Grant SNM: Enabling Scalable Production and Processing of Nanoparticles for Emerging Energy Applications (NSF-CMMI-1344562)

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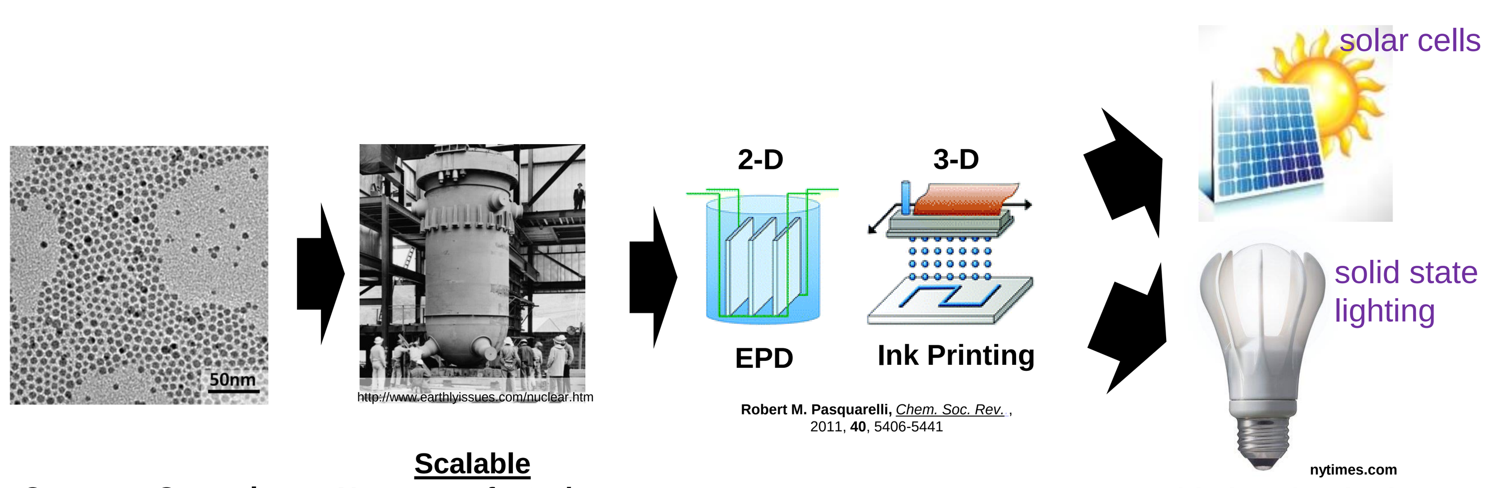
Introduction

Background: Over the last two decades, nanoparticle synthesis has progressed significantly, to the point of creating a multitude of new shapes and compositions, with tight size controls. Unfortunately, the conventional synthesis procedure ('hot-injection') does not easily scale, limiting the incorporation of nanoparticles into technology.

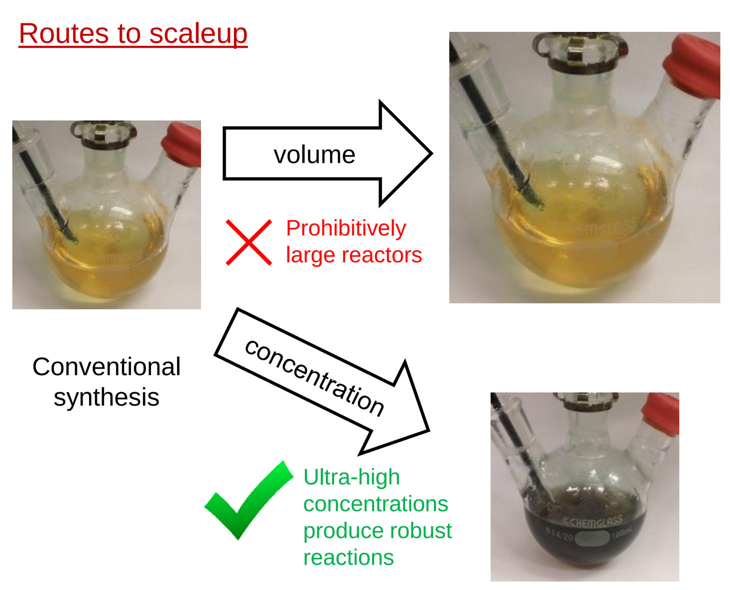
Challenge: Develop a scalable synthesis for colloidal nanoparticles.

