Lola Montez ca. 1850

21st-Century Tools for 19th-Century Nanotechnology: Understanding and Conserving the Daguerreotype

Nicholas P. Bigelow, University of Rochester

Ralph Wiegandt,
George Eastman House International Museum of Photography & Film

Brian McIntyre, University of Rochester

Emily Thompson, Clemson University

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Directorate for Mathematical & Physical Sciences
Division of Chemistry
Division of Materials Research

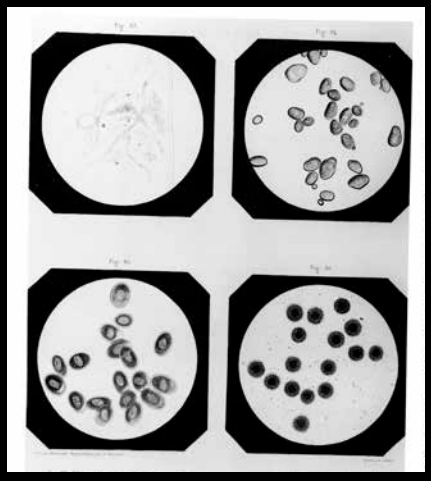
The Daguerreotype

Louis Jacques Mande Daguerre
Jean Baptiste Sabatier-Blot
1844, daguerreotype GEH collections

Daguerreotype

Unidentified Young Girl: Southworth & Hawes: ca 1850
1/6 plate

Unidentified Young Girl: Southworth & Hawes: ca 1850
whole plate



Daguerreotypes are a very precious record of our history and are intrinsically artistic and cultural objects

Plate 2: two areas of interest imaged at higher magnification.

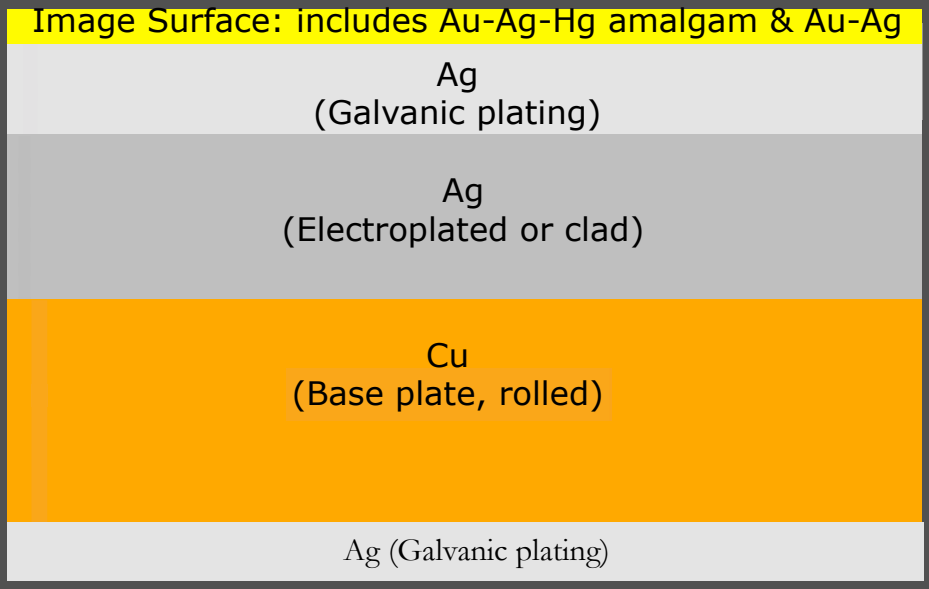
The clock tower imaged at 15x optical magnification. Based on this micrograph and historic information, the light fell on this plate at 1:55 PM on September 24, 1848.


STEAMBOAT
PAINTING
BOILER YARD
QUEEN CITY
SHEET IRON
COPPER SHOP

Daguerreotype Process

- Silver plate over copper substrate: mechanically clad, or electroplated with silver
- Polished to a mirror surface
- Made light sensitive by exposure to iodine and possibly bromine vapor
- Sensitized plate put into camera
- Exposure time variable; dependent on method of sensitization; UV sensitive. Under 10 seconds –latent image of reduced silver halide prints out
- Latent image is "developed" by heated mercury fumes which combine with the reduced silver, forming micron sized light scattering particles
- Plate fixed with sodium thiosulfate
- Fixed image was immediately processed with a gold chloride-sodium thiosulfate solution

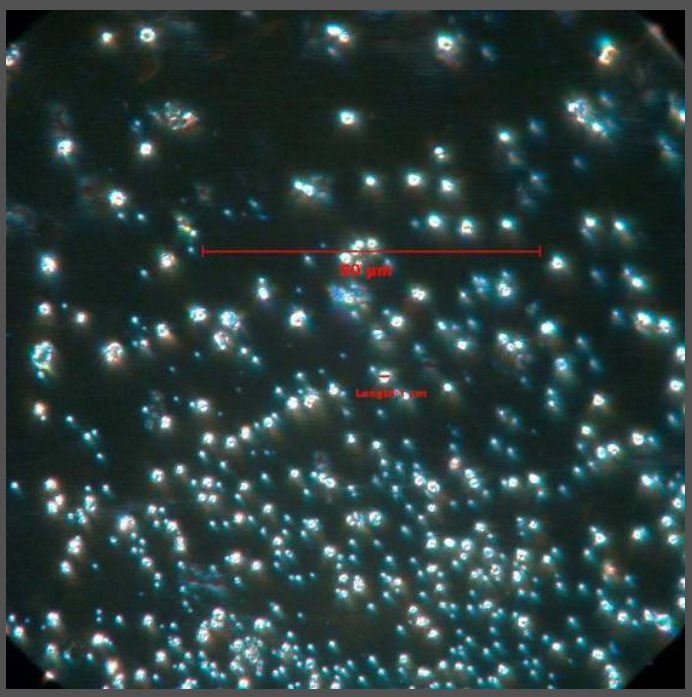
The basic structure of a daguerreotype



Where is the "image"

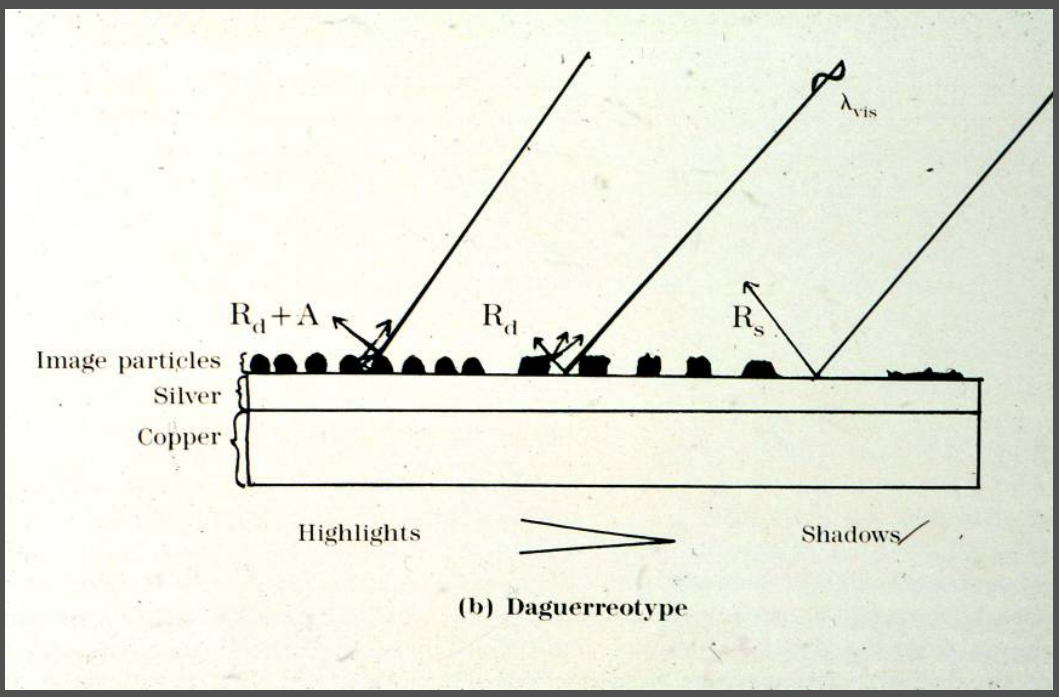
Daguerreotype magnification comparison: 50X

Enter powerful tools of nanoscience
Microscopy, FIB, EDX



Daguerreotype magnification comparison: 1500X

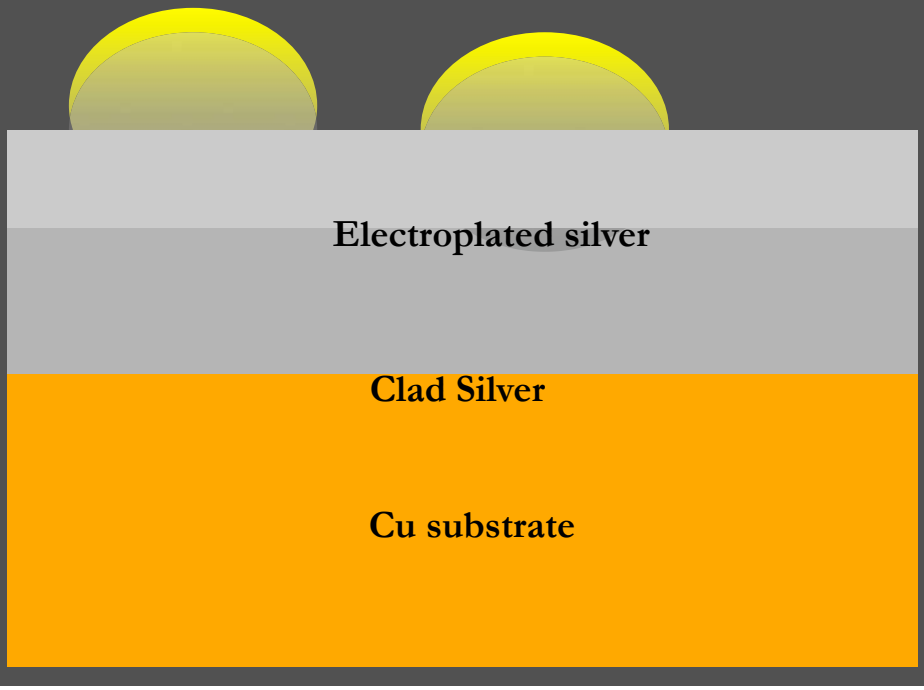
The Mirror with a Memory



(b) Daguerreotype

Image particles are "nano" structures:

Serendipitously discovered nano-science



Daguerreotypes are delicate objects

Factors in the condition of the daguerreotype

- Original processing chemistry
- Possibility of coatings/coating residues
- Previous cleaning
- Environmental effects
  - Macroclimate in storage
  - Microclimate of case materials
  - Light exposure
  - What else? What is the object really like chemically, structurally, mechanically????

Addison Gallery of American Art, Andover, MA c. 2005

Dramatic condition change noted during exhibition

Before Exhibition (March 2005)

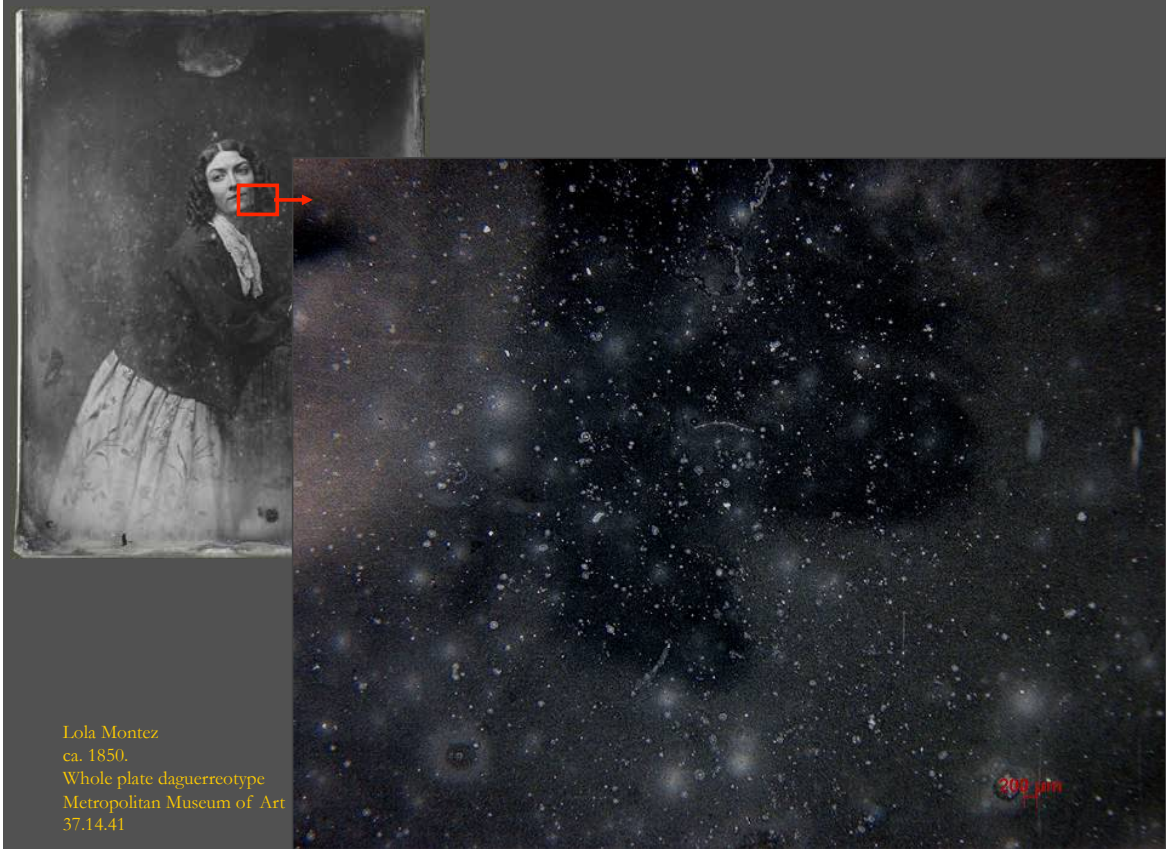
After ~ 1 Month on Display (July 2005)

Lola Montez

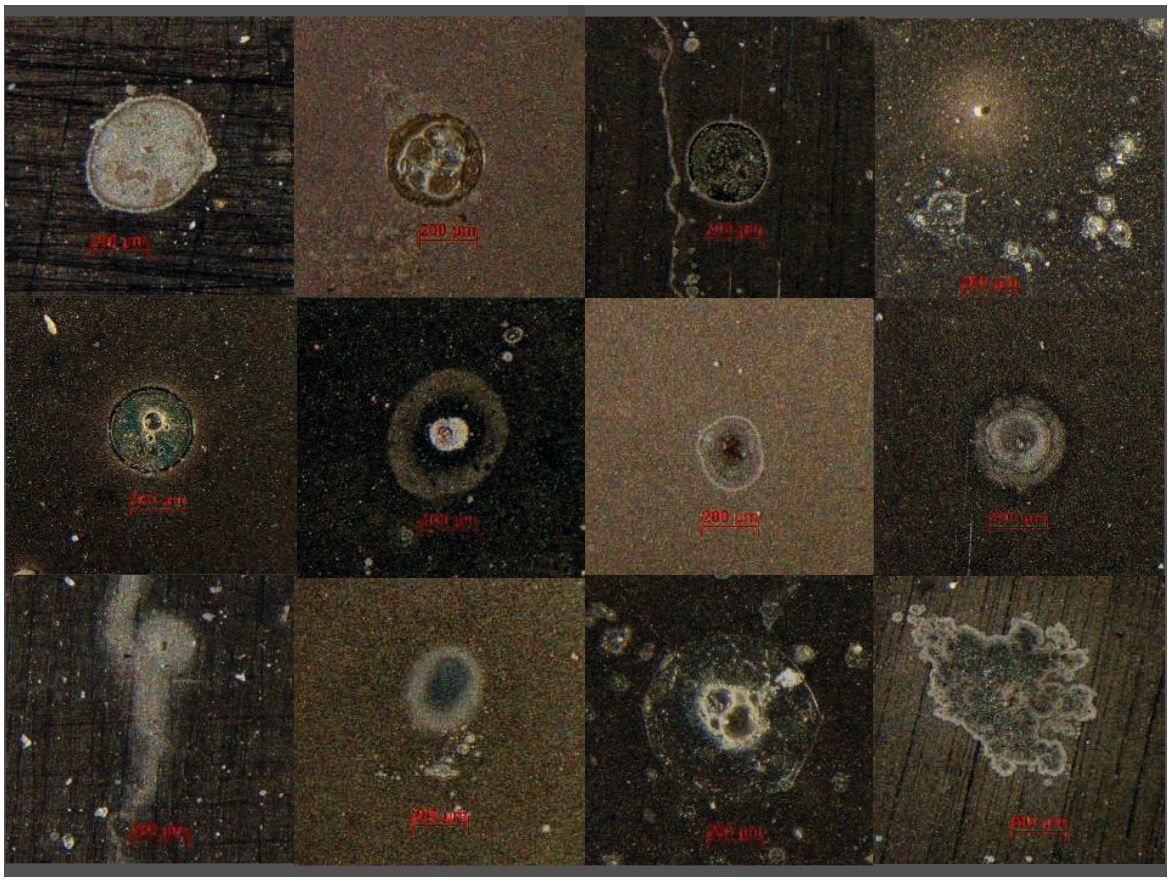
Late 1930's

Lola Montez, ca. 1850. Whole plate daguerreotype. The Metropolitan Museum of Art. 37.14.41

c. 1998



Lola Montez
ca. 1850.
Whole plate daguerreotype
Metropolitan Museum of Art
37.14.41



There are many processes at work:

We need to understand the many degradation modalities and fundamentals

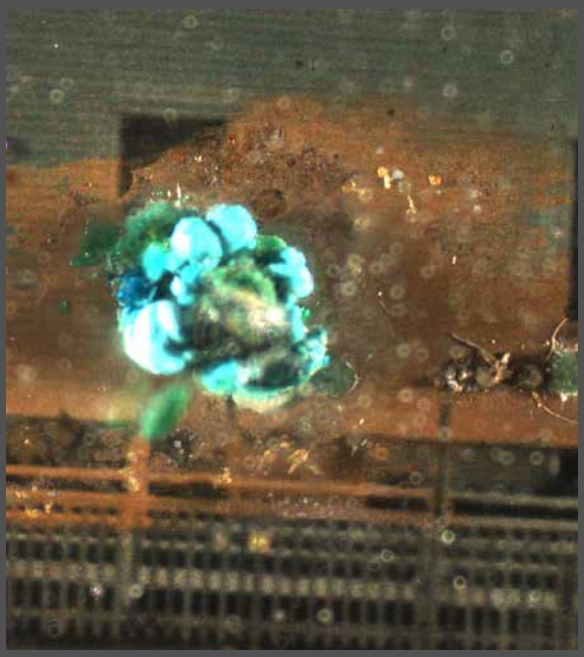
How does the image formation process actually work at a nano-scale?

