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16.982 Bio-Inspired Structures
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Chemical Synthetic Routes for Metal and Semiconductor Nanoparticles and Structures

Additional Synthetic Approaches

- Sonochemical
- Electrochemical
- Photochemical
- Chemical Vapor Deposition

Aspects of Nanoparticle Growth in Solution

Arrested precipitation

Precipitation under starving conditions: a large number of nucleation centers are formed by vigorous mixing of the reactant solutions.

If concentration growth is kept small, nuclei growth is stopped due to lack of material.

Particles had to be protected from Oswald Ripening by stabilizers

Oswald Ripening

The growth mechanism where small particles dissolve, and are consumed by larger particles. As a result the average nanoparticle size increases with time and the particle concentration decreases. As particles increase in size, solubility decreases.

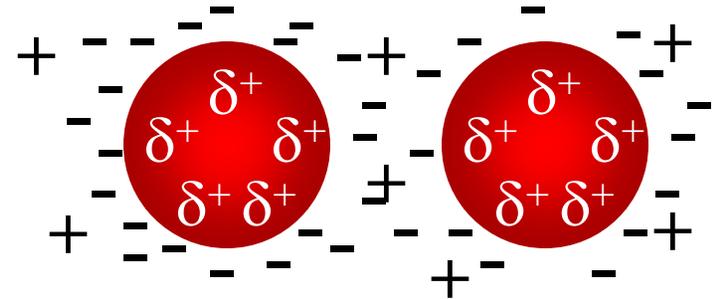
Synthetic Approaches for Metal and Semiconductor Nanoparticles via Chemical Routes

1. Metal Compound
 - Positively charge metal salt, or
 - Metal centers of complexes
2. Solvents (depends on the nature of the salt)
 - Water
 - Polar organic solvents
 - Non-polar organic solvents
3. Reducing agent (determined by the nature of the metal compound)
 - Gaseous hydrogen
 - Hydridic compounds
 - Reducing organics, e.g. alcohols
 - Many others

Stabilization of Nanoclusters Against Aggregation

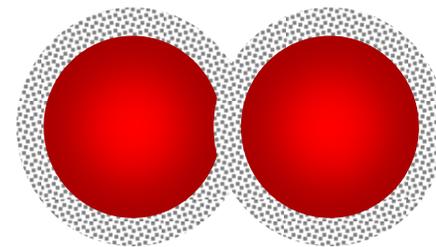
1. Electrostatic stabilization

Adsorption of ions to the surface. Creates an electrical double layer which results in a Coulombic repulsion force between individual particles



2. Steric Stabilization

Surrounding the metal center by layers of material that are sterically bulky, Examples: polymers, surfactants, etc



Synthetic Approaches for Metal and Semiconductor Nanoparticles via Chemical Routes

4. Stabilizers

Role of stabilizers:

Stabilizing agents/ligands/capping agents/passivating agents

- prevent uncontrollable growth of particles
- prevent particle aggregation
- control growth rate
- controls particle size
- Allows particle solubility in various solvents

Other Common Stabilizers

1. Organic ligands

- Thiols (thioethanol, thioglycerol, mercaptoethylamine, etc)
- Amines
- phosphates

