Universidad de Oviedo

Lomonosov Moscow State University

Nanostructured materials: synthesis, structural and magnetic properties

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TNT2008 Trends in NanoTechnology Oviedo (Spain) September 01-05, 2008

USC UNIVERSIDADE DE SANTIAGO DE COMPOSTELA

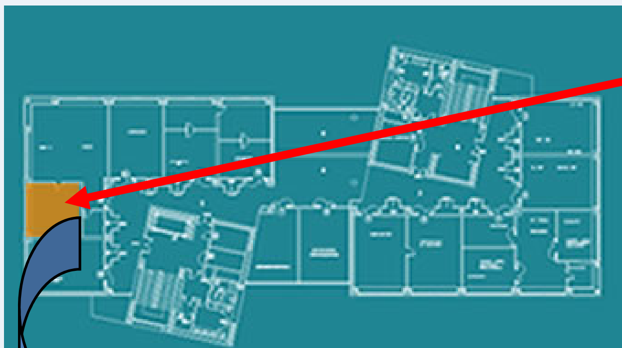
Outline of the work:

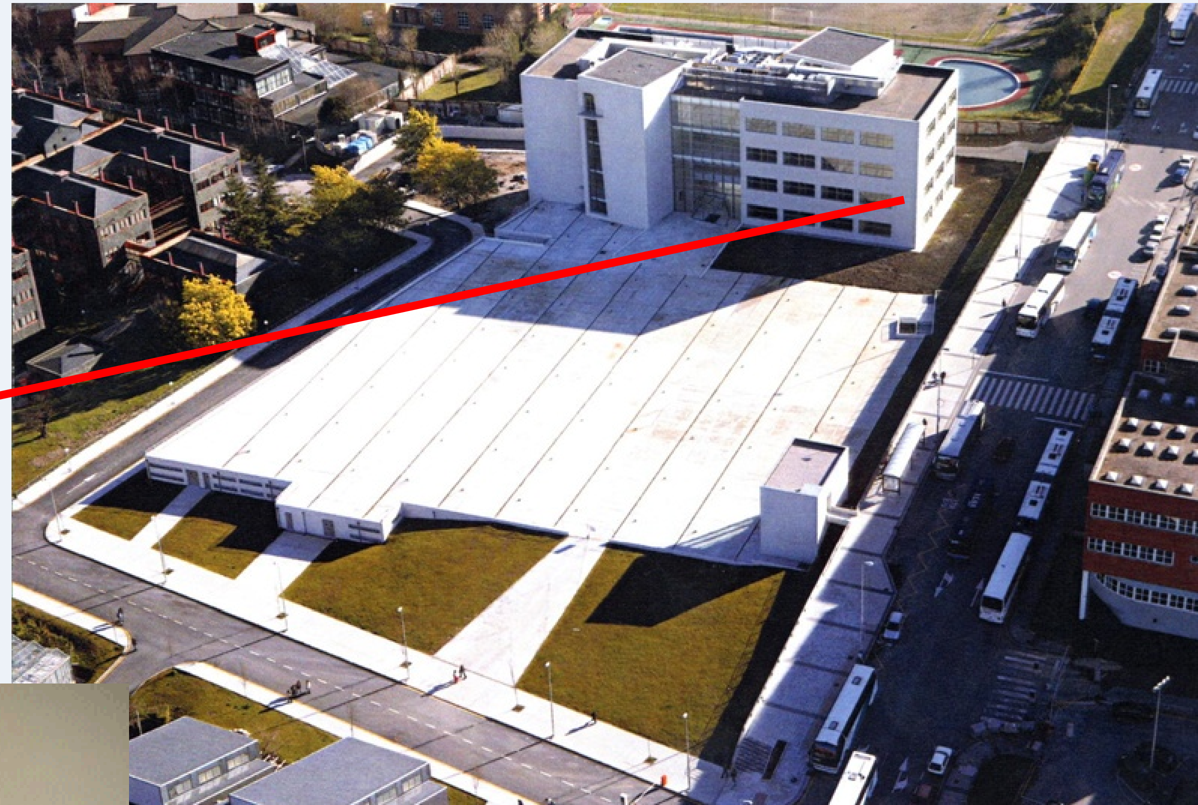
- Synthesis and characterization of nanoporous anodic alumina membranes (NAAMs) as templates.
- Fabrication of magnetic/metallic nanowires by electrodeposition in NAAMs.
- Synthesis of anodic Titanium oxide nanotubes for UV self-cleaning sensors of organic contaminants, (oils, hydrocarbons).
- Hexagonally ordered nanoholes array magnetic films by replicating NAAMs.
- MCE: Arrays of nanostructured ferromagnetic nanowires for magnetic refrigerant devices.

http://www10.uniovi.es/SCTs/servicios/cristo/membranas/servicioCC16presentacion.html

Universidad de Oviedo

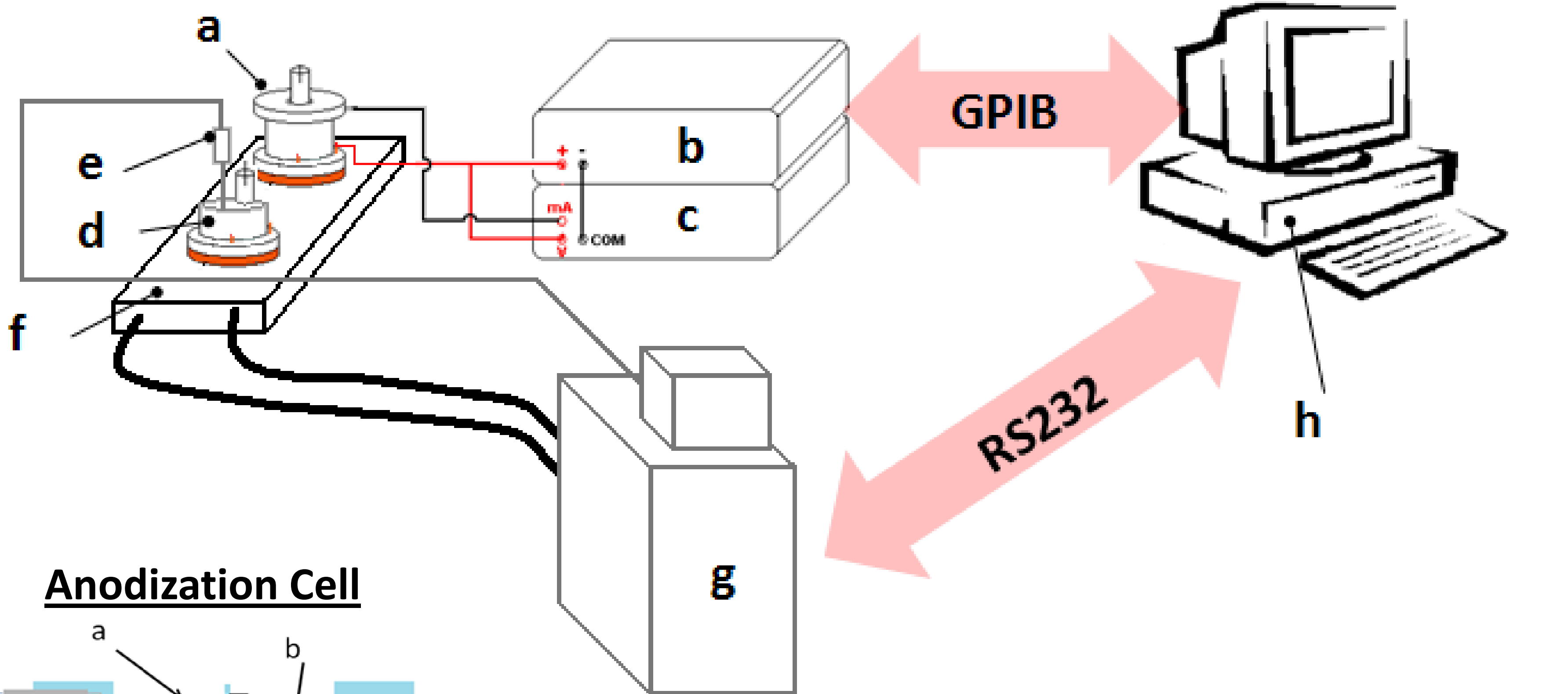
Scientific-Technological Common Services SCT´s UniOvi.



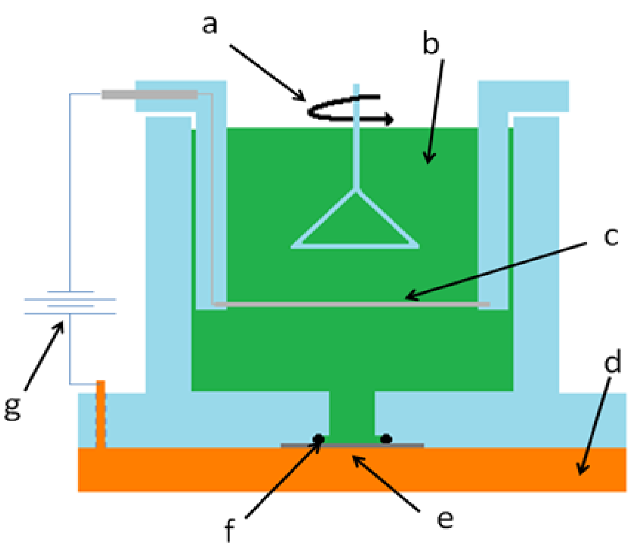


Nanostructured Functional Materials & Nanoporous Membranes Laboratory at University of Oviedo

Home-made experimental anodization setup:



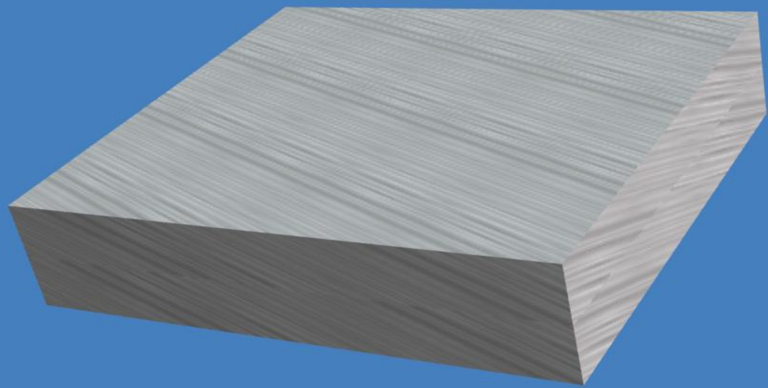
Anodization Cell



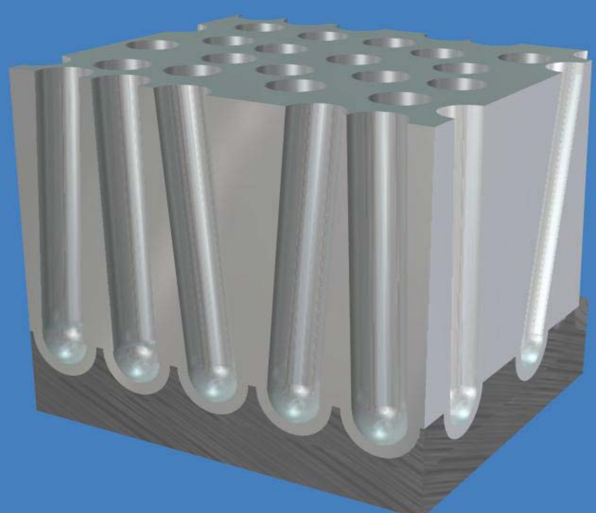
Potentiostatic anodization: Constant dc Voltage between the two electrodes (sample and Pt grid).
Controll of the anodization parameters as:
type of electrolite, pH, Temperature, value of the applied voltage.
Agitation system for continuous renewing the solution.

