Building College-University Partnerships for Nanotechnology Workforce Development

Metal Nanoparticles

Metal Nanoparticles: How are they manufactured, what useful properties do they have and what are some examples of products?

Dr. James Delattre
NanoHorizons. LLC

Lecture Outline

- **History of Synthetic Metal Nanoparticles**
- **Contemporary Definitions**
- **Methods of manufacture**
- **Useful properties**
- **Commercial examples available <u>TODAY</u>**

History of Synthetic

Metal Nanoparticles

History of Synthetic Metal Nanoparticles

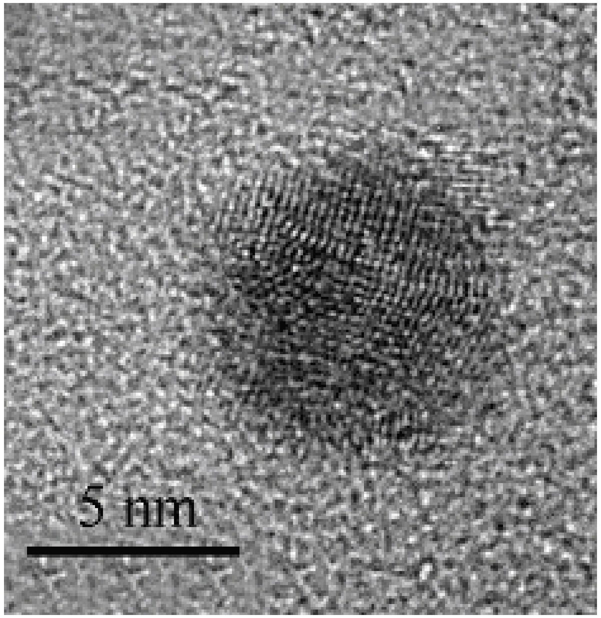
Michael Faraday's Recognition of Ruby Gold: the Birth of Modern Nanotechnology

His 1857 Lecture to the Royal Society in London

In his studies of the interactions of light and matter, Faraday prepared gold 'sols' that were "very minute in their dimensions" and stated that "known phenomena appeared to indicate that a mere variation in the size of its particles gave rise to a variety of resultant colours."

http://www.goldbulletin.org/assets/file/goldbulletin/downloads/Faraday_4_40.pdf

History of Synthetic Metal Nanoparticles



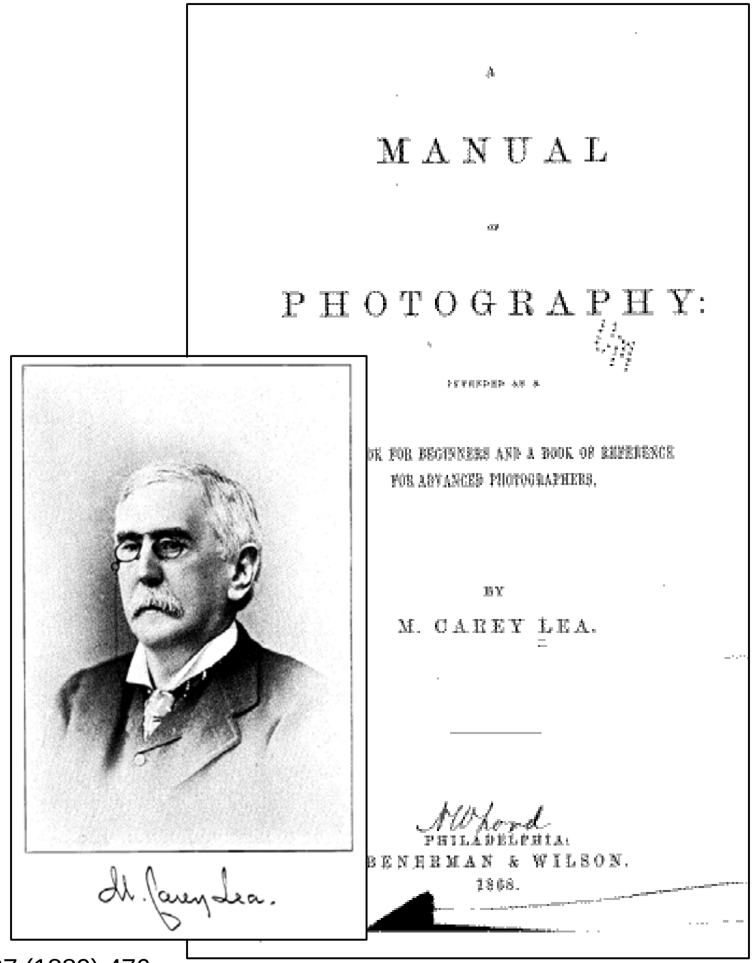
Portrait of Michael Faraday. Reproduced by Courtesy of the Royal Institution of Great Britain

Nearly 100 years later Turkevich used electron microscopic investigations to reveal that the ruby-colored colloids made by Faraday's preparative routes produce particles of gold with average sizes in the 6 2 nm range.

http://www.goldbulletin.org/assets/file/goldbulletin/downloads/Faraday_4_40.pdf

History of Synthetic Metal Nanoparticles

- Mathew Carey Lea of Philadephia first synthesized colloidal silver in 1880s[1]
- Used widely in photographic film industry throughout 20th century[2]
- Still used today in X-ray films[3]



A

MANUAL

OF

PHOTOGRAPHY:

K FOR BEGINNERS AND A BOOK OF REFERENCE

FOR ADVANCED PHOTOGRAPHERS.

BY

M. CAREY LEA.

PHILADELPHIA:

BENERMAN & WILSON.

1868.

[1] MC. Lea, "On Allotropic Forms of Silver", *American Journal of Science*, 37 (1889) 476

[2] D.Whitcomb, "Mathew Carey Lea: Chemist, photographic scientist", *Chemical Heritage Newsmagazine*, 24(4) (2006/7).

[3] DR.Whitcomb, "Nanosilver Particles in Medical X-ray Diagnostic Films", Eastman Kodak Company (2005). www.particlesociety.org/Whitcomb.pdf

History of Synthetic Metal Nanoparticles

- **1969**: Carey Lea colloidal silver produced using same methodology as 1889 [1]
  - Size determination and characterisation using electron microscopy (TEM) confirms the size from historical characterisation methods [2]
  - Confirmed as metallic silver by X-ray diffraction
  - *Carey Lea* colloidal silver **average size 7 - 10 nm**
  - Confirmation that historical colloidal silver is composed of nanoscale silver particles

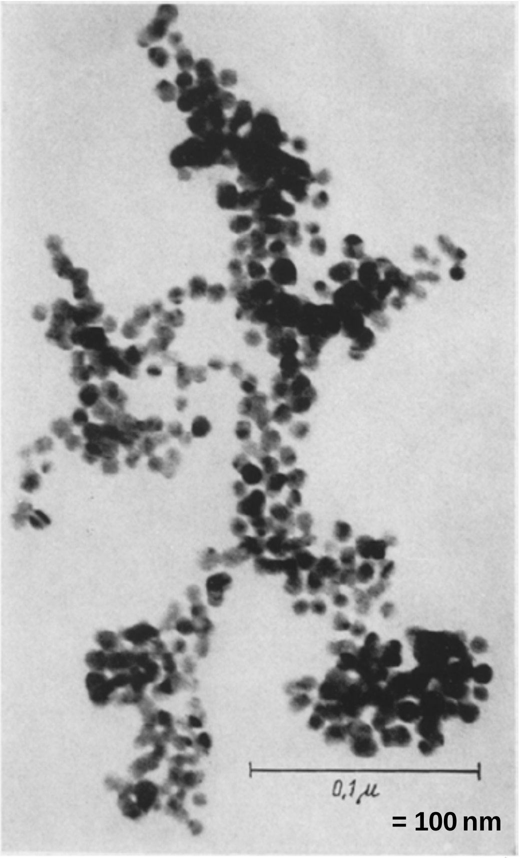
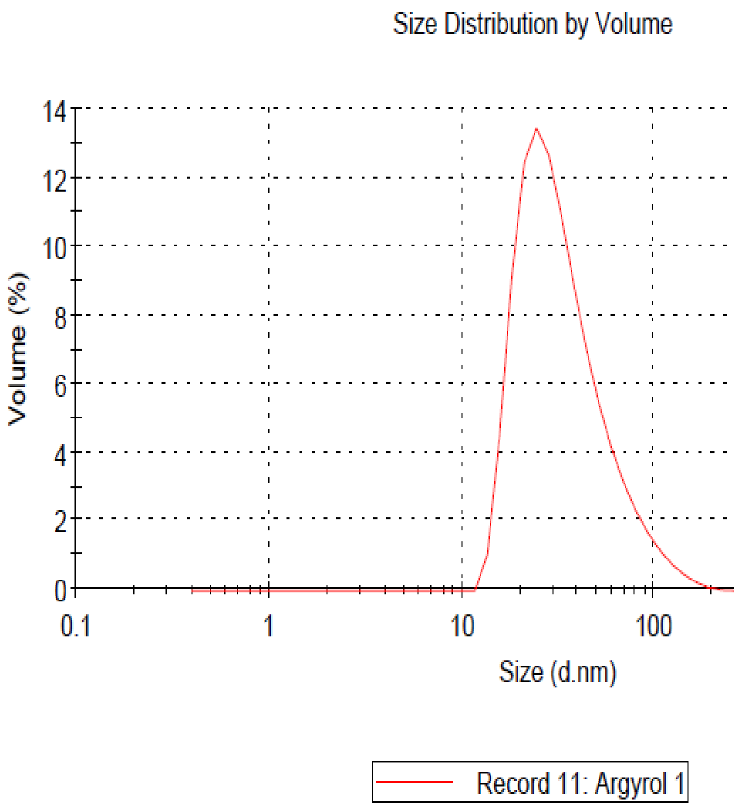


Fig. 1. Electron micrograph of a *Carey Lea* silver sol

1Lea, MC. "Allotropic Forms of Silver." *American Journal of Science*, 37 (1889), 476.
2Frens, G. & Overbeek, J.Th.G."Carey Lea's colloidal silver", *Kolloid-Zeitschrift und Zeitschrift für Polymere,* 233(1-2) (1969) pp922-929.

History of Synthetic Metal Nanoparticles



In 1902, Alfred C. Barnes developed a new antiseptic silver compound, Argyrol, and formed the firm of Barnes & Hille in Philadelphia. The success of this endeavor provided Dr. Barnes with a sizable fortune which was used to amass America’s largest private collection of modern art including works by Picasso, Monet, Matisse, Cezanne and Renoir.

