Multifunctional magnetic materials

Denys Makarov

Definition

What is multifunctional material?

Multifunctional material is defined to be any material or material-based system which integrally combines two [or possibly more] properties, one of which is normally structural and the other functional, e.g. optical, electrical, magnetic, thermal etc...

https://www.scitechnol.com/scholarly/multifunctional-materials-journals-articles-ppts-list.php

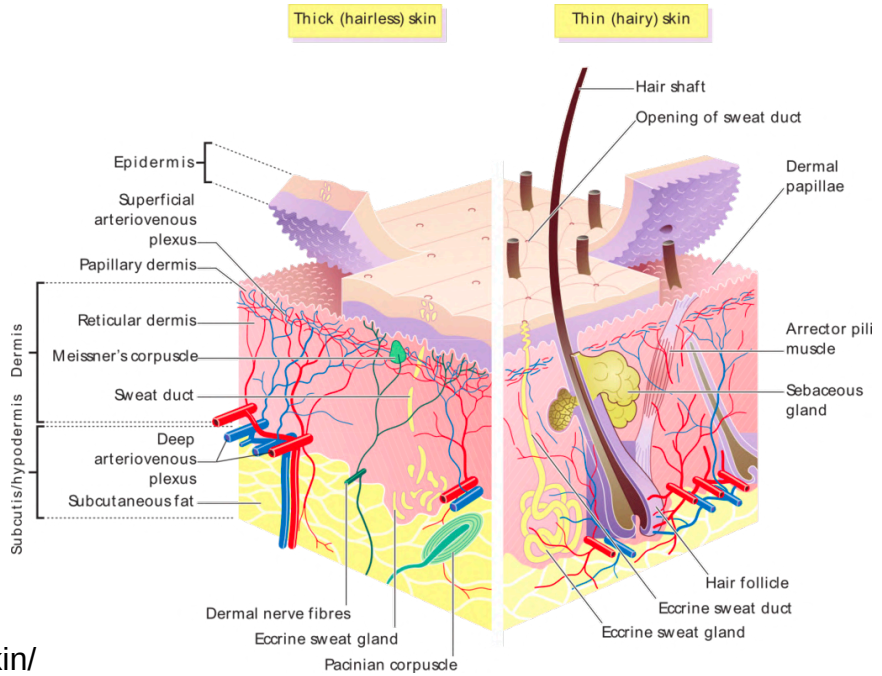
Definition

Multifunctional materials are the materials that perform multiple functions in a system due to their specific properties

The applications of such new "smart" materials include energy, medicine, nanoelectronics, aerospace, defence, semiconductor, and other industries

Multifunctional materials can be both naturally existing and specially engineered

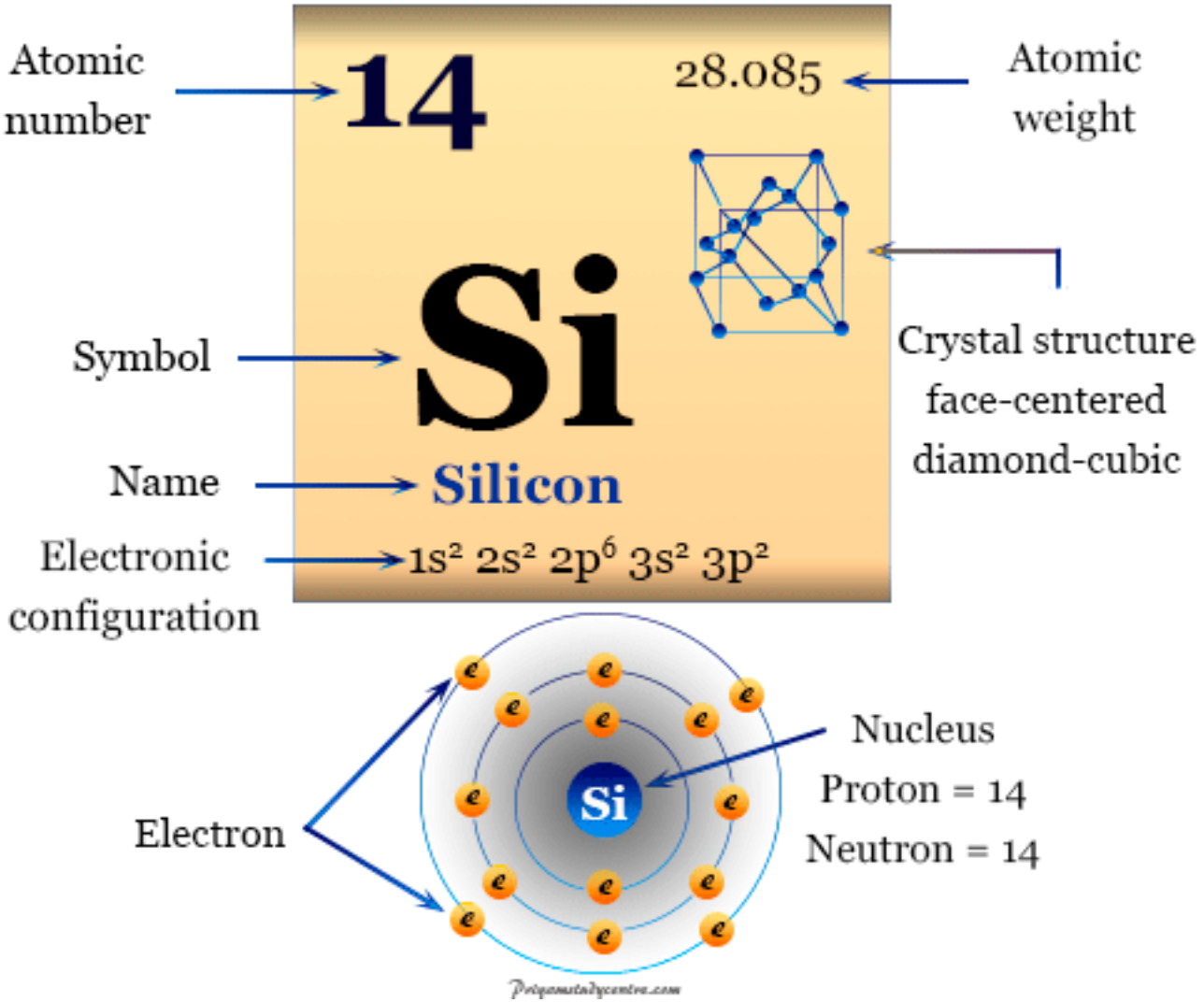
What is the most well known natural multifunctional material?



https://www.e-education.psu.edu/eme807/node/698

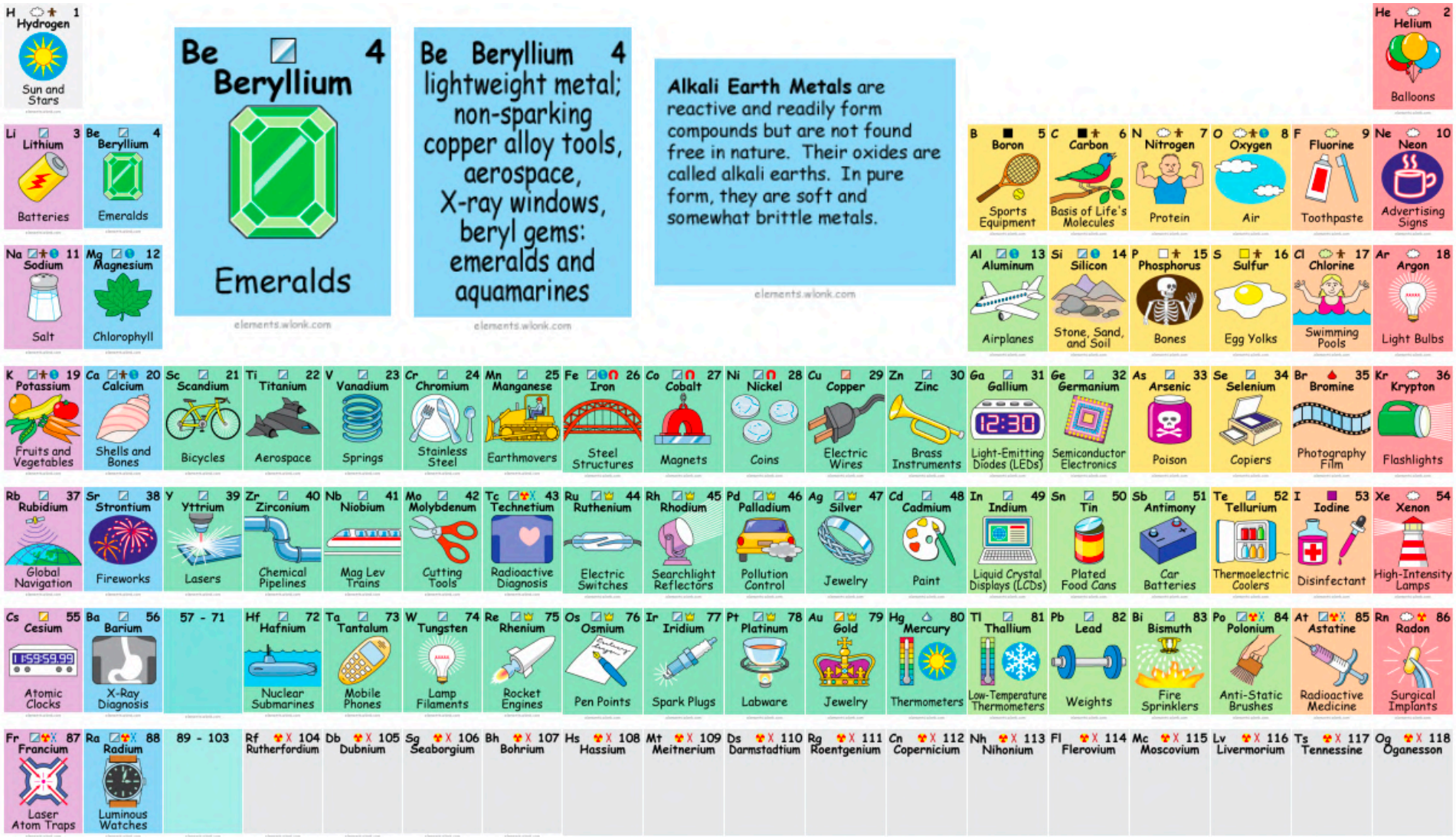
https://courses.lumenlearning.com/boundless-ap/chapter/the-skin/

Do you know not multifunctional materials?

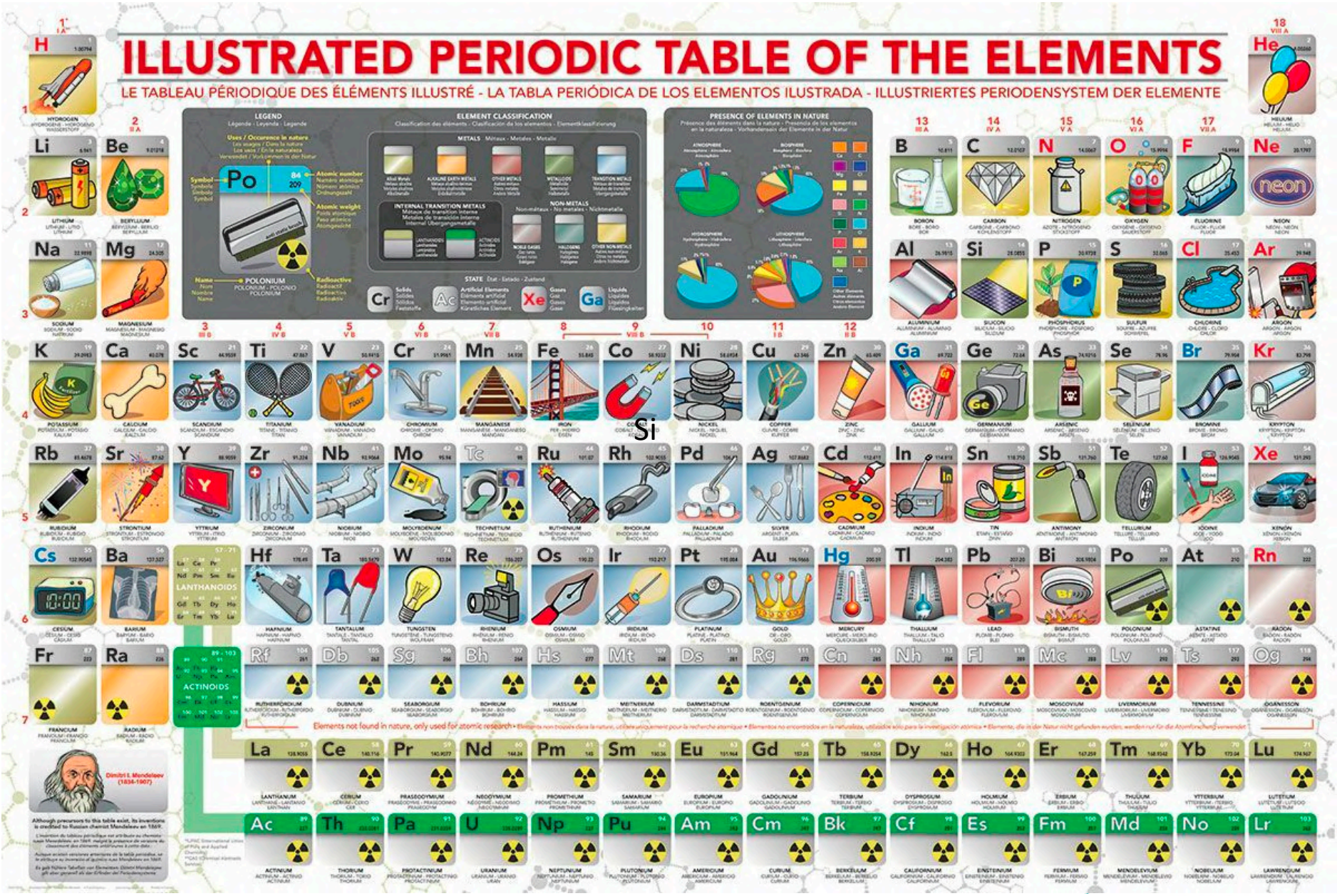


Semiconductor => electronics Suitable band gap => optics (detectors), communication

Do you know not multifunctional materials?



Do you know not multifunctional materials?



Definition / Semantics

Smart materials Intelligent materials Advanced Materials

Multifunctional materials Advanced functional materials

Multiferroic materials Magnetoelectric materials

Magnetic composites

Most probably, these are (in some sense) synonyms

Ferroic materials / Order parameter

The behavior of any physical system from cosmological objects in field theories through living organisms in biology up to synthetic objects in condensed and soft matter is determined by the order parameter that lives in spacetime

Order parameter in ferromagnets: magnetisation

In ferromagnets, order parameter brakes the time reversal symmetry

There are (at least) 4 ferroic order parameters

Ferroic materials / Order parameter

A material is termed as ferroic if there is a spontaneous property, called the order parameter, that arises in uniform alignment of some microscopic property of the unit cell throughout macroscopic regions of a crystal

The order parameter O can be switched into at least two different directions by some external field A

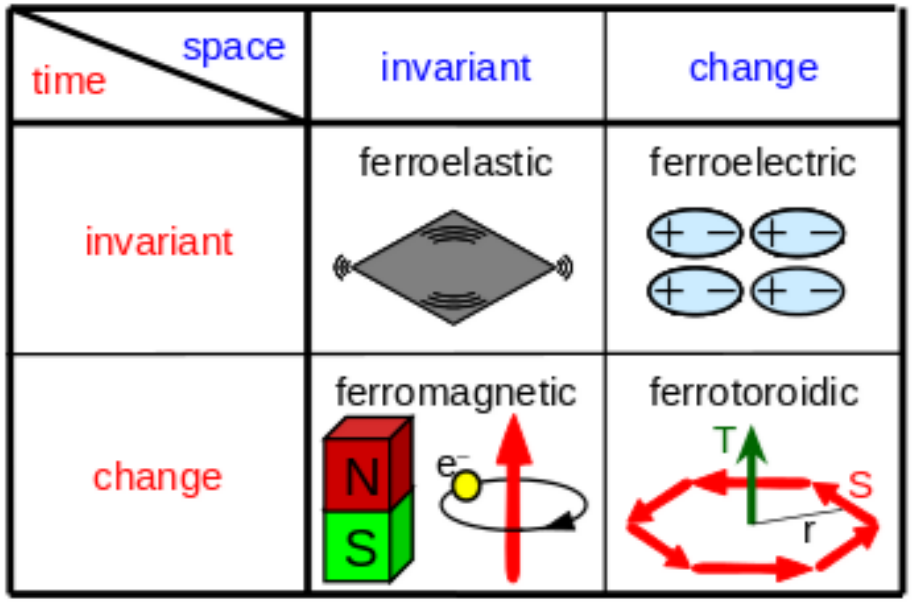
This works because a ferroic contributes a term
$F = -OA$
to the free energy so that an alignment of O parallel to A minimizes this energy

Regions with different orientation of the order parameter can coexist.
They are called domains

Long-range ordering is present below a critical temperature only

Manfred Fiebig: https://www.hikari.uni-bonn.de/research/multiferroics/new-forms-of-ferroic-order

Ferroic materials / Order parameter



Type	Micro. property	Macro. property	Force field
Ferroelastic	Deformation	Strain	Stress
Ferromagnetic	Magnetic moment	Magnetization	Magnetic field
Ferroelectric	El. dipole moment	Polarization	Electric field
Ferrotoroidic	Magnetic vortex	Toroidization	Toroidal field