Synthesis of Nanoporous Anodic Alumina Templates:

(two-step anodization process)

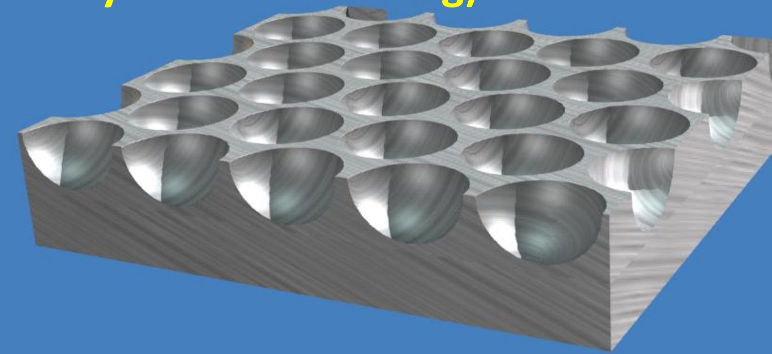


a) starting foil: high purity Al (99,999%)

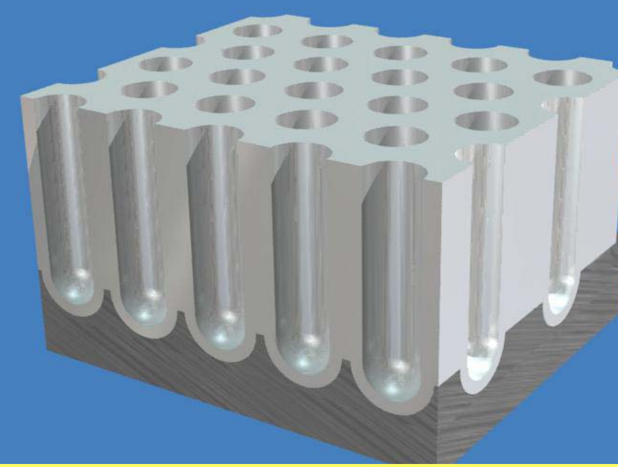


b) first anodization process:
(nanopores randomly oriented)

c) Aluminium template:
(after removing alumina porous layer by chemical etching)

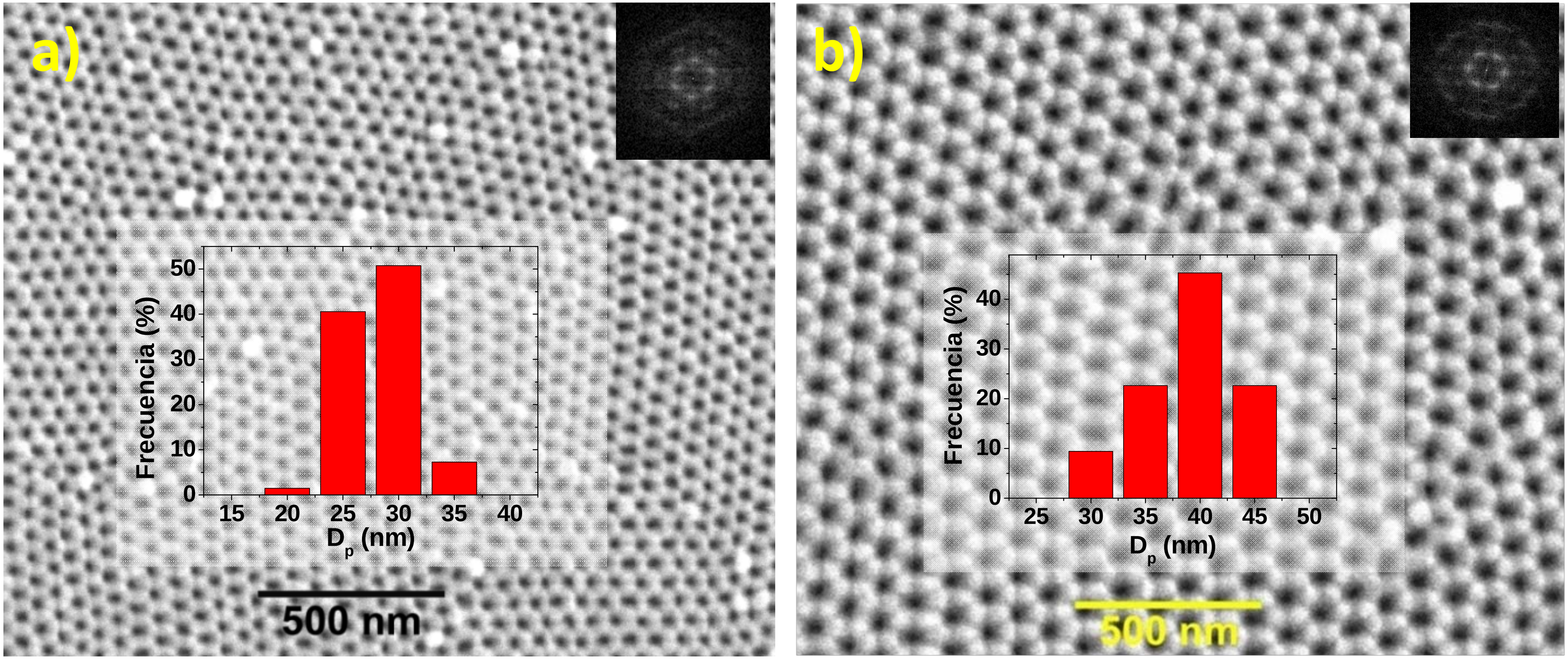


d) second anodization process:
(nanopores self-ordered grown hexagonally centered)



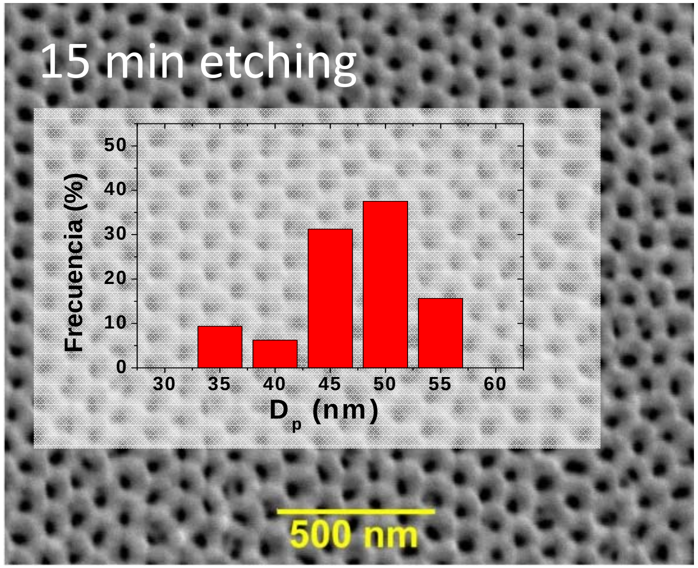
Highly-ordered alumina pore structures:
Masuda & Fukuda Science (1995)

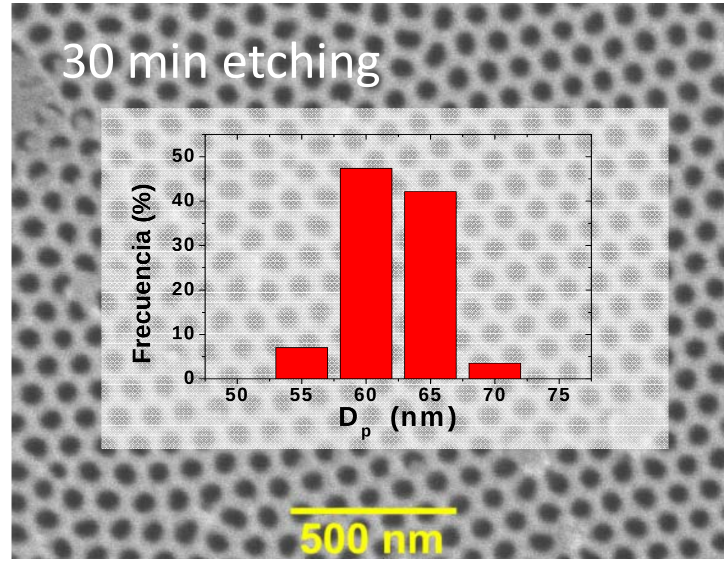
Sample	Electrolite	T (ºC)	V_{anod} (V)	First anodization time (hours)	Second anodization time (hours)	d_{pores} (nm)	$D_{interpores}$ (nm)	Porosity (%)
a)	H_2SO_4 0,47 M	1	25	10	1	26±3	62±4	16
b)	$(COOH)_2$ 0,3 M	2-3	40	92	2	37±4	102±6	12