2. Surfactants

3. Polymers

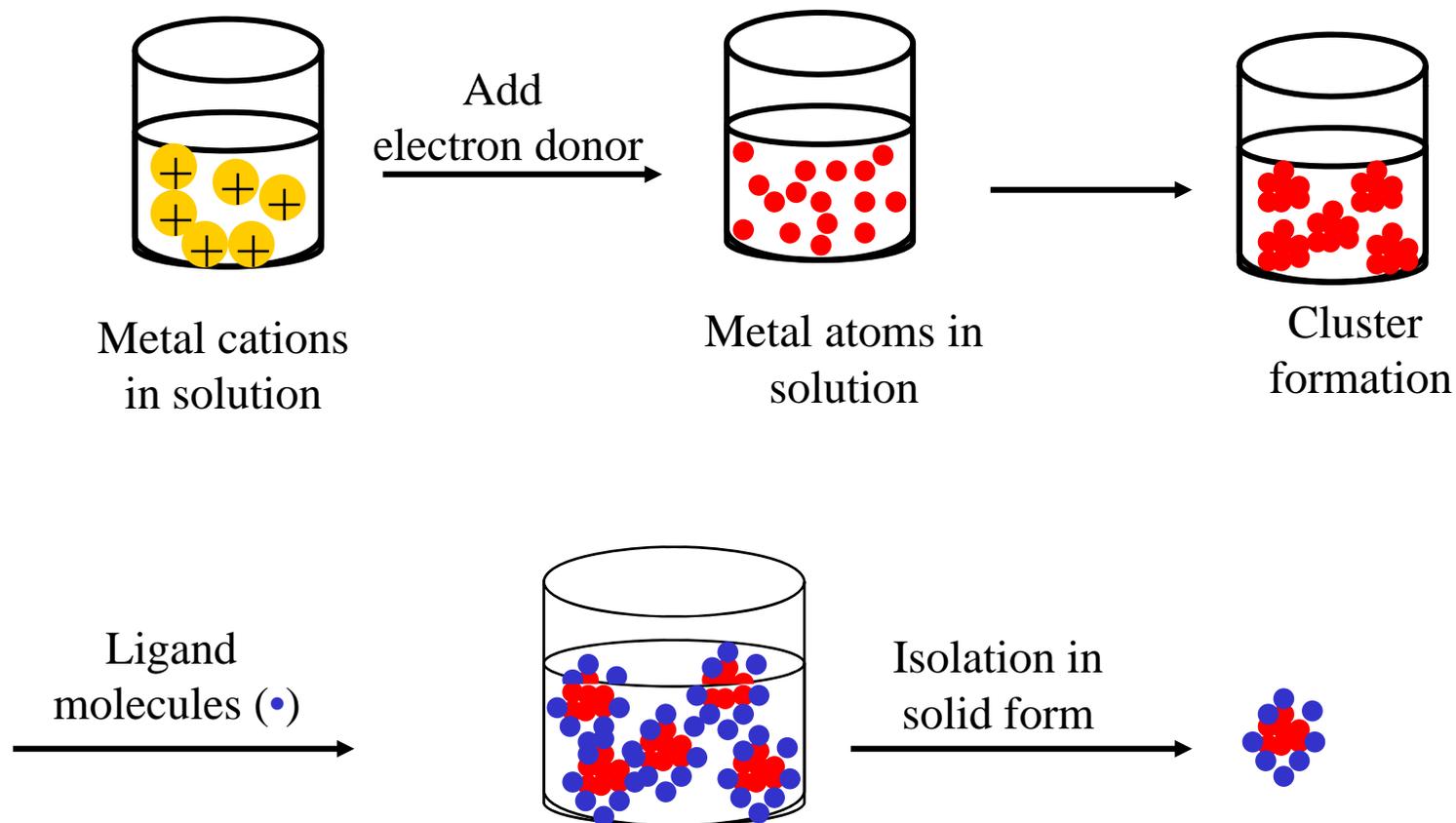
4. Solvents

ether

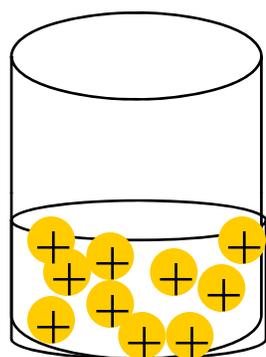
thioether

5. Polyoxoanions

Schematic Procedure for Cluster Synthesis

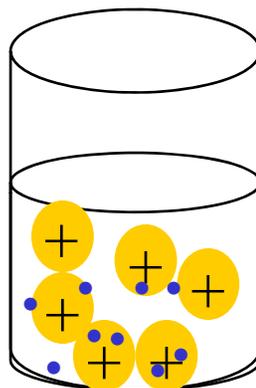


Schematic Procedure for Cluster Synthesis

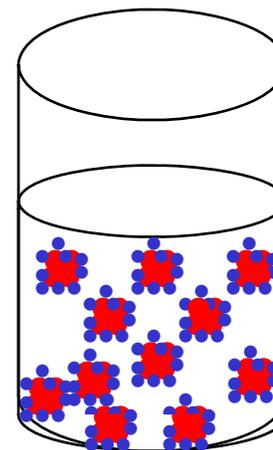


Metal cations
in solution

Add
Ligand
molecules (•)