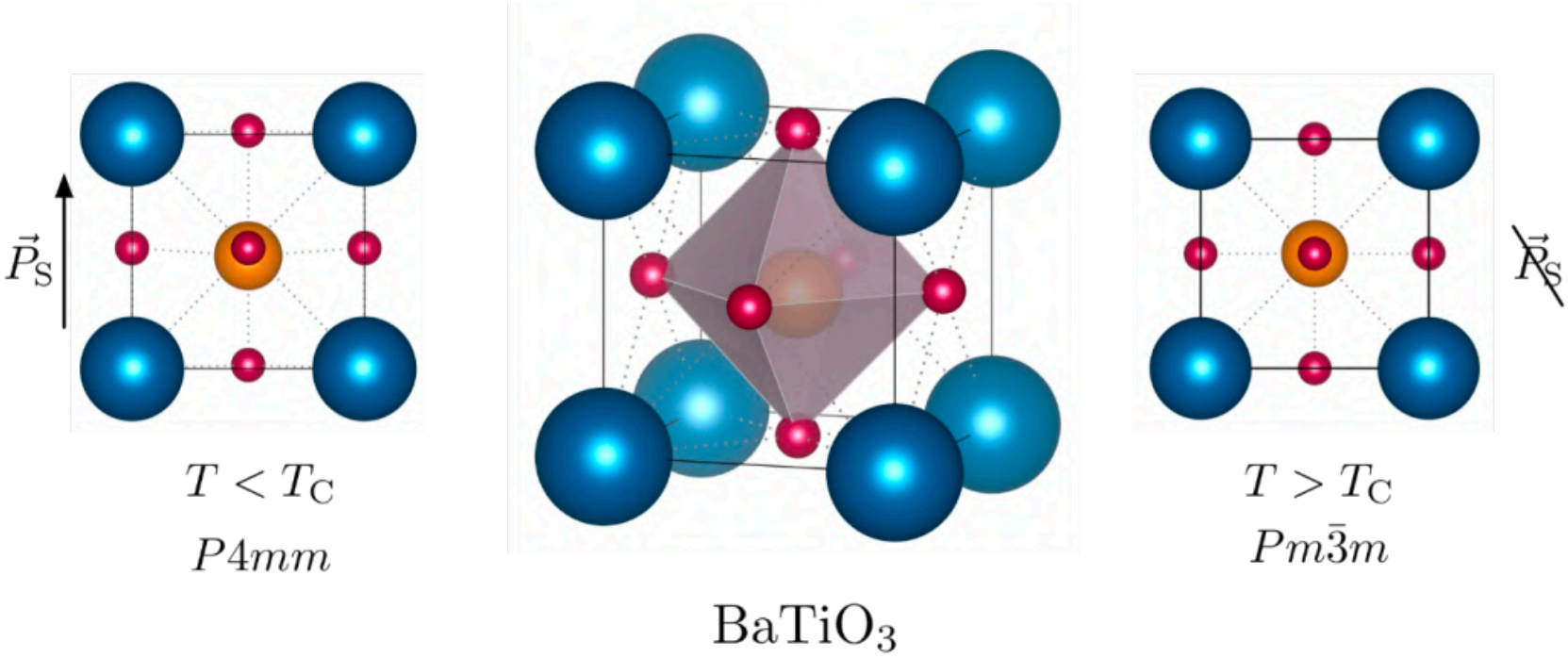
N. A. Spaldin, M. Fiebig & M. Mostovoy
The toroidal moment in condensed-matter physics and its relation to the magnetoelectric effect
J. Phys.: Condens. Matter **20**, 434203 (2008)

Manfred Fiebig: https://www.hikari.uni-bonn.de/research/multiferroics/new-forms-of-ferroic-order

Ferroelectric barium titanate: $BaTiO_3$

parent phase: ideal cubic ABO_3 perovskite structure => no electric polarisation

ferroelectric phase: the Ti^{4+} ion is shifted away from the center of the octahedron causing a polarization (only one ferroic order; no magnetism; empty *d* shell)

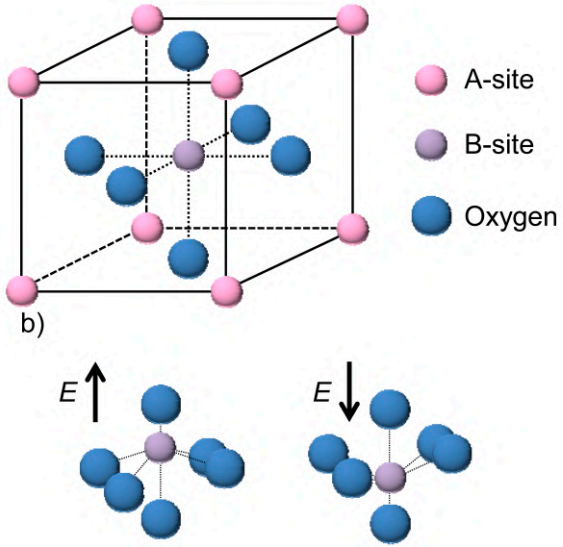


https://blogs.hrz.tu-freiberg.de/pyro/pyroelektrizitaet/

Mutiferroic $BiFeO_3$ (BFO)

In BFO, the ferroelectric displacement is driven by the A-site cation, and the magnetism arises from a partially filled *d* shell on the B site

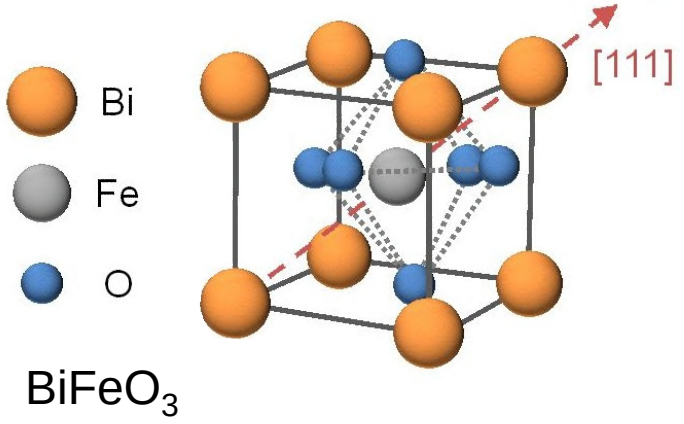
In BFO, the A-site cation (Bi^{3+}) has a so-called stereochemically active $6s^2$ lone-pair of electrons, and off-centering of the A-site cation is favoured by an energy-lowering electron sharing between the formally empty A-site *6p* orbitals and the filled O *2p* orbitals



cubic phase

rhombohedrally distorted perovskite structure

J. B. Neaton et al., *Phys. Rev. B*. **71**, 014113 (2005)



$BiFeO_3$

https://www.intechopen.com/chapters/44929

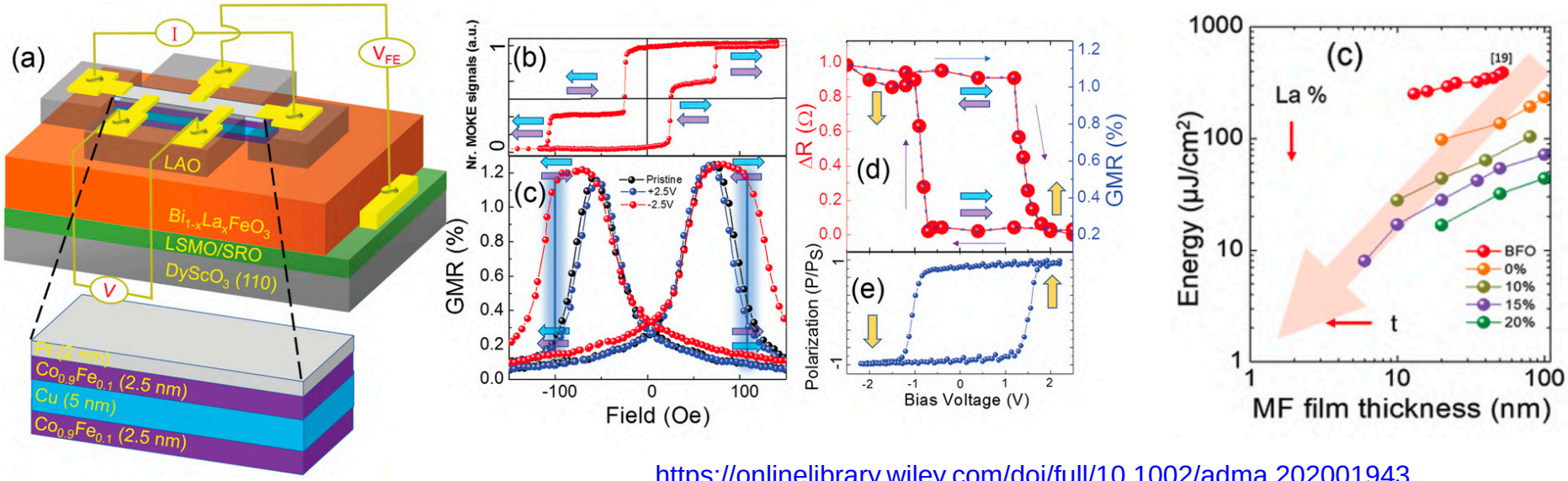
BFO based ultralow power electronics

Spin transfer torque magnetic random access memory (STT-MRAM) is among the most promising spintronic memory for computing

Still, it suffers from resistance scalability (resistance scales inversely proportional to the area and drive current densities) and intrinsically high energy/bit operation (>100 fJ/bit)

Magneto-electric memory can operate with capacitive displacement charge and potentially reach 1-10 aJ/switching operation

$Bi_{1-x}La_xFeO_3$ thin films



https://onlinelibrary.wiley.com/doi/full/10.1002/adma.202001943

Mutiferroic vs Magnetoelectric materials

Multiferroics are defined as materials that exhibit more than one of the primary ferroic properties in the same phase

In magnetoelectric materials electric field modifies the magnetic properties and vice versa

All ferromagnetic ferroelectric multiferroics are linear magnetoelectrics

Magnetoelectric materials are not necessarily multiferroic

Magnetoelectric Cr_2O_3

I. Dzyaloshinskii, *ZETF* **37**, 881 (1959)

Free energy expansion in powers of *E* and *H* according to Landau & Lifshitz (1958):

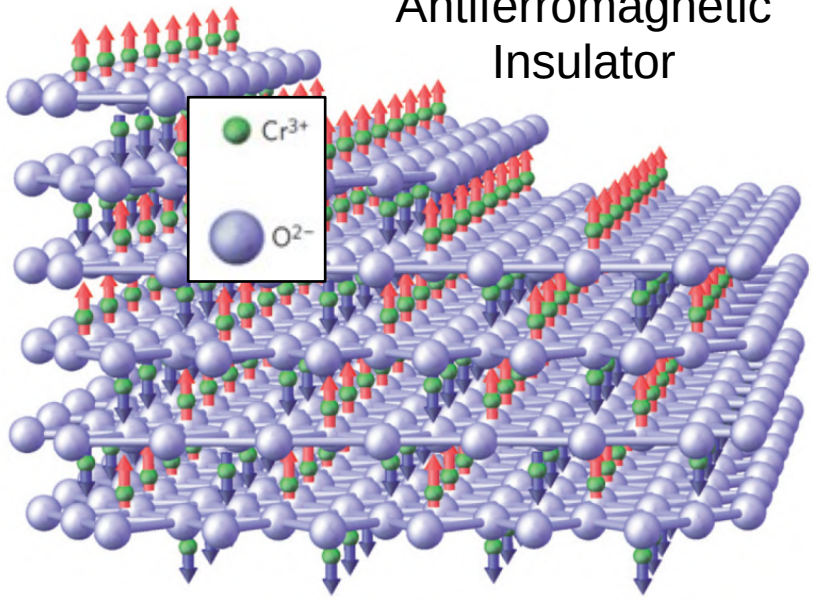
$$F(E,H) = F_0 - \frac{\varepsilon_{ij} E_i E_j}{8\pi} - \frac{\mu_{ij} H_i H_j}{8\pi} - \alpha_{ij} E_i H_j - \cdots$$

Electric response to electric field

Magnetic response to magnetic field

Cr_2O_3

Magnetoelectric Antiferromagnetic Insulator



X. He et al., *Nature Mat.* **9**, 579 (2010)

Linear magnetoelectric effect

➡ Only allowed if time- & space inversion symmetries individually broken

α_{ij}

Magnetoelectric tensor

www.etsy.com

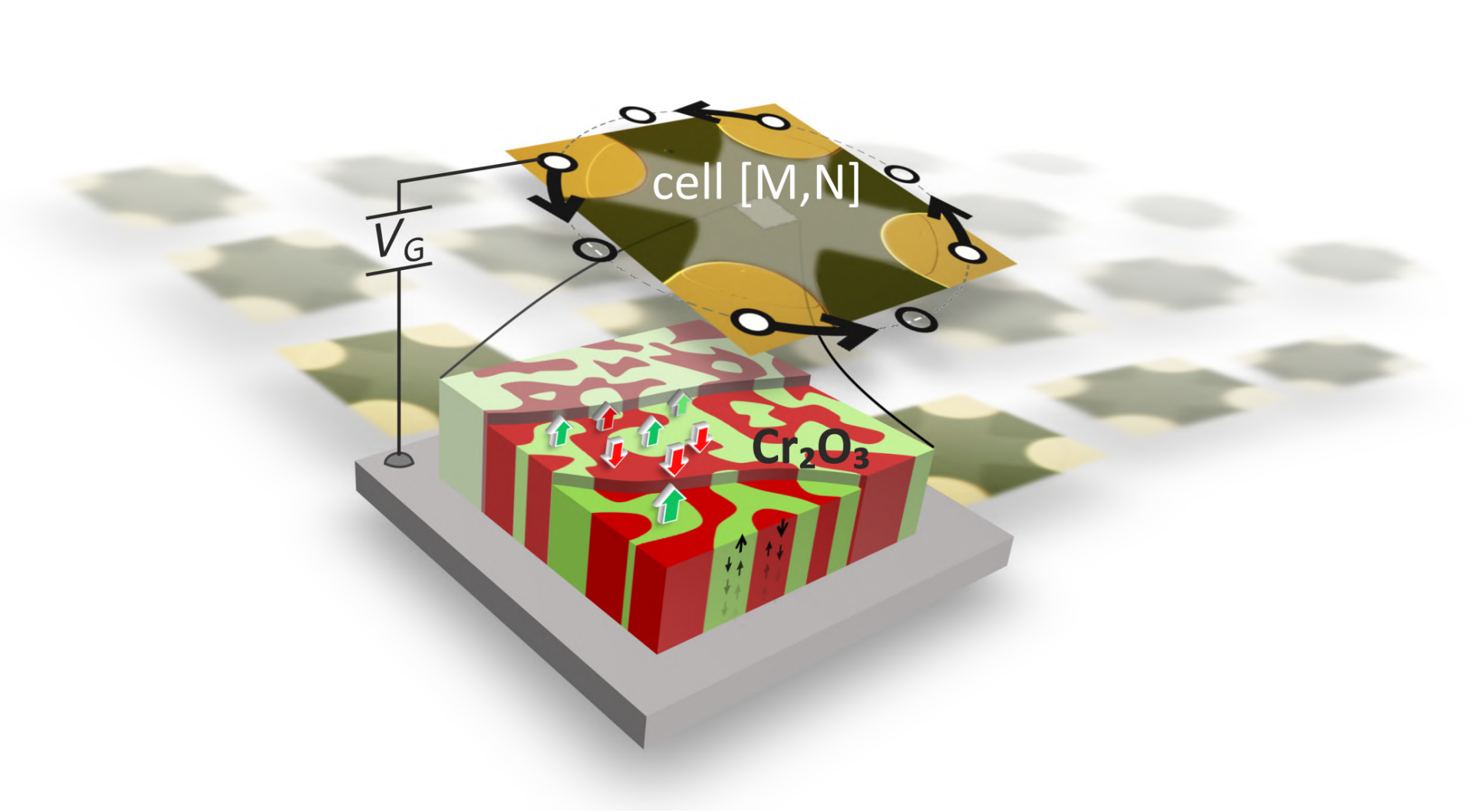
Multifunctional

Optoelectronics

Solar cells

Pigment

Magnetoelectric Cr_2O_3



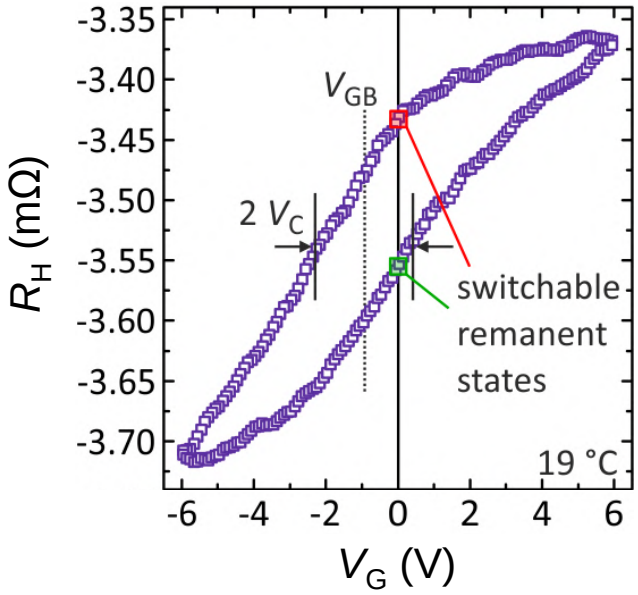
T. Kosub, DM et al., *Nature Commun.* **8**, 13985 (2017)

