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Synthesis and functionalization of rod-like iron oxide nanoparticles

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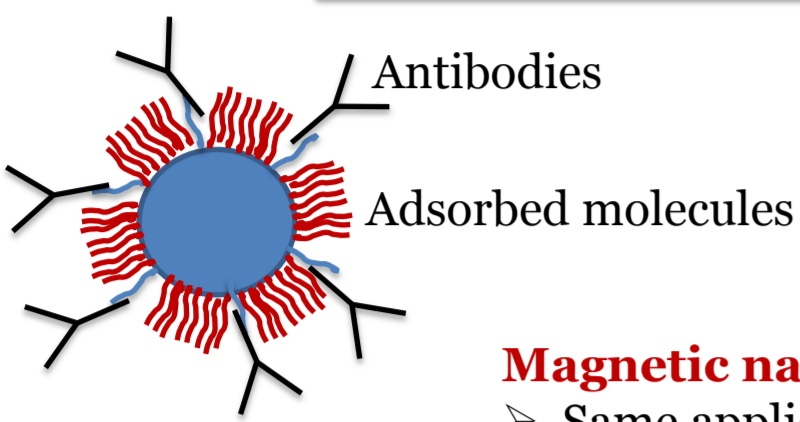
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Introduction



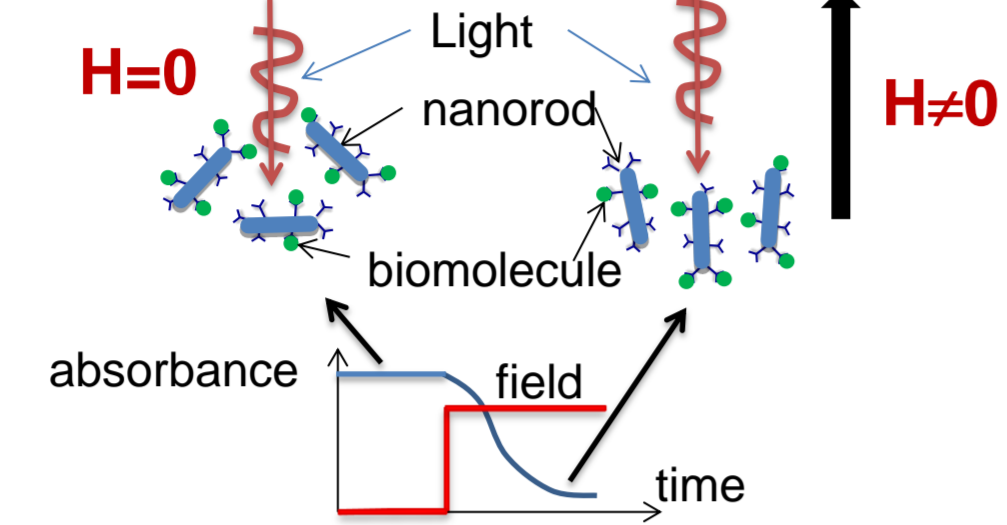
Magnetic micro- or nanobeads:

- MR imaging;
- Cell separation;
- Hyperthermia;
- Detection of biomolecules by ELISA

Magnetic nanorods:

- Same applications with **enhanced magnetization**
- Detection of biomolecules by **magneto-optic effects**

- Follow light absorption by nanorod suspension in response to **H**
- Relate C_{ads} to change of relaxation time



Start-up CMD (Exeter, UK)

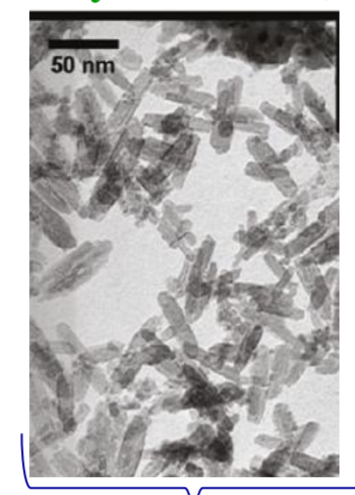
Objectives / State of the art

We seek for iron oxide nanorods:

- High specific surface → small enough
- High interaction with **H** → large enough
- Strong MO response → $L/d > 5$
- Well dispersed in water → graft **polymers/polyelectrolytes**

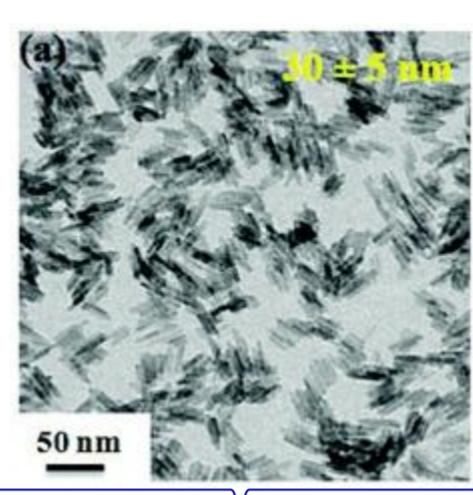
If using **B=1 mT**
 $d \sim 5 \text{ nm}$
 $L \sim 25 \text{ nm}$

Milosevic et al.
J. Phys. Chem. (2011)



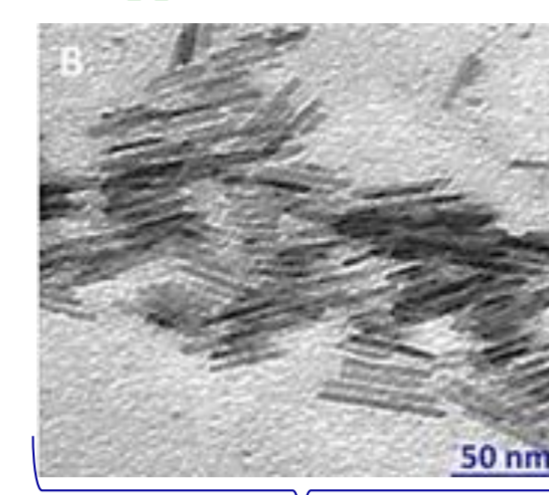
No stabilization

Mohaparta et al.
Nanoscale (2015)



Stabilization by PEI

Orza et al.
ASC Appl. Mater. Int. (2017)



