Outline

Preparation of Nanocrystals
Passivation of Nanocrystals
Obtaining Narrow Size Distributions
Characterization
Controlling the Shape of Nanocrystals

Self-Assembly of Nanocrystals
Entropy as the driving force
Experimental Variables: size, shape & magnetic interactions

Magnetic properties of NC arrays
Isolation and Purification of Nanocrystals

**Electrostatic Stabilization**

- Electrostatic repulsion
- Van der Waals attraction

Barrier to aggregation is proportional to energy of mixing between the tethered capping group and solvent.

**Steric Stabilization**

Capping groups provide surface passivation (covalently bound ligands) & sufficient repulsion.

Engineering Interparticle Separation
TBPO < TOPO < THPO

Barrier to aggregation is proportional to energy of mixing between the tethered capping group and solvent.
Preparation of Colloidal Metals in Constrained Environments

Notes:
- Separate nucleation from growth
- Temporally discrete nucleation event
- Slow controlled growth on existing nuclei

Details of Co Synthesis

Cobalt Carbonyl (0.5g) + Dichlorobenzene (3 ml)

Inject (rate & temperature) into

Trioctylphosphene oxide (TOPO) + Oleic Acid + DCB

0.1-0.2 g 0.2 ml 12 ml

Centrifuge

Nanocrystal Particles

Disperse in solvents

SELF ASSEMBLY

*critical parameters
**Issues in La Mer synthesis**

- Reaction time - controls particle size
- Injection (temperature and rate) - controls nucleation and hence particle size distribution
- Surfactant
- Solvent (s)
- Concentration of metal precursor, surfactant

- Control of shape
- Alloying
- Control and/or prevention of oxidation
- Control of interparticle separation
- Self-assembly

**Structure of Co Nanoparticles**

- ε-Cobalt (11 nm particles)

![Image of ε-Cobalt (11 nm particles)](image)

COUNTS (arb. u.)

DEG

30 40 50 60 70 80

6.09 Å

![Image of ε-Cobalt (11 nm particles)](image)
Kinetic Control of Nanocrystals Shape?

![Images showing Cohcp and Co0 crystalline structures with time labels (15'', 300'', 1000'')]

Selective bonding of surfactants to specific Co surfaces?

- **Oleic Acid**
  - Formula: \( R \overset{\|}{\mathrm{C}} \overset{\\mathrm{O}}{\mathrm{\ddot{O}}} \mathrm{H} \)
- **TOPO**
  - Formula: \( \mathrm{R} \overset{\\mathrm{P}}{\mathrm{= O}} \mathrm{H} \)
- **Oleyl Amine**
  - Formula: \( \mathrm{R} \overset{\\mathrm{N}}{\mathrm{H}} \mathrm{H} \)
- **Thiol**
  - Formula: \( \mathrm{R} \overset{\\mathrm{S}}{\mathrm{H}} \mathrm{H} \)
Nanocrystal shape control with multiple surfactants?

- Oleic Acid
- TOPO
- Plates?

Oleic Acid
- Oleyl Amine
- Rods?

Nanocrystals shape control: the role of surfactants

- Oleic acid
- Tri-n-octylphosphine oxide
- Oleyl amine

1:1 1:1.6 1:2.7

- Spheres
- Plates or rods?

- Rods or Disks?
General Requirements for Shape Controlled Synthesis

- Suitable organo-metallic precursor that rapidly decomposes to yield monomers at temperatures where the surfactants are stable.
- Two surfactants must be found that differentially adsorb to the growing particle surface leading to rod formation.
- One surfactant must promote monomer exchange between particles to allow for size distribution focussing.

Puntos, Krishnan & Alivisatos, Science, 291, 2115 (2001);
Bao, Breeman & Krishnan (unpublished)
Self Assembly of Colloidal Nanocrystals

- Under appropriate conditions particles in suspension spontaneously self-assemble
- First order Fluid -> Solid phase transition
- To control the structure of the colloid “crystalline” phase need to
  a) Control interaction among particles
  b) Control particle Kinetics
- ENTROPY plays an important role in this spontaneous self-assembly.

Self Assembly: Entropy as the Driving Force

(Phase Transitions in Hard Sphere and/or charge-stabilized colloids)

<table>
<thead>
<tr>
<th>Hard Materials</th>
<th>Soft Materials (Colloids)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Thermodynamic Equilibrium</td>
<td>“Hard Sphere” systems (weak repulsive potential)</td>
</tr>
<tr>
<td>Minimize Gibbs Free Energy</td>
<td>E \ll TS</td>
</tr>
<tr>
<td>F = E - TS</td>
<td>Free energy determined by entropy (S) which is a function of the packing fraction, ( \phi )</td>
</tr>
<tr>
<td>E &gt;&gt; TS</td>
<td>S (( \phi ))</td>
</tr>
<tr>
<td>i.e. internal energy determines equilibrium phase and thermal fluctuations are treated as perturbations.</td>
<td>As volume fraction increases, particle motion is restricted by collisions</td>
</tr>
<tr>
<td></td>
<td>Freezing (first order phase transition)</td>
</tr>
</tbody>
</table>
Self Assembly: Entropy Driven First-Order Phase Transformation

Remarkable Feature
Two observed close-packed densities.

