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Controlled adsorption of metallic nanoparticles on polymeric microcapsules with a view to growing secondary continuous metal films

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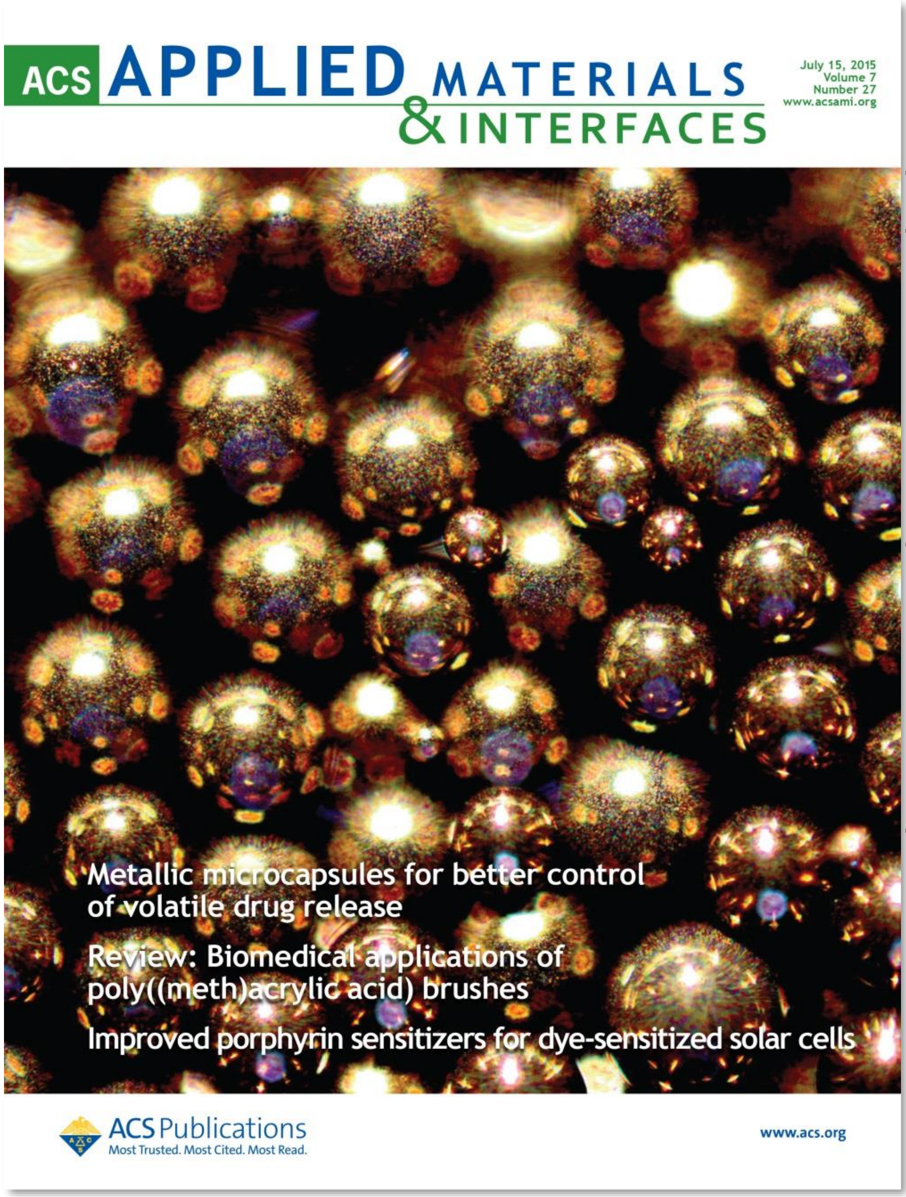
Controlled adsorption of metallic nanoparticles on polymeric microcapsules with a view to growing secondary continuous metal films

3-4-2016

James Hitchcock

Why Metal Coat Microcapsules?

- We metal coat liquid core / polymeric shell microcapsules and emulsion droplets
- A key aspect of this technology is control of the adsorption of the primary catalytic nanoparticles
- Resulting capsules are **non permeable** to small, volatile molecules which is very hard to achieve using conventional encapsulation techniques (David Weitz - fluorinated polymeric capsules formed microfluidics)
- Procter and Gamble sponsored the original work – ‘permanent’ encapsulation of perfume ‘high notes’
- We are now looking to use the technology for cancer treatments



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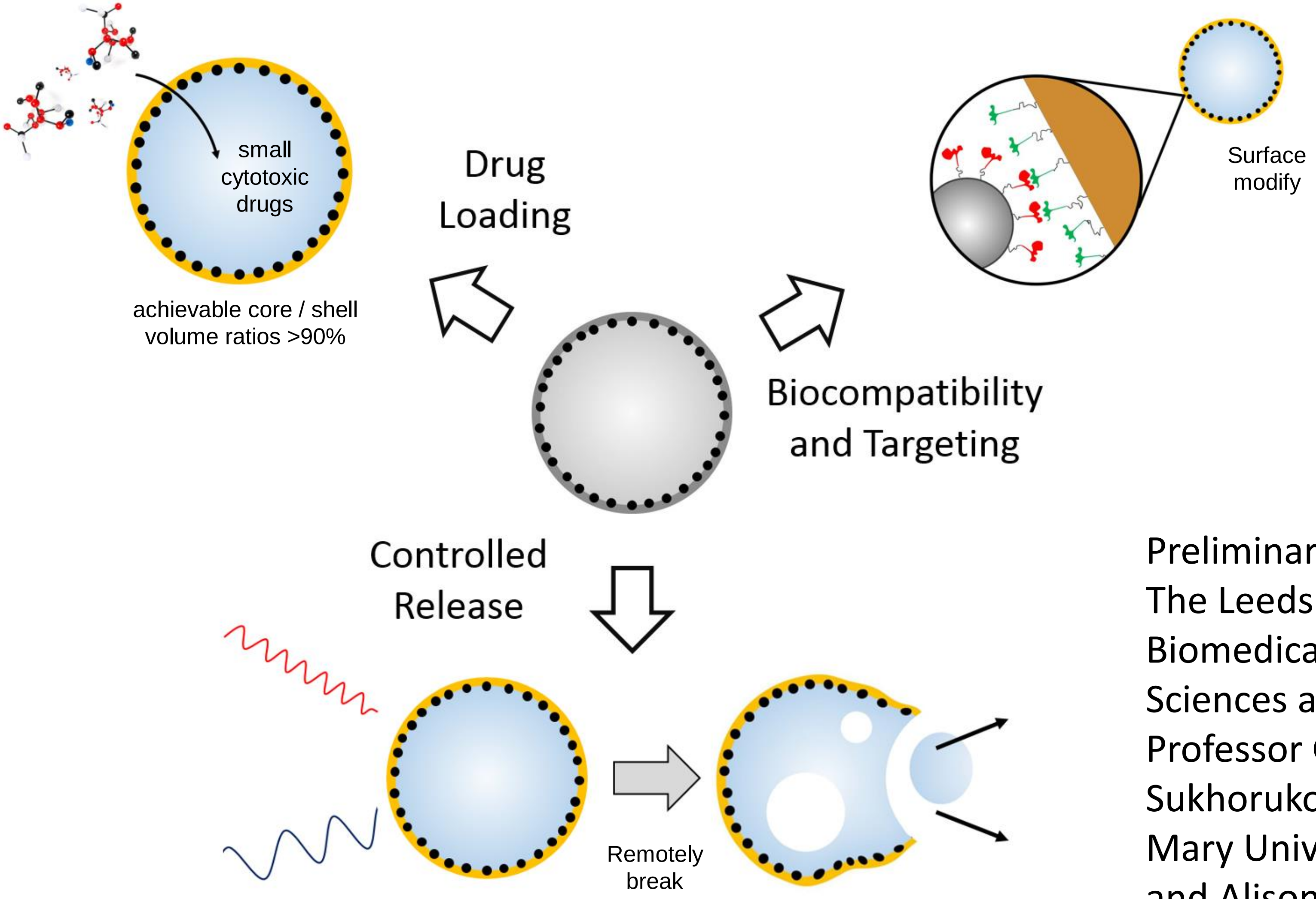
Potential Targeted Cancer Treatment



