Umwelt Bundesamt

Federal Ministry for the Environment, Nature Conservation, Building and Nuclear Safety

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Importance of physical-chemical properties of ENM (intrinsic/extrinsic) for environmental hazard and risk assessment

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University of Birmingham

Scientific Stakeholder meeting on nanomaterials in the Environment, 10 and 11 Oct 2017

Intrinsic versus extrinsic properties

Constant throughout life
=> Intrinsic to an individual

Context dependent
=> changes with seasons,
with exposure location etc.

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Harder to imagine for NMs

Intrinsic properties are inherent to the nano-form of a material, and include e.g. structure and structural strain, shape, porosity, structural configuration and bandgap.

Extrinsic properties which are those connected to the surface area of the NM, including e.g. surface interactions and transformations of NM surface and biomolecules (e.g. unfolding, receptor activation, membrane damage, fibrillation etc.) as a result of binding.

Composition aspects such as inherent molecular toxicity, charge, hydrophobicity and coating (although also linked to both the intrinsic and extrinsic axes).

Nano Today (2014) **9**, 266—270

ECHA JRC RIVM approach

Intrinsic

„What they are?“
Chemical composition
Surface characteristics, including coating chemistry, functionalisation, surface charge
Particle size distribution (number average)
Specific surface area
Particle shape (e.g. aspect ratio)
Impurities
Crystalline phase(s) and size
Redox potential / band gap
Hydrophobicity/wettability
Rigidity
solubility
Isoelectric point

Extrinsic

„Where they go, what they do?“
Rate of dissolution (in environment)
Dispersibility/agglomeration and dispersion stability
Dustiness (depends on moisture)
Biological (re)activity (or surface reactivity)
Photoreactivity
Zeta potential
Surface affinity

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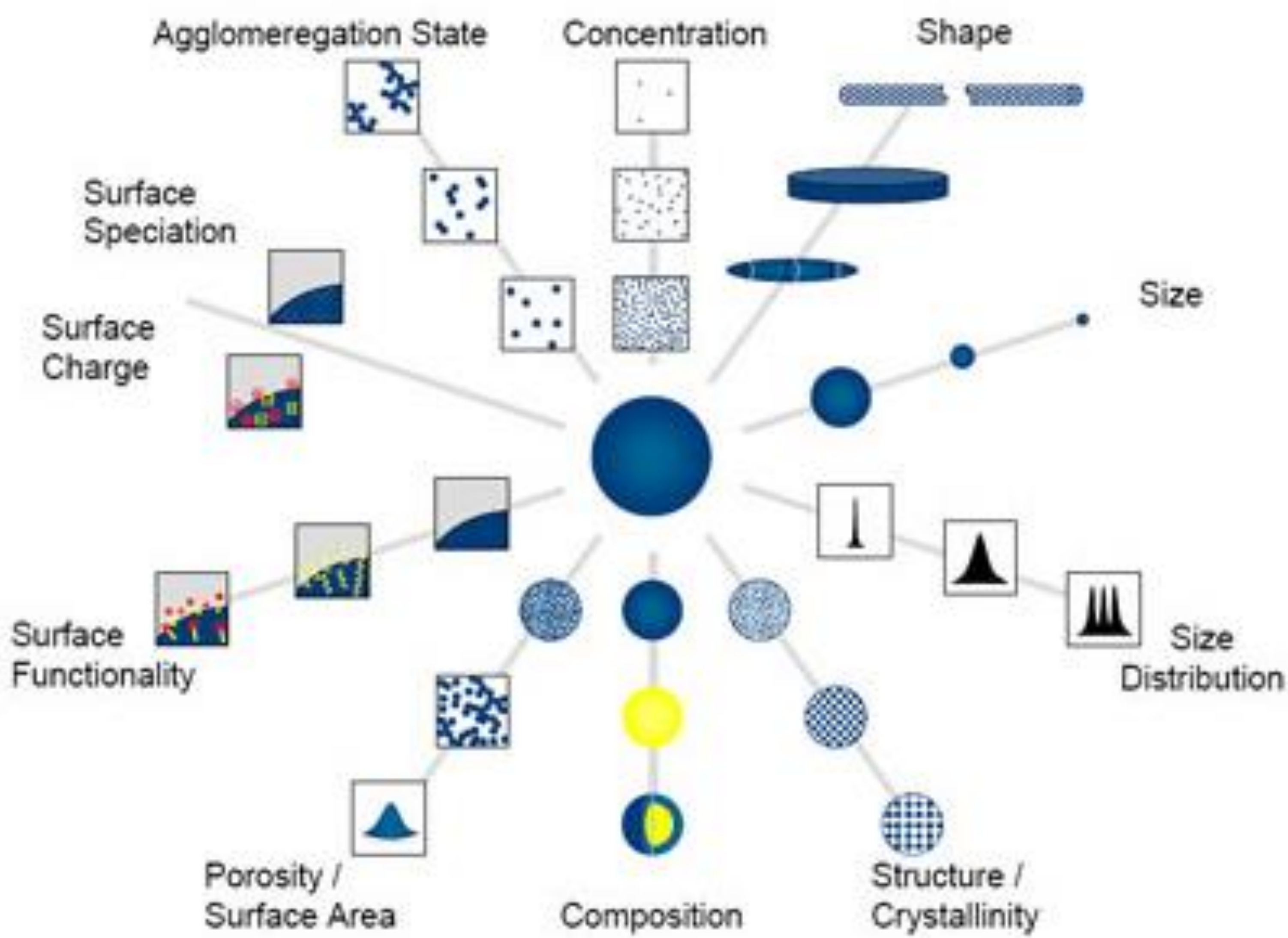
Discuss this tomorrow on Table 1 of Knowledge Cafe

Dynamic nature of NMs in environment



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Hasselhov, 2009

Parameter / Descriptor	Context dependent?	Potential impacts of surroundings
Size /size distribution	Yes	In environment, most likely decreased by binding of NOM (stabilization). Protein binding may lead to either increased or decreased size via bridging or steric stabilisation. pH/ionic strength may alter agglomeration.
Surface area	Yes	Aggregation/agglomeration will reduce available surface area.
Purity (particle / dispersant)	Maybe	Impurities / dispersants may be more effectively released from NM surface under different environmental conditions.
Dissolution potential	Yes	pH, ionic strength, redox potential and adsorbed biomolecules affect dissolution rate.
Photochemical activity	Most likely	Differences in pH and ionic strength and presence/absence of organic matter may affect electron transfer and result in protonation of different excited states.
Surface charge / chemistry	Yes	Binding of ions/ biomolecules may confer a different charge / charge distribution and surface groups but this may be dynamic.
Hydrophobicity	Yes	Binding of biomolecules typically results in a more hydrophilic surface presentation, although may be dynamic.
Redox activity	Most likely	Different surfaces / coatings / bound ligands may result in different radical species being generated.(Li, 2013)
Shape	Most likely	Agglomeration will result in different overall shape. Bundling/ unbundling of nanotubes is an example.
Crystal structure	Unlikely	Structure is a bulk property, established during the formation of an NM and cannot change by processes occurring on the surface, unless if the NM dissolves completely and re-precipitates.
Porosity / surface defects	Most likely	Dependent on pore size or nature of defect, most likely decreased due to biomolecule absorption; may be influenced by dissolution if NMs do not dissolve congruently or are a mixed phase.

