Alice Mieting

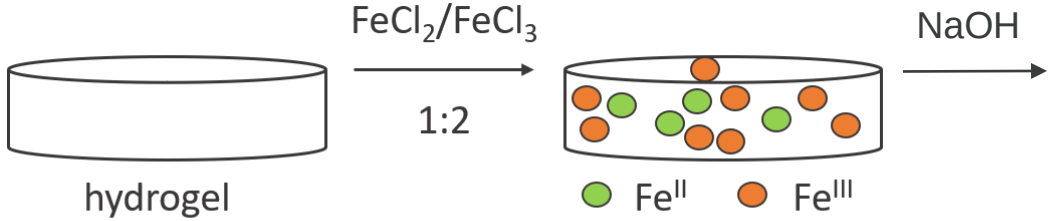
Precipitation of iron oxide in hydrogel with superparamagnetic and stimuli-responsive properties

CSAC2021: 1st International Electronic Conference on Chemical Sensors and Analytical Chemistry
01 – 15 July 2021 | Online

Ferrogel: Iron oxide functionalized hydrogels

Synthesis: In-situ co-precipitation of iron oxide in hydrogels

Characterization: particle properties (size, extent of agglomeration, uniformly distribution)
swelling properties (ionic strength, pH, specific ions)
physical properties (magnetization, electric conductivity)

