

Gold in a Metallic Divided State—From Faraday to Present-Day Nanoscience**

Peter P. Edwards* and John Meurig Thomas*

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Dedicated to Professor Roald Hoffmann on the occasion of his 70th birthday

This article celebrates the 150th anniversary of the reading of a ground-breaking lecture by Michael Faraday to the Royal Society of London on the interaction of light with metal particles that are “very minute in their dimensions.” Faraday’s systematic studies and perceptive interpretations marked the birth of modern colloid chemistry, and thence the emergence of the nanoscience and nanotechnology of gold nanoparticles and self-assembled monolayers, a field of intense current activity worldwide.

Background

On February 5, 1857, Michael Faraday (see photo in Figure 1) delivered the Bakerian Lecture of the Royal Society entitled “Experimental Relations of Gold (and other Metals) to Light”.^[1] It described a vast repository of experi-



Figure 1. Portrait of Michael Faraday, age 39, by H. W. Pickersgill (Royal Institution of Great Britain).

ments with metal hydrosols, thin metal films, metal island films, and aerosols, performed mainly with gold, but also with silver, copper, platinum, tin, iron, lead, zinc, palladium, aluminum, rhodium, iridium, mercury, and arsenic. Although the term colloid was not coined until 1861 (by Graham^[2]), Faraday’s is a landmark paper because it heralded the birth of modern colloid science, especially with respect to the behavior of comminuted metals, their suspensions, and the attendant formation of thin films of metal.

On page 160 of his paper, commenting on the fact that his more dilute preparations were clear, Faraday goes on to say: “The latter, when in their finest state, often remain unchanged for many months, and have all the appearance of

solutions. But they never are such, containing in fact no dissolved, but only diffused gold. The particles are easily rendered evident, by gathering the rays of the sun (or a lamp) into a cone by a lens, and sending the part of the cone near the focus into the fluid; the cone becomes visible, and though the illuminated particles cannot be distinguished because of their minuteness, yet the light they reflect is golden in character, and is seen to be abundant in proportion to the quantity of solid gold present”. This is the first clear description^[3] of what is now called the Tyndall effect (Tyndall’s own work^[4] on this effect was not published until 1869, some 15 years after Faraday’s).

Faraday explored (qualitatively, as was his invariable practice^[5]) the relations between matter, on the one hand, and electrical, magnetic, and optical phenomena on the other. He pondered the question: “to what extent experimental trials might be devised ... which might contradict, confirm, enlarge or modify ... that wonderful production of the human mind, the undulatory theory of light”. He reasoned that there was merit in observing the action of light on metal particles which were small compared to the wavelength of light; gold sprang to mind because “known phenomena appeared to indicate that a mere variation in the size of its particles gave rise to a variety of resultant colours”. Faraday was familiar with the nature of ruby glass, which had been used for centuries for stained glass windows, and Purple of Cassius,^[7] which for a time was presumed to possess medicinal qualities (supposedly the Elixir of Life). Each of these derives its color and properties from the presence of colloidal gold of various diameters.

[*] Prof. Dr. P. P. Edwards
Inorganic Chemistry Laboratory
University of Oxford
South Parks Road, Oxford OX1 3QR (UK)
Fax: (+44) 1865-272-656
E-mail: peter.edwards@chem.ox.ac.uk
Homepage: <http://www.chem.ox.ac.uk/researchguide/ppedwards.html>

Prof. Dr. Sir J. M. Thomas
Department of Materials Science and Metallurgy
University of Cambridge
Pembroke Street, Cambridge CB2 3QZ (UK)
Fax: (+44) 1223-334-567
E-mail: jmt2@cam.ac.uk

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Faraday prepared his colloidal dispersions of gold by a two-phase preparation, reducing an aqueous solution of a gold salt, such as sodium tetrachloroaurate ($\text{Na}[\text{AuCl}_4]$), with a solution of phosphorus in carbon disulfide, since phosphorus was regarded as “a very favourable agent”. The reduction proceeds rapidly at room temperature and the bright yellow color of the $\text{Na}[\text{AuCl}_4]$ solution is replaced within minutes of mixing by the deep ruby coloration characteristic of colloidal gold. Faraday concluded that the gold was dispersed in the liquid in a very finely divided form, the presence of which could be detected by the reddish opalescence when a narrow intense beam of light is passed through the liquid (Figure 2). With perhaps just a hint of frustration, Faraday noted: “The state of division of these particles must be extreme; they have not as yet been seen by any power of the microscope”.