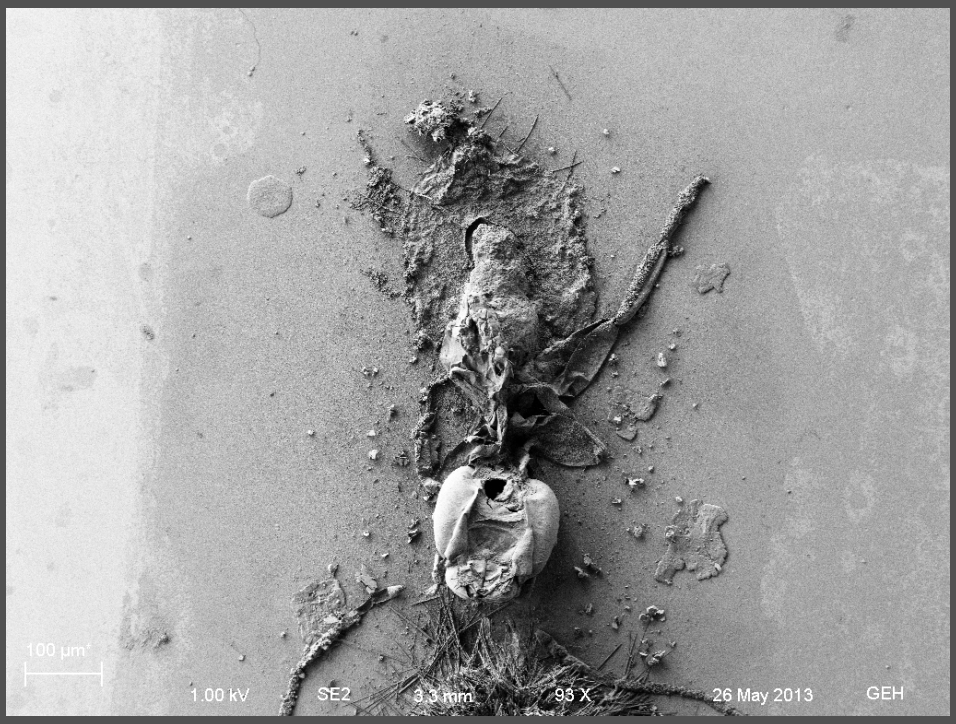
Do we really understand the daguerreotype?

Since “first light” the daguerreotype carries with it a history not only of its creation, but of its “life”

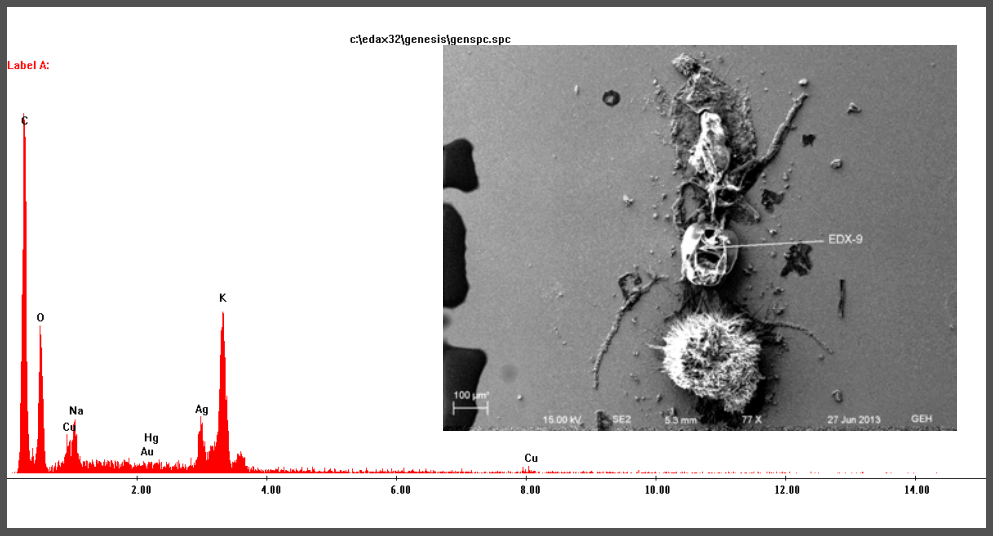
1/6th Plate format: in half-case, missing lid, appears to have original paper binding intact, never opened

Walter's Bug: It *was* alive



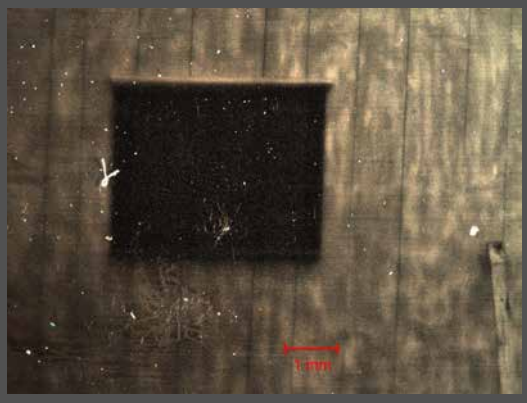


Energy Dispersive X-Ray Analysis

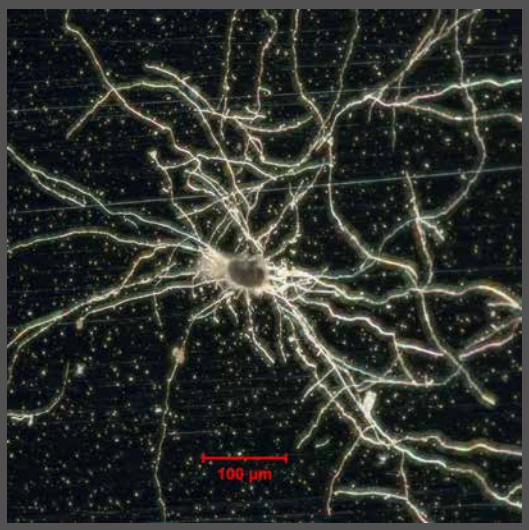


Strong carbon signal, copper, sodium, and potassium, with silver

The plate is populated with many biological fiber-like structures in addition to the insects.

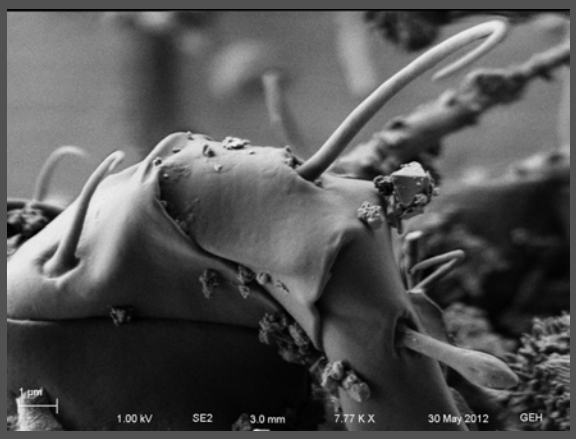


30 X magnification



200 X magnification; dark-field
Fibers are engorged with NPs

A remarkable discovery:
The daguerreotype surface
engages readily with life forms *at the cellular level*

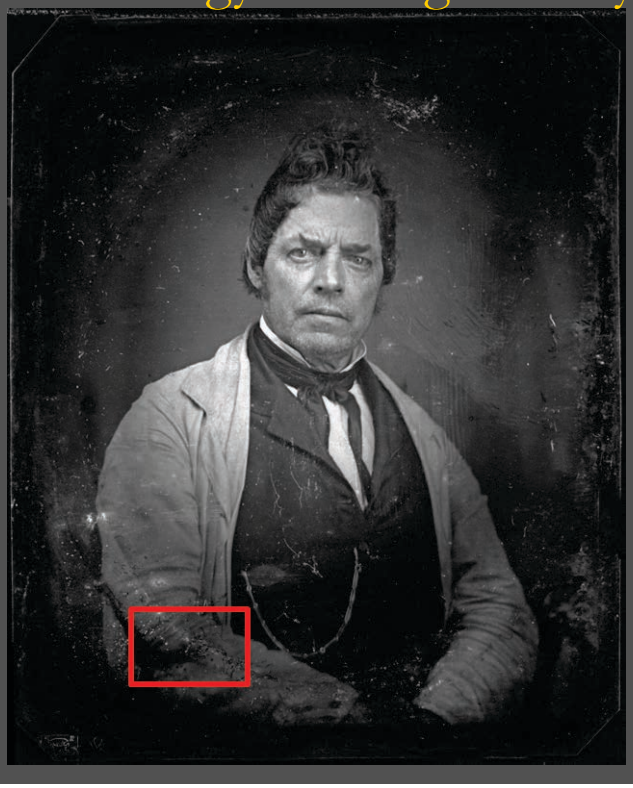


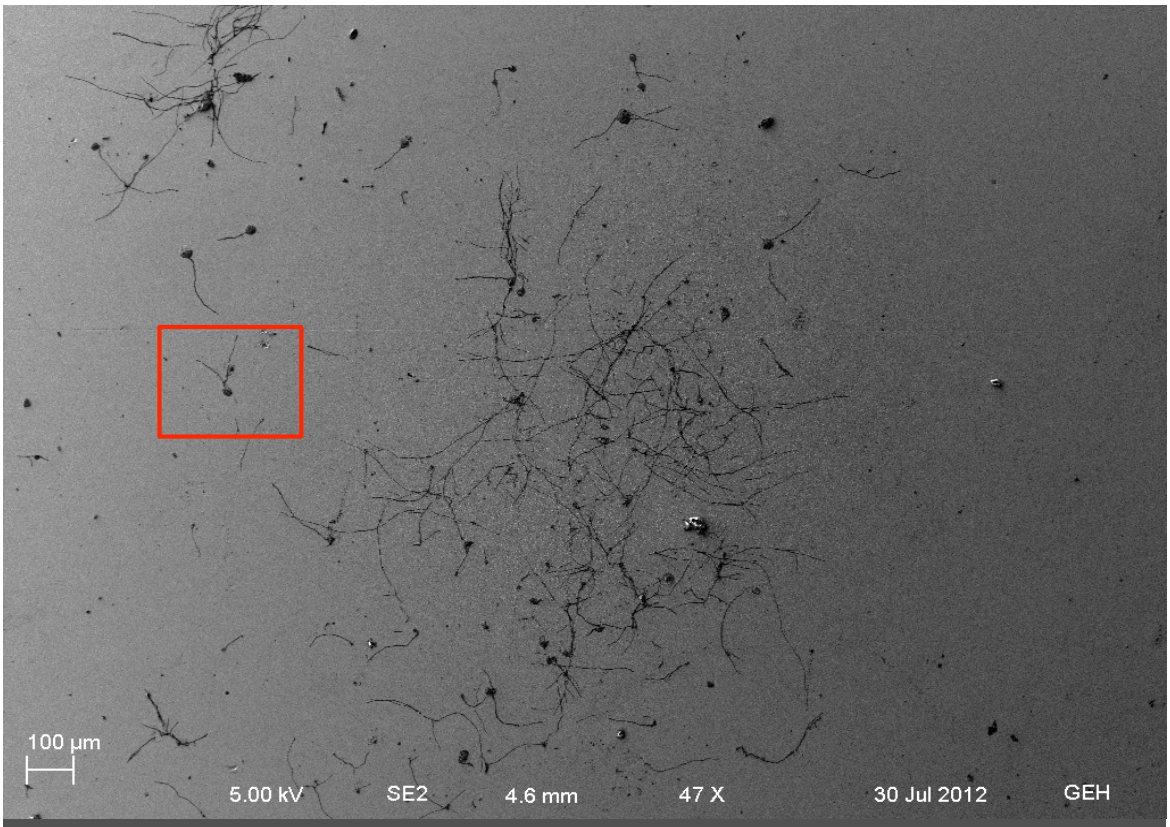
- Hosts and engages with living organisms and the chemistry of life:
  - Fungi
  - Bacteria
  - Plants
  - Enzymes
  - Proteins
  - Nucleic acids
  - Cytoplasmic fluids

The observation of biological activity on the daguerreotype surface might seem surprising

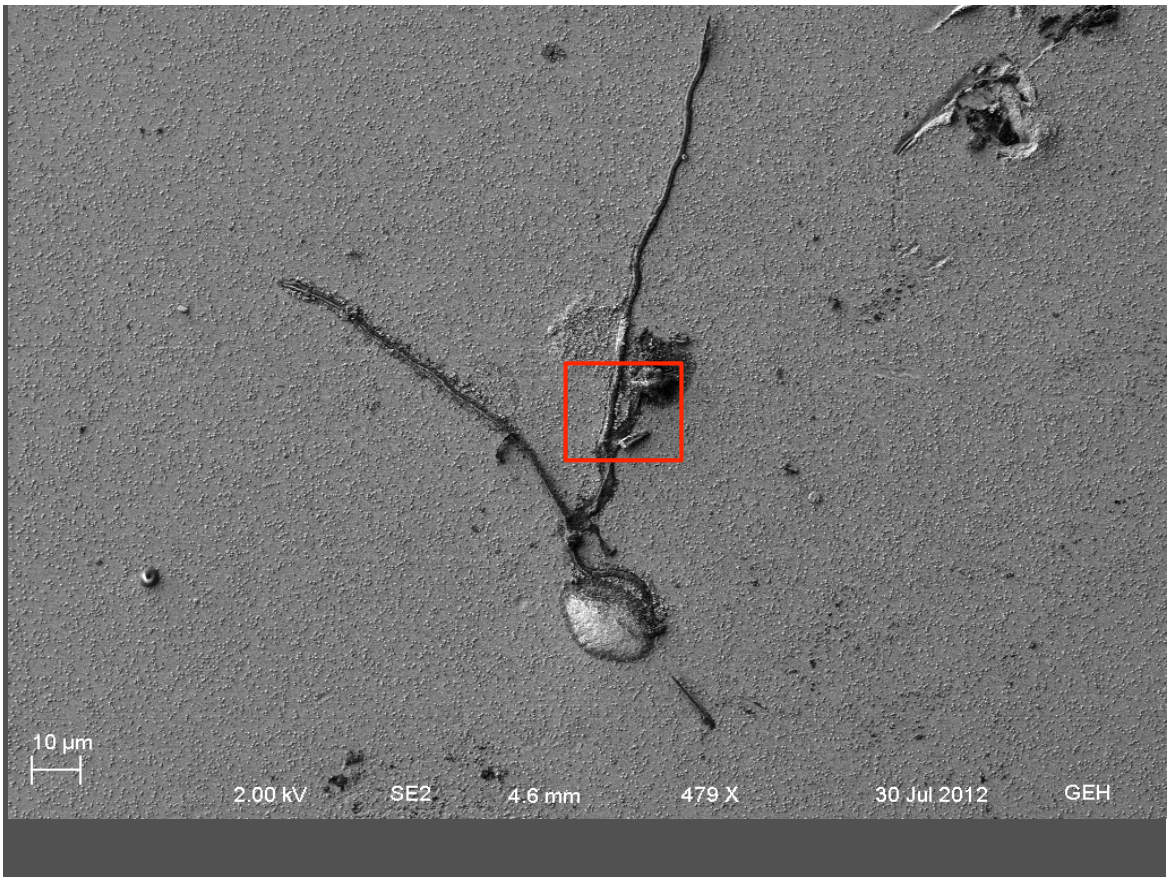
The observation of biological activity on the daguerreotype surface might seem surprising

