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(54) Title: A METHOD FOR TUNING THE MAGNETIC COERCIVITY OF A NANOPOROUS FILM, A DEVICE AND USES THEREOF

(57) Abstract: The present invention relates to a method for tuning the magnetic coercivity of a nanoporous film, a device and uses thereof. The method comprises: - providing a thick nanoporous film having a thickness above 10 nm and an average nanopore wall thickness, at least regarding the interstitial separation between nanopores measured along at least one plane, which is below 15 nm; and - subjecting said thick nanoporous film to an electric field to vary its magnetic coercivity by voltage-inducing changes in the magnetic anisotropy thereof. The device comprises a thick nanoporous film and a voltage source to vary the magnetic coercivity of the thick nanoporous film by voltage-inducing changes in the magnetic anisotropy thereof, according to the method of the present invention. The invention also comprises the use of the device of the invention as a component of a magnetic device actuated with voltage.



A METHOD FOR TUNING THE MAGNETIC COERCIVITY OF A NANOPOROUS FILM, A DEVICE AND USES THEREOF

FIELD OF THE INVENTION

5 The present invention relates, in a first aspect, to a method for tuning the magnetic coercivity of a thick nanoporous film, by voltage-inducing changes in the magnetic anisotropy thereof.

 A second aspect of the present invention relates to a device comprising a thick nanoporous film and a voltage source to vary the magnetic coercivity of the thick
10 nanoporous film by voltage-inducing changes in the magnetic anisotropy thereof, according to the method of the first aspect of the present invention.

 A third aspect of the present invention relates to different uses of the device of the second aspect of the present invention.

15 BACKGROUND OF THE INVENTION

 The coercivity is a parameter of paramount importance in magnetic materials. Either a decrease or an increase of coercivity can be desirable depending on the target application:

 (i) A decrease of coercivity enhances the energy efficiency in writing information
20 in magnetic recording media and other applications based on magnetic actuation. Indeed, 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.
25 This can be accomplished by reducing the coercivity of the actuated material.

 (ii) Conversely, the strength of permanent magnetic materials (e.g., CoPt magnets) is proportional to the maximum energy product, which in turn depends on coercivity. In this case, a larger coercivity improves the quality of a permanent magnet.

 Coercivity is generally controlled by varying the composition of the magnetic
30 material or its microstructure (grain size, crystallographic defects, microstrains, etc.). For a given sample, coercivity can be modified by thermal treatments (since the magnetocrystalline anisotropy depends on temperature). This has led to the concept of "thermally-assisted writing". Generation of heat, however, is not energetically cost-effective. Alternatively, coercivity might be modified by applying voltage.

35 Several approaches to tailor magnetism by means of an electric field have been proposed so far: (i) strain-mediated magnetoelectric coupling in piezoelectric-

magnetostrictive composite materials [Wang, Y., Hu, J., Lin, Y. & Nan, C.W. Multiferroic magnetoelectric composite nanostructures. *NPG Asia Mater.* 2, 61–68 (2010)], (ii) multiferroic materials in which the ferroelectric and ferromagnetic order parameters are coupled to each other [Ramesh, R. & Spaldin, N. A. Multiferroics: progress and prospects in thin films, *Nat. Mater.* 6, 21–29 (2007)] and (iii) electric-field induced oxidation-reduction transitions (magneto-ionics) [Bauer, U. et al. Magneto-ionic control of interfacial magnetism. *Nat. Mater.* 14, 174–181 (2015); Gilbert, D. A. et al. Structural and magnetic depth profiles of magneto-ionic heterostructures beyond the interface limit. *Nat. Commun.* 7, 12264 (2016)]. However, each of these approaches faces some drawbacks: (i) clamping effects with the substrate, need of epitaxial interfaces and risk of fatigue-induced mechanical failure, (ii) the dearth of available multiferroic materials and the reduced strength of magnetoelectric coupling, even at low temperatures and (iii) precise control of the chemical 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, preferably 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 [Chiba, D. et al. Magnetization vector manipulation by electric fields, *Nature* 455, 515–518 (2008)] and some metallic elements and alloys [Weisheit, M. et al., Electric field-induced modification of magnetism in thin-film ferromagnets. *Science* 315, 349–351 (2007); Brovko, O. O., Ruiz-Díaz, P., Dasa, T. R. & Stepanyuk, V. S. Controlling magnetism on metal surfaces with non-magnetic means: electric fields and surface charging. *J. Phys.: Condens. Matter* 26, 093001 (2014)] 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 [Ohno, H. et al. Electric-field control of ferromagnetism. *Nature* 408, 944–946 (2000)]; changes of coercivity and, in some cases, reorientation of the magnetic easy axis in thin films [Bonell, F. et al. Large change in perpendicular magnetic anisotropy induced by an electric field in FePd ultrathin films. *Appl. Phys. Lett.* 98, 232510 (2011)]. 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 [Brovko, O. O., Ruiz-Díaz, P., Dasa, T. R. & Stepanyuk, V. S. Controlling magnetism on metal surfaces with non-magnetic means:

electric fields and surface charging. J. Phys.: Condens. Matter 26, 093001 (2014)] and, therefore, only occur within a few nm from the surface. This restricts the effect to nanoparticles (often superparamagnetic at room temperature) or ultra-thin films (consisting of a few monolayers), both difficult to be integrated in real devices.

5 On the other hand, 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
10 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 [Quickel, T. E. et al. Mesoporous bismuth ferrite with amplified magnetoelectric coupling and electric field-induced ferrimagnetism. Nat. Commun. 6, 6562 (2015); Gosh, S. Charge-response of magnetization in nanoporous Pd–Ni alloys. J.
15 Magn. Mater. 323, 552–556 (2011)], particularly for pure magnetoelectric effects, i.e., neither mediated by strain nor resulting from oxidation/reduction reactions.

It is, therefore, necessary to provide an alternative to the state-of-the-art which covers the gaps found therein, by providing a method for tuning the magnetic coercivity of a nanoporous film which clearly improves the ones known in the art, which is not
20 restricted to nanoparticles or ultra-thin films, and which is not based on magnetoelectric effects mediated by strain nor resulting from oxidation/reduction reactions.

SUMMARY OF THE INVENTION

To that end, the present invention relates, in a first aspect, to a method for tuning
25 the magnetic coercivity of a nanoporous film, wherein said nanoporous film is made of a metal, of a metallic alloy, or of a semiconductor material, comprising:

- providing a thick nanoporous film having a thickness above 10 nm and an average nanopore wall thickness, at least regarding the interstitial separation between nanopores measured along at least one plane, which is below 15 nm; and
- 30 - subjecting said thick nanoporous film to an electric field to vary its magnetic coercivity by voltage-inducing changes in the magnetic anisotropy thereof.

According to the method of the first aspect of the present invention, either an increase or a decrease of the coercivity can be provided to the nanoporous film due to corresponding voltage-induced changes in the magnetic anisotropy thereof, which can
35 either increase or decrease upon accumulation of surface electrostatic charges.

For a preferred embodiment, the method of the first aspect of the present invention comprises providing the thick nanoporous film with a three-dimensional isotropic porosity, wherein said average nanopore wall thickness refers to the interstitial separation between nanopores measured along three orthogonal planes.

5 For different embodiments, said thick nanoporous film has a thickness above one of 20 nm, 100 nm, 200 nm, 300 nm, 400 nm, and 500 nm.

For an embodiment, the thick nanoporous film has an average nanopore wall, at least regarding the interstitial separation between nanopores measured along at least one plane, which is below 10 nm.

10 Given the surface origin of voltage-induced magnetic changes in metals, metal alloys or semiconductors, the large surface-area-to-volume ratio and the ultra-narrow pore walls of the provided thick nanoporous film allow the whole film, and not only the topmost surface, to effectively contribute to the observed magnetoelectric effect. This overcomes the stringent 'ultrathin-film requirement' from previous studies, where small voltage-driven
15 coercivity variations were reported.