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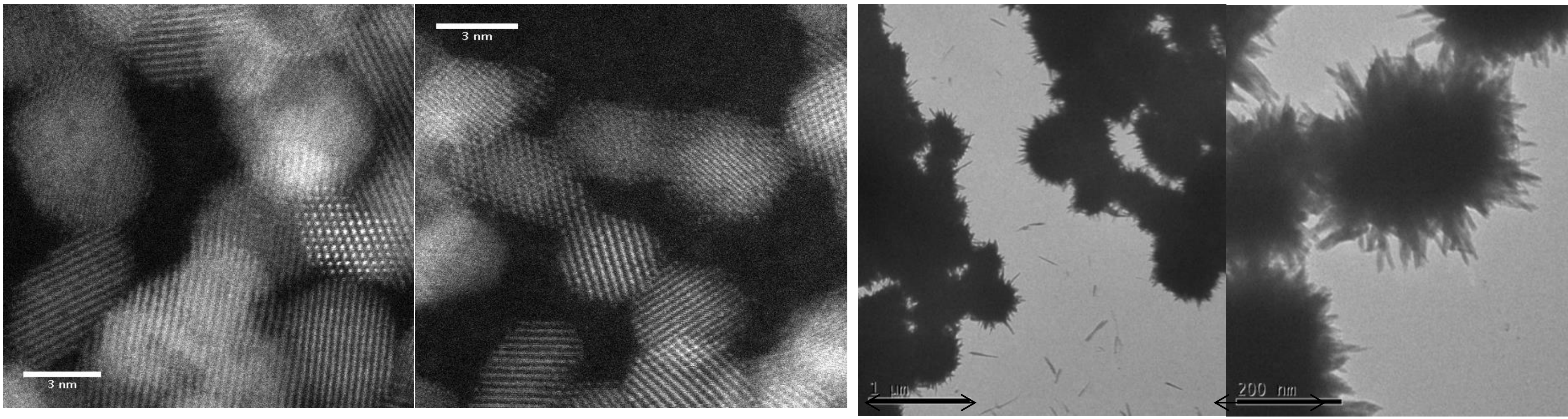
NMs ageing in the environment



3nm **1µm** **200nm**

- CeO_2 NMs + 5mM KH_2PO_4 + 5mM citric acid + 5mM ascorbic acid @ pH 5.5
- Characterisation by XRD, UV-vis, TEM

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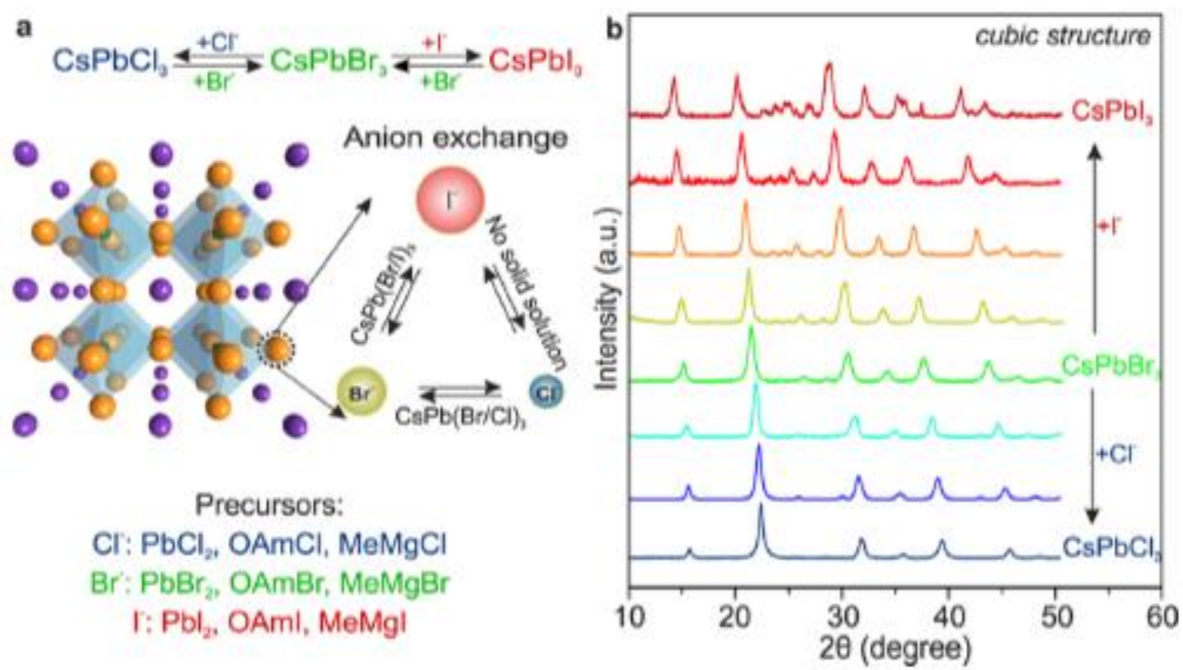
NanoMILE

Perovskite materials

- Dissolution / Behaviour under reducing and non-reducing conditions
- Impact of light intensity on perovskites
- Acid−Base and Redox Properties
- **Anion exchange**

Thermodynamic metastability



Nedelcu et al. (2015) NanoLett. 15, 5635−5640.

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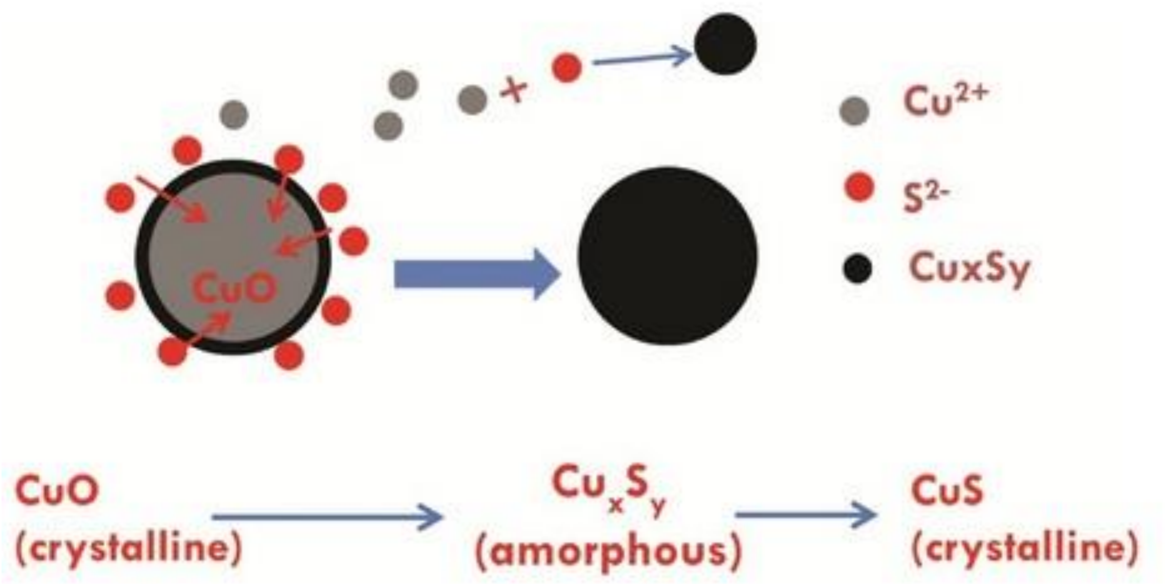
Intrinsic = Context independent

Are there any properties that are truly independent of context and unchanging over time?



Should rate of change in defined (standardised) contexts be what we consider instead?