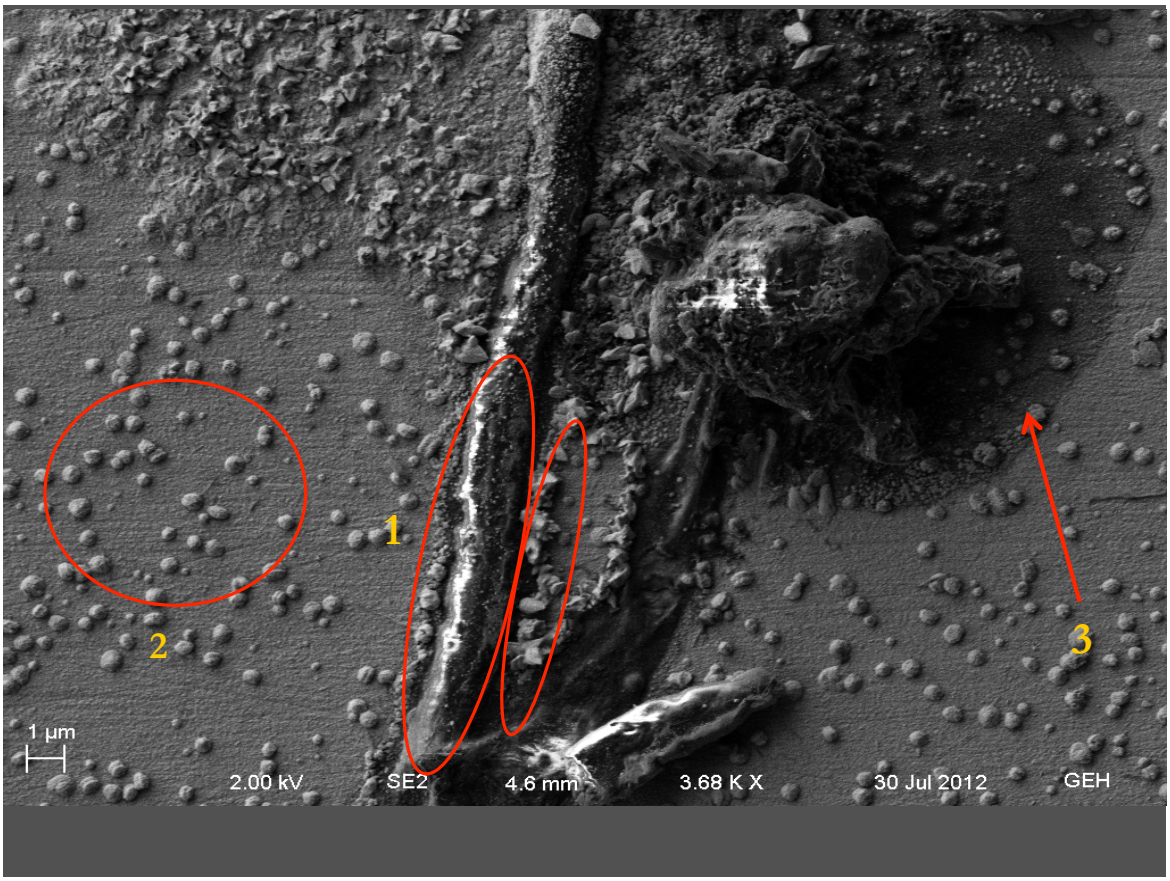
The biology of a daguerreotype

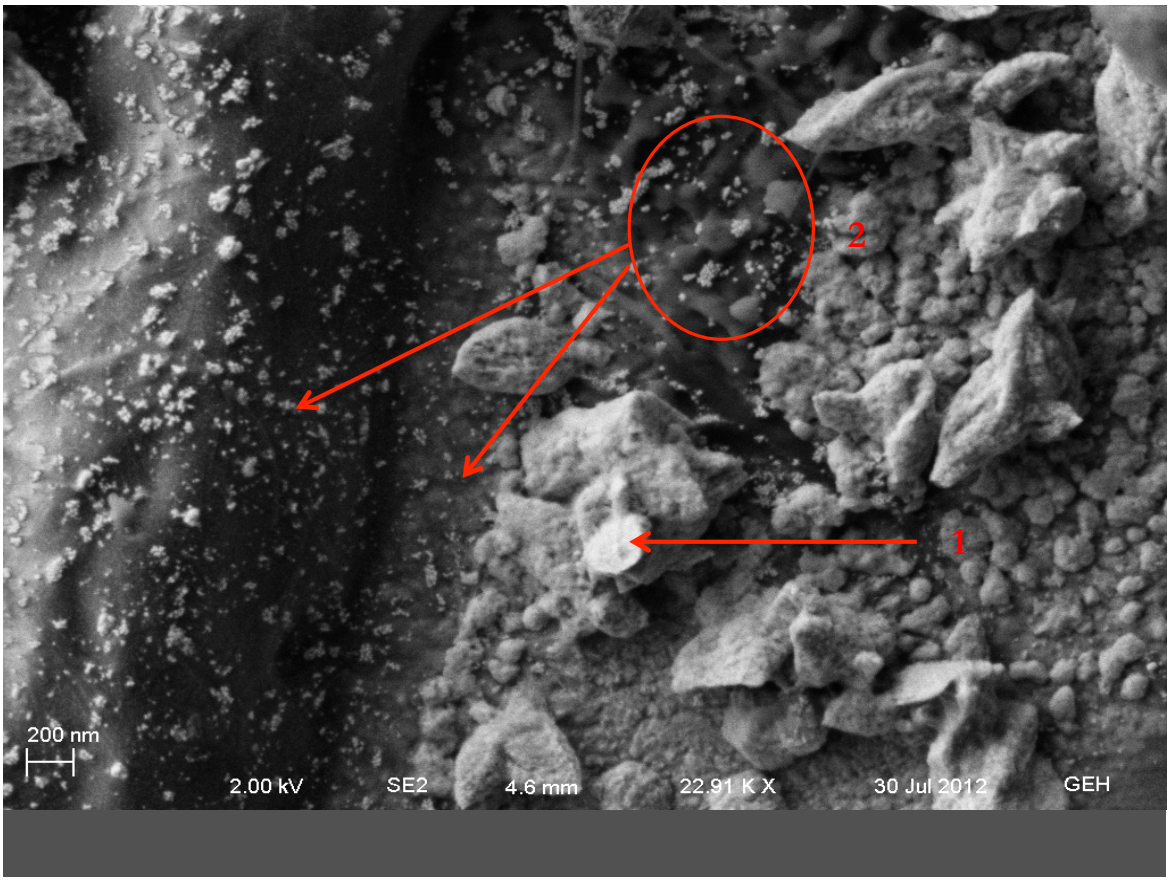


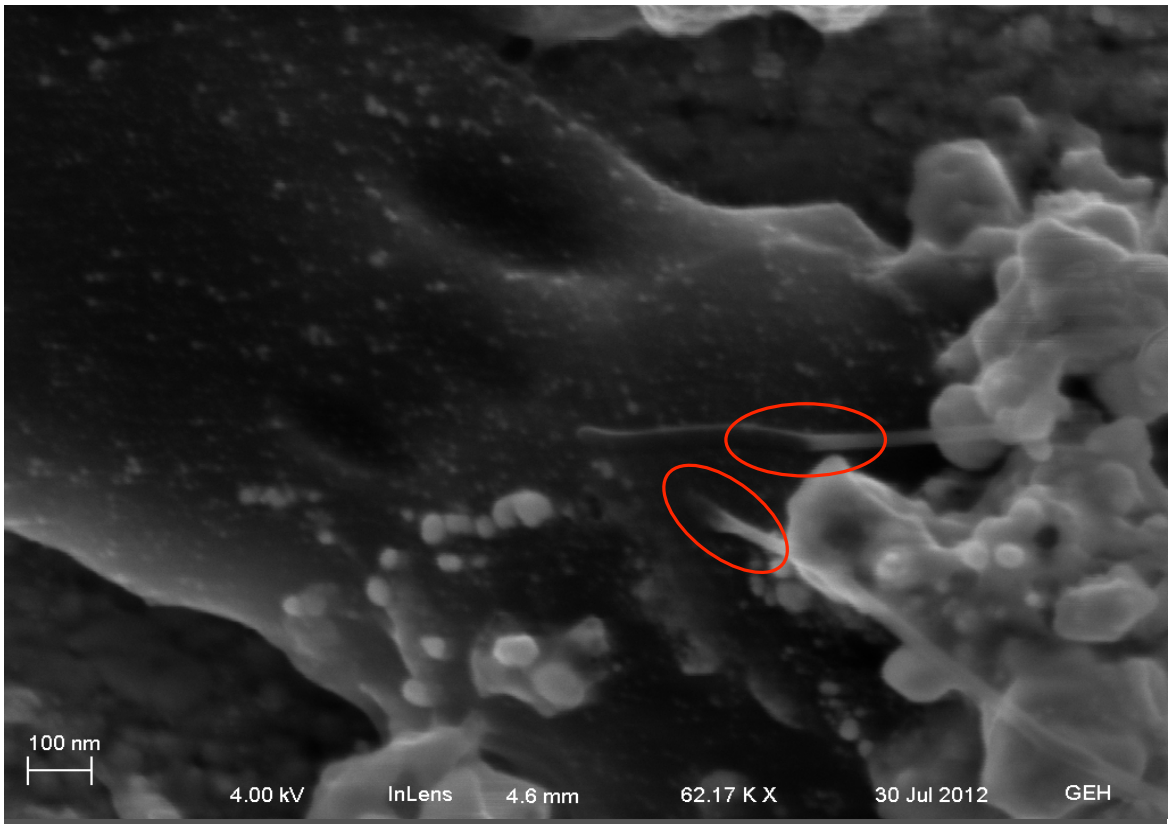


In a Scanning Electron Micrograph (SEM) non-conductive items are dark

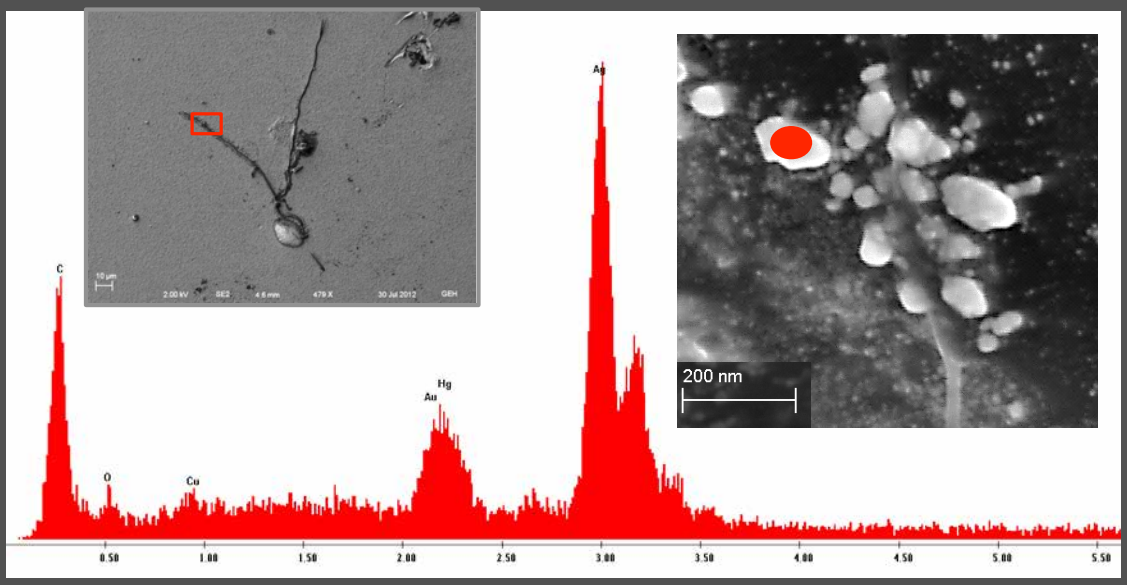



1
2
3
1 µm
2.00 kV
SE2
4.6 mm
3.68 K X
30 Jul 2012
GEH

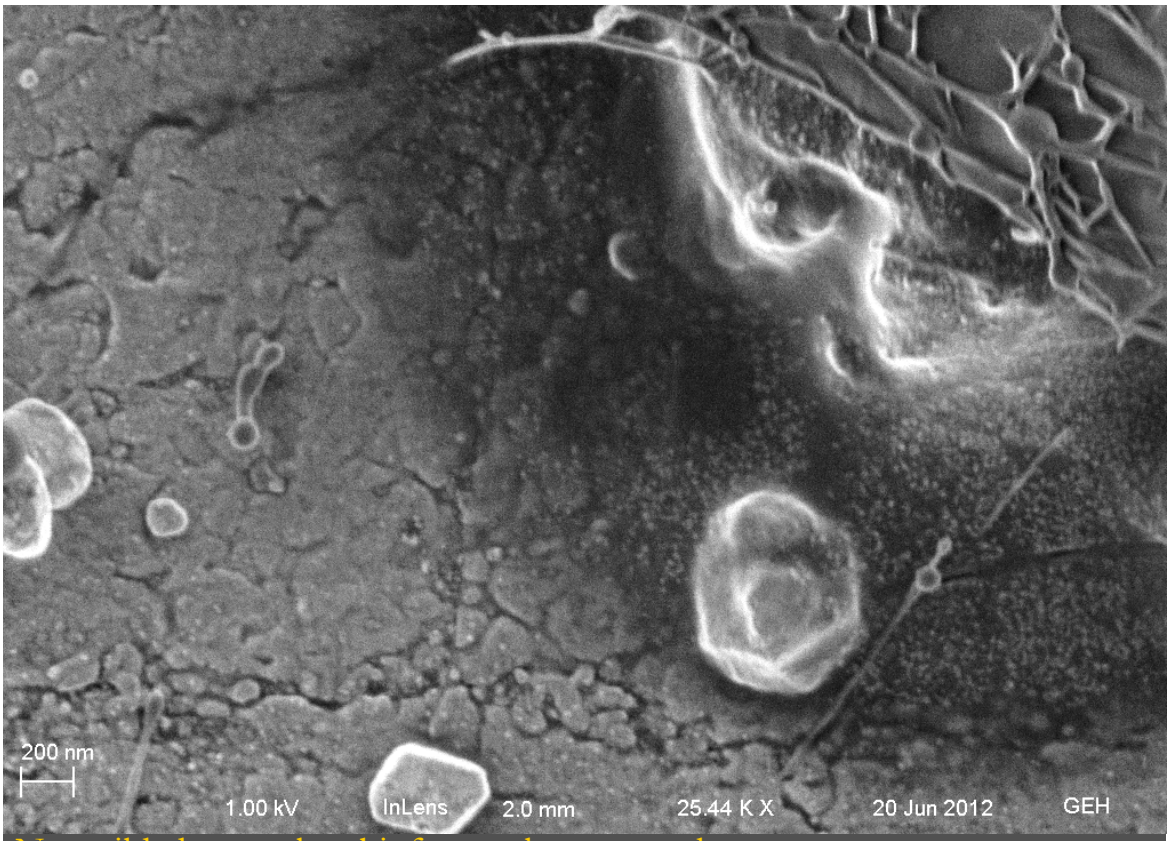

2
1
200 nm
2.00 kV
SE2
4.6 mm
22.91 K X
30 Jul 2012
GEH



Energy Dispersive X-Ray Analysis (EDX)



The bioform is transporting and processing metals from the daguerreotype



Non-gilded example – bioforms also present here

Is the bioform processing of metallic nano-particles well known?

Of interest to others?

Important?

