Nanoscience technology and advanced materials
PHYS 6014

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Lecture 2
What are the differences between matter at the nanoscale and the bulk?

What are the main properties of metal nanoparticles that they change at the nanoscale?

How the nanoparticle size and shape change affects their optical properties?

What are the differences between metal and semiconductor nanoparticles?

Name few applications of semiconductor nanoparticles.
Outline

Synthesis of nanoparticles—fundamentals

Functionalization of nanoparticles

Examples of synthetic protocols to produce nanoparticles of different sizes and shapes
Synthesis of nanoparticles—fundamentals
Synthetic Approach

Top-down approach

Physical and lithographic principles of microtechnology are used for the construction of nanometre scale objects.

Bottom-up approach

Ionic, atomic, or molecular units are assembled through various processes to form structures in the nanometer range.
Some examples of top down and bottom up approaches

**Top down approach:** Mechanical methods (e.g. Ball milling), thermal fabrication methods (e.g. annealing), high energy and particle fabrication methods (e.g. laser ablation), chemical fabrication methods (e.g. etching), lithographic methods (e.g. electron beam lithography), natural fabrication methods (e.g. erosion).

**Bottom up approach:** Gas phase methods (e.g. chemical vapour deposition), non-biological liquid phase methods (e.g. reduction of metal salts), bottom-up lithographic methods (e.g. STM writing), biological and inorganic methods (e.g. formation of DNA of sugars, phosphate and nucleosides).
Bottom-up approach

bottom-up approach is driven mainly by the reduction of Gibbs free energy

$$\Delta G = \Delta H - T\Delta S$$

nanostructures and nanomaterials produced are in a state closer to a thermodynamic equilibrium state

To have $\Delta G$ as negative as possible, $\Delta H$ should get small and $\Delta S$ large

$\Delta H$ is related to the surface energy and $\Delta S$ is related to the objects and the space that they occupy
Surface energy

Surface energy is the energy required to create a unit area of surface

\[ \gamma = \left( \frac{\partial G}{\partial A} \right)_{n,T,P} \]

A restoring force is needed to pull the surface atoms back to their original positions

\[ \gamma = \frac{1}{2} N_b \varepsilon \rho_a \]

\( \gamma \equiv \text{surface energy} \)
\( \varepsilon \equiv \text{bond strength} \)
\( N_b \equiv \text{number of broken bonds} \)
\( \rho_a \equiv \text{density of surface atoms} \)

For an fcc structure with a lattice constant of \( \alpha \), the crystallographic face with the lowest surface energy is the 111.

\[ \gamma \{111\} \]

\[ \gamma_{\{111\}} = 2\sqrt{3} \frac{\varepsilon}{a^2} \]
‘Magic’ numbers

<table>
<thead>
<tr>
<th>Number of shells</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
</tr>
</thead>
<tbody>
<tr>
<td>Number of atoms in cluster</td>
<td>13</td>
<td>55</td>
<td>147</td>
<td>309</td>
<td>561</td>
</tr>
<tr>
<td>Percentage of surface atoms</td>
<td>92</td>
<td>76</td>
<td>63</td>
<td>52</td>
<td>45</td>
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</tbody>
</table>

\[ \Delta G = \Delta H - T \Delta S \]
Mechanisms for the reduction of surface energy

the surface energy can be reduced through:

- **surface restructuring** through combining surface dangling bonds into strained new chemical bonds

- **surface relaxation**, the surface atoms or ions shift inwardly which occur more readily in liquid phase than in solid surface due to rigid structure in solids

- **surface adsorption** through chemical or physical adsorption of terminal chemical species onto the surface by forming chemical bonds or weak attraction forces such as electrostatic or van der Waals forces

- **composition segregation** or impurity enrichment on the surface through solid-state diffusion
Challenges to the synthesis of colloidal nanoparticles

Retain stability in solution of the as prepared nanoparticles (compensate the huge surface energy so that particles do not aggregate).