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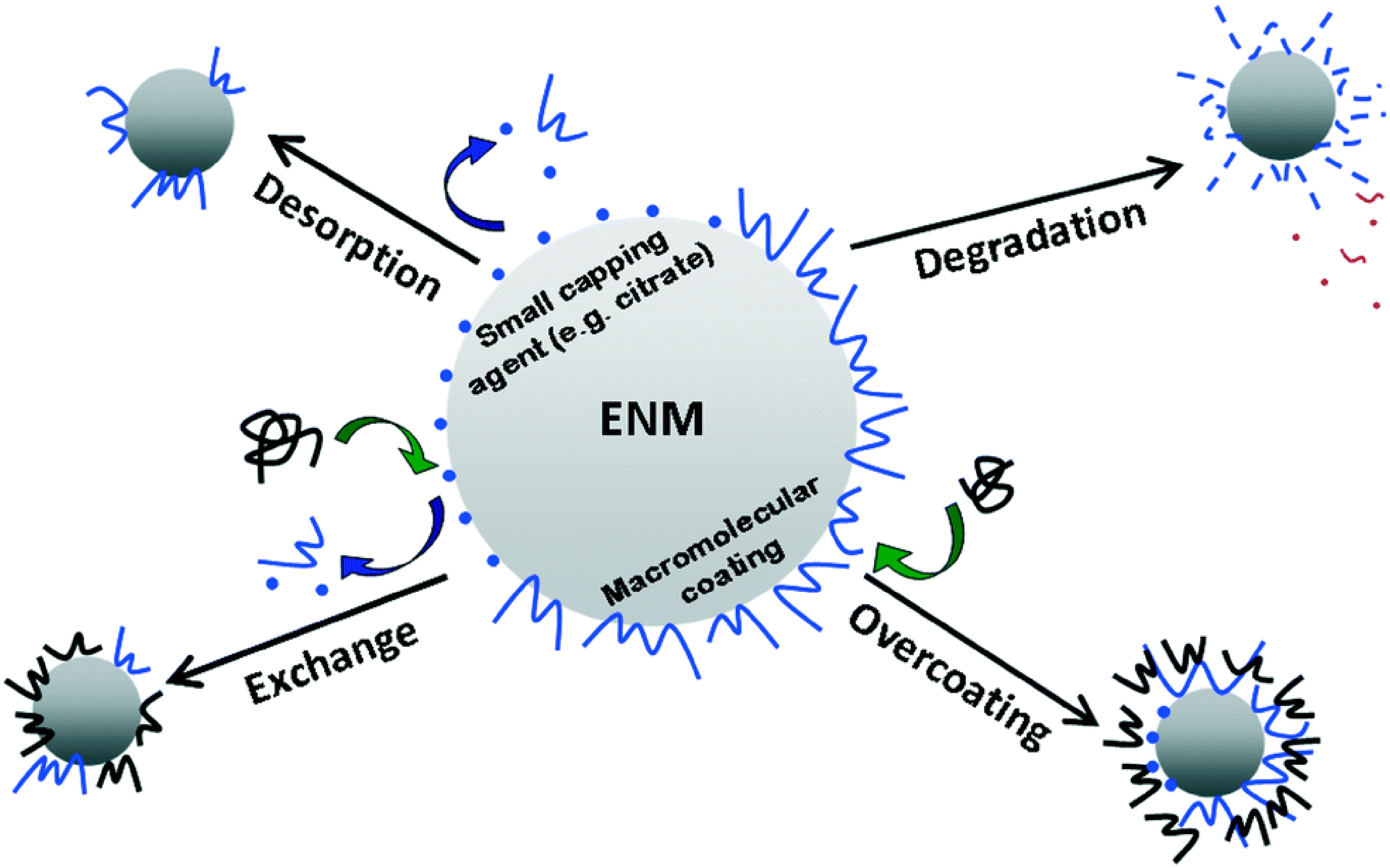
Extrinsic = Context dependent

Turns out nearly everything can be affected by the surroundings!



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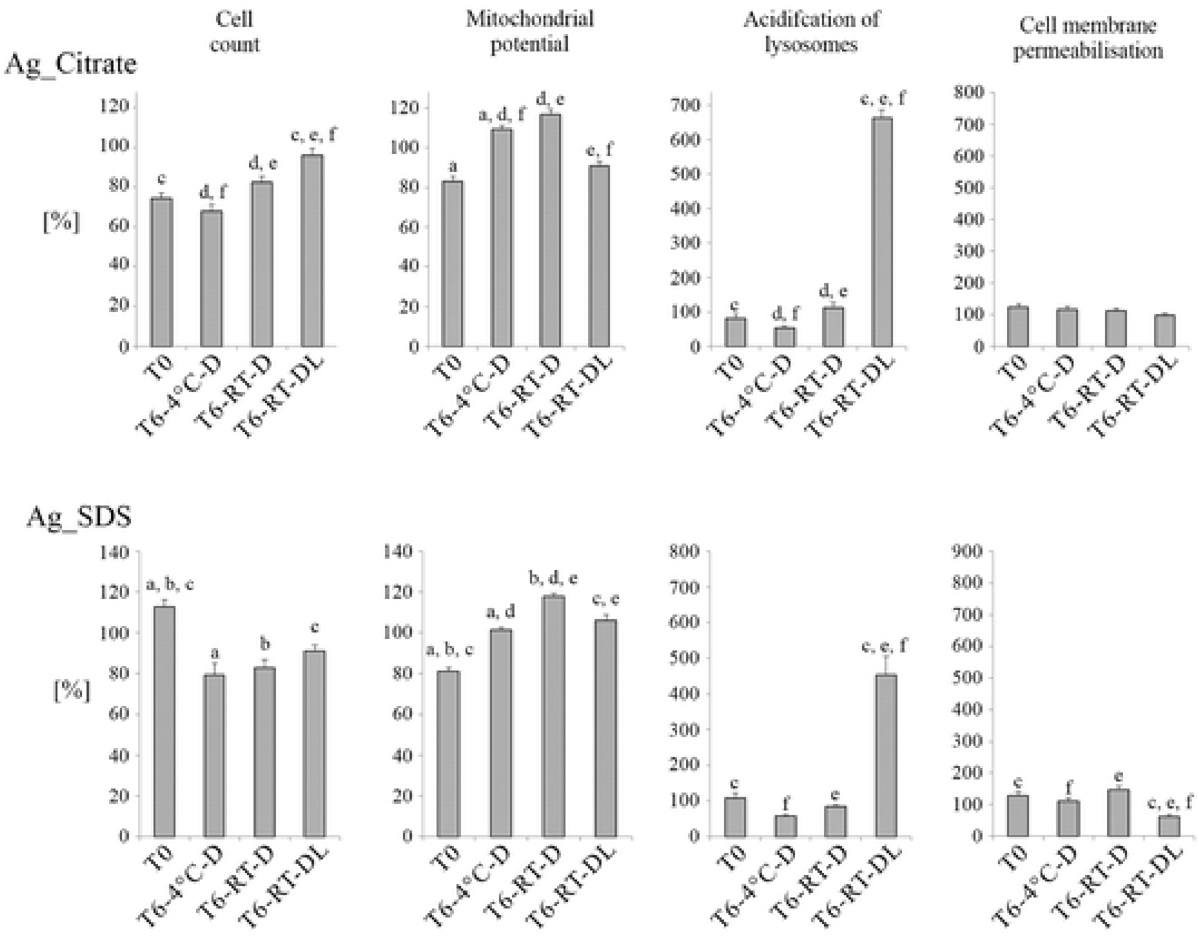
Ageing during storage an issue



Looked at the effect of storage conditions and coating structure on AgNP stability.

