



Plasmonics sheds light on the nanotechnology of daguerreotypes

Naomi J. Halas^{a,b,c,d,e,f,1}

The capturing of images has become one of our most universal and commonplace technologies. As a digital electronic technology, it has permanently transformed society by revolutionizing personal recording and interpersonal communication. It has also revolutionized modern science, changing the way data are obtained and expanding our ability to study complex physical and biological processes. It is easy to forget that, in the recent past, the capturing of static and dynamic images involved time-consuming multistep chemical processes. The chemical recording of images begins with the preparation of a surface with photoactive chemicals that create regions of contrast upon exposure to light or, alternatively, realistic coloration patterns corresponding to the captured image, followed by additional chemical processing steps that would slow or altogether halt the photoactive chemistry, preserving the image as a relatively permanent record. The very first chemically captured images were demonstrated by Daguerre in the 1830s and dominated the first era of photography until more streamlined methods were developed (Fig. 1A). These first images have unique optical characteristics, including high resolution across their contrast range, a high sensitivity to viewing angle, and occasionally, subtle coloration. Because of the long exposure times required for capturing an image, the subject matter was frequently buildings or landscapes imaged under natural lighting, and many of these images show the surprisingly realistic coloration of a blue sky background. The subject matter of these earliest photographic images—daguerreotypes—have in many cases been permanently altered or even destroyed by natural and human events, making many of them invaluable historical records. Our understanding of the underlying physical and chemical processes that constitute these first images is essential for the development of effective preservation methods. Until now, however, the actual nanometer-scale physical and chemical composition that results in the unique optical

properties of daguerreotypes has remained essentially unknown. In PNAS, Schlather et al. (1) report a detailed study that elucidates the nanoscale origin of the major characteristics of daguerreotype images. Their unique sensitivity to viewing angle provides a critical clue to the nature of the chemistry of daguerreotypes: That the image-rendering chemistry involves the creation of nanoparticles capable of redirecting incident light in a spectrally dependent manner, rather than merely absorbing light and creating a flat contrast, as one would anticipate with molecular chromophores used in subsequent photographic processes. Discovering that metallic nanoparticles formed during exposure to light, giving rise to the characteristics of daguerreotype images (Fig. 1B), and determining precisely how their size, shape, concentration, and chemical concentration determine the unique properties of daguerreotypy, are the essence of their report.

Our ability to understand the optical properties of subwavelength metallic particles lies at the origins of modern electromagnetic theory. Michael Faraday (2) provided the first scientific study of colloidal gold particles, which appear as a deep vivid red when suspended in aqueous solution. Faraday synthesized them accidentally from gold leaf but, through light-scattering experiments, observed that the red-colored medium was likely particulate in nature. Subsequently, Gustav Mie (3) explained the red color of gold nanoparticles by applying Maxwell's equations to the problem of a plane wave incident on a gold sphere much smaller than the wavelength of incident light. The strong resonant absorption of gold nanoparticles is due to their collective electronic resonance, known as their surface plasmon resonance, common to coinage or noble metals. Before the development of efficient computational approaches to solving Maxwell's equations, studies of plasmon-resonant particles was largely limited to systems that could be solved analytically, such as spherical or ellipsoidal solid or multilayered nanoparticles (4–7). With

^aDepartment of Electrical and Computer Engineering, Rice University, Houston, TX 77005; ^bDepartment of Physics and Astronomy, Rice University, Houston, TX 77005; ^cDepartment of Chemistry, Rice University, Houston, TX 77005; ^dLaboratory for Nanophotonics, Rice University, Houston, TX 77005; ^eSmalley–Curl Institute, Rice University, Houston, TX 77005; and ^fDepartment of Materials Science and NanoEngineering, Rice University, Houston, TX 77005

Author contributions: N.J.H. wrote the paper.

The author declares no conflict of interest.

This open access article is distributed under [Creative Commons Attribution-NonCommercial-NoDerivatives License 4.0 \(CC BY-NC-ND\)](https://creativecommons.org/licenses/by-nc-nd/4.0/).

See companion article on page 13791.

¹Email: halas@rice.edu.

Published online June 25, 2019.