Our approach: We believe the solution is through concentrating the reaction medium to near physical solubility limits and using the 'heat-up' method. These new highly-viscous regimes alter the kinetics of the reaction and diverge from the classical Le Mer model on solution-phase synthesis. The heat-up method is readily scalable since it requires no temporal event. Our test system is $Cu_{2-x}S$ nanoparticles. Through our methods, we demonstrate consistency of results on unexplored large-scale reactions.



Quantum Control — Scalable Nanomanufacturing — Solution Processing — Enabled Technologies

Synthesis at the Solubility Limit



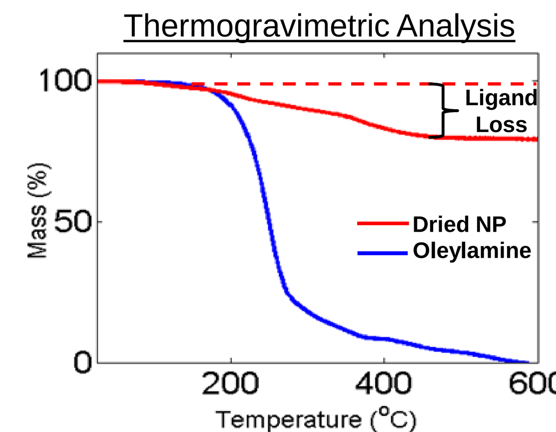
Our Solution

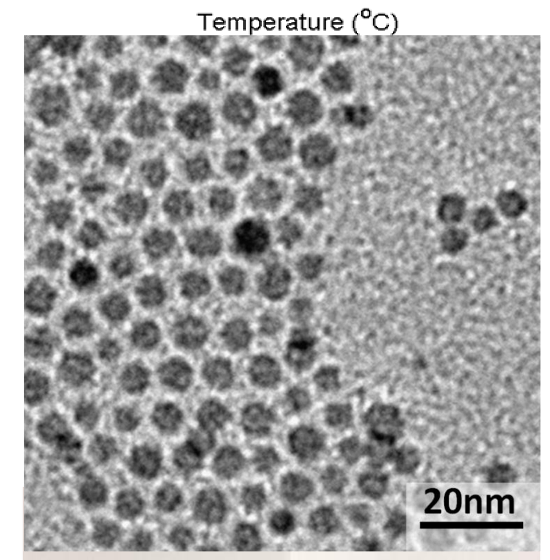
- Use ultra-high concentrations, pushing the solubility limits. This is an unexplored frontier in nanoparticle synthesis.
- Use the "heat-up" method for direct scalablity.

Advantages

- Enhanced thermal stability
- Greater yield per volume
- Linear volumetric scaling
- Decouple particle nucleation from growth
- Independence of precursor reactivity

