

Self assembly of golden core-cage nanoparticles



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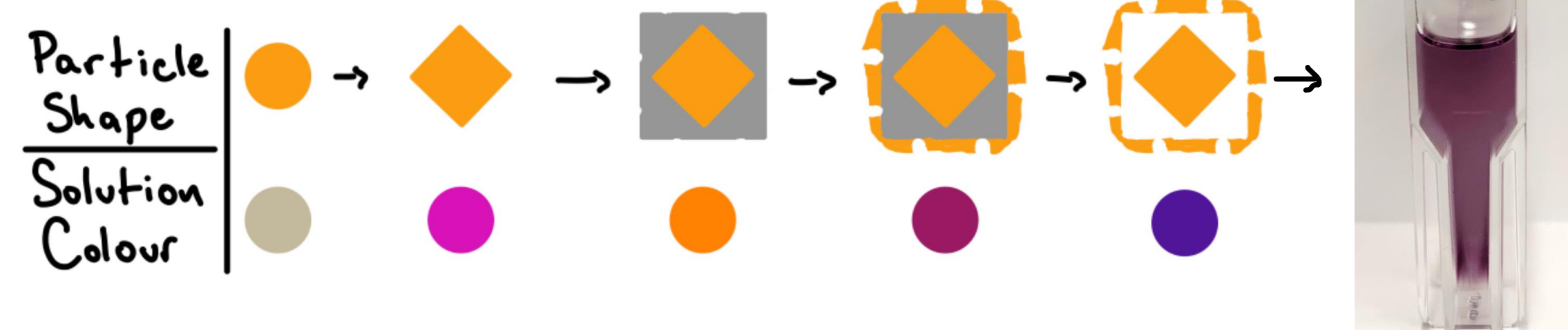
INTRO:

Plasmonic metal nanoparticles of complex shapes are of high importance in sensing, catalysis, and imaging. The organisation of these nanoparticles in chains or lattices allows for tuning of optical properties and enhancement of the electric field (E-field) in interparticle gaps, making plasmonic nanoparticle assembly very attractive for investigation. With new synthesis strategies for plasmonic nanoparticles with complex geometries, studies of more complex plasmonic coupling modes can be enabled, with more tunable optical resonance and stronger E-field hot spots. Self assembly into chains and lattices of nanoparticles with simple geometries, such as spheres and cubes, has been previously studied.

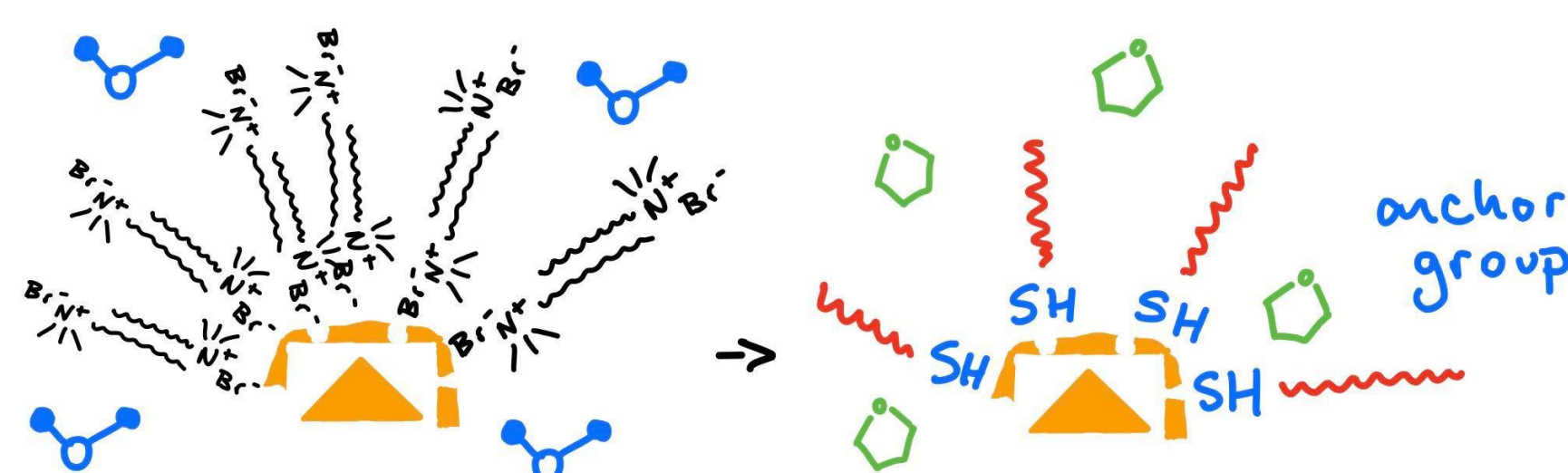
This work will study optical response and distribution of E-field hot spots in self assembled chains of core-cages, a more complex structure comprised of a gold octahedral core trapped inside a golden cage.