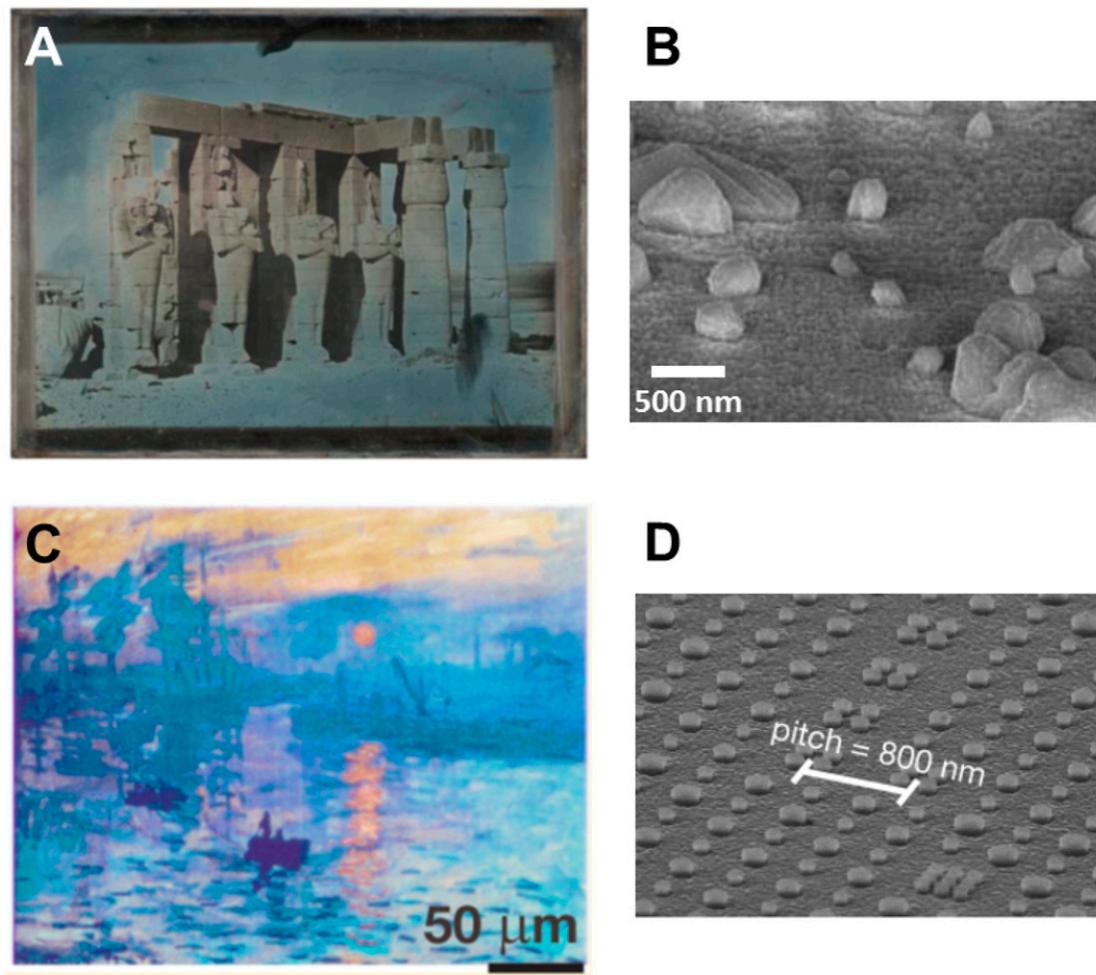


Fig. 1. Examples of 19th- and 21st-century images composed of plasmonic nanoparticles and nanostructures. (A) Daguerreotype *Ramesseum, Thebes, 1844*. Girault de Prangey, The Metropolitan Museum of Art. Purchase, Mr. and Mrs. John A. Moran Gift, in memory of Louise Chisholm Moran, Joyce F. Menschel Gift, Joseph Pulitzer Bequest, 2016 Benefit Fund, and Gift of Dr. Mortimer D. Sackler, Theresa Sackler, and Family, 2016 (2016.604). (B) Representative scanning electron microscope (SEM) image of Ag–Hg nanostructures deposited on Ag support film that constitutes the daguerreotype image. Reprinted with permission from ref. 1. (C) Realistic reproduction of Monet’s *Impression, Sunrise* using an expanded palette of colors composed of aluminum nanostructures. Reprinted with permission from ref. 20. Copyright 2014 American Chemical Society. (D) Tilted SEM image of a region of nanoparticles that constitutes the image in C. Reprinted with permission from ref. 20. Copyright 2014 American Chemical Society.

the far more recent availability of numerical modeling approaches such as finite-difference time-domain (8), finite-element or boundary-element methods, more complex geometries, such as metallic nanoparticles of arbitrary shape on extended metallic substrates of arbitrary thickness, could be accurately analyzed. In combination with advances in chemical synthesis and planar fabrication of metallic nanoparticles and nanostructures, this has resulted in the development of the field of plasmonics, one of the most active areas of modern optics (9–12). These modern computational methods, combined with electron microscopy to accurately image the constituent nanoparticles that create the image, are essential for achieving an understanding of daguerreotype image characteristics.

