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# Highly cyclable voltage control of magnetism in cobalt ferrite nanopillars for memory and neuromorphic applications (1)

Special Collection: Challenges and Perspectives in Materials Chemistry—A Celebration of Prof. Sir Anthony K. Cheetham's 75th Birthday

Muireann de h-Óra 🕿 💿 ; Aliona Nicolenco; P. Monalisha 💿 ; Tuhin Maity; Bonan Zhu 💿 ; Shinbuhm Lee; Zhuotong Sun; Jordi Sort 🕿 💿 ; Judith MacManus-Driscoll 💌 💿

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Muireann de h-Óra,<sup>1,a)</sup> D Aliona Nicolenco,<sup>2,3</sup> P. Monalisha,<sup>2</sup> D Tuhin Maity,<sup>4</sup> Bonan Zhu,<sup>5</sup> D Shinbuhm Lee,<sup>1,6</sup> Zhuotong Sun,<sup>1</sup> Jordi Sort,<sup>2,7,a</sup> D and Judith MacManus-Driscoll<sup>1,a</sup>

#### AFFILIATIONS

- <sup>1</sup> Department of Materials Science and Metallurgy, University of Cambridge, CB3 OFS Cambridge, United Kingdom
- <sup>2</sup>Departament de Física, Universitat Autònoma de Barcelona, 08193 Bellaterra, Spain
- <sup>3</sup>Cidetec, Gipuzkoa Science and Technology Park, P.O. Miramon/Miramon Pasealekua, 196 20014 Donostia, San Sebastián, Spain
- <sup>4</sup>Indian Institute of Science Education and Research Thiruvananthapuram, Thiruvananthapuram, Kerala 695551, India
- <sup>5</sup>Department of Chemistry, University College London, 20 Gordon St., London WC1H 0AJ, United Kingdom
- <sup>6</sup>Department of Physics and Chemistry, DGIST, Daegu 42988, South Korea
- <sup>7</sup>Institució Catalana de Recerca i Estudis Avançats, Pg. Lluís Companys 23, 08010 Barcelona, Spain

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<sup>a)</sup>Authors to whom correspondence should be addressed: mad71@cam.ac.uk; jordi.sort@uab.cat; and jld35@cam.ac.uk

### ABSTRACT

Tuning the properties of magnetic materials by voltage-driven ion migration (magneto-ionics) gives potential for energy-efficient, nonvolatile magnetic memory and neuromorphic computing. Here, we report large changes in the magnetic moment at saturation ( $m_S$ ) and coercivity ( $H_C$ ), of 34% and 78%, respectively, in an array of CoFe<sub>2</sub>O<sub>4</sub> (CFO) epitaxial nanopillar electrodes (~50 nm diameter, ~70 nm pitch, and 90 nm in height) with an applied voltage of -10 V in a liquid electrolyte cell. Furthermore, a magneto-ionic response faster than 3 s and endurance >2000 cycles are demonstrated. The response time is faster than for other magneto-ionic films of similar thickness, and cyclability is around two orders of magnitude higher than for other oxygen magneto-ionic systems. Using a range of characterization techniques, magnetic switching is shown to arise from the modulation of oxygen content in the CFO. Also, the highly cyclable, self-assembled nanopillar structures were demonstrated to emulate various synaptic behaviors, exhibiting non-volatile, multilevel magnetic states for analog computing and high-density storage. Overall, CFO nanopillar arrays offer the potential to be used as interconnected synapses for advanced neuromorphic computing applications.

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#### INTRODUCTION

Research in digital memory is growing with the increase in popularity of artificial intelligence, machine learning, the Internet of Things, and Big Data. This, in turn, has caused an energy demand that has triggered innovation toward non-volatile memory technologies that do not require a continuous power supply. Magnetic memory is a promising non-volatile technology for storing data, but conventional magnetic memory concepts use electrical current to control magnetic properties (i.e., through electromagnets or spin-torque effects), and this can lead to significant energy loss by heat dissipation.<sup>1,2</sup> On the other hand, magnetoelectric (ME) devices, where electric fields are used to tune the magnetism, could offer energy-efficient non-volatile memory.<sup>3</sup> However, no truly practical magnetoelectric devices for memory yet exist.