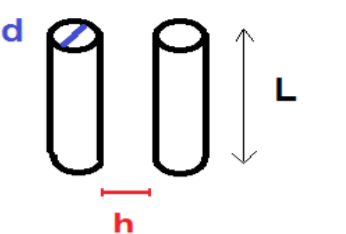
Stabilization by PEG-NH2

Key question

Why nanorods are so unstable as compared to nanobeads?

van der Waals interaction is much stronger for rods than for beads (larger contact area)

$$U_{vdw} = -\frac{A_H L}{24\sqrt{2}d} \left(\frac{d}{h}\right)^3 \sim -60k_B T$$



$L \sim 30 \text{ nm}$, $d \sim 6 \text{ nm}$;
 $h \sim 0.5 \text{ nm}$ – two water layers separating particle surfaces

To get $U_{vdw} \sim 1k_B T$ → separate nanorods at $h \sim 7-8 \text{ nm}$ using a polymer



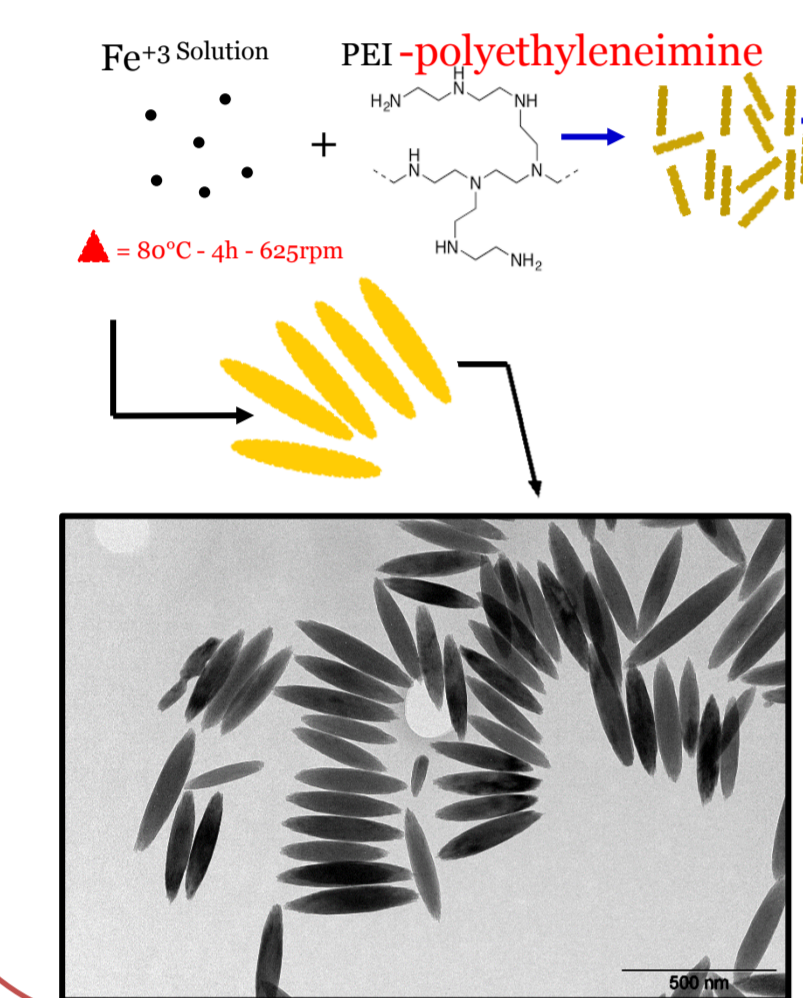
Detailed study of nanorod stability is missing

Our work: go further in realization and understanding of nanorod dispersion

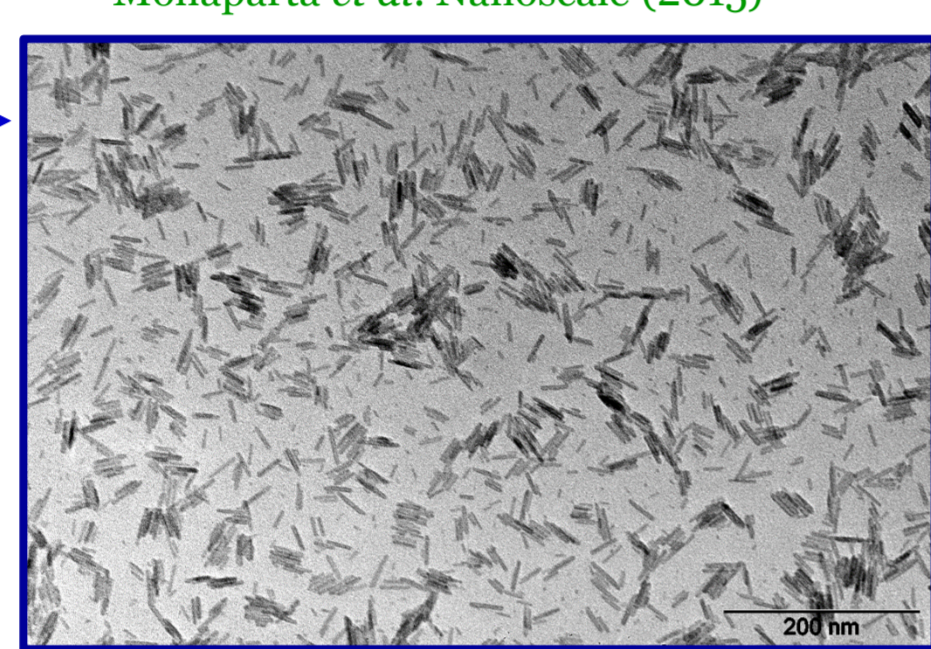
Two step synthesis

Akaganéite $\beta\text{-FeOOH}$

Hydrolysis of $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ at 80°C



The protocol with PEI
Mohaparta et al. Nanoscale (2015)