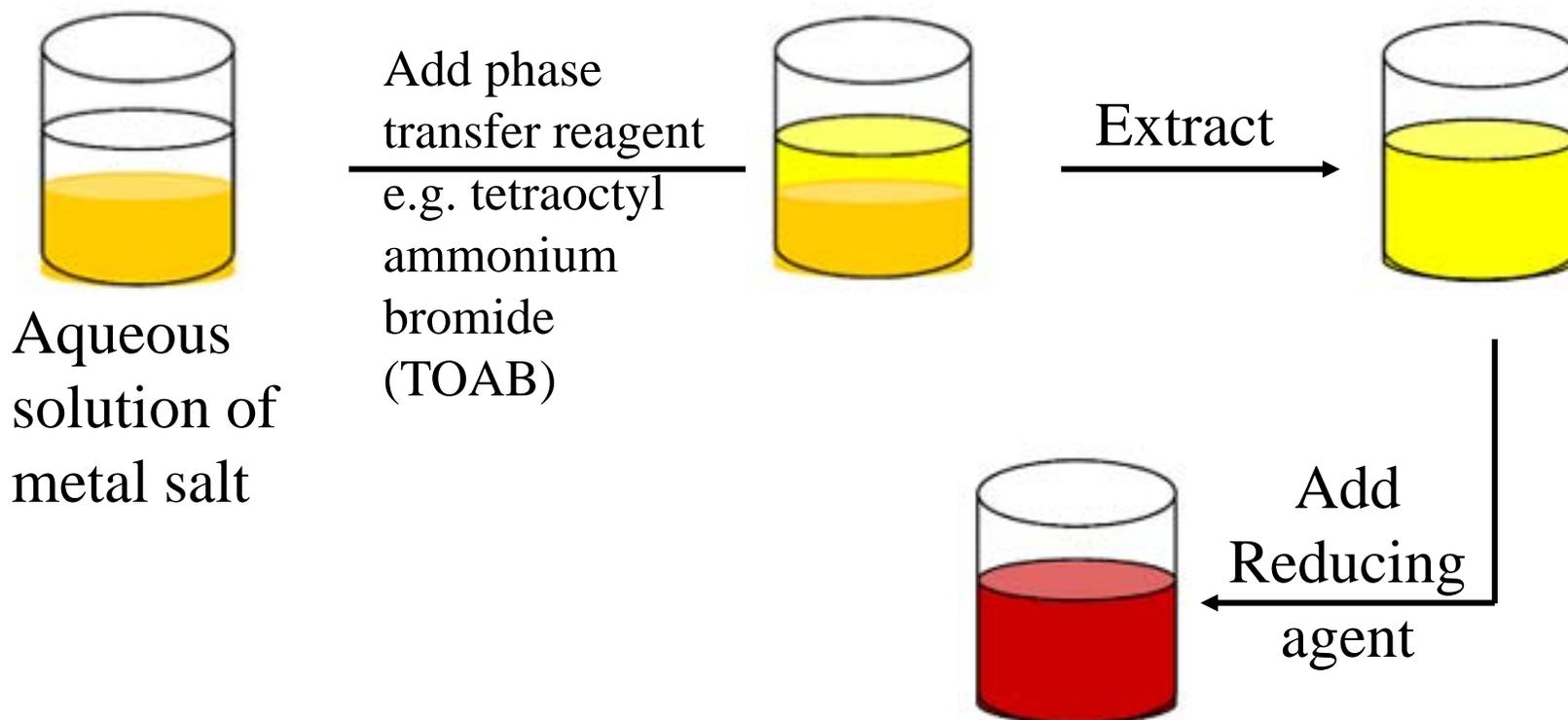
Add
electron
donor



Stabilized
Metal particles
in solution

Synthesis of Metal Nanoparticles in Organic Media

Biphasic reduction procedure



TEM Image of Au Nanoparticles Prepared in the Presence of a Surfactant (CTAB)

Image removed due to copyright restrictions.

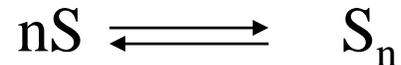
J. Phys. Chem. B. **2001**, *105*, 4065

CTAB = cetyltrimethylammonium bromide

Nucleation and Growth

Homogeneous nucleation occurs via a stepwise sequence of bimolecular additions until a nucleus of critical size is obtained.

a. Nucleation from supersaturated solution



b. Diffusion-Controlled Growth



LaMer et al. *J. Am. Chem. Soc.* **1950**, 72, 4847

Highly monodisperse nanoparticles are formed if the processes of nucleation and growth can be successfully separated

- Nucleation process must be fast
- Growth process must be slow

Nucleation

Nucleus Radius is calculated as follows:

$$\Delta G = 4\pi\sigma(r^2 - [2r^3 / 3r^*])$$

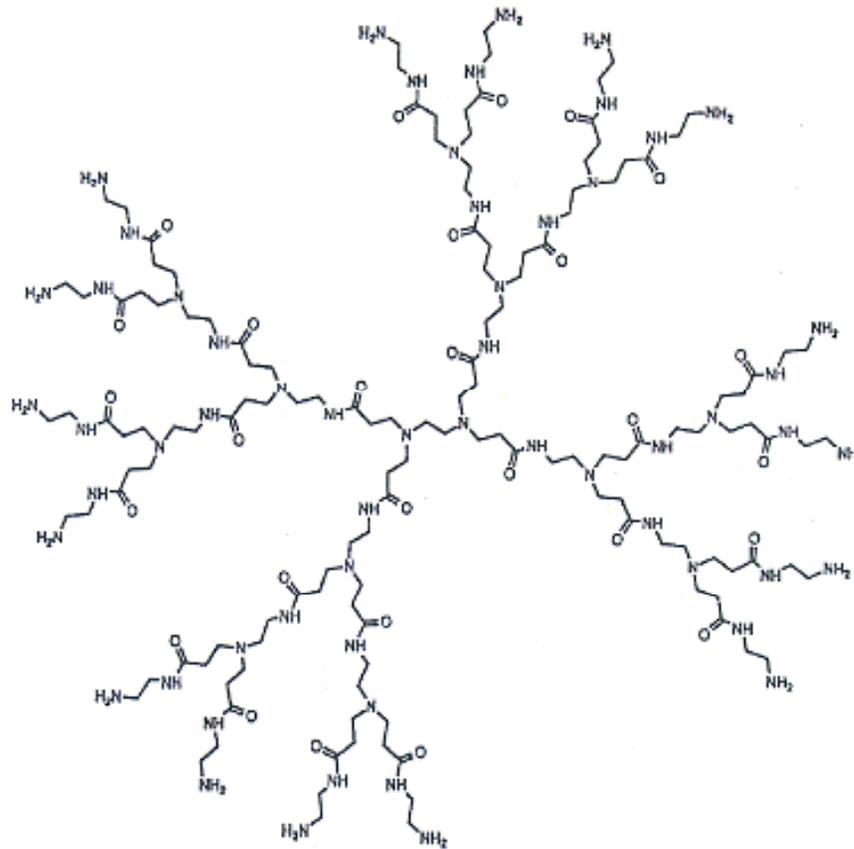
Where r = nucleus radius
 r^* = critical nucleus radius
 σ = surface tension

