Design and Manufacture of Functional Microcapsules and Engineered Products

Proceedings

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Facile two-step encapsulation of small species in a metallic shell

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INSTITUTE OF PARTICLE SCIENCE & ENGINEERING

Microencapsulation of perfume oils

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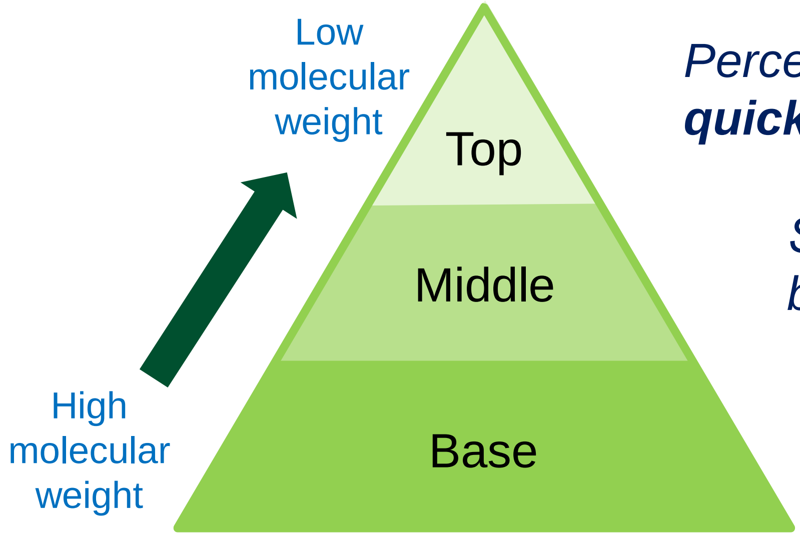
- Fragrances consist of complex mixture of molecules with various physiochemical properties
- Controlled release of fragrances remains a challenge as consumers are attracted to a product that provides a long lasting effect
- Fragrances are comprised of some highly volatile species (top notes)

Creative Commons photo by **Jessica Lucia** (theloushe)

Fragrance Pyramid



*Perceived immediately on application, **evaporate quickly***

Scent emerges prior to top notes' dissipation, body of the perfume

Appears close to the departure on middle note, give depth to the perfume

Challenges with encapsulating small species

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Most microcapsule membranes are highly permeable

- Can lead to leaching of the encapsulated active ingredient which is undesirable
- This is particularly prominent for small actives such as those found in drugs, vitamins, fragrance and flavour oils
- Current shell materials (polymeric/lipid based membranes/ particulate) have relatively high diffusion coefficients
- Attempts to decrease diffusion rates by using a thicker shell wall often reduce the volume of the capsule core → less efficient

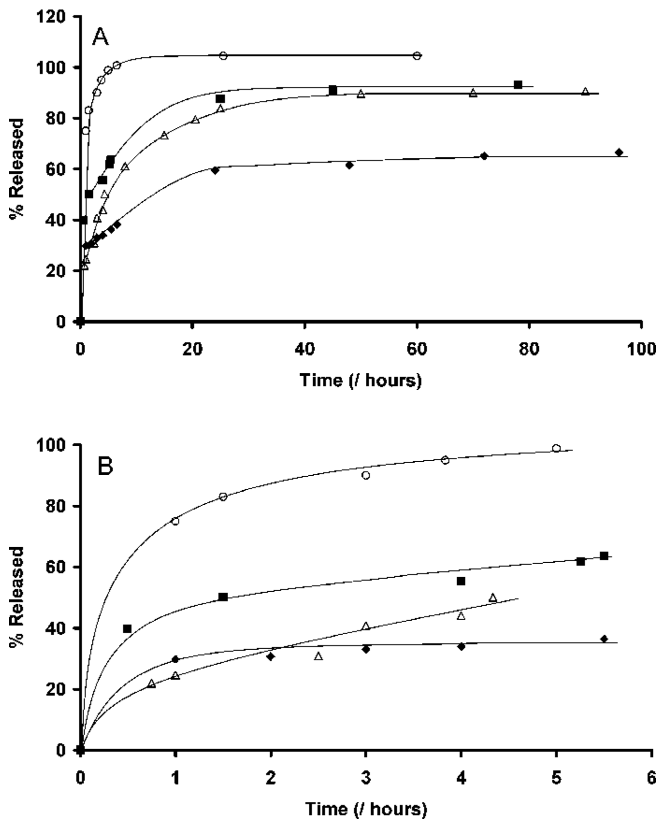

Figure 1. Effect of polymer type on the release profile of 4-nitroanisole

1) Dowding, P. J.; Atkin, R.; Vincent, B.; Bouillot, P. Oil Core/ Polymer Shell Microcapsules by Internal Phase Separation from Emulsion Droplets. II: Controlling the Release Profile of Active Molecules. Langmuir 2005, 21 (12), 5278−5284

Metallic encapsulation

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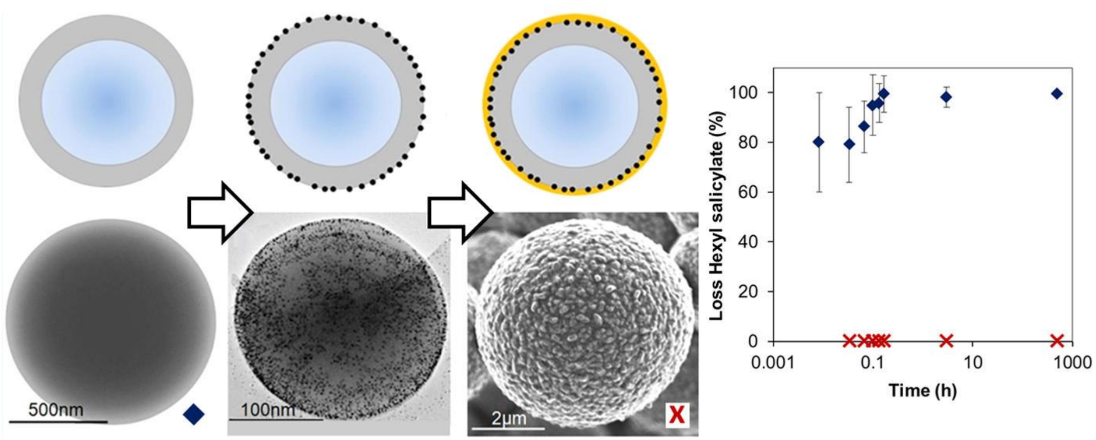
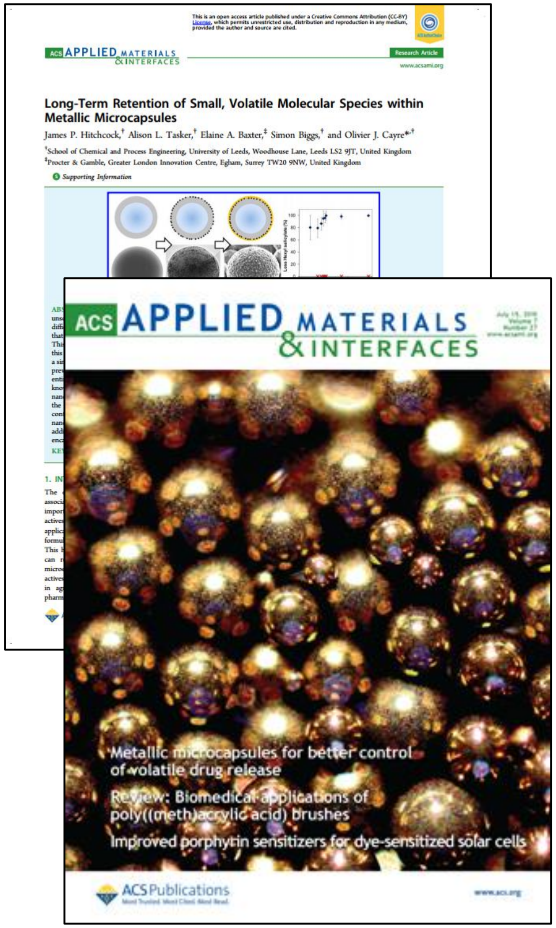
Co-solvent evaporation method used to produce polymer shell-oil core microcapsules on which an impermeable metal film is grown

Drawbacks:

- Not the most efficient way to create polymer shell (high % of oil phase is DCM which evaporates) but worked well as template
- Harmful expensive solvents used
- Choice of oils and stabilisers is limited due to wetting characteristics
- Involves several steps, some difficult to scale up





J. P. Hitchcock, A. L. Tasker, E. A. Baxter, S. Biggs and O. J. Cayre, *ACS Applied Materials & Interfaces* **2015**, *7*, 14808-14815.