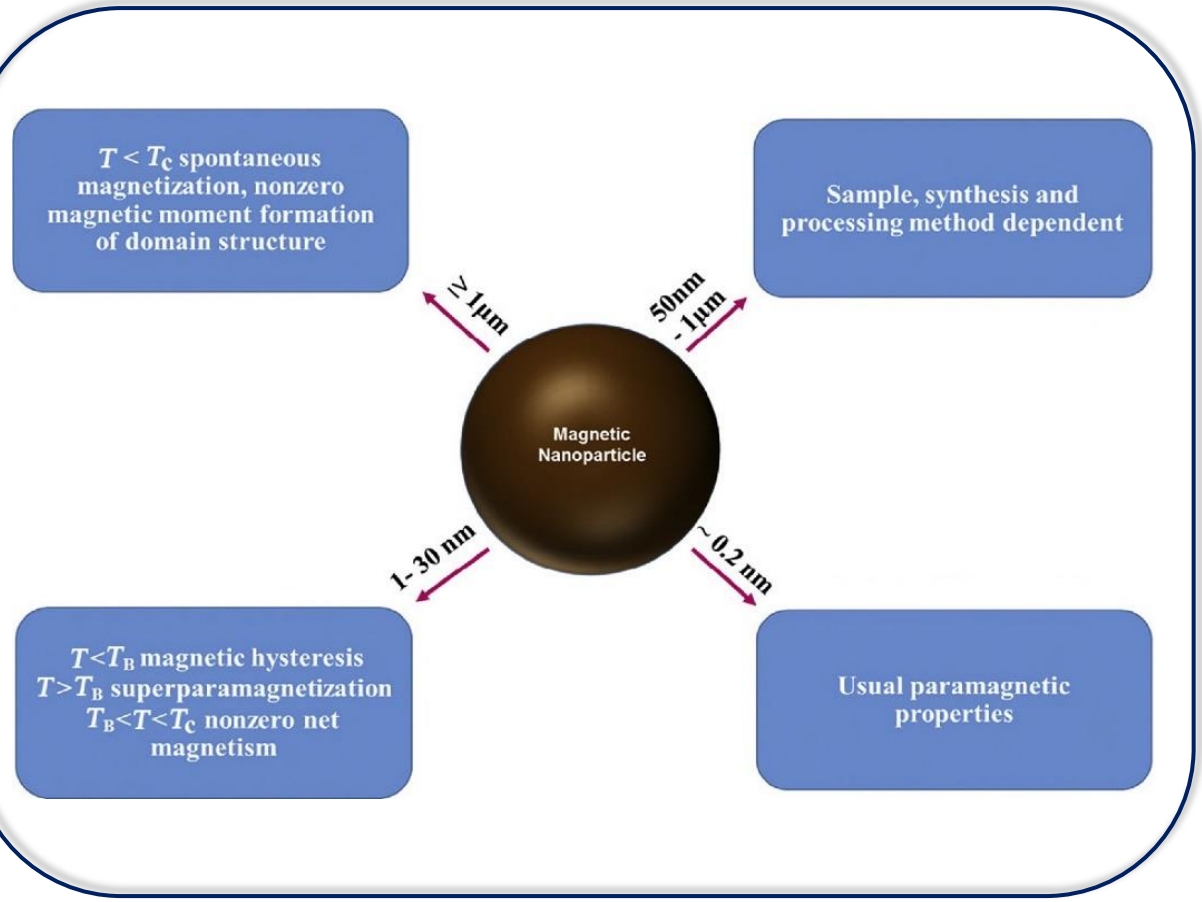


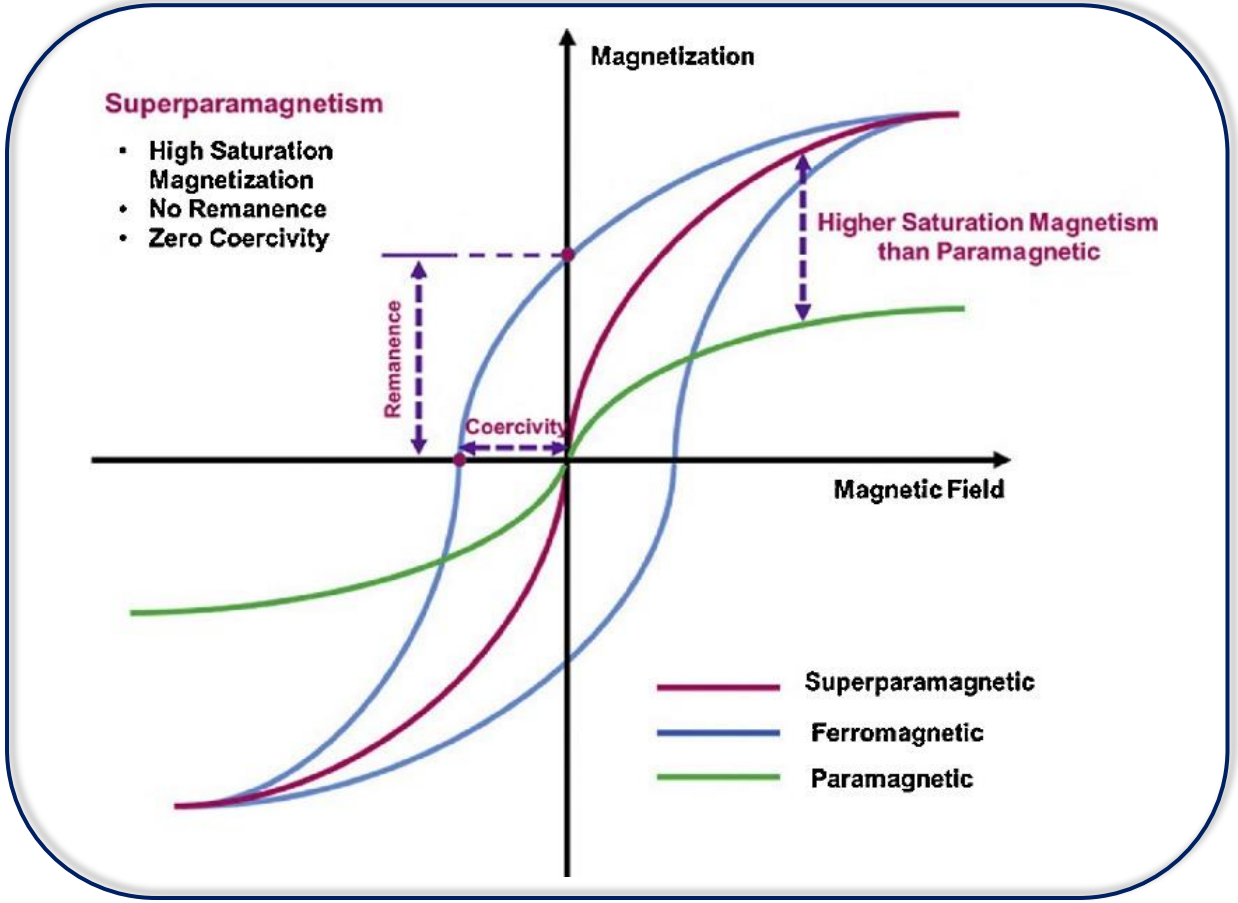
In-situ method: Co-Precipitation

- Particle size and shape distribution
- Impact on particle size and shape
- (Long-term) stability in aqueous environment
- Reproducibility of physical properties

