Gas-Phase Production of Core-Shell Nanoparticles by Decoupled Processes

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Motivation: Biofunctional Composite Nanoparticles

Iron Oxide Core
Magnetic core

Alternating magnetic field
Brownian and Neél relaxation

MRI contrast enhancement and
RF thermal tumor treatment

Bi-Material Composites

Tri-Material Composites

Gold conductive nanolayer
on silica insulating layer

Surface plasmon resonance

Tuned infrared resonance for
laser ablation of tumors

Gold
Silica
Iron Oxide

Silica and Gold Coating

Nanotechnology Applications in Energy

Catalytic Treatment of Exhaust
- Reduction of CO in exhaust
- Production of H₂ for NOₓ Treatment

Fuel Cells
- Catalysts for proton exchange membranes
- Catalysts for direct methanol fuel cells

Fuel Production
- Hydrogen from biomass
- Hydrogen from water
- Liquid fuels from biomass

Current synthesis techniques rely heavily on wet-chemistry methods.
Gas-Phase Synthesis Approach

Gold (or Silver) Nanoparticles Coated with Silica

Evaporation  Nucleation  Agglomeration and Sintering  Silica Precursor  Ultraviolet Radiation  Collection

Iron Oxide Nanoparticles Coated with Silica

Iron Precursor  Plasma Dissociation  Nucleation  Silica Precursor  Ultraviolet Radiation  Collection

Silica Nanoparticles Coated with Gold

Silica Precursor  Thermal Dissociation  Nucleation  Evaporation  Condensation  Collection
Silica Coated Silver Synthesis Schematic
Photoinduced Chemical Vapor Deposition (Photo-CVD)

- Evaporation Furnace
- Dilution $N_2$
- Sintering Furnace
- Bipolar Charger
- Polydisperse Aerosol
- DMA1
- Monodisperse Aerosol
- CaF$_2$ Window
- U.V. Excimer Lamp $\lambda=172$nm
- Xe$_2^*$
- DMA2
- Coating Chamber
- Chamber Furnace
- Electrostatic Precipitator
- Filter
- Purge
- N$_2$ Carrier Gas
- TEOS Bubbler
- CPC

**Abbreviations**
- DMA – Differential Mobility Analyzer
- TDMA – Tandem Differential Mobility Analyzer
- CPC – Condensation Particle Counter
Silica Coating of Silver Nanoparticles

Boies et al. (2009) Nanotechnology

Silica Precursor Bubbler

Coating Chamber

N₂ Carrier Gas

DMA

Xe₂*

U.V. Excimer Lamp

λ = 172 nm

Metal Evaporation

CPC

Repeable 1 hour

[Graph showing normalized dN/dLog(d_p) vs. particle mobility diameter (nm)]

[TEM image showing 40 nm (2.5 nm coating)]

5 nm

40 nm
(2.5 nm coating)
Silica Coating Thickness on Silver Nanoparticles

- Purge Flow $\uparrow$
- Residence Time $\downarrow$
- Concentration $\downarrow$
- Coating Thickness $\downarrow$

Boies et al. (2009) Nanotechnology
Coating Chemistry

Infrared (IR) Spectroscopy

Increased Oxygen

Si-O-Si Peak →

C-H Peak ↓

CH₃ ↓

Other hydrocarbons ↓

OH ↑

Note: Oxygen in excess of 5.1 sccm causes nucleation

Boies et al. (2009) Nanotechnology
Energy-Dispersive X-Ray (EDX) Verification of Coating

Particles coated at 300°C

Boies et al. (2009) Nanotechnology
Polydisperse Ag particles produced at $10^7$ #/cm$^3$

Particles processed at 400˚C

Boies et al. (2009) Nanotechnology
Diffusion Limited Growth Theory

Continuum Regime \((Kn<0.1) \rightarrow 1/D_p\) Growth

Free Molecule Regime \((Kn>10) \rightarrow\) No Dependence

At Atmospheric Pressure, 20 nm \(\rightarrow Kn=6.5\), 30 nm \(\rightarrow Kn=4.3\), 40 nm \(\rightarrow Kn=3.3\)

\[ Kn = \frac{2\lambda}{D_p} \]

\(Kn\) - Knudsen number
\(\lambda\) - Mean free path
Hot-Wire Gold Particle Production Schematic

- **N$_2$**
- **98 mm**
- **20 mm**
- **3 mm**
- **3 μm**
- **0.404 mm**
- **Pt Core**
- **Au Shell**
- **R$_{core} \leq \frac{1}{2} R_{shell}$$\ R - Resistance**

- **Condensation Particle Counter**
- **Po - 210 Charger**
- **Electrostatic Precipitator**
- **Differential Mobility Analyzer**
Gold Decoration of Silica

Particle size distribution of gold-decorated silica nanoparticles at different residence times

Boies et al, 2010 J Aero Sci
Hot-Wire Evaporation Decoration: Densification of Coating

Densified Gold Decoration Collected after TDMA

High Density – Gold Islands Remain
UV-Vis Spectra of Gold Decorated Silica
Gold Mobility on Particle Surface at Elevated Temperature

120°C  274°C  438°C  609°C

811°C  906°C  957°C  1040°C
Gold Mobility on Particle Surface at Elevated Temperature

At Low Temp

At 957 °C
Iron oxide production

Plasma torch

Fe precursor

Iron oxide production

Ejector

U.V. excimer lamp

TEOS bubbler

Silicon dioxide coating

Gold coating

Collection/Characterization
Core: Iron Oxide Production

Particles 3-5 nm

Magnetization

Production rate ~mg/min
Shell 1: Silica Coating

TEOS Flow ↑  Particle Size ↑

Similar to Coating of Silver Nanoparticles

7 slm N₂ Purge Flow
Shell 3: Gold Decoration

- Silica Shell
- Iron Oxide Core
- Au Particles
- Silica Shell
- Iron Oxide Core
Synthesized Composite Nanoparticles

Silica Coated Iron Oxide

Tri-Layer Gold, Silica, Iron Oxide

Organic Coated Aluminum

Platinum Decorated Silica

Organic Coated Sodium Chloride

Silver Decorated Silica

Boies et. al, In Prep Nanotech

Boies et. al, In Prep Nano Let

He et. al, In Prep J Nanopart Res

Boies et al., Not Published

Zhang et. al, 2006 J Nanopart Res
Future Directions
Homogenous Mixed Metals

Spark Discharge

Evaporation, Dissociation

Mixed Metal Core-Shell Nanoparticles

Possible Morphologies

Bi-Material Composites

Tri-Material Composites

Materials of Interest
Gold
Platinum
Rubidium
Iron
Nickel
Iron Oxide
Titanium Oxide
Carbon

On-Line Testing of Catalytic Properties

Polydisperse particles

Differential Mobility Analyzer

Size selected particles

CO Detection
Catalyst Decorated Nanoparticle Substrates

Carbon Nanoparticles or Nanotubes Decorated with Gold and Platinum

Methane

Thermal Dissociation

Nucleation

Evaporation

Condensation

Impaction

Gas Flow

Heat/Photo Dissociation

Evaporation

Condensation

Impaction

Gas Flow

Critical Parameters to Study

• Control of particle size and morphology of decoration
• Catalytic effect of varying platinum and gold and other metal compositions
• Film formation of particles by impaction
• Production rate and quality of core particles and nanotubes
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