Metallic encapsulation

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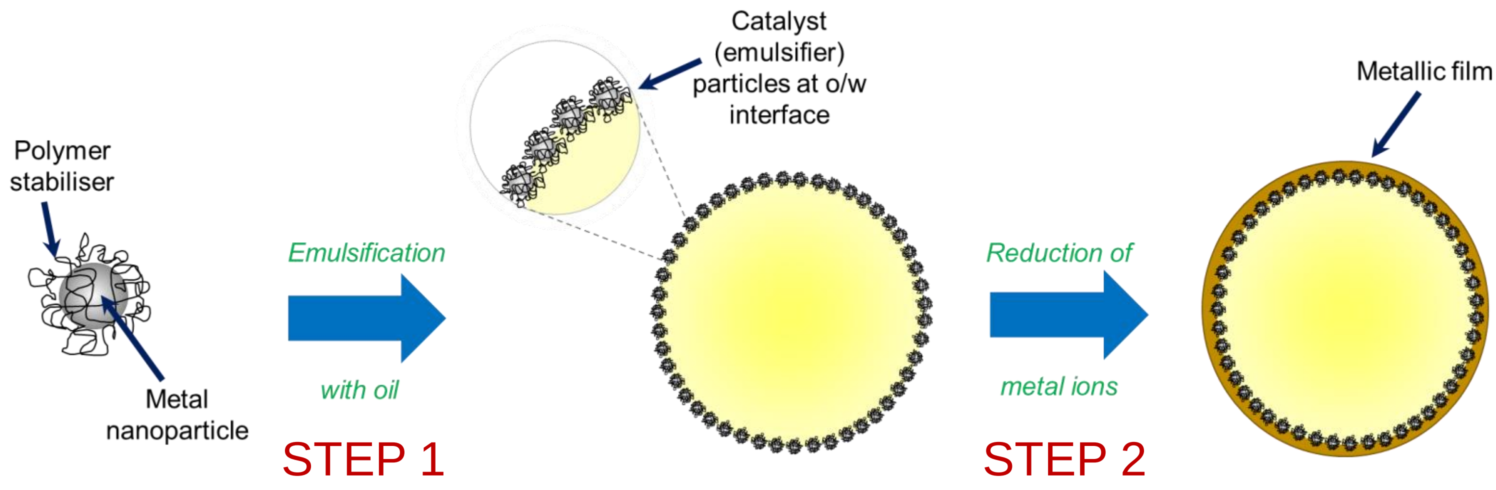
Emulsion template method

- Metallic film deposited directly onto emulsion droplet stabilised by nanoparticles
- Removes the need for a polymer shell
- 2 – step procedure (rather than 3)
- Prevents waste from solvent evaporation used in previous method
- Allows up to 100% of the active material to be encapsulated



Aims of work

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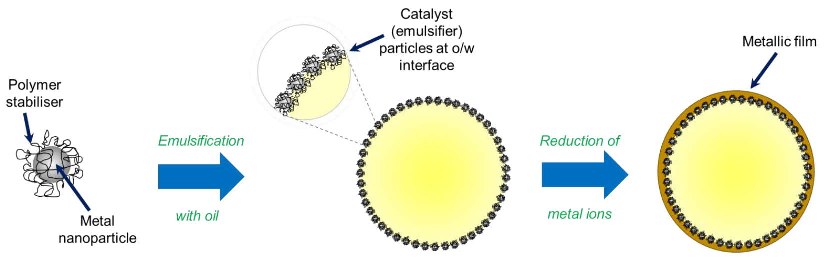
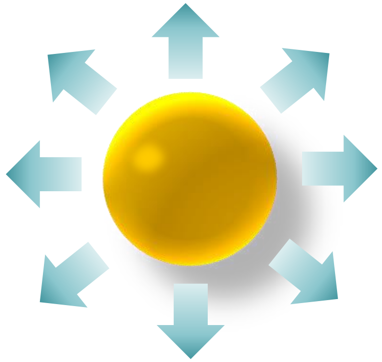
1) Synthesise microcapsules via electroless deposition on an emulsion template

- Platinum catalyst emulsifier used to create emulsion droplets
- Electrolessly plate gold directly onto the surface of the oil droplet



2) Demonstrate impermeably via release studies

- Using gas chromatography to monitor the release of oil from the capsules within an ethanol environment



Aims of work

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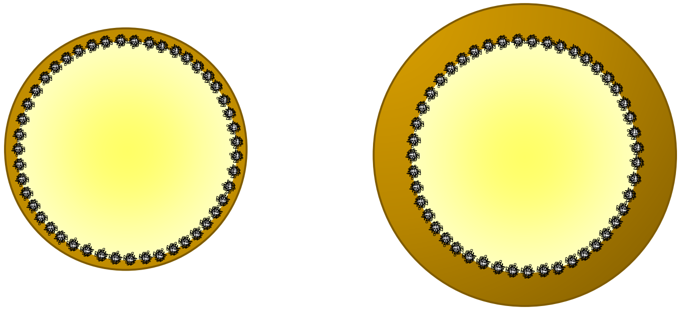
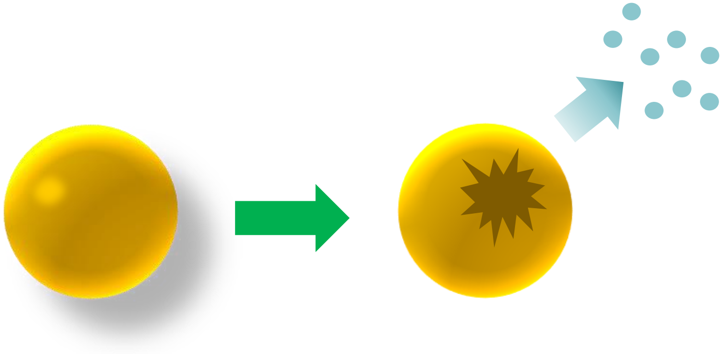
3) Control shell thickness

