Spontaneously Induced Magnetic Anisotropy in an Ultrathin Co/MoS_2 Heterojunction

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Supplementary Information

Co (3 ML) ultrathin films on MoS_2

In the main manuscript, we show a XMCD-PEEM image of Co films of thickness 5 ML and above. The reason not to discuss domain images from thinner Co layers is that there is no domain to discuss. For each magnetic order (ferro-, antiferro- and ferri-),

there is a constant competition with thermal fluctuation; not until that fluctuation is suppressed or overcome can we observe the magnetic order. For the Co/MoS_2 heterojunction discussed here, we find the critical thickness of the Co layer to overcome thermal fluctuation to lie between 3 and 5 ML (data given in a later section). For this reason, when taking XMCD images from the heterojunction with Co (3 ML) as displayed in Figure S1, the two images recorded with opposite photon helicity show no obvious contrast reversal. Although this argument applies to both Co/MoS_2 and Co/SiO_2, we note that the Co becomes partially oxidized on SiO_2, which could also contribute to an absence of ferromagnetic order at the parts of the image corresponding to Co/SiO_2 (Ref. [S1]).

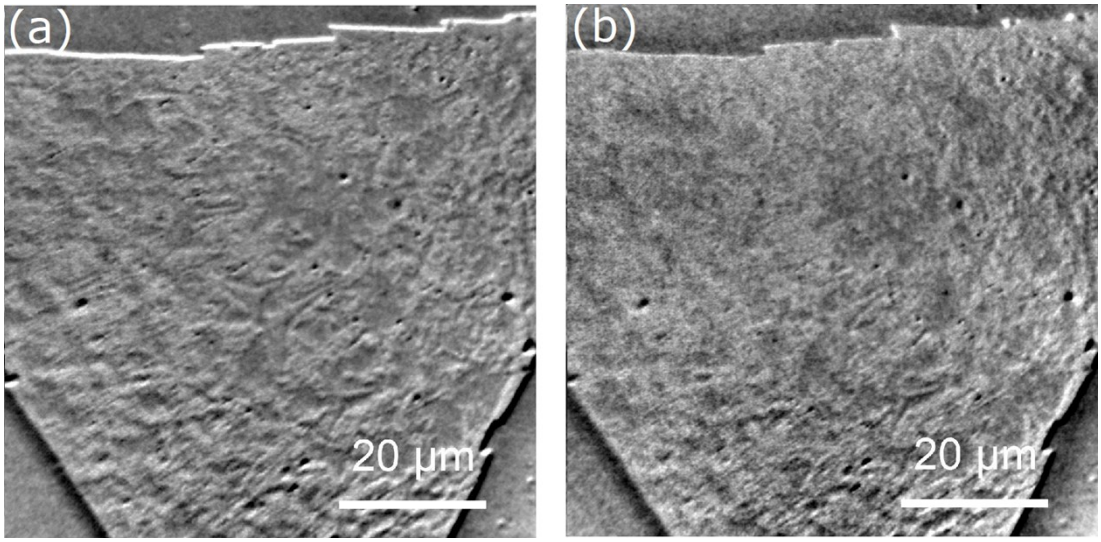

Figure S1. XMCD enhanced PEEM images acquired using (a) RCP light (Co L_3 – Co L_2) and (b) LCP light (Co L_3 – Co L_2), with no obvious contrast reversal between the two images.

Co film morphology vs. magnetic domains

As the contrast of XMCD-PEEM image is proportional to the cosine of the angle between the photon beam polarization and the magnetization, a corrugated surface morphology could introduce an additional uncertainty in the image analysis. To examine a possible impact of the Co film morphology on the domain analysis, we deposited additional Co (2 ML) on top of the surface shown in Figure S1. In Figures S2 (a) and (b), we observed not only an additional contrast arisen but also a contrast reversal after flipping the photon polarization. This observation confirms that the

ferromagnetism of the Co layer became turned on. Figure S2(c) is the PEEM image recorded with the XMCD effect switched off; i.e., the image is recorded with linearly polarized photons at an energy far from the Co *L*-edge absorption resonance to avoid any contribution from absorption asymmetry. Comparing Figures S2(a) and S2(b) with S2(C), we find no correlation between the magnetic domain and the film morphology. A closer examination of the magnified images as displayed in Figure S3(a) and S3(b) yields the same conclusion.

