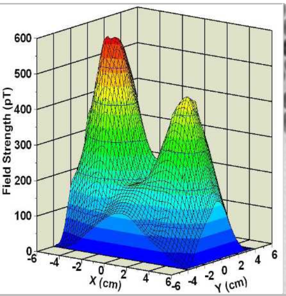
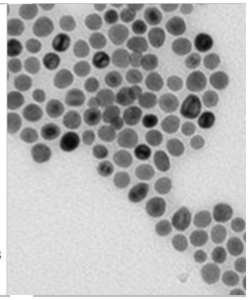
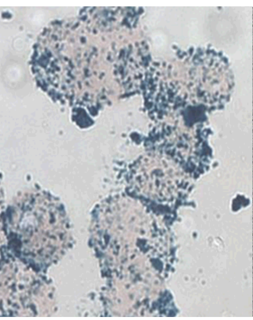
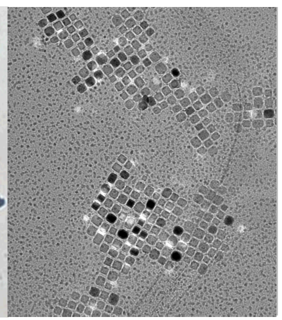
SAND2016-3927C

Controlling Magnetic Properties of Nanoparticles with the Extended LaMer Mechanism









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Nanoparticle Size is Critical in Biomedical Applications

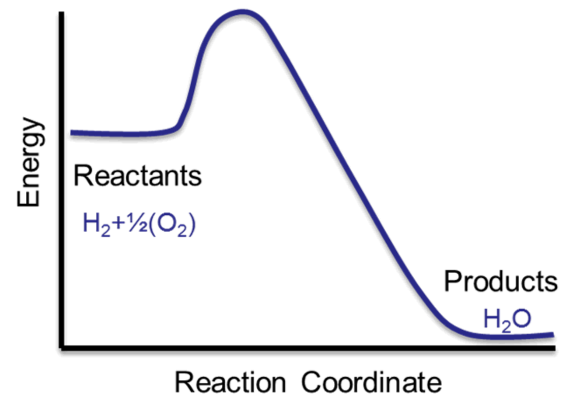
- Magnetic properties vary dramatically with size (e.g. particle moment, colloidal stability, relaxation time, etc).
- Many applications use magnetic nanoparticles: Magnetic resonance imaging (MRI), Magnetic Particle Imaging (MPI), Magnetic Relaxometry (MRX), Hyperthermia.
- Market acceptance and regulatory approval for medical use requires consistent performance.
- Many of these depend upon the superparamagnetic relaxation time (MPI, MRX, hyperthermia) which has extraordinary size dependence.

MRX system for biodetection
www.seniorscientific.com

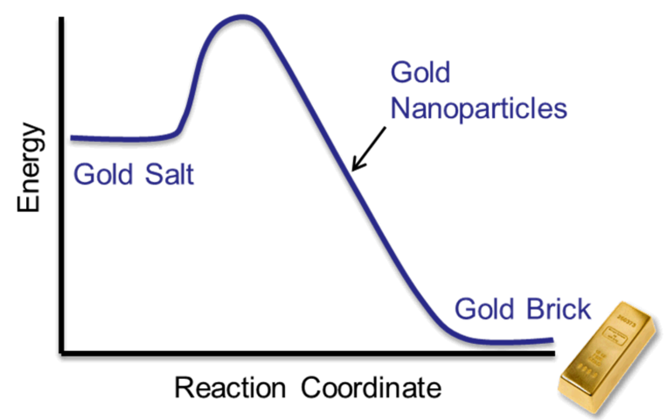
Nanoparticle Size Control

- Nanoparticles are a kinetic product.
- Kinetic control of nanoparticle size
  - Reproducibility
  - Focus on systematic size variation

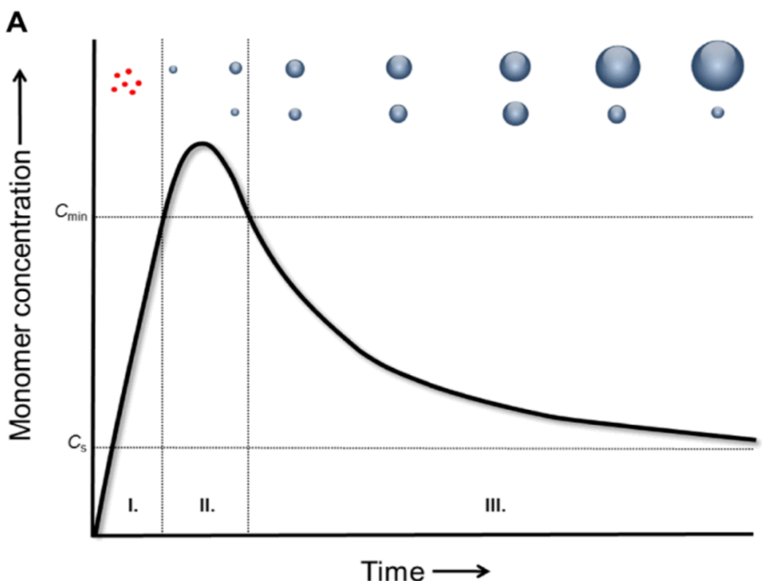
"Normal" Chemistry



Nanoparticle Chemistry



LaMer Mechanism



LaMer and Dinegar, JACS 1950. 72(11): p. 4847-4854.

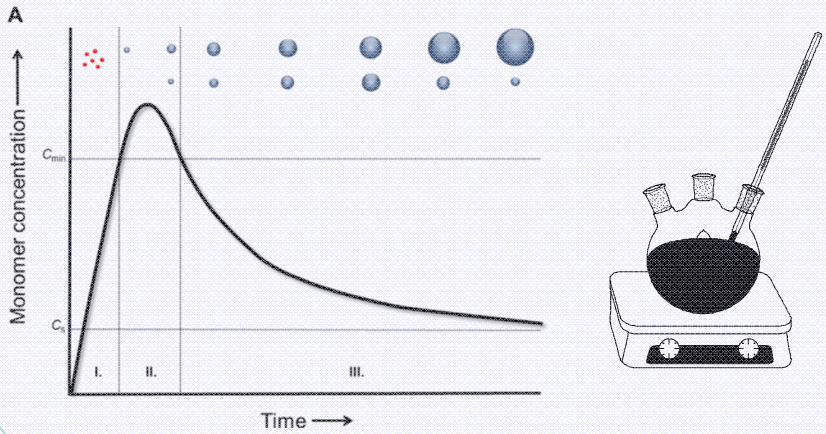
- Closed system
  - Eventual size at reaction completion is determined by the number of nuclei formed.
  - Nucleation is chaotic, non-linear and very hard to systematically control.
  - Nucleation is hard to reproduce using different hardware or in different locations (altitude, humidity).