T. Kosub, DM et al., *PRL* **115**, 097201 (2015)

Linear magnetoelectric effect in AF-MERAM

Isothermal switching by gate voltage

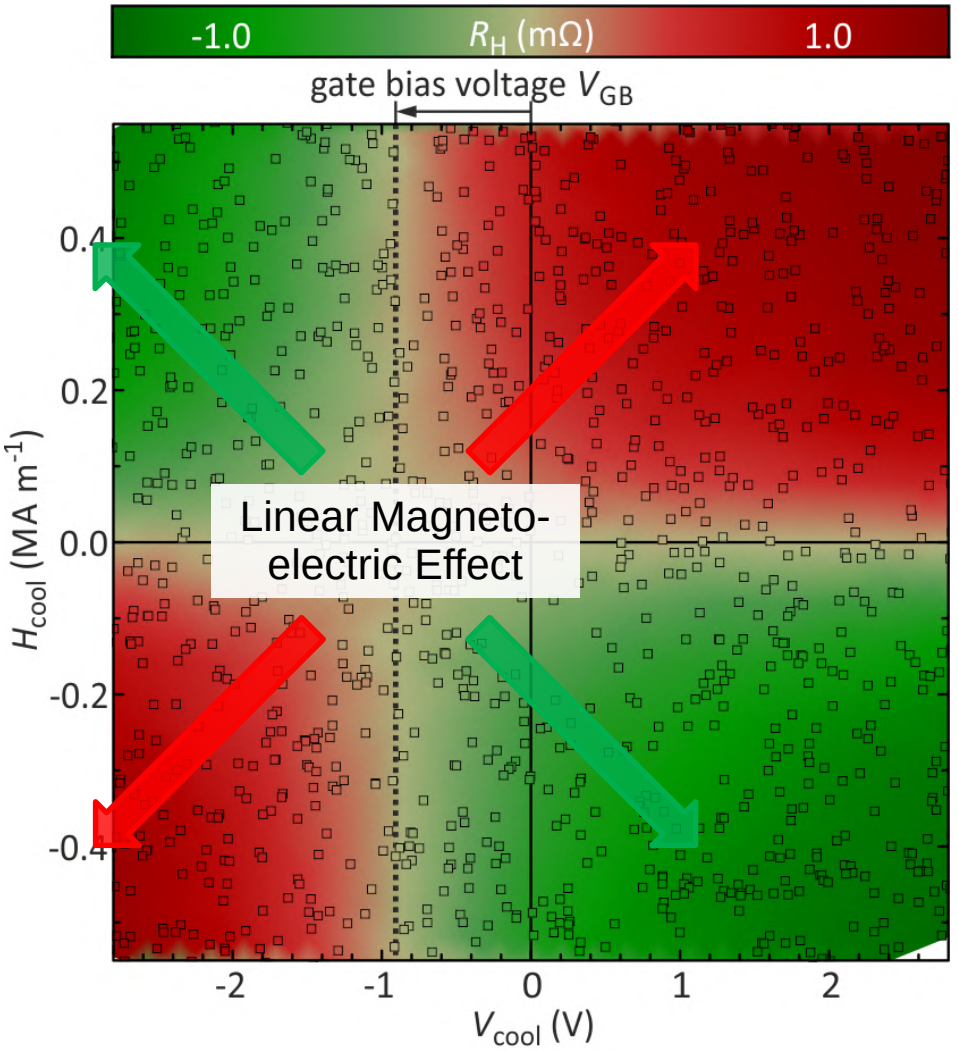
Read out signal



Writing gate voltage

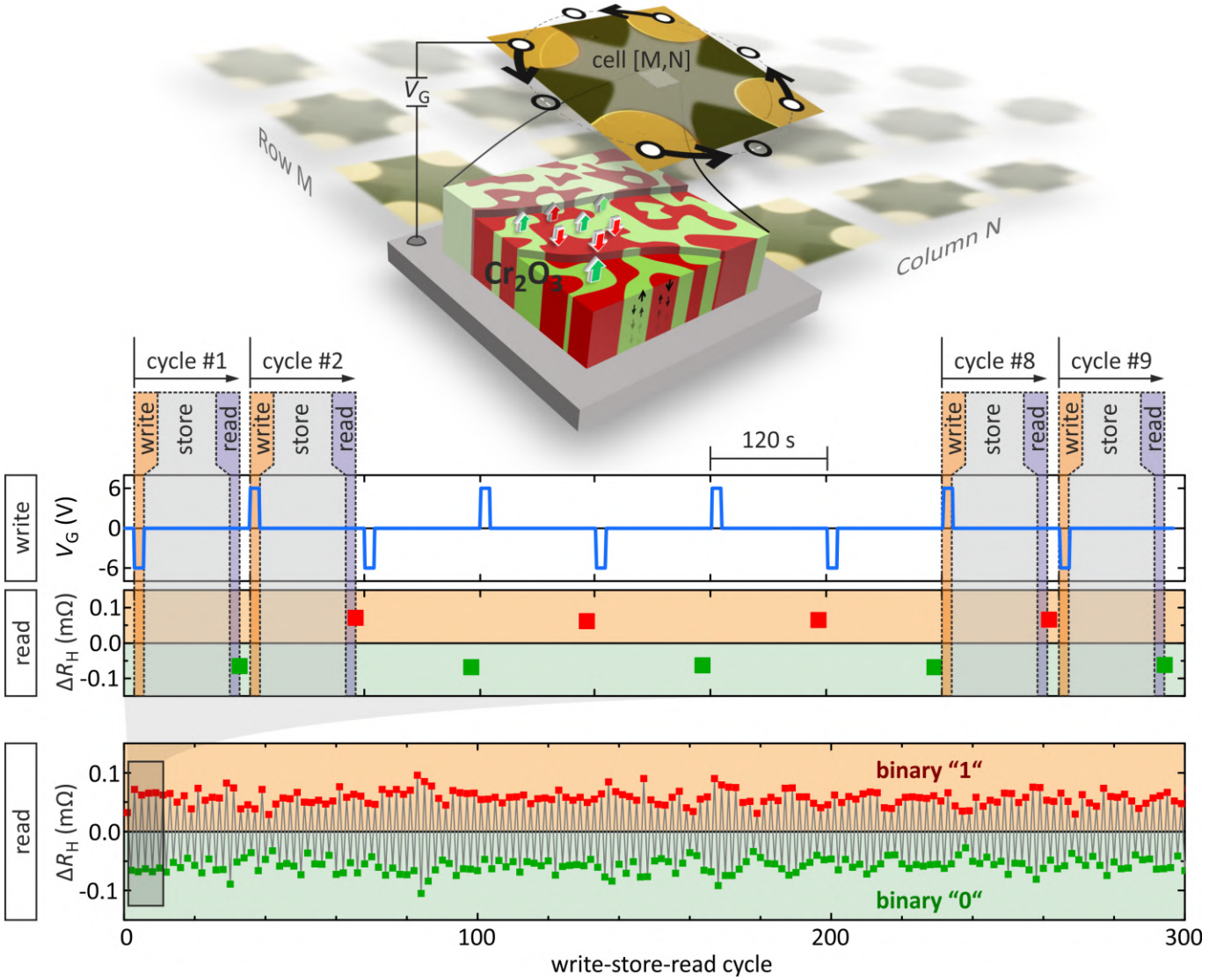
200-nm-thick Cr_2O_3
on Al_2O_3 substrate

Magnetoelectric field cooling



T. Kosub, DM et al., *Nature Commun.* **8**, 13985 (2017)

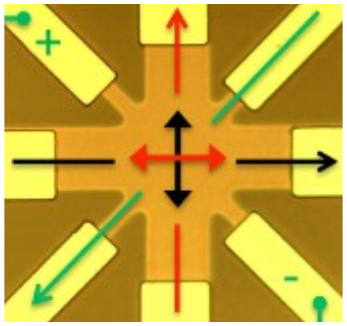
Realization of an AF-MERAM cell

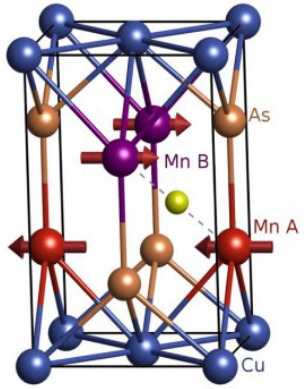


T. Kosub, DM et al., *Nature Commun.* **8**, 13985 (2017)

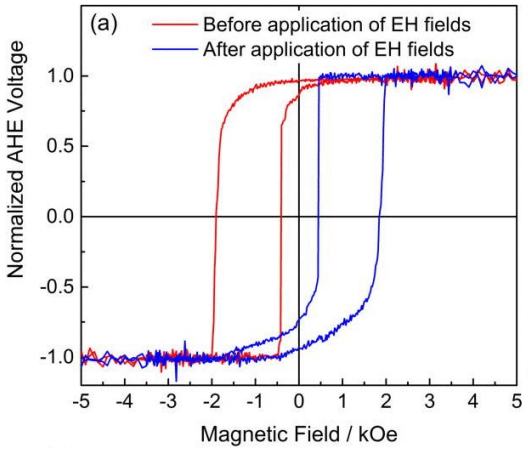
Families of Magnetic RAM

write with:	read from: ferromagnet	read from: antiferromagnet
charge current	MRAM	AF-MRAM
electric field	MERAM	AF-MERAM

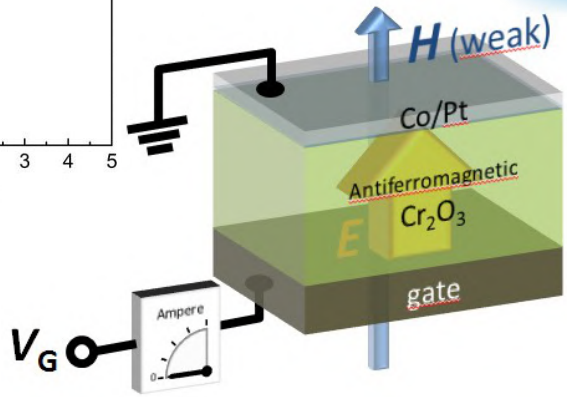


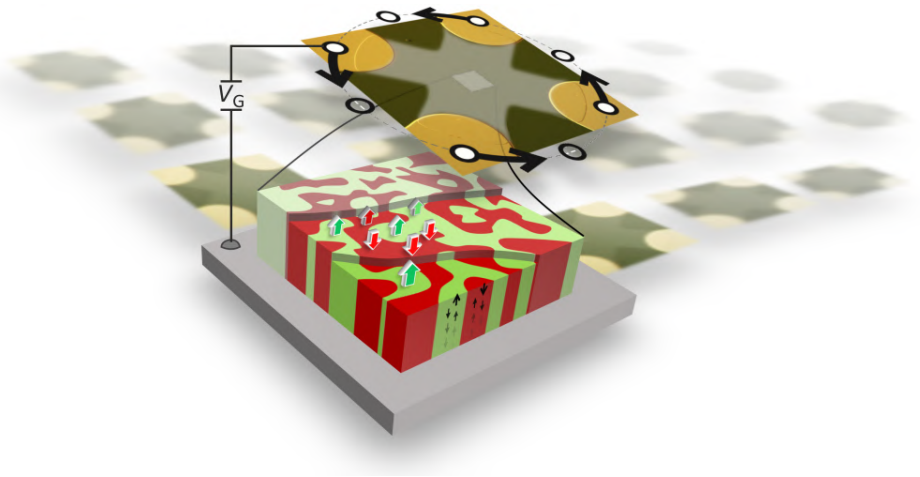


P. Wadley et al., *Science* (2016)



T. Kosub, DM et al.,
Nature Commun. **8**, 13985 (2017)





X. He et al., *Nature Mat.* **9**, 579 (2010)
K. Toyoki et al., *APL* **106**, 162404 (2015)

Magnetostrictive materials

Magnetism and mechanical deformation

Magnetostriction: change of the shape or dimensions of a magnetic material upon magnetisation (in an applied magnetic field)

Anisotropic magnetostriction (Joule magnetostriction): elongation/contraction (for positive/negative magnetostrsiction coefficient) of the material in an applied field

Typically small: relative elongation is in the order of 10×10^{-6}

Terfenol-D ($TbDyFe_2$ alloy): about 2000×10^{-6} at 2 kOe and room temperature

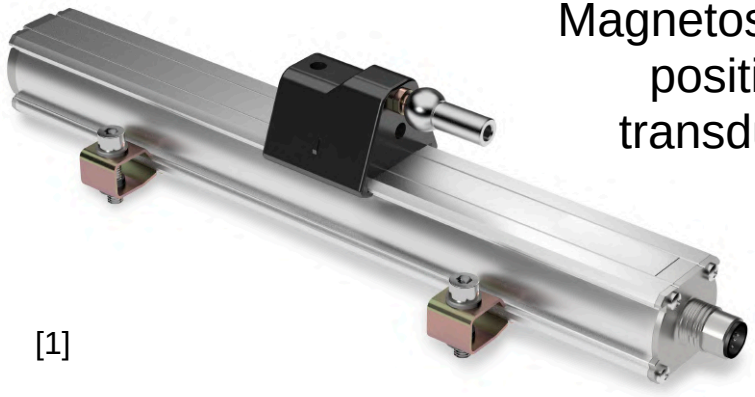
FeAl alloy: about 300×10^{-6} at 0.2 kOe

Isotropic magnetostriction: isotropic volume change in an applied field (much smaller than Joule magnetostriction)

https://www.tf.uni-kiel.de/servicezentrum/neutral/praktika/anleitungen/m205

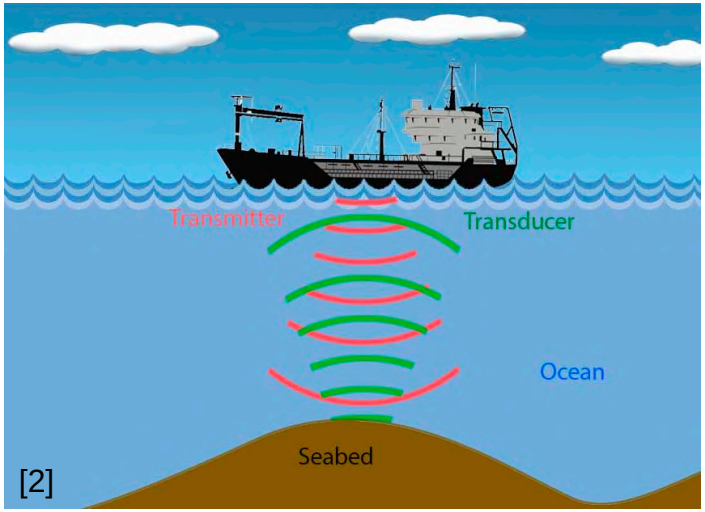
Magnetostriction: applications

Magnetostrictive position transducer



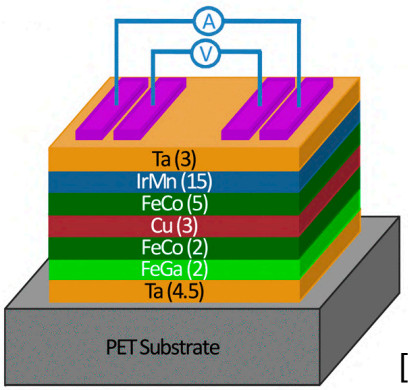
[1]

Magnetostrictive sonar



[2]

Magnetostrictive spin valves



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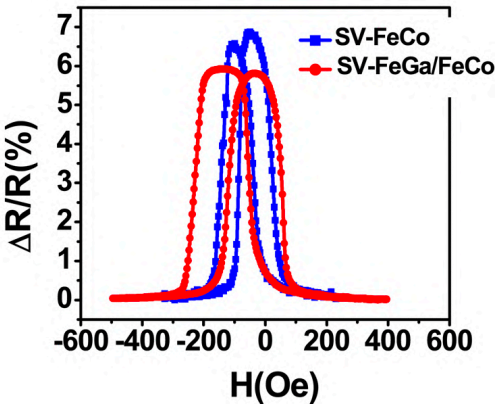
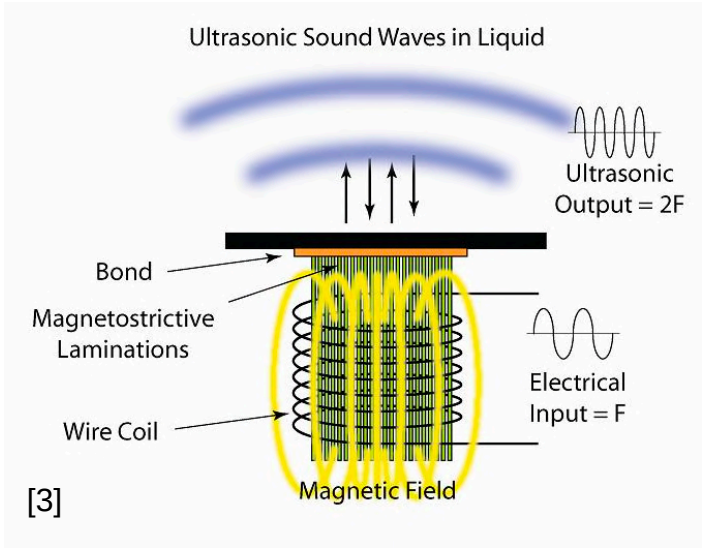




[3]

[1] https://www.powertransmissionworld.com/a-new-contacless-magnetostrictive-position-transducer/

[2] https://news.vidyaacademy.ac.in/wp-content/uploads/2019/02/Active-sonar.jpg

[3] https://techblog.ctgclean.com/2012/01/ultrasonics-transducers-magnetostrictive-hardware/

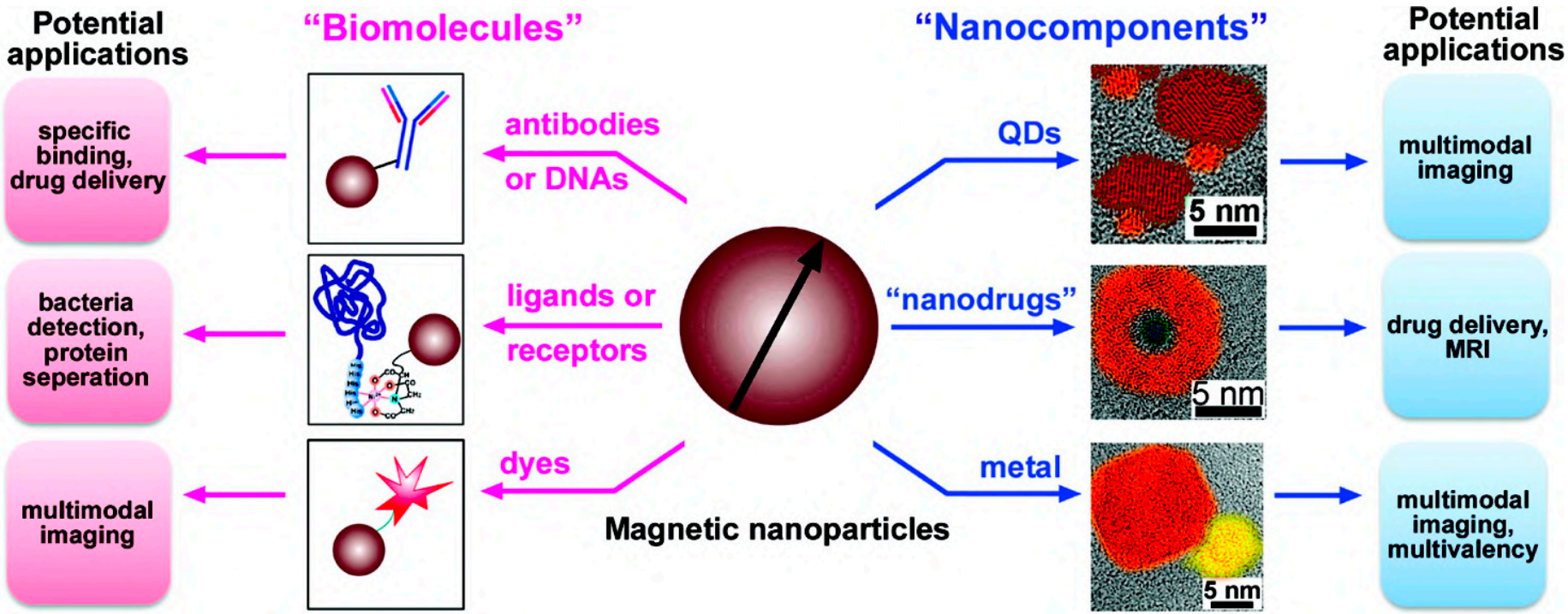
[4] https://aip.scitation.org/doi/10.1063/1.4943770