Fabrication and Modification

- Physical methods
- Wet chemical preparation
- Microbial methods



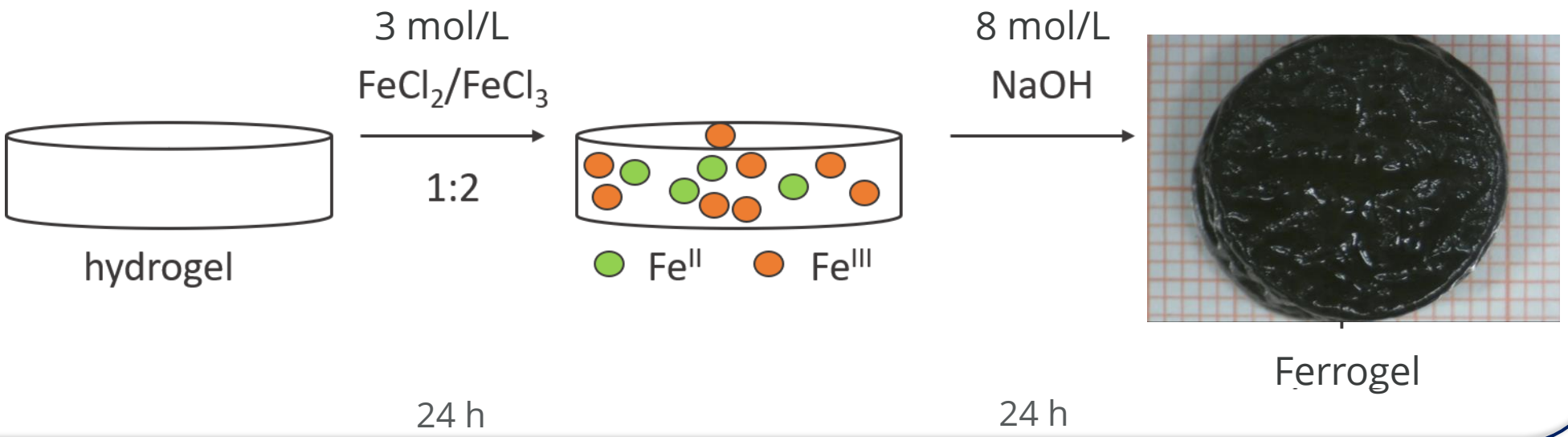


Mohammed et al. *Particuology*, 2017

In-situ ferrogel

Sensory:
1,6 mol/L AAm
1,5 mol-% BIS
0,27 mol-% APS
2,1 mol-% TEMED

Actuatory:
2,8 mol/L AAm
0,03 mol-% BIS
0,32 mol-% APS
0,5 mol-% TEMED

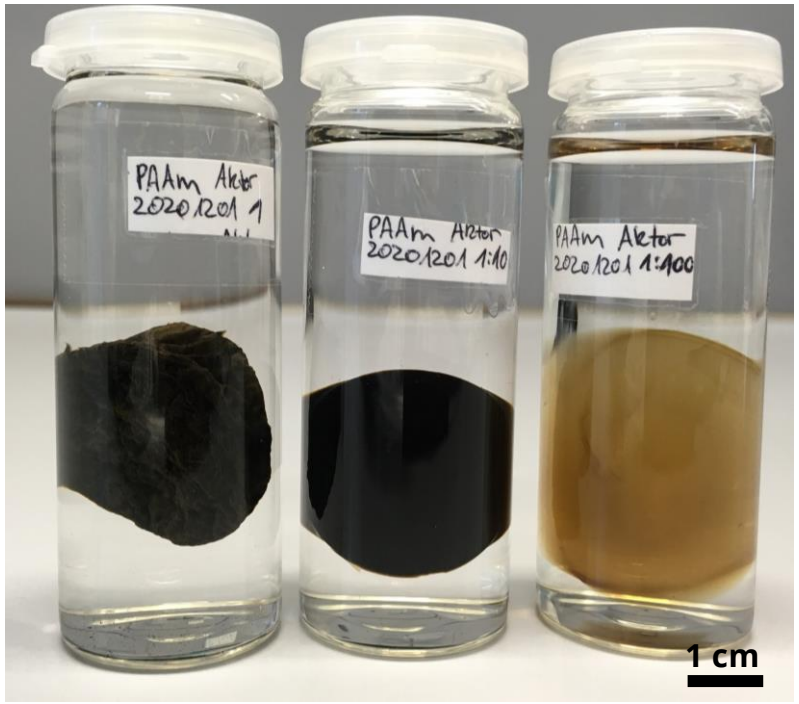


→ Two types of hydrogel: 1,5 mol% vs. 0,03 mol% BIS

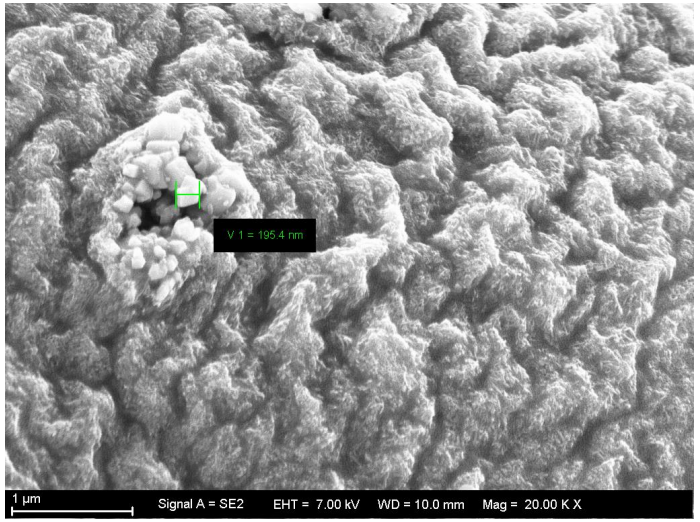
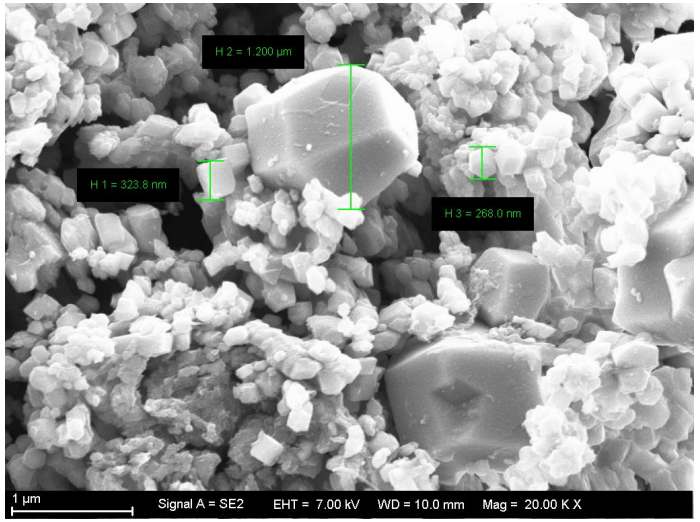
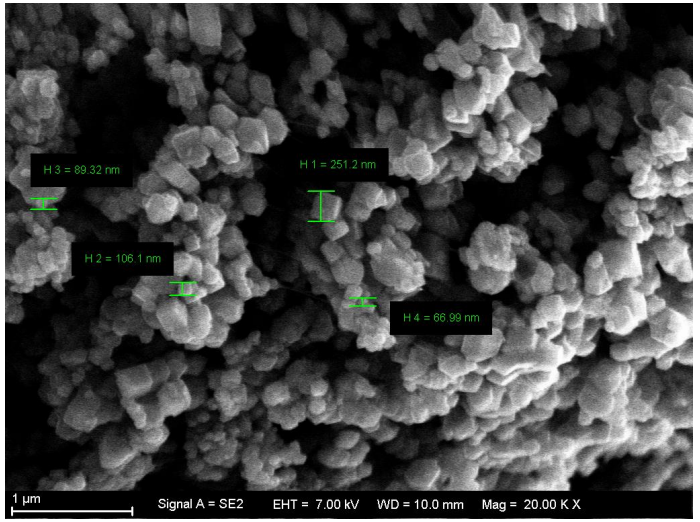
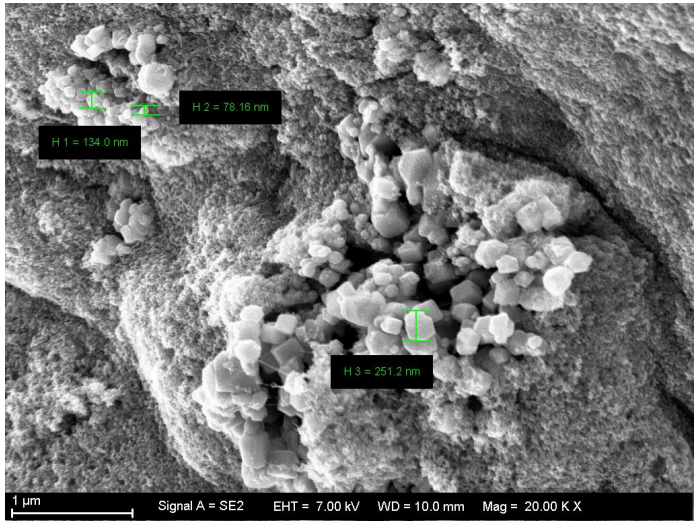
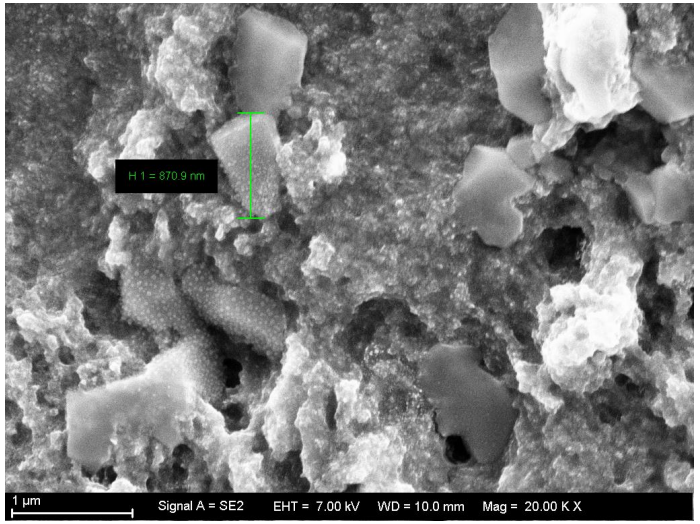
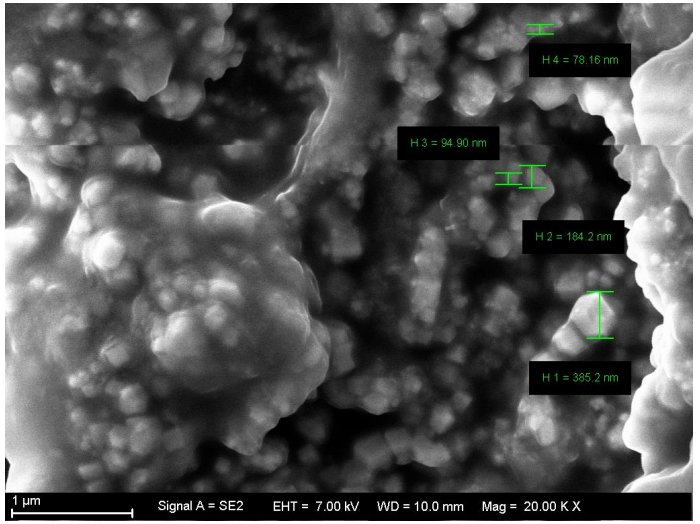
→ Dilutions of iron salts and base : 1 1:10 1:100