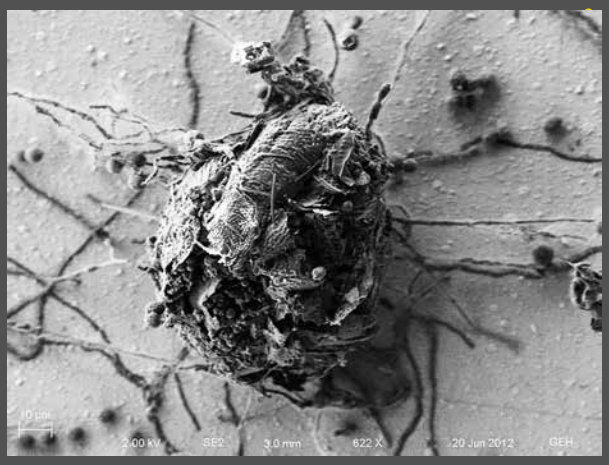
Current Research: Technology and Education Topics in Applied Microbiology and Microbial Biotechnology 2010

"Mycofabrication, mechanistic aspect and Multifunctionality of Metal Nanoparticles - Where are we? And where should we go?"

Fungi	Mode of Synthesis	Nanoparticles	Reference
Verticillium sp.	Intracellular	Au	Mukherjee *et al.*, 2001 [29]
Fusarium oxysporum	*Extracellular*	*CdS*	*Ahmad* et al., *2002 [30]*
Phoma sp. 3.2883	Intracellular	Ag	Chen *et al.*, 2003 [31]
Colletotrichum sp.	Extracellular	Au	Shankar *et al.*, 2003 [16]
Usnea longissima	Extracellular	Usnic acid	Shahi & Patra, 2003 [34]
Fusarium oxysporum	Extracellular	Zirconia	Bansal *et al.*, 2004 [32]
Trichothecium sp.	Extra/Intra	Au	Ahmad *et al.*, 2005
Fusarium oxysporum	Extracellular	Si, Ti	Bansal *et al.*, 2005 [33]
Fusarium oxysporum *Verticillium sp.*	Extracellular	Magnetite	Bharde *et al.*, 2005 [37]
Fusarium oxysporum	Extracellular	Ag	Duran *et al.*, 2005 [38]
Aspergillus fumigates	Extracellular	Ag	Bhainsa & D' Souza, 2006 [34]
Fusarium oxysporum f. *sp. lycopersici*	Intra- & Extracellular	Pt	Riddin *et al.*, 2006 [26]
Verticillium luteoalbum	Intracellular	Au	Gericke& Pinches, 2006 [39]
Fusarium semitectum	Extracellular	Ag	Basavaraja *et al.*, 2007 [40]

Aspergillus flavus	Intracellular	Ag	Vigeshwaran *et al.*, 2007 [41]
Fusarium oxysporum	*Extracellular*	*CdSe quantum dots*	*Kumar* et al., *2007a [42]*
Fusarium oxysporum	Extracellular	Ag	Kumar *et al.*, 2007b [43]
Fusarium oxysporum	Extracellular	Ag	Mohammadian *et al.*, 2007 [44]
Aspergillus niger	Extracellular	Ag	Gade *et al.*, 2008 [24]
Fusarium acuminatum	Extracellular	Ag	Ingle *et al.*, 2008 [28]
Trichoderma asperellum	Extracellular	Ag	Mukherjee *et al.*, 2008 [27]
Penicillium sp.	Extracellular	Ag	Sadowski *et al.*, 2008 [45]
Fusarium semitactum	Extracellular	Au, Au-Ag alloy	Sawale *et al.*, 2008 [46]
Helminthosporum solani	Extracellular	Au	Kumar *et al.*, 2008 [69]
Phoma glomerata	Extracellular	Ag	Birla *et al.*, 2009 [47]
Fusarium solani	Extracellular	Ag	Ingle *et al.*, 2009 [48]
Coriolus versicolor	Extracellular	Ag	Sanghi and Verma, 2009 [70]
Cladosporium cladosporioides	Extracellular	Ag	Balaji *et al.*, 2009 [71]
Fusarium oxysporum	Extracellular	Pt	Govender *et al.*, 2009 [72]

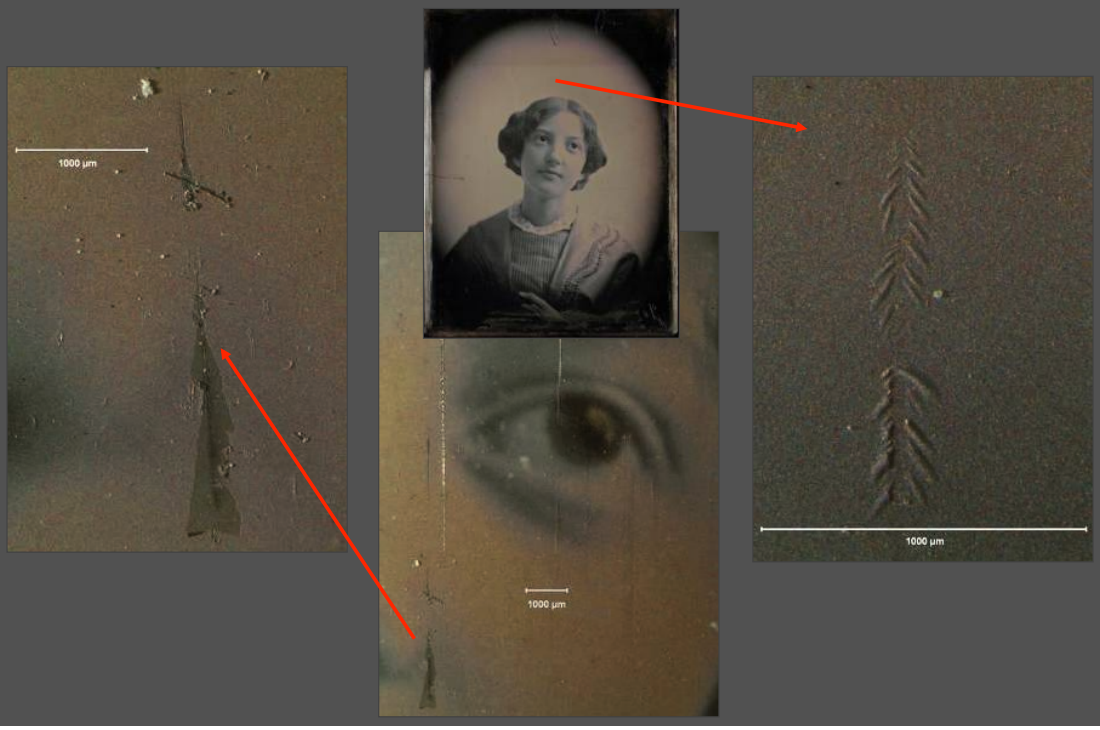
The daguerreotype surface has the elemental building blocks for bottom-up self assembling nanostructures



Gold and silver nanoparticles are favored elements for nano bio- engineers in creating self-assembling structures

Biological forms and chemistry can serve as the scaffolding and mechanisms for self-assembled gold and silver complexes

Unstable surface: exfoliation
What is the cause of exfoliation?



The gilding of daguerreotypes as nano-technology fabrication mechanism

Literary Gazette; and Journal of the Belles Lettres, Arts, Sciences, &c. (London) No. 1231 (22 August 1840): 545. This text appears as part of a column under the header: "PARIS LETTER. Academy of Sciences, August 18, 1840."

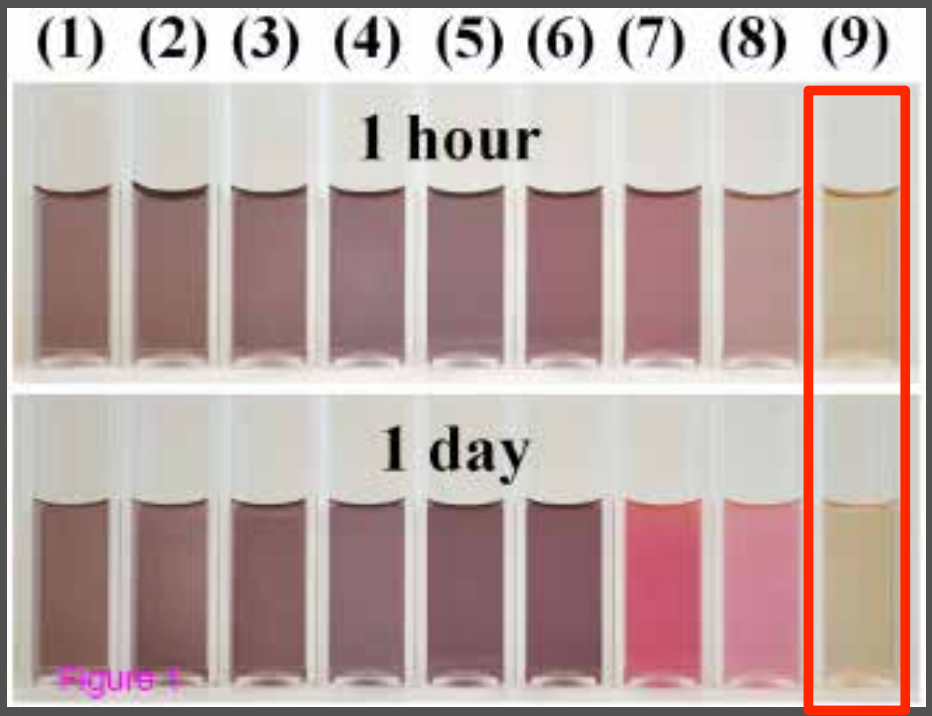
M. Fizeau communicated a method of fixing photographic impressions obtained with the daguerreotype, by means of a chlorure of gold. The mixture employed was one gramme of chlorure of gold dissolved in half a litre of pure water (distilled), to be mixed with three grammes of hyposulphite of soda, also dissolved in half a litre of water. The two mixtures to be poured gradually together, and well stirred

Tunability and Stability of Gold Nanoparticles Obtained from Chloroauric Acid and Sodium Thiosulfate Reaction

Tunability and Stability of Gold Nanoparticles Obtained from Chloroauric Acid and Sodium Thiosulfate Reaction

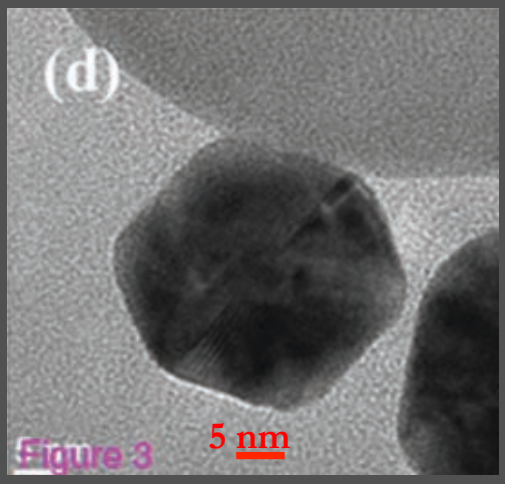
Nanoscale Research Letters 2012, 7:337 doi:10.1186/1556-276X-7-337

Guandong Zhang (gdzhan04@louisville.edu)
Jacek B. Jasinski (jbjasinski@gmail.com)
Justin L. Howell (howell.houwel@gmail.com)
Dhruvinkumar Patel (dnpatel01@gmail.com)
Dennis P. Stephens (dps2501@gmail.com)
Andre M. Gobin (andre.gobin@louisville.edu)

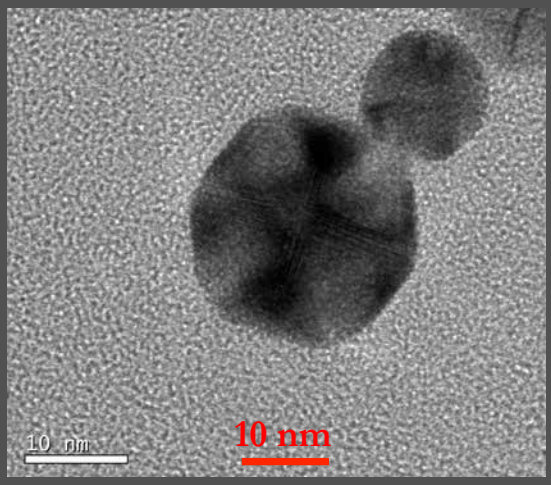


Particles do not aggregate - functionalized

University of Louisville

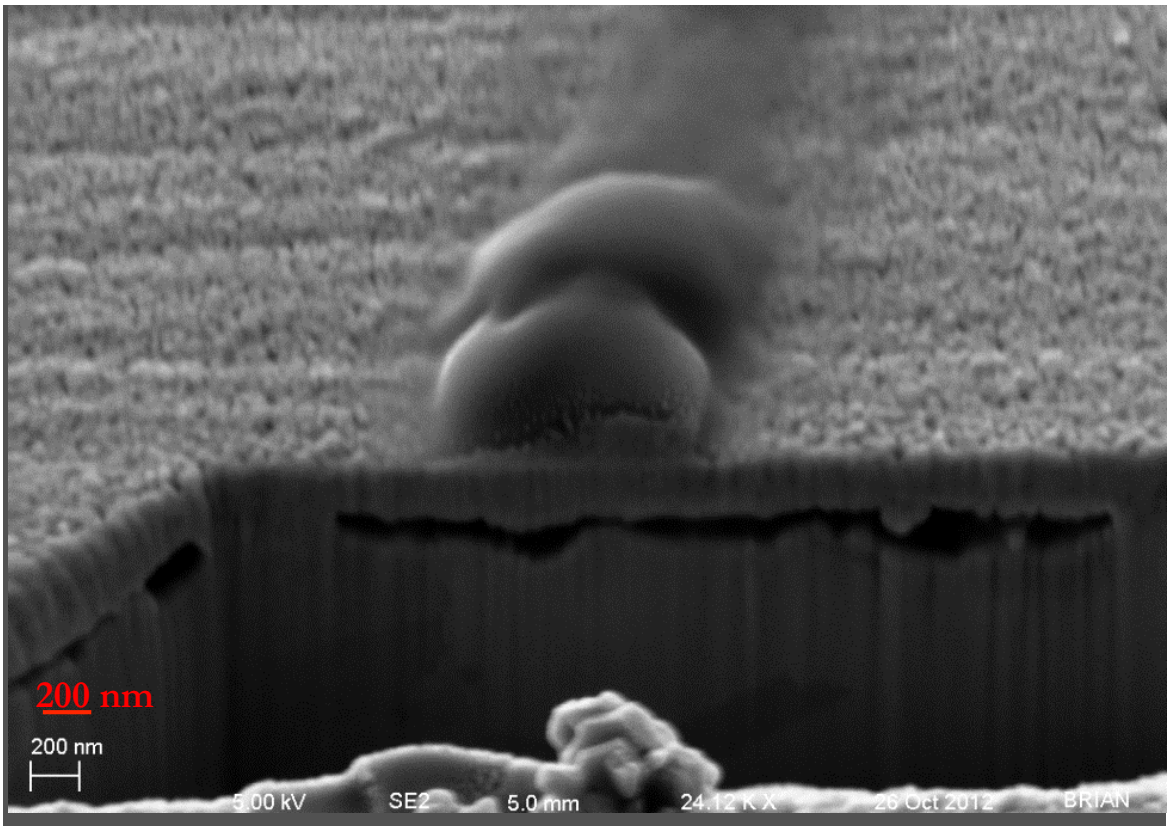


GEH UR SCIART



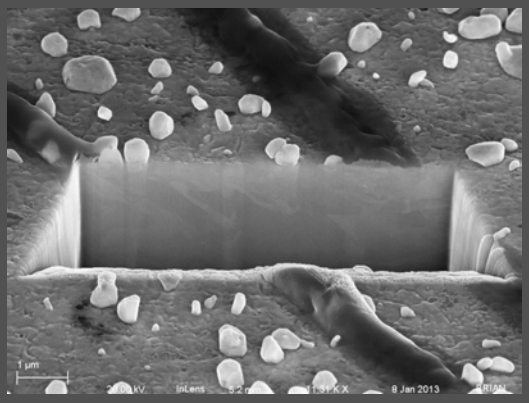
The entire gilding process is more complex than originally thought and intrinsically involves gold nano-particles.