small cytotoxic drugs

achievable core / shell volume ratios >90%

Drug Loading

Surface modify

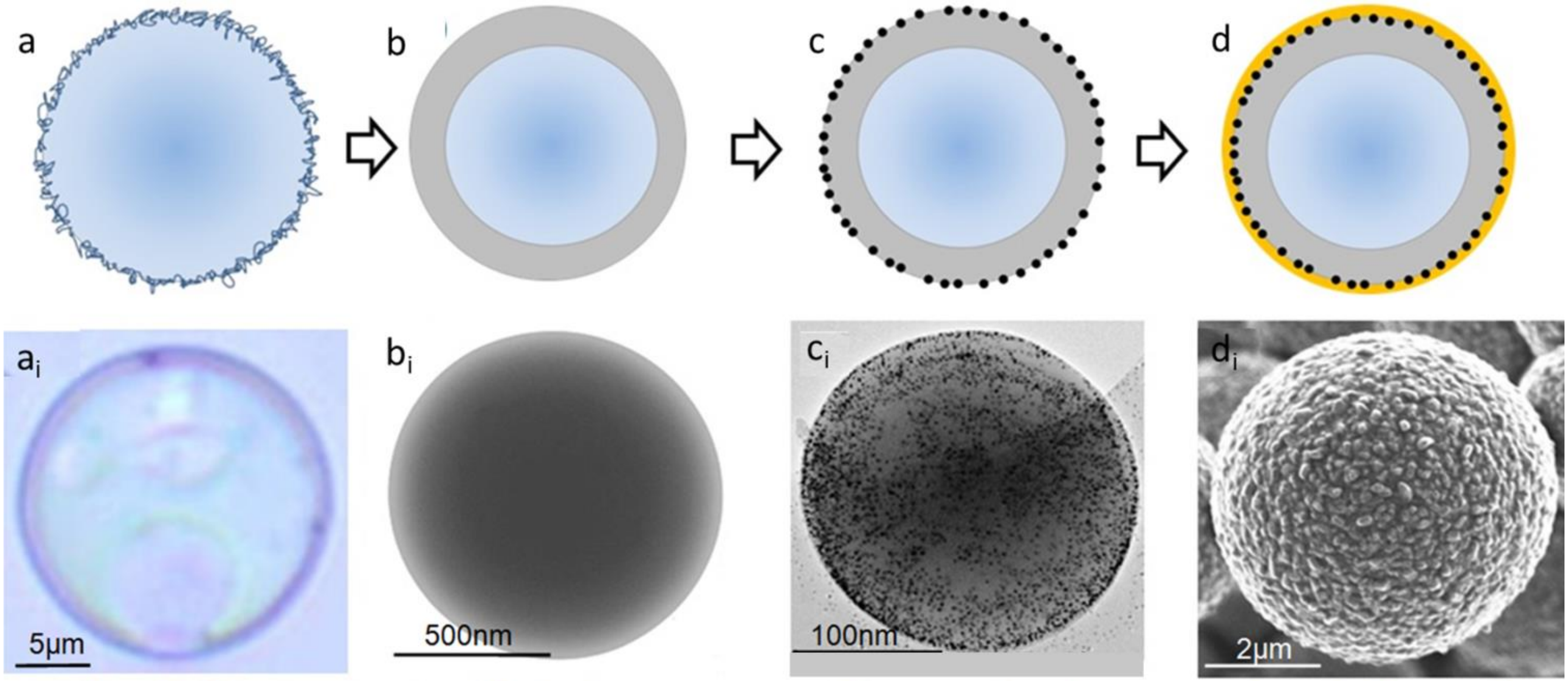
Biocompatibility and Targeting

Controlled Release

Remotely break

Preliminary work with The Leeds Institute of Biomedical & Clinical Sciences at St James Professor Gleb Sukhorukov (Queen Mary University) (Hui) and Alison and Simon Queensland Australia

Synthesis of Metal Coating Polymer Microcapsules



Stabilised oil/water emulsion droplet

Core/shell polymeric capsule

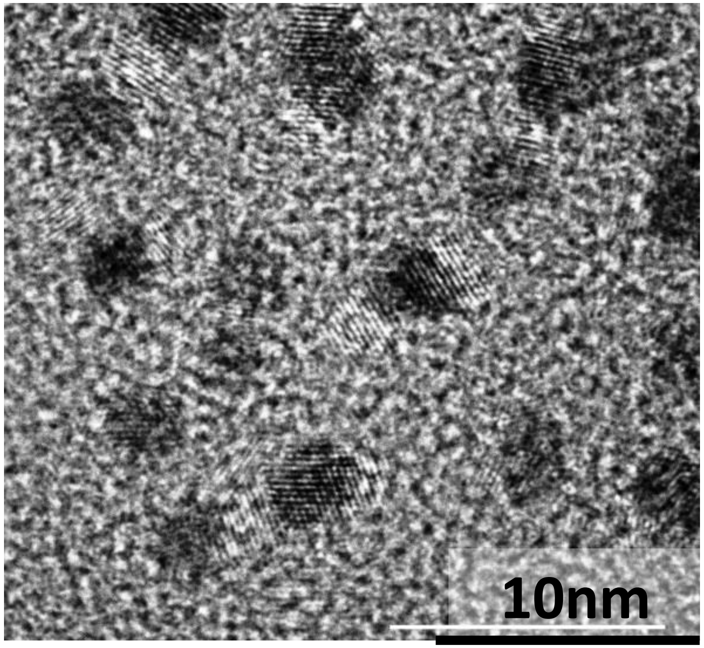
Adsorption of catalytic metallic nanoparticles

Growth of a secondary metallic film

PVP stabilized Platinum Nanoparticles (Pt-NPs)

- Gold films grown on polyvinylpyrrolidone (PVP) stabilized platinum nanoparticles (Pt-NPs)
  - NP synthesis - metal salt reduction > nucleation, growth and polymeric steric stabilisation.
  - PVP is polar and tends to adsorb well to most surfaces (so Pt-NPs are nicely surface active)

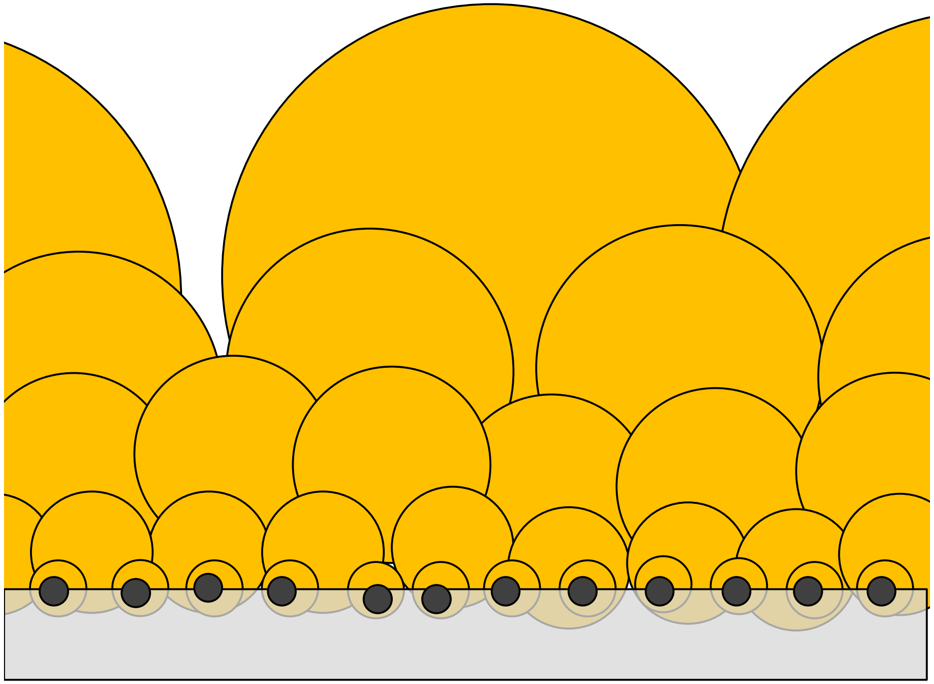
- Key aspect of technology – understanding and controlling the adsorption of NPs which catalyse the growth of the secondary film



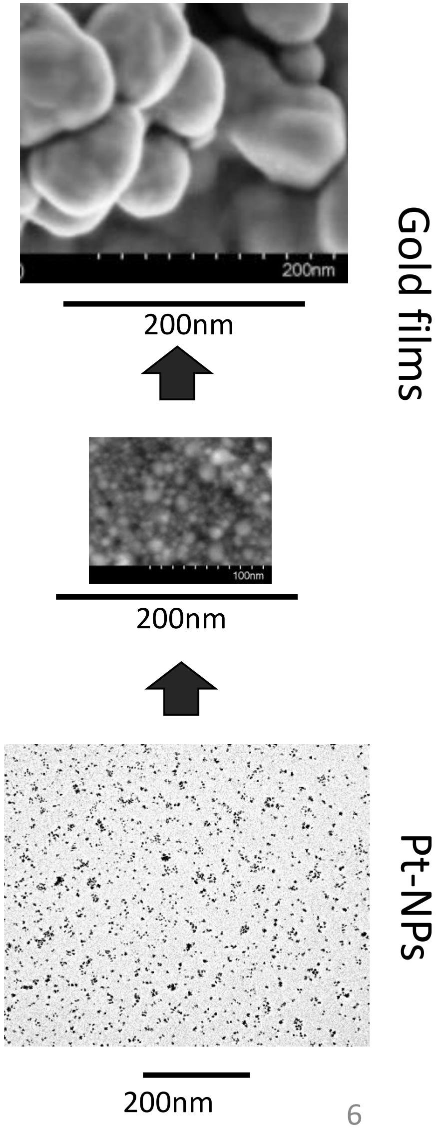
$$NaBH_4 + H_2PtCl_6 + 3H_2O \rightarrow Pt + H_3BO_3 + 5HCl + NaCl + 2H_2$$

Nanoparticle Adsorption - Key Step

- Require the NPs to have a high energy of adsorption onto the polymeric microcapsule surfaces – low detachment on washing
- Efficient use of Pt-NPs - high cost
- Tune NP adsorption density of NPs
  - Minimize thickness of secondary metallic film – require high NP surface density
  - Minimize NP usage – require thicker secondary metal film to bridge the gaps between NPs



$$2HAuCl_4 + 3H_2O_2 \rightarrow Pt \rightarrow 2Au + 3O_2 + 8HCl$$



Characterisation of Pt-NP Adsorption

- Used spin coated 2D polymeric films as a model system to look at Pt-NP adsorption kinetics using QCM and TEM

- Use TEM to characterize /measure NP adsorption density onto the 3D capsule surfaces.

2D model system

Pt-NP adsorption on spin coated polymeric films

Low Adsorption Density when using Standard NP Formulations

- Both TEM and QCM showed that only very low Pt-NP adsorption densities were achievable using Pt-NP formulations routinely used in the literature.

- Calculations of ratio of number of NPs to number of polymeric chains show that most examples of polymerically stabilised NP synthesis in the literature introduce 100’s to 10,000’s times more polymer chains than the number of NPs they are synthesising (calc)

- PVP is surface active and therefore may adversely affect the adsorption on the nanoparticles.

- We therefore studied the influence the polymer concentration in the NP synthesis has on the resulting Pt-NP adsorption density using both QCM and TEM.