Magneto-ionic devices are a type of magnetoelectric system where magnetism is controlled by electric-field-driven ion motion. Ions that have been commonly explored include  $O^{2-}$ ,  $H^+$ , Li<sup>+</sup>, or

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 $N^{3-}$ ,<sup>4–7</sup> and they are introduced into the magnetic materials either from a solid or from a liquid electrolyte.<sup>8–13</sup> A high electric field at a magnetic material electrode–electrolyte interface (resulting from the formation of the electrical double-layer, EDL) acts as the driving force for ion migration.<sup>14</sup>

As magneto-ionic systems are voltage-controlled rather than current-controlled, they are energy efficient with potential writing energies as low as  $\sim 10^{-3}$  fJ = 1 aJ.<sup>5,15,16</sup> This is  $10^2$  times lower than standard complementary metal oxide semiconductor devices (CMOS) and 10<sup>5</sup> times lower than magnetic-based devices like magneto-resistive random-access memories or hard disk drives.<sup>17</sup> Magneto-ionic systems also enable non-volatile, and reversible modulation of magnetic anisotropy, coercive field,<sup>18</sup> exchange bias field,<sup>19</sup> and magnetic easy axis.<sup>20</sup> The high tuning capability of the different parameters makes magneto-ionic systems suitable not only for ultralow power magnetic memory<sup>18,21</sup> but also for a range of other energy-efficient devices,<sup>22</sup> including devices for neuromorphic computing.<sup>23</sup> Here, biological synaptic functions can be emulated in the current-voltage response behavior.<sup>24</sup> Thus, they show similar behavior to the biological brain where ion motion is triggered by electrical stimuli in liquid media.<sup>25–27</sup> Compared to memristive synapses (which use voltage-induced changes of electric resistivity to potentiate or depress post-synaptic signals), magneto-ionic synapses operate through the induced changes of magnetization (a vector) to modulate synaptic weight. Since magnetization is a vector (whereas resistivity is a scalar), this adds a new degree of freedom for the control of the neuromorphic system.<sup>1</sup>

A range of configurations have been studied to optimize magneto-ionic effects, with planar films and bilayers being the most common.<sup>29</sup> However, porous polycrystalline films (e.g., CFO) have also been studied to maximize the surface area to volume ratio so that ion transfer between liquid or solid electrolytes<sup>8–11,30–34</sup> is enhanced. Remarkably, studies on magneto-ionic effects in arrays of patterned or self-assembled dots or islands are rather scarce. If magneto-ionics could be demonstrated to be applicable to dense, high surface area nanopillar arrays, the phenomenon could be used in patterned magnetic recording media or as an array of interconnected synapses.3 <sup>-39</sup> The non-volatility and energy efficiency of the magneto-ionic effect in the nanopillar arrays could be a key enabler for next-generation data storage,<sup>1,22,28</sup> provided durability, cyclability, and magnitude of the magnetic response were satisfied also.

While there are obvious benefits of magneto-ionics as a concept, they currently have some practical limitations. Since ion migration is a thermally activated process, the slow rates of field-assisted oxygen ion migration at room temperature mean that switching times are proportionately slow. The times to switch magnetic states range from  $10^{-5}$ – $10^{5}$  s.<sup>5,6,40</sup> Operation above room temperature increases magneto-ionic rates but this is not practical for most electronics.<sup>5,16</sup> The cyclability of magneto-ionic devices is another challenge with an upper limit of >10 000 cycles, which has been demonstrated only with H<sup>+</sup> insertion at Co/GdO<sub>x</sub> interface;<sup>6,40</sup> however, this has the limitation of requiring a reliable and constant source of H<sup>+</sup> from humid air. Cyclability at room temperature with more stable O<sup>2-</sup> driven magneto-ionics rarely exceeds 100.<sup>13</sup> Here, a key limitation is the degradation of the chemical structure, which is modified upon cycling and often causes phase transitions and chemical reduction that are not always fully reversible.<sup>5</sup>

Herein, we propose that higher cyclability and large magnetoionic effects are possible by implementing three key materials features: (a) a single-crystal-like epitaxial material, (b) a nanostructured material, and (c) a magnetic oxide material with intrinsic oxygen ions. The epitaxial material is less defective than polycrystalline material and should uniformly enhance oxygen diffusion in and out during voltage application. A nanostructured material offers a higher surface to volume ratio than non-nanostructured material and thus should allow a larger fraction of the material to have its oxygen content changed upon voltage application, leading to large magneto-ionic effects. A magnetic oxide (as opposed to a metal) could be chosen, which does not undergo a phase change or large volume change upon voltage application, offering the chance of better cyclability. As oxygen ions are readily stored in an oxide material, there is also no need for an additional source/drain layer.

