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Nanoparticle Synthesis and Assembly

Introduction

Materials formed by nanoparticles exhibit novel interactions with each other and the local environment due to the high impact of surface properties on their behavior. Chemical methods for achieving the “bottom up” approach to nanomaterials experience a challenge in controlling the particle size and morphology, the distribution of particle sizes, as well as placing nanomaterials in desired positions during integration into devices. Solution synthesis routes have the potential for creating nanomaterials of controlled size and shape, as well as control of the interface to permit directed assembly of the materials into higher order structures.

The operations in the synthesis of nanoparticles and in their directed assembly all relate to crystallization processes, where the impact of growth factors (such as concentration, defects, and specific adsorption of surface stabilizers) can be characterized and manipulated. Nanomaterials provide a rich subject for exploration of the interactions between the particles and the free space of solutions, liquid crystals, and polymer melts, leading to the formation of novel materials and composites.

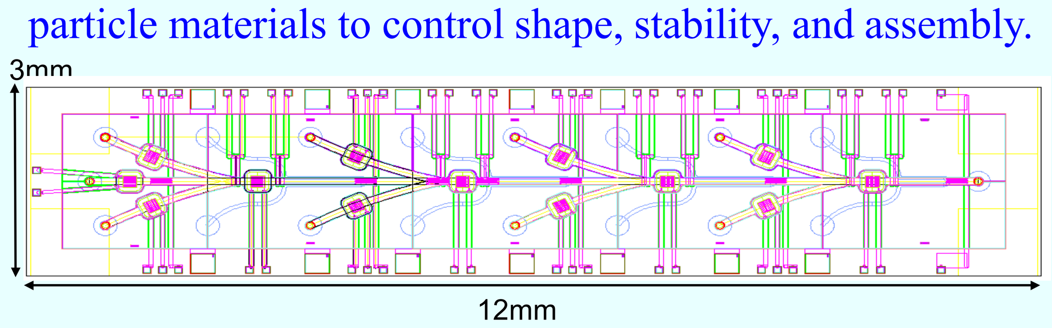
Associated Capabilities

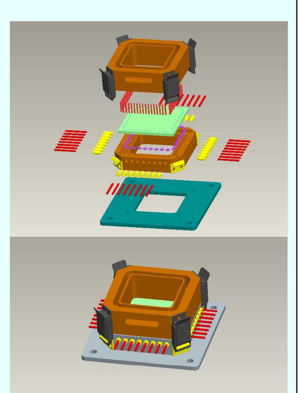
Expertise in the following areas:

- Solution Chemistry expertise
- Nanoparticle synthesis techniques
- Dispersion and aggregation methods for nanoparticles and suspensions
- Rheological characterization of suspension properties
- Interparticle interaction energy calculation
- Surface Wetting characterization and surface energy parameter calculation

Development of Microfluidic Discovery Platform

This discovery platform has been developed to study the nucleation and growth of nanoparticle systems, to gain improved fundamental understanding of the synthesis of nano-particle materials to control shape, stability, and assembly.





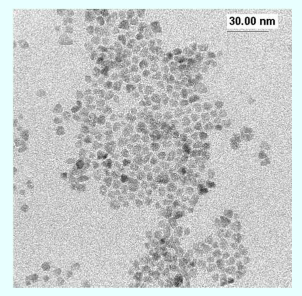
POC: Nelson S. Bell, CINT Core, 505-844-6234, nsbell@sandia.gov

Contributors: Martin Piech, Greg Jamison, Paul Clem, Francois Leonard (SNL/CA), Frank A. Jones (SNL/CA), Alec Talin (SNL/CA), Murat Okandan, and Ron Renzi (SNL/CA)