Note: $\Phi_h > \Phi_r$

As $\phi_S$ drives FO transformation

Size-dependent magnetic behavior of Co nanocrystals

<table>
<thead>
<tr>
<th>Properties and magnetic characteristic lengths of the 3d transition-metal ferromagnete</th>
<th>$M_s$ (emu/cc)</th>
<th>$K_u$ (erg/cc)</th>
<th>$J$ (erg/cc)</th>
<th>$T_c$ (°C)</th>
<th>$l_H$ (nm)</th>
<th>$l_K$ (nm)</th>
<th>$l_s$ (nm)</th>
<th>$D_{ext}$ (nm)</th>
<th>$D_s$ (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe</td>
<td>1714</td>
<td>$8 \times 10^5$</td>
<td>$1.7 \times 10^6$</td>
<td>770</td>
<td>14.5</td>
<td>17.5</td>
<td>3.5</td>
<td>14</td>
<td>16.0</td>
</tr>
<tr>
<td>Co</td>
<td>1422</td>
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<td>$2.2 \times 10^6$</td>
<td>1131</td>
<td>17.5</td>
<td>5.5</td>
<td>4.2</td>
<td>70 ($\sim 7.6$)</td>
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</tr>
<tr>
<td>Ni</td>
<td>484</td>
<td>$5 \times 10^5$</td>
<td>$1.0 \times 10^5$</td>
<td>358</td>
<td>19.5</td>
<td>45.0</td>
<td>8.0</td>
<td>55</td>
<td>39.1</td>
</tr>
</tbody>
</table>

- super paramagnetic
- super paramagnetic
- perfect crystal
- perfect crystal
- thermal process
- single domain rotation
- single domain cURLing mode
- domain wall motion
Self-assembly of intermediate size (8-10 nm) Co nanocrystals (superparamagnetic)

Classical Entropy-driven 1st Order Phase Transition

Self-assembly of very small (3-5 nm) Co nanocrystals

Tentative Model(s): Steric Forces Dominate
**Working Hypotheses**

Projection of Particles In Special Orientations (652)

ZL. Wang et al, 2001

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**Self-assembly of Bimodal size distributions**

Two different NC Sizes
Role of Surfaces

Entropy-induced Wetting: Depletion forces determine self-assembly
Self Assembly of Co Nanoparticles: Large FM particles

Magnetostatic interactions dominate self-assembly

Self Assembly of Co Nanoparticles: Disks

5 x 20 nm Disks

Magnetostatic interactions dominate self-assembly
Self-assembly of NCs: Solvent-Nonsolvent Pair Precipitation

- Efficiency of steric stabilization strongly dependent on interaction of alkyl group (surfactant) with the solvent.
- Gradual addition of a non-solvent or the evaporation of a solvent from a solvent-nonsolvent mixture can produce size-dependent flocculation.

Dispersion on Surfaces: Solvent Surface Tension

- Low Surface Tension (Hexane)
- High Surface Tension (DCB)
Self Assembly of Co Nanoparticles

Size-dependent magnetic behavior of Co nanocrystals

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<th>I_K (nm)</th>
<th>I_L (nm)</th>
<th>D_m (nm)</th>
<th>D_s (nm)</th>
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</thead>
<tbody>
<tr>
<td>Fe</td>
<td>1714</td>
<td>8x10^5</td>
<td>1.7x10^4</td>
<td>770</td>
<td>14.5</td>
<td>17.5</td>
<td>3.5</td>
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Defects act as nucleation sites.
Defects act as pinning sites.
Perfect crystal.
Defective crystal.

Superparamagnetic.
Single domain.
Multi-domain.
Dreaded process.
Single domain rotation.
Single domain curling mode.
Domain wall motion.
Low Field

High Field

Zero Field Cooled

KV > 27k_BT

KV ~ 27k_BT

KV < 27k_BT

t = 1

t = 2

t = 3

Cooled Under Field

KV > 27k_BT

KV ~ 27k_BT

KV < 27k_BT

t = 1

t = 2

t = 3
Magnetic Behavior of Co Nanocrystal Arrays: ZFC & FC

Ideal
Non-interacting
Superparamagnetic
Nanocrystals
(monodisperse)

Dipolar Ferromagnets?
Ferromagnetism in the absence of exchange interactions

Luttinger and Tisza (1946)
Roser and Corruncini (1990)
Bouchaud and Zerah (1993)
Work in progress: ZFC - FC- TRM measurements

Collaborators: Per Norbladt and Petra Jonsson, Uppsala University

Work in progress: ZFC - MEM measurements

Collaborators: Per Norbladt and Petra Jonsson, Uppsala University
Summary

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Controlling the Shape of Nanocrystals

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Entropy as the driving force
Experimental Variables: size, shape & magnetic interactions

Magnetic properties of NC arrays

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