We show magneto-ionic switching of  $CoFe_2O_4$  nanopillar electrodes, with dimension ~50 nm, pitch ~70 nm, and height ~90 nm, from a propylene carbonate liquid electrolyte. We observe large changes in the magnetic moment at saturation,  $m_{S_1}$  and coercivity,  $H_C$ . As far as known, the cyclability of the switching is superior to previously reported oxygen magneto-ionic studies.<sup>40,42</sup> The magnetic switching is shown to arise from oxygen content modulation in the CFO, as confirmed by x-ray photoelectron spectroscopy (XPS), x-ray diffraction (XRD), and conducting atomic-force microscopy (C-AFM). We also demonstrate nanopillar-based synaptic devices and mimicked synaptic functionalities for neuromorphic computing applications. The synaptic device exhibits non-volatile and multilevel magnetic states, which are promising for analog and high-density data storage, offering promise for future computing in the form of interconnected arrays of synapses.

#### **EXPERIMENTAL METHODS**

Self-assembled vertically aligned nanocomposite (VAN) films of CFO + MgO, in a 50:50 molar ratio (precursor materials to create the nanopillar films), were grown by pulsed laser deposition (PLD) on 0.5 wt. % Nb-doped SrTiO<sub>3</sub> (Nb:STO) (001) substrates at 770 °C. A KrF laser ( $\lambda$  = 248 nm) at a fluence of 2 J cm<sup>-2</sup> and a repetition rate of 5 Hz was used. The PLD targets for the depositions were formed using solid-state sintering from powders of cobalt oxide (Co<sub>3</sub>O<sub>4</sub>) and iron oxide (Fe<sub>3</sub>O<sub>4</sub>), and for the VAN target, magnesium oxide (MgO) was also added. Targets were sintered at 1250 °C for 6 h in air.

Reference epitaxial planar CFO films were also grown. Here, the substrate temperature was  $625 \degree C$ , which is lower than the VAN film where the temperature was moderately higher to enable sufficiently distinct nanopillars to form. To achieve the CFO nanopillar structure, the MgO was then wet chemically etched from the VAN structure by submerging the sample in 10 wt. % ammonium sulfate at  $60\degree C$  for 2 h. The sample was continuously sonicated during the etching to ensure the full removal of MgO from the VAN structure.

The magneto-ionic experiments were conducted at room temperature on both the planar and nanopillar films using a simple electrochemical cell as shown schematically in Fig. 1. The cell was designed to be able to do operando magnetic measurements in the VSM. An area of the film was scratched to make the electric 12 February 2024 16:15:00



FIG. 1. Schematic of electrochemical cell used for the magneto-ionic measurements by VSM *in situ*. The cell was filled with a liquid electrolyte (propylene carbonate with traces of dissolved Na<sup>+</sup> and OH<sup>-</sup> species). The CFO film was submerged in the liquid. The substrate, Nb:STO with CFO nanopillars, was used as the working electrode, while a Pt wire acted as the counter electrode (shown in the inset). The cell vibrated vertically on a sample holder in the VSM while measurements were taken.