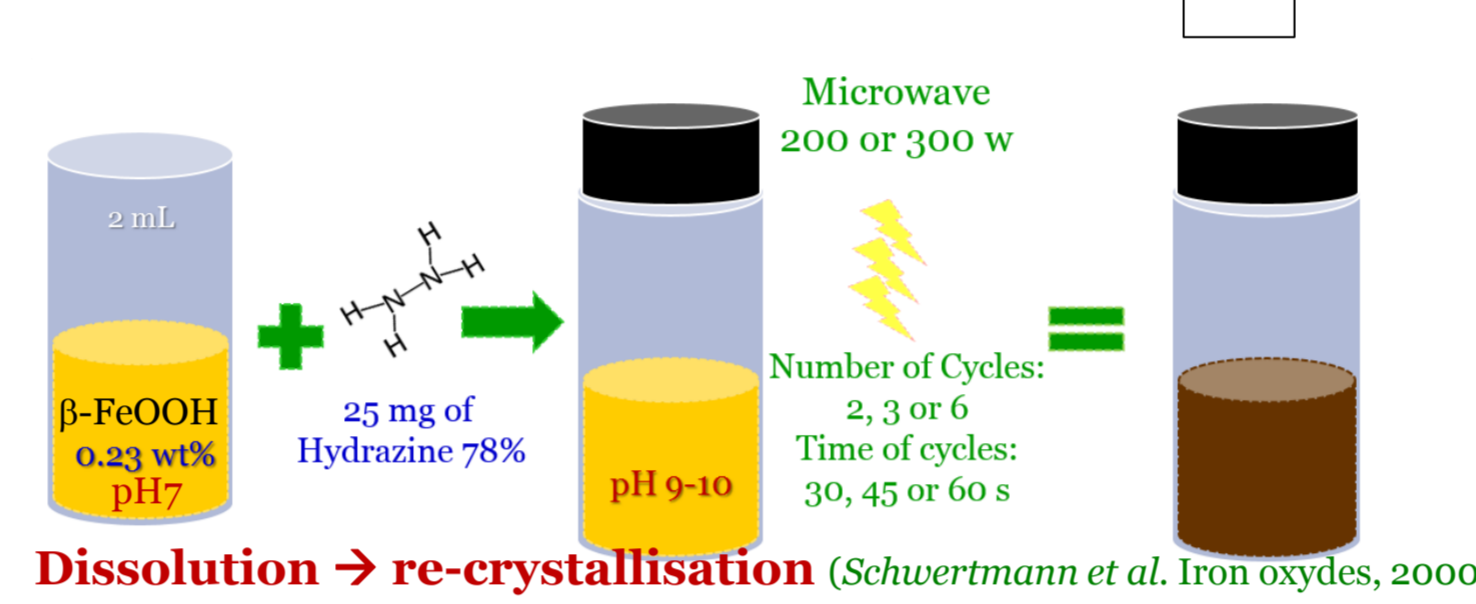
NH2 groups → affinity with specific crystal phases → **anisotropic crystal growth**

The protocol without PEI
Blesa et al. Reactivity of Solids (1986)