Identify ways to synthesize particles with narrow size distribution and good crystallinity.
A simple example of colloidal nanocrystal synthesis

Aqueous Solution
NaAuCl₄

Aqueous Solution
Trisodium Citrate

200 nm
<table>
<thead>
<tr>
<th>Precursors</th>
<th>Formula</th>
</tr>
</thead>
<tbody>
<tr>
<td>Metal anode</td>
<td>Pd, Ni, Co</td>
</tr>
<tr>
<td>Palladium chloride</td>
<td>PdCl₂</td>
</tr>
<tr>
<td>Hydrogen hexachloroplatinate IV</td>
<td>H₂PtCl₆</td>
</tr>
<tr>
<td>Potassium tetrachloroplatinate II</td>
<td>K₂PtCl₄</td>
</tr>
<tr>
<td>Silver nitrate</td>
<td>AgNO₃</td>
</tr>
<tr>
<td>Silver tetraoxylchlorate</td>
<td>AgClO₄</td>
</tr>
<tr>
<td>Chloroauric acid</td>
<td>HAuCl₄</td>
</tr>
<tr>
<td>Rhodium chloride</td>
<td>RhCl₃</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Reduction Reagents</th>
<th></th>
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<tbody>
<tr>
<td>Hydrogen</td>
<td>H₂</td>
</tr>
<tr>
<td>Sodium citrate</td>
<td>Na₃C₆H₅O₇</td>
</tr>
<tr>
<td>Hydroxylamine hydrochloride</td>
<td>NH₄OH + HCl</td>
</tr>
<tr>
<td>Citric acid</td>
<td>C₆H₈O₇</td>
</tr>
<tr>
<td>Carbon monoxide</td>
<td>CO</td>
</tr>
<tr>
<td>Phosphorus in ether</td>
<td>P</td>
</tr>
<tr>
<td>Methanol</td>
<td>CH₃OH</td>
</tr>
<tr>
<td>Hydrogen peroxide</td>
<td>H₂O₂</td>
</tr>
<tr>
<td>Sodium carbonate</td>
<td>Na₂CO₃</td>
</tr>
<tr>
<td>Sodium hydroxide</td>
<td>NaOH</td>
</tr>
<tr>
<td>Formaldehyde</td>
<td>HCHO</td>
</tr>
<tr>
<td>Sodium tetrahydroborate</td>
<td>NaBH₄</td>
</tr>
<tr>
<td>Ammonium ions</td>
<td>NH₄⁻</td>
</tr>
</tbody>
</table>
### Different nanocrystal morphologies

<table>
<thead>
<tr>
<th>Structures</th>
<th>Shapes</th>
<th>Schematic drawings</th>
<th>Metals</th>
</tr>
</thead>
<tbody>
<tr>
<td>single-crystal</td>
<td>perfect/truncated cube</td>
<td></td>
<td>Pd, Ag, Au, Pt, Cu, Rh, Bi, Fe</td>
</tr>
<tr>
<td></td>
<td>perfect/truncated octahedron</td>
<td></td>
<td>Pd, Ag, Au, Pt</td>
</tr>
<tr>
<td></td>
<td>perfect/truncated tetrahedron</td>
<td></td>
<td>Ag, Au, Pt, Rh</td>
</tr>
<tr>
<td>rectangular bar</td>
<td></td>
<td></td>
<td>Pd, Ag, Pt</td>
</tr>
<tr>
<td>octagonal rod</td>
<td></td>
<td></td>
<td>Pd, Au, Fe, Co, Ni</td>
</tr>
<tr>
<td>rectangular or octagonal wire</td>
<td></td>
<td></td>
<td>Pb, In, Sn, Sb, Fe, Co</td>
</tr>
<tr>
<td>singly twinned</td>
<td>right bipyramid</td>
<td></td>
<td>Pd, Ag</td>
</tr>
<tr>
<td>multiply twinned</td>
<td>decahedron</td>
<td></td>
<td>Pd, Ag, Au</td>
</tr>
<tr>
<td></td>
<td>icosahedron</td>
<td></td>
<td>Pd, Au</td>
</tr>
<tr>
<td></td>
<td>five-fold twinned pentagonal rod</td>
<td></td>
<td>Pd, Ag, Au, Cu</td>
</tr>
<tr>
<td></td>
<td>five-fold twinned pentagonal wire</td>
<td></td>
<td>Ag, Au, Cu</td>
</tr>
<tr>
<td></td>
<td>triangular/hexagonal plate</td>
<td></td>
<td>Pd, Ag, Au, Cu, Pb, Bi, Co, Ni</td>
</tr>
<tr>
<td></td>
<td>disc</td>
<td></td>
<td>Sn, Co</td>
</tr>
</tbody>
</table>

