





Institute of Condensed Matter and Nanosciences
Louvain School of Engineering



AFM-based characterisation of ferromagnetic, ferroelectric and multiferroic nanostructures

Bernard NYSTEN

Bio and Soft Matter (BSMA)

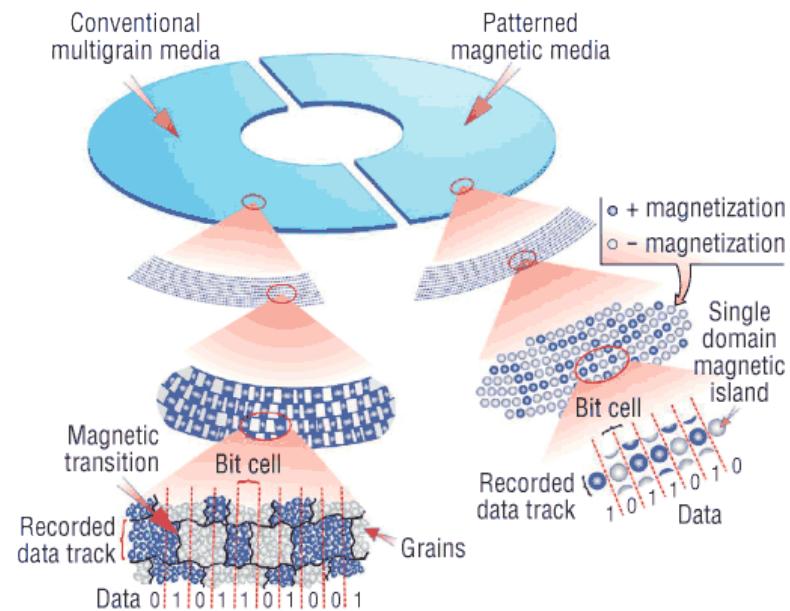
Context: Increase of data storage capacity

Conventional media

- Maximum storage density:
200 Gb/inch²
(superparamagnetic limit)

Perpendicular recording media

- Storage density up to 1 Tb/inch²



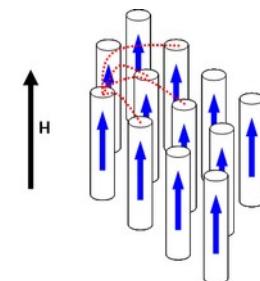
Context: Development of organic electronics

Search for flexible, light-weight data storage media



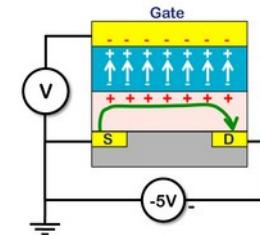
Perpendicular magnetic recording media

- Arrays of magnetic nanowires
- Drawback: increase of storage density limited by **inter-wire dipolar interaction**



Flexible data storage media

- Use of **ferroelectric polymers** in FeFET structures



Development of multiferroic materials

- Use of magnetic writing and electric reading or vice-versa
- ⇒ **Magnetic control of electrical polarization or vice-versa**

Nano-structured functional objects

- Need for **adapted characterisation tools** and procedures

Context

The tools

- Atomic force microscopy, *in-situ* and *in-field* magnetic force microscopy, *in-field* piezoresponse force microscopy

Arrays of magnetic nanowires

- Magnetic reversal in dilute arrays
- Interaction field measurement on single nanowires

Nanopatterned magneto-electric nanocomposites

- Room temperature magnetic switching of electrical polarization in nanopatterned magneto-electric nanocomposites

Conclusions



In-situ & In-field

Magnetic Force Microscopy (MFM)
&
Piezoresponse Force Microscopy (PFM)

Atomic force microscopies (AFM)

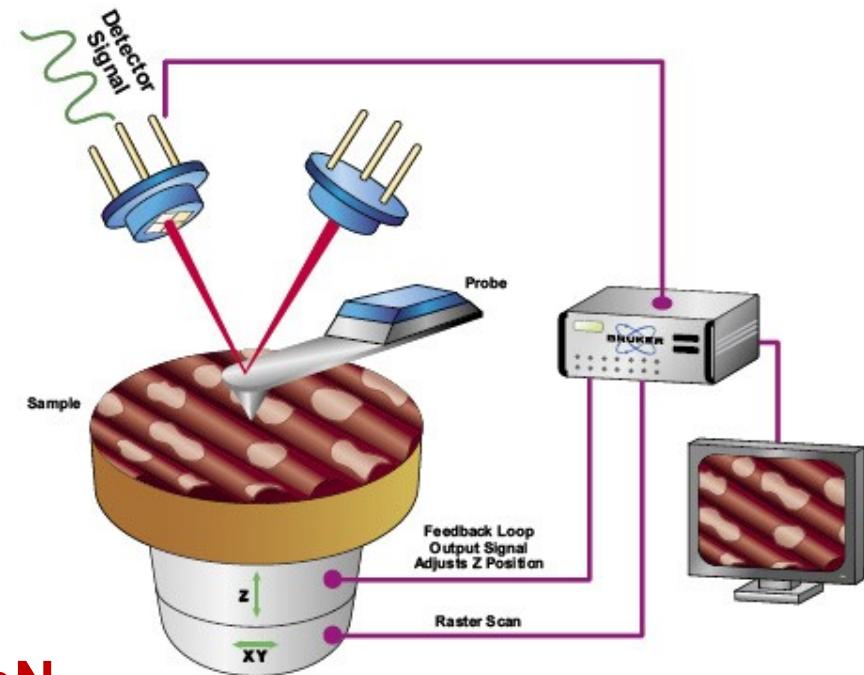
Main components

- Probe: cantilever spring & tip
- Cantilever deflection detection system
- Piezoelectric scanner

Resolution

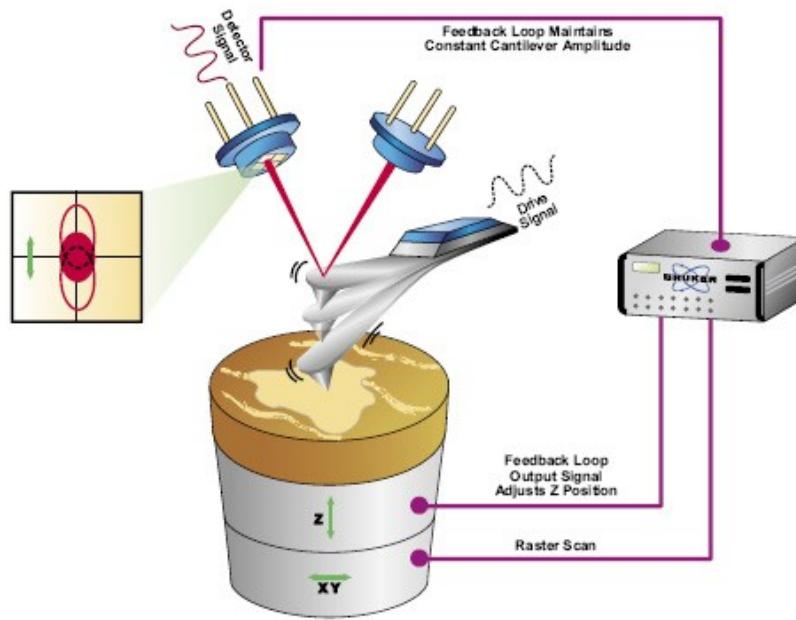
- Sample displacement (x,y,z): $< 1 \text{ \AA}$
- Cantilever deflection (d): $\leq 1 \text{ \AA}$
- Force: $F = k_c d$
for $k_c = 0.01 \text{ N.m}^{-1}$ $F \sim 1 \text{ pN}$

(!!! thermal noise at RT $\sim 8 \text{ pN} !!!$)

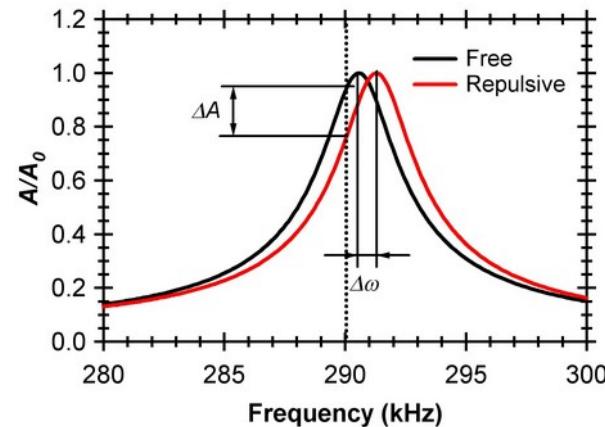
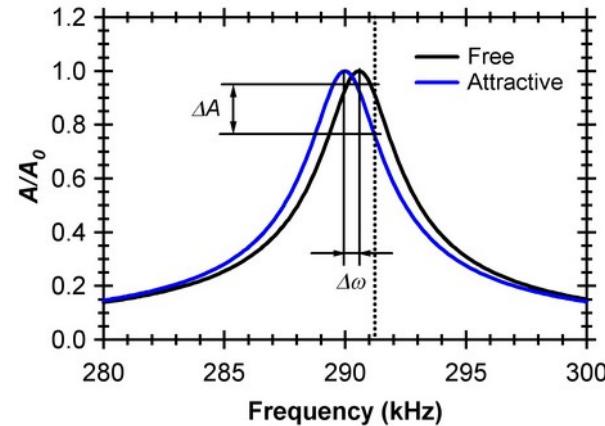


<http://blog.brukerafmprobes.com/category/guide-to-spm-and-afm-modes/>

Amplitude-modulated AFM (AM-AFM)



$$\omega_e = \sqrt{k_c - \frac{\partial F_{ts}}{\partial z}} / m$$

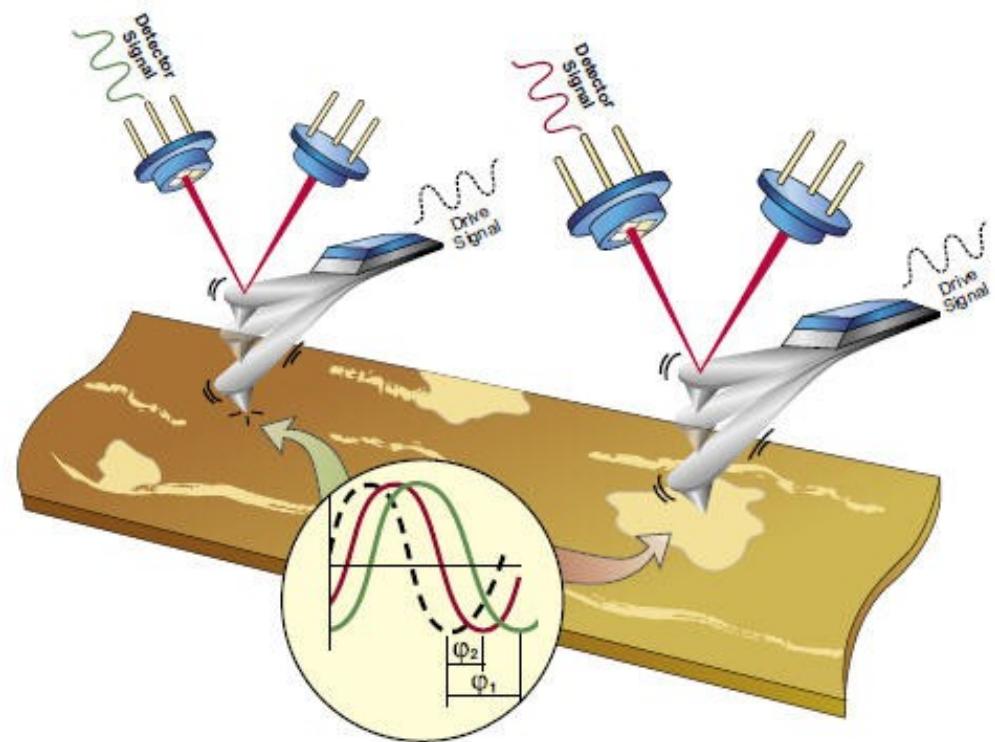


<http://blog.brukerafmprobes.com/category/guide-to-spm-and-afm-modes/>

AM-AFM with phase detection

$$\Delta\phi \approx -\frac{Q}{k_c} \frac{\partial F_{ts}}{\partial z}$$

- Repulsive force field:
 - force gradient < 0
 - $\Delta\phi > 0$
- Attractive force field
 - force gradient > 0
 - $\Delta\phi < 0$



<http://blog.brukerafmprobes.com/category/guide-to-spm-and-afm-modes/>

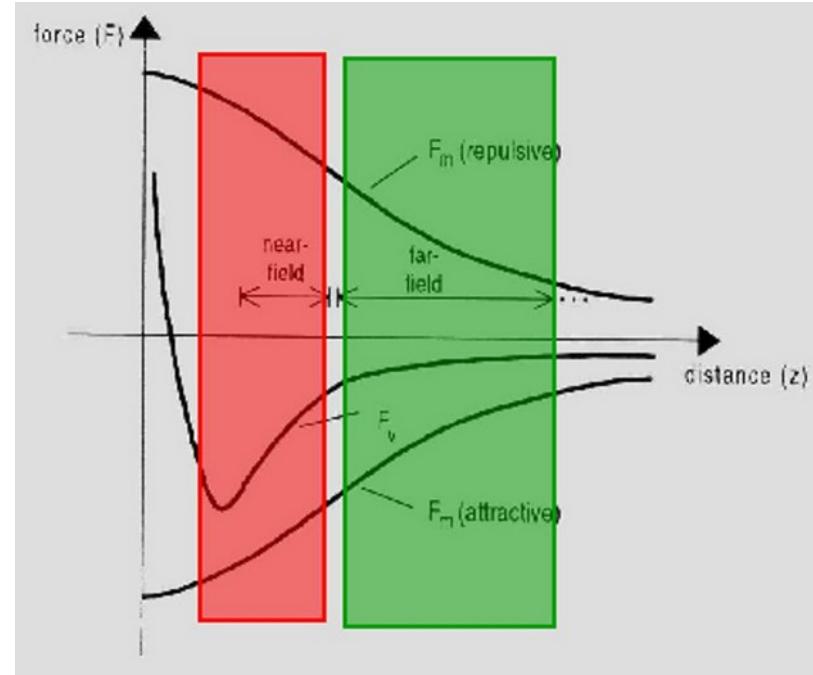
Magnetic force microscopy (MFM)

“Near field”:

- $F_{mag} > F_{vdw}$
but $\text{grad } F_{mag} < \text{grad } F_{vdw}$
- Interactions dominated by topography

“Far field”:

- $F_{mag} > F_{vdw}$
and $\text{grad } F_{mag} > \text{grad } F_{vdw}$
- Magnetic interactions dominate