Effect of polymeric stabilizer used to make the NPs on resulting NP surface adsorption (TEM)

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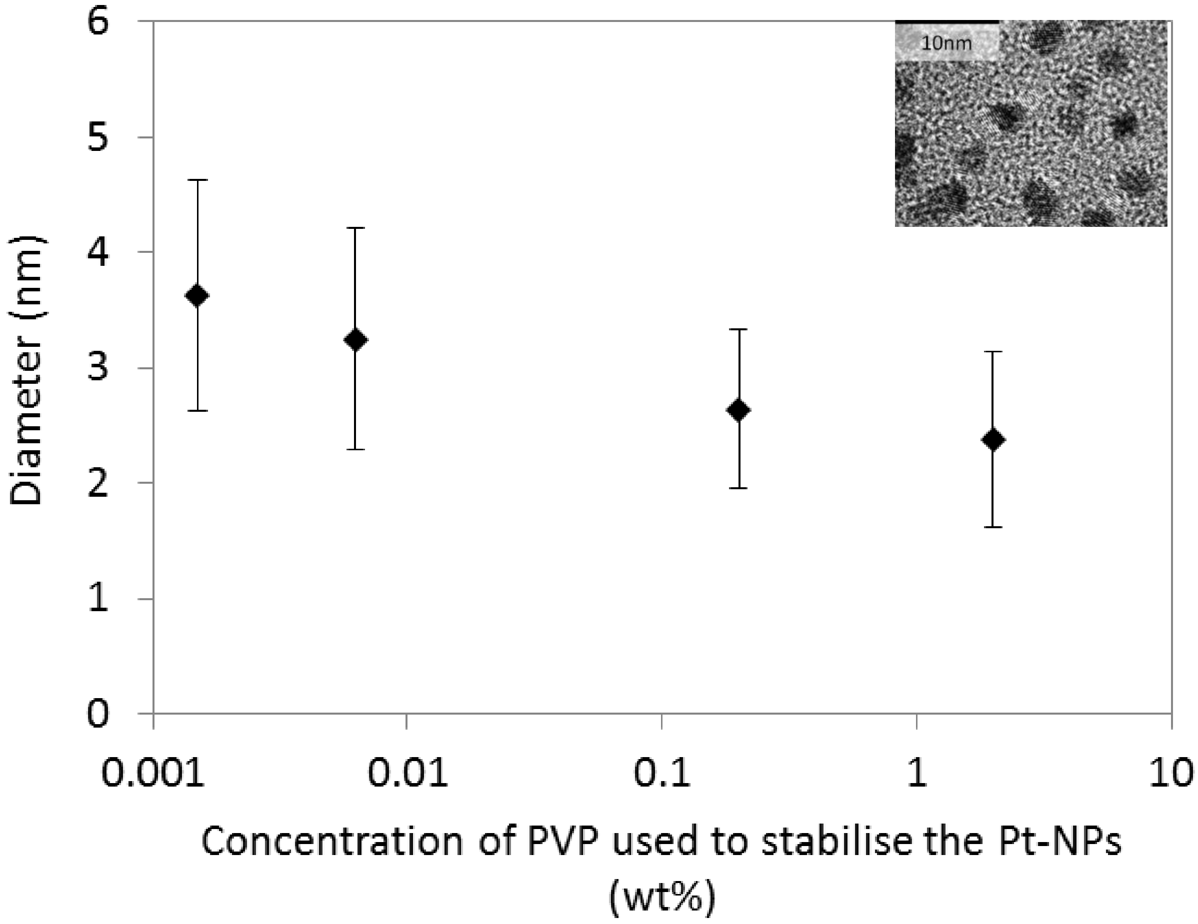


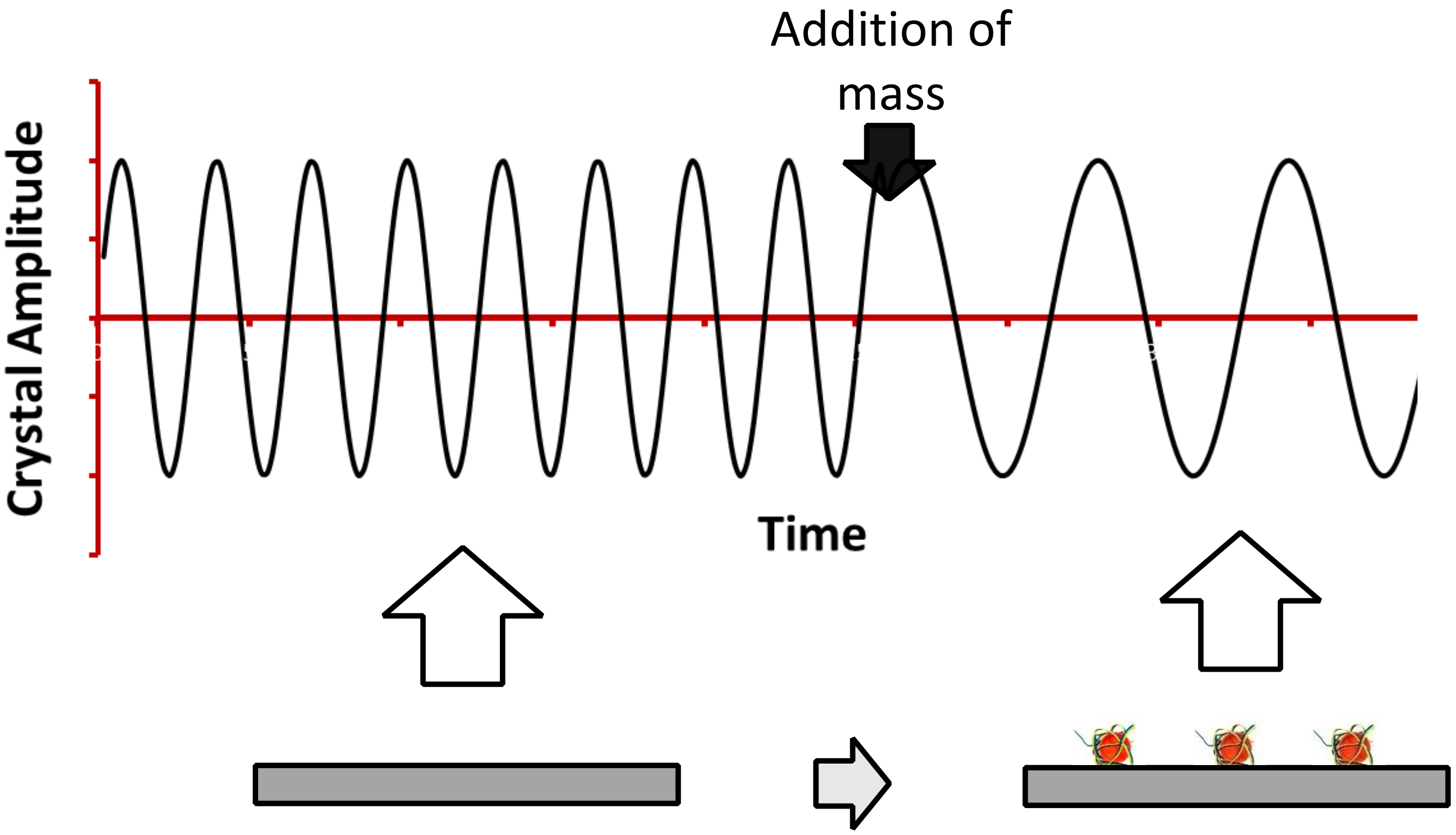
A range of Pt-NP dispersions were synthesized using different concentrations of polymeric stabilizer.

Below 0.0015wt% unstable

Approximately 1:1 PVP : Pt-NP

Interesting implications for NP morphology

Quartz Crystal Microbalance (QCM)