### Crystallographic Planes

- **{100}**
- **{111}**
- **{110}**

**Twin planes**
Nanocrystal Synthesis: Nucleation and Growth

\[ \Delta G_v = -\frac{kT}{\Omega} \ln \left(\frac{C}{C_o}\right) = -\frac{kT}{\Omega} \ln(1 + \sigma) \]

- \( \Delta G_v \): free energy change per volume
- \( k \): Boltzman constant
- \( T \): temperature
- \( \Omega \): atomic volume
- \( C \): concentration of solute
- \( C_o \): equilibrium concentration or solubility
- \( \sigma \): supersaturation, \( \sigma = (C - C_o)/C_o \)

See G. Cao – Nanostructures and Nanomaterials, Imperial College press 2004
Nucleation and growth-schematically

I - the concentration of atoms steadily increases with time as the precursor is decomposed

II - the concentration of atoms reaches a point of supersaturation, the atoms start to aggregate into small clusters (i.e., nuclei) via self- (or homogeneous) nucleation. These nuclei then grow in an accelerated manner and the concentration of atoms in solution drops.

III - If the concentration of atoms drops quickly below the level of minimum supersaturation, no additional nucleation events will occur. With a continuous supply of atoms via ongoing precursor decomposition, the nuclei will grow into nanocrystals of increasingly larger size until an equilibrium state is reached between the atoms on the surface of the nanocrystal and the atoms in the solution.
Nucleation Process

\[ \Delta G_v \quad \text{Free energy change per volume} \]

Free energy change for forming solid particle with radius \( r_{\text{nuc}} \):

\[ \Delta G_{\text{nuc}} = \Delta G_v \frac{4}{3} \pi r_{\text{nuc}}^3 + \gamma 4\pi r_{\text{nuc}}^2 \]

\( \text{Volume} \quad \text{Surface} \)

\[ \frac{\partial \Delta G_{\text{nuc}}}{\partial r} \bigg|_{r=r^*} = 0 = \Delta G_v 4\pi r^*^2 + 8\gamma\pi r^* \]

\[ r^* = -\frac{2\gamma}{\Delta G_v} \]

\[ \Delta G^* = \frac{16\pi\gamma^3}{3\Delta G_v^2} \quad \text{critical free energy, nucleation barrier} \]

See G. Cao – Nanostructures and Nanomaterials, Imperial College press 2004
Nucleation Rate

Nucleation rate:

\[ J = A \exp\left( -\frac{\Delta G^*}{kT} \right) \]

\[ = \left( \frac{C \ kT}{3\pi\lambda^3 \eta} \right) \exp\left( -\frac{\Delta G^*}{kT} \right) \]

- \( \lambda \): the diameter of the growth species (monomers)
- \( \eta \): viscosity of the solution
- \( C \): initial concentration

Fast nucleation is favored by:

High initial concentration (high supersaturation): \( C \uparrow \)
Low viscosity: \( \eta \downarrow \)
Low critical energy barrier \( \Delta G^* \downarrow \)
High T (usually true, but not always because higher T leads to lower supersaturation)

For a given concentration of solute, a larger number of nuclei mean smaller sized nuclei
Evolution from nuclei to seeds

Once a cluster has grown past a critical size, structural fluctuations become so energetically costly that the cluster becomes locked into a well-defined structure.

