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Examination of a 19th Century Daguerreotype Photograph using High Resolution Scanning Transmission Electron Microscopy for 2D and 3D Nanoscale Imaging and Analysis

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Nanoscale structures on the surface and near surface of daguerreotype photographs have been characterized by scanning transmission electron microscopy-energy dispersive spectroscopy (STEM-EDS) and STEM-based tomographic imaging and analysis. The examined features include photo contrast-inducing nanoparticles, the protective gilding layer, and pores within the silver substrate.

In 1839, the daguerreotype photographic process was first presented to the scientific community in France. The technology spread rapidly and was widely used around the globe until roughly 1860. Image formation can be generalized into four steps: 1) exposing silver-plated copper to an iodine plus or minus another halogen vapor(s), 2) further exposing the sensitized plate to visible light within a camera, 3) development of an image after the plate is treated with heated mercury vapor, and 4) deposition of a gilding layer *via* gold chloride solution and heating [1].

Daguerreotypes have been the subject of a few detailed scanning electron microscopy-based studies over the years [e.g. 2]. However, a detailed description of the nanochemistry associated with the contrast-inducing image particles and gilding layer in daguerreotypes has not been described. In this study we present the elemental distribution within HgAg nanoparticles, the AuAg protective nanofilm coating, as well as Ag sulfide along pore surfaces in the substrate using STEM-EDS and STEM-based tomographic methods. Additionally, we present direct microstructural evidence for nanotwinning in the gilding layer.

An FEI Helios NanoLab 660 Dual Beam™ was used to deposit an initial layer of carbon with the electron beam over a region of a daguerreotype plate (Figs. 1a and b) rich in particles. This carbon film provides a conformable and dense coating that protects the upper surface during subsequent ion milling. A second layer of ion beam deposited platinum (or additional carbon) completes the protective coating. Site-specific electron transparent wafers were then extracted from highlight regions of the photograph. Lamellae were Pt-welded to an FIB Lift out grid and were thinned to 70_-_100 nm in thickness.

Lamellae were examined using an FEI Titan 80-300 transmission electron microscope at 300 keV and an FEI Titan G2 80-200 for nanotomography. Hyperspectral EDS data cubes were collected in STEM mode using a Si(Li) EDS or a high solid angle SDD analyzer and processed using multivariate statistical (MVS) algorithms designed to maximize contrast in the spatial domain [3] as implemented in the AXSIA software package [4].

Spatial simplicity-based MVS results reveal nanoparticle cores are encapsulated by the gilding layer, instead of simply being coated on their outer surfaces (Fig. 1). Incipient Ag sulfide films are found lining voids directly beneath the photo surface, and additionally, within the nanoparticle cores (Fig 1b). NB: Certain commercial equipment, instruments, or materials are identified in order to specify the experimental procedure adequately. Such identification is not intended to imply recommendation or endorsement by the National Institute of Standards and Technology.

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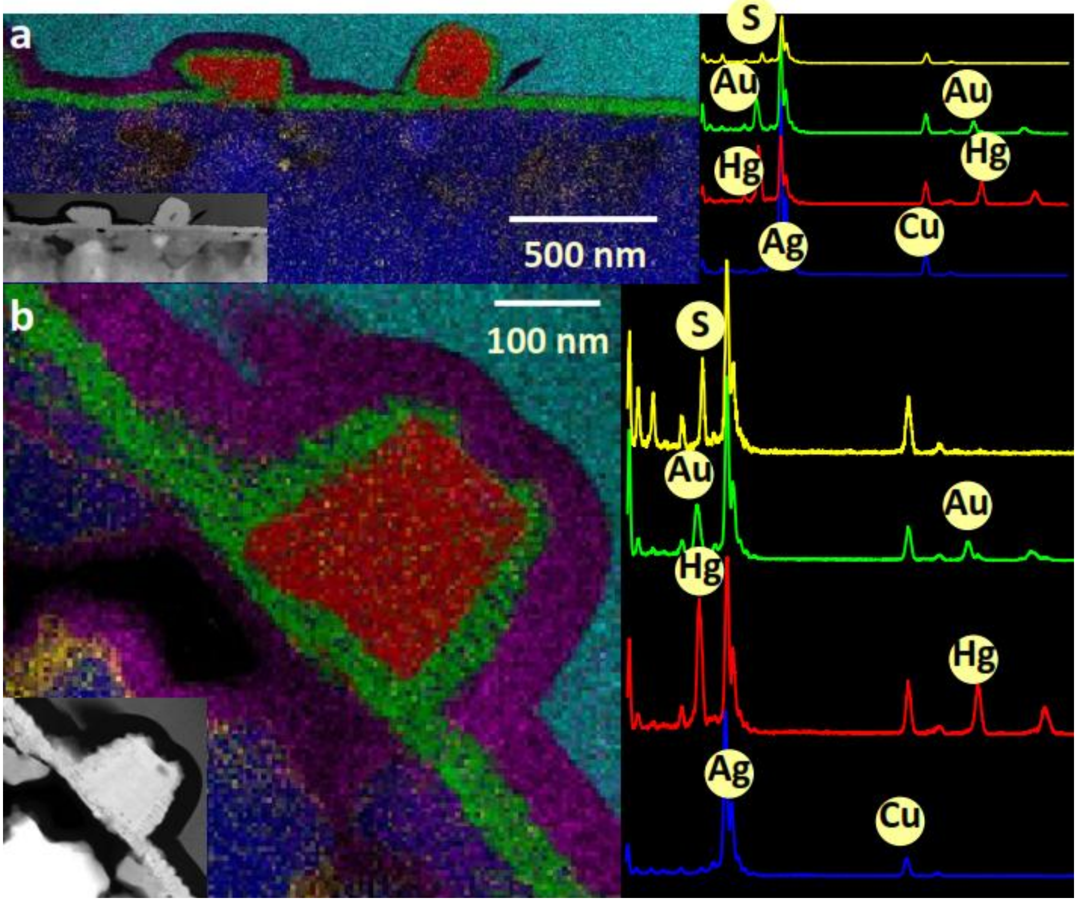

Figure 1 (a and b). Composite component image (left) and component X-ray spectra (right) of daguerreotype photograph cross section where: Blue-represents Ag substrate, Red-represents HgAg nanoparticles, Green-represents AuAg gilding overlayer. Magenta and cyan represent C and Pt deposited in the focused ion beam. Inset: High angle annular dark-field images.

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