3D porous alumina, a controllable platform to tailor magnetic nanowires.

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1. Introduction

The understanding of the magnetic properties of nanostructures is a field under continuous evolution. Not only the low dimensional characteristics of the materials confer unique properties to those structures, but also the high degree of freedom when fabricating them increases the possibilities of tailoring their magnetic properties. The recent development of novel technologies that provide ways of both fabricating and characterizing at the nanoscale have open a door to the obtainment of nanostructures with specifically designed magnetic properties. In this chapter we will review some of these tailored nanostructures that are sometimes referred to as 3D-nanostructures, such as diameter modulated nano-wires and composition modulated nano-wires. Then, we will compare these structures to actual three-dimensional nanostructures, that is, those that take advantage in their design of the three spatial dimensions. At the end of the chapter, we will discuss in depth one fascinating three-dimensional self-sustained magnetic nanostructure which has been developed within our research group based on template growth inside three-dimensional tailored alumina, which, as it will be shown, is obtained using only industrially scalable and highly tunable fabrication methods.

The importance of fabricating nano-sized structured magnetic materials, as it is discussed in different sections of this book, has attracted wide attention because not only do they present different properties than bulk materials due to their low dimensions, but they also have a great potential for miniaturizing technological applications. Moreover, the fabrication of low dimensional structures presents extra degrees of freedom, which affect their characteristics, such as the nanometer diameter in the case of nanowires, the aspect-ratio of the structures, the different behavior of an isolated nano-sized entity

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compared to their collective behavior (a single nanowire and an array of nanowires, for instance), multilayer arrangements combining different materials, etc. The control over nano-magnetism has a wide range of applications [1], and therefore it has received a great deal of attention in recent years. Small sized magnetoresistive devices or permanent magnets, miniaturized sensors, advanced information storage means, such as perpendicular recording media, are quite relevant nowadays. Controlling their magnetic properties such as anisotropy, coercive field, remnant and saturation magnetization is fundamental to understand the basis of magnetism and also to proceed with their applications. For instance, the control of the movements of the magnetic domain walls has been proposed as a way to store information, or the control of magnetic anisotropy which is related to the alignment of the magnetic spins can be also used for recording data. Moreover, magnetic nanowires fabricated via template-assisted techniques can be directly implemented into conventional devices while still embedded in their containing matrices, making their usage much more straightforward than in the case of using isolated nanowires as far as easiness of contact fabrication and intensity of the signal are concerned. Nevertheless, the ultimate aim of using arrays of magnetic nanowires in most cases is to store information using each of the nanowires as an entity, controlling individually the wall motion of the magnetic domains, to obtain ultra-high density magnetic recording media. Therefore, the state of the art nano-fabrication tools and nano-electronics are needed in order to implement these next-generation storage devices and much research is being devoted to the development of such technology. It is important to say that these cutting edge technological developments will not be the subject of this chapter. Here we will focus on the different advances that have been made in the fabrication of 3D magnetic nanowires themselves. Most of these developments have been envisaged as a way of controlling and understanding the magnetic domain walls dynamics, which are affected by the shape anisotropy, dipolar interaction, wire diameter, inhomogeneities, etc. To date, there are still many open questions and these implementations are in most cases looking for the perfect candidates to gain control over the creation and movement of the walls.

In order to produce nanowires of magnetic materials, different approaches can be taken. For instance, methods such as chemical routes (such as solvothermal synthesis) or physical methods (Molecular Beam Epitaxy, for instance) to obtain metallic nanowires have been used [2, 3]. In this chapter, we will focus mainly in a certain approach: the fabrication of magnetic nanowires inside a template, thanks to techniques such as electrochemical deposition [4, 5], or Atomic Layer Deposition (ALD) [6], that can get inside and fill the pores of such templates. One of the main advantages of these techniques is that the aspect ratio of the nanowires can be higher than in the case of chemical methods. Historically, the first templates used for this purpose were ion track etched polymers [7],

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or mica [8, 9], where nanowires of reduced diameters in the range of the nanometers were fabricated.

Then, in 1995, a new family of templates was developed by Masuda and Fukuda, [10] based on anodic aluminum oxide (AOO). Their fabrication consists of a rather straightforward process consisting of two anodization steps, which produces highly ordered porous templates. Depending on the anodization conditions, a wide range of pore diameters can be obtained, and this has been deeply studied in order to decrease the diameter, achieving pores of only 12 nm [11]. Nowadays, it is possible to fabricate these templates with controlled pore diameters in the whole range from 8 nm to 350 nm by using different electrolytes to give rise to different diameters [12], as it was made in [13] to study the thermal conductivity of alumina templates as a function of their porosity. The most typically used electrolytes are sulfuric acid for nano-pores of around 20 nm in diameter, oxalic acid for around 40 nm and phosphoric acid for 120 nm and over [14]. Another important parameter that depends on the electrolyte used is the inter-pore distance because once certain ordered alumina template has been fabricated, the pore diameter can be increased by simply chemical etching, and then the maximum achievable pore diameter will be determined by the inter-pore distance. In such a way, alumina templates with pores up to 400 nm can be obtained. Of the two anodization steps, the first one gives rise to a hexagonal ordering of the pores, and the second one, which maintains this ordering, defines the length of the final pores. In principle, if the anodization conditions are mild, pores with tens or even a hundred microns in length and homogeneous in diameter can be easily achieved.

