predicted that the magnetocrystalline anisotropy energy at this interface can be changed by as much as 50% upon reversal of the ferroelectric polarization in PVDF. Combined with a judicious choice of the Co film thickness this effect could reverse the easy axis direction from in-plane to out-of-plane, leading to magnetic moment switching in response to applied electric field. We showed that induced screening charges in the ferromagnet are responsible for the effect. Oxidation of the Co interface appears to be detrimental due to quenching the interface magnetization of Co. Our results provide a new insight into the mechanism of magnetoelectric coupling in the interfaces between organic ferroelectrics and metallic ferromagnets, and we hope that they will stimulate new experimental studies.

Methods

The MAE is induced by the spin-orbit interaction in the system. We calculate the MAE within the force theorem as a difference between the sum of single-particle energies corresponding to magnetization in-the-plane, along the [100] direction, E_{\parallel} , and out-of-plane, along the [001] direction, E_{\perp} , calculated for the same self-consistent potential, *i.e.*, $\text{MAE} = E_{\parallel} - E_{\perp}$.^{43,44} The energy is obtained from first-principles calculations based on the density-functional theory. We use the projector augmented

wave method implemented in the Vienna *ab initio* simulation package (VASP)⁴⁵ within the generalized gradient approximation. Spin-orbit interaction is included in VASP as a perturbation using the scalar-relativistic eigenfunctions of the valence states.⁴⁶

A convergence criterion of 10^{-3} meV was used for the total energy calculations. Because of the high precision required, convergence tests were performed for both the plane wave energy cutoff and the k-point sampling. For the Co/PVDF supercell good convergence of MAE was achieved at a 400 eV plane wave expansion cutoff and a Monkhorst-Pack grid of $6 \times 20 \times 2$ k-points. For example, MAE for polarization toward the interface is 0.38 meV for $3 \times 12 \times 1$ k-mesh and 0.39 meV for $6 \times 20 \times 2$ mesh. For polarization away from the interface the MAE is 0.57 meV for $3 \times 12 \times 1$ k-mesh and 0.57 meV for $6 \times 20 \times 2$ mesh. Both orbital and spin moments calculated for this system also show excellent convergence, with an accuracy of $\sim 10^{-3} \mu_B$. Convergence of moments was tested both with and without spin-orbit coupling. For the Co/Cu supercell good convergence is reached at the k-point sampling of $5 \times 16 \times 2$. In particular, the calculated MAE per volume unit cell is 0.33 meV for $5 \times 16 \times 2$, 0.34 meV for $5 \times 18 \times 2$, and 0.33 meV for $6 \times 20 \times 2$ k-mesh. We used the same energy convergence criterion and plane-wave cutoff as before.

As follows from our previous results (refs 28, 29), PVDF is physisorbed on the Co surface. The structure of the Co/PVDF and Co/O/PVDF interfaces was determined using DFT-D, in which the van der Waals interactions are included semiempirically.⁴⁷ The details of the interface optimization are given in the Supporting Information for ref 28.

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Conflicts of interest — The authors declare no competing financial interest.

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