- By varying the concertation of metal salt used in the electroless deposition



4) Release mechanisms

- Looking at different mechanisms to rupture the capsules



Platinum nanoparticle synthesis

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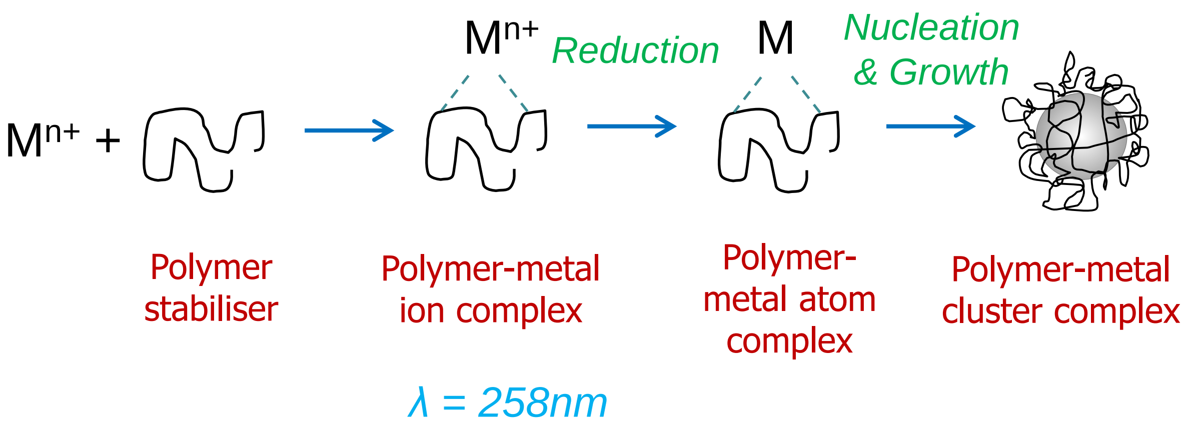
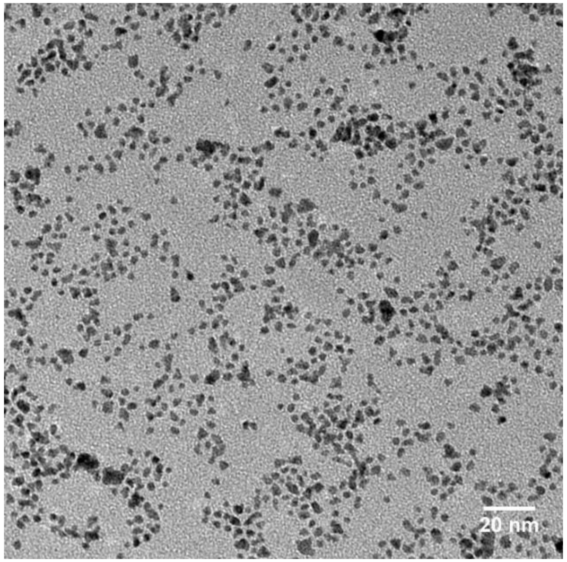
Platinum NPs were synthesised via the in-situ reduction of $H_2PtCl_6{\bullet}H_2O$ in the presence of polyvinylpyrollidone (PVP)

$$NaBH_4 + H_2PtCl_6 + 3H_2O \longrightarrow Pt + H_3BO_3 + 5HCl + NaCl + 2H_2$$

Synthesis adapted to ensure **low amount of PVP**





TEM micrograph of Pt-PVP NPs

Formed ~3nm PVP stabilised Pt nanoparticles (Pt-PVP NPs)

Adapted from Surface and Nanomolecular Catalysis, CRC Press, 2006, ISBN 1420015753, 9781420015751
*Tu, W.-x., X.-b. Zuo, and H.-f. Liu. Chinese Journal of Polymer Science (CJPS), 2008. **26**(1): p. 23-29.*

Step 1: Emulsification of NPs with oil

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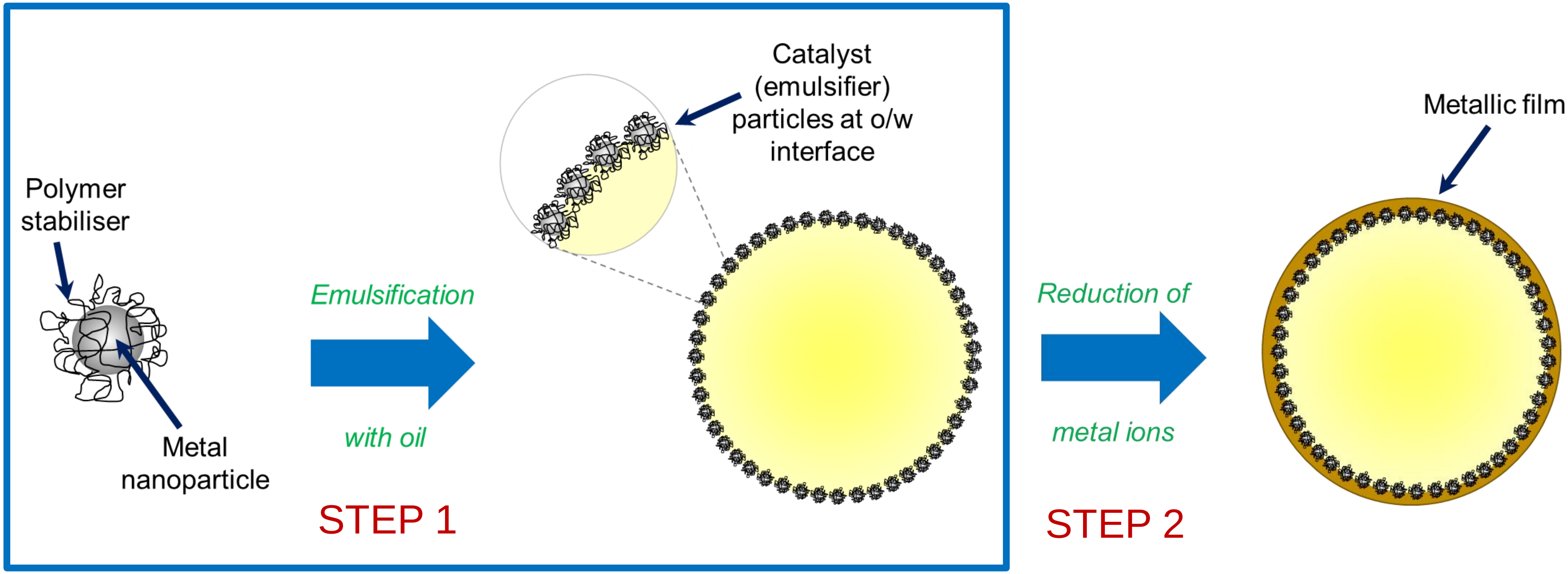
- O/W emulsions were created using an ultrasonic processor
- Hexadecane and PVP stabilised Pt NPs were used to create the emulsion



Step 1: Emulsification of NPs with oil

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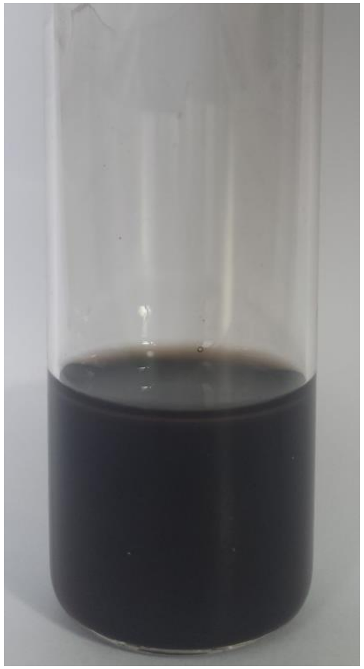
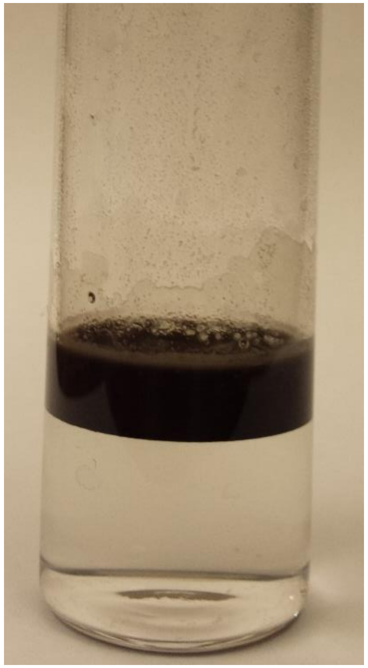
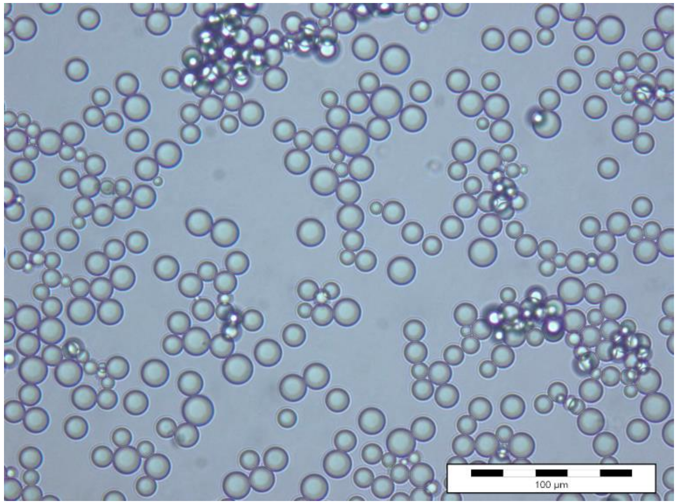
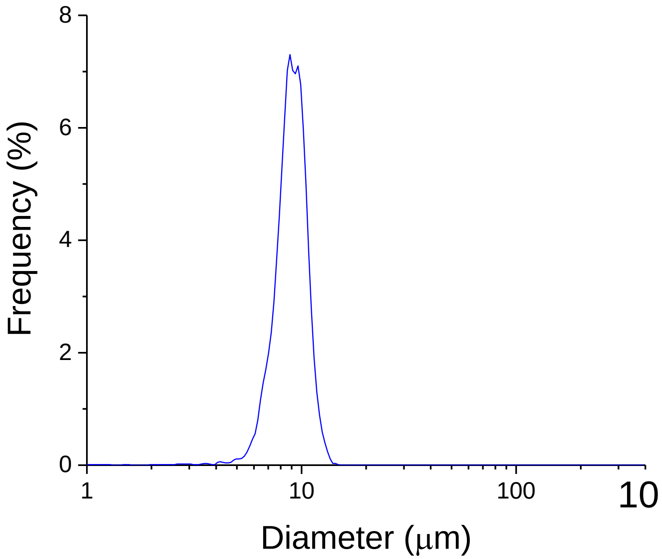
- Emulsion creams due to density difference of hexadecane.
- Colourless bottom aqueous phase shows that nanoparticle have been adsorbed at the interface