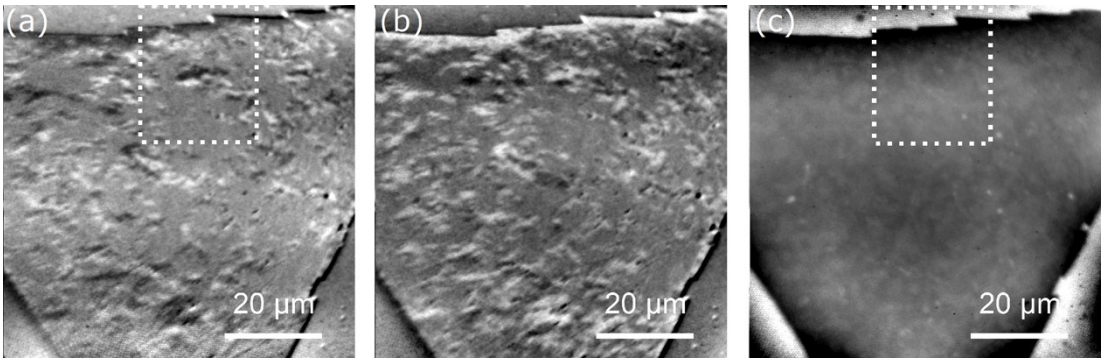

Figure S2. PEEM images acquired using (a) RCP light (Co L_3 – Co L_2), (b) LCP light (Co L_3 – Co L_2), and (C) Linearly polarized light with photon energy equal to 770 eV, an energy far from Co *L*-edge resonances.

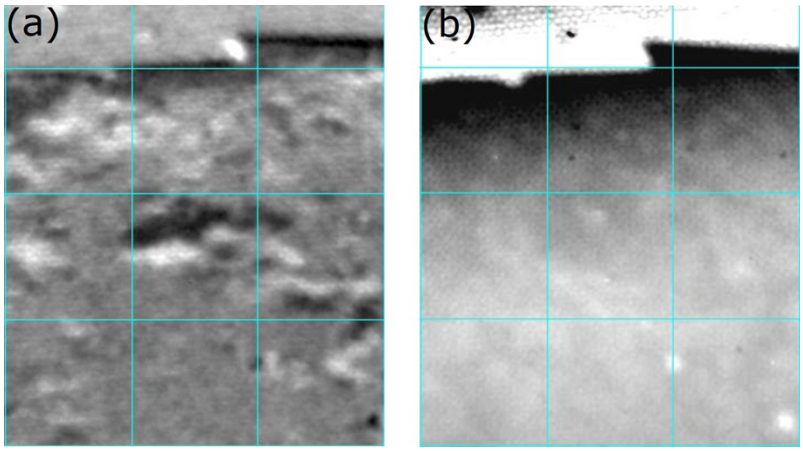

Figure S3. Magnified images taken from the squares marked with a white dashed line in (a) Figure S2(a) and (b) Figure S2(c).

Preparation of the polycrystalline monolayer MoS_2

In Figure 4 of the main text, we compare the domain structures of Co films, deposited on single grain MoS_2 and on polycrystalline MoS_2. The polycrystalline monolayer MoS_2 was prepared inside a tubular furnace according to the solid-source CVD method. The substrate used for the growth was Al_2O_3, which was heated via a two-step process. The first step was to set the temperature of the furnace to 150 ^oC for 10 min, then ramping the temperature to 680 ^oC with a linear ramp of slope, and keeping the temperature constant for 15 min. Argon served as carrier gas to bring S to react with MoO_3 at 680 ^oC. The detailed process is described in Ref. [S1]. Figure S4 proves that the lattice structure is polycrystalline; the lattice parameter is consistent with the bulk variant.