connection to the sample substrate. Contacts were made by indium welding a Cu wire to the exposed substrate. A Pt wire was used as the counter electrode, which was then held at a constant distance from the sample using a hot-melt polymer adhesive. The sample was then placed in a small Eppendorf tube and filled with propylene carbonate (PC) treated with metallic sodium to remove any traces of water, which left a small amount of Na<sup>+</sup> and OH<sup>-</sup> ions ( $\approx$ 5 ppm Na<sup>+</sup> as determined by Inductively Coupled Plasma (ICP) spectroscopy). A MicroSense (LOT-QuantumDesign) Vibrating Sample Magnetometer (VSM) was used to measure the magnetic properties. The voltage was applied using an Agilent B2902A power supply in situ. All in situ magnetic measurements (hysteresis loops, cyclic measurements, and neuromorphic measurements) were taken in an in-plane (IP) configuration (i.e., applying the magnetic field parallel to the Nb:STO substrate plane) at room temperature. Ex situ measurements (XPS, XRD, and C-AFM) were done by first treating the sample in a larger electrochemical cell setup. Using crocodile clips, the film and Pt wire were attached to the power supply before being submerged in a Na<sup>+</sup> treated PC contained in a quartz beaker. This system allowed for easy transfer between the cell and the measurement devices. The planar and nanopillar CFO films were treated with a negative gate voltage for 30 min to achieve the "treated" state (oxygen removal from the nanopillars) and afterward with a positive gate voltage for 30 min to achieve the "recovered" state (oxygen addition to the nanopillars), ex situ. A range of characterization measurements were carried out to determine the structural changes between the as-prepared, treated, and recovered states of the two sets of samples. The XRD patterns were recorded using a Materials Research Diffractometer (MRD) from Malvern PANalytical and a Panalytical Empyrean vertical diffractometer. XPS was done using a Phoibos 150 analyzer in ultra-high vacuum conditions (base pressure 5  $\times$  10<sup>-5</sup> mbar) with a monochromatic Al Ka x-ray source. XPS spectra were calibrated using the carbon peak that arises from "adventitious" carbon on the film after exposure to air. C-AFM was performed using a Bruker Veeco Dimension Pro to investigate the electrical properties. Contact angle measurements were done using a Marca KRÜSS, model DSA 100.

#### **RESULTS AND DISCUSSION**

Figure 2 shows microstructural information about the nanopillar films before and after etching MgO out of VAN film. Figure 2(a) shows a schematic of the film structure before and after etching and Fig. 2(b) shows the corresponding XRD spectra. The film is epitaxially aligned with (00*l*) peaks of CFO and MgO on the Nb-STO (001) substrate. The CFO (004) peak remains unchanged in both intensity and peak position relative to the substrate, indicating no change in strain or microstructure of the CFO after etching out the MgO. The MgO (002) peak vanishes after etching, indicating complete MgO removal.

Figure 2(c) shows an AFM image of the CFO nanopillar sample after etching out the MgO. Clear oblong features of uniform height are visible and correspond to the nanopillars. Figure 2(d) shows a top-view scanning electron microscope (SEM) image of the film after etching, clearly showing that the nanopillars, size, and the shape are in agreement with the AFM image. Figure 2(e) shows a cross-sectional secondary electron SEM image of the etched film. The height of the nanopillars is ~90 ± 10 nm. Pores are visible as the darker features between the lighter-featured nanopillars. The pores penetrate the film through to the substrate, confirming the x-ray result of Fig. 2(b), i.e., the MgO was fully etched out.

Figure 3(a) shows the in-plane hysteresis loops of the CFO nanopillar films in the as-prepared state (0 V), after treatment with applied negative gate voltages of -2, -4, -6, and -10 V (oxygen removal from the film), and then after recovering (oxygen reintroduction to the film) with an applied positive gate voltage of +10 V. The loops were measured *in situ*, i.e., during voltage application. The loop shapes indicate that the magnetic domains in the nanopillars are neither IP nor out-of-plane (OOP) but likely have a range of orientations. This is confirmed by OOP magnetization measurements,



FIG. 2. Formation and structure of nanopillar films. (a) Schematic of the self-assembled nanocomposite growth and the etching of the matrix. (b) X-ray diffraction pattern of the CFO:MgO nanocomposite before and after etching the MgO matrix from the VAN film. The \* denotes an artifact peak from the XRD detector. (c) AFM image of the free-standing nanopillars after the matrix had been etched. (d) Top view and (e) cross-sectional secondary electron SEM of the free-standing nanopillars. Nanopillars are outlined with the visible portion highlighted in orange.