This straight forward self-ordering process to fabricate large areas of nanoporous templates has been the subject of many studies and as a result, new template architectures have been developed [15]. On the one hand, a higher ordering in the templates has been achieved by pre-texturing the surface (avoiding the first anodization step) with a master and then performing the anodization [16]. In such a way, different patterns can be obtained, with non-hexagonal pore ordering [17], non-circular pore geometries (square or triangular, for instance) via nano-indentation by stamps [18-20] or holographical pre-patterning of the aluminum [21], etc. On the other hand, mixing mild anodization conditions with more aggressive conditions (for instance, increasing the applied anodization voltage to reach the so-called hard anodization regime) while growing the pores in the second step, gives rise to diameter modulated pores [22]. In such a way, a whole new family of so-called three-dimensional templates at the nano-scale has been created from this technique, which will be explained in detail later in the chapter. Then, by replicating their hollow template with magnetic materials, one can give rise to novel nanostructures with tailored magnetic properties.

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In this chapter, we will review the influence of fabricating three-dimensional (3D) structures of magnetic materials at the nanoscale. We will not discuss effects such as three-dimensional nano-magnets in the wide description of the concept, as it was already discussed in a thorough review article of 2017 by Fernández-Pacheco *et al.* [1], the types of domain walls or effects at the nanoscale such as 3D arrays of magnetic vortices [23] or 3D spin textures [24]. We will focus on how to produce a controlled nanometric structure of magnetic materials, mainly via template-assisted fabrication using 3D templates, but also other methods. And, which effect does this structuration in its magnetic properties, which in most cases will differ greatly from the properties that are expected from the forming material. For instance, the magnetization and the magnetic easy axis can be controlled with these structures due to the shape anisotropy. This can be used in applications, such as magnetic recording or spintronics. The control of the domain wall is crucial in the development of high-density data storage devices, which are also defined as 3D magnetic data storage. Nevertheless, it is still not fully understood how the dynamics of the process work, what is the exact influence of the shape anisotropy, the interaction between the adjacent nanowires, etc. As it was already mentioned, most of the developments in this field were triggered by the objective of controlling the domain wall motion when the magnetization is reversed, trying to obtain efficient and well-defined pinning sites for these walls, and this has been studied in the different nanowire geometries that will be presented along with the work.

To begin with, different nanostructures that are sometimes referred to as “3D-magnetic nanostructures” such as diameter modulated nanowires, or multilayer nanowires (composed of different materials) will be discussed, with special detail as their fabrication methods are concerned and also describing how the magnetic properties have been modified in each case. Then, we will focus on what we define as self-sustaining 3D magnetic nanonetworks, that is, artificial arrangements of magnetic nanostructures that can be self-sustained given that they are interconnected in the three dimensions of space and do not need of a matrix to hold them in position. These structures can be envisaged as the natural evolution of the previous ones, but their properties can differ greatly from those found in modulated nanowire arrays.

2. Modulated magnetic nanowires

After the study of the behavior of different magnetic materials (such as cobalt [25], nickel [26], Ni-Fe [27], etc.) in the form of nanowires, the next approach was to study the magnetic nanowires with modulated diameter or composition. In these cases, the magnetic properties differ from those of conventional nanowires and a deep study on

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their behavior has opened the door to further understanding of domain wall movement and interaction not only between adjacent nanowires, but also between different sections of a single nanowire.

2.1. Magnetic nanowires with modulated diameter

As it was described in the introduction, templates with a certain modulation in the diameter can be produced, in the case of using AAO, by using two different anodization processes, such as hard anodization and mild anodization (or even changing the anodization electrolytes) while growing the pores. In such a way, the pore diameter, which depends on the anodization conditions, changes from a small diameter in the regions where mild anodization has been used, to wider diameters in those where the hard anodization was implemented. Therefore, modulating the pore length where each of the processes is applied (by controlling the times each of the conditions is applied), a diameter modulation is obtained, as it was shown in 2006 in reference [22]. In the following years, these templates were used for growing inside magnetic materials via electrochemical deposition, reproducing the modulation in the diameter and giving rise to diameter modulated nanowires. In this case, the different magnetic properties associated with different diameters within the same material would be present in the resulting magnetic material. This modulation in the diameter is crucial for the understanding, for instance, of the magnetization reversal dynamics, which is driven by the nucleation of the domain walls. How a magnetic domain wall nucleates and propagates depends on the nanowire diameter, and thus, having a nanowire with different diameters is an excellent test bank to understand the transitions from one kind of domain wall to another. In the case of nickel, the magnetic reversal takes place via transverse wall propagation for diameters under 55 nm, while for diameters over 55 nm it occurs via vortex formation and propagation. When a nanowire with diameters both over and under 55 nm is studied, then both processes compete in the magnetization reversal, and as it was studied theoretically, starting with a vortex wall formation in the larger diameter region which propagates and then evolves to a transverse reversal when the diameter decreases [28]. Then, it is necessary to apply a higher nucleation field to continue the propagation of the wall at the interface, and thus the domain wall is pinned at this point.

Not only electrochemistry can be used to replicate the morphology of modulated AAOs, but also Atomic Layer Deposition (ALD) has been used to obtain arrays of modulated magnetic iron oxide nanotubes [6]. In this work, the strong shape anisotropy of these modulated nanotubes (with diameters varying between 70 nm and 150 nm) affects their coercive field, which has higher values for those tubes with smaller diameters. If only one

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wide segment is introduced in the middle of a long narrow tube, the coercive field drops over 30% of its original value, which is a proof of the influence of these diameter modulations on the magnetic reversal.