The Gilding Has Many Consequences

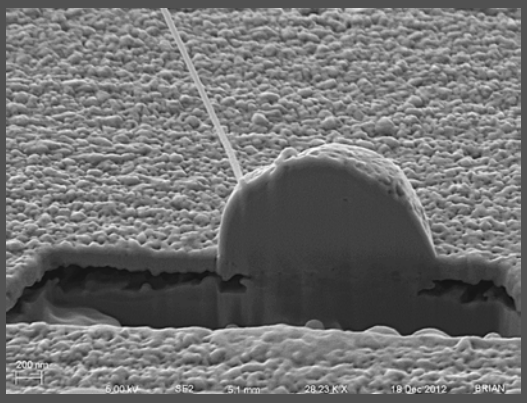


Nano-archaeology: Focused Ion Beam Cross-sectioning

FIB trench of historic ungilded daguerreotype

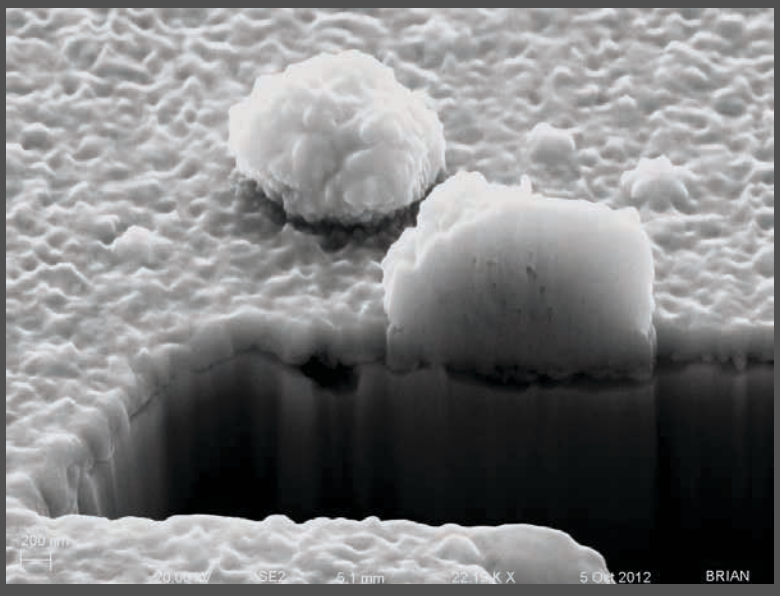


Fib trench of historic gilded daguerreotype

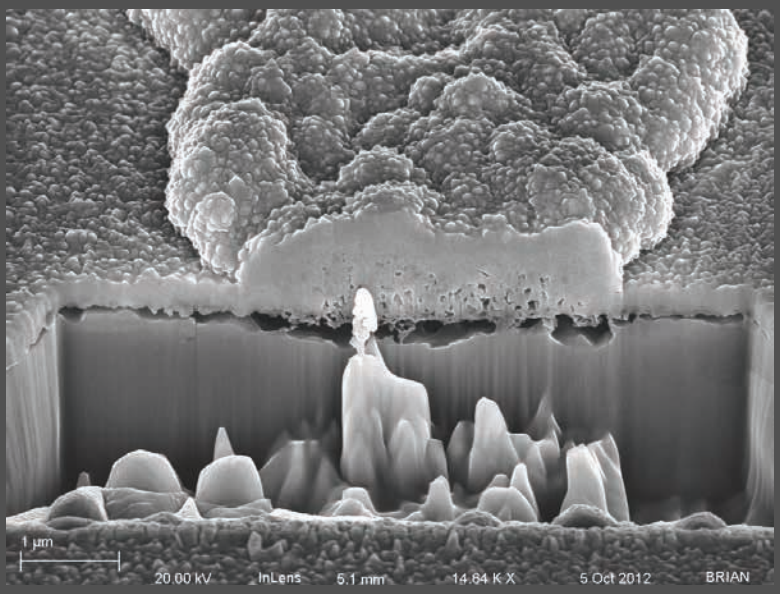


Focused Ion Beam

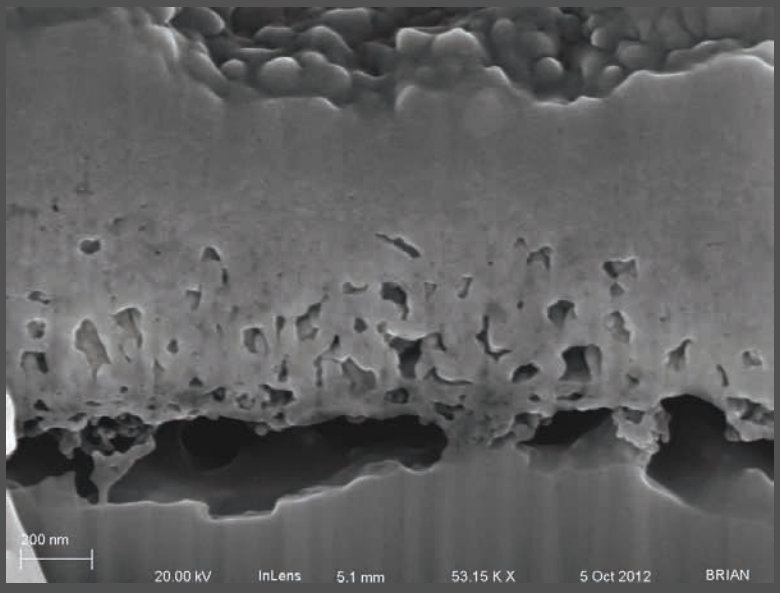
Image particle: note subsurface voids beneath the silver plate and beneath the image particle



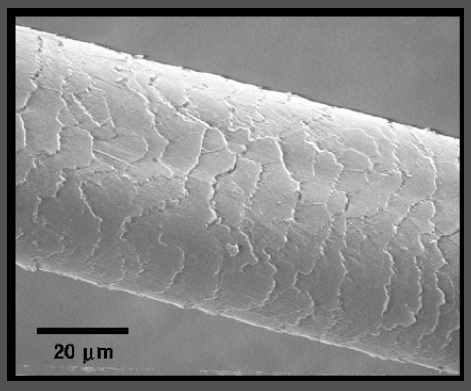
Large image particle in a dark region of the daguerreotype: not the extended diminuation of silver at the plating interface below the particle; top surface is gold rich

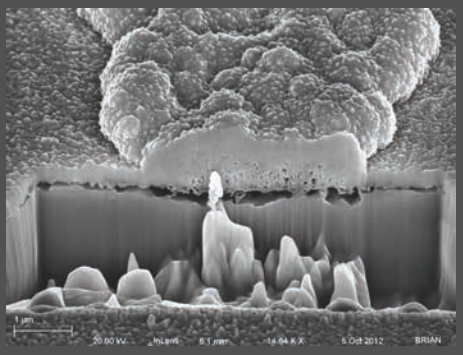


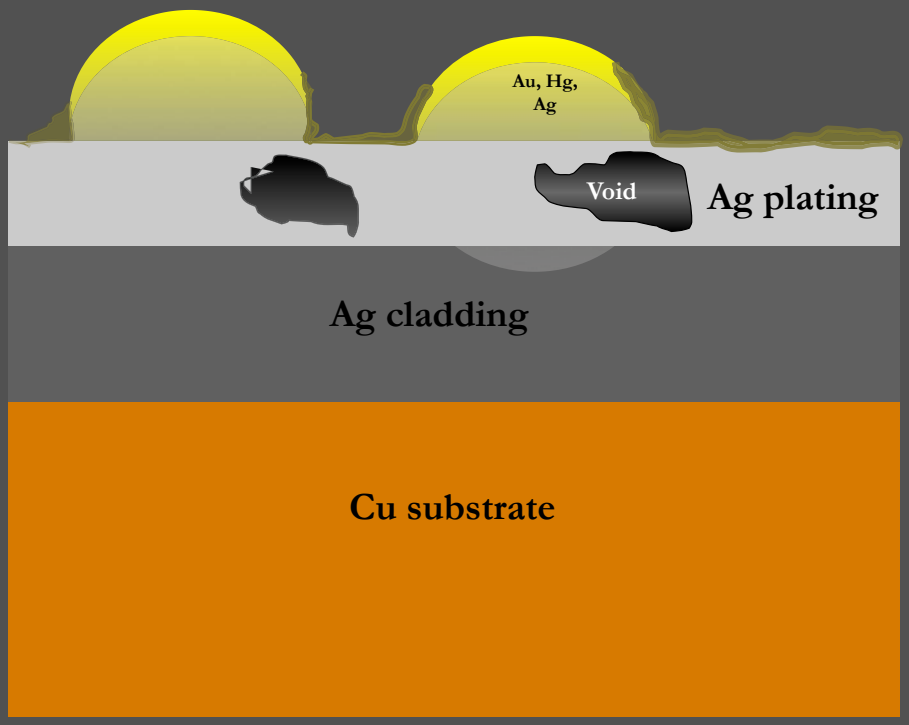
Unprecedented view of the silver substructure of a daguerreotype. The particle becomes more gold rich at the top.



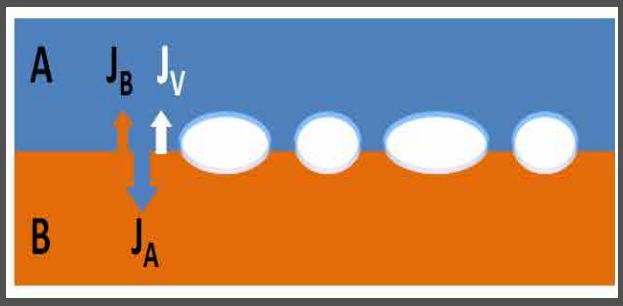
Size comparison with human hair



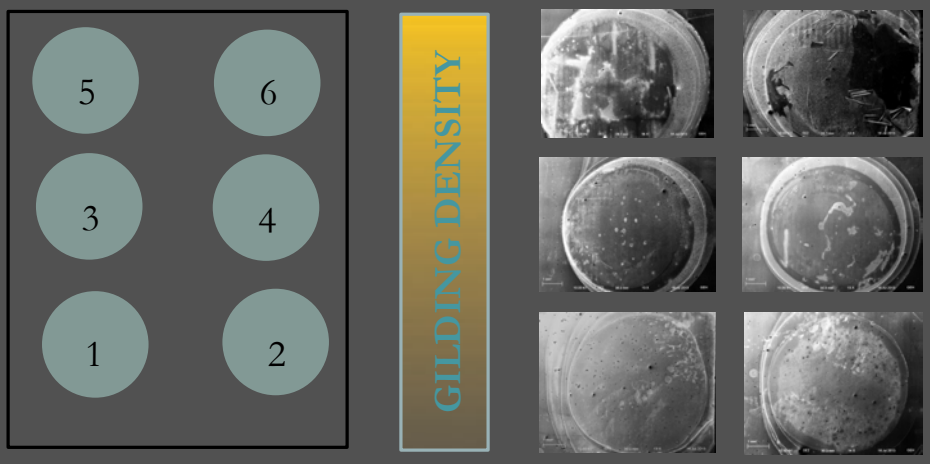




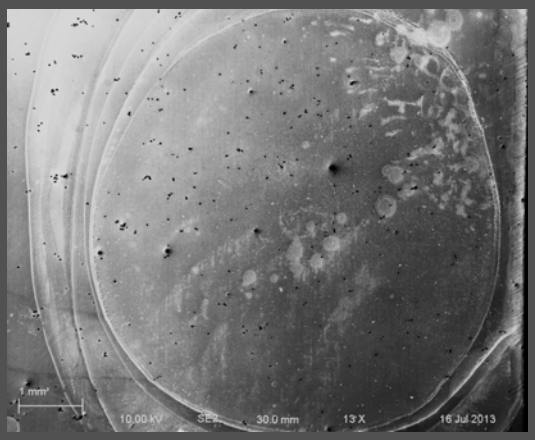
Kirkendall Effect

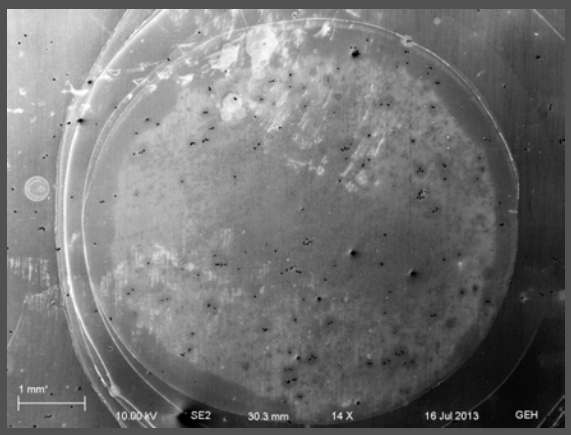


Localized drop-wise gilding with progressive addition of gold solution during heating "daguerreochips"



1 and 2


1 mm
10.00 kV SE2 30.0 mm 13 X 16 Jul 2013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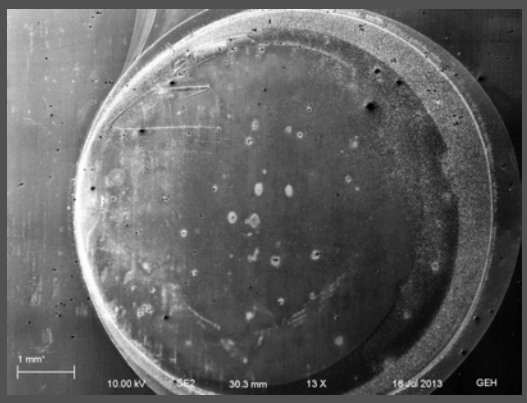
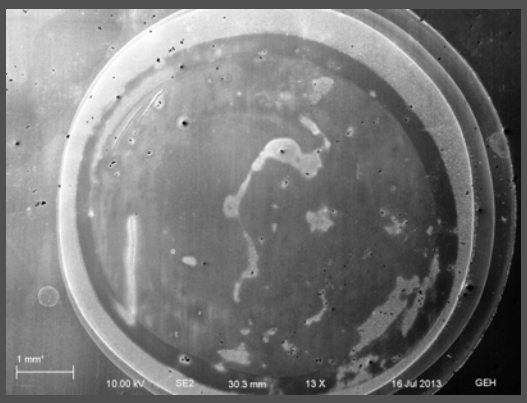
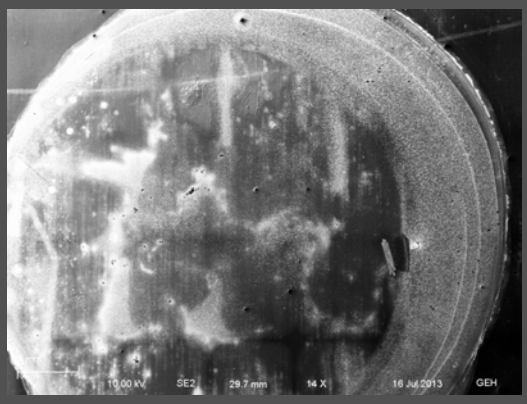
10.00 kV SE2 30.3 mm 14 X 16 Jul 2013 GEH