Liter-Scale Nanoparticle Reaction

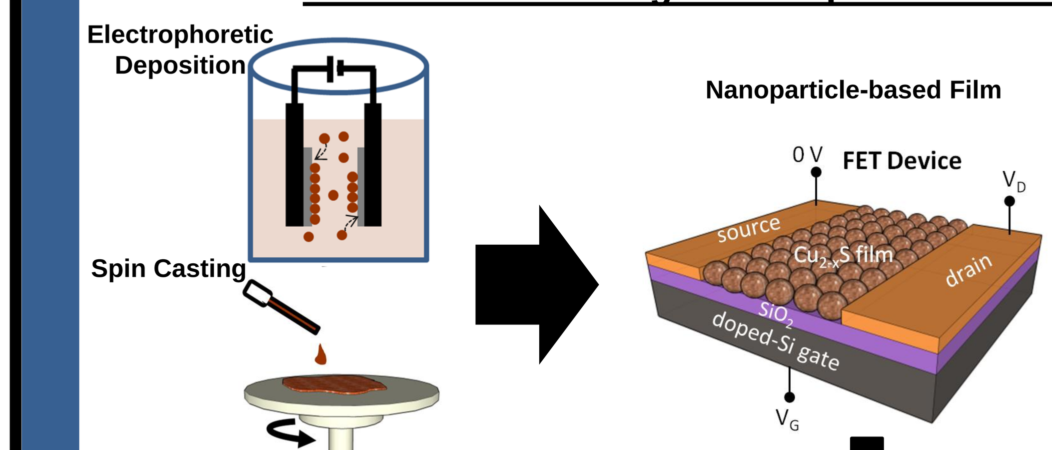




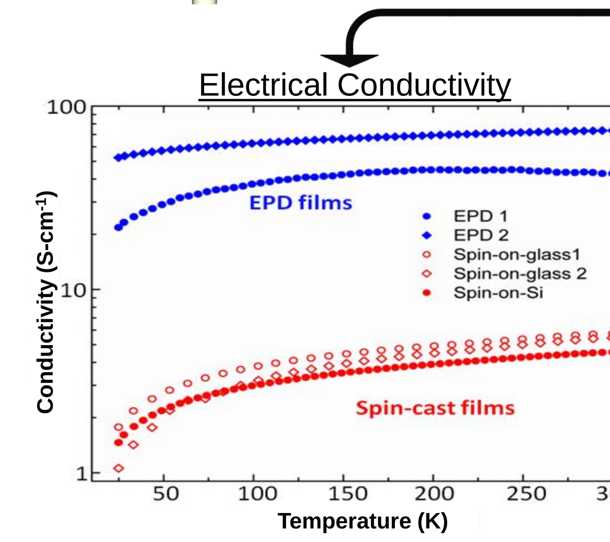
- 1-Liter reaction producing 85g of nanoparticles (more than 1 billion-trillion particles)
- Yield >90% - Determined by comparing the difference of ligand loss from total mass collected to the theoretical yield.

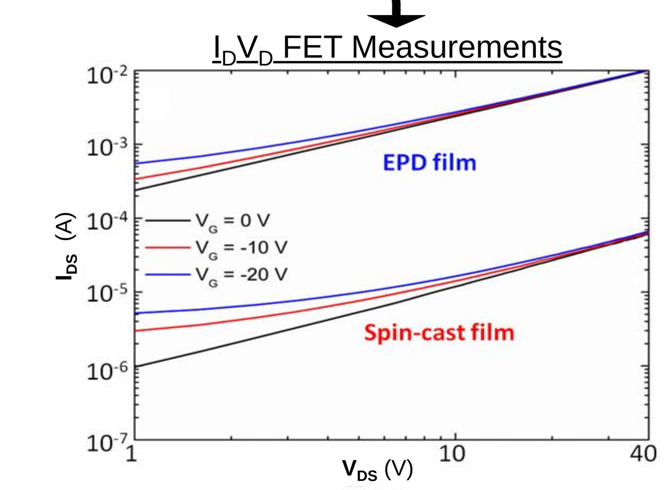
Applications for Scalable Synthesis of Nanoparticles

Solution Processing of Nanoparticles onto Electrical Devices



- Scalable deposition method for assembly of colloidal nanoparticles in to devices.
- High electrical conductivity from solution-processed films
- Room temperature processing – no anneal step necessary