For an embodiment of the method of the first aspect of the present invention, the nanoporous film is made of a single metal which is a ferromagnetic metal, such as Ni, Co, Fe or other ferromagnetic alloys (e.g., containing Ni, Co or Fe in their compositions).

According to an embodiment of the method of the first aspect of the present
20 invention, the nanoporous film is made of a metallic alloy, wherein at least one of the constituent elements of the metallic alloy is a ferromagnetic metal, such as Ni, Co, or Fe.

For a preferred implementation of said embodiment, the metallic alloy is a metallic binary alloy in which at least one of the two constituent elements is said ferromagnetic metal and the other is a noble metal, such as Cu or Pt.

25 According to different embodiments, the metallic binary alloy is a Cu-Ni alloy, a Co-Pt alloy, or a Fe-Pt alloy.

The method of the first aspect of the present invention comprises, for an embodiment, performing the above mentioned subsection of the thick nanoporous film to an electric field, by introducing the thick nanoporous film into a non-aqueous liquid
30 electrolyte, and applying voltage thereto to build up an electrical double layer around the nanopore walls.

For an alternative embodiment, the method of the first aspect of the present invention comprises filling the nanopores with a dielectric material, and performing the subsection of the thick nanoporous film to an electric field. If the dielectric is a ferroelectric
35 material, by applying a voltage between said ferroelectric material and the thick nanoporous film (according to the method of the present invention), the variation of the

magnetic coercivity of the thick nanoporous film is maintained by the electrical charges stored in the ferroelectric material.

In general, the method of the first aspect of the present invention comprises performing the subjection of the thick nanoporous film to an electric field at room temperature, although alternative embodiments for performing said step at other
5 temperature values are also embraced by the present invention.

A second aspect of the present invention relates to a device, comprising:

- a thick nanoporous film made of a metal, of a metallic alloy, or of a semiconductor material, wherein said thick nanoporous film has a thickness above 10 nm and an average
10 nanopore wall thickness, at least regarding the interstitial separation between nanopores measured along at least one plane, which is below 15 nm; and

- a voltage source configured and arranged to subject said thick nanoporous film to an electric field to vary its magnetic coercivity by voltage-inducing changes in the magnetic anisotropy thereof, according to the method of any of the previous claims.

15 For different embodiments, said thick nanoporous film has a thickness above one of 20 nm, 100 nm, 200 nm, 300 nm, 400 nm, and 500 nm.

For an embodiment, the thick nanoporous film has an average nanopore wall, at least regarding the interstitial separation between nanopores measured along at least one plane, which is below 10 nm.

20 An electrodeposition method for making magnetic-electrocatalytic, pseudo-ordered mesoporous alloy films, and several preparation and synthesis examples, are disclosed in Patent application GB1607416. The contents of said patent application regarding said method and examples are incorporated herein by reference, to describe corresponding embodiments for carrying out the step of providing a thick nanoporous film
25 of the method of the first aspect of the invention, and the manufacturing of the thick nanoporous film of the device of the second aspect of the invention, for which the film is a magnetic-electrocatalytic, pseudo-ordered mesoporous metallic binary alloy film.

The present invention is applied to the provision not only of mesoporous films but also of microporous and macroporous films, for different embodiments. The method
30 described in GB1607416, or slight variations thereof, can also be used for the manufacturing of said micro- and macro-porous films.

A third aspect of the present invention relates to the use of the device of the second aspect as a component of a magnetic device.

For another embodiment of the third aspect of the present invention, the magnetic
35 device includes magnetic recording media, spin valves, tunnel junctions, magnetic

sensors, spintronic devices, magneto-electric devices, computation devices, or magnetic actuators.

BRIEF DESCRIPTION OF THE FIGURES

5 In the following some preferred embodiments of the invention will be described with reference to the enclosed figures. They are provided only for illustration purposes without however limiting the scope of the invention.

Figure 1: This Figure illustrates the production of the thick nanoporous film according to an embodiment of the method of the first aspect of the invention for which said production is carried out by electrodeposition. (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 Pluronic®P-123 tri-block co-polymer 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, observed by scanning transmission electron microscopy (STEM) –image taken from the middle depth of the films. (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 magnetoelectric measurements. Note that the scale bars in (b), 10 15 20 (c) and (d) are 25 nm, 5 nm and 5 nm⁻¹, respectively.

Figure 2: (a) Schematic illustration of the experimental setup used for the step of subjecting to an electric field the thick nanoporous film produced as described according to Figure 1, and also for performing magnetoelectric measurements. (b) Representation 25 of the formation of the electrical double layer around the pore walls during the electric field application and the magnetoelectric measurements. (c) Representative hysteresis loops of the nanoporous Cu-Ni films acquired under application of different voltage values.

Figure 3: (a) Dependence of the coercivity, H_C , on the applied positive voltage for nanoporous Cu-Ni films. (b) Dependence of the susceptibility around the coercivity (see 30 definition in the text), χ , and the remanence-to-saturation magnetization ratio, M_R/M_S , as a function of voltage. Note that the lines are guides to the eye.

Figure 4: (a) Representative hysteresis loops of the nanoporous Cu-Ni films acquired under 25 application of different negative voltage values. (b) Dependence of the coercivity, H_C , on the negative applied voltage. (c) Dependence of the susceptibility 35 around coercivity (see definition in the text), χ , and the remanence-to-saturation

magnetization ratio, M_R/M_S , as a function of negative voltage. Note that the lines in (b) and (c) are guides to the eye.

Figure 5: Dependence of the coercivity, H_C , on the applied voltage (both for negative and positive values), for the fully-dense and nanoporous Cu-Ni electrodeposited films with the same composition ($\text{Ni}_{75}\text{Cu}_{25}$ at.%) and thickness (600 nm). Note that the most pronounced changes occur for the nanoporous alloy, due to the large surface-area-to-volume ratio.

Figure 6: Cyclic voltammetry curves, measured while immersing the Cu-Ni films in the anhydrous electrolyte (propylene carbonate), for both nanoporous and fully-dense films. No evidence for oxidation/reduction was observed.

Figure 7: (a) Cyclic voltammetry curves from the nanoporous Cu-Ni films acquired while immersing the films in the aqueous electrolyte (0.1M NaOH). (b) Dependence of the coercivity, H_C , on the applied voltage when using the aqueous electrolyte. The line in (b) is a 5 guide to the eye. The changes in coercivity are smaller than in the case of anhydrous electrolyte, revealing that oxidation is not the main cause of the observed magneto-electric effects.

Figure 8: Representative morphology of the surface of nanoporous Co-Pt films observed by high-resolution scanning electron microscopy (SEM). Panels (a) and (b) correspond to samples with different at.% Pt content.

Figure 9: Representative hysteresis loops of the nanoporous Co-Pt films acquired under application of different positive voltage values using the aforementioned anhydrous electrolyte.

Figure 10: Dependence of the coercivity, H_C , on the applied positive voltage for the nanoporous Co-Pt films immersed in the non-aqueous electrolyte.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

The intrinsic magnetoelectric effects in nanoporous Cu-Ni and Co-Pt films grown by micelle-assisted electrodeposition are investigated. It is demonstrated that a drastic reduction/increase of coercivity can be obtained in the nanoporous metallic alloys (with very narrow pore walls) under the application of voltage across an electrical double layer using a non-aqueous liquid electrolyte, according to an embodiment of the method of the first aspect of the present invention. 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 are ascribed by ab-initio calculations to

changes in the magnetic anisotropy energy stemming from electric field-induced spin-dependent modifications of the magnetic density of states at the surface.