FIG. 3. Magneto-ionic data for CFO nanopillar films. (a) Hysteresis loops (20 min duration) of CoFe<sub>2</sub>O<sub>4</sub> nanopillars at 0 V (as-prepared state), after applying -2, -4, -6, and -10 V (treated state), and +10 V (recovered state). (b) Change in saturation magnetization, m<sub>S</sub>, and coercivity, H<sub>C</sub>, as a function of applied negative gate voltage. (c) Representation of cycling of magnetic moment, m, at  $\pm 10$  V with a period of 60 s for the first 10 cycles (cycles no. 0–10), cycles no. 100–110, and cycles no. 2000–2100. Note, the magnetic moment in (c) has been centered around zero and normalized between 0.5 and -0.5.

which were also undertaken (not shown) and appeared similar to Fig. 3(a). Figure 3(a) shows that the negative gate voltage induces an increase in  $m_S$  while the positive gate voltage induces a reduction in  $m_S$ . Figure 3(a) inset shows that  $m_S$  does not saturate after 20 min of each voltage application, indicating that oxygen loss or recovery is not complete.

Relative to the as-prepared (0 V) sample when -10 V is applied to the nanopillar sample, there is a 34% increase in  $m_{\rm S}$  from 3.05  $\pm$  0.02 memu to 4.10  $\pm$  0.01 memu and a 78% increase in  $H_{\rm C}$  from 713  $\pm$  7 Oe to 1270  $\pm$  30 Oe. When +10 V is then applied to the sample, the magnetic properties are almost entirely recovered with minimal change from the initial as-prepared (0 V) state. The large changes in magnetic properties when voltage is applied suggest that the liquid electrolyte is able to wet, spread, and penetrate the surface of the nanopillar film. This is confirmed in Fig. S1 from the supplementary material, which shows that the contact angle between the sample and a drop of propylene carbonate is 50.1  $\pm$  0.2°. As the sample is hydrophilic,<sup>43</sup> a high surface interface between the nanopillars and electrolytes can be assumed.

The dramatic change in magnetic properties can be attributed to the  $O^{2-}$  diffusion out of the CFO into the liquid electrolyte.<sup>30,44</sup> The application of negative gate voltage results in a sufficiently large electric field<sup>14</sup> at the oxide-electrolyte electrical double-layer (EDL), causing the oxygen ions to migrate toward the surface of the CFO.<sup>45</sup> This, combined with the high  $O^{2-}$  ion mobility in the electrolyte, leads to the de-oxygenation of the CFO at the nanopillar surfaces and thus a change in  $m_S$  and  $H_C$ .<sup>30</sup> It has previously been shown in porous CFO polycrystalline material that the increase in  $m_S$  is due to the decrease in the oxygen content after magneto-ionic voltage application, leading to a reduction in average cation valence,<sup>30</sup> i.e., Fe<sup>3+</sup> is reduced to Fe<sup>2+</sup> in the tetrahedral positions.<sup>46,47</sup> The increase of  $H_C$  in the treated sample is probably related to the variation of the Fe<sup>3+</sup>/Fe<sup>2+</sup> ratio with voltage (which is known to modify the effective magnetic anisotropy).<sup>48–50</sup>

To investigate the cyclability of the magneto-ionic effect in the CFO epitaxial nanopillars, the samples were cycled between -10

and +10 V at 60 s/cycle. Figure 3(c) shows that the CFO pillars can be consistently cycled between the different magnetic states for >2000 cycles. The cyclability is two orders of magnitude higher than in previously studied polycrystalline CFO films and other oxygen magneto-ionic systems.<sup>13,30</sup>

Figure 3(c) shows that the changes in the magnetic moment with voltage occur very quickly, in less than 3 s (the time taken to acquire each data point). Fast cycling produces an average difference in the magnetic moment of ~0.018 memu between -10 and +10 V for the first 10 cycles, which decays to ~0.008 memu after 2000 cycles. Previously, similar switching speeds in oxygen-driven magneto-ionic systems were achieved in very thin (<10 nm) films, whereas here, we have much thicker ~90 nm pillar films,<sup>51</sup> which could be advantageous for improved stability. Indeed, the surfaces of the nanopillar film in the as-prepared, treated, and recovered states show no significant microstructural changes when observed by AFM (see Fig. S2 from the supplementary material).