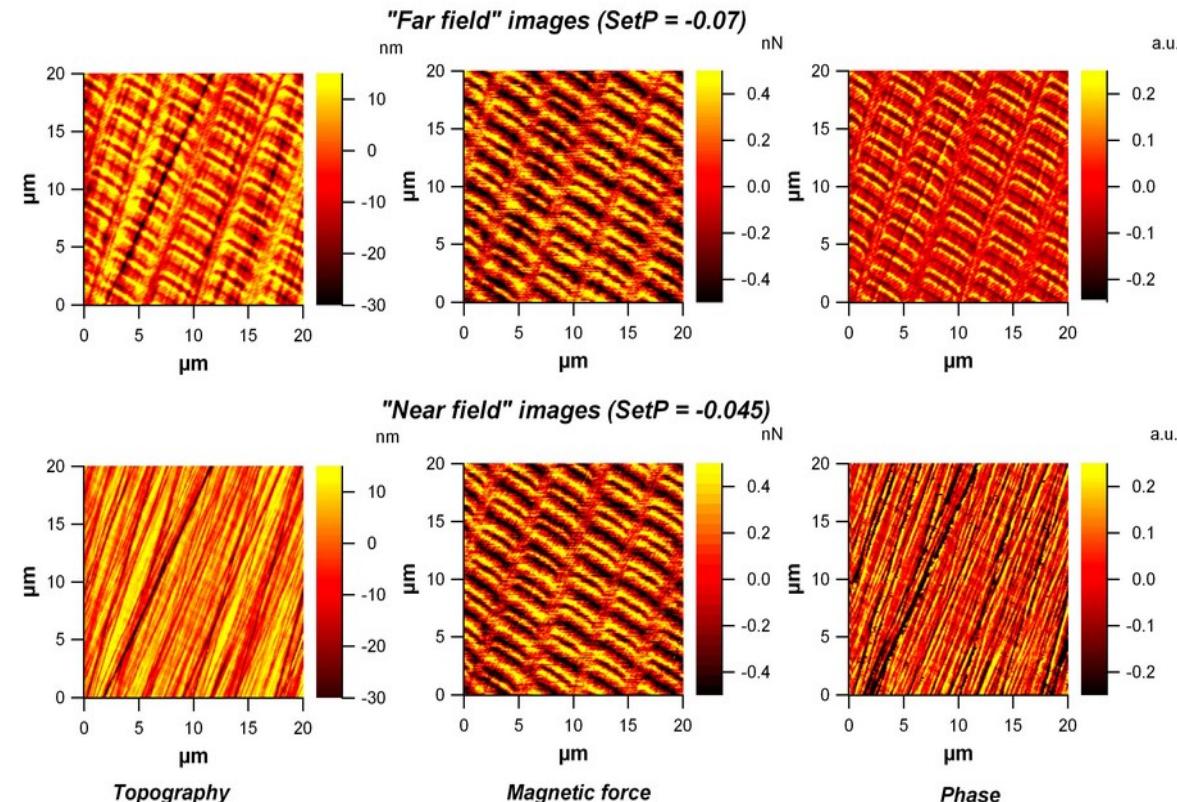


$$\omega_e = \sqrt{k_c - \frac{\partial F_{ts}}{\partial z}}$$

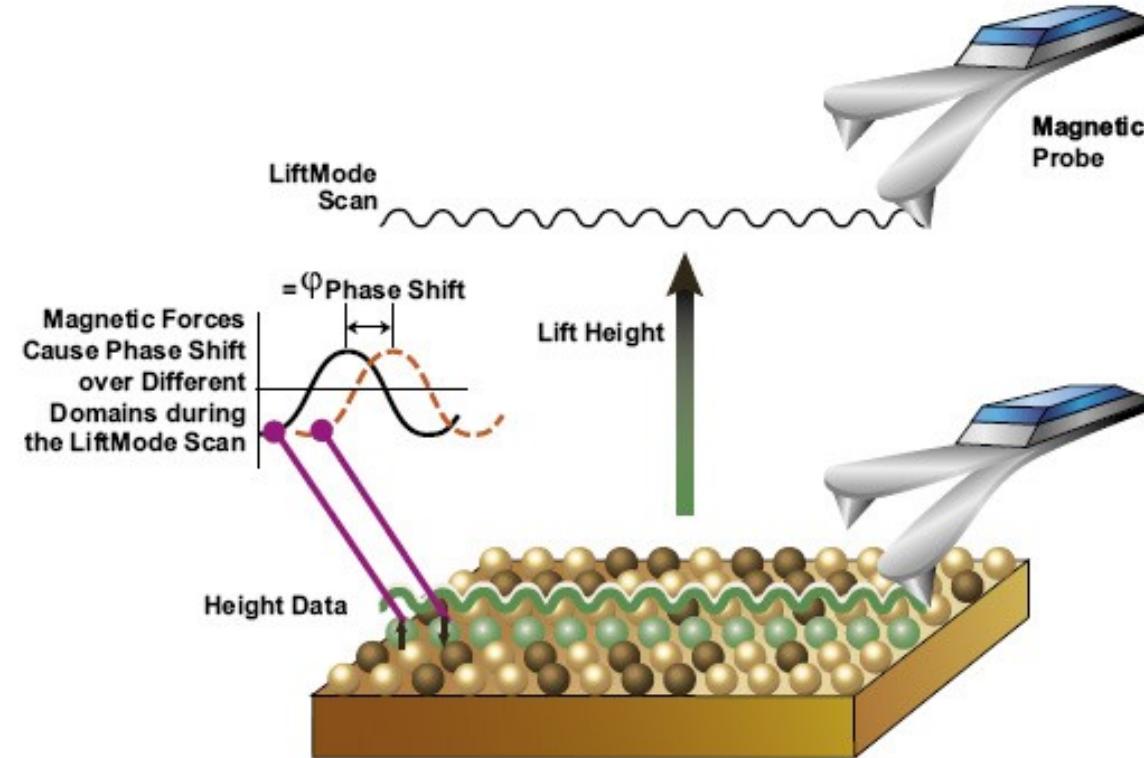
$$\Delta \phi \approx -\frac{Q}{k_c} \frac{\partial F_{ts}}{\partial z}$$

MFM: “Near field” vs “Far field”

Hard disk surface



Decoupling topographic and magnetic information



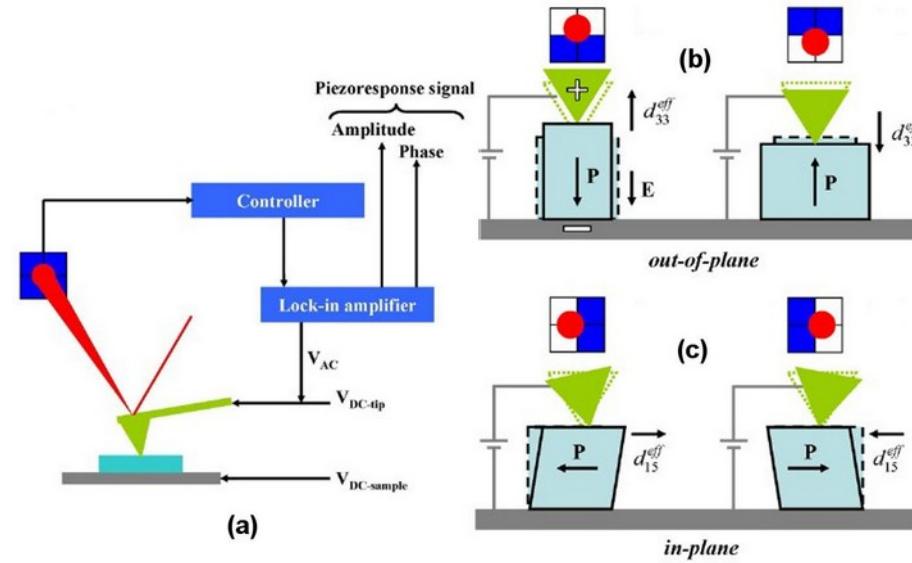
<http://blog.brukerafmprobes.com/category/guide-to-spm-and-afm-modes/>

Piezoresponse force microscopy (PFM)

Tip-sample bias voltage: $V_{ts} = V_{DC} + V_{AC} \sin(\omega t)$

Tip deflection modulation due to the converse piezoelectric effect:

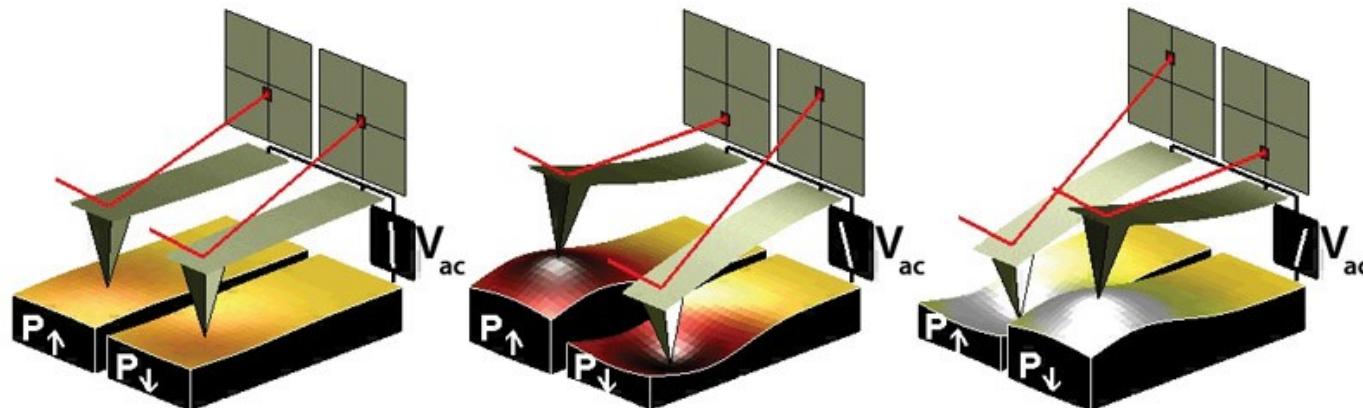
$$d \propto d_{33}^{eff} V_{DC} + d_{33}^{eff} V_{AC} \sin(\omega t + \phi)$$



<https://www.azonano.com/article.aspx?ArticleID=2682>

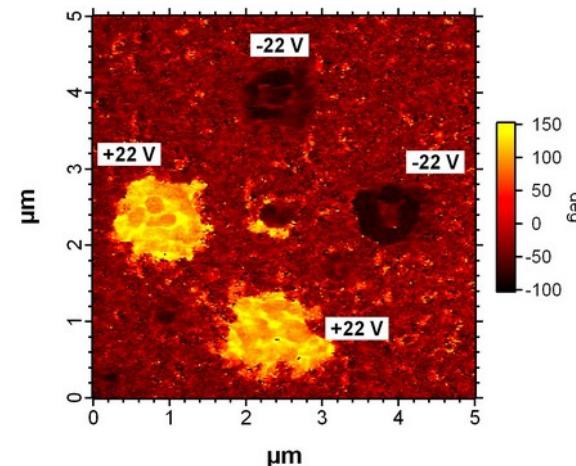
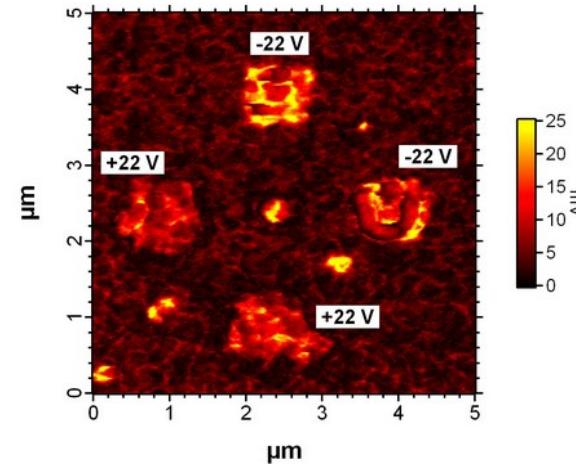
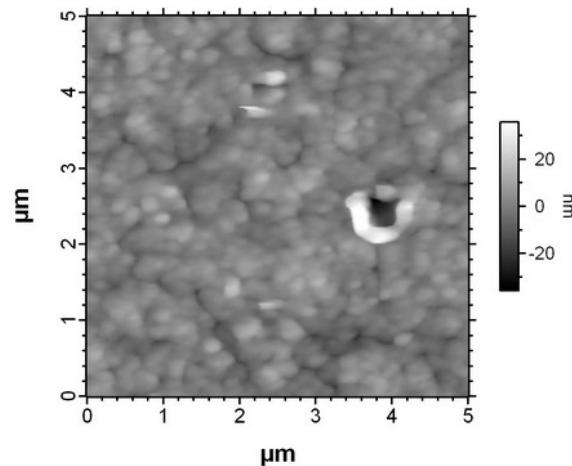
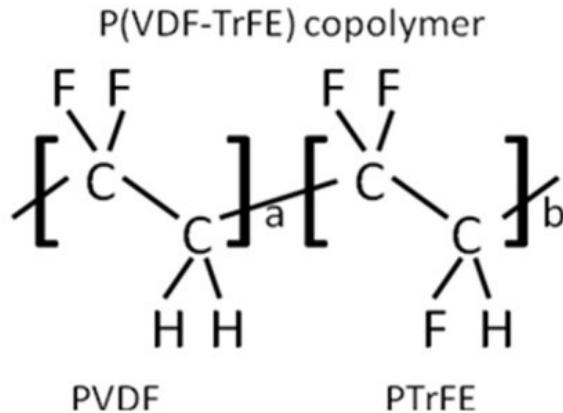
PFM: Phase and domain orientation