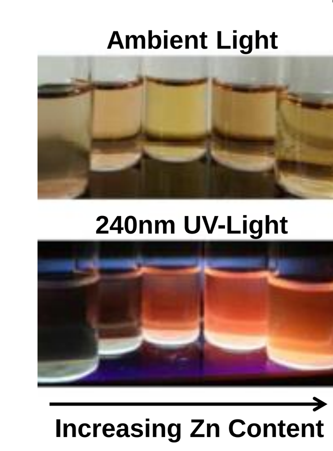


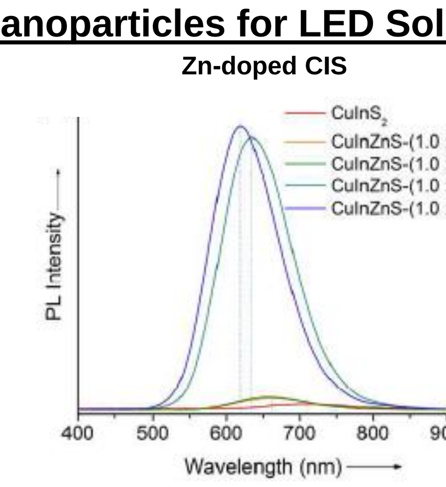


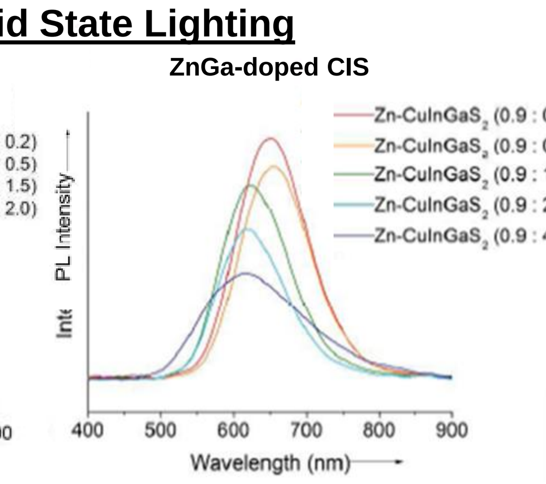
- EPD film conductivities comparable to physically deposition methods for $Cu_{2-x}S$.
- High conductivities associated with inter-particle coupling.
- No saturation – suggests high [carrier]
- P-type behavior

O. O. Otelaja, D. Ha, T. Ly, H. Zhang, and R. D. Robinson, ACS Appl. Mat. Interfaces., 2014, 6 (21), pp 18911

Nanoparticles for LED Solid State Lighting







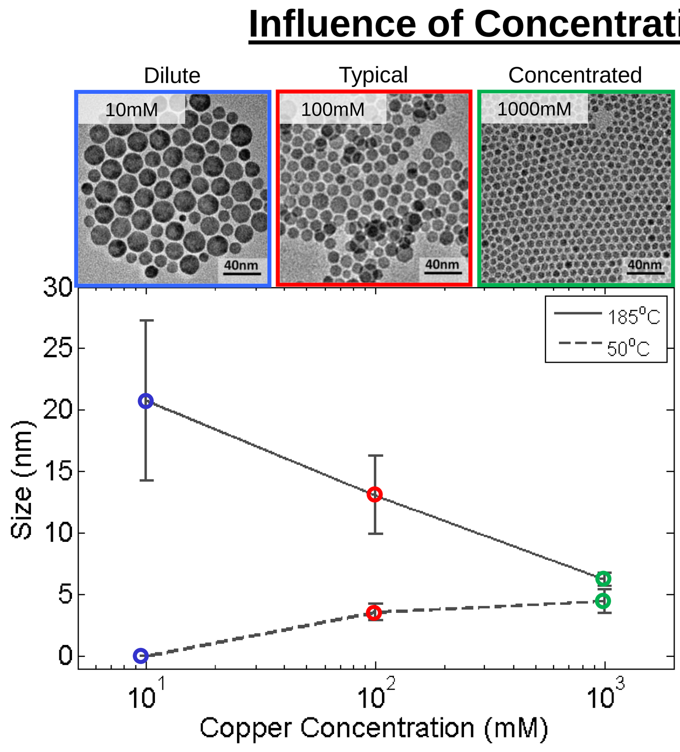
- Heat-up method to dope nanoparticles allows for a facile scalable synthesis.
- Different dopants can be introduced simultaneously, prior to nanoparticle growth.
- Robust process in controlling doping levels in material.
- Significant enhancement in photoluminescence by Zn incorporation.
- Particle emission tunability from chemistry (Ga doping)

