

Self-Assembled Gold Nanoparticle Thin Films with Nonmetallic Optical and Electronic Properties

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Self-assembled multilayer thin films consisting of alternating layers of ~6-nm Au nanoparticles and α,ω -dithiols have been prepared on glass substrates. They have been studied by UV/Vis spectroscopy, ellipsometry, scanning tunneling microscopy, and temperature-dependent conductivity measurements. The electronic and optical properties of the thin film material are nonmetallic, and the Au particles maintain their individual character without fusion to larger units. Electronic conduction within the films occurs via activated electron hopping.

Introduction

Self-assembled nanostructures represent a rapidly emerging field of great fundamental and practical interest and are receiving worldwide attention.¹ Much of the recent work is driven by prospective applications in microelectronics, nonlinear optics, catalysis, sensor science, and other areas. Currently, the study of thiol-protected Au nanocrystals has been leading to some interesting new developments in the field.² Whetten and co-workers have reported the spontaneous formation of highly ordered two- and three-dimensional superlattices from monodisperse fractions of such particles.^{2f} These nanostructures can be regarded as a new class of materials whose properties can, in principle, be tuned at will by manipulating the size and spacing of their constituents. Recently, it has been found that a range of ordered superstructures of particles can be obtained by similar self-assembly methods.^{2k,m} Murray and co-workers have developed elegant ways of preparing functionalized^{2g} and poly-hetero-

functionalized particles²ⁱ which are of interest for innovative catalytic applications. In a recent joint publication with the Whetten group, they demonstrated electrochemically that Au nanoparticles in solution exhibit Coulomb-staircase charging behavior due to the extremely small absolute double-layer capacitance of the individual particles (i.e., nanoparticles provide a feasible way of monitoring single electron events).^{2j}

A promising route to more complex nanostructures is based on the controlled covalent attachment of nanoparticles to suitably functionalized surfaces or to each other. This approach is very versatile and can lead to long-range ordered bulk nanocomposites,³ thin film structures,⁴ or even well-defined superstructures formed by two or more particles.⁵ Interesting but relatively unexplored materials are obtained by successive multilayer formation on functionalized substrates.⁴ In these systems the particles are first covalently attached to a functional group on the surface of the substrate followed by derivatization with a bifunctional compound which acts as a linker unit for a subsequent layer of particles. This procedure can be repeated many times to build up an arbitrary number of well-defined layers. Mono- and multilayer structures of Au nanoparticles exhibit interesting spectroscopic and electrochemical properties such as Raman enhancement,^{6a} and electrochemical addressability across an insulating

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organic monolayer.^{4b,6b,c} Quartz crystal microbalance measurements have corroborated the successive growth of saturating monolayers.^{4c}

The solution-phase reaction of Au nanoparticles with organic dithiols leading to the self-assembly of cross-linked nano-networks with nonmetallic electronic conductivity has been reported in a previous communication.³ Bard and co-workers have extended this method for the fabrication of self-assembled spherical ultramicroelectrodes by confining the self-assembly process to the tip end of a quartz micropipet.⁷ The present paper focuses on the unusual optical and electronic properties of multilayer thin films formed by stepwise self-assembly of ~6-nm Au particles and organic dithiols on mercaptosilane-functionalized glass substrates. The thin films produced have been studied by UV/Vis spectroscopy, ellipsometry, scanning tunneling microscopy, and temperature-dependent conductivity measurements. The results show that the Au particles are well-protected by the dithiol linker molecules and do not fuse into larger units. The thin film material obtained clearly exhibits nonmetallic properties (i.e., electron-hopping conductivity and optical constants very different from those of metals).

Materials

All chemicals used were of highest purity grade available and used as purchased from Aldrich, Fluka, and BDH.

Experimental Section

Preparation of Au Sols. Solutions of ~6-nm Au particles in toluene were prepared as described previously.^{2a,3} Briefly, 30 mL of a 30 mM aqueous solution of hydrogen tetrachloroaurate was mixed with 80 mL of a 50 mM solution of tetraoctylammonium bromide in toluene and stirred vigorously. After quantitative transfer of the tetrachloroaurate to the organic phase, 25 mL of a freshly prepared 0.5 M aqueous solution of sodium borohydride was added with vigorous stirring. After the solution was further stirred for 2 h, the ruby-colored organic phase was separated, washed once with 0.1 M sulfuric acid to remove excess borohydride, washed twice with 1 M sodium carbonate solution, washed five times with water, and dried over anhydrous magnesium sulfate. Before use the solution was diluted with toluene to give a gold content of ~250 mg/L.