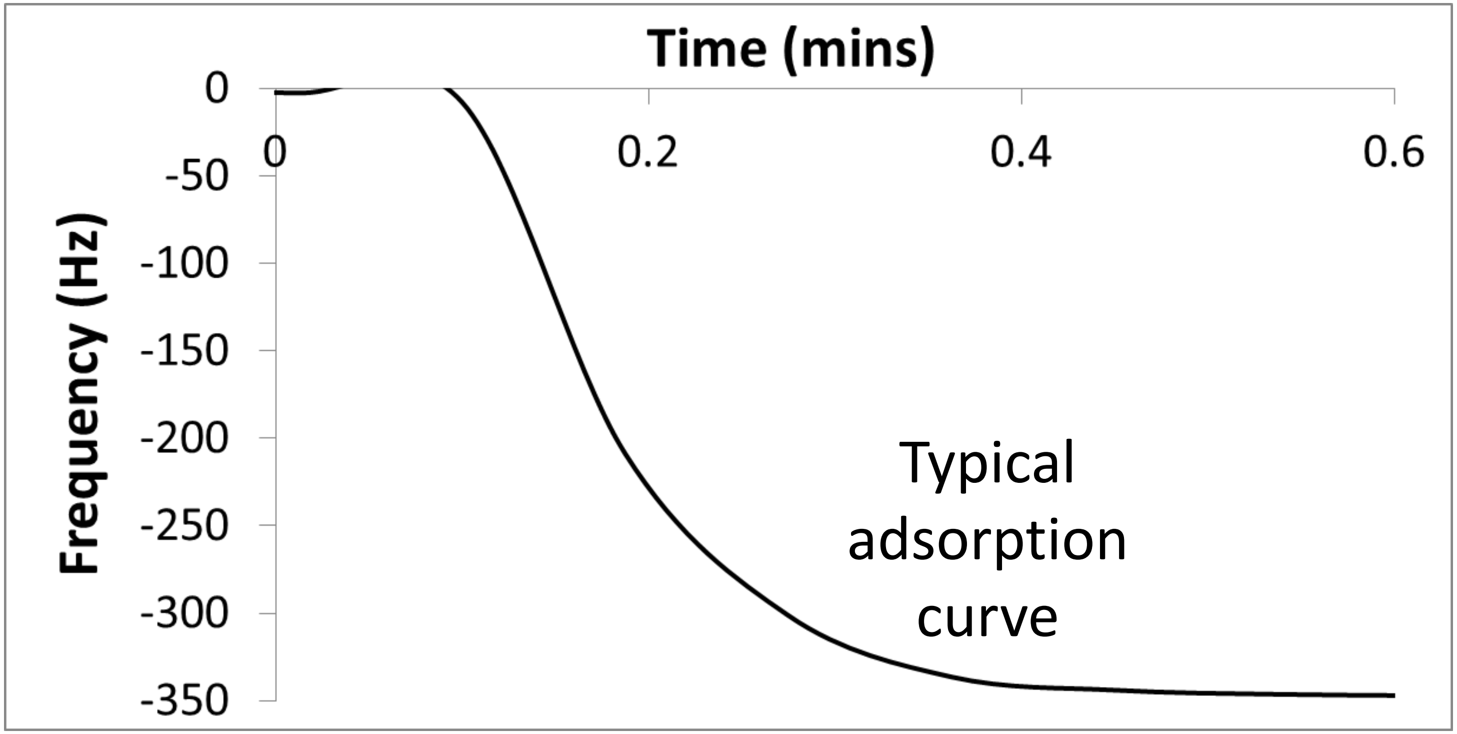


Piezoelectric crystal

Clean crystal original frequency

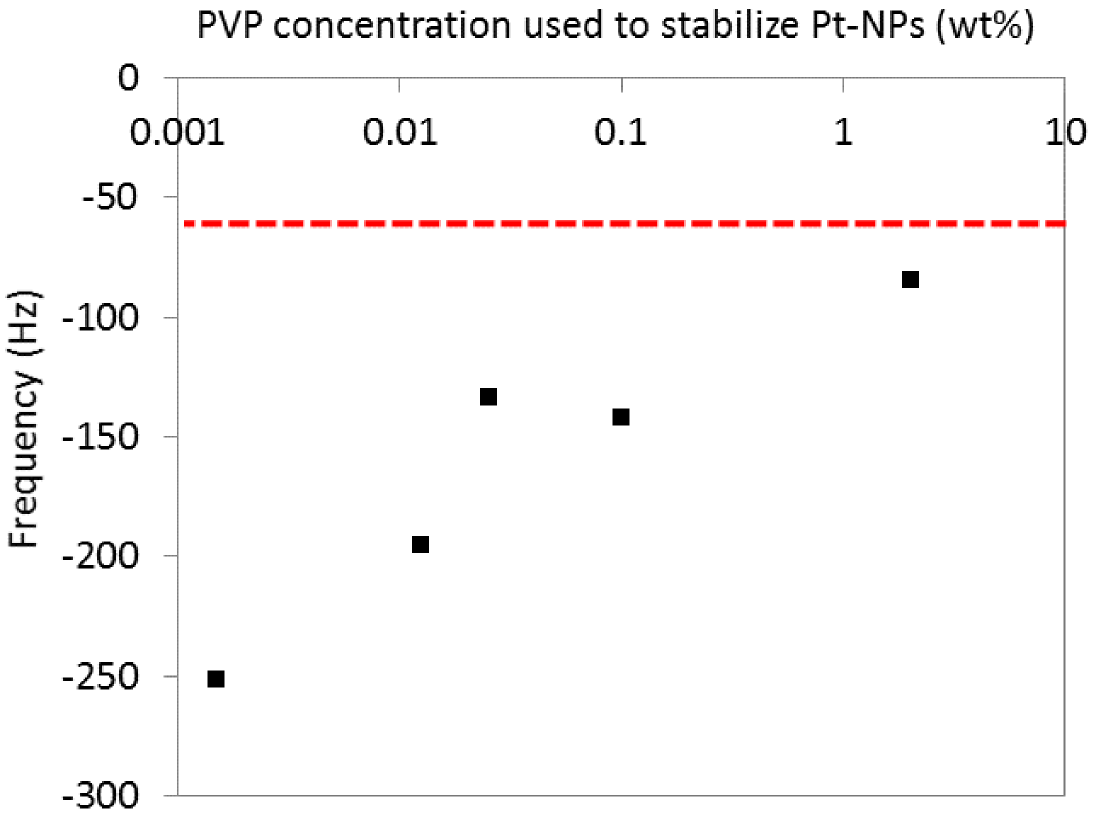
Frequency drops with the addition of mass

Quartz Crystal Microbalance (QCM)



Piezoelectric crystal

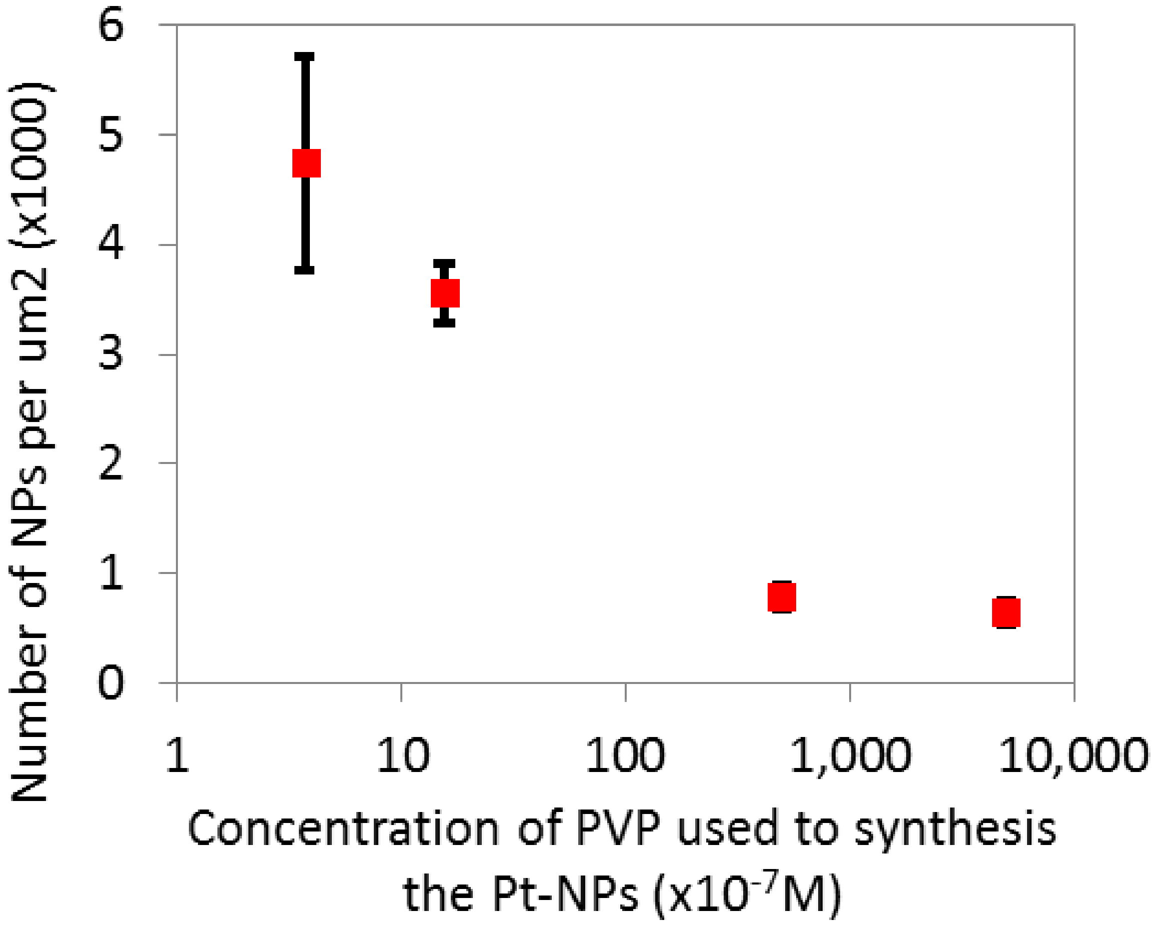
Effect of polymeric stabilizer used to make the NPs on resulting NP surface adsorption (QCM)



Lower concentrations of polymeric stabilizer leads to an increase in frequency change and therefore increased adsorbed mass (more NPs adsorbing).

At higher polymer concentrations the adsorbed mass becomes similar to the adsorption of pure polymer (0.2-2wt% commonly used in literature).

Effect of polymeric stabilizer on NP adsorption (TEM)



This trend was also confirmed through a different series of experiments that studied the density of adsorbed nanoparticles onto polymer-coated carbon grids via TEM

Why are we seeing this relationship?