Adsorption of nanoparticles at the interface

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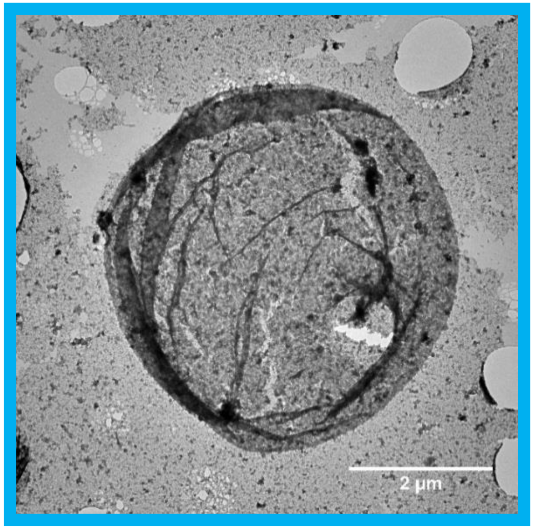
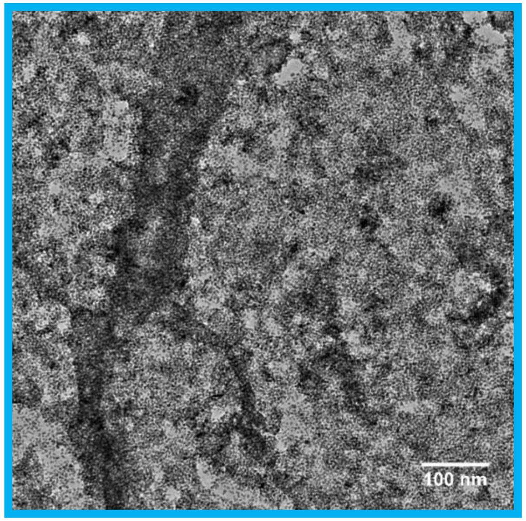
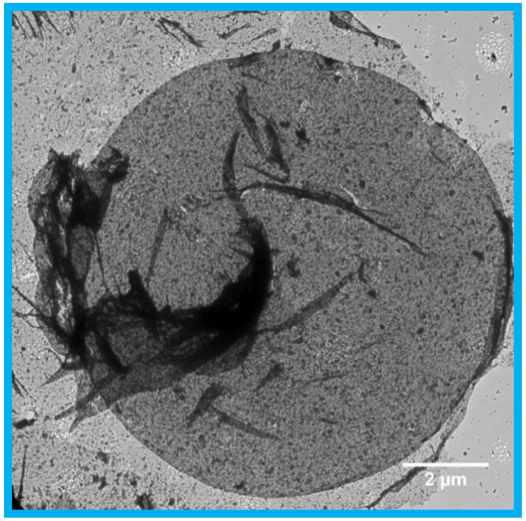
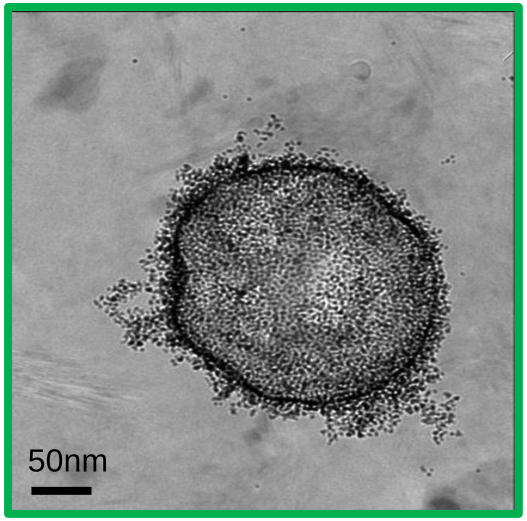






- Droplets dried and imaged on TEM
  - Buckling observed
  - Shows robust films → entanglement of polymer chains
- Droplets on cryoTEM show dense packing at interface
- Interfacial rheology studies show an increase in elasticity over time



Step 2: Metallic coating of emulsion droplets

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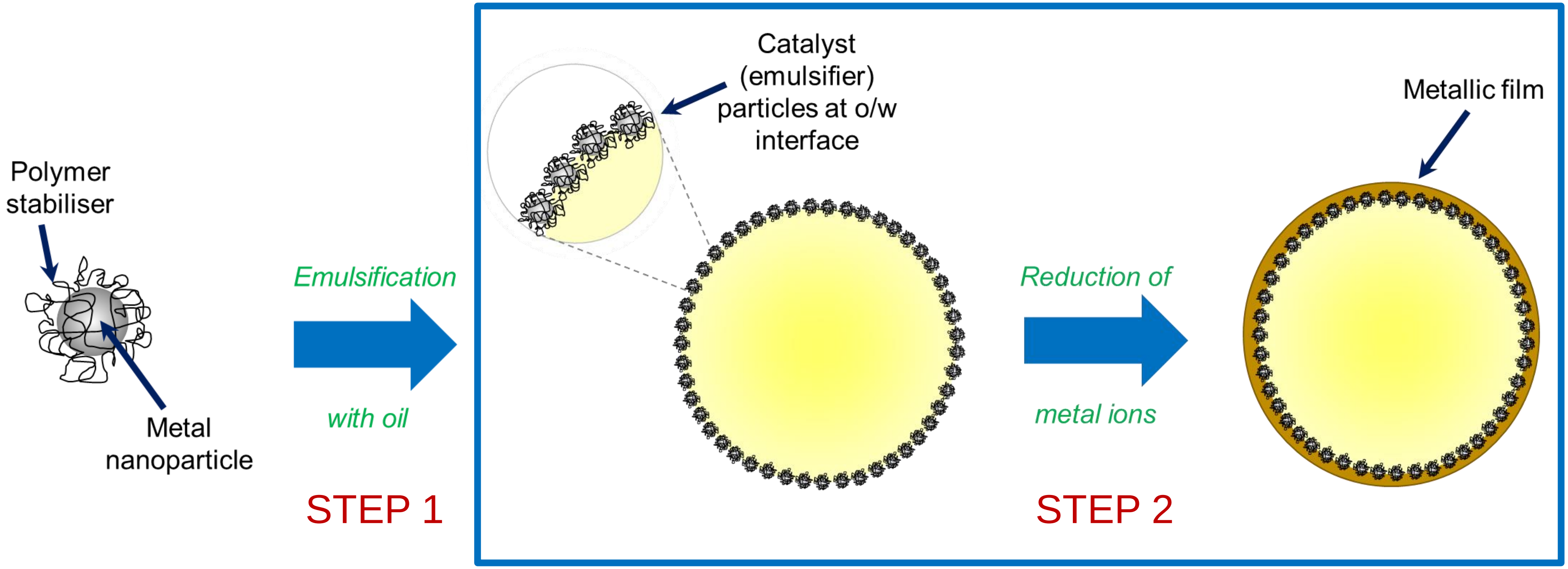
Gold coating was applied via electroless deposition, using the platinum NPs as a catalyst