Our Approach

- Control everything that can reasonably be controlled.
- Accept that nucleation can’t be conveniently controlled.
- Nucleate, then grow to appropriate size through precursor addition.

Extended LaMer

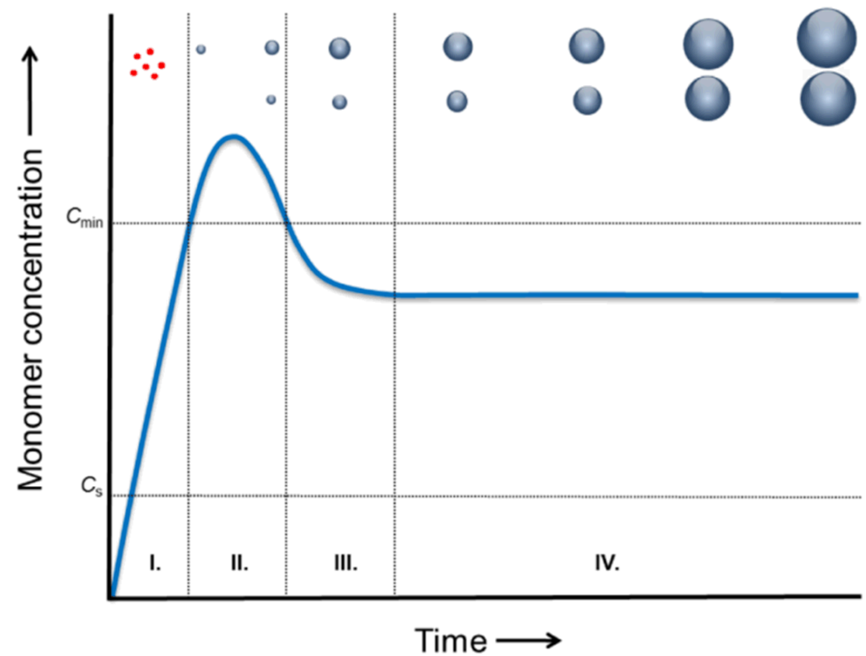
Classic LaMer



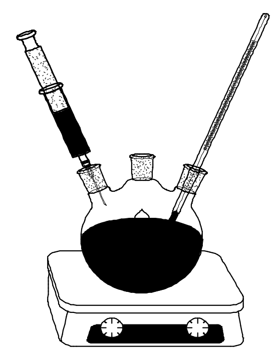
Two goals of this work

- Systematic size control
- Improved reproducibility

Extended LaMer



Continuous addition of precursor



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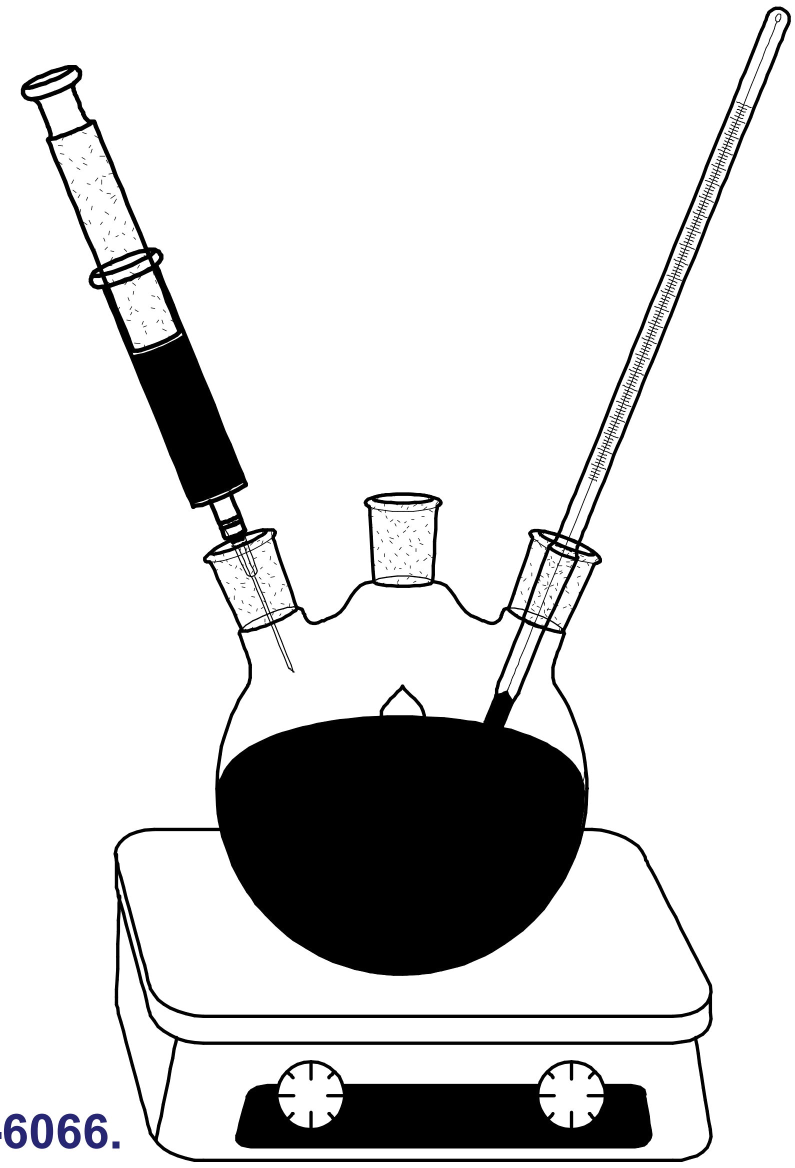
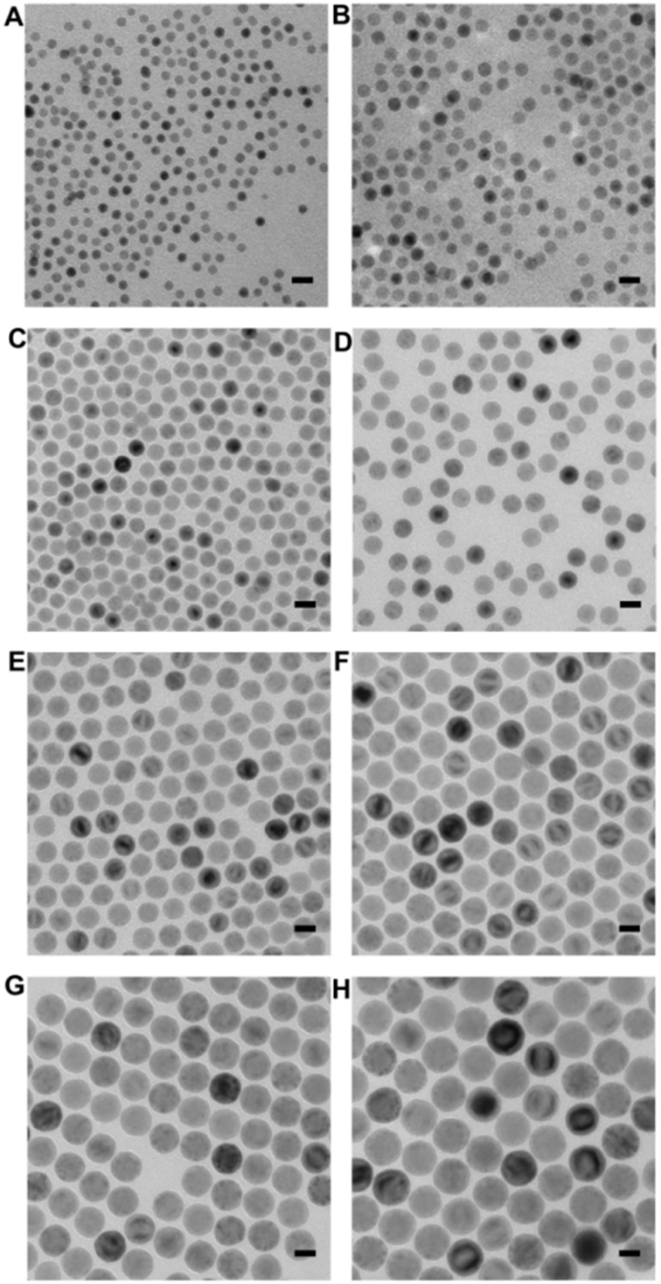
Reaction Scheme