$$\Delta G_{(\text{nucleus})} = n(\Delta G_{\text{formation, bulk}} - \Delta G_{\text{formation, free atom}}) + \sigma A$$

Where A = particle surface area

Dendrimer-Templated Nanocluster Synthesis

Structure of poly(amidoamine) dendrimer (PAMAM)



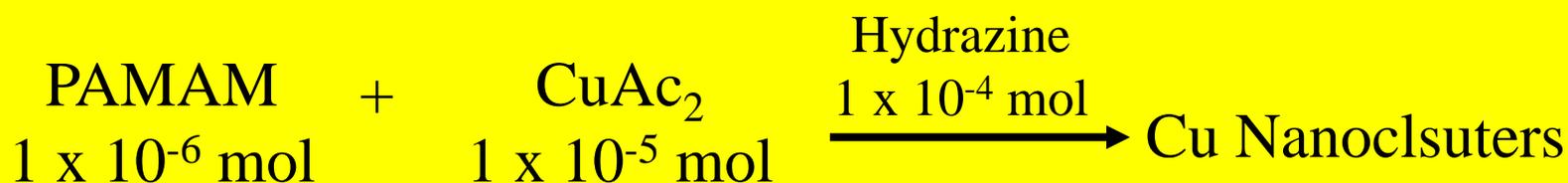
Generation 2 PAMAM Dendrimer

Dendrimer-Templated Nanocluster Synthesis

Pioneered in 1998, by

Donald A. Tomalia (Michigan Molecular Institute)

Richard M. Crooks (TAMU)



Formation of Cu nanoclusters can be monitored by UV-vis spectrophotometry

Reaction is pH dependent:
Presumably H^+ ions compete with Cu^{2+} ions for the tertiary amine sites

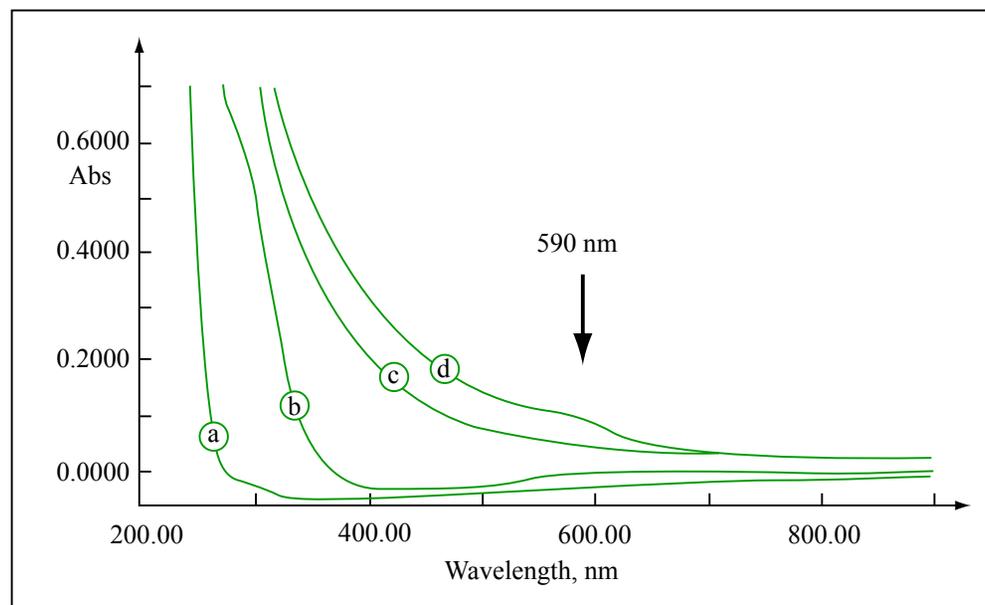


Figure by MIT OpenCourseWare.