Monolayer formation with High Energy of Adsorption (Pt-NPs)

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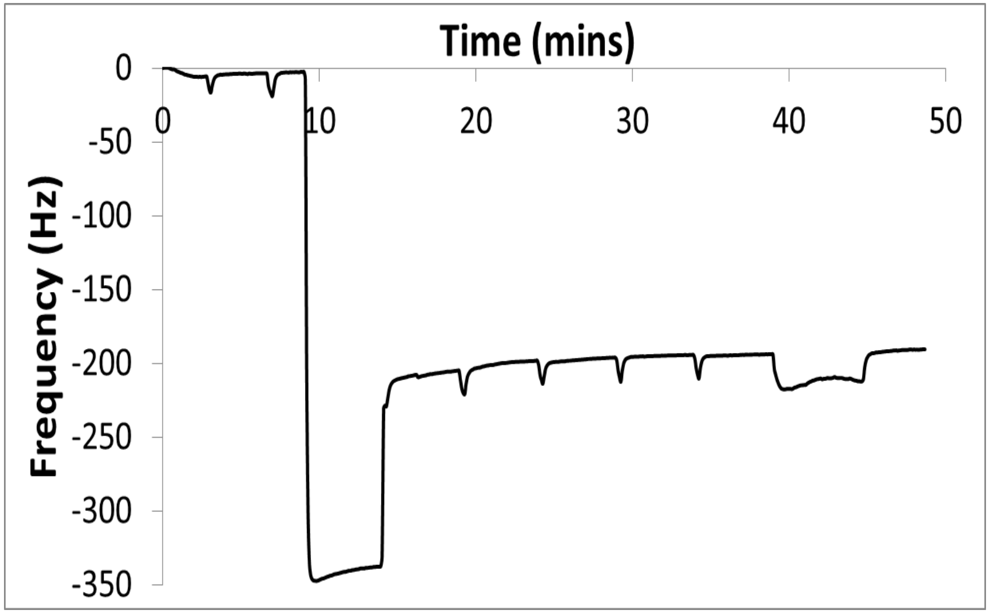
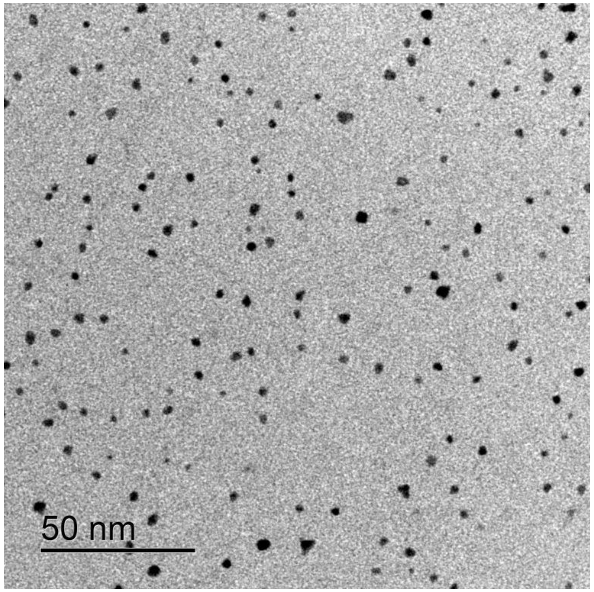




QCM shows that multiple wash cycles do not remove either adsorbed bare PVP or Pt-NPs from a PEMA interface – permanently adsorbed E_{ad} >> kT - good for us

QCM shows plateauing in excess Pt-NP suspension and TEM confirms that once we get a monolayer further adsorption is restricted – steric hindrance

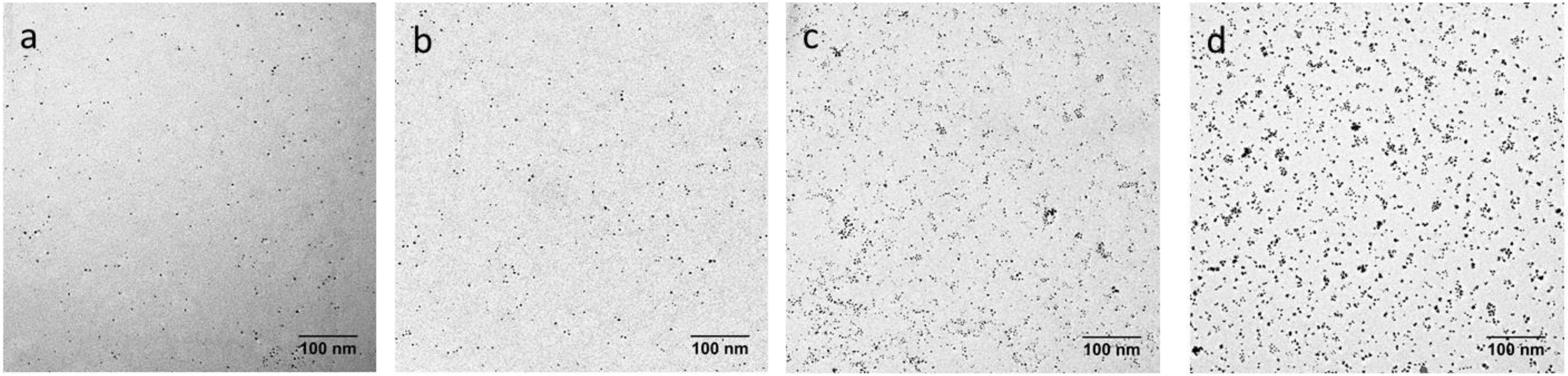
Effect of polymeric stabilizer on NP adsorption (TEM)

On the basis of the high adsorption energy of both bare PVP and Pt-NPs and their ability to restrict further adsorption of either species through steric hindrance

- Seems likely that the observed change in NP adsorption density is due to a change in ratio of adsorbed bare PVP and adsorbed Pt-NP.
- (a)-(d) are all fully coated but the ratio of NPs to polymer is increasing

This is a visualization of the contribution the NPs are making to the mass change in the QCM data. PVP hydrocarbon chains provide little contrast on TEM.

Very difficult to remove excess PVP - similar size and chemistry



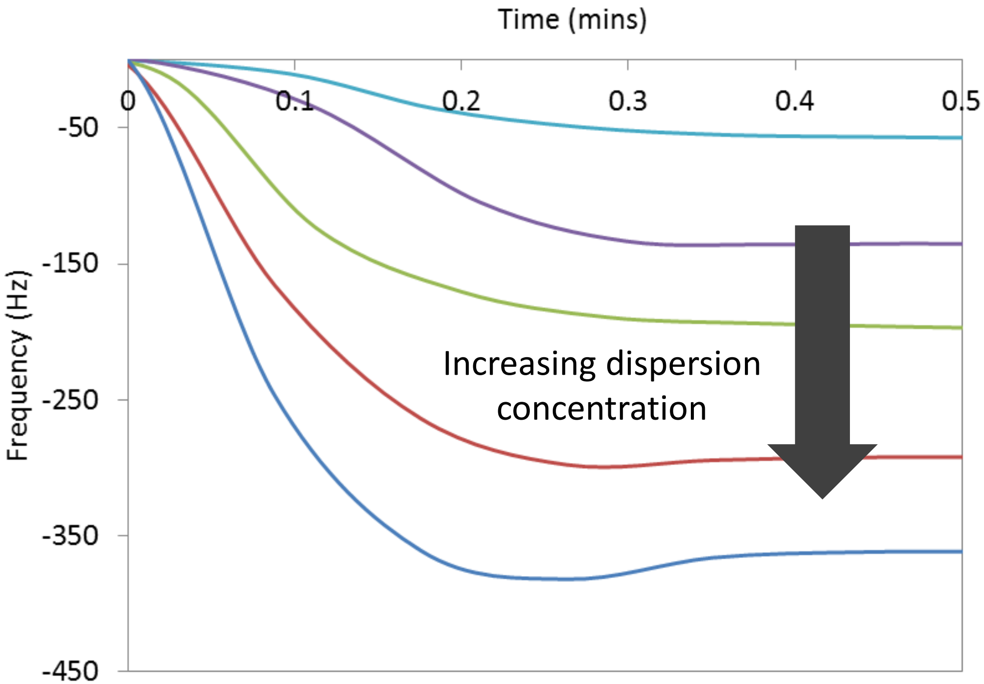
2wt% PVP

0.2wt% PVP

0.006wt% PVP

0.0015wt% PVP

Concentration of NPs vs NP adsorption density (QCM and TEM)



Frequency change vs time for Pt-NP (0.006wt%PVP) at different suspension concentrations

We would like to be able to reproducibly obtain the same NP density independent of the number of capsules that need coating

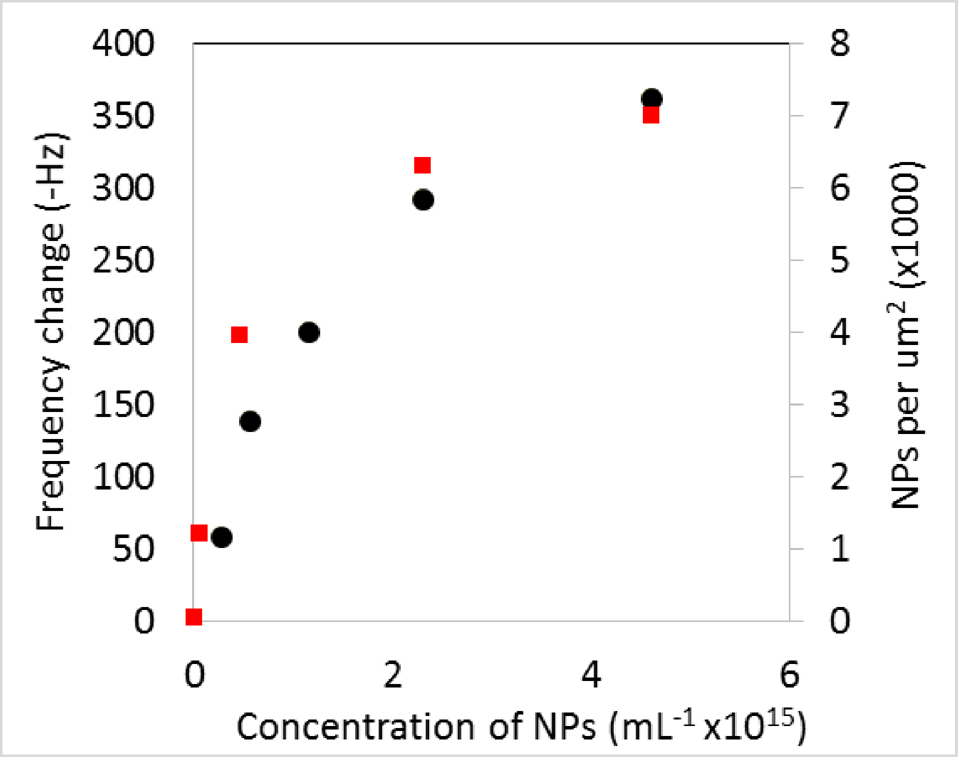
Looked at how the Pt-NP suspension concentration effects resulting adsorption density