Conditions assessed include:

Room Temp – Light (RT-DL)
Room Temp – Dark (RT-D)
4°C-Dark (4°C-D)

Times: 0, 3 and 6 months

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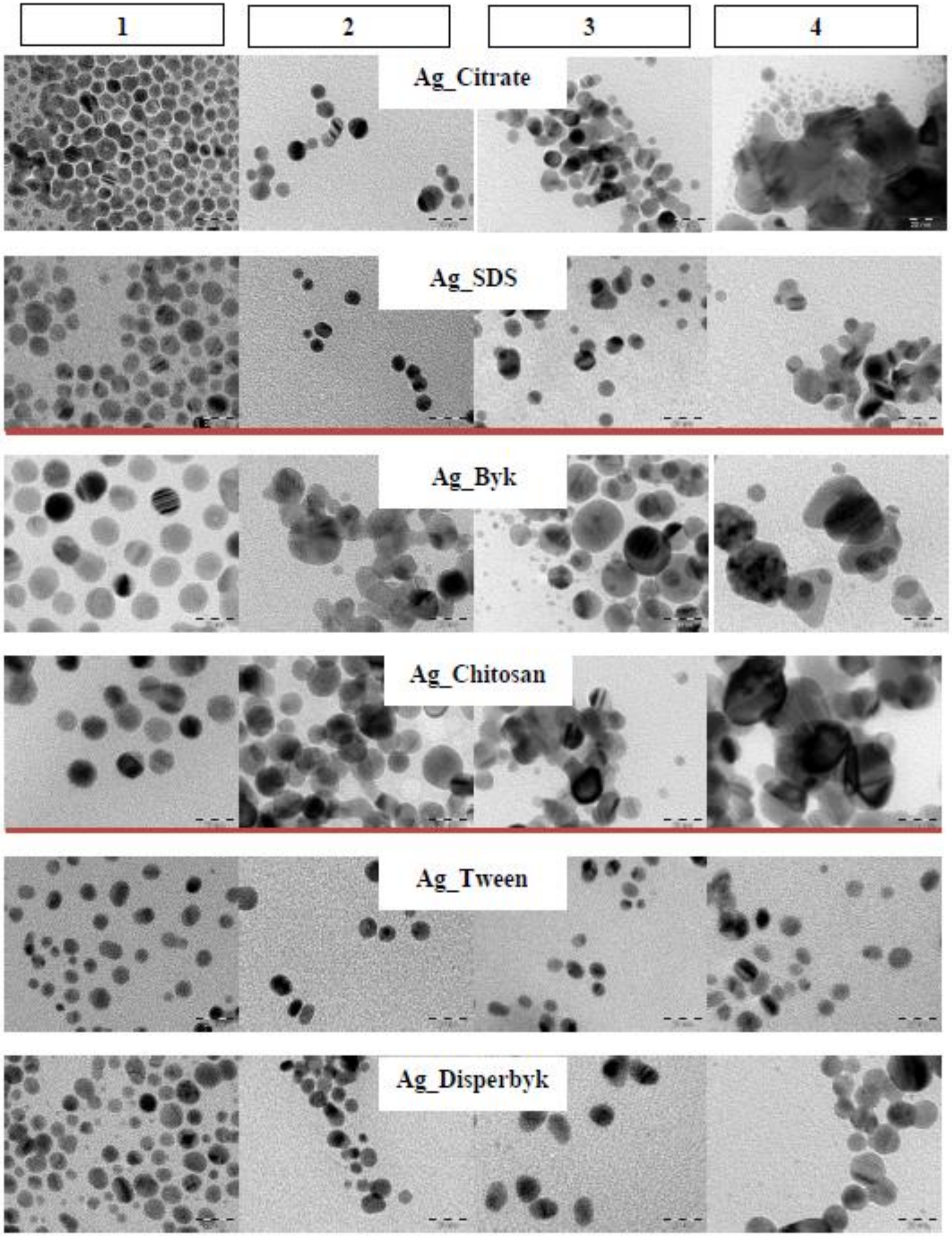
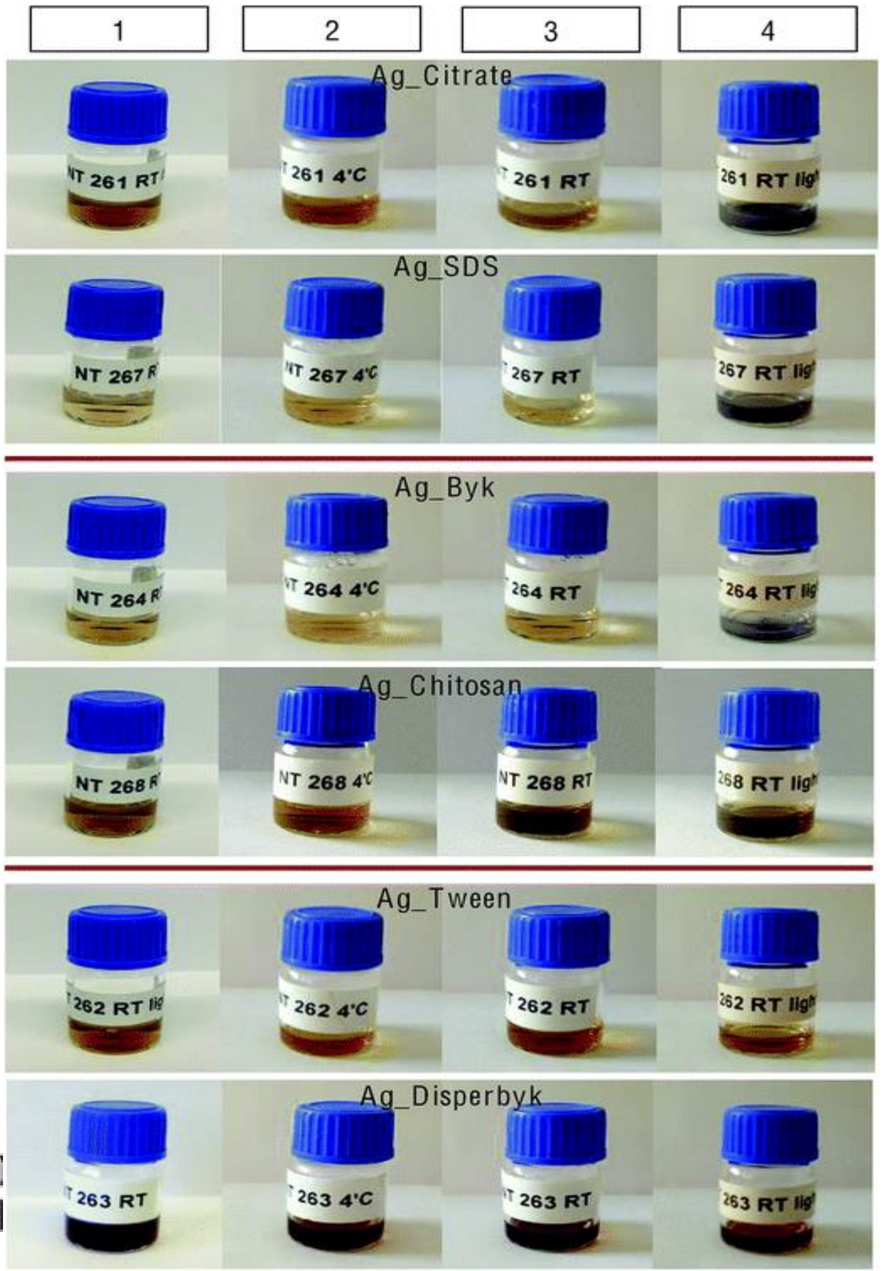
Izak-Neu et al., RSC Adv., 2015, **5**, 84172