Sensory Ferrogel

Actuatory Ferrogel



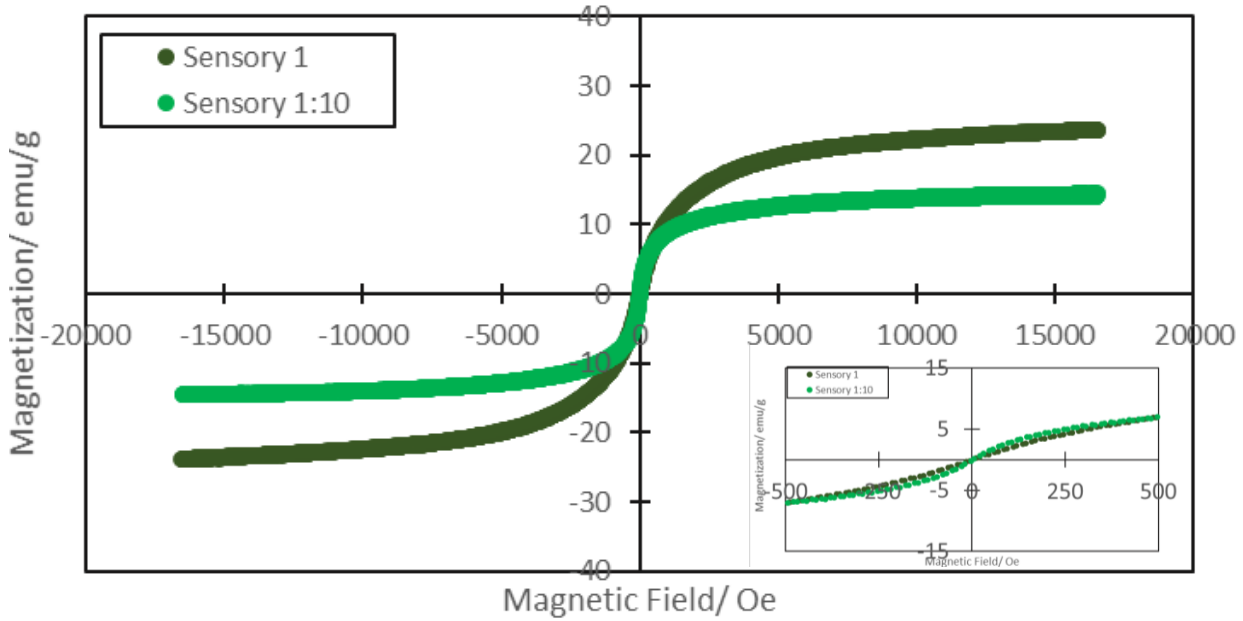
→ black to lightbrown
→ brittle to soft

	1	1:10	1:100
Sensory Ferrogel			
Actuatory Ferrogel			

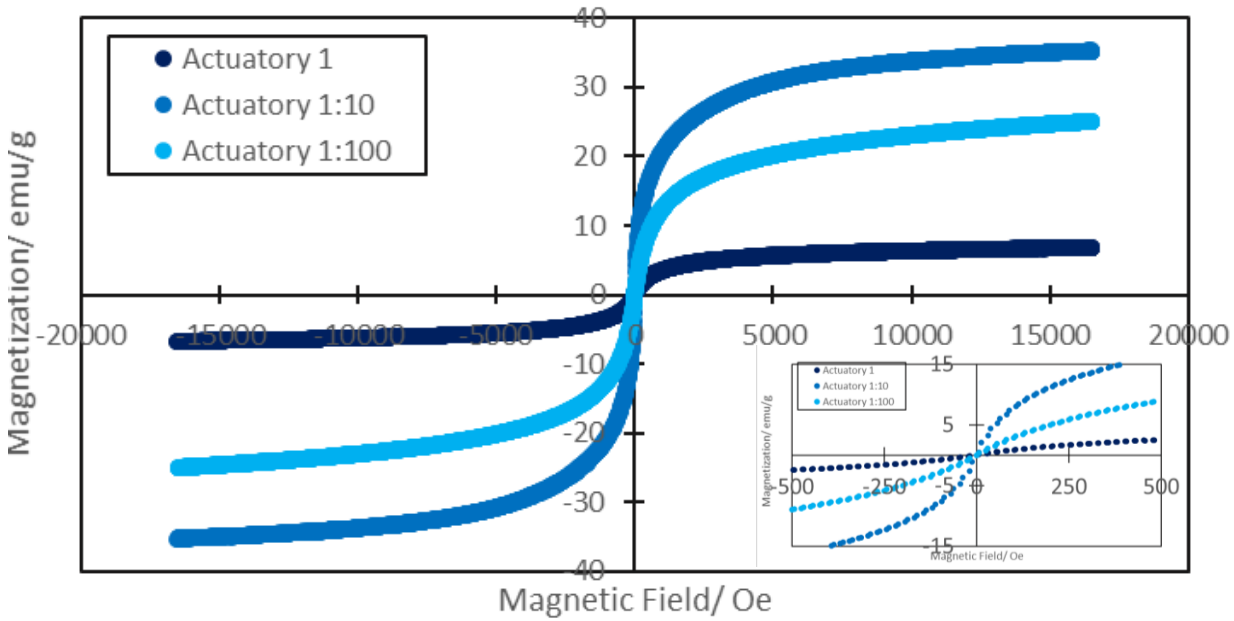
→ cubic particles 50 bis 300 nm, 1 µm
→ TEM for ~10 nm sized particle

