

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

Cambridge Particle Conference
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Motivation: Biofunctional Composite Nanoparticles

Iron Oxide Core
Magnetic core

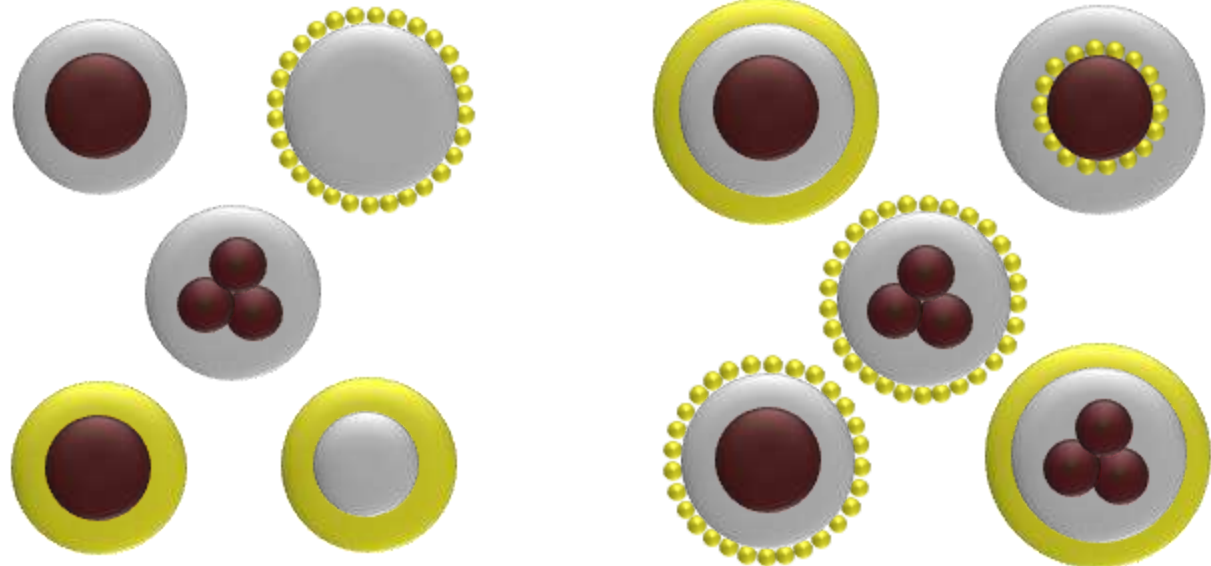
→ Alternating magnetic field
Brownian and Néel relaxation

→ MRI contrast enhancement and
RF thermal tumor treatment

Bi-Material
Composites

Tri-Material
Composites

 Gold
 Silica
 Iron Oxide



Silica and Gold Coating

Gold conductive nanolayer
on silica insulating layer

→ Surface plasmon
resonance

→ Tuned infrared resonance for
laser ablation of tumors

Nanotechnology Applications in Energy

Catalytic Treatment of Exhaust

- Reduction of CO in exhaust
- Production of H₂ for NO_x Treatment

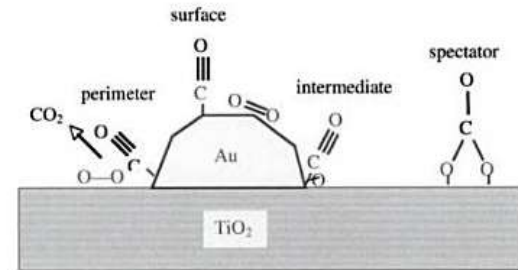
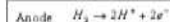


Fig. 15.2 Mechanism of CO oxidation on supported fold catalysts, as proposed by Haruta et al. [16].

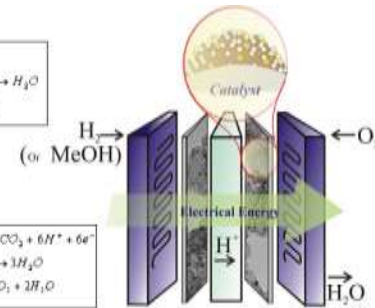
Fuel Cells

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

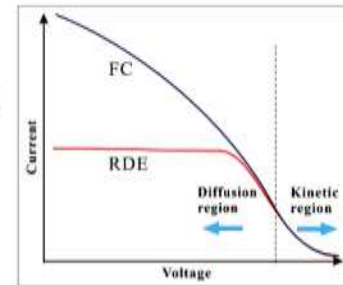
In PEMFC



In DMFC



Astruc, 2008

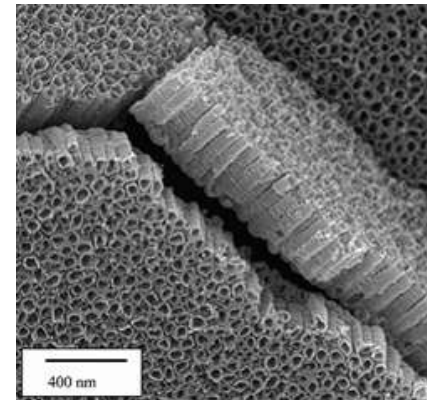


Zhong et. al, 2010 *Nanotechnology*

Fuel Production

- Hydrogen from biomass
- Hydrogen from water
- Liquid fuels from biomass

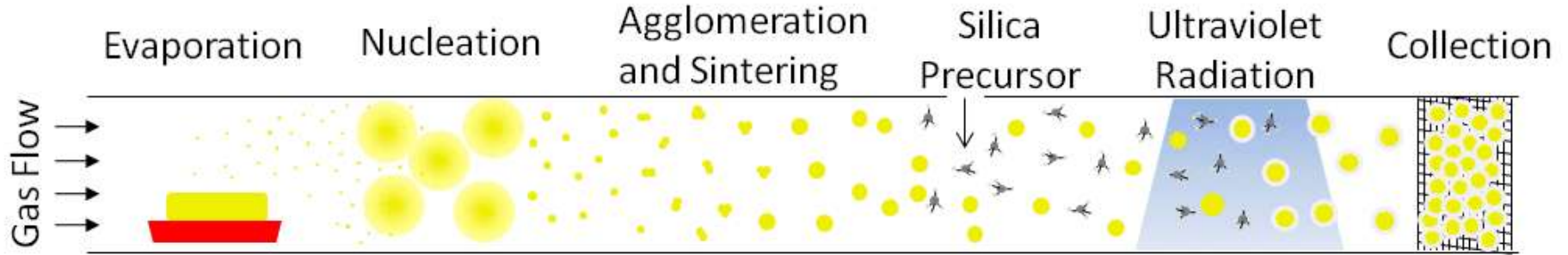
Current synthesis techniques rely heavily on wet-chemistry methods.



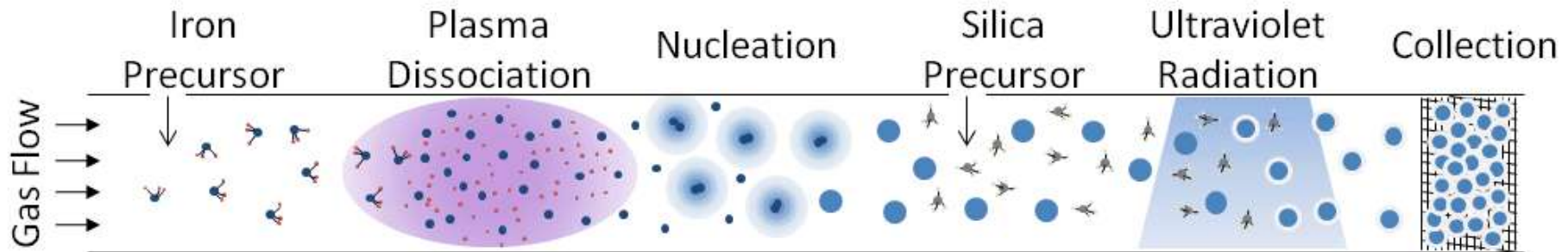
Mor et. al, 2004 *Nanoletters*

Gas-Phase Synthesis Approach

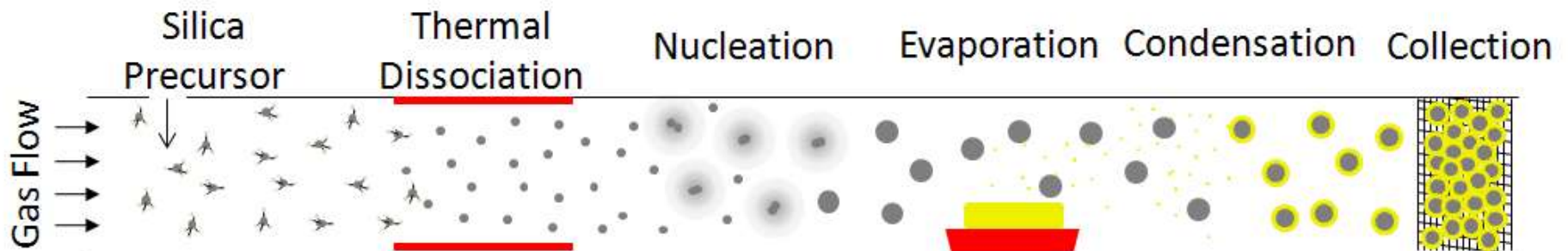
Gold (or Silver) Nanoparticles Coated with Silica