In the case of magnetic nanowires modulated in diameter grown by electrochemical deposition, there has been a number of works that have explored how these variations in diameter can be used, through domain wall pinning, to control the magnetization reversal. Different measurements, both in single nanowires (such as spatially resolved magneto-optical Kerr effect, MOKE, magnetometry, X-ray magnetic circular dichroism (XMCD)[29], or Magnetic Force Microscopy, MFM [30]) and in arrays of nanowires (Superconducting Quantum Interference Device, SQUID measurements or First-order reversal curves, FORC [31]) have been performed on a variety of modulated nanowires. In the case of arrays of nanowires, the interactions between neighboring nanowires play an important role that has to be taken into account. Nickel nanowires with different geometries have been extensively studied [32], showing that the interaction between nanowires is higher when there is a modulation in their diameter when compared to nanowires with the same spacing between them and the same diameter [33]. Nevertheless, this effect could also be due to the bigger diameters of the modulated waveguides in the regions where the diameter is increased, given that with increasing nanowire diameter, without varying the distance between their centers, the interaction is also higher. Actually, these modulated nanowires show properties which are a combination of those that would be obtained in arrays of nanowires with the diameters present in the modulation [33], opening the door to a way of tuning the magnetic properties. In more recent work from 2017, Arzuza *et al.* studied magnetic properties of nickel nanowires with their diameter single-modulated between 35 and around 55 nm, which are under and above the threshold for vortex propagation domain walls, respectively [31]. In order to study the behavior of the nanowires as an array, the First-Order-Reversal-Curve (FORC) was measured, finding that the magnetization reversal in the case of diameter modulated nanowires occurs through two different processes, a helicoidal vortex wall (which is more complicated than a vortex domain wall) and a transverse mode. Moreover, FORC measurements show higher interaction fields in the case of modulated nanowires, along with a non-uniform stray field, a consequence of the shape modulation. This stray field is the main difference between these modulated nanowires and homogeneous ones.

In 2014 a study on different geometries of the modulated Co nanowires (square and exponential connection between the low diameter and high diameter sections of the nanowire), showed that also the shape has an influence in the magnetic properties [34]. In general, the main differences between non-modulated and modulated nanowires were the same than what was reported before, with higher magnetostatic interactions in the

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case of the modulated ones, induced by local stray fields. But within the modulated nanowires, there are subtle differences, given that in this case, the ends of the wider segments of the modulated nanowires, where the magnetic charges appear and induce the stray fields, are different for each studied morphology, and that reverts on coercivity and remanence angular evolutions particular of each case, which modifies the interactions between neighboring nanowires.

Other magnetic materials have been also fabricated as modulated nanowires, showing differences with their single-diameter nanowire counterparts. For example in CoFe alloy[35], an increase of the squareness (SQ , defined as the ratio of remanence to saturation) and a reduction in the coercive field was found, which, according to the authors, suggest a higher magnetostatic interaction due to the stray field present in the modulated nanowires. Isolated $\text{Fe}_{28}\text{Co}_{67}\text{Cu}_5$ were also investigated as isolated entities with MFM to get an insight on the effect that the diameter modulation has on the spin orientation, suggesting curling of the magnetization at the junction region [30]. In 2016, a study on the behavior of FeCoCu modulated nanowires with two different geometries (one with the big diameter sections longer than the smaller diameter sections, and the second just the other way round) was performed, obtaining from MOKE measurements from single nanowires that the domain walls were somehow pinned at the diameter modulations. In that way, metastable magnetic states are produced during the propagation of the vortex domain walls along them [36]. The spin configuration of nanowires of the same material, which has the magnetization easy axis along the nanowire length, was also studied in a so-called bamboo-like structure (with diameter modulations each 400 nm along the nanowire's length, see **Figure 1**). In other work, by Bran *et al.*, similar structured nanowires were studied, comparing FeCoCu and Co, which was chosen because it presents the easy axis perpendicular to the nanowire length [29]. The combination of photoemission and XMCD allowed an insight on the magnetic structure and spin configuration of both the surface and the bulk of the nanowires. On the one hand, in the case of FeCoCu bamboo-like nanowires, the shape anisotropy dominates, with vortex structures at the end and at the diameter modulations. This confirms the previous results of magnetization reversal through vortex domain wall propagation with certain pinning at the modulations. On the other hand, for the cobalt nanowires, the structure was different, with vortices of alternating chirality that do not seem to appear at determined positions of the nanowire, that is, which are not connected with the diameter modulations.

Studies on single-modulated $\text{Ni}_{80}\text{Fe}_{20}$ permalloy showed that the magnetic interaction is higher in the case of having the same length of the nanowire of each of the diameters and that the reversal of the magnetization takes place through the propagation of vortex

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domain walls that are nucleated at both ends and in the junction region [37]. This hypothesis was simulated and nanowires with these characteristics were fabricated and measured, showing a good agreement between the predictions and the experiments.

(Figure1)

All these results and studies show that these kinds of modulated nanowires are ideal to provide a configurable test bench for gaining a further understanding on domain wall dynamics and nucleation phenomena within a single nanowire and in an array of nanowires. As it has been shown, the properties of the nanowire arrays of modulated nanowires present a combination of the expected properties of nanowires of both diameters. Moreover, the domain wall pinning has been demonstrated in certain cases, mainly when studying single nanowires with modulated diameters, and the different ways of magnetic domain reversal have been studied from both the theoretical and experimental points of view.

2.2. Composition modulation: Multilayered nanowires

Another way of presenting a so-called three-dimensional structuration at the nano-scale when talking about nanowires is to fabricate multilayered structures, varying the composition of the layers, as in reference [38], where these structures are defined as “3D arrays of magnetostatically coupled nanopillars”. These structures can also be done with electrochemical deposition methods, and, as it was the case for the diameter modulated nanowires, it has been also used to find a way to control the magnetization reversal of the nanowires and, in the best case, find a way to control the wall movement and introduce pinning states in well-defined places.