The properties of plasmonic nanoparticles are strongly modified when positioned on an underlying substrate, whether the substrate material is either dielectric or metallic (13–15). They are also controlled by nanoparticle size, shape, orientation, and chemical composition (16–18). In the context of daguerreotypy, the development process involves the nucleation and growth of Ag–Hg alloyed nanoparticles on an underlying Ag photographic plate. The size and

density of the nanoparticles resulting from the development process differ depending upon illumination properties, creating the areas of contrast that constitute the replicated image. The exquisite spatial resolution characteristic of daguerreotype images results from the nanoscale variations of the nanoparticles that constitute the developed image. With our current understanding of plasmonics has come revolutionary advances in the design and use of plasmonic nanostructures for permanent color printing (19, 20). By control of nanoparticle size, shape, orientation, and interparticle distances, plasmonic pixels can be fabricated that span the visible region of the spectrum, composing complex images (Fig. 1 C and D).

If the understanding established in this article had been available much earlier, would photography have evolved to incorporate more and different types of plasmonic media, materials, and effects as modern chemical photography moved forward? One can only speculate about the possible evolution of daguerreotypy in the overall development of photography if this had been the case. Clearly, in recent years, there have also been many important discoveries of new light-driven effects involving plasmonic nanoparticles that include the tuning of plasmonic nanoparticles to

different colors (21), to plasmonic systems that can modify nearby chromophores, changing their light-absorbing properties (22) or their fluorescence lifetimes (23). Recent advances in plasmonic photocatalysis have greatly expanded our understanding of how plasmonic nanoparticles and nanostructures can promote chemical reactions, lower reaction barriers, and determine reaction outcomes (24–27). Entirely new light-induced chemistries, due to plasmonics, are being identified (25, 28–30). If these chemistries had been available during earlier eras of chemical image capture, those technologies may have been substantially expanded.

Of course, chemical methods of recording images have been surpassed by electronic ones, leaving the use of these earlier chemistry-based photographic approaches to smaller communities, such as that of artistic photography. In this modern era of electronic image acquisition and storage, we see important emerging roles for plasmonic nanoparticles and nanostructures

in expanding imaging device capabilities (31–33). Plasmonic nanostructures can be used as active nanoscale antennas to respond selectively to only certain wavelength bands of light and can facilitate spectrally selective photodetection and image acquisition (34–36). Plasmonics in electronic imaging systems will grow in importance even further as imaging systems extend to regions of the spectrum beyond visible light, where chemically specific information can be captured in an image. Plasmonics can contribute to light detection systems by replacing expensive low-bandgap semiconductors with less expensive and more sustainable silicon-based systems. In these cases, light interaction is controlled by the properties of the plasmonic nanostructures themselves. In a very real sense, plasmonics has provided an electronic analog of the plasmonic nanostructures that we now know to be the underlying elements of the very first method of image capture: The daguerreotype.