Hereinafter, the main results from the present invention are described in detail. The typical morphology of the cross-section of the electrodeposited Cu-Ni films, observed by scanning transmission electron microscopy (STEM), is shown in Fig. 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 (Fig. 1c). The corresponding selected area electron diffraction (SAED) patterns (Fig. 1d) indicate the formation of a face-centered cubic (FCC) solid solution, as it corresponds to electrodeposited Cu-Ni. X-ray diffraction (XRD) measurements (Fig. 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 $2\theta = 51\text{-}52^\circ$, is not detected. Moreover, 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 $\text{Cu}_{25}\text{Ni}_{75}$ (at. %). The nanoporous character of the Cu-Ni films brings about a drastic increase of the surface area-to-volume ratio (S/V). 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 $1 \times 1 \text{ mm}^2$ 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 ultra-thin (2 nm thick) film and about 10^{12} times larger than the volume of a single nanoparticle with a diameter of 10 nm.

Figure 2a illustrates the experimental setup used for the step of subjecting to an electric field the thick nanoporous film produced as described according to Figure 1 (DC power source and corresponding electrode and counter-electrode), and also for performing the magnetoelectric measurements (laser, optical detector, and electromagnets). The formation of the electrical double layer surrounding the pore walls is depicted in Fig. 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, i.e. the thick nanoporous film electrodeposited on a conductive substrate acting as an electrode (connected to the

positive terminal of the illustrated DC voltage source), and the counter-electrode (depicted conductive plate connected to the negative terminal of the illustrated DC voltage source). The use of a liquid electrolyte is very convenient to generate high electric fields. Namely, the large dielectric constant ($\epsilon_r = 64$ for propylene carbonate) and the formation of the so-called electrical double-layer (with thickness ~ 1 nm) promote significant charging effects when applying moderate voltages. Representative hysteresis loops, measured at different positive voltages, from 0 V to 14 V, are shown in Fig. 2c. A progressive narrowing of the hysteresis loop is clearly observed as the voltage is increased. The coercivity, H_C , decreases from approximately 97 Oe to 66 Oe, which represents a relative variation close to 32% (see Fig. 3a). This is a remarkably larger change compared to previous works from the literature on ultra-thin 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 , and the normalized differential magnetic susceptibility around the coercivity, $\chi = (dm/dH)_{H=H_C}$ (where m denotes here the normalized Kerr amplitude signal) are shown in Fig. 3b. The effects on H_C , M_R/M_S and χ for negative voltages are significantly smaller and opposite to those observed with positive voltage (see Fig. 4). 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 Fig. 5, 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 non-aqueous electrolyte as for the magnetoelectric measurements. The results, shown in Fig. 6, indicate absence of clear oxidation/reduction peaks, with current densities of the order of $\mu\text{A}\cdot\text{cm}^{-2}$, varying smoothly with potential. This suggests that capacitive processes, rather than faradaic ones, dominate during in-situ magnetoelectric measurements. Remarkably, no peaks attributed to metal oxides or phase separation were observed by XRD after the magnetoelectric measurements (see Fig. 1e). Additionally, the Cu/Ni ratio of the films did not vary after the measurements, confirming that no partial dissolution of the Cu-Ni porous film took place during the voltage application.

To further confirm that, in contrast to prior art proposals, in the method of the first aspect of the present invention 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 NaOH solution). In this case, oxidation indeed takes place upon application of a positive potential, as evidenced by cyclic voltammetry (Fig. 7a), where relatively high current densities ($\sim \text{mA}\cdot\text{cm}^{-2}$) are attained for $V > \pm 1\text{V}$. However, in spite of oxidation, the changes in H_C were always $< 6\%$ and actually H_C slightly increased (not decreased) after partial oxidation (Fig. 7b).

Concerning the Co-Pt system, Figure 8 shows a representative on-top SEM images of two different Co-Pt nanoporous films, with different Pt content, i.e., approximately 50 at.% Pt in panel (a) and 80 at.% Pt in panel (b). Application of voltage in this system was done in the same way as for Cu-Ni, i.e., by means of an electrical double-layer formed when the film was immersed in the non-aqueous electrolyte. Representative hysteresis loops for different values of the applied voltage are shown in Figure 9. The dependence of the coercivity on voltage for this system is shown in Figure 10. Remarkably, in this case the trends in coercivity are opposite to those observed for the nanoporous Cu-Ni films. That is, application of a positive voltage increases (and not decreases) the value of coercivity. Similar experiments as those performed for Cu-Ni rule out that the effect is due to oxidation of the nanoporous Co-Pt layers.

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. Hence, the electrostatic charges that are accumulated at the surface (within the so-called Thomas-Fermi screening length, $\lambda_{\text{TF}} \sim 0.5 \text{ nm}$) 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) and, consequently, cause changes in the surface magnetization and the magnetic anisotropy energy (MAE). Magnetic effects can propagate a few nm towards the interior of the alloy, within the spin-spin correlation length, which exceeds 20 nm in many metallic systems. Given the 3D nanoporous morphology of the films, the electric field affects the nanopore walls from “all directions” (see Fig. 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 ultra-thin $\text{Cu}_{1-x}\text{Ni}_x$ films have been predicted theoretically (in particular, changes in the Curie temperature [Ovchinnikov, I. V. & Wang, K. L. Theory of electric-field-controlled surface ferromagnetic transition in metals. Phys. Rev. B 79, 020402 (2009)]), 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 ab-initio calculations were carried out. Different

configurations of randomly arranged Cu and Ni atoms were averaged in order to simulate an alloy. The results show an almost linear dependence of the surface magnetic moment with the applied electric field, which can be quantified as:

$$\mu_0 \Delta M = \alpha_s E, \quad (1)$$

- 5 where ΔM is the surface magnetization, E the applied electric field and α_s is the so-called surface magnetoelectric coefficient. Note that E of the order of $1 \text{ V} \cdot \text{\AA}^{-1}$ indeed corresponds to the values obtained from voltages around 10 V (as in the herein disclosed experiments), assuming that the electrical double layer is approximately 1 nm thick. The applied electric field also induces changes in the density of states and an increase of the change of the
10 surface orbital moment m_L , which can be related to an increase of the MAE using Bruno's relation [Bruno, P. Tight-binding approach to the orbital magnetic moment and magnetocrystalline anisotropy of transition-metal monolayers. Phys. Rev. B 39, 865–868 (1989).]:

$$\text{MAE} \propto \Delta m_L. \quad (2)$$

- 15 The changes in total and orbital magnetic moments are confined to the surface atoms. Overall, the effect would be negligible, as shown in Fig. 5 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_R/M_S and χ (i.e., the overall shape and width of the loop). However, in the case of the present invention,
20 due to the complex morphology of mesoporous Cu-Ni films, the correlation between MAE, H_C and χ 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
25 competing anisotropies make the correlation between H_C and MAE rather complex. Nonetheless, the variation of H_C and χ with the electric field can be considered consistent with changes in the calculated MAE of the system.

- Ab-initio calculations on Pt-based hard magnetic alloys (e.g., CoPt) have been reported in the literature [Manchanda, P. et al., Magneto-electric control of surface
30 anisotropy and nucleation modes in L10-CoPt Thin Films. IEEE Magn. Lett. 5, 2500104 (2014)]. The effect of voltage on the magnetic anisotropy is indeed opposite to the one observed for Cu-Ni, thus in agreement with the experimental observations herein disclosed.

- A person skilled in the art could introduce changes and modifications in the
35 embodiments described without departing from the scope of the invention as it is defined in the attached claims.

Claims

1.- A method for tuning the magnetic coercivity of a nanoporous film, wherein said nanoporous film is made of a metal, of a metallic alloy, or of a semiconductor material,
5 comprising:

- providing a thick nanoporous film having a thickness above 10 nm and an average nanopore wall thickness, at least regarding the interstitial separation between nanopores measured along at least one plane, which is below 15 nm; and
- subjecting said thick nanoporous film to an electric field to vary its magnetic
10 coercivity by voltage-inducing changes in the magnetic anisotropy thereof.

