

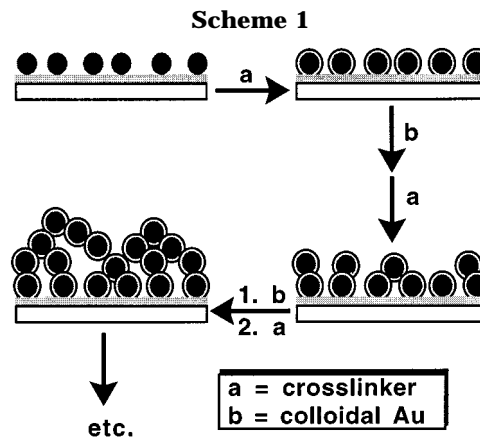
Stepwise Construction of Conductive Au Colloid Multilayers from Solution

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Two-dimensional (2-D) and 3-D arrays of colloidal Au^{1–7} and Ag⁸ nanoparticles have become a popular target in nanometer-scale materials synthesis. A focus of this work has been the optical, electric, and dielectric properties as a function of array structure; of particular interest is the question of when (or if) bulk metal behavior is found. For example, the resistivity of Au nanoparticle arrays separated by organic cross-linkers varies—depending on the particle diameter, the spacer length, and the number of particle layers—from as high as $3.6 \times 10^8 \Omega \text{ cm}$ for a thin film of 2.4-nm diameter Au spaced by 1,16-hexadecanethiol³ to as low as $6 \Omega \text{ cm}$ for 38 layers of 8-nm diameter colloidal Au particles spaced by 1,6-hexanedithiol.⁴ To date, none of the particle arrays have approached the resistivity of pure Au ($2.4 \times 10^{-6} \Omega \text{ cm}$), and none of the electrical or optical properties have been described as a function of the number of particles in the array. We describe herein the optical, electrical, and topographic properties of Au colloid multilayers as a function of particle coverage (θ). Prepared in solution through layer-by-layer assembly, these films are significant in three respects: (i) Au colloid multilayers undergo a large decrease in near-IR transmittance and a nearly million-fold decrease in



resistance (from $>10^7 \Omega$ to $<10^2 \Omega$), behavior analogous to that observed in evaporated, discontinuous Au films.^{9,10} Surprisingly, this change occurs over just a factor of 2 increase in θ . (ii) Twelve layers of 11-nm diameter Au particles spaced by bifunctional, two-carbon cross-linkers exhibit resistivities of $5 \times 10^{-4} \Omega \text{ cm}$, 4 orders of magnitude more conductive than any previously described monolayer-protected Au particle arrays.^{3–5} (iii) To our knowledge, they comprise the first examples of highly conductive Au films of controlled thickness deposited from aqueous solution without any redox chemistry, photochemistry, or heating. As such, they may be of value for electronic device fabrication in solution,¹¹ especially those involving biological molecules.¹²

Scheme 1 depicts the protocol for formation of Au colloid multilayers, a strategy that draws heavily on our previous experiences with surface-confined colloidal Au nanoparticles.² Thus, when a 11-nm diameter¹³ colloidal Au monolayer on a (3-aminopropyl)trimethoxysilane (APTMS)-coated or equivalent mercaptosilane-coated glass slide is exposed to a molecule having two functional groups that bind to or induce flocculation of colloidal Au [2-mercaptoethanol, 2-mercaptoethylamine, HS(CH₂)₆SH, APTMS, poly(vinylpyrrolidone), etc.],¹⁴ immersion in colloidal Au leads to additional particle binding.^{2a} Repetitive dips into bifunctional organic cross-linker and colloidal Au solutions (5–15 min for the cross-linker, 5–60 min for the colloid, with copious rinsing between immersions) rapidly leads to formation of Au colloid multilayers. Note that no interlayer registry of particles is expected. Scheme 1 is very general and can be used with colloidal Au nanoparticles of any diameter, although the lower particle concentrations for standard preparations of both large and small particles lead to longer derivatization times.^{14b}

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(13) Particle dimensions (221 particles sized): $10.7 \text{ nm} \pm 1.3 \text{ nm}$ (long axis); $9.4 \text{ nm} \pm 1.1 \text{ nm}$ (short axis).