180° phase shift between oppositely oriented domains

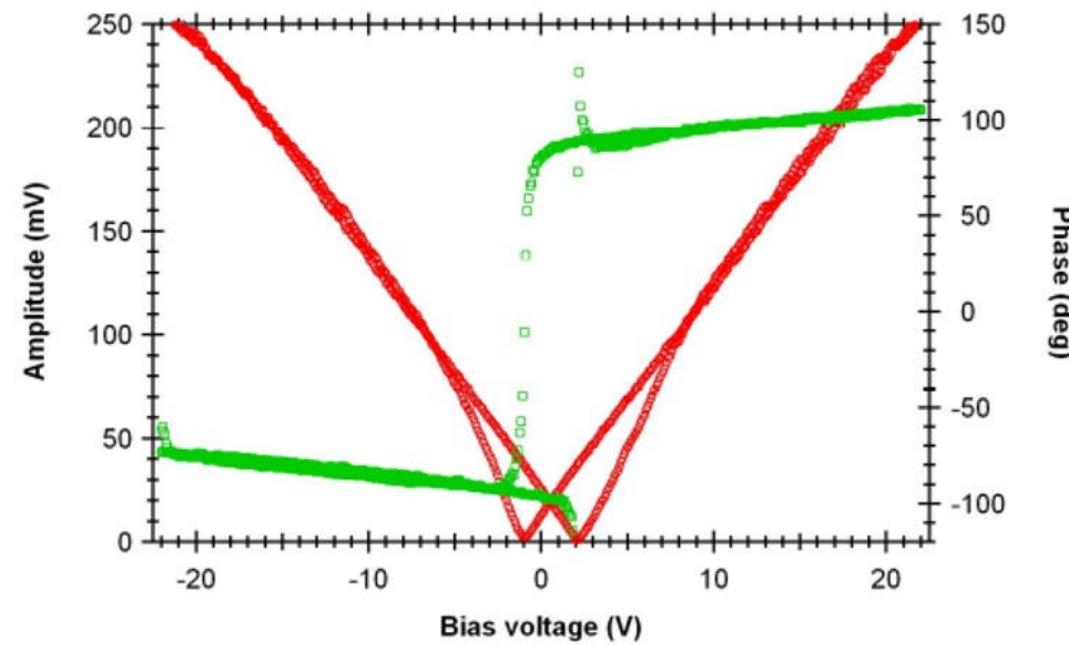
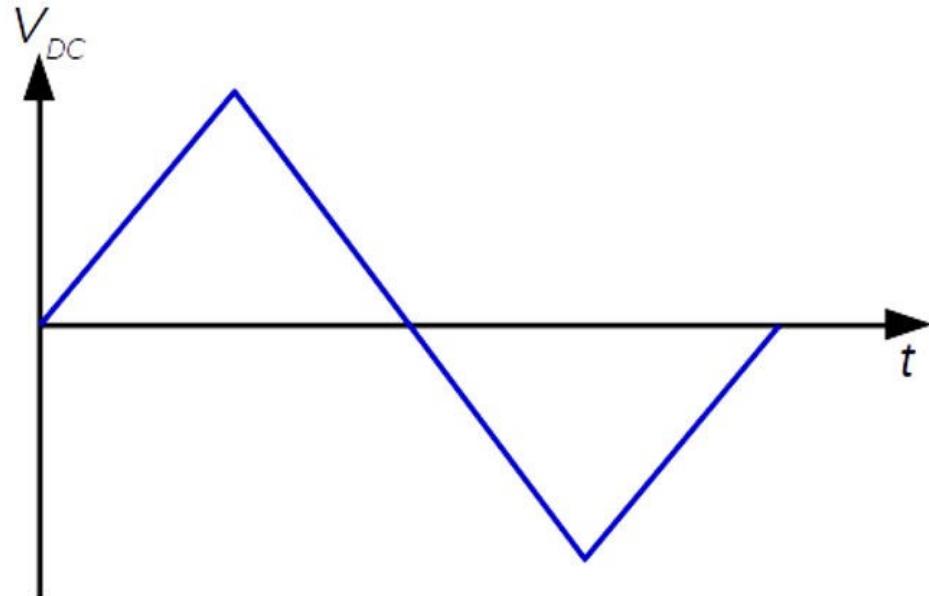


<https://www.asylumresearch.com/Applications/PFMApNote/PFMApNote.shtml>

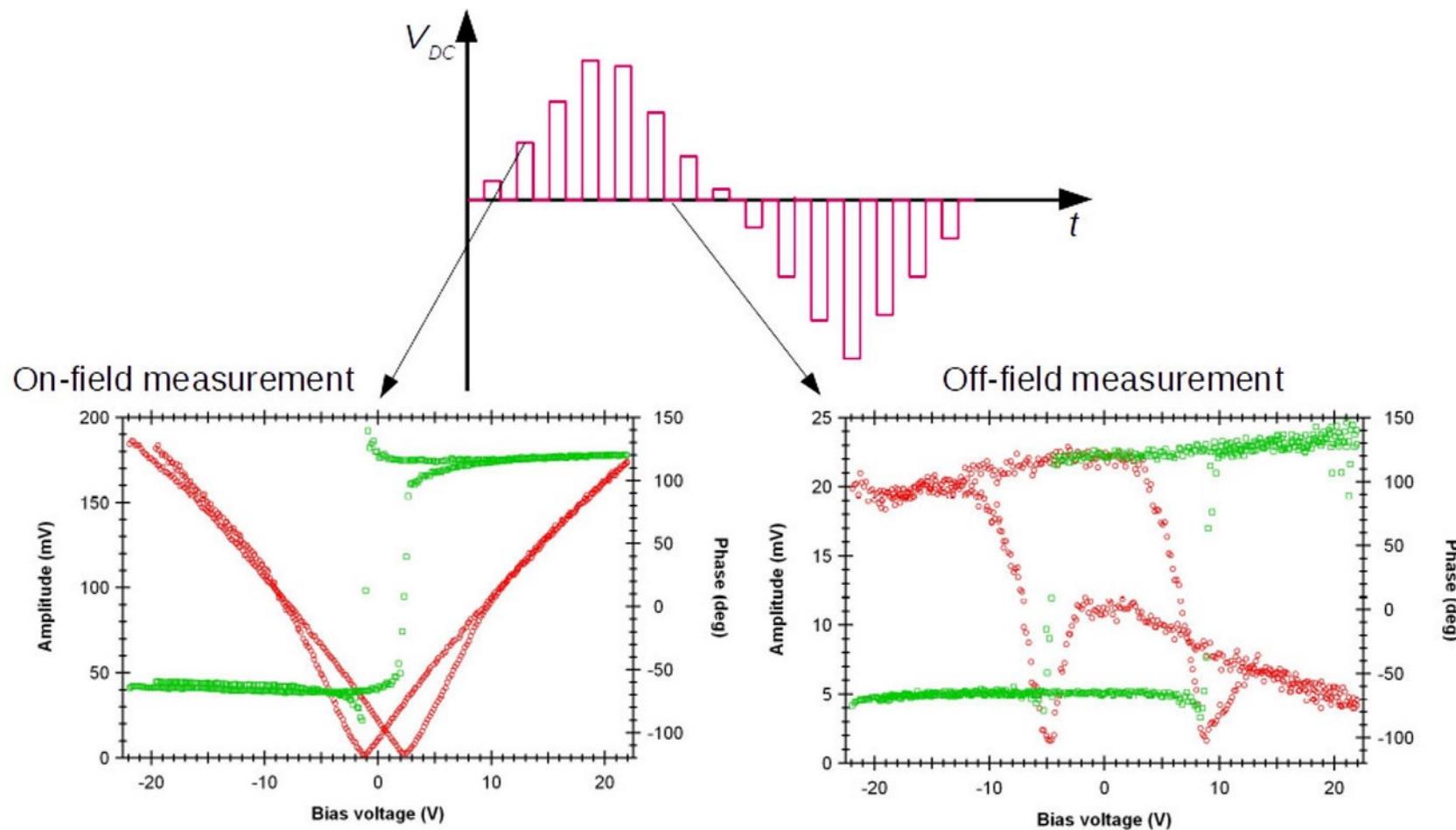
PFM: PVDF-TrFE 100 nm thin film



PFM: Standard spectroscopy



PFM: Pulsed spectroscopy

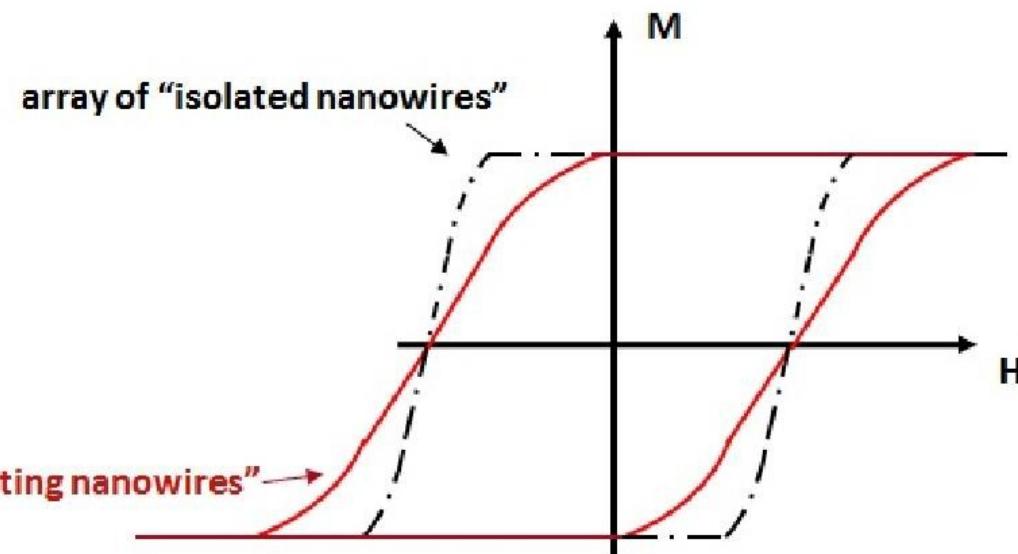
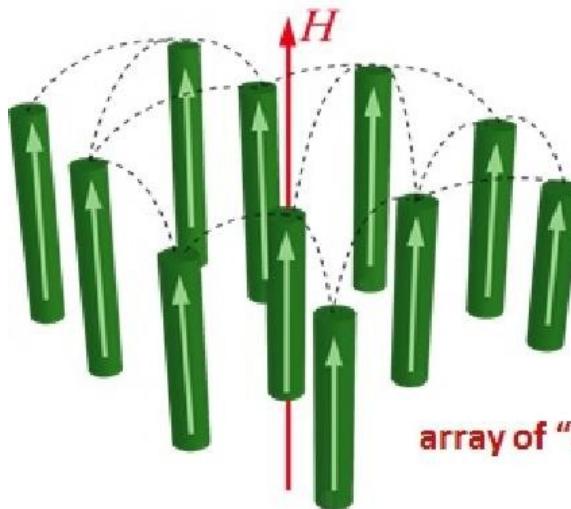




Magnetization Reversal Process in Dilute Arrays of Magnetic Nanowires

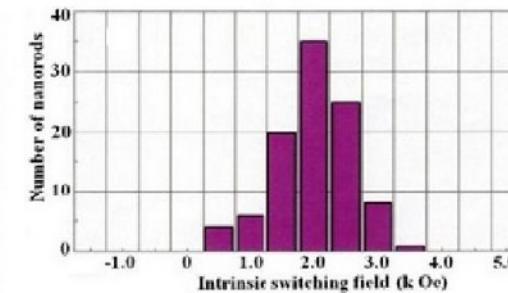
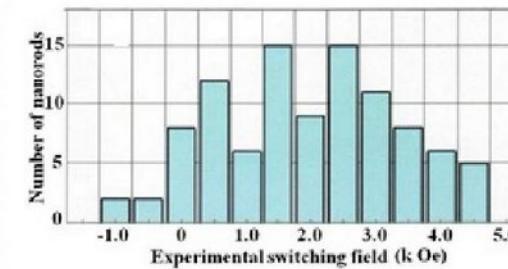
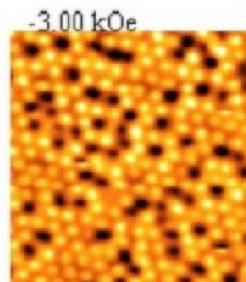
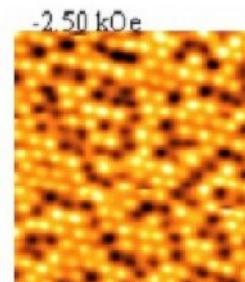
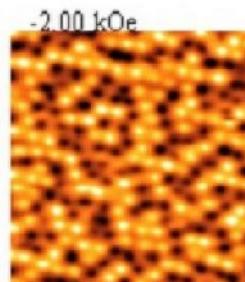
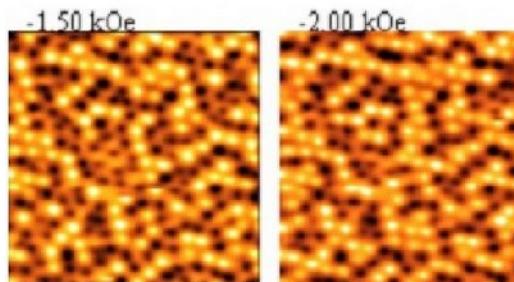
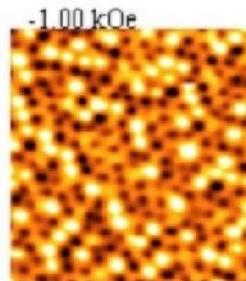
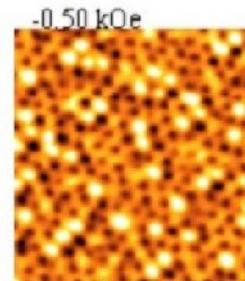
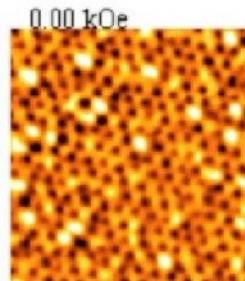
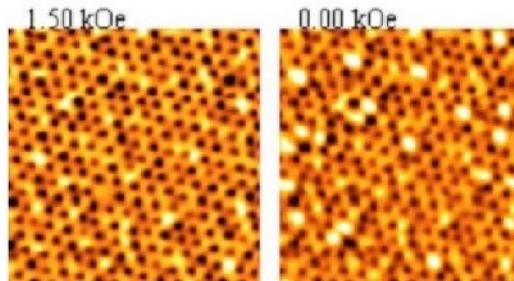
Dense arrays of magnetic nanowires

Broadening of the switching field distribution (SFD) due to the **dipolar interaction** between nanowires



Dense arrays of magnetic nanowires

Broadening of the switching field distribution (SFD) due to the **dipolar interaction** between nanowires

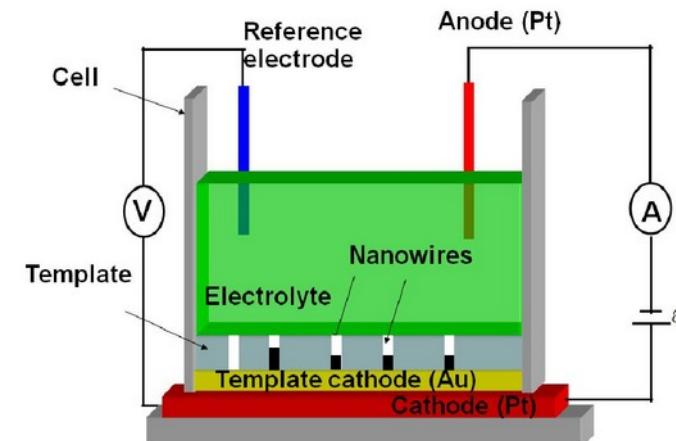
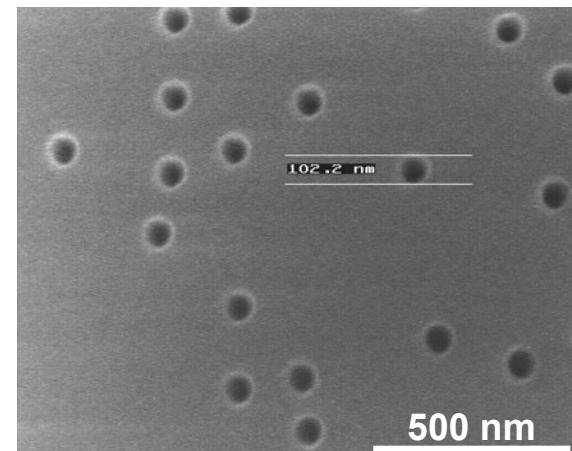


Wang et al., Nanotechnology 2008, 19, 455703

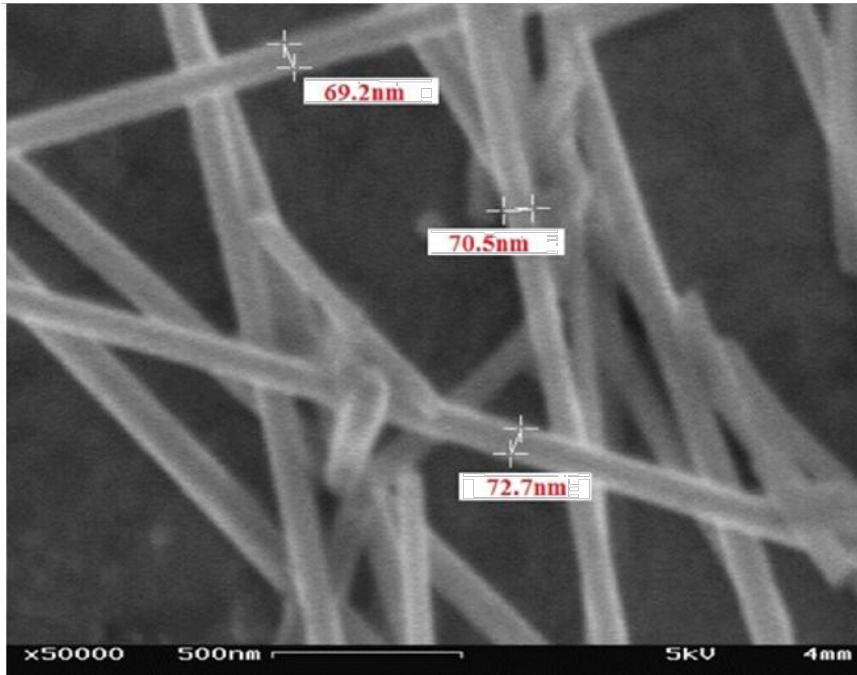
Synthesis of dilute arrays of magnetic NWs

Template method

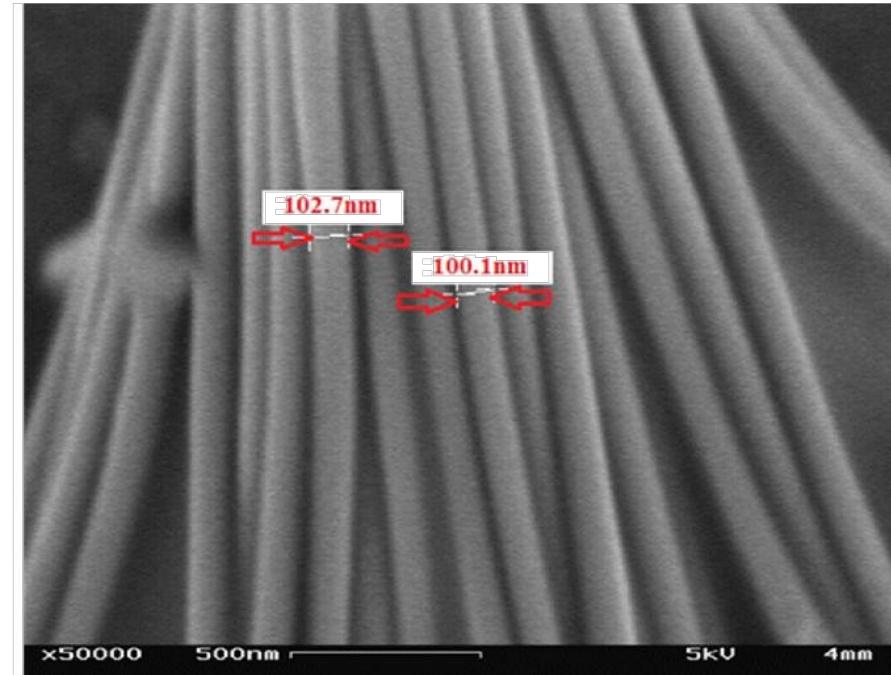
- Electrochemical deposition within pores of track-etched polycarbonate (PC) membranes
- Pore diameter: 40 to 150 nm
- Pore density: 10^8 to 10^9 cm $^{-2}$
- Ni:
 - $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$ (263 g/l) @ -1.1 V
- $\text{Ni}_{80}\text{Fe}_{20}$:
 - $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$ (131 g/l), $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ (5.6 g/l) @ -1.0 V
- $\text{Co}_{55}\text{Fe}_{45}$:
 - $\text{CoSO}_4 \cdot 6\text{H}_2\text{O}$ (80 g/l), $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ (40 g/l) @ -0.9 V



Magnetic NWs released from template

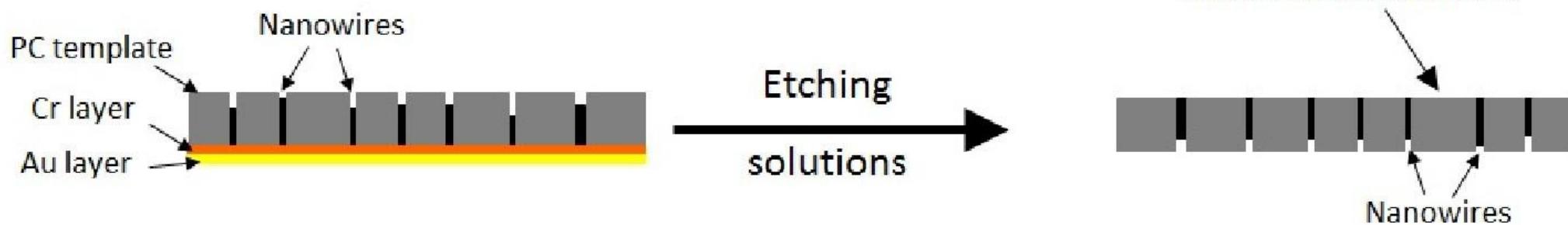


Pore diameter: 70 nm



Pore diameter: 100 nm

Sample preparation for MFM analysis

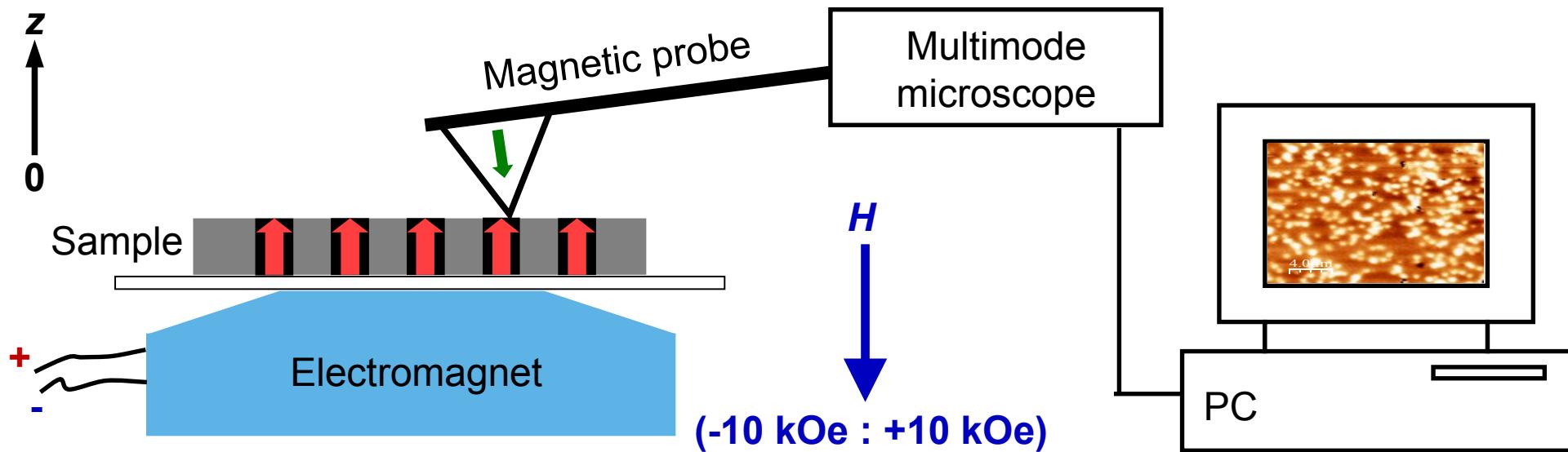


Etching of metallic cathode

- Au: KI (100 g/l) + I₂ (25 g/l) aqueous solution
- Cr: KMnO₄ (52 g) in 600 mL of 5 M NaOH solution

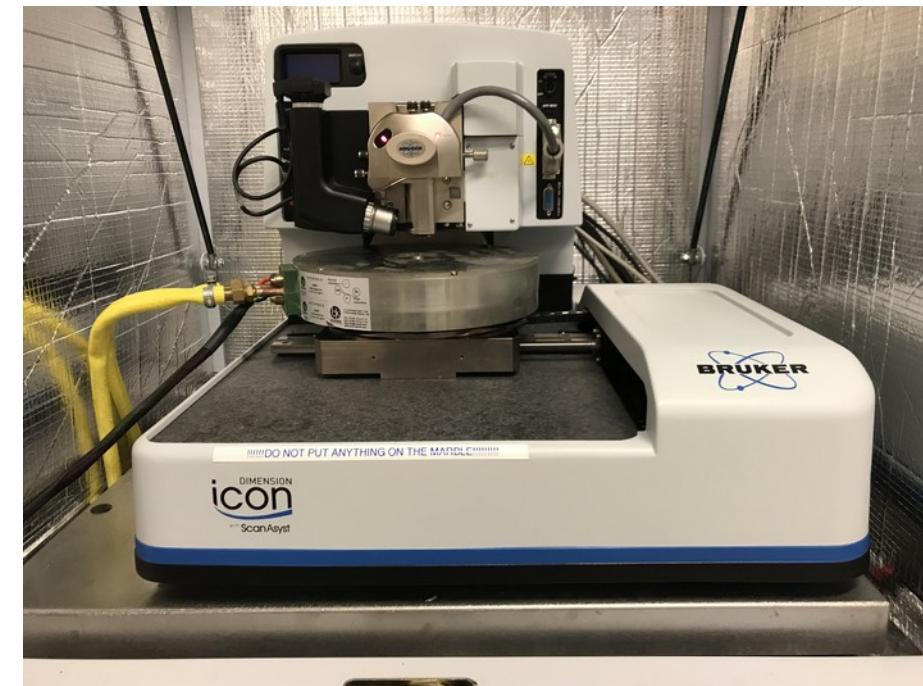
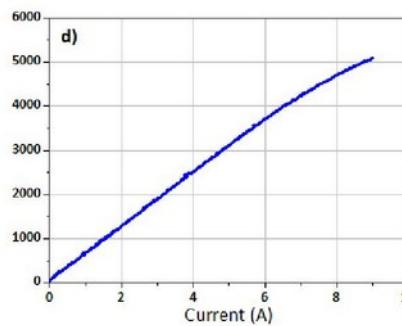
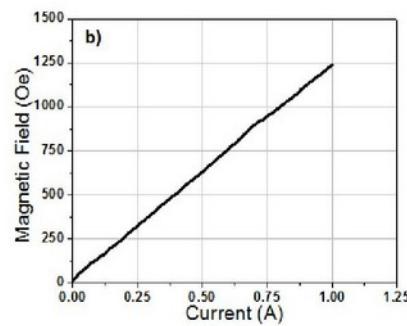
Experimental setup for *in-situ* analysis

Adaptation of custom-build magnets
on Agilent 5500 or Bruker Dimension Icon multimode AFMs.



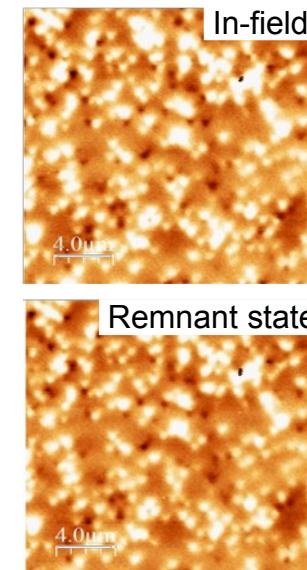
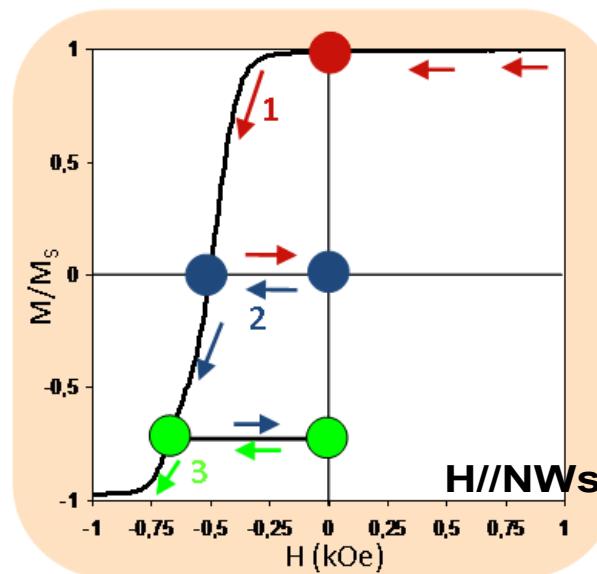
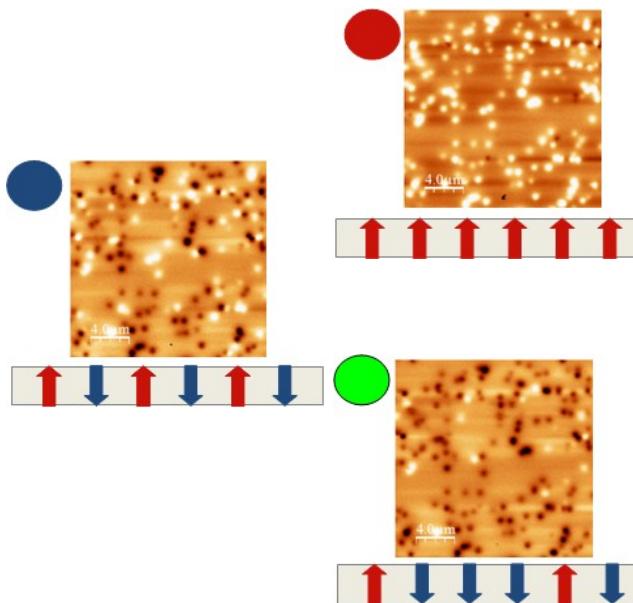
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MFM experimental procedure

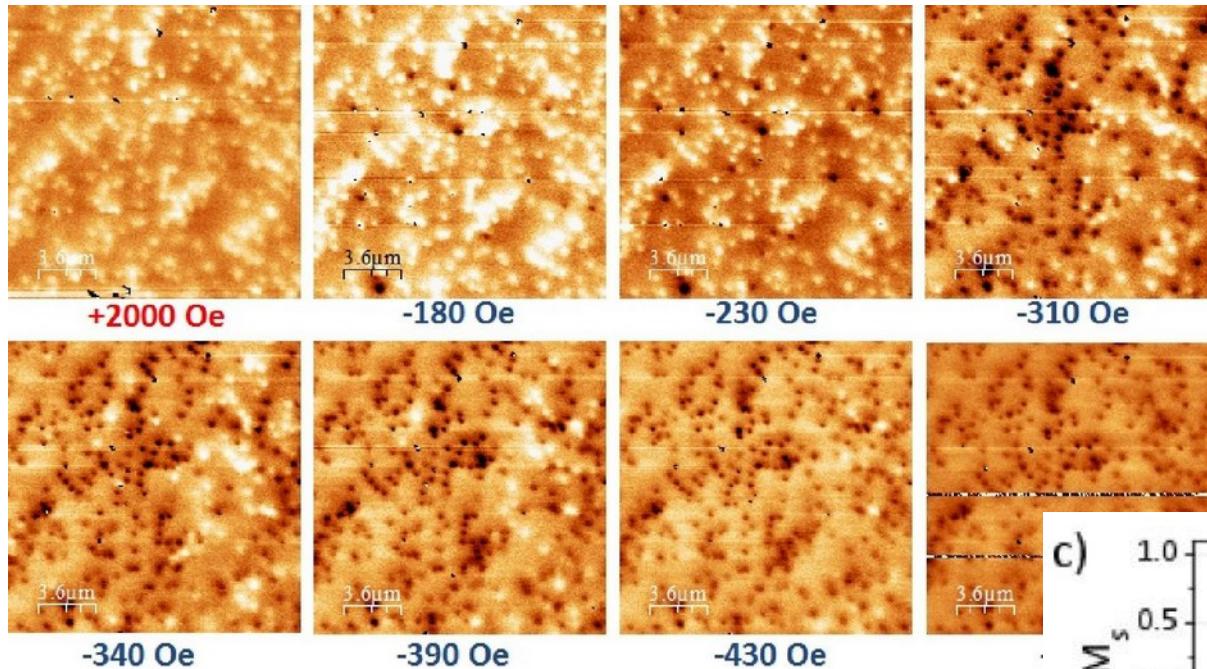
1. Saturation of sample magnetization in +0z direction
2. Tip magnetization in -0z direction
3. Imaging same region with increasing applied field in -0z.
4. Determination of magnetization curve and switching field distribution (SFD) on the basis of switched NWs (n_{down}).



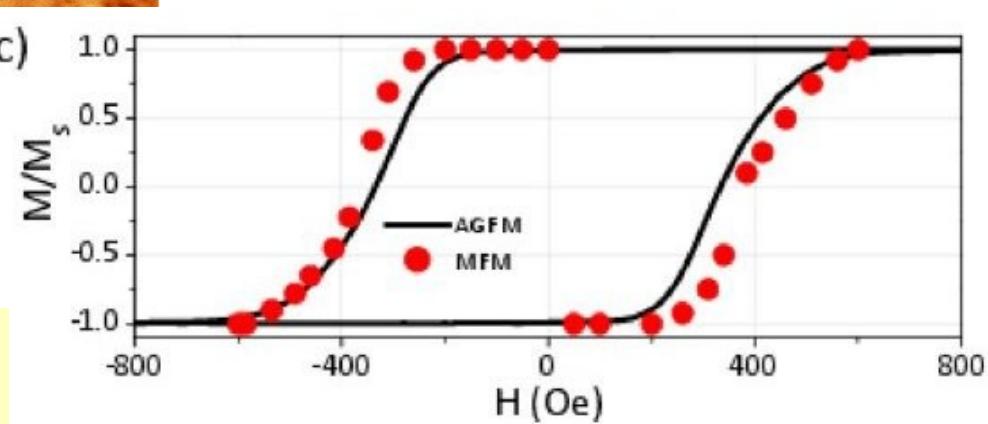
$$\frac{M(H)}{M_s} = \frac{n_{down} - n_{up}}{n_{down} + n_{up}}$$

$$SFD(H) = n_{down}(H)$$

Results: NiFe 100 nm NWs

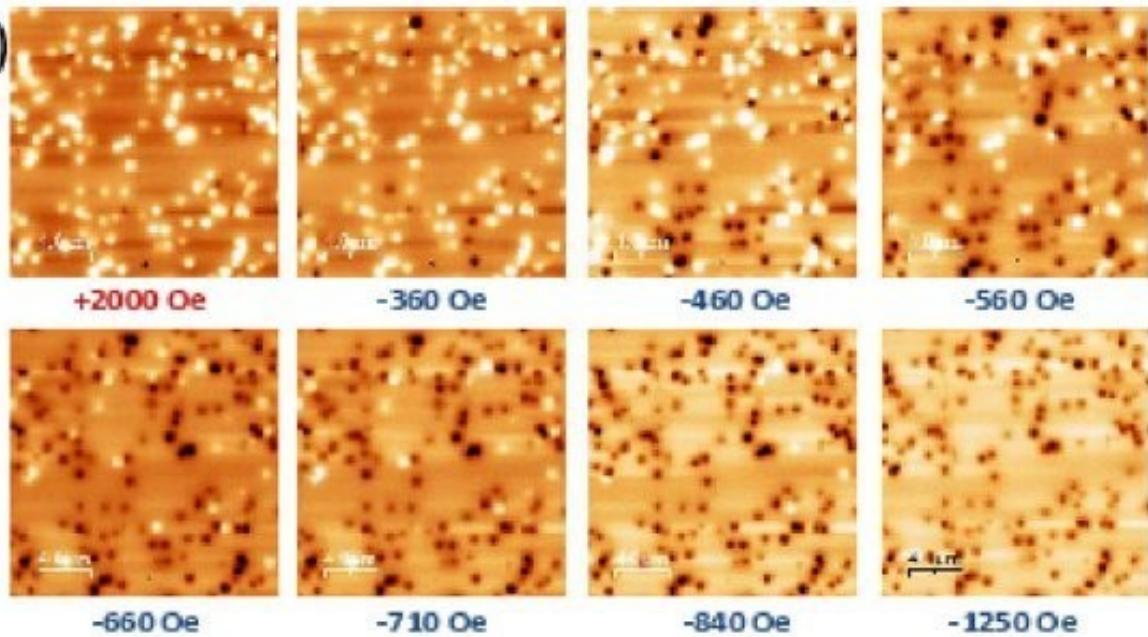


$$\frac{M(H)}{M_s} = \frac{n_{down} - n_{up}}{n_{down} + n_{up}}$$

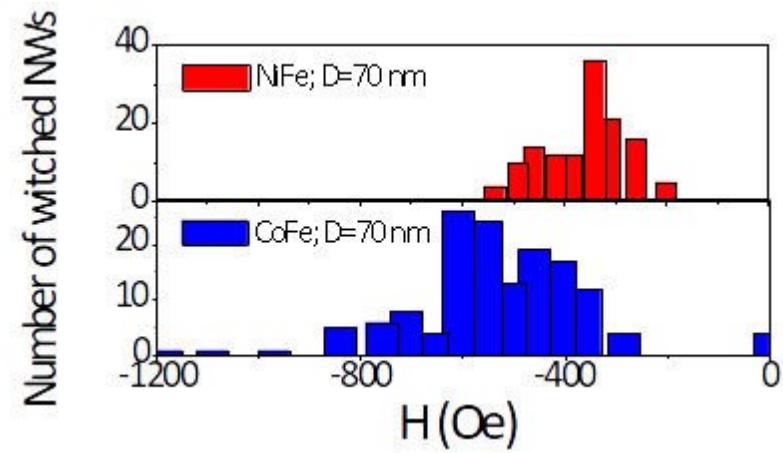


Results: CoFe 70 nm NWs

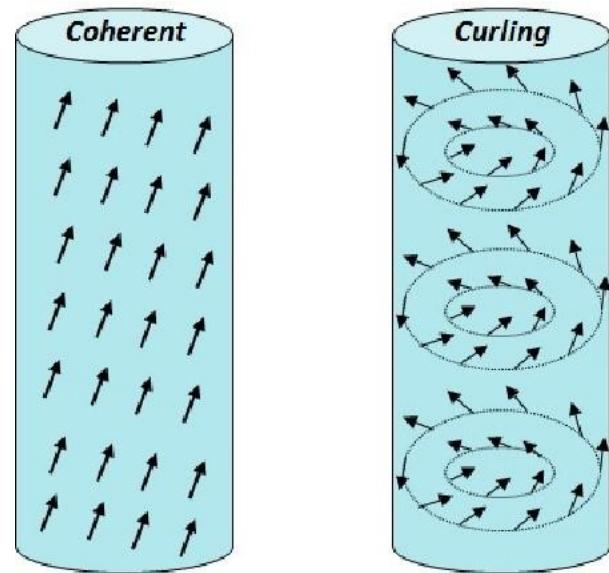
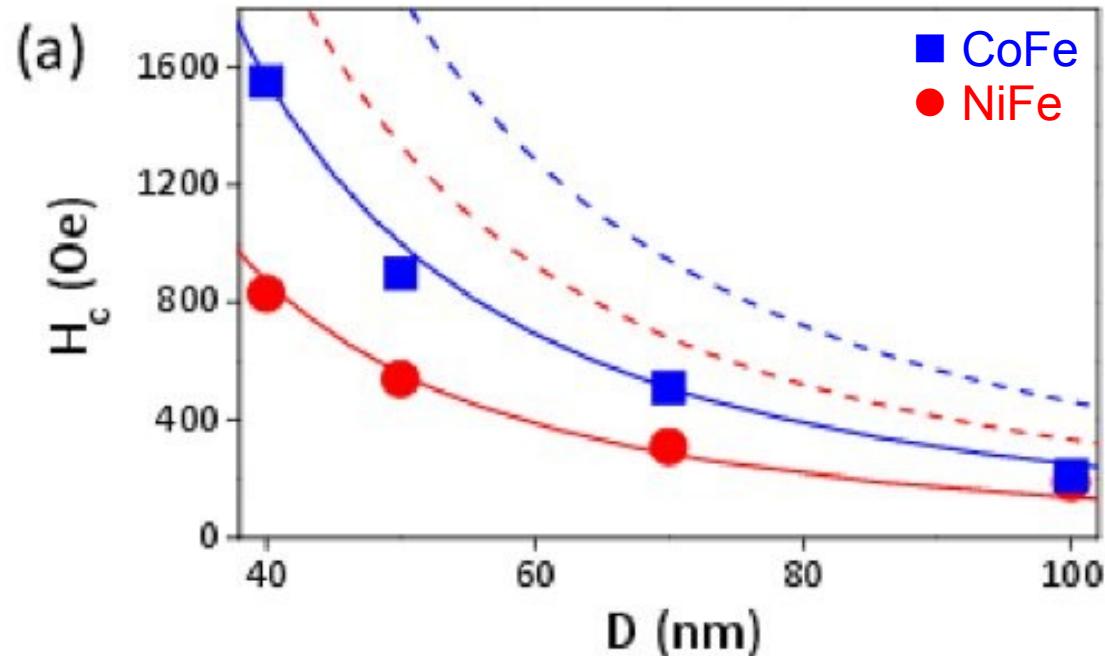
a)



$$SFD(H) = n_{down}(H)$$



Diameter dependence of coercive field

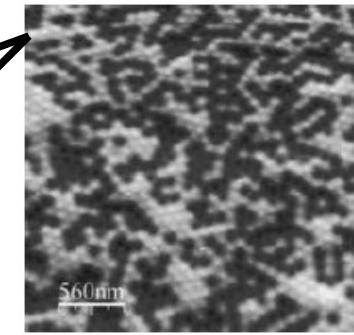
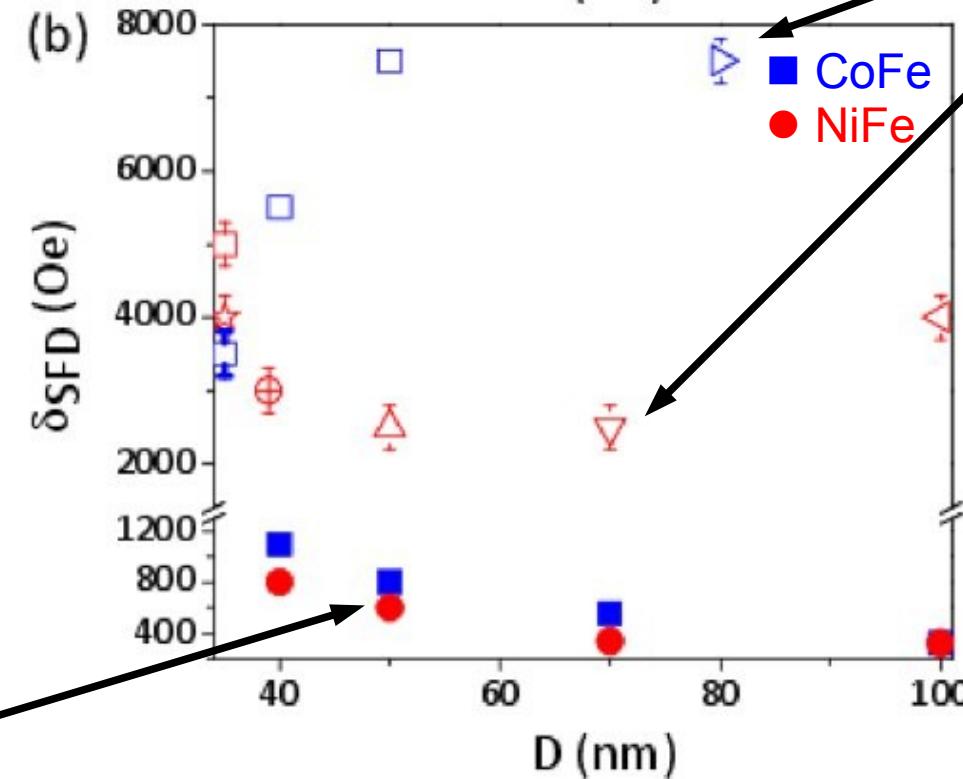
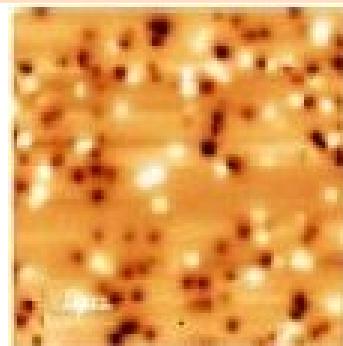


$H_c \propto D^{-2}$ compatible with curling mode magnetization reversal

Diameter dependence of SFD width

Access to the intrinsic SFD

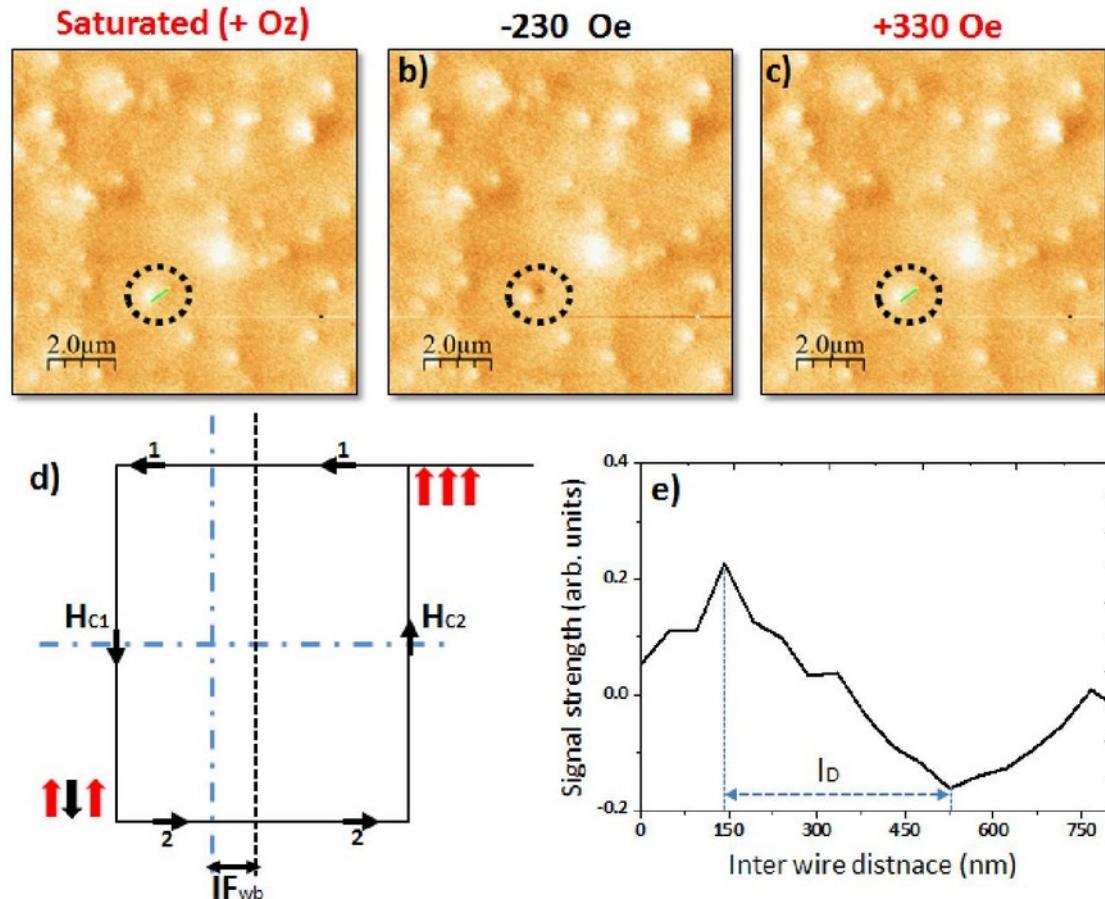
Dilute arrays
No dipolar interactions



Dense arrays
Dipolar interactions

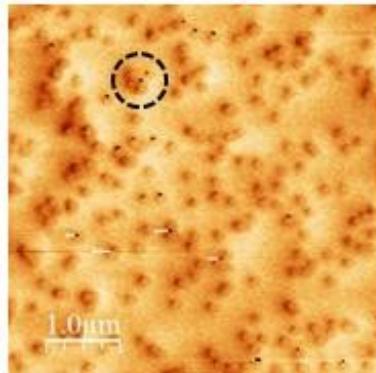
Nielsch et al., J. Magn. Magn. Mater. 2002, 249, 234

Interaction field between individual NWs

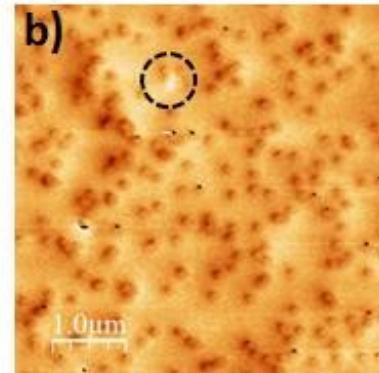


Interaction field between individual NW

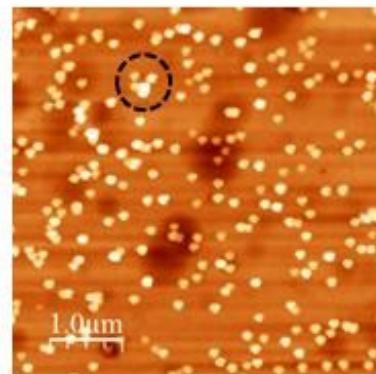
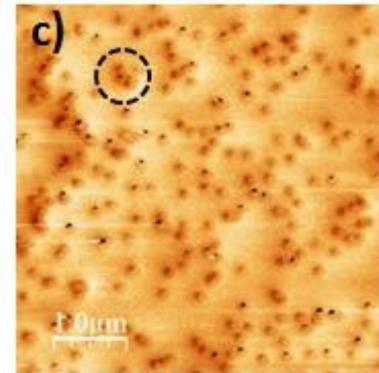
Saturated (- Oz)



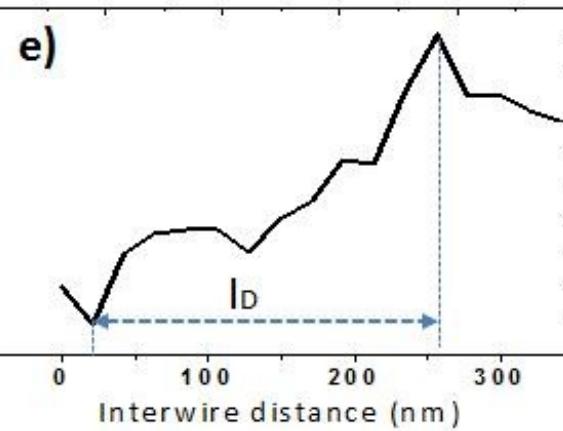
+230 Oe



-900 Oe

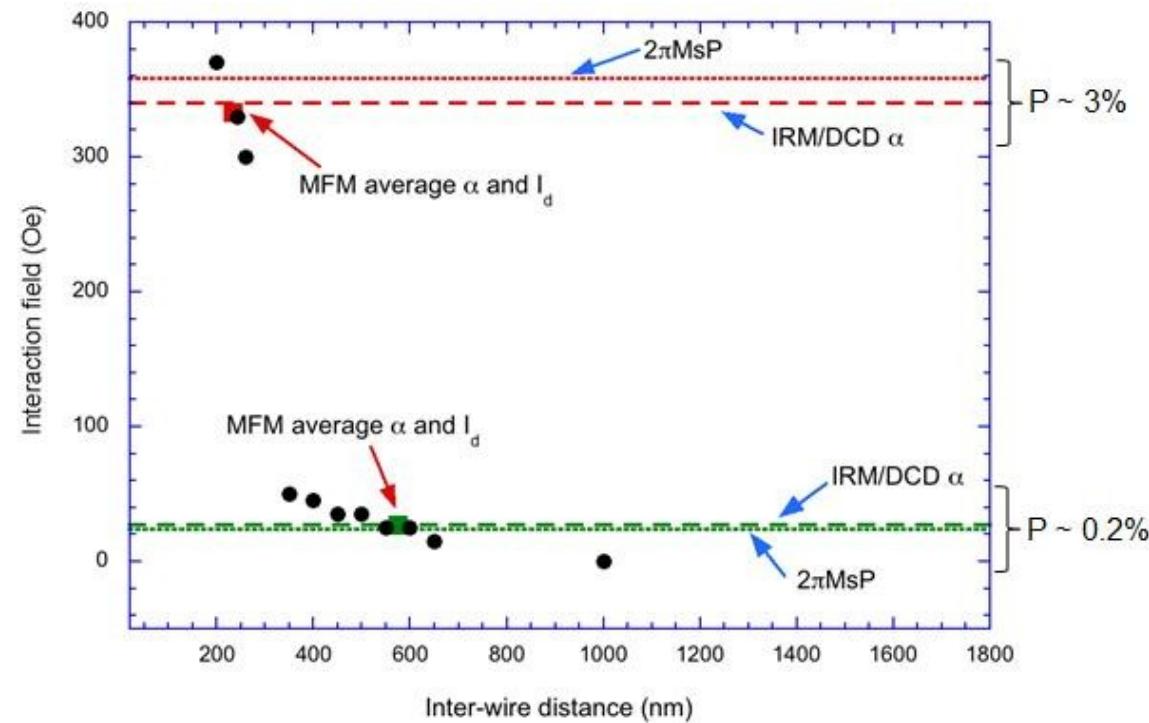


Signal strength (arb units)



IF dependence on inter-wire distance

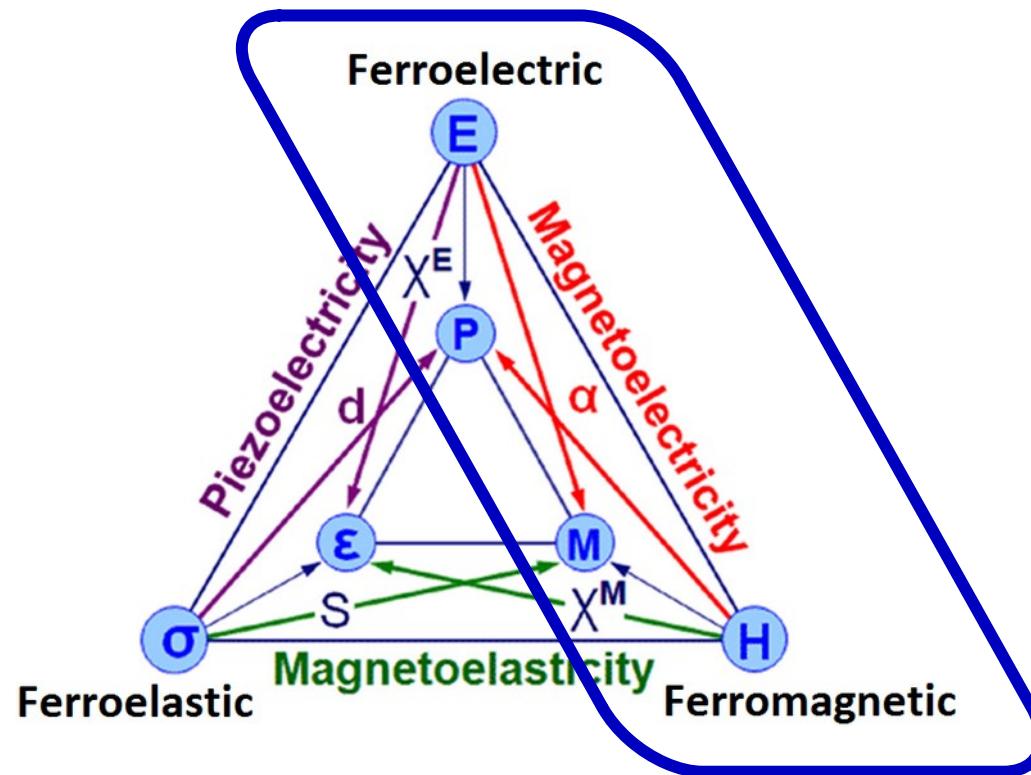
Comparison between experimental data on dilute and semi-dilute arrays and modelling





Magnetic Switching of Electrical Polarization in Magneto-Electric Nanocomposites

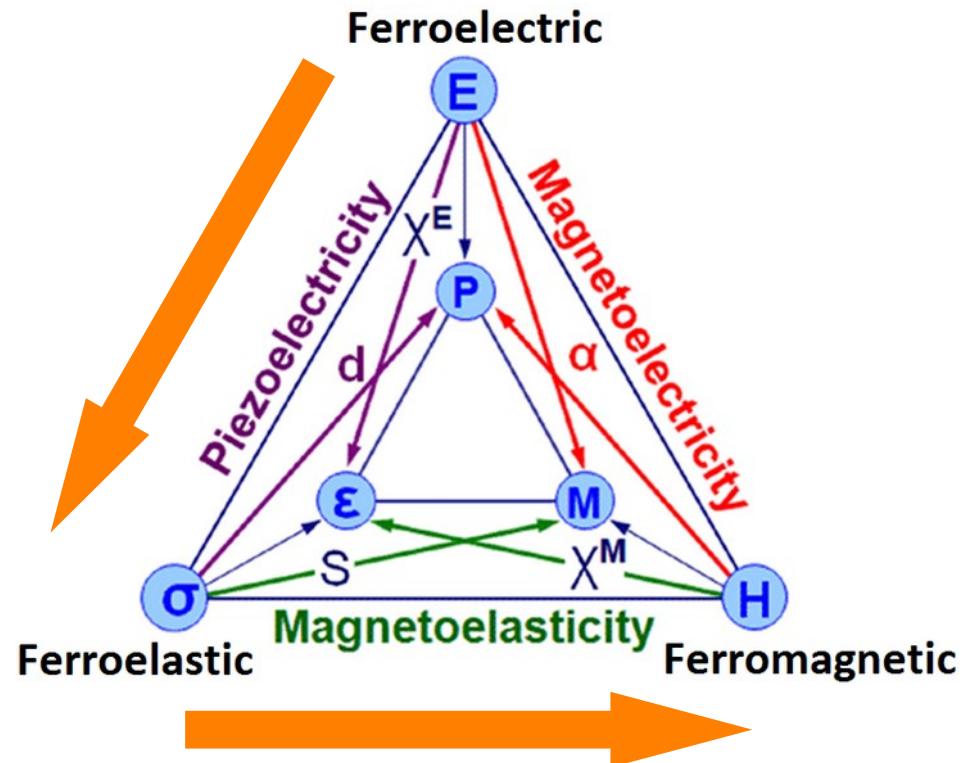
Coupling between ferroelectric and ferromagnetic properties



Magneto-electric coupling

Electrical control of ferromagnetic order

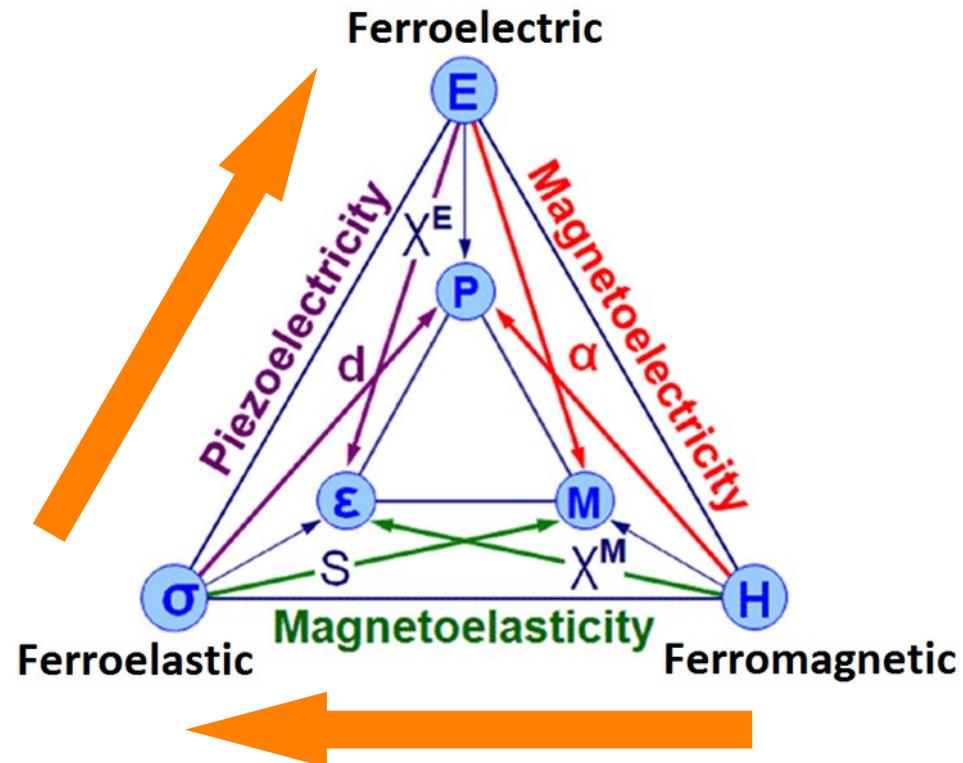
electric field → strain → magnetic polarization



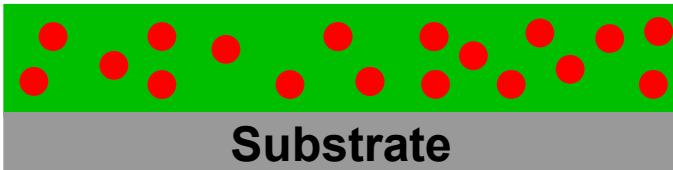
Magneto-electric coupling

Magnetic control of ferroelectric order

magnetic field → strain → electrical polarization



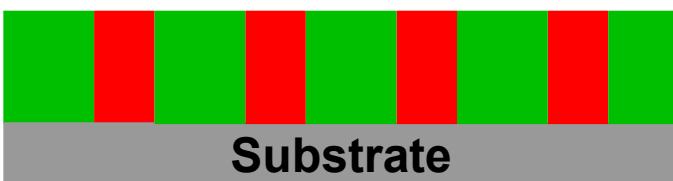
Design of hybrid magneto-electric layers



- Particle aggregation
- Poor control of particle distribution in the matrix



- Reduction of magnetostriction due to the clamping of the layer on the substrate

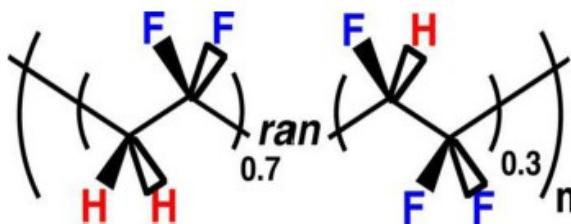


- Avoids above mentioned problems
- Maximizes contact area

Ferromagnetic Ferroelectric
material material

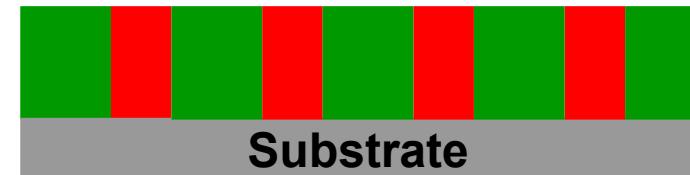
PVDF-TrFE

- Good ferroelectric properties
- Easy processability



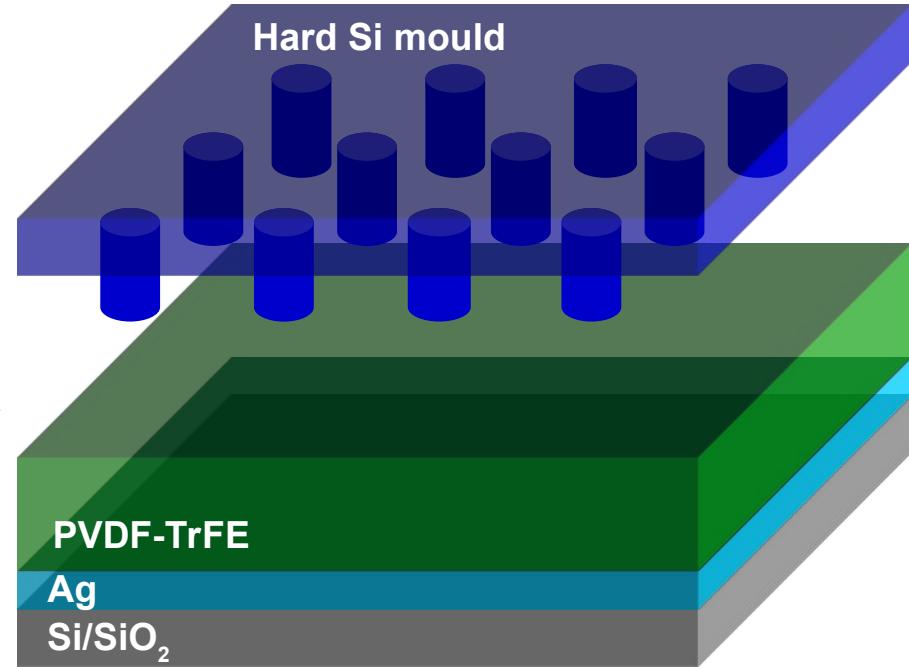
Nickel

- Large magnetostriuctive coefficient
- Easy electrochemical deposition

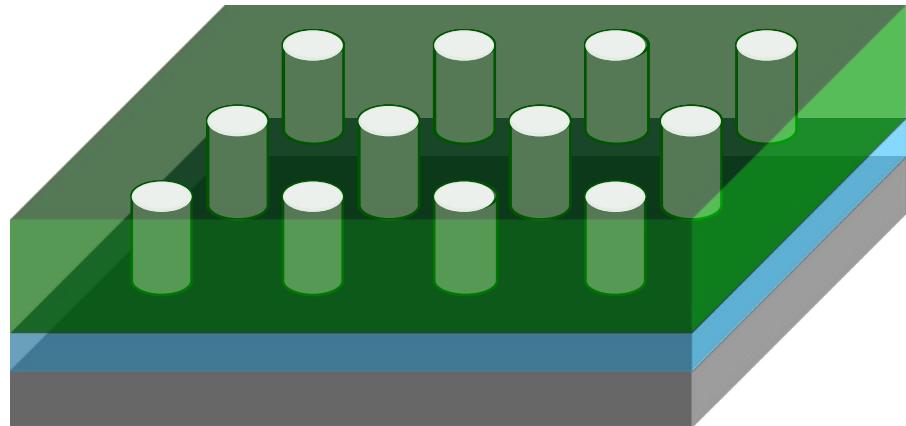


Ferromagnetic Ferroelectric
material material

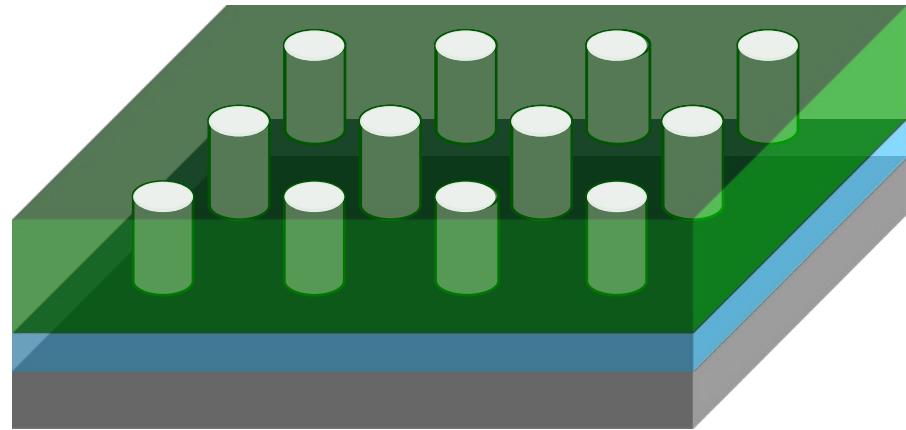
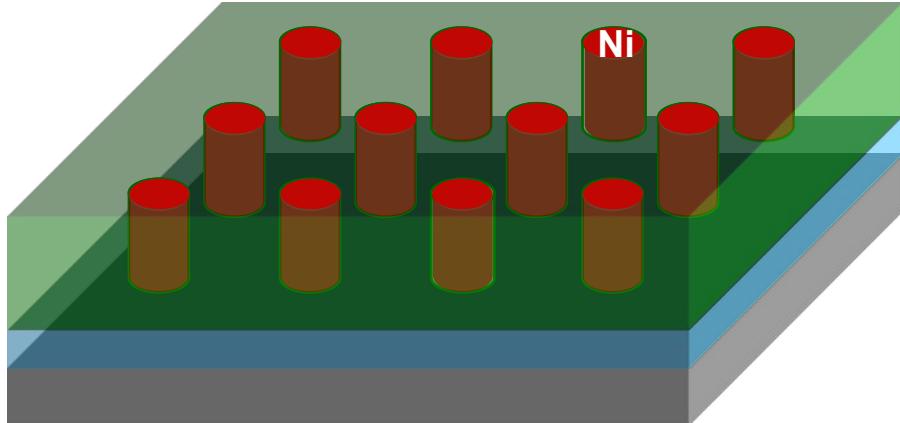
Magneto-electric layer fabrication



Nanoimprint lithography

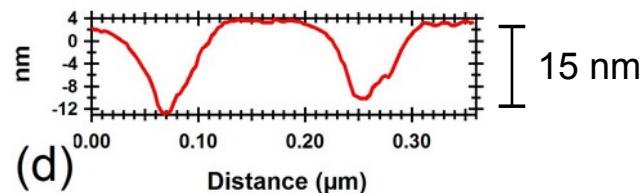
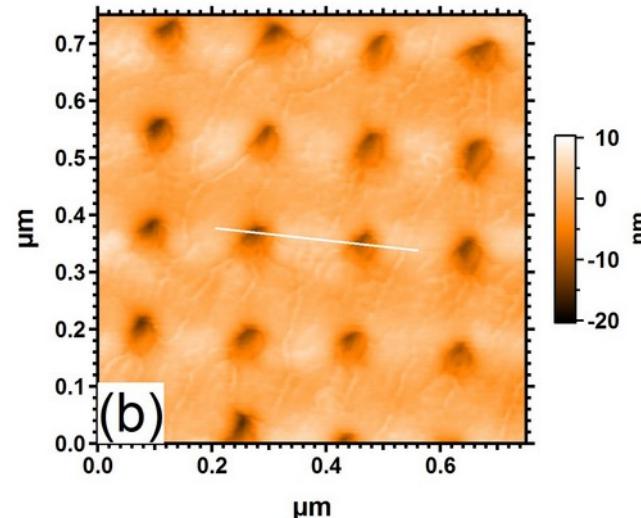
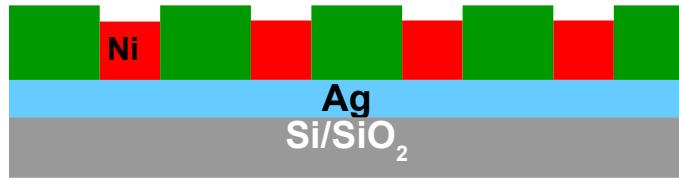
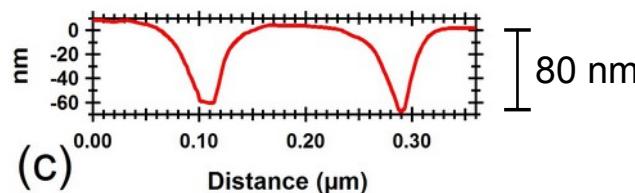
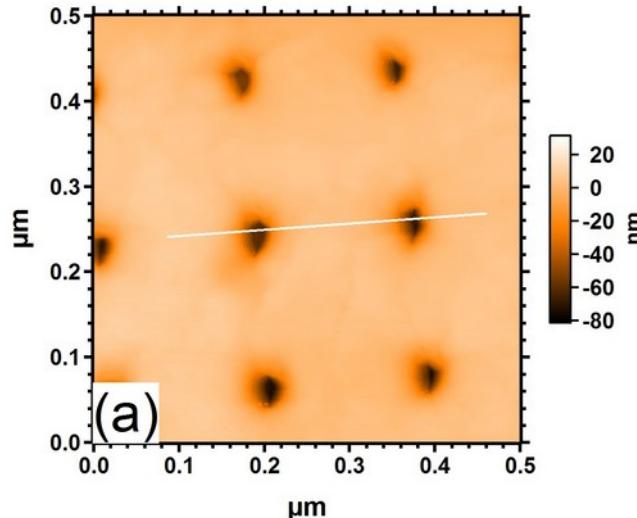
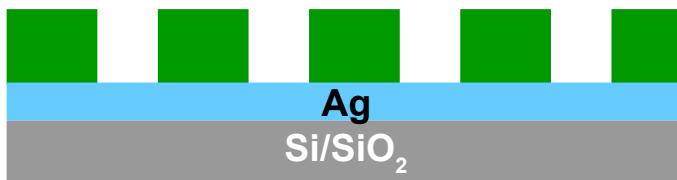


Magneto-electric layer fabrication



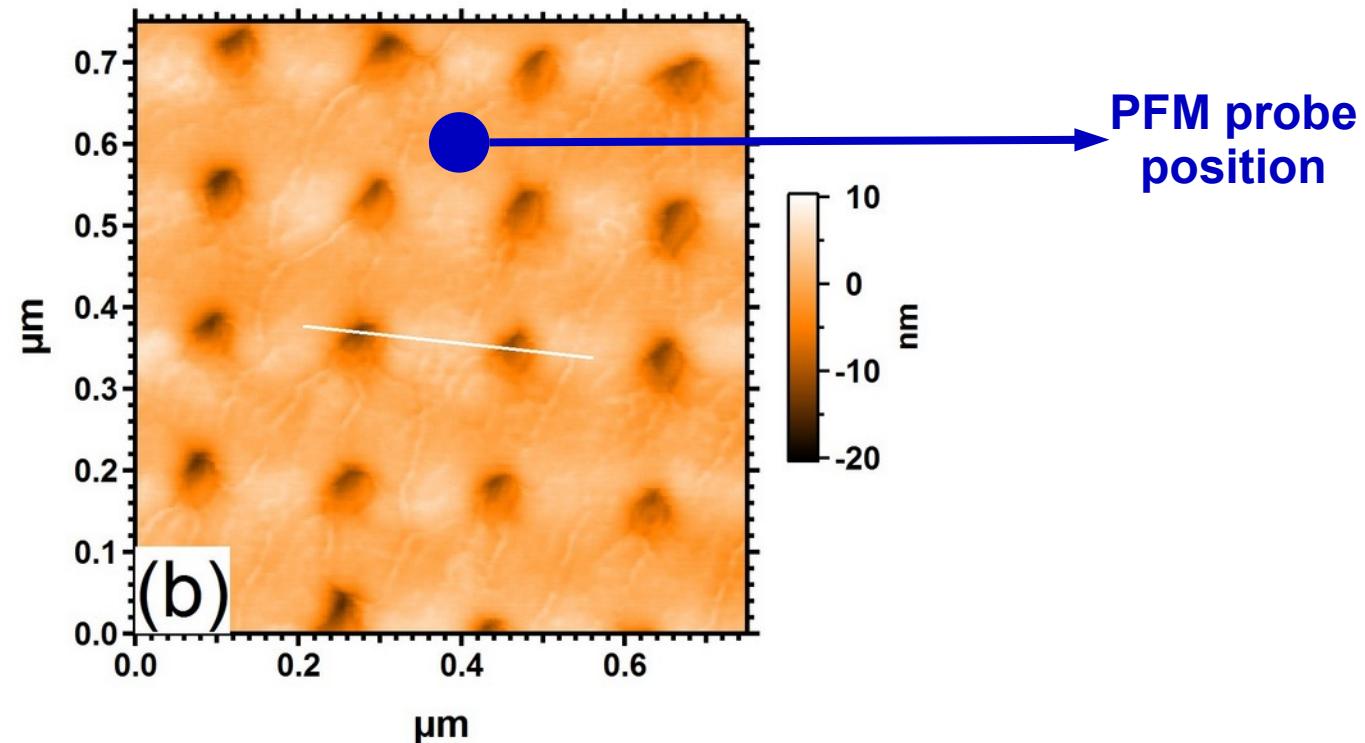
Ni
electrodeposition

Magneto-electric layer morphology



In-field magneto-electric properties

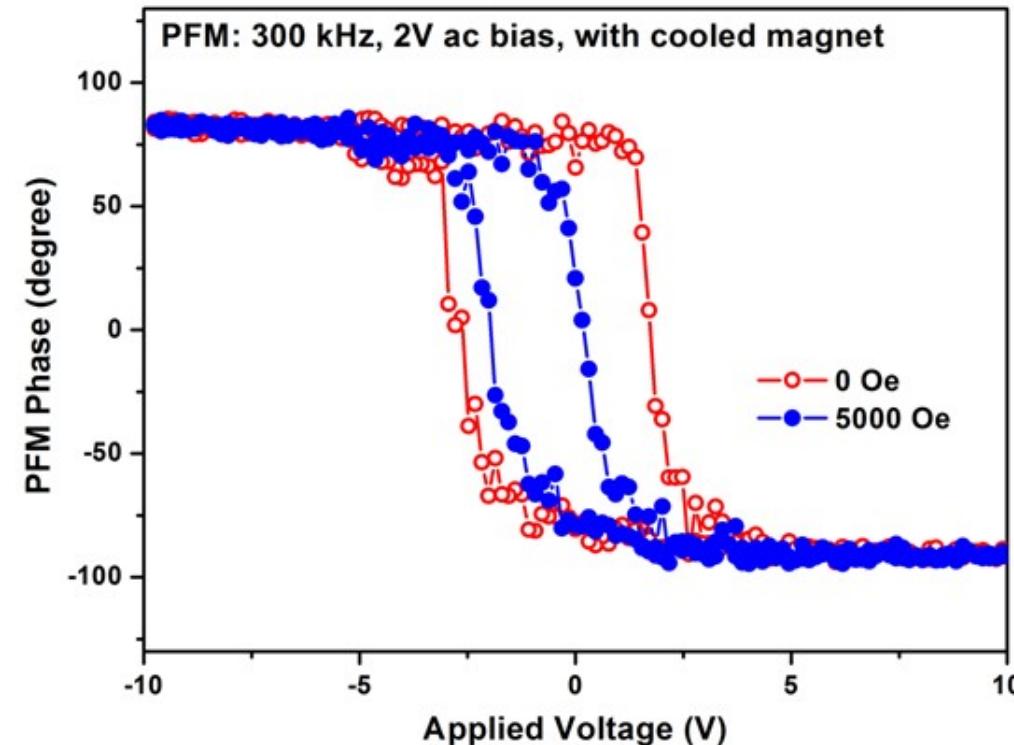
PFM spectroscopy under transverse magnetic field
(using same setup as for *in-situ* MFM analyses)



In-field magneto-electric properties

Giant magneto-electric coupling effect

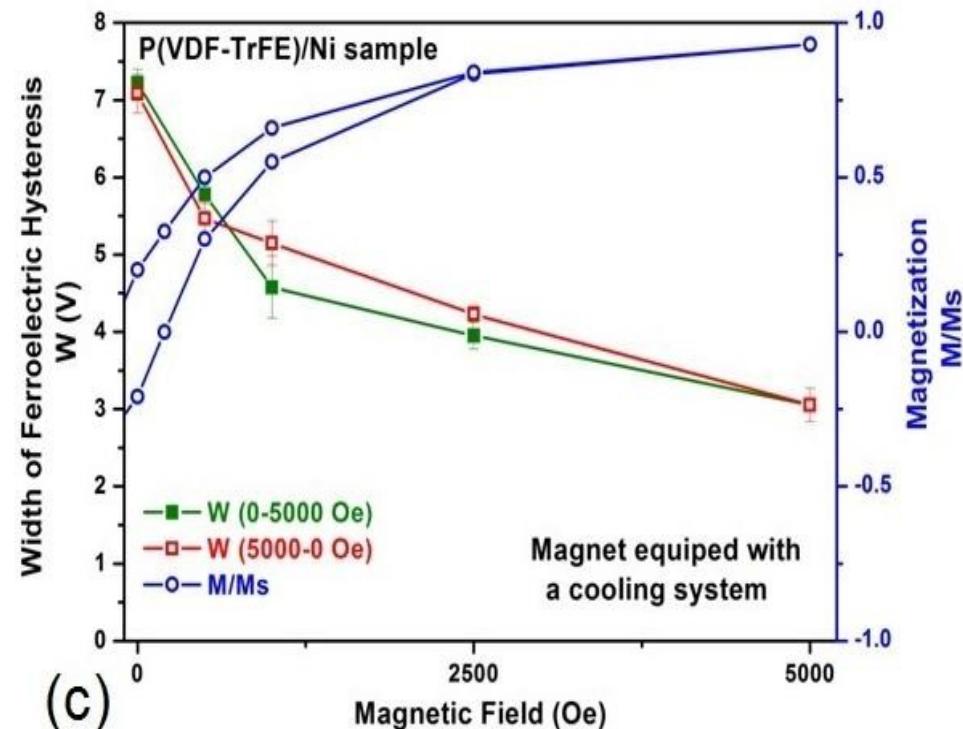
- Decrease of hysteresis loop width with increasing magnetic field



In-field magneto-electric properties

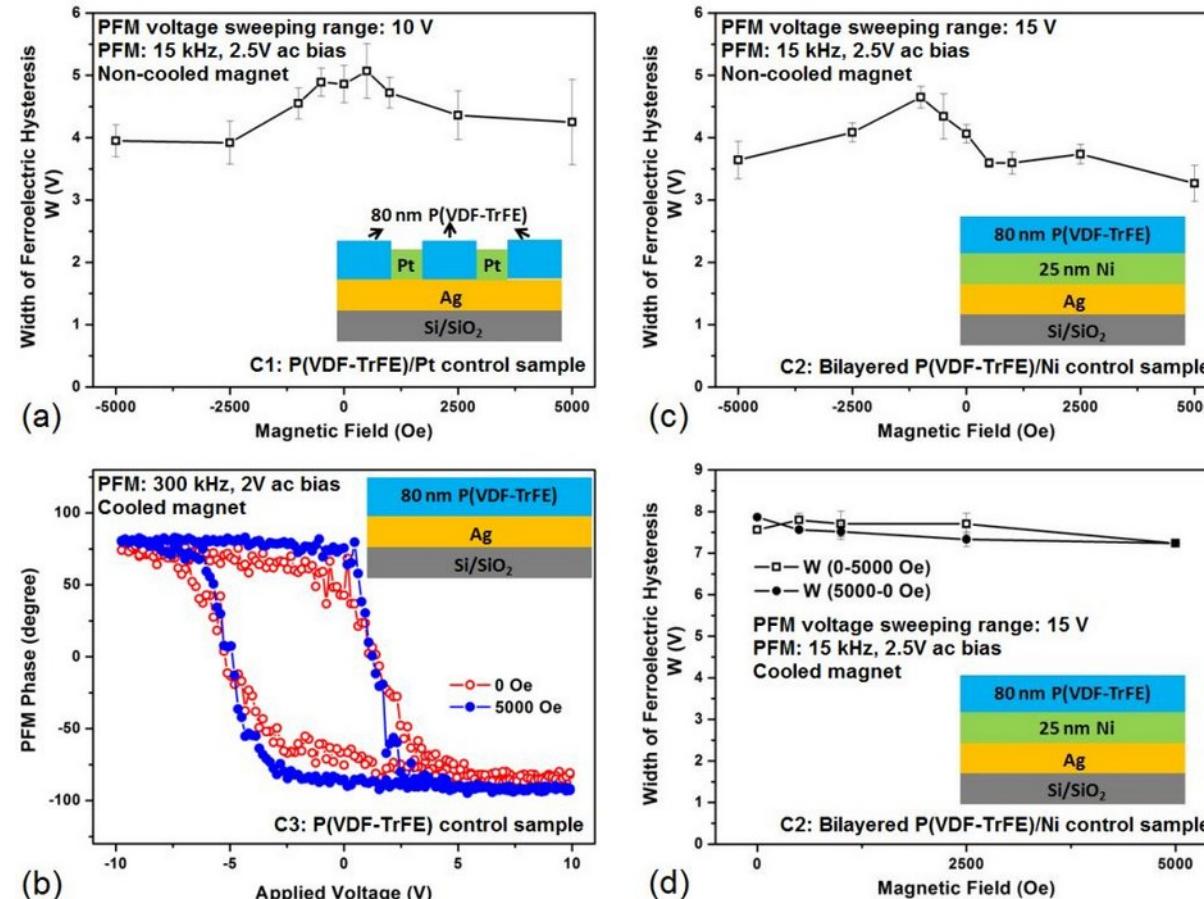
Giant magneto-electric coupling effect

- Decrease of hysteresis loop width with increasing magnetic field



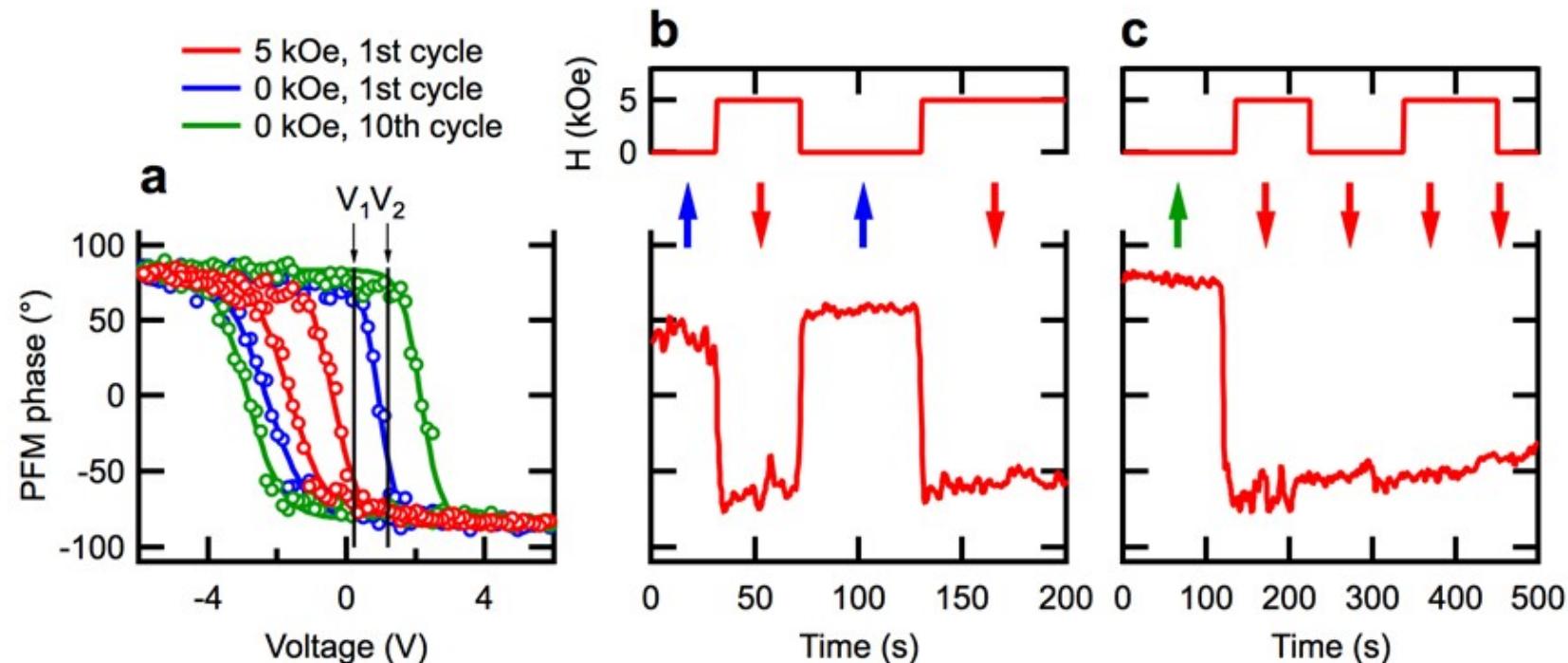
In-field magneto-electric properties

Control experiments



Magnetic control of electrical polarization

Polarization reversal by on/off switching of the magnetic field



In-situ and *in-field* MFM on dilute arrays of magnetic nanowires

- Access to the intrinsic switching-field distribution
- Measurement of inter-wire interaction field on individual nanowires
 - Tabasum M. R. *et al.*, *J. Appl. Phys.* **2013**, *113*, 183908
 - Tabasum M. R. *et al.*, *J. Superconduct. Novel Magn.* **2013**, *26*, 1375
 - Tabasum M. R. *et al.*, *Nanotechnology* **2014**, *25*, 245707

In-field PFM on hybrid magneto-electric layers

- Characterisation of a giant magneto-electric coupling effect
- Evidence of magnetic control of electrical polarization
 - Cai R. *et al.*, *Adv. Mater.* **2017**, *29*, 1604604
 - Poddar S. *et al.*, *ACS Nano* **2018**, *12*, 576
 - Cai R. *et al.*, *Adv. Funct. Mater.* **2020**, *30*, 1910371

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Thank you for your attention