Iron Oxide Nanoparticles Coated with Silica

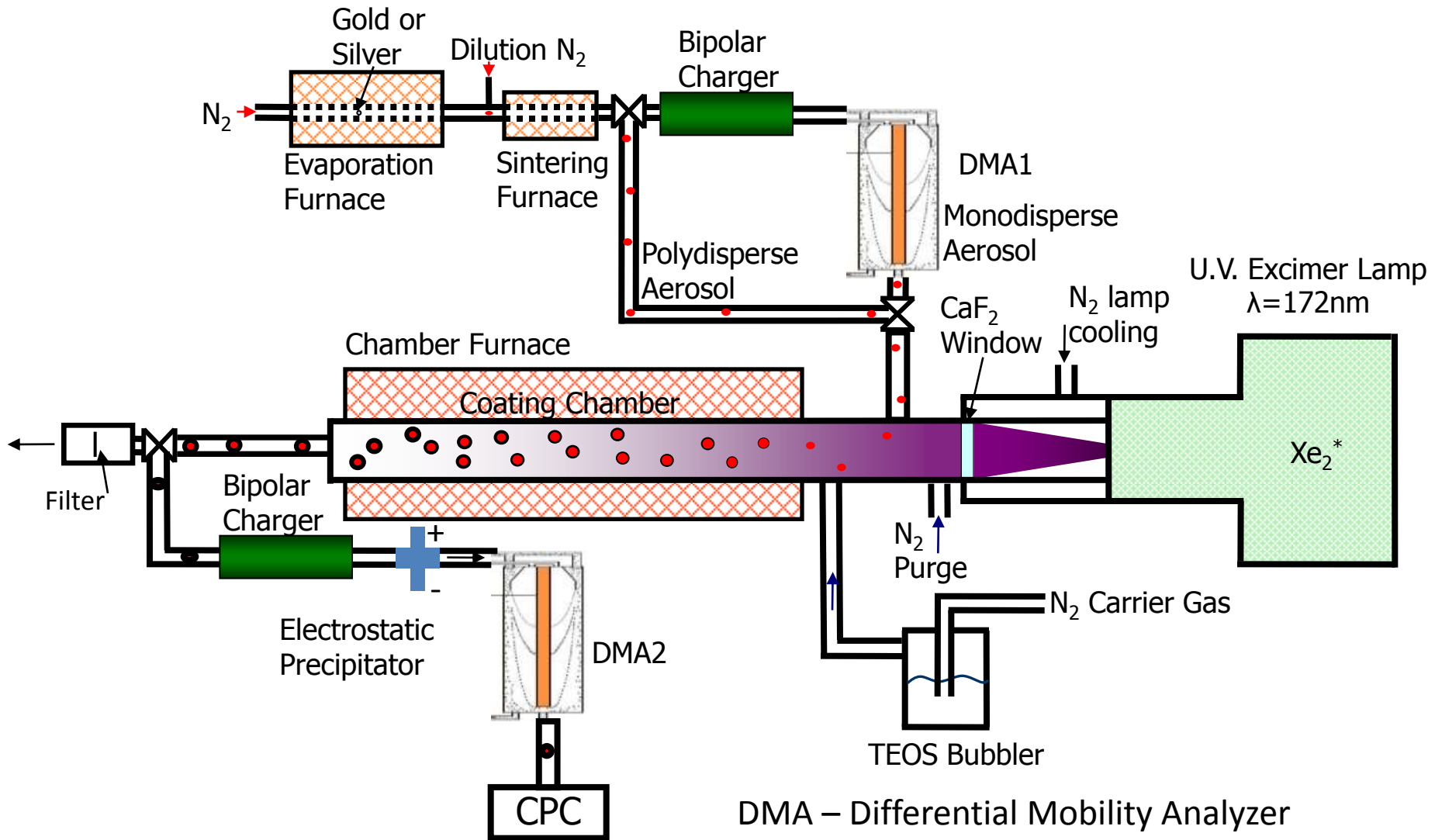


Silica Nanoparticles Coated with Gold



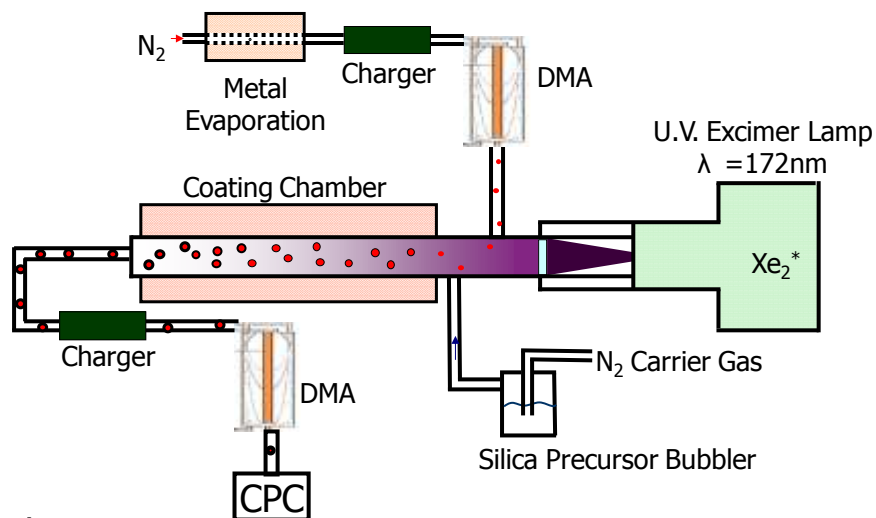
Silica Coated Silver Synthesis Schematic

Photoinduced Chemical Vapor Deposition (Photo-CVD)

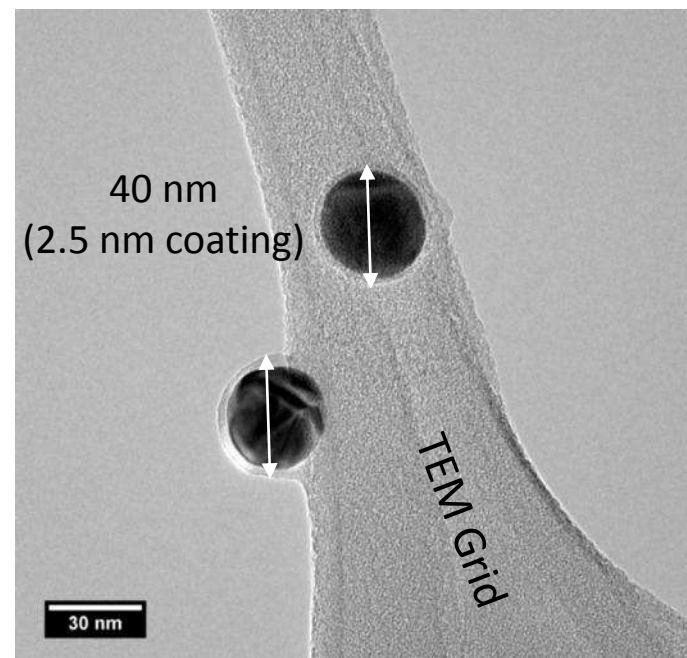
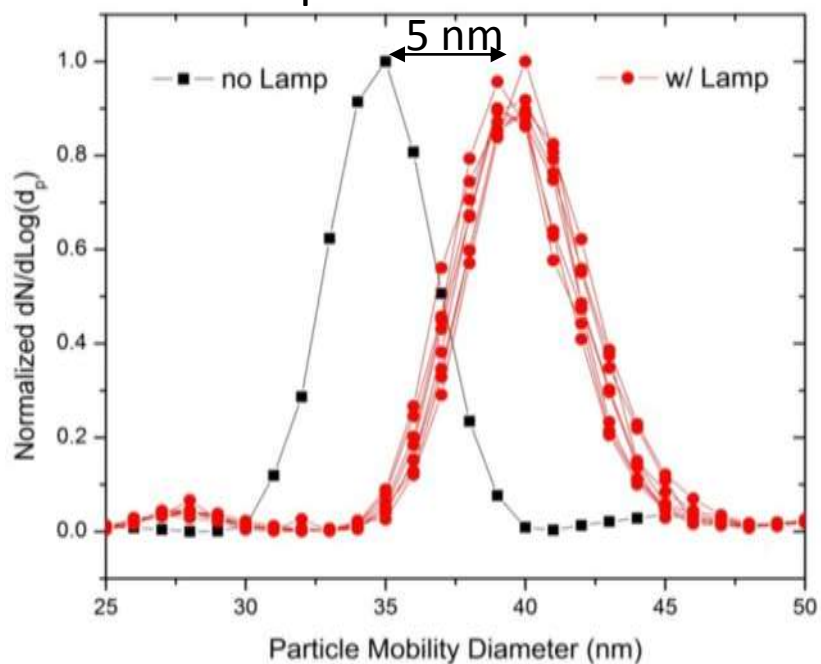


DMA – Differential Mobility Analyzer
TDMA – Tandem Differential Mobility Analyzer
CPC – Condensation Particle Counter