J. Am. Chem. Soc. **1998**, *120*, 4877

J. Am. Chem. Soc. **1998**, *120*, 7355

Reverse Micelles

Water-in-oil droplets

$$\text{Water pool } w = \frac{[\text{H}_2\text{O}]}{[\text{surfactant}]}$$

Particle size is controlled by the size of the water droplets in which synthesis takes place

Consider that:

$$R = 3V/A$$

V = volume , R = radius,
A = surface area

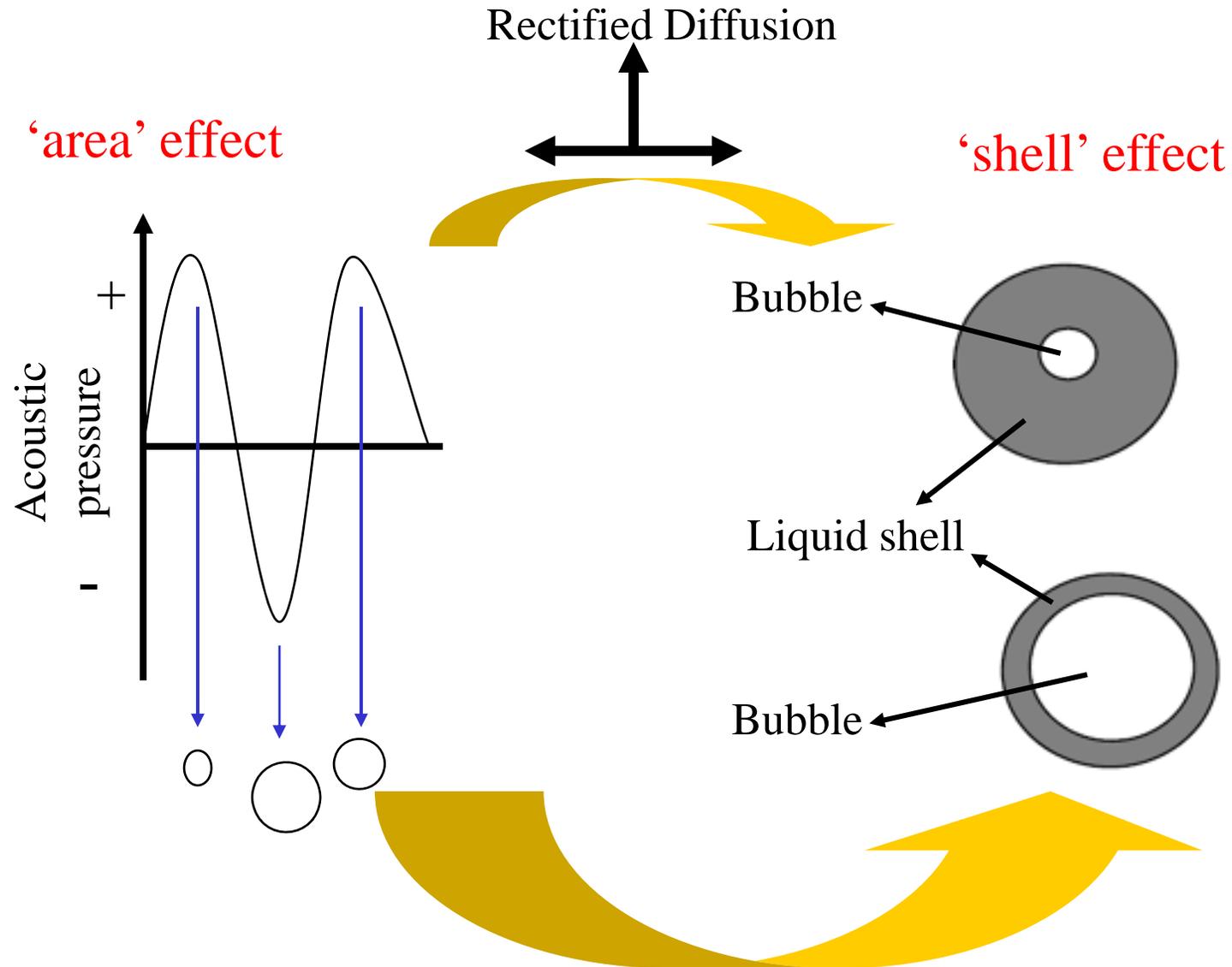
$$R_w = \frac{3V_{\text{aq}}[\text{H}_2\text{O}]}{\sigma[s]}$$

σ = head polar group area
 V_{aq} = volume of water

Parameters Affecting Particle Growth/ Shape/ Structure

- Type of capping agent/stabilizers
- Concentration of the reactants
- pH value of the solution
- Duration of heat treatment

Sonochemical Approaches for Nanoscale Particle Synthesis



Sonochemical Approaches for Nanoscale Particle Synthesis

Step 1:

- Bubble expands when surrounding medium experiences –ve pressure
- Bubble collapses when surrounding medium experiences +ve pressure
- Bubble collapse leads to extreme temperatures (5,000 – 50, 000 K), and pressure (100 atm) within the bubble

Step 2:

Solvent or solute molecules present within the bubbles are decomposed under these extreme conditions and generate highly reactive radicals

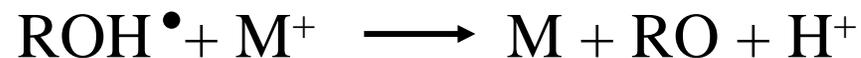
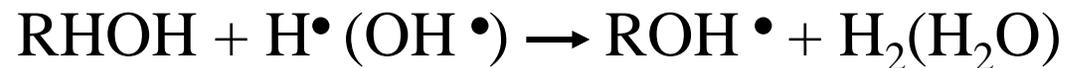
Formation of Highly Reactive Radicals