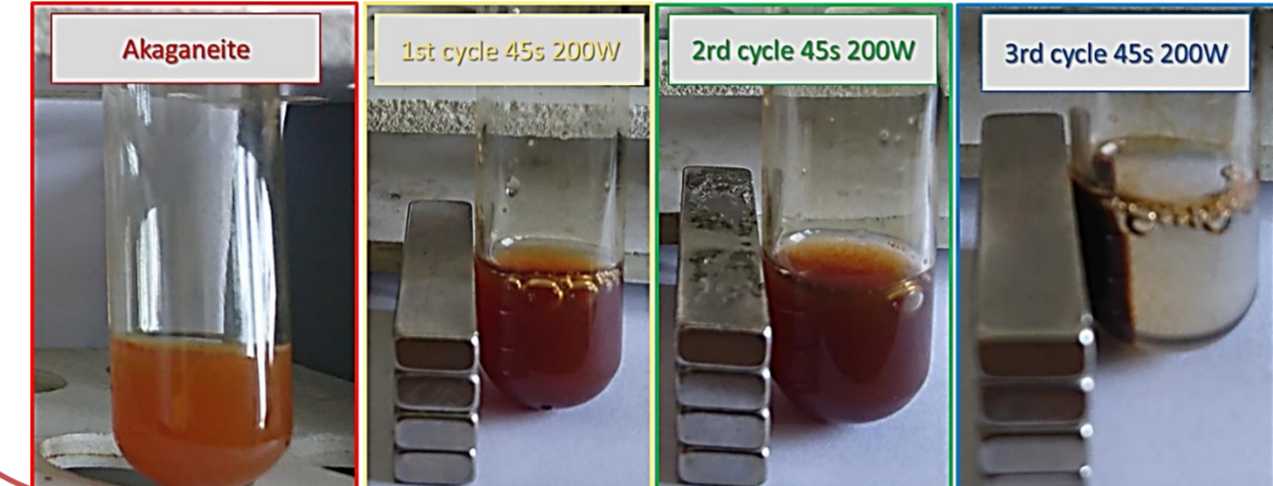
1

2

Reduction of $\beta\text{-FeOOH}$ to iron oxide



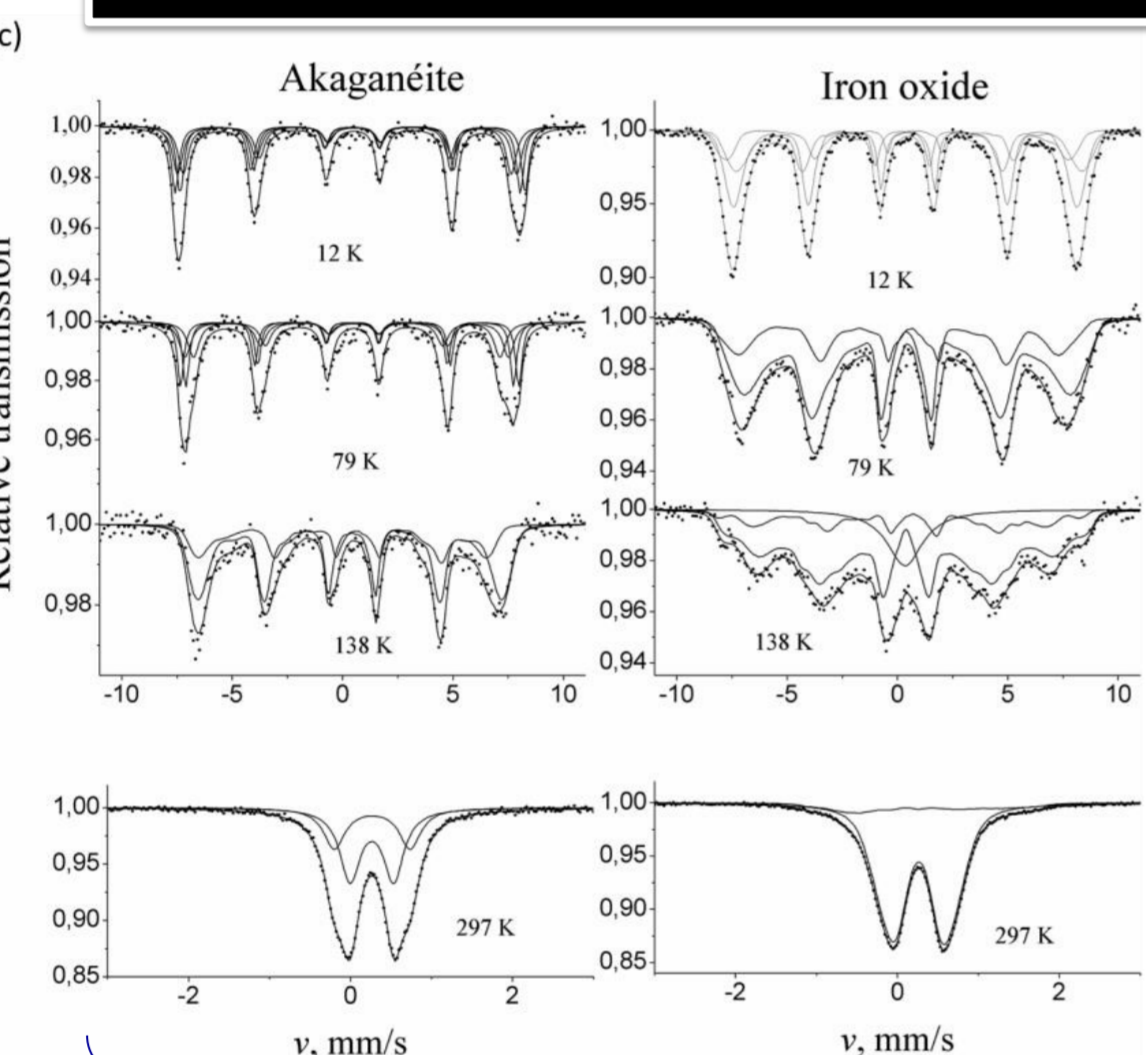
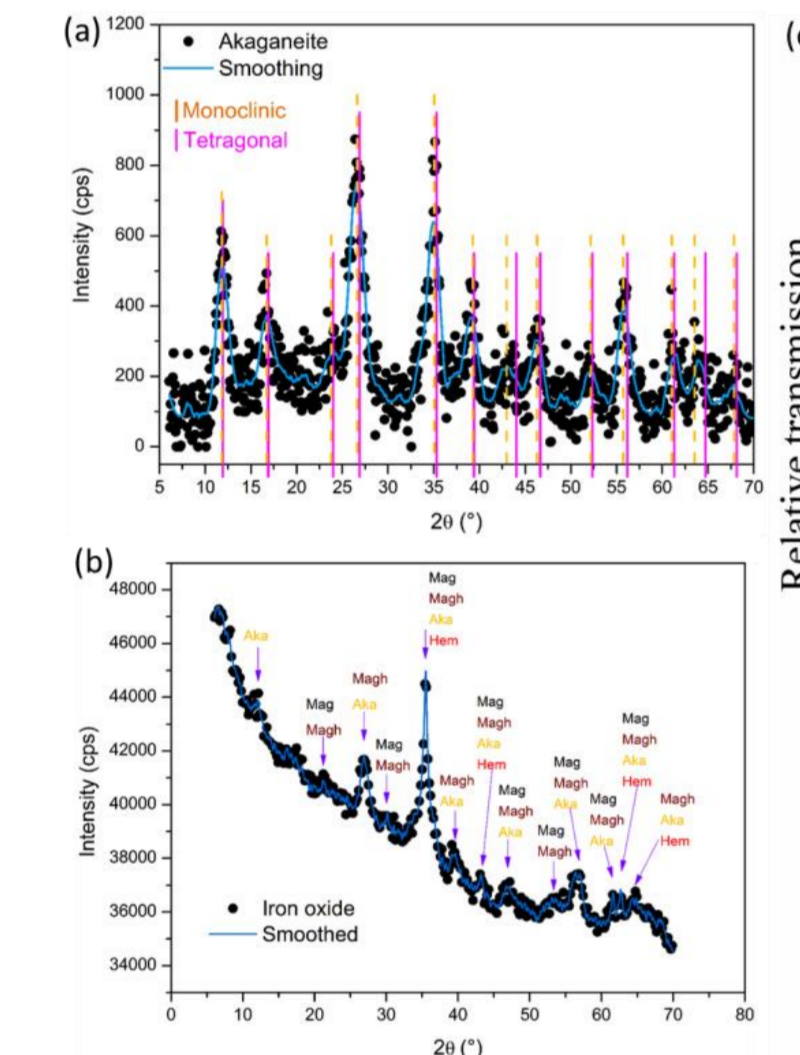
Dissolution → re-crystallisation (Schuertmann et al. Iron oxides, 2000)