Preparation of Self-Assembled Multilayer Thin Films. Glass microscope slides were cleaned thoroughly with hot (~100 °C) piranha solution (1:3 H₂SO₄:H₂O₂ [Caution! This solution is a strong oxidizing agent which causes severe burns in contact with skin and reacts violently with organic compounds. Storage after use should be avoided and great care and appropriate protective clothing must be employed when handling this mixture.]) for 20 min and functionalized with 3-(mercaptopropyl)-trimethoxysilane following the method of Goss et al.⁸ The -SH functionalized slides were rinsed with copious amounts of toluene and immersed overnight in the Au sol, followed by thorough rinsing with toluene and immersion in a 2 mM solution of dithiol in toluene for at least 1 h. Dithiols used were 1,6-hexanedithiol, 1,9-nonanedithiol, and 1,12-dodecanedithiol. The SAM of Au particles was visible as a slight pink tint. Subsequent layers were deposited by repeated alternate immersion in Au sol and dithiol solution, respectively. The resulting film structure is schematically illustrated in Figure 1. After the first monolayer of particles had been deposited on the functionalized glass surface an immersion time of 3 h in the Au sol was found to be sufficient to obtain saturated layers (for a quantitative quartz crystal microbalance study see ref 4c). Upon deposition of more than one monolayer, the color changed from pink (monolayer) through purple (two to three layers) to deep blue (four to seven layers) and finally a golden metallic luster was obtained (eight layers and more).

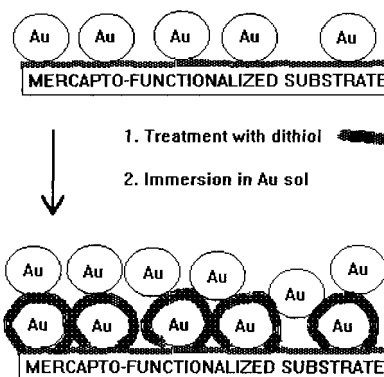


Figure 1. Scheme of the assembly strategy for the Au nanoparticle thin film structure.

UV/Vis Spectroscopy. UV/Vis spectra were obtained using a Pye Unicam PU 8800 UV/Vis spectrophotometer. Glass microscope slides were cut into rectangles of 0.9 cm × 2.6 cm to fit into the sample holder. A blank glass slide was used as a reference for each measurement.

Ellipsometry. A Gaertner Ellipsometer (model L 126 B) equipped with a He/Ne laser ($\lambda = 632.8$ nm) was used to monitor film growth and determine the optical constants of the materials. Glass slides for ellipsometric studies were sand-blasted on one side prior to film deposition to minimize the reflectivity of the underside of the substrate. The complex refractive index of the substrate was found to be $N = 1.51 - 0.01i$ which is typical for glass. Prior to measurement, the samples were dried thoroughly in a stream of nitrogen and all measurements were carried out with dithiol-terminated surfaces to avoid coalescence of surface-bound unprotected Au particles. Measurements were taken using two different angles of incidence, 70° and 50°, for higher reliability of the calculated film thickness and optical constants. Commercial software (R. Greef, TDELTA PSI, ELLGRAPH, AUTOFIT Software, Optochem, Southampton, U.K.) was employed to interpret the results.

Scanning Tunneling Microscopy (STM). A Burleigh Instructional STM was used to obtain images of conductive multilayer thin films on glass substrates. The tip was a Pt90/Ir10 wire (Goodfellow, U.K.) cut with a hardened steel cutter.

Conductivity Measurements. To measure the lateral electronic conductivity of the thin films on glass microscope slides, the samples were electrically contacted with a coating of conductive paint (Silver Loaded Paint, GC Electronics, U.K.), leaving a rectangular gap of 26 mm × 6 mm across which resistance measurements were taken with a digital multimeter (Fluke). Three films each of 20 layers were grown using 1,6-hexanedithiol, 1,9-nonanedithiol, and 1,12-dodecanedithiol as linking agents. For low-temperature measurements an electrically contacted sample comprising 38 layers of particles linked with 1,9-nonanedithiol was wrapped carefully with PTFE tape and sealed in a glass cylinder equipped with a pentane thermometer. The device was then immersed in a Dewar flask which contained a mixture of ethanol and liquid nitrogen. The temperature range measured was between 120 and 300 K. Control samples of the conductive coating alone showed no significant change in conductivity over this temperature range. Measurements were taken during the slow warming-up phase to ensure thermal equilibrium between sample and thermometer.

Results and Discussion

Multilayer Assembly. The deposition of successive layers of Au nanoparticles on glass substrates (Figure 1) was followed by ellipsometry and UV/Vis spectroscopy. The UV/Vis spectrum of a ruby-colored solution of ~6-nm Au particles in toluene shows the well-known plasmon absorption peak at 525 nm characteristic of Au particles larger than ~3 nm (Figure 2). This peak is red-shifted and substantially broadened upon particle aggregation, giving the multilayer thin films a bluish appearance. Solutions containing coupled ensembles of gold particles

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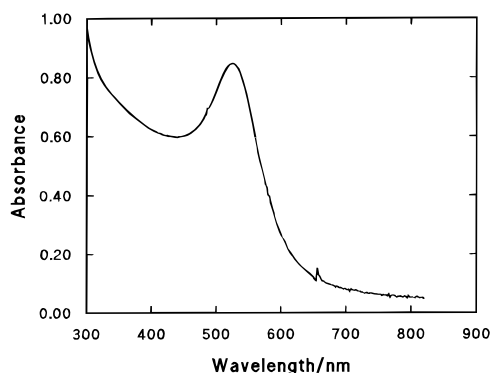


Figure 2. UV/Vis spectrum of ~ 6 -nm Au nanoparticles in toluene.