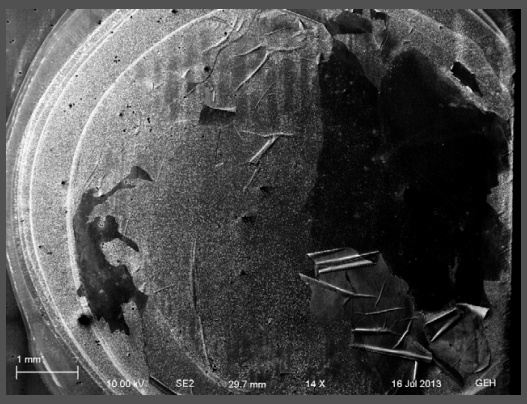
3 and 4


1 mm
10.00 kV SE2 30.3 mm 13 X 16 Jul 2013 GEH

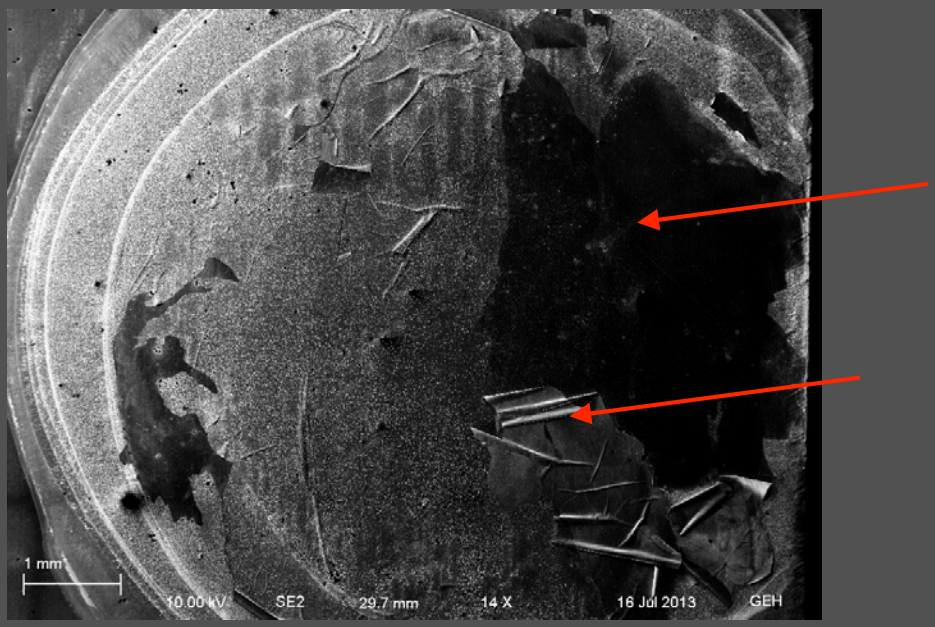

1 mm
10.00 kV SE2 30.3 mm 13 X 16 Jul 2013 GEH

5 and 6

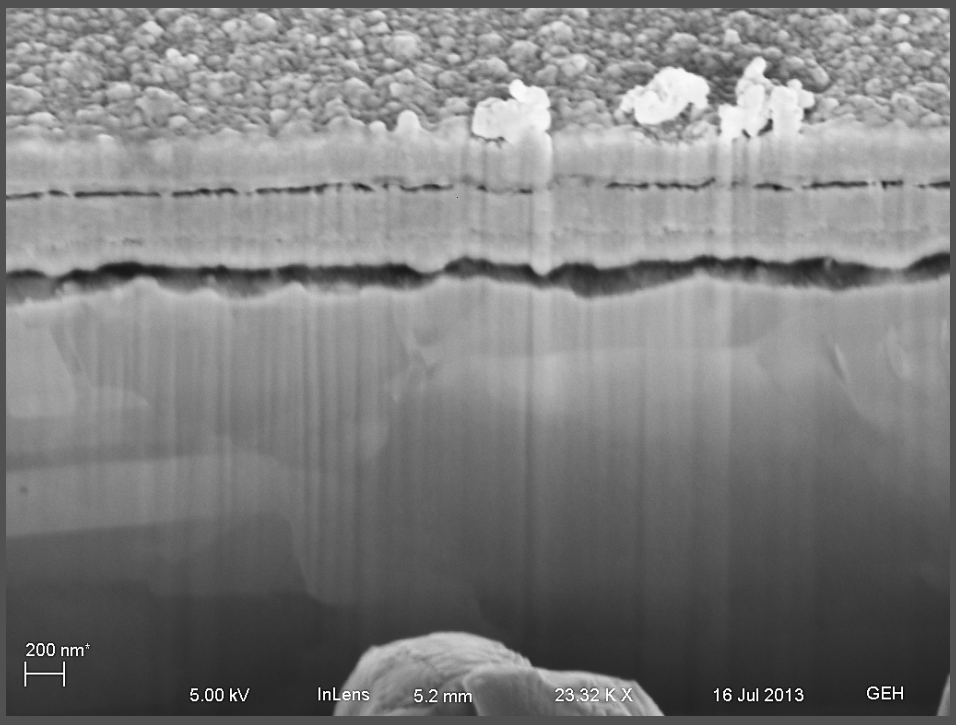


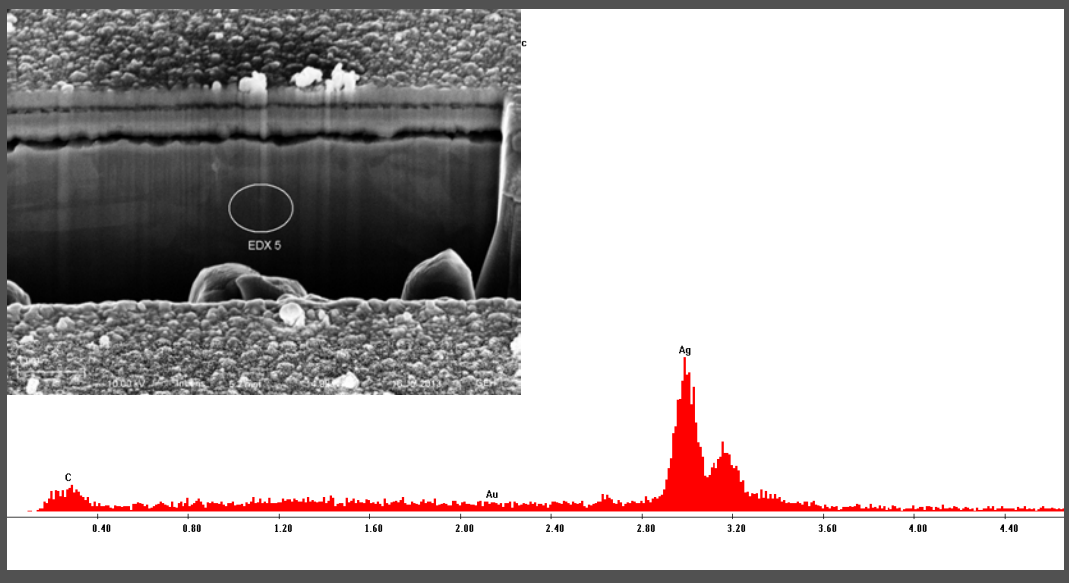


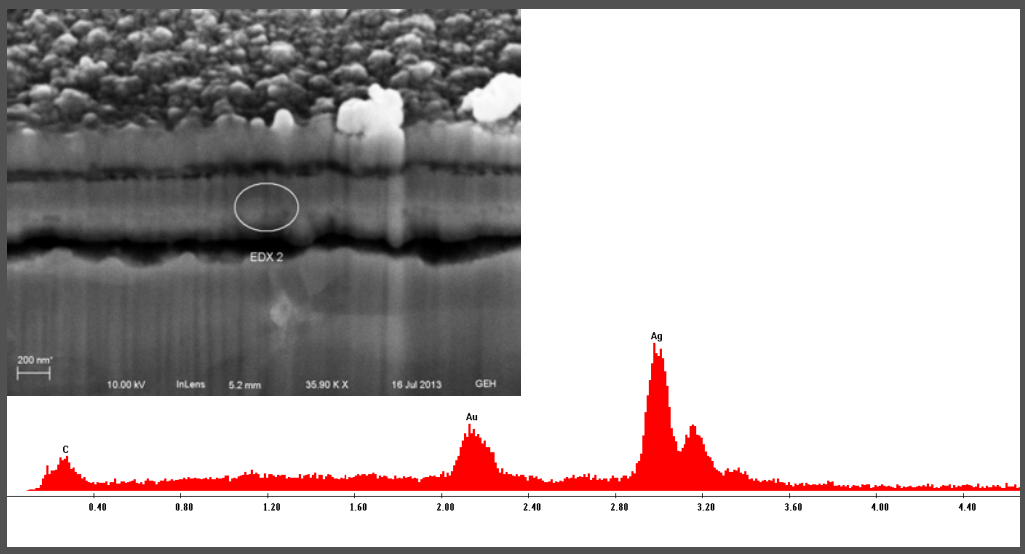
Gilding to the extent that the gilding layer delaminated and rolled up

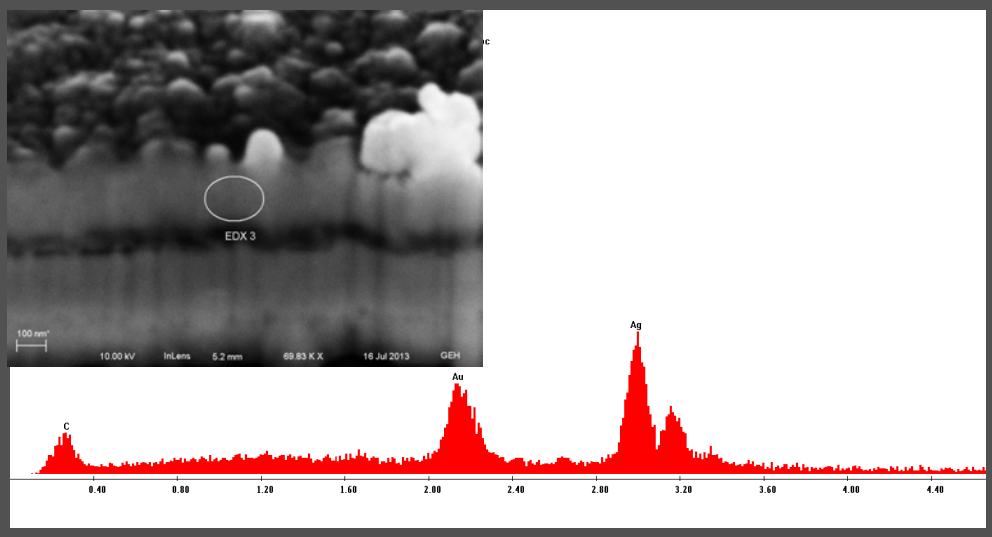


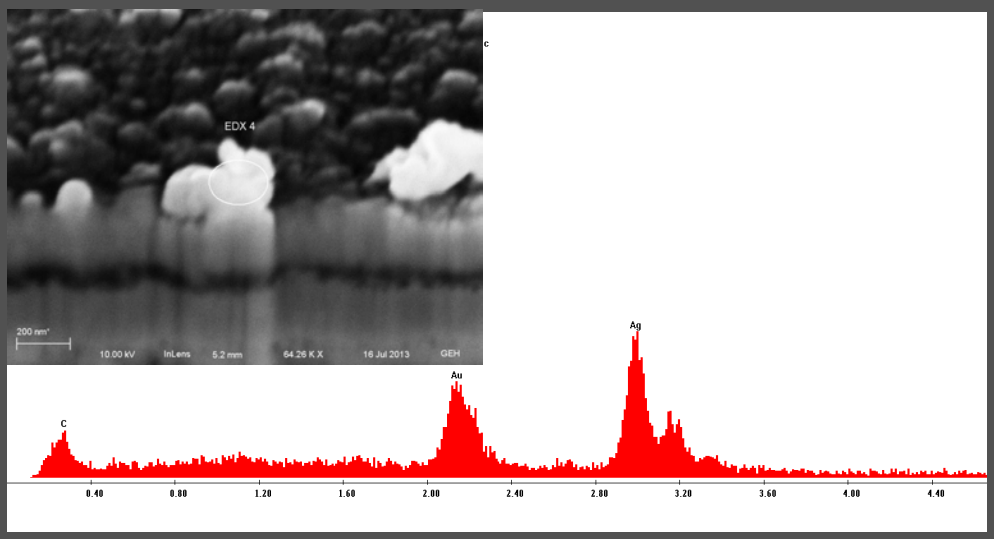
Fib Section of 6



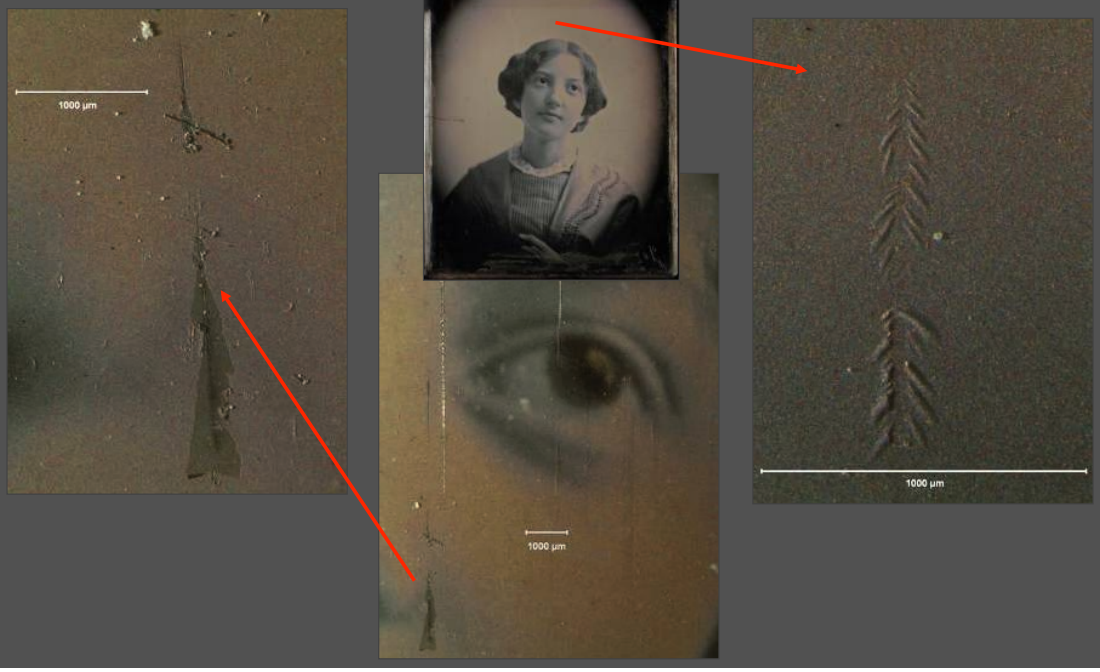



EDX 2
200 nm
10.00 kV InLens 5.2 mm 35.90 K X 16 Jul 2013 GEH
C
Au
Ag
0.40 0.80 1.20 1.60 2.00 2.40 2.80 3.20 3.60 4.00 4.40

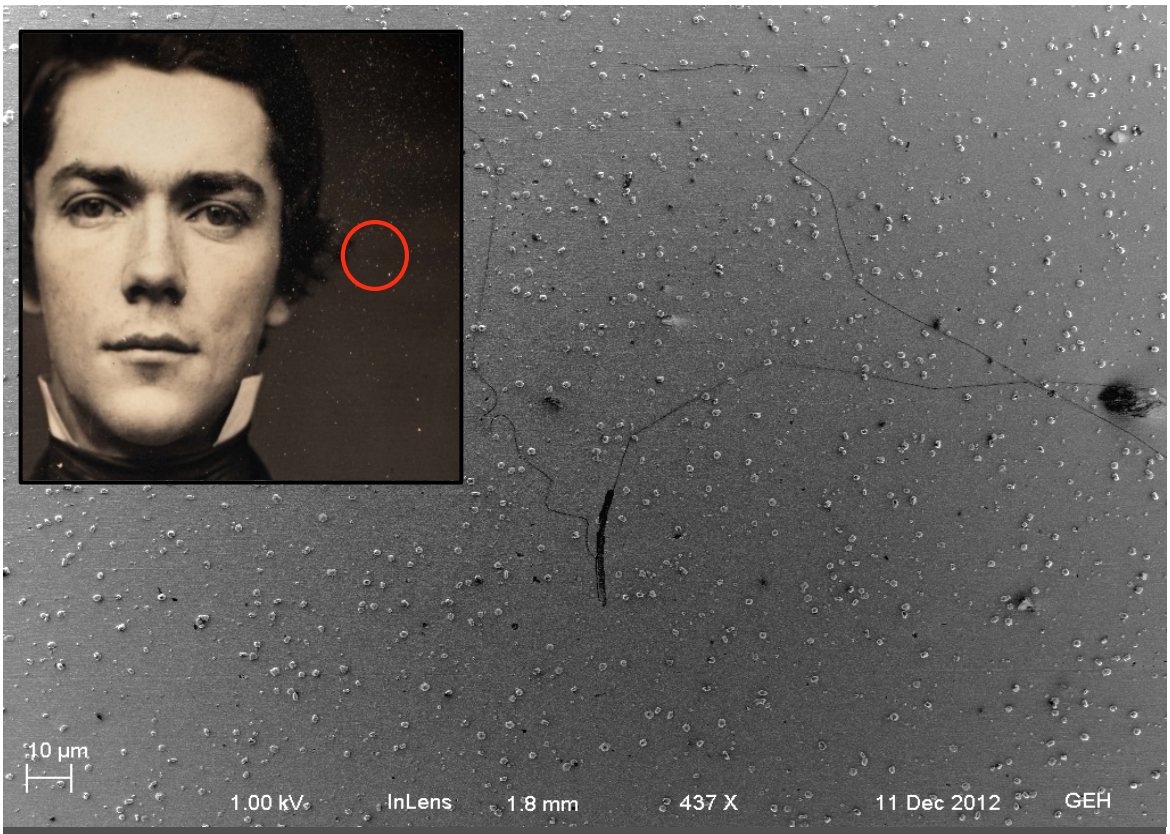

EDX 3
100 nm
10.00 kV InLens 5.2 mm 69.83 K X 16 Jul 2013 GEH
C
Au
Ag
0.40 0.80 1.20 1.60 2.00 2.40 2.80 3.20 3.60 4.00 4.40