METHODS:

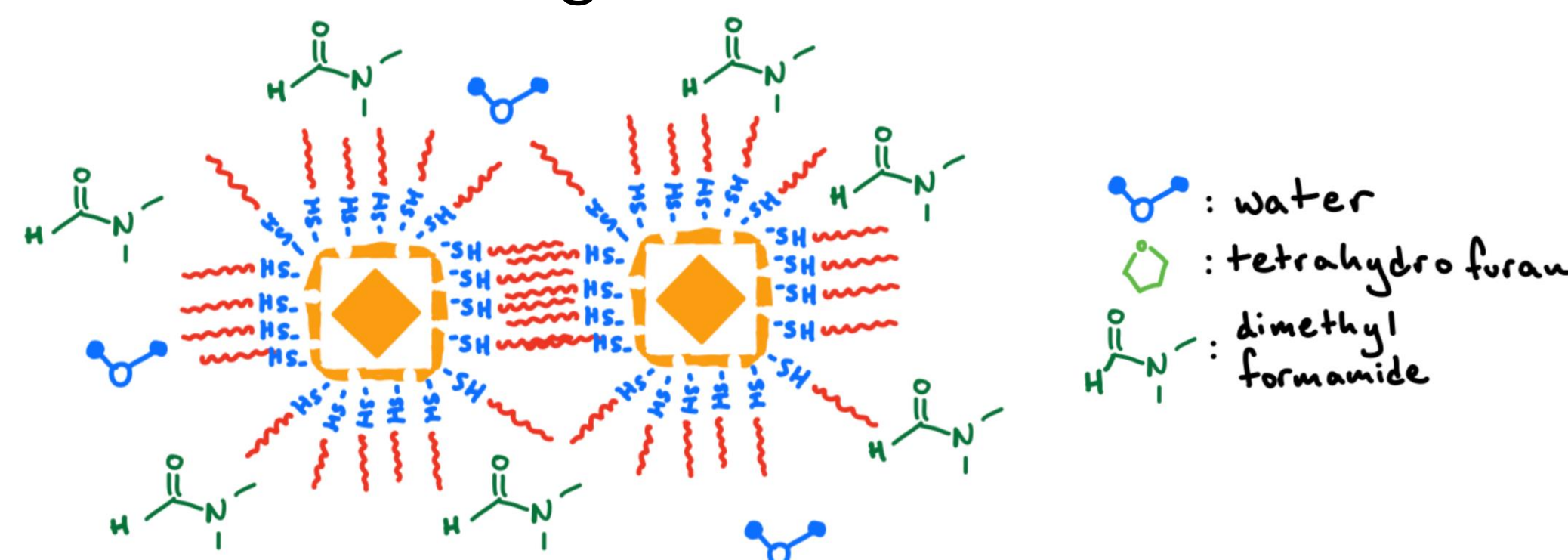
1. Nanoparticles with gold octahedral core and golden cage exterior were synthesized (1)



2. Ligands were exchanged from cetyltrimethylammonium bromide to thiol terminated polystyrene. (2)



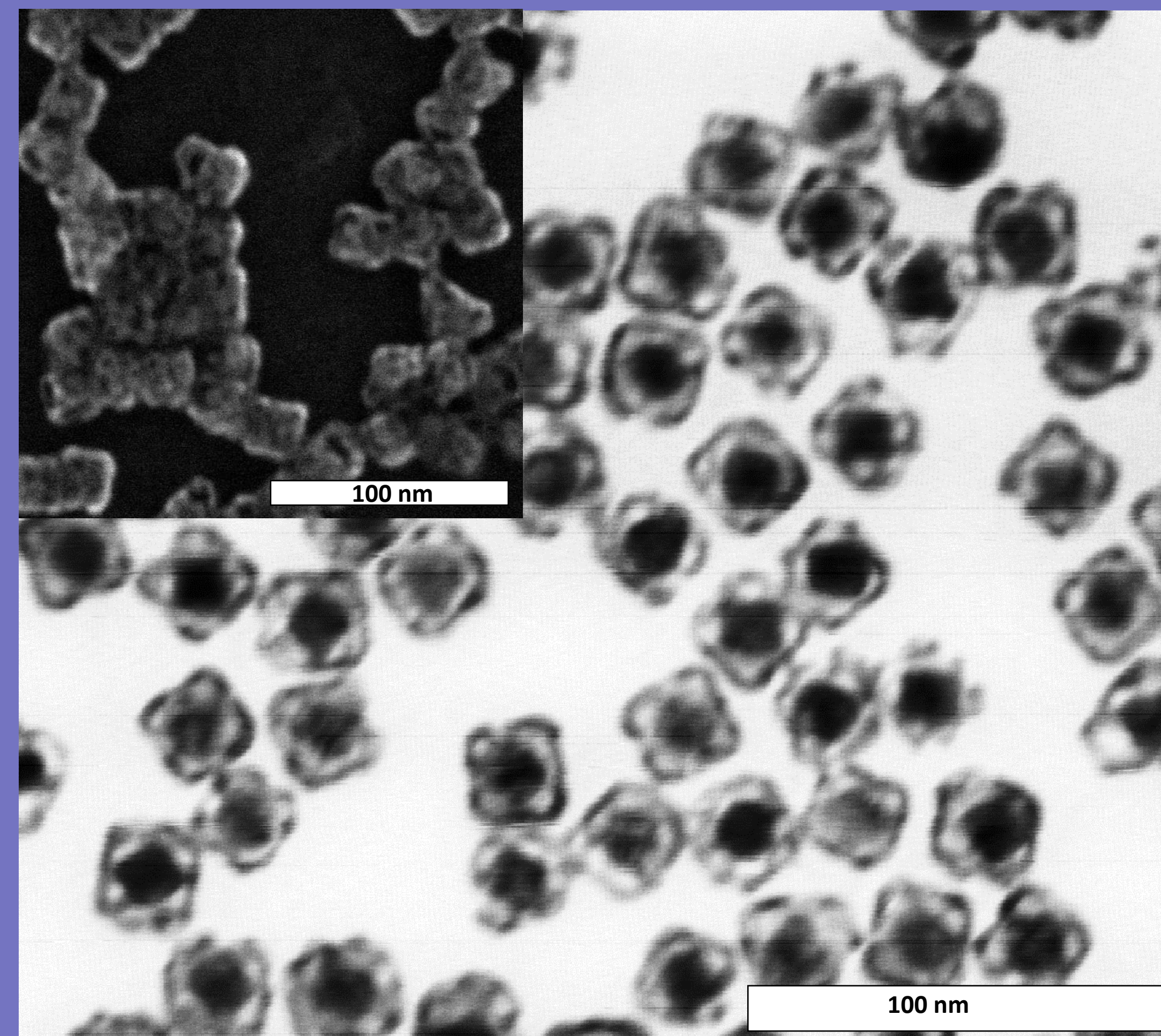
3. Self assembly was initiated by changing polarity of solvent to more polar by the slow addition of water, in a ratio of 15% water to 85% organic solvent.



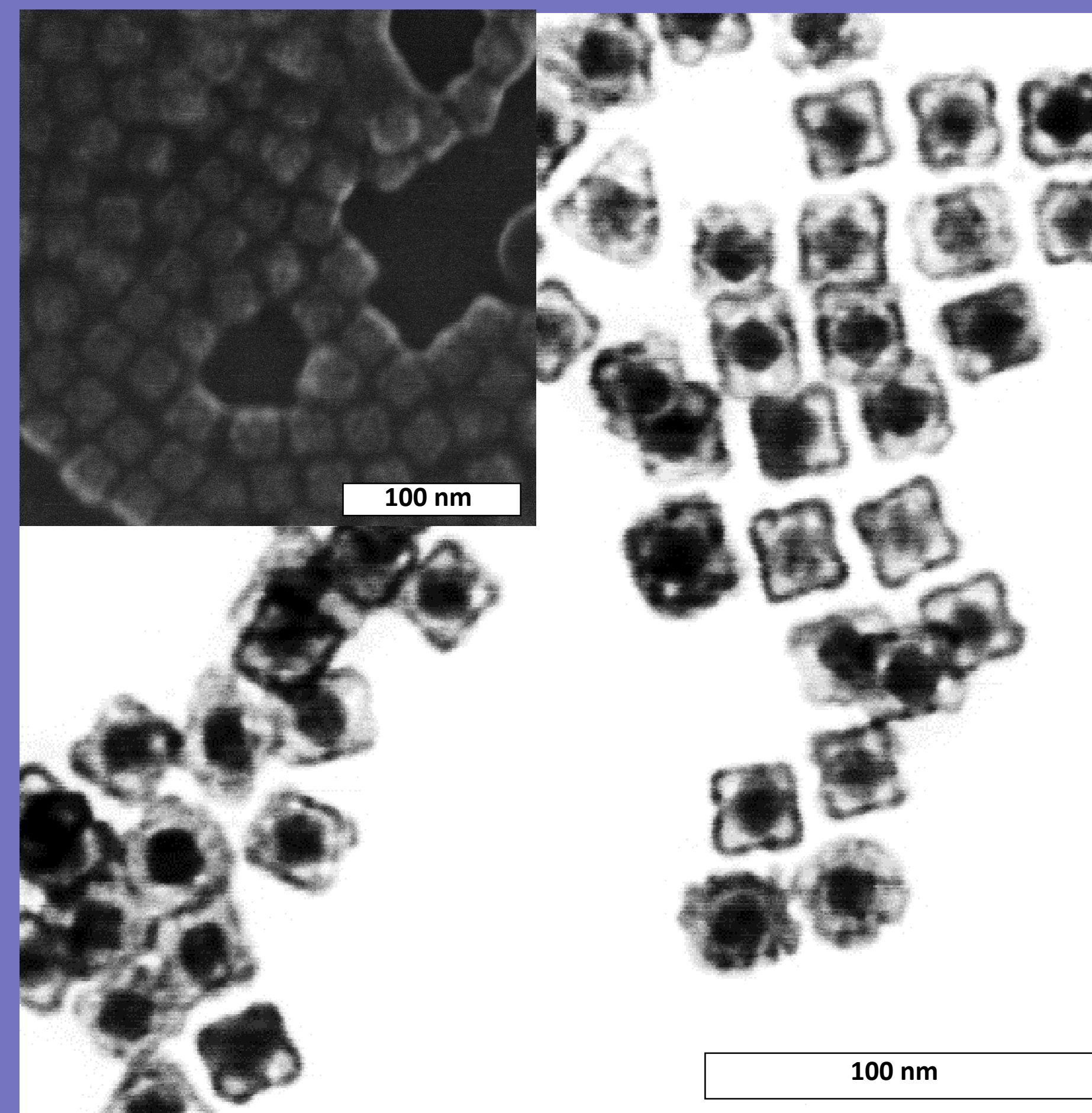
Results: Gold nanoparticles surrounded by nonpolar organic ligands self-assemble into chains when the polarity of a solvent shifts to more polar by the slow addition of water.

Pre self assembly – SEM/TEM

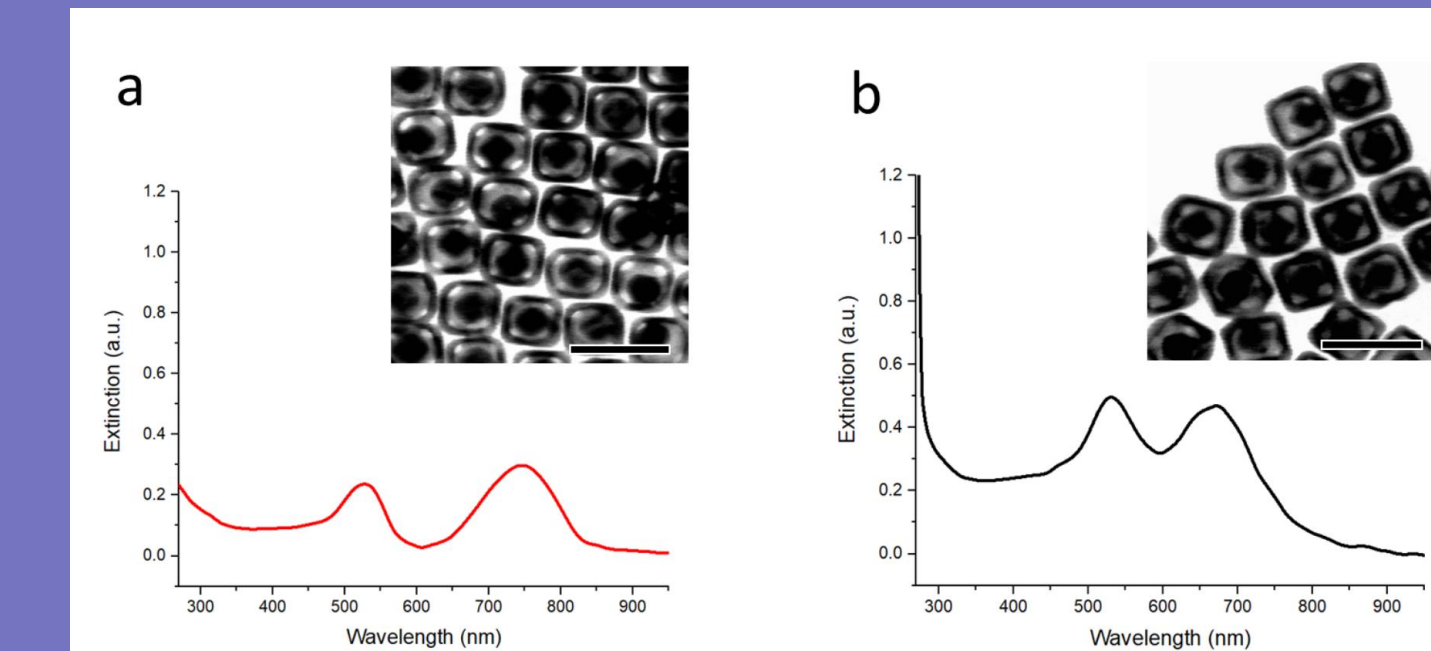
CTAB ligands



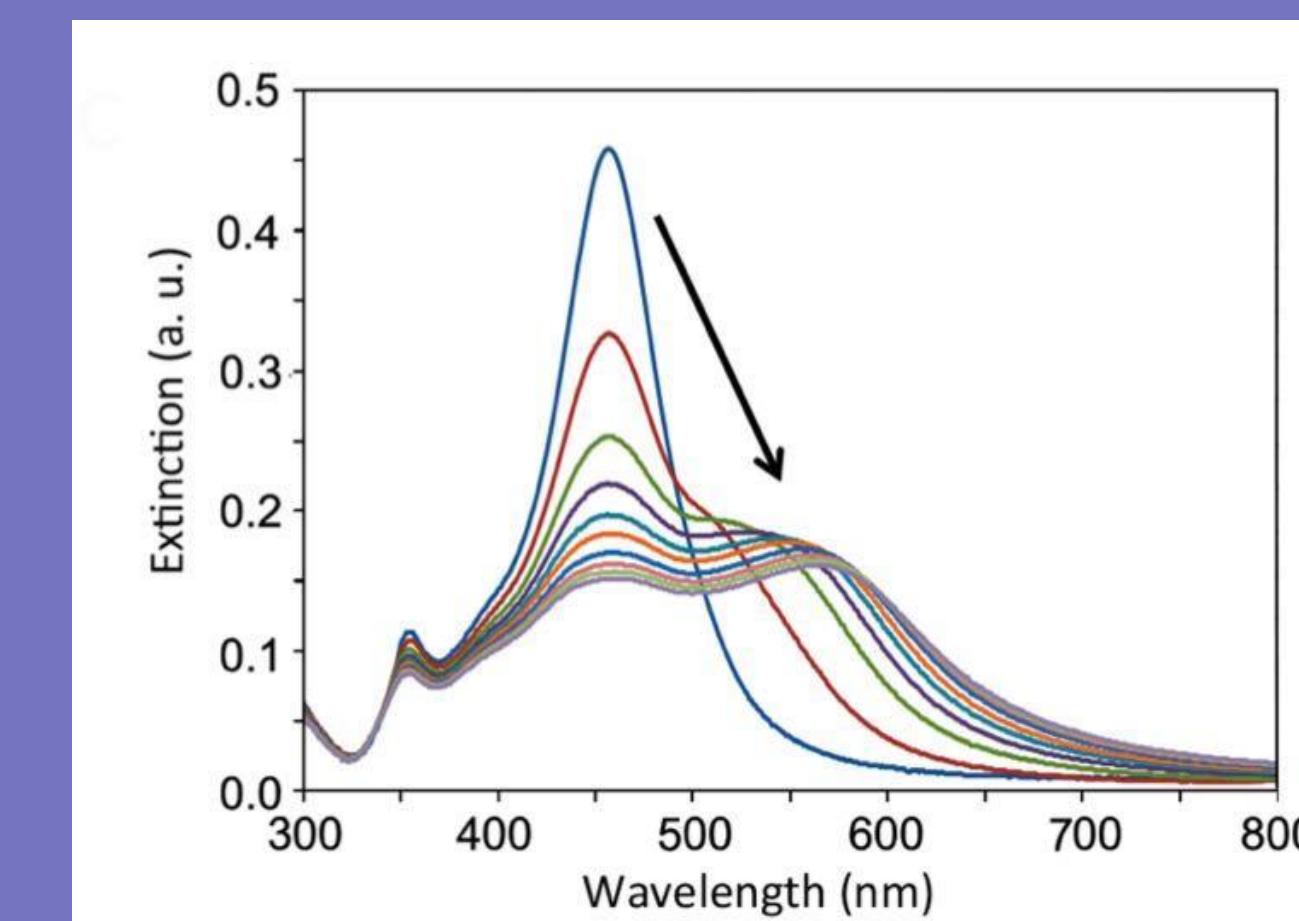
Polystyrene ligands



Predicted peaks depending on wall thickness (1)

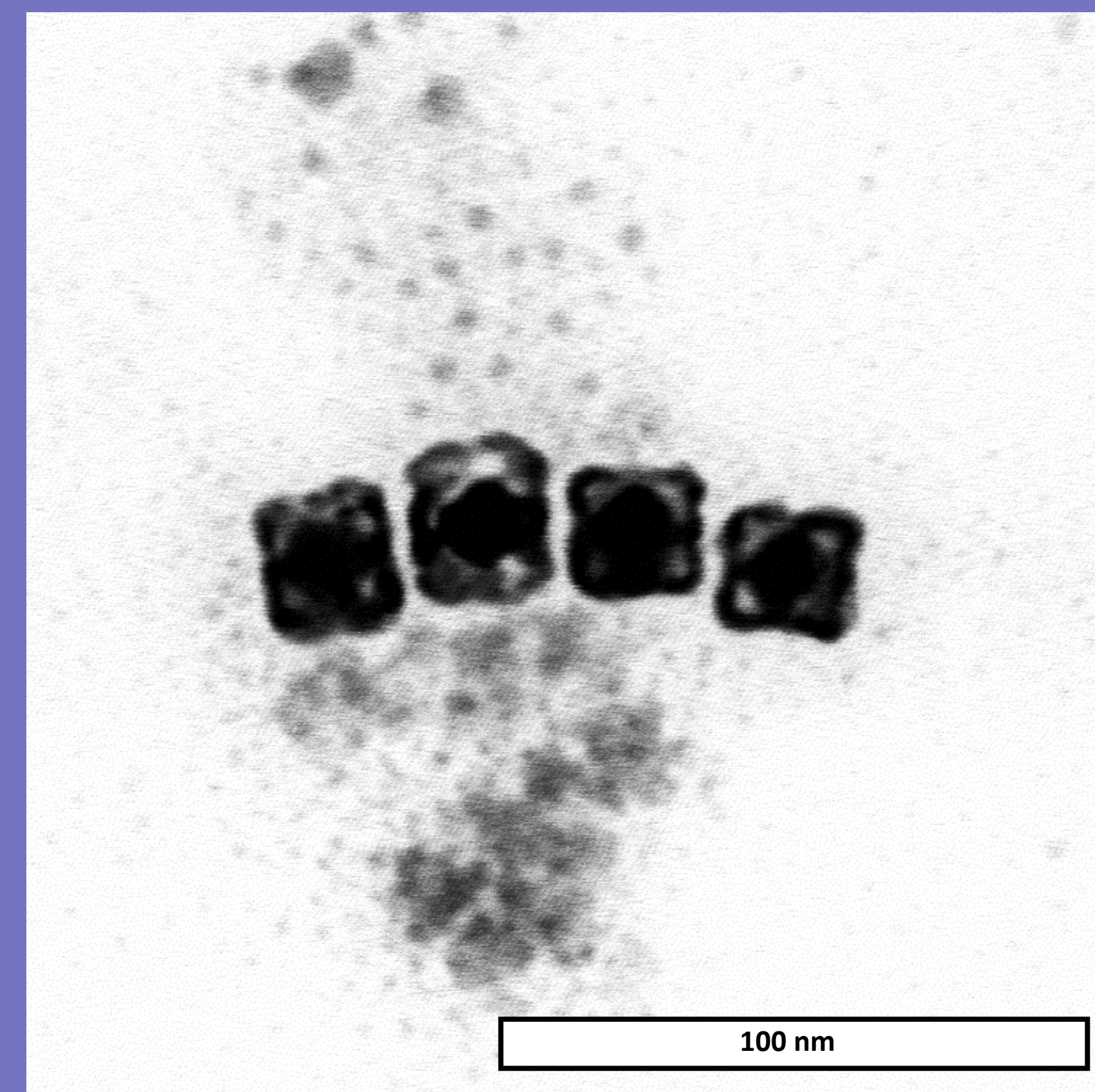


Predicted spectrum shift (2)



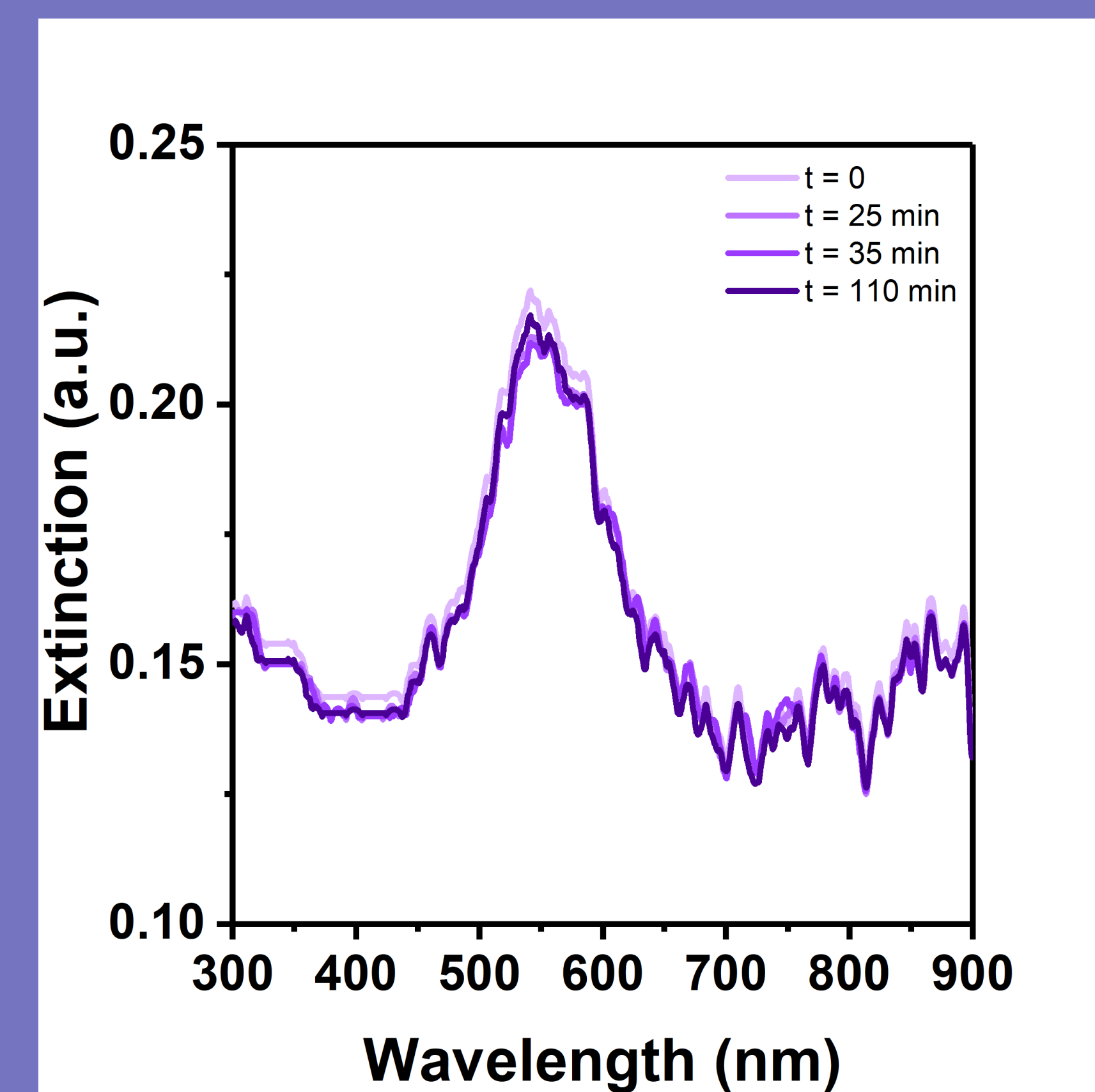
Post self assembly - TEM

Two hours post self assembly initiation



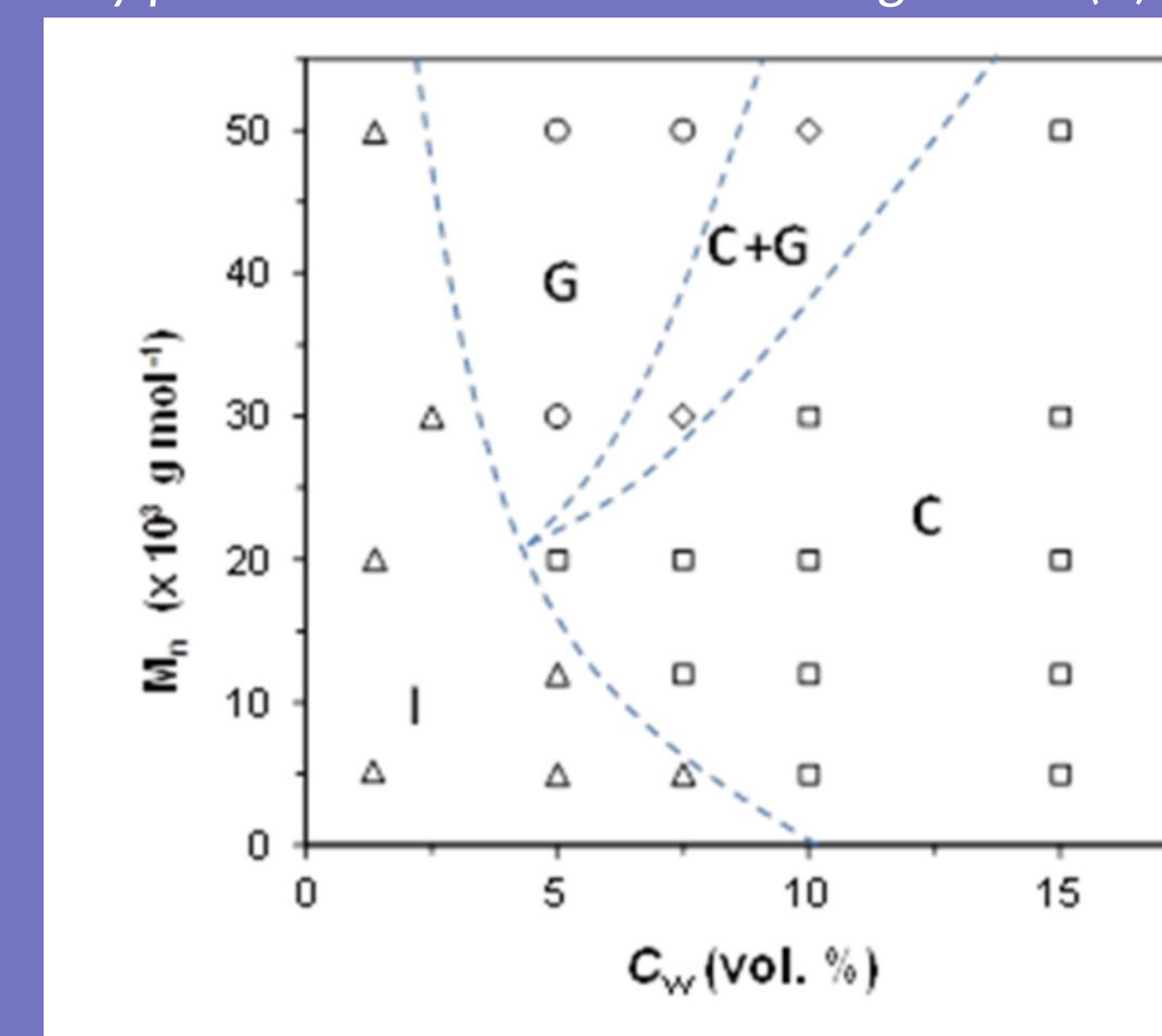
*This may be a drying effect, as no spectral change was observed

UV-Vis



Phase-like diagram

Why particles assemble as chains or globules (6)



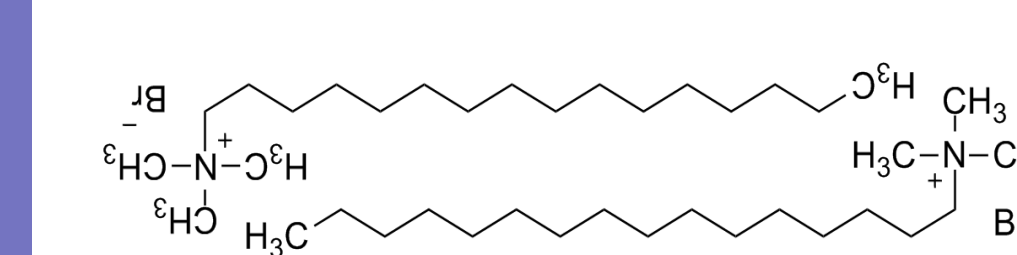
Conclusions

Since the UV-vis peaks did not shift over a significant amount of time (over two hours, which was more than sufficient in similar studies), the evidence provided are not sufficient to produce an accurate model for the self assembly of gold core-cage nanoparticles. This may be for a few reasons:

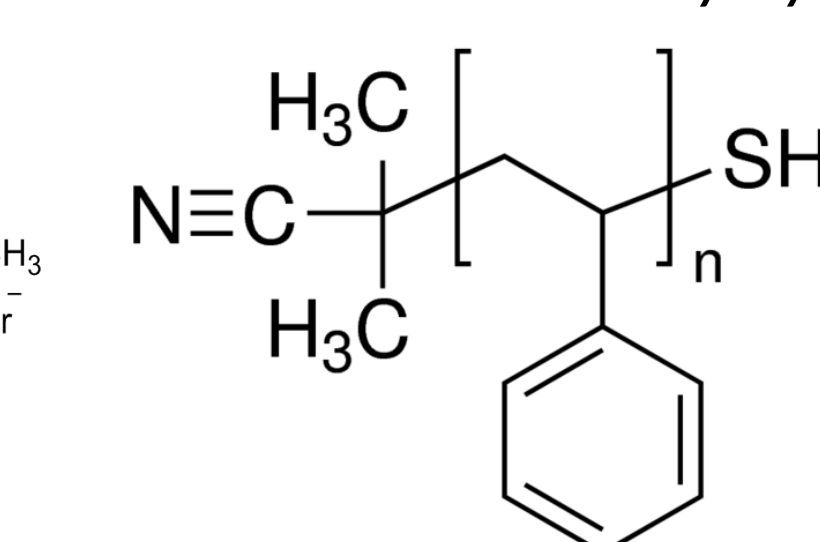
1. Gold core cage nanoparticles should usually have two prominent UV-Vis peaks. The particles I produced only had one prominent peak and a secondary, smaller peak. This may be a result of the ratio of the gap inside the particle to the cage wall thickness, or the silver cube interior not fully dissolving into solution.
2. Self assembly may have occurred in a small amount of particles, but not enough to influence the overall spectroscopy of the sample. This may explain why some TEM images captured organized structures after ligand exchange and self assembly initiation had been performed.

