Lecture 6. Synthesis and Fabrication of Nanomaterials

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(a) Some nanoparticle samples (Gold nanoparticles)

(b) Case Study: Shaped Nanoparticles (nanocubes, etc)

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(a) Nanoporous template: AAO membrane
   Nanowire samples (Au, Ni, Cu)

(b) Case study: Electrodeposition in nanoporous templates

Self-assembly and Nanotechnology
Section I:

Synthesis of Nanoparticles
Growth of colloidal nanocrystals by reduction in the presence of surfactants

**General Strategy**

- Metal precursor solution
- Reducing Agent
- Capping (stabilizing agent)
- Solvent (heated)

**Example: Gold nanocrystals**

- Tetrachloroauric acid (HAuCl\(_4\))
- Boil with Trisodium citrate

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**Self-assembly and Nanotechnology**
Molecular surfactant templated growth of nanoparticles

Self-assembly and Nanotechnology
Different solute interaction possibilities can occur

Non-polar compound

Polar compound

Amphiphilic compound

Self-assembly and Nanotechnology
Synthesis of Nanoparticles Using Reverse Micelles

AOT: Sodium bis (2-ethylhexyl)sulfosuccinate

Radius of micelle (nm) = 0.15 \[\text{water} / \text{[AOT]}\]

Molar ratio


Self-assembly and Nanotechnology
Nanoparticle Synthesis in Reverse Micelles

AOT: Reverse micelles (0.2 M AOT + 0.4 M water in cyclohexane)
Titanium isopropoxide Ti[OCH(CH₃)₂]₄ 0.2 M added under vigorous stirring

Langmuir, 13, 16, 1997

Self-assembly and Nanotechnology
Nanoparticles Stabilization against Aggregation (VDW force is high)

- **Electrostatic** (adsorption of ions)
- Coat particles with Organic molecules / polymers
  - Capping (stabilizing agent)
  - e.g. Trioctylphosphine oxide (TOPO)

Self-assembly and Nanotechnology
Nanoparticle Size Controlled by Ratio of Au(III) / citrate

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<th>Amount of trisodium citrate solution (1%, mL)</th>
<th>Color</th>
<th>λₘₐₓ</th>
<th>Size (nm)</th>
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Reference: Chemical Physics Letters (2004), 395(4-6), 366-372

Self-assembly and Nanotechnology
The diameter of gold nanoparticles determines the wavelengths of light absorbed. The colors in this diagram illustrate this effect.
Quantum Dots

Fluorescence induced by exposure to ultraviolet light in vials containing various sized Cadmium selenide (CdSe) quantum dots.

A quantum dot is a semiconductor nanostructure that confines the motion of conduction band electrons, valence band holes, or excitons (pairs of conduction band electrons and valence band holes) in all three spatial directions.
Different sized quantum dot nanoparticles are shown above, first in ultraviolet light and then in ambient light. The length of the synthesis reaction determines particle size for CdSe, increasing from left to right. In colloidal suspension, this semiconductor behaves in the same way as a metal.
Shape Control over the Growth of Colloidal Nanocrystals

A. Kinetic control: High energy facets grow faster than low energy facets

B. Kinetic shape control through selective adhesion

C. Intermediate energy facet eliminates high energy facet.

D. Controlled branching of nanocrystals


Self-assembly and Nanotechnology
Case Study I:
Shaped Nanoparticles - Nanocubes
Shaped Nanoparticles

Spherical vs. shaped nanoparticles

Novel properties: size and shape dependent optical, electrical, etc.

Several examples

◆ Younan Xia’s group, U Washington
  ![Ag nanocubes](image)

◆ Catherine J. Murphy’s group, U South Carolina
  ![Au nanoparticles](image)

◆ A Paul Alivisatos’s group, UC Berkeley
  ![Tetrapod-shaped CdSe](image)

*Self-assembly and Nanotechnology*
Shaped Nanoparticles – Polyol Synthesis

Solution-phase synthesis

Including: metal precursor, solvent, reducing agent, capping agent, etc.

