Appendix

Appendix A: Ferromagnetic resonance measurements

This part is transcribed from the paper [6]. The measurements, analysis of the results and the model were made by Yenni Velázquez-Galvan and Joaquím De la Torre Medina. The measurements were made on the same samples that were used in this work.

For those FMR measurements a microstrip line wave-guide configuration has been used, as depicted in Figure 71 [108, 4]. A 500 mm wide and 500 nm thick microstrip was evaporated on the free surface of the PC membrane after electrodeposition. FMR measurements were performed at room temperature at a constant frequency in the range of 100 MHz to 50 GHz, by sweeping the magnetic field applied in the OOP direction from 10 kOe down to zero field.

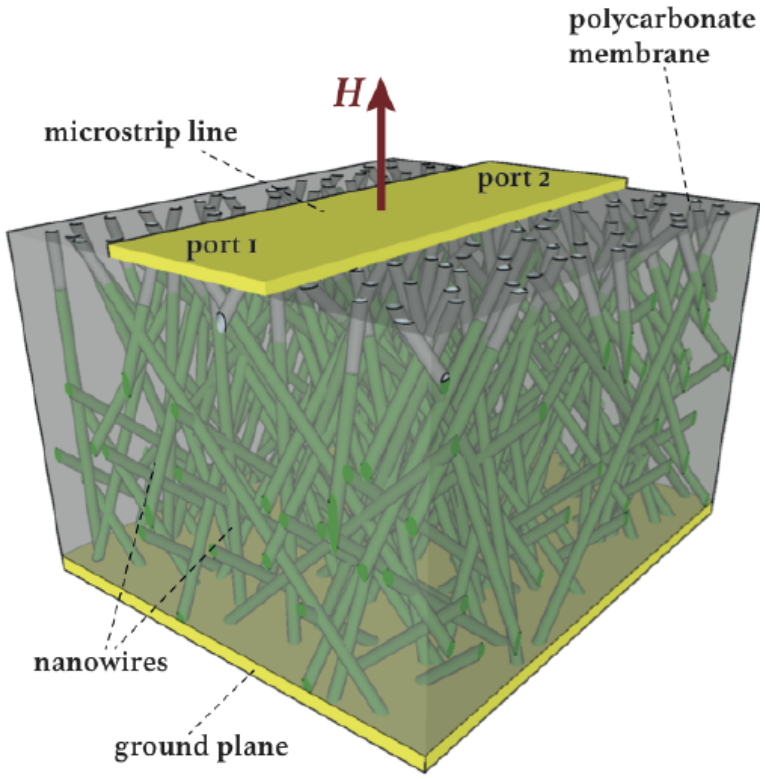

Figure 71: Schematic representation of a 3D PC template prepared by successive irradiation steps (under an angular range of ±45° relative to the out-of-plane direction, before and after PC film rotation by 90°), featuring cylindrical nanopores with a mean diameter of 40 nm and partially filled with magnetic CNWs. Schematic of a stripline transmission line for FMR measurement fabricated using similar partially filled membrane. Image From [6]

Information about the magnetic properties of the distinct CNWs networks can be obtained from FMR measurements. Figure 72 (a) shows the comparison between the absorption spectra for the Ni and NiFe CNWs networks at the excitation frequency f = 20 GHz. As observed, the resonance field (H_r) given by the minimum of the spectra is lower for the NiFe than for the Ni sample, which is consistent with a larger anisotropy field for the former. Indeed, this feature is also observed in Figure 72 (b) as the f vs. H_r dispersion relation for the Ni CNWs network is located at lower frequencies in

comparison with the NiFe CNW network.

On the other hand, the effect of the solution pH on the magnetic anisotropy of Co CNWs is clearly observed from both absorption spectra and their corresponding relation dispersions shown in Figure 72 (c) and (d). For Co CNWs networks the observed behaviour in these figures is very similar to what is reported previously for Co parallel NWs arrays [1]. That is, the resonance frequencies for the samples with pH 3.6 and 5 are lower than those for the MS case (pH 2.0), which is consistent with the configuration where the c-axis is oriented perpendicular to the nanowire axis. Conversely, the higher resonance frequencies observed for the pH 6.4 sample is consistent with the reinforcement of the magnetisation along the nanowires axis by the addition of the MC contribution.