Different compositional configurations have been proposed and studied, such as having layers that alternate ferromagnetic and non-ferromagnetic materials, for instance Nickel and Copper (as in ref [39]), Fe and copper[40], FeCoCu and copper [36], FeGa and copper [41], cobalt and gold [38], etc. Other configuration consists of combining two or more magnetic materials with different properties, such as Co and Ni [23]. In all cases, when they are fabricated via electrochemical composition inside alumina templates, the parameters that determine the behavior of the nanowires, that is, the length of the different segments, the nanowire diameter, inter-pore distance, and materials properties, can be easily controlled, either by the electrochemical process itself, or by choosing the appropriate alumina template (pore diameter, inter-pore distance, etc.).

In the case of using ferromagnetic and non-ferromagnetic segments along the nanowire, what one obtains are ferromagnetic discs along each of the nanowires. The interaction between the multilayered nanowires shows a different behavior than that of conventional nanowires, as it can be seen through FORC measurements [39]. Moreover, certain properties, such as the total magnetic anisotropy, change with the thicknesses of these ferromagnetic discs. It has been shown that maintaining the ferromagnetic layer constant (FeCoCu), if one increases the non-ferromagnetic (copper) layer thickness the coercivity, remanence, and susceptibility increase. On the other hand, for constant copper thickness, the susceptibility decreases with increasing the FeCoCu thickness [36]. In such a way, the characteristics of the nanowire array can be tailored, obtaining a decrease in the magnetic interactions for thicker non-ferromagnetic layers. The main cause is that the stray fields between neighboring magnetic disks within the same nanowire or from adjacent wires depend on the distance between such disks and their dimensions. Similar results were reported in the case of Co/Au multisegmented nanowires, the coercivity and squareness of the measured hysteresis loops are larger than in the case of pure Co nanowires [38], that is, cobalt nano-disks coupled via magnetostatic interaction. A deeper insight on the interactions between the ferromagnetic nanodisks (FeGa in this case) and non-ferromagnetic sections (Cu) within a nanowire was also discussed in Reference [41], where the complex magnetic interactions are described in order to further tailor the properties of such structures. In this work, dipolar interactions are also described, as well as the 3D spin structure displayed by these nanowires, which is quite complex and could be tailored by the geometrical characteristics of the nanowires. A more recent work, where a similar approach was taken, was presented in 2018 [40]. In this case, multi-segmented nanowires in which the ferromagnetic section (made of iron) was kept constant in length and samples with different lengths of non-ferromagnetic sections (copper) were studied. It was shown that for small copper segments (around 15 nm in length), the magnetic behavior is driven by the dipolar coupling between the ferromagnetic iron disks (these structures are shown in **Figure 2**). On the contrary, when the non-magnetic sections are longer the interactions within a single nanowire are less intense and the magnetic behavior is dominated by the dipolar interactions between nano-disks from neighboring nanowires.

(Figure 2)

When two different magnetic materials are used for these multilayered nanowire structures, such as nickel and cobalt, the interfaces between adjacent nano-disks provide well defined pinning sites, as it is shown in Figure 2.b and 2.c [23], where again the simulations and the experiments agree and help us to understand the domain wall dynamics in these structures. Further studies on these isolated nanowires have also given

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an insight into the dynamics of the domain walls in these cases, which propagate via three-dimensional vortices. The characterization of those nano-magnetic structures has triggered the development of novel measurement systems, able to follow in time the real-time motion of the domain walls (which cannot be made by more conventional methods such as MFM). Therefore, developments in ultrafast methods such as scanning transmission X-ray spectroscopy (STXM) or X-ray magnetic circular dichroism photoemission electron microscopy (XMCD-PEEM) are emerging in the field.

As it has been shown here, the fabrication of multilayered nanowires via template-assisted electrochemical growth is a quite configurable and a wide variety of structures can be obtained with high quality in the interfaces. Moreover, the method provides the possibility of growing high aspect-ratio multilayered nanowires, which in return gives more precise measurements than in other kinds of segmented nanowires due to the larger signals produced. These kinds of nanowires have shown to provide pinning sites that are well-defined at the interfaces of the different materials that compose the nanowire, and they also have been really useful to study the stray fields within the different segments of a single nanowire, providing a deeper understanding of the domain wall motion and the interactions between magnetic domains.

2.3. Relative orientation modulation: Radial nanowire array

Different works have dealt with radially distributed nanowire arrays, such as those from R. Sanz *et al.* [42, 43] in 2007. In a more recent work dealing with this same kind of structures from J. García *et al.* this geometry was defined as a 3D ordered array of magnetic nanowires [44], although it does not enter in what we define a 3D geometry which will be exposed in section 3. These structures consist of a single-magnetic material nanowire array which has been formed using an AAO fabricated in a wire as a template (see **Table I** for a schematic view on the geometry). Once this template is electrochemically filled with a magnetic material, the nanowires have the conventional hexagonal ordering with their neighbors, but in a long range, they have a cylindrical disposition due to the wire where it was fabricated, obtaining nanowires oriented in all the radial directions with respect to the axis of the original aluminum wire. In the study carried out with this kind of cylindrical nickel and cobalt nanowire arrays in the aforementioned works, they showed similar behavior to the conventional nanowire arrays, although the geometry of the cylindrical nanowire array produces a hysteresis loop which is in between the parallel and perpendicular hysteresis loops of the planar nanowire array. Therefore, this geometry shows a dependence on the angle that the nanowires form with the applied magnetic field, as well as from the angle that the nanowires present among them.