Effect of number of cycles, duration and microwave power

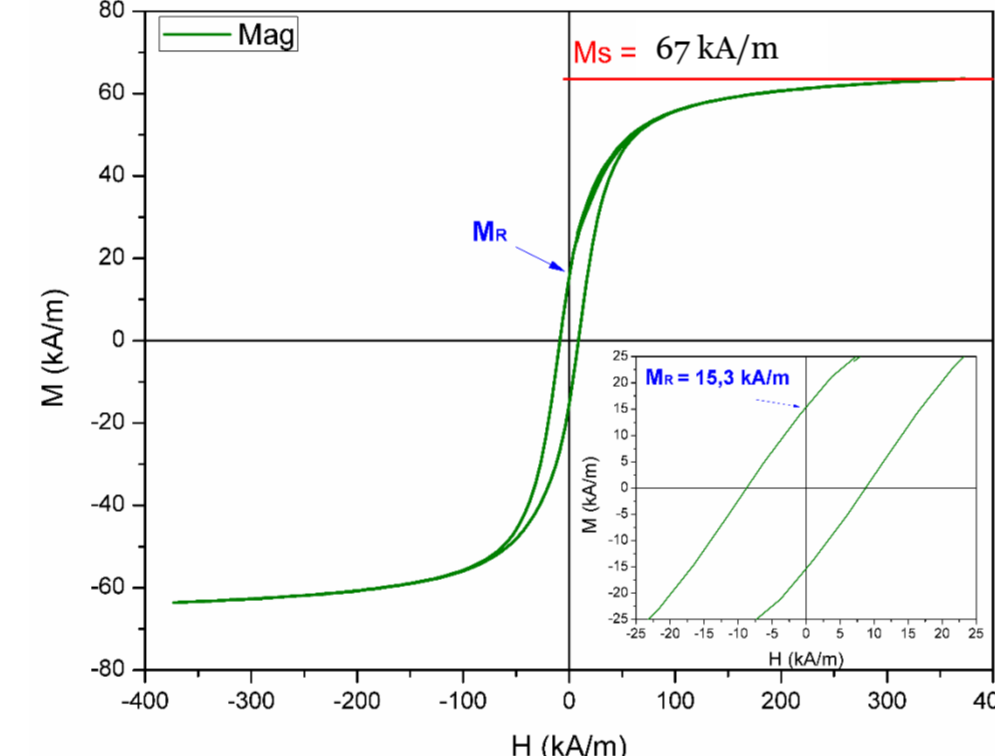
Number of cycles	Time (s)	Power (w)	Magnetization	Form	TEM
2	60	200	weak	cubic/rod	
6	30	200	strong	cubic/rod	
3	30	300	strong	cubic/rod	
2	60	300	strong	cubic/rod	
3	45	200	strong	rod	

Characterization of bare nanorods



Low hyperfine field: **no hematite**

Iron oxide room temperature magnetization

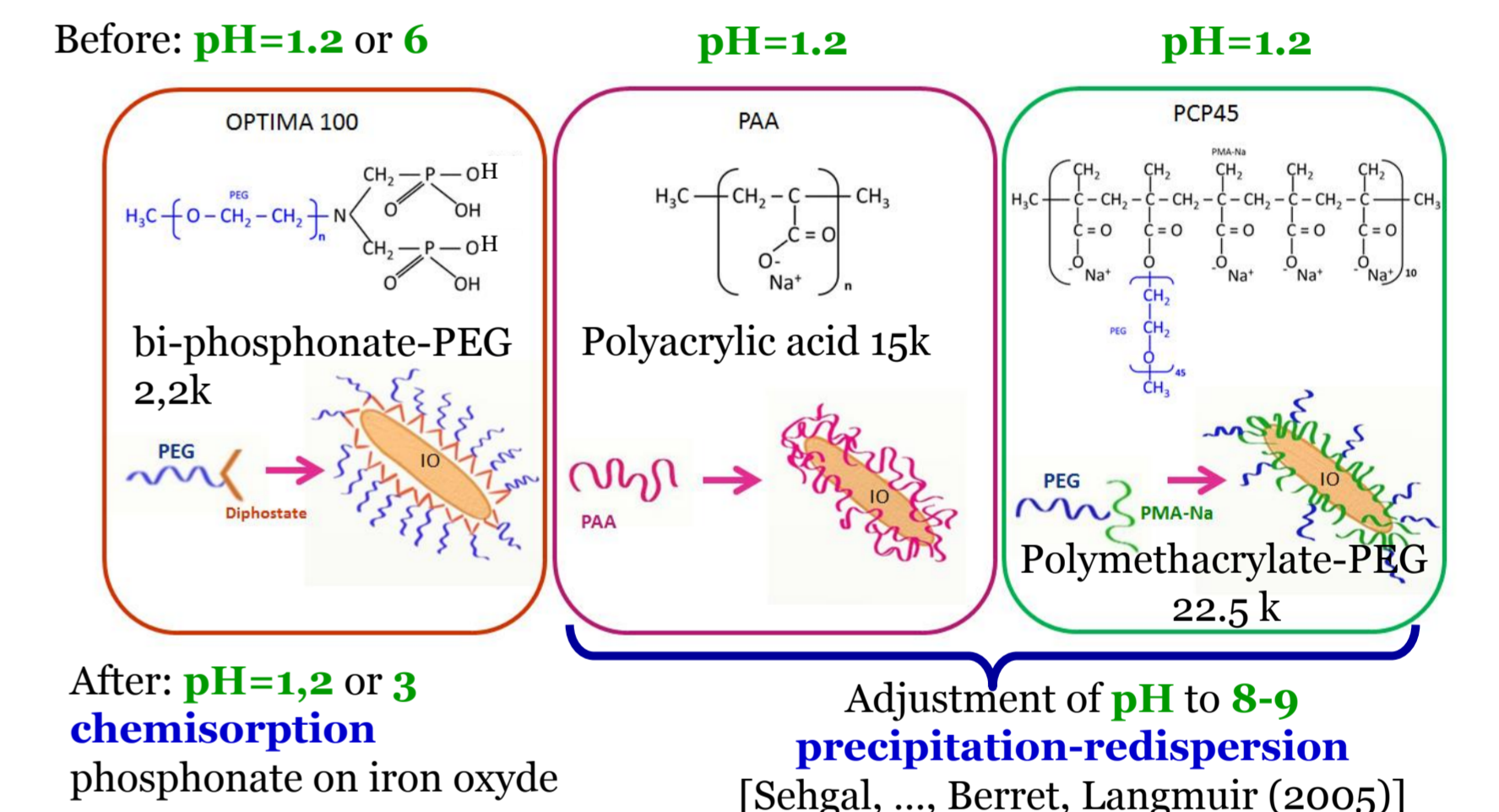


Saturation magnetization: $M_s = 67 \text{ kA/m}$ Why so small?
 Remnant magnetization: $M_r = 15 \text{ kA/m}$ Why remnance?