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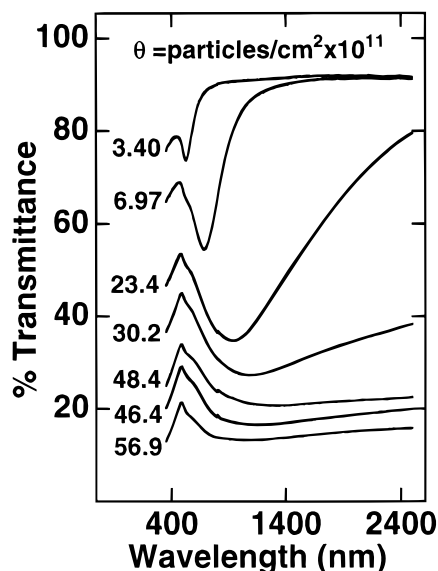


Figure 1. Au particle coverage (θ) dependence of UV-vis/near-IR transmission spectra of Au colloid multilayers [prepared by successive, repeated immersion of a glass slide derivatized with APTMS, and a 11-nm diameter Au colloid monolayer into (a) 4 mM 2-mercaptoethanol (8–10 min) and (b) 17 nM, 11-nm diameter Au (30–60 min)].

Tapping-mode atomic force microscopy (AFM) and field emission scanning electron microscopy (FE-SEM) have been used to monitor the growth of colloidal Au films. Images acquired after repeated exposures to 2-mercaptoethanol/colloidal Au (Supporting Information) indicate a porous geometry, with neither close-packed coverage within a layer (in accord with previous findings)² nor registry between layers. Both AFM and FE-SEM images clearly indicate areas of uninterrupted particle contact after just two 2-mercaptoethanol/Au treatments, suggesting the possibility of macroscopic conductive paths.

Further support for metal-like attributes comes from visible/near-infrared optical transmission spectra (Figure 1), shown as function of θ for samples immersed between 1 and 12 times in 2-mercaptoethanol/11-nm Au.¹⁵ The spectra for low coverages match those previously obtained for small colloidal Au aggregates or immobilized 2-D Au nanoparticle arrays:^{2,16} strongly absorbing in the visible and transparent in the near-infrared. As the particle coverage increases, near-infrared transmission decreases markedly and becomes only weakly wavelength dependent. Similar behavior is seen in thin Au films.⁹ It is remarkable that 12 layers of burgundy-colored, 11-nm diameter colloidal Au particles yield a shiny and reflective surface that, to the eye, is indistinguishable from bulk Au films.

At sufficiently high coverages, Au colloid multilayers undergo an insulator-conductor transition. Figure 2 shows a plot of dc resistance (plotted on a semilog scale) vs θ .¹⁷ Samples containing 25×10^{11} particles/cm² are

(15) Optical spectra were acquired using a Varian Cary 5 spectrophotometer; particle coverages were calculated by atomic absorption measurements (Perkin-Elmer 1100B outfitted with a graphite furnace) on 50% aqueous aqua regia-digested surfaces, assuming all Au particles were prolate spheroids, with $10.7 \times 10.7 \times 9.4$ nm axes.

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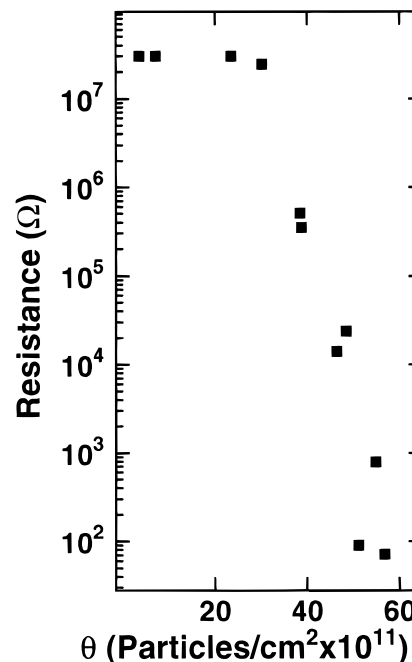


Figure 2. log plot of dc resistance versus Au particle coverage (θ) for Au colloid multilayers. See Figure 1 for details of sample preparation.

insulating, with a resistance in excess of $10^7 \Omega$ (the highest value we can presently measure is 200 M Ω). Increasing θ leads to an enormous decrease in resistance; when θ is doubled to 50×10^{11} /cm², the resistance drops below 100 Ω , a change of over 5 orders of magnitude. Considering the porous nature of these films and the presence of organic adsorbed 2-mercaptoethanol on the particles,¹⁸ these films are remarkably conductive: the most conductive samples (12 treatments) have a resistivity of $5 \times 10^{-4} \Omega$ cm, a value roughly $1/200$ that of pure Au.¹⁹ Au colloid multilayers on glass substrates are thus more conductive than In-doped SnO₂, for example, and can be used for routine voltammetric measurements.^{14a} It is interesting to note that a sample comprising 12 layers of 11-nm diameter Au particles separated by a two-carbon spacer is 4