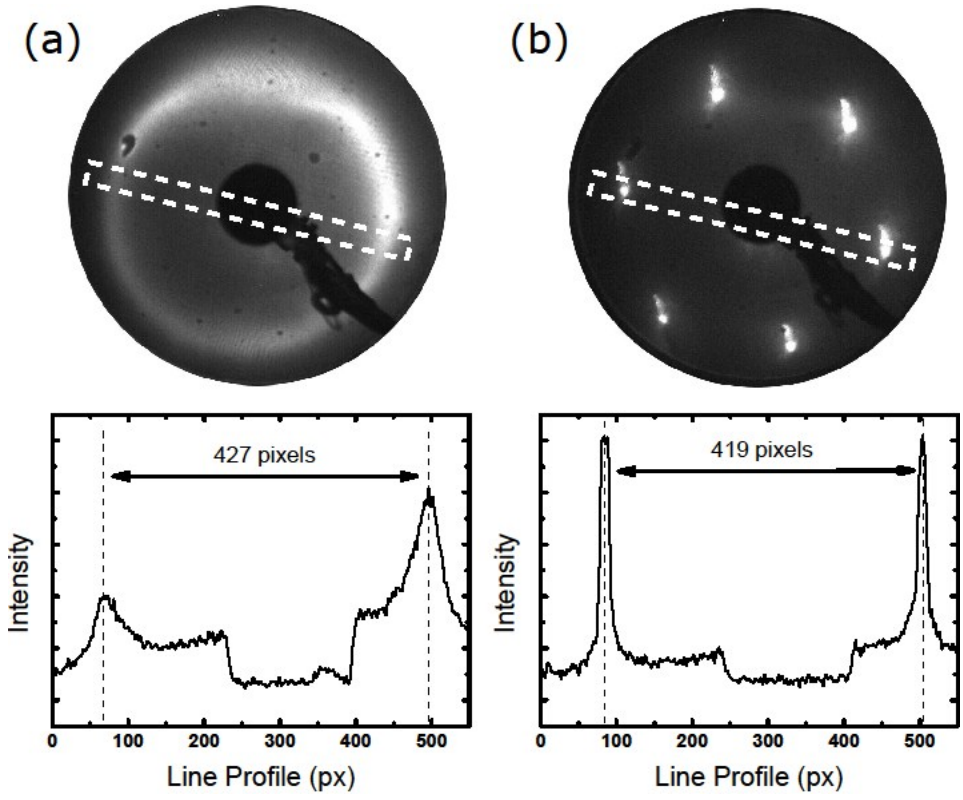

Figure S4. LEED patterns and the corresponding line profiles at electron energy 70 eV of (a) polycrystalline MoS_2 and (b) bulk MoS_2. The white dashed-line areas indicate the integration areas for the line profiles.

Magneto-optical Kerr effect: Co magnetization in-plane

By analyzing the histogram derived from the XMCD-PEEM image, we suggest that the magnetization of the Co layer in Co/MoS_2 is in-plane. As the monolayer MoS_2 flake

is too small and the bulk MoS_2 surface is too rough, neither sample was suitable for our measurement of the magneto-optical Kerr effect (MOKE), but polycrystalline MoS_2 can be prepared with a larger area and is known to be flat. Figure S5 depicts the result of a thickness-dependent MOKE measurement on Co (*x* ML)/MoS_2 (polycrystalline). The results shown in Figure S5 are consistent with the PEEM measurements, namely that the onset of ferromagnetic order in-plane occurs at Co (5 ML).

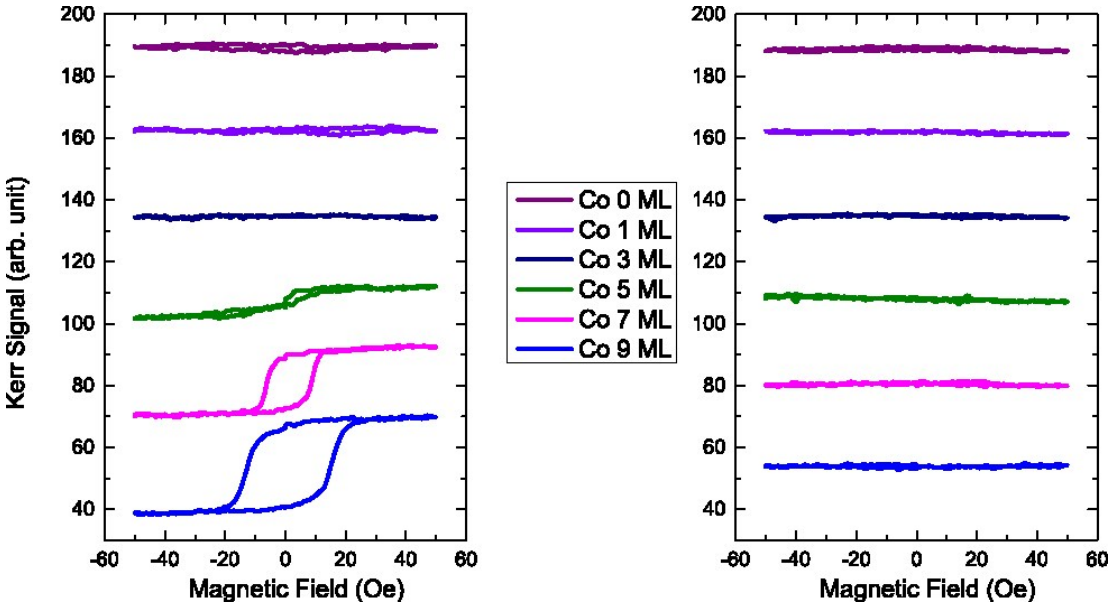

Figure S5. MOKE measurement of Co (*x* ML)/MoS_2 (polycrystalline), *x* = 0, 1, 3, 5, 7, 9. The plot at left shows the onset of in-plane ferromagnetic hysteresis when the Co layer attained 5 ML. No hysteresis was observed along the direction of the surface normal, as shown in the plot at right.