Depending on the liquid medium, sonication leads to the generation of oxidizing and reducing radicals

In aqueous solution

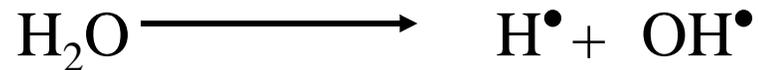


In solutes like alcohols, sonication leads to secondary radicals



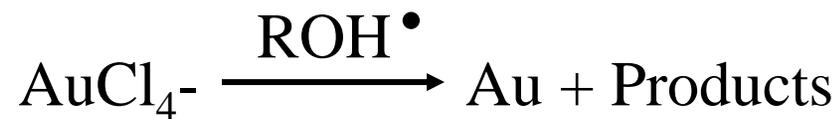
Examples of Metal Nanoparticles Prepared by Sonication

Ag nanoparticles prepared in aqueous solution at 1 MHz



J. Phys. Chem. **1987**, 91, 6687

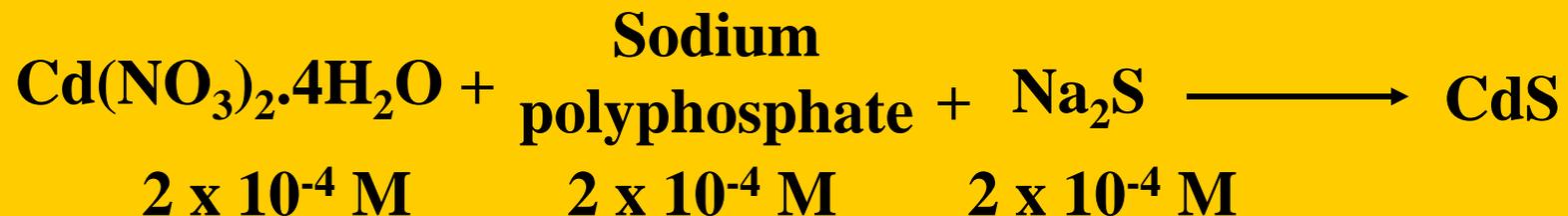
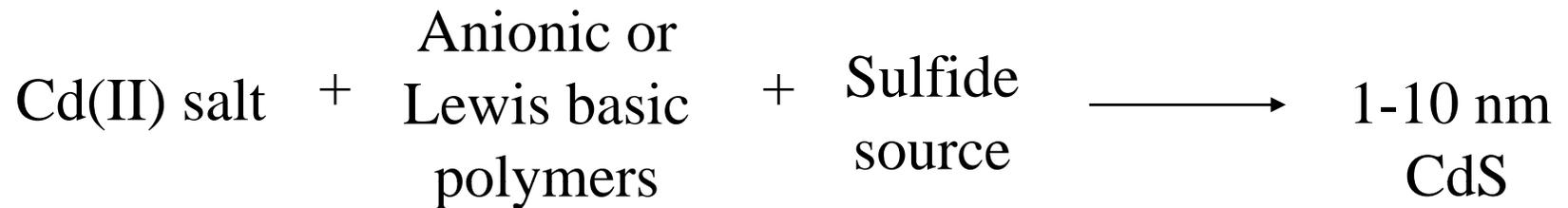
Au nanoparticles prepared by sonication



Langmuir **2002**, 18, 7831-7836

Synthesis of CdS Nanoparticles

General:



Chem. Mater. **1999**, *11*, 3595

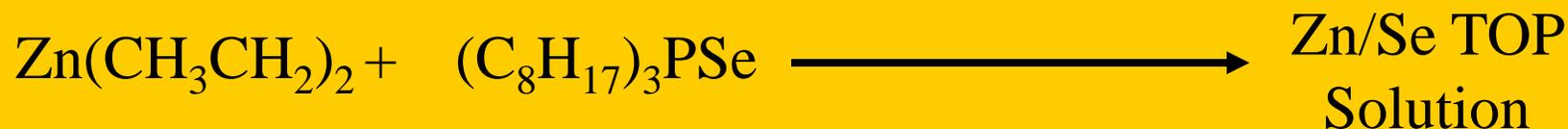
Synthesis of CdSe Nanoparticles



HAD-TOP-TOP = hexadecylamine-trioctylphosphine oxide-trioctylphosphine

J. Am. Chem. Soc. **1993**, *115*, 8706

Synthesis of ZnSe Nanoparticles



J. Phys. Chem. B. **1998**, *102*, 3655

TOPO binds too strongly to Zn

TOP binds too weakly

Amines, however have intermediate strength

Synthesis of III-V Semiconductor Nanoparticles

Synthesis of III-V semiconductor nanoparticles is quite complex
Requires high temperature



