Richard Feynman

(1959)

"...Why can't we make them very small?"

"...all the way down!..."

"...atoms the way we want, the very atoms, the way we can arrange the atoms by atom, the possibility of maneuvering things, I can see, do not speak against the principles of physics, as far as I am afraid to consider the final..."
Atoms and molecules are generally less than a nm and we study them in chemistry.

Quantum chemistry does not apply, but the fundamental laws hold, and the system are not large enough for classical laws of physics.
(Small Wonders, Endless Frontiers, Review NNI, NRC, 2002)

Small Wonders, Endless Frontiers, Review NNI, NRC, 2002

Nanotechnology Timeline

Examples
Nanophotonic & Nanoelectronic &
Already some

Nano 2012

Nano 2007

Nano Now

Nanomechanical materials & devices
Nanoscale switches & coatings
NEMS based sensors
Lasers & ultrasound
High-end, flexible, nano-bio materials
Nanophotonic & nano-optical
Nano power sources
Nanoelectronics &
Nanotechnology
Overview of Nanoparticle

• **Basic Concept**
  – Introduction of nanoparticles 125-70,000 atoms, < 100 nm
  – Size Dependent Properties
  – Colloidal Stability

• **Wet Chemistry**
  – Metal Nanoparticles
  – Semiconductor
  – Ceramics
  – Polymer nanoparticles

• **Other Methods**
  – Mechanochemical Process
  – VLC mechanism
  – Combustion method
1. Metal: Electron mean path

Dimensions correlating with the continuous distribution of the energy states.

**Figure 2.5** Formation of a zero-dimensional (0D) quantum dot by the formal reduction of bulk.

**Important Parameter**
Figure 1. Comparisons of box approximation, expected from a particle-in-a-box representation of the quantum rods. The dotted line shows the dependence of the bandgap on the shape of the synthesized by Kan et al., a plot of the bandgap for the quantum rods studied by Kan et al., a plot of varying length/diameter ratio. The vertical, dotted line and the corresponding quantum rods, are the grey area from particle-in-a-box calculations of cylindrical quantum rods obtained from rectangular quantum wells, the thickness of the quantum well over the bulk value against $P$, the increase in the bandgap of different structures. $p$, $q$, Geometries of the quantum wells, wires, rods and dots.
Calorimetric measurements show that the energy dependence of supported Pb particles vary much more quickly than predicted by the Gibbs-Thomson relationship. This shows that the surface energy increases substantially as the radius decreases below 3 nm.

2. Semiconductor: Exciton Radius

Ex) Case

Important Parameter: Semiconductor

Size Increase
Size Dependent Optical Properties

- The figure shows the trend of property A vs. size for different shapes. The trend is marked by different colors indicating various properties.

- The legend indicates the color codes for different particle sizes and shapes.

- The graphical representation illustrates the change in property A with respect to size, highlighting the significant variation in properties for different particle shapes.
Melting Point of Gold

\[ T_m = 1064.0^\circ C \]

Gold Atomic Size: 1.79 Å (50Åm: 6%)
(Degussa P-25) Degussa P-25
Photocatalyst TiO₂

Catalytic Activity
• Size Dependent Chemical Reaction

Population (%)

Band gap (eV)

Activity

Cluster Diameter (nm)

0.0
0.5
1.0
1.5
2.0
2.5
3.0
3.5
4.0
4.5
5.0
5.5
6.0
6.5
7.0
7.5
8.0
8.5
9.0
9.5
10.0

Au clusters with a band gap of 0.2-0.6 eV

Au clusters on TiO₂

2.0
2.5
3.0
3.5
4.0
4.5
5.0
5.5
6.0
6.5
7.0
7.5
8.0
8.5
9.0
9.5
10.0

V/m²TIO(110)

V/m²TIO²

20
**Electrostatic Force & Steric Repulsive Force**

Need other forces for colloidal stability → Thermodynamics → Agglomeration (Stable)