Regarding the control experiment of the MOKE hysteresis loops of Co(7 ML)/SiO2, we make the comparison between the loops taken from Ref. [S1] and the Figure S5 above. The two hysteresis loops have visible differences; the loop acquired from Co/MoS_2 has a lower squareness and an approximately 40% smaller magnitude in coercivity (10 Oe on Co/MoS_2, 16 Oe on Co/SiO_2). An additional observation here is that, while MOKE suggests that an external magnetic field can magnetize a 7ML thick of Co layer, the PEEM image depicted in Figure 3(b) indicates that Co (7 ML)/SiO2 exhibits no spontaneous magnetic order in micrometer size.

Mo 3*d* and S 2*p* μ-XPS

Figures S6(a) and (b) report the Mo 3*d* and S 2*p* μ-XPS results. The shapes of both spectra are consistent with that of pristine MoS_2 reported in Ref. [29], but not with that of Co-doped MoS_2 ascribed in Ref. [40]. We hence suggest that the Co atoms do not break the Mo-S bonds but weakly hybridize with those topmost S atoms in the MoS_2 substrate.

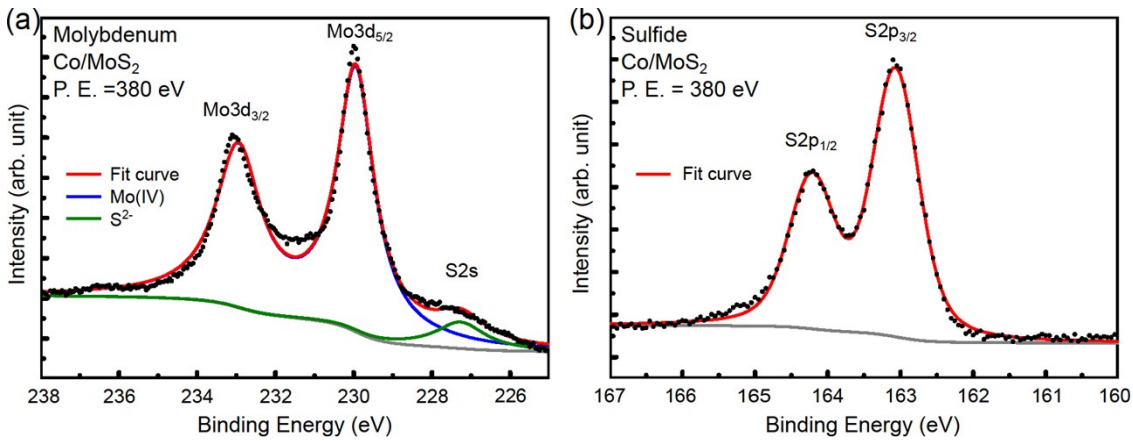

Figure S6. μ-XPS of (a) Mo 3*d* and (b) S 2*p* core levels of a Co(4 ML)/MoS_2.

Lattice structure of Co

The growth mode of Co films on MoS_2 is a relevant issue to determine the origin of the magnetic anisotropy. We performed LEED measurements in a series on Co films grown on bulk MoS_2. Figure S7(a) shows the LEED pattern of the bare surface of bulk single crystal MoS_2. The sharpness of the LEED pattern and the absence of a diffuse background is an effective indication that the probed area was smaller than a single grain. Upon cobalt deposition (3 ML), the diffraction pattern became blurred (Figure S7(b)). The LEED pattern became even more diffuse when the Co deposition attained 5 ML (Figure S7(c)). This observation strongly implies that the Co adlayer was amorphous. We believe that Co deposited on a monolayer of triangular MoS_2 would follow the same growth mode. As a consequence, the observed magnetic anisotropy in Co/MoS_2 (flake) cannot be ascribed simply to an epitaxial growth of Co.