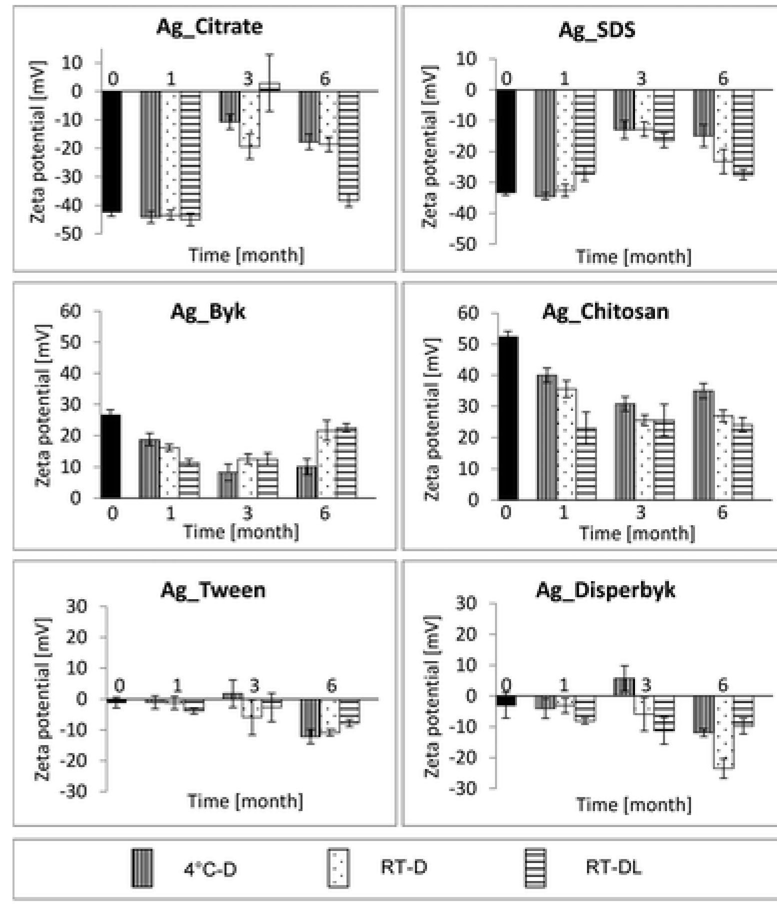
(1) T0,
(2) T6:4 °C-D,
(3) T6:RT-D,
(4) T6:RT-DL
(scale bar 20 nm).

- ❑ Agglomeration
- ❑ Dissolution
- ❑ Loss of stabiliser
- ❑ Surface chemistry evolution

NanoTOES
Nanotechnology: Training of Experts in Safety



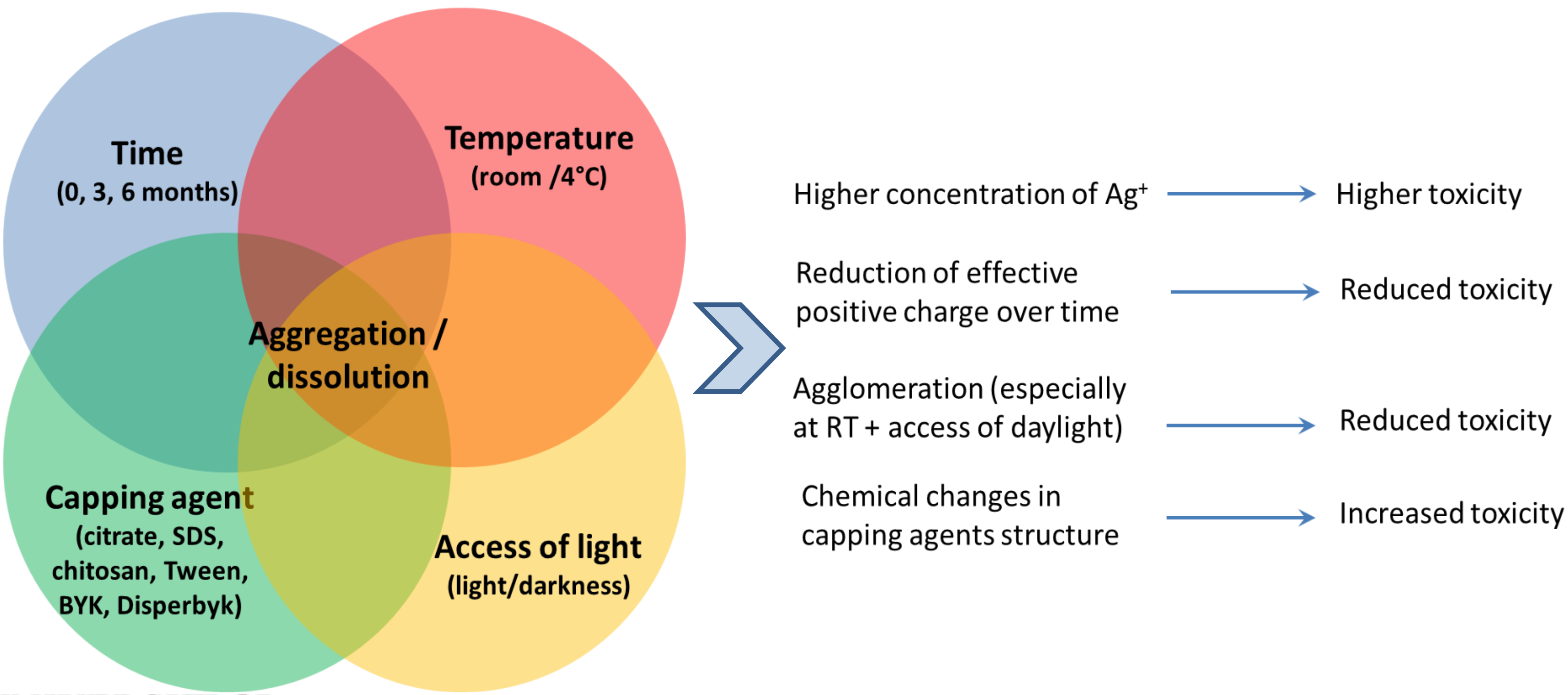
(1) T0, (2) T6:4 °C-D, (3) T6:RT-D; (4)T6:RT-DL



Zeta potential

Monitor “ageing” of NMs

- **Recommendation** to add temporal assessment of NP properties from when NPs are synthesized / purchased / “opened” and during the experimental studies



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Izak-Neu et al., RSC Adv., 2015, **5**, 84172-84185

Record of NM Provenance

Information about NM synthesis appropriate for sample provenance:

(1) Record of sample synthesis: reference or details of synthesis as known (e.g., process, vendor, lot number, chemicals, and chemical sources)

(2) Characterization results: data reports including relevant dates and processing of samples for analysis

(3) Important dates and times: synthesis, arrival in laboratory, opening of sample container, primary analysis measurements, and expiry date