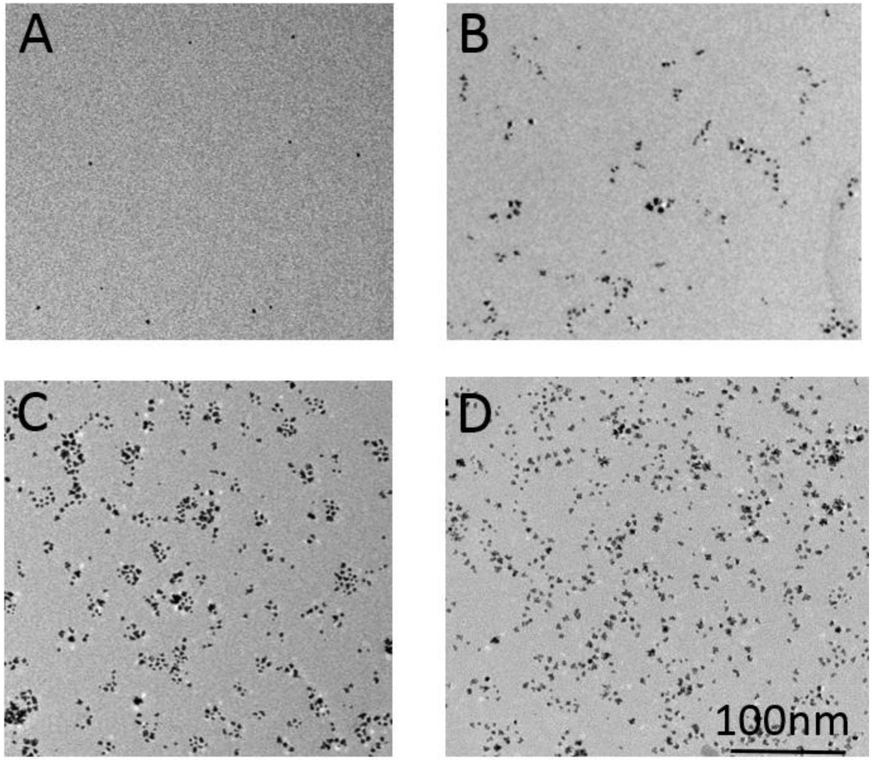
Looks like typical Langmuir isotherm something you might see with a small surfactant at low concentration

This is unexpected high surface energy should see same frequency change for all concentrations over different time frames

Same trend confirmed using TEM

Concentration of NPs vs NP adsorption density (QCM and TEM)





Not due to PVP relaxation / unfurling a interface

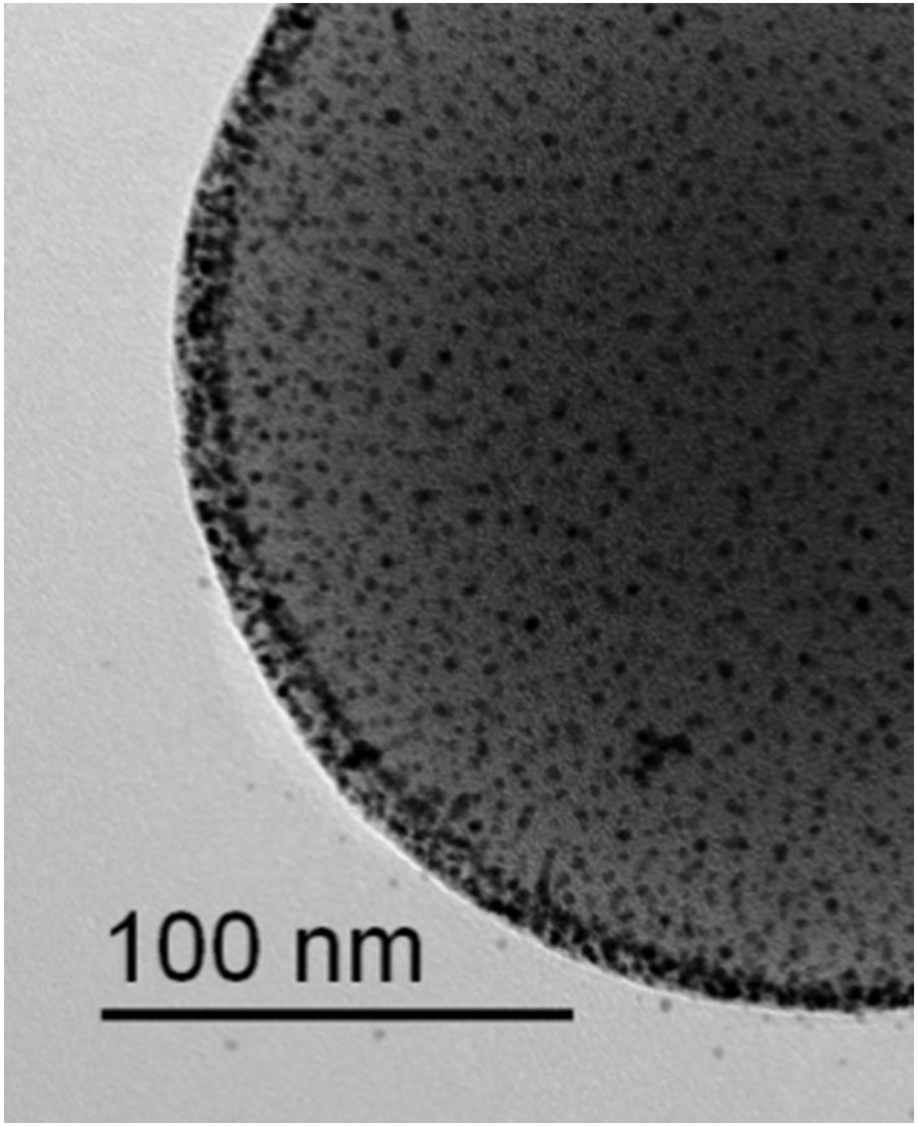
- Effect on QCM frequency change small for pure PVP
- Relaxation times order of magnitude greater than adsorption times required here

Not due to depletion of Pt-NPs from the continuous phase

- Calculations of numbers of Pt-NP introduced show massive excess for all concentrations

NP adsorption onto polymeric capsules (3D)

Pt-NP adsorption densities on polymeric microcapsules



Can use TGA or UV-Vis to monitor depletion of NPs from the continuous phase to infer adsorption density.

To directly measure the adsorption density using TEM is non trivial:

- Need to image only the very small capsules in order to achieve transparency
- The surface is not flat and therefore need to correct for this
- We are actually imaging both sides of the capsule

Correcting for Surface Curvature

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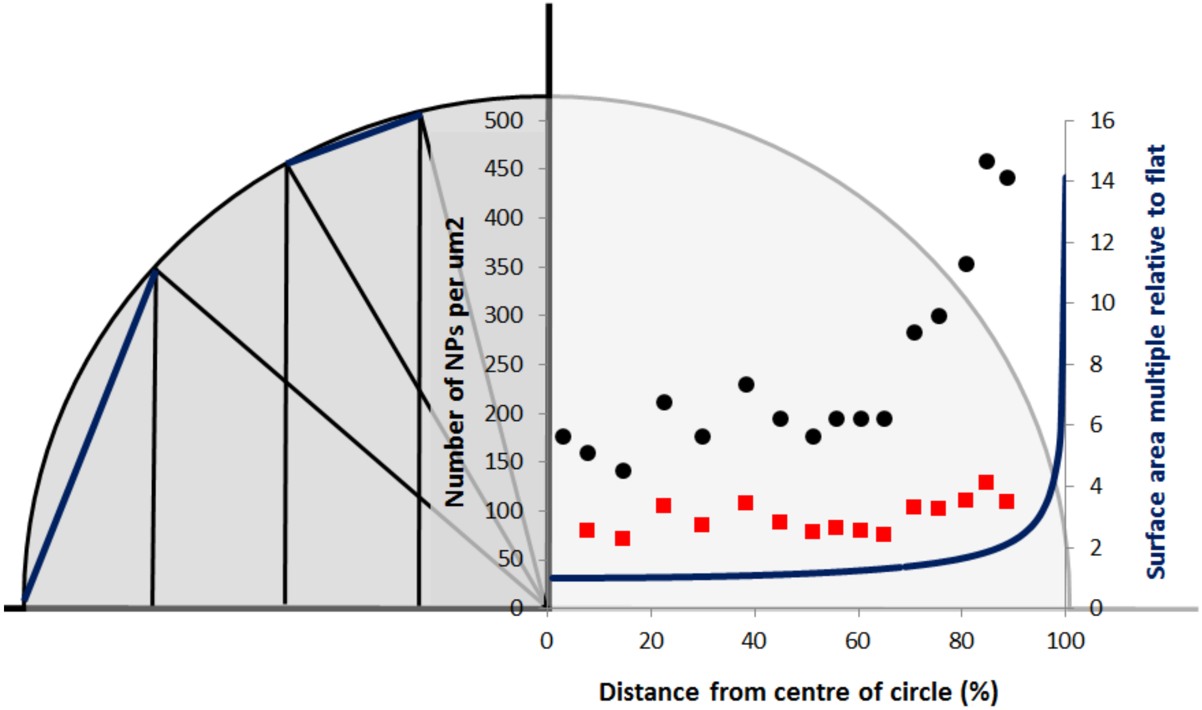
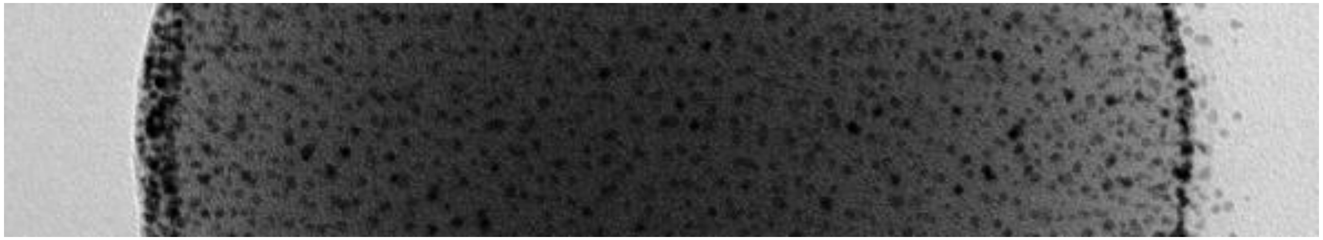
Correcting apparent surface area to actual surface area