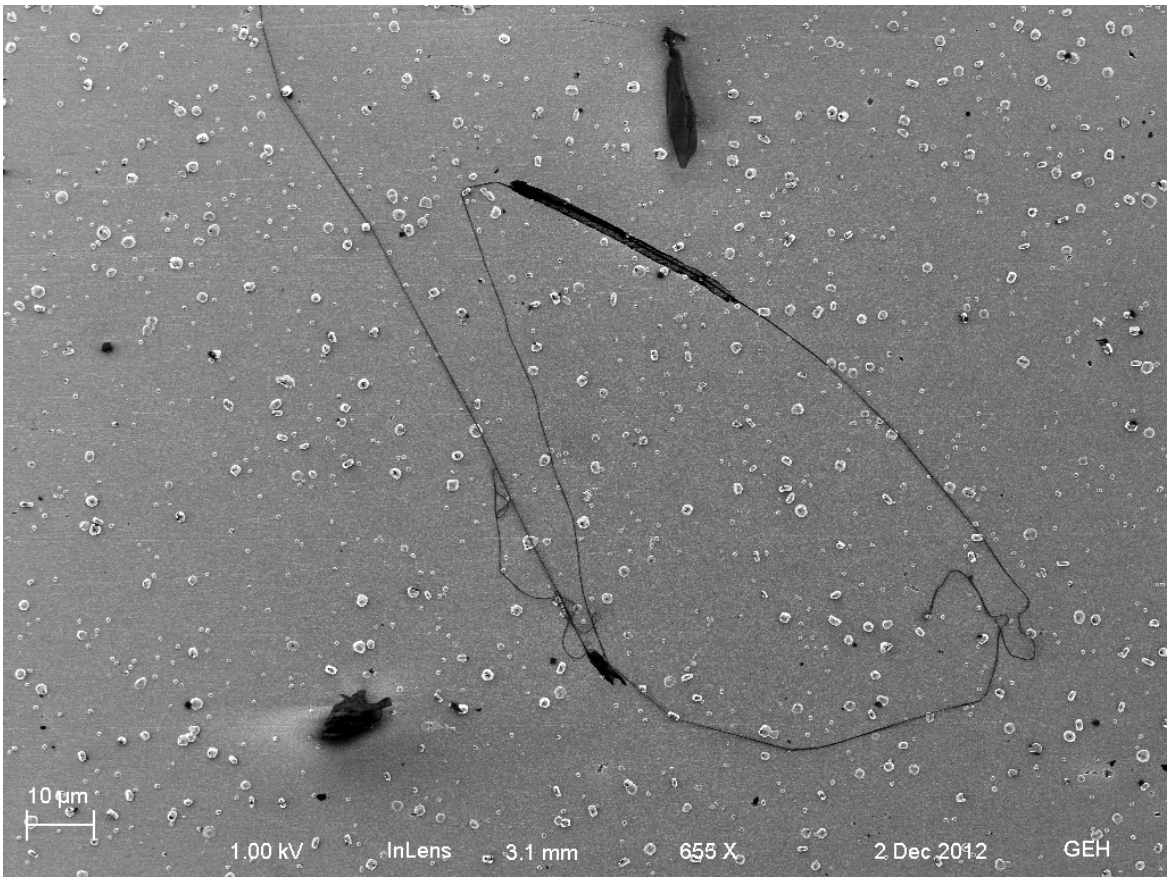


RECALL – Unstable surface: exfoliation

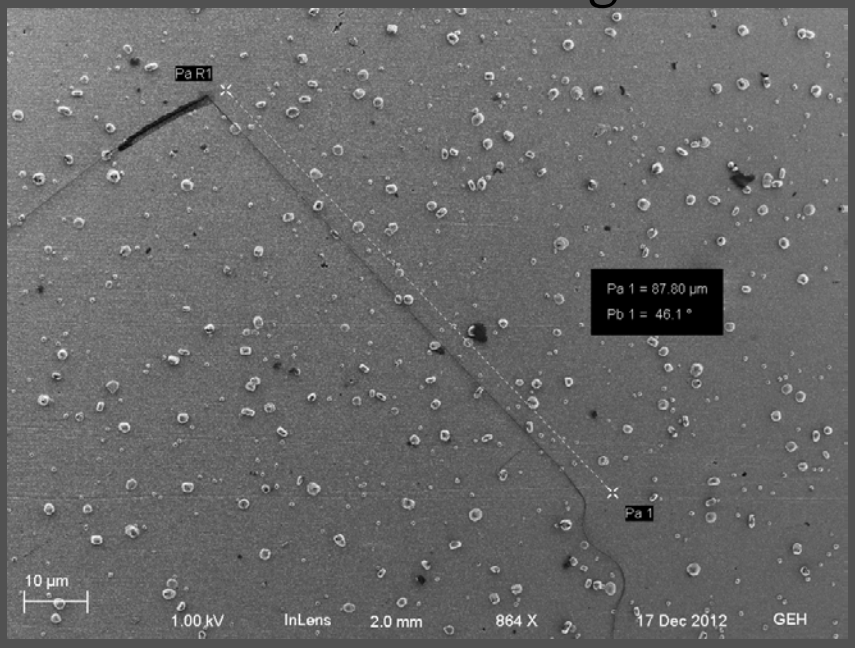


The daguerreotype as a nanofactory – evolving since "First Light"

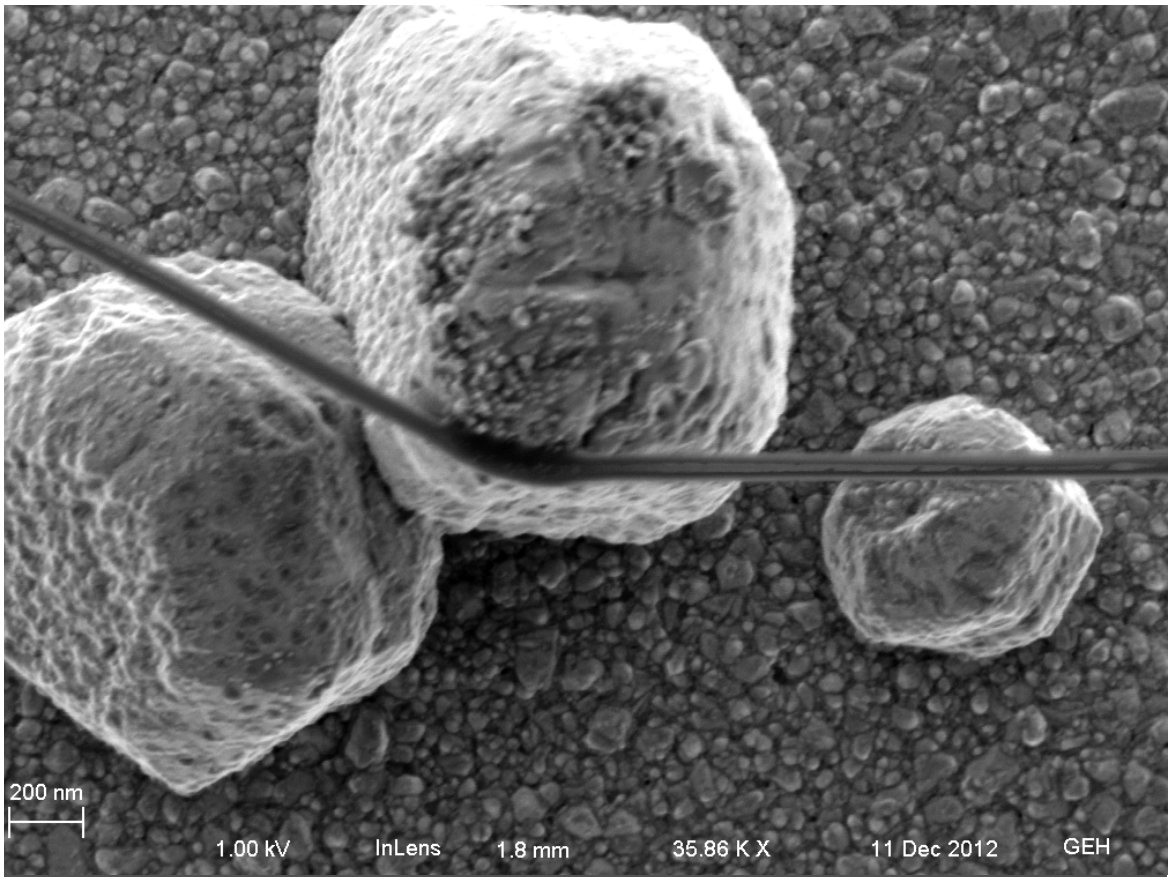


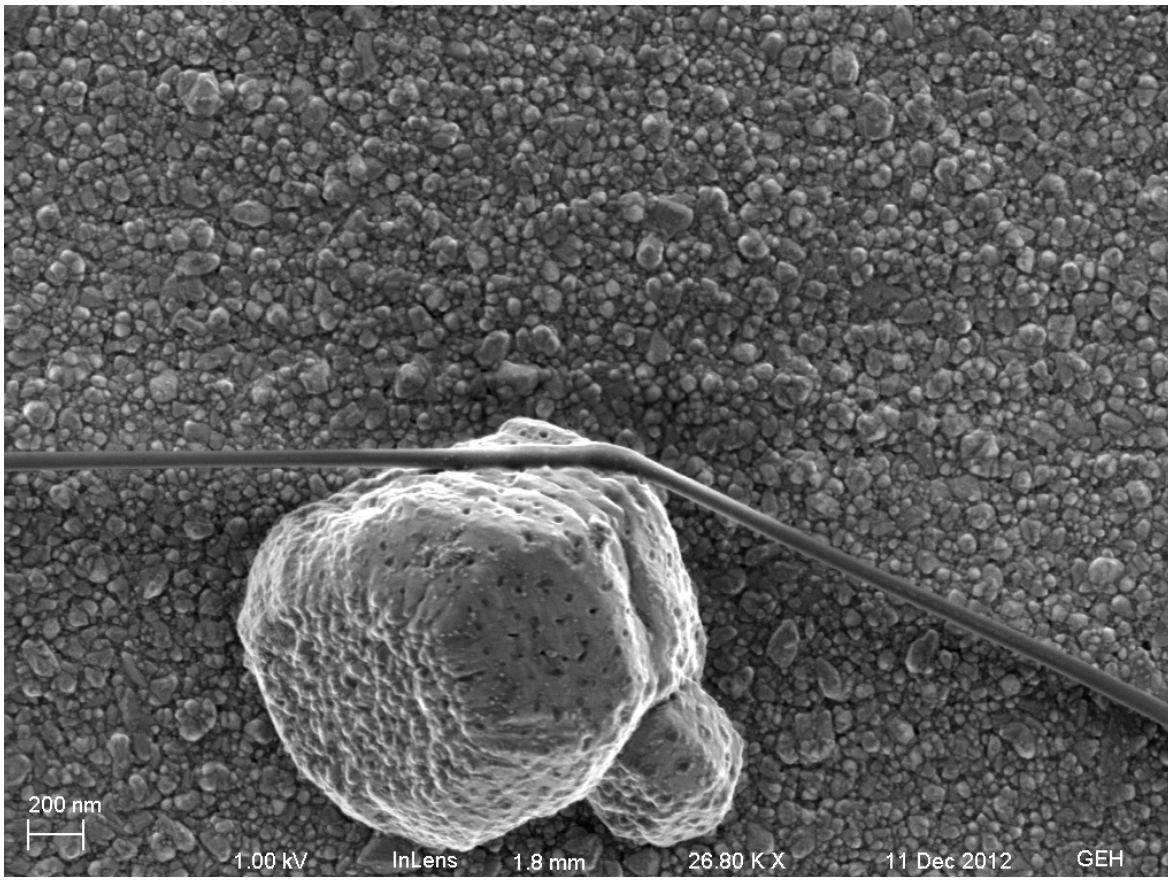


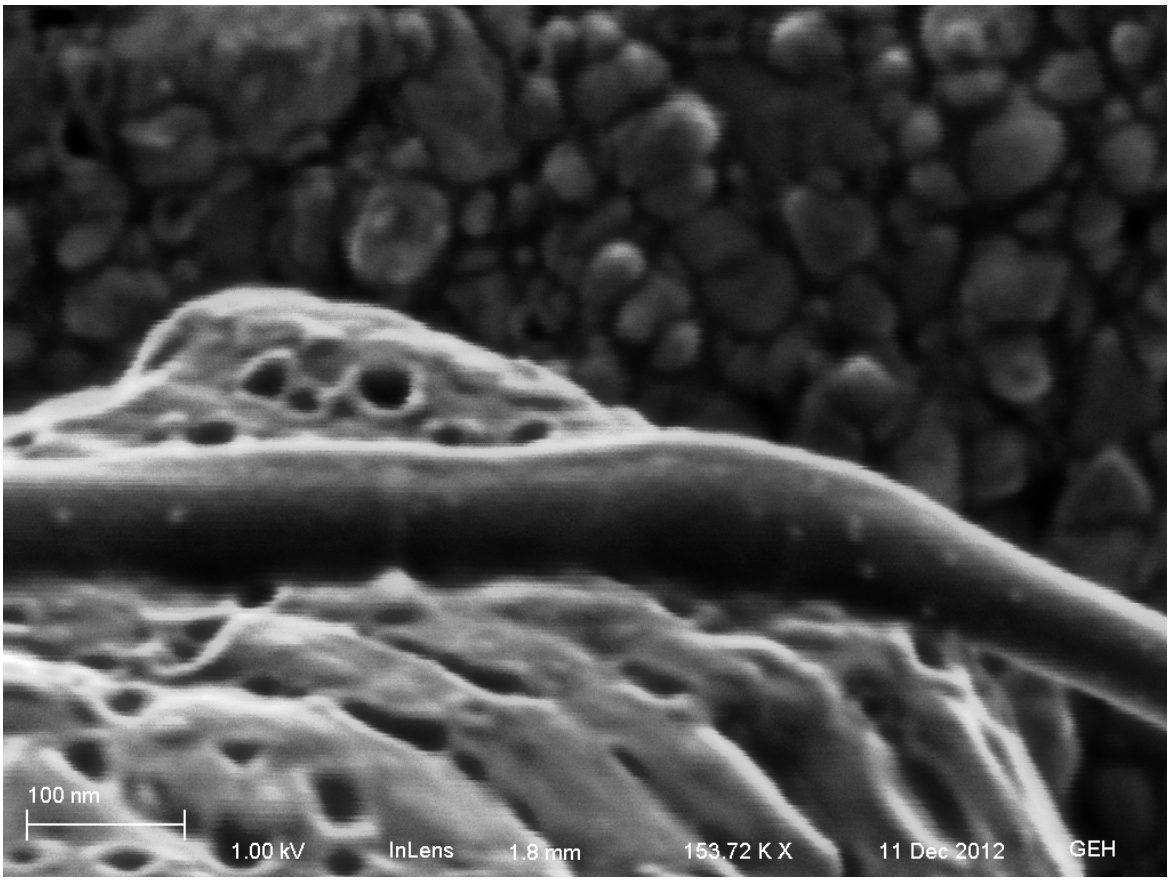
Aspect ratio: 50-70 nm diameter: 88microns in length



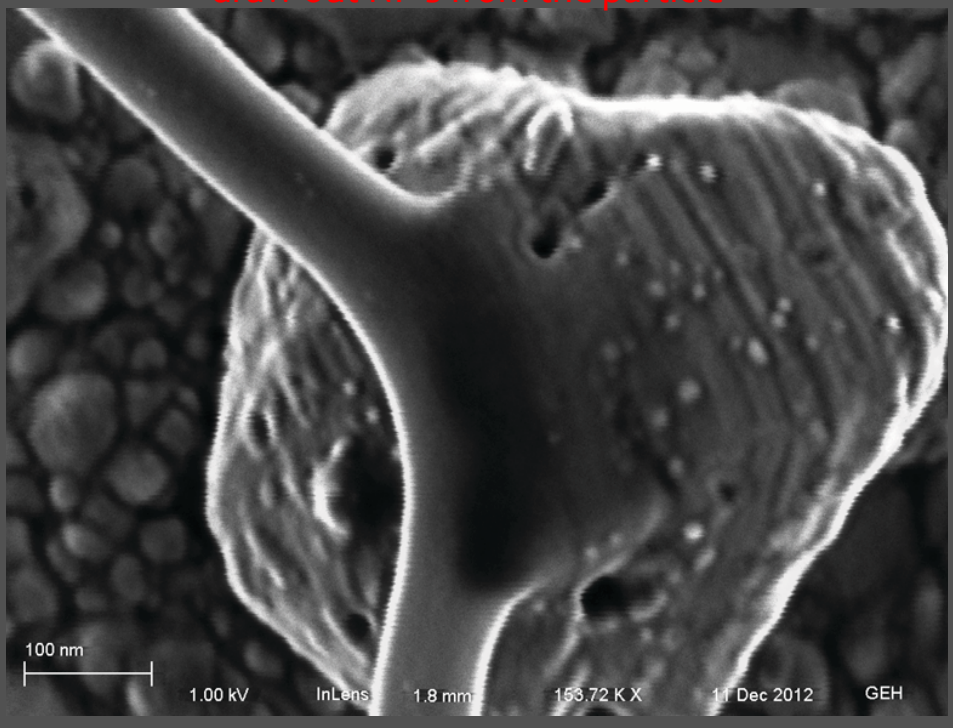
Nano-fiber is raised from the surface –with sporadic encounter with image particles