Nanoparticle Synthesis and Morphological Control

Shape Control in the Formation of ZnO Nanorods

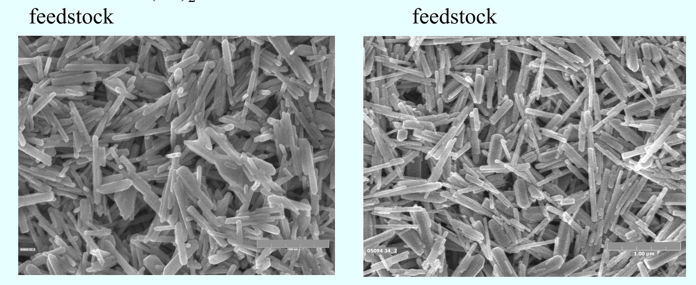
- Zinc oxide is a valuable semiconductor for applications in gas sensing and biological study.
- Many routes for forming ZnO nanorods cannot control the axial ratio, or place the width of a nanorod near the quantum confined regime.
- CINT Users will be evaluating the alignment of ZnO Nanorods using dielectrophoretic assembly processes.
- The phenomenon of Ostwald ripening from ZnO nanodots in ethanol shows improved ability to control nanorod width.



$Zn(Ac)_2 + 2\ TMA\text{-}OH \rightarrow ZnO + H_2O + 2\ TMA^+ + 2\ (Ac)^-$

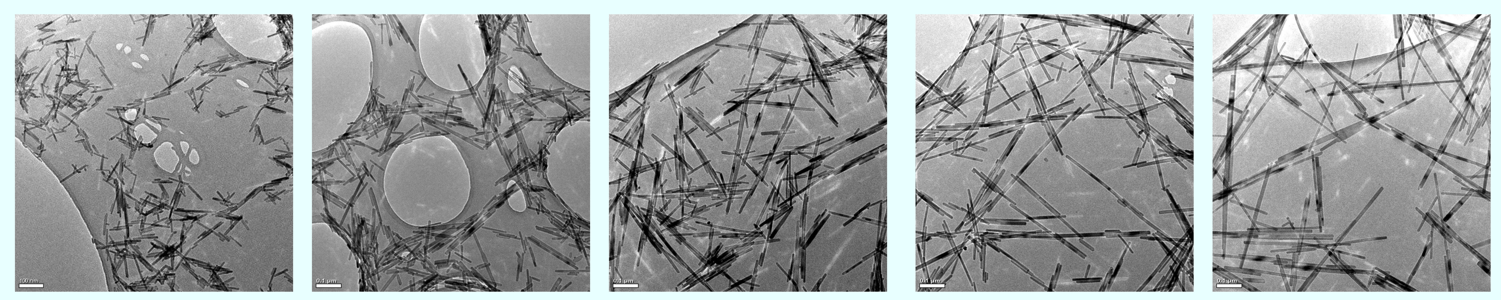
Reaction in a pressure vessel at 150 °C ripens the nanodots into nanorods.

Rods from $Zn(Ac)_2$ / TMA-OH feedstock — Rods from ZnO nanodots feedstock



1. B. Cheng and E.T. Samulski, “Hydrothermal Synthesis of One-dimensional ZnO Nanostructures with Different Aspect Ratios,” *Chem. Comm.* (2004) 986-987.

Ethylenediamine growth additive promotes the formation of nanorod morphologies



Reaction Time: 4 hours, 8 hours, 16 hours, 24 hours, 72 hours

Photoluminescence and Current-Voltage Properties of Individual ZnO Nanorods

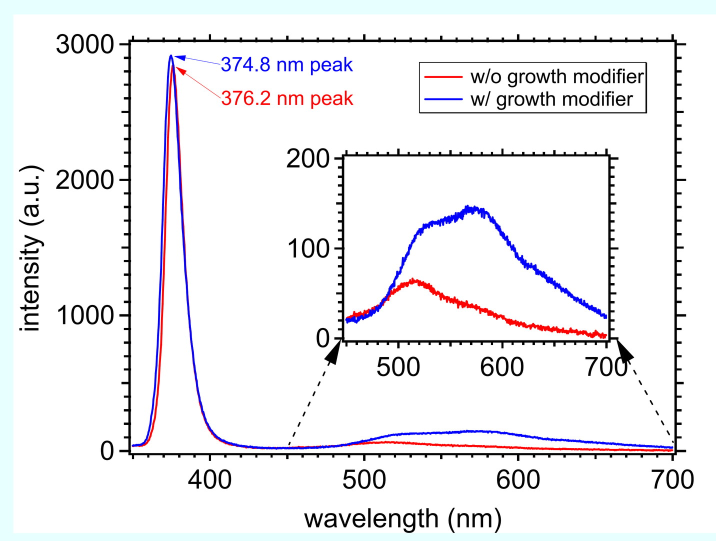


Figure 1: Photoluminescent spectra of the two sets of nanorods. The sharp UV peak shows the near-band-edge excitation. The inset is a blow up of the 450-700 nm range of the peaks typically associated with the defect structure

