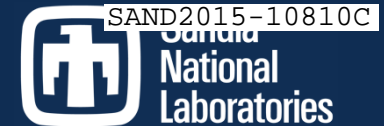


Exceptional service in the national interest



Effect of Seed Age on Gold Nanorod Formation: A Real Time, Microfluidic Investigation.

John Watt, Bradley G. Hance, Rachel S. Anderson, Dale L. Huber
*Center for Integrated Nanotechnologies,
Sandia National Laboratories, Albuquerque, New Mexico, USA*

jd watt@sandia.gov

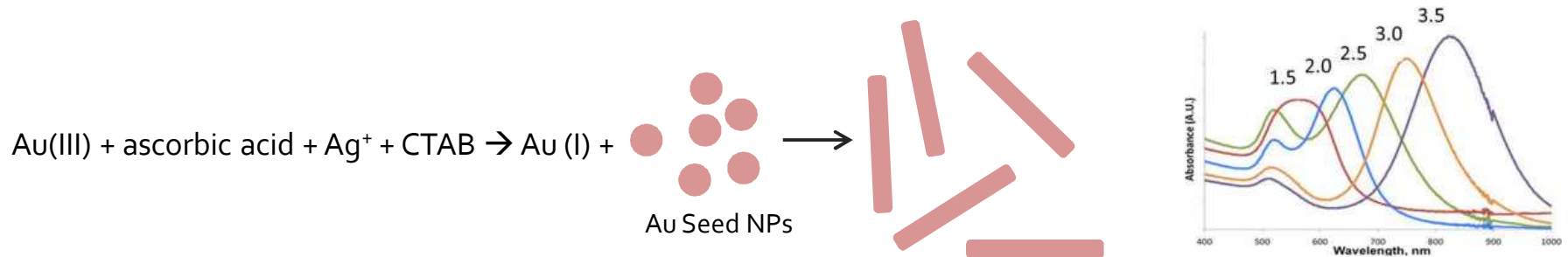


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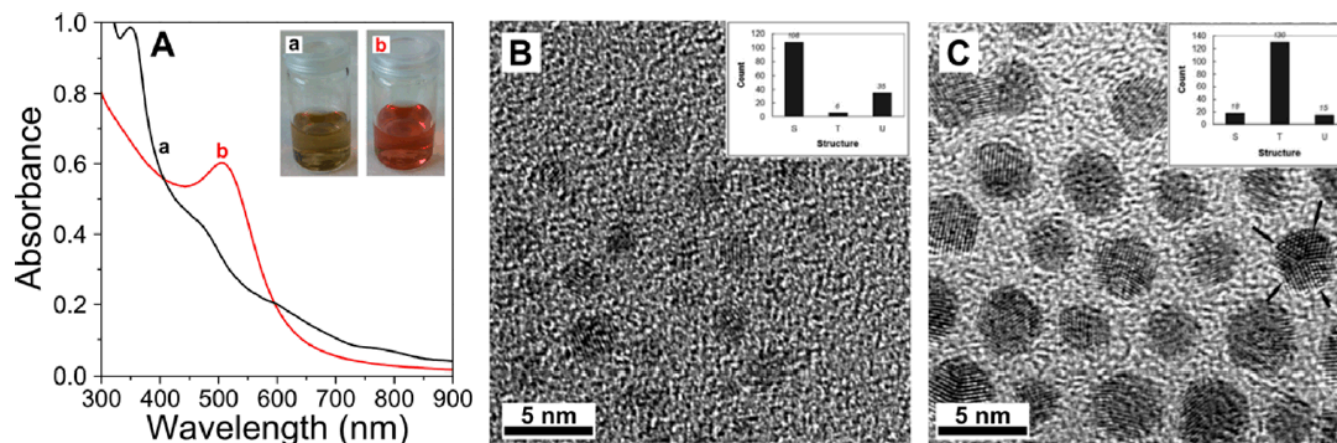
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- Well established syntheses:
 - Seeded growth using cetyltrimethylammonium bromide (CTAB) is the most popular.
 - Fine tuning of the longitudinal plasmon resonance.



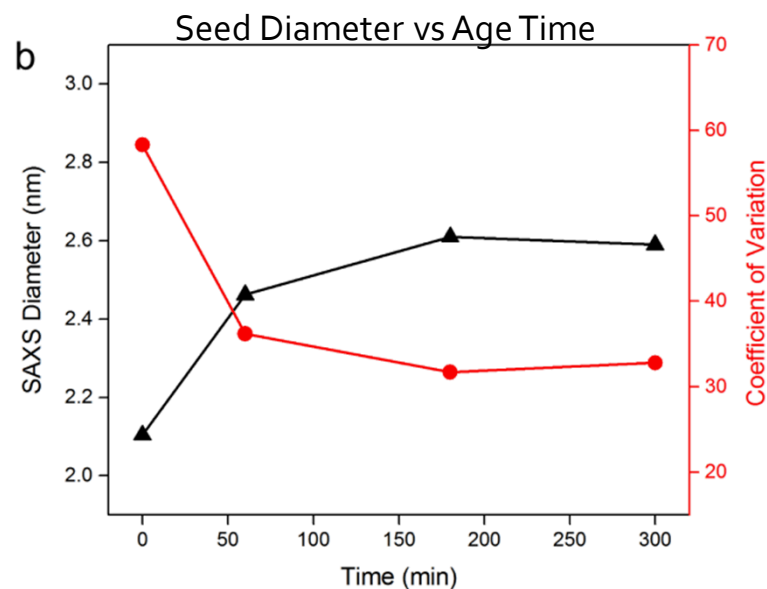
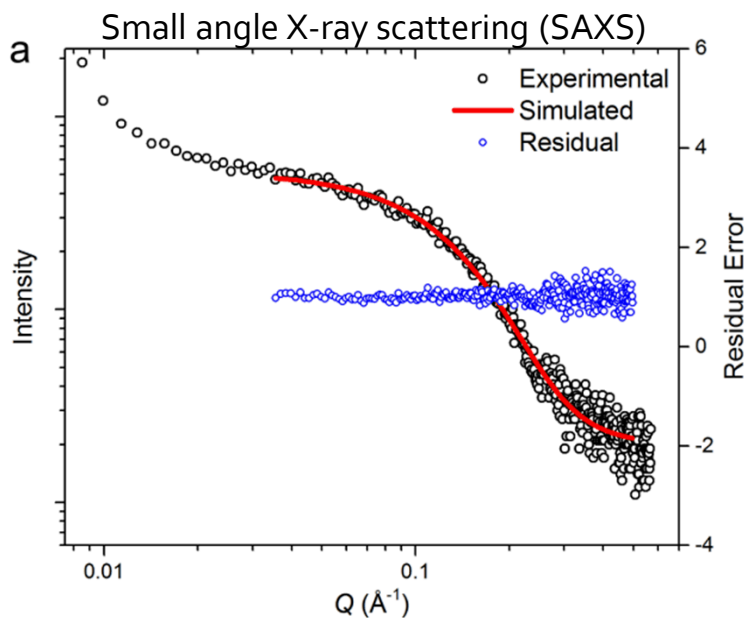
- Selective capping by CTA-Br-Ag⁺, lateral deposition of Ag, formation of ion channels of the CTAB layer, incomplete CTAB coverage etc. all assume some structural anisotropy is already present.
- Reproducibility is a big problem e.g.;
 - Impurities in CTAB are important – **buy the same Lot #.**
 - Metal salt (HAuCl₄, AgCl) stock solutions need to be stored out of direct sunlight.
 - pH