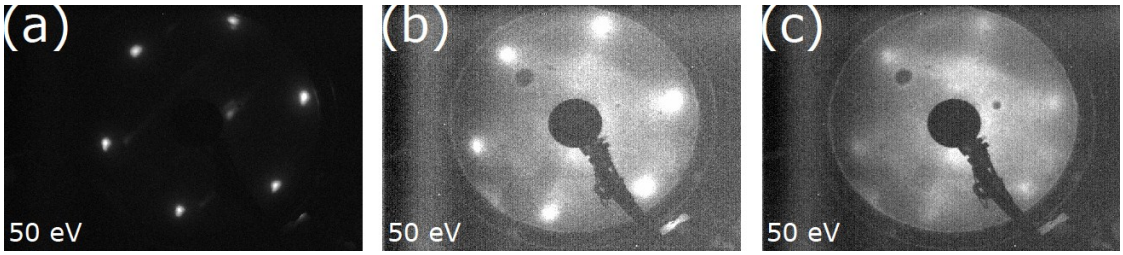

Figure S7. LEED patterns of (a) Bare surface of bulk MoS_2 single crystal, (b) Co (3 ML) on bulk MoS_2 and (c) Co (5 ML) on bulk MoS_2.

Fe/MoS_2 and Fe/Co/MoS_2

The charge transfer between Co and MoS_2 was confirmed with XPS, but no charge transfer occurred between Fe and MoS_2 according to Ref. 24,25. For the purpose of comparison, we acquired XMCD images on Fe/MoS_2 (flake) to seek a possible ferromagnetic signature. As shown in Figure S8(a) and (b), we were unable to find a magnetic contrast with Fe (5 ML).

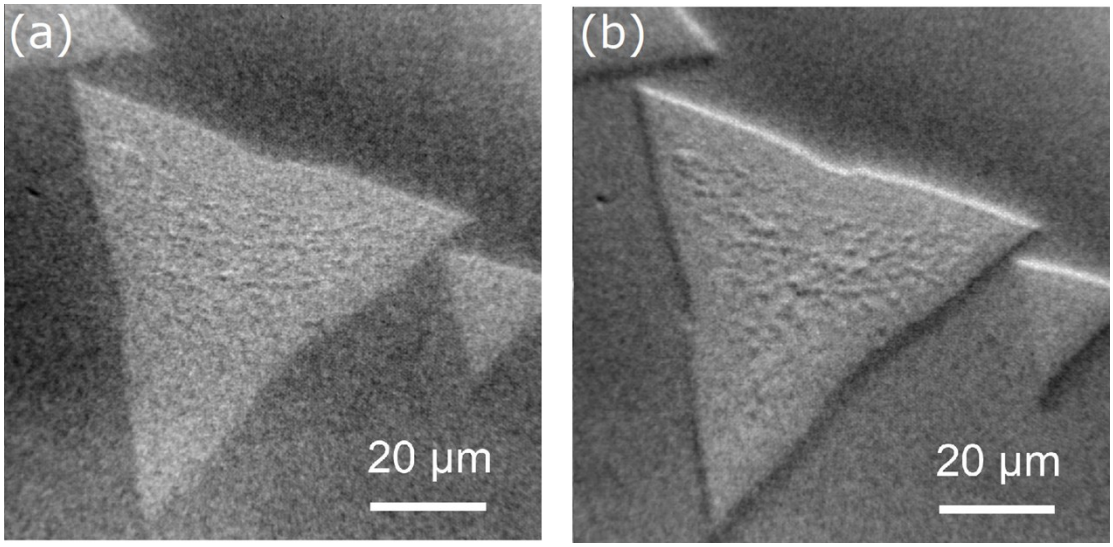

Figure S8. XMCD-PEEM images of Fe (5 ML)/MoS_2 acquired using (a) RCP(Fe L_3 – Fe L_2) and (b) LCP(Fe L_3 – Fe L_2). Neither domain nor contrast reversal is observed.

Interestingly, if Fe is deposited on Co/MoS_2 (flake) of which the ferromagnetic order has been turned on, the Fe film would have its ferromagnetic order actuated even at 3 ML. Figure S9 displays the element-specific domain images. With the

domains in the two images showing a correspondence one to one, there is ferromagnetic coupling between the Co and Fe layers.