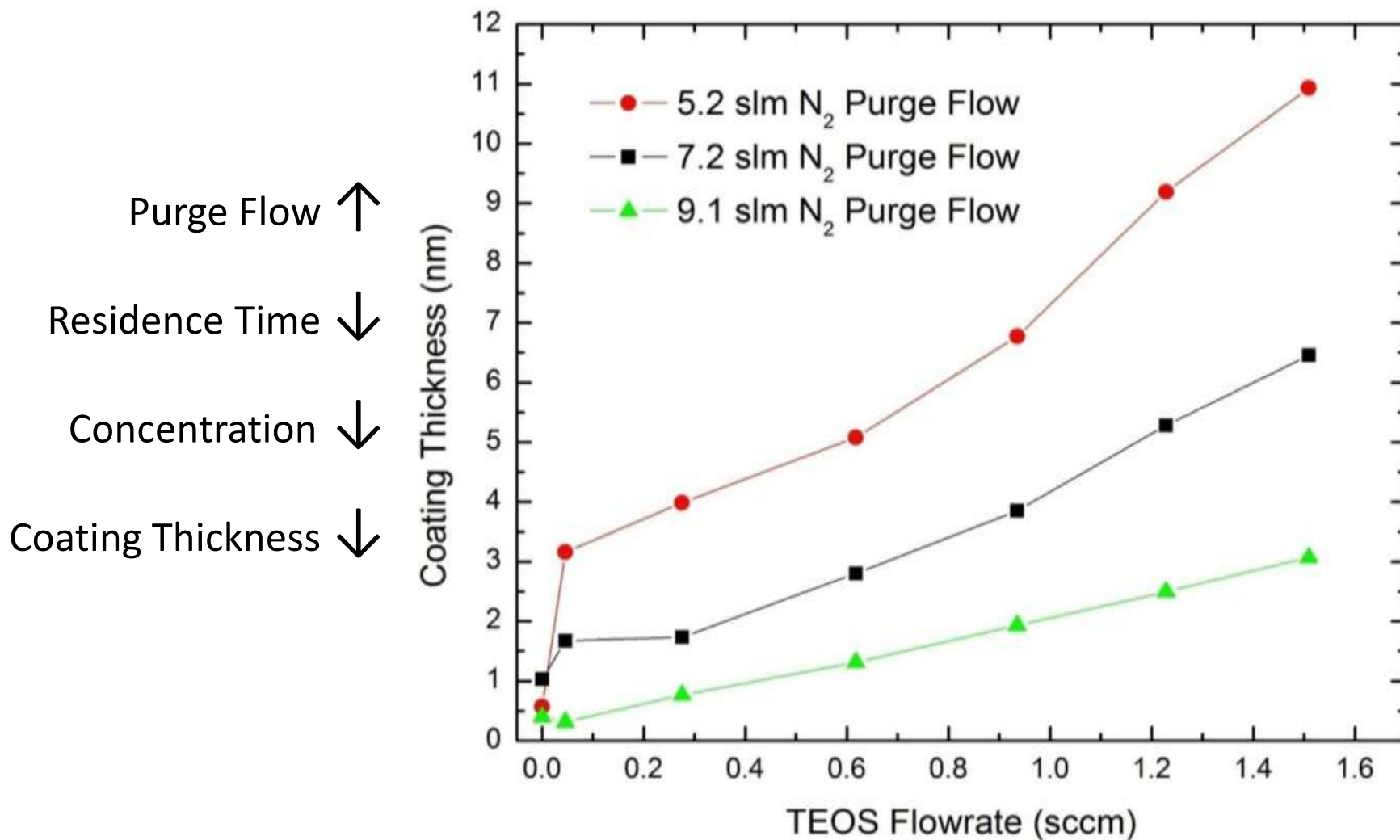
Silica Coating of Silver Nanoparticles



Repeatable 1 hour



Silica Coating Thickness on Silver Nanoparticles



Coating Chemistry

Infrared (IR) Spectroscopy

Increased Oxygen

Si-O-Si Peak —

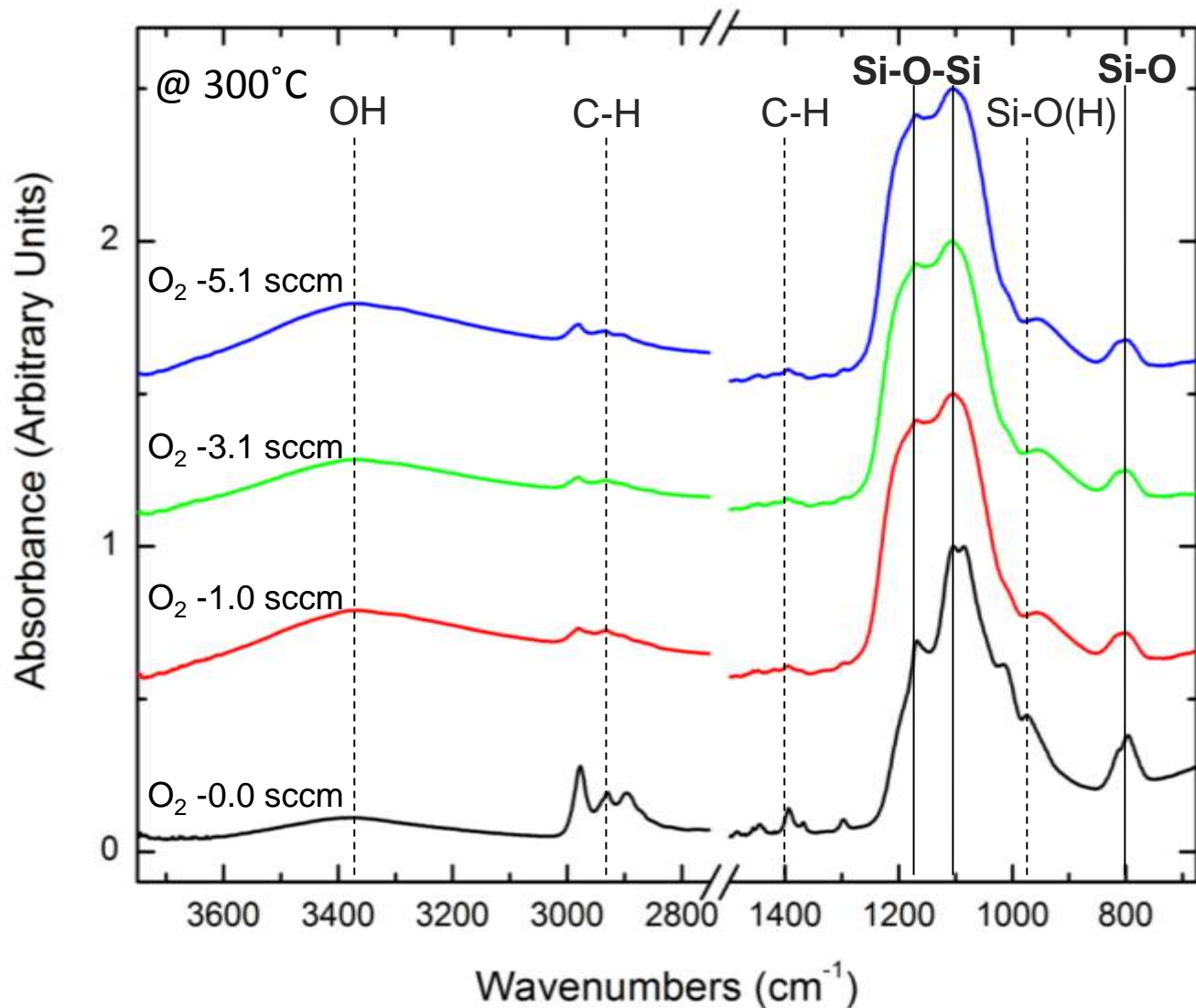
C-H Peak ↓

CH₃ ↓

Other hydrocarbons ↓

OH ↑

Note: Oxygen in excess of 5.1 sccm causes nucleation

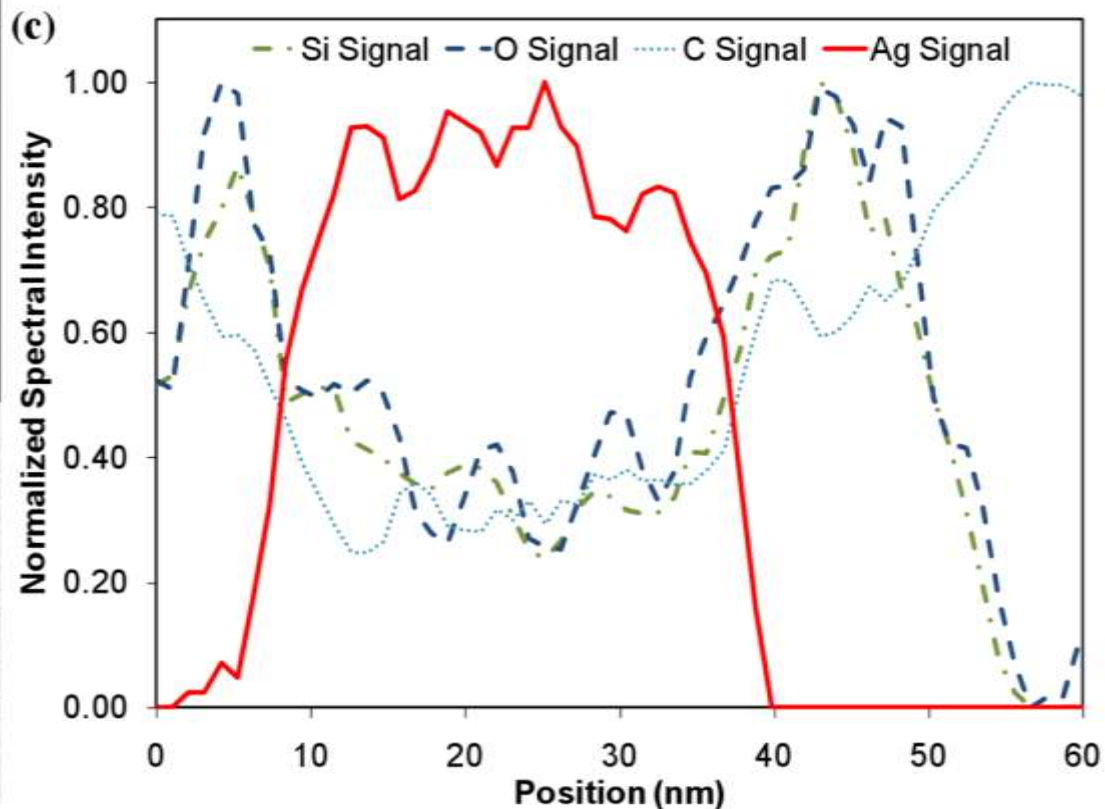
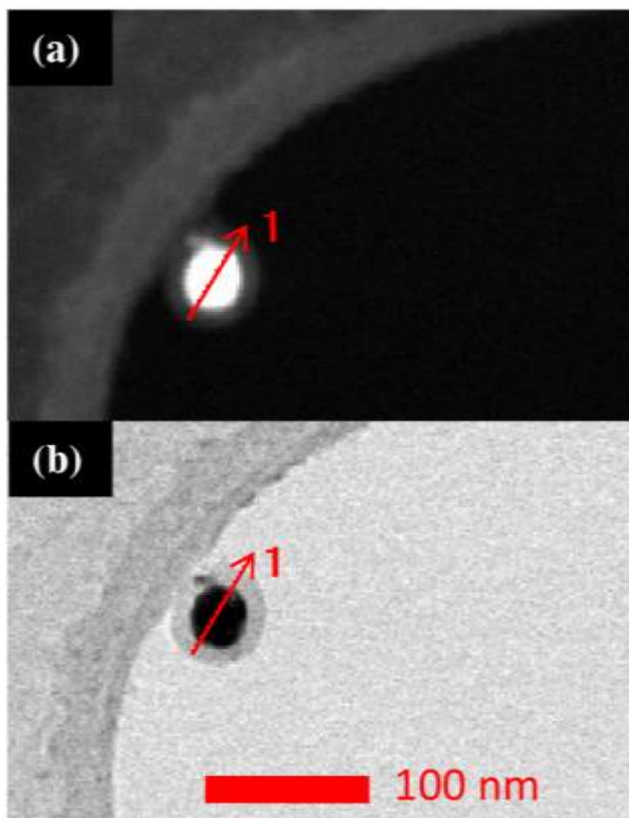


Energy-Dispersive X-Ray (EDX)

Verification of Coating

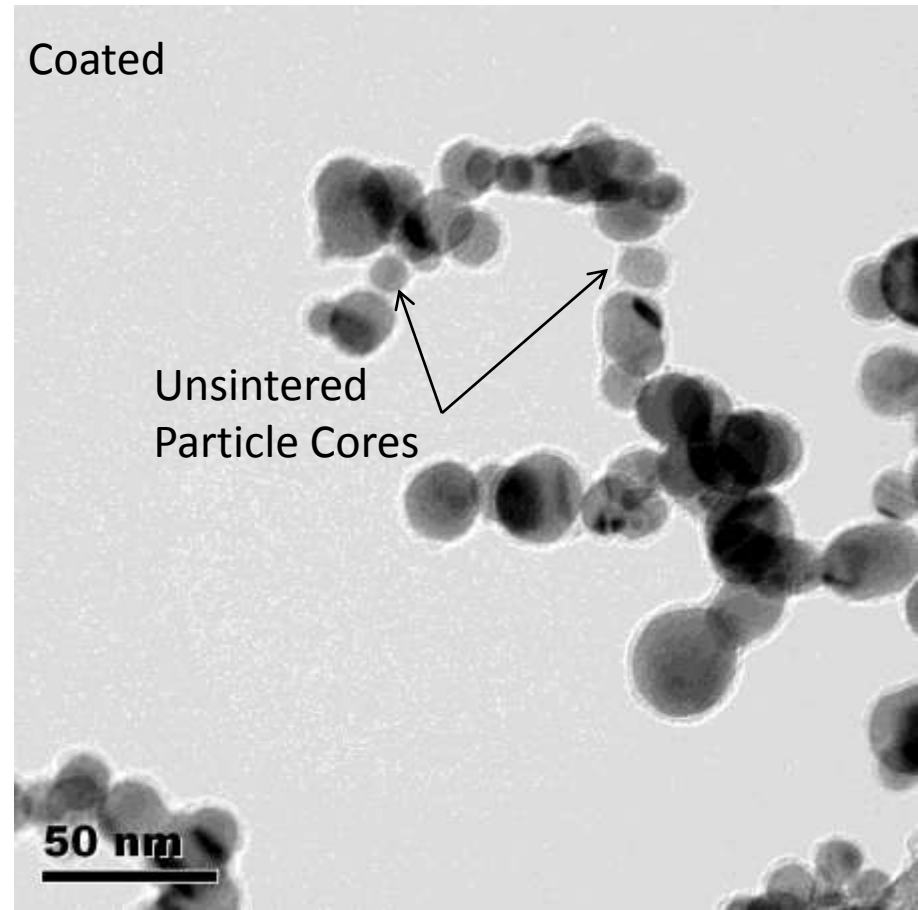
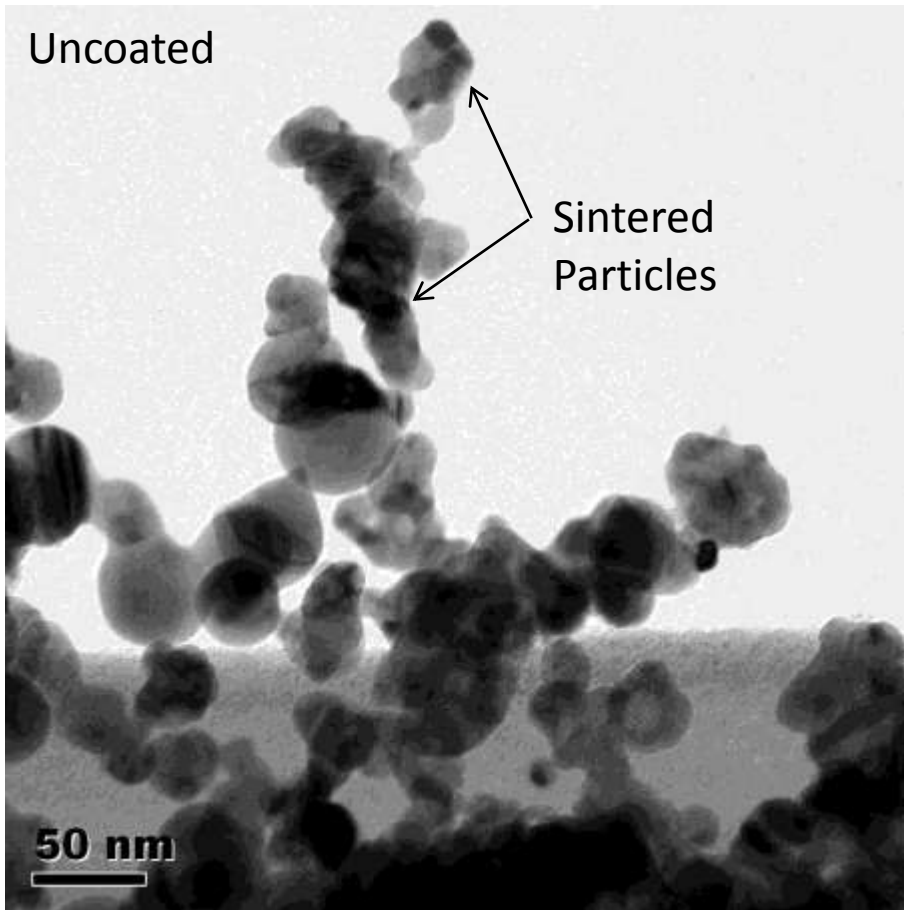
Dark- (a) and bright- (b) field images

EDX Line Scan of Core-Shell Particle



Particles coated at 300°C

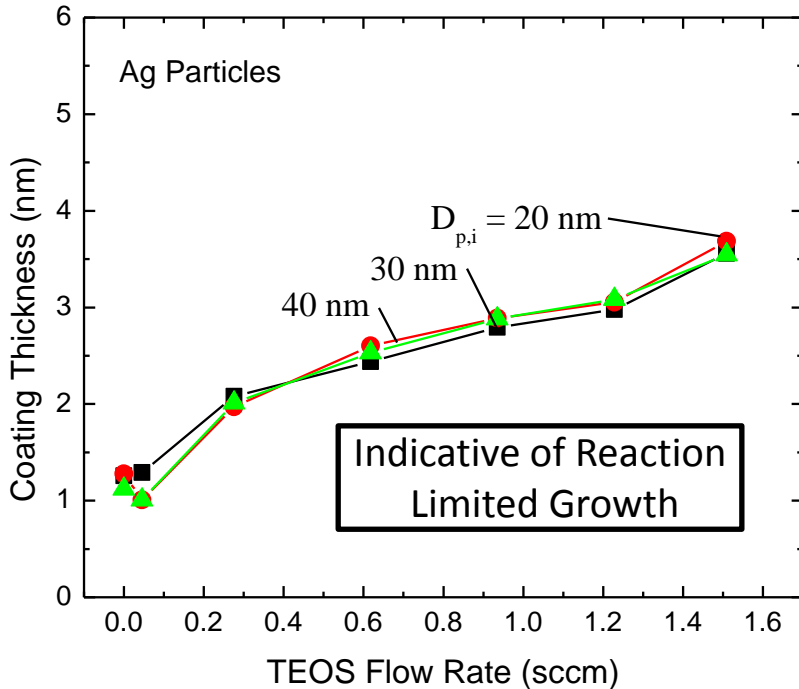
Polydisperse Ag particles produced at 10^7 #/cm³



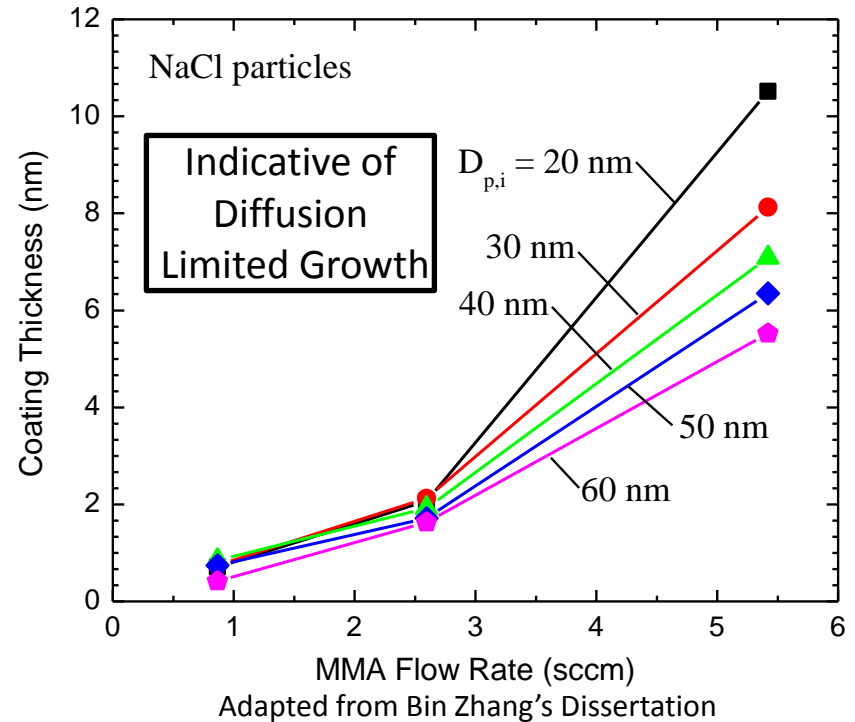
Particles processed at 400°C

Photo-CVD Coating

Silica Coating



MMA Coating



Diffusion Limited Growth Theory

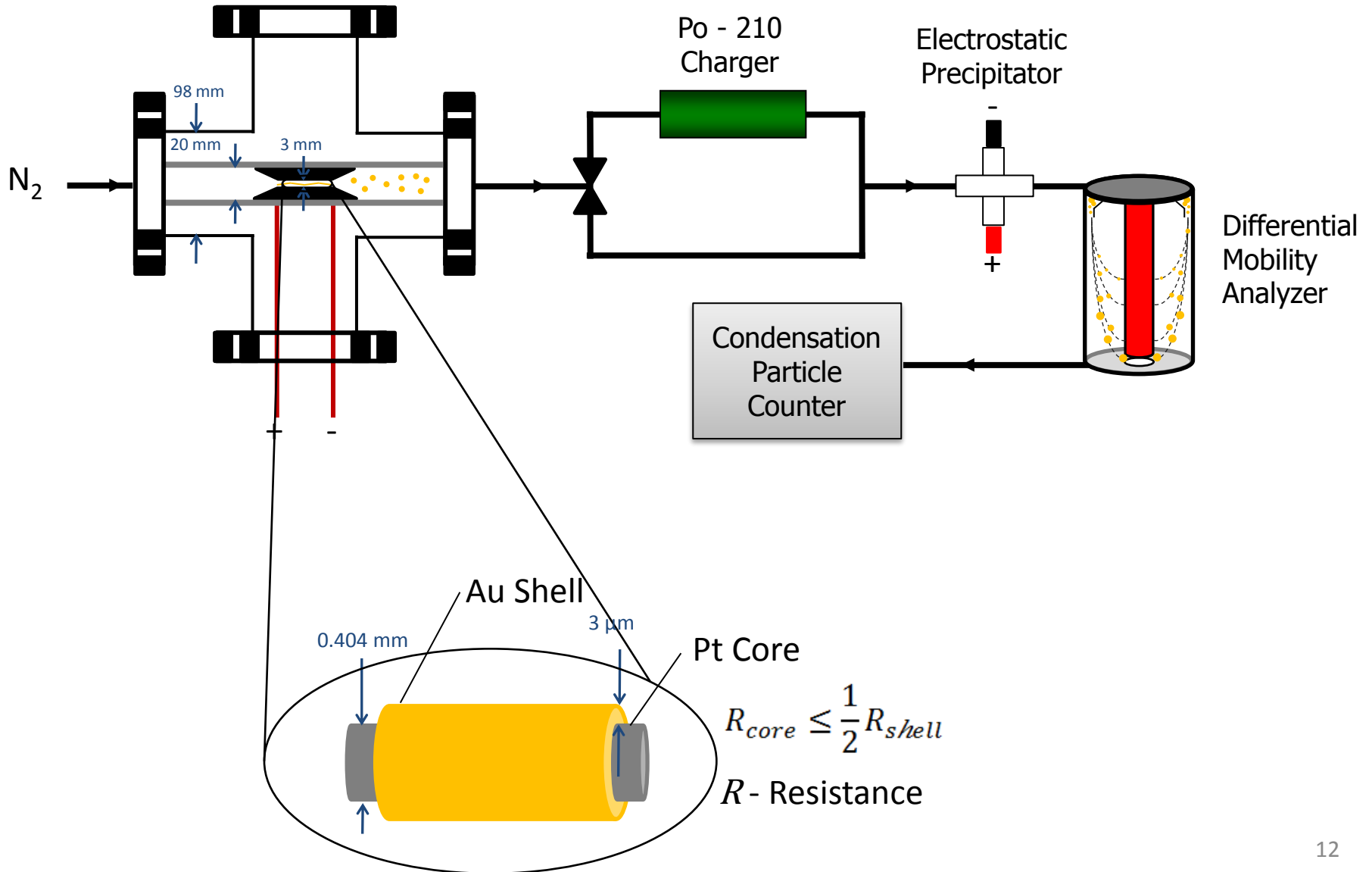
Continuum Regime ($Kn < 0.1$) $\rightarrow 1/D_p$ Growth

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

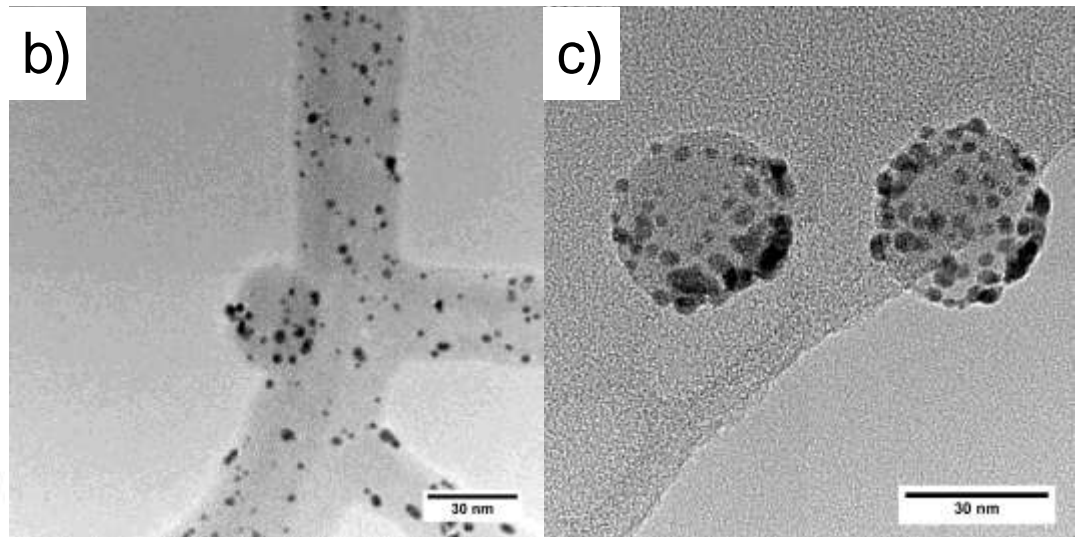
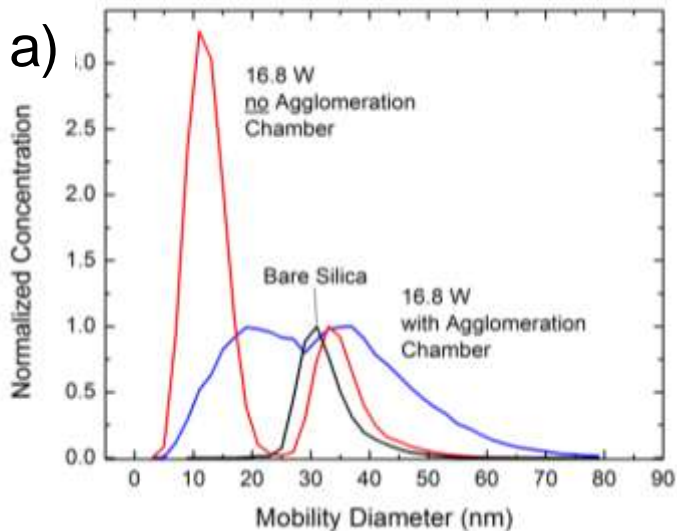
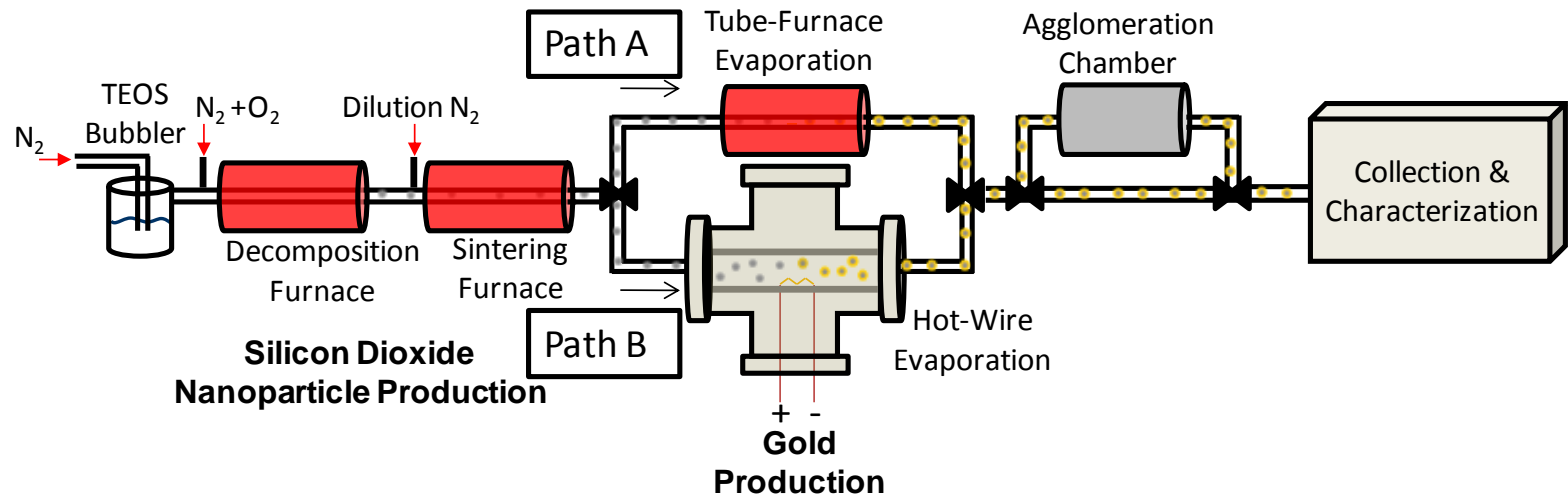
At Atmospheric Pressure, 20 nm $\rightarrow Kn = 6.5$, 30 nm $\rightarrow Kn = 4.3$, 40 nm $\rightarrow Kn = 3.3$

$$Kn = 2\lambda/D_p \quad Kn - \text{Knudsen number} \quad \lambda - \text{Mean free path}$$