- Use a stoichiometric Fe oleate source derived from $Fe(acac)_3$.
- Constant temp. controlled to ± 0.25 ° C
- <u>Temperature stabilized in absence of precursor.</u>
- Continuous dropwise addition into constant temperature hot solvent.
- We control size with time of addition (stoichiometry), not heating rates.

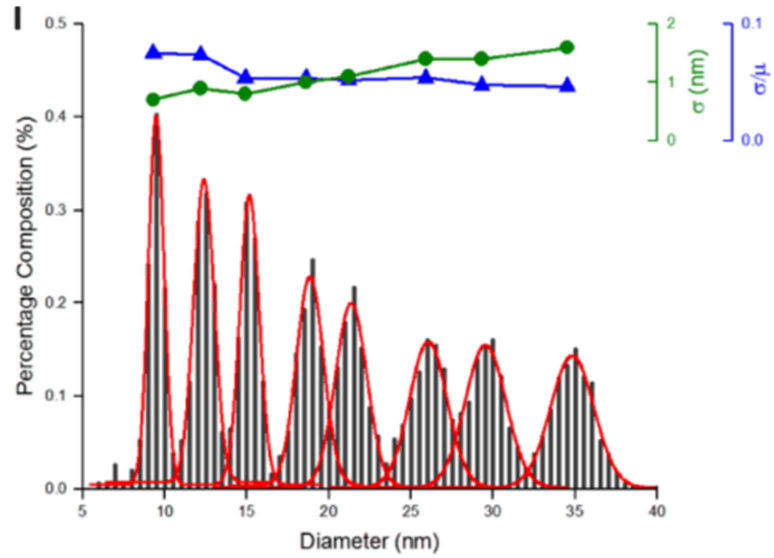


Vreeland, et al. Chem. Mat. 2015, 27 (17), 6059-6066.