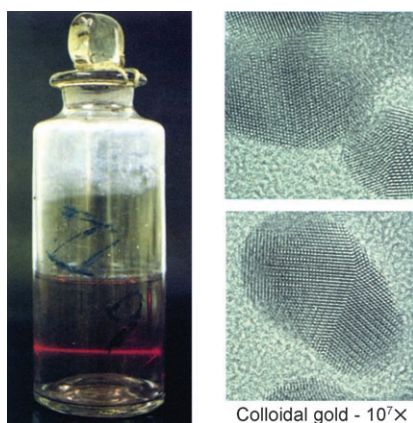


Figure 2. Faraday's colloidal suspension of gold (his “gold fluid”^[1]) with a red laser beam clearly visible by the Tyndall effect, plus high-resolution transmission electron microscope images of individual colloidal gold particles. (Adapted from J. M. Thomas, *Nova Acta Leopoldina*, **2003**, 88, 109–139).

Nearly a century later electron microscopic investigations^[8] on Faraday's ruby-colored gold colloids did indeed reveal that these preparative routes produce particles of gold of average diameter (6 ± 2) nm; a later high-resolution electron microscopic study^[9] showed that Faraday's fluid preparations^[10] contain a distribution of particle sizes, some with diameters as small as 3 nm, others as large as 30 nm. Faraday's

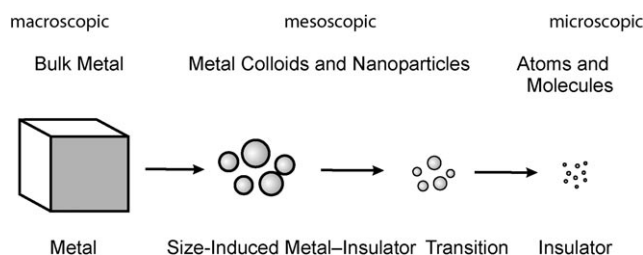


Figure 3. A metal divided; a representation of the fragmentation or division of a bulk metal illustrating the macroscopic, mesoscopic, and microscopic regimes of matter. (Modified from P. P. Edwards, *Proc. Indian Natl. Sci. Acad. Part A* **1986**, 52, 265–291.)

systematic studies of gold therefore led him to conclude that “the gold is reduced in exceedingly fine particles, which becoming diffused, produce a beautiful ruby fluid ... the various preparations of gold, whether ruby, green, violet or blue in colour, ... consist of that substance in a metallic divided state.”

A schematic representation of the successive division or fragmentation of a single macroscopic grain of, for example, bulk gold into the mesoscopic and microscopic particle size regimes is given in Figure 3.

The recent explosion of activities centered on the nanoscience and nanotechnology of gold, prompted by important synthetic and investigative developments of gold nanoparticles and self-assembled thin films, has led to a renaissance of interest in this area initiated by Faraday. Equally spectacular developments in the unexpected, extraordinary catalytic performance of nanoparticulate gold have also spawned worldwide research activity. As an indicator of the recent “reawakening” of

activities on colloidal and nanoparticulate gold, we show in Figure 4 the timeline of citations relating to Faraday's original Bakerian Lecture of 1857 together with similar citation data for papers with “gold colloids” and “gold nanoparticles”. In this special anniversary year of Faraday's insightful paper, one can report the true emergence of a major new activity in the science and technology of gold particles that are “very minute in their dimensions.”

On this historic anniversary of Faraday's Bakerian Lecture, we present a brief overview in this Essay of ongoing research—and controversies—into several forefront research areas centered around gold in a state of extreme division.