3. Magnetic structures with a 3D geometry

As we said in the introduction, we will define 3D magnetic nanostructures as those that are interconnected in the three dimensions of space, forming a self-sustaining arrangement that does not need a matrix to hold them. In this section we will introduce different ways of producing 3D geometries, such as those fabricated in ion-irradiated polymeric templates, in lithographically patterned resist or in modified alumina templates. Those structures have the common features of having nanowires along different spatial directions, along with an interconnected structure that allows them to be self-sustained structures once their templates have been eliminated.

3.1. Self-sustaining interconnected nanowire networks from ion-irradiated 3D polymeric templates

A truer three-dimensional arrangement of nanowires is that resulting from filling a polymer template which has been ion-irradiated in two different orientations producing nano-pores in both direction than are interconnected [45]. The most common way of producing such templates is by performing two subsequent irradiations, both with a certain angle of the incident beam with respect to the surface of the polymer, which can be tailored at will. Such a template, when filled by ALD or electrochemical methods, produces an array of nanowires which form a certain angle among them and cross at certain points, and thus, once the ion-damage polymer has been removed, a self-standing structure of crossing nanowires is obtained. Moreover, the diameter of the nanowires can be also tailored by controlling the etching of the membranes once the irradiation process has been made. Nevertheless, what cannot be controlled is the separation or ordering of such nanowires, given that the template is created by the ionic tracks left by the irradiation, and only the density of the beam can be controlled, but not the individual tracks. These kinds of structures (as shown in **Figure 3**), sometimes referred to as 3D interconnected nanowire networks, have been studied for different applications, such as thermoelectricity [46], microbatteries [47], and magnetism. For instance, in 2015 a work by Araujo *et al.* was presented, where Ni and Ni/NiFe were grown inside a template of this kind, with the nanopores forming 30° with each other [48]. The measurements on these structures resulted in magnetic properties quite different from the ones obtained in parallel-aligned nanowire arrays, as far as their anisotropy and demagnetization fields (see Figure 3.c). On the one hand, the properties depended strongly on the relative angle of the nanowires among them, which is one of the tunable parameters in their fabrication.

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This, combined with the possibility of changing the material forming the nanowires, gives this configuration a high tunability. In a more recent work, of 2016, NiCo was used to produce a magnetic 3D interconnected network [49] and the magneto-transport of such nano-structure was studied, obtaining different responses at different angles between the magnetic field and the plane of the 3D interconnected network, which can be tuned by varying the composition of the NiCo alloy. Nevertheless, the tunability in these structures is limited to changing the material, given that modifications in the geometry of the 3D interconnections are not so straightforward, assuming that only the relative angle and the porosity can be changed when producing the template, but other parameters, such as the exact position of the connections cannot be tuned and the maximum angle between the nanowires is also limited by the preparation technique of the irradiation of the polymer.

(Figure 3)

3.2. 3D nanostructures fabricated in lithography patterned resists

Another way of obtaining 3D nanostructures is via lithography. Recent developments in this field have provided the tools to fabricate nanometric structures, such as the two-photon lithography technique. With this technology, different geometries can be produced, in a photoresist by illuminating it with a focused laser and producing 3D structures within it. Then, the illuminated areas can be removed and the patterned photoresist can be used as a template to grow inside magnetic materials with techniques that reproduce the obtained structure, such as electrochemical deposition. In 2018, a work where cobalt 3D structures were fabricated following this route was presented by Williams *et al.* [50]. One of the main advantages of this fabrication method is the versatility to realize different 3D structures that are not achievable by anodic alumina or track-etched polymer membranes, being able to access to complex 3D geometries and 3D networks. This allows the fabrication of structures which have been previously only imagined in theoretical studies, and which would give rise to nanostructured metamaterials with modified properties. Nevertheless, the two-photon lithography technique has also some limitations. For instance, the sizes that can be achieved cannot go under some hundreds of nanometers in size (approximately 430 nm is the smallest lateral feature that Williams *et al.* could fabricate), given that it depends on the wavelength of the writing laser. Also, the fabrication of such structures is also time-consuming, given that it is a serial fabrication method. This technique was used to fabricate tetrapods of cobalt (see **Figure 4**), which were then studied to see the effect of this angled nanowires in the magnetic properties of the structures, which showed a complex domain structure.

(Figure 4)

3.3. Self-sustaining interconnected nanowire networks 3D structures from 3D AAO templates

In this section we will present a technique, developed by our group, to create a 3D nano-structure that can be tailored as desired, presented in 2014 [51]. This method is based in the aluminum anodization, obtaining an array of parallel nanowires which are connected each certain length among them. This scaffold structure can be used as a template and filled via electrochemistry methods with different materials [52, 53]. In the case of filling it with a magnetic material, one can finely tune the properties of the 3D magnetic nano-network generated. This control over the magnetic properties is driven by the shape and it is purely magnetostatic. This approach can produce the tuning of the magnetic easy axis and coercivity to the desired direction. It is worth to mention that, this can be achieved on virtually any magnetic material, alloy or multilayers that can be prepared inside this 3D-porous alumina template, as we showed in a recent publication [54]. We will enter in more detail in these kinds of 3D magnetic-nano-structures, performances and behavior.