LIGANDS:

Cetyltrimethylammonium
Bromide (5)



Thiol-terminated Polystyrene (5)



PLASMONICS:

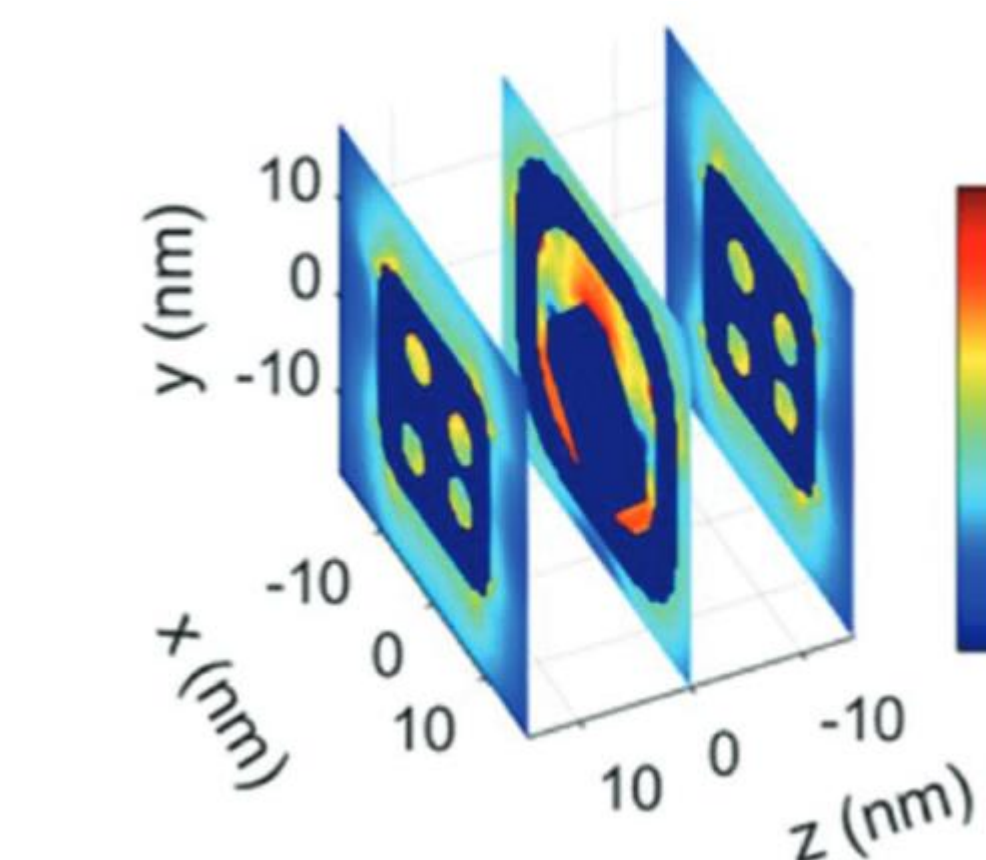
Localized surface plasmon resonance (LSPR) is an optical phenomenon that occurs in metallic nanoparticles subject to radiation with amplitude larger than their size. When the incident light reacts with electrons on the surface of a metal nanoparticle, plasmon oscillations are produced with different frequency depending on the material, size, and shape of the nanoparticle.(3) Shape affects resonance frequency much more than size. (4)

Oscillations produced in the surface electrons enhance the electric field (E-field) around particles. As particles approach at distances much smaller than the wavelength of incident light, the E-field between them interferes constructively, causing “hot spots” between particles.

FUTURE PLANS:

1. Create more reliable method for synthesis and self assembly of gold core cages.
2. Simulate electric field model for nanocage self assembly. (1)

Figure corresponds to FDTD calculation of E-fields under wavelength of 556 nm

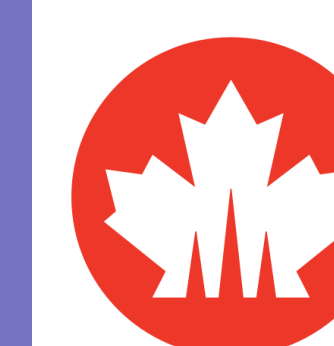


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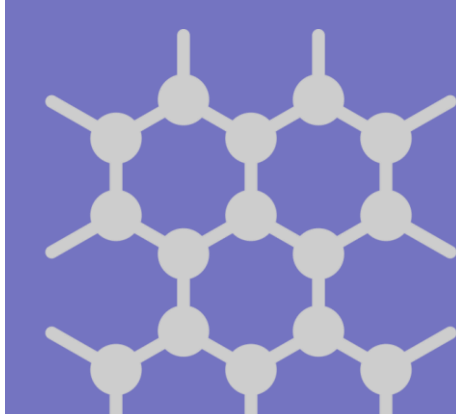
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- 5) Photos of compounds from Sigma Aldrich.
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Acknowledgments



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