$$2HAuCl_4 + 3H_2O_2 \xrightarrow[Pt]{} 2Au + 3O_2 + 8HCl$$



Step 2: Metallic coating of emulsion droplets

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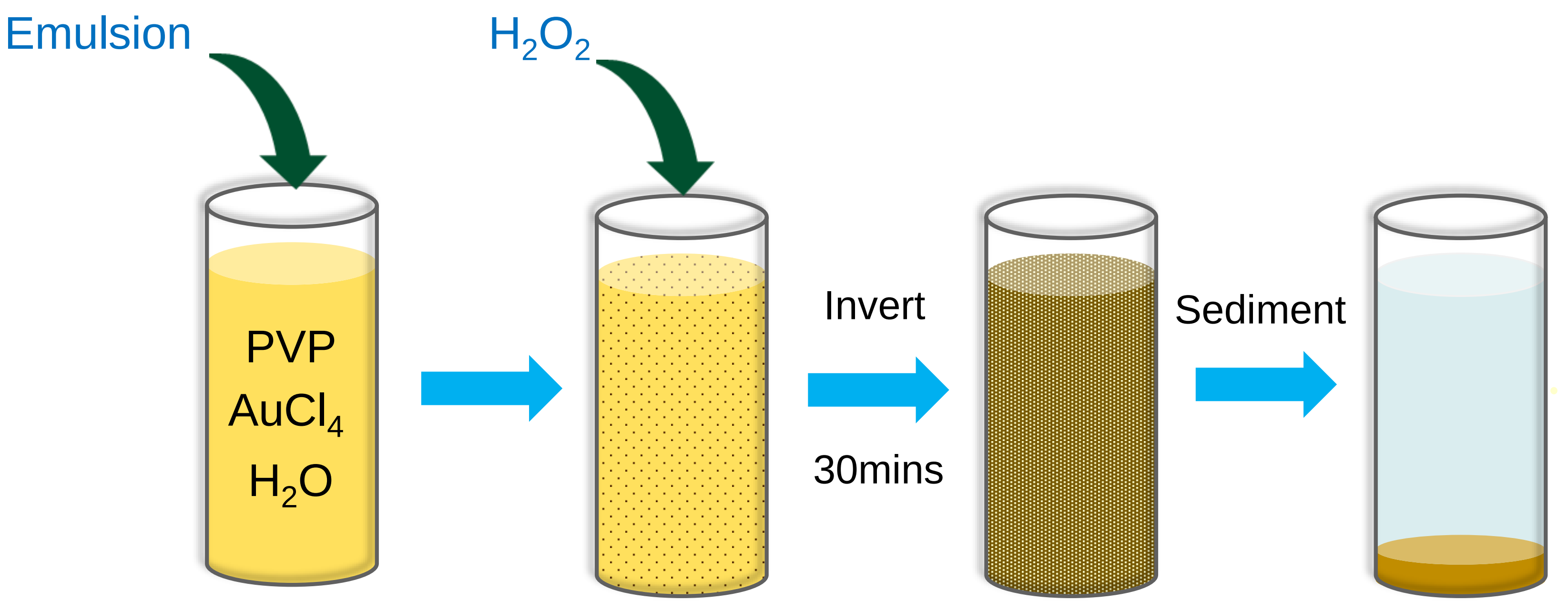
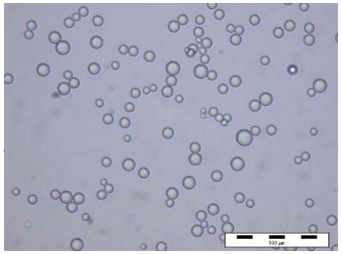
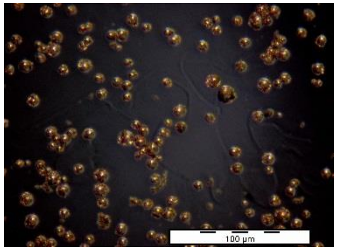
0.5 ml of emulsion was added to a plating solution consisting of 5ml PVP (0.2wt%), 10ml water, 2ml $AuCl_4$, 1ml H_2O_2 and inverted on the carousel for 30 mins.







Release of core oil

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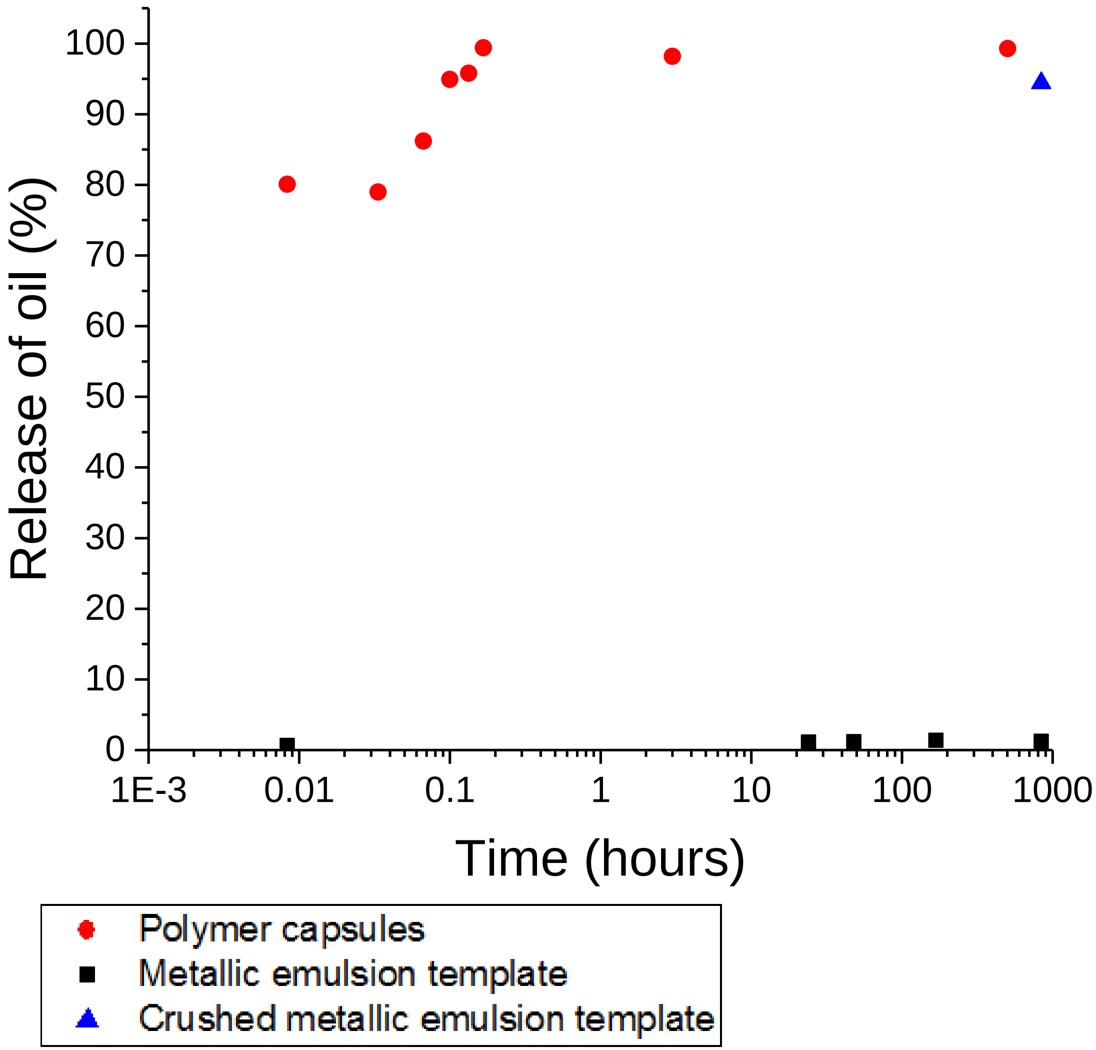
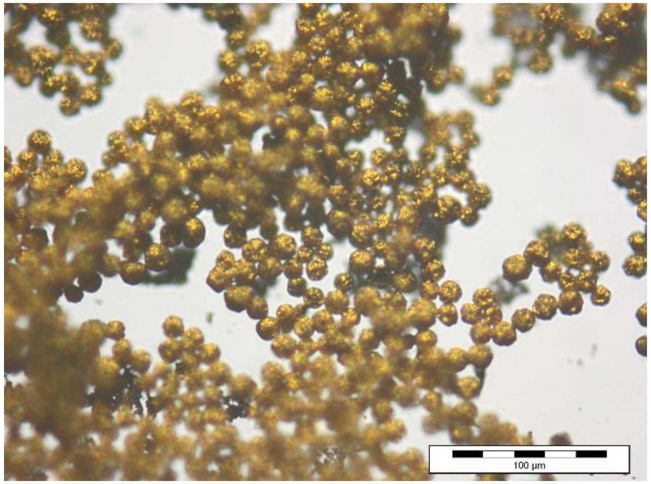
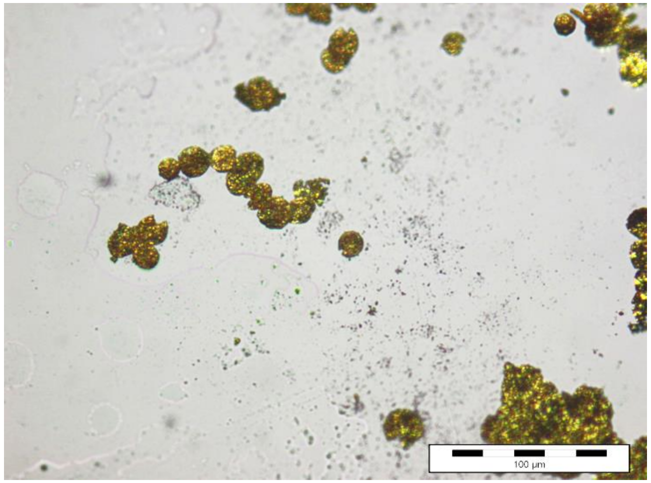