3.4.1. Fabrication process and morphological description of the structures

The first step is the fabrication of the 3-D template, which is based in two-step anodization of aluminum, as described in [51]. The first anodization is used to produce ordered pores on the aluminum, and the second one consist of pulsed anodization alternating between mild and hard anodization, similarly as it was done to produce the modulated templates. The difference is that, after the anodization process, the templates are etched in phosphoric acid. Given that the etching rates of the mild and hard regions are different, controlling the time of reaction one can etch away the hard regions up to a point where these regions produce connections between adjacent nano-pores and thus a 3D-AAO interconnected nano-structure is produced. This structure can be described as an array of parallel nanotubes of around 50 nm in diameter interconnected with a network of perpendicular nanotubes of around 40 nm in diameter. The distance between the connecting nanotubes can be finely tuned given that they are formed in the areas of hard anodization, and those are defined by the high voltage pulses applied in the second step, and thus changing the pulses, the interconnections can be made closer to each other or more separated. Then, after dissolving the remaining aluminium and evaporating a layer of chromium and gold on one side of the 3D-template, those can be filled via electrochemical deposition. It is worth to note that all the fabrication methods used here (anodization and electrochemical growth) are cost-effective and easily scalable to the

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industry. Once the matrix is filled, the alumina template can be dissolved and the self-standing 3D-magnetic structure can be studied. A scheme of this process, described in [52] for 3D cobalt nano-structures fabrication is shown in **Figure 5**. Studies on the magnetic behavior of such structures showed that these magnetic 3D nanowire interconnected networks can be designed to obtain a certain magnetic anisotropy and coercivity, given that tuning the spacing of the nanowire transversal connections controls the magnetic properties [54].

(Figure 5)

Finally, it is worth saying that the cylindrical nanowire geometry discussed in section 2.3, from reference [43, 44], can be also combined with this 3D nano-network structure, as it has been demonstrated in [55], where a 3D nano-network structure in a cylinder was processed [55], although these have not yet been filled with magnetic material and studied.

Type of structure	Main features	Advantages	Disadvantages
Modulated	Domain wall pinning	Easy fabrication One material	Moderate control over the magnetization parameters
Multilayered	Domain wall pinning	Easy fabrication of the template	At least two materials growth Higher control of the magnetic anisotropy
Cylindrical	Radial properties modified with respect to NW-arrays	Easy fabrication of the template	Only cylindrical properties are modified. Other geometries are not accessed.
Interconnected 3D network in ion-track-membranes	Properties modified with respect to NW-arrays. Self-sustained structure	Self-standing structure. Tunability of the diameter, and relative angle of the nw	Need of an accelerator to fabricate the template. No control over the ordering of the nanowires.
Interconnected 3D by two photon lithography	Virtually any geometry can be produced.	Highly tunable structures obtained.	Time-consuming fabrication method Limited resolution at the nanoscale
Interconnected 3D network in anodic alumina (3D-AAOs)	Highly tunable geometry should give rise to tunable magnetic properties. Self-sustained structure.	Self-standing structure. High tunability of the interconnexion distance. Easily scalable fabrication methods.	To be analyzed

Summary and outlook

The possibility that technology gives us of realizing nano-metric structures in a controlled way, with high tunability, has opened a door to new possibilities in nanomagnetism. The possibility of creating 3D-nano networks of magnetic materials with modified properties could lead to novel applications in a wide range of fields. In the latest years, different nano-magnetic geometries have provided a way to study the different parameters that play a role in controlling the nano-magnetism independently. Diameter modulated nanowires for studying the domain wall movement, multilayer nanowires to see the interactions between different sections of the same nanowire, 3D magnetic nanostructures that show the importance of the interaction between the isolated nanowires, etc. Thanks to these structures, advancements in wall pinning and domain wall movement have been achieved, along with a further understanding of the models that help us to recreate those effects. Nevertheless, along with those novel structures, novel measurement techniques are also being developed, in order to see with enough resolution the magnetic domains or to follow in real time the domain wall movement. Those developments are crucial to finally understand and control the nano-magnetic structures and be able to design actual devices for using their possibilities for magnetic information storage or random access memories, and if the field keeps as active as in recent years, it seems that such applications will be a reality in the near future.

Authors and Acknowledgments

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Dr. Olga Caballero-Calero is a Tenured Scientist at the IMN-CSIC where she works in at the FINDER group. Currently, the main topics of her research are the fabrication of novel thermoelectric devices for the harvesting of wasted heat for its use as electricity, as well as the study of novel nanostructures of different materials and study their change in properties due to nano-structuration.

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Regarding technology transfer, she holds the copyright of 4 patents and is the co-founder of a spin-off company.

This work was supported by the MAT2017-86450-C4-3-R and Infante project. The authors would like to acknowledge valious discussions with Dr. Ruy Sanz. The authors would like to thank Mr. Pedro Campos Resende for his drawings in figure 5.

Figures

Figure 1: a) SEM image of bamboo-like nanowires with diameter modulation embedded in the AAO membrane (from reference [36], under creative commons license) b) TEM image of a Ni nanowire with one modulation in diameter and c) sketch of the stray field lines (dashed arrows) outside the nanowire and the magnetization (grey arrows) within the nanowire (b and c reproduced with permission from reference [32])

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Figure 2: a) SEM image of a multilayered nanowire arrays, in this case, formed by alternative layers of Cu and Fe (taken from [40], under creative commons license) b) measured image of a pinned domain wall in the interface of Co and Ni layers of a multilayered nanowire obtained via Differential Phase Contrast Virtual Bright Field detection (VBF-DPC, developed in ref [23]). C) shows the micromagnetic simulations (color cones for the magnetization direction, black arrows for the stray field) of the domain wall structure (b and c reprinted with permission from [23]).

Figure 3: a) and b) SEM images of 3D Ni interconnected networks, after the dissolution of the template. In the inset of a), an optical image of the macroscopic network can be seen. c) shows the hysteresis loop when the external field is applied out of plane (OOP, red) and in-plane (IP, blue) for a 3 Ni interconnected network (reproduced from reference [49], protected under a creative commons license).