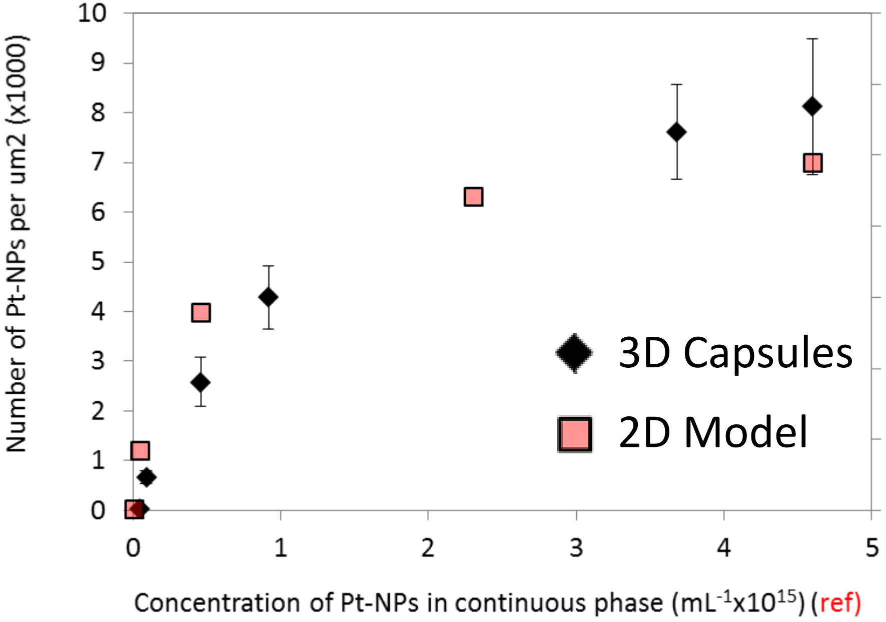
Pt-NP adsorption densities on polymeric microcapsules

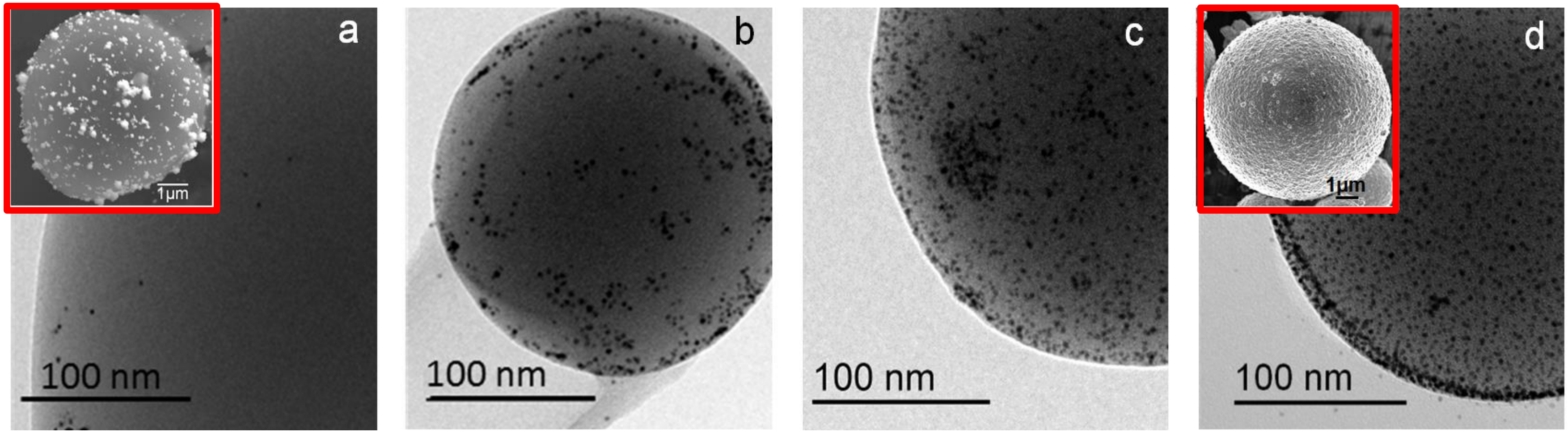
- See the same trend as on the model 2D system – as long as excess Pt-NPs the density at equilibrium is independent of surface area introduced

- So we have control over the Pt-NP density

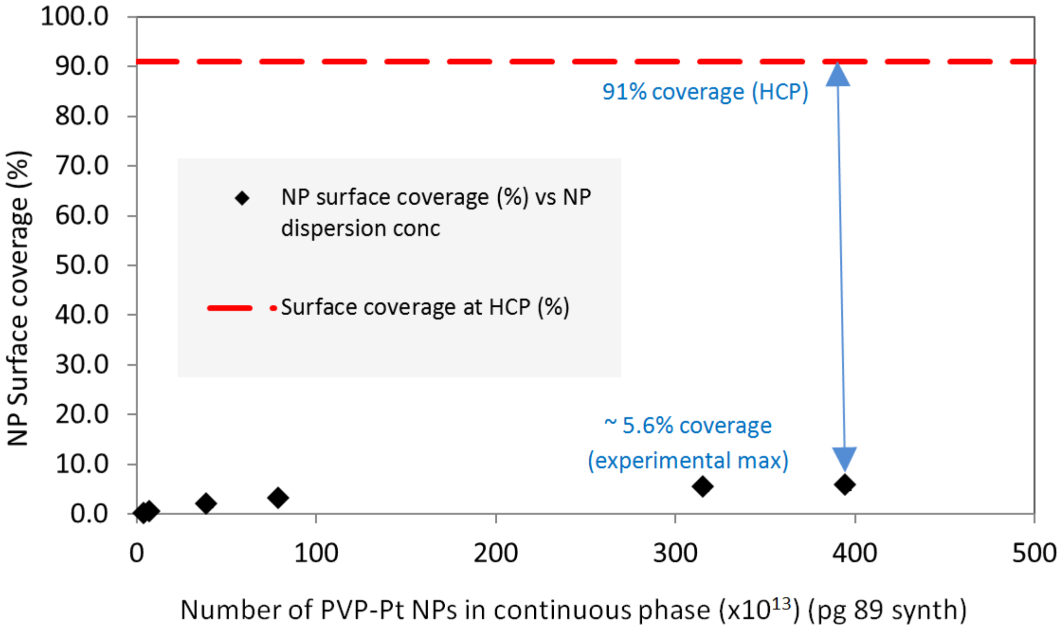
- Aim was to have control over subsequent gold film morphology

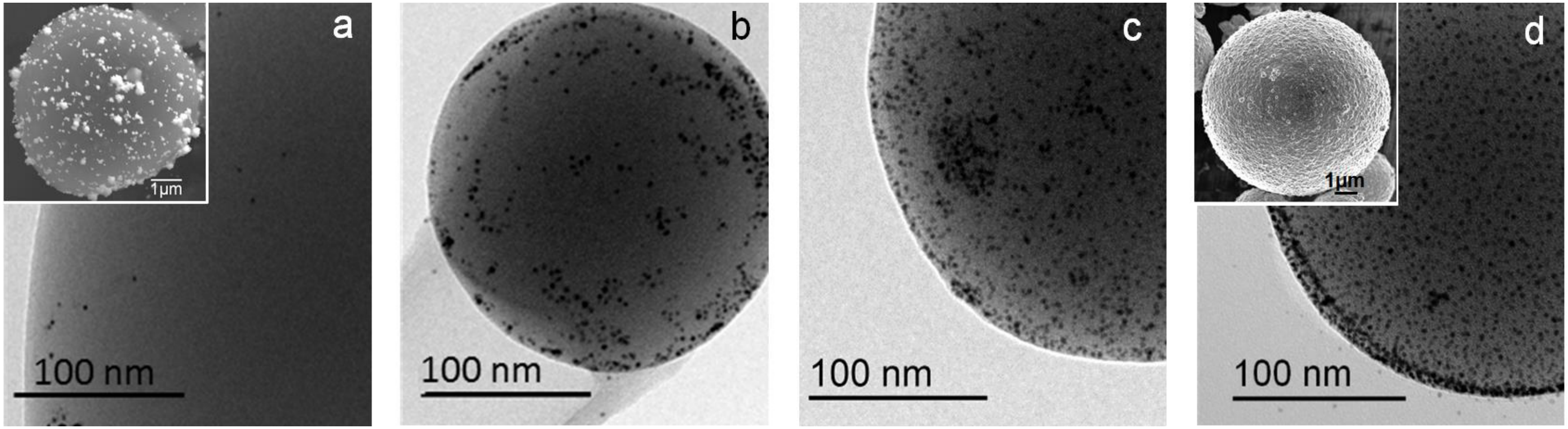
- Insets show resulting gold film growth





Why ~6% Maximum Pt-NP Coverage?