This critical point marks the birth of a seed

Structure of the seeds:

- single-crystal
- singly twinned crystal
- multiply twinned crystal
Evolution from nuclei to nanoparticles

$R$ is the ratio between the growth rates along the $<100>$ and $<111>$ directions.
Growth rate of nanocrystals

(i) generation of growth species

(ii) diffusion of the growth species from bulk to the growth surface

(iii) adsorption of the growth species onto the growth surface

(iv) surface growth through irreversible incorporation of growth species onto the solid surface

Diffusion control growth–Surface control growth

Monolayer growth

Poly-nuclear growth
Revision

What is the top–down and what is the bottom–up approach?

What drives the bottom–up chemical synthesis of inorganic colloidal nanocrystals? Suggest ways that the surface energy can be reduced.

For a fcc structure, which plane is more favorable energetically?

What are magic numbers?

Describe the nucleation and growth process. Calculate the critical free energy for the nucleation process?

Describe the nucleation and growth rate.
Explain the top-down and the bottom up approach. What are their differences? Give two examples of production methods that involve these approaches.
**Top down approach:** Physical and lithographic principles of microtechnology are used for the construction of nanometre scale objects from the bulk.

1. **Mechanical methods** (e.g. Ball milling–Production of nanoparticles by mechanical attrition to produce grain size particles. High energy ball milling uses steel balls to transfer kinetic energy by impact to the sample–Usually involved in the formation of ferroelectric barium titanate nanoparticles.

2. **Lithographic methods** (e.g. electron beam lithography–usually employed for the formation of nanoparticle patterns on surfaces. For example dimers of plasmonic nanorod antennas).

**Bottom up approach:** Ionic, atomic, or molecular units are assembled through various processes to form structures in the nanometer range.

1. **Gas phase methods** (e.g. chemical vapour deposition–Involves the formation of nanomaterials from the gas phase, usually at elevated temperatures, onto a solid substrate catalyst–for example the formation of carbon nanotubes).

2. **Chemical liquid phase methods** (e.g. reduction of metal salts–for example the reduction of gold salt to gold nanoparticles using sodium borohydride),
Surface stabilization
Types of colloidal nanoparticle's stabilization

- Electrostatic stabilization
- Steric stabilization
- Electrosteric stabilization
Electrostatic Stabilization

Repulsion due to electric potentials of two particles

Repulsion due to osmotic flow:
• **Steric Stabilization**

\[ \Delta S < 0 \]

\[ \Delta G = \Delta H - T \Delta S > 0 \]

The physical basis for the steric stabilization is:

i) A *volume restriction effect* arising from the decrease in possible configurations in the region between the two surfaces

ii) An *osmotic effect* due to the relatively high concentration of adsorbed molecules in the region between the two particles
Type of interactions of the surfactant with the surface of the nanoparticle

(a)

(b)

a) Chemisorption – An anchored ligand which covalently binds to the surface of the nanoparticle (i.e. a thiol–gold bond or a amine–silver bond)

b) Physisorption – The ligand is adsorb at the surface of the nanocrystal (i.e. hydrophobic, van der Waals interactions)
The stability of sterically stabilised nanoparticles depends on:

i) Type of interaction of the ligands with the surface of nanoparticles
ii) Solubility of the ligand/particle system (i.e. solvent polarity, temperature)
iii) Degree of surface coverage of the ligands.