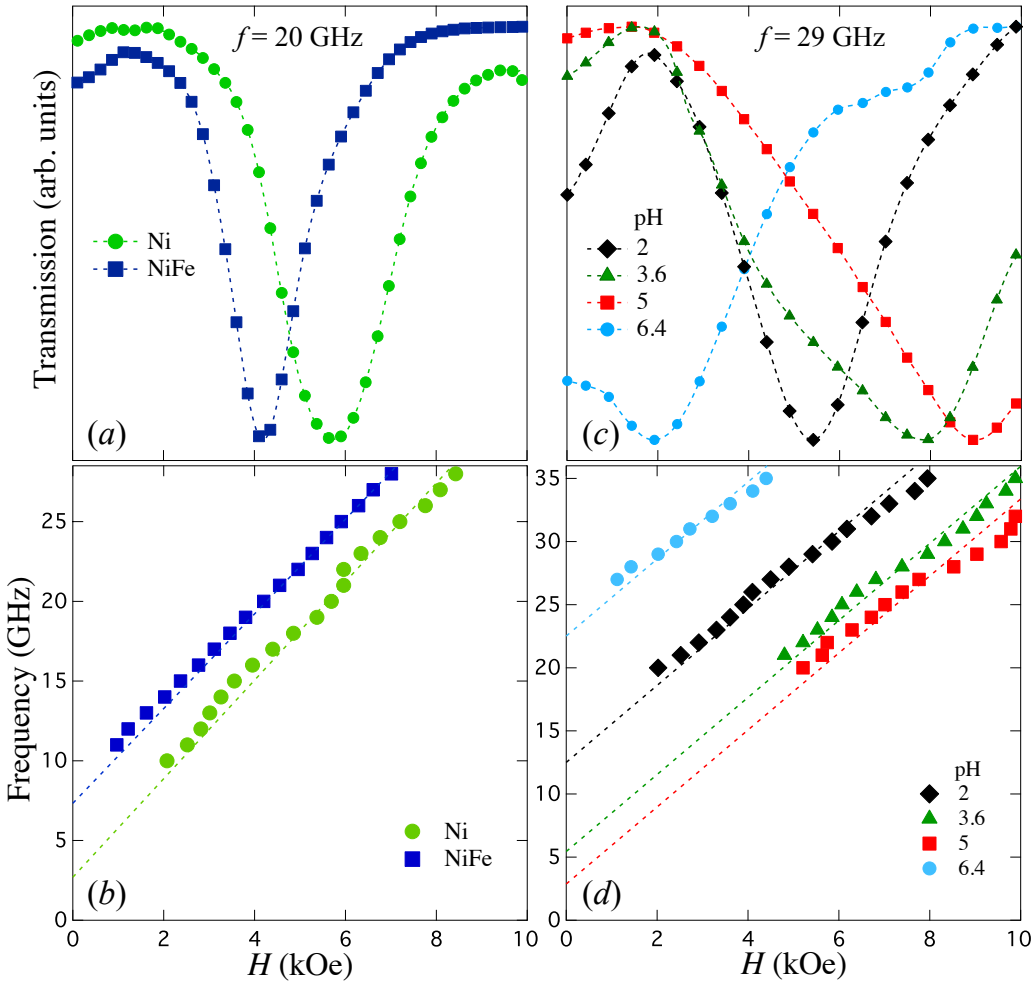

Figure 72: (a) Comparison of the measured FMR spectra with a magnetic field applied in the OOP direction on Ni and NiFe CNW networks at 20 GHz. (b) Comparison of the corresponding dispersion relations for Ni and NiFe CNW networks. The dashed lines correspond to the fits to Eq. (1). (c) FMR spectra recorded at 29 GHz on Co CNWs networks grown at pH values of 2.0, 3.6, 5.0 and 6.6. (d) The corresponding dispersion relations for the absorption spectra in (c). Image From [6]

The magnetic properties of CNWs networks can be characterized quantitatively by determining its corresponding effective anisotropy field H_{eff}. To this end, consider a uniform distribution for the NWs orientation in the range $-\theta \leq \theta_0 \leq \theta$ with respect to the normal of the membrane plane or z-axis (OOP : out-of-plane). In this range, θ is the maximum angle of all possible orientations of the NWs

represented by θ_0. The orientation of the NWs spans along both the x- and y-axes and interconnections between NWs take place randomly. In order to determine the FMR condition that accounts for all the possible orientations of the NWs in this range, let us consider first the FMR condition for an array of NWs tilted to an angle θ_0 with respect to the OOP direction:

$$\left(\frac{f}{\gamma}\right)^2 = [H_{eff}\cos(2\theta_0) + H_r\cos(\theta_0 - \theta_H)] \times [H_{eff}\cos^2(\theta_0) + H_r\cos(\theta_0 - \theta_H)] \quad (79)$$

where γ is the gyromagnetic ratio, H_r is the resonance field and θ_0 and θ_H are respectively the angles that the saturated magnetisation and the applied field make with respect to the NWs axis. Since FMR measurements are carried out in the saturated state with H along the OOP direction, then the angle $\theta_0 = \theta_H$ between the OOP direction and the NWs axis lie in the range $-\theta \leq \theta_0 \leq \theta$. Since billions of NWs are probed at the same time in the measurements, recorded FMR spectra provide average field values for a specific excitation frequency. Considering the symmetry of the NWs orientations with respect to the OOP direction, negative angles in the range $-\theta \leq \theta_0 \leq 0$ provide FMR contributions that are equivalent to those for positive angles. After some algebraic manipulation and performing the angular average of Equation 79 over the range $0 \leq \theta_0 \leq \theta$, the average resonance condition reads:

$$\left(\frac{f}{\gamma}\right)^2 = H_r^2 + \frac{1}{2}H_{eff}H_r\left(1 + \frac{3}{\theta}\int_0^\theta \cos(2\theta_0)\ \mathrm{d}\theta_0\right) + \frac{1}{4}H_{eff}^2\left(1 + \frac{1}{\theta}\int_0^\theta (2\cos(2\theta_0) + cos(4\theta_0))\ \mathrm{d}\theta_0\right) \quad (80)$$

