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Supplementary Information

Hydroxide-based magneto-ionics: electric-field control of reversible paramagnetic-to-ferromagnetic switch in α-$Co(OH)_2$ films

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1. Sample Synthesis

The electrodeposition of cobalt hydroxide from cobalt nitrate bath is originated due to a local pH increase around the working electrode when nitrate ions are reduced, according to the following two possible chemical reactions:

$$NO_3^- + H_2O + 2e^- \rightarrow NO_2^- + 2\ OH^- \quad (1)$$

$$NO_3^- + 7H_2O + 8e^- \rightarrow NH_4^+ + 10\ OH^- \quad (2)$$

This reduction occurs at lower overpotentials than the metal Co deposition, producing an increase of OH^- groups in the vicinity of the working electrode, hindering the cobalt metal deposition and promoting the formation of cobalt hydroxide. In some cases, especially when acidic electrolytes are employed, metallic cobalt co-deposition within the hydroxide can occur. It has been reported that the ratio of cation/nitrate anion plays an important role. Thus, to assure the cobalt deposition suppression, ammonia nitrate (NH_4NO_3) is introduced. This is crucial to achieve fully paramagnetic samples.[1]

As a first attempt, α-$Co(OH)_2$ films were electrodeposited using electrolytes with a $Co(NO_3)_2 \cdot 6H_2O$ concentration of 0.1M.[2] Their morphology consist of hexagonal platelets randomly oriented with the basal planes perpendicular to the substrate surface (**Fig. S1a**).[3-4] This morphology leads to films with a large surface-to-volume ratio (i.e. porosity). Even though certain porosity could be beneficial, such as enhancing the magnetoelectric effects,[5-7] these films present uneven surfaces due to size dispersion of platelets. For this reason, their roughness needs to be minimized for thin-film based device applications.

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When $Co(NO_3)_2 \cdot 6H_2O$ concentration in the electrolyte was increased to 1 M, the sample morphology improved with a more uniform surface (**Fig. S1b**). Close examination of the films still revealed a certain degree of porosity from the perpendicular growth of the platelets, but the films were more densely packed (**Fig. S1b inset**). However, cracks appeared all over the surface, produced by stress relaxation during sample growth.[8] When SDS was incorporated to the electrolyte, the film morphology was preserved and, importantly, crack formation was suppressed (**Fig. 1a** in main text). It has been reported that SDS acts as a stress-relieve agent during electrodeposition, avoiding crack formation.[8-9]

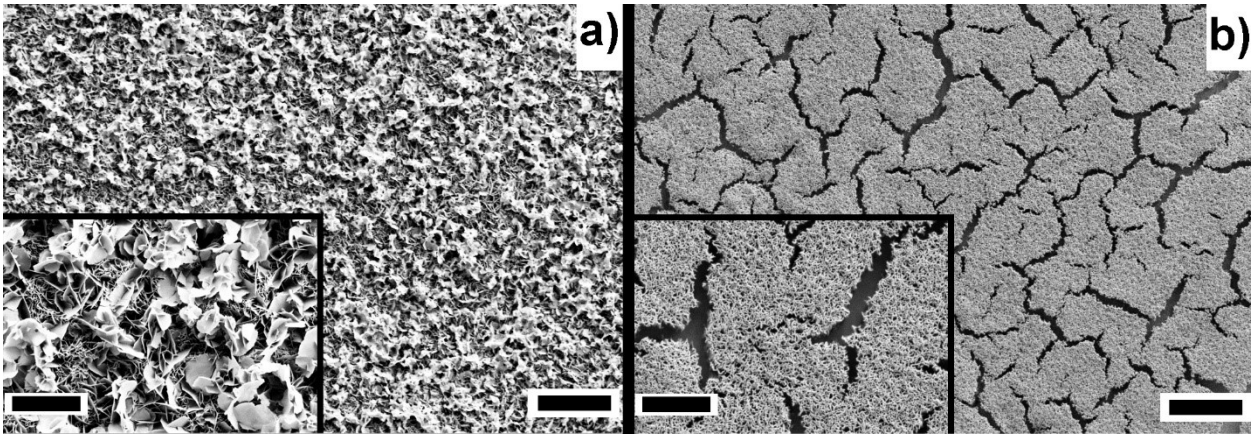

Fig. S1: Low and high resolution (inset) SEM images of the samples synthesized from an electrolyte containing a) 0.1 M and b) 1 M $Co(NO_3)_2 \cdot 6H_2O$. Scale bar is 10 μm in images (a-b), and 4 μm in (a-b) insets.