2.- The method according to claim 1, wherein said nanoporous film is made of a metallic alloy, wherein at least one of the constituent elements of the metallic alloy is a ferromagnetic metal.
15

3.- The method according to claim 2, wherein said metallic alloy is a metallic binary alloy in which at least one of the two constituent elements is said ferromagnetic metal and the other is a noble metal.

20 4.- The method according to any of the previous claims, comprising performing said subsection of the thick nanoporous film to an electric field, by introducing the thick nanoporous film into a non-aqueous liquid electrolyte, and applying voltage thereto to build up an electrical double layer around the nanopore walls.

25 5.- The method according to any of claims 1 to 3, comprising filling the nanopores with a dielectric material, and performing said subsection of the thick nanoporous film to an electric field.

30 6.- The method according to claim 5, wherein said dielectric material is also a ferroelectric material, the method comprising performing said subsection of the thick nanoporous film to an electric field by applying a voltage between said ferroelectric dielectric material and the thick nanoporous film, so that the variation of the magnetic coercivity of the thick nanoporous film is maintained by the electrical charges stored in said ferroelectric material.

7.- The method according to any of the previous claims, comprising performing said subjection of the thick nanoporous film to an electric field at room temperature.

5 8.- The method according to any of the previous claims, comprising providing said thick nanoporous film with a three-dimensional isotropic porosity, wherein said average nanopore wall thickness refers to the interstitial separation between nanopores measured along three orthogonal planes.

10 9.- The method according to any of claims 2 to 8, wherein said ferromagnetic metal is selected from Ni, Co, and Fe.

10.- The method according to claim 3 or to any of claims 4 to 9 when depending on claim 3, wherein said noble metal is selected from Cu and Pt.

15 11.- The method according to claim 10, wherein said metallic binary alloy is a Cu-Ni alloy, a Co-Pt alloy, or a Fe-Pt alloy.

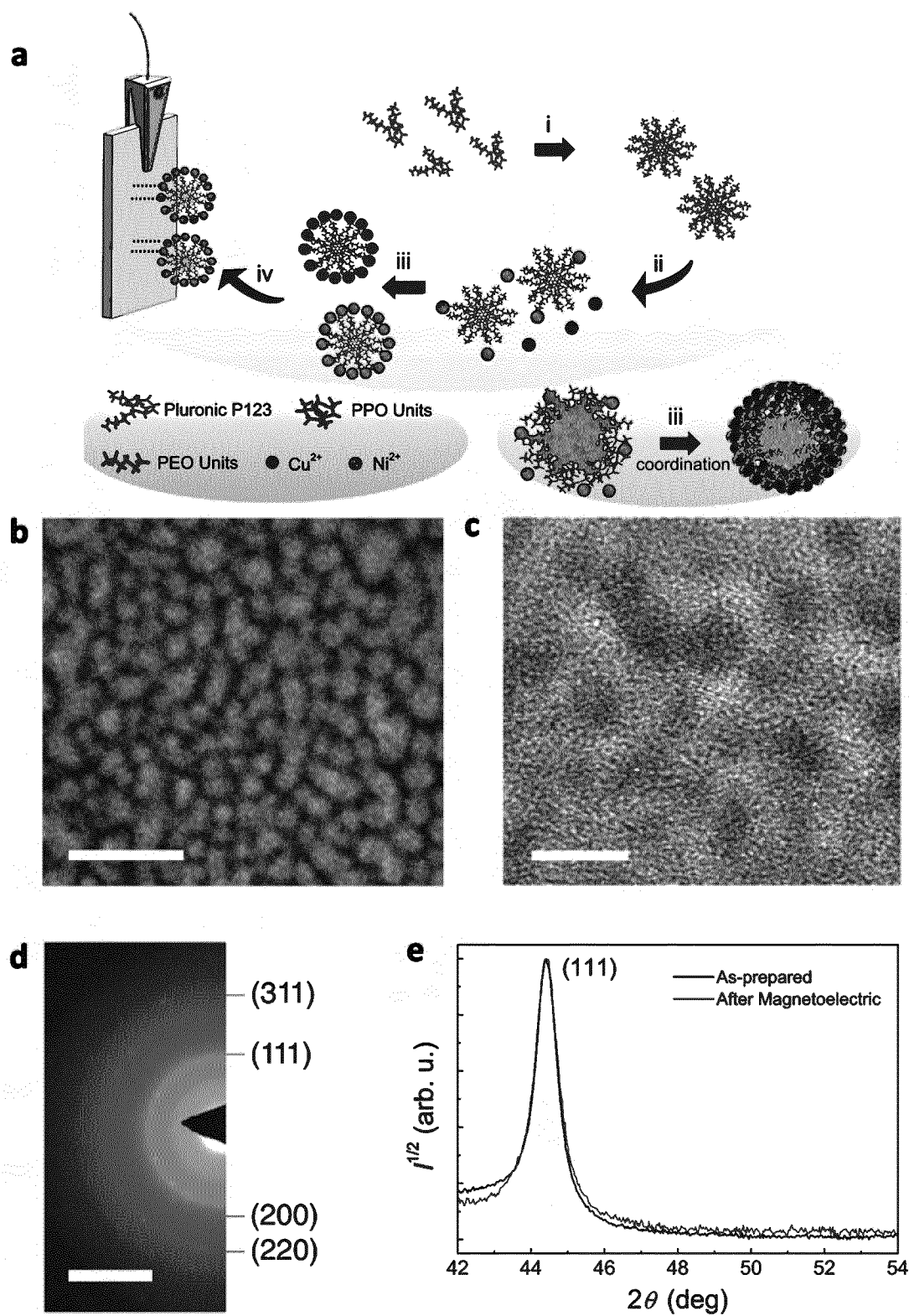
12.- A device, comprising:

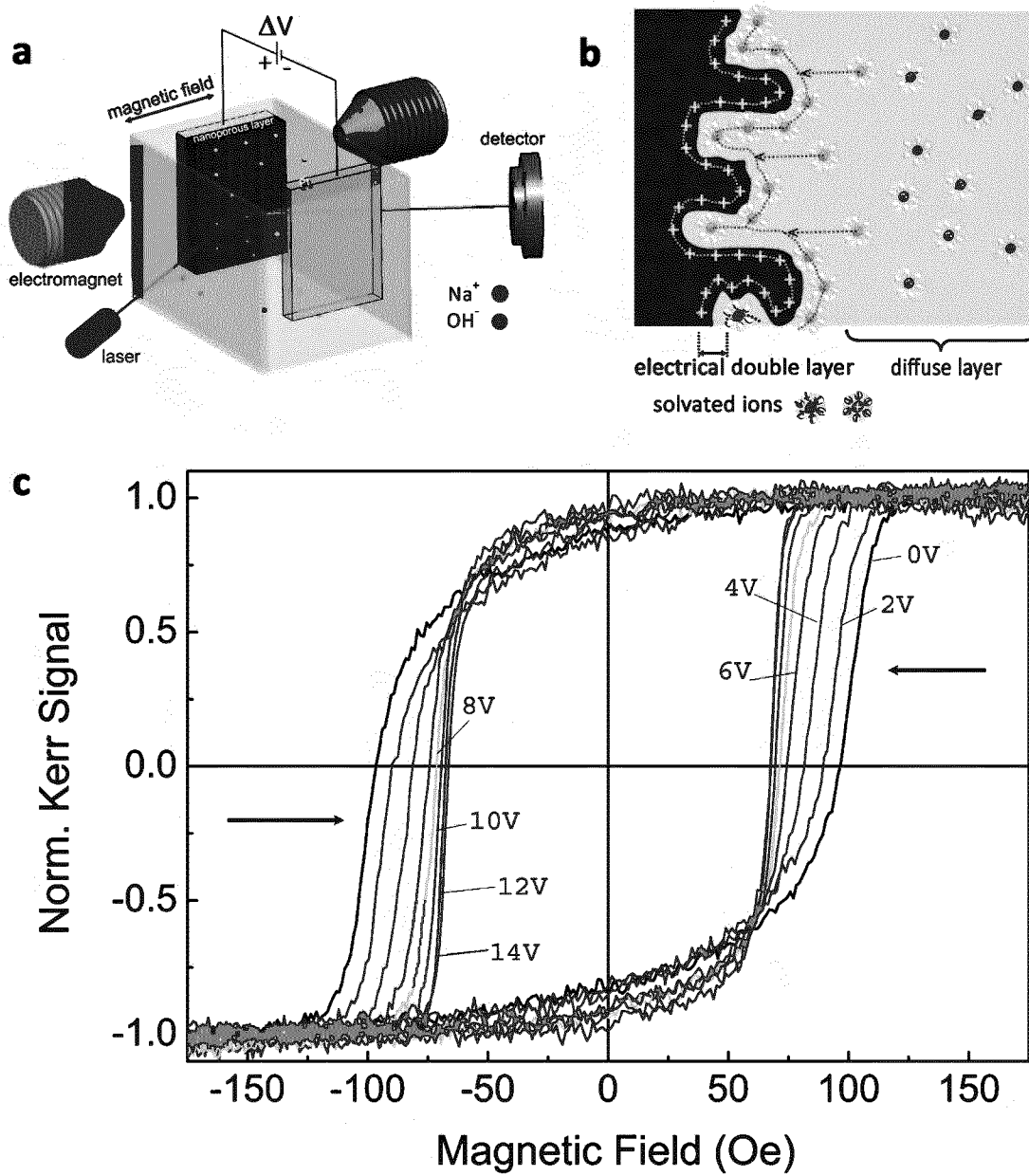
20 - a thick nanoporous film, wherein said nanoporous film is made of a metal, of a metallic alloy, or of a semiconductor material, wherein said thick nanoporous film has a thickness above 10 nm and an average nanopore wall thickness, at least regarding the interstitial separation between nanopores measured along at least one plane, which is below 15 nm; and

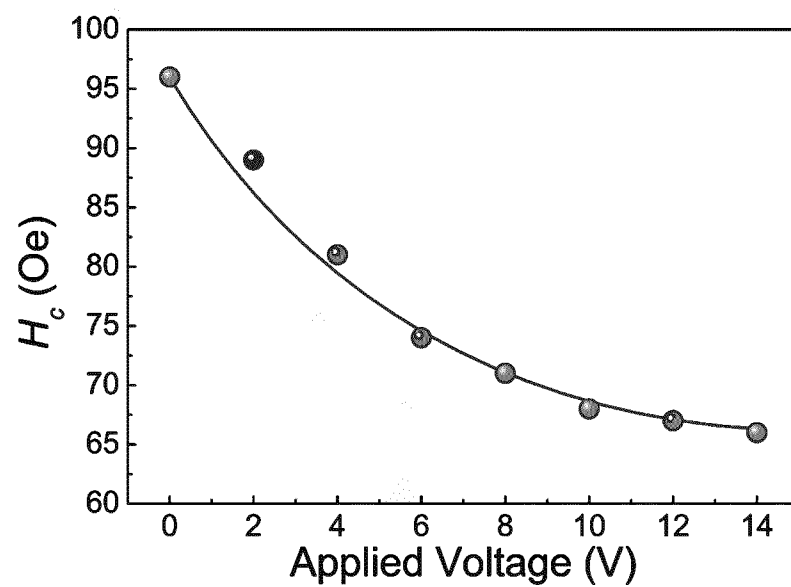
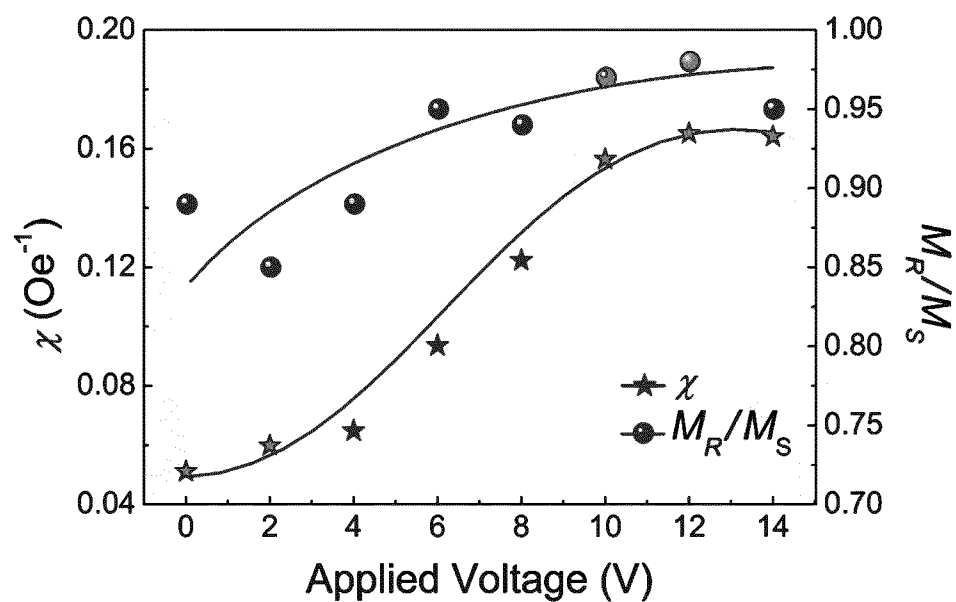
25 - a voltage source configured and arranged to subject said thick nanoporous film to an electric field to vary its magnetic coercivity by voltage-inducing changes in the magnetic anisotropy thereof, according to the method of any of the previous claims.

13.- Use of the device according to claim 12, as a component of a magnetic device.

30 14.- Use according to claim 13, wherein the magnetic device includes magnetic recording media, spin valves, tunnel junctions, magnetic sensors, spintronic devices, magneto-electric devices, computation devices, or magnetic actuators.