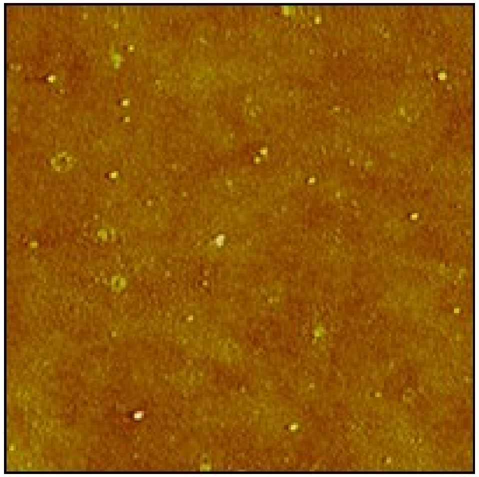
History of Synthetic Metal Nanoparticles

1942 Argyrol Ad

Why Synthetic Metal Nanoparticles?

Because naturally occurring metal nanoparticles can form by reduction of terrestrial metal ions by organic acids

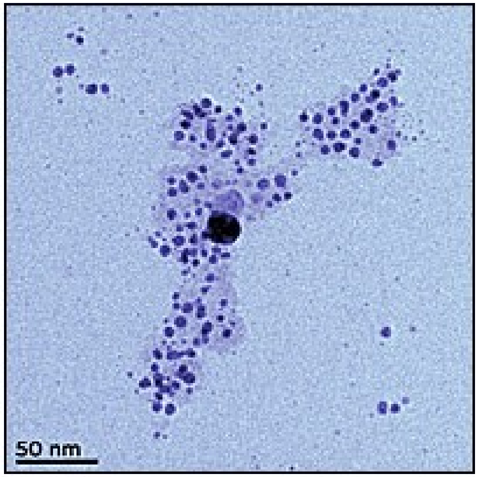
http://www.nist.gov/mml/mmsd/silver-051011.cfm



AFM (Atomic force microscopy) image of silver nanoparticles formed from silver ions in solution with humic acid. Color tone in this image indicates height (0 to 10 nanometers) above the base plane, so brighter spots are taller, larger nanoparticles. Image is roughly 1,700 nm on a side.

Credit: MacCuspie, NIST

View hi-resolution image



Transmission electron microscopy (TEM) image of silver nanoparticles formed from silver ions in solution with humic acid. The acid tends to coat the nano particles (visible here as a pale cloud), keeping them in a colloidal suspension instead of clumping together. (Color added for clarity.)

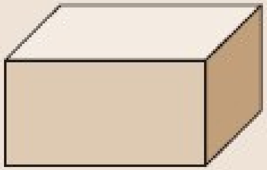
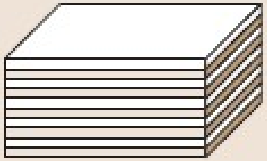
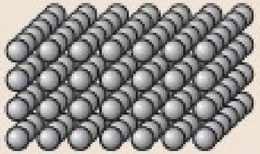
Credit: SUNY, Buffalo

View hi-resolution image

Contemporary Definitions of

Metal Nanoparticles

Contemporary Definitions

$L_{X,Y,Z} > L_0$	No nanostructures	No confinement	Bulk material	
$L_{X,Y} > L_0 > L_Z$	Two-dimensional (2-D) nanostructures	One-dimensional (1-D) confinement	Wells	
$L_X > L_0 > L_{Y,Z}$	One-dimensional (1-D) nanostructures	Two-dimensional (2-D) confinement	Wires	
$L_0 > L_{X,Y,Z}$	Zero-dimensional (0-D) nanostructures	Three-dimensional (3-D) confinement	Dots	

Credit: Nanoparticle Synthesis, Prof. Jimmy C. Yu, Department of Chemistry, The Chinese University of Hong Kong

Contemporary Definitions

More than 24 distinct nano-related definitions have been proposed mostly by standards organizations and government agencies

Summary of current definitions for Nanotechnology, Nanoscale, and Nanoparticles

Organization	Size (nm)	Dimensions	Manufactured	Insoluble	Unique Property	Surface Area	Other
ASTM[i]	> 1– < ~ 100	2 or 3	Not Included	Not Included	May or may not	Not Included	
British Institute of Standards (BSI)[ii]	1–100	1 or more	Not Included	Not Included	Not Included	Not Included	
CEPA[iii]	1–100	1 or more	Yes	Not Included	Yes	Not Included	
Health Canada[iv] (Working Definition)	1–100	1 or more	Yes	Not Included	Yes*	Not Included	*Unique properties even if < or > than 1–100 nm
DEFRA[v]	< 200	2 or 3	Not Included	Not Included	Not Included	Not Included	
EPA (PPDC)[vi]	1–100	Not Included	Yes	Not Included	Not Included	Not Included	
EU Cosmetics Regulation (Article 2	1–100	1 or more	Yes	Yes	Not Included	Not Included	Also biopersistant

Report of the ICCR Joint Ad Hoc Working Group on Nanotechnology in Cosmetic Products: Criteria and Methods of Detection ICCR-4, 2010

Contemporary Definitions:
Cautionary Note on Regulatory Definitions

"First, we have the problem of definitions…Unfortunately, the generally accepted definition of nanotechnology—"the understanding and control of matter at dimensions between approximately 1 and 100 nanometers, where unique phenomena enable novel applications" is what the US National Nanotechnology Initiative uses—is one of expedience, not of science. It serves the purpose of stimulating new research and technology innovation in an exciting new area brilliantly. *But it doesn't clearly define a set of products and processes that have common and specific safety issues; and it was never intended to.*

As a result, attempts to apply the generally accepted definition of nanotechnology to material and product safety ends up in a messy mismatch. Materials that are probably benign come under suspicion, while others that we should be worried about potentially slip the net."

- Prof. Andrew Maynard
  Director, University of Michigan Risk Science Center
  "Ten things everyone should know about nanotechnology safety"
  2020 Science

Metal Nanoparticles:

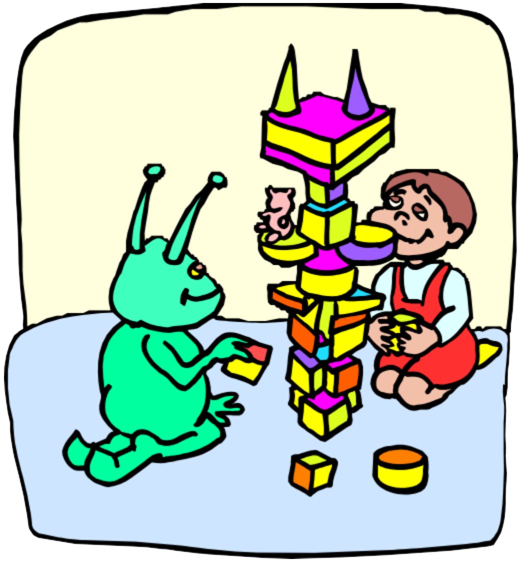
Methods of Manufacture

Manufacturing Methods:

Two General Approaches to Nanoparticle Synthesis

- **Top ⇨ Down:**
  - **Start with the bulk material and "cut away material" to make the what you want**

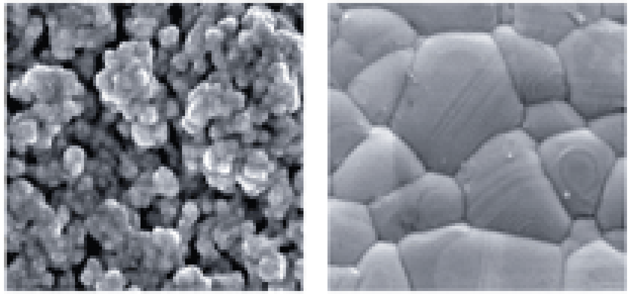
- **Bottom ⇨ Up:**
  - **Building what you want by assembling it from building blocks (such as atoms and molecules).**
  - **Atom-by-atom, molecule-by-molecule, or cluster-by-cluster**



Credit: Nanoparticle Synthesis, Prof. Jimmy C. Yu, Department of Chemistry, The Chinese University of Hong Kong

Top-Down Approaches

- **Milling (rarely achieves nanoscale)**
- **Sputter/laser/e-beam deposition**
  (energy + metal target = NPs)
- **Pulsed Wire Evaporation**
- **Nanolithography**