↑ Dried capsules before crushing



↑ Dried, crushed capsules shows oil inside

* Polymer capsule data (red circles) collected by Dr Alison Tasker

Aims of work

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3) Control shell thickness

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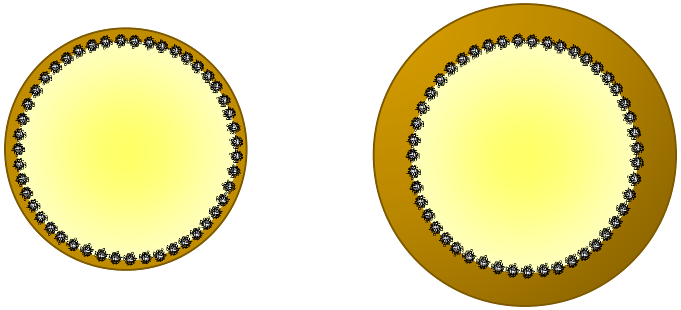

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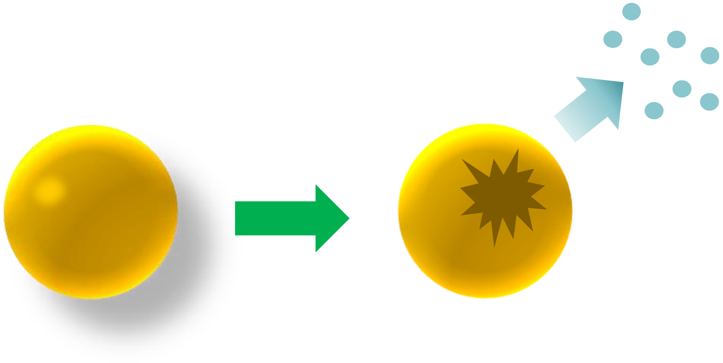

Controlling metal shell thickness

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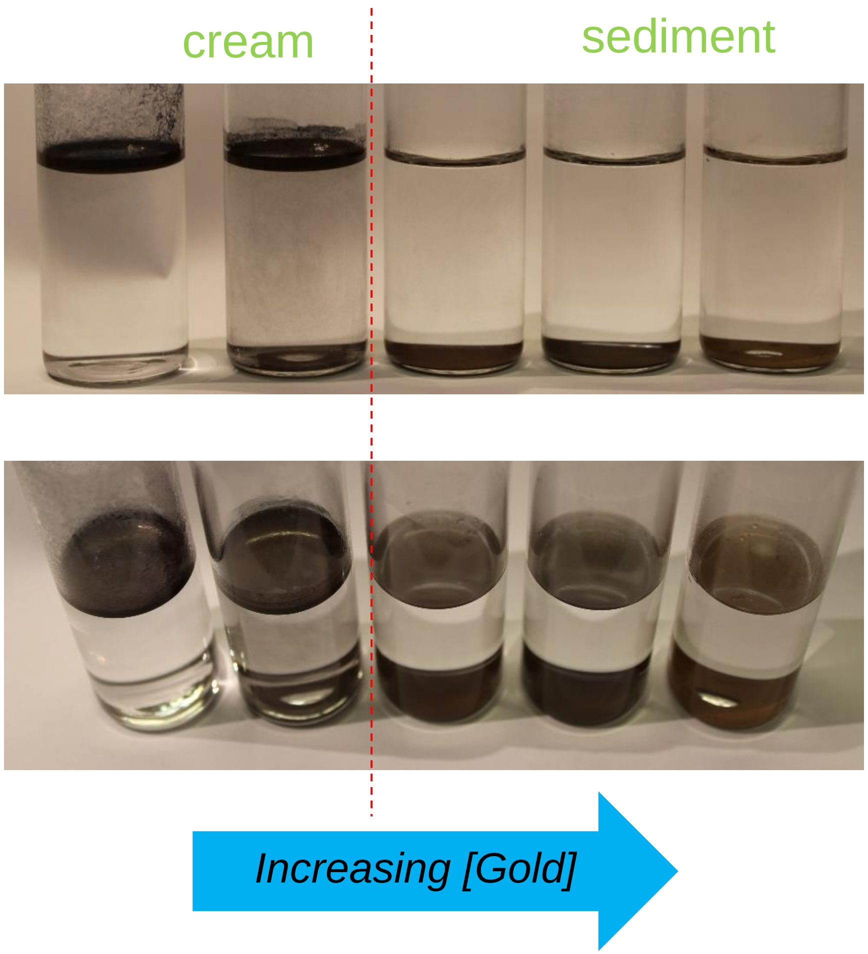
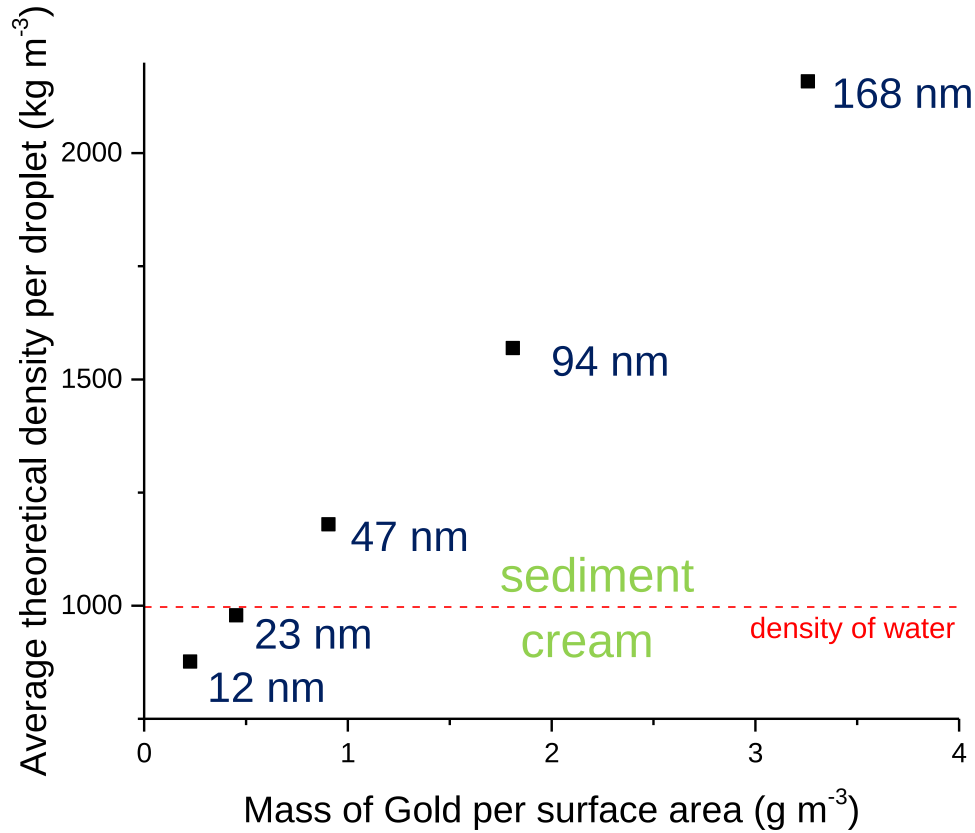
Can control metal film thickness (and therefore capsule density) by changing the **concentration of gold salt** in plating solution