**Figure 1**

**Figure 2**

a**b****Figure 3**

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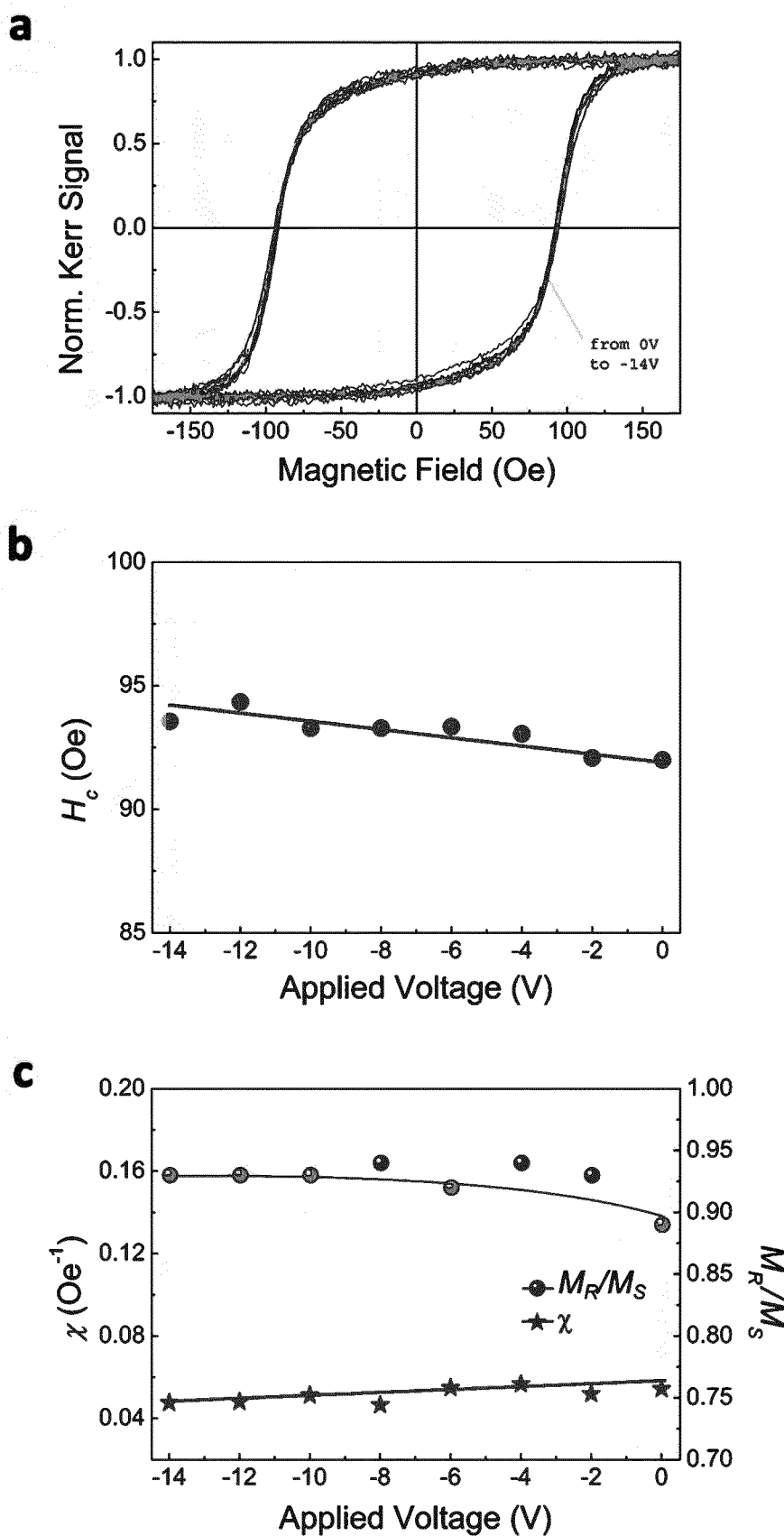
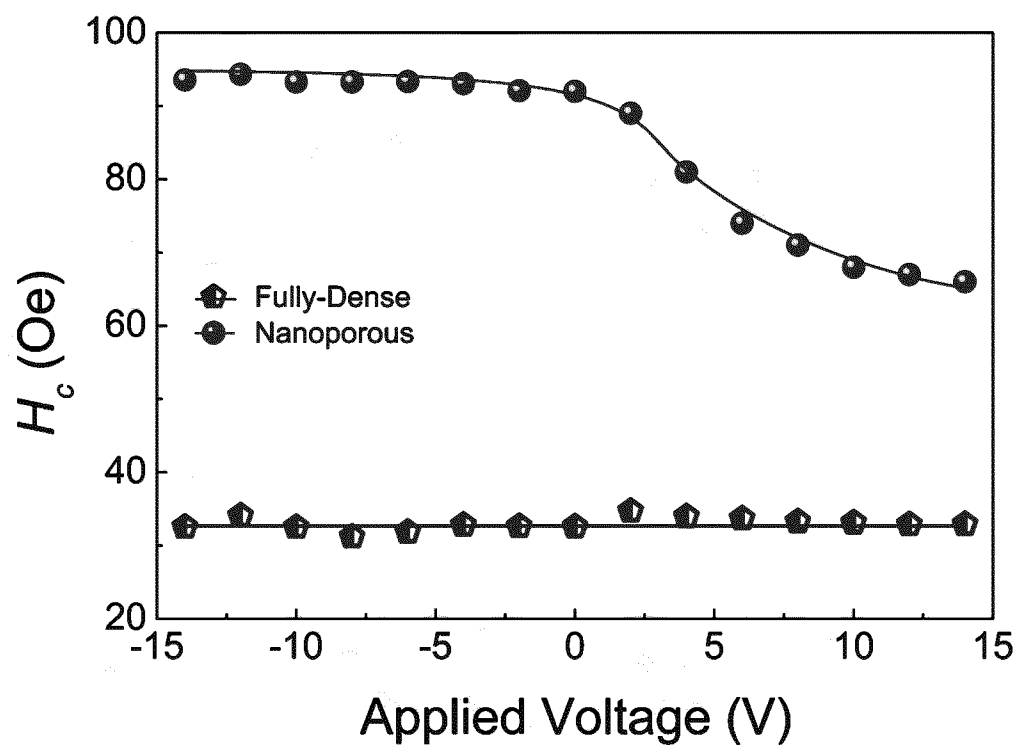
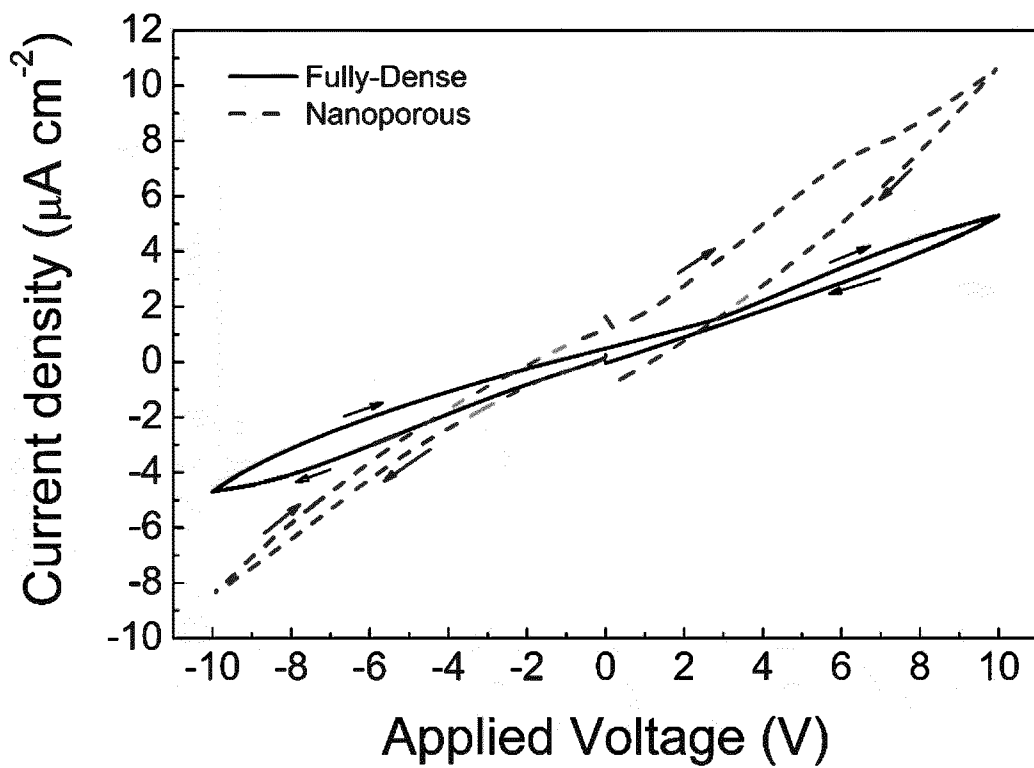
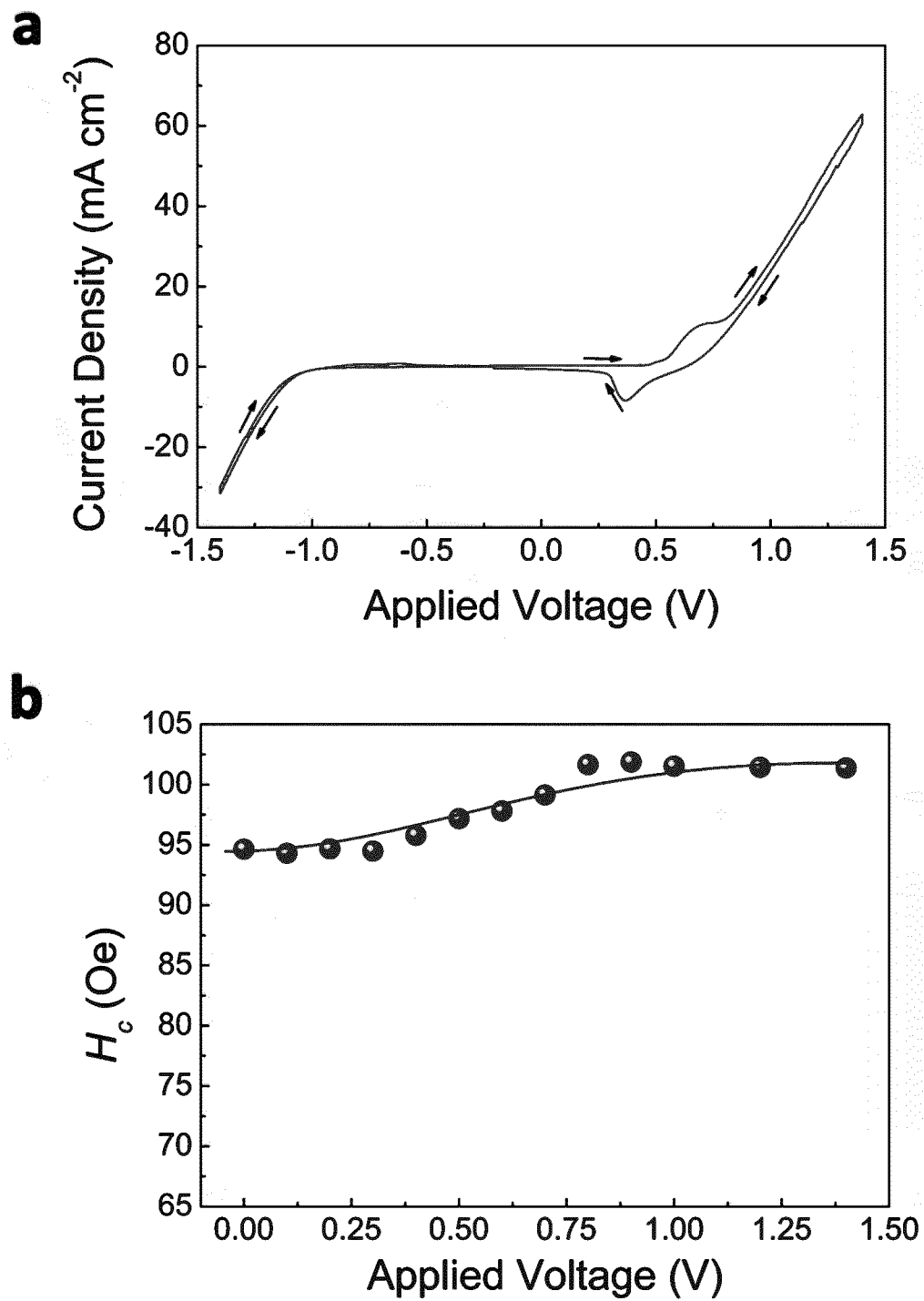
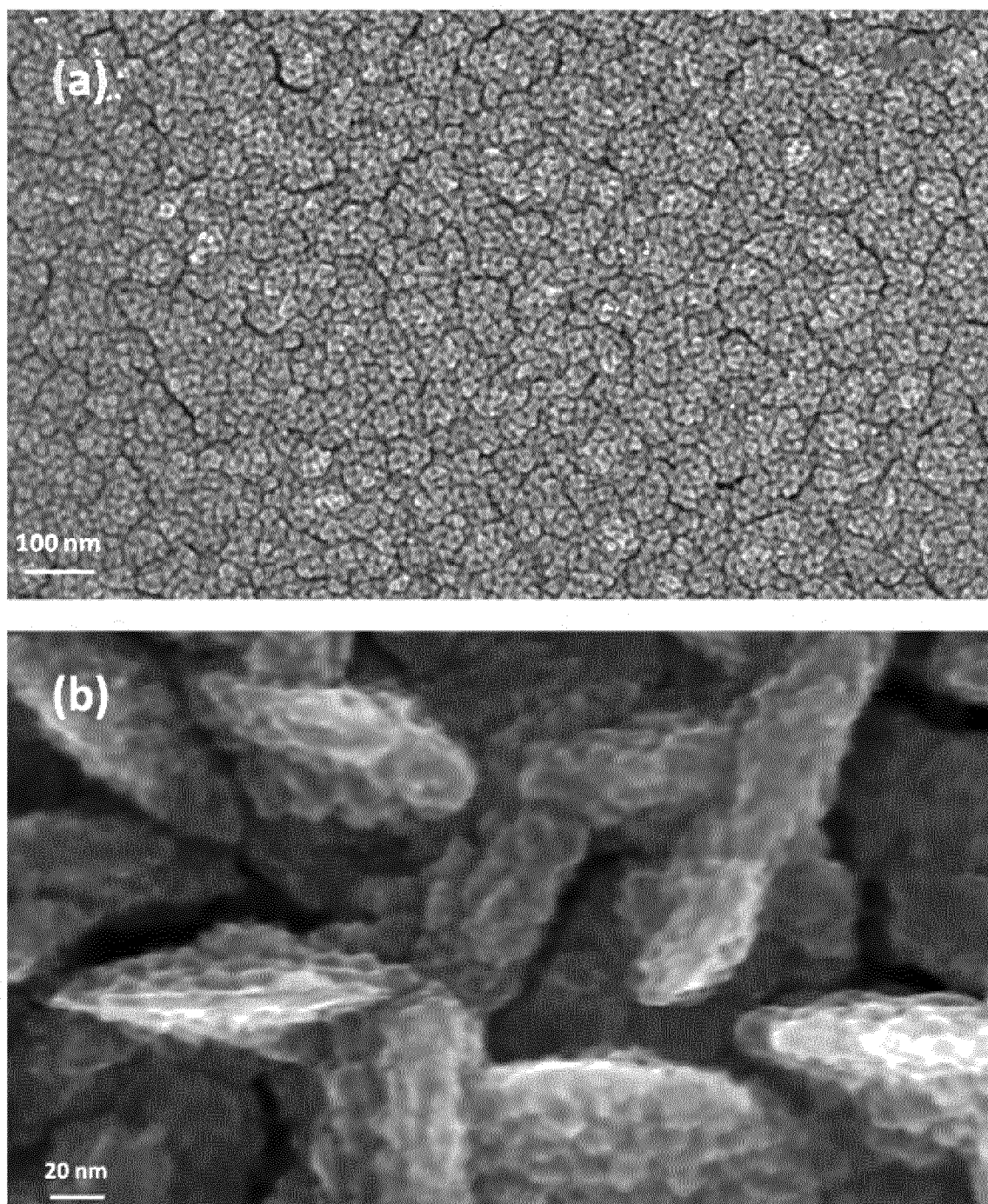