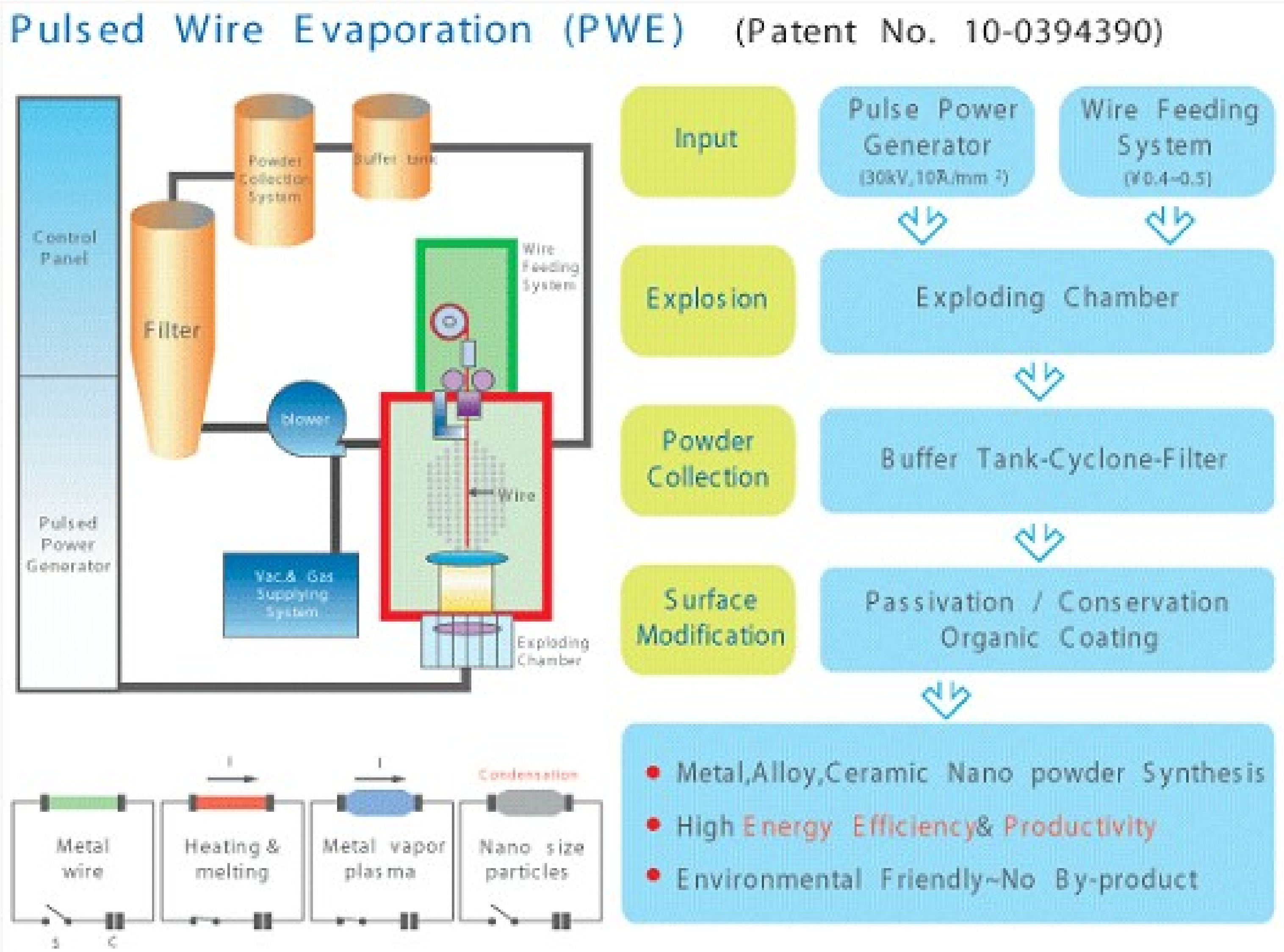
ACTICOAT silver　　Regular silver

- **Pros**
  - **Can be inexpensive**
  - **Scalable**
  - **Pure target = pure NPs (in theory)**
- **Cons**
  - **10 ~ 1000 nm; broad distribution**
  - **Highly varied particle shape or geometry**
  - **Oxidation / impurities**

http://www.smith-nephew.com/key-products/advanced-wound-management/acticoat/

Principle of Pulsed Wire Evaporation

nano technology NANO POWDER MAKER



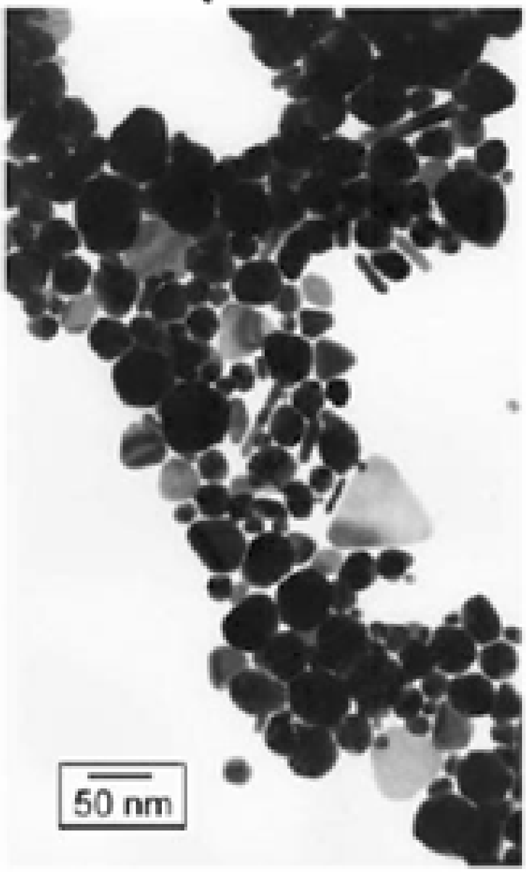
Bottom-Up Approach

- Liquid Phase Synthesis from Chemical Precursors
  - Chemical Reduction
  - Electrochemical Reduction
- Vapor Phase Synthesis from Chemical Precursors
  - Chemical Vapor Deposition
  - Flame Spray Pyrolysis
- Self-Assembly of Clusters, Particles

- Pros
  - Good control of size distribution
  - Shape control in some cases
- Cons
  - Impurities often intermixed in NPs
  - Limits on scalability in some cases

Manufacturing Methods:
Bottom-Up Chemical Reduction

Faraday Au Colloids



Au nanoparticles are synthesized through reduction reaction

$AuCl_4^- + P \longrightarrow Au\ (NP)$

Metal salt | Reducing reagent | Solvent - water

- **Size, shape, crystallinity**
- **Large surface area for <u>conventional application</u>**

Source: Nanoscale manufacturing curriculum for ATE

Manufacturing Methods:
Bottom-Up Chemical Reduction

Table 3.1. Summary of precursors, reduction reagents and polymer stabilizers.

Precursors	*Formula*
Metal anode	Pd, Ni, Co
Palladium chloride	$PdCl_2$
Hydrogen hexachloroplatinate IV	H_2PtCl_6
Potassium tetrachloroplatinate II	K_2PtCl_4
Silver nitrate	$AgNO_3$
Silver tetraoxylchlorate	$AgClO_4$
Chloroauric acid	$HAuCl_4$
Rhodium chloride	$RhCl_3$
Reduction Reagents	
Hydrogen	H_2
Sodium citrate	$Na_3C_6H_5O_7$
Hydroxylamine hydrochloride	$NH_4OH + HCl$
Citric acid	$C_6H_8O_7$
Carbon monoxide	CO
Phosphorus in ether	P
Methanol	CH_3OH
Hydrogen peroxide	H_2O_2
Sodium carbonate	Na_2CO_3
Sodium hydroxide	NaOH
Formaldehyde	HCHO
Sodium tetrahydroborate	$NaBH_4$
Ammonium ions	NH_4^-
Polymer stabilizers	
Poly(vinylpyrrolidone), PVP	
Polyvinylalcohol, PVA	
Polyethyleneimine	
Sodium polyphosphate	
Sodium polyacrylate	
Tetraalkylammonium halogenides	

Metal Nanoparticle Properties Including:

- **Composition**
- **Particle size**
- **Crystal structure**
- **Shape**
- **Zeta Potential**
- **Reactivity**
- **Solubility**

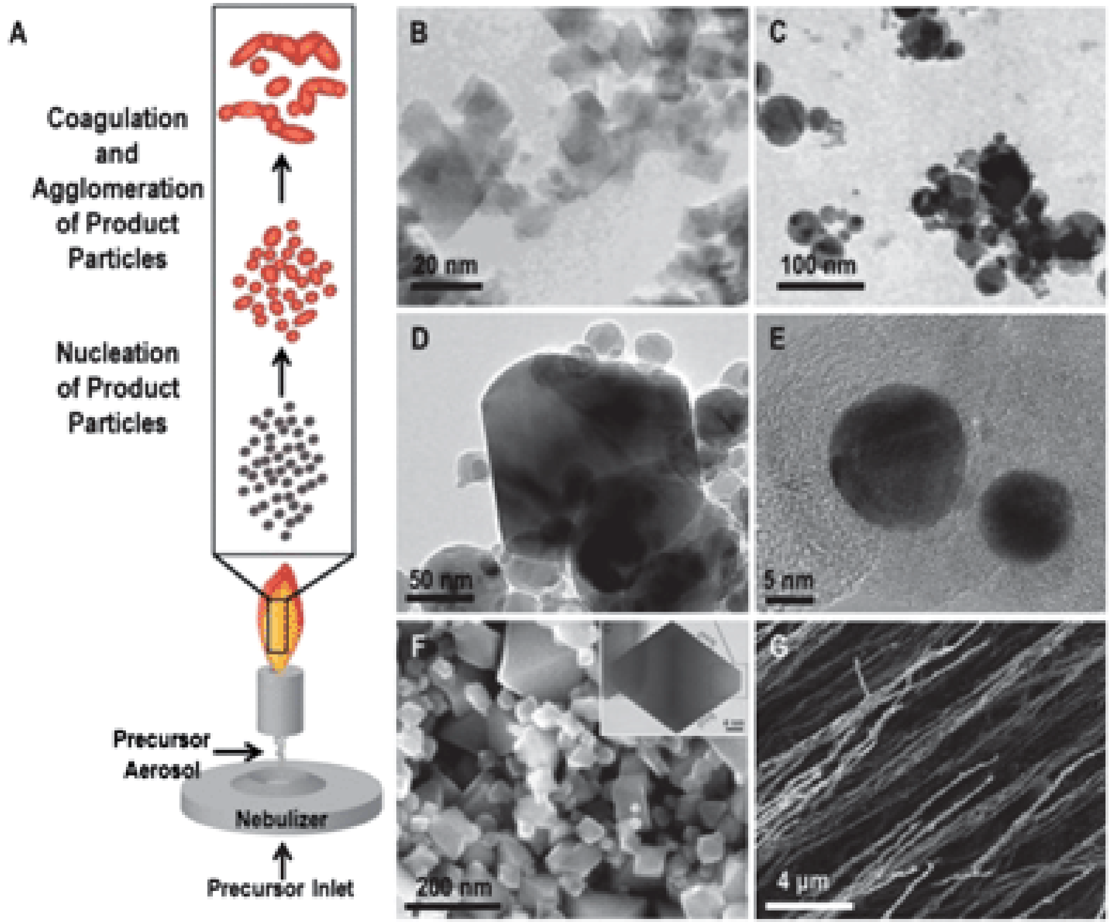
can be controlled (though not independently) by modifying metal precursors, solvents, reducing agents and polymer stabilizers