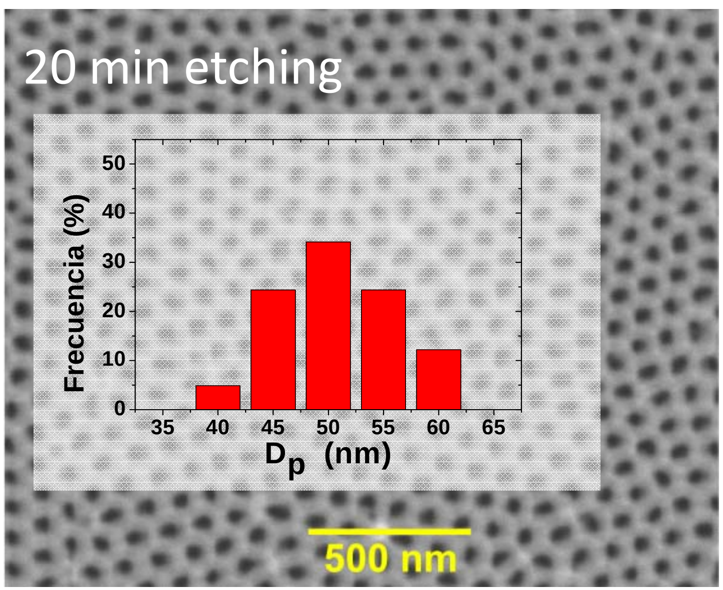


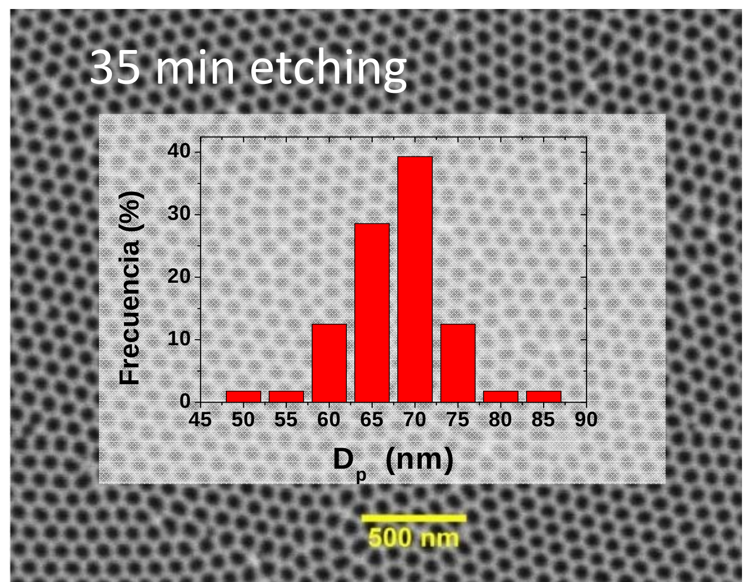
Nanopores widening

NAAM (Oxalic) after a controlled etching in phosphoric acid 5% wt. and at 30ºC

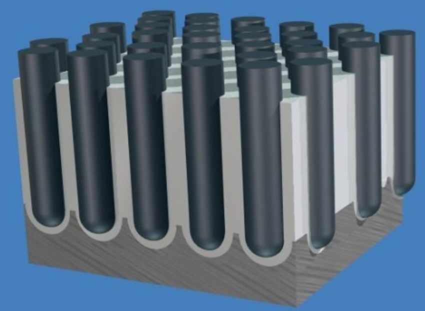






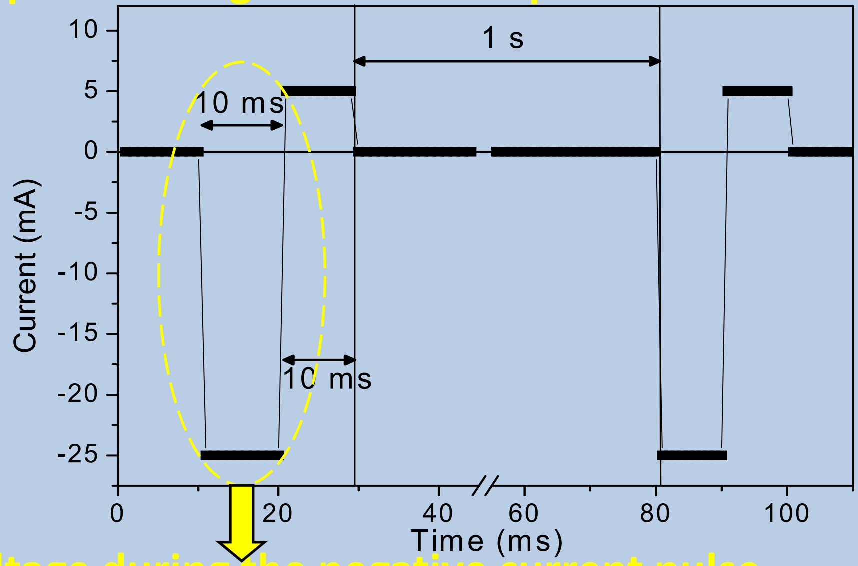


Synthesis of Metallic Nanowires by Pulsed Electrodeposition

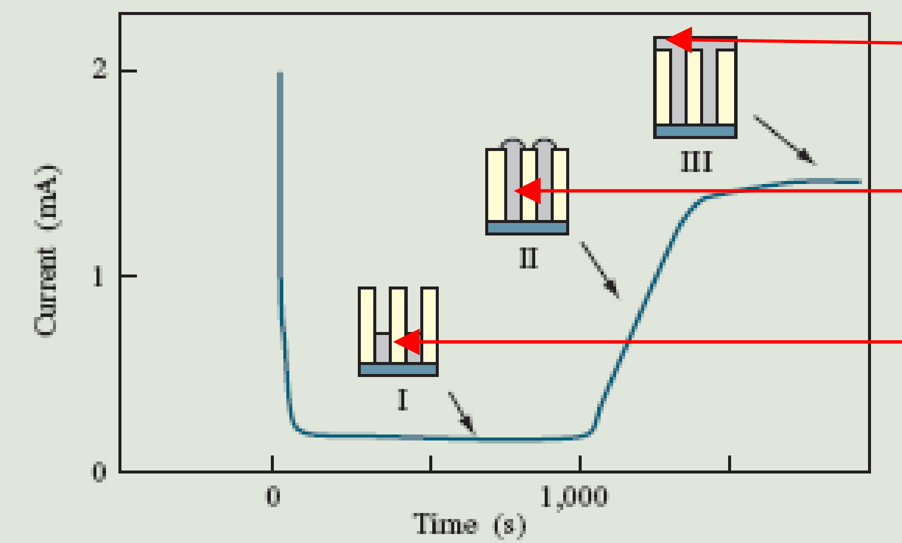


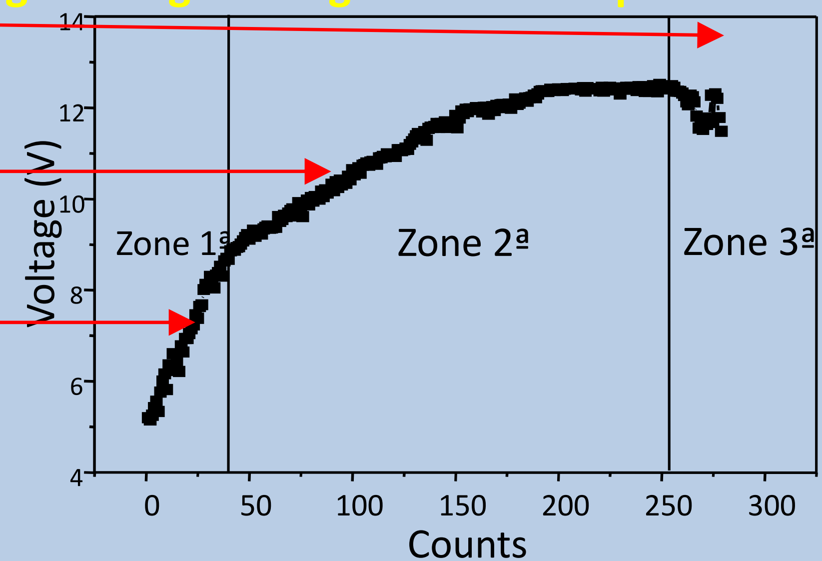
Vertically aligned & ordered array of nanowires in anodic alumina templates

Current pulse during the electrodeposition



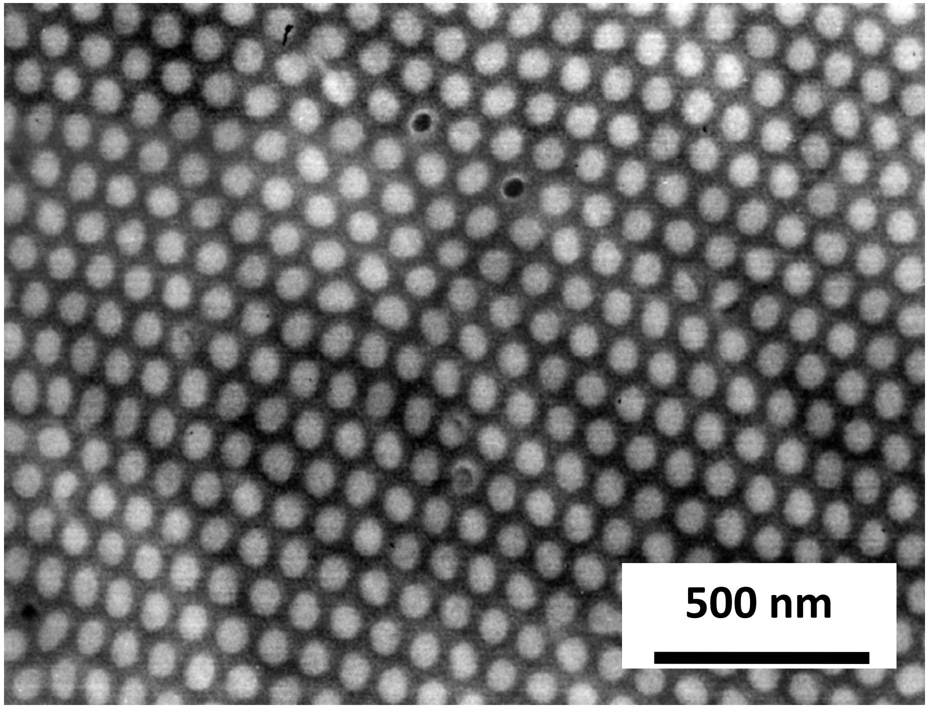
Voltage during the negative current pulse



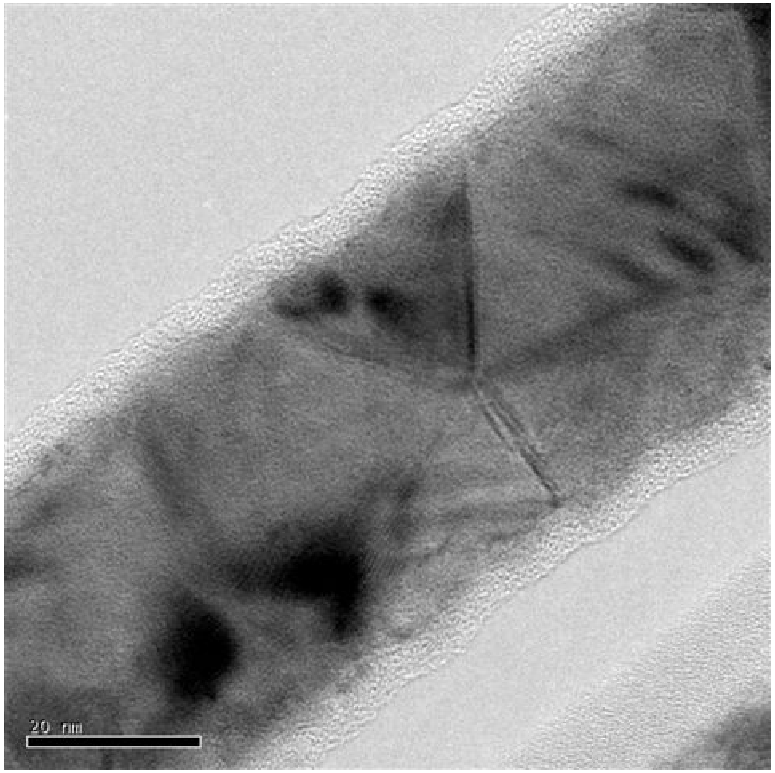


Nielsch Adv. Mater. 2000; Pirota J.A.& C. 2004; L. Sun et al. IBM J. Res. & Dev. 2005