**Capping agents**: surfactants or polymers, modifying the kinetics of atoms assembly/growth to generate shapes

**Polyol method**: easy and efficient method

Solvent: ethylene glycol

Also as a reducing agent when heated

Capping agents: polymers mostly used

**Purposes**:

- Self-assembly or directed assembly to create 1D, 2D, and 3D structures
- Self-assembly with polymers or block copolymers to obtain novel nanocomposites
Shaped Nanoparticles – Some Preliminary Results

SEM images of Ag nanoparticles using poly(vinyl pyrrolidone) (PVP)

SEM images of Ag nanoparticles using Block copolymers

Pluronic block copolymers PEO-PPO-PEO

Self-assembly and Nanotechnology
Shaped Nanoparticles – Nanocubes

SEM images of Ag nanoparticles using poly(allylamine hydrochloride) (PAH)

Self-assembly and Nanotechnology
Section II:
Synthesis of Carbon Nanotubes
Carbon Nanotube: A Form of Carbon

Graphite (stable)

Bucky ball (metastable)

Nanotube = rolled sheet of graphite

Smalley & Kroto, 1997 Nobel

Cited: >4000 times

Review on Nanotubes:

Self-assembly and Nanotechnology
Different Types of Nanotubes

- Zig-Zag
- Armchair
- Chiral

**a1** zig zag vector
**a2** reflection over armchair line

Self-assembly and Nanotechnology
Different Types of Nanotubes

The \( (n,m) \) nanotube naming scheme can be thought of as a vector \( (Ch) \) in an infinite graphene sheet that describes how to 'roll up' to graphene sheet to make the nanotube. \( T \) denotes the tube axis, and \( a_1 \) and \( a_2 \) are the unit vectors of graphene in real space. It is based upon similar diagrams found in the literature (for instance, Odom et al. Topics Appl. Phys., 2001, 80, 173).

Self-assembly and Nanotechnology

Science, 297, 2 Aug 2002
Single Wall and Multi Wall Nanotubes

SWNT (single Wall nanotube)  
Diameter ~ 1.4 nm

MWNT (multiwall)  
Diameter 10-20 nm

Up to cm long

Must read Paper:

Self-assembly and Nanotechnology
Methods for Fabricating Nanotubes

- Arc Vaporization
- Laser Vaporization
- CVD
- Flame
Arc Discharge

~ 1mm spaced carbon electrodes

Metal doped electrodes (Fe, Co, Ni, Mo): SWNT

Pure Graphitic electrodes: MWNT (other fullerenes etc)

DC (20 V, 100 A)
Generates an arc

During this process, the carbon contained in the negative electrode sublimates because of the high temperatures caused by the discharge. Because nanotubes were initially discovered using this technique, it has been the most widely used method of nanotube synthesis.

The yield for this method is up to 30 percent by weight and it produces both single- and multiwall nanotubes, however they are quite short (50 microns)
CVD: Metal Catalysts

HiPco: CO, Fe(CO)$_5$
Commercial Process
97% Pure, 450 mg /hr

- C based gas
  - (acetylene, ethylene, methane)
  - Catalyst (Fe, Co, Ni)
  - Temperature 700-1000 C

Self-assembly and Nanotechnology
Laser Ablation, pulsed laser, 500 Torr Ar.

Mechanism Ablation, arc discharge: Still Controversial

- Atomize Carbon (Explode or Dissociate on Metal)
- Preclude initial recombination (metal-C bond, high energy)
- Confinement (Prevent over expansion, Background Pressure Key * Note deposition is not in vacuum)
- Cooling (crucial for SWNT, MWNT) (In a metal Dissolution to form a supersaturated solution)
- \( sp_2 \) hybridization, sheet bends to reduce dangling bonds (high energy)

In the laser ablation process, a pulsed laser vaporizes a graphite target in a high temperature reactor while an inert gas is bled into the chamber. The nanotubes develop on the cooler surfaces of the reactor, as the vaporized carbon condenses. A water-cooled surface may be included in the system to collect the nanotubes.

