Synthetic Strategies to Colloidal Nanocrystals and Heterostructures

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Colloidal Nanocrystals and Heterostructures

What are they?

Particles with a size of the order of nanometres.

- Tera- (T): $10^{12}$
- Giga- (G): $10^9$
- Mega- (M): $10^6$
- Kilo- (k): $10^3$
- Deci- (d): $10^{-1}$
- Centi- (c): $10^{-2}$
- Milli- (m): $10^{-3}$
- Micro- (μ): $10^{-6}$
- Nano- (n): $10^{-9}$
- Pico- (p): $10^{-12}$
The Micro world

Ant \( \sim 5 \text{ mm} \)

Human hair \( \sim 10-50 \text{ mm wide} \)

Fly ash \( \sim 10-20 \text{ mm} \)

Red blood cells with white cell \( \sim 2-5 \text{ mm} \)

The Nano world

\( \sim 10 \text{ nm} \) diameter

ATP synthase

DNA \( \sim 2 \text{ nm diameter} \)

Atoms of silicon spacing \( \sim \text{tenths of nm} \)

Nanotube electrode

Nanotube transistor

Iron atoms on copper surface Corral diameter \( \sim 14 \text{ nm} \)

Carbon nanotube \( \sim 2 \text{ nm diameter} \)

Head of a pin 1-2 mm

MicroElectroMechanical devices 10-100 mm wide

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Is Nanotechnology a completely new technology?

- as a science, nanotechnology is about 80 years old.
- nanofabrication has been used in the semiconductor industry for about 15 years.
- ultrafine chemicals have also been produced in bulk for a number of years.
NOVEL AND USEFUL PROPERTIES

THERMODINAMIC PROPERTIES

- decreasing of the melting point;
- increasing of pressure required for solid-solid transitions;
- crystalline phases unstable for extended solids

A SIGNIFICANT FRACTION OF ATOMS RESIDES AT THE SURFACE AND NOT IN THE BULK OF THE MATERIAL
OPTOELECTRONIC PROPERTIES OF NANOCRYSTALS

Optical transitions in semiconductors
Absorption of metallic nanocrystals (Au NCs)

- CdSe
- Absorbance (a.u.)
- PL Intensity (a.u.)
- Wavelength (nm)
- Size
- Lenght/width diameter
- 2.5 nm
- 18 nm
- 4.8 nm
- 12.6 nm
ENERGETIC LEVELS OF A BULK SOLID, A NANOCRYSTAL AND A MOLECULE

[Diagram showing energy levels for bulk, nanocrystal, and molecule, with labels for HOMO and LUMO, and a color scale ranging from "red" to "blue"]
the charge carrier motion is restricted to a small material volume
The red-ox potential can be tuned with the size of nanocrystals. 

Usefull application of nanocrystals in Catalysis
MAGNETIC PROPERTIES OF NCs

Nanostructured ferromagnetic materials behave as single magnetic domain whose magnetization can be easily influenced by thermal fluctuations of the local environment, depending on the particle size and on a variety of surface effects.
FERROFLUIDS

Stable Colloidal Suspension of Magnetic Material (Nanoparticles) in a Liquid Carrier

Each Nanoparticle Constitutes a Single Magnetic Domain - SuperParaMagnetism -

Applications: magnetic seals, lubricants, loudspeakers, dumpers, inks, medicine,...
HOW ARE THEY SYNTHESIZED?

Several methods are possible, e.g.

- Precipitation
- Milling
- Reduction
- Condensation

They can be synthesized in the solid, liquid or gaseous phase.

SOME EXAMPLES... >>
Synthesis of Maghemite

Wet chemical coprecipitation

Base

Fe²⁺, Fe³⁺

Sedimentation

Oxidation/Redispersion

γ-Fe₂O₃

Bare particles

+ Polymer

PRODUCT

PRECIPITATION
MILLING

Transmission electron micrograph of ~30nm zinc oxide

Particle size distribution curve for MCP ~30nm ZnO nanopowder showing a mean particle size of 30nm
TiO$_2$ Nanorods $\approx 10$ nm
“Nanochemistry and Nanophysics”

Nanochemistry can be described as a special discipline of inorganic or solid state chemistry. It focuses on the synthesis of nanoparticulate systems. The nanochemist can be considered to work towards this goal from the atom "up", whereas the nanophysicist tends to operate from the bulk "down":

Surfactants are amphiphilic molecules composed of a polar head group and one or more hydrocarbon chains with hydrophobic character.