The Remarkable Catalytic Performance of Nanoparticles of Gold^[11]

Because the properties of all solids depend on the type of motion that its electrons may execute,^[12,13] which in

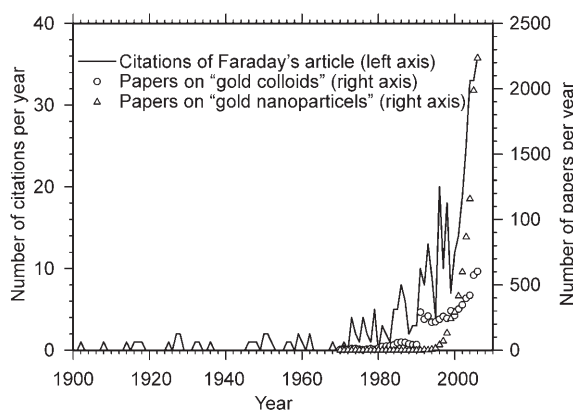


Figure 4. The time evolution of citations from Faraday's 1857 Bakerian Lecture together with citation data for “gold colloids” and “gold nanoparticles”. Data assembled by Drs. Vladimir Kuznetsov (Inorganic Chemistry Department, Oxford) and Werner Marx (Max Planck Institute for Solid State Research, Stuttgart).

turn depends on the space available for their motion (that is, their degree of spatial confinement), it is to be expected that materials of nanometer dimension will exhibit unusual properties governed by their precise size. Optical, thermal, and chemical properties are indeed much influenced by the dimension when it falls in the nanoscale range.

Among the first reports of exceptional catalytic activity displayed by nanoparticles of gold were the channeling phenomena observed when single crystals of graphite, decorated by minute particles of Au, are rapidly oxidized in air with channels excavated (by gasification) by the nanoglobules of the metal (Figure 5).^[14] In 1987, however,

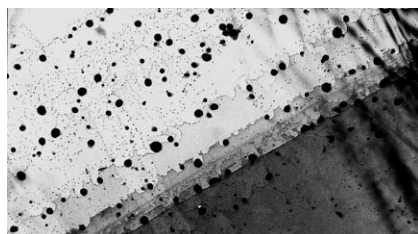


Figure 5. In the presence of 1 bar of air, monatomic steps on the surface of a graphite single crystal are gasified (at ca. 650 °C) preferentially where they are decorated by nanoparticles of gold (ca. 5 nm diameter). These nanoparticles excavate shallow channels at the surface. This electron micrograph shows globules of gold (ca. 30 nm diameter formed by coalescence of small ones) at the completion of the period of oxidation. Fresh, smaller nanoparticles (ca. 5 nm) were then deposited to decorate the excavated channels.^[14]

came the dramatic report of Haruta et al.,^[15] who found that nanoparticles of Au (2 to 4 nm in diameter), uniformly dispersed on an oxide support such as Fe₂O₃ or NiO, could catalyze the conversion of carbon monoxide in air or oxygen at temperatures as low as –77 °C. Later, gold nanoparticles, acting alone, were found to catalyze the selective oxidation of alcohols^[16] in water and (in alkaline water) to oxidize carbon monoxide^[17] at room temperature.

In the intervening years many other commercially significant reactions such as the epoxidation of propylene have been found to be catalyzed by nanoparticles of gold. But perhaps the most important, from the viewpoint of sustainable development, is the recent

work of Christensen et al.,^[18] who showed how nanoparticle gold, supported on the inert spinel MgAl₂O₄, very efficiently leads to the formation of acetic acid by aqueous-phase oxidation of ethanol in air. This transformation is of profound significance in the context of sustainability since materials such as acetic acid and ethylene (which are currently converted industrially by addition^[19] to yield the important solvent ethyl acetate) are each fossil-derived. Nanoparticle gold catalysts now offer a means of converting^[18] biomass, via ethanol, into other commodity-scale products besides acetic acid, for example, ethylene butadiene and acetaldehyde.

Although the general view that nanoparticles should exhibit properties different from those of bulk analogues is universally accepted, the degree of difference between bulk and nanoparticle gold is exceptional. Bulk and nanoparticle platinum and palladium show many similarities catalytically;^[20] this is not so for gold, which, in its extended, single-crystal state does not dissociatively chemisorb either O₂ or H₂. Yet Au nanoparticles exhibit exceptional activities in oxidation with O₂, and they have recently been found^[11] to catalyze the production of hydrogen peroxide from mixtures of O₂ and H₂. Why is this so? Many plausible explanations abound.