(17) Two electrical contact pads (≈ 900 Å of Au) of 0.2 cm width and 0.9 cm in length were sputter-coated onto the ends of masked, 2.5-cm length, Au colloid multilayer-coated glass slides, yielding an electrode spacing of 2.1 cm. Resistance measurements were carried out in 2-point probe fashion using a Fluke Digital Multimeter (Model 77). Resistance values measured by this method yielded values ($\pm 2 \Omega$) identical with average values obtained by a home-built four-point probe measurement.¹⁴

(18) The possibility that colloidal Au particles in successive layers “squeeze out” the organic molecules—thereby leading to direct particle contact—can be discounted by several separate lines of reasoning: (i) If such behavior obtained here, it would have been observed in previously reported colloidal Au multilayer films,^{3,4} leading to much lower resistances than those reported. (ii) Au multilayer conductivity is dependent on the alkyl chain length: the lowest measured dc resistance of Au colloid multilayers linked by 2-mercaptoethylamine is a few hundred ohms, and APTMS-linked multilayers are insulators at equivalent particle coverages.^{14b} (iii) Such behavior is inconsistent with AFM and FE-SEM^{14b} data showing the presence of connective paths over large areas after 5–6 exposures to Au. If there were direct particle contact, these samples would conduct, contrary to what is observed.

(19) A typical resistance measured for the most conducting samples was 80 Ω . The cross sectional area, A , was 0.9 cm (width) \times 150 nm (the maximum possible film thickness) = 1.35×10^{-5} cm², and the sample length (L) was 2.1 cm. Using the formula for resistivity (ρ), $\rho = RAL^{-1}$, a value of $\rho = 5.1 \times 10^{-4} \Omega$ cm is calculated. The corresponding value for pure bulk Au at 20 °C is $\rho = 2.44 \times 10^{-6} \Omega$ cm (Weast, R. C., Ed. *CRC Handbook of Chemistry and Physics*, 69th ed.; CRC Press Inc.: New York, 1988; p E-93).

orders of magnitude more conductive than 38 layers of 8-nm diameter Au particles linked by a six-carbon spacer. Electron transfer between particles likely occurs by activated hopping between nearest neighbors, as previously observed for granular metal films.²⁰

The number of particles bound per treatment does not change with particle coverage, evidenced by a nearly linear plot of θ vs number of immersions in Au (Supporting Information). In other words, each step in the multilayer assembly adds the same amount of Au, and as a result the volume fraction (f) of colloidal Au does not appreciably change as function of θ ;^{14,21} similar observations were reported for thiol-capped colloidal Au particles using quartz crystal microgravimetry.⁴ While the exact mechanism of conductivity in these samples has not yet been determined, it is worth noting that the

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(21) The geometry of these films is complex. Nevertheless, we^{14b} and others^{14a} find an essentially linear relationship between *maximum* film height (as measured by AFM) and number of exposures to colloidal Au (with a best-fit slope of 10.6 nm/exposure).^{14b} Likewise, a plot of *mean* film height (again, as measured by AFM) versus number of Au exposures is also roughly linear.¹⁴ The film volume (v) is defined as the product of the cross-sectional area (a , which is constant) and the film thickness (z). If the number of Au treatments is n and $z = yn$ (where y is a constant), then $v = ayn$. The volume fraction f is defined as the ratio of the Au volume (g) to v . Since $g = q\theta a$, where q is the volume per particle (a constant), $\theta =$ the number of particles/cross-sectional area, and a is defined as above, and $\theta = rn$ (where r is a constant, Supporting Information), then $f = g/v = (qrn)/(ayn) = a$ constant. Thus, we conclude that f remains roughly constant. An upper limit of $f \approx 0.5$ can be obtained by integration of light areas in a FE-SEM image and assuming that the volume under each integrated element is completely filled with Au.

volume fraction of Au particles in these samples falls between the 2-D ($f \approx 0.6$) and 3-D ($f \approx 0.3$) percolation regimes.²²

From a materials perspective, the ability to form highly conductive Au surfaces from solution under extremely mild conditions may be of practical value, particularly for devices with molecular components. Likewise, Au colloid multilayers are well-suited to fundamental studies on optical, electric, and dielectric properties of thin Au films, including the effects of particle diameter, alkyl chain length, and temperature.

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Supporting Information Available: Three figures showing (i) AFM images and line scans of Au colloid multilayers (3 and 6 layers), (ii) FE-SEM images of Au colloid monolayers and multilayers (12 layers), and (iii) a plot of θ versus number of Au colloid/2-mercaptoethanol treatments (3 pages). See any current masthead page for ordering information and internet access instructions.

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