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Figure 4: a) scheme of the illumination process within a positive resist of the tetrapod structure. Center, the scheme of the resulting structure once the hollow photoresist is filled with cobalt via electrodeposition and the resist is dissolved. B) an SEM image of an actual cobalt tetrapods c) and d) show the Magneto-Optical Kerr effect (MOKE) loops obtained in a tetrapod array with the fields applied along different directions (all images reproduced with permission from [50])

Figure 5: Illustration of the empty 3D-template, then its preparation with the gold layer, its filling with the magnetic material and the 3D nano-structure left after the dissolution of the alumina Z is the distance between the transversal channels, which can be maintained over the whole structure or varied.

- [1] A. Fernández-Pacheco, R. Streubel, O. Fruchart, R. Hertel, P. Fischer, R.P. Cowburn, *Nature Communications*, 8 (2017) 15756.
- [2] A. Rudolph, M. Soda, M. Kiessling, T. Wojtowicz, D. Schuh, W. Wegscheider, J. Zweck, C. Back, E. Reiger, *Nano Letters*, 9 (2009) 3860-3866.
- [3] A. Šutka, T. Käämbre, U. Joost, K. Kooser, M. Kook, R.F. Duarte, V. Kisand, M. Maiorov, N. Döbelin, K. Smits, *Journal of Alloys and Compounds*, 763 (2018) 164-172.
- [4] A. Fert, L. Piraux, *Journal of Magnetism and Magnetic Materials*, 200 (1999) 338-358.
- [5] C. Schönenberger, B. Van der Zande, L. Fokkink, M. Henny, C. Schmid, M. Krüger, A. Bachtold, R. Huber, H. Birk, U. Staufer, *The Journal of Physical Chemistry B*, 101 (1997) 5497-5505.
- [6] K. Pitzschel, J.M.M. Moreno, J. Escrig, O. Albrecht, K. Nielsch, J. Bachmann, *ACS nano*, 3 (2009) 3463-3468.
- [7] T. Whitney, P. Searson, J. Jiang, C. Chien, *Science*, 261 (1993) 1316-1319.
- [8] G.E. Possin, *Review of Scientific Instruments*, 41 (1970) 772-774.
- [9] L. Sun, C. Chien, P. Searson, *Journal of materials science*, 35 (2000) 1097-1103.
- [10] H. Masuda, K. Fukuda, *Science*, 268 (1995) 1466-1468.
- [11] C. Manzano, J. Martín, M. Martín-González, *Microporous and Mesoporous Materials*, 184 (2014) 177-183.

CABALLERO-CALERO, Olga; MARTÍN-GONZÁLEZ, Marisol. 3D porous alumina: a controllable platform to tailor magnetic nanowires. *Magnetic Nano-and Microwires*. Woodhead Publishing, 2020. p. 3-20.

- [12] G.D. Sulka, Nanostructured materials in electrochemistry, 1 (2008) 1-116.
- [13] B.a. Abad, J. Maiz, M. Martin-Gonzalez, The Journal of Physical Chemistry C, 120 (2016) 5361-5370.
- [14] J. Martín, C.V. Manzano, M. Martín-González, Microporous and Mesoporous Materials, 151 (2012) 311-316.
- [15] F. Li, L. Zhang, R.M. Metzger, Chemistry of materials, 10 (1998) 2470-2480.
- [16] H. Masuda, H. Yamada, M. Satoh, H. Asoh, M. Nakao, T. Tamamura, Applied Physics Letters, 71 (1997) 2770-2772.
- [17] S.-H. Chen, D.-S. Chan, C.-K. Chen, T.-H. Chang, Y.-H. Lai, C.-C. Lee, Japanese Journal of Applied Physics, 49 (2010) 015201.
- [18] H. Masuda, H. Asoh, M. Watanabe, K. Nishio, M. Nakao, T. Tamamura, Advanced Materials, 13 (2001) 189-192.
- [19] W. Lee, R. Ji, C.A. Ross, U. Gösele, K. Nielsch, Small, 2 (2006) 978-982.
- [20] J.T. Smith, Q. Hang, A.D. Franklin, D.B. Janes, T.D. Sands, Applied Physics Letters, 93 (2008) 043108.
- [21] Z. Sun, H.K. Kim, Applied Physics Letters, 81 (2002) 3458-3460.
- [22] W. Lee, R. Ji, U. Gösele, K. Nielsch, Nature materials, 5 (2006) 741.
- [23] Y.P. Ivanov, A. Chuvilin, S. Lopatin, J. Kosel, ACS nano, 10 (2016) 5326-5332.
- [24] J.-G. Zhu, Y. Zheng, G.A. Prinz, Journal of Applied Physics, 87 (2000) 6668-6673.
- [25] A. Chumakov, S. Grigoriev, N. Grigoryeva, K. Napolskii, I. Roslyakov, A. Eliseev, A. Okorokov, H. Eckerlebe, Journal of Physics: Conference Series, IOP Publishing, 2010, pp. 012033.
- [26] K. Nielsch, R. Wehrspohn, J. Barthel, J. Kirschner, S. Fischer, H. Kronmüller, T. Schweinböck, D. Weiss, U. Gösele, Journal of Magnetism and Magnetic Materials, 249 (2002) 234-240.
- [27] H. Chiriac, A. Moga, M. Urse, T.-A. Óvári, Sensors and Actuators A: Physical, 106 (2003) 348-351.
- [28] S. Allende, D. Altbir, K. Nielsch, Physical Review B, 80 (2009) 174402.
- [29] C. Bran, E. Berganza, E. Palmero, J. Fernandez-Roldan, R. Del Real, L. Aballe, M. Foerster, A. Asenjo, A.F. Rodríguez, M. Vazquez, Journal of Materials Chemistry C, 4 (2016) 978-984.
- [30] Ó. Iglesias-Freire, C. Bran, E. Berganza, I. Mínguez-Bacho, C. Magén, M. Vázquez, A. Asenjo, Nanotechnology, 26 (2015) 395702.
- [31] L. Arzuza, R. López-Ruiz, D. Salazar-Aravena, M. Knobel, F. Béron, K. Pirota, Journal of Magnetism and Magnetic Materials, 432 (2017) 309-317.
- [32] K. Pitzschel, J. Bachmann, S. Martens, J.M. Montero-Moreno, J. Kimling, G. Meier, J. Escrig, K. Nielsch, D. Görlitz, Journal of Applied Physics, 109 (2011) 033907.
- [33] A. Rotaru, J.-H. Lim, D. Lenormand, A. Diaconu, J.B. Wiley, P. Postolache, A. Stancu, L. Spinu, Physical Review B, 84 (2011) 134431.
- [34] I. Minguez-Bacho, S. Rodriguez-López, M. Vázquez, M. Hernández-Vélez, K. Nielsch, Nanotechnology, 25 (2014) 145301.
- [35] A. Esmaeily, M. Venkatesan, A.S. Razavian, J. Coey, Journal of Applied Physics, 113 (2013) 17A327.
- [36] E.M. Palmero, C. Bran, R.P. del Real, M. Vázquez, Journal of Physics: Conference Series, IOP Publishing, 2016, pp. 012001.
- [37] M.S. Salem, P. Sergelius, R.M. Corona, J. Escrig, D. Görlitz, K. Nielsch, Nanoscale, 5 (2013) 3941-3947.
- [38] C. Bran, Y.P. Ivanov, J. Kosel, O. Chubykalo-Fesenko, M. Vazquez, Nanotechnology, 28 (2017) 095709.
- [39] F. Béron, L.-P. Carignan, D. Ménard, A. Yelon, IEEE Transactions on Magnetics, 44 (2008) 2745-2748.