Characterization: Nickel nanowires in NAAMs

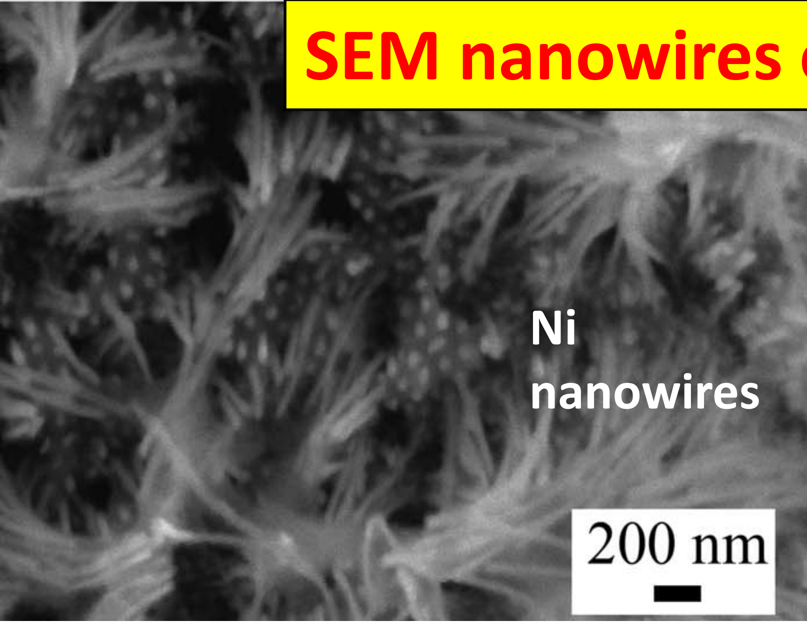


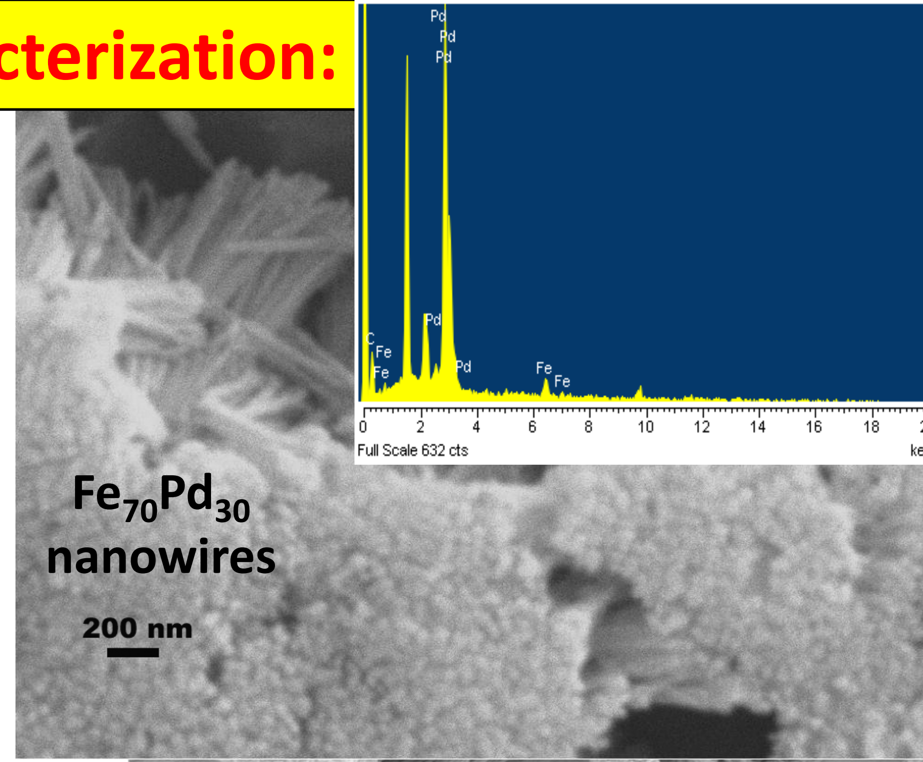
HR-SEM of an uniform Ni filled NAAM template by pulsed electrodeposition
d pore = 35 nm = d nanowire
Dinterpore = 105 nm = Dnw interspacing
Nanowires length = order of microns

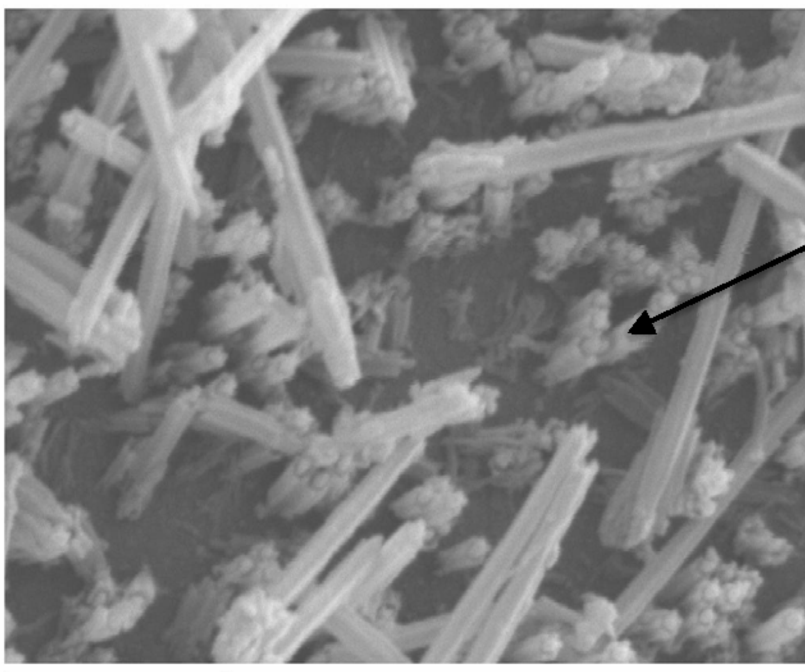


TEM image of an isolated Ni nanowire showing its polycrystalline nanostructure.

SEM nanowires characterization:

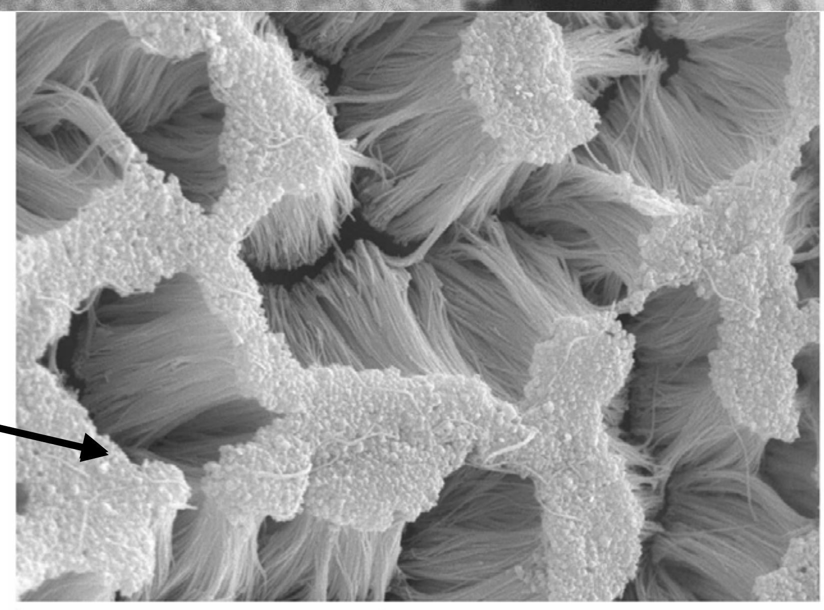




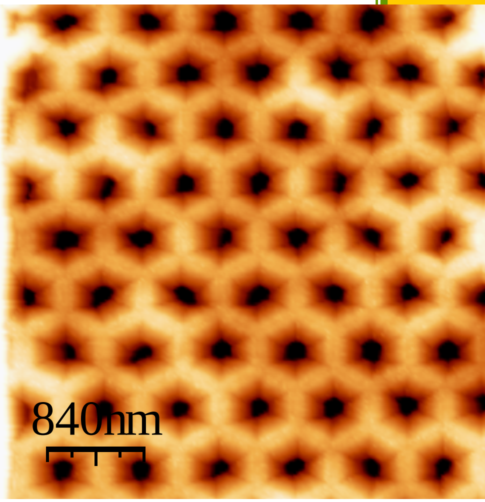


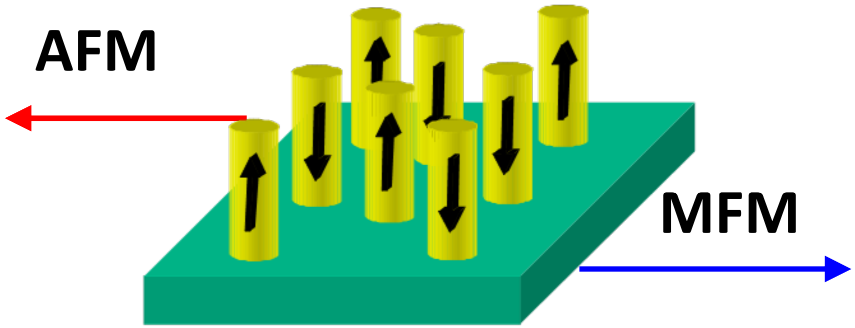
$Ni_{80}Fe_{20}$ nanowires

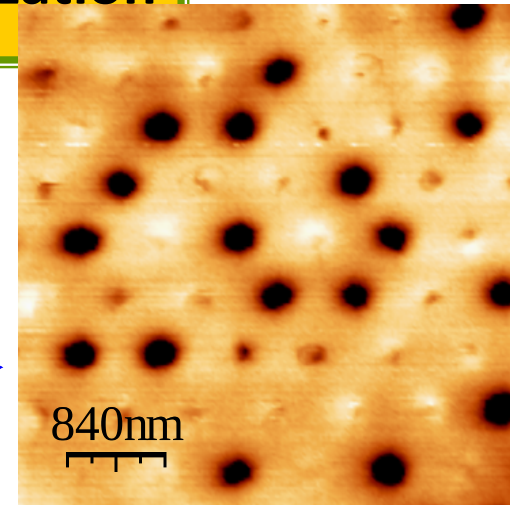
Co nanowires arrays (after etching in NaOH)



AFM and Magnetic MFM characterization



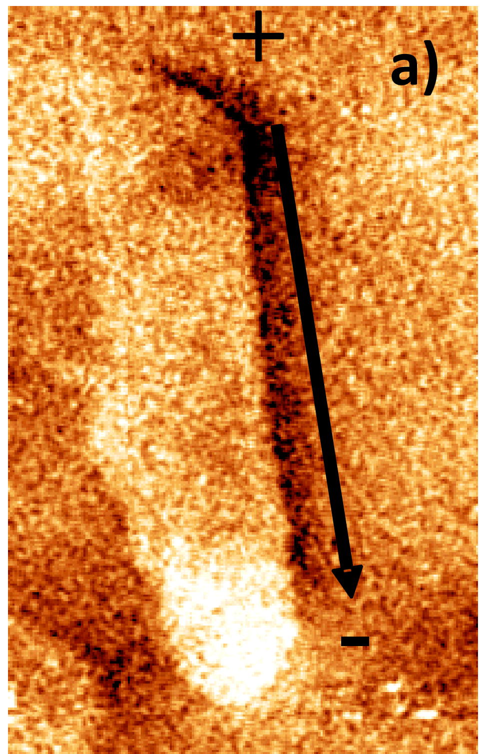


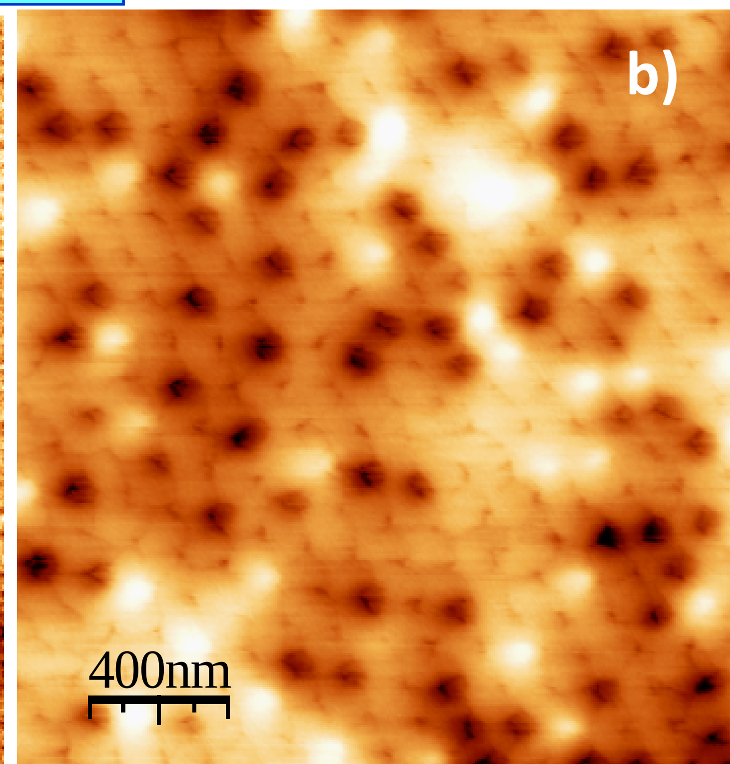


- single domain nanomagnets

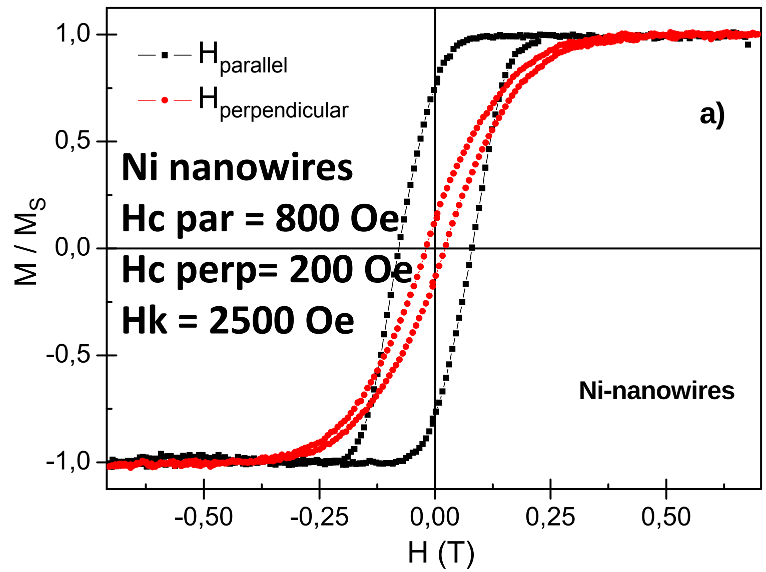
a) MFM image of an isolated Ni nanowire showing its dipolar magnetic structure. The nanowire has 4 μm length and 35 nm diameter.