- Small gold nuclei (typically < 5 nm) act as sites for anisotropic growth.
- Structure has a direct effect on the resulting nanorod;
 - Citrate capped/reduced seeds (~ 5 nm) lead to multi-twinned nanorods.
 - CTAB capped seeds ~ 2 nm lead to single crystal nanorods.



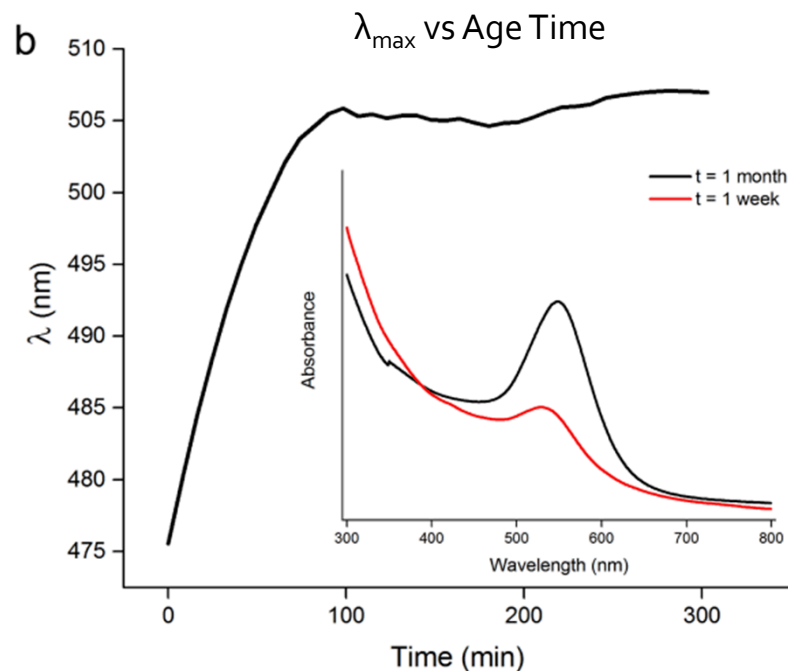
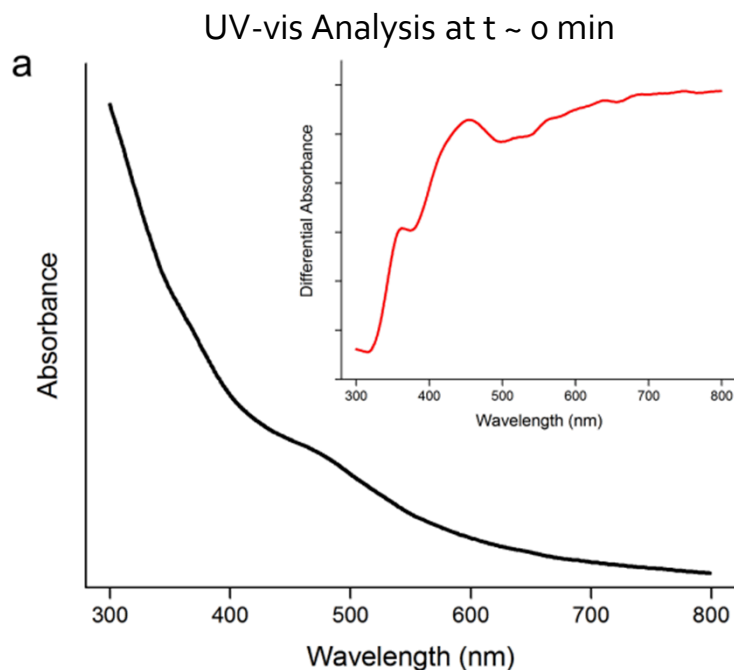
- Large free surface energy, subject to aging effects.
- Seed ages range from 5 min to up to 30 days.
- Seed age should have a direct effect on nanorod formation.

- Synthesized by rapid reduction of HAuCl_4 by NaBH_4 in CTAB at 30 °C.
- TEM analysis unsuccessful due to uncontrollable aging.