GaP particles prepared in this manner lacked monodispersity



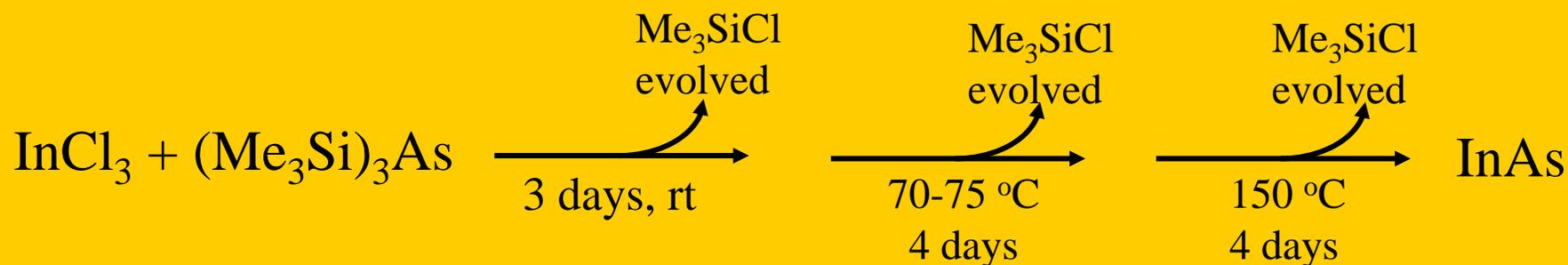
Chem. Mater. **1989**, 1, 4

J. Am. Chem. Soc. **1990**, 112, 9438

Synthesis of InP and InCl₃



Synthesis of InAs via Dehalosilylation

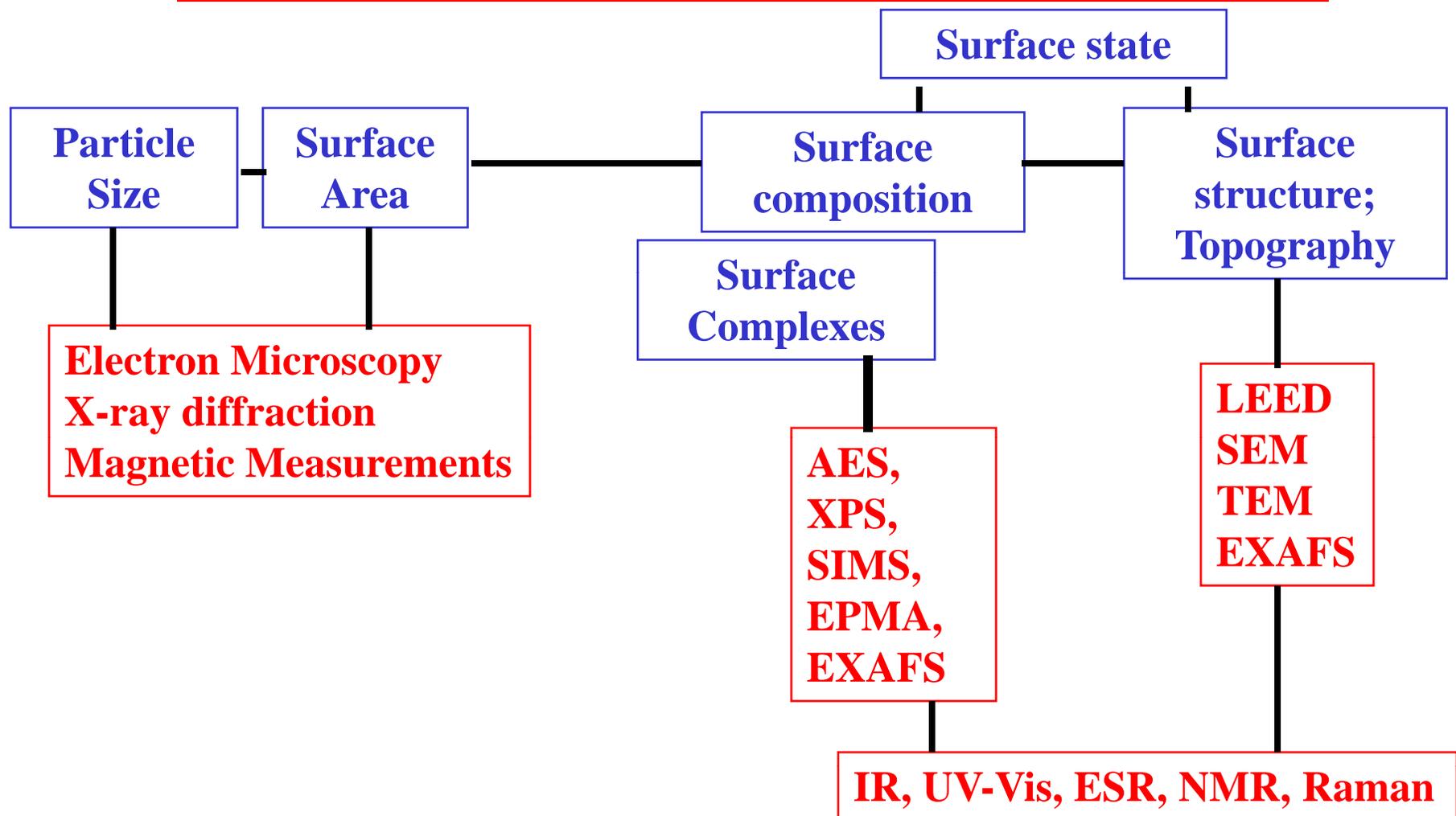


Chem. Mater. **1989**, *1*, 4

Factors Affecting the Nature of the Nanoparticle

- Particle size and shape
- Surface properties
- Particle-solvent interactions
- Particle-particle interactions