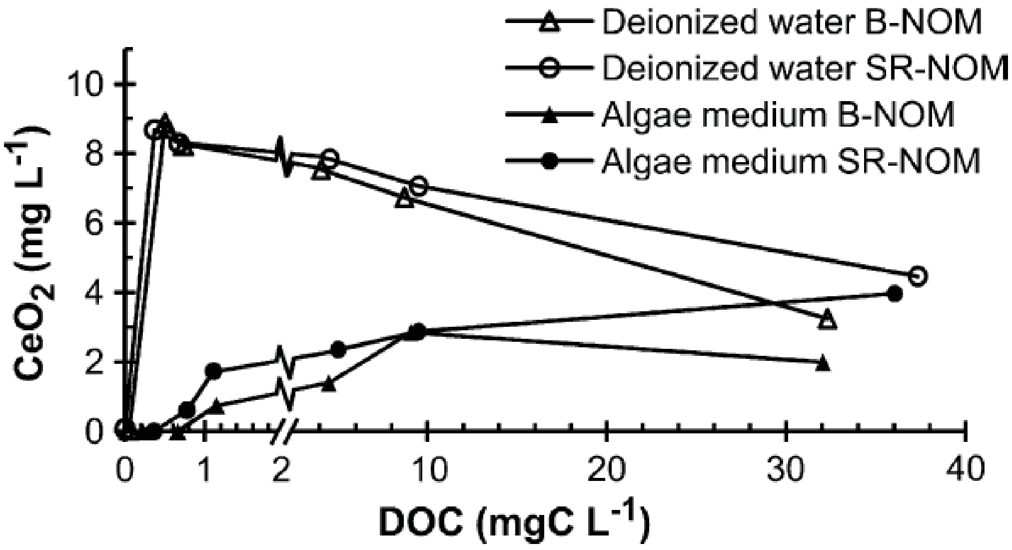
(4) Storage time, conditions, and containers: temperature, humidity, media, light shielded, shipping, or transport)

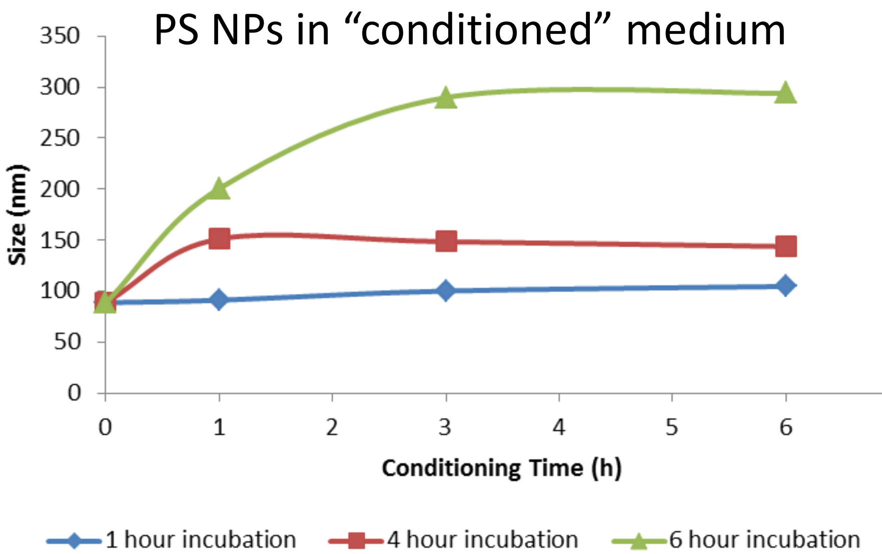
(5) Record of additional processing: e.g., dried, washed, heated, sonicated, functionalized (including the method and number of times processed).

Baer, Biointerphases. 2016 11(4): 04B401.

Characterisation in relevant media over relevant timeframes

- Dispersion medium typically determines agglomeration degree and affect dosimetry!





Quik et al., Chemosphere, 2010, 81: 711-715

Nasser et al, J Proteomics, 2016

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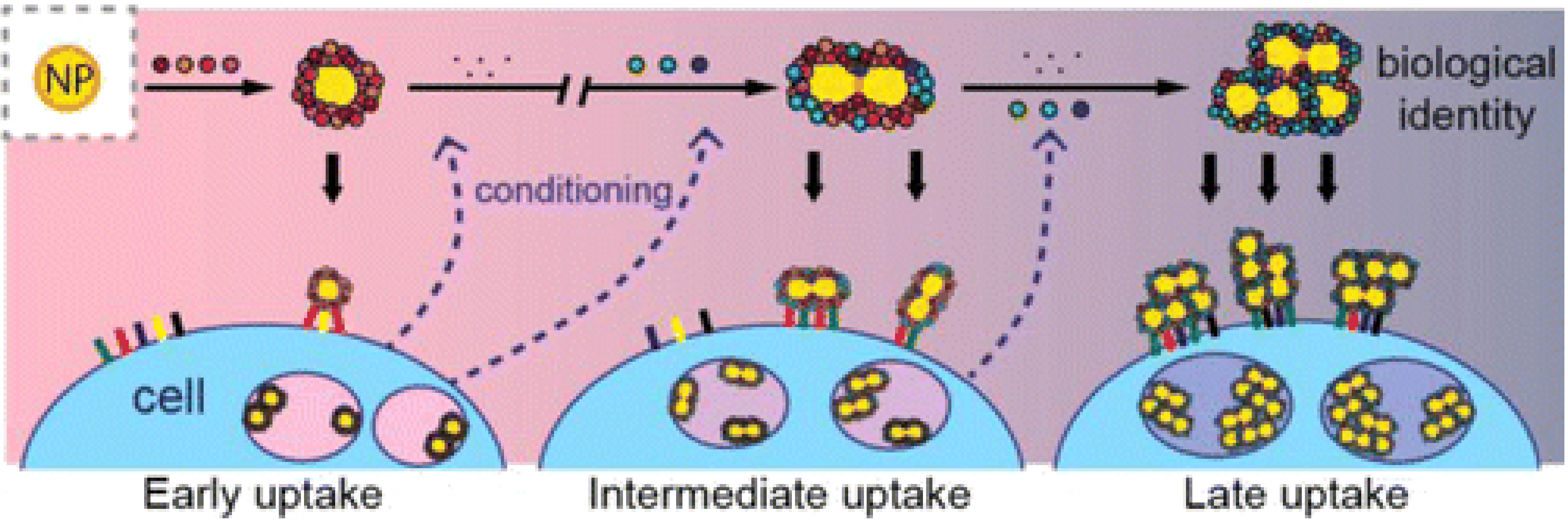
Dynamic nature of the system
e.g. Cells / organisms “condition” media
=> evolution of form over time



Cells respond to the presence / uptake of NMs, leading to secretion of proteins and other biomolecules that cause the “initial” corona to evolve and which can lead to altered uptake and impacts.   Not currently considered in assessing toxicity.