G. Z. Cao, Nanostructures & Nanomaterials, London: Imperial College Press, 2004.

Bottom-Up Approach

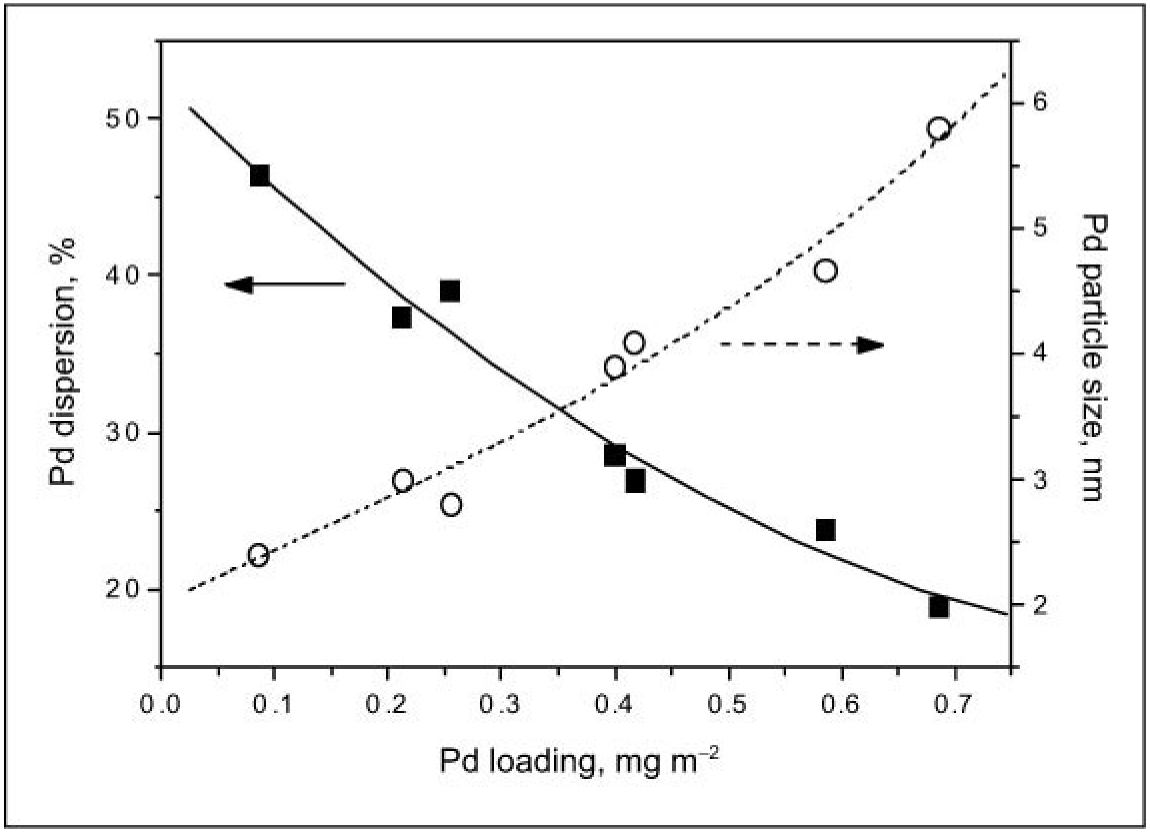
- Strategies for high dispersion
  - thermodynamic equilibrium approach
    - supersaturate
    - nucleate
    - controlled growth
  - kinetic approach
    - limiting the amount of precursors for the growth
    - confining in a limited space
    - diffusion limited growth

Manufacturing Methods:
Bottom-Up Flame Spray Pyrolysis



Aerosol-assisted synthesis and assembly of nanoscale building blocks, NE Motl, J. Mater. Chem. A, 2013,1, 5193-5202

Manufacturing Methods:
Bottom-Up Flame Spray Pyrolysis

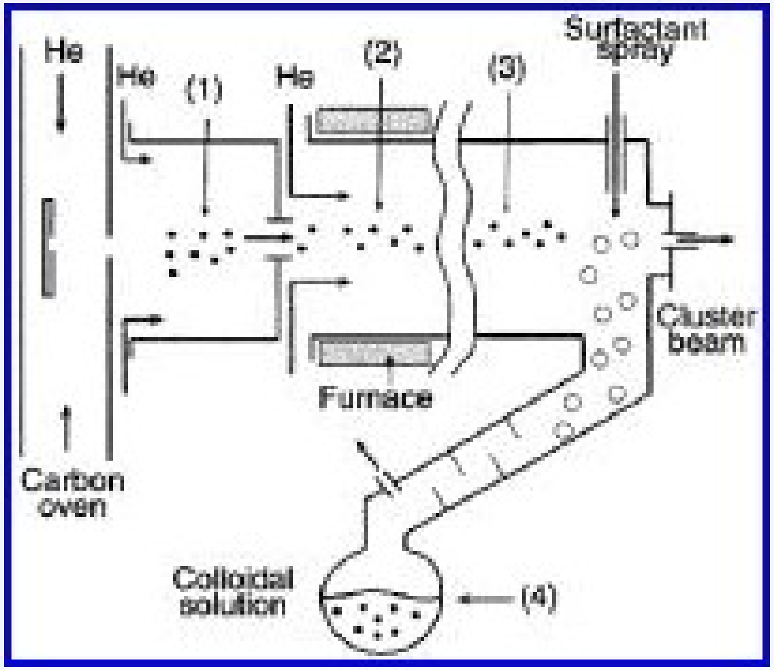


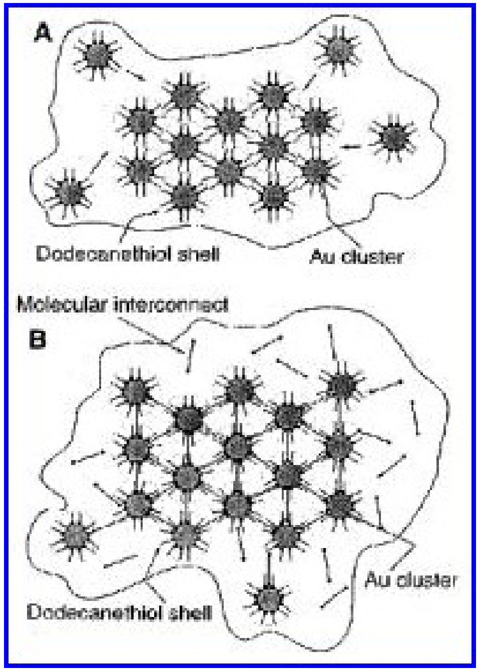
Flame Synthesis of Supported Platinum Group Metals for Catalysis and Sensors

Reto Strobel, ETH-Zurich, Platinum Metals Review, Jan 2009.

Pd dispersion and corresponding Pd particle size of flame-made Pd/Al_2O_3 with different Pd contents and Al_2O_3 surface area.

Surface Functionalization & Self Assembly





- Fundamental problem: The thermodynamically stable state of metals, semiconductors, and polymers is bulk material, not colloidal particles. Stable colloidal dispersions r*equire* an interfacial stabilizer, which is a chemical that reduces the interfacial free energy between the particle and the solvent and makes short range forces between the particles repulsive.

R. P. Andres, Science (1996)

Useful properties of metal nanoparticles and commercial products

Useful Properties:
Photocatalytic “self cleaning” cement

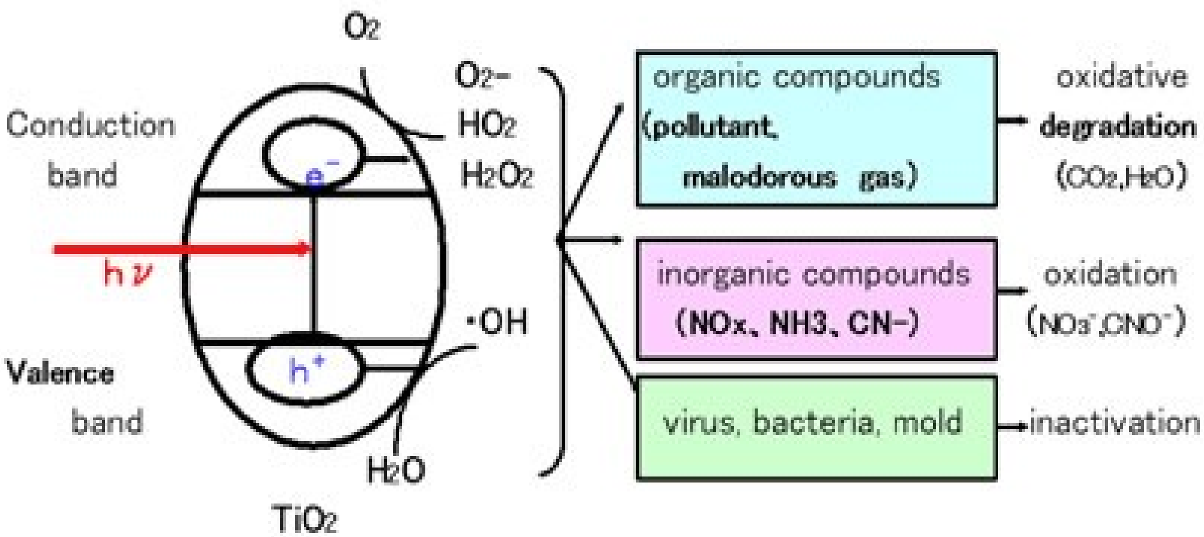
Fig. (5). Photo of concrete partly coated with titania slurry solution (1% of $Ag\text{-}TiO_2$).

Photocatalytic and Self-Cleaning Properties of Ag-Doped TiO2, Open Materials Science Journal, B. Tryba, 2010.

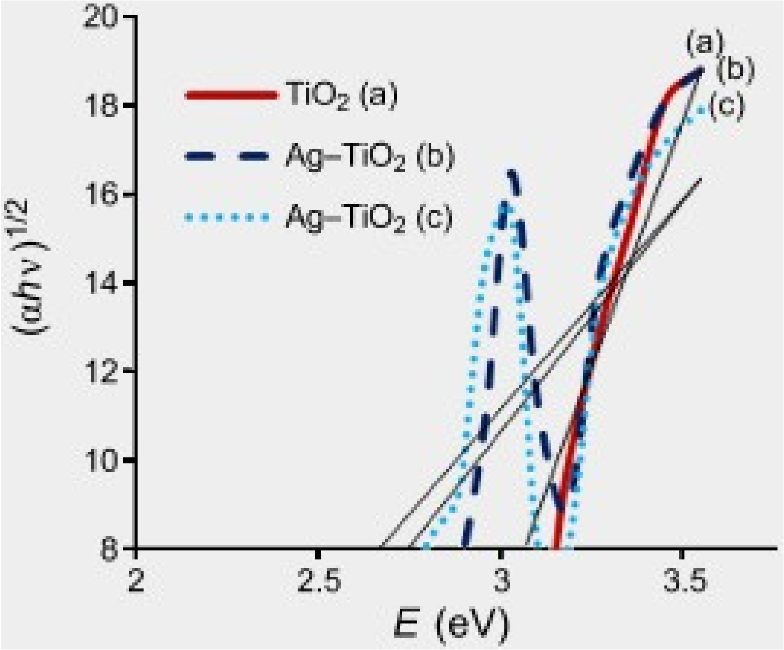
Useful Properties:
Photocatalytic “self cleaning” cement

ISK ISHIHARA SANGYO KAISHA,LTD.