At first it was thought that the (oxide) support played a crucial part in providing either charge or oxygen or water to boost the catalytic activity of the gold. But definitive work by Lopez et al.,^[21] who compared the catalytic performance of Au nanoparticles on reducible oxides such as Fe₂O₃, TiO₂, and NiO with that on nonreducible oxides such as SiO₂, Al₂O₃, and MgAl₂O₄, have ruled out this explanation as being of no more than of minor consequence. Among the other popular proposals are: 1) the presence of a metal-to-nonmetal transition in very small plate-like particles;^[22] 2) the existence of bilayers (as opposed to monolayers) of Au, with high intrinsic activity associated with quantum confinement effects;^[23] 3) strain in Au arising from the mismatch of the lattices at the interface with the support;^[24] 4) the presence of cationic Au in the nanoparticles;^[25] and 5) the effect of low-coordination sites of

Au atoms and the roughness of the nanoparticle surface.^[21,26]

Thorough analysis,^[21] focusing on the oxidation of carbon monoxide, points to the view that the presence of low-coordination sites on the surface of many small particles is one of the key determinants. This certainly seems to be more important^[26] than the quantum size effect. A compilation of measured CO oxidation activities for nanoparticle gold catalysts as a function of particle size reveals the enormous effect of the particle dimension (Figure 6): for particles in the range 2 to

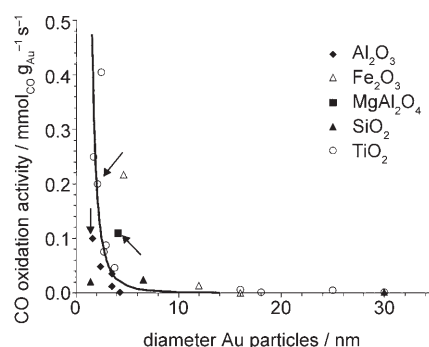


Figure 6. Plot showing the onset of high catalytic activity in CO oxidation in nanoparticles of gold.^[21] (The three points marked by arrows are from the measurements of Lopez et al.,^[21] the remainder are from the work of several other investigators.)

4 nm the catalytic performance exceeds by more than two orders of magnitude that for particles 20 to 30 nm in size. By comparison, the influence of support materials is rather modest, and whilst reducible supports yield higher activities than the nonreducible ones, the effect is small, amounting to a factor of 2 to 4. This shows that the effects of charge or oxygen transfer from the support are not crucial. Figure 6 unmistakably indicates that a property directly related to the size of the gold nanoparticles is the dominant effect in the remarkable catalytic performance of gold.

Using density functional theory (DFT), Lopez and Nørskov^[27] have calculated the adsorption energy of CO and O on a number of different gold surfaces and analyzed the origin of bonding trends. It transpires that small clusters of the metal, unlike close-packed gold surfaces, can form strong bonds to a variety of adsorbates, includ-

ing CO, H₂, and O₂, the latter both dissociatively and molecularly. The strengths of the Au–CO and Au–O bonds vary strongly with the coordination number. Whereas atoms of gold in the surface of an extended (111) plane have electronic d states that are so low in energy that they are unable to interact strongly with oxygen states (so that O₂ does not dissociate on Au(111)), atoms of gold at steps and corners of nanoparticles have a lower coordination number and hence possess d states that are closer to the Fermi level, thus leading to a strong interaction.

Computed reaction profiles^[27] for CO oxidation on a Au₁₀ nanoparticle composed of three close-packed atoms on top of seven underlying ones also prove revealing. Two possible reaction paths within the traditional Langmuir–Hinshelwood (LH) mechanism were considered: one wherein O₂ is dissociatively chemisorbed, the other wherein it is molecularly adsorbed, as a peroxo group. Both types of LH mechanisms are found to be extremely facile on the Au₁₀ cluster, and reaction barriers are less than 0.8 eV, indicating that surface oxidation should take place well below room temperature.

Another quantum-mechanical investigation,^[28] using the Born–Oppenheimer local-spin-density molecular dynamics method (BOLSDMD) also explored the well-known Eley–Rideal (ER) mechanism of surface catalysis, in which a collision between a gaseous CO molecule and an adsorbed peroxo moiety leads to oxidation. Here it transpired that both the ER and LH modes of catalysis should proceed rapidly on Au₈ clusters supported on a magnesium oxide substratum.