<table>
<thead>
<tr>
<th>Example</th>
<th>Media</th>
<th>Dispersed Phase</th>
<th>Phase</th>
</tr>
</thead>
<tbody>
<tr>
<td>Milk, Butter</td>
<td>Liquid</td>
<td>Liquid</td>
<td>Emulsion</td>
</tr>
<tr>
<td>Jellies, Glue</td>
<td>Liquid</td>
<td>Polymers</td>
<td>Gels</td>
</tr>
<tr>
<td>Soap</td>
<td>Liquid</td>
<td>Micelles</td>
<td>Colloids</td>
</tr>
<tr>
<td>Fog, Aerosol Sprays</td>
<td>Gas</td>
<td>Liquid</td>
<td>Aerosol</td>
</tr>
</tbody>
</table>

Rapidly, and are not readily filtered

A suspension of finely divided particles in a continuous medium in which the particles are approximately 5 to 5,000 angstroms in size do not settle out of the substance.
Zeta potential

- Diffuse layer: mobile by thermal vibration
- Stern layer: immobile adsorbed layer
- Stern layer + Diffuse layer

Electric double layer

Electrostatic force

Force for Colloidal Stability
Prohibit coagulation btw. particles

$\Delta G < 0$

Entropy : Deg. of freedom ($\Delta S > 0$)
Enthalpy : Osmosis pressure ($\Delta H < 0$)

-a - Repulsion between particles
Steric Repulsive Force

Force for Colloidal Stability
Double Layer Thickness

\[
\left( \frac{\frac{1}{N} \frac{Z}{N} \frac{Z}{F}}{\frac{Z}{N} \frac{Z}{F}} \right) = \frac{1}{K}
\]

Solution

\[
\psi_0 \cdot \exp(-Kx) = \psi
\]

Poisson Equation

Randomized the uniform distribution (\text{thermal E})

2. Entropic Factor

Favors a locally ordered ionic arrangement

1. Electrostatic Interaction

Surface Potential
<table>
<thead>
<tr>
<th>Particle Morphology</th>
<th>RH Ratio</th>
<th>Zeta Potential of Solvent at 20 °C</th>
<th>Dielectric Constant of Solvent at 20 °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Spherical, discrete</td>
<td>4.5</td>
<td>32</td>
<td>3</td>
</tr>
<tr>
<td>Spherical, aggregated</td>
<td>6.7</td>
<td>36</td>
<td>2</td>
</tr>
<tr>
<td>Aggregated</td>
<td>11.4</td>
<td>48</td>
<td>1</td>
</tr>
<tr>
<td>Fine (aggregated)</td>
<td>18.3</td>
<td>80</td>
<td>0</td>
</tr>
</tbody>
</table>

Different Solvent (Mixed solvent = n-PrOH + H₂O)

TiO₂

Control the Particle Size
Hamaker constant \( (A) \approx 10^{-20} \) J (water and aliphatic alcohol)

- Higher barrier \( \leftrightarrow \) Smaller size
- Lower barrier \( \leftrightarrow \) Larger size

Zeta potential of precipitate

Only dependent on Dielectric constant of solvent

Energy barrier for colloidal stability

\[
\sum_{i=1}^{n} \frac{12h}{\lambda d} - V = q
\]

Control the Particle Size
- Well dispersed
- Spherical shape (no irregular shape)
- Smaller particle size
- Reduce agglomeration

HPC: Hydroxypropyl cellulose (m.w. = 100,000)

Dispersant Effect (Steric Force)
- Amorphous Particles
- Crystallized Particles

TEM Micrograph of TiO$_2$
How to Synthesize Nanoparticles
Major efforts in nanoparticle synthesis can be grouped into two broad areas: gas phase synthesis and sol-gel processing. Additional nanoparticle synthesis techniques include sonochemical processing, cavitation processing, microemulsion processing, and high-energy ball milling.
Sol-gel processing is a wet chemical synthesis approach that can be used to generate nanoparticles by gelation, precipitation, and hydrothermal treatment.
Advantages & Disadvantages

**Disadvantages**
- Use of toxic solvents
- Expensive raw materials
- Sensitivity to atmosphere condition

**Advantages**
- Easy achieved
- High homogeneity
- Low-temperature synthesis
- Precise composition control
- Large area scale
To make monodisperse particles, the time $t$ should be decreased. Diagram:

- **1.** Water (NH$_3$)
- **2.** Stirring
- **3.** SiO$_2$ monomer
- **4.** SiO$_2$ particles

**Diagram:**

- **X-axis:** Reaction Time
- **Y-axis:** Concentration of dissolved materials (monomers)

**Legend:**
- Growth
- Nucleation
- C$_{\text{min}}$
- C$_{\text{max}}$
Monodisperse SiO$_2$ from MTMS

MTMS: Methyltrimethoxysilane
$\text{MTMS} = 0.6 \text{M}, \text{[NH}_3\text{]} = 1 \text{M}$

Particle Size vs. Temp.