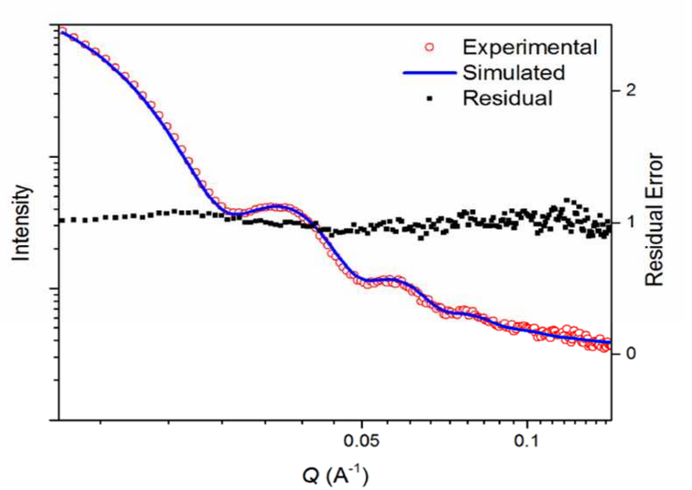


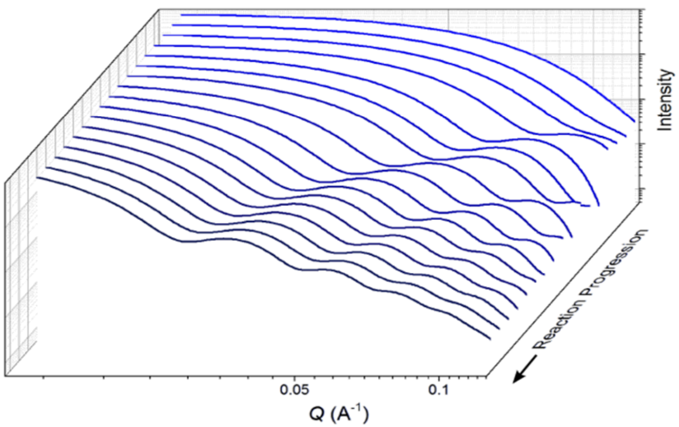
Size Monitored by TEM

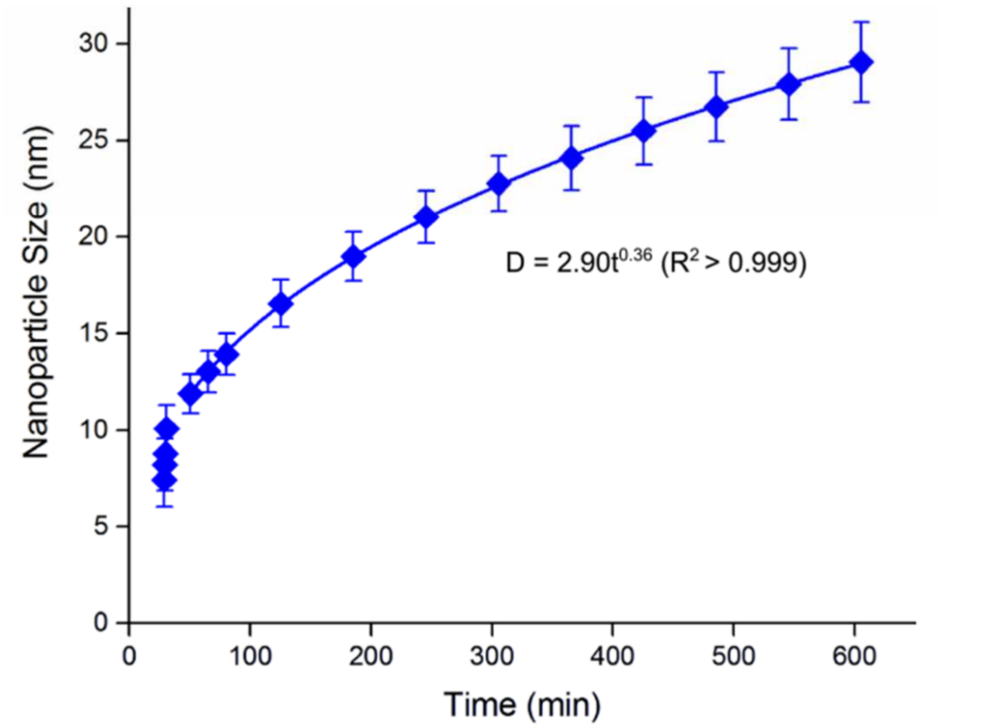
- Scale bars are 20 nm
- Aliquots are from a single reaction
- Particle are round and single crystal (HRTEM)
- Size focusing occurs early in the reaction



Size Control with Extended LaMer

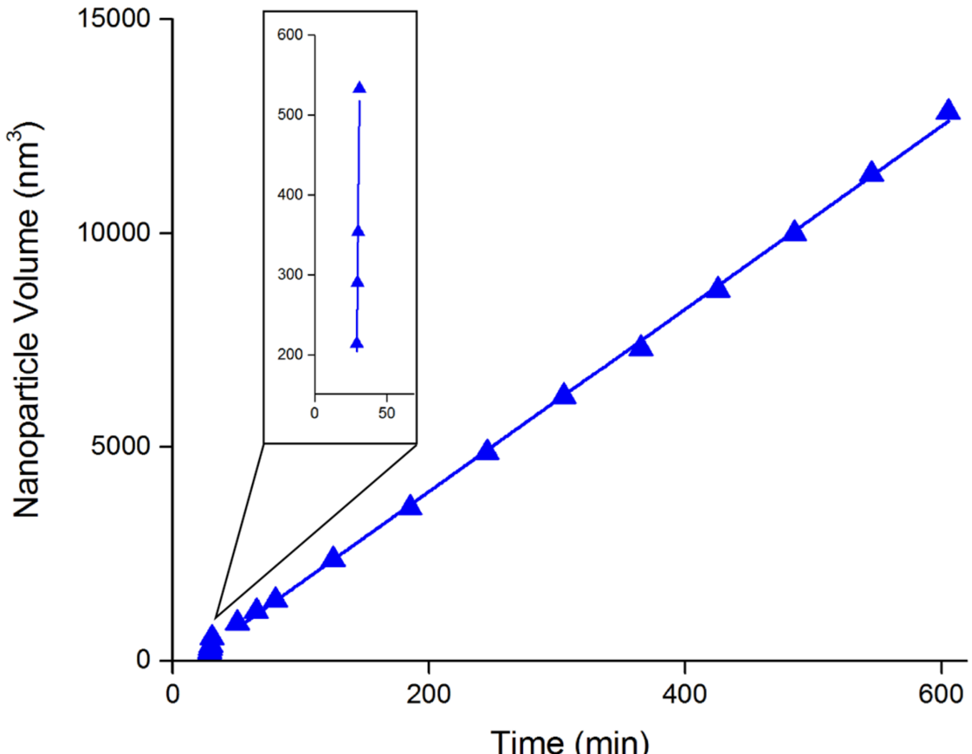


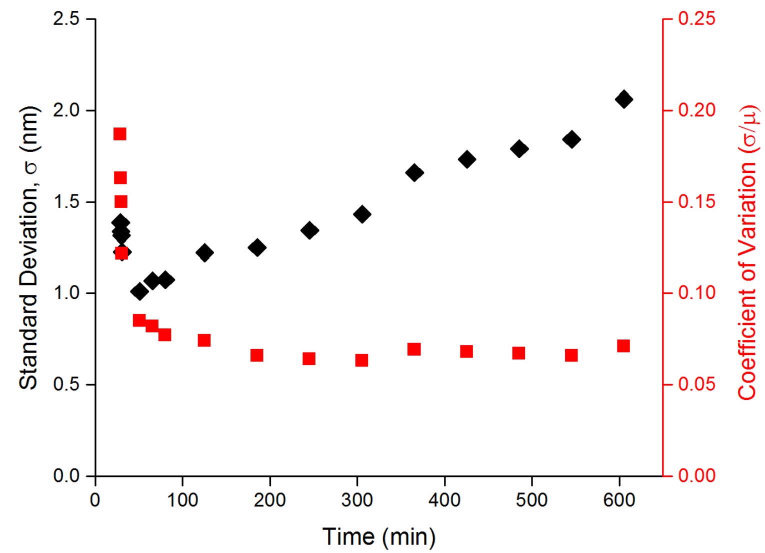




- Use benchtop SAXS to determine particle size of aliquots.
- Yields near real time size determination.