Reaction mechanism of TiO_2 photocatalysis



Useful Properties:
Photocatalytic "self cleaning" cement



Band gap obtained by extrapolating the linear portion of the $(\alpha h\nu)^{1/2}$ versus photon energy (eV) curve of (a) TiO_2 and (b) 3% and (c) 7% Ag-doped TiO_2 nanoparticles.

Silver nanoparticles precipiated on TiO_2 will "plasmon sensitize" TiO_2 photocatalyst …

lowering the band gap and increasing photocataytic oxidative 'self cleaning' efficiency.

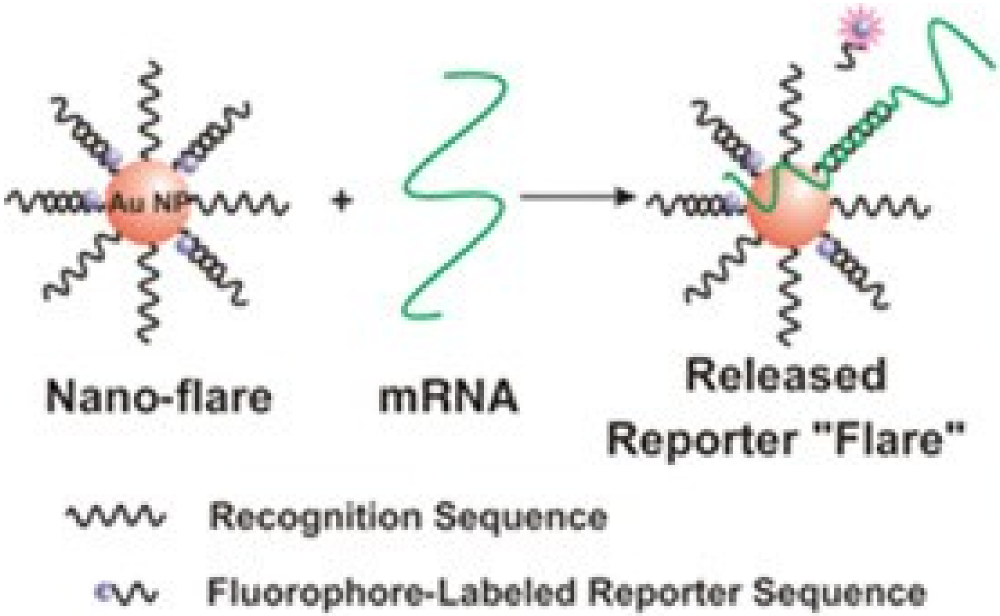
K. Gupta, Beilstein J. Nanotechnol. **2013,**

Useful Properties:

Nanoparticle-based Fluorescent Biodetection

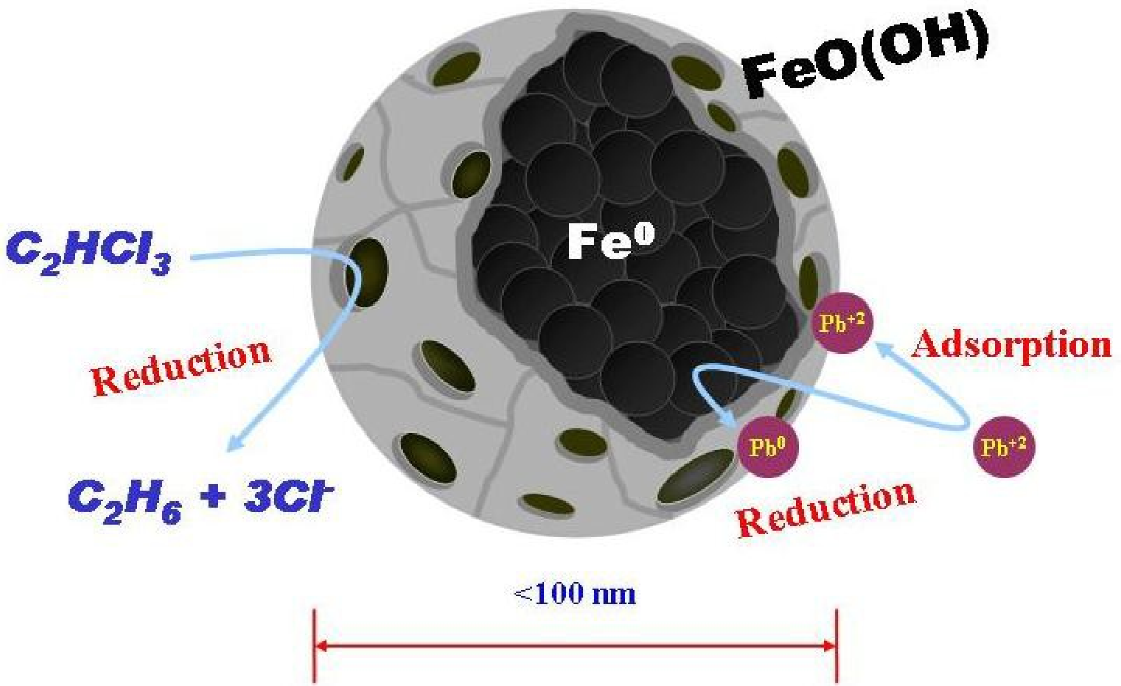
AuraSense™

Millipore SmartFlare™ Detection Probes
Live Cell RNA Detection



Nano-flares: Probes for Transfection and mRNA Detection in Living Cells D.S. Seferos et al., JACS, Dec 2007.

Useful Properties:
Enhanced reactivity – Zero Valent Iron



Zero Valent Iron Nanoparticles are highly reactive and chemically reduce halogenated hydrocarbons and heavy metals. Widely used to remediate contaminated land and ground water.

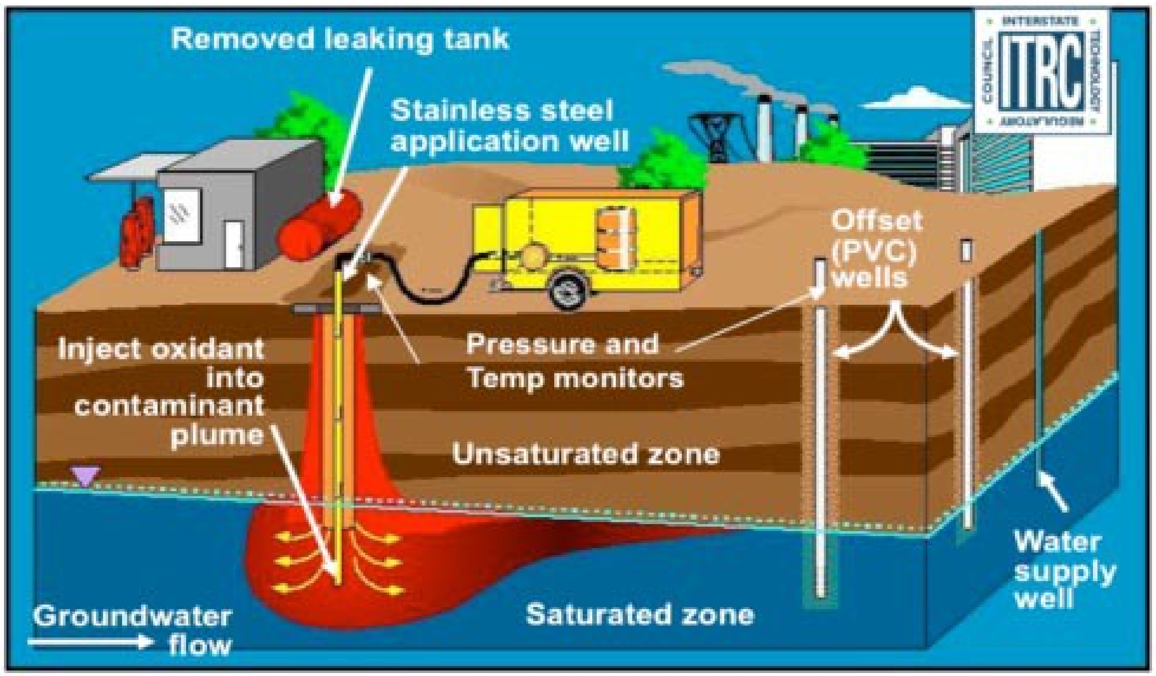
http://www.lawandenvironment.com/uploads/image/zero%20valent%20iron.jpg

Useful Properties:

Enhanced reactivity – Zero Valent Iron

REGENESIS

Advanced Technologies for Contaminated Site Remediation



In-Situ Chemical Oxidation (ISCO)

http://www.regenesis.com/contaminated-site-remediation-products/chemical-oxidation/Regenox/

Useful Properties:

Electrical Conductivity and Capacitance

Leather Touch Screen Gloves

Capacitive touchscreens work by sensing the conductive properties of your skin. Revolutionary nanotechnology integrated into the leather of the gloves mimics the conductive properties of the human skin; this makes the gloves touchscreen compatible. The nanotechnology functions independent from the human skin, this enables us to fully insulate the gloves with a layer of soft 100% wool lining.

Leather is coated with a combination of carbon black, silver nanoparticles and a conductive polymer adhesive.