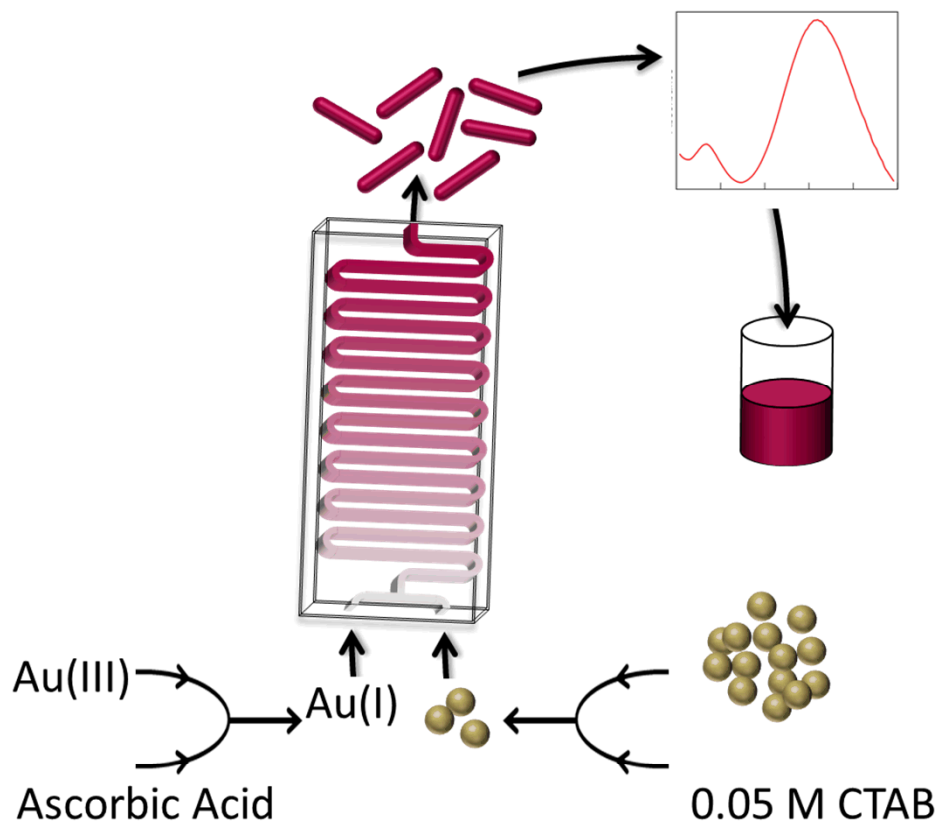


- Small angle X-ray scattering (SAXS) shows that there is a **significant population of gold nanoparticles < 2 nm at $t \sim 0$.**

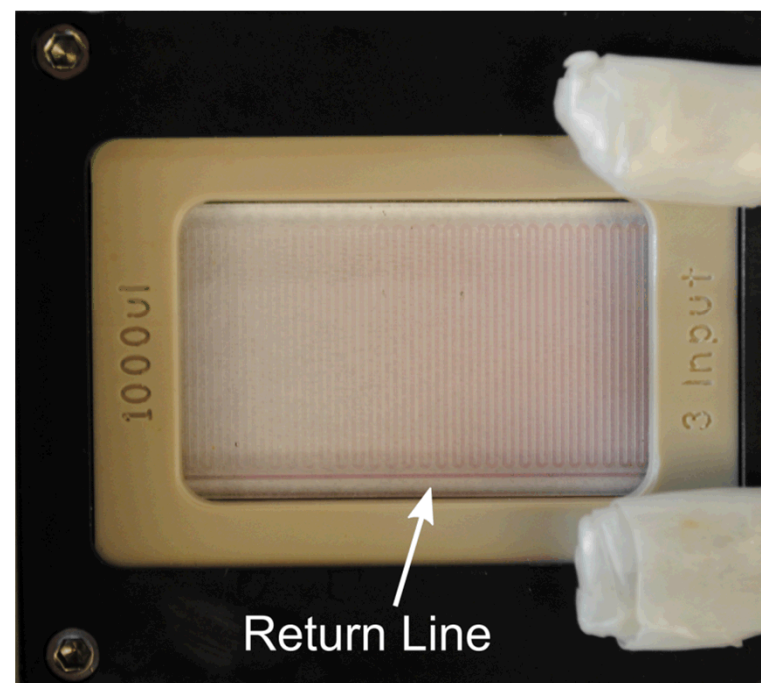
- UV-vis analysis at $t \sim 0$ shows molecular like transitions characteristic of NPs < 2 nm in size.

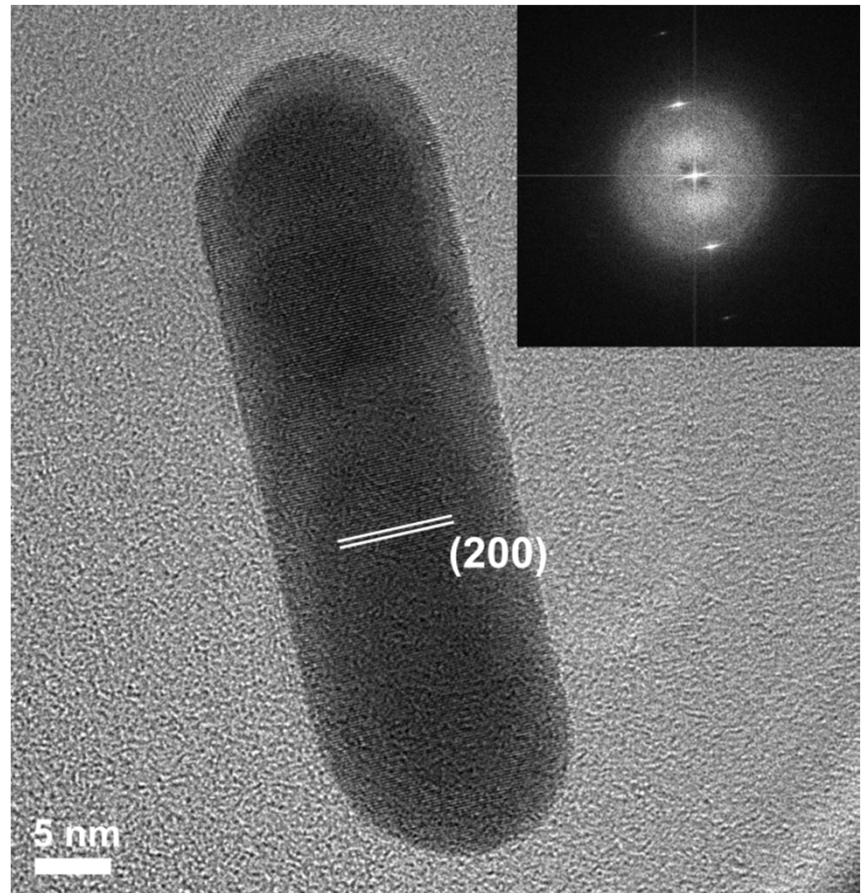
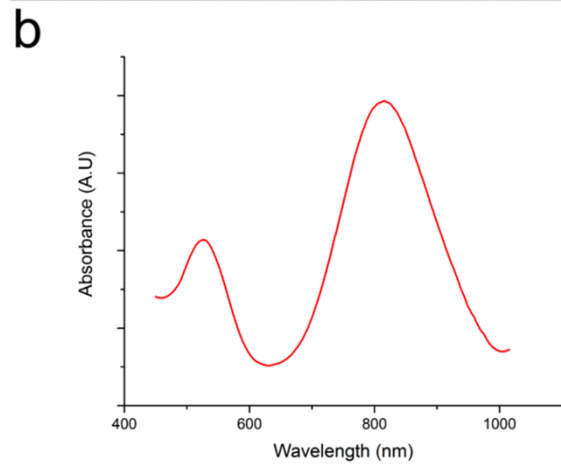
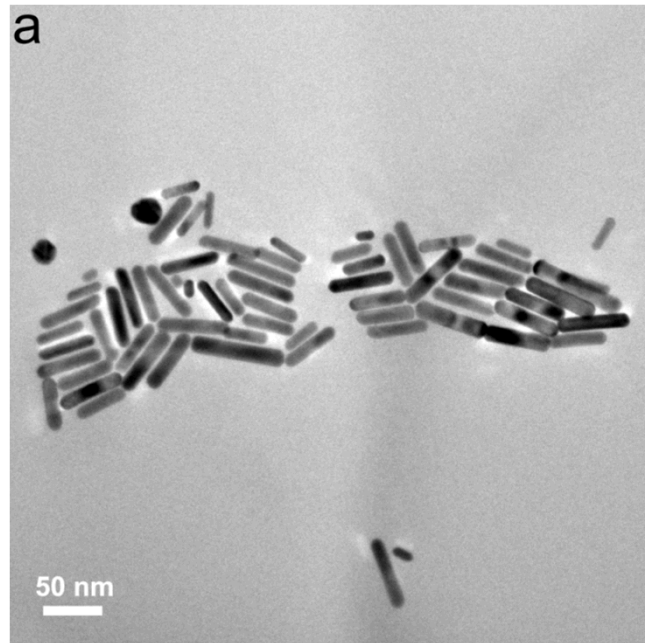


- Seeds 'ripen' with age.

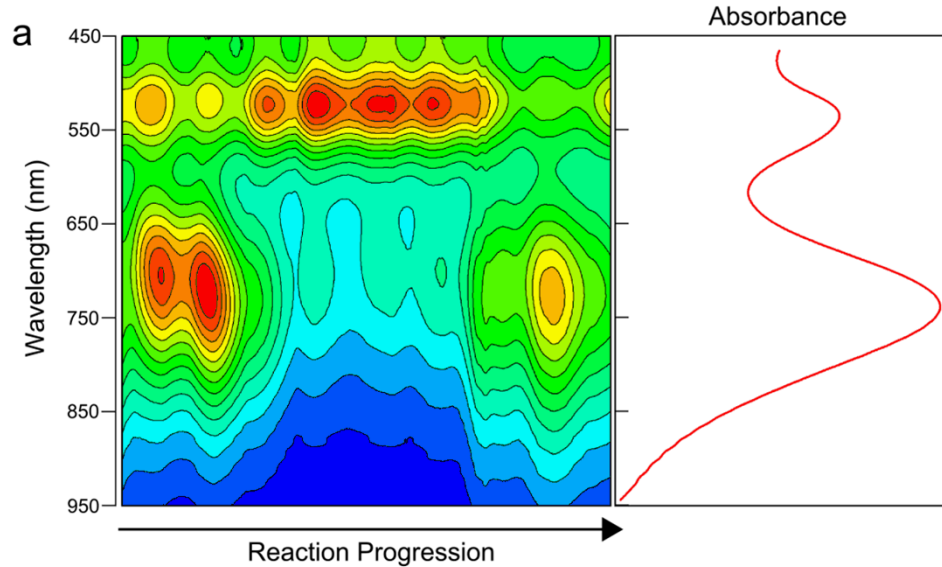


- Gold seeds synthesized with CTAB/ NaBH_4 .
- Aged at 30°C .
- Injected continuously.

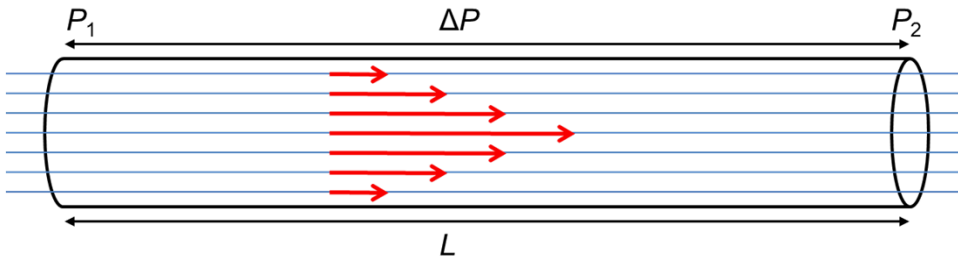




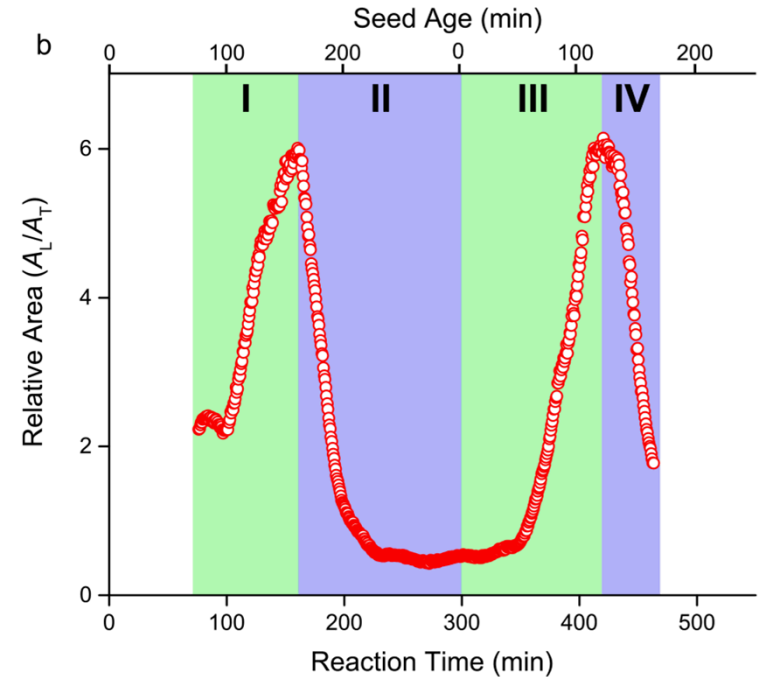
In-situ Aging – 2D Contour Plot



$$v = \frac{\Delta P}{4\mu\Delta x}(R^2 - r^2)$$

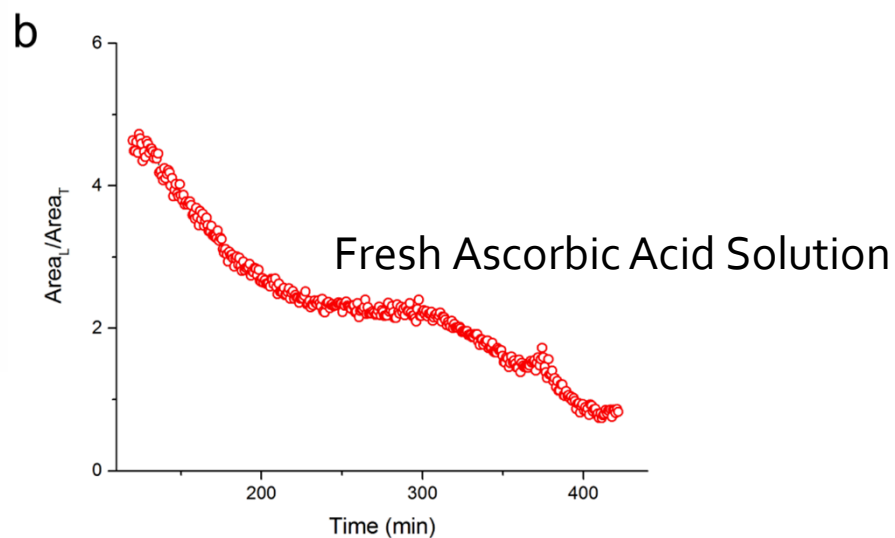
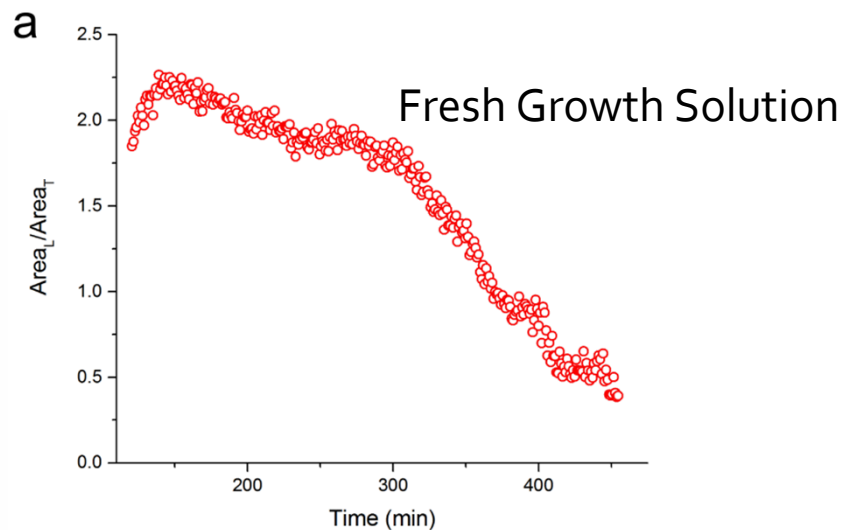
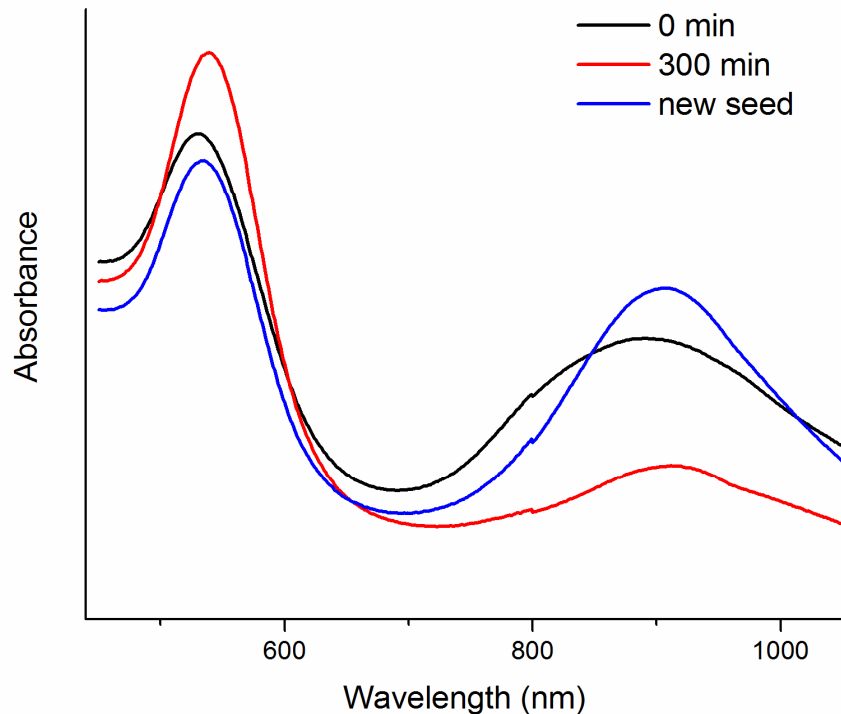


Nanorod Yield vs Seed Age

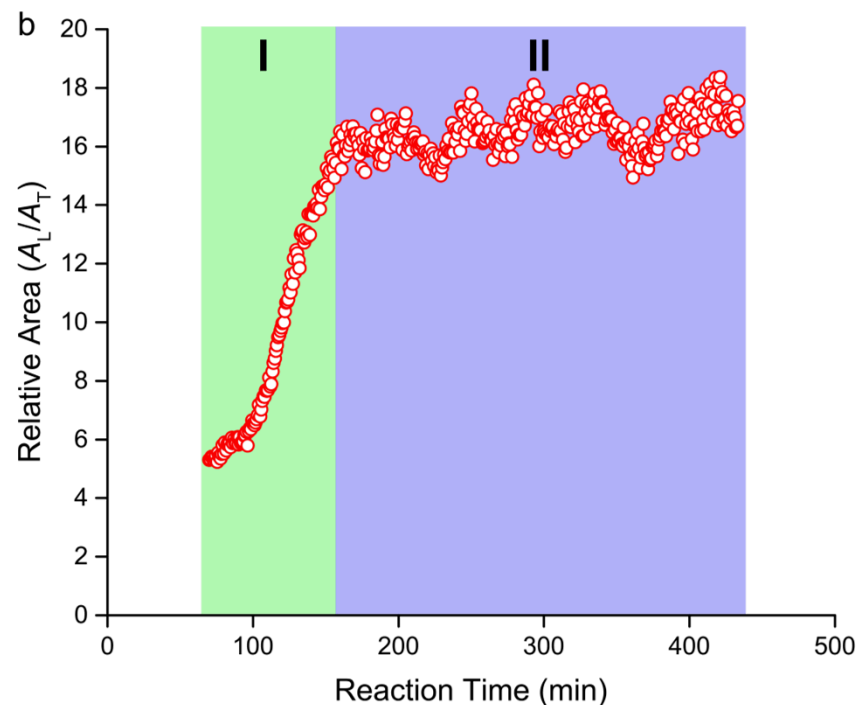
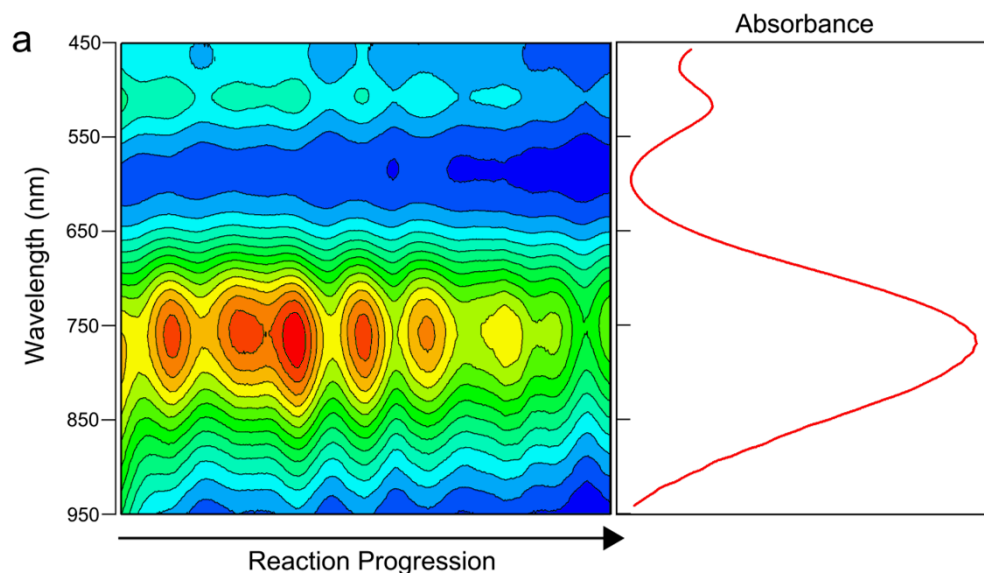


- Direct observation of the effect of seed age on gold nanorod formation.
- As seeds age, nanorod yield decreases.

- Ex-situ confirmation.

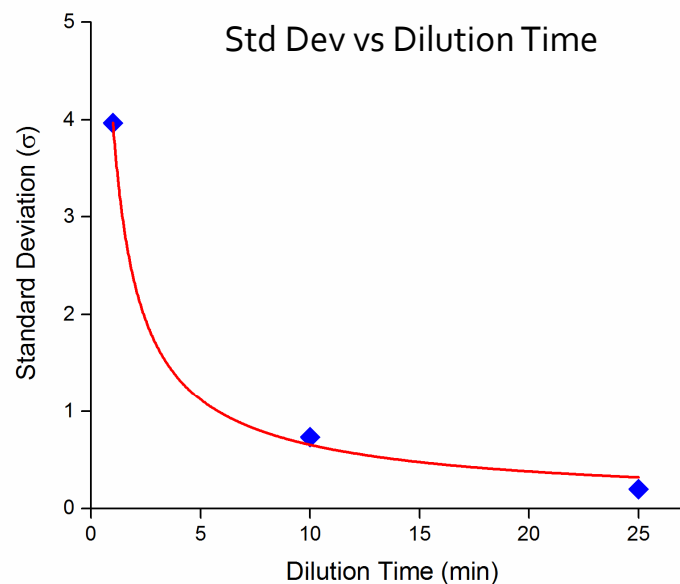
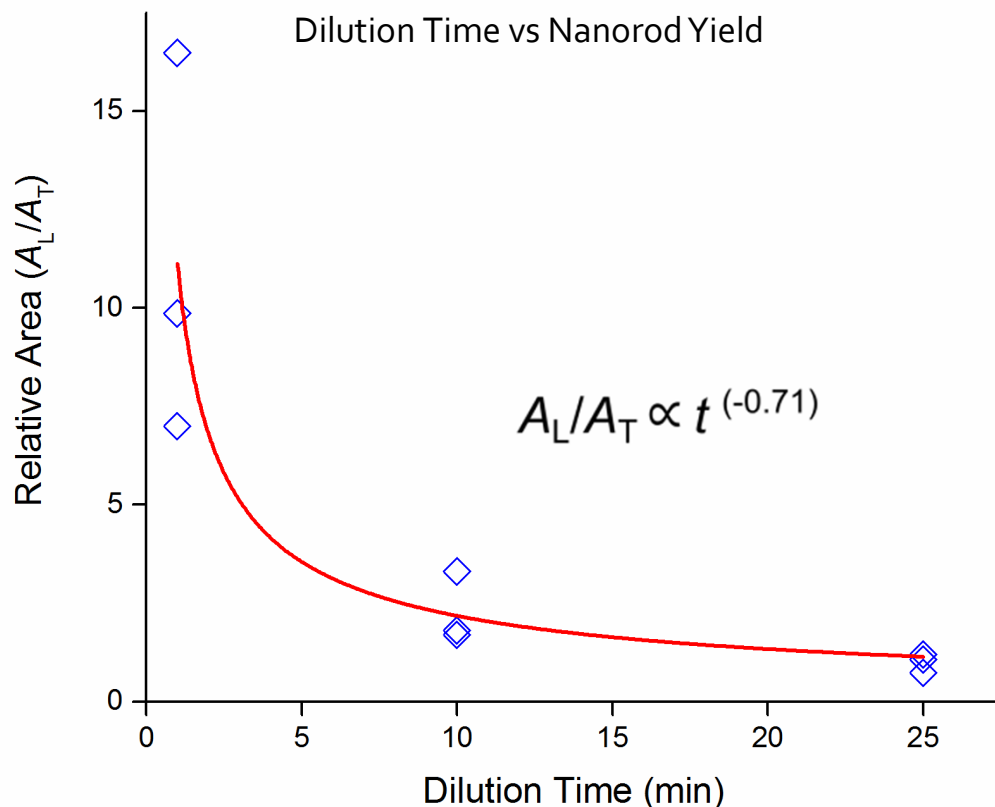


- Thirty fold dilution of seed solution 1 min following synthesis.