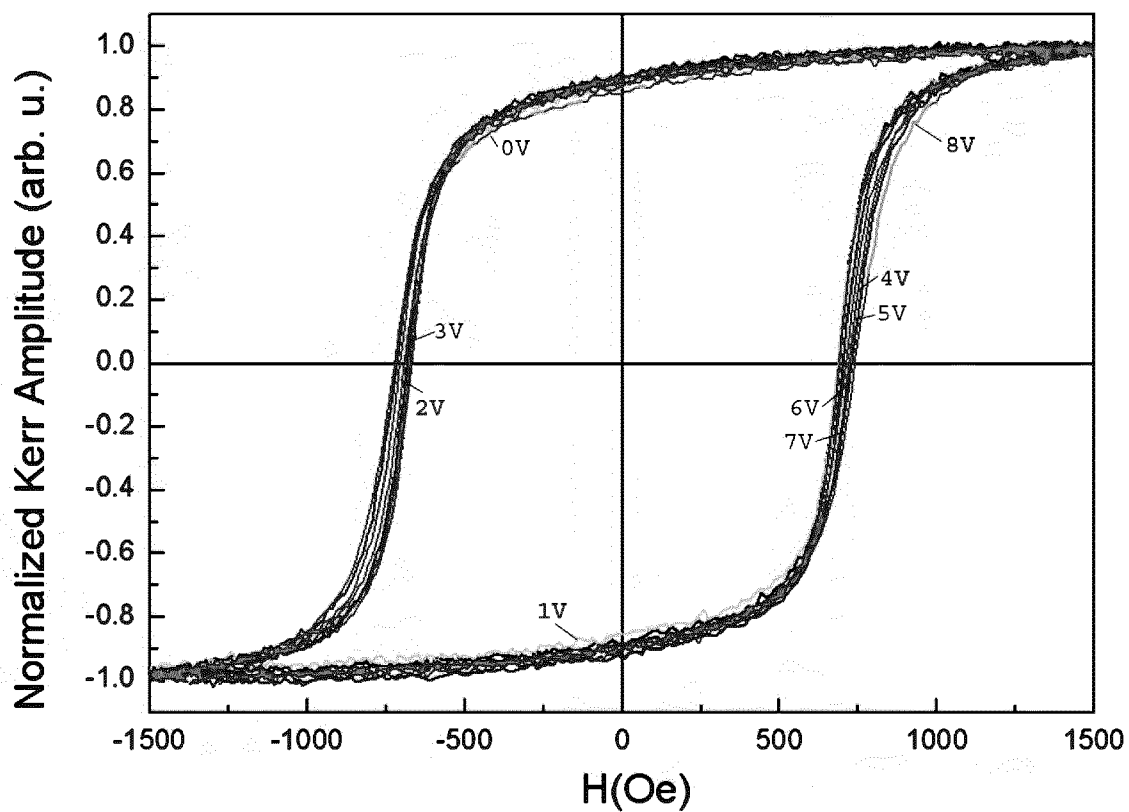
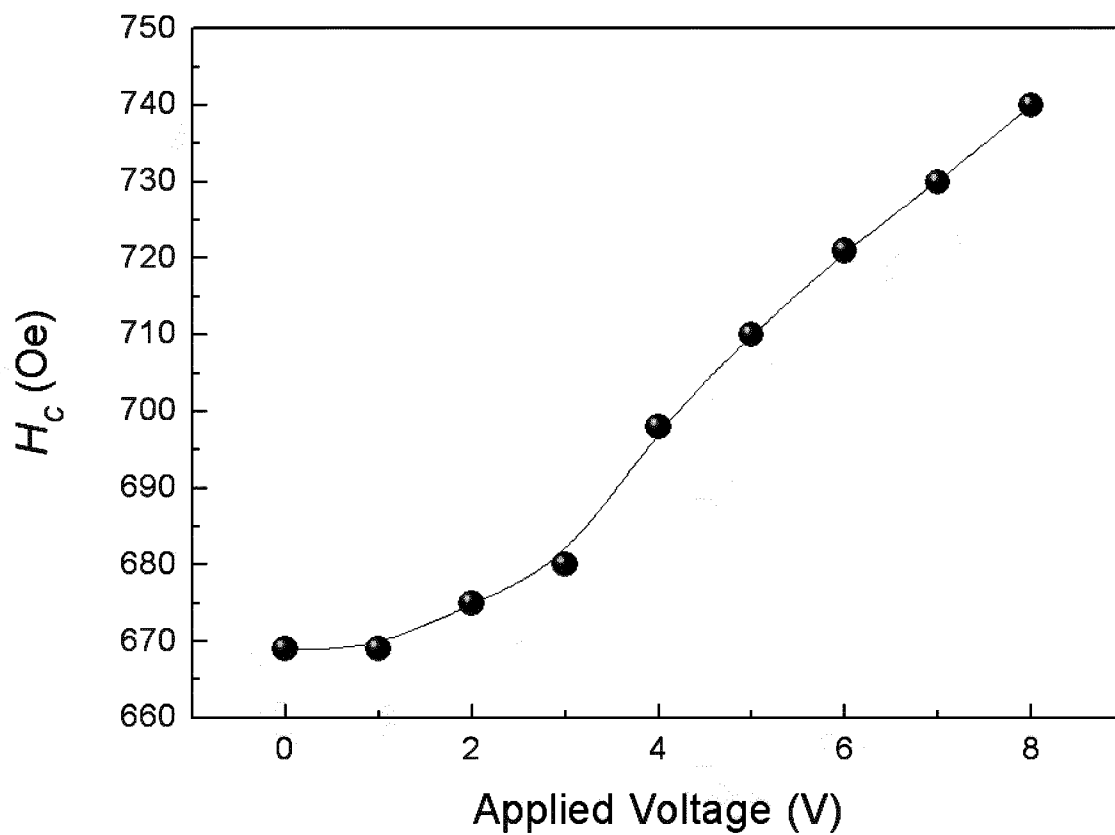
Figure 4