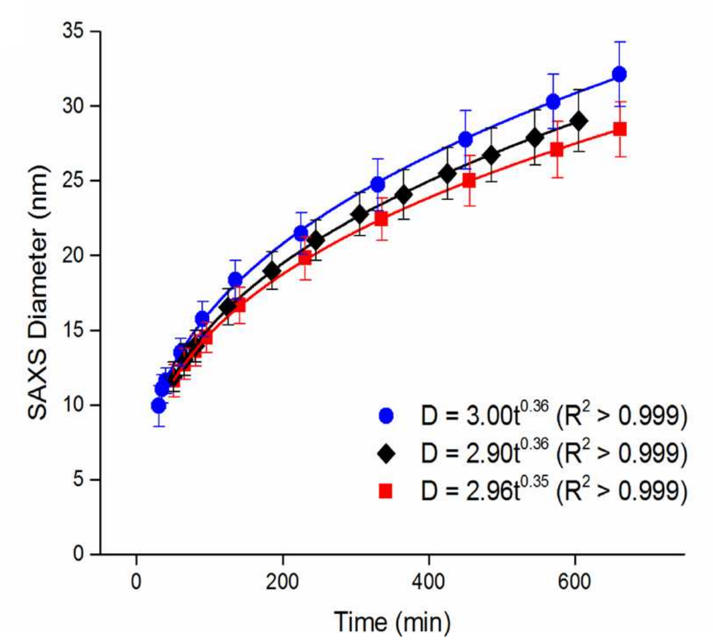
Size Control with Extended LaMer



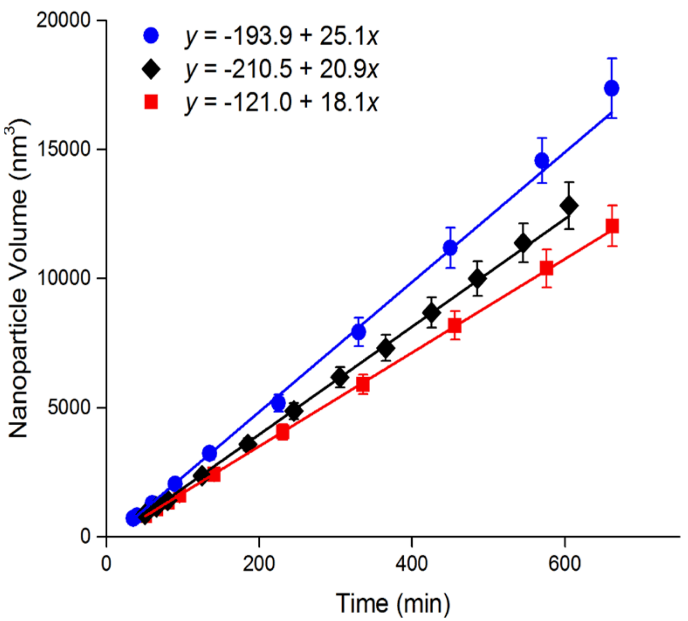


- SAXS gives us great statistics.
- Clearly see two growth regimes.
  - Rapid growth in early stage is catalytic
  - Size focusing as a result of differential reactivity
  - Highly exothermic just after nucleation
- After period of rapid growth, steady state reaction

Reproducibility

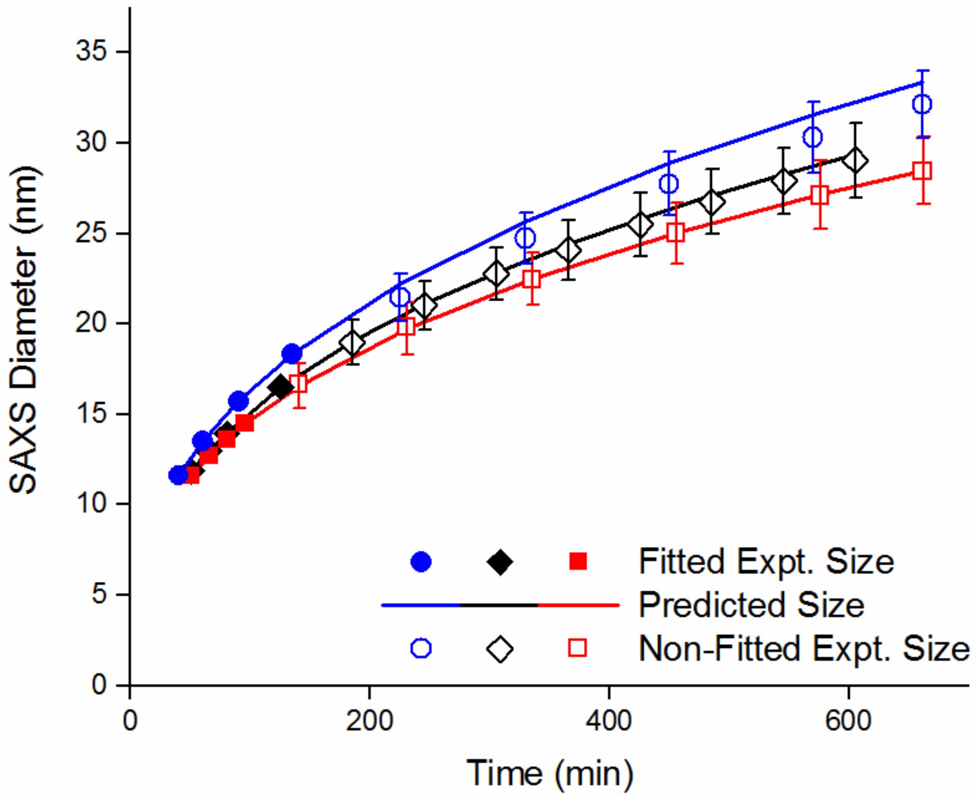


- Reaction repeated in triplicate
- New precursor synthesized for each reaction
- Particle diameter grows as $t^{1/3}$
- Batch-to-batch coefficient of variation .04



- Particle volume grows linearly with t
- Similar starting points, differing slopes
- Why does slope differ?
  - Each reaction has the same rate of addition
  - Steady state requires rate of addition to equal rate of reaction
  - All reactions produce material at the same rate
- Variation in growth rate must mean that a different number of particles are nucleated