In-situ ferrogel: conditioned and air dried
Images made by Sitao Wang

Sensory Ferrogel



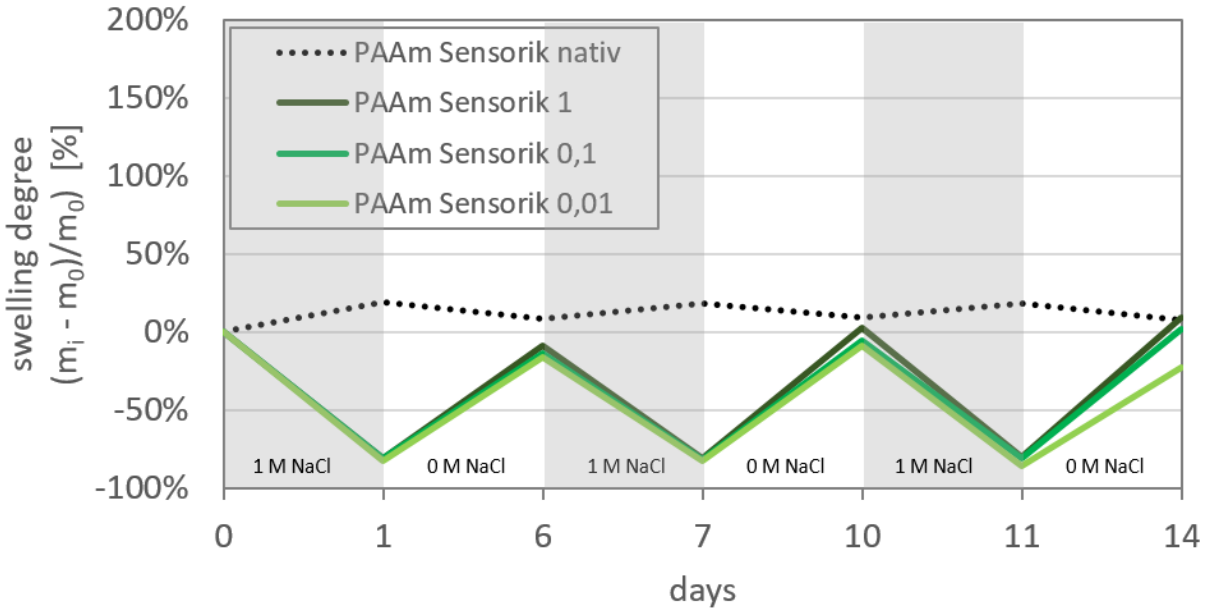
Actuatory Ferrogel



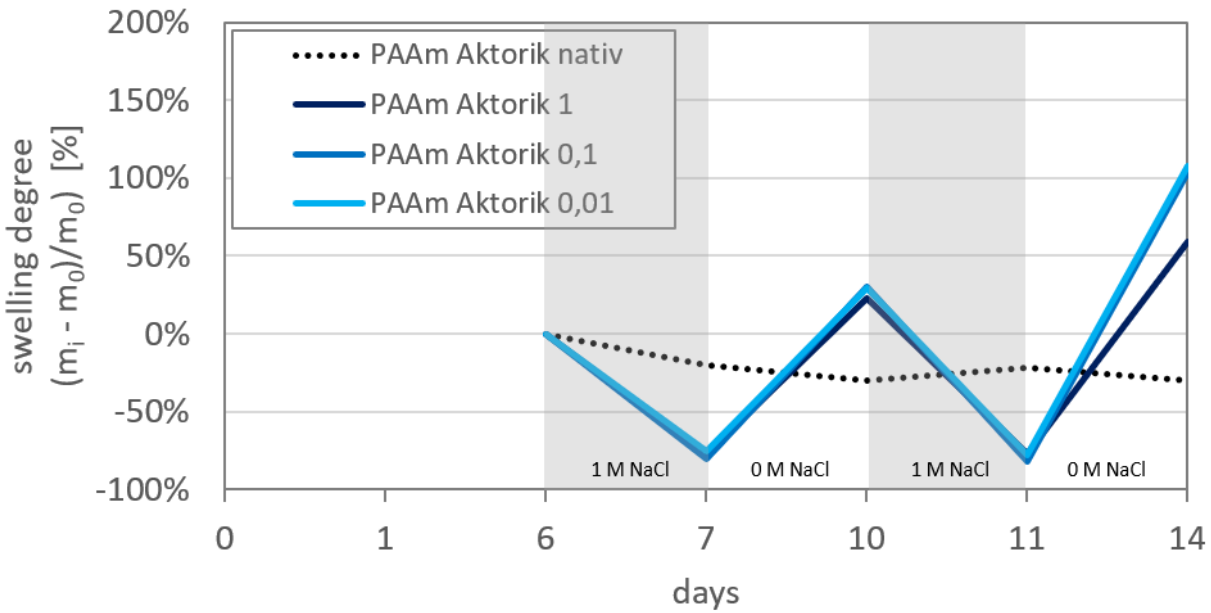
→ Superparamagnetic behaviour

In-situ ferrogel: conditioned and air dried
VSM measurements made by Mia Schliephake

Sensory Ferrogel



Actuatory Ferrogel



→ Swelling properties comparable to ion-sensitive hydrogels:
Ionic strength ↑ → masking of bonded ionized groups → deswelling

→ ~ 80 % **deswelling** in 1M NaCl

→ 50 - 100 % **swelling** in ultrapure water

→ Dissolution of actuatory Ferrogel 1 and 0,1

0 M NaCl = ultrapure water

$$2FeCl_3 + FeCl_2 + 8BOH \rightarrow Fe_3O_4\,(s) + 4H_2O + 8BCl$$

$$Fe^{3+} + 3OH^- = Fe(OH)_3\,(s)$$

1) hydroxides precipitating

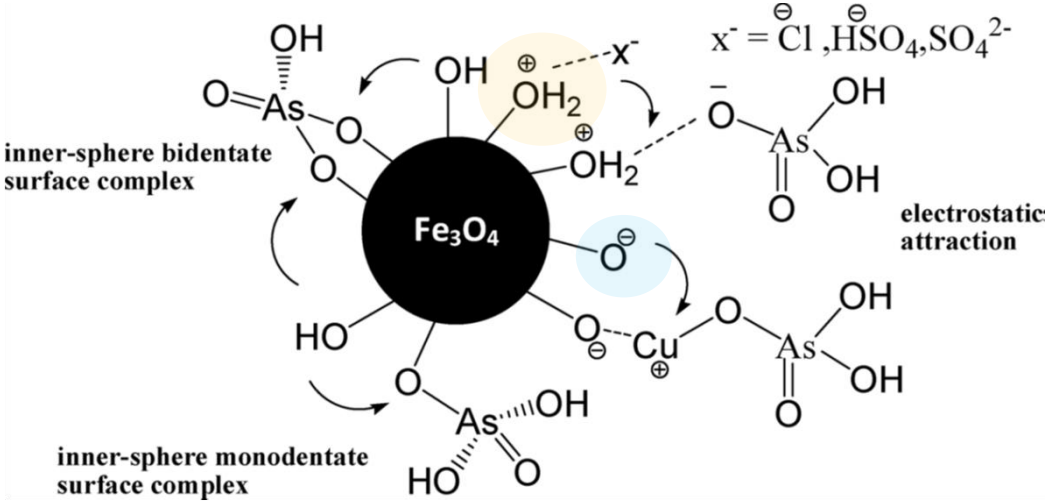
$$Fe(OH)_3\,(s) = FeOOH\,(s) + H_2O$$

2) decomposing due to ↑ ionic strength

$$Fe^{2+} + 2OH^- = Fe(OH)_2\,(s)$$

$$2FeOOH\,(s) + Fe(OH)_2\,(s) = Fe_3O_4\,(s) + 2H_2O.$$

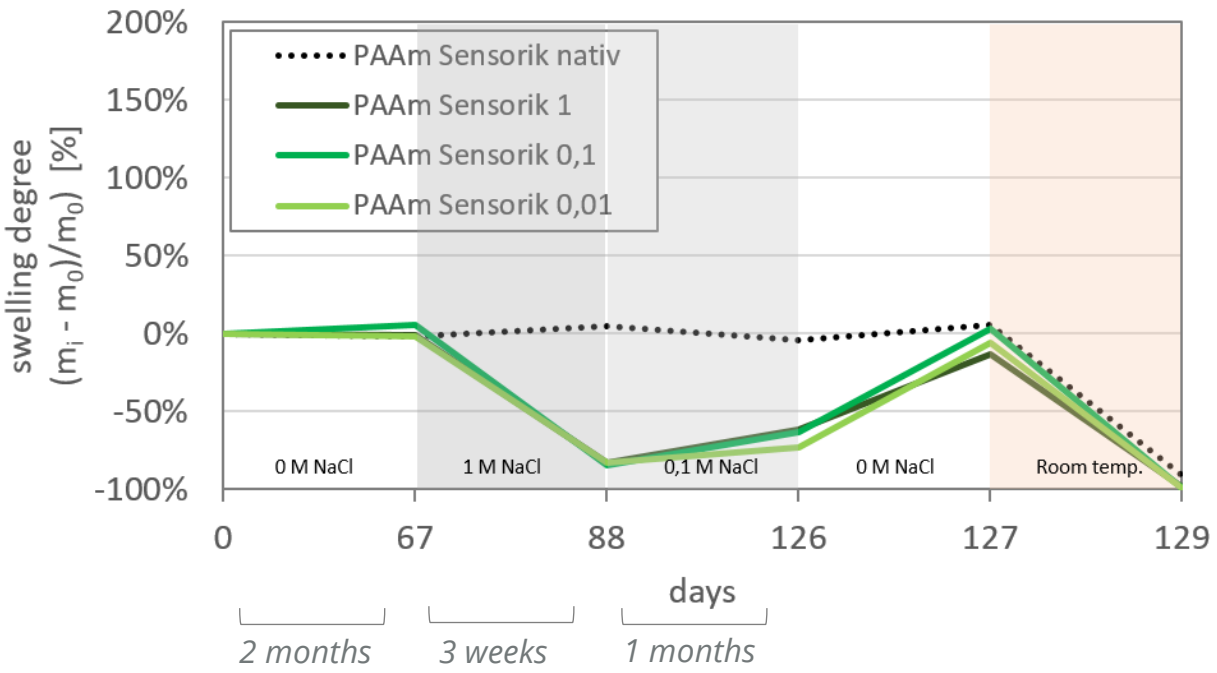
3) Solid state reaction (10-30 min at RT)