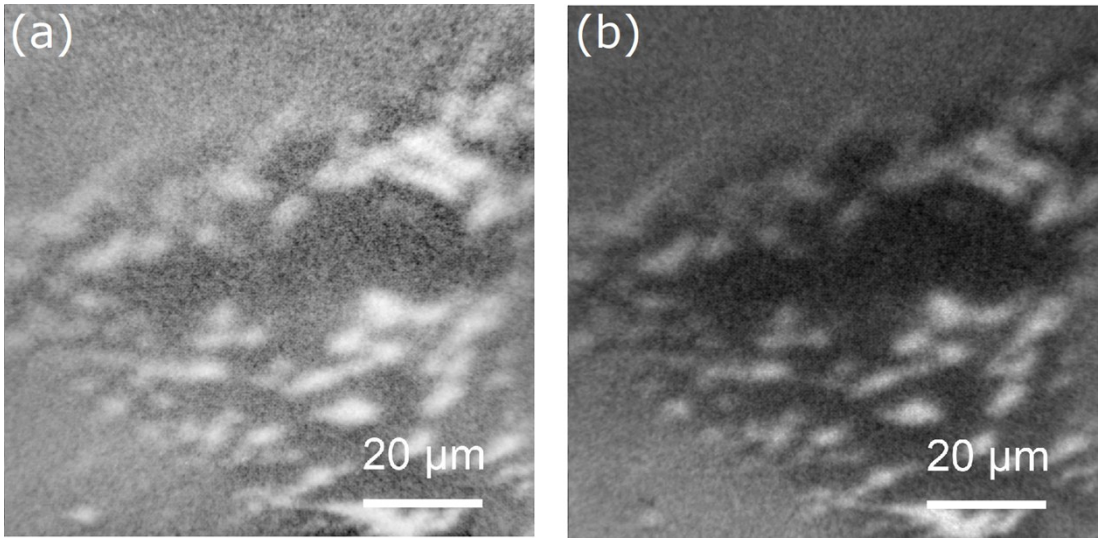

Figure S9. XMCD-PEEM images of Fe(3 ML)/Co(9 ML)/MoS_2 acquired using (a) Co L_3 (LCP – RCP) and (b) Fe L_3 (LCP –RCP).

Absence of XMCD signal in Co/SiO_2

No magnetic domain was observed when Co stood on the SiO_2 surface. Although it is possible that magnetic domains in Co/SiO_2 were much larger than the PEEM field of view, the nearly overlapped Co *L*-edge spectra acquired under opposite photon polarization states indicate otherwise. The X-ray absorption spectral (XAS) evidence indicates a lack of ferromagnetic order in Co/SiO_2 near 25 °C.

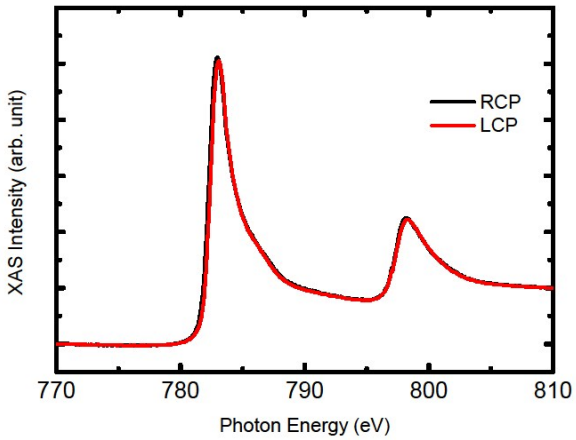

Figure S10. XAS of Co (5 ML)/SiO_2. No asymmetry was observed between the two *L*-edge resonances upon polarization reversal.

Uniformity of Co films

The calibration of a Co monolayer (ML) was based on the medium-energy electron-diffraction (MEED) oscillation period recorded during Co deposition on single-crystal Cu(001), as described in the Method section of the main manuscript. To determine the uniformity of the Co film, we deposited Co (1 ML) on MoS_2/SiO_2 and characterized it using micro-area XAS. Four micro-area spectra were recorded from spots marked in Figure S11(a), respectively. The resemblance of all four spectra, in both intensity and spectral features, indicates that the thickness of the Co film is uniform within our detection limit (sub-monolayer), for both Co/MoS_2 (flake) and Co/SiO_2.

The AFM (Figure S12) image shows the morphology of Pd(2 nm)/Co (0.6 nm; 3.5 ML)/MoS_2 or SiO_2. The Pd layer is deposited to prevent the oxidation of Co. The observed film morphology is similar to that found on Fe/MoS_2 (Ref. [24] Figure 3) showing uniformly distributed nanoclusters. These nanoclusters have no obvious correlation to the shape of micrometer-sized magnetic domains.

