Nanoparticles and Nanotubes: Synthesis and Applications

Richard L. Axelbaum

Department of Energy and Environmental Engineering
Washington University in Saint Louis

2nd International Conference on Energy and the Environment
Hong Kong, 2008
Synthesis of Nanoparticles

- **Aerosol Processing**
  - Flame
  - Furnace reactor
  - Gas condensation
  - Plasma reactor
  - Laser ablation

- **Solution Phase**

- **Mechanical Grinding**
Key aspects of Aerosol Science

- **Coagulation and agglomeration**
  - \( \frac{dN}{dt} \sim - \beta N^2 \)

- **Condensation and nucleation**
  - Kelvin relation: \( \ln\left(\frac{p}{p_s}\right) = 2\sigma \gamma /r R_u T \)
  - for small \( r \), \( p \gg p_s \)

- **Sintering**
  - change in surface area (\( a \)) with time
  - \( \frac{da}{dt} = -1/\tau_f (a - a_{\text{sphere}}) \)
  - where \( \tau_f \) is the characteristic time for mass transfer
Nanoparticle Synthesis via Aerosol Routes

NUCLEATION  

COLLISIONAL GROWTH  

SINTERING CRystallization  

VAPOR (molecular state)  

CLUSTERS  

PARTICLE (stable clusters)  

CONDENSATIONAL GROWTH  

Primary particle

Nanoparticle agglomerate
Flow Reactor

Example: $\text{TiCl}_4 + \text{O}_2 \rightarrow \text{TiO}_2 + 2 \text{Cl} \quad \Delta H_R = -39 \text{ kcal}$

By controlling $T$, reaction rate and sintering rate can be controlled.

Dilution can control agglomeration at expense of throughput

Broad size distribution
**Electro-spray Pyrolysis**

- **Process Characteristics**
  - Can produce near mono-dispersed, unagglomerated and high purity product
  - Easy to control the particle size and product characteristics
  - Extremely low throughput

![Diagram of Electro-spray Pyrolysis](image)
Electrospray Generated Iron Oxide NP

![Graph showing the size distribution of iron oxide nanoparticles before and after furnace exposure.](image-url)
Tightening Monodispersity with MDMA

Input has a broad log-normal size distribution

Output has a narrow, mono-disperse size distribution

Sodium/Halide Flame and Encapsulation
Process

Generic Chemistry:

- **Metals**
  \[ \text{AlCl}_3 + 3\text{Na} + \text{Inert} \rightarrow \text{Al} + 3\text{NaCl} + \text{Inert} \]

- **Ceramics**
  \[ \text{AlCl}_3 + \text{NH}_3 + 3\text{Na} + \text{Inert} \rightarrow \text{AlN} + 3\text{NaCl} + 1.5\text{H}_2 + \text{Inert} \]

- **Composites**
  \[ 5\text{AlCl}_3 + \text{NH}_3 + 15\text{Na} + \text{Inert} \rightarrow 4\text{Al-AlN} + 15\text{NaCl} + 1.5\text{H}_2 + \text{Inert} \]

→ Starting materials are readily available
→ Reactions are exothermic
→ High thermodynamic yields
Aerosol Growth Process

Single component growth:  e.g., $\text{TiCl}_4 + \text{O}_2 \rightarrow \text{TiO}_2 + 2\text{Cl}_2$

Two-component growth:  e.g., $\text{TiCl}_4 + 4\text{Na} \rightarrow \text{Ti} + 4\text{NaCl}$

salt-encapsulated Ti  

--- 40 nm
Applications in Medicine

Targeted Delivery of NP laden Therapeutics

Treatment of Aneurysms

Tumor

Smoothening of damaged blood vessels

From Stereotaxis

From FeRx Corporation
Magnetic behavior is strongly dependant on grain size.

Particle size below ~10 nm is required for superparamagnetic behavior.
Process for Synthesizing Nb-coated Superparamagnetic Iron

Run Conditions

- NbCl$_5$ Mole Fraction: 0.75%
- Na Mole Fraction: 1.2%
- Fe/NbCl$_5$ Mass Ratio: 1:1
- Re$_{jet}$: 3279
- T$_{ad}$: 795 °C
VSM Results

Increasing temperature →
Carbon Nanotubes: Structure and Properties

**Carbon nanotubes**
- Single or multi-walled
- Diameters down to 0.4 nm, lengths up to ~ 5 cm

**Properties**
- Metallic, semiconductive, or insulative
- Nanowires (conductors)
- High tensile strength
- 60 times stronger than steel and 5 times lighter
- Regular surface and high surface area
- High thermal conductivity along axis

Potential Applications of CNTs

- Electrostatic charge dissipation
- Electromagnetic shielding
- High-strength, lightweight composites
- Multi-functional composites
- Hydrogen storage
- Catalyst support media
- Gas sensors
- AFM tips
- Nano-transistors
- Field emission displays

- Fuel cells
- Biomedical applications
  - Drug delivery
  - Cancer treatment

*Baughman et al. (2005) Science*
Carbon Fibers and SWNTs
High $Z_{st}$ Inverse Diffusion Flame Synthesis

Ferrocene

QuickTime™ and a decompressor are needed to see this picture.
Effect of Catalyst on Yield

Fe/O Catalyzed Synthesis

Fe/Si/O Catalyzed Synthesis
Fe/Si/O Catalyzed SWNTs

SEM

TEM