Mössbauer spectra:
 11% → ordered magnetic phase (**ferrimagnetic** $\gamma\text{-Fe}_2\text{O}_3/\text{Fe}_3\text{O}_4$ giving remnance)

89% → disordered magn. phase (**superparamagn.** $\gamma\text{-Fe}_2\text{O}_3/\text{Fe}_3\text{O}_4$ contributing to low Ms)

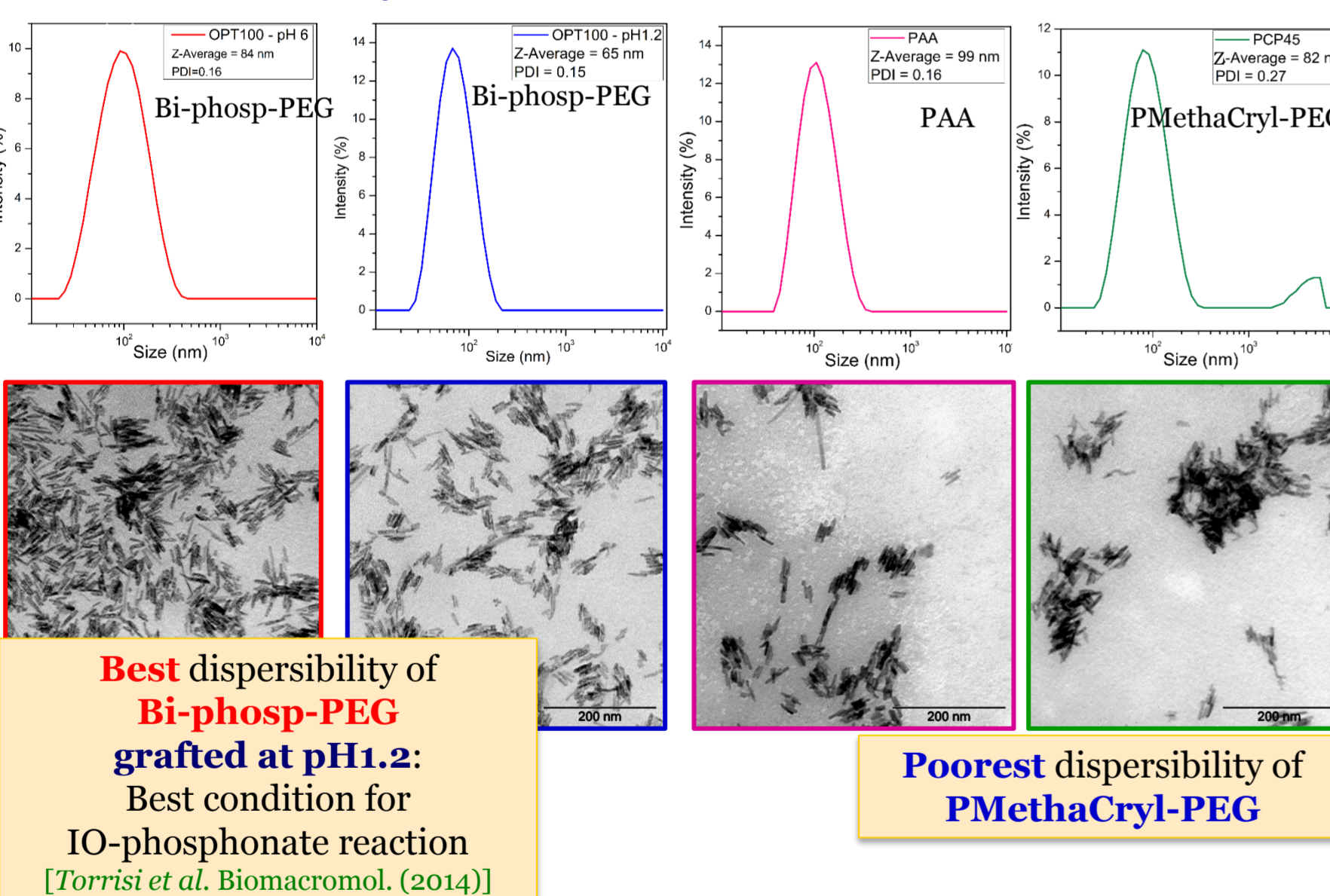
Dispersion of IO nanorods in water



Adjustment of **pH to 8-9**
precipitation-redispersion
 [Sehgal, ..., Berret, Langmuir (2005)]