Debates as to the root cause of the remarkable catalytic performance of nanoparticle gold still rage,^[29] as do the exciting new applications opened by its existence.^[11] One cannot but feel that ever more critical experiments under in situ conditions in addition to quantum calculations are called for. After all, it was only very recently discovered^[30] by in situ studies at ambient pressures that the time-hallowed LH mechanism for the oxidation of carbon monoxide on palladium (previously studied at extremely low pressures) appear to be supplanted by the Mars–van Krevelen

(sacrificial oxide) mechanism, wherein a thin veneer of palladium oxide releases its bulk oxygen for catalysis. This was discovered by experiments conducted under in situ conditions at atmospheric pressure.

Experimental steps in this direction—but not yet fully in situ—have very recently been taken by Hutchings et al.^[25] and by Shaikhutdinov et al.^[31] The first of these studies (combining the techniques of ¹⁹⁷Au Mössbauer and X-ray absorption spectroscopies with high-resolution electron microscopy) has uncovered clear evidence that cationic gold plays a crucial role in catalyzing CO oxidation at room temperatures; and the second study, working with in situ scanning electron microscopy using CO + O₂ at rather lower pressures, showed that sintering of nanoparticle gold (on both ceria and titania supports) occurs during CO oxidation. Such studies, carried out under more realistic in situ conditions,^[32] hold the key to a deeper understanding of the extraordinary catalytic behavior of “divided” gold.

The Size-Induced Metal–Insulator Transition^[33, 34, 53]

Within our modern vision of the electronic structure of the metallic state, it is entirely reasonable to suppose that in the process of subdivision of a bulk element such as gold (Figure 3), a stage will be reached when the individual particle does not behave like a smaller, identical copy of the bulk metal itself.^[35, 36] We now know that the characteristic properties of the metallic state require the existence of a partially filled electronic energy band with an energy-level spacing sufficiently small to allow the facile flow of electrical current.

The electron-energy spectrum of a metal sample of macroscopic size is usually considered to be a continuum. However, for a metal particle of mesoscopic size (around 1–10 nm), with a small number of conduction electrons, the assumption of an electron-energy continuum becomes invalid and the electronic energy levels become discrete. The average spacing (δ) between adjacent electronic energy levels, known as the Kubo gap, increases inversely

with the total number of conduction electrons (N) in a particle: $\delta \approx E_F/N$, where E_F is the Fermi energy. The smaller the particle size is, the larger the energy separation between allowed energy levels is, and at low temperatures this level spacing may become comparable to thermal energy, kT . For the smaller particles within the nanoparticle size regime, the consequence of $\delta \approx E_F/N$ may even be evident at room temperature. This leads to strongly size-dependent structural, optical, and electronic properties and, ultimately, to the complete cessation of metallic conductivity *within* a particle.^[36] Importantly, key physical properties can be tailored for applications in information storage devices and optoelectronics simply by varying the individual metal particle size.^[37, 38]

There is also considerable theoretical interest^[36] in understanding the electronic and chemical behavior of individual metal nanoparticles near a presumed critical diameter for the inevitable size-induced metal-to-insulator transition (SIMIT; Figure 3). However, attempts to understand and harness the properties of divided gold were hitherto severely limited by the absence of reliable synthetic routes to monodispersed gold particles of tailored dimensions.

The synthesis of stable, isolable thiolate-monolayer-protected gold colloids and clusters by Schiffrin, Brust, and colleagues just a dozen years ago represented a seminal contribution in the development of modern metal colloid science (Figure 7).^[39] These authors showed that the classical two-phase

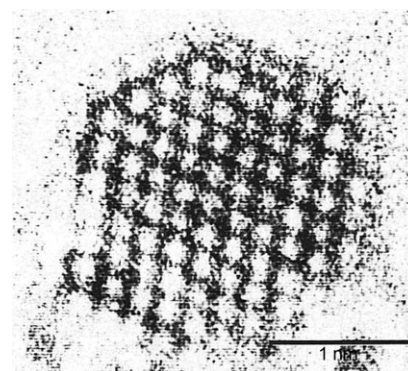


Figure 7. A high-resolution transmission electron microscopy (HRTEM) image of an individual thiolate-protected gold particle.