Prediction of Growth

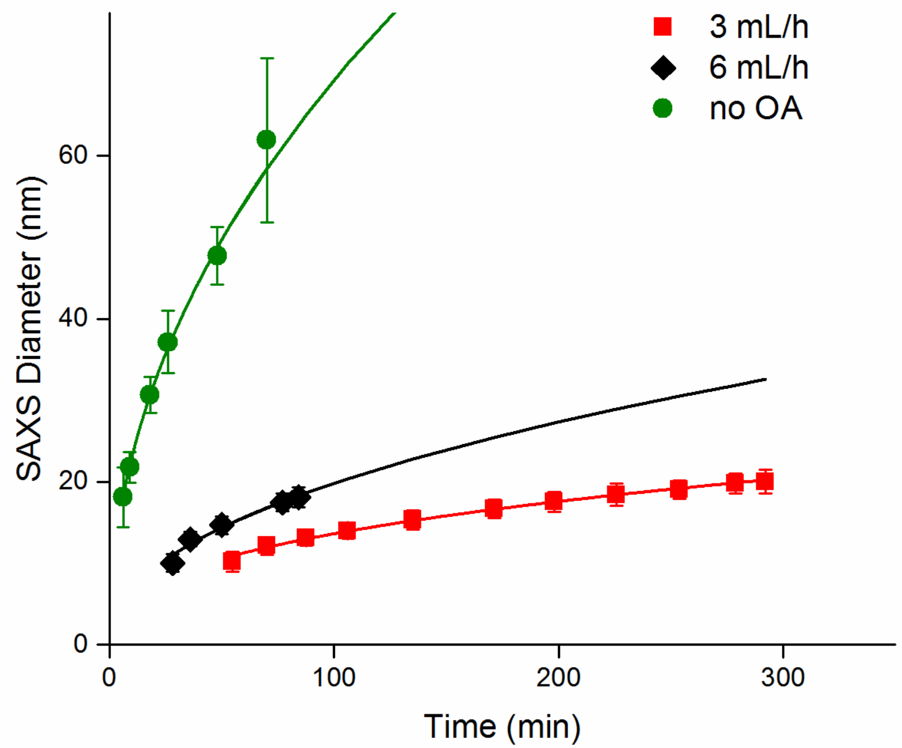


- Same data as before

- Take first four data points after steady state reached
- Extrapolate and compare extrapolation to actual data.
- Every data point is within 1.5% of predicted value.

- Why does this work better?
- Extrapolation accounts for different number of nuclei formed.

Size Control Varying Surfactant Concentration



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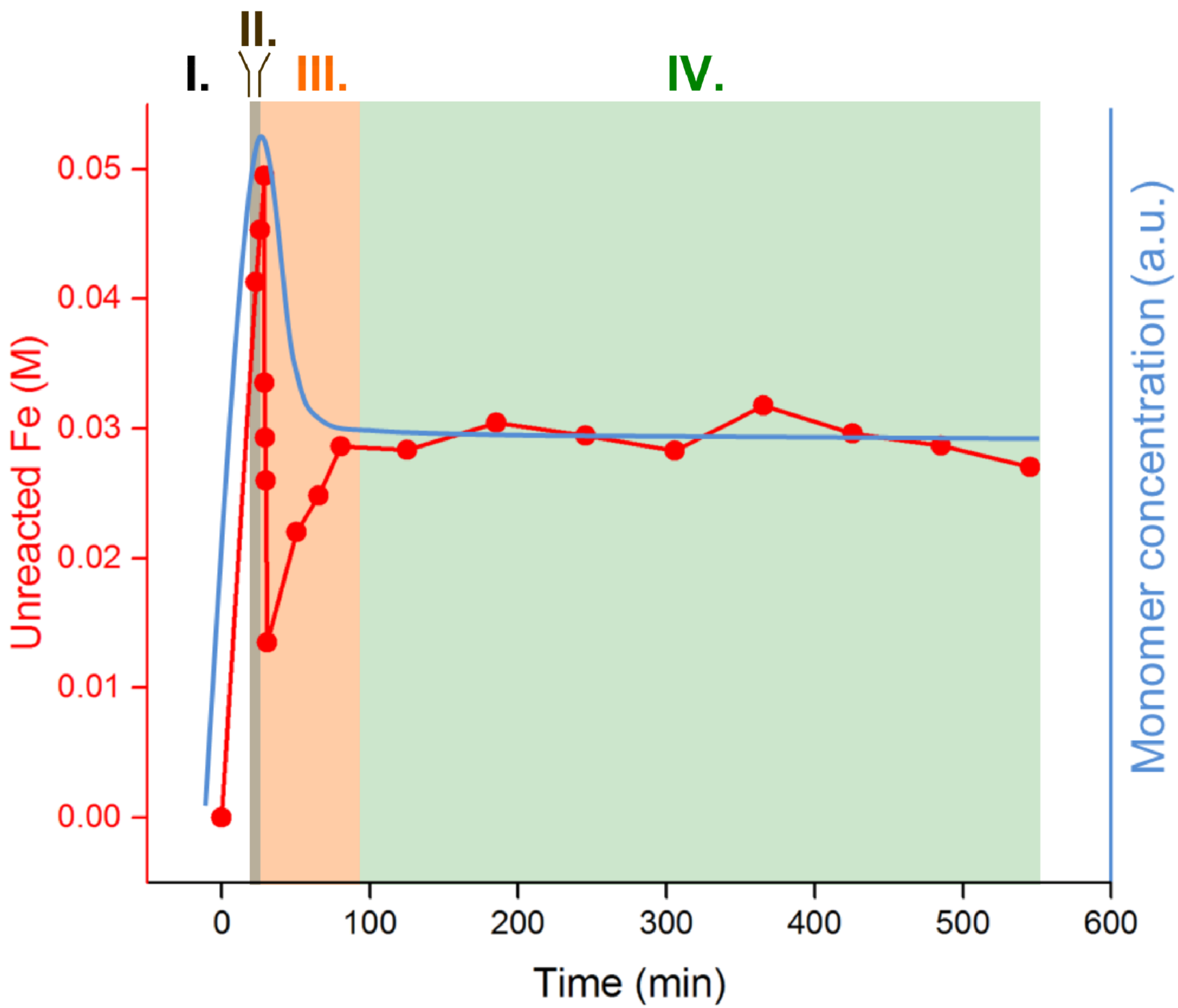
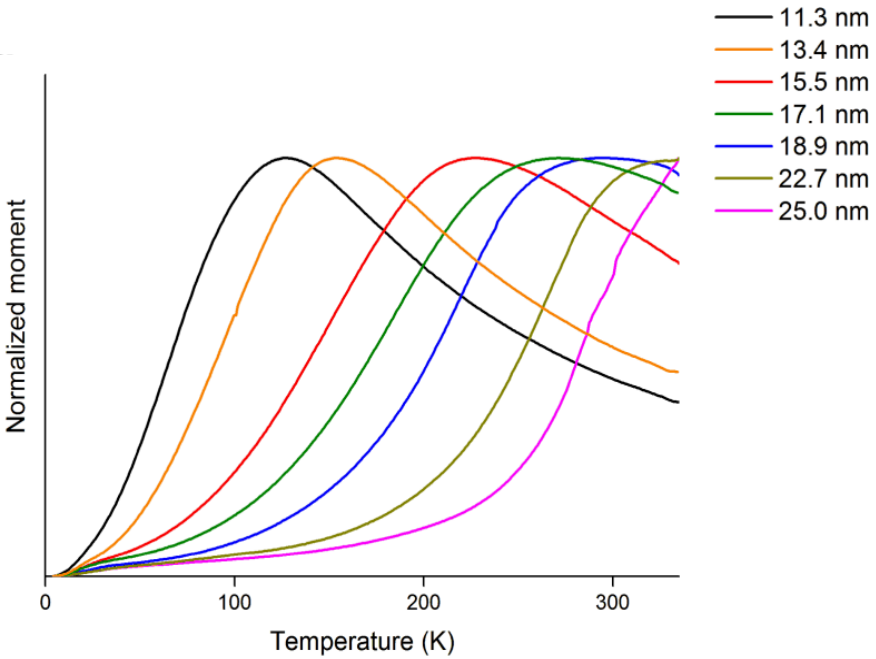
Comparison of Real Data to Predicted Extended LaMer Behavior