Common Methods for Nanoparticle Characterization



UV-Visible Spectroscopy

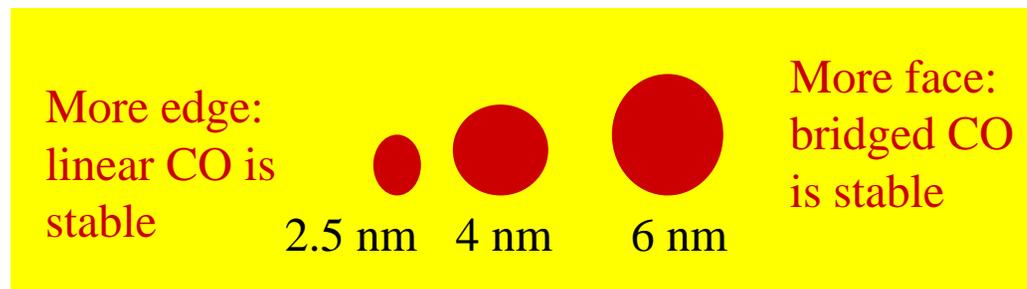
- Particularly effective in characterizing semiconductor and metal particles
- Useful for metal nanoparticle characterization whose surface plasmon absorbance lies in the visible range, e.g. Cu, Au, Ag
- Can be used to determine particle size:
(For semiconductor nanoparticles: as the radius decreases, the band gap increases and λ_{\max} shifts to lower energy.)
- Particle aggregation
- Information about the surface, e.g. presence of adsorbates

Infrared Spectroscopy

IR has been used as a surface probe for nanostructures

Example illustrated by Bardley:

Adsorbing CO onto the metal nanoparticle surface resulted in IR depending on particle size



As particle size increased, the ratio of terminal CO to bridging CO decreased

Bradley, et al. *Chem. Mater.* **1992**, 4, 1234

Nuclear Magnetic Resonance (NMR)

Two uses:

1. Probing the ligands that surround metal core
2. Probing the intra-core metallic atoms (difficult)

Probing the intra-core metallic atoms

Nuclear spin relaxation time, and nuclear resonance frequency, are sensitive to any metallic property the particle may exhibit

Change in frequency (known as ‘Knight shift’) is a consequence of the interaction of the metal nucleus with the conduction band electrons

If particles are very small, in favorable cases, the Knight shift allows resonances for surface and interior metal particles to be identified

Microscopy

- **TEM:** High voltage beam passes through a very thin sample. The sample areas that do not allow passage of electrons allow image to be presented
- **STM:** Involves dragging a sharp needlelike probe across a sample very close to the surface. The tunneling current between the sample and probe tip can be monitored . As probe approaches an elevated portion, the probe moves up and over, and produces a surface map.
- **AFM:** The probe tip is essentially touching the surface, and the surface can be mapped by the weak interaction between the tip and the sample.

Transmission Electron Microscopy

- Provides direct visual information of size, shape, dispersity, structure and morphology
- Routine magnifications $\geq 40,000$ to 0.2 nm

Drawbacks

- Samples are dried and examined under high vacuum conditions
- Therefore, no direct information is gained on how particles exist in solution
- Only a finite number of particles can be examined and counted, which may not be a representative of the sample as a whole
- Requires electron beam in which case, some nanoparticles may undergo structural rearrangement, aggregation or decomposition.

Scanning Tunneling Microscopy (STM)

Makes possible the determination of the total diameter of the nanoparticle, including the stabilizing ligand shell
Effective probe of the electronic properties of nanoparticles

Reetz et al. *Science* **1995**, 267, 367-369

A combined STM/TEM study of Pd nanoparticles stabilized by $R_4N^+Br^-$.

Determined thickness of stabilizing ligand shell by subtracting the STM determined diameter from the TEM determined diameter

Shortcomings to STM

- Nanoparticles may not stick well to the substrate surface, preventing good images from being obtained
- Geometry of the tip shape may lead to inaccurate measurements or artifacts in the image
- Tunneling mechanism is not well understood
- Samples have to be dried
- Specific techniques applied to imaging are not mature, i.e. standard literature protocols have not been established

Atomic Force Microscopy

- Technique is purely mechanical
 - A cantilevered tip attached to a spring is dragged across a sample
 - Increase or decrease in tip height is measured yielding a surface height profile as a function of distance
 - Can be carried out on non-conducting samples

Shortcomings

- Can reliably determine particle height but not diameter
- Cannot distinguish between subtle shape differences, or image particles that are not spatially close to each other