colloid preparation of Faraday could be combined with contemporary phase-transfer chemistry to yield, in a simple procedure, very small colloidal gold particles coated/protected by a monolayer of functional thiolate ligands. This synthetic route has become an extremely popular starting point for a particularly broad range of metal colloid and nanoparticle activities.^[40]

Such individual mesoscopic conductors, well-separated from each other by an insulating monolayer sheath constitute ideal systems to study the size confinement of metallic, conduction electrons. According to arguments first advanced by Fröhlich^[41] (interestingly, some 70 years ago) and then developed extensively by Kubo,^[42] the electrical conductivity *within* a particle is expected to decrease rapidly when the characteristic de Broglie wavelength of the conduction electrons is of the same order as the physical dimension of the particle itself. This can be viewed as electron localization throughout the tiny particle of metal as valence (conduction) electrons become highly confined and quantum effects dominate.

Measuring the electrical conductivity of such individual mesoscopic and microscopic particles obviously requires the use of novel experimental techniques. The microwave absorption procedure is a unique method of measuring the conductivity of separated, dispersed particles that requires no physical electrode contact with the sample and uses an observation frequency high enough to avoid interparticle charge-carrier hopping.

Recent experiments^[43] on individual gold colloid particles of diameters close to 4 nm revealed electrical conductivities within the particles of a factor 10^7 below that of the corresponding bulk metal. This is a striking example of a SIMIT in tiny particles of gold arising from the localization of conduction electrons owing to size-induced confinement.

Similarly, copper particles grown by progressive, controlled reduction of isolated copper oxide particles reveal that below a shell thickness of 3 nm, the copper shell conductivity has a value below Mott's so-called "minimum metallic conductivity" and shows clear non-metallic behavior (i.e., although each

particle has a measurable conductivity, it is far below that of bulk, metallic copper and exhibits a completely different temperature dependence).^[44]

However, recent studies of vacuum-evaporated gold nanoparticles without surface stabilizing/protecting agents reveal the presence of a characteristic plasmon peak in the optical absorption spectrum, reflecting the continuing metallic nature of the gold particles, even for diameters as small as 0.25 nm.^[45] This critical finding vividly illustrates the subtlety, and importance, of surface chemical effects in effecting—or indeed enhancing—any SIMIT.^[46]

A striking feature of thiol-stabilized gold colloids is their tendency to spontaneously form highly ordered 2D and 3D thin-film arrays of metal particles simply by slow evaporation of the host organic solvent on a suitable substrate (Figure 8).^[47,48] In recent years this has

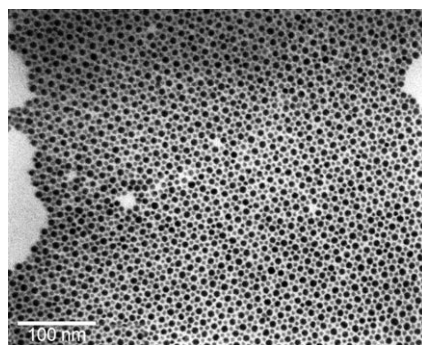


Figure 8. Self-assembled thin films of nanoparticulate gold.^[47]

become a field of intense research worldwide. Of greatest interest is the potential to precisely tune both the optical and electronic properties of the films by controlling both the individual particle size and the interparticle spacing, the latter now with molecular-scale precision through the choice of appropriate protecting or capping molecules surrounding the gold particle.^[49,50]

In a recent timely contribution Pelka et al. reported extensive studies on self-assembled thin films of gold nanoparticles of 4–5 nm diameter, prepared on glass, using aliphatic dithiols of different hydrocarbon chain lengths as interparticle linker molecules.^[51] Importantly, the dc conductivity of these films (σ), measured down to 4.2 K, shows a strong

dependence on the intervening spacer length, effectively traversing the different mechanisms of electrical conductivity through the films: from thermally activated electron hopping between gold particles in films with longer-chain linker molecules, changing to electron tunnelling at low temperatures, ultimately to become metallic when the interparticle linker is shorter (Figure 9).