Magnetic composites

Magnetic particles and polymers

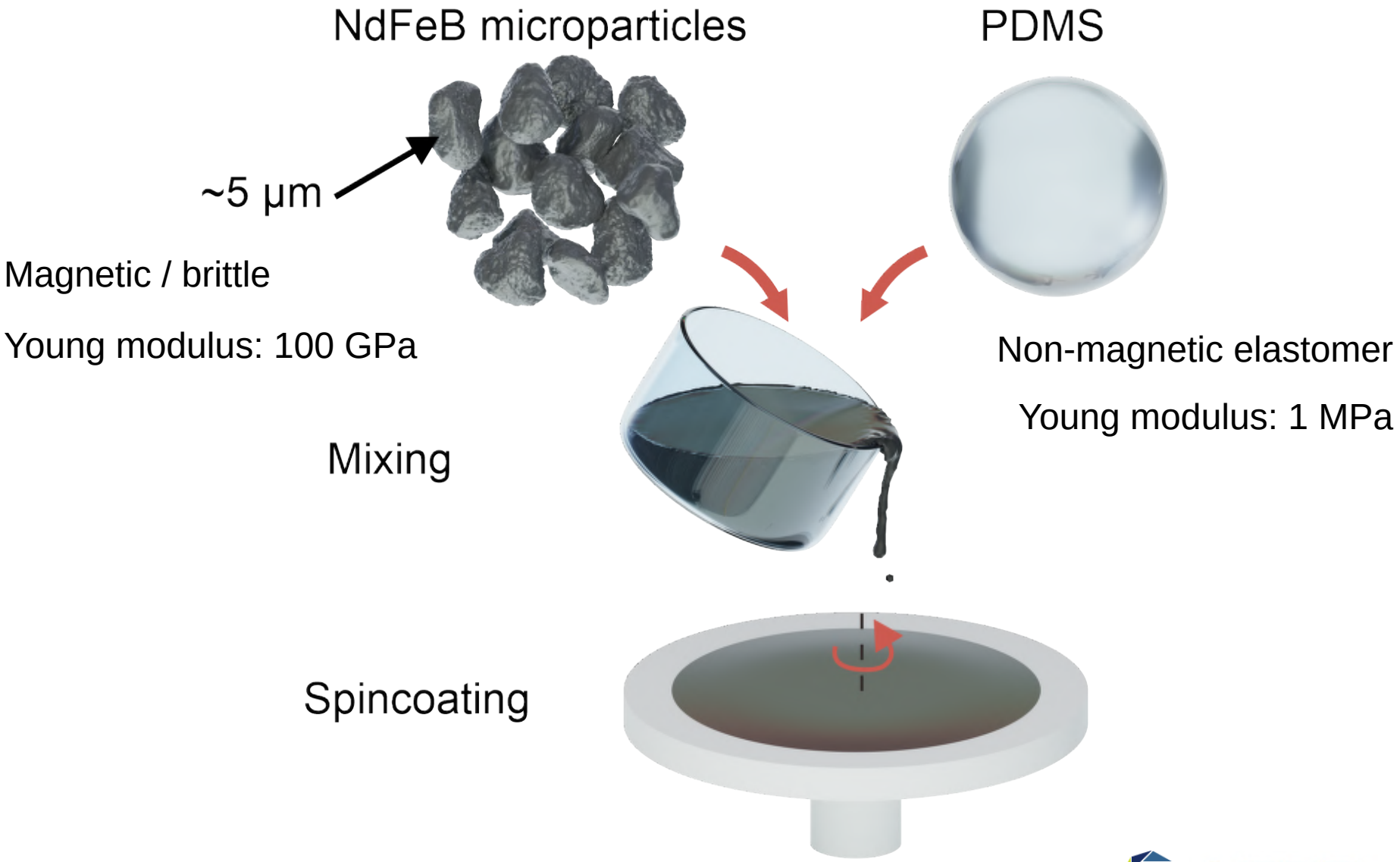
Multifunctional magnetic nanoparticles

Lecture by Annelies Coene



J. Gao et al., *Acc. Chem. Res.* **42**, 1097 (2009)

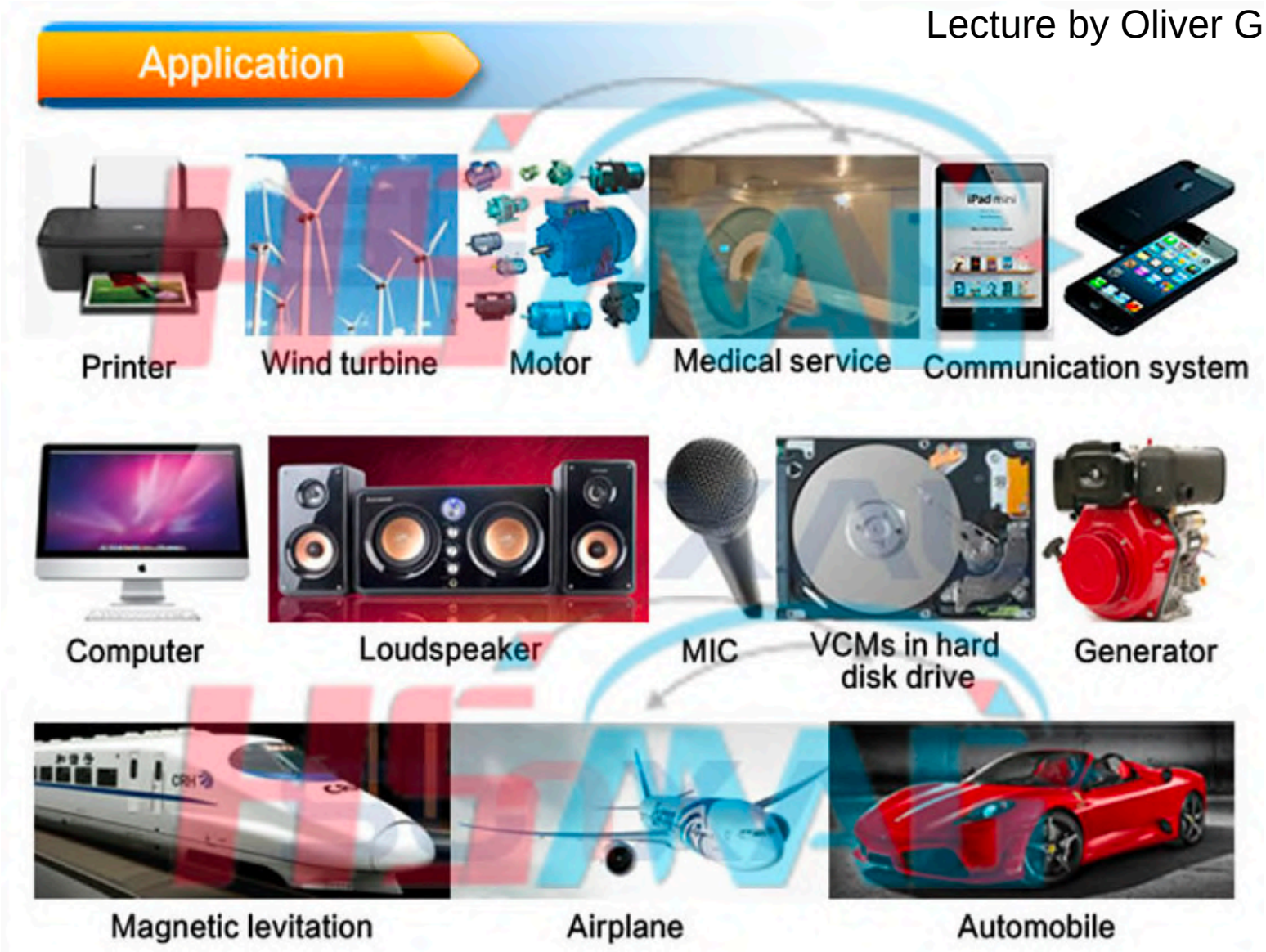
Magnetic particles and polymers



X. Wang et al., *Communications Materials* **1**, 67 (2020)

NdFeB - hard permanent magnet: applications

Lecture by Oliver Gutfleisch

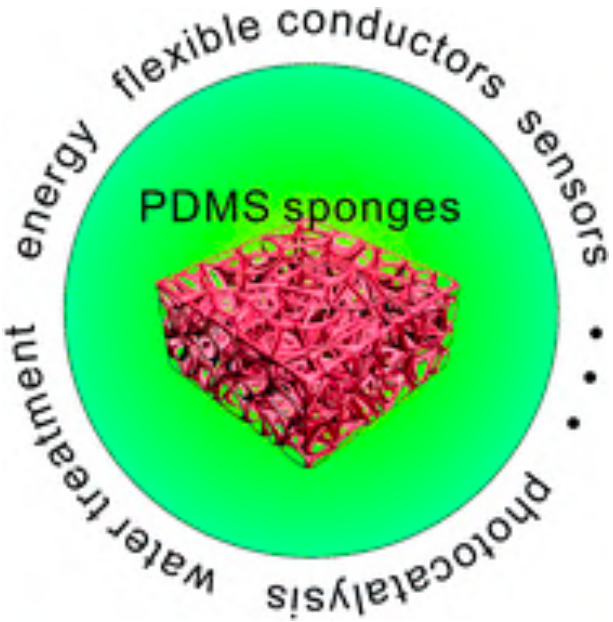


https://www.hsmagnets.com/blog/ndfeb-magnets-application/

PDMS: polydimethylsiloxane

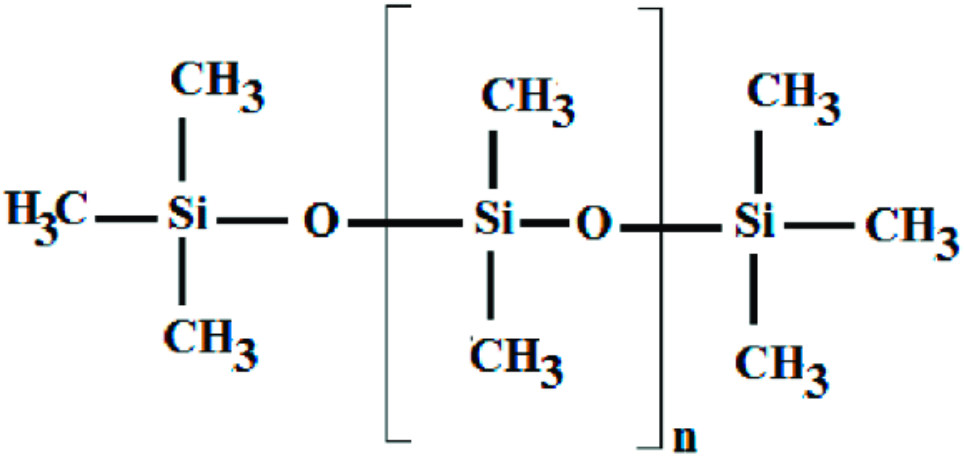
Elongation: 50%; Young's modulus: 1 MPa

www.nonpaints.com



http://www.siliconeall.com/product/html/?637.html

https://pubs.rsc.org/en/content/articlelanding/2017/ta/c7ta04577h

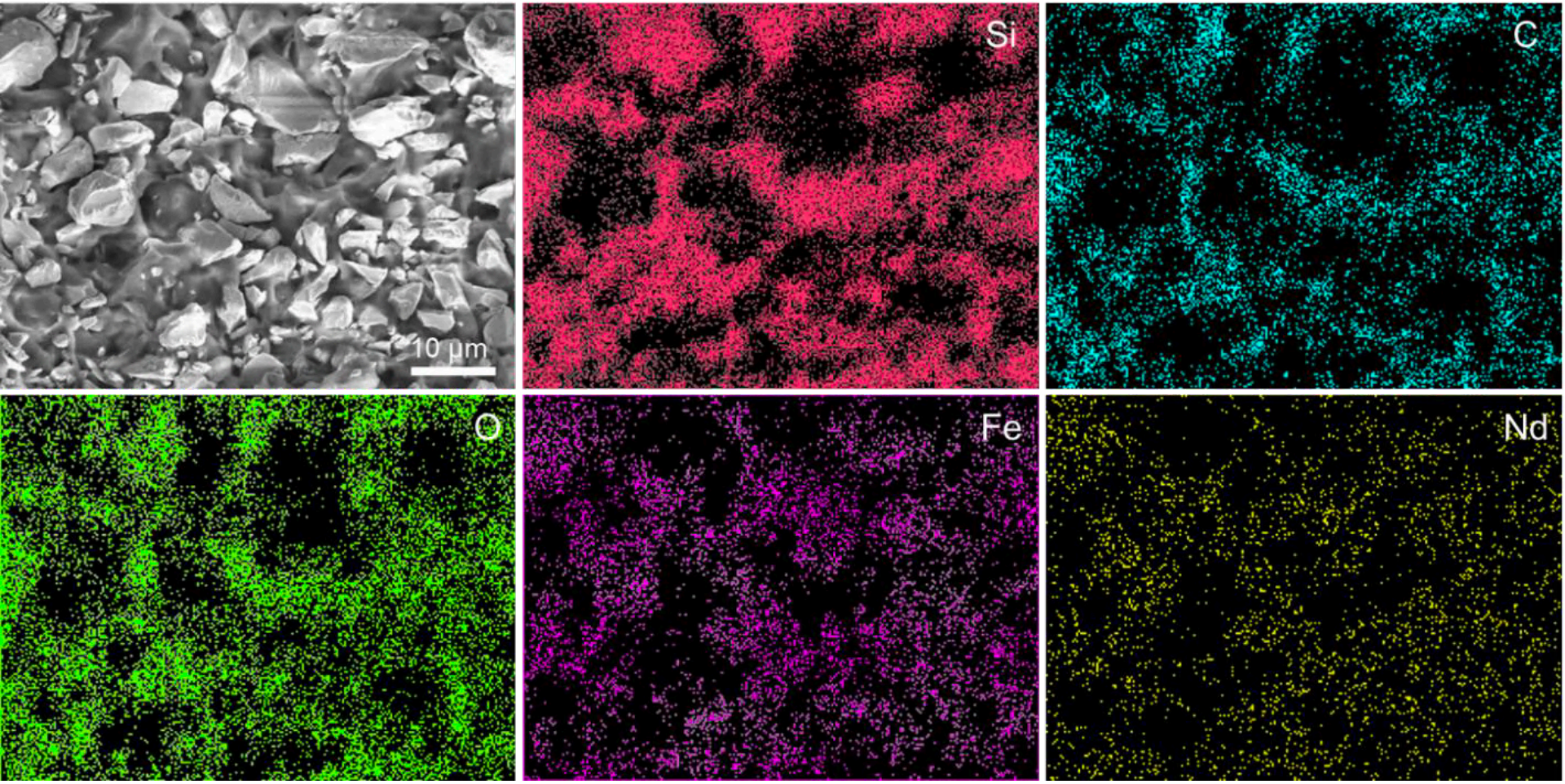


Biocompatible rubber

Cosmetics, fluidics,
smart skins, smart textiles…

Hard magnetic composite: NdFeB in PDMS

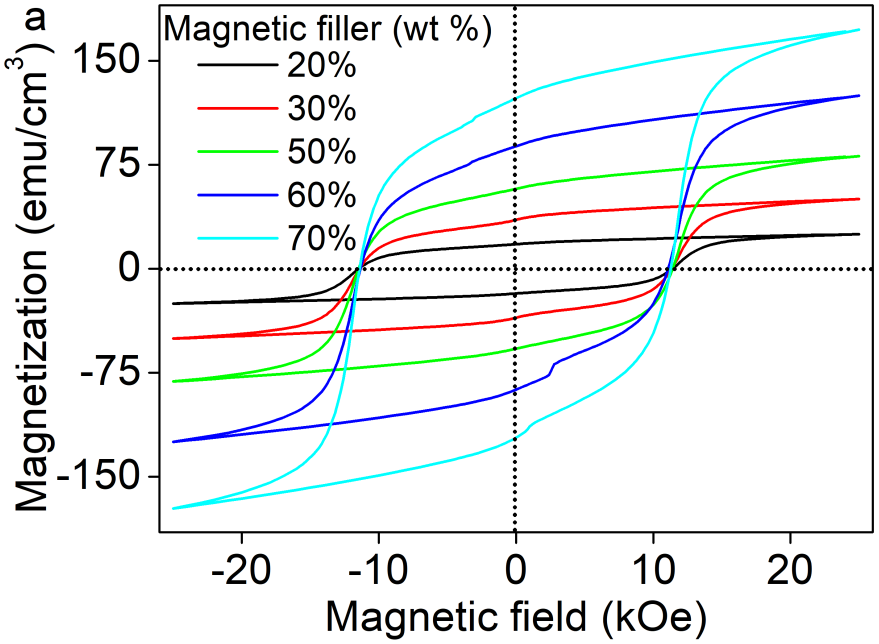
Elemental mapping (EDX)

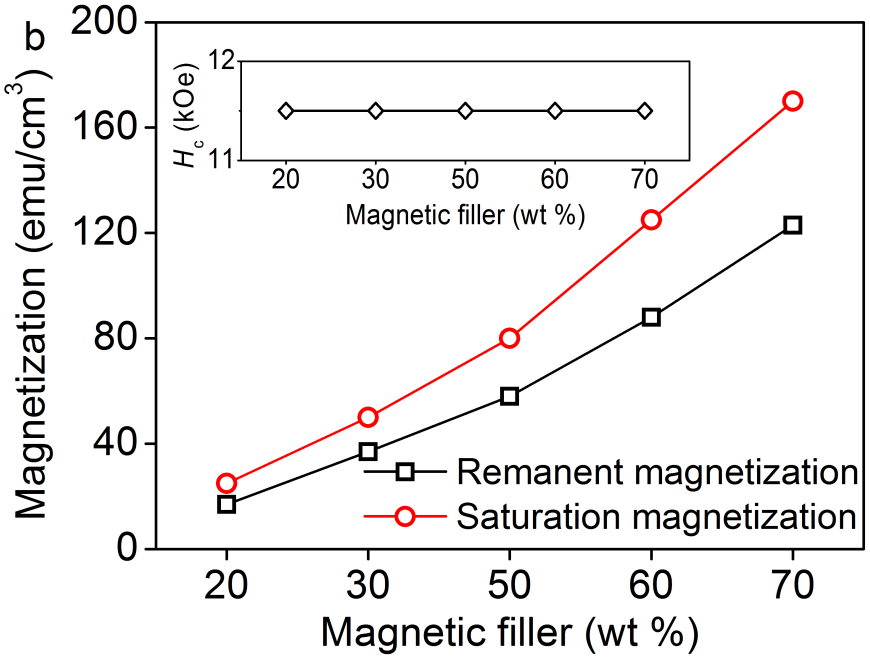


J. Ge, DM et al., *Nature Communications* **10**, 4405 (2019)

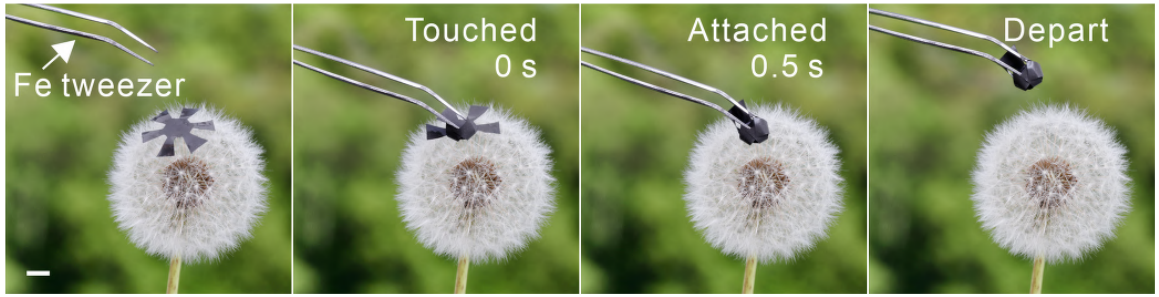
Hard magnetic composite: NdFeB in PDMS

NdFeB microparticles (5 um diameter) in PDMS





X. Wang, DM et al., *Communications Materials* **1**, 67 (2020)


Fe tweezer
Touched
0 s
Attached
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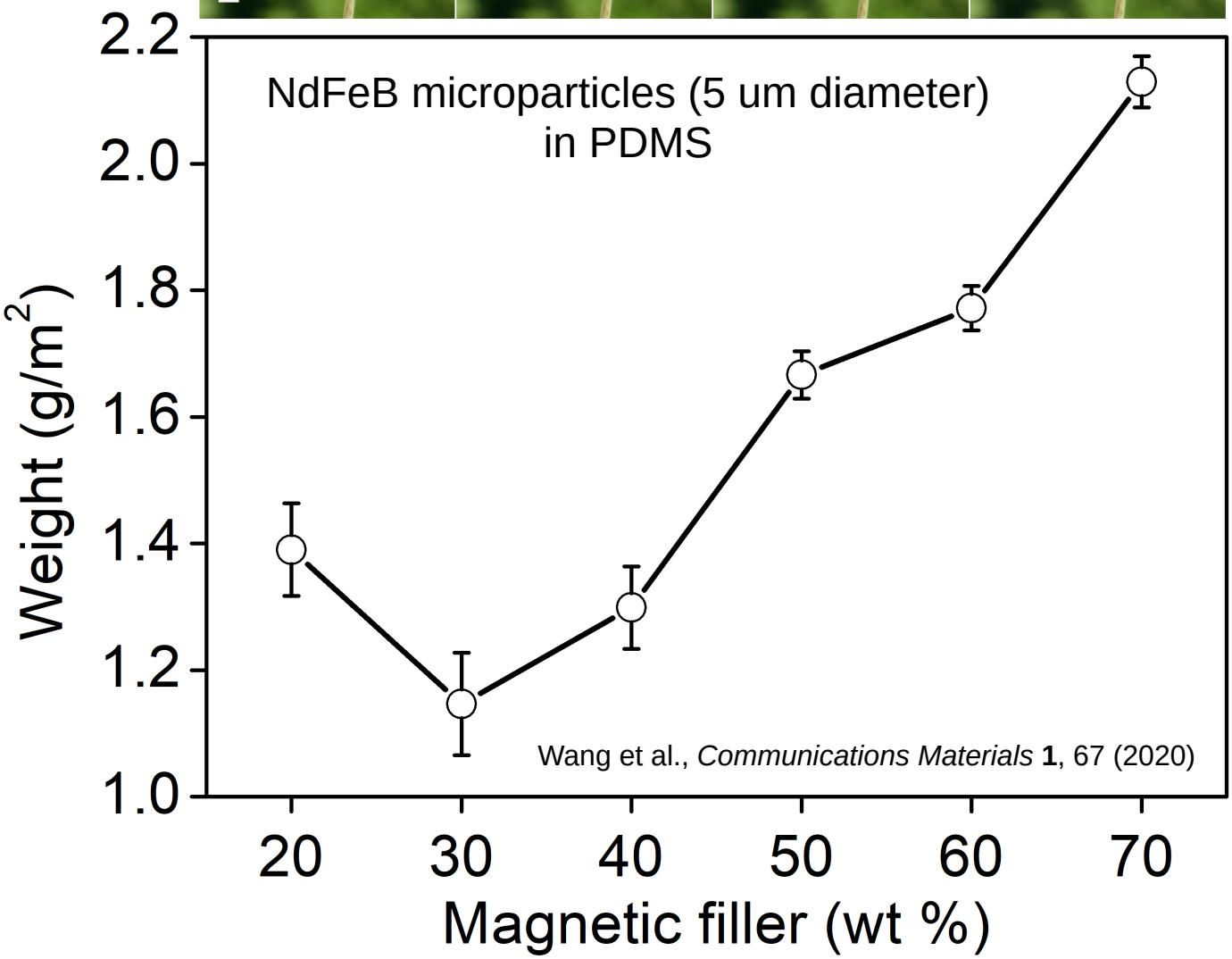
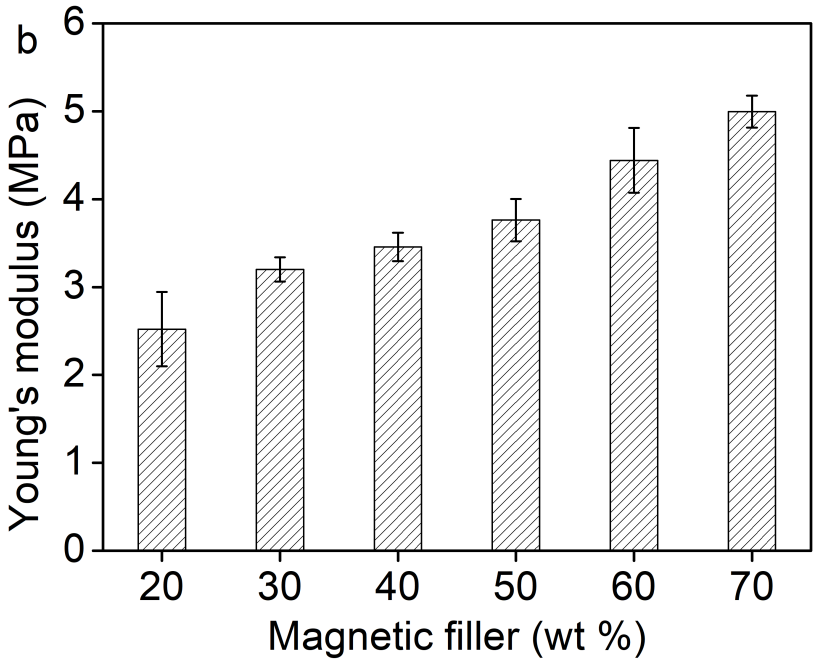
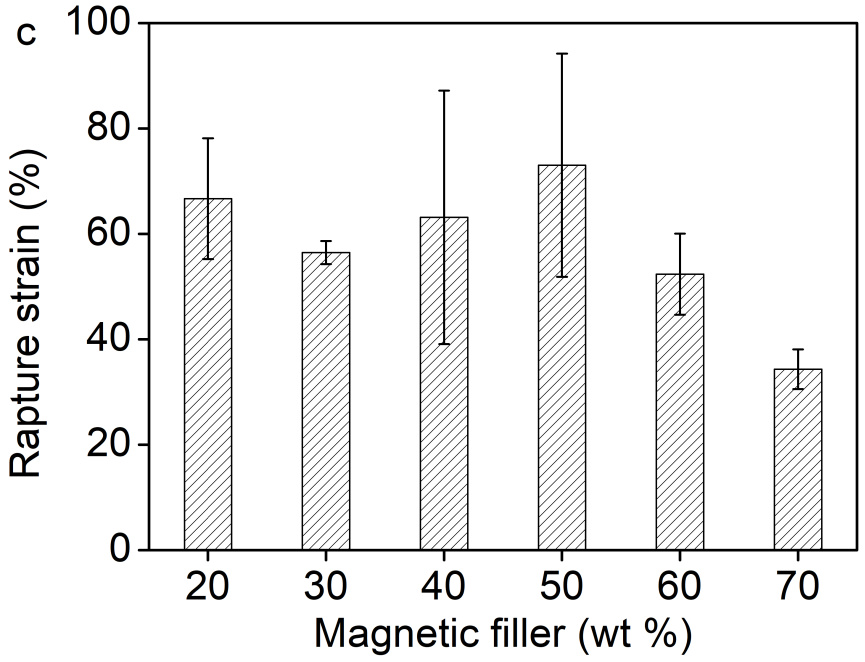
Depart


NdFeB microparticles (5 um diameter)
in PDMS
Wang et al., Communications Materials 1, 67 (2020)
Weight (g/m2)
2.2
2.0
1.8
1.6
1.4
1.2
1.0
20
30
40
50
60
70
Magnetic filler (wt %)

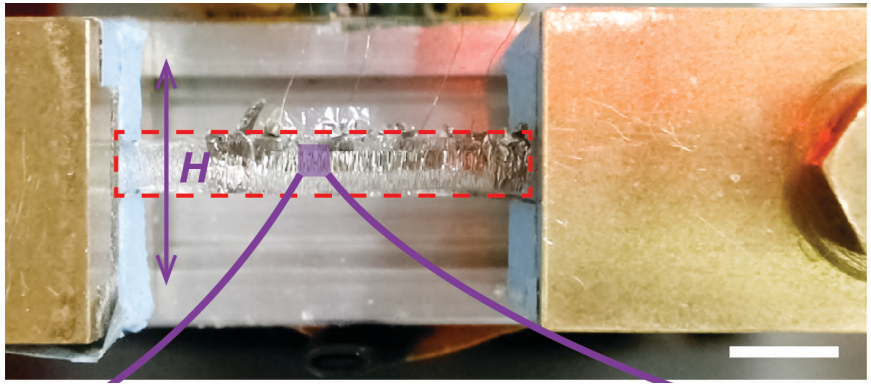
Hard magnetic composite: NdFeB in PDMS

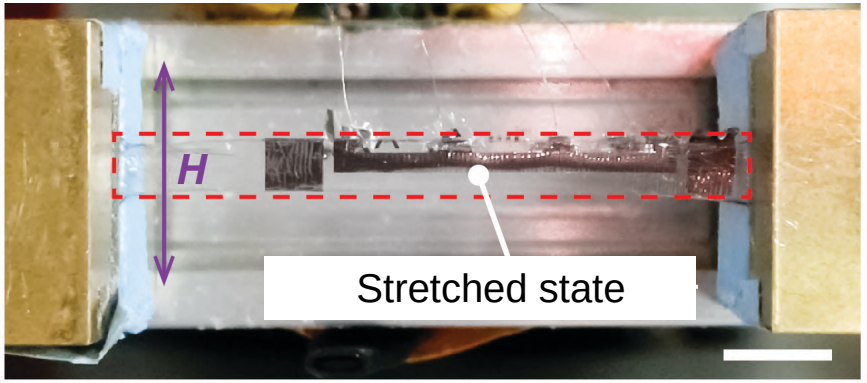
X. Wang et al., *Communications Materials* **1**, 67 (2020)



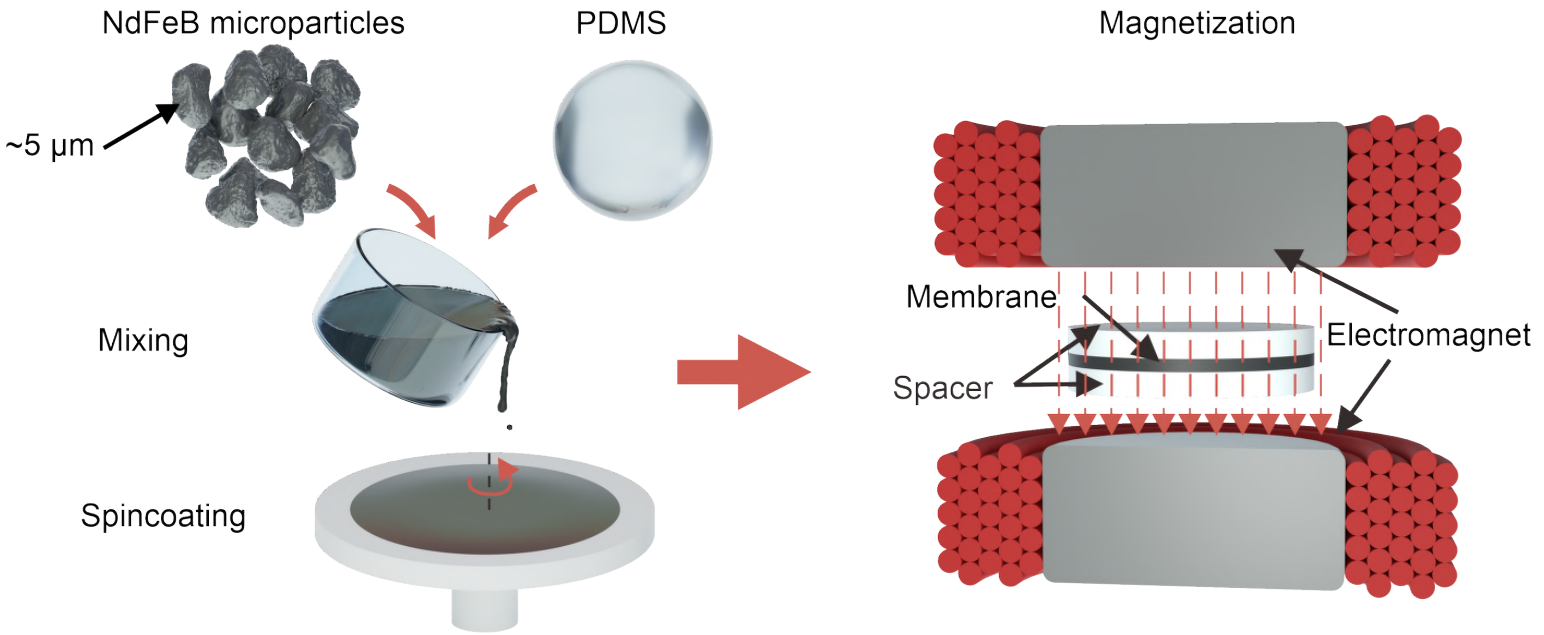


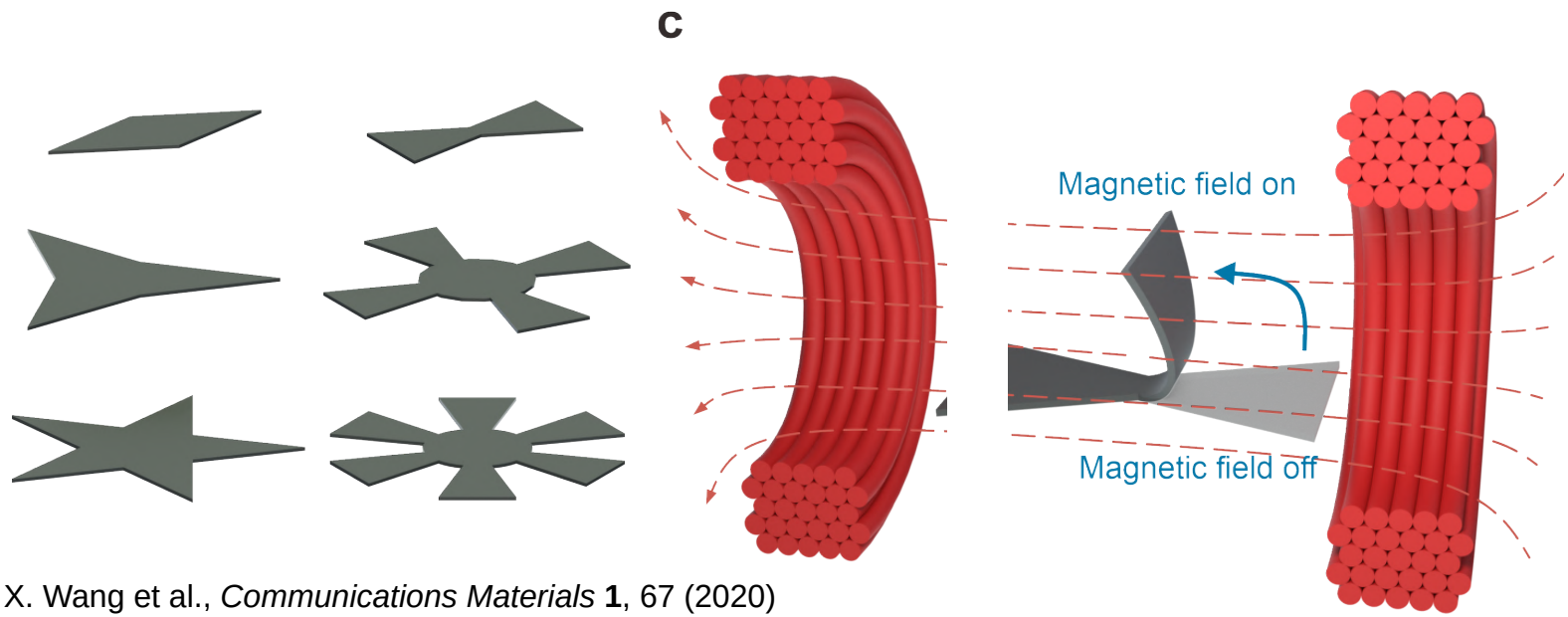
M. Melzer, DM et al., *Nature Communications* **6**, 6080 (2015)