Characterization of polymer coated IO nanorods

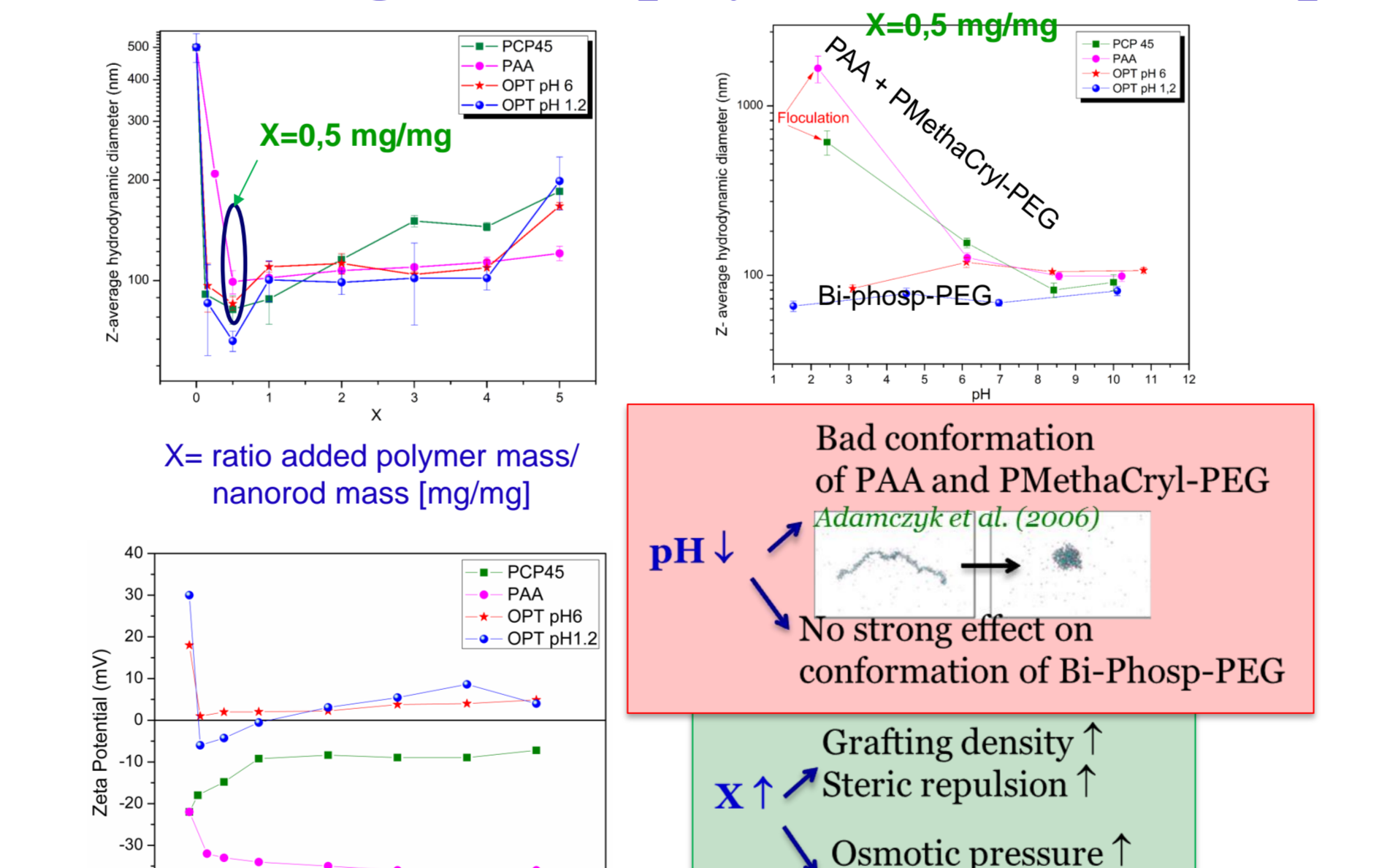
DLS intensity distribution of diameters



Best dispersibility of Bi-phosph-PEG grafted at pH 1.2:
 Best condition for IO-phosphonate reaction [Torrist et al. Biomacromol. (2014)]

Poorest dispersibility of PMethaCryl-PEG

DLS z-average versus polymer amount X and pH



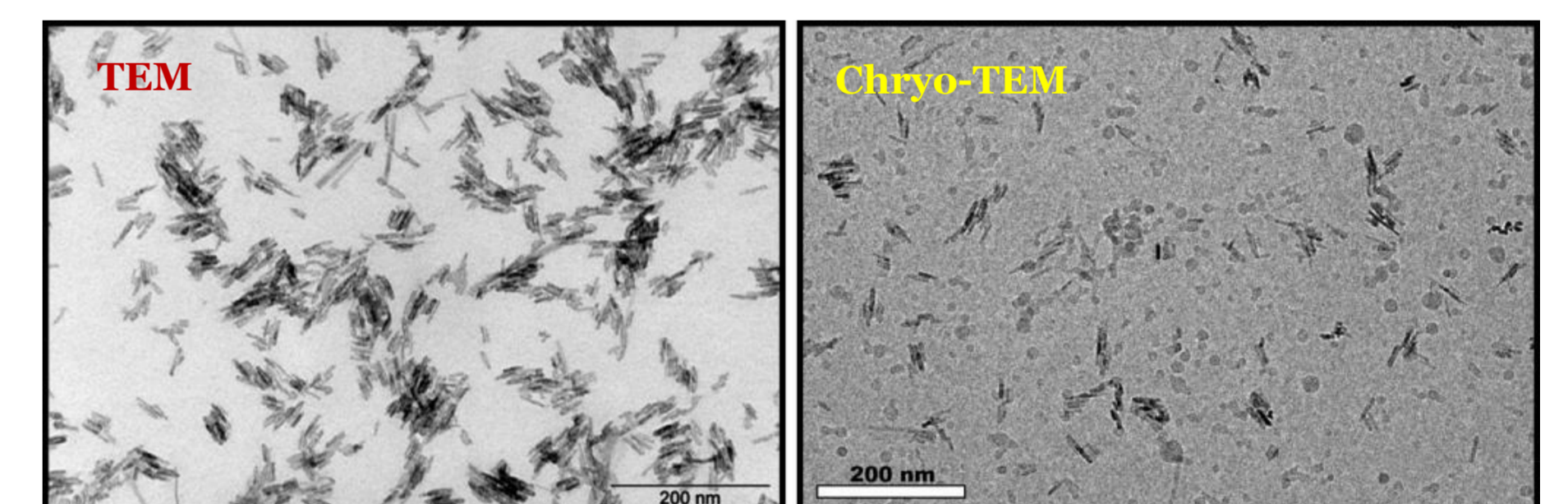
X = ratio added polymer mass/nanorod mass [mg/mg]

Bad conformation of PAA and PMethaCryl-PEG [Adamczyk et al. (2006)]

No strong effect on conformation of Bi-Phosph-PEG

Grafting density ↑
 Steric repulsion ↑
 Osmotic pressure ↑
 depletion attraction ↑

Best stabilization: PEG-bi-Phosphonate grafted at acidic pH at X=0.5 mg/mg



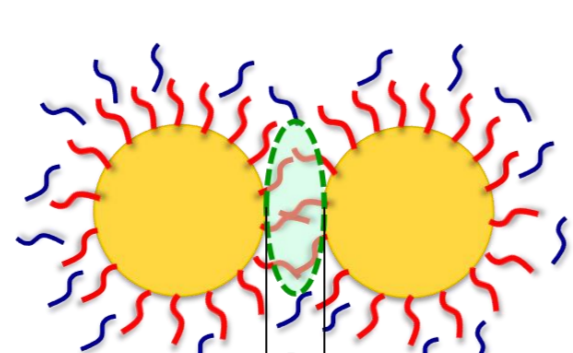
- Smaller aggregates in cryo-TEM pictures
- Lateral aggregation of rods

What leads to this aggregation?