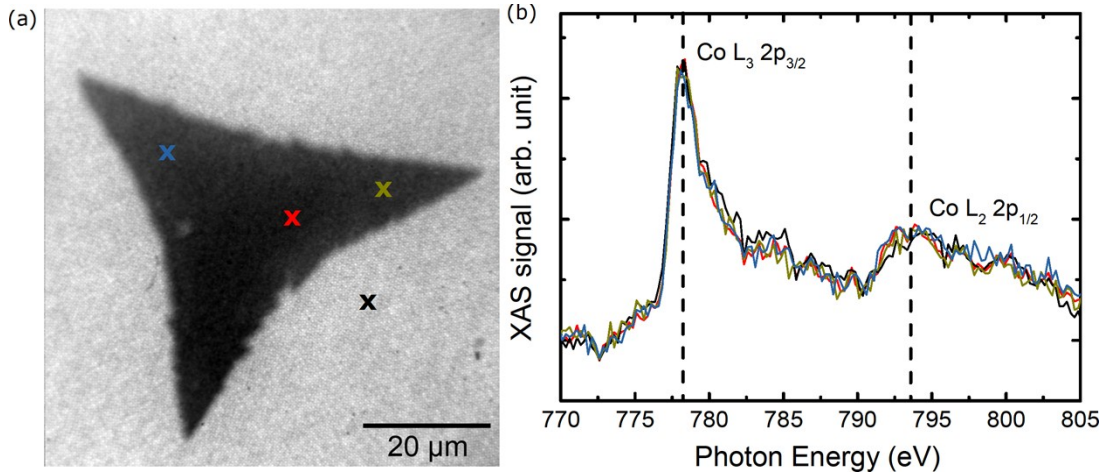

Figure S11. PEEM image of Co (1 ML) on MoS_2 and SiO_2. Each colored "x" sign label in (a) marks the position at which the corresponding Co *L*-edge spectrum in (b) was recorded. All spectra display a high degree of similarity in their spectral features and intensity.