See for example, *Conductive leather materials and methods for making the same.* US Patent App 8507102 B1

http://www.mujjo.com/blog/tag/leather-gloves-with-nano-technology/

Useful Properties:

Catalysis – Carbon Dioxide to Methanol Conversion

Biofuels LPMEOH™ Liquefaction

$2\ H_2 + CO \rightarrow CH_3OH$

$CO_2 + 3\ H_2 \rightarrow CH_3OH + H_2O$

$CO + H_2O \rightarrow CO2 + H_2$

CO/CO2 to methanol conversion over nanoscale copper catalysts on a zinc oxide support

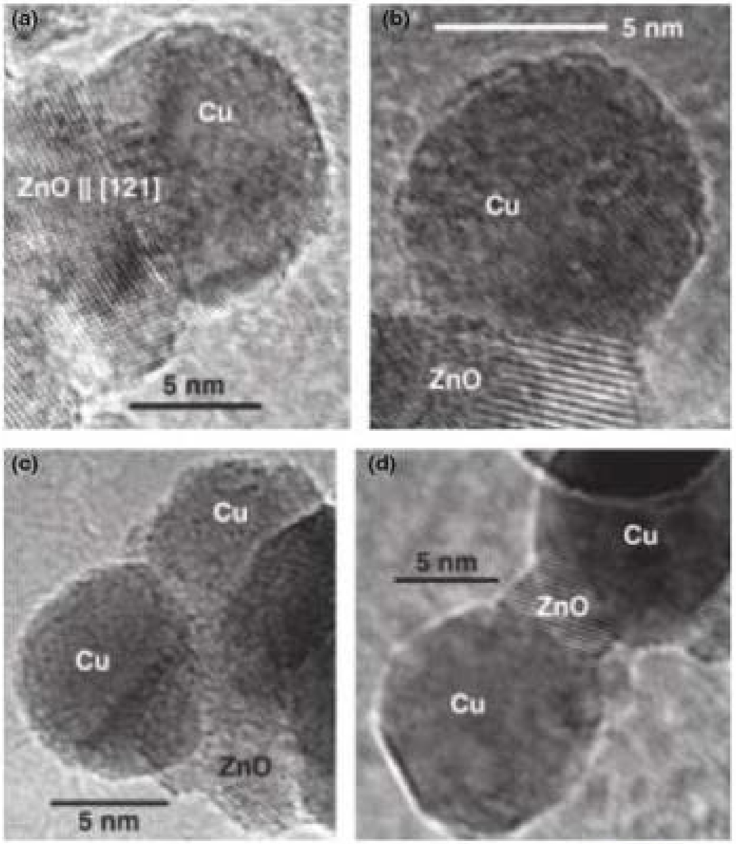


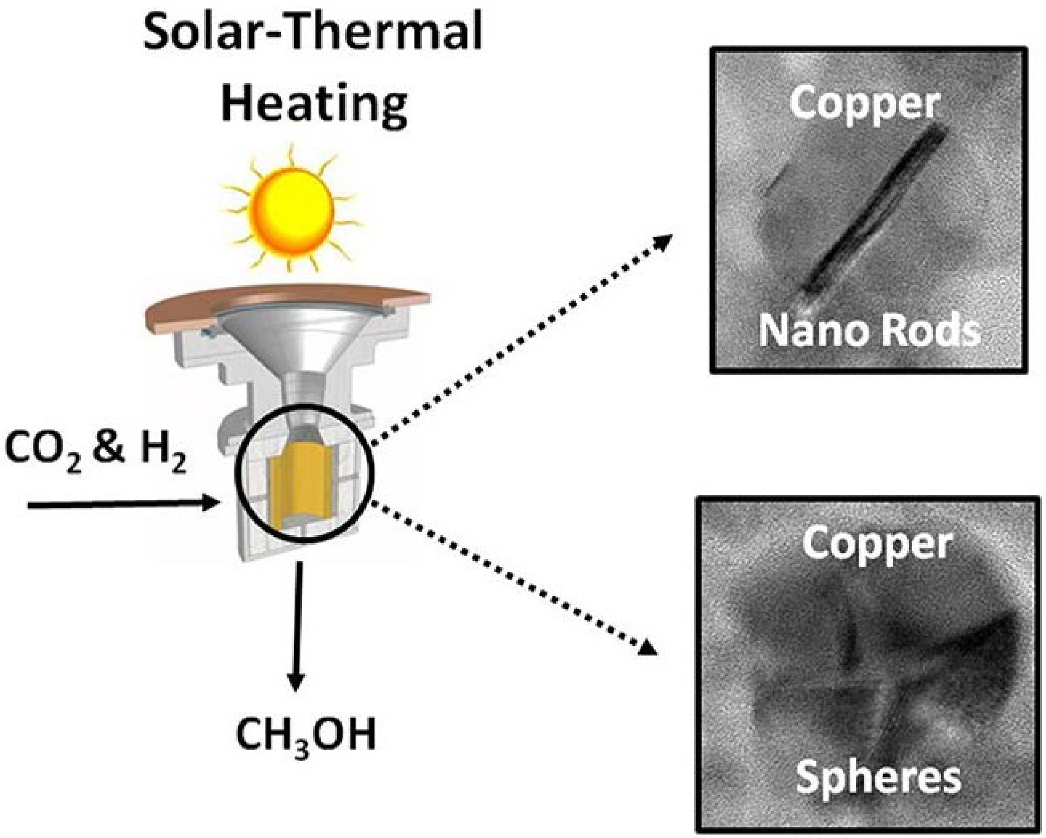
Figure 19.18. HRTEM images of a Cu/ZnO catalyst obtained from a copper zinc hydroxycarbonate precursor aged for 120 min. (Reprinted with permission from Ref. 70, Copyright 2005, Wiley-VCH.)

Nanocatalysis: Synthesis and Applications , ed. Vivek Polshettiwar, Wiley 2013.

Useful Properties:

Catalysis – Carbon Dioxide to Methanol Converstion

Schematic diagram showing how nanostructured copper catalysts can be incorporated into a carbon friendly CO2 to methanol reactor using solar energy to heat the catalyst bed. Electron microscopy (right) shows that the reactive copper catalysts used for this work consist of a variety of particle shapes, such as rods and spheres, dispersed on a zinc oxide support.



http://www.netl.doe.gov/research/coal/energy-systems/gasification/gasifipedia/methanol

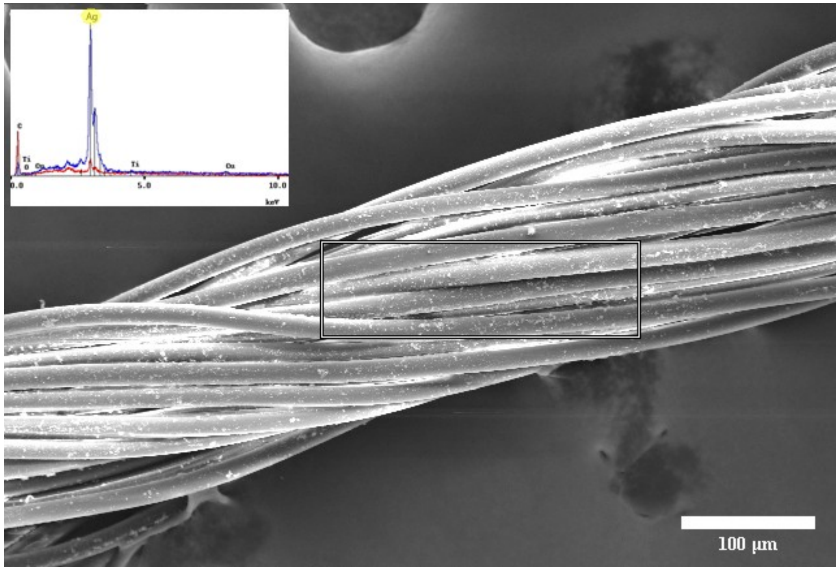
Useful Properties:

Antimicrobial Silver for Textiles Applications

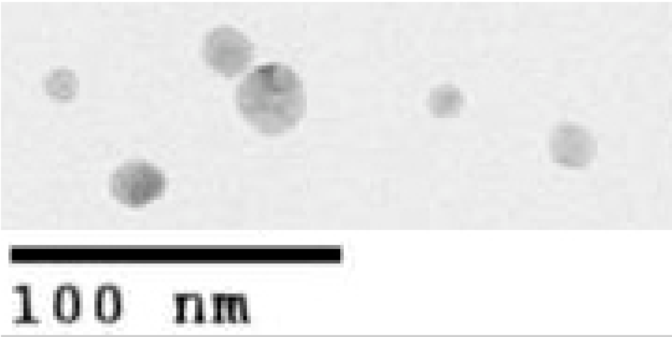
NanoHorizons

Visible results through invisible science

- Founded by Prof. Fonash in 2002
- Manufacturer of nanoscale silver antimicrobial additives and fibers
- Surface functionalized particles encapsulated in proprietary polymer stabilizers
- Available under the SmartSilver brand



SMART SILVER

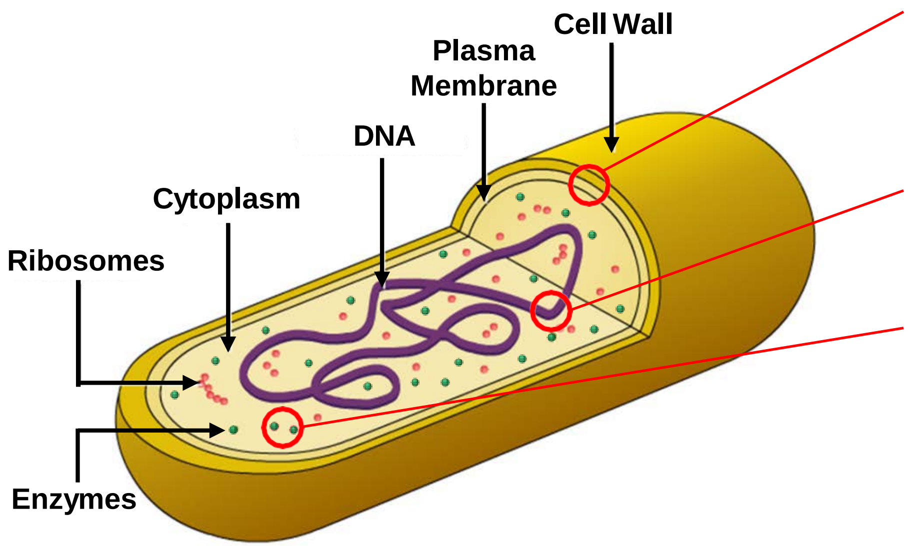


Useful Properties:

Antimicrobial Silver for Textiles Applications

- Oxygen in air & water reacts with metallic silver to produce silver ions (Ag^+).
  - Silver Ions = active antimicrobial agent for all silver based antimicrobial additives.
- Silver ions bind to components within bacteria that contain negatively charged groups.
  - Including proteins and enzymes necessary for a bacteria to live, grow, and replicate.
- Silver ions binds to multiple bacterial components which significantly interferes with the normal functioning of the bacteria; bacteria die

Bacterial Cell



Major Modes of Action for Silver Ions on Bacterial:

(1) Cellular Membrane [1, 2, 3]

- Causes structural and functional changes in the bacterial membranes leading to their inability to properly function.

(2) Replication [1, 2]

- Binds to bacterial DNA thus prevent them from multiplying.

(3) Metabolic Pathways [1, 2]

- Binds to and inactivates metabolic enzymes required by bacteria to live and grow.

(1) Jung, Woo Kyung, et al. "Antibacterial Activity and Mechanism of Action of the Silver Ion in Staphylococcus aureus and Escherichia coli." *Applied Environ Microbiology* (2008): 2171-2178.