Interaction energy between nanorods

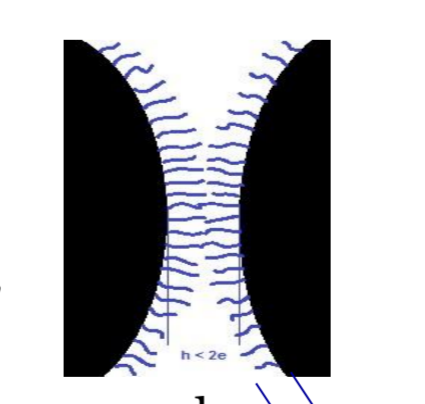
- Magnetic attraction due to remnant magnetization ($\sim 15 \text{ kA/m}$): $U_{mag} \ll k_B T$ (rods are too Brownian)
- Electrostatic repulsion due to electric double layer overlap: $U_{el} \ll k_B T$ (short Debye length $\kappa^{-1} < 1 \text{ nm}$)
- van der Waals attraction: *van der Schoot & Odijk J. Chem. Phys. [1992]*

$$U_{vdw} = -\frac{1}{24\sqrt{2}} \cdot A_H \frac{L}{d} \left(\frac{d}{h}\right)^{3/2}$$

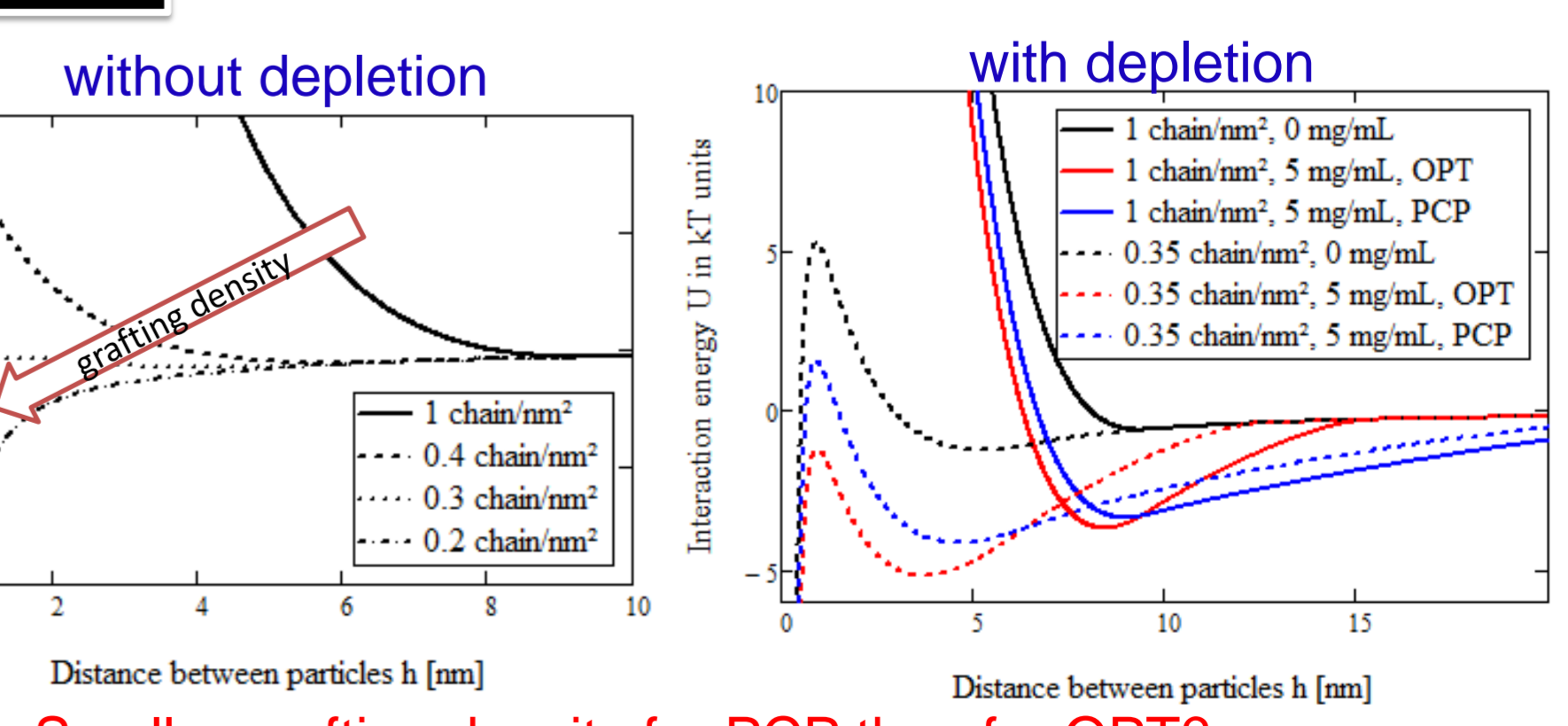


- Steric repulsion due to polymer layers overlap: *Patel & Russel, Coll. Surf. (1988) + Derjaguin approximation*

$$U_s = L(d/2)^{1/2} \int_h^{2d} \frac{u(x)}{(x-h)^{1/2}} dx = 2k_B T \frac{L(d\delta)^{1/2}}{a^2} k_1 \left(\frac{7k_2}{5k_1}\right)^{5/12} N_e (a^2 n)^{1/6} \int_{h/(2\delta)}^{y^2} \frac{y^{-5/4} + 5y^{7/4} - 17/7}{[y-h/(2\delta)]^{1/2}} dy$$



- Depletion attraction due to osmotic pressure asymmetry (Russel "Colloidal dispersions" 1989): $U_{dep} = -\Pi V_{ex}$
- Osmotic pressure: $\Pi \approx n_p k_B T (1 + B_2 n_p)$
 Excluded volume: $V_{ex} = L \left(\frac{d}{2} + \Delta + \delta\right) (\varphi - \sin \varphi)$ with $\varphi = 2 \arccos \left(\frac{d+h}{d+2\Delta+2\delta}\right)$



Smaller grafting density for PCP than for OPT?

- Conclusions:**
- Two-step nanorod synthesis + grafting of 3 different polymers/polyelectrolytes;
 - Optimum polymer amount for minimal aggregation (**X=0.5**) → interplay: steric repulsion vs depletion;
 - Nanorods/PAA or Polymethacryl-PEG: stable at $8 < \text{pH} < 11$; Nanorods/bi-phosphonate-PEG: stable at $1.5 < \text{pH} < 11$.
 - Best stability with bi-phosphonate-PEG grafted at acidic pH
 - Theoretical estimations suggest stronger nanorod aggregation for smaller grafting density (PCP vs OPT)