Voltage-Induced Coercivity Reduction in Nanoporous Alloy Films: A Boost toward Energy-Efficient Magnetic Actuation

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Magnetic data storage and magnetically actuated devices are conventionally controlled by magnetic fields generated using electric currents. This involves significant power dissipation by Joule heating effect. To optimize energy efficiency, manipulation of magnetic information with lower magnetic fields (i.e., lower electric currents) is desirable. This can be accomplished by reducing the coercivity of the actuated material. Here, a drastic reduction of coercivity is observed at room temperature in thick (≈600 nm), nanoporous, electrodeposited Cu–Ni films by simply subjecting them to the action of an electric field. The effect is due to voltage-induced changes in the magnetic anisotropy. The large surface-area-to-volume ratio and the ultranarrow pore walls of the system allow the whole film, and not only the topmost surface, to effectively contribute to the observed magnetoelectric effect. This waives the stringent “ultrathin-film requirement” from previous studies, where small voltage-driven coercivity variations were reported. This observation expands the already wide range of applications of nanoporous materials (hitherto in areas like energy storage or catalysis) and it opens new paradigms in the fields of spintronics, computation, and magnetic actuation in general.

1. Introduction

The continuous progress in information and communication technologies critically depends on an optimized utilization of electric power. Magnetism and spintronics have largely contributed to the digital revolution by dramatically enhancing the electric power. Magnetism and spintronics have largely contributed to the digital revolution by dramatically enhancing the electric power. Magnetic data storage and magnetically actuated devices are conventionally controlled by magnetic fields generated using electric currents. This involves significant power dissipation by Joule heating effect. To optimize energy efficiency, manipulation of magnetic information with lower magnetic fields (i.e., lower electric currents) is desirable. This can be accomplished by reducing the coercivity of the actuated material. Here, a drastic reduction of coercivity is observed at room temperature in thick (≈600 nm), nanoporous, electrodeposited Cu–Ni films by simply subjecting them to the action of an electric field. The effect is due to voltage-induced changes in the magnetic anisotropy. The large surface-area-to-volume ratio and the ultranarrow pore walls of the system allow the whole film, and not only the topmost surface, to effectively contribute to the observed magnetoelectric effect. This waives the stringent “ultrathin-film requirement” from previous studies, where small voltage-driven coercivity variations were reported. This observation expands the already wide range of applications of nanoporous materials (hitherto in areas like energy storage or catalysis) and it opens new paradigms in the fields of spintronics, computation, and magnetic actuation in general.

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2. Results and Discussion

2.1. Morphology and Structure of the Electrodeposited Films

The typical morphology of the cross-section of the electrodeposited Cu–Ni films, observed by scanning transmission electron microscopy (STEM), is shown in Figure 1b. STEM observations demonstrate the occurrence of open-cell porosity, with highly interconnected ligaments whose lateral size is typically around 5–7 nm. The overall film’s thickness is around 600 nm. Further structural analysis, performed by high-resolution transmission electron microscopy (HRTEM), reveals the occurrence of crystalline planes within the pore walls (Figure 1c). The corresponding selected area electron diffraction (SAED) patterns (Figure 1d) indicate the formation of a face-centered cubic (FCC) solid solution, similar to electrodeposited Cu–Ni dense films. X-ray diffraction (XRD) measurements (Figure 1e) corroborate that the films grow forming a FCC solid solution and they are actually textured along the (111) direction, i.e., the (200) FCC peak, expected at around $2\theta = 51° - 52°$, is not detected. Moreover, even if the Gibbs free energy of mixing between Cu and Ni is slightly positive, no phase separation into Cu-rich and Ni-rich regions takes place during electrodeposition. Compositional analyses, carried out by energy-dispersive X-ray (EDX) spectroscopy, reveal that the composition of the films is Cu$_{33}$Ni$_{67}$ (at%). The nanoporous character of the Cu–Ni films brings about a drastic increase of the S/V ratio. Indeed, simple geometrical reasoning can be used to show, for example, that the S/V ratio of a 600 nm thick porous film covering an area of $1 \times 1$ mm$^2$ and being made of an array of vertically oriented pores, with 5 nm pore diameter and 5 nm interpore distance would be about 120 times larger than the S/V ratio of a fully dense layer of 600 nm covering the same area. Interestingly, the total volume of “active material” (i.e., influenced by the action of an electric field) in the nanoporous layer case would be around 250 times larger than that of an ultrathin (2 nm thick) film.

2.2. Control of Coercivity Using Voltage

Figure 2a illustrates the experimental setup used for the magnetoelectric measurements. The formation of the electrical double layer surrounding the pore walls is depicted in Figure 2b. The sample was mounted in a home-made electrolytic cell filled with anhydrous propylene carbonate with Na$^+$ solvated species, and the magnetic properties were measured along the film plane by magneto-optic Kerr effect (MOKE), while applying different constant voltages between the sample and the counter-electrode. The use of a liquid electrolyte is very convenient to generate high electric fields. Namely, the large dielectric constant ($\varepsilon_r = 64$ for propylene carbonate) and the formation of the so-called electrical double-layer (with thickness $\leq 1$ nm) promote significant charging effects when applying moderate voltages. Representative hysteresis loops, measured at different positive voltages, from 0 to 14 V, are shown in Figure 2c. A progressive narrowing of the hysteresis loop is clearly observed as the voltage is increased. The coercivity, $H_C$, decreases from $\approx 97$ to 66 Oe, which represents a relative variation close to 32% reactions, their kinetics, and the reversibility of the process. Thus, there is clearly a technological demand for alternative approaches to manipulate magnetism with an electric field at room temperature.

Interestingly, a number of exciting experiments performed in recent years have shown the possibility to modify the magnetic properties of diluted magnetic semiconductors and some metallic elements and alloys directly with an applied electric field, via accumulation of electrostatic charges at their surface. This is very promising for the development of low-power magnetic actuators and spintronic devices. Among the magnetic effects caused by electric field one can mention: change of Curie temperature in diluted magnetic semiconductors such as (Ga,Mn)As or (In,Mn)As; changes of coercivity and reorientation of the magnetic easy axis in thin films. In semiconductors these effects are mostly observed at low temperatures and are due to electric-field induced modification of the charge carriers’ concentration. In metals, magnetoelectric phenomena are related to spin-dependent screening (i.e., electrons with different spin characters respond differently to the applied electric field) and, therefore, only occur within a few nm from the surface. This restricts the effect to ultrathin films (consisting of a few monolayers), which can be difficult to be integrated in real devices.

Given the surface origin of voltage-induced magnetic changes in metals, it is envisaged that an increase of the surface area-to-volume (S/V) ratio in nanoporous materials could trigger a significant enhancement of magnetoelectric effects, provided that the pore walls are kept sufficiently narrow. During the last few years, the advances in the synthetic pathways to produce nanoporous materials with controllable pore size and composition have boosted a wealth of applications in diverse fields such as catalysis, bioimplants, dampers, gas sensing or energy storage, where materials with a high surface area are essential. However, although many of the cutting-edge technological applications in spintronics and magnetic actuators also rely on surface or interface magnetic phenomena, the use of nanoporous materials in these technologically relevant fields has been largely overlooked, particularly for pure magnetoelectric effects, i.e., neither mediated by strain nor resulting from oxidation/reduction reactions.

In this work, we explore intrinsic magnetoelectric effects in nanoporous Cu–Ni films grown by micelle-assisted electrodeposition (Figure 1a). We demonstrate that a drastic reduction of coercivity can be obtained in the nanoporous metallic alloy (with very narrow pore walls) under the application of voltage across an electrical double layer using a nonaqueous liquid electrolyte. The nanoporous morphology of the investigated material allows for much larger accumulation of surface electric charges compared to fully dense films. Since the whole porous structure is affected by the electric field, this results in a much more pronounced voltage-induced reduction of coercivity compared to previous studies. The purely magnetoelectric effects in Cu–Ni are ascribed by ab initio calculations to changes in electronic characters respond differently to the applied electric field. In metals, magnetoelectric phenomena are related to electric-field induced modification of the charge carriers’ concentration. In diluted magnetic semiconductors such as (Ga,Mn)As or (In,Mn)As, changes of coercivity and reorientation of the magnetic easy axis in thin films. In semiconductors these effects are mostly observed at low temperatures and are due to electric-field induced modification of the charge carriers’ concentration. In metals, magnetoelectric phenomena are related to spin-dependent screening (i.e., electrons with different spin characters respond differently to the applied electric field) and, therefore, only occur within a few nm from the surface. This restricts the effect to ultrathin films (consisting of a few monolayers), which can be difficult to be integrated in real devices.
This is a remarkably larger change compared to previous works from the literature on ultrathin metallic films, reporting variations of only up to 4.5%. The loops also tend to become progressively more square-shaped as the applied voltage is increased. The corresponding variation of the remanence-to-saturation magnetization ratio, $M_R/M_S$, 

Figure 1. a) Illustration of the micelle-assisted electrodeposition procedure, where PPO and PEO denote, respectively, the poly(ethylene oxide) and poly(propylene oxide) blocks of the PluronicP-123 triblock copolymer and (i–iv) denote the different synthetic steps: (i) stirring for clear solution, (ii) addition of metal salt, (iii) coordination of dissolved metal species with the hydrophilic shell domains of the micelles, (iv) electrodeposition. b) Cross-section image of the electrodeposited nanoporous Cu–Ni films (which are about 600 nm thick), observed by scanning transmission electron microscopy (STEM)—image taken after making a slice of the film and observing it along the perpendicular to film direction (cross-section), at a depth of about 300 nm from the outer film surface. c) High-resolution transmission electron microscopy (HRTEM) image of the nanoporous Cu–Ni alloy. d) Corresponding selected area diffraction (SAED) pattern. e) X-ray diffraction (XRD) patterns of the nanoporous films before and after the magneto-electric measurements.
and the normalized differential magnetic susceptibility around the coercivity, \( \chi = \frac{(d m/dH)_H}{H_C} \) (where \( m \) denotes here the normalized Kerr amplitude signal) are shown in Figure 3b. The effects on \( H_C, M_R/M_S \), and \( \chi \) for negative voltages are significantly smaller and opposite to those observed with positive voltage (see Figure S1 in the Supporting Information). No significant variations in the Kerr signal amplitude were observed for either positive or negative applied voltages. To corroborate the crucial role played by the porosity on the observed magnetoelectric effects, the same experiments were performed on fully dense Cu–Ni films with the same composition and thickness, prepared by electrodeposition. As shown in Figure S2 (Supporting Information), the variations of \( H_C \) in that case are negligible, both for positive and negative applied voltages.

In order to rule out that oxidation/reduction reactions might govern the observed variations of \( H_C \), cyclic electrochemical voltammetry experiments were performed, both for the nanoporous and the fully dense Cu–Ni films, using the same nonaqueous electrolyte as for the magnetoelectric measurements. The results, shown in Figure S3 (Supporting Information), indicate absence of clear oxidation/reduction peaks, with current densities of the order of \( \mu A \ cm^{-2} \), varying smoothly with potential. This suggests that capacitive processes (i.e., charge accumulation), rather than faradaic ones (involving charge transfer -electrons- across the electrode–electrolyte interface), dominate during in situ magnetoelectric measurements. This is in agreement with the XRD results since no diffraction peaks corresponding to metal oxides/hydroxides were observed after the magnetoelectric measurements (see Figure 1e). Also no evidence for phase separation (i.e., occurrence of peaks from Ni-rich and Cu-rich FCC solid solutions) was encountered after the magnetoelectric measurements. Additionally, the Cu/Ni ratio of the films did not vary after the measurements, confirming that selective dissolution of either Cu or
Hence, the electrostatic charges that are accumulated at the surface (within the so-called Thomas–Fermi screening length, \( \lambda_{TF} \approx 0.5 \text{ nm} \)) can induce modifications in the electronic band structure (i.e., in the charge density of unpaired \( d \) electrons with energy close to the Fermi level\(^{13,16} \)) and, consequently, cause changes in the surface magnetization and the magnetic anisotropy energy (MAE)\(^{36,30,31} \). Magnetic effects can propagate a few nm toward the interior of the alloy, within the spin–spin correlation length, which exceeds 20 nm in many metallic systems.\(^{32} \) Given the 3D nanoporous morphology of the films, the electric field affects the nanopore walls from “all directions” (see Figure 2b). Interestingly, since the pore walls are very narrow and fully interconnected, the overall porous structure (i.e., the entire porous film) contributes to the observed voltage-induced large reduction of coercivity.

Although magnetoelectric phenomena in ultrathin Cu\(_x\)Ni\(_{1-x}\) films have been predicted theoretically (in particular, changes in the Curie temperature)\(^{32} \), this is the first experimental demonstration of such effects for this type of alloys. To get a deeper understanding of the fundamental origin of magnetoelectric effects in Cu–Ni we carried out ab initio calculations\(^{33,34} \), including spin–orbit interactions, on (111) slabs of Cu\(_{25}\)Ni\(_{75}\) (Figure 4a, b). Different configurations of randomly arranged Cu and Ni atoms were averaged in order to simulate an alloy (three examples are depicted in Figure 4a). The results show an almost linear dependence of the surface magnetic moment with the applied electric field (Figure 4c), which can be quantified as

\[
\mu \Delta M = \alpha_s E
\]

where \( \Delta M \) is the surface magnetization, \( E \) is the applied electric field, and \( \alpha_s \) is the so-called surface magnetoelectric coefficient.

To further confirm that oxidation/reduction processes are not responsible for the observed trends in magnetic properties, hysteresis loops were also acquired while applying voltage using an aqueous electrolyte (0.1 M \( \text{NaOH} \) solution). In this case, oxidation indeed takes place upon application of a positive potential, as evidenced by cyclic voltammetry (Figure S4a, Supporting Information), where relatively high current densities (\( \approx 1 \text{ mA cm}^{-2} \)) are attained for \( V > \pm 1 \text{ V} \). However, in spite of the oxidation, the changes in \( H_C \) were always <6% and actually \( H_C \) slightly increased (not decreased) after partial oxidation (Figure S4b, Supporting Information).

### 2.3. Ab Initio Calculations

The fundamental physical origin of intrinsic magnetoelectric effects in metallic alloys remains still not fully understood. However, in metals, electric fields are screened very effectively and such screening is known to be spin-dependent due to exchange interactions\(^{16} \). Hence, the electrostatic charges that are accumulated at the surface (within the so-called Thomas–Fermi screening length, \( \lambda_{TF} \approx 0.5 \text{ nm} \)) can induce modifications in the electronic band structure (i.e., in the charge density of unpaired \( d \) electrons with energy close to the Fermi level\(^{13,16} \)) and, consequently, cause changes in the surface magnetization and the magnetic anisotropy energy (MAE)\(^{36,30,31} \). Magnetic effects can propagate a few nm toward the interior of the alloy, within the spin–spin correlation length, which exceeds 20 nm in many metallic systems.\(^{32} \) Given the 3D nanoporous morphology of the films, the electric field affects the nanopore walls from “all directions” (see Figure 2b). Interestingly, since the pore walls are very narrow and fully interconnected, the overall porous structure (i.e., the entire porous film) contributes to the observed voltage-induced large reduction of coercivity.

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where \( \Delta M \) is the surface magnetization, \( E \) is the applied electric field, and \( \alpha_s \) is the so-called surface magnetoelectric coefficient. Note that \( E \) of the order of 1 V Å\(^{-1} \) indeed corresponds to the values obtained from voltages around 10 V (as in our experiments), assuming that the electrical double layer is \( \approx 1 \text{ nm} \) thick.\(^{29} \) Fitting the data in Figure 4c, we obtain that \( \alpha_s = 3.6 \times 10^{-14} \text{ G cm}^2 \text{ V}^{-1} \) when the magnetic moment is in-plane, and \( \alpha_s = 3.0 \times 10^{-14} \text{ G cm}^2 \text{ V}^{-1} \) when the magnetic moment is pointing out-of-plane. These values are of the same order of magnitude as the ones calculated for a pure Fe(001) film.\(^{39} \) Similar trends are obtained considering the (001) plane (see Figure S5 in the Supporting Information). The applied electric field also induces changes in the density of states (Figure S6, Supporting Information) and an increase of the change of the surface orbital moment \( m_\text{L} \) (Figure 4d), which can be related to an increase of the MAE using Bruno’s relation\(^{35} \)

\[
\text{MAE} \propto \Delta m_\text{L}
\]

The changes in total and orbital magnetic moments shown in Figure 4 are confined to the surface atoms. Overall, the effect would be negligible, as shown in Figure S2 (Supporting Information) for a fully dense film. The use of a nanoporous material allows enhancing the effect to make it measurable. Changes in MAE are generally correlated with variations in \( H_C, M_B/M_S, \) and \( \chi \) (i.e., the overall shape and width of the loop)\(^{13,16} \). However, in our case, due to the complex morphology of mesoporous Cu–Ni films, the correlation between MAE, \( H_C \), and \( \chi \) is not straightforward. An increase of positive MAE indicates an enhancement of perpendicular magnetocrystalline anisotropy per Ni atom. Magnetocrystalline anisotropy
competes with the shape anisotropy (which promotes magnetic easy axis along the nanopores ligaments directions, which are randomly distributed). Such competing anisotropies make the correlation between $H_C$ and MAE rather complex. Nonetheless, the variation of $H_C$ and $\chi$ with the electric field can be considered consistent with changes in the calculated MAE of the system.

3. Conclusions

In conclusion, our work demonstrates that the coercivity of nanoporous Cu–Ni thick films can be drastically decreased by simply applying an electric field. The large surface-area-to-volume ratio and the ultranarrow pore walls of the system play a crucial role in the discovered effect. Such electrically driven modification of magnetic properties is very appealing for energy-efficient magnetic actuation. Indeed, a reduction in coercivity implies that lower currents are needed to switch the magnetization of the system (either when using an electromagnet or in spin-torque devices), hence considerably reducing energy loss in the form of heat dissipation (Joule effect). The voltage-induced decrease of coercivity could also be used as an alternative to thermally assisted magnetic writing in magnetic recording applications, since the latter is less energetically effective. Thus, the results from this work will likely expand the already wide range of applications of nanoporous materials (so far, mainly in chemistry), to areas like magnetically actuated micro-electromechanical systems, magnetic recording or spintronics, where their potential has been hitherto largely overlooked.

4. Experimental Section

Nanoporous Cu–Ni Film Growth: The electrodeposition of nanoporous Cu–Ni films was performed in a thermostatted three-electrode cell using a PGSTAT302N Autolab potentiostat/galvanostat (Ecochemie). Contrary to other more sophisticated methods, here the nanoporosity is induced during single-step micelle-assisted electrodeposition (see Figure 1a), a
procedure which has been used in recent years for the growth of only very few types of nanoporous layers, i.e., Pt-based alloys[36–38] and Cu[39] but not magnetic alloys. Together with the lyotropic liquid crystals, this synthetic approach can be categorized as a soft templating method. Above the “critical micellar concentration” (c.m.c.) (e.g., 0.004 wt% for Pt123 at room temperature[40]), the micelles start to spontaneously form in the aqueous solution, get progressively in contact and tend to self-assemble at the solid–liquid interface, interfering and guiding the electrodeposition process, leading to the growth of mesoporous metallic films (see Figure 1a). Si/SiO2 chips coated with Ti (10 nm)/Au (90 nm) adhesion/seed layers were used as cathodes (0.23 cm² working area), a platinum spiral served as counter electrode and a double junction Ag/AgCl (E = 0.210 V/SHE) with 3 M KCl inner solution and 1 M NaSO4 outer solution was employed as the reference electrode (Metrohm AG). The pH was left as-prepared (pH = 6.0). Electrodeposition was carried out galvanostatically at 25 °C, at a current density (j) of ~80 mA cm⁻², during 120 s, under mild agitation (200 rpm) to favor mass transport of the electroactive species toward the cathode. N₂ was bubbled through the solution to get rid of oxygen before each deposition. The electrodeposited films (600 nm thick) were rinsed with Milli-Q water and ultrasonicated in ethanol for 5 min to remove remaining micelles from the growth process.

**Fully Dense Cu–Ni Film Growth:** The electrodeposition of fully dense Cu–Ni films is described elsewhere.[27]

**Magnetoelectric Measurements:** Hysteresis loops at different DC voltage values were measured at room temperature, along the film plane, in a MOKE setup from Durham Magneto-Optics (see Figure 2a). An external Agilent B2902A power supply was employed to generate voltage. The sample was mounted vertically in a quartz SUPRASIL cell of states for spin up minus the density of states for spin down projected in the direction of the magnetization.

**Supporting Information**

Supporting Information is available from the Wiley Online Library or from the author.

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**Conflict of Interest**

The authors declare no conflict of interest.

**Keywords**

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[1] I. Zútic, J. Fabian, S. D. Sarma, Rev. Mod. Phys. 2004, 76, 323.
[2] C. Chappert, A. Fert, F. N. Van Dau, Nat. Mater. 2007, 6, 813.
[3] J.-M. Hu, Z. Li, L.-Q. Chen, C.-W. Nan, Nat. Commun. 2011, 2, 553.