CABALLERO-CALERO, Olga; MARTÍN-GONZÁLEZ, Marisol. 3D porous alumina: a controllable platform to tailor magnetic nanowires. *Magnetic Nano-and Microwires*. Woodhead Publishing, 2020. p. 3-20.

- [40] S. Moraes, D. Navas, F. Béron, M. Proenca, K. Pirola, C. Sousa, J. Araújo, *Nanomaterials*, 8 (2018) 490.
- [41] A.J. Grutter, K.L. Krycka, E.V. Tartakovskaya, J.A. Borchers, K.S.M. Reddy, E. Ortega, A. Ponce, B.J. Stadler, *ACS nano*, 11 (2017) 8311-8319.
- [42] R. Sanz, M. Vazquez, K. Pirola, M. Hernandez-Velez, *Journal of applied physics*, 101 (2007) 114325.
- [43] R. Sanz, M. Hernández-Vélez, K.R. Pirola, J.L. Baldonado, M. Vázquez, *Small*, 3 (2007) 434-437.
- [44] J. García, V. Prida, V. Vega, W.d.O.d. Rosa, R. Caballero-Flores, L. Iglesias, B. Hernando, *Journal of Magnetism and Magnetic Materials*, 383 (2015) 88-93.
- [45] M. Rauber, I. Alber, S. Müller, R. Neumann, O. Picht, C. Roth, A. Schökel, M.E. Toimil-Molares, W. Ensinger, *Nano letters*, 11 (2011) 2304-2310.
- [46] M.F. Wagner, F. Völklein, H. Reith, C. Trautmann, M.E. Toimil-Molares, *physica status solidi (a)*, 213 (2016) 610-619.
- [47] A. Vlad, V.-A. Antohe, J.M. Martinez-Huerta, E. Ferain, J.-F. Gohy, L. Piraux, *Journal of Materials Chemistry A*, 4 (2016) 1603-1607.
- [48] E. Araujo, A. Encinas, Y. Velázquez-Galván, J.M. Martínez-Huerta, G. Hamoir, E. Ferain, L. Piraux, *Nanoscale*, 7 (2015) 1485-1490.
- [49] T. da Câmara Santa Clara Gomes, J. De La Torre Medina, M. Lemaitre, L. Piraux, *Nanoscale research letters*, 11 (2016).
- [50] G. Williams, M. Hunt, B. Boehm, A. May, M. Taverne, D. Ho, S. Giblin, D. Read, J. Rarity, R. Allenspach, *Nano Research*, 11 (2018) 845-854.
- [51] J. Martín, M. Martín-González, J. Francisco Fernández, O. Caballero-Calero, *Nat Commun*, 5 (2014) 5130.
- [52] B. Abad, J. Maiz, A. Ruiz-Clavijo, O. Caballero-Calero, M. Martin-Gonzalez, *Scientific reports*, 6 (2016).
- [53] A. Ruiz-Clavijo, O. Caballero-Calero, M. Martín-González, *Nanomaterials*, 8 (2018) 345.
- [54] A. Ruiz-Clavijo, S. Ruiz-Gómez, O. Caballero-Calero, L. Pérez, M. Martín-González, *physica status solidi (RRL)—Rapid Research Letters*, Accepted for Publication, doi: 1.01002/pssr201900263 (2019).
- [55] P.M. Resende, R. Sanz, A. Ruiz-de Clavijo, O. Caballero-Calero, M. Martin-Gonzalez, *Coatings*, 6 (2016) 59.