Which gives:

$$\left(\frac{f}{\gamma}\right)^2 = H_r^2 + C_1H_{eff}H_r + C_2H_{eff}^2 \quad (81)$$

where C_1 and C_2 are constants that result from the averaging process:

$$C_1 = \frac{1}{2}\left(1 + \frac{3}{2\theta}\sin(2\theta)\right) \quad (82)$$

and

$$C_2 = \frac{1}{4}\left(1 + \frac{1}{\theta}\sin(2\theta) + \frac{1}{4\theta}\sin(4\theta)\right) \quad (83)$$

Equation 81 can be used as a fitting function for the determination of the effective field (H_{eff}), however, H_{eff} can be directly obtained from the extrapolated zero field resonance frequency ($f(H_r = 0) = f_0$) as this function is a straight line, that is:

$$H_{eff} = \frac{f_0}{\gamma\sqrt{C_2}} \quad (84)$$

For the case of Ni, NiFe and Co (pH 2.0) CNWs networks only magnetostatic contributions are present in the anisotropy field, then $H_{eff} = H_{ms}$. However, for the case of Co CNWs networks with magnetocrystalline contributions $H_{eff} = H_{ms} \pm H_{mc}$, so the magnetocrystalline field can be easily determined as $H_{mc} = \pm(H_{eff} - H_{ms})$ by using the previously determined magnetostatic field (H_{ms}) for the Co (pH 2.0) sample. The $\pm$ sign in this expression is used when the c-axis is oriented in the direction parallel (perpendicular) to the NWs axis. In this way, H_{eff} and H_{mc} are obtained using Equation 84, but with the respective expression for the effective field depending on the CNW network considered under analysis. The effective field for the Ni, NiFe and Co (pH 2.0) CNWs networks

determined using Eq. (2) are respectively 1.16, 3.2 and 5.44 kOe. Since the constant $C_2 < 1$ in this equation, then the corresponding f_0 values for CNWs networks are lower than the expected ones for the case of parallel NWs arrays that are given by the expression $f_0 = \gamma H_{eff}$ [108]. This decrease of f_0 for CNWs networks is consistent with the contributions of tilted parallel NWs array to different orientations [4]. Besides, Figure 73 shows the variation of the anisotropy fields H_{eff} and H_{mc} vs. the solution pH for Co CNW networks measured with the external field in the OOP direction. These fields have been determined using Equation 84 for $\theta = \frac{\pi}{4}$, where error bars around this angle take into account the $\pm 5^{\circ}$ angular dispersion of the ions bombardment in the track etching process of the PC membrane. The magnetostatic field $H_{ms} = H_{eff}$ for the pH 2.0 sample, obtained using Equation 84, has been used as input parameter into this same equation in order to obtain the corresponding H_{mc} value from H_{eff} for the case of Co CNWs networks with pH > 2. As seen in Figure 73, H_{ms} is negative for the samples with pH 3.6 and 5.0 and positive for the pH 6.4 sample, so this field lies in the range from -4.20 to 4.35 kOe. Particularly, H_{eff} has the lowest value for the Co (pH 5.0) sample as it is nearly isotropic.

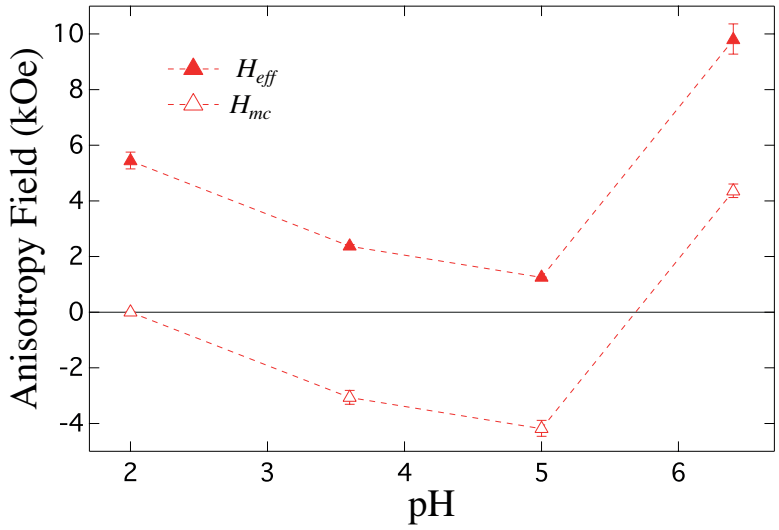

Figure 73: Variation of the effective anisotropy field H_{eff} and its magnetocrystalline contribution H_{mc} with the pH of the electrolyte solution used to deposit Co CNWs networks. The error bar takes into account the $\pm 5^{\circ}$ angular dispertion of the heavy ions bombardment of the polycarbonate template. Dotted lines are guides for the eye. Figure from [6].