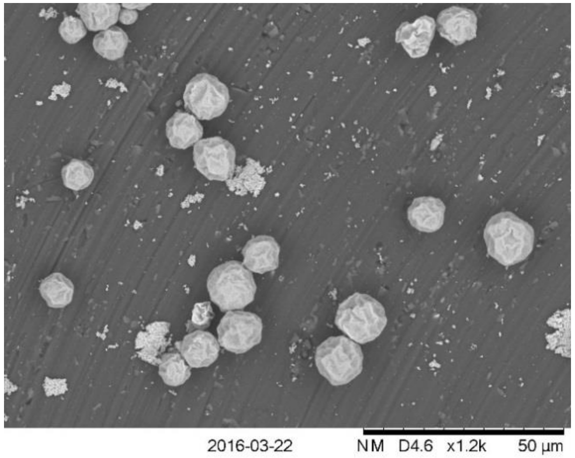


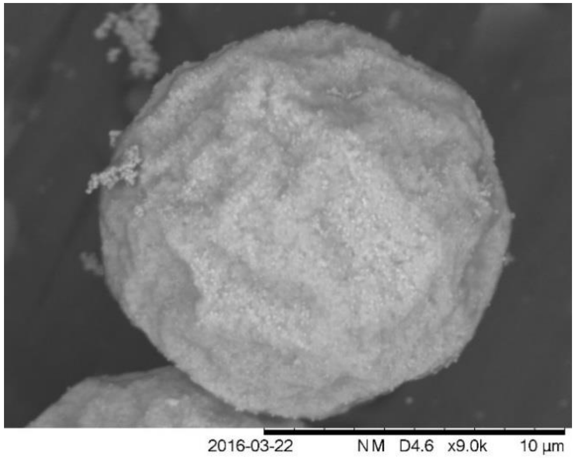


Controlling metal thickness

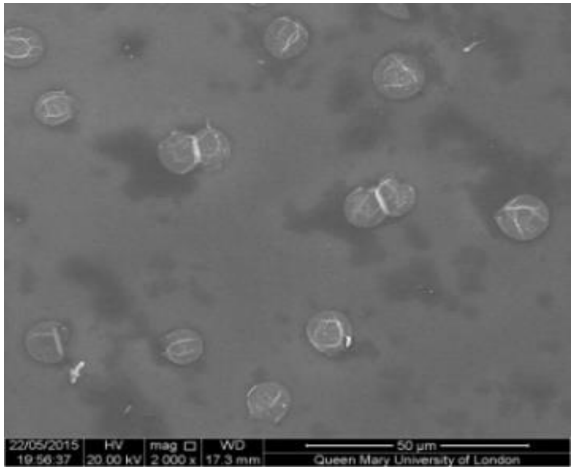
Effect of varying gold salt concentration: SEM

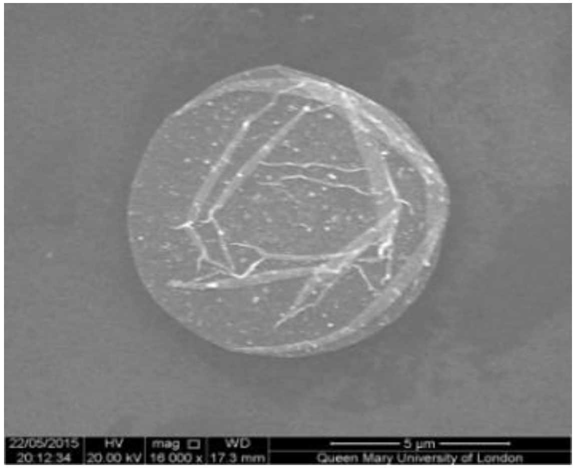
High gold concentration → thicker coating





Low gold concentration → thinner coating





Release mechanisms

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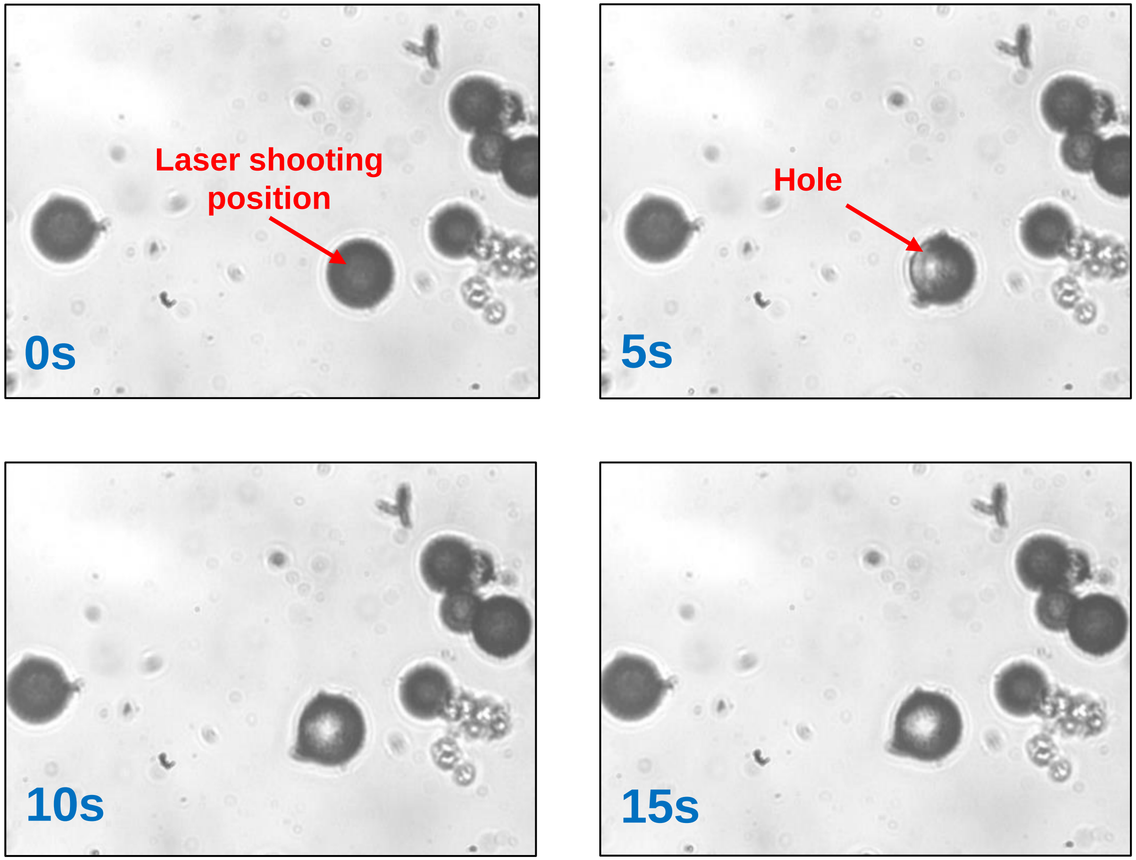
Laser irradiation (wet state)