- 1 A. E. Schlather, P. Gieri, M. Robinson, S. A. Centeno, A. Manjavacas, Nineteenth-century nanotechnology: The plasmonic properties of daguerreotypes. *Proc. Natl. Acad. Sci. U.S.A.* **116**, 13791–13798 (2019).
- 2 M. Faraday, The Bakerian Lecture: Experimental relations of gold (and other metals) to light. *Philos. Trans. R. Soc. Lond.* **147**, 145–181 (1857).
- 3 G. Mie, Articles on the optical characteristics of turbid tubes, especially colloidal metal solutions. *Ann. Phys.* **25**, 377–445 (1908).
- 4 A. L. Aden, M. Kerker, Scattering of electromagnetic waves from 2 concentric spheres. *J. Appl. Phys.* **22**, 1242–1246 (1951).
- 5 D. Atlas, M. Kerker, W. Hitschfeld, Scattering and attenuation by non-spherical atmospheric particles. *J. Atmos. Terr. Phys.* **3**, 108–119 (1953).
- 6 C. F. Bohren, How can a particle absorb more than the light incident on it. *Am. J. Phys.* **51**, 323–327 (1983).
- 7 A. E. Neeves, M. H. Birnboim, Composite structures for the enhancement of nonlinear-optical susceptibility. *J. Opt. Soc. Am. B* **6**, 787–796 (1989).
- 8 A. Taflove, M. E. Brodwin, Numerical-solution of steady-state electromagnetic scattering problems using time-dependent maxwells equations. *IEEE Trans. Microw. Theory Tech.* **23**, 623–630 (1975).
- 9 N. C. Lindquist, P. Nagpal, K. M. McPeak, D. J. Norris, S. H. Oh, Engineering metallic nanostructures for plasmonics and nanophotonics. *Rep. Prog. Phys.* **75**, 036501 (2012).
- 10 S. A. Maier, H. A. Atwater, Plasmonics: Localization and guiding of electromagnetic energy in metal/dielectric structures. *J. Appl. Phys.* **98**, 01101 (2005).
- 11 M. Pelton, J. Aizpurua, G. Bryant, Metal–nanoparticle plasmonics. *Laser Photonics Rev.* **2**, 136–159 (2008).
- 12 M. I. Stockman, Nanoplasmonics: Past, present, and glimpse into future. *Opt. Express* **19**, 22029–22106 (2011).
- 13 P. K. Aravind, H. Metiu, The effects of the interaction between resonances in the electromagnetic response of a sphere-plane structure—applications to surface enhanced spectroscopy. *Surf. Sci.* **124**, 506–528 (1983).
- 14 M. W. Knight, Y. Wu, J. B. Lassiter, P. Nordlander, N. J. Halas, Substrates matter: Influence of an adjacent dielectric on an individual plasmonic nanoparticle. *Nano Lett.* **9**, 2188–2192 (2009).
- 15 F. Le et al., Plasmons in the metallic nanoparticle-film system as a tunable impurity problem. *Nano Lett.* **5**, 2009–2013 (2005).
- 16 L. M. Liz-Marzán, Tailoring surface plasmons through the morphology and assembly of metal nanoparticles. *Langmuir* **22**, 32–41 (2006).
- 17 A. Comin, L. Manna, New materials for tunable plasmonic colloidal nanocrystals. *Chem. Soc. Rev.* **43**, 3957–3975 (2014).
- 18 R. W. Yu et al., Structural coloring of glass using dewetted nanoparticles and ultrathin films of metals. *ACS Photonics* **3**, 1194–1201 (2016).
- 19 A. Kristensen et al., Plasmonic colour generation. *Nat. Rev. Mater.* **2**, 16088 (2016).
- 20 S. J. Tan et al., Plasmonic color palettes for photorealistic printing with aluminum nanostructures. *Nano Lett.* **14**, 4023–4029 (2014).
- 21 R. Jin et al., Photoinduced conversion of silver nanospheres to nanoprisms. *Science* **294**, 1901–1903 (2001).
- 22 K. A. Willets, Probing nanoscale interfaces with electrochemical surface-enhanced Raman scattering. *Curr. Opin. Electrochem.* **13**, 18–24 (2019).
- 23 H. Hu, H. Duan, J. K. W. Yang, Z. X. Shen, Plasmon-modulated photoluminescence of individual gold nanostructures. *ACS Nano* **6**, 10147–10155 (2012).
- 24 P. Christopher, H. Xin, S. Linic, Visible-light-enhanced catalytic oxidation reactions on plasmonic silver nanostructures. *Nat. Chem.* **3**, 467–472 (2011).
- 25 E. Cortés, Activating plasmonic chemistry. *Science* **362**, 28–29 (2018).
- 26 D. F. Swearer et al., Heterometallic antenna-reactor complexes for photocatalysis. *Proc. Natl. Acad. Sci. U.S.A.* **113**, 8916–8920 (2016).
- 27 L. Zhou et al., Quantifying hot carrier and thermal contributions in plasmonic photocatalysis. *Science* **362**, 69–72 (2018).
- 28 U. Aslam, V. G. Rao, S. Chavez, S. Linic, Catalytic conversion of solar to chemical energy on plasmonic metal nanostructures. *Nat. Catal.* **1**, 656–665 (2018).
- 29 A. E. Schlather et al., Hot hole photoelectrochemistry on Au@SiO₂@Au nanoparticles. *J. Phys. Chem. Lett.* **8**, 2060–2067 (2017).
- 30 J. M. Dieterich, E. A. Carter, Quantum solutions for a sustainable energy future. *Nat. Rev. Chem.* **1**, 0032 (2017).
- 31 H. A. Atwater, A. Polman, Plasmonics for improved photovoltaic devices. *Nat. Mater.* **9**, 205–213 (2010).
- 32 N. I. Zheludev, Y. S. Kivshar, From metamaterials to metadevices. *Nat. Mater.* **11**, 917–924 (2012).
- 33 J. Olson et al., High chromaticity aluminum plasmonic pixels for active liquid crystal displays. *ACS Nano* **10**, 1108–1117 (2016).
- 34 S. P. Burgos, S. Yokogawa, H. A. Atwater, Color imaging via nearest neighbor hole coupling in plasmonic color filters integrated onto a complementary metal-oxide semiconductor image sensor. *ACS Nano* **7**, 10038–10047 (2013).
- 35 B. Y. Zheng, Y. Wang, P. Nordlander, N. J. Halas, Color-selective and CMOS-compatible photodetection based on aluminum plasmonics. *Adv. Mater.* **26**, 6318–6323 (2014).
- 36 A. Dorodnyy et al., Plasmonic photodetectors. *IEEE J. Sel. Top. Quantum Electron.* **24**, 4600313 (2018).