Hot-Wire Gold Particle Production Schematic

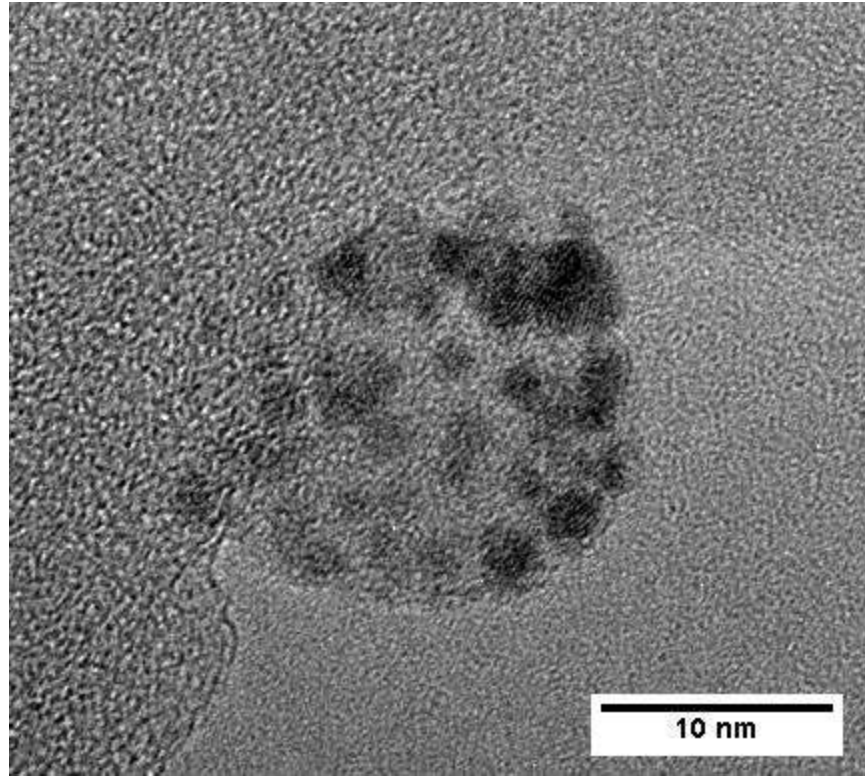


Gold Decoration of Silica



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

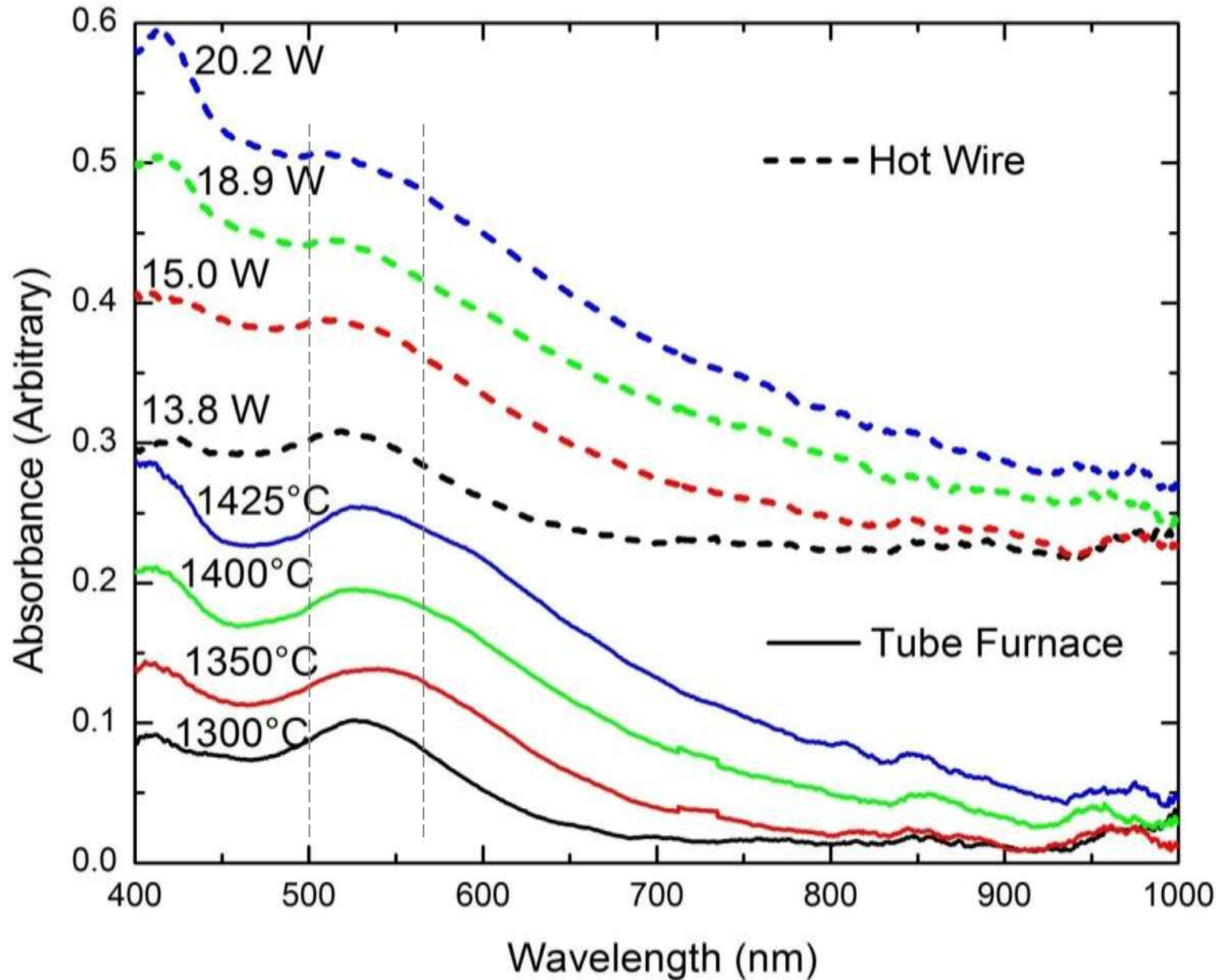
Hot-Wire Evaporation Decoration: Densification of Coating