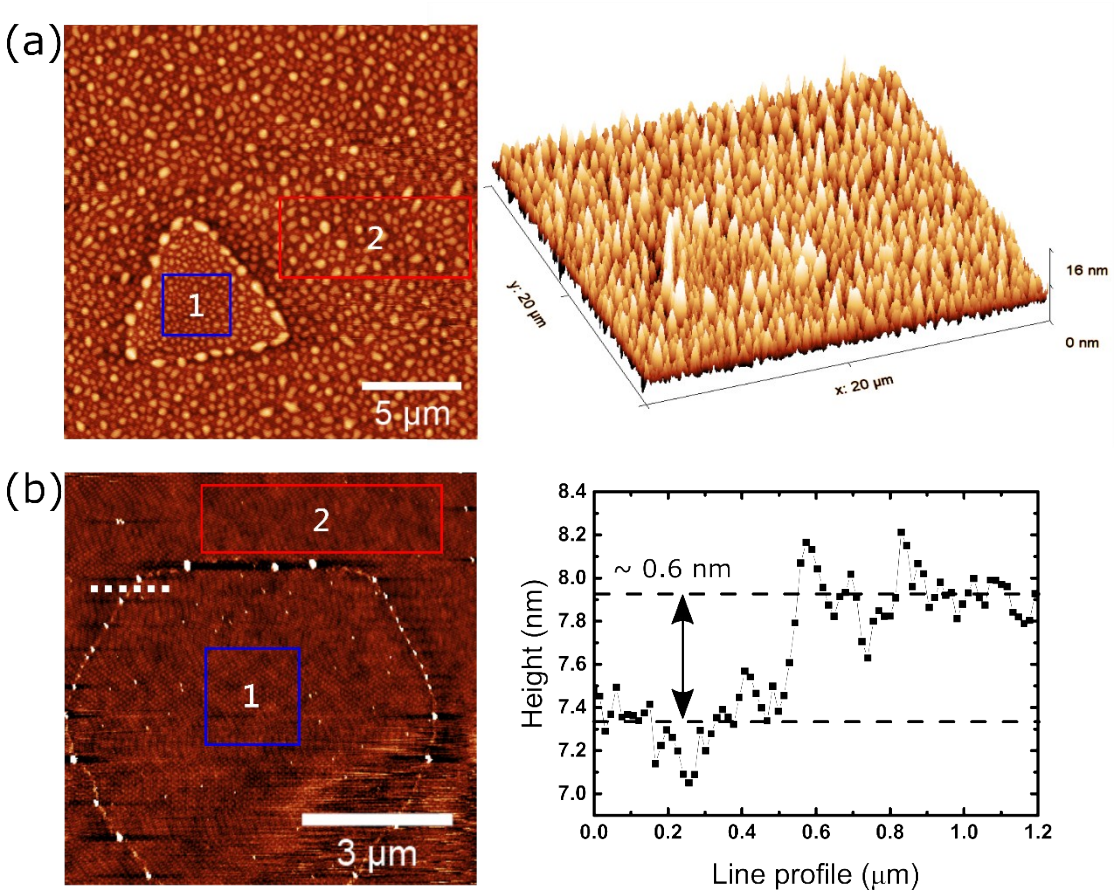

Figure S12 AFM images. (a) The AFM morphology of Pd(2 nm)/Co(0.6 nm)/SiO_2 or MoS_2. The triangular region is the Pd/Co stands on MoS_2, and the rest is Pd/Co stands on SiO_2. Region 1(Co/MoS_2) has a mean roughness of 1.1 nm, and region 2(Co/SiO_2) has a mean roughness of 1.8 nm. The Pd layer is added to prevent oxidation. **(b)** The AFM morphology of bare monolayer MoS_2 flake. The mean roughness of region 1(MoS_2) and region 2(SiO_2) is 0.4 nm and 0.3 nm, respectively. The 0.6 nm height difference between SiO_2 and MoS_2 flake indicates the flake is monolayer.

Additional examples of the magnetic anisotropy in Co domains

In the main manuscript, Figure 4 shows that the Co domain boundaries tend to be parallel with the lattice of MoS_2. Figure S12 offers additional support of our statement in showing more domain boundaries exhibiting a similar behavior.

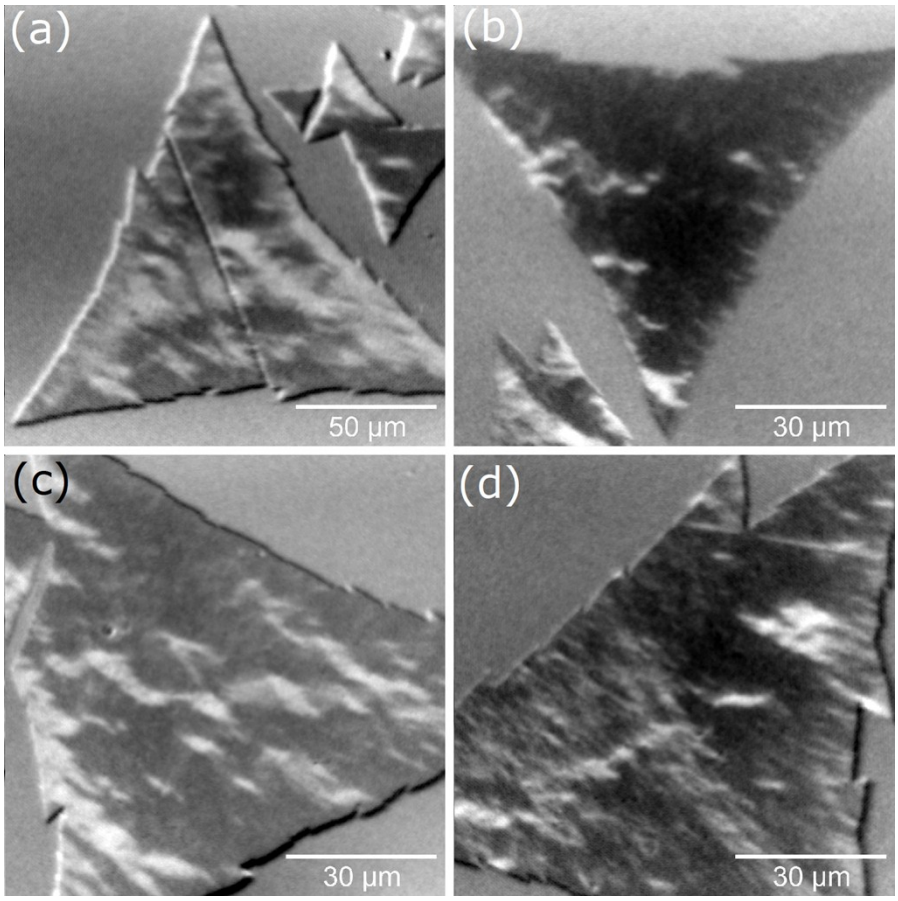

Figure S13. Additional examples that show Co domain boundaries having the same tendencies as displayed in Figure 4 of the manuscript. All Co samples presented here had a thickness of 9 ML.

References

S1. Entani, S., Kiguchi, M., Ikeda, S. & Saiki, K. Magnetic properties of ultrathin cobalt films on SiO_2 substrates. *Thin Solid Films* **493**, 221-225 (2005).

S2. Chen, M.*, et al.* TMD FinFET with 4-nm thin body and back gate control for future low-power technology. In: *2015 IEEE International Electron Devices Meeting (IEDM)* (2015).