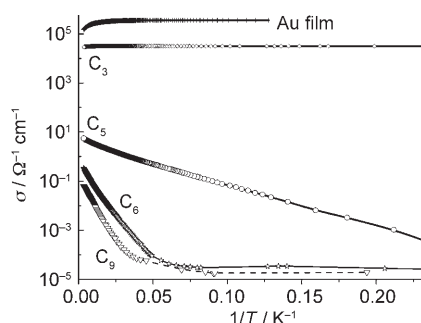


Figure 9. Temperature dependence of σ measured for six consecutively deposited layers of cross-linked gold clusters as compared to that of a 30-nm thiol-protected continuous gold film deposited on glass by the techniques of molecular-beam epitaxy.^[51] Note: the sample C_3 has the shortest cluster–cluster distance, and an increase in the spacer length occurs for C_3 through C_9 . The materials clearly reveal a transition from metal to insulator from samples C_3 to C_9 .

These results demonstrate quite clearly that the electronic and optical properties of such films can be precisely controlled by changing the interparticle distance to effect the transformation from metallic to insulating (nonmetallic) films of gold. Interestingly, in Faraday's own studies on gold films^[1] he noted: "Very thin films ... did not sensibly conduct the electricity of a single pair of Grove's plates; thicker films did conduct"; this is clearly the forerunner of modern researches on thin films of gold and silver undergoing an insulator-to-metal transition!

Finally, Corbierre et al. have very recently described a fascinating new fabrication method for assembling 1D arrays of gold nanoparticles on surfaces.^[52] This important new innovation combines both top-down (electron-beam lithography) and bottom-up (nanoparticle nucleation and growth) approaches, allowing for the precise patterning of gold nanoparticles in true 1D arrays (Figure 10). Importantly, the

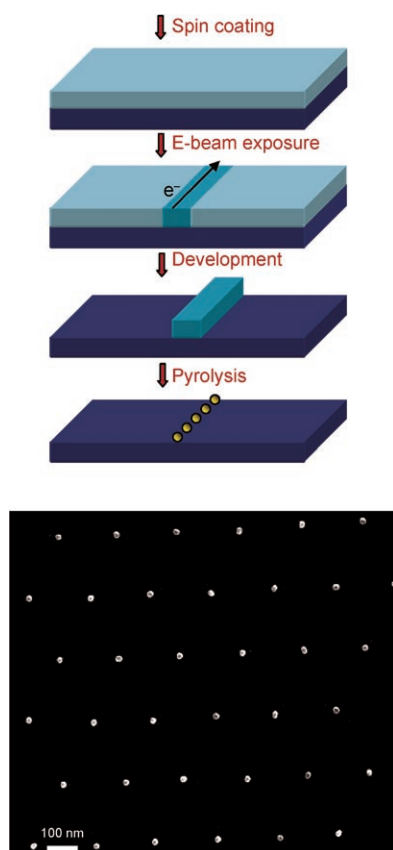


Figure 10. Uniform 1D arrays of tunable gold nanoparticles (orange spheres). Top: schematic representation of the fabrication method; bottom: a field-emission gun scanning electron microscopy (FEG-SEM) image of 20-nm-diameter gold nanoparticles.

interparticle distances, as well as the patterns composed of nanoparticles, are precisely tunable, for example, by varying the electron-beam parameters; this highly versatile technique will surely open many new avenues in plasmonics and electronics.

Concluding Remarks

Faraday's Bakerian Lecture of 1857^[1] was a particularly important event in the development of science and technology. In that famous and influential work, he presented to the world the first systematic study of gold and other metals "in a state of extreme division" as diffused and aggregated gold particles in solution (colloids) and both thin (nonconducting) and thick (conducting) films of gold. Faraday, characteristically modest, described himself as "only an experimentalist"

and investigated these ancient scientific curiosities and offered far-reaching ideas and uniquely perceptive interpretations into the very nature of the metallic, divided state. His profound influences can still be instantly recognized in the modern burgeoning field of nanoscience and nanotechnology based on gold nanoparticles and self-assembled monolayers. These interdisciplinary research activities are now the subject of intense activity worldwide, and show great promise for an extraordinary variety of optical, electronic, magnetic, catalytic, and biomedical applications involving chemistry, physics, biology, and medicine.^[40] It is fitting to celebrate Faraday's monumental contributions over 150 years ago to the nature of gold in its metallic, divided state, for these epitomize his indefatigable searches for connections between curiosity and discovery, basic and applied science (surely, better seen as "science applied"), and imagination and application.

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