Densified Gold Decoration Collected after TDMA

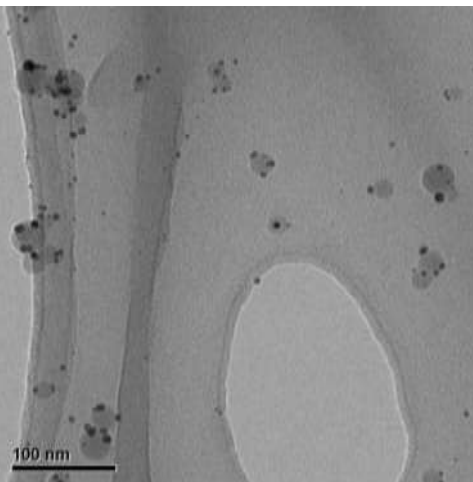
High Density – Gold Islands Remain

UV-Vis Spectra of Gold Decorated Silica

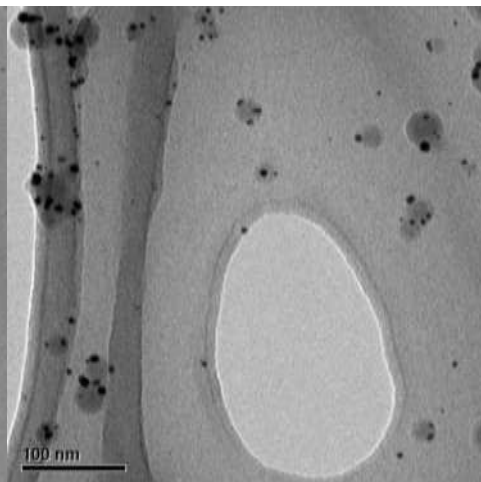


Gold Mobility on Particle Surface at Elevated Temperature

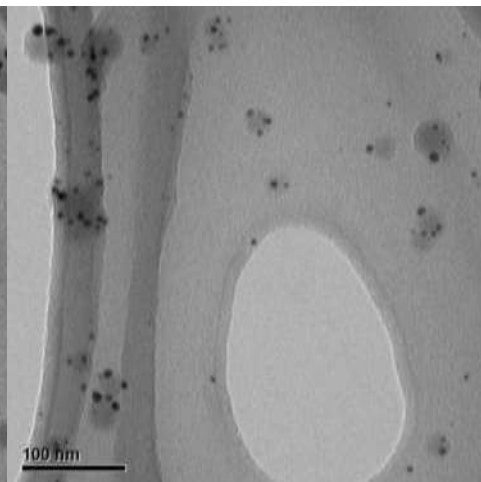
120°C



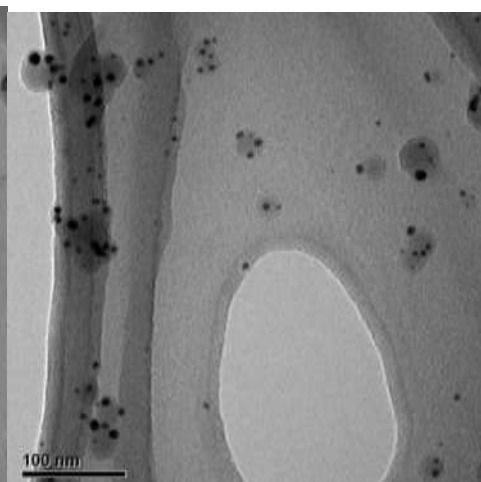
274°C



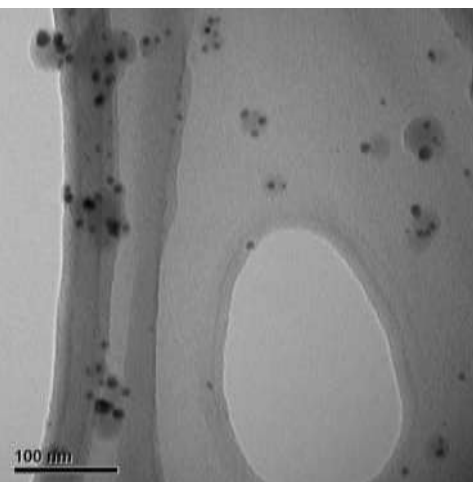
438°C



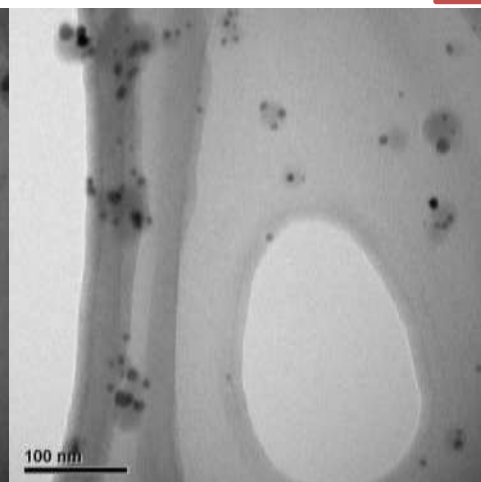
609°C



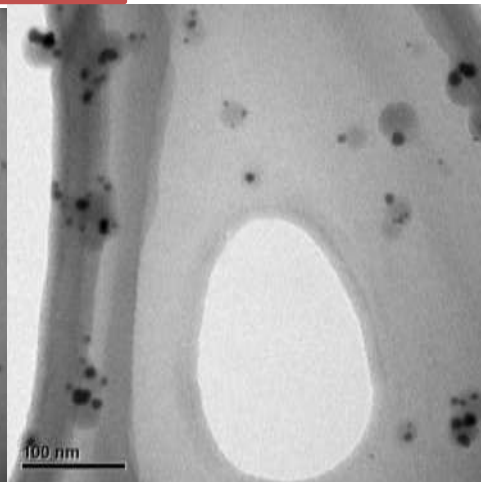
811°C



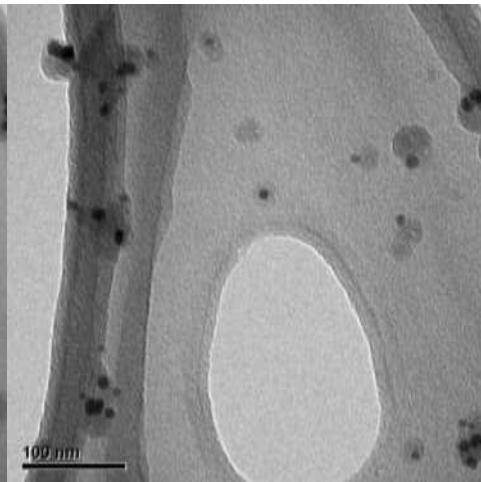
906°C



957°C

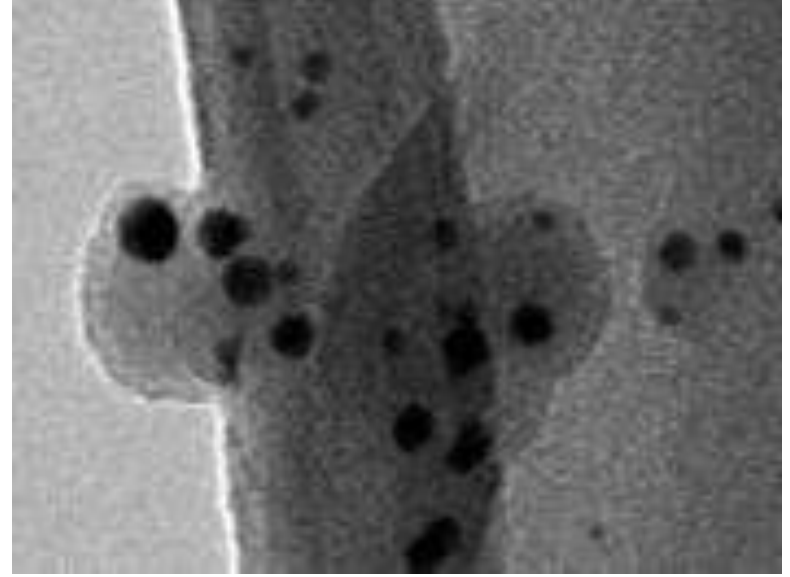
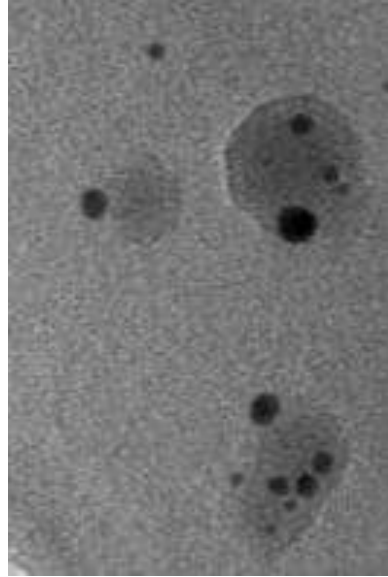


1040°C

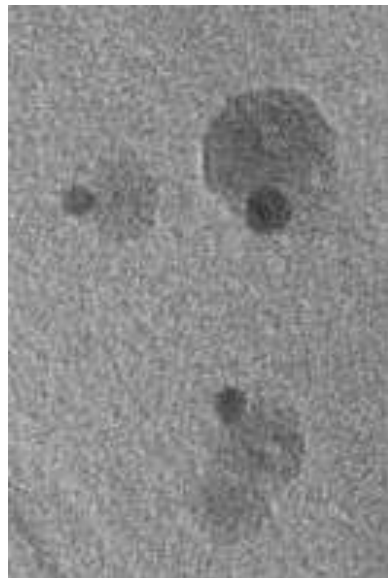


Gold Mobility on Particle Surface at Elevated Temperature

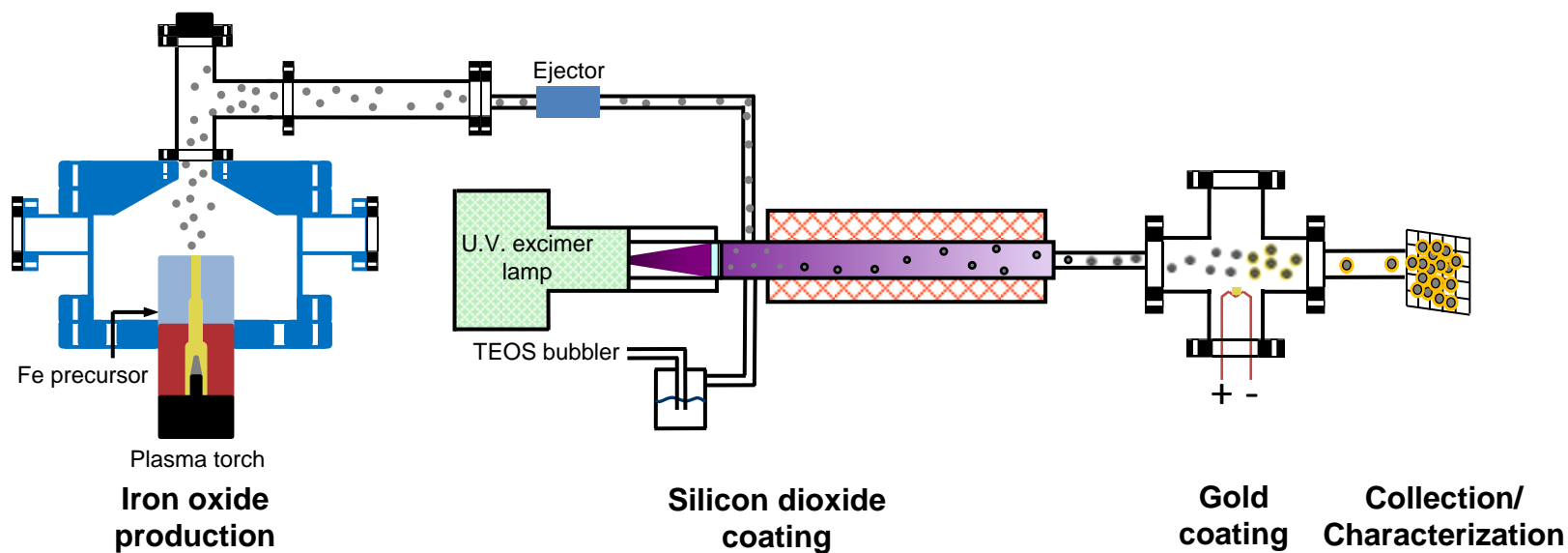
At Low Temp



At 957 ° C

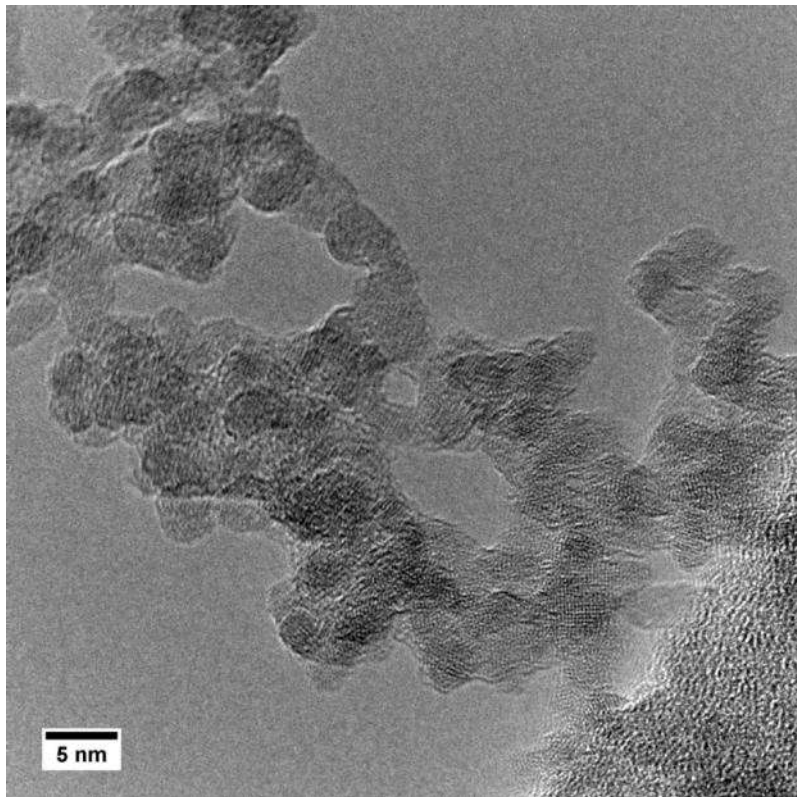


Tri-Layer Nanoparticle Synthesis

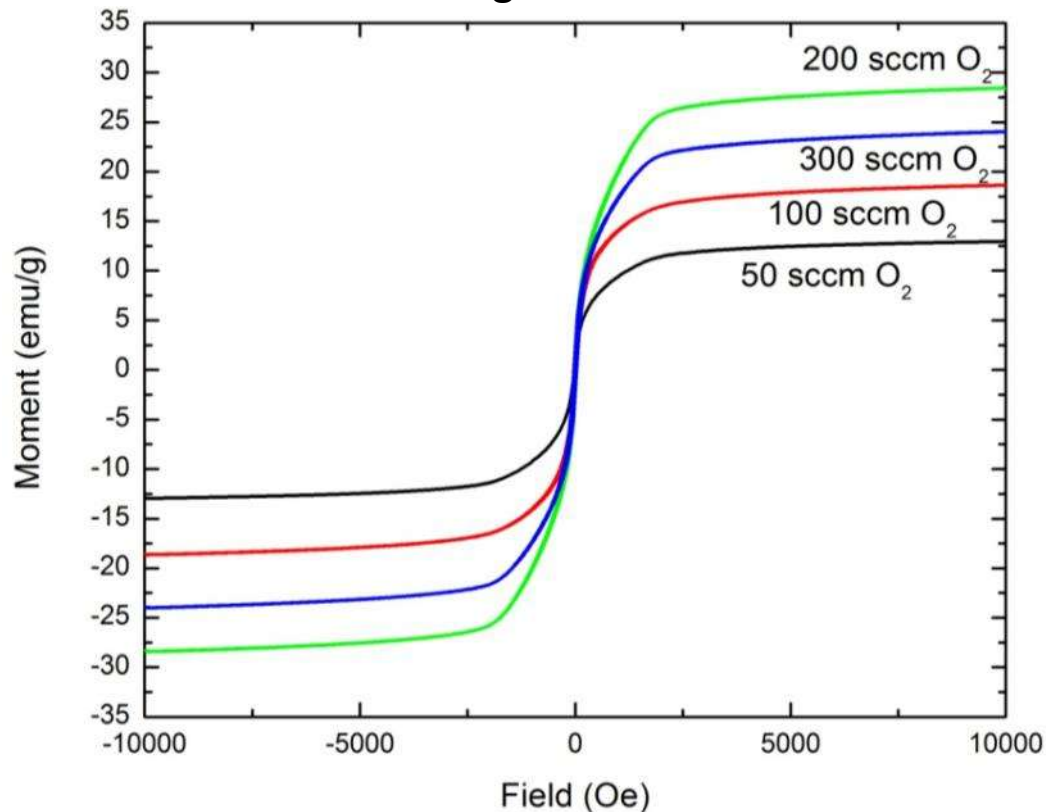


Core: Iron Oxide Production

Particles 3-5 nm



Magnetization

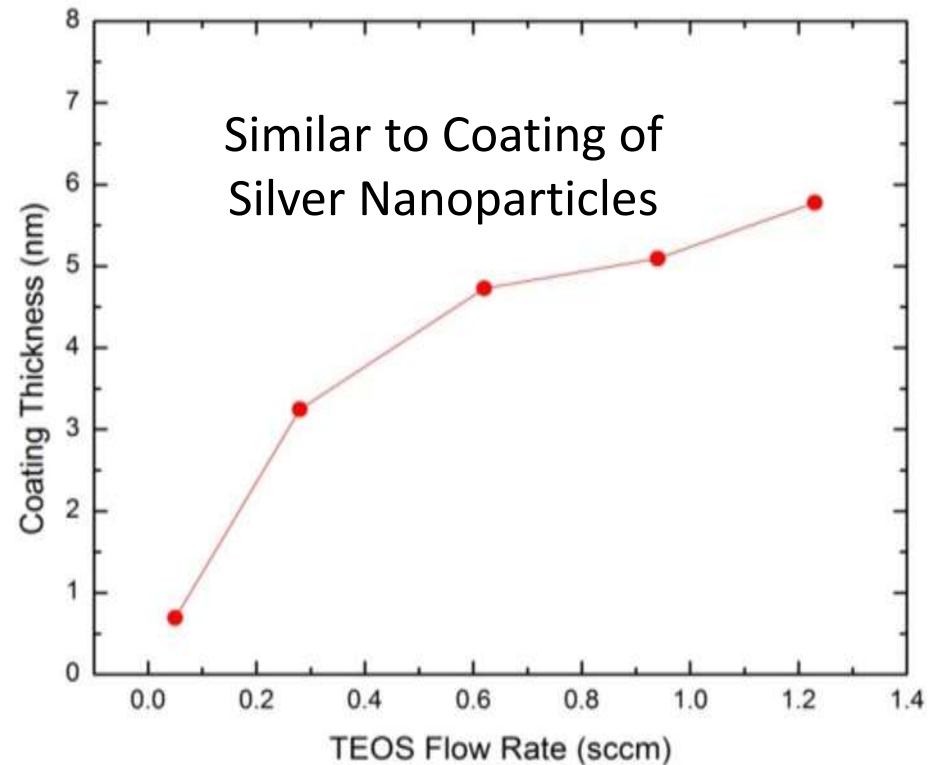
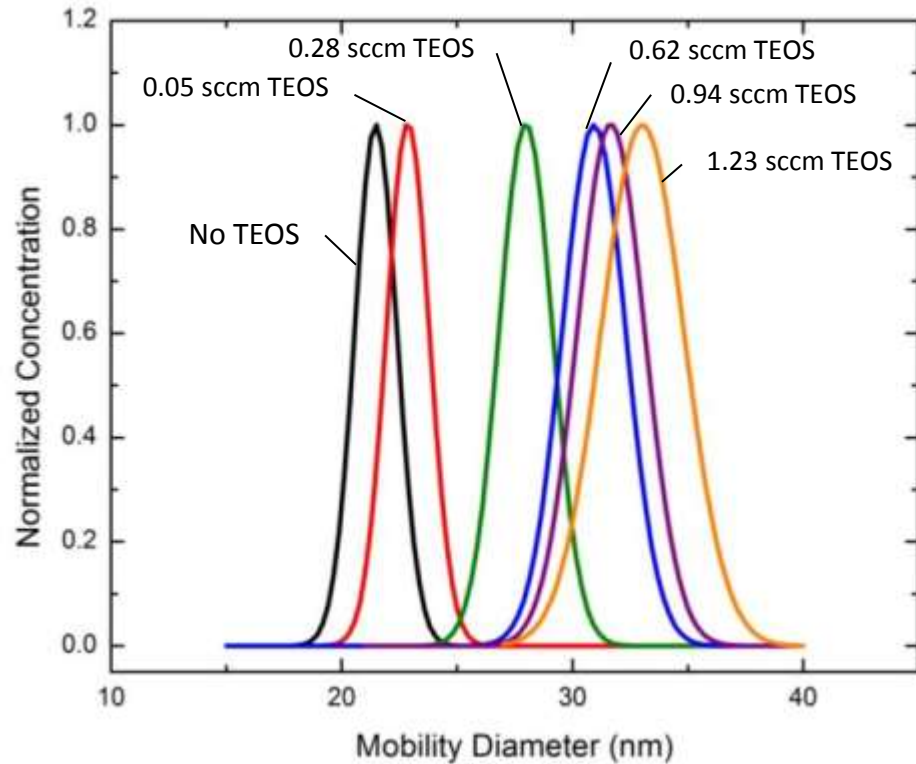


Production rate ~mg/min

Shell 1: Silica Coating

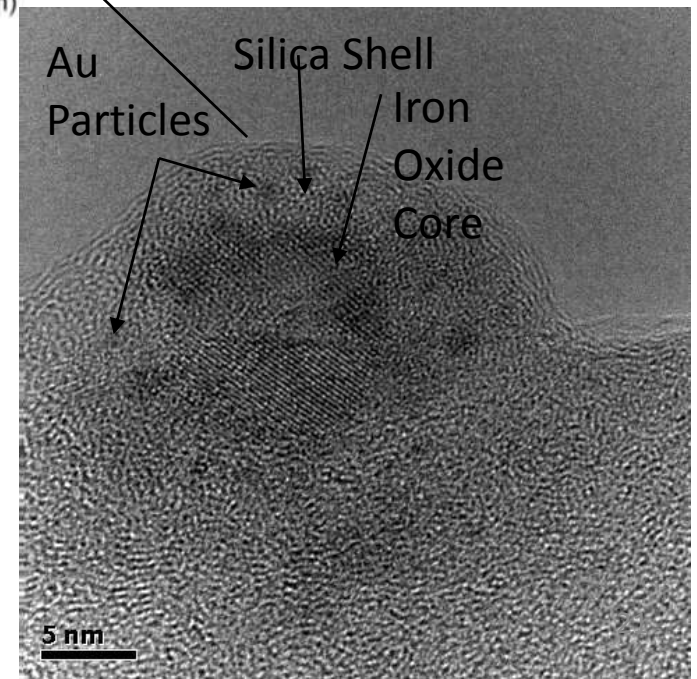
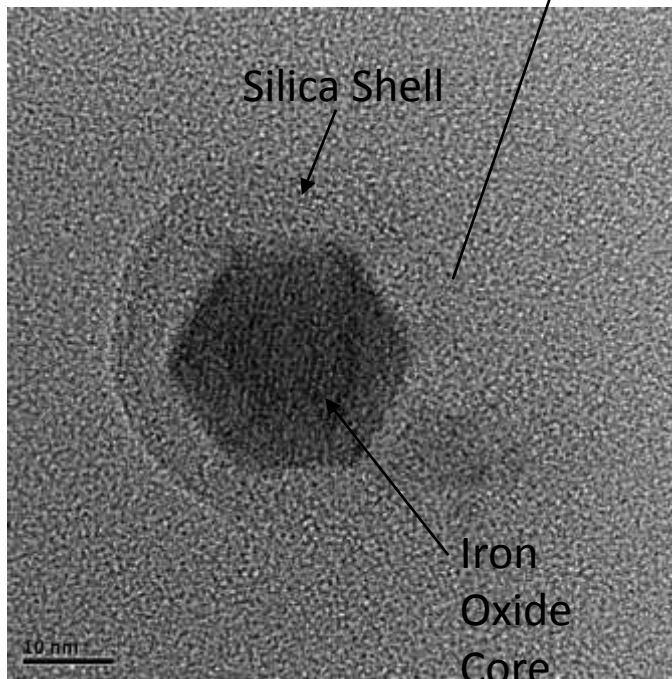
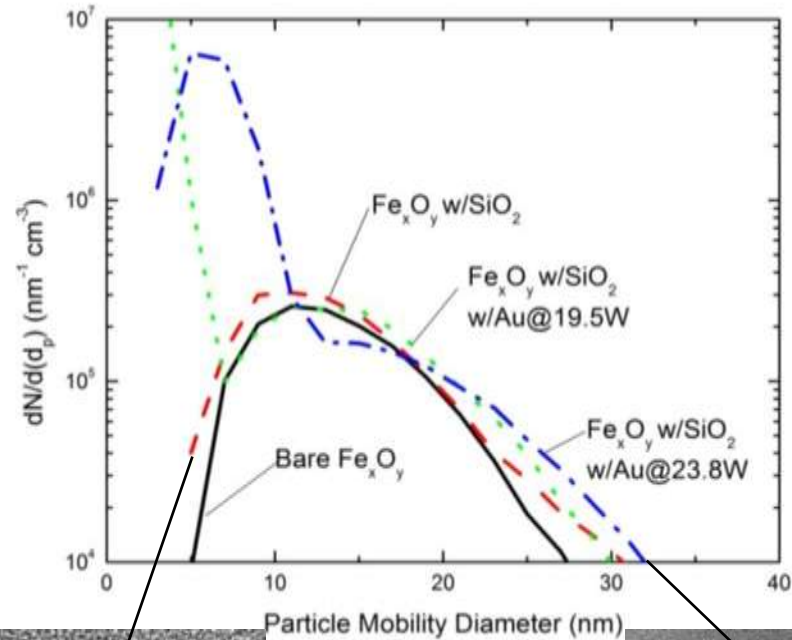
TEOS Flow ↑