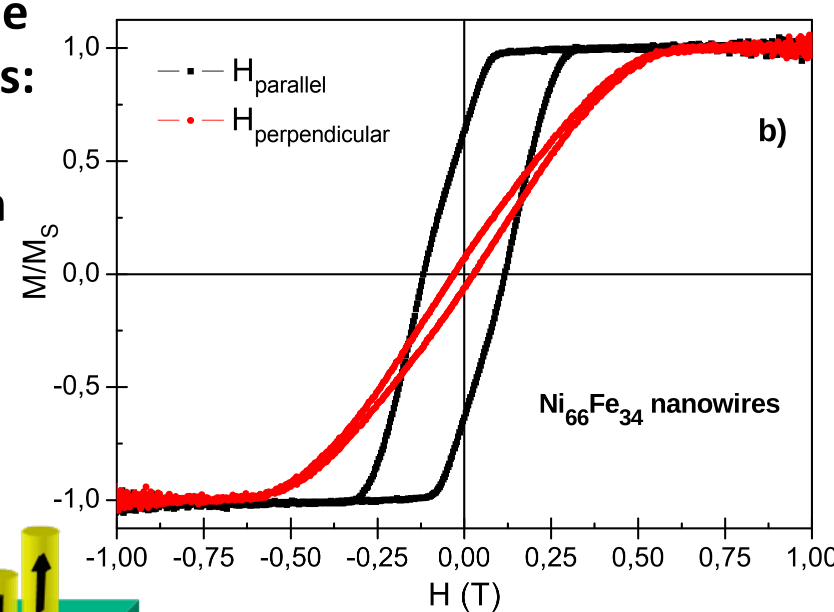
b) MFM image of an array of $Ni_{69}Fe_{31}$ nanowires embedded in an AAM template in its remanent magnetic state



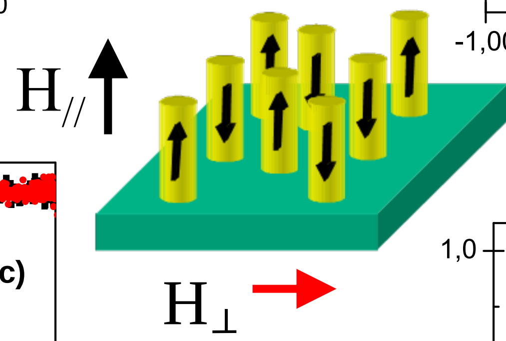


Oxalic made membranes:
d = 35 nm
D = 105 nm

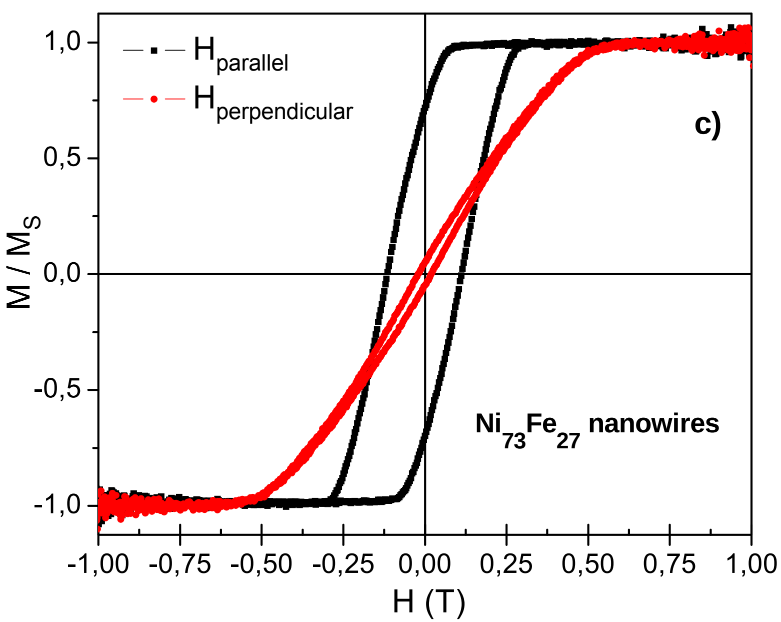


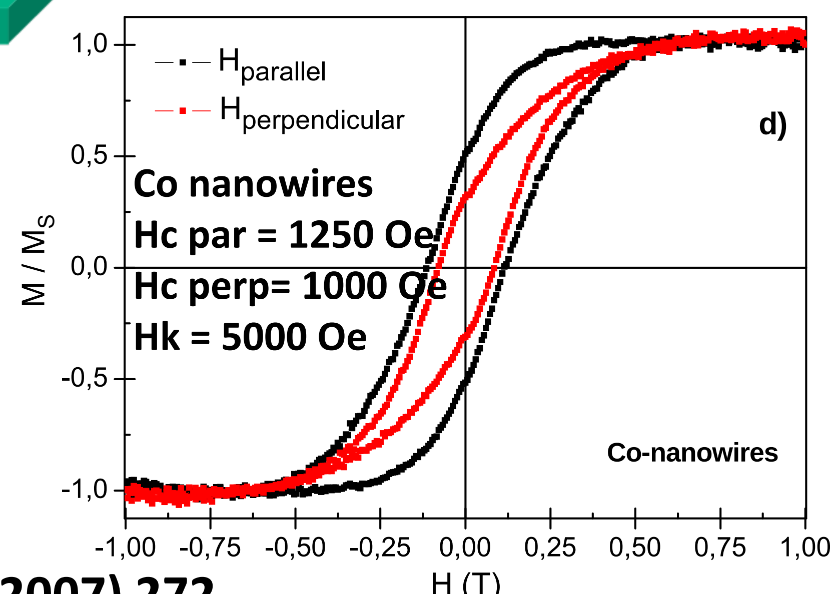


Shape anisotropy



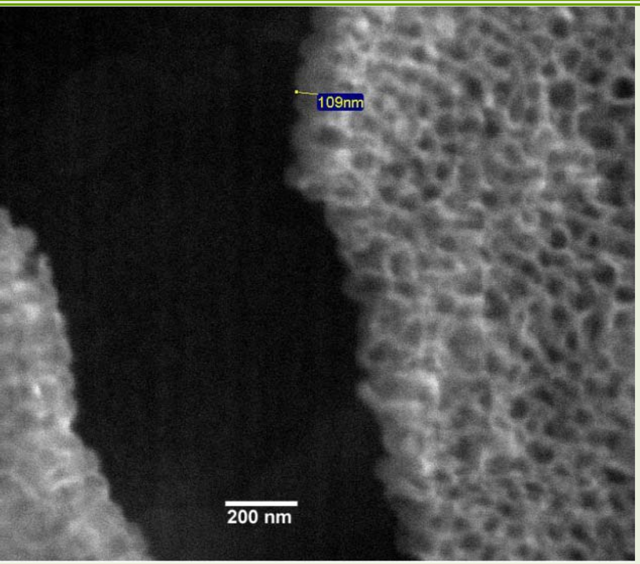
Shape anisotropy / Magnetocrystalline

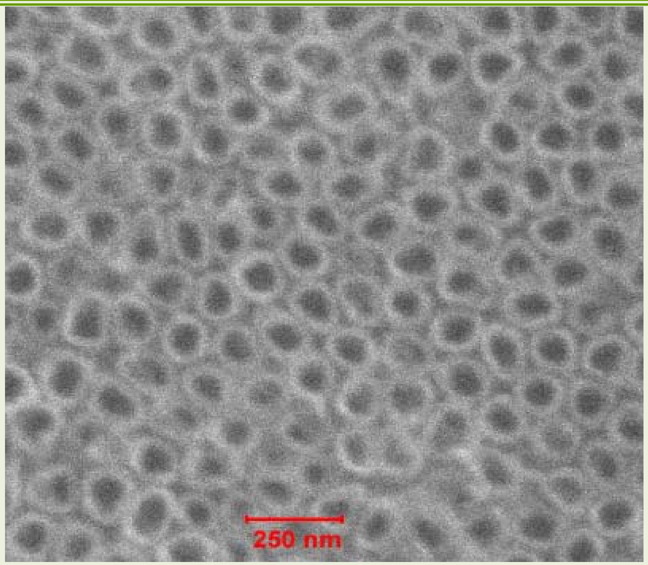


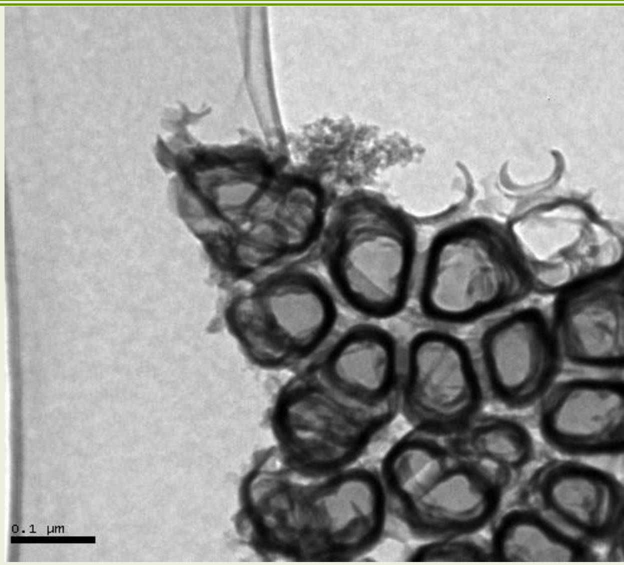


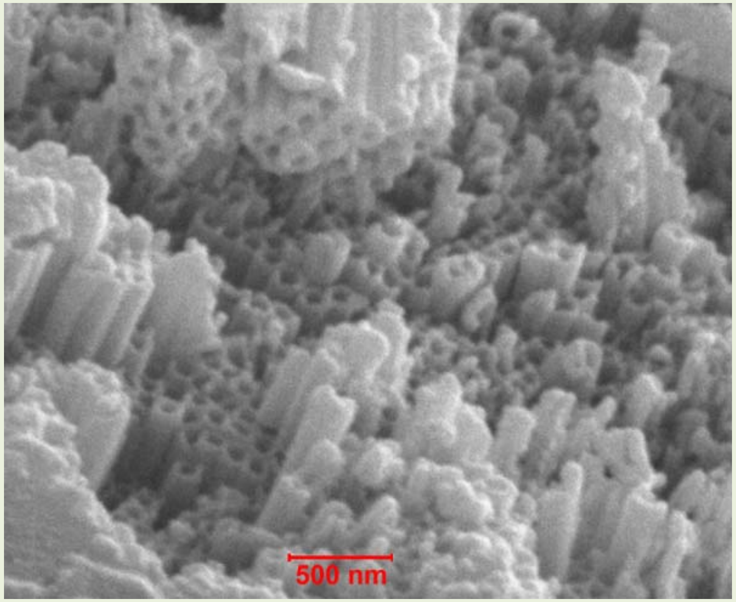
V.M. Prida et al, J. Nanosci. Nanotechnol. 7, (2007) 272