Self-assembly and Nanotechnology

Role of Catalytic Particles in Nanotube Growth

Extrusion or Root Growth

\[ C_nH_m = C + H_2 \]

Tip Growth

Explains Hollow Tube

Self-assembly and Nanotechnology
Purification to get carbon nanotubes of precise composition and size

- Oxidation: Damage to SWNT (closed structure less reactive) less than other carbon / metal compounds
- Acid treatment, Ultrasonication (Metal removal)
- Magnetic removal of catalysts
- Microfiltration (SNWT trapped), fullerenes solvated in CS2
- Functionalization, Cutting using fluorination and pyrolysis
- Chromatography (HPLC-SEC)
Section III:
Synthesis of Nanowires

Self-assembly and Nanotechnology
Most commonly used methods

- CVD (Chemical Vapor Deposition)
- Solution phase synthesis
- Electrodeposition
Vapor Liquid Solid (VLS) growth (in CVD)

I: Metal catalyst reacts with vapor of Ge (from the decomposition of GeI$_2$)

II: Au and Ge form a liquid eutectic when temp above (361 C)

III: Droplet becomes supersaturated in Ge, Ge starts to precipitate on liquid Au, at the solid liquid interface.

Example: Birth of a Ge Nanowire from an Au Catalyst Particle

Au catalyst + GeI$_2$ vapour

SEM images of Ge nanowires

Y. Wu, P. Yang, JACS 2001, 123, 3165

Self-assembly and Nanotechnology
Case Study II:
Electrodeposition of Nanowires/Nanorods in Nanoporous Templates

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Lab Session II (after spring break)
Promising Nano-Building Blocks – Nanowires (Nanorods)

Nanoparticles (1-100nm)

Nanowires (nanorods)

Anisotropic nanoparticles

Surface functionalization
Assembly/integration
Integrated structures or devices

M^{n+} + n \text{e} \rightarrow M
Reduction

diameter (d) = 15-200nm

length \leq 50 \mu m

- Templates commercially available, and easy to make
- Very large scale production \((10^9-10^{10} \text{ wires/cm}^2)\)
- Relatively easy to fabricate and very good to pattern

Fabrication of Large-scale One- and Multi-component Nanowires

**Process flow**
- Evaporate Ag
- Electroplate electrolytic solutions ($M^{n+}$)
- Etch Ag
- Dissolve template

**Nanowires with one- and multi-component segments**

- One-component nanowires (gold nanowires, $d=50$nm)
- Multi-component nanowires (Gold-Nickel-gold, $d=200$nm)

Gu, Ye, Gracias. *Journal of Materials (JOM)* **2005**, 57, 60-64
Hybrid Nanowires with Controlled Size and Functionality

- Nanowires with different diameters
  - Au nanowire, $d=50\text{nm}$
  - Au nanowire, $d=15\text{nm}$

- Symmetrical and asymmetrical nanowires
  - Au-Polypyrrole nanowire, $d=200\text{nm}$

- Inorganic-organic nanowire: metal-polymer nanowires
  - Polypyrrole

- Nanowires with functional segments
  - With ferromagnetic segments (e.g., Nickel)
  - With sensor segments
  - Tin (Sn) → $\text{SnO}_2$: excellent sensor materials
  - Sn → SnO$_2$; excellent sensor materials
  - Anneal
Summary and perspective

- Section I: Nanoparticles synthesis
- Section II: Carbon Nanotube synthesis
- Section III: Nanowires/nanorods
- Molecular based nanomaterials (organic molecules, polymers,...)
- Bio-related nanomaterials and nanostructures (DNA, peptide, virus, etc)
- New nano-building blocks •••

Self-assembly and Nanotechnology