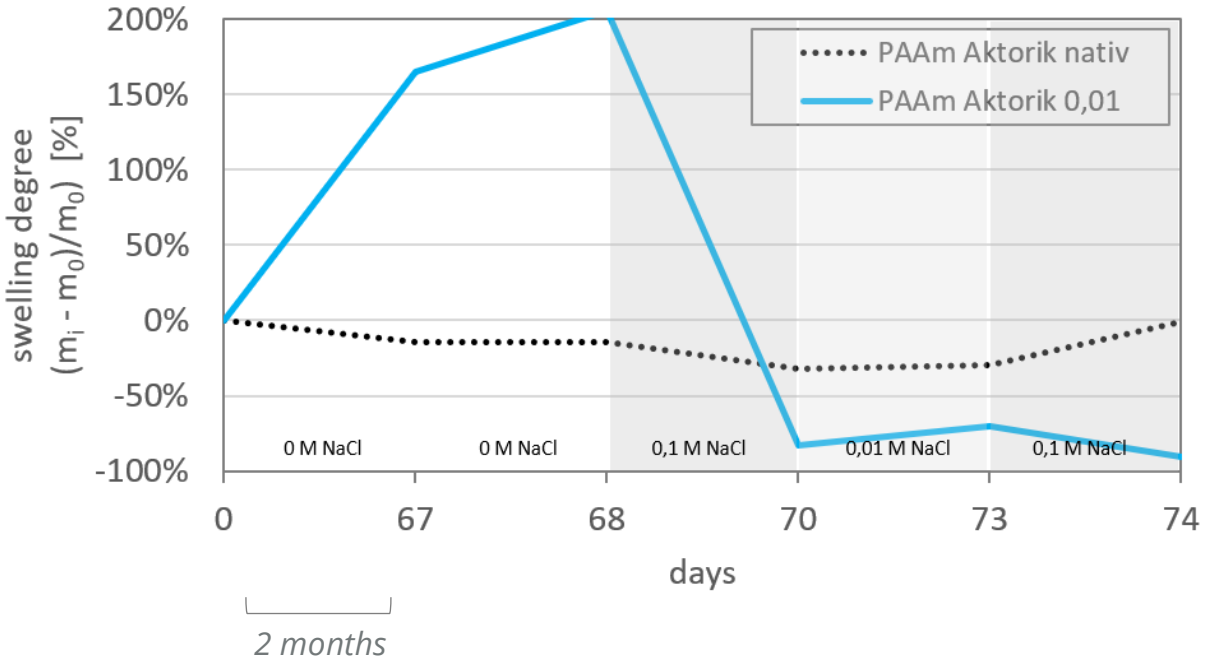
Darezereshki et al. *Environmental Nanotechnology, Monitoring & Management, 2018*