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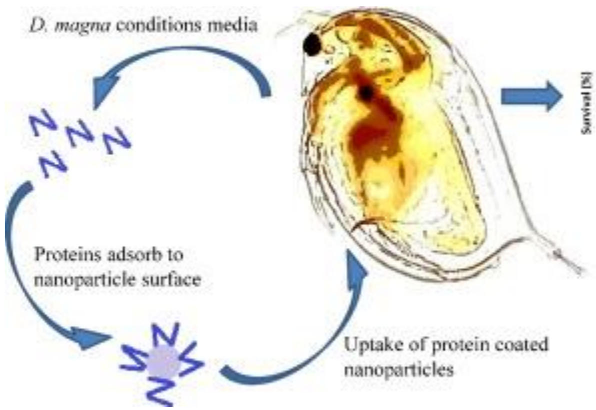
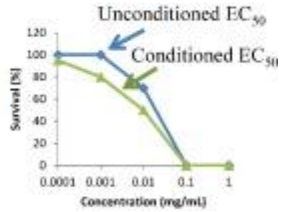
Albanese and Chan, *ACS Nano*, 2014, 8: 5515–5526
DOI: 10.1021/nn4061012

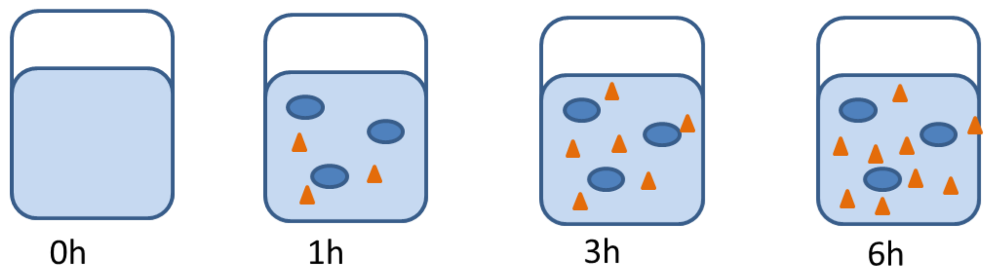
Secreted biomoelcule corona



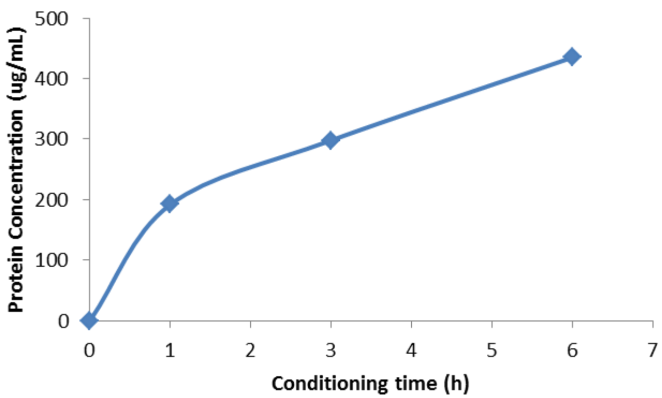


Conditioning HH Combo Media

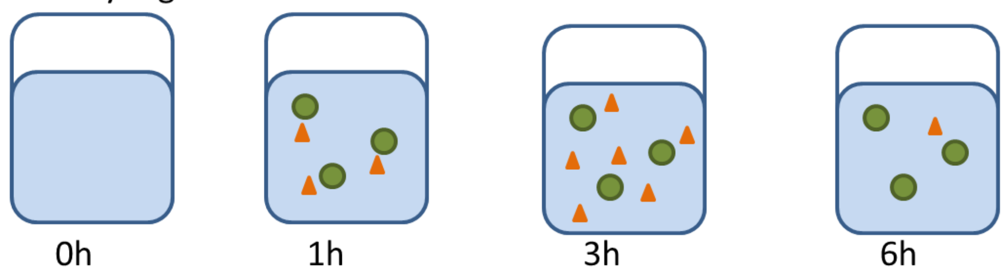
Conditioned by D.magna



Proteins Released by D.magna



Conditioned by Algae



At end of conditioning time remove daphnia/algae leaving only proteins

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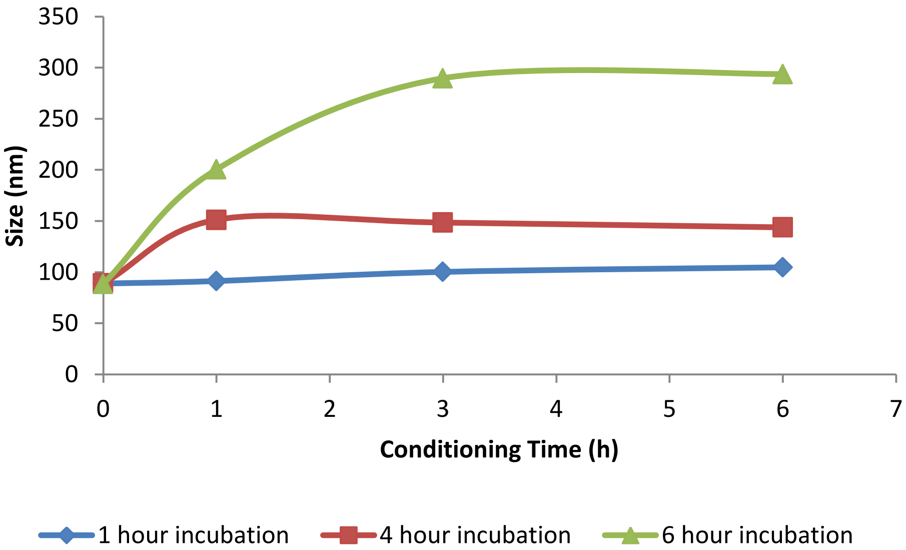
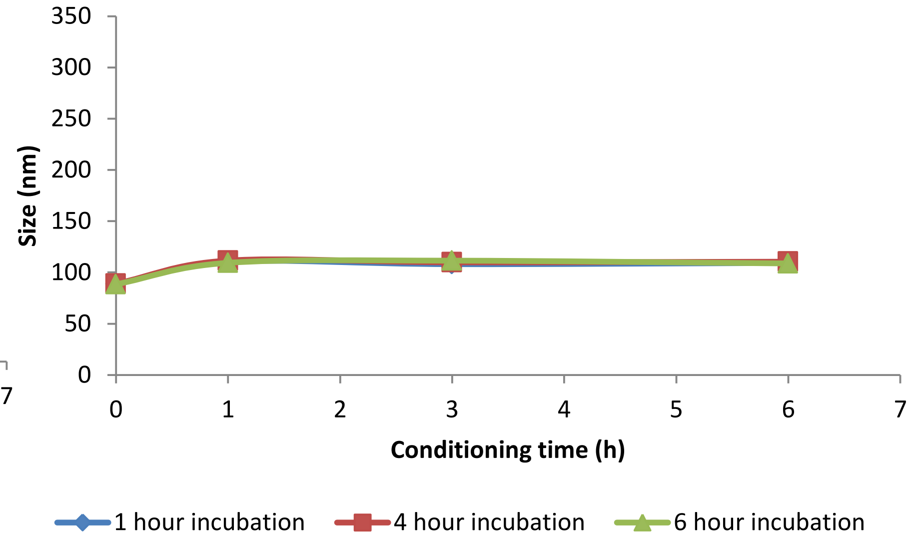
Work from PhD student Fatima Nasser

FUTURE NANO NEEDS

Secreted biomolecule corona

Incubation of Particles in Conditioned Media and Particle stability





- Longer incubation time of NPs in conditioned media increases NP-protein interaction
- As conditioning time increases (as well as incubation time),agglomeration also increases indicating proteins acting as a potential destabilizer

- Low dose of proteins present in media causes no significant changes in NP stability