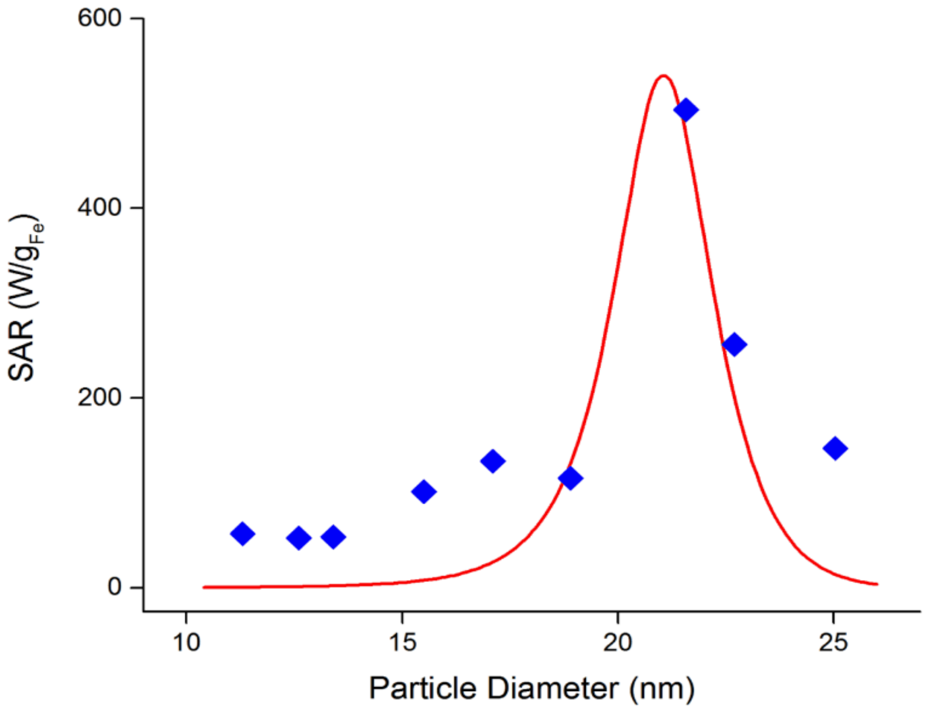
- Unreacted iron concentration is related to monomer concentration by some unknown rate constant.
- Plotting unreacted Fe vs time gives us a LaMer style plot.
- Behavior just after is catalytic
  - Growth is extremely rapid for particles below 10 nm
  - Continues despite decrease in concentration of iron
- Soon transitions to LaMer behavior (diffusion of reactive intermediate).