Mechanically soft Magnetically hard actuators





X. Wang et al., *Communications Materials* **1**, 67 (2020)

Durability of magnetic soft actuators

X20 slower

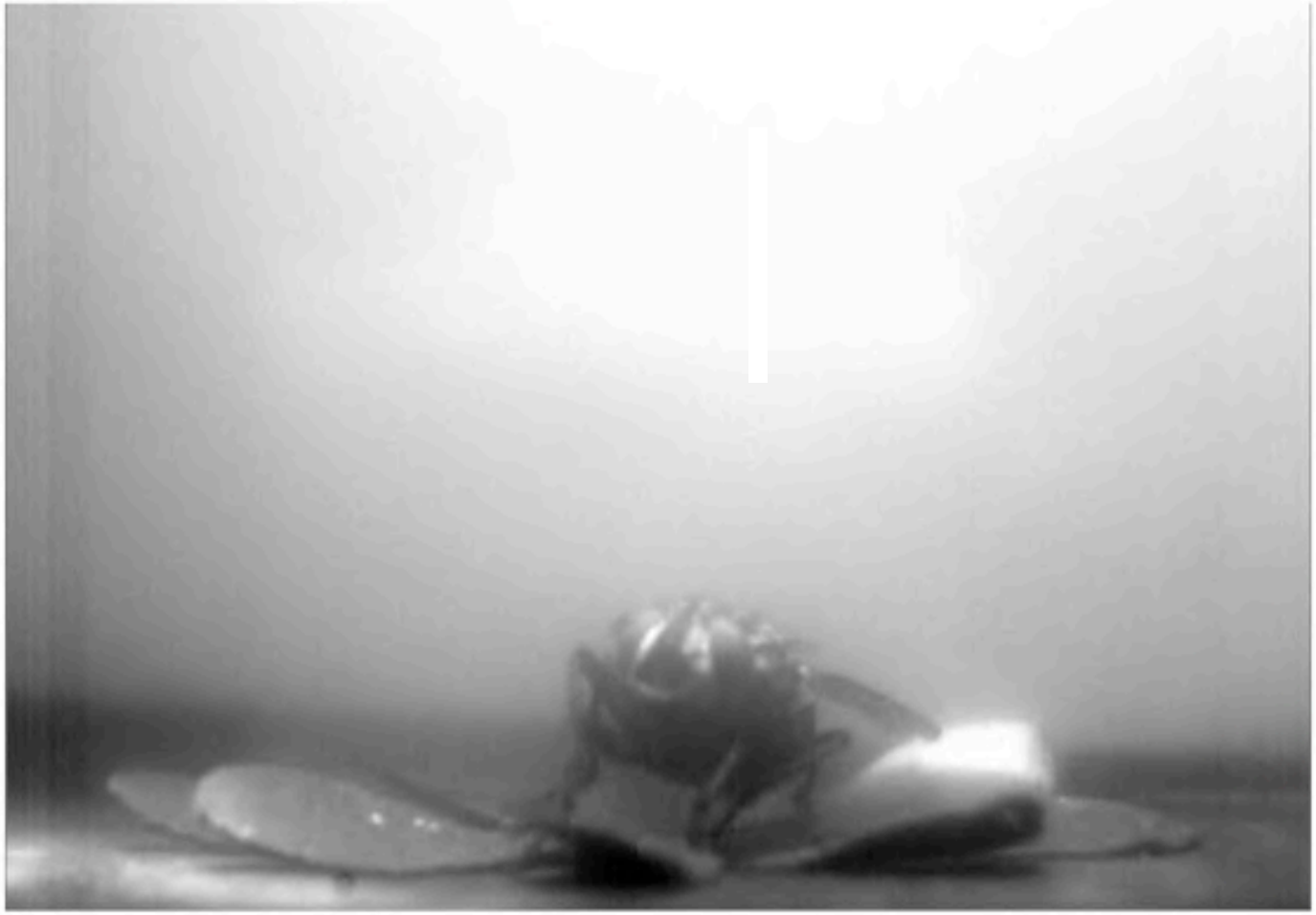
Test start

After 2.1 million cycles

X. Wang et al., *Communications Materials* **1**, 67 (2020)

Interaction with delicate objects

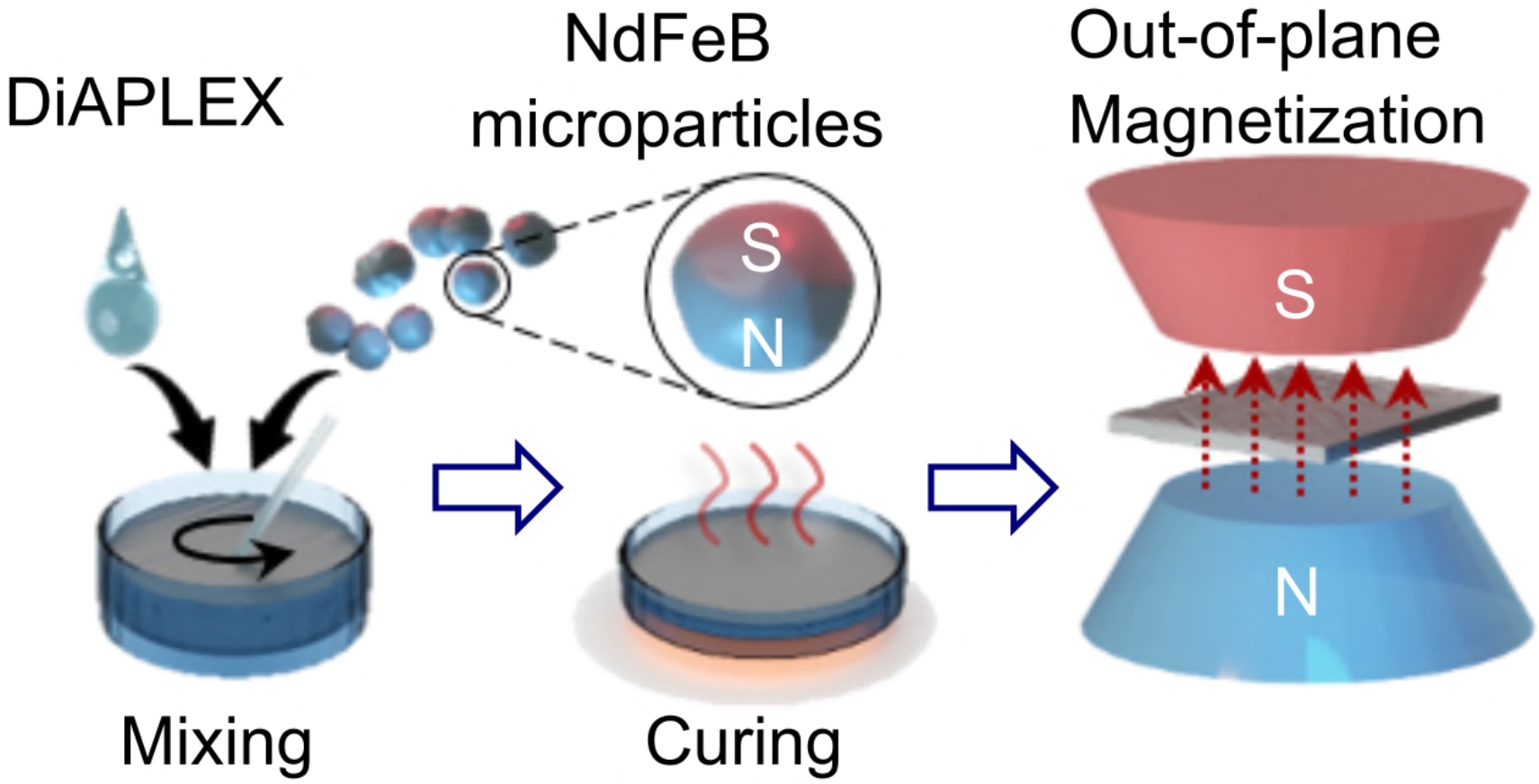
80 times slower



X. Wang et al., *Communications Materials* **1**, 67 (2020)

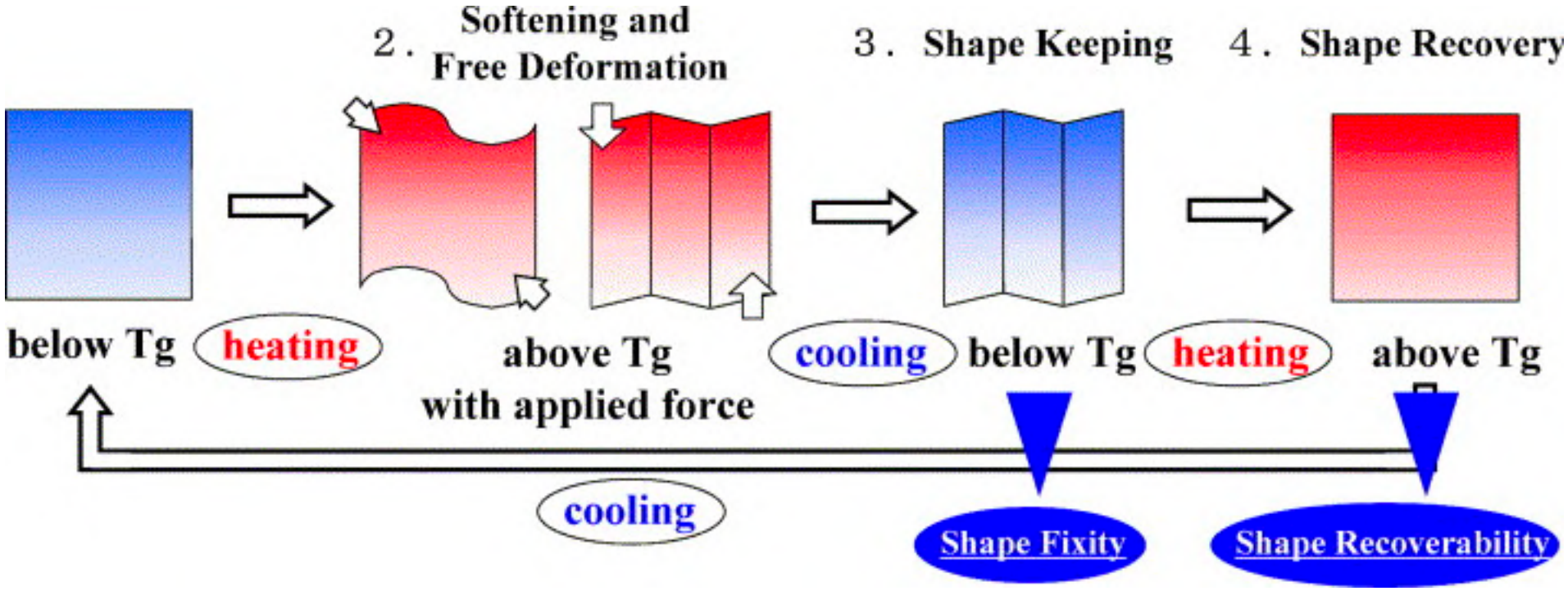
Photothermal and magnetic field driven composites

Photothermal and magnetic field driven composites



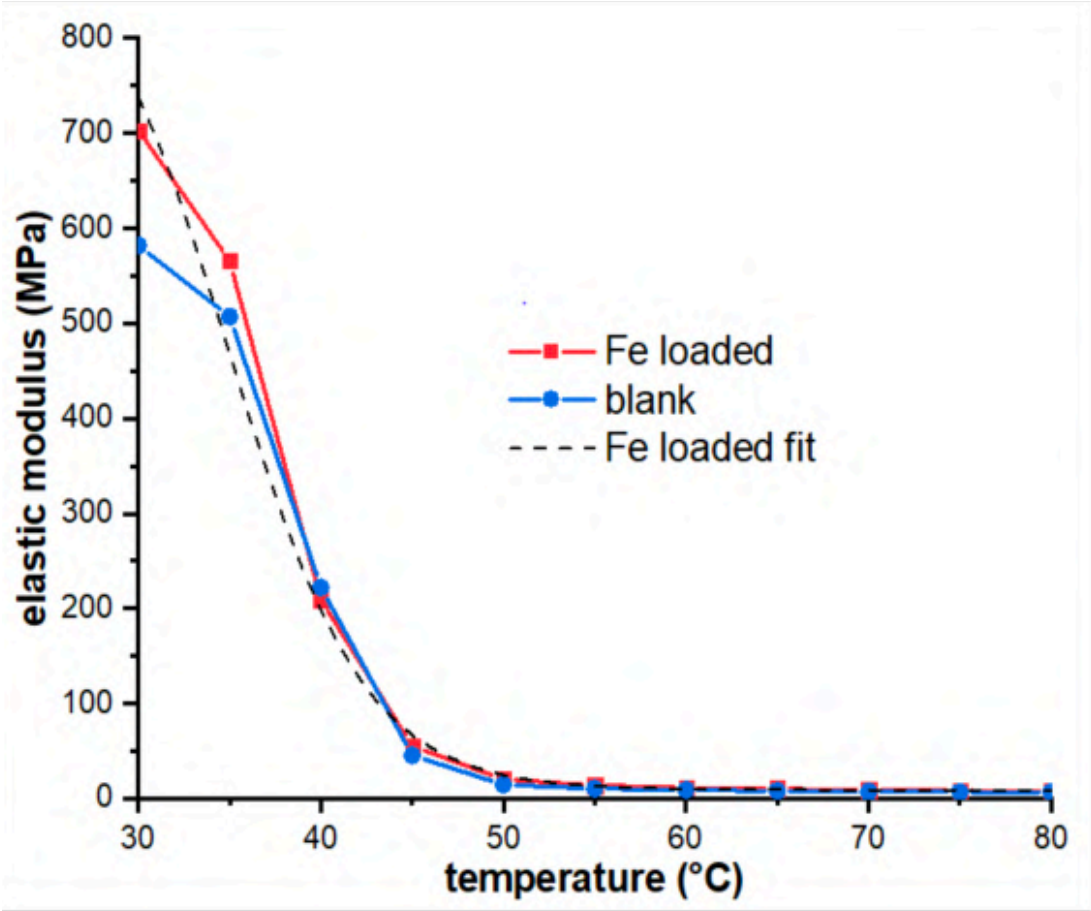
M. Ha, DM et al., *Adv. Mater.* **33**, 2008751 (2021)

DIAPLEX: shape memory polymer



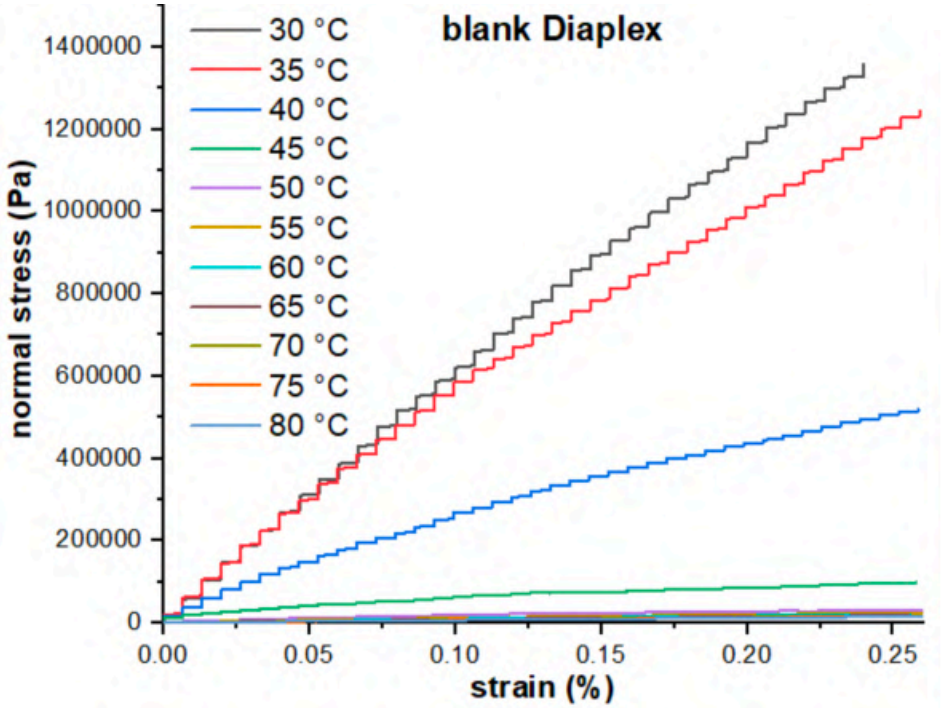
https://www.sciencedirect.com/science/article/abs/pii/S1359835X0400065X

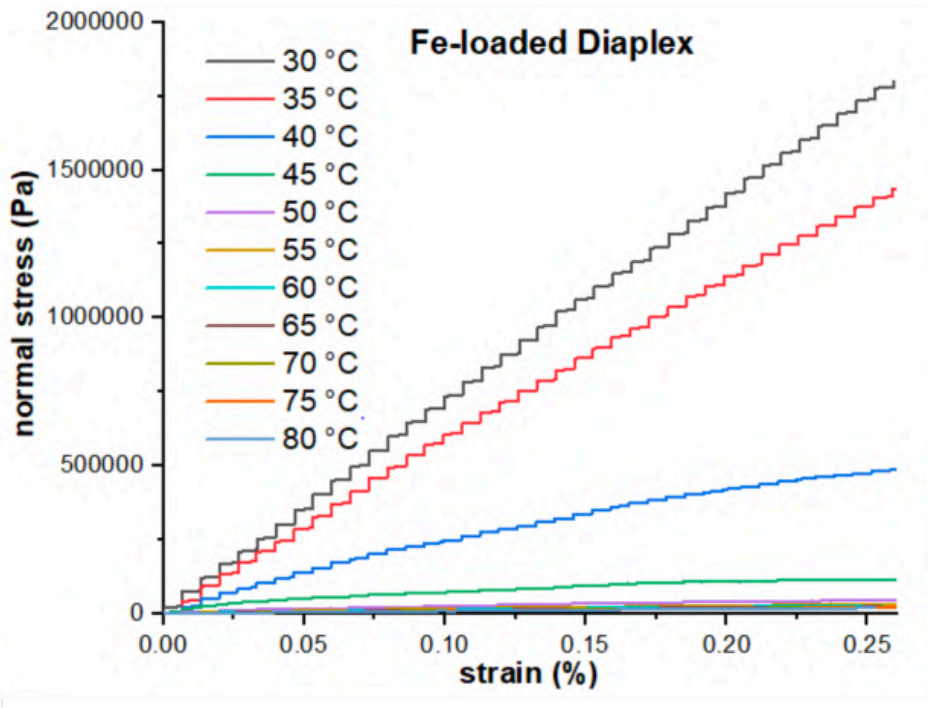
DIAPLEX: shape memory polymer



J. Liu et al., *Science Advances* **5**, eaaw2897 (2019)

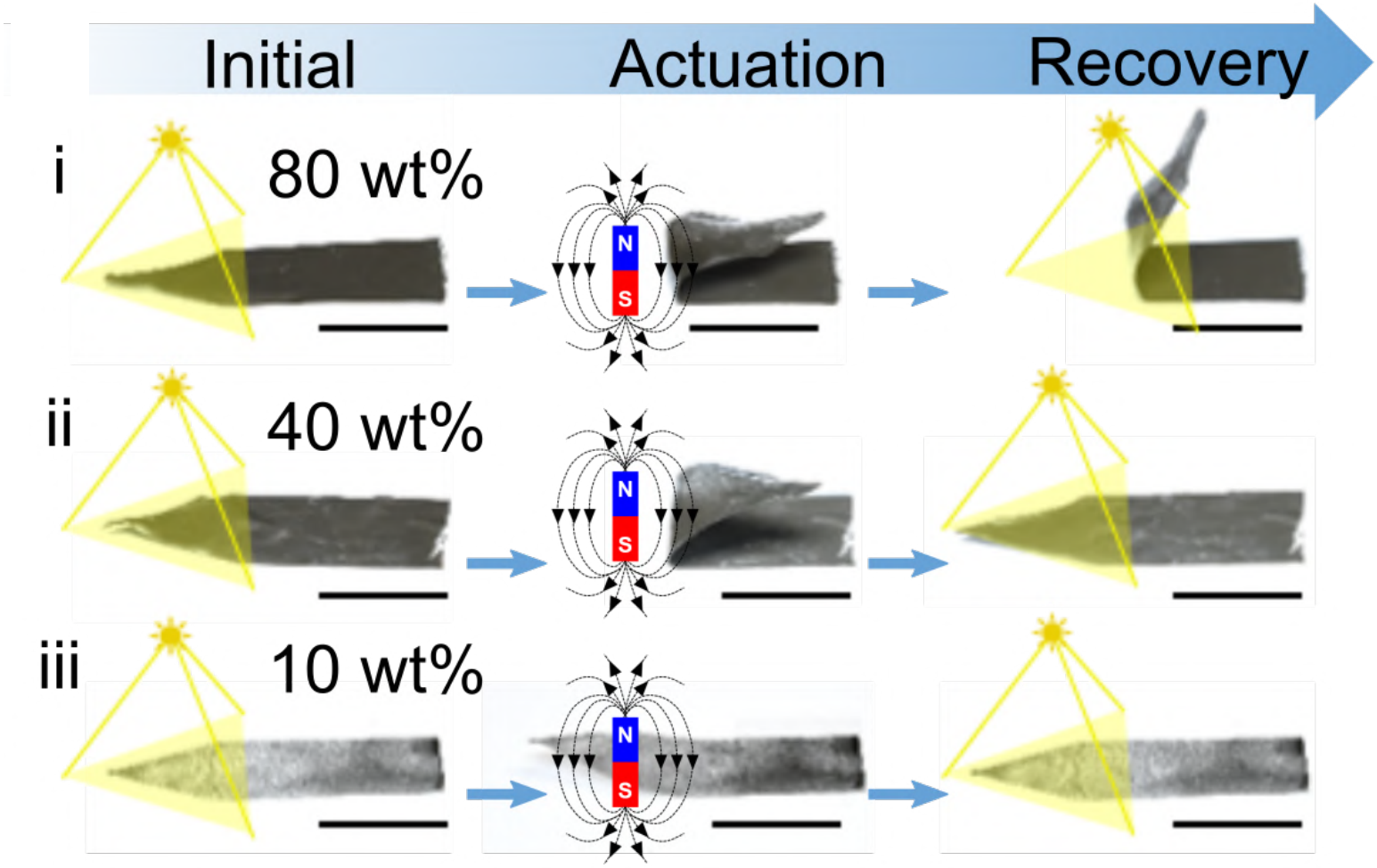
DIAPLEX: shape memory polymer





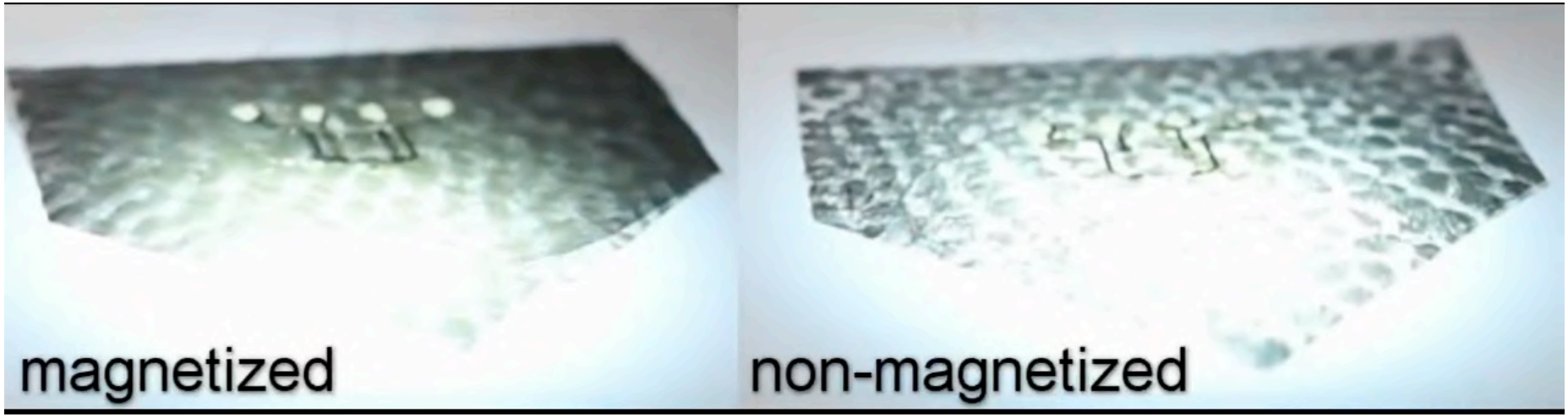
J. Liu et al., *Science Advances* **5**, eaaw2897 (2019)