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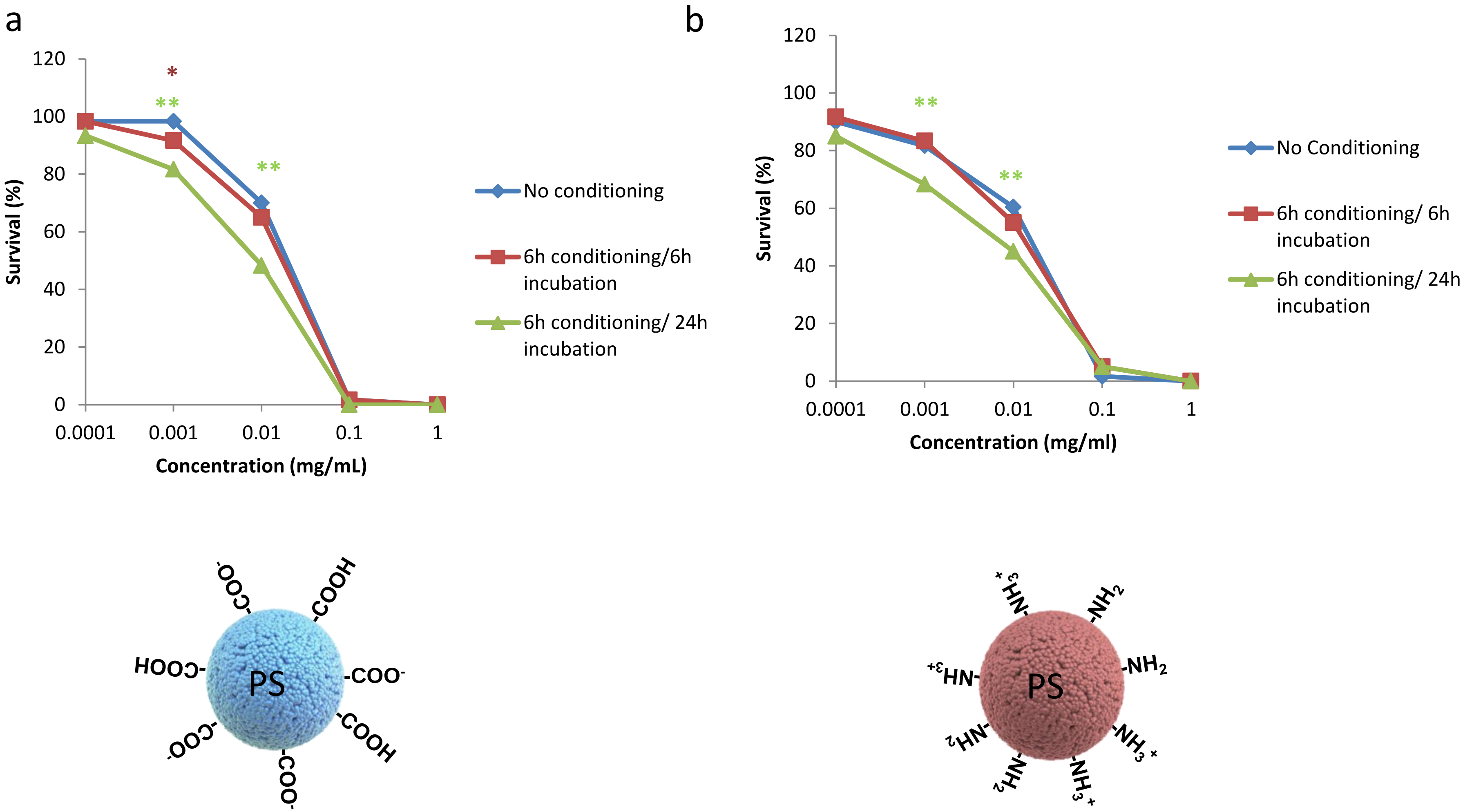
Eco-corona impacts EC_{50}



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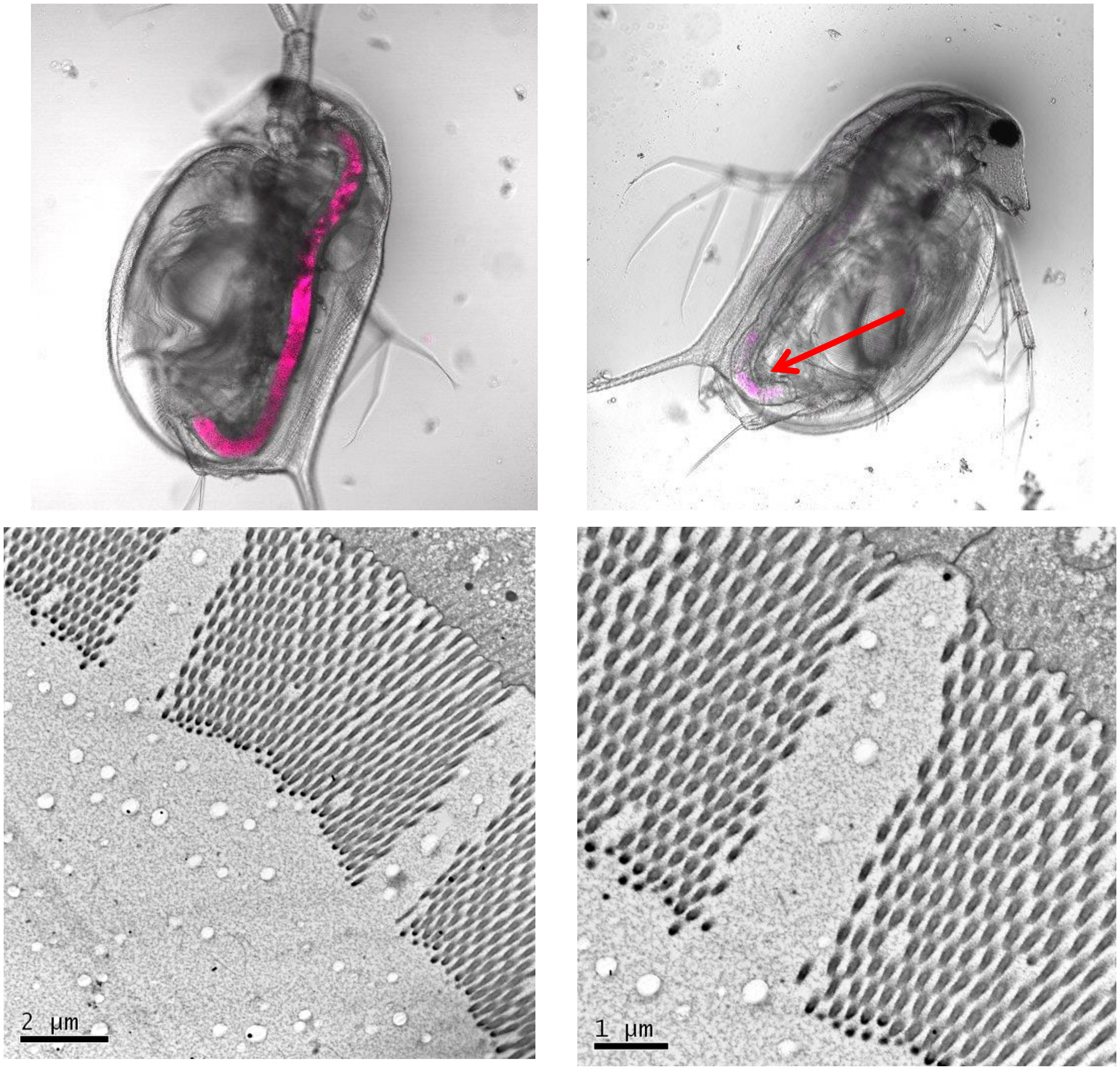
NM Retention in gut – impacts?



No evidence of translocation of PS NPs

Size matters
– 500nm taken up more than 50nm NPs
- Smaller NPs retained more!

Shape matters

Conditioning matters

Acknowledgements

MARIE CURIE ACTIONS
ecofriendlyNano
SEVENTH FRAMEWORK PROGRAMME
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Analytical and Characterisation Excellence
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NERC
SCIENCE OF THE ENVIRONMENT
HORIZON 2020
NanoFASE
Fate and Exposure models for you - www.nanofase.eu
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NANOGENTOOLS

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