By shooting single capsule, hole was obtained

Tests carried out at Queen Mary University London by Prof. G. Sukhorukov and Hui Gao

Release mechanisms

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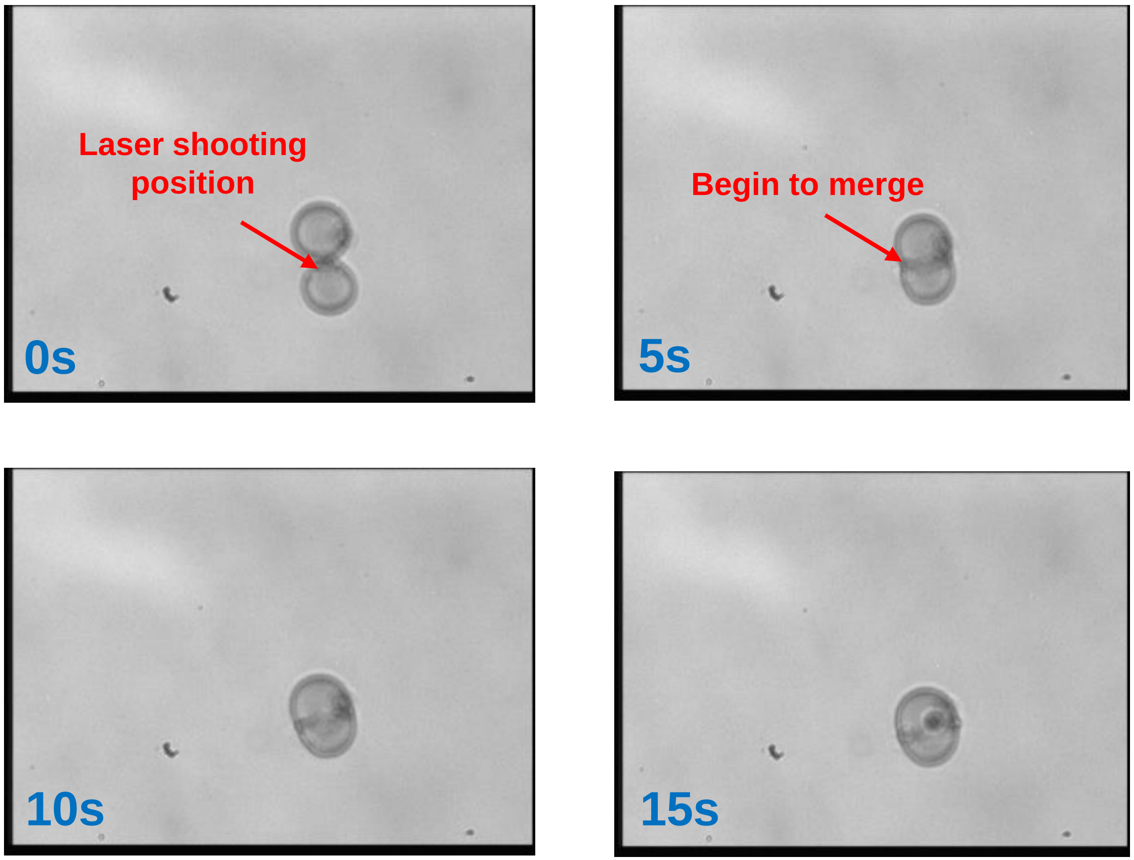
Laser irradiation (wet state)



By shooting the connecting point of two capsules with NIR laser → merge together into one capsule

Tests carried out at Queen Mary University London by Prof. G. Sukhorukov and Hui Gao

Release mechanisms

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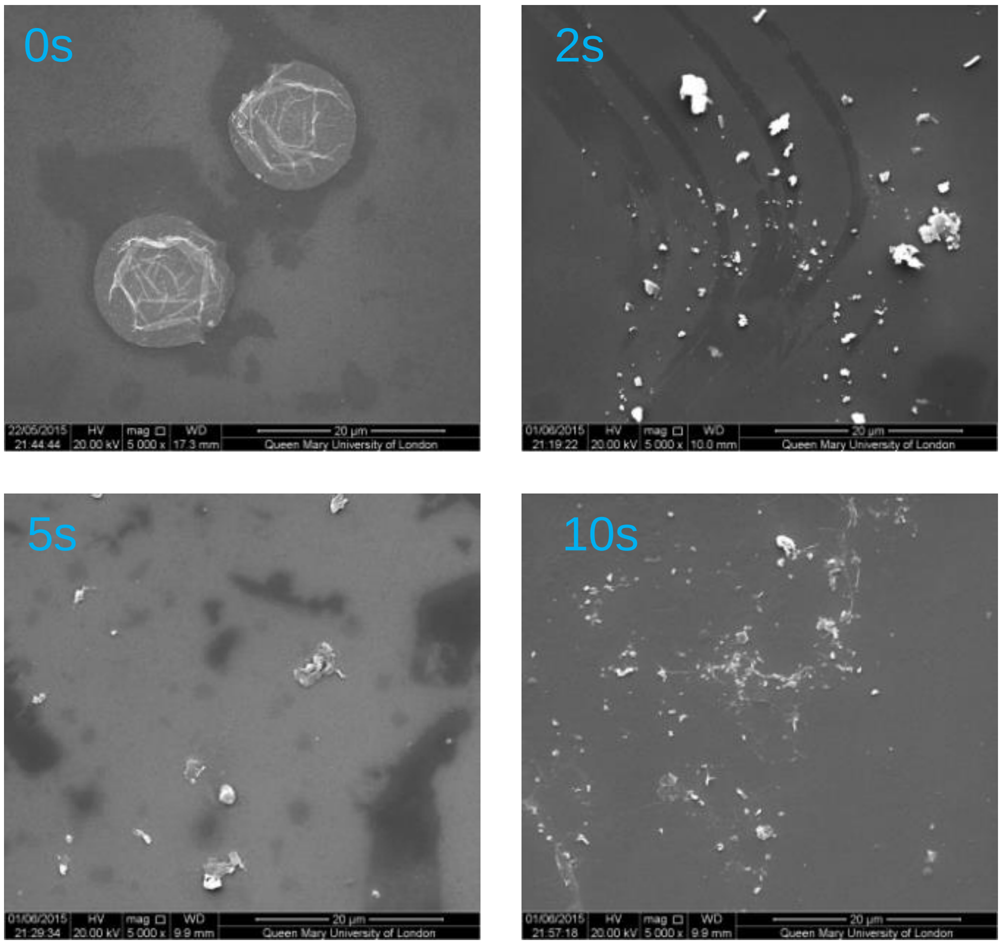
Ultrasound treatment



- Capsules broken within a few seconds
- Plan to do further work with thicker shells
- Further work on varying energy input to find threshold for breaking

From Queen Mary University London

Conclusions & future work

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Conclusions

- Polymer stabilised platinum nanoparticles act as efficient emulsifiers
- A metallic film can be grown on an emulsion template and encapsulate the oil.
- Capsules show permeability in ethanol environment
- Shell thickness can be controlled
- Alternative targeted release mechanisms are being explored. Both laser and ultrasound can rupture the shell walls.

Future Work

- Release studies of different shell thicknesses
- Further work on laser and ultrasound treatment
- Effect of electrolyte concentration on emulsion

Acknowledgments & Thanks

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- Thank you to Dr Olivier Cayre and everyone in the Colloid an Polymer Engineering Group and the Institute of Polymer Science at the University of Leeds
- Professor Gleb Sukhorukov and Hui Gao from Queen Mary University of London for the laser and ultrasound treatment work
- Dr. Alison Tasker and Dr. James Hitchcock for the data on polymer capsules
- Thank you to the EPSRC for funding the research

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Queen Mary University of London

EPSRC Engineering and Physical Sciences Research Council