“They: i) act as terminating or stabilizing agents insuring slow growth rate, ii) prevent the agglomeration, iii) confer stability and processability.”

“BOTTOM-UP” APPROACH: hot-injection method
SYNTHESIS OF NANOCRYSTALS

THERMODYNAMIC FACTORS
(e.g.: relative stability of the crystals)

KINETIC FACTORS
(diffusion of reactants, surface adhesion of surfactants)

Experimental conditions to be controlled:

✓ nature and relative concentration of molecular precursors;
✓ catalysts;
✓ organic stabilizers;
✓ growth temperature
Example CdSe

Preparation of semiconductor nanocrystallites:
Solutions of (CH₃)₂Cd and tri-\(n\)-octylphosphine selenide (TOPSe) are injected into hot tri-\(n\)-octylphosphine oxide (TOPO) in the temperature range 120-300 °C. This produced TOPO capped nanocrystallites of CdSe.

Quantum-dots

Size- and material-dependent emission spectra of several surfactant-coated semiconductor nanocrystals in a variety of sizes (A).

Blue series: different sizes of CdSe (Diameter: 2.1, 2.4, 3.1, 3.6, 4.6 nm)

Green series: InP nanocrystals (Diameter: 3.0, 3.5, and 4.6 nm)

Red series: InAs nanocrystals (Diameter: 2.8, 3.6, 4.6, 6.0 nm)

(B) A true-color image of a series of silica-coated core (CdSe)-shell (ZnS or CdS) nanocrystal probes in aqueous buffer, all illuminated simultaneously with a handheld ultraviolet lamp

Synthesis: There are many wet chemical methods of synthesis for semiconductor nanoparticles, a organic and an inorganic method are presented here:

\[
\text{Cd}^{2+} + \text{Se}^{2-} \xrightarrow{\text{Stabilizer } L_n} \text{CdSeL}_n
\]

**Optimized synthesis parameters:**

9 < pH < 12.5

Surfactant: Thioalcohols/Thioacids

Atmosphere: inert gas

\[
\text{[Me}_2\text{Cd}] + [(\text{TMS})_2\text{Se}] \xrightarrow{\text{TOP/TOPO}} \text{CdSe}
\]

**Optimized synthesis parameters:**

230 < T < 260°C

Surfactant: TOP/TOPO

Atmosphere: inert gas

(1) Aqueous Cd\(^{2+}\)+S\(^{2-}\) → stabilizer

(2) Cd(CH\(_3\)_2 + (TMS\(_2\)S → hot TOPO

Cd\(^{2+}\) rich surface

CdS

organic surface passivation

inorganic surface passivation

CdS

CdS

CdS

CdS

Cd(\(\text{OH}\))\(_2\)
Size control

Nucleation and Growth

- Nucleation and growth of crystals

% Pearlite

Nucleation rate \( \uparrow \) as \( \Delta T \uparrow \)

Growth rate \( \uparrow \) as \( T \uparrow \)

log (time)

Exam:

- Pearlite colony
- \( T \) just below \( T_E \)
- \( \Delta T \) small
- \( T \) large

- \( T \) moderately below \( T_E \)
- \( \Delta T \) moderate
- \( T \) moderate