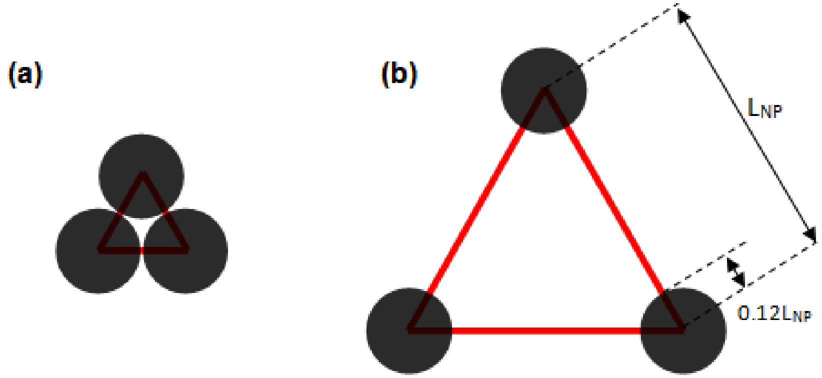




Theoretical Pt-NP separation at 5.6% coverage?

Calculation of ratio of hexagonal packed NP separation (L_{NP}) to NP radius (r) for a chosen surface area coverage (Γ_{cov}):

old coated PVMA capsules as
in plating solution (SEM)

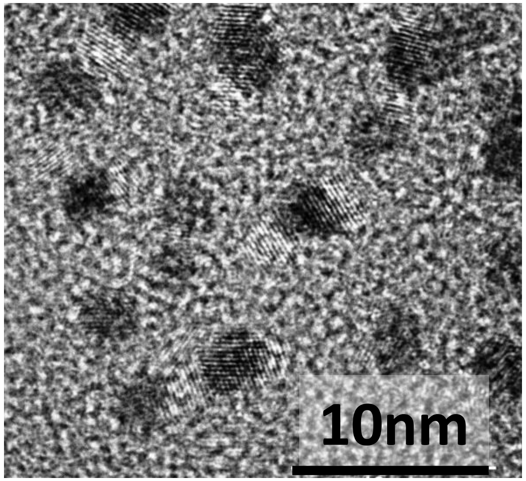


Scaled schematic diagram showing (a) HCP – 91% surface coverage and (b) 5.6% surface coverage

NP radius r
Surface area coverage Γ_{cov}
NP separation L_{NP}

$$\frac{r}{L_{NP}} = \sqrt[4]{\frac{3\Gamma_{cov}{}^{2}}{4\pi^{2}}}$$

Therefore for 5.6% coverage $\Gamma_{cov} = 0.056$ and $\frac{r}{L_{NP}} = 0.12$



Polymeric stabilizer accounts for the NP spacing

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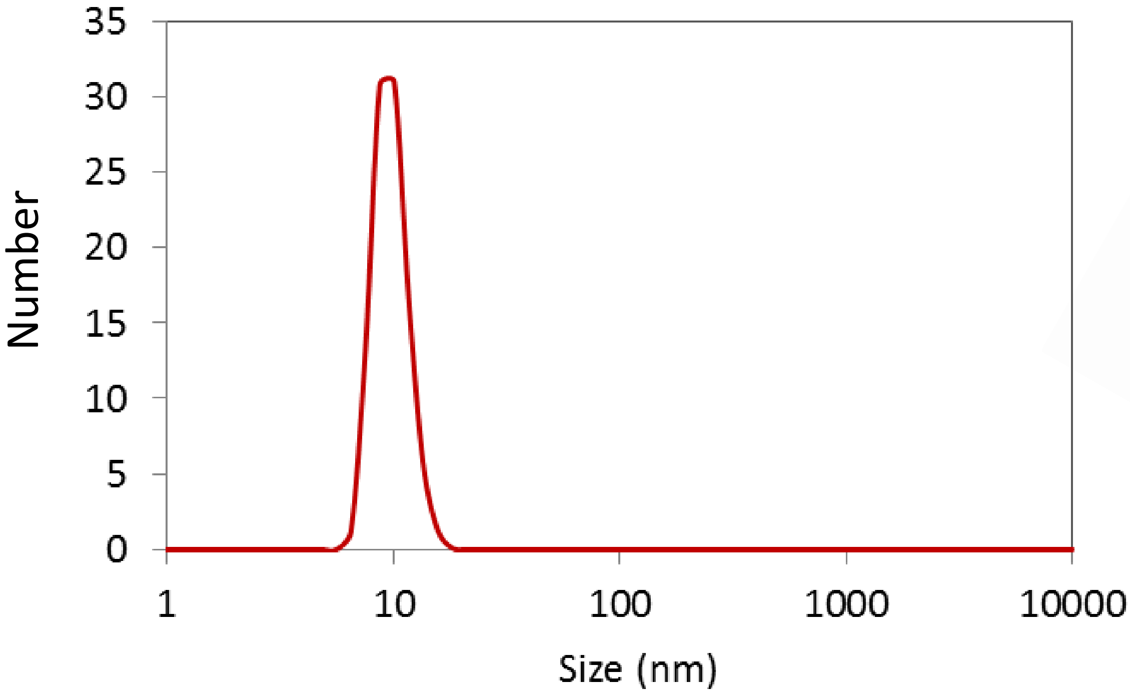
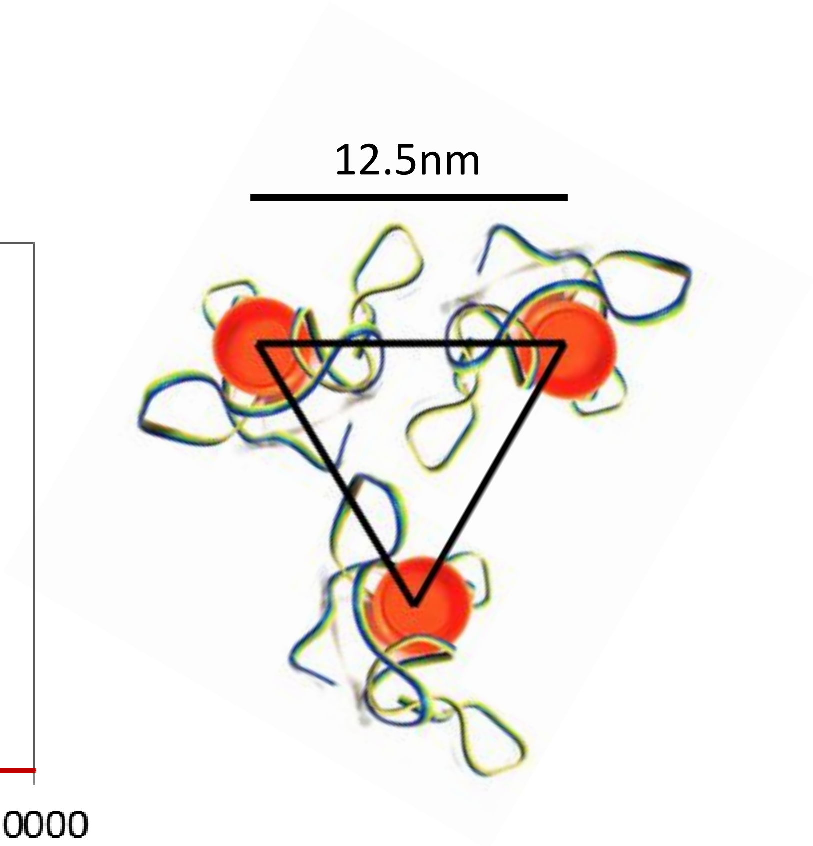
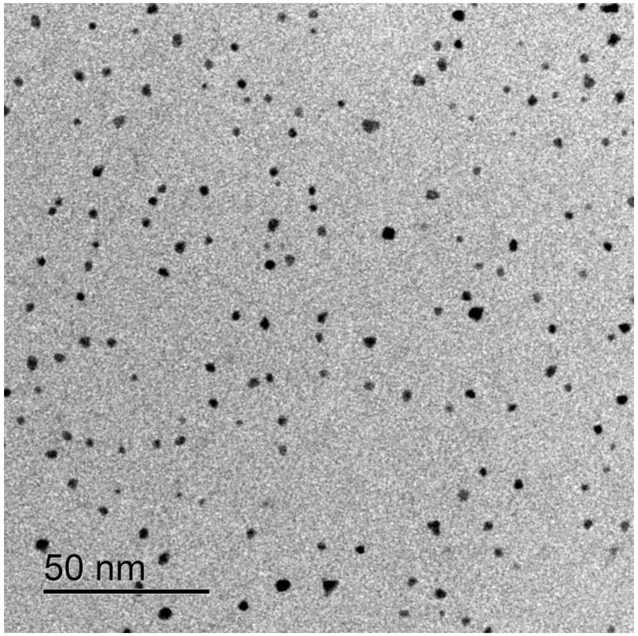
- At 5.6% coverage $\frac{r}{L_{NP}} = 0.12$
- NP diameter 3nm therefore HCP inter-nanoparticle spacing would be 12.5nm
- DLS gives a hydrodynamic diameter of ~10nm





Conclusion:

- We synthesize small (2-4nm) polymerically stabilized NPs with good size distribution.
- Show that NP films form in seconds and adsorb at PEMA interfaces with energies many times the background thermal energy
- Demonstrate control over adsorption density by varying the polymeric concentration in original NP synthesis
- Demonstrate control of NP adsorption density by changing the concentration of the NP suspension
- We achieve Pt NP core adsorption densities of ~6%
- Key message – watch out for excess polymeric stabiliser
  - quite often stuck with it in the resulting NP suspension, similar surface chemistries and often size
  - likely to adversely effect NP adsorption densities.



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Appendix