Mascolo et al. *Materials,* 2013

Sensory Ferrogel



Actuatory Ferrogel



→ Swelling properties are maintained

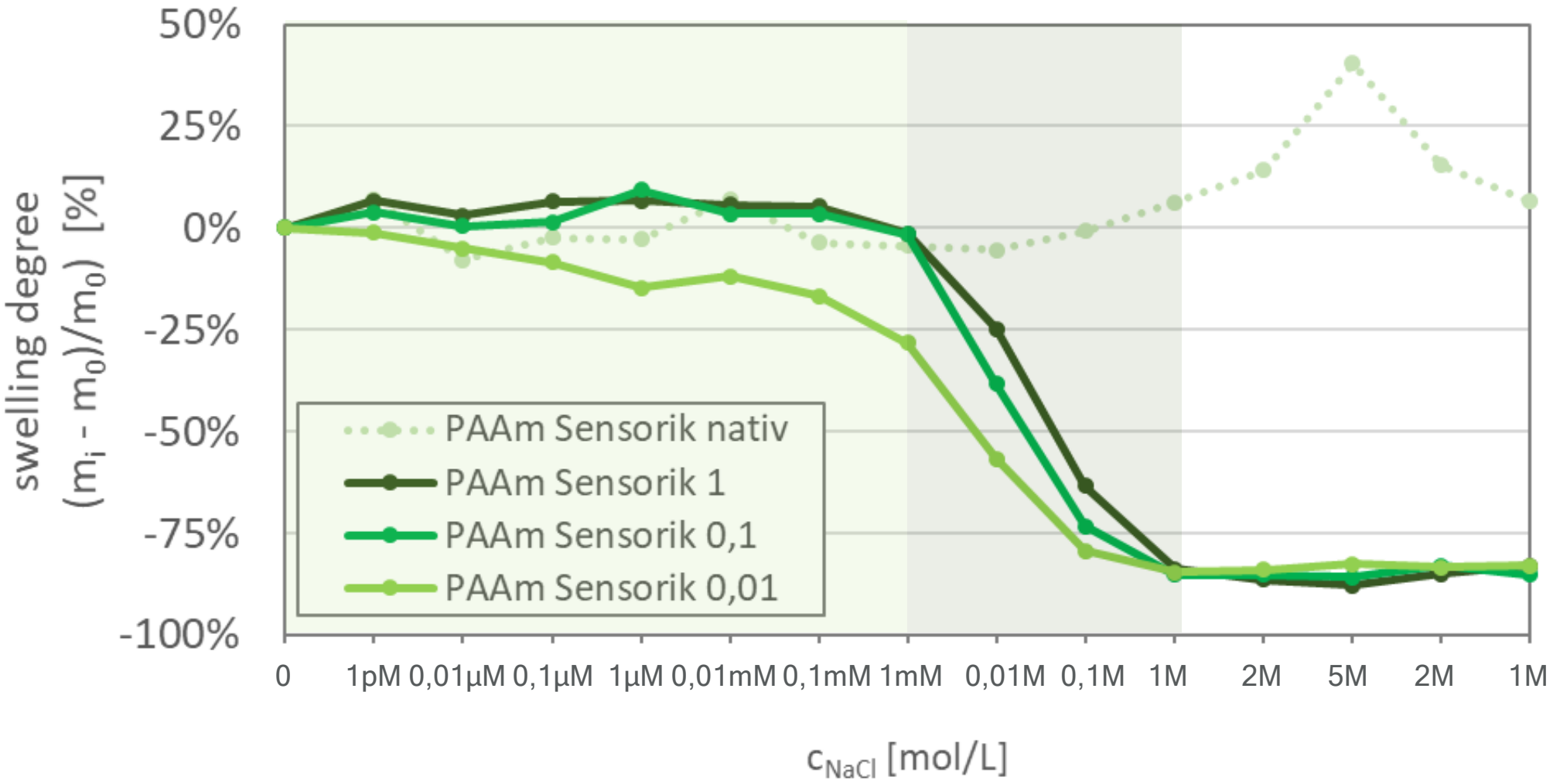
→ Stability in ultrapure water

→ **no** long-term stability in ultrapure water

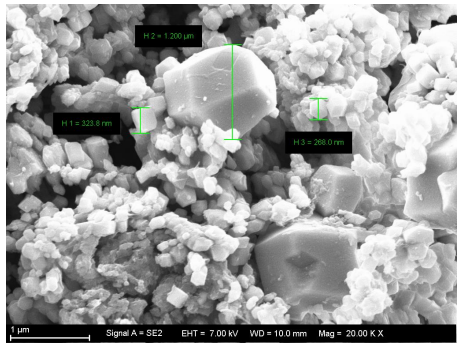
→ ~ 300 % deswelling in 0,1M NaCl

0 M NaCl = ultrapure water

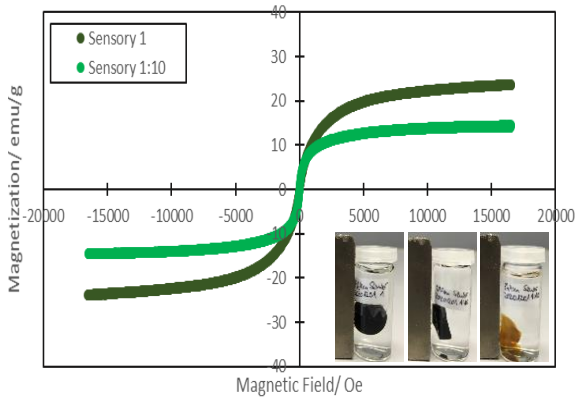
Sensory Ferrogel



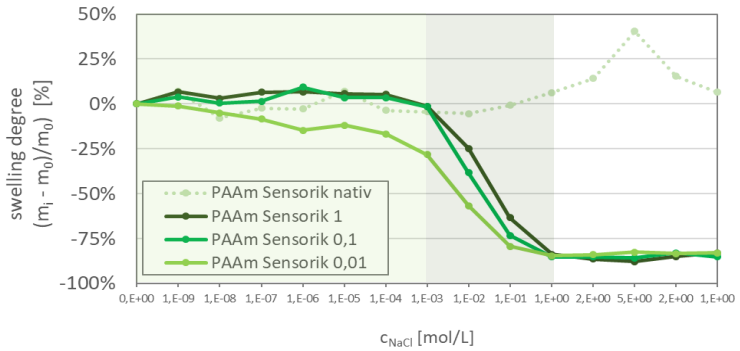
Nm sized particles



Superparamagnetic behaviour



Ionic sensitive deswelling



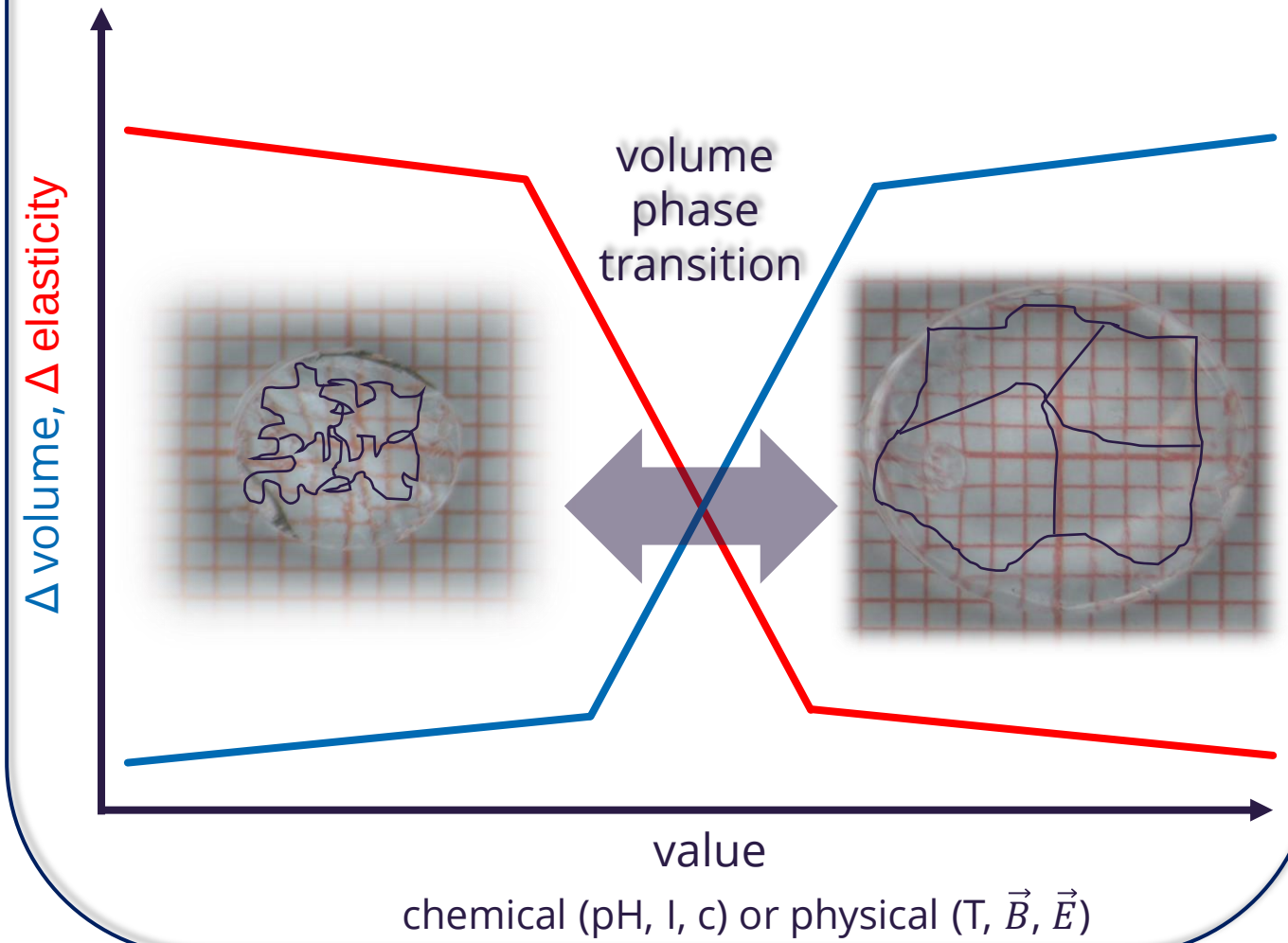
Sensory Ferrogel

→ stimuli-responsive ferrogel for
- → piezoresistive sensors
- → Magnetic field guided control in microfluidics or medicine
- → thermoresponsive deswelling due to HF magnetic fields