- \( T \) way below \( T_E \)
- \( \Delta T \) large
- \( T \) small

Ostwald ripening

Anderson-205-10.5
Size control
Shape control

Star-like PbSe

γ-Fe$_2$O$_3$ tetrapods

FePt faceted NCs

rise-shaped CdSe

Scale bar = 100 nm
Shape control

Pencil-shaped CdS NCs

Ag spheroids

Rectangular-shaped Au nanorods

TiO$_2$ NCs

Scale bar = 100 nm
STRATEGIES FOR SHAPE SELECTION

1. Growth in templates

2. Growth promoted by a catalyst

3. Oriented attachment

4. Growth by selective adhesion

5. Growth in the presence of external fields

6. Seeded growth
In water:

- **WATER**
- **ORGANIC SOLVENT**

**SURFACTANTS ACT BY:**

- **POsing PHYSical CONSTRAINS TO THE UNCONTROLLED NCs ENLARGEMENT DURING THE SYNTHESIS;**
- **COMPLEXING AGENT AVOIDING THE AGGREGATION OF THE NCs AFTER THE SYNTHESIS**
Gold particles in micelles

Synthesis: A-B diblock copolymer is used for micelle formation
Polymer: Poly(styrene-block-2-vinyl-pyridine)
Idea: An inorganic compound such as HAuCl4 is bound selectively to the Polyvinylpyridine block of the polymer and thus solubilized within the core of the micelle. Afterwards, the compound is transformed by chemical reaction to the metal.

Synthesis in a Structured Medium

A number of matrices have been used for the preparation of semiconductor nanoparticles including: zeolites, layered solids, molecular sieves, micelles/microemulsions, gels, polymers, and glasses. These matrices can be viewed as nano-chambers which limit the size to which crystallites can grow. The properties of the nanocrystallites are determined, not only by the confinements of the host material but also by the properties of the system, which include the internal/external surface properties of the zeolite and the lability of micelles.

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HYBRID NANOCRYSTALS

a CdSe; b CdSe/CdS; c CdSe/CdS/ZnS

d Fe/Fe$_3$O$_4$; e FePt/SiO$_2$; f Au nanorods/SiO$_2$

Large interphase between the two materials
Lattice constants do not differ significantly
SKETCH OF POSSIBLE MECHANISMS FOR CORE-SHELL NANOCRYSTAL HETERO_STRUCTURES

1. Growth of a single, a multiple or an asymmetric shell on nanocrystal core.

2. Shell formation following a redox reaction with the initial core.

3. Formation of a uniform shell upon thermal annealing of an initially amorphous and/or discontinuous coating.
Dumbbell-like $\text{Fe}_3\text{O}_4$-Au dimers

Dumbbell-like PbS-Au-PbS ternary NCs

PbSe nanorod-$\text{Fe}_3\text{O}_4$-Au ternary NCs

CoPt$_3$-Au dimers
formation of a heterodimer by phase segregation of two immiscible materials

coalessence of an initially amorphous shell

selective nucleation on a starting seed

growth of a trimer upon formation of a domain which bridges two preformed NCs

formation of a trimer by fusion of two reactive domains from distinct dimers

formation of a trimer by selective nucleation on a preformed heterodimer seed
Dumbbell-like CdSe nanorods with PbSe tips at the ends

Matchstick-like CdS nanorods with one PbSe tip

Matchstick-like CdSe nanorods with one Au tip

Cds Nanocrystals made of Cds rods with CdTe tip on one end and a branching point on the opposite end

USE OF ROD-LIKE SEEDS
In DOE, TOPO, hexane-1,2-diol and Cd(acac)$_2$
TEM and SEM for hybrid NCs
Nanoparticles

What are they used for?

The potential number of applications is enormous, e.g. Adhesives, e.g. varied strength from “post it” to “solid weld” Coatings, e.g. sunscreens now incorporate nanoparticles. Medical, e.g. new methods of delivering drugs etc. etc.

Ultimately they will be applied in all industries just as micron-sized particles are used today.

...WE’LL SEE THE NEXT TIME...>>
A GOOD NANOMATERIAL

- narrow size distribution;
- fewer internal defects;
- uniform surface;

- Well defined physical properties, such as strong plasmon absorption for metal NCs or luminescence for semiconductor materials

Once the synthesis is stopped by lowering the reaction temperature, a surfactant coating layer around the NCs remains tightly bound to their surface and guarantees their full solubility in a variety of organic solvents.
REVIEWS