Particle Size (nm)

$80 \degree C$

$50 \degree C$
TEOS : Tetraethylorthosilicate

H2O/ethanol=0.2, [NH3]=0.7M, 22°C

Particle Size vs. TEOs Conc.

Monodispersed SiO2 From TEOs

Stober Method
Photonic Crystal

- Reflectance vs. Particle size

![Micrograph of Photonic Crystal with 354 nm label](image)

- Bragg’s Law
  \[ \lambda_{\text{Bragg}} = 2n_{\text{eff}} d_{111} \]
  \[ n_{\text{eff}} = \sqrt{n_{\text{SiO}_2}^2 f + n_{\text{air}}^2 (1-f)} \]
  \[ d_{111(\text{FCC})} = \sqrt{2/3D} \quad f = \text{filling ratio} \]
<table>
<thead>
<tr>
<th>Synthesis, Decomposition</th>
<th>Continuous System</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hydrolysis, Extraction, Polymerization</td>
<td>Non-aqueous Solution</td>
</tr>
<tr>
<td>Synthesis, Modification, Coating</td>
<td>Organic and Biomaterials</td>
</tr>
<tr>
<td>Oxide, Nitride, Carbide</td>
<td>Radio-, Mechano-processing</td>
</tr>
<tr>
<td>(Btito, Strtio, Lino) (1989)</td>
<td>5. Combined with Electrical Photo-</td>
</tr>
<tr>
<td>Pzt, Zro, Btito, Hap, Ferite (1978)</td>
<td>4. Etching, Corrosion, Polishing</td>
</tr>
<tr>
<td>Oxide, Sulphide, Fluoride... (1978)</td>
<td>3. Crystalized Thin/Thick Films</td>
</tr>
</tbody>
</table>

Development of Hydrothermal Processing

Hydrothermal Synthesis
Hydrothermal Reactor

- Mediate Temperature
- High Temperature & High Pressure
The method, hydrothermal synthesis, is carried out using autoclaves. The autoclave must be treated under 200 degree Celsius because the internal Teflon container is not durable over the temperature. A weighed amount of starting materials and water is mixed and sealed in the autoclave. The autoclave is kept in a temperature-controlled oven for planned time. Internal pressure depends on the temperature.
Hydrothermal Crystallization

- Temperature & holding time
- pH control
- Adding Pb, Ba, Sr source

ZrTiO₄ Gel
ZrO₂ Gel
TiO₂ Gel

Ternary Hydrolysis or Metal Salt (Microwave heating)

Perovskite Nanoparticles
Perovskite Nanoparticles

\[
\begin{align*}
(f) \ Ba(Tl_{1.5}, Zr_{0.5})O_3 \\
(e) \ Pb(Tl_{1.5}, Zr_{0.5})O_3 \\
(d) \ PbZrO_3 \\
(c) \ PbTiO_3 \\
(b) \ SrTiO_3 \\
(a) \ BaTiO_3
\end{align*}
\]
1 Dimensional Nanostructure!

- Most materials can be made soluble in the proper solvent by heating and pressurizing the system close to its critical point.
- Easily control a solubility of solute.
- Lower supersaturation state.