Anodic TiO_2 nanotubes: self-cleaning contaminant sensors







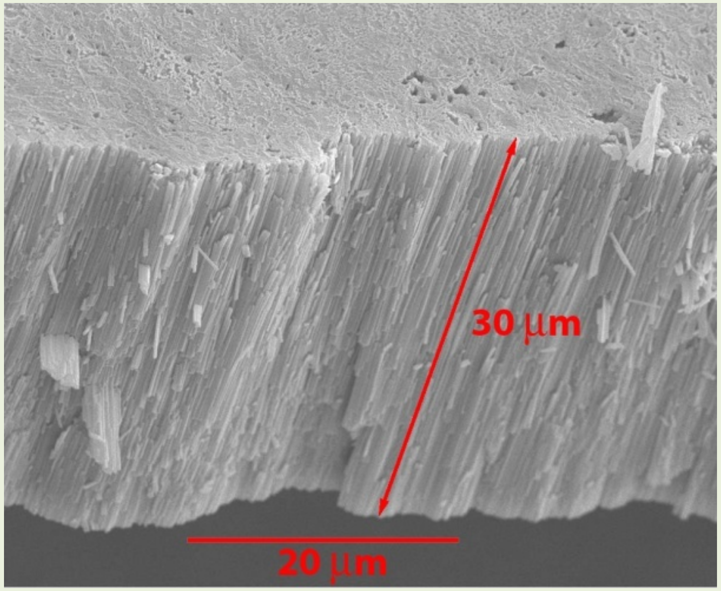


dnt = 40-100 nm

Wthick = 20-60 nm

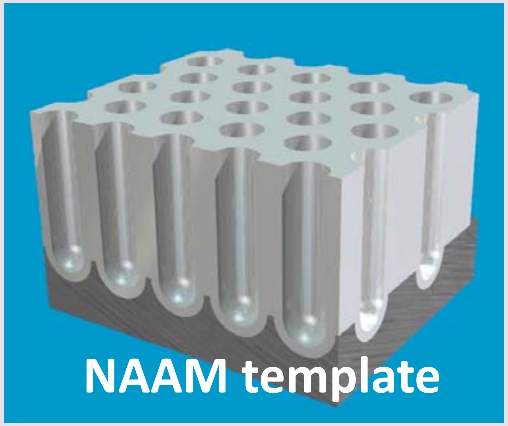
L = 200 nm-microns

Self-cleaning under UV radiation.

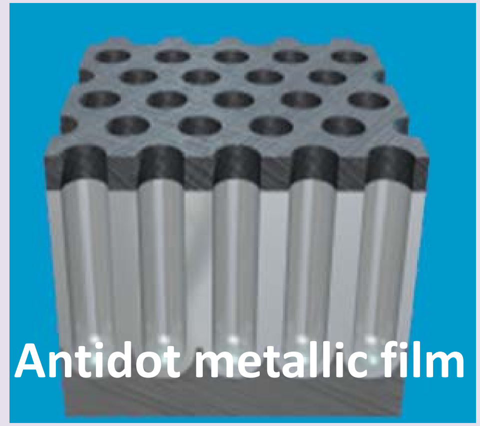


Research Project PCTI-FICyT: FC06-PC041; *V. Vega et al*, Nanoscale Res. Lett. 2, (2007) 355

Magnetic/metallic films with hexagonally ordered nanoholes array

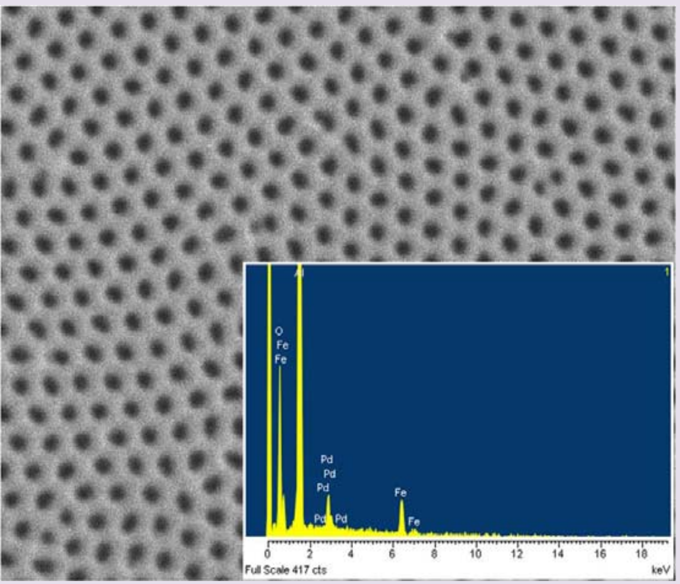


Vacuum Thermal evaporation

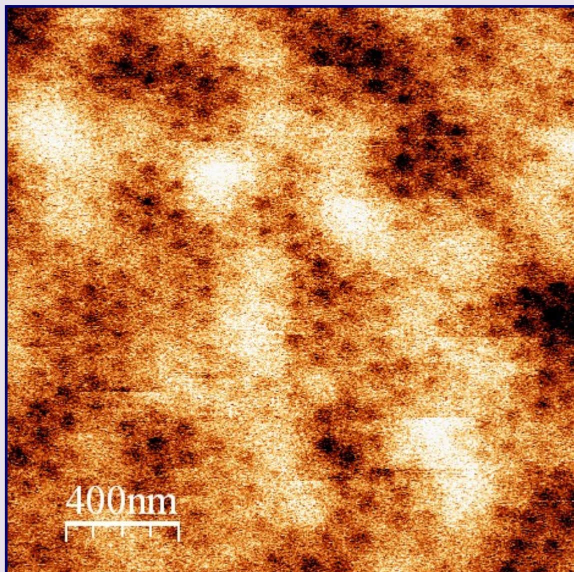


Hexagonally ordered nanoholes magnetic films fabricated as replicas of ceramic nanoporous alumina templates

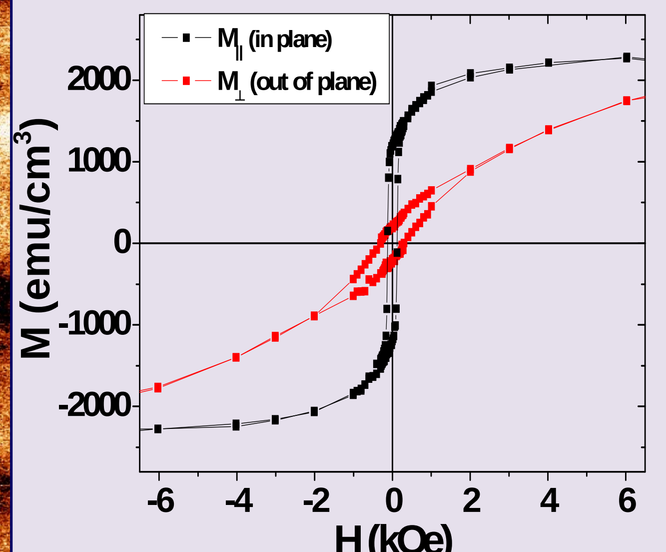
SEM



MFM



VSM



* *V. Vega*, **POSTER PA-49**
Project: UNOV-08-MB-1.

Thickness (nm)	H_c par (Oe)	M_r/M_s PAR	H_c perp (Oe)	M_r/M_s PERP	$H_{k\ PERP}$ (kOe)
49	125	0.51	300	0.08	10

Magnetocaloric Effect in Nano-materials: application to self-assembled Magnetic Nanowires

Aim:

Nanostructured ferromagnetic alloys in form of thin films, or as arrays of self-ordered nanowires embedded in NAAM templates exhibiting high uniaxial shape anisotropy, are able to overcome thermal fluctuations even in very small sizes.

This effect is a clear disadvantage in bulk thermoelastic alloys that are not suitable for their use in rapid actuation of microsensors or actuators because of the response speed of actuators is significantly limited by the heat conduction of the material itself.

MCE: related to the capacity of a magnetic material for changing its temperature under the applying or removing a magnetic field.

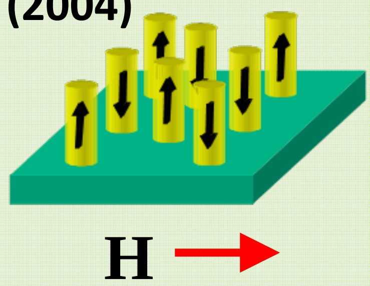
Purpose: employ of Nanostructured materials in magnetic refrigeration devices.

Theoretically simulations predict the coexistence of both regimes, positive and negative magnetocaloric effect (**MCE**) in a material having a single magnetic phase transition.

Model: ensemble of single domain particles, whose easy magnetization axes lie parallel aligned and the uniaxial oriented particles are perpendicularly magnetized with respect to their easy axis. (Non-interacting model) simulated for different temperatures.

The MCE regime can be controlled by the applied magnetic field.

V. Franco and A. Conde,
J. Magn. Magn. Mater.
(2004)



Basic equations: $E = -\mu_0 M_s VH(\hat{e}_m \cdot \hat{e}_h) + KV(\hat{e}_m \wedge \hat{e}_k)^2$

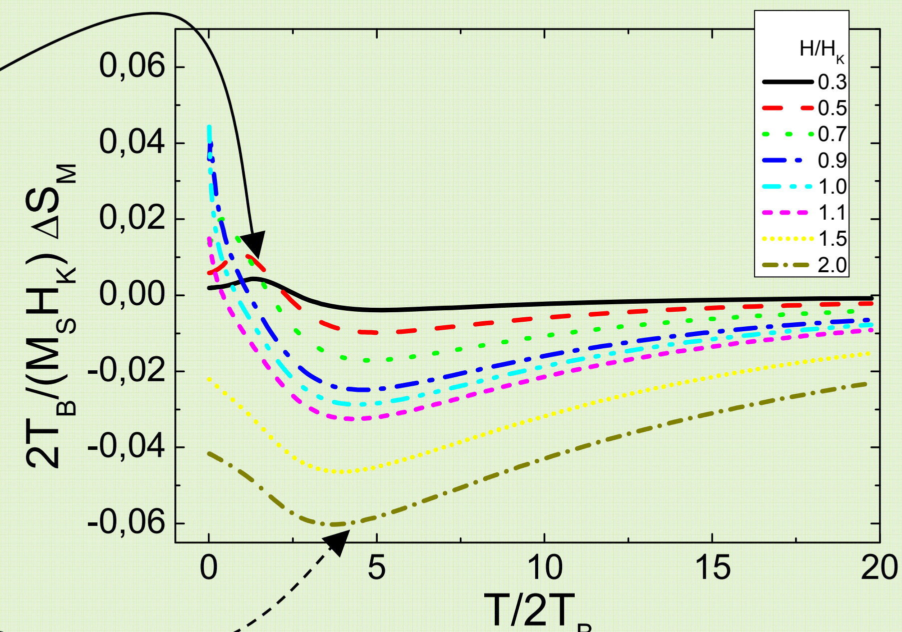
reduced magnetization ($m=M/M_S$) calculated as (superparamagnetic-like hysteresis loops):