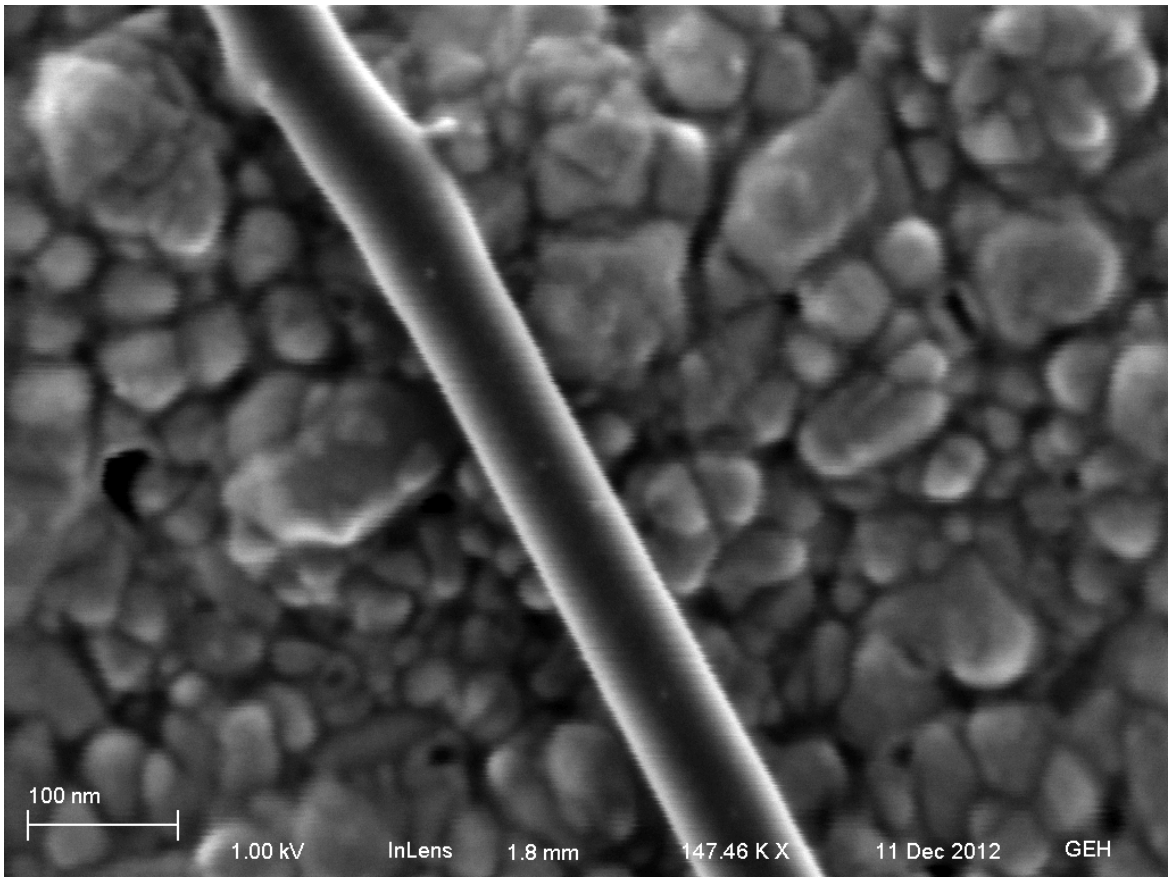

200 nm
1.00 kV
InLens
1.8 mm
35.86 K X
11 Dec 2012
GEH

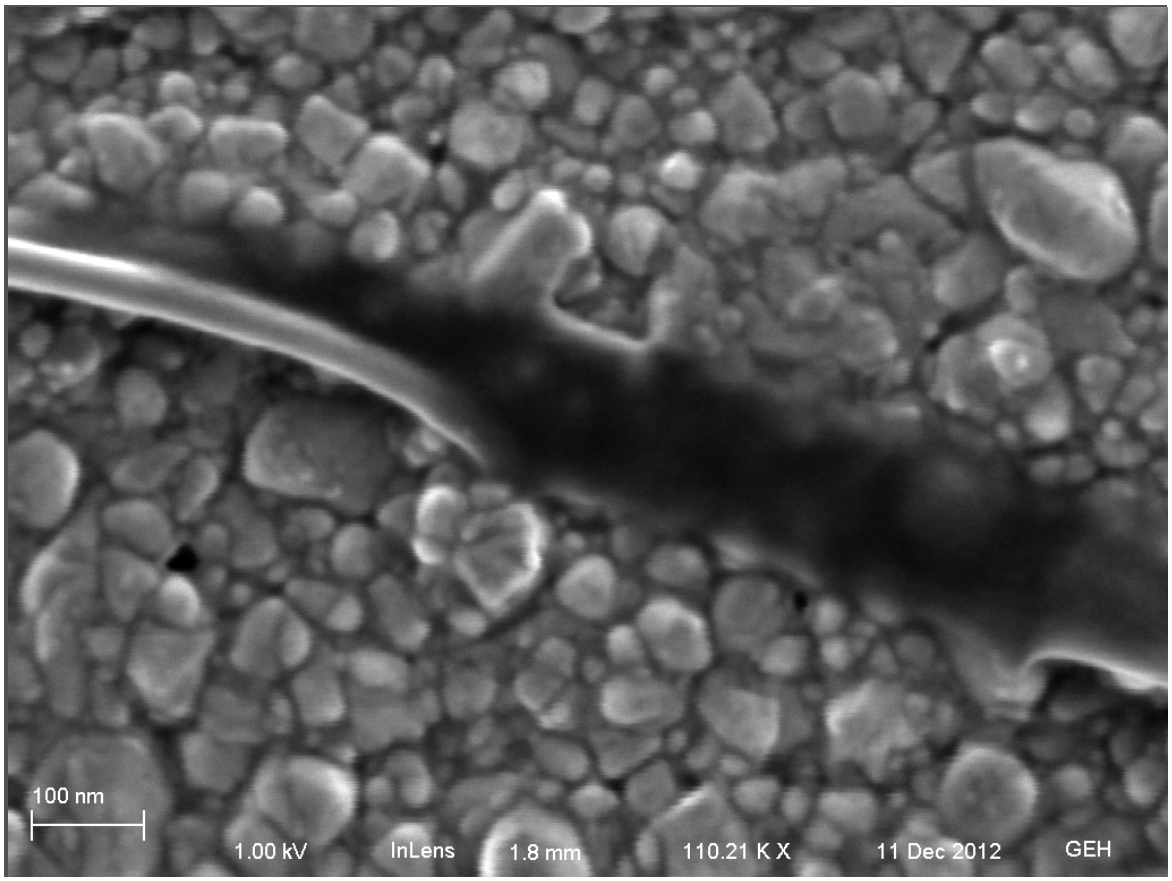

200 nm
1.00 kV
InLens
1.8 mm
26.80 K X
11 Dec 2012
GEH



Fiber engagement with Ag-Hg image particle –appears to draw out NP's from the particle




100 nm
1.00 kV
InLens
1.8 mm
147.46 K X
11 Dec 2012
GEH


100 nm
1.00 kV
InLens
1.8 mm
110.21 K X
11 Dec 2012
GEH

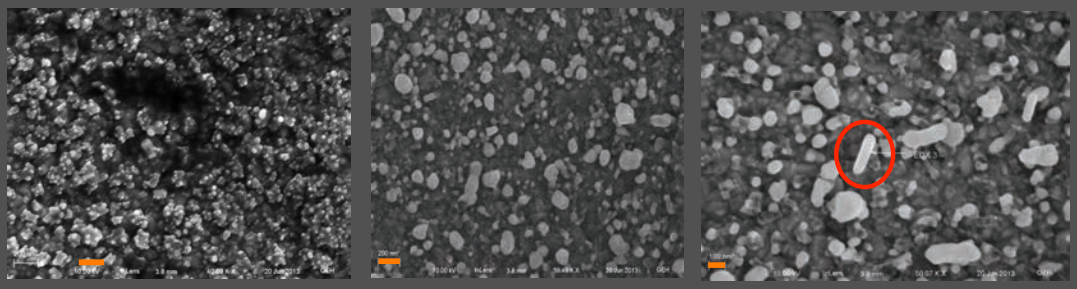
Examples of other ongoing studies:

-Plasmonic effects
-Light induced change
-Cleaning

Daguerreotypes exhibit quantum optical characteristics

- Color in darkfield light microscopy is due to localized plasmon resonance of gold and silver nanoparticles
- This may be a source for natural color effects seen in daguerreotypes

The impact of UV light on the nano structured surface



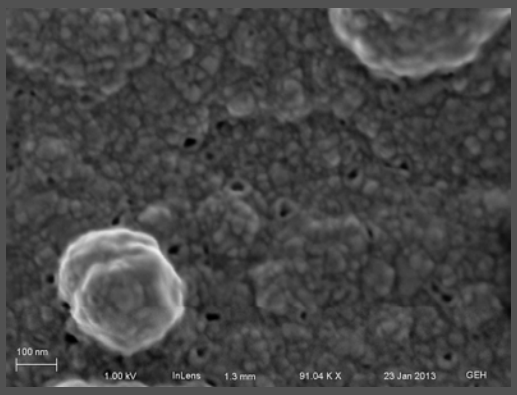
(left) SEM image of surface not affected by UV light. Scale bar is 200 nm.

(middle) SEM image of surface affected by UV light, showing increase in image particle size. Scale bar is 200 nm.

(right) SEM image of surface affected by UV light. Scale bar is 100 nm. Particle circled shows change in morphology.

Comparison of two surfaces

The nano-structure of the Cornelius plate



The nano-structure of the study plate with the nanofiber

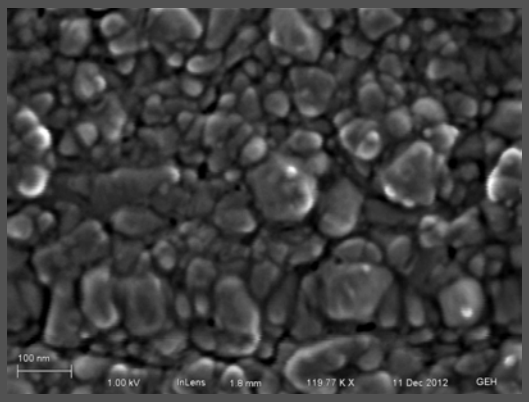


Plate after test cleaning

Plate after the two cleaning processes as indicated.

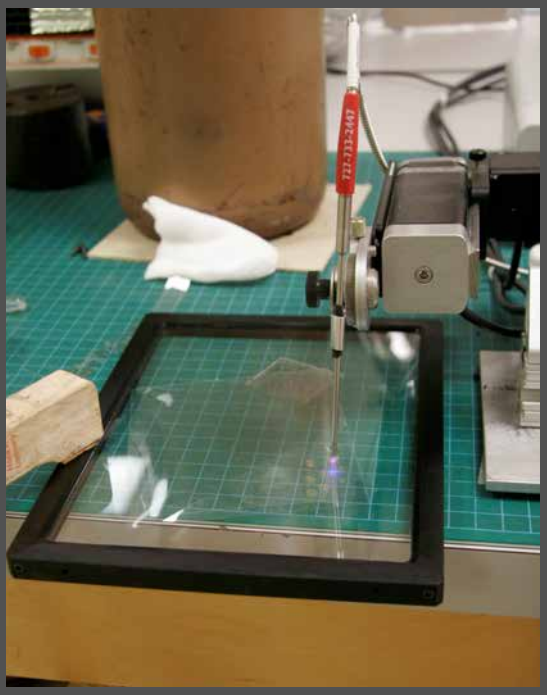
Electro-cleaned

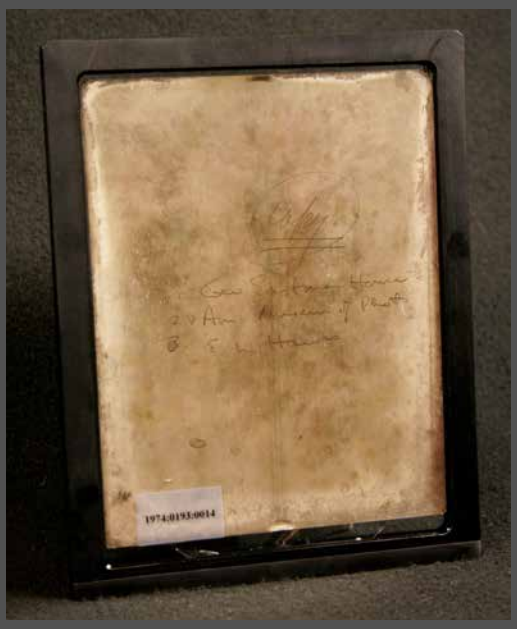
Thiourea cleaned

What do we do now?

- Are there surface intervention treatments that can effectively remove reactive chemistry and retain the original nano-structure of the daguerreotype?
- Are original cases and framing materials effective in preventing the nano-scale reactions as we have see here –for which there is no known scientific rationale for the degradation to not progress.
- Is it possible to slow or halt nano-chemical reactions now –and wait for new science to emerge that may provide better solutions to these critical issues for the preservation of the daguerreotype?

The answer is yes –but it requires adopting new practices

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Scientists Were Active in the Story

for example

•William Henry Fox Talbot

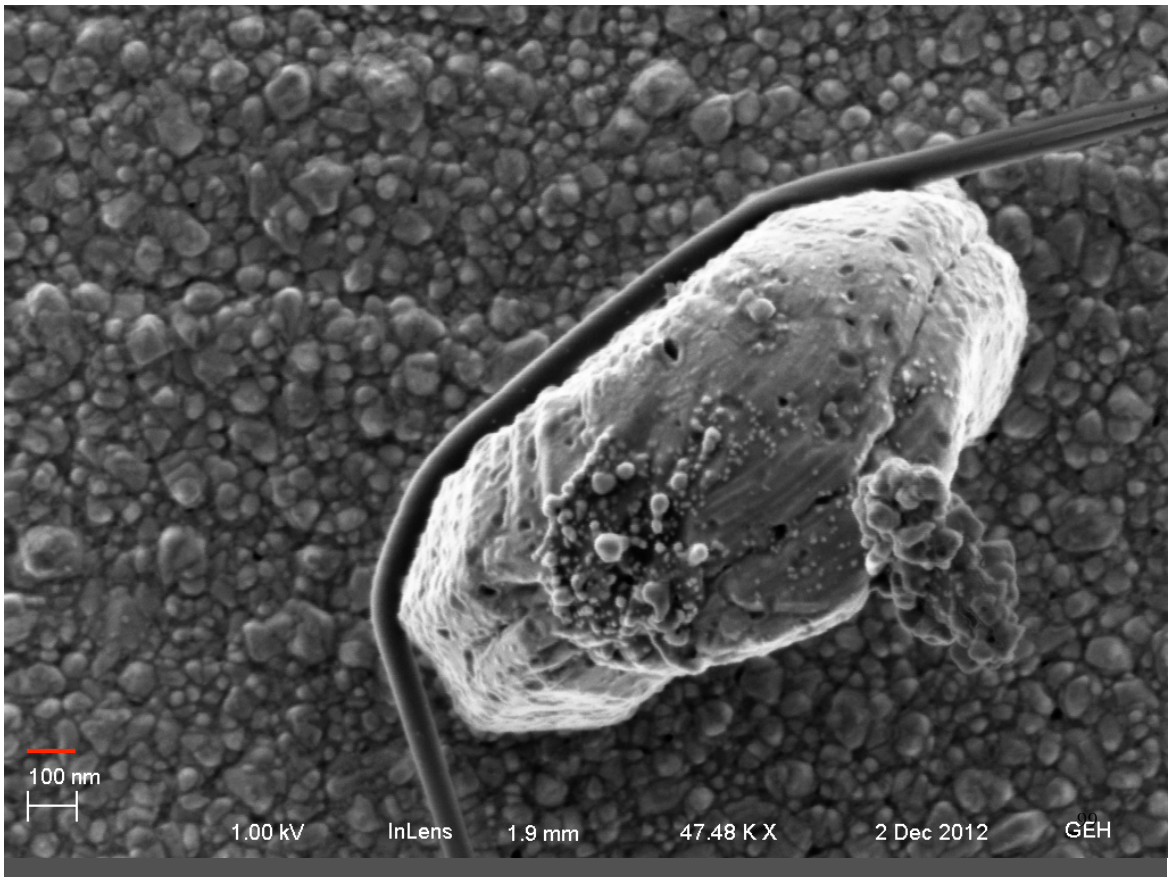
•William Hayden Wollaston

•Étienne Louis Malus

This work gives back to Science
And supports Conservation

Science is key to interpreting and conserving art.

Art and its conservation can lead to *new* science and insights that reach beyond the object itself.


100 nm
1.00 kV
InLens
1.9 mm
47.48 K X
2 Dec 2012
GEH