Solvothalmy Synthesis

Solvothermal synthesis utilizes a solvent under pressures and temperatures above its critical point to increase the solubility of solid and to speed up reaction between solids.
Solvothermal/Syntheseis
Additive (dispersant, complex agent)
Heterogeneous Nucleation

Broad size distribution
Random size
Random shape

Reducing agent

\[
\begin{align*}
\text{(III)} N + 4H_2O & \quad \text{↔} \quad 2Ni^{2+} + 4OH^- \\
2Ni^{2+} + N_2H_4 & \quad \text{↔} \quad 2Ni^{2+} + N_2 + 4OH^{-}
\end{align*}
\]

Reduction in Solution

Introduction – Reduction in Solution
<table>
<thead>
<tr>
<th>Reducing agent</th>
<th>Conditions</th>
<th>Hydrazine hydrochloride</th>
<th>NaBH₄ borane</th>
<th>N₂H₄·H₂O</th>
<th>H₂O₂</th>
<th>Polys</th>
<th>Water</th>
<th>Other reagents</th>
<th>Metal species</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fast</td>
<td>ambient</td>
<td>50°C &lt; T &lt; 60°C</td>
<td>100°C &lt; T &lt;</td>
<td>180°C</td>
<td>&lt; 110°C</td>
<td>&lt; 120°C</td>
<td>&lt; 120°C</td>
<td>&lt; 120°C</td>
<td></td>
</tr>
<tr>
<td>Slow</td>
<td>ambient</td>
<td>70°C &lt; T &lt; 100°C</td>
<td></td>
<td>120°C</td>
<td>&lt; 120°C</td>
<td>&lt; 120°C</td>
<td>&lt; 120°C</td>
<td>&lt; 120°C</td>
<td></td>
</tr>
<tr>
<td>Very Fast</td>
<td>ambient</td>
<td>80°C &lt; T &lt; 100°C</td>
<td></td>
<td>120°C</td>
<td>&lt; 120°C</td>
<td>&lt; 120°C</td>
<td>&lt; 120°C</td>
<td>&lt; 120°C</td>
<td></td>
</tr>
</tbody>
</table>

Table 1: Guidelines for the choice of reducing agents and reaction conditions in the precipitation of metal particles.
Complex agent

Seed (Heterogeneous Nucleation)

Temperature, Concentration, pH, Chemical composition... etc.

Processing parameter

How to control the particles
Heterogeneous Nucleation (T)
Heterogeneous Nucleation (2)
\[ \text{In}^\varepsilon = \frac{nF\bar{E}}{RT} \]

- Reaction: \( \bar{E} > 0 \)
- Redox potential \( \rightarrow \) Driving Force: \( \bar{E} \)

**Heterogeneous Nucleation (3)**
Seed-Mediated Growth in Solution

Formation mechanism

Seed-mediated growth for gold and silver

Nanorod Growth

CTAB + Rod-like template
Ascorbic acid + Weak reducing agent
Citrate + capping agent (inhibit particle growth)
NaBH₄ + Strong reducing agent
Evaporation-Condensation

Physical: Evaporation-Condensation

GNP (Glycine Nitrate Process)

Spray Pyrolysis

Chemical: Spray Pyrolysis

Chemical Vapor Reaction

Mechanical: Milling

Synthesis Techniques
Spray Pyrolysis Process

Stages of Spray Pyrolysis Process

Sintering  Decomposition  Drivinc  Precipitation  Evaporation

Heat Transfer  Solution  Precipitate  Solvent Vapor  Solvent Vapor
**NIO Nanoparticle**

- Solution flow rate
- Solution concentration
- Droplet radius
- Nozzle to substrate distance
- Ambient temperature
- Substrate temperature

**Experimental Variables**

**Considerations**

- Transport of the leaching agent is the liquid with the liquid product.
- The reaction must be fast, with a large volume change.
- The product must be solubilized in the liquid.
- The precursor must not react with the liquid.
Overall Reaction:

$\text{SiH}_4 \rightarrow \text{SiH}_{2m}^+ + (2n-m)\text{H}_2$

Particle nucleation:

Aerosol Synthesis
Advantages:
- Easy achievement
- High homogeneity
- Low temperature synthesis
- No post-processing treatment
- No liquid byproducts

Disadvantages:
- Use of toxic systems
- Expensive raw materials
- Sensitivity for atmosphere condition
$\text{SiO}_2\text{ nanoparticles}$

$\text{Flame Hydrolsysis}$

$\text{Starting Materials}$

- Methane
- Oxygen
- Hexamethyldisiloxane
- Fuel Gas: $\text{Si}$
- Oxidizer: $\text{Si precursor}$
Bigger particles

Higher precursor conc.