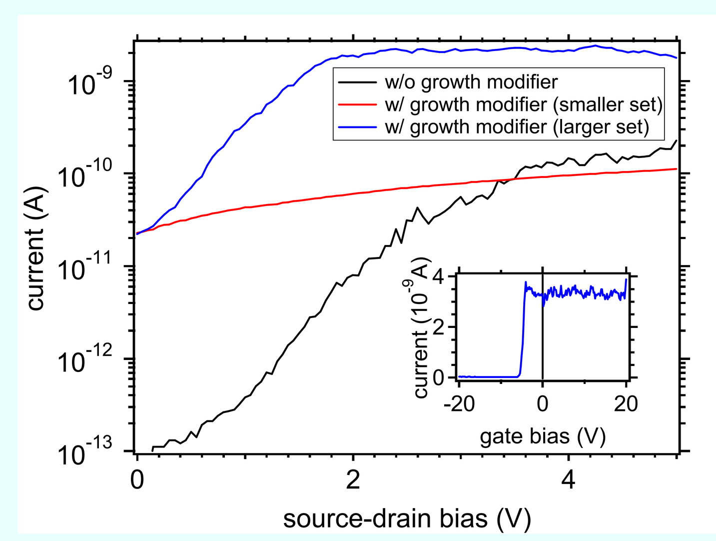


Figure 2: Typical current-voltage curves in forward bias for the two sets of nanorods. The curves from the samples with the growth modifier show the two differing behaviors: the smaller nanorods with low conductivity and the larger nanorods with higher conductivity and saturation current. The inset shows the gate bias dependence of the larger nanorods at 2V source-drain bias. The gate dependence is consistent with an n-type FET.

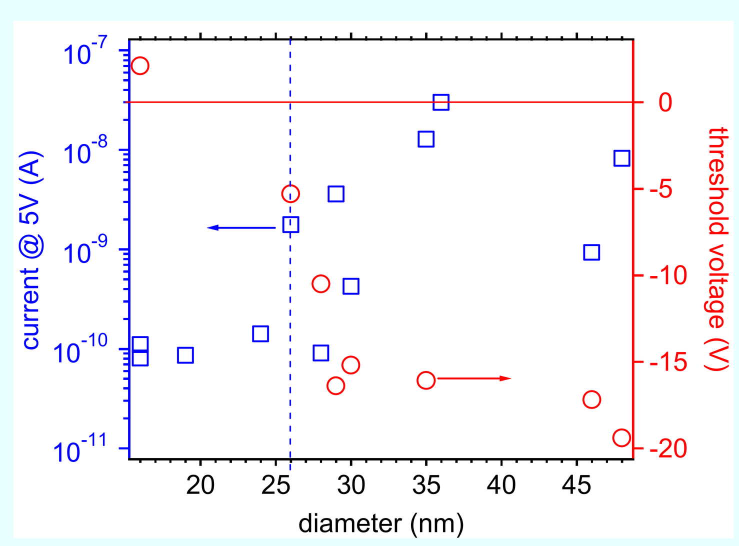


Figure 3: Electrical dependence on the diameter of the nanorods. The squares (□), associated with the left axis, represents the current at 5 volts source-drain current. The dotted vertical line is a guide to show the difference in current above the cut-off point. The circles (○), associated with the right axis, represent the threshold current based on gate dependent measurements. For devices with more than one nanorod, the largest diameter is given.

Observations: Growth from nanodots lead to high aspect ratio nanorods using ethylene-diamine as a growth promoting agent. The impact of the growth modifier is being investigated. Nanorods were spun down over electrodes and evaluated for individual PL and I-V properties. Ethylenediamine synthesized rods are of lower width and do not demonstrate an effect from surface adsorption. Rather, conduction is impacted by the depletion distance of the material, rather than the surface state or quantum confinement due to size constraint.

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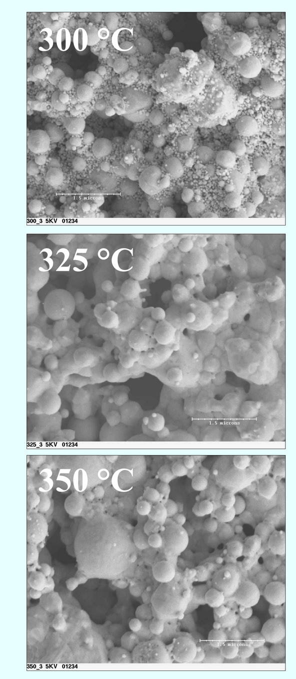
Nanoparticle Dispersion and Integration

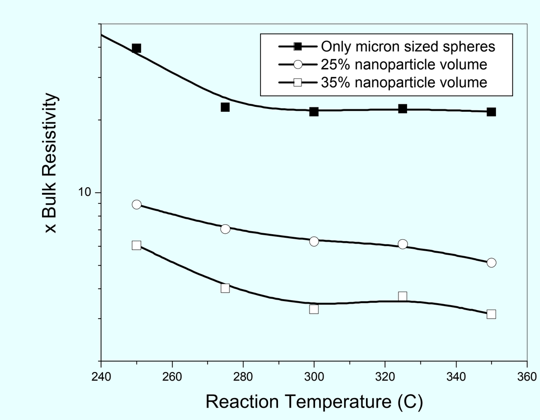
Low Temperature Silver Conductor Pastes using Nanoparticles as Reactive Components.

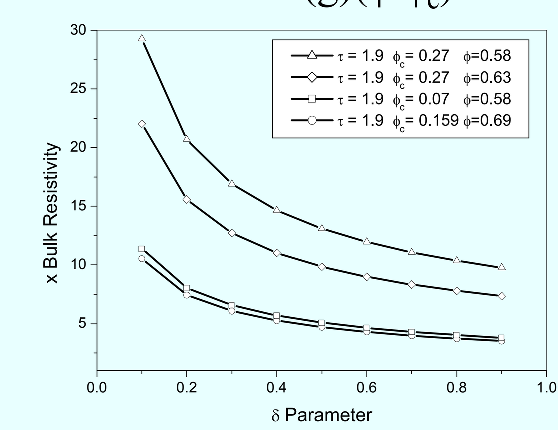
- Using nanoparticles as novel components in traditional materials is a route to novel products. Silver nanoparticles react at low temperature based on nanosized melting point depression.
- A percolation theory treatment describes the conductivity behavior of the mixture of micron and nanosized particles.
- The removal of organic processing aids is the critical factor in developing the highest conductivity.



$$T_m = \frac{Mk\Theta_b^2\delta^2 a^2}{36\hbar^2\left[1-\left(1-na/R\right)^3\right]} + \frac{1}{8}\Theta_b$$

$$\Sigma = A\,(g)(\phi-\phi_c)^\tau$$





O. Dominguez E, Y. Champion, and J. Bigot, “Surface Effects on the Sintering Behavior of Nanometric Metallic Particles,” *Rev. Mex. Fis.* **45 S1** (1999) 74-77.

Photocontrol of Colloidal Aggregation

Photosensitive Surface Polymers Control Aggregation State of Model Silica Particles