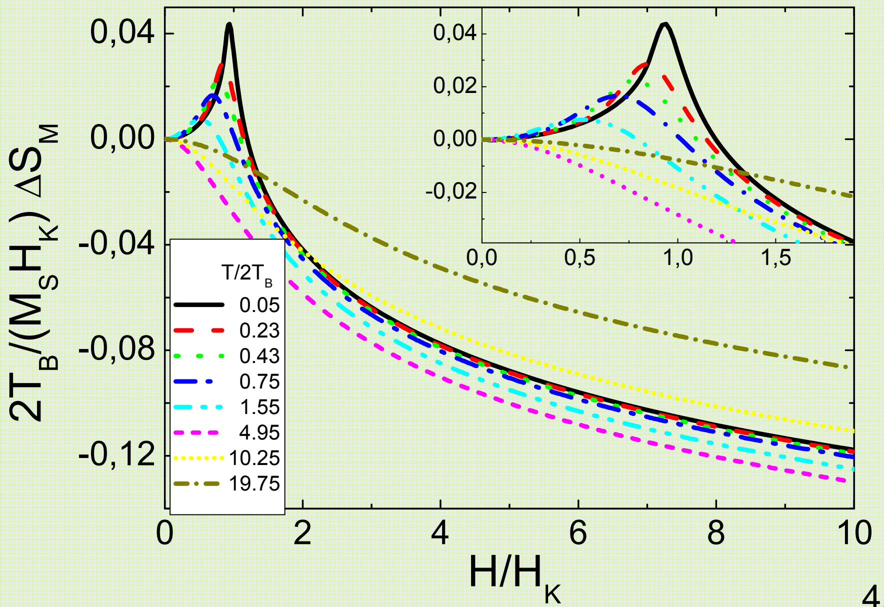
$$<m> = \frac{\iint e^{\frac{-E}{kT}} (\hat{e}_m \cdot \hat{e}_h) \sin\theta d\theta d\phi}{\iint e^{\frac{-E}{kT}} \sin\theta d\theta d\phi}$$

and the magnetic entropy change, from Maxwell relation: $\Delta S_M = \int_0^H \left(\frac{\partial M}{\partial T} \right)_H dH$

Magnetocaloric Effect

ΔS_M for low applied fields ($H<H_K$) exhibits a positive peak (negative MCE) at low temperatures, and another negative peak (positive MCE) at higher temperatures





Magnetic field dependence of ΔS_M curves: at low temperatures, the positive peak is located close to the anisotropy field, H_K.

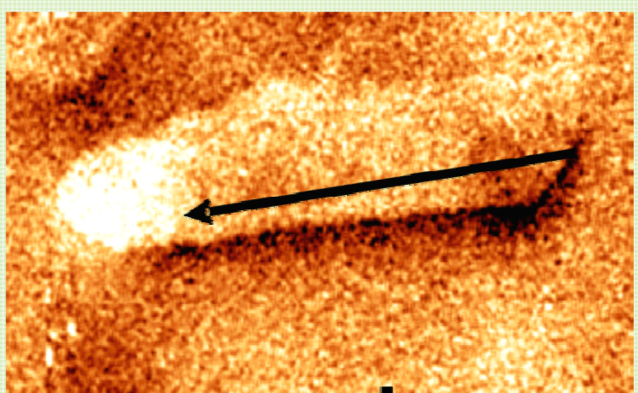
As temperature increases, the field H at the maximum value of the entropy change shifts to lower values.

For all temperatures, high applied magnetic fields cause a progressive decrease of ΔS_M when the temperature increases.

Experimental system: array of magnetic single domain Ni nanowires

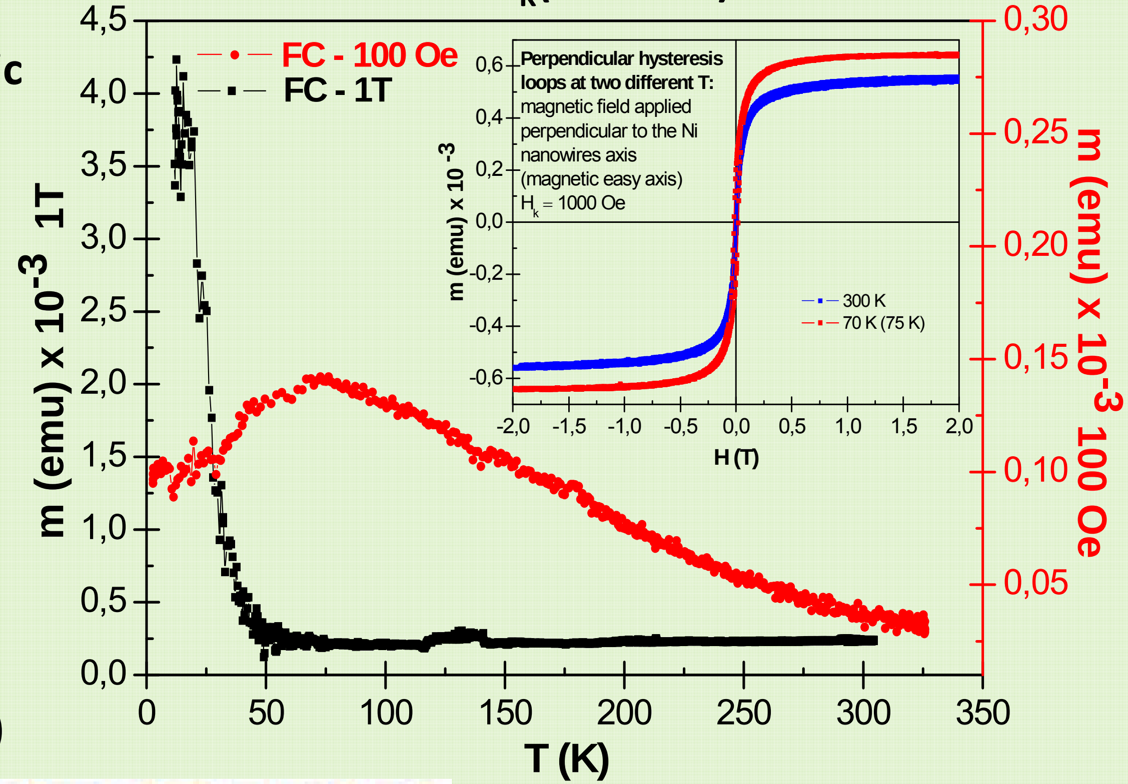
35 nm diameter

105 nm interwire spacing

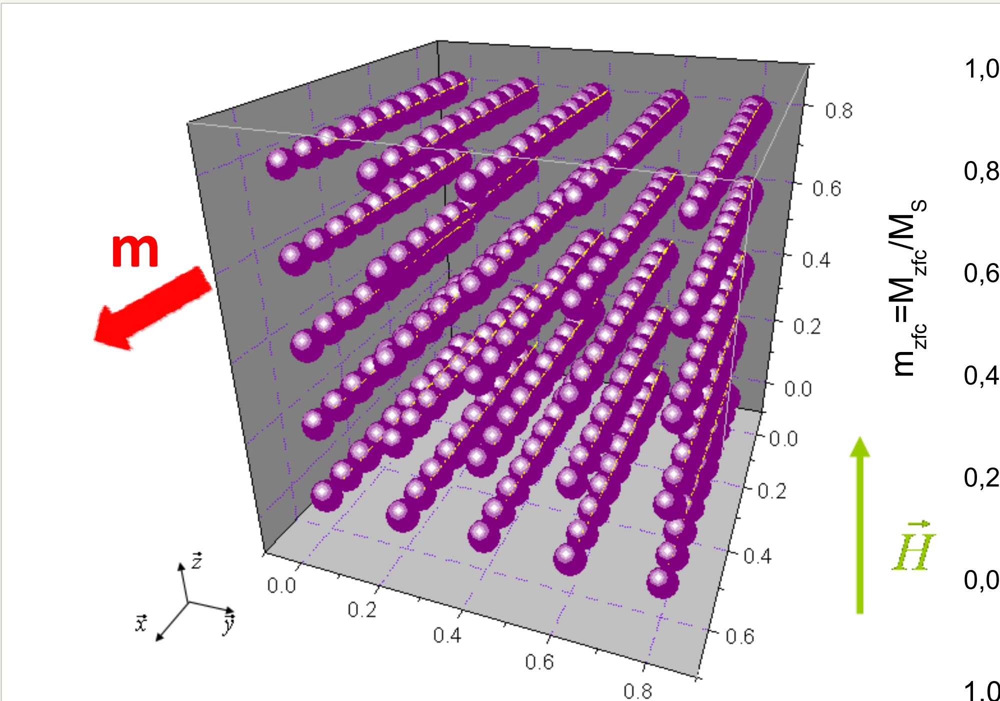


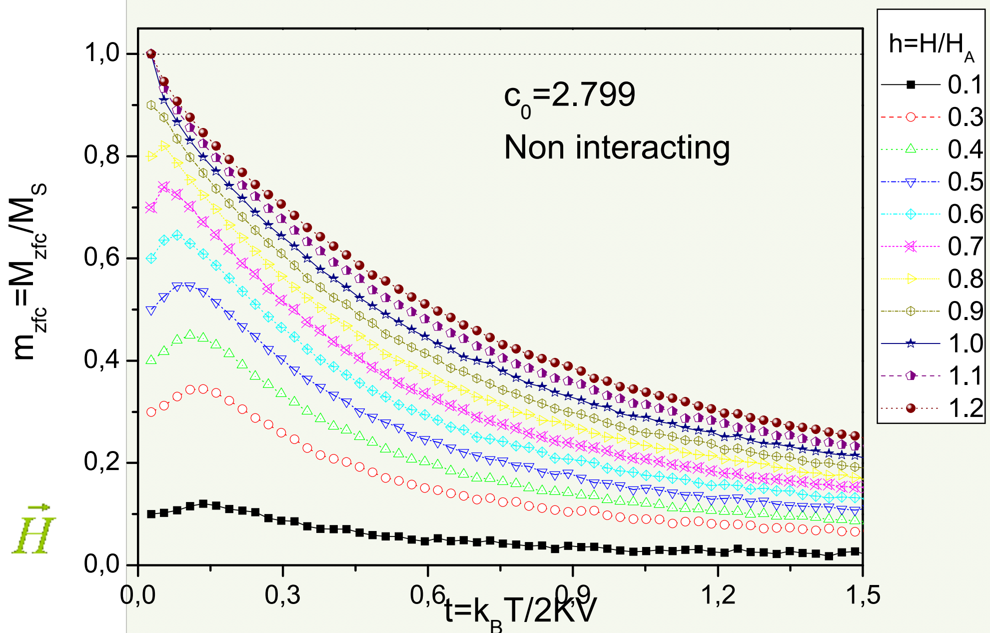
***V. Franco et al*, Phys. Rev. B (2008)**

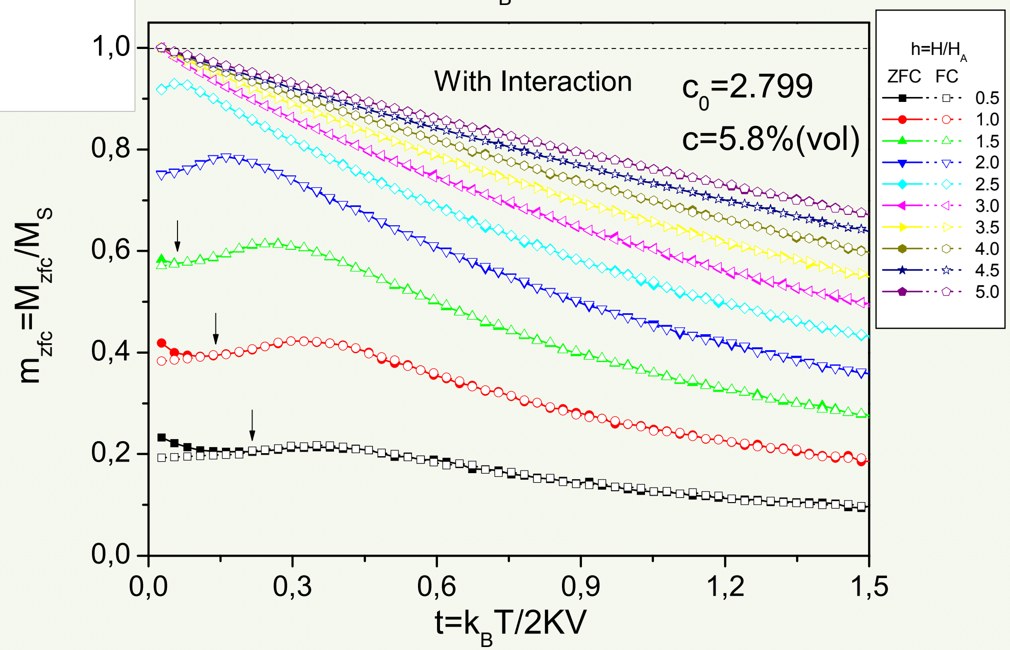
100 Oe < H_K(2500 Oe) < 1T



Improved model: MC simulations including nanoparticles dipolar interactions







Characteristics of the system:

Array of nanoparticles uniaxially aligned

$K=5.7*10^5 erg/cm^3$

$M_S=638.24\ emu/cm^3$

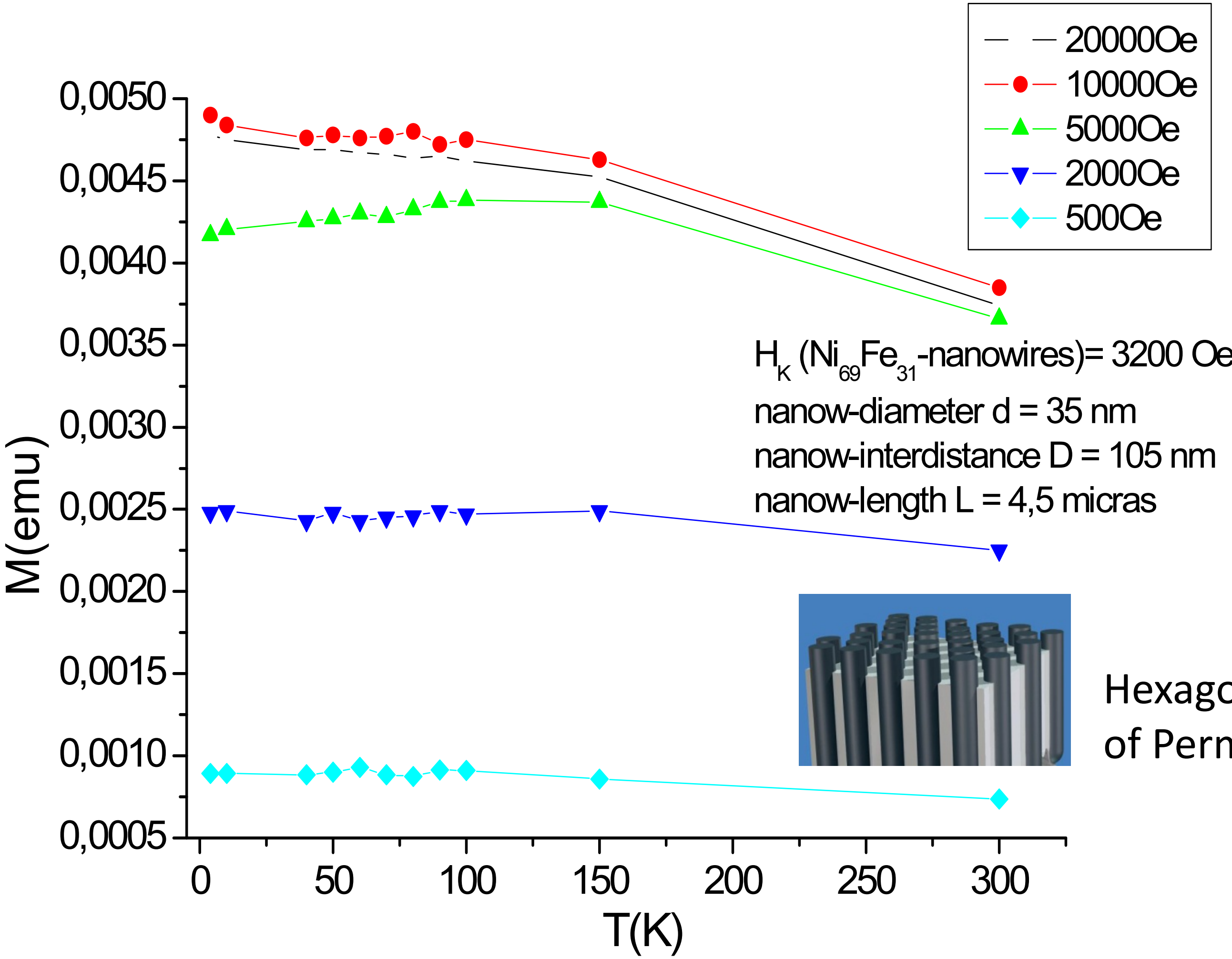
đ=3.5nm → $V=2.245*10^{-20}cm^3$

$H_A \equiv 2K/M_S$ = 1786.162 Oe

$c_0 \equiv 2K/M_S^2$ = 2.799

$$E_T = \sum_i \left(E_A^{(i)} + E_Z^{(i)} + \tfrac{1}{2}\sum_{i \neq j} E_D^{(i,j)} \right)$$

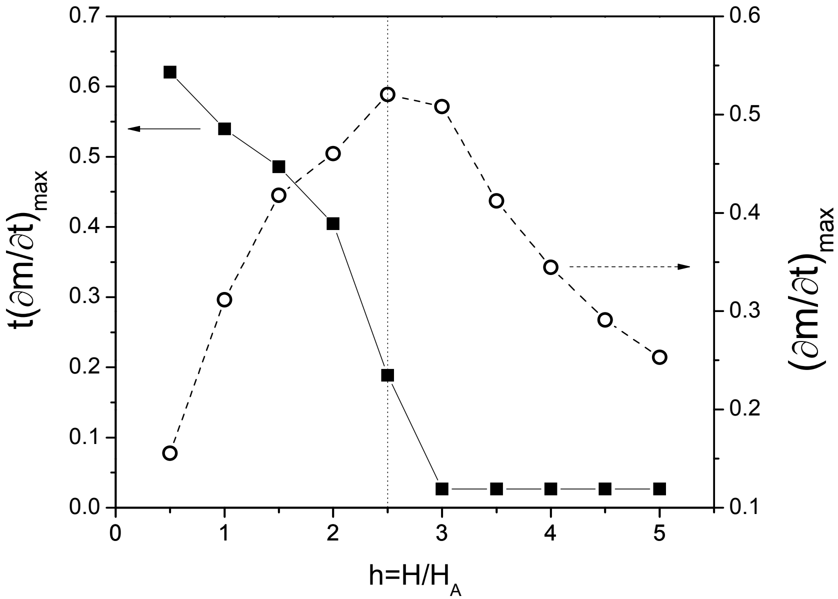
Experimental results:



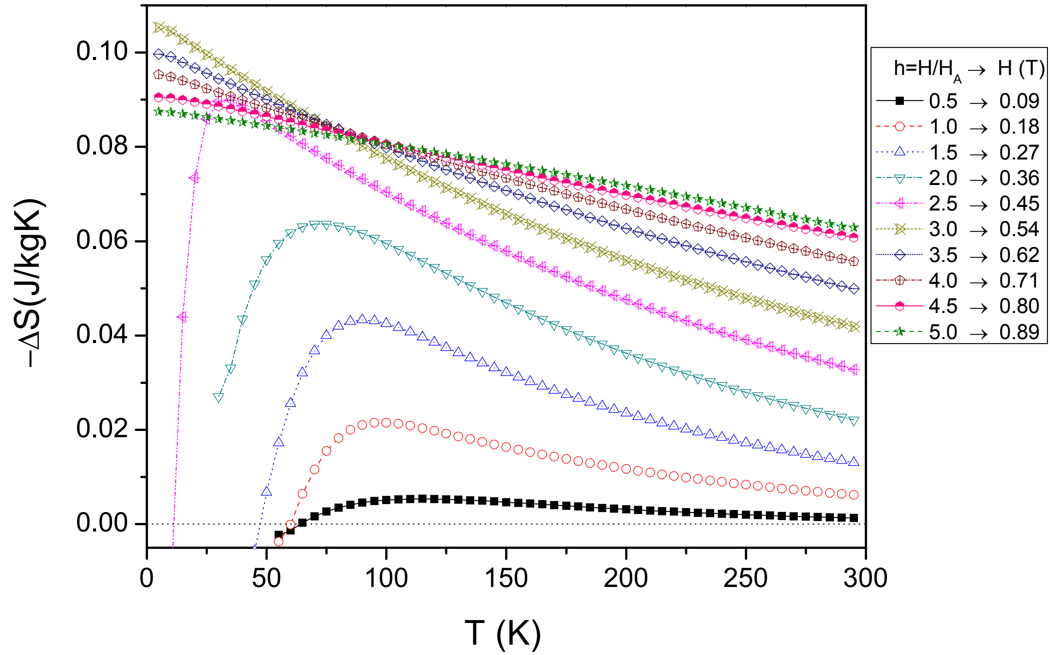
Hexagonally centered array of Permalloy nanowires

Research project : (Strategic Action for Nanoscience & Nanotechnology) NAN2004-09203-C04-01, NAN2004-09203-C04-03 and NAN2004-09203-C04-04

Susceptibility

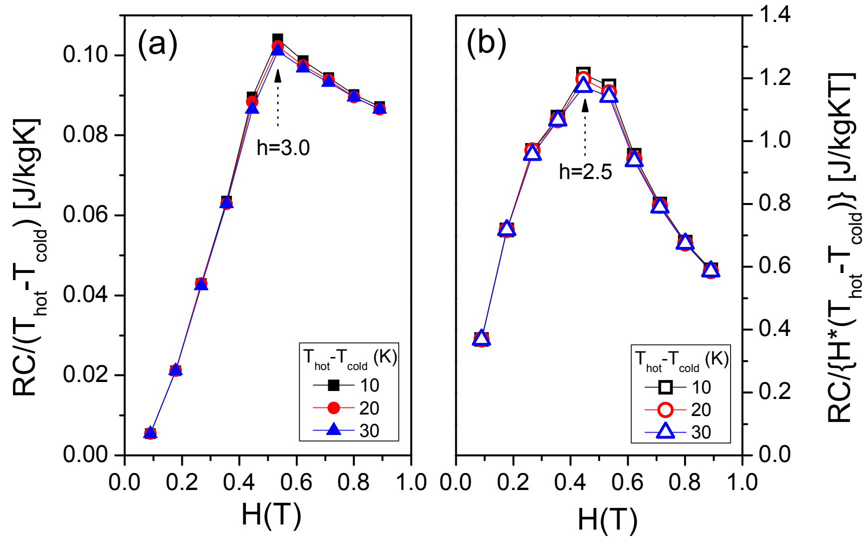


MCE



Refrigerant Capacity:

$$RC = \int_{T_{cold}}^{T_{hot}} \left[\Delta S_M(T,H)\right]_{\Delta H} dT$$



Energetic efficiency:

$\{RC/(T_{hot}-T_{cold})\}/h$

Summary:

- We syntetize highly ordered nanoporous alumina membranes by following a two-step anodization process.
- Using the alumina nanopores as templates, we can produce different kind of nanostructured materials as magnetic nanowires or antidot films.
- We also syntetize highly aligned Titanium Oxide nanotubes by a single anodization procedure.
- The employ of nanostructured magnetic nanowires, with single magnetic phase and well defined magnetic anisotropy, for their use in magnetic refrigeration devices is being studied.

THANK YOU FOR YOUR ATTENTION !!!

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