Precursor conc. 4.8 vol%

Precursor conc. 2.4 vol%
Mechanochemical Process

Mechanochemical activation changes the amount of free energy. Accumulated energy changes the viewpoint of changes of the viewpoint of changes of free energy.
Vibrating mill

Planetary mill

Mechanical activation devices
Mechanical Activation

- Milling of BaCO₃

- Increase Kinetics

Smaller TiO₂ Particle

Reagent Kinetics

Sucrose

- 2BaTiO₃ + TiO₂
- Ba₂Ti₄O₉ + CO₂
- BaCO₃ + TIO₂
- BaTiO₃ + CO₂
Particle Size Increase with Temperature

Reaction completed at 1200°C

Calcination Temperature (°C)

Particle Size (nm)

SEM Micrographs

Particle Morphology
Polymeric Nanoparticles

- **Emulsion Polymerization**

The "ingredients" for an emulsion polymerization include 1) a water soluble initiator, 2) a chemical emulsifier, and 3) a monomer that is only slightly soluble in water, or completely immiscible.

The two differences between emulsion and suspension polymerization are: 1) that a suspension polymerization is a mechanical process, and must have a stabilizing agent until the droplets are far apart, and 2) the emulsion polymerization is a chemical process which requires a surfactant to make the monomer "emulsify."

Disadvantage- the surfactant is a soap and it contaminates the polymer.
Advantage- better heat control; the size of the emulsion polymer is usually 0.05 to 5 microns, and the size of the droplets is usually in the 10- 1000 micron diameter range.

Water-soluble initiators are used rather than monomer-soluble initiators. The end product is usually a stable latex--an emulsion of polymer in water rather than a filterable suspension.
## Overview of Polymeric Nanoparticles (PNP) Applications

<table>
<thead>
<tr>
<th>Application</th>
<th>Material</th>
<th>Purpose</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cancer Therapy</td>
<td>Polyalkylcyanoacrylate nanoparticles with anticancer agents, Oligonucleotides</td>
<td>Targeting, Reduce Toxicity, Increase uptake, Improve stability</td>
</tr>
<tr>
<td>Intracellular Targeting</td>
<td>Polyalkylcyanoacrylate/polyester nanoparticles with anti-parasitic, antibacterial or antiviral agents</td>
<td>Target reticuloendothelial systems for intracellular infection</td>
</tr>
<tr>
<td>Prolonged Systemic Circulation</td>
<td>Polyesters with adsorbed polyethylene glycols, pluronics or derivatized polyesters</td>
<td>Prolong systemic drug effect, Avoid uptake by the reticuloendothelial system</td>
</tr>
<tr>
<td>Vaccine Adjuvant</td>
<td>Polymethyl methacrylate nanoparticles with vaccines, Oral and intra-muscular immunizations</td>
<td>Enhance immune response, Alternate acceptable adjuvant</td>
</tr>
<tr>
<td>Peroral Absorption</td>
<td>Polymethyl methacrylate nanoparticles with proteins and therapeutic agents</td>
<td>Enhance bioavailability, Protect from gastrointestinal enzymes</td>
</tr>
<tr>
<td>Ocular Delivery</td>
<td>Polyalkylcyanoacrylate nanoparticles with steroids, Anti-inflammatory agents, Antibacterial agents for glaucoma</td>
<td>Improve retention of drug/reduce washout</td>
</tr>
<tr>
<td>Other Applications</td>
<td>Polyalkylcyanoacrylate nanoparticles with peptides, Nanoparticles with adsorbed enzymes, Polyalkylcyanoacrylate nanoparticles for transdermal applications, Nanoparticles with radioactive or contrasting agents</td>
<td>Cross blood-brain barrier, Enzyme immunoassays, Improve absorption, Imaging</td>
</tr>
</tbody>
</table>
Typically in the range of 4-10%.

The solid contents of the miniemulsions used for the experiments are
so far, the size of the particles could be controlled between 70-250nm.

Solid Droplets

Liquid Droplets

Heating

Ultra-sonic

Stirring

Water

Surfactant

Dissolved Polymer

PF 11112: (R₁: 3,7,11-

PF 2/6: (R₁: alkyl: 2-ethylhexyl)

PF: [n [R₁ R₂]

Me-LPPP: