Thermal Electro-Chemical Synthesis of Metallic (Ag) Nanocrystals

Michael Z. Hu[1] & Clay E. Easterly[2]

[1]Separations & Materials Research

[2]Advanced Biomedical Science & Technology

Oak Ridge National Laboratory

E-mail: hum1@ornl.gov

Phone: 865-574-8782

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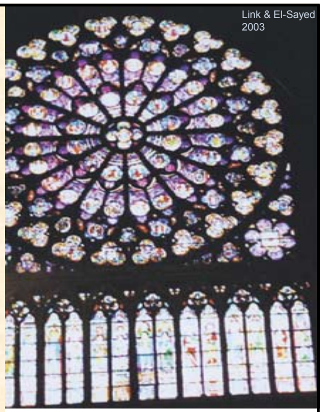
Colors for Your Eyes!

Secret for shining gold lustre coating:
Ag and Cu nanoparticles dispersed homogenously in glassy matrix of ceramic glaze

Link & El-Sayed 2003



Rose window of the Cathedral of Notre Dame, Paris

Au nanoparticles were used as a pigment of ruby-colored stained glass dating back to 17th century.
Metallic nanoparticles have fascinated scientists since the Middle Ages because of their colorful colloidal solutions.

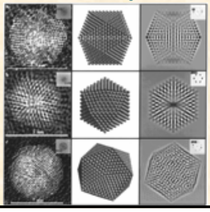
A Wide Range of Advanced Applications of Metallic Nanocrystals

- Catalysis
- Micro-/nano-electronics & optical devices
  - optics, ultrafast optical switches
  - data storage (magnetic, optical)
- Analytical analysis
  - SERS
- Sensors
  - Bio sensing, tagging, or detection
  - Chemical vapor sensing
  - Sensing heavy metal ions
  - Monitoring toxic chemicals
- Energy storage and conversion
  - fuel cells
- Nanocrystal assemblies drastically expands the range of applications
  - Collective optical or magnetic properties due to long-range dipolar interactions

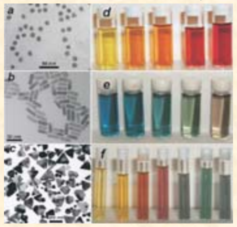
Ag nanocrystal applications:

- Surface-enhanced Raman scattering (SERS)
  - signal enhancement
  - single molecule detection
- Antibacterial & anti-inflammatory
  - Wound dressing/bandages
  - Burn prevention
  - Glass coating (dirt repelling)
  - Against viruses (HIV-1)
  - Targeted therapy
- Enhanced photo luminescence

Henglein et al., 1999



Liz-Marzan, 2004



(a) Au nanospheres, (b) Au nanorods, (c) Ag nanoprisms (mostly truncated triangles) (d)AuAg alloy nanoparticles with increasing Au concentration, (e) Au nanorods of increasing aspect ratio, (f)Ag nanoprisms with increasing lateral size

Size, shape-dependant properties

Issues:

- Size & size uniformity
- Dispersibility
- Surface chemistry
- Shape
- Crystal microstructure

Synthesis Methods for Metallic (Ag) Nanoparticles/Nanocrystals

- **Chemical reduction processes**
  - Ag (I) to Ag(0) by reducing agents (e.g., NaBH4 and formaldehyde)
    [Yin et al. 2002; Green et al. 2002; Jiang et al. 2001; Yonezawa et al. 2000; Wang et al. 1999; Vorobyova et al. 1999; Huang et al. 1998; Wang et al. 1998]
  - Ag^{2+} reduction by citrate ions, which serve multiple roles as reductant, complexant, and stabilizer
    [Pillai and Kamat 2004]
  - Reduction of silver nitrate by hydroxylamine hydrochloride and by polyacrylamide
    [Leopold and Lendl 2003; Qin et al. 2002]
  - Spontaneous reduction of Ag(I) in organic solvents
    [Rodriguez-Gattorno et al. 2002; Liu et al. 2002]
- **Coprecipitation** (thermal decomposition of organometallic precursors)
- **Pulse sonochemical or sonochemical reduction techniques**
  [Liu et al. 2001; Salkar et al. 1999]
- **Electrochemical techniques**
  [Rodriquez-Sanchez et al. 2000; Zhou et al. 1999; Zhu et al. 2001]
- **Photochemical or radiolytic reduction**
  [Keki et al. 2000; Li et al. 2000; Henglein and Giersig, 1999; Henglein 1998]

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Chemical Reduction Processes In Various Liquid Media

- **Aqueous solutions** (with or without the presence of surfactants, polymer dispersants, or capping stabilizer molecules)
  [Yin et al. 2002; Jiang et al. 2001; Yonezawa et al. 2000; Chou and Ren 2000; Wang et al. 1999; Huang et al. 1998]
- **Non-aqueous solvents** (e.g., DMSO, ethanol, ethylene glycol, toluene and DMF)
  [Rodriguez-Gattorno 2002], [Murthy et al. 1997], [Sun& Xia 2002; Silvert et al. 1996], [Chaki et al. 2002], [Liu et al. 2002; Pastoriza-Santos and Liz-Marzan 1999]
- **Two-phase arrested growth method**
  [Korgel et al. 1998; Heath et al. 1997]
- **Water-in-oil microemulsions or reversed micelles**
  [Pileni 2000; Rong et al. 1999; Vorobyova et al. 1999; Pavlyukhina et al. 1998; Pileni et al. 1998; Manna et al. 1997; Taleb et al. 1997]
- **Liquid crystalline systems**
  [Patakfalvi and Dekany 2002; Zhang et al. 2001]
- **Supercritical carbon dioxide systems**
  [Sun et al. 2001; Ohde et al. 2001]

Use of protective agents (steric capping molecules or ligands) to control the size/growth and stabilize the nanoparticles, such as trialkylphosphine/amine, triethylamine, alkanethiols, long-chain unsaturated carboxylates, CS2, quaternary ammonium disulfide; poly(vinylpyrrolidone).

Ag Nanocrystals: improve Properties

"Clean" nanocrystals are needed:

- **Antibacterial properties of Ag ions and radicals**
  - **Infections due to bio-warfare**
  - **Impregnated into plastic vascular catheters, toothbrushes, air conditioning systems**
  - **Swimming pool**
- **Pro-healing, anti-inflammatory properties**
  - **Burn injury, wound**

Reactive Species of Silver Released from Silver Products

http://www.burnsurgery.com/Modules/nano/sec4.htm

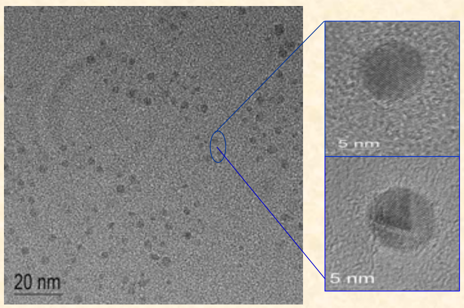
Medical Name	Initial forms of Silver	Silver Species in Solution	Conc. Silver* after 24 hrs
Nanocrystal Silver Delivery	Metallic Ag Nanocrystal	Ag+ AgO/Ag+ clusters	50-100µg/ml
1% SSD	Ag+	Ag+	30µg/ml
(0.5%) Silver Nitrate	Ag+	Ag+	30µg/ml
Arglaes	$AgKaPO_4$	Ag+	20µg/ml
Silverion	Ag Metal	Ag+	<1µg/ml

* concentration of silver in solution (one square inch of surface / 5 ml water)

- Rapid deactivation of silver by tissue proteins or Cl^-
- A continuous silver release → much more effective use of silver ions
- Ag nanocrystal
  →high surface areas
  →more reactive to water and oxygen
  →release Ag cations very rapidly and for long periods
  →more rapid killing effect is due to increased speed of silver delivery to the bacterial wall and possible presence of Ag radical species
- Low toxicity of pure metal Ag to human tissue

Formation of "Naked" Metallic Nanocrystals by A Novel *Thermal ElectroChemical Process*

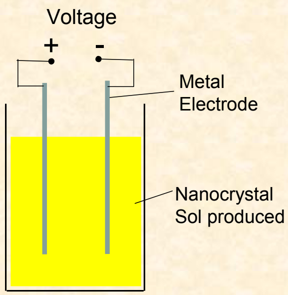
Special niche applications
- home-land security
- others (optical and antibacterial properties)

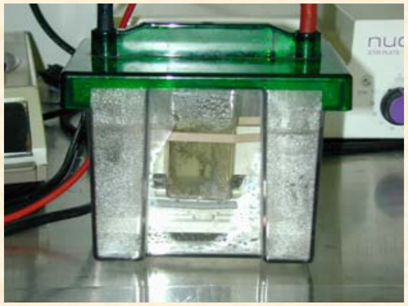


This process, developed at ORNL, generates possibly a new class of Ag nanocrystals.

- **Size < 10 nm**
- **Free from any organic capping molecules**
- **Colloidally stable**

Experimental setup



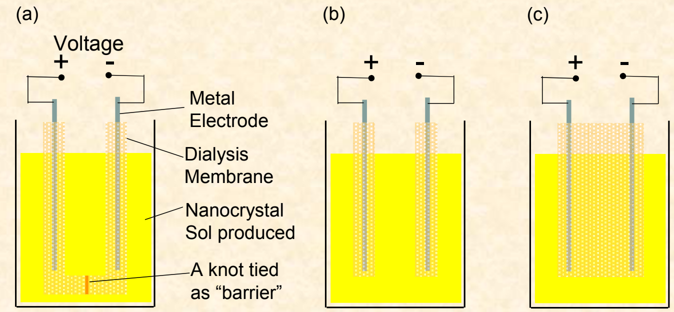


Fractal growth between electrodes

- Membranes surrounded the electrodes are necessary to
  - ✓ Reduce the fractal growth of solids from electrode surface
  - ✓ Control the nanocrystal growth in bulk solution
  - ✓ Regulate the diffusion rate of ions/clusters

- Simple electrode corrosion generates of nanoparticles with diameters in tens to hundreds of nanometers
- Fractal growth eventually bridge the electrodes, generating "micro-arching"

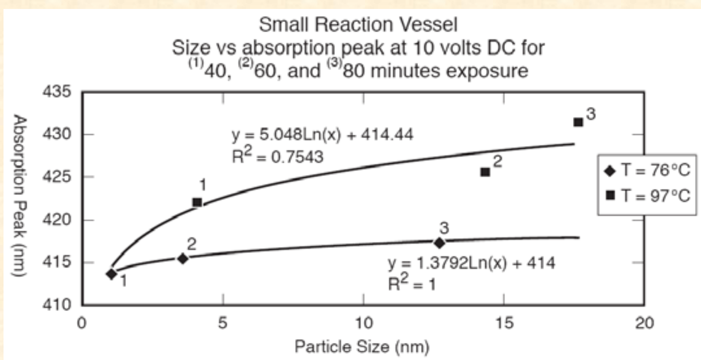
Various Reactor Designs



Schematic for the thermal electrochemical synthesis reactor. (a) electrodes encapsulated with one U-shaped membrane tube with a center barrier (i.e. a tied knot), (b) electrodes encapsulated with two separate membrane tubes with the bottom sealed or tied, (c) electrodes encapsulated in one big membrane tube.

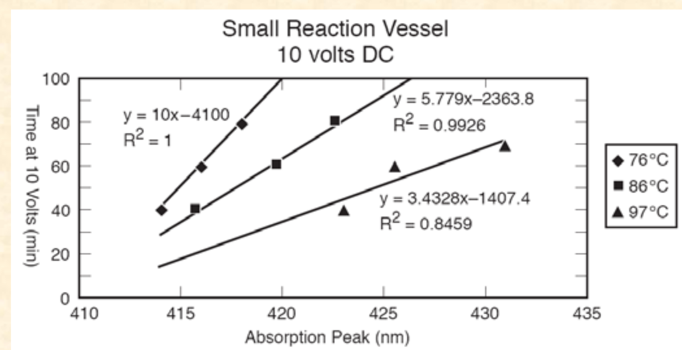
Process Parameter Studies

Correlation of nanoparticle size by DLS and UV/vis absorption peak position.



Process Parameter Studies

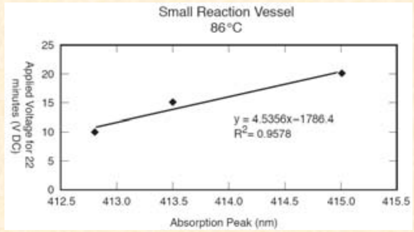
Temperature and reaction time effects on nanocrystal formation. Correlation between reaction time/temperature and UV/vis absorption peak position.



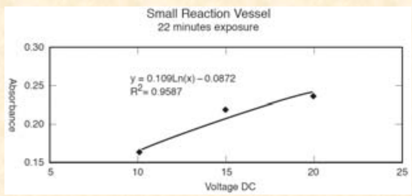
Process Parameter Studies

Voltage effect on

(a) UV/vis absorption peak position (or nanocrystal size) and

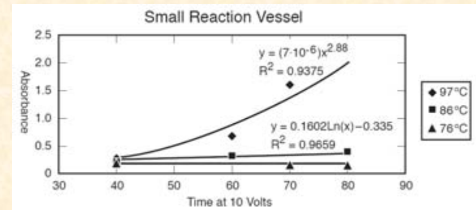


(b) absorbance (or nanocrystal concentration).

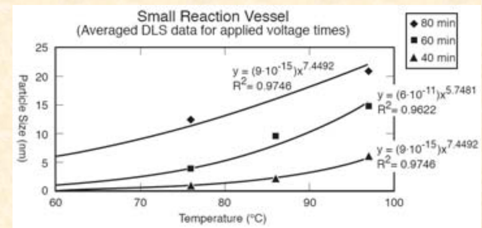


Process Parameter Studies

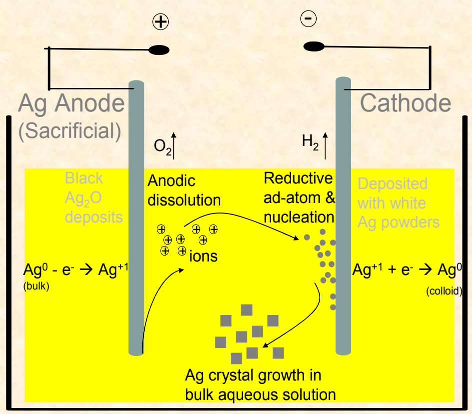
UV/vis absorbance changes (with reaction time and temperature) during nanocrystal formation process.



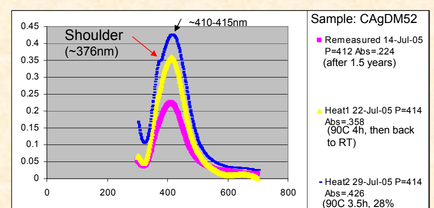
Correlation of DLS particle size with reaction time and temperature.



Silver Nanocrystal Formation Process and Mechanism



UV/VIS: Evolution of self-assembled nanostructures by heat-assisted concentration

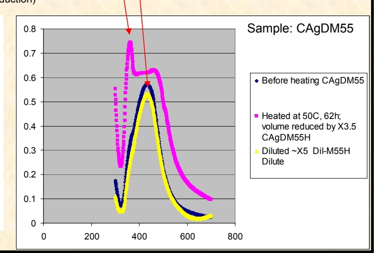


New peak (~**364nm**), corresponding to nano-needles, evolve after heated concentration of Ag nanocrystal sol

Dynamic equilibrium

This peak (~**435nm**) corresponds to Ag nanoparticles (a few nanometers)

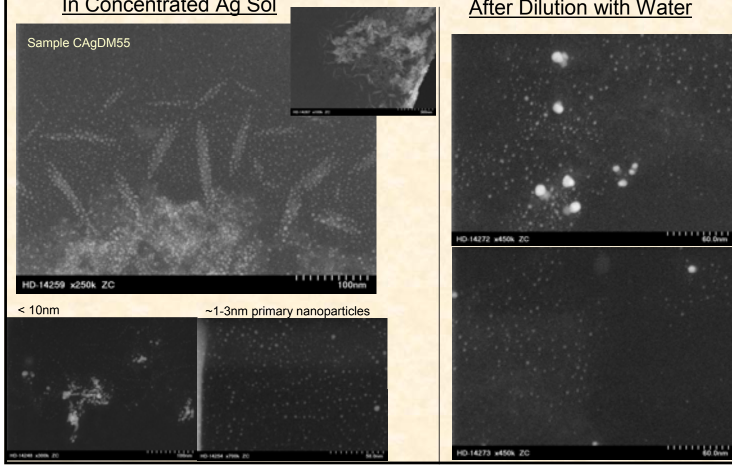
- **Ag nanocrystal sol can be concentrated by oven heat, while still maintaining the stable nanosize for majority population**
- **However, beyond a "critical nanoparticle concentration", primary nanoparticles will assembled into a new nanostructure (i.e., nano-needles)**
- **The self-assembled nano-needles can be reversibly dispersed into nanoparticles by simple dilution**



STEM images of self-assembled nano-needles and primary nanoparticles

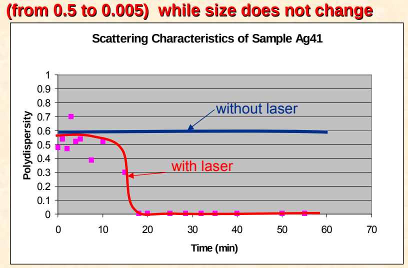
In Concentrated Ag Sol

After Dilution with Water



Laser-Induced Phenomenon: Ag Nanoparticle Homogenization

2 orders-of-magnitude reduction in polydispersity! (from 0.5 to 0.005) while size does not change



Polydispersity: a parameter in dynamic light scattering measurement to quantify particle size distribution.
- < 0.02, for monodisperse or nearly monodisperse samples
- 0.02-0.08, for narrow size distributions
- > 0.08, for broader distribution

- **Mechanism of homogenization ?**
  - **Photon excitement, surface plasmon resonance effect**

Electromagnetic radiation induced dipoles

  - **Thermal energy**
  - **Ostwald ripening**
- **Size dependency?**
- **Effect of laser type/wavelength?**
- **Dynamics of homogenization?**
- **Nanocrystal properties?**

Summary

- **A novel thermal electro-chemical (TEC) method has been developed for synthesis of "naked" Ag nanocrystals (mostly 1-5 nm in diameter)**
- **Concentrated sol can be obtained by simple oven heat evaporation. A concentration dependant self-assembly of nanocrystals into nano-needles has been observed**
- **A laser-induced particle size homogenization process has been discovered**
- **Preliminary in-vitro tests show that Ag nanocrystals are effective in killing and inhibiting the bacterial growth**

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