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**Figure 5****Figure 6**

**Figure 7**

**Figure 8**

**Figure 9****Figure 10**

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2018/061900

A. CLASSIFICATION OF SUBJECT MATTER
INV. H01F10/12 H01L43/00
ADD.

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
H01F H01L

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

EPO-Internal, WPI Data, INSPEC, COMPENDEX

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	GHOSH ET AL: "Charge-response of magnetization in nanoporous Pd-Ni alloys", JOURNAL OF MAGNETISM AND MAGNETIC MATERIALS, ELSEVIER, AMSTERDAM, NL, vol. 323, no. 5, 1 March 2011 (2011-03-01), pages 552-556, XP027525958, ISSN: 0304-8853 [retrieved on 2010-11-24] abstract; figure 4 page 553, column 1, paragraphs 1,2 page 553, column 2, paragraph 1 ----- -/--	1-14



Further documents are listed in the continuation of Box C.



See patent family annex.

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Date of the actual completion of the international search

12 September 2018

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24/09/2018

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Authorized officer

Primus, Jean-Louis

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2018/061900

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	STEFAN TOPOLOVEC ET AL: "SQUID magnetometry combined with in situ cyclic voltammetry: A case study of tunable magnetism of -Fe₂O₃ nanoparticles", JOURNAL OF MAGNETISM AND MAGNETIC MATERIALS, vol. 329, 1 March 2013 (2013-03-01), pages 43-48, XP055092838, ISSN: 0304-8853, DOI: 10.1016/j.jmmm.2012.09.071 abstract; figure 3 page 43, column 2, paragraph 3 - page 44, column 1, paragraph 1 -----	1-14
X	THOMAS E. QUICKEL ET AL: "Mesoporous bismuth ferrite with amplified magnetoelectric coupling and electric field-induced ferrimagnetism", NATURE COMMUNICATIONS, vol. 6, no. 1, 10 March 2015 (2015-03-10), XP055506340, DOI: 10.1038/ncomms7562 abstract; figures 3,5 -----	1-14
A	M. WEISHEIT ET AL: "Electric Field-Induced Modification of Magnetism in Thin-Film Ferromagnets", SCIENCE, vol. 315, no. 5810, 19 January 2007 (2007-01-19), pages 349-351, XP055506335, US ISSN: 0036-8075, DOI: 10.1126/science.1136629 abstract; figure 1 -----	1-14
A	US 2014/197910 A1 (TOLBERT SARAH H [US] ET AL) 17 July 2014 (2014-07-17) paragraphs [0025] - [0027]; figure 1 -----	1-14

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/EP2018/061900

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 2014197910	A1	17-07-2014	NONE
