State-of-the-art Flame Synthesis of Nanoparticles

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Nanoparticles

1 - 100 nm (at least into two dimensions)

The thickness (diameter) of a human hair is 50,000 - 100,000 nm!
Ratio of Surface Atoms to Total Atoms in a Single Particle (Ichinose et al., 1992)

Surface Atoms %

Particle Diameter, nm

0 2 4 6 8 10 12

0 20 40 60 80 100
The Melting Point Decreases with Decreasing Nanoparticle Size

Applications of Nanoparticles

- Large surface area per gram (adsorbents, membranes)
- Stepped surface at the atomic level (catalysts)
- Easily mix in gases and liquids (reinforcers)
- Superfine particle chains (recording media)
- Easily carried in an organism (new medicines)
- Cosmetics that last way into the night ...

Some people believe that nanoparticles are a new state of matter!
How are they made?

- Many processes & synthesis conditions…
  - Plasma-arc
  - Laser ablation
  - Chemical Vapor Deposition
  - Wet-phase chemistry
  - etc.

- Need synthesis technique that is:
  - *Rapid, continuous & scaleable*

- Flame synthesis…
  - carbon black
  - TiO$_2$ 10$^6$ t/year
  - SiO$_2$
  - C$_{60}$/C$_{70}$ 10$^3$ t/year

*Scale-up limitations*
Particle formation & growth – flames

- Chemical reaction
- Nucleation
- Aggregation
- Coagulation

[TiCl₄] [H₂] [H₂O] [O₂] [HCl]
Vapor flames

- Can make many interesting materials:
  - Fillers for composites, catalysts etc.
- However, limited compositions
  - C, TiO$_2$, SiO$_2$, Al$_2$O$_3$
Vapor flames

Reactants in vapor phase

Chemical reaction

Nucleation

Coagulation

Aggregation
Spray flames

Droplets contain:
- Organic solvent (comb. energy)
- Reactant precursor compound

Reactants in **LIQUID** phase

Keep aerosol processes
Spray flames

[Diagram showing a spray flame with labeled components: Filter housing, Exhaust vent, Spray flame, Support flame, Shield gas, MFCs, Oxygen, Methane, Oxygen, Oxygen, Precursor liquid, Syringe pump, PI]
Flame synthesis

Spray flames

- Spray Flame Pyrolysis (FSP)
- Liquid enables composition flexibility
- Opens up many possibilities…
Single-phase particles & aggregates
Mixed-phase & composition
Embedded, surface clusters & shells
Surface functionalization
Formulations
Immobilization, films & 2D coatings
Devices

Increasing VALUE
Increasing COMPLEXITY
Increasing FUNCTION
Tailor-made particle structures (size, morphology, crystallinity etc.)
with a large variety chemical compositions
Flame Spray Pyrolysis
In-situ deposition of noble metals

For applications in

- catalysts
- sensors
- optical devices, etc.

Au on TiO$_2$

Concentration vs. crystallite size

Doubling gold concentration

- doubles Au crystallite size
- leaves support unchanged

Concentration vs. crystallite size

Doubling gold concentration

- doubles Au crystallite size
- leaves support unchanged
- Gold particle size is independent of ceramic supporting surface area

Flame Spray Pyrolysis
Glucose sensor

- Hydrogen peroxide
- Biomolecules (glucose, choline, ...)

Proton Exchange Membrane Fuel Cell

- Hydrogenation
- Oxidation
- Reforming
- Electrodes for fuel cells

Hydrogenation of cyclohexene

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Mixed-phase & composition

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Increasing VALUE

Increasing COMPLEXITY

Increasing FUNCTION
Direct deposition on sensor substrate

Mädler et al., European patent, Dec. 9th 2004.
Layer morphology – top view

Deposition time: 180 s

SnO$_2$

500 $\mu$m
Layer morphology – top view

Deposition time: 180 s
Layer morphology – cross section

$\text{SnO}_2$

$\text{Al}_2\text{O}_3$

Deposition time: 180 s

5 $\mu$m
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Mixed-phase & composition

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Examples for FSP materials

Metal oxides
SiO$_2$, TiO$_2$, Al$_2$O$_3$, Bi$_2$O$_3$, CeO$_2$, ZnO

Mixed metal oxides
SiO$_2$/TiO$_2$, V$_2$O$_5$/TiO$_2$, ZnO/SiO$_2$, Zn$_2$SiO$_4$, BaTiO$_3$, Ce$_x$Zr$_{(1-x)}$O$_y$

Noble metals on oxides
Au, Pt, Pd on TiO$_2$, SiO$_2$, Al$_2$O$_3$

Scale-up

HMDSO/EtOH spray flame producing 300 g/h of silica.

Scale-up

Lecture summary

- Nanoparticles for Materials
- Flame Spray Pyrolysis & metal-oxide materials
  - Vapor $\rightarrow$ Spray flame: extend range of accessible compositions
  - Flame Spry Pyrolysis (FSP)
  - Metal-oxide nanomaterials for many applications
  - Metal on metal-oxides
  - Sensors and emerging areas…

- Nanoparticle Technology is a frontier for scientific advances and business opportunities