Our reference CFO planar epitaxial films of 90 nm thickness show a different behavior to the nanopillar films. In the as-prepared state [Fig. S3(a)], the magnetic domains are aligned IP. Upon voltage application, the *m*-*H* data again indicates an increase in the ferromagnetism due to the formation of  $\text{CoFe}^{2+/3+}_2\text{O4-x}$  after oxygen removal, but the increase is larger,  $\Delta m_{S-\text{planar}} = 370\%$ , than for the nanopillar films,  $\Delta m_{S-\text{pillar}} = 34\%$ . Thus, the initial change in  $m_S$ upon -10 V application is higher compared to the nanopillar films. However, there is no full recovery of the planar film *M*-*H* loop upon positive voltage application. The reason for this is unclear at present but is common to planar films.<sup>52,53</sup> This could be related to a reaction layer that forms at the CFO (001) planar film surface after oxygen removal but does not form on the nanorods owing to the (100) surface being the predominant surface that is exposed to the electrolyte. Further work is required to understand more about what influences recoverability.

Considering the almost complete recoverability and hence excellent cyclability of the nanopillar films, we now focus on the structural and chemical changes that occur for the different states of



FIG. 4. Structural and chemical analyses of CFO nanopillar films. (a) (i) X-ray diffraction patterns for CFO nanopillar sample as-prepared (black), treated with -10 V for 30 min (blue), and recovered with +10 V for 30 min (orange). The peak denoted \* represents a contamination peak from Ag paste from sample processing. The CFO (004) peak is shown magnified in (ii) to better show the peak shift when treated and recovered. The dashed lines represent the central peak position. (b) XPS of the Fe 2p<sub>3/2</sub> peak for the sample (i) as-prepared, (ii) treated with -10 V for 30 min, and (iii) recovered with +10 V for 30 min.

voltage application. The XRD image of Fig. 4(a-i) shows the (004) CFO XRD peak position for the as-prepared, -10 V treated, and +10 V recovered films. We see a small shift in the peak for each state. The shift can also be clearly seen in the CFO (008) peak (not shown), further confirming the change in structure. A summary of lattice parameter changes calculated from the XRD patterns is presented in Table I. The respective values for both the nanopillars and planar films are presented in Table I.

Compared to the as-prepared lattice parameter of the asprepared CFO nanopillars,  $8.384 \pm 0.006$  Å, the treated nanopillars show an 0.43% increase, which is consistent with a decrease in oxygen content.<sup>44,54-57</sup> The finding is supported by XPS [Fig. 4(b)], which shows the Fe  $2p_{3/2}$  spectra of the CFO nanopillars. There is only Fe<sup>3+</sup> present in the as-prepared nanopillars [Fig. 4(b-i)], but there is also a significant fraction of Fe<sup>2+</sup> after treating (-10 V) [Fig. 4(b-ii)]. Since Fe<sup>2+</sup> has a larger ion radius than Fe<sup>3+</sup>, an increase in lattice parameter is expected.<sup>58,59</sup> After recovery, the lattice parameter almost fully recovers, with only a small (0.06%) lattice expansion remaining. The XPS data [Fig. 4(b-iii)] no longer show any measurable Fe<sup>2+</sup> remaining, indicating excellent reversibility of oxygen.

The XRD patterns of the planar films are shown in Fig. S4 of the supplementary material. As presented in brackets in Table I,

 
 TABLE I. The summary of lattice parameters calculated from the XRD patterns and % changes for the planar and nanopillar films.

Sample	% Change in c-lattice parameter cf as-prepared
Nanopillars [planar] as-prepared	
Nanopillars [planar] treated (-10 V)	0.43 [0.11]
Nanopillars [planar] recovered (+10 V)	0.06 [0.08]

the corresponding lattice changes upon treatment and recovery for the planar films are much smaller (0.11% and 0.08%, respectively) than for the nanopillar films, indicating less oxygen content change, which is consistent with the lower surface area to volume ratio and larger diffusion lengths. The observed expansion of the c-lattice parameter with oxygen removal and concomitant increase in Fe<sup>2+</sup> content is confirmed by density functional theory calculations (supplementary material Note 1 and Figs. S5 and S6).

Next, C-AFM was used to further investigate the migration of oxygen ions in the CFO nanopillars under 0, -10, and +10 V (Fig. 5). All C-AFM scans were done with a -5 V bias on the measurement tip. The results reveal that the sample in the as-prepared state is highly insulating. The current is in the pA range, with little variation in the current across the film. The sample was then treated for 30 min at -10 V to achieve the treated state. The treated film has a current flow on the order of nA, three orders of magnitude higher than in the initial state. This increase in current flow can be attributed to the oxygen migration out of the films and is consistent with previous work on voltage-actuated CFO.<sup>30</sup> The sample was then recovered with +10 V for 30 min. The current flow decreases from the treated state, revealing a good correlation between magnetization changes and electric conductivity changes, which is an important aspect of the potential use of nanopillars in neuromorphic applications.

Finally, the CFO nanopillars were investigated as artificial synapses for neuromorphic applications. In the human brain, synapses play the role of signal transmission across neurons, with synchronized learning and memory capability. Here, we use sample magnetic moment as the synaptic weight to mimic synaptic functionalities. As shown in Fig. 6(a), after applying to the CFO nanopillar films, a series of negative voltage pulses of different amplitudes (in a sequence of  $\Delta V = -6, -8, -10$ , and -12 V), of duration (t<sub>p</sub> = 150 s), and with 600 s spacing, we observe multilevel magnetic states.<sup>60</sup>



FIG. 5. Conductive Atomic Force Microscopy (C-AFM) images of nanopillar films after different voltage application treatments, i.e., in the as-prepared (state I), after applying -10 V to reach state II, and again in the recovered state after +10 V (state III). The lighter colors represent a higher electric current flow across the sample.



**FIG. 6.** (a) Non-volatile and distinct multilevel conductance states realized by applying a series of negative gate voltage pulses of different amplitudes (in the sequence of  $V_G = -6, -8, -10$ , and -12 V) and of the same duration ( $t_p = 150$  s), spaced apart by 600 s. (b) Changes in the magnetic moment,  $\Delta m$ , [analogous to excitatory postsynaptic conductance (EPSC)] triggered by spikes of the same duration ( $t_p = 150$  s shown in gray) and different amplitudes ( $V_G = -6, -8, -10, \text{ and } -12$  V), and (c) the maximum change in  $\Delta m$  and the slope of the increase in  $\Delta m$  with applied voltage vs voltage. (d) Experimental transfer curve at a sweeping rate of 0.017 V/s in the direction of the arrows. (e)  $\Delta m$  triggered by presynaptic spikes of the same amplitude ( $V_G = -10$  V) and different durations (50, 150, 250, and 350 s), and (f) the maximum change in  $\Delta m$  and the slope of the increase in  $\Delta m$  with applied voltage.

The synapse can tune its synaptic weight depending on activity, which is termed synaptic plasticity, and this forms the basis for all learning and memory.<sup>61</sup> The phenomenon of tuning synaptic plasticity by varying spike amplitude is known as spike amplitude-dependent plasticity (SADP). As shown in Fig. 6(b), SADP was also mimicked. Here, a series of voltage pulses with the same duration time (150 s) and different amplitudes ( $\Delta V = -6$ , -8, -10, and -12 V) were applied to the sample, and the corresponding increase of magnetic moment was measured. The peak value ( $\Delta m_{\text{Max}}$ ) increased with pulses of increasing voltage, evidencing spike-amplitude-dependent plasticity (SADP).<sup>62</sup> After the region where a voltage pulse was applied for 150 s, the magnetic moment decayed slightly before settling at a stable level. The sample was then recovered to the original state by applying the same gate voltage of the opposite sign until the initial magnetic moment was reached between each measurement (not shown).

Figure 6(c) shows the change in the magnetic moment with increasing applied voltage. An approximately linear relationship is observed. dm/dt, the activation slope, also increases linearly with applied voltage. Higher voltages cause the oxygen ions to migrate faster from the CFO to the electrolyte, due to the creation of a larger electric field at the CFO–propylene carbonate interface. The faster-moving ions cause a sharper slope for higher voltages.

Figure 6(d) shows the sample magnetization vs applied voltage curve measured by the sweeping voltage at a rate of 0.017 V/s in the direction of the arrows. The curve shows the reversibility of

the sample magnetization with hysteresis behavior, making it suitable to mimic synaptic behaviors. The portion of the curve that remains open at the end point corresponds to the small portion of the magnetic moment that is not recoverable from the initial cycle [Fig. 3(a) initial and recovered loops]. Note that this small irreversibility occurs when voltage is applied for several minutes to the sample. However, if the voltage actuation time is fast enough (e.g., <1 min), then the sample is fully recoverable and cyclable [Fig. 3(c)]. The magnetic moment increased as the gate voltage was swept from 0 to -10 V and continued to increase as the voltage reversed from -10 to 0 V. This is indicative of the cumulative effect of magneto-ionics, i.e., the O<sup>2-</sup> ions continue to migrate with negative gate voltage even if the amplitude of the voltage decreases. The magnetic moment then decreases when the voltage is positive.

It is well known that the duration of the voltage pulses can also be used to tune the synaptic weight (sample *m*) defined as spikeduration dependent plasticity (SDDP). Figure 6(e) shows the dependence of magnetic moment on pulse duration for -10 V applied for 50, 150, 250, and 350 s. The magnitude of the moment increases with an increase in pulse duration. This is plotted in Fig. 6(f). The  $\Delta m$ value increases with an increase in duration due to higher oxygen migration for a longer pulse. Overall, the successful demonstration of artificial synapses in the CFO nanopillar offers good prospects for future neuromorphic devices, where the array of nanopillars could be used as an array of interconnected synapses.

#### CONCLUSIONS

Here, we have shown highly cyclable voltage control of magnetic properties in CoFe<sub>2</sub>O<sub>4</sub> by electrochemical removal and reintroduction of oxygen mediated by a PC electrolyte. The CoFe<sub>2</sub>O<sub>4</sub> was in the form of epitaxial nanopillar arrays of ~50 nm dimension, ~70 nm pitch, and ~90 nm height, by etching out MgO from a vertically aligned nanocomposite CoFe2O4/MgO film that was grown by selfassembly by pulsed laser deposition. Large changes in  $m_S$ , 34%, and  $H_C$ , 78%, with an applied voltage of -10 V were achieved as a result of changes in oxygen content in the CFO. The magnetic switching is almost fully reversible when an opposite voltage of +10 V was applied. Cyclability to >2000 cycles was demonstrated, one of the highest cycling performances reported for magneto-ionic systems, with fast, <3 s, and distinct magnetic switching. The mechanism of switching was shown to be oxygen migration out of and into CFO with concomitant switching of the Fe valence state between Fe<sup>3+</sup> and  $Fe^{2+}$ , which modulates  $m_s$  and  $H_C$ . The magnetic nanopillars were also demonstrated to show synaptic behavior for neuromorphic computing applications. Non-volatile, distinct multilevel analog magnetic states, spike amplitude, and spike duration-dependent synaptic plasticity were controlled by voltage pulsing. The changes in magnetic properties were also accompanied by changes in electric conductivity, as evidenced by C-AFM, which may enable both magnetic and electrical readings of the synaptic weight. This study highlights the high potential of CFO nanopillars to be used as interconnected synapses in future high density ultra-fast energy efficient memory devices.

#### SUPPLEMENTARY MATERIAL

See the supplementary material for contact angle measurement, AFM of the as-prepared, treated, and recovered sample, planar film magnetic measurements and XRD, and density functional calculations of the response of ionic and electronic structures of CoFe<sub>2</sub>O<sub>4</sub> upon removal of lattice oxygen.

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#### **Conflict of Interest**

The authors have no conflicts to disclose.

#### **Author Contributions**

Muireann de h-Óra: Data curation (equal); Formal analysis (equal); Funding acquisition (equal); Investigation (equal); Methodology (equal); Writing - original draft (equal); Writing - review & editing (equal). Aliona Nicolenco: Conceptualization (equal); Data curation (equal); Formal analysis (equal); Investigation (equal); Methodology (equal); Project administration (equal); Visualization (equal); Writing - review & editing (equal). P. Monalisha: Data curation (equal); Investigation (equal); Methodology (supporting); Writing - original draft (supporting); Writing - review & editing (equal). Tuhin Maity: Visualization (equal); Writing - review & editing (equal). Bonan Zhu: Formal analysis (equal); Investigation (equal); Software (equal); Writing - review & editing (supporting). Shinbuhm Lee: Writing - review & editing (supporting). Zhuotong Sun: Investigation (supporting). Jordi Sort: Conceptualization (equal); Project administration (equal); Supervision (equal); Visualization (equal); Writing - original draft (equal); Writing - review & editing (equal). Judith MacManus-Driscoll: Project administration (equal); Supervision (equal); Writing original draft (equal); Writing – review & editing (equal).

#### DATA AVAILABILITY

The data that support the findings of this study are available from the corresponding authors upon reasonable request.

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