(2) Rai, M. K., et al. "Silver nanoparticles: the powerful nanoweapon against multidrug-resistant bacteria." *Journal of Applied Micorbiology* (2012).

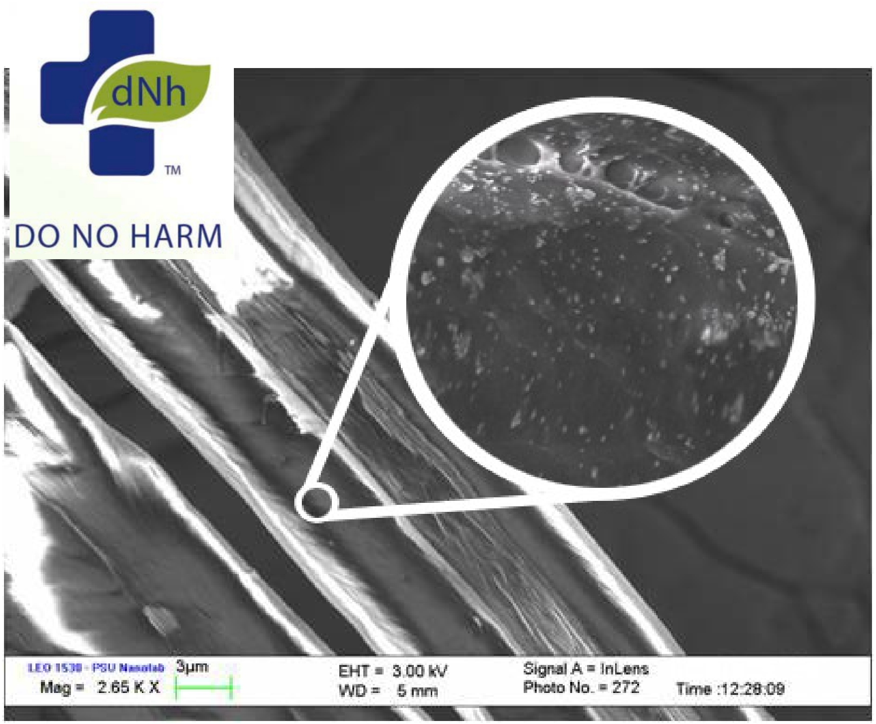
(3) Feng, Q. L., et al. "A mechanistic study of the antibacterial effects of silver ions on Escherichia coli and Staphylococcus aureus." *Journal of Biomedical Materials Research* (2000): 662-668.

Useful Properties:

Antimicrobial Silver for Textiles Applications

NanoHorizons' SmartSilver® in Do No Harm™ Medical Scrubs

SmartSilver® particles at 40,000 Magnification Covalently Bonded Within the Cotton Fiber of Medical Scrubs



Useful Properties:

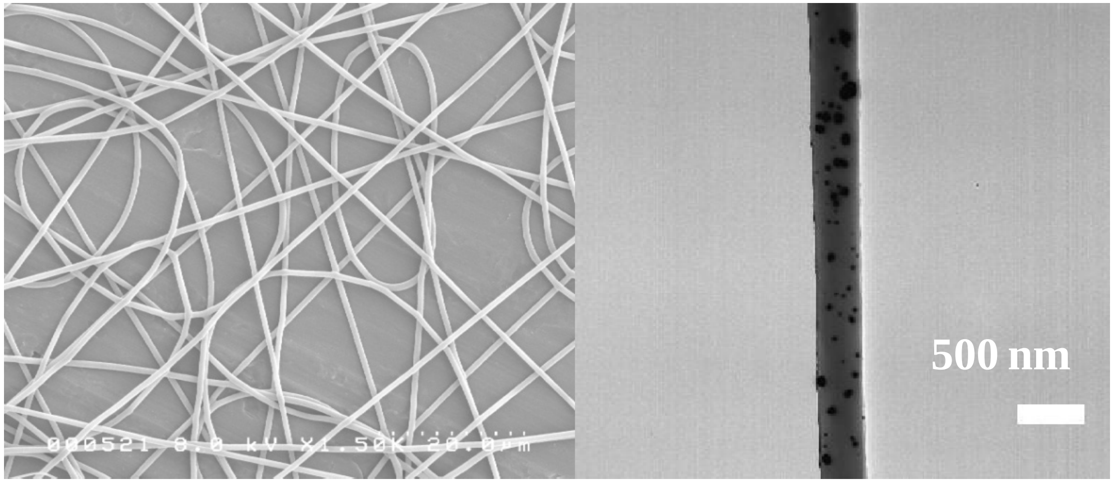
Antimicrobial Silver for Textiles Applications

- SmartSilver® additives are delivered as a ready-to-use masterbatch, textile finish or dispersible additive

- SmartSilver® particles are nanoscale, so they can be integrated into fine-structured materials such as fibers and foams without impacting processing or mechanical properties

SmartSilver® nanoparticles are small enough to be electrospun into 300 nm fibers without negatively impacting physical properties

Courtesy: Kyoto Institute of Technology and NanoHorizons



Useful Properties:

Nanoscale Silver for Biofilm Resistant Polymers

- Almost all current *in vitro* tests used for evaluating antimicrobial polymers focus exclusively on planktonic (“floating”) cells.
- Antimicrobial medical devices are increasing being evaluated for their ability to resist the growth of *biofilms*
- New *biofilm resistance* test methods developed for antimicrobial catheters allow quantification of both planktonic bacteria and biofilm formation

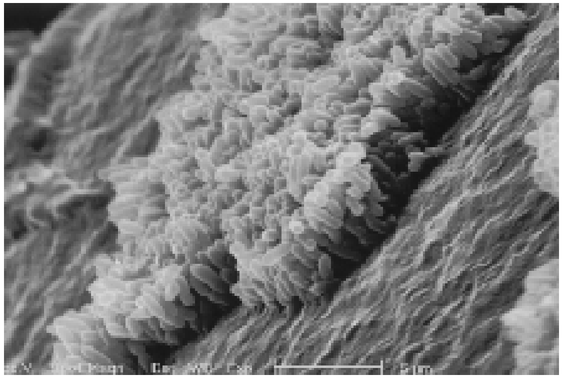
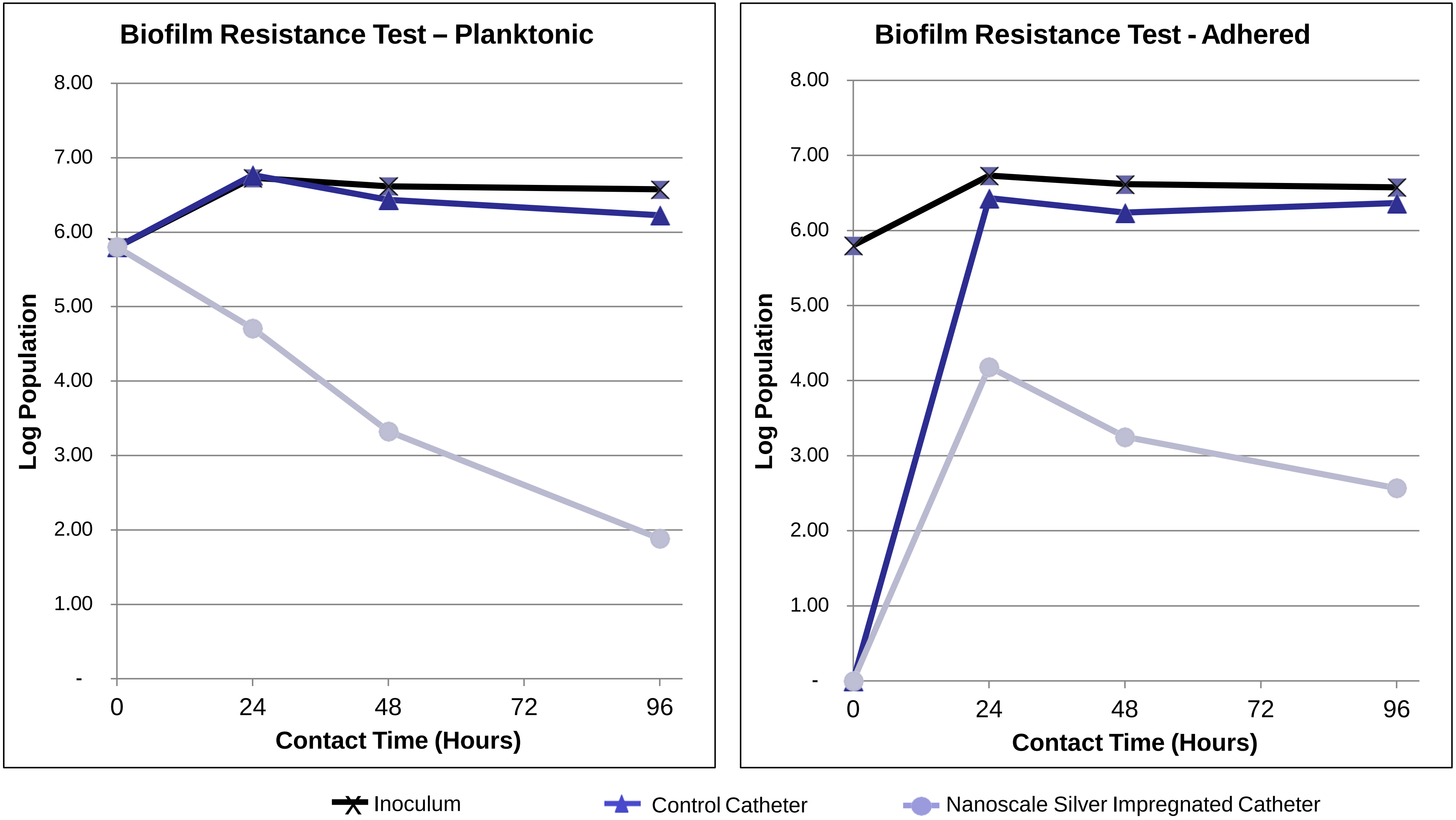


Figure 1. A biofilm on a urinary catheter (Adapted from Stickler and Morgan, J Med Microbiol 55 (2006), 489-494)

Useful Properties:

Nanoscale Silver for Biofilm Resistant Polymers

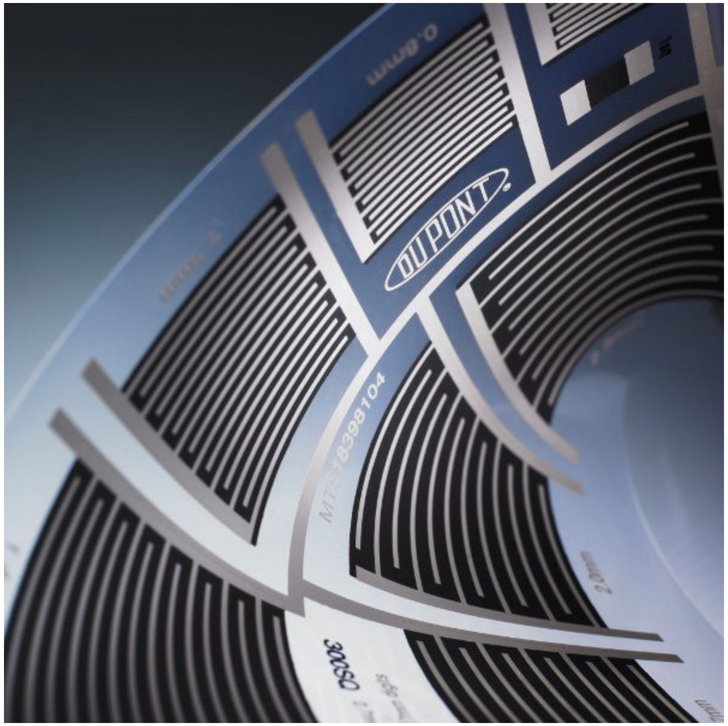


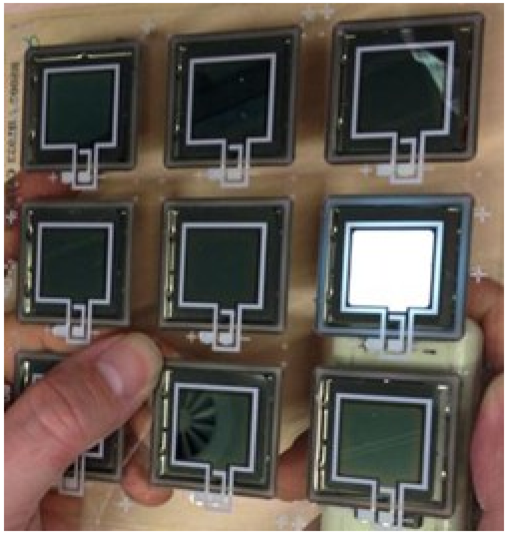
Useful Properties:

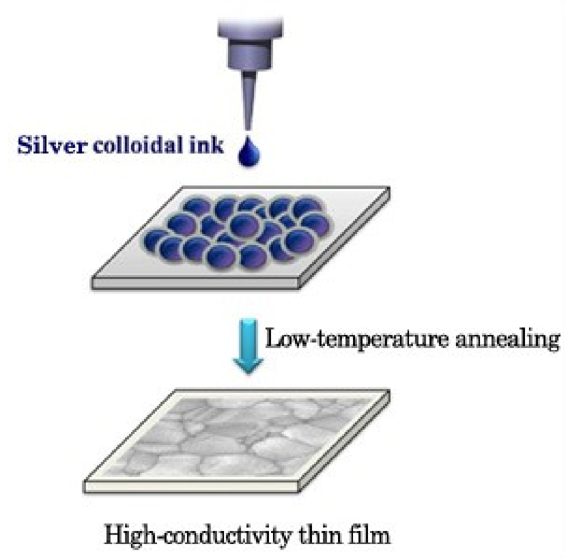
Conductive Inks for OLEDs and Micro-nanoelectronics

“Dupont nano-silver conductive materials for OLED lighting”
March 29, 2014.

Dupont Microcircuit materials introduces a new nano silver conductor ink developments for OLED lighting. Combines high conductivity, and excellent adhesion, low print thickness and smooth sintered surface.





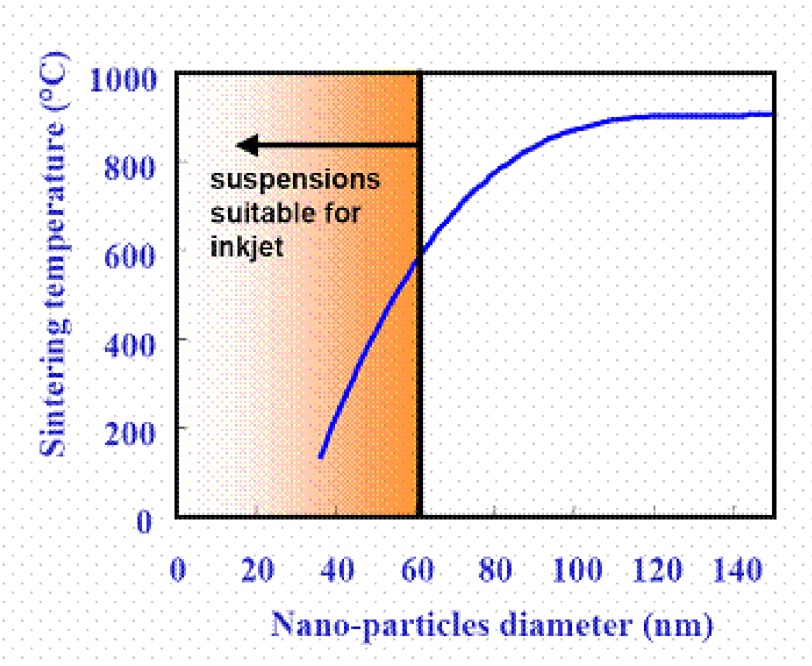


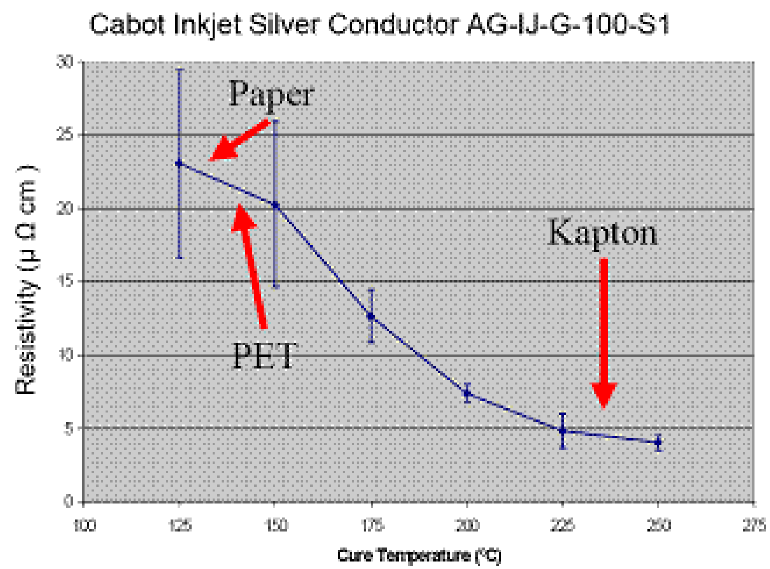
T. Dong, Phys. Chem. Chem. Phys. **11**, 6269 (2009)

http://www2.dupont.com/MCM/en_US/index.html

Useful Properties:

Conductive Inks for OLEDs and Micro-nanoelectronics





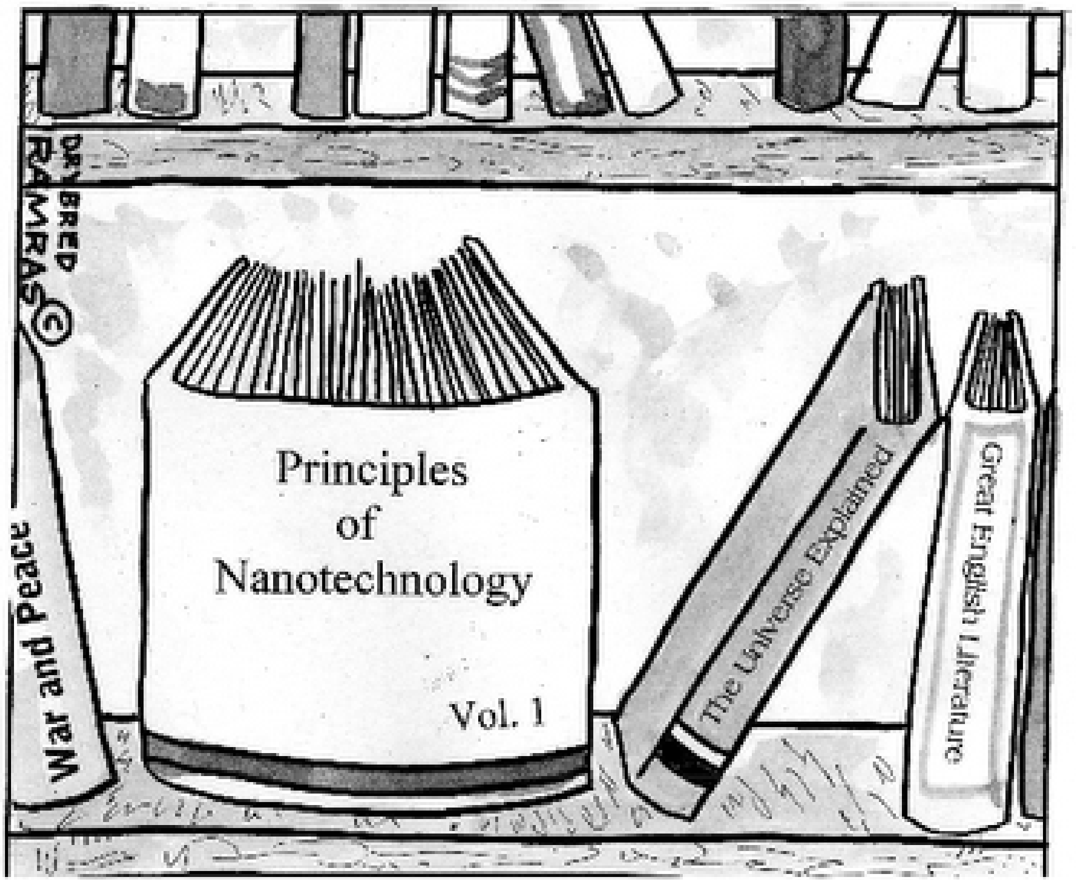
Reduced melting temperature of nanoparticles. (Right) Resistivity as a function of curing temperature from Cabot-PEDS.

http://mems.soe.ucsc.edu/printed_materials.html

Lecture Goals

- Introduction to metal nanoparticles
- Gain historical perspective
- Familiarity with definitions (complex)
- Common methods of manufacture
- Useful properties of metal nanoparticles
- Real world commercial examples

Thank You!



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