S. D. Perera, H. Zhang, X. Ding, A. Nelson, and R. D. Robinson, J. Mater. Chem. C, 2014, 10.1039/C4TC01887G

Critical Reaction Parameters

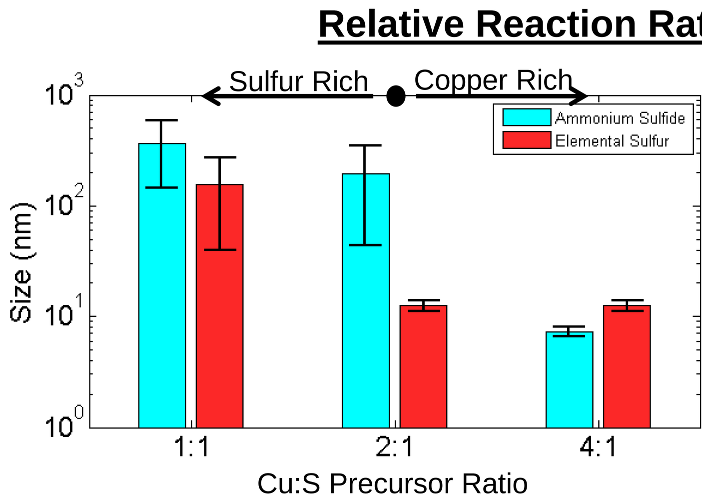
Kinetics and Diffusion

Influence of Concentration on Size and Dispersity



- Considerable size focusing of particles at higher concentrations.
- Size decreases at high concentrations – suggests greater number of collisions, generating more nuclei sites.
- Low T produces same particle size for 100 and 1000 mM – indicating similar monomer conversion.
- Under dilute conditions, particle stability is poor – no particles at low T and huge particles at high T.

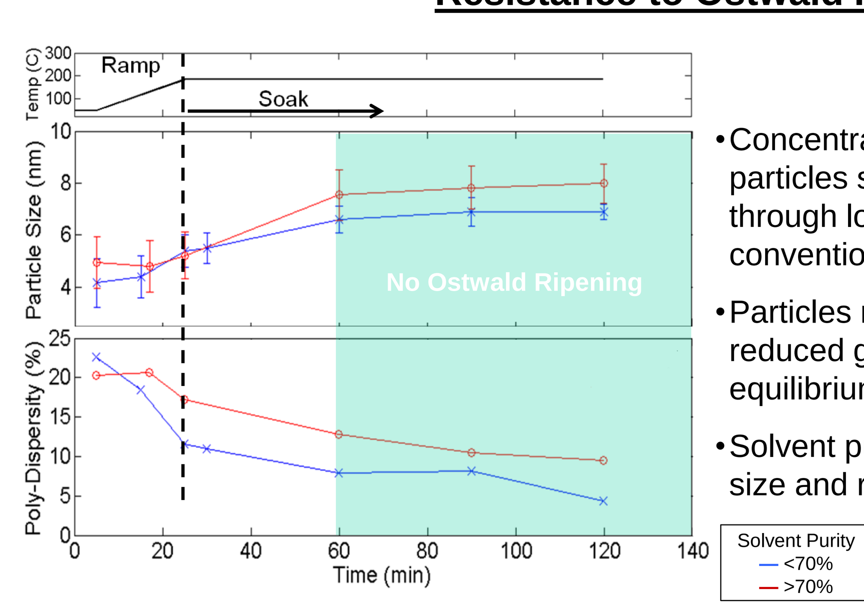
Relative Reaction Rates (Concentrated)



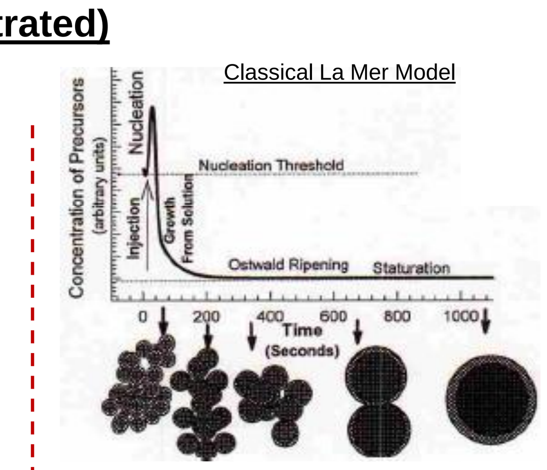
- Metal-rich solutions reduce particle size and dispersion – likely from sulfur-diffusion limited growth
- More-reactive sulfur precursors require a greater metal ratio to maintain control.
- Stoichiometry studies give insight into relative reactivity mechanisms and limitations.