Advantages of steric stabilization vs. electrostatic stabilization

a) Particles with a high coverage of ligands are always re-dispersible

b) Very high concentration of particles can be accommodated in a solution

c) It is not electrolyte sensitive

d) Particles can be well-dissolved in different solvents by appropriate choice of the stabilizer
Electrosteric stabilization

Schematic representation of electrosteric stabilization: (a) charged particles with nonionic polymers and (b) polyelectrolytes attached to uncharged particles.
Examples of nanocrystal synthesis
CdSe Nanocrystal Synthesis–Thermal decomposition

Precursors: CdO + Se–TOP
Surfactants: TOPO, TOP, Alkyl amine
Solvent: TOPO

\[ \text{CdO} + \text{Se–TOP} \rightarrow \text{CdSe} + \text{TOPO} \]

Triocetylphosphine oxide (TOPO)
Triocetylphosphine (TOP)

Stir plate
Heating mantle
Temperature controller
A Wide Field View of 7-nm CdSe Nanocrystals
Shape Control by Selective Adhesion of Surfactants

Triocetylphosphine oxide (TOPO)

Hexyl phosphonic acid (HPA)

Wurtzite (hcp)

Anisotropic Growth

Surfactant binds selectively on crystal surfaces, changing surface energy

Monolayer of 4x40 nm CdSe nanorods
Control of Length and Diameter
Wurtzite and Zinc Blende Structures

- The stability of cubic zincblende and hexagonal wurzite structure is similar.
- Nucleation in zincblende structure, growth in wurzite structure.
- The (111) face of zincblende is equivalent to the (001) face of wurzite.
Branching: CdTe Nano-tetrapod

zincblende core  ➔ wurzite arm

50 nm

10 nm
Varying the reaction conditions

Ar

Stir plate

Less amount of organics

Se instead of Te

Scale bars: 100nm

Synthesis of gold nanorods - Seeding procedure

Surfactant as directing agent

Preferential surfactant binding to Au{100} face

A

100 nm

50 nm

100 nm

Ms. Dorota Bartczak
By changing the type of seeds, amount of reducing agents organics bind preferential to a particular crystallographic plane.

perfect/truncated octahedron$^4$

Pd, Ag, Au, Pt

Kanaras group

CrystEngComm, 2010, 12 (12), 4312 – 4316
Seed-growth on a template

Gold salt
Reducing agent

Gold shells grown on silica particles

100 nm
Gold nanoshells
Galvanic replacement reaction

3Ag(s) + AuCl$_4^-$ → Au (s) + 3Ag$^+$ + 4Cl$^-$
Nanocages

Nanocage size is about 80 nm
Revision

Name the different ways that nanoparticles are stabilised in solution and explain them. Which type of stabilization is the ideal one to avoid aggregation?

Give two examples of nanocrystal synthesis based on thermal decomposition and explain. How the shape of CdSe nanocrystals to nanorods can be controlled?

Explain one example of nanoparticle synthesis that involves a seeding procedure.

What is a galvanic replacement reaction and what types of nanoparticles we could synthesize?
Name two ways that a surfactant can interact with the nanoparticle surface
a) Chemisorption – An anchored ligand which covalently binds to the surface of the nanoparticle (i.e. a thiol–gold bond or a amine–silver bond)

b) Adsorption– the ligand is adsorb at the surface of the nanocrystal (i.e. hydrophobic, van der Waals interactions)
What is the difference between metal and semiconductor nanoparticles? Draw a graph and explain.
In any material, there will be a size below which there is substantial variation of fundamental electrical and optical properties with size, which will be seen when the energy level spacing exceeds the temperature. For a given temperature, this occurs at a very large size in semiconductors, as compared to metals. This can be understood by considering that the bands of a solid are centered about atomic energy levels, with the width of the band related to the strength of the nearest neighbor interactions. As a function of increasing size, the center of a band develops first and the edges develop last. Thus, in metals, where the Fermi level lies in the center of a band, the relevant energy level spacing is still very small, and at temperatures above a few kelvin, the electrical and optical properties more closely resemble those of a continuum, even in relatively small sizes (tens or hundreds of atoms). In semiconductors, however, the Fermi level lies between two bands, so that the edges of the bands dominate the low-energy optical and electrical behavior. Optical excitations across the gap depend strongly on the size, even for crystallites as large as 10,000 atoms.