Systematic Control of Magnetic Properties

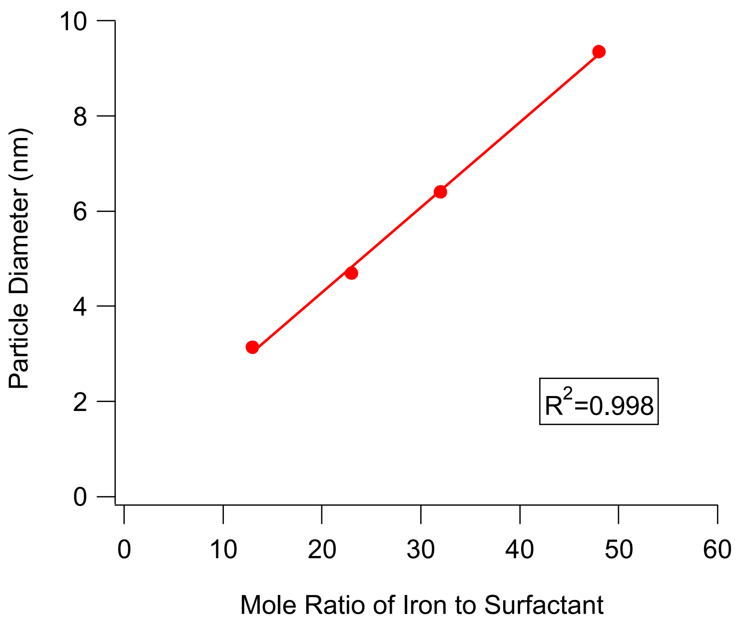


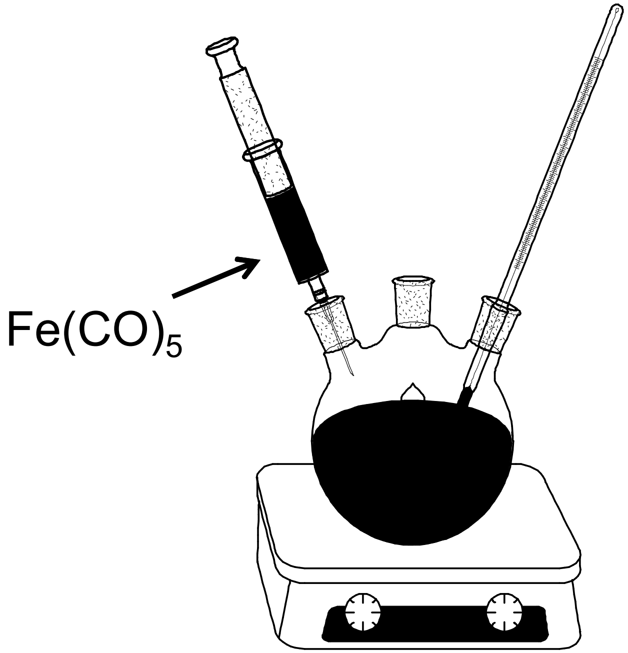
Blocking Temperature

Hyperthermia



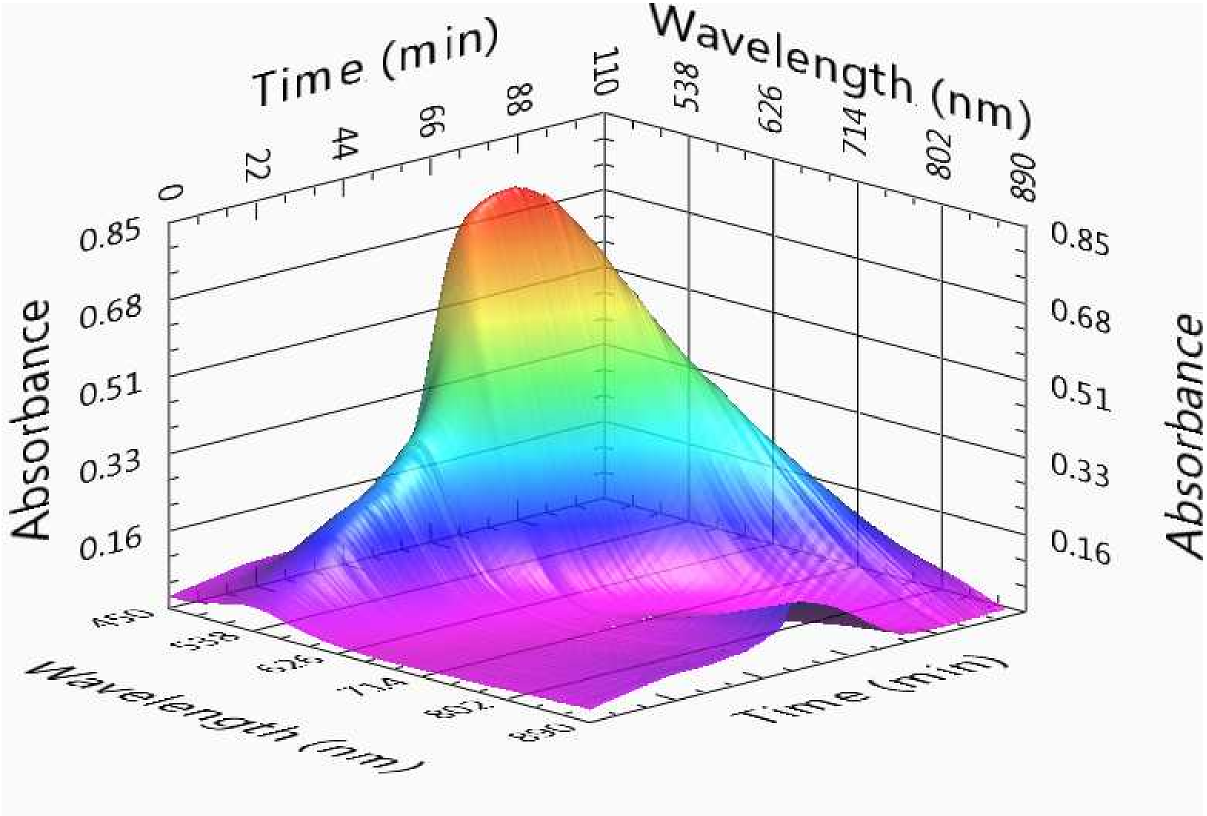
Extended LaMer Approach is General

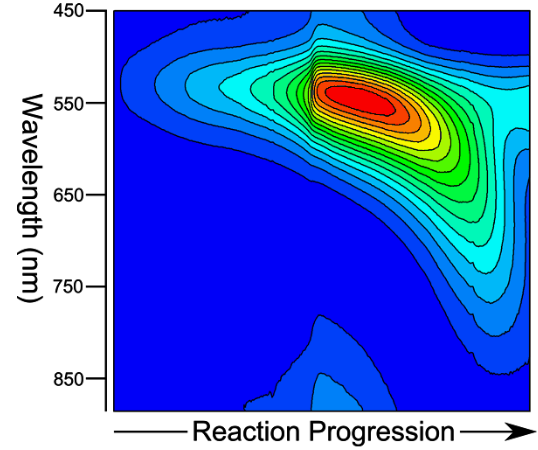




- Fe (0) nanoparticles can be produced using the same continuous addition approach
- Surfactant is 2,4-pentanedione (acac).

Gold Nanoparticles Growth Through the Extended LaMer Mechanism

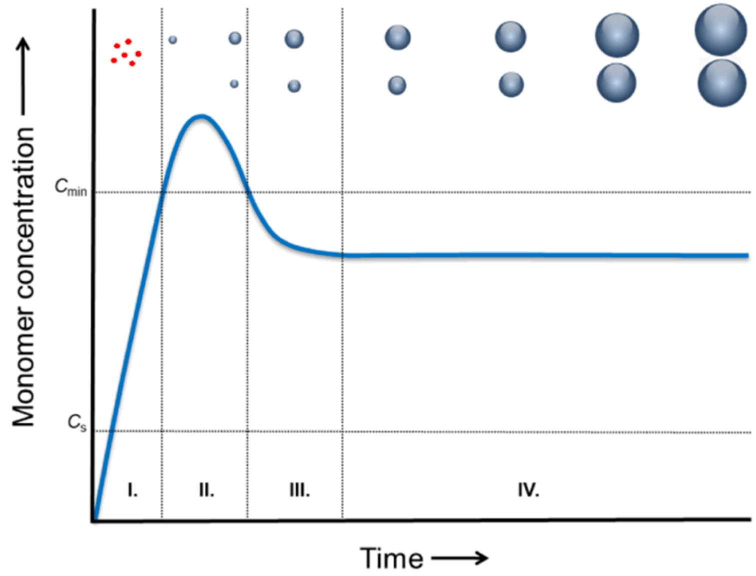




Real time monitoring using UV-vis spectroscopy

Conclusions

- Extended LaMer mechanism allows us to better control the size of particles produced.
- Reactions are both reproducible and predictable.
- Can systematically control size dependent properties.
- Approach is general and is being applied to other systems including Fe (0) and gold.



- **Research supported by the U.S. Department of Energy, Office of Basic Energy Sciences, Division of Materials Sciences and Engineering**

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- **This work was performed, in part, at the Center for Integrated Nanotechnologies, a U.S. Department of Energy, Office of Basic Energy Sciences user facility.**

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