Magnetic origami: photo- and magnetic field responsive



M. Ha et al., *Adv. Mater.* **33**, 2008751 (2021)

Photothermal and magnetic field actuation



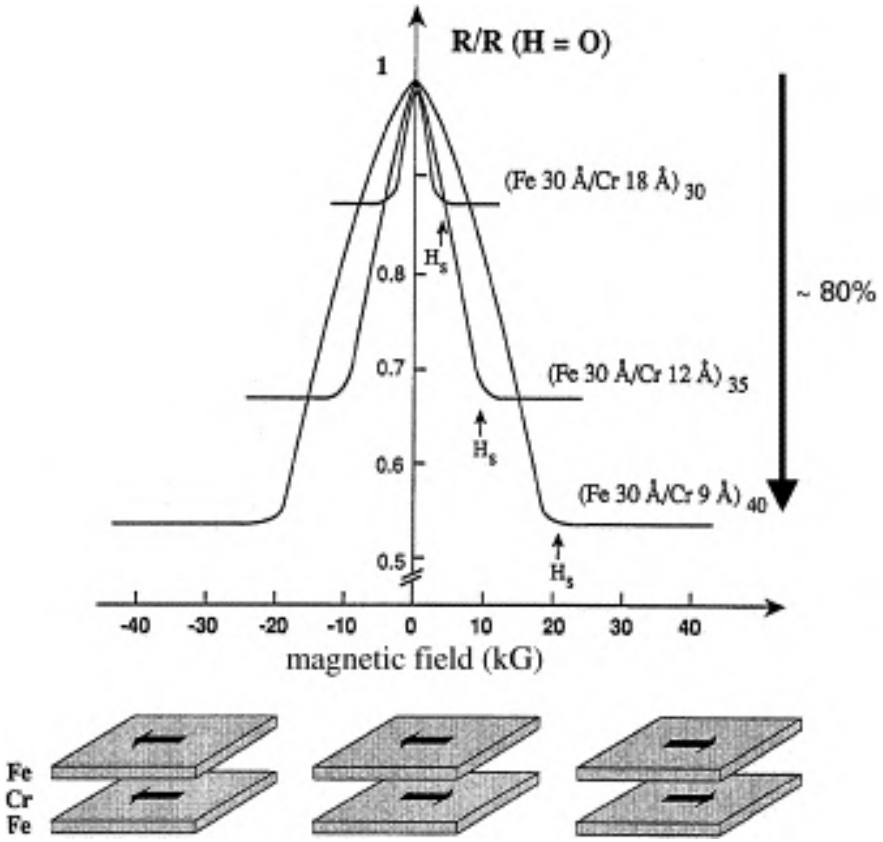
M. Ha et al., *Adv. Mater.* **33**, 2008751 (2021)

Photothermal and magnetic field actuation

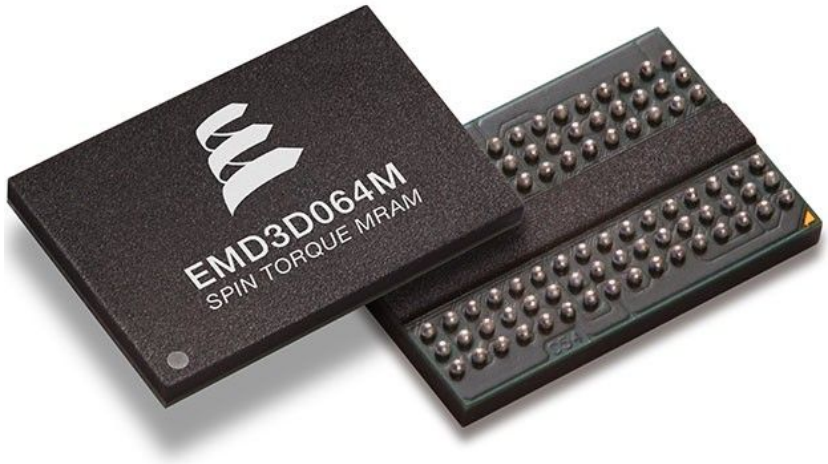
M. Ha et al., *Adv. Mater.* **33**, 2008751 (2021)

Magnetic composites for sensor applications

Spintronics



A.Barthélémy et al., JMMM 242-245, 68 (2002)



Giant magnetoresistive (GMR) sensors

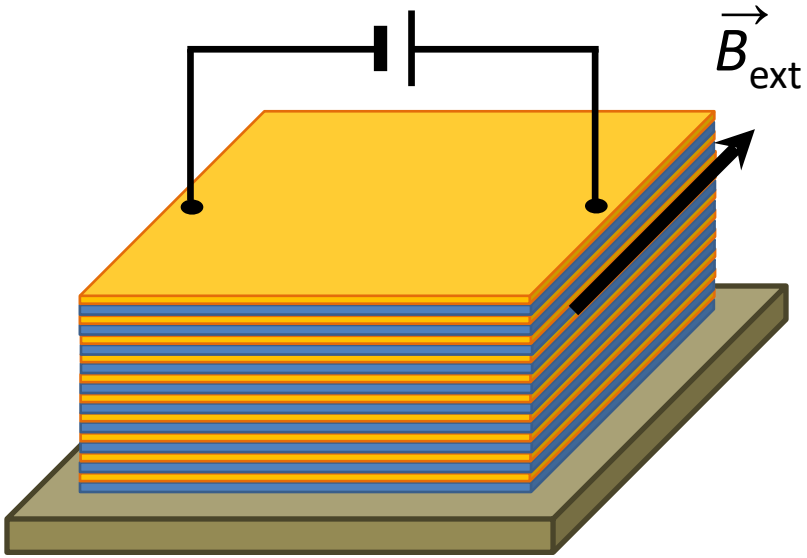
20 to 50 doublelayers of ferro- and nonmagnetic conductors

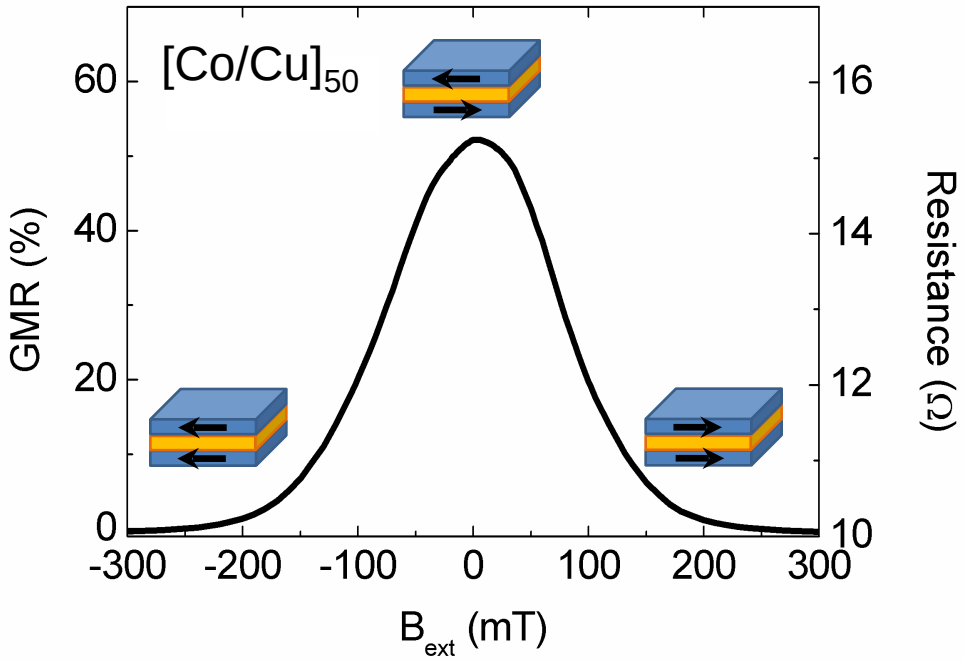
Current-in-plane measurement

Sensitive to in-plane fields

Giant **M**agneto-**R**esistance

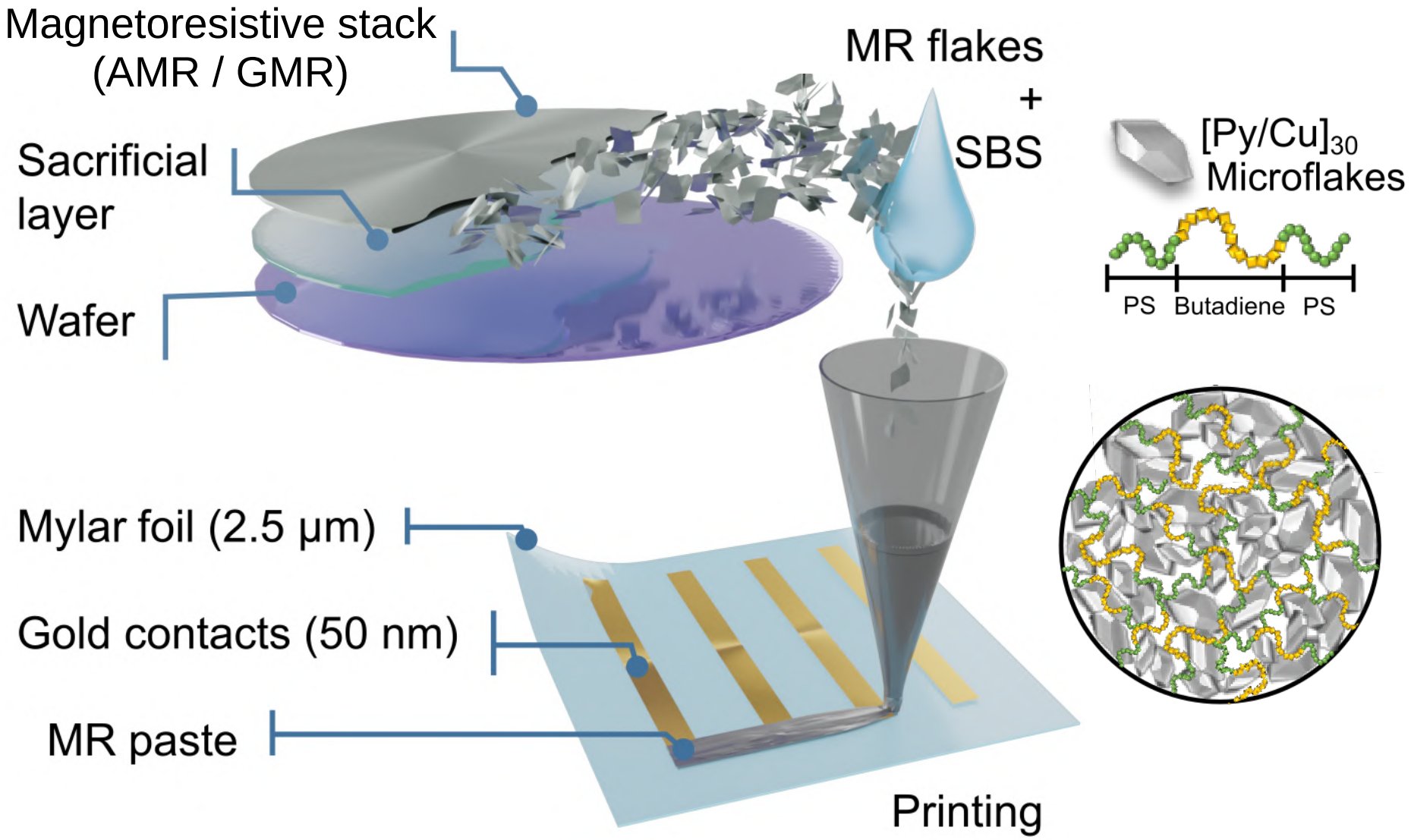
$$GMR(B_{ext}) = [R(B_{ext}) - R_{sat}] / R_{sat}$$





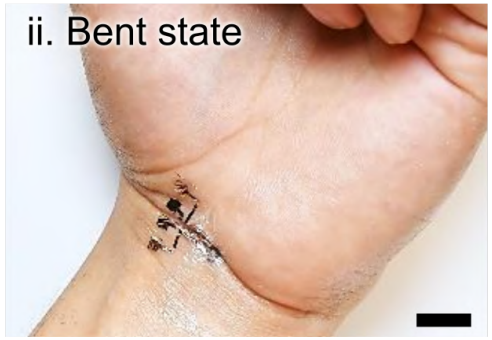
Phys. Rev. Lett. **57**, 2442 (1986)

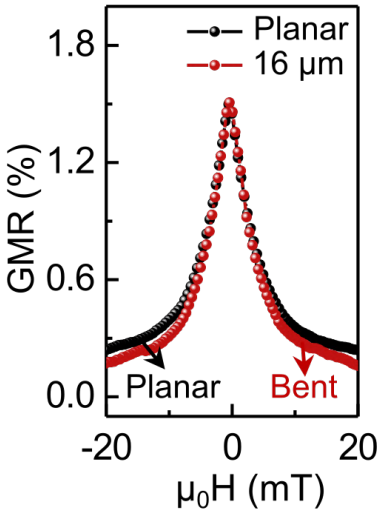
Printed skin-conformal magnetoelectronics

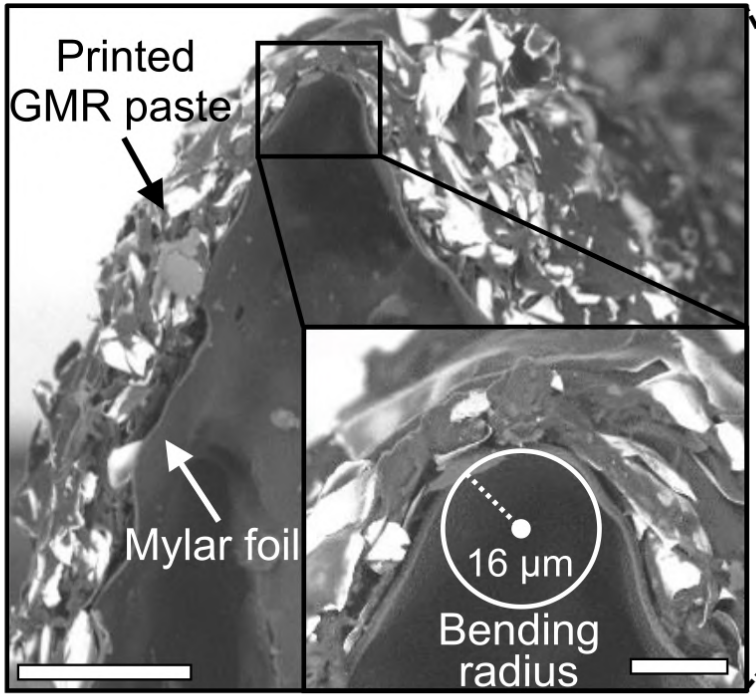


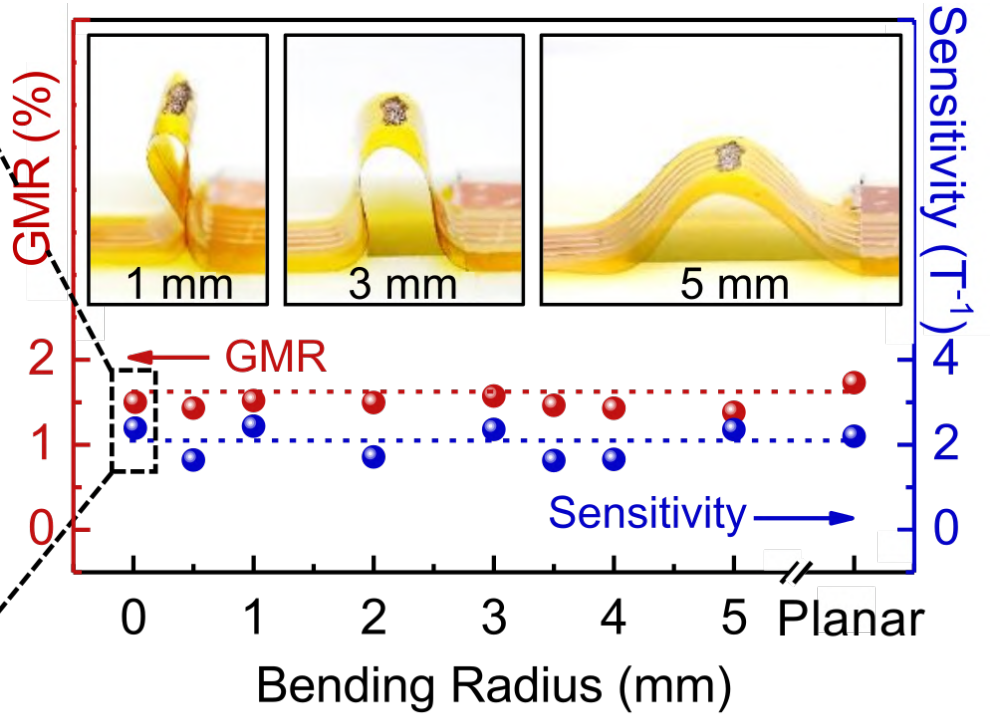
M. Ha et al., *Adv. Mater.* **33**, 2005521 (2021) & E. S. Oliveros Mata et al., *Appl. Phys. A* **127**, 280 (2021)