- Remote control of aggregation allows for the directional growth and assembly of diverse units into components with macroscopically interesting properties.
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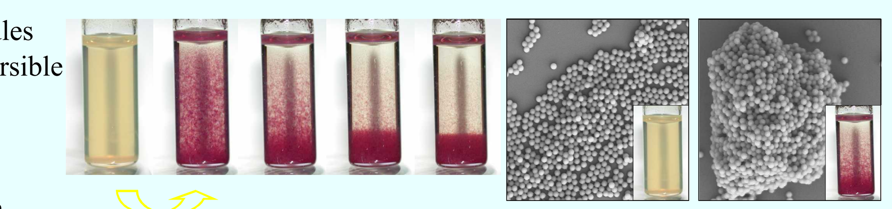
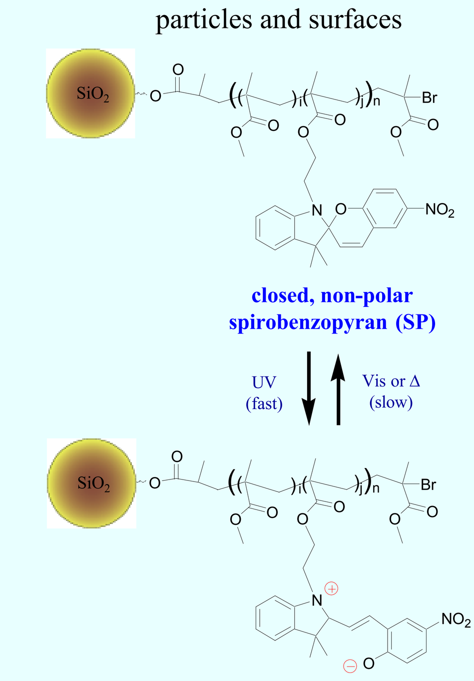
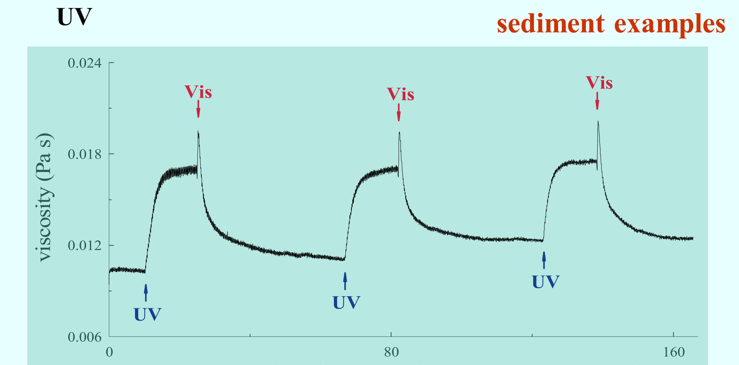
Goal incorporation of photochromic molecules into the material system to impart reversible photo-tuning of intermolecular and/or interparticle forces

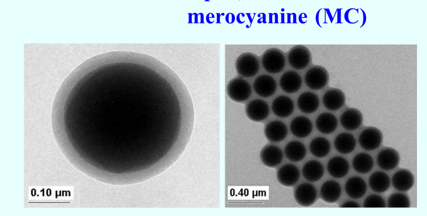


Approach introduction of photo-active SP molecules into polymeric matrices chemically grown from colloidal particles and surfaces

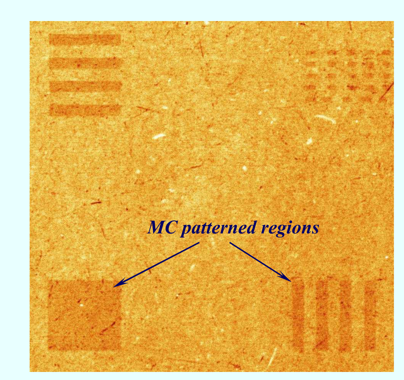




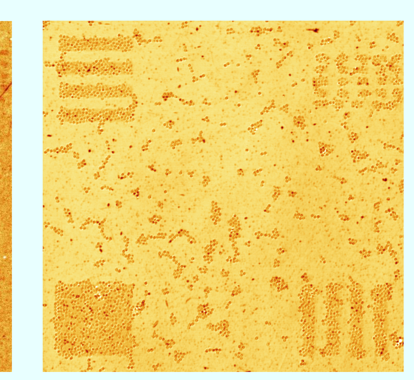
30% v/v toluene suspension of SiO_2-*graft*-$SP_{0.2}$-*co*-$MMA_{0.8}$ colloids



30 nm thick $SP_{0.2}$-*co*-$MMA_{0.8}$ (*i.e.*, 20 mol% SP) brushes on 284 nm core SiO_2 particles



$SP_{0.2}$-*co*-$MMA_{0.8}$ film on SiO_2 surface patterned using two-photon adsorption process



after settling toluene dispersion of $SP_{0.2}$-*co*-$MMA_{0.8}$ derivatized 1 µm SiO_2 colloids, rinsing and drying

Applications

- photo-induced defect annealing in colloidal crystal composites
- optically tuned microfluidic rheology
- stimuli–responsive sensors
- nanostructure/pattern deposition