Sensitivity and Control

Resistance to Ostwald Ripening (Concentrated)



- Concentrated solutions maintain particles size and dispersion through long soaks – contrary to conventional Ostwald ripening
- Particles reach a plateau of reduced growth – possible equilibrium with monomers.
- Solvent purity affects particle size and reproducibility.

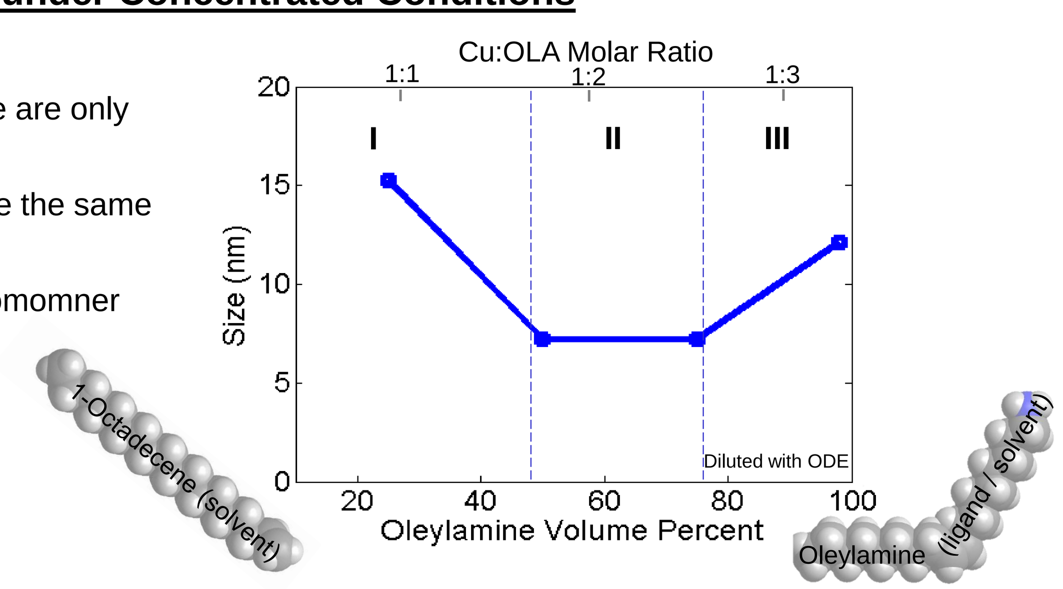


1. Burst Nucleation
2. Size Focusing
3. Ostwald Ripening

C.B. Murray, C.R. Kagan, M.G. Bawendi, Annu. Rev. Mater. Sci., 2000, 30:545-610

Effects of Solvent Purity under Concentrated Conditions

- I — Ligand deficient region in which particle are only stabilized at larger sizes.
- II — Equilibrium region in which particles are the same over large variations in OLA.
- III — Increased probability of monomer – momomner collision.



Future Work

- 1 kg batch reaction of high-quality nanoparticles.
- Characterize concentration effects on particle nucleation, growth, and ripening.
- Implement electrophoretic deposition to extract nanoparticles from solution.
- Understand the governing physical factors of nanoparticle reactions.
  - Shear analysis
  - Temperature profiles

Conclusion

- Heatup method + high concentrations yield a robust scientific platform for scaleup
- Concentrations at the solubility limit enable consistent, tunable, scalable nanoparticle production.
- Concentrated solutions are more resistant to Ostwald ripening than dilute solution.
- Solvent purity is an underappreciated parameter for tuning nanoparticle size and dispersity.

Acknowledgements

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