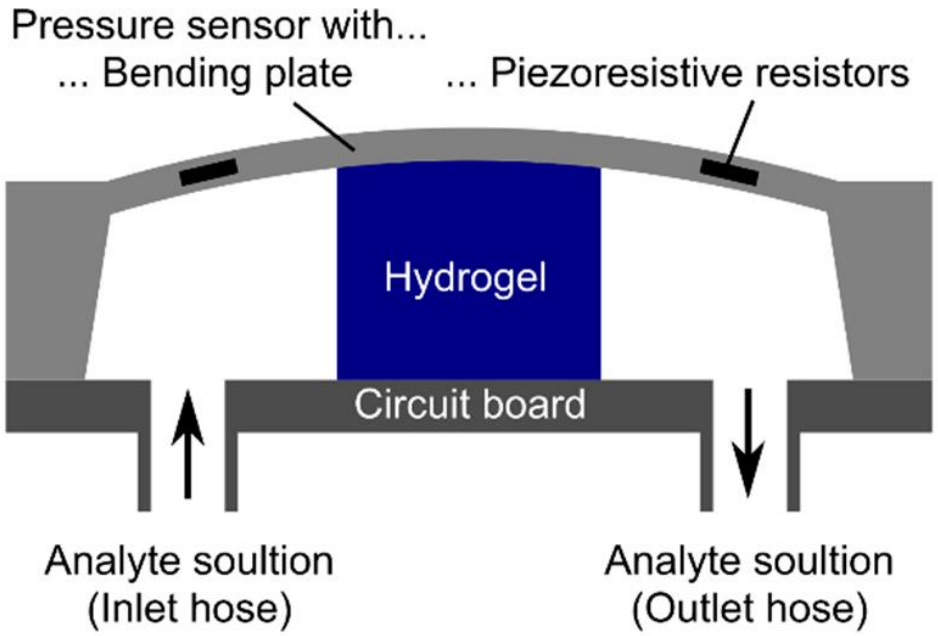
Actuatory Ferrogel

→ stimuli-responsive ferrogel for
- → Water remediation

Hydrogel
hydrophilic 3D polymer network



Microsystem
pressure sensor



Sensors **2019**, 19, 971

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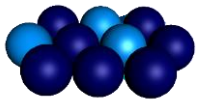
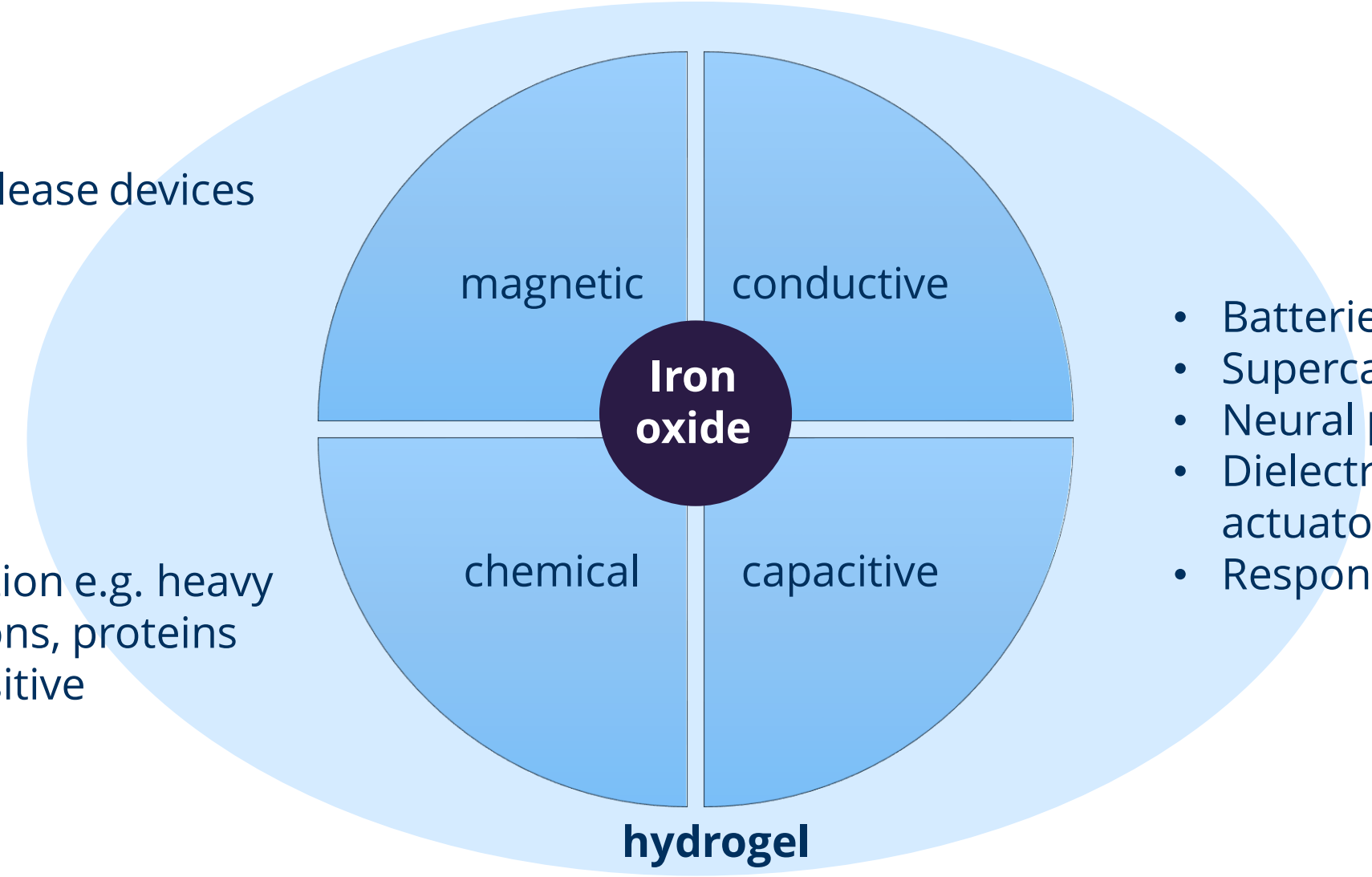
Thank you for your attention!



Applications of iron oxide functionalized hydrogels

- Drug-release devices

- Adsorption e.g. heavy metal ions, proteins
- pH sensitive



- Batteries
- Supercapacitors
- Neural protheses
- Dielectric elastomer actuators
- Responive sensors

Magnetite

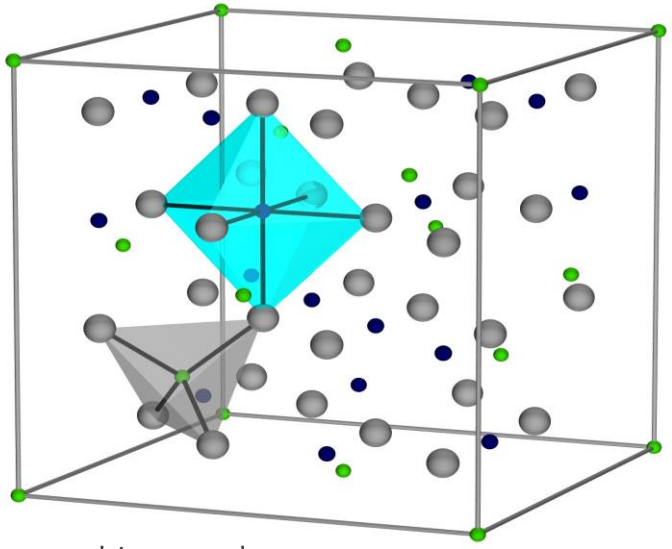
iron^{II,III} oxide

Fe_3O_4

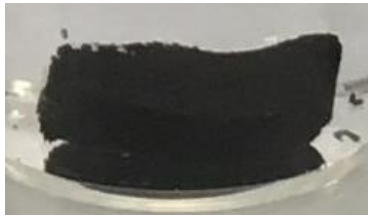
$[Fe^{3+}{}_8]_t\,[Fe^{2+}{}_8Fe^{3+}{}_8]_o\,O_{32}$

oxidation

$[Fe^{3+}{}_8]_t\,[Fe^{3+}{}_{5,33}\square_{2,67}Fe^{3+}{}_8]_o\,O_{32}$



cubic crystal structure



ferromagnetic

Maghemite

iron^{III} oxide

γ-Fe_2O_3

ferrimagnetic

Hematite

Beta-FeOOH → iron^{III} oxide α-Fe_2O_3

trigonal crystal structure

antiferrimagnetic