Particle Size ↑



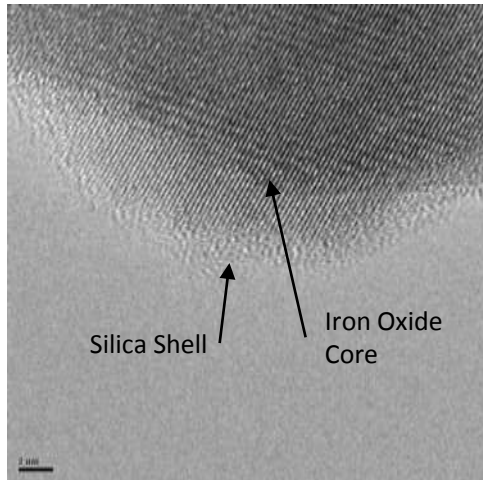
7 slm N₂ Purge Flow

Shell 3: Gold Decoration



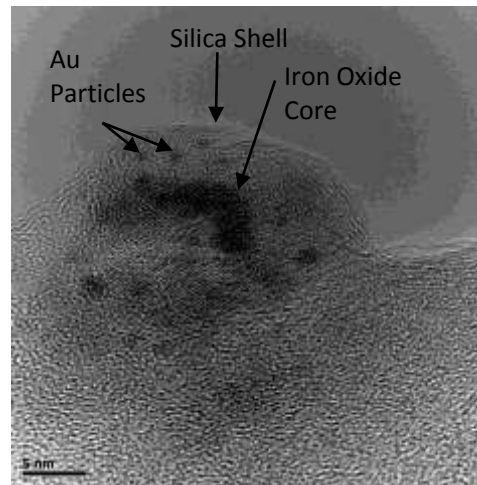
Synthesized Composite Nanoparticles

Silica Coated Iron Oxide



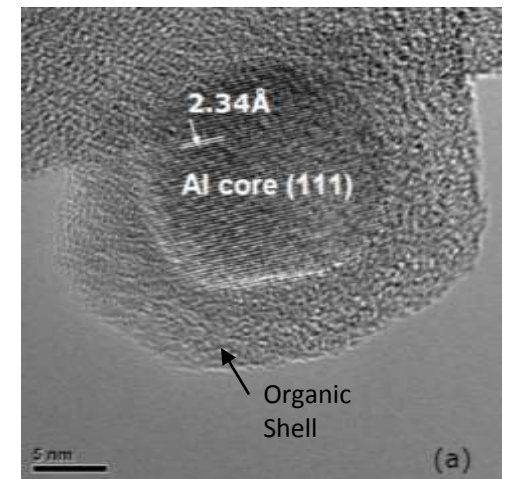
Boies *et. al*, In Prep Nanotech

Tri-Layer Gold, Silica, Iron Oxide



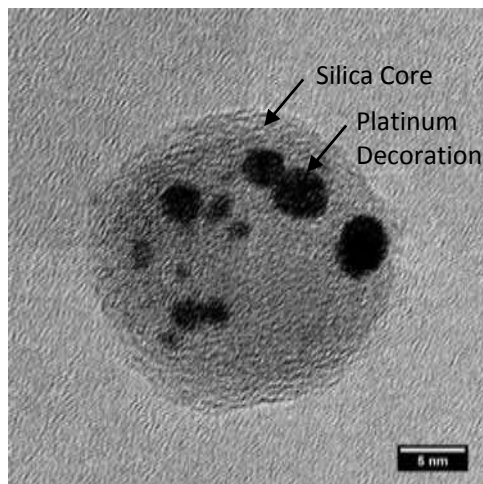
Boies *et. al*, In Prep Nano Let

Organic Coated Aluminum



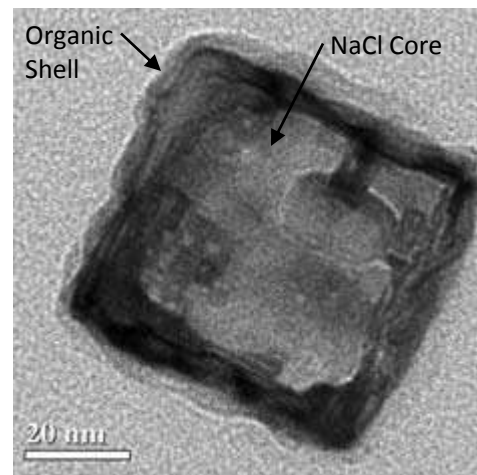
He *et. al*, In Prep J Nanopart Res

Platinum Decorated Silica



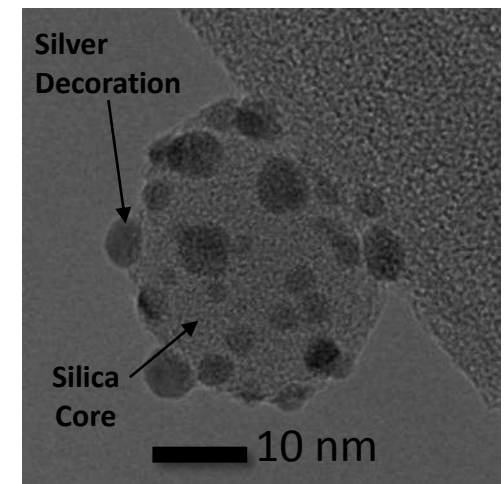
Boies *et al.*, Not Published

Organic Coated Sodium Chloride



Zhang *et. al*, 2006 J Nanopart Res

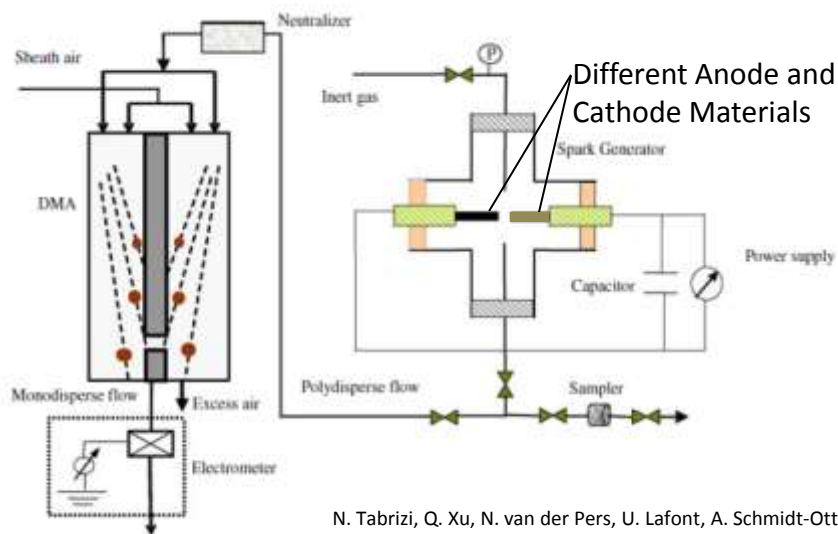
Silver Decorated Silica



Future Directions

Homogenous Mixed Metals

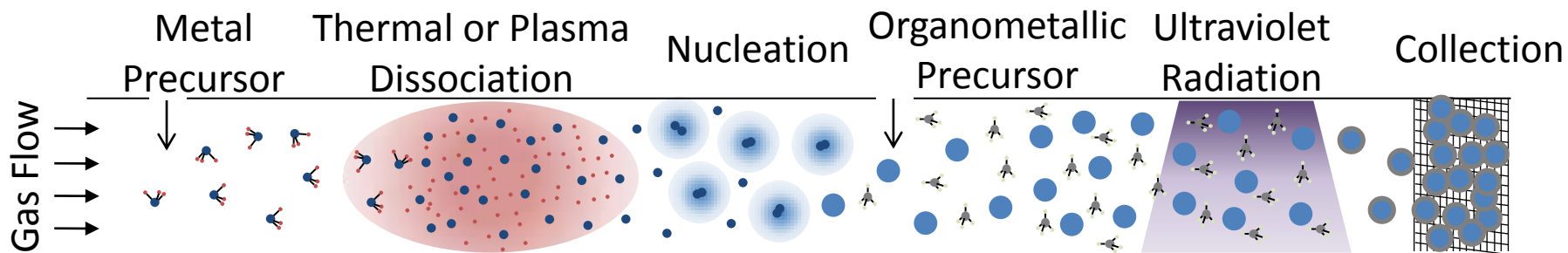
Spark Discharge



N. Tabrizi, Q. Xu, N. van der Pers, U. Lafont, A. Schmidt-Ott, Synthesis of mixed metallic nanoparticles by spark discharge. *Journal of Nanoparticle Research* **2010**, *11*, 1209.

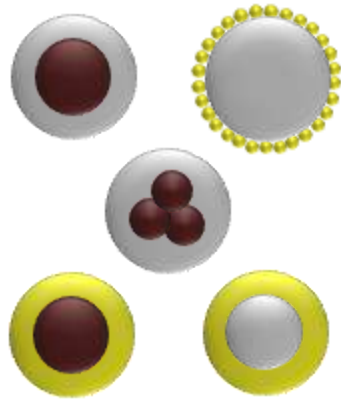
Evaporation, Dissociation

Mixed Metal Core-Shell Nanoparticles

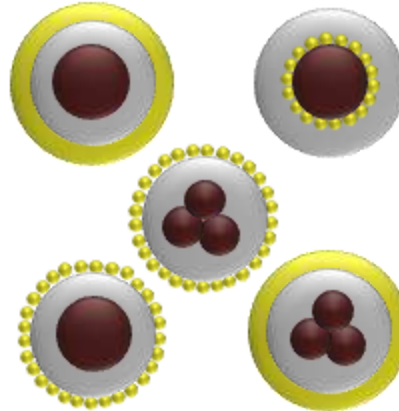


Possible Morphologies

Bi-Material Composites



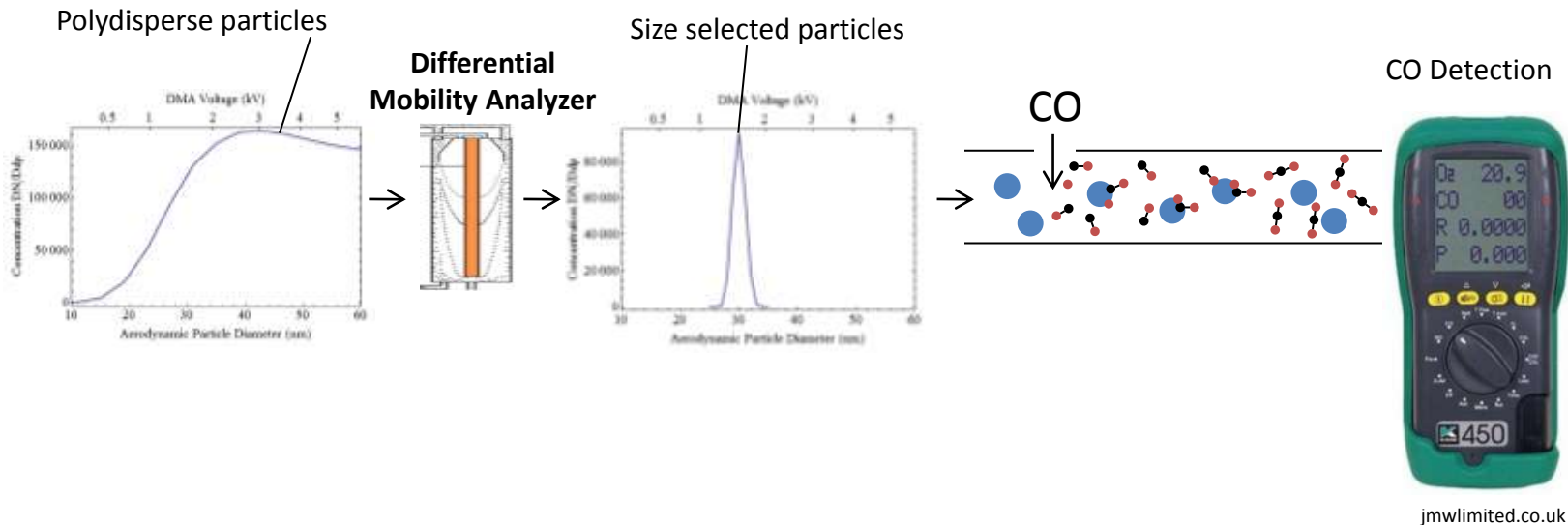
Tri-Material Composites



Materials of Interest

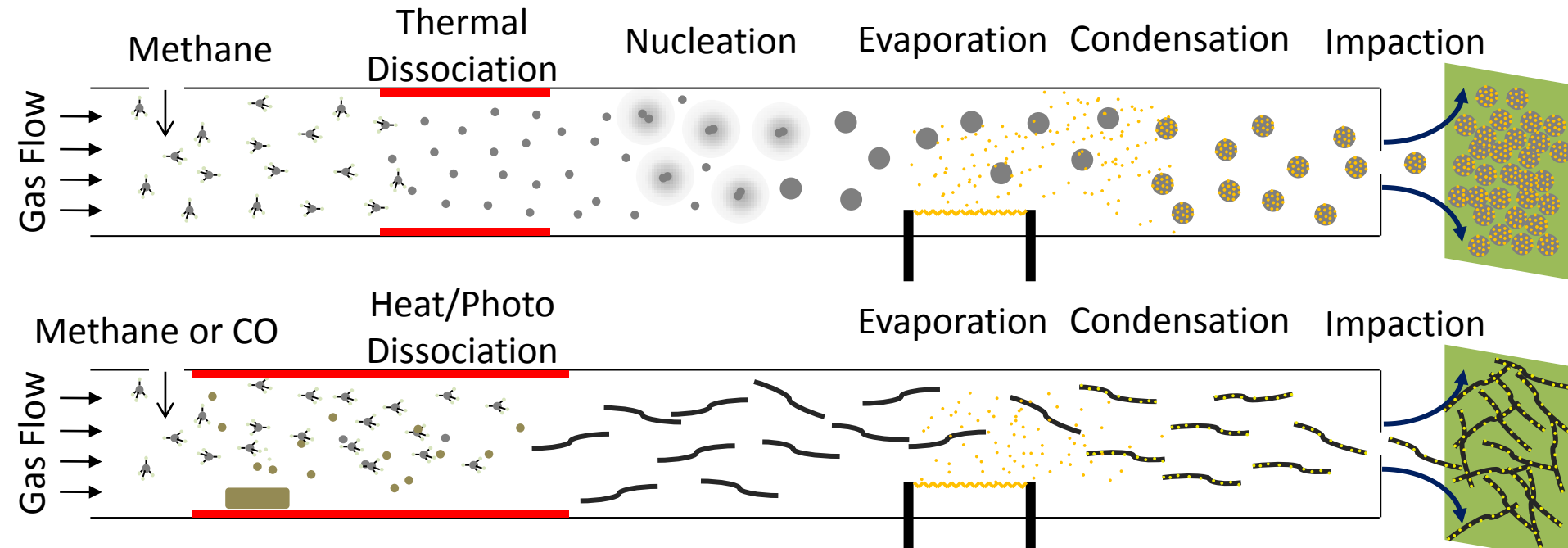
Gold
Platinum
Rubidium
Iron
Nickel
Iron Oxide
Titanium Oxide
Carbon

On-Line Testing of Catalytic Properties

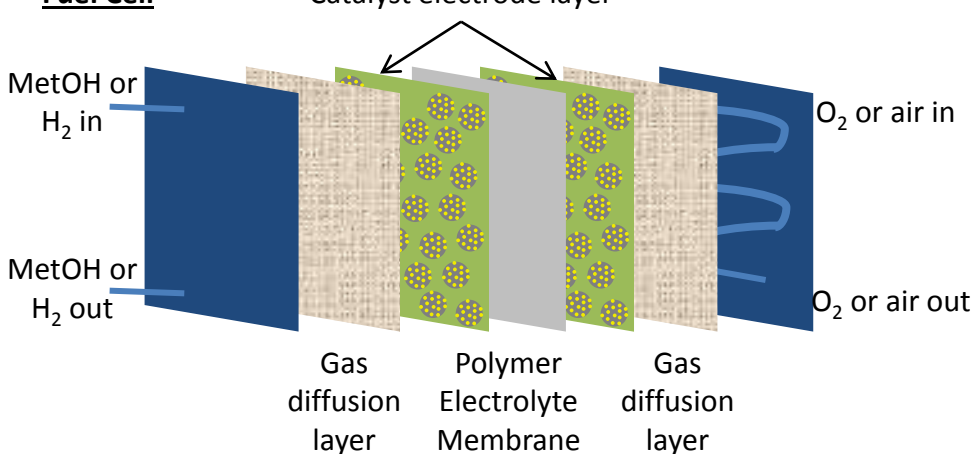


Catalyst Decorated Nanoparticle Substrates

Carbon Nanoparticles or Nanotubes Decorated with Gold and Platinum



Fuel Cell



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 impactation
- Production rate and quality of core particles and nanotubes

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- National Science Foundation Grant-0730184
- Nitto Denko Technical Corporations
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- Institute of Technology Characterization Facility, a NSF-funded Materials Research