Printed skin-conformal magnetoelectronics









M. Ha et al., *Adv. Mater.* **33**, 2005521 (2021) & E. S. Oliveros Mata et al., *Appl. Phys. A* **127**, 280 (2021)

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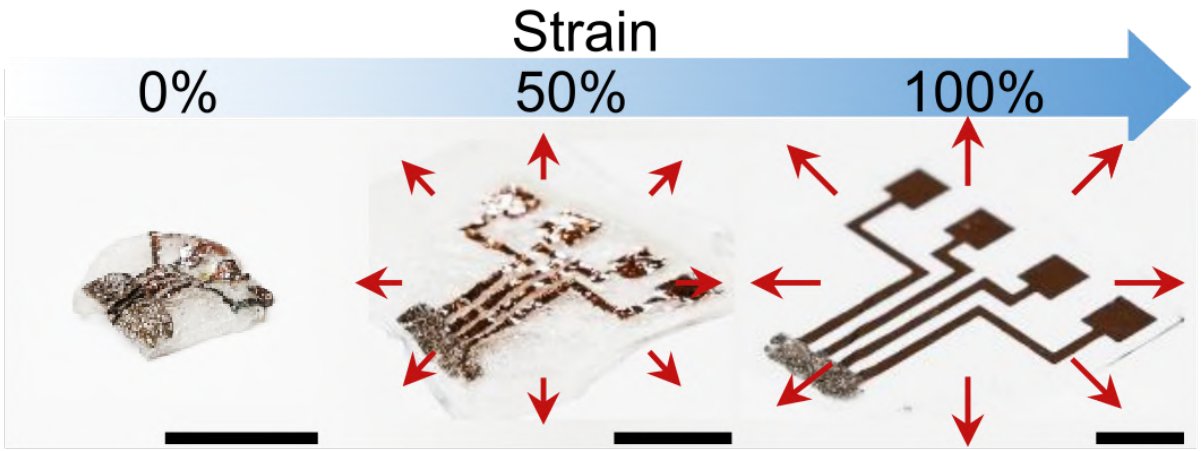
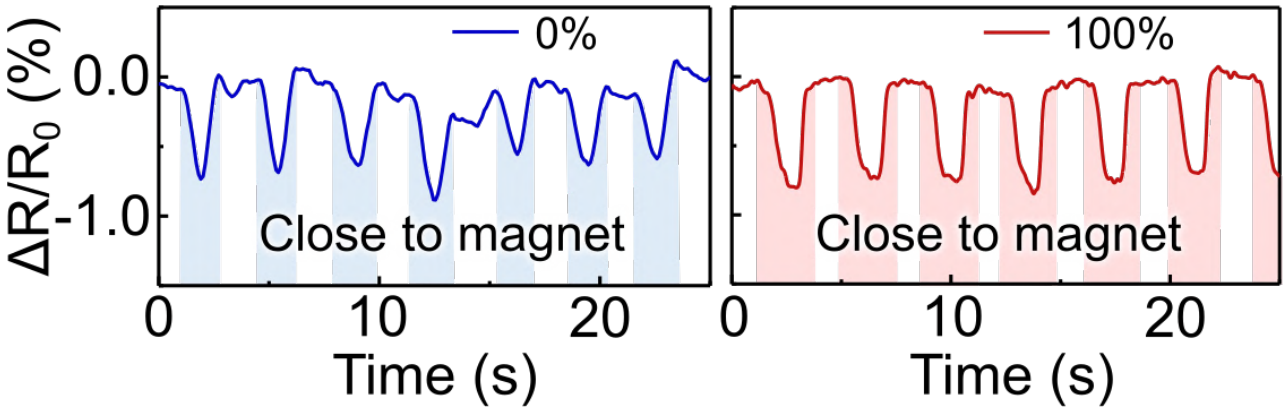
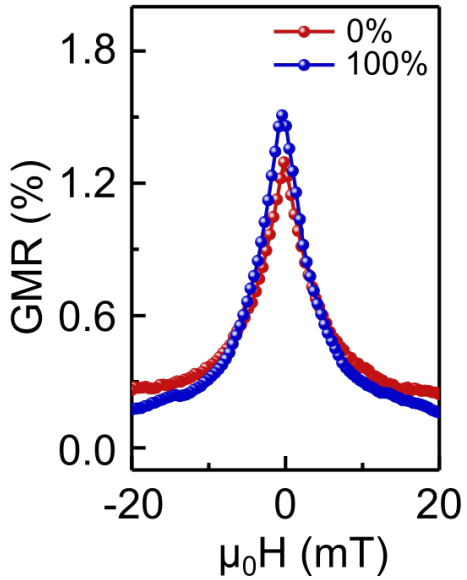
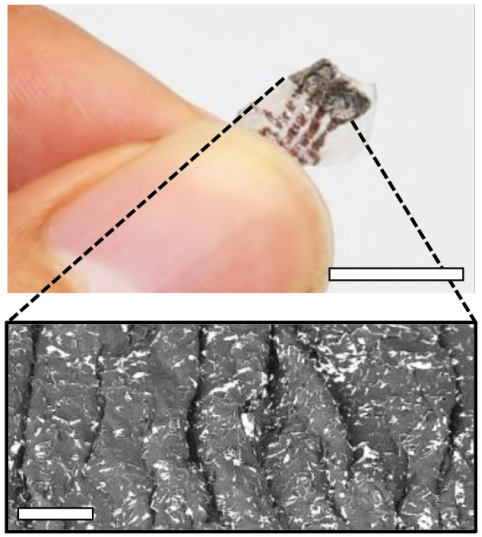




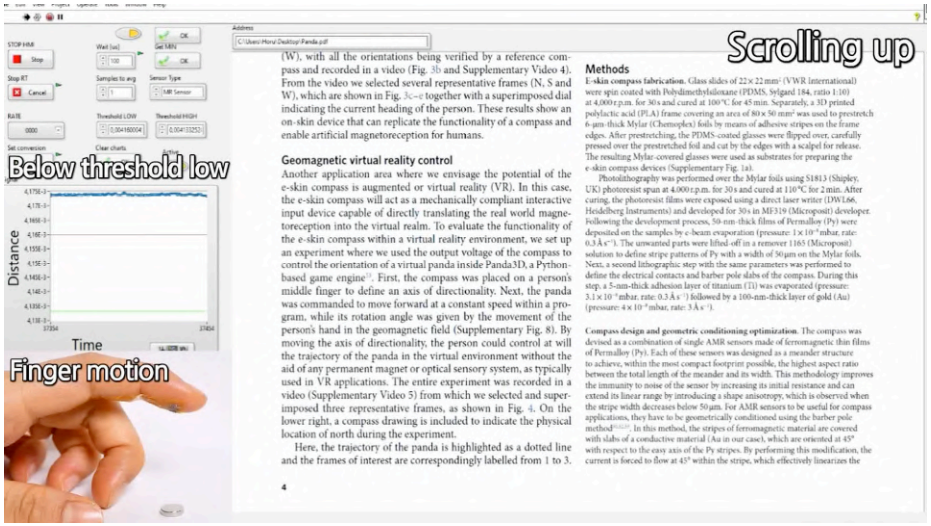




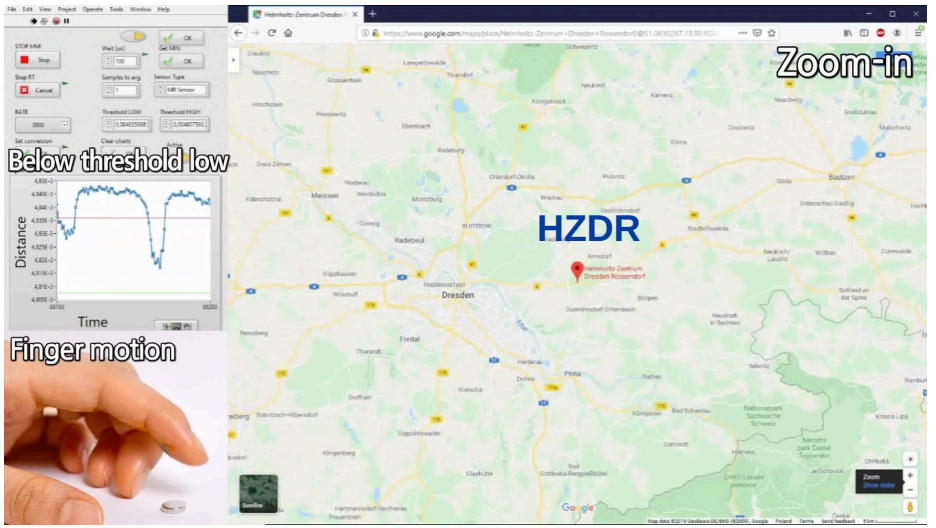
M. Ha et al., *Adv. Mater.* **33**, 2005521 (2021) & E. S. Oliveros Mata et al., *Appl. Phys. A* **127**, 280 (2021)

Printed skin-conformal magnetoelectronics

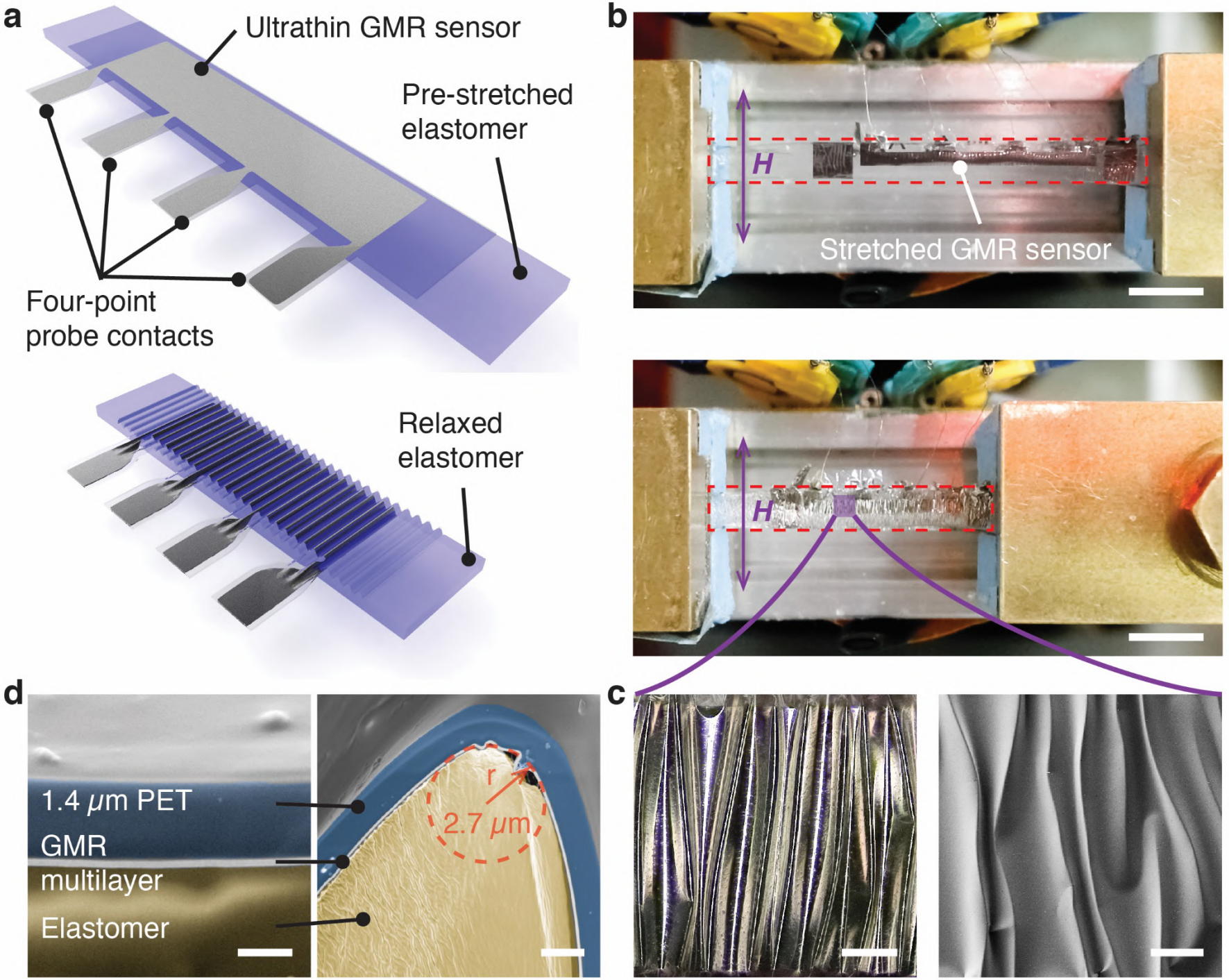
Scrolling documents



Interacting with a map

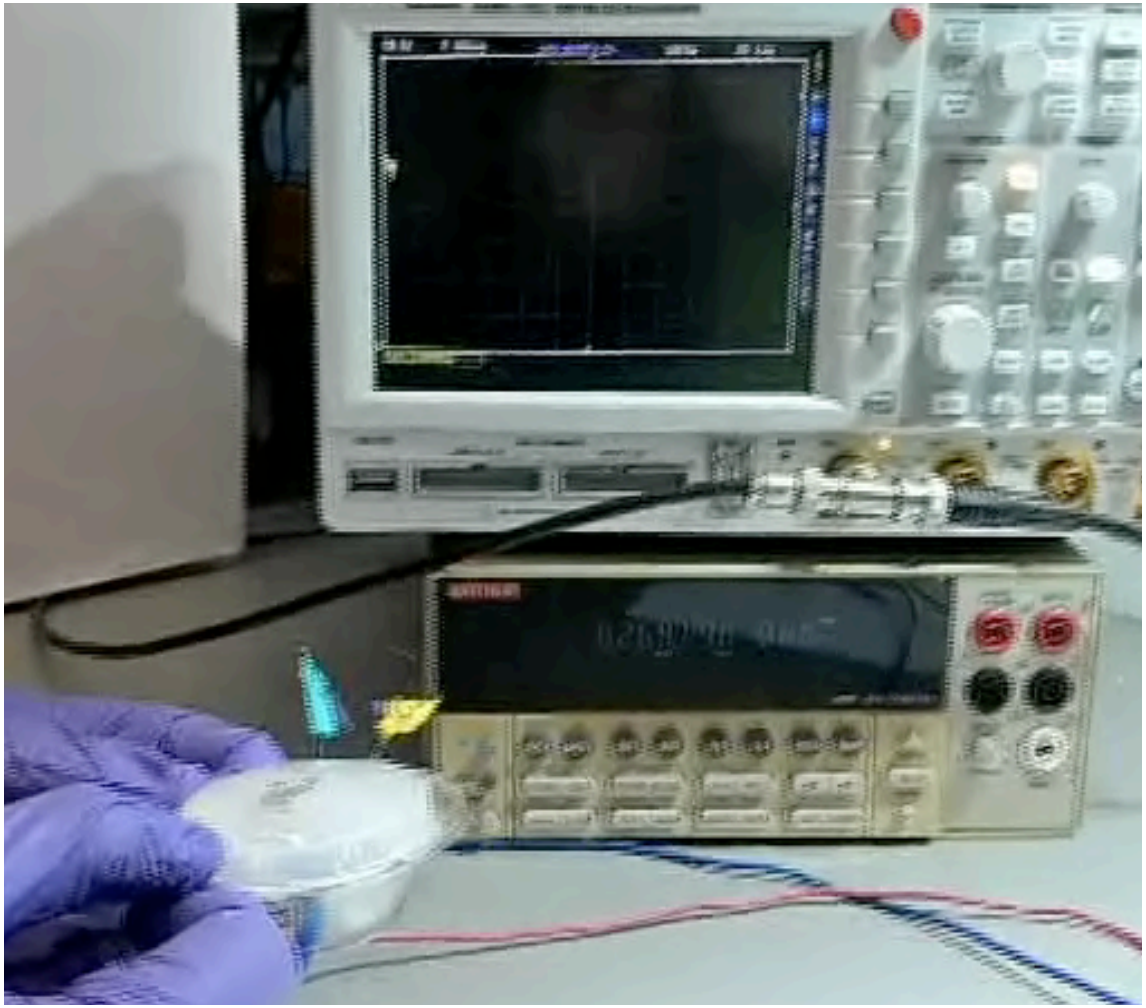


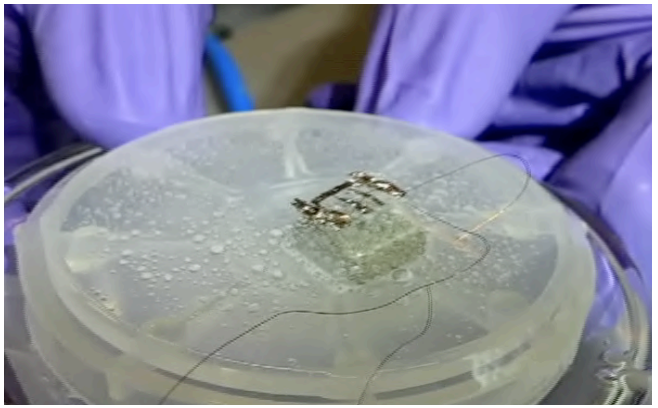
M. Ha et al., *Adv. Mater.* **33**, 2005521 (2021) & E. S. Oliveros Mata et al., *Appl. Phys. A* **127**, 280 (2021)


a
Ultrathin GMR sensor
Pre-stretched elastomer
Four-point probe contacts
Relaxed elastomer
b
H
Stretched GMR sensor
H
d
1.4 μm PET
GMR multilayer
Elastomer
r
2.7 μm
c

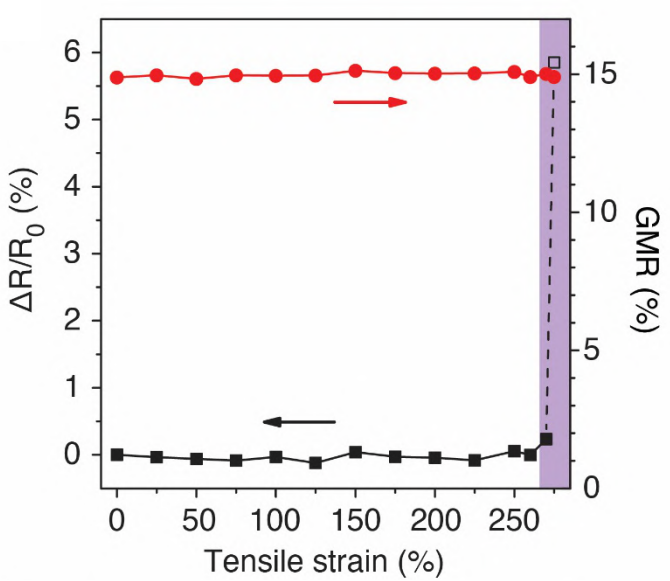
Strain-invariant magnetoelectronics for smart skins

Sensor applied to the elastomeric VHB rubber





Stretching performance



Melzer, DM et al., *Nature Commun.* **6**, 6080 (2015)

Thank you for your attention