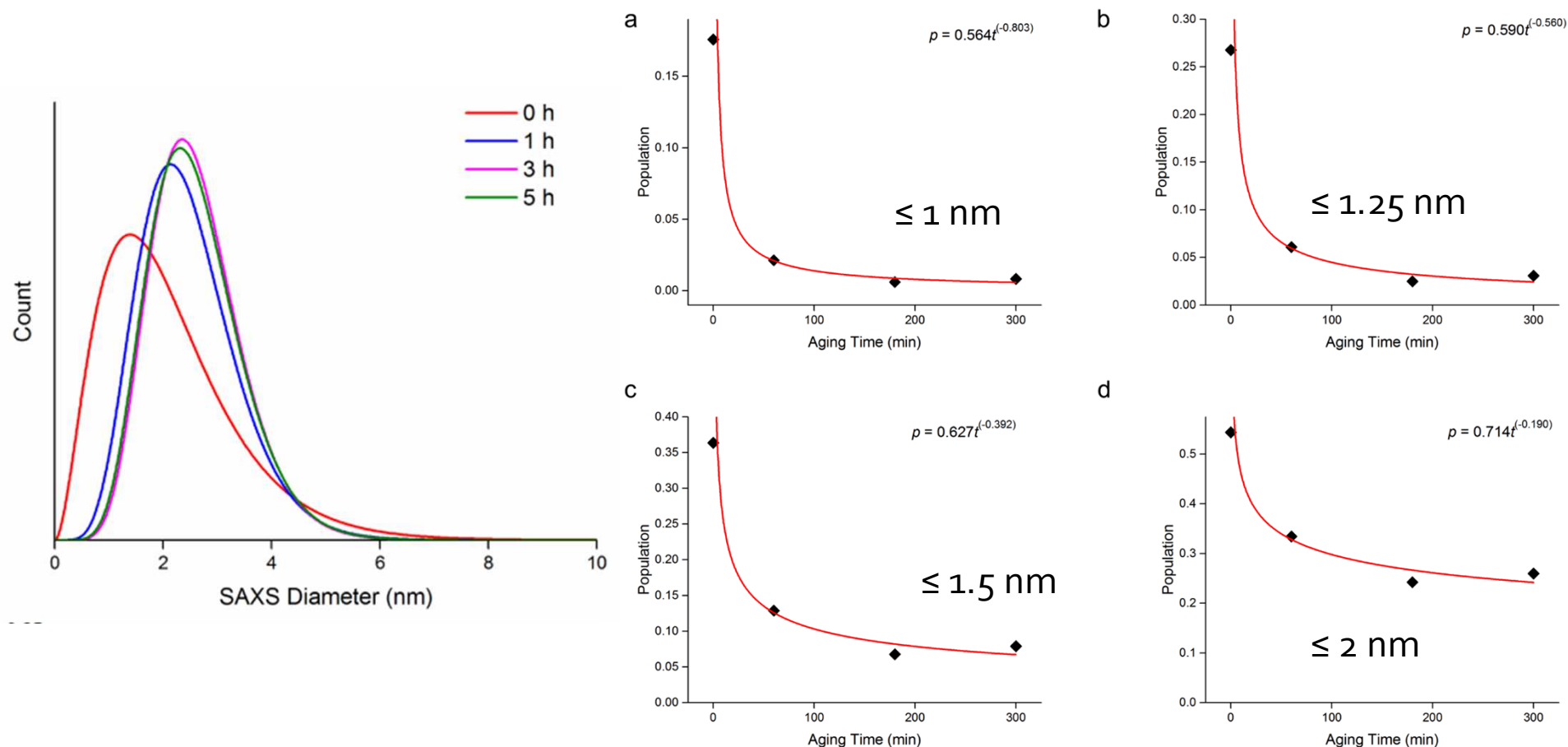


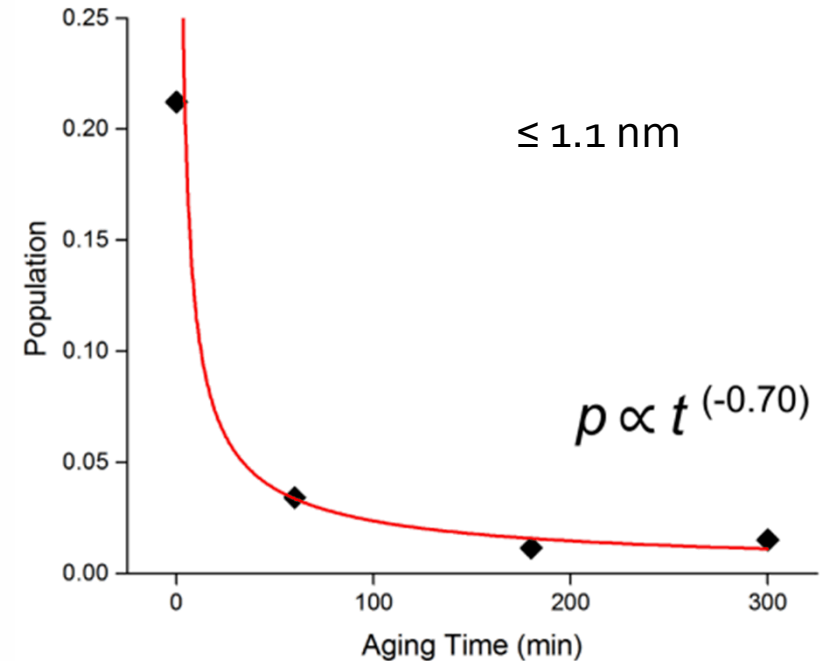
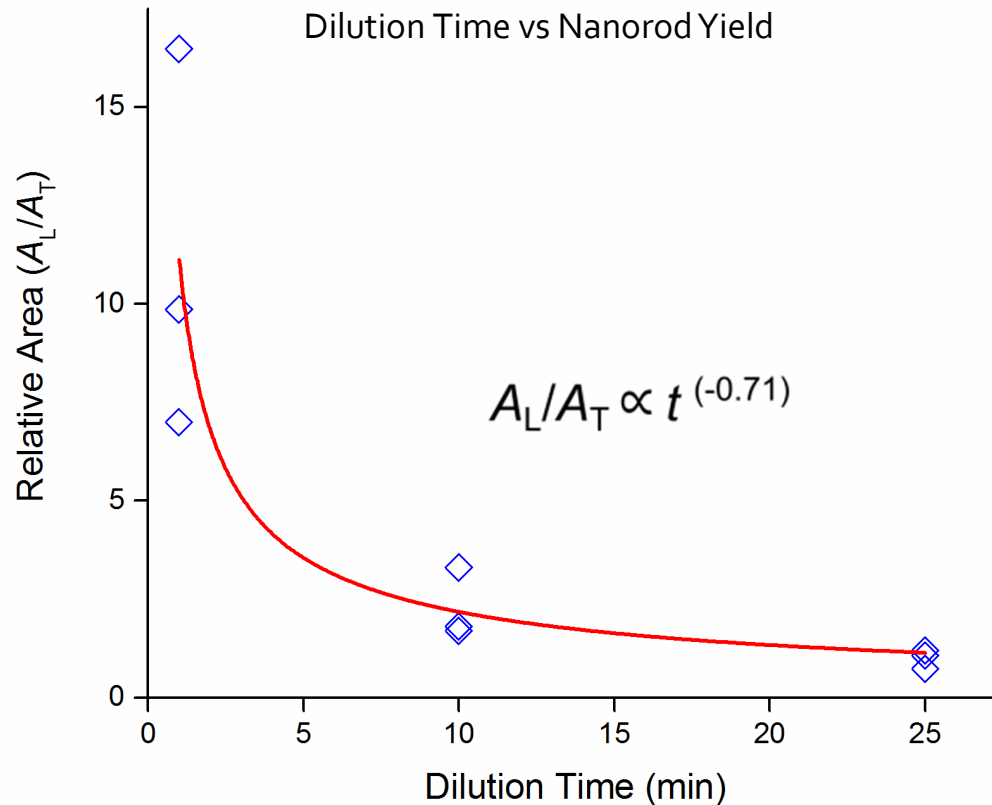
- Continuous production of gold nanorods in good yield.
- A fresh seed solution is critical for the formation of gold nanorods.

- Additional dilutions made at 1 min, 10 min, 25 min and injected continuously on-chip to form gold nanorods.
- Average yield after steady state is reached.



- From SAXS analysis we can observe how certain populations of seeds change with time.





- The rate of disappearance of **nanoparticle seeds < 1.1 nm in size**, matches closely with the rate of decrease in nanorod yield.

- Ultrasmall < 1.1 nm gold seed nanoparticles are responsible for gold nanorod formation.
- Soft template method requires a larger size and can therefore not be applied.
- Au(I) to Au(0) reduction was recently shown to only occur at the gold surface.
- Small gold nanoparticles are known to be catalytically active.
- High surface curvature, incomplete CTAB bilayer coverage, high surface energy.
 - Leads to the emergence of anisotropy.
- Dilution can halt aging and allow us to investigate the structure of the seeds closer to their natural state.

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