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2. Magnetic Switching

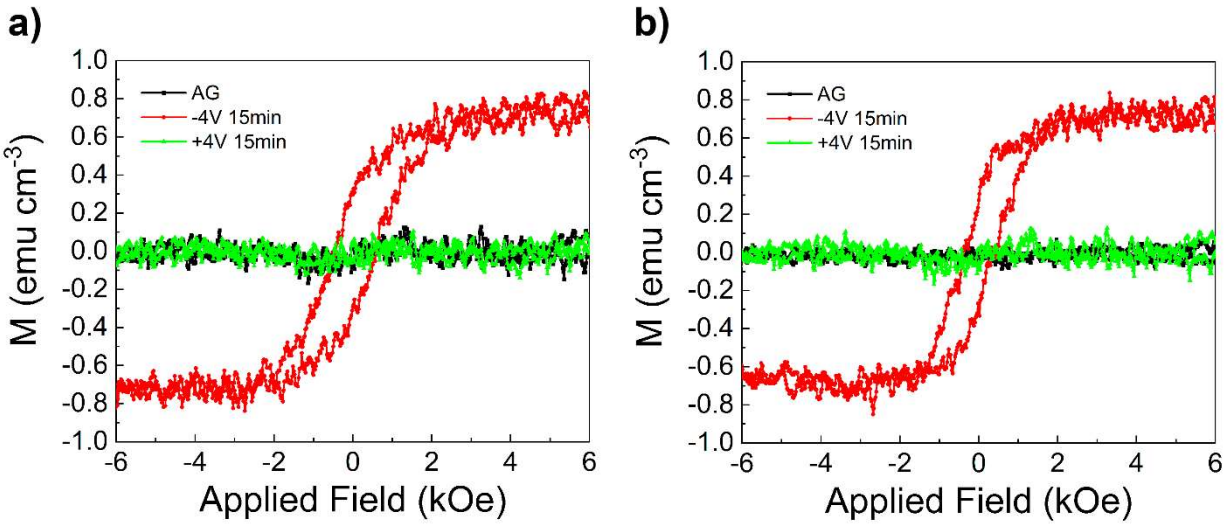

Fig. S2: Magnetic hysteresis loops for two consecutive switching cycles in α-$Co(OH)_2$ films after gating it at -4V and +4V for 15min each for a) one cycle and b) two cycles, respectively. Note that the AG in panel b) corresponds to the +4V 15 min state from panel a).

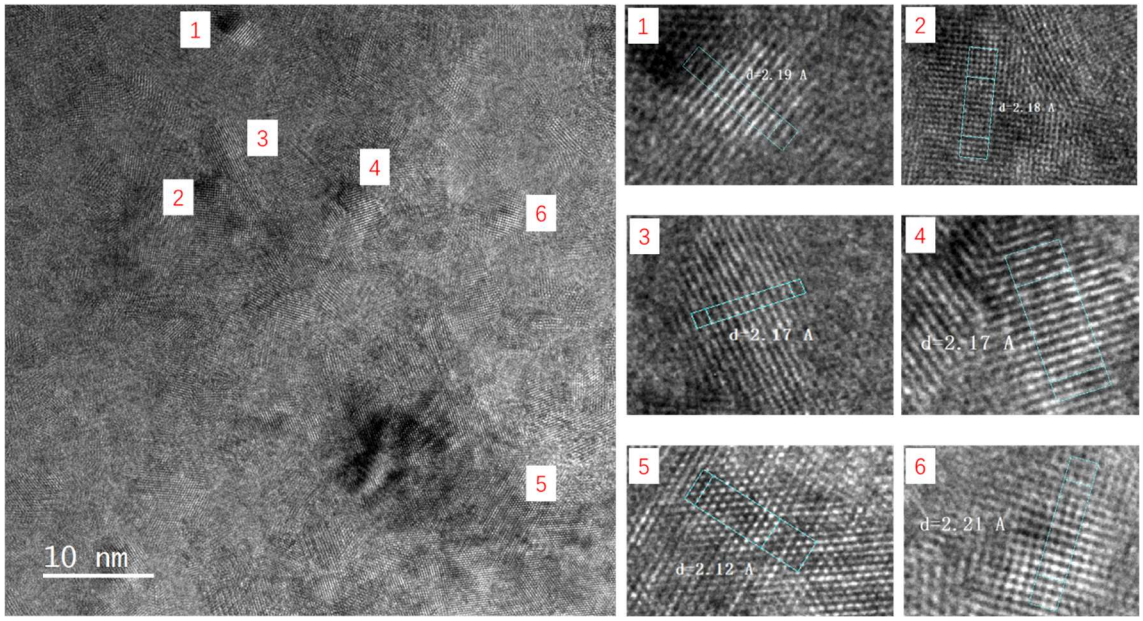

Fig. S3: High resolution scanning transmission electron microscopy and zoom-in images of labeled regions collected from an α-$Co(OH)_2$ sample after a gating procedure of -8V for 3.5h. The *d*-spacing corresponds to (100) hcp Co.

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References

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