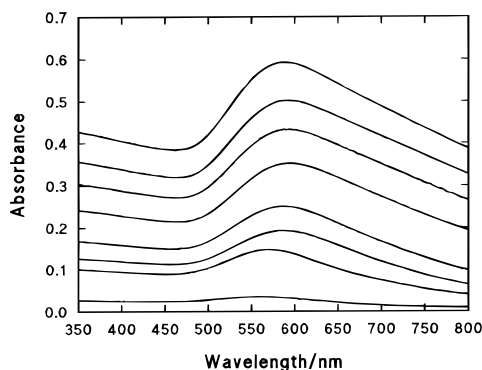


Figure 3. UV/Vis spectra of the first eight layers of ~ 6 -nm Au nanoparticles deposited on glass and linked with 1,9-nonanedithiol.

have been reported to show a similar effect.^{3,5b,d,f} The spectra of eight consecutive layers linked with 1,9-nonanedithiol are shown in Figure 3. The deposition of further layers leads to the formation of a brass-colored mirror. Unlike similar thin film preparations which employ gold hydrosols,^{4d} our spectra show no further broadening and loss of peak features after the deposition of a few layers. This indicates structural differences between hydrosol-based preparations and the thin films described here, probably implying a more metal-like character of the former. The particles in solution are stabilized by a layer of tetraoctylammonium bromide ion pairs with the bromide being strongly adsorbed to the Au surface.^{2m} It is assumed that most of this coating is replaced upon attachment of the thiol ligands, but the possibility of ionic inclusions within the multilayer structure cannot be ruled out at present. The UV/Vis data (Figure 4a) and the ellipsometric study of the film formation process (Figure 4b) indicate regular layer-by-layer growth. When 1,9-nonanedithiol is used as a linker molecule, the incremental increase in apparent thickness per monolayer of particles is 7–8 nm which is consistent with the particle size of ~ 6 nm and a ligand shell of ~ 1 nm thickness. Within the accuracy of these experiments, no significant differences in film thickness could be established using other dithiols. The complex refractive index of the material was determined as discussed below. Both UV/Vis and ellipsometric data indicate that the surface coverage of the first layer was less than that of subsequent layers, which might be due to incomplete surface functionalization of the glass substrate. However, similar observations have been made by quartz crystal microgravimetry for multilayer formation on dithiol-derivatized Au surfaces, for which dense packing of the bifunctional molecule should be expected.^{4c} Hence, the higher loading of subsequent layers could also be due to

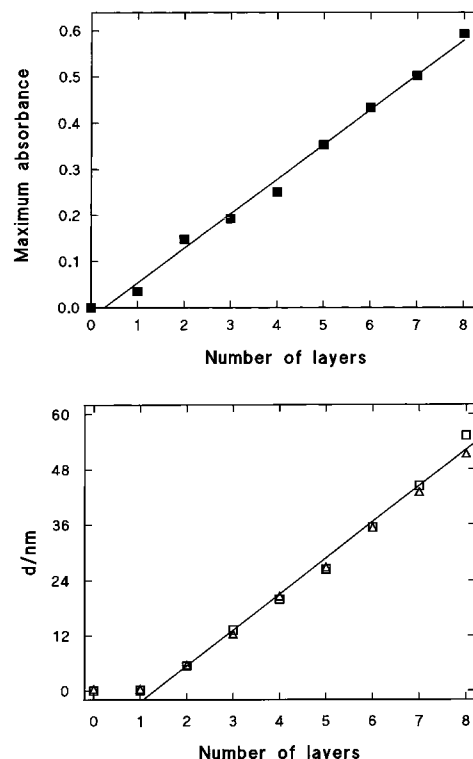


Figure 4. (a) Maximum absorbance value (between 550 and 600 nm) of the UV/Vis spectra in Figure 3 vs the number of layers deposited. (b) Ellipsometric thickness of the same material using a He/Ne laser (632.8 nm) at two different angles of incidence, 70° (\square) and 50° (\triangle). Substrate refractive index: $N_s = 1.51 - 0.01i$; film refractive index: $N_f = 2.63 - 1.55i$. Both techniques indicate regular layer-by-layer growth and the thickness measured is in reasonable agreement with the particle size.

the increased surface roughness on the nanometer scale after deposition of the first layer. An important feature of the thin film material prepared is that the individual Au particles do not fuse together but seem to be well-protected and covalently linked to each other by their dithiol ligand shell as previously observed in bulk materials precipitated from solution.³ An STM image of the dithiol-terminated surface (Figure 5) shows that over a relatively large surface area (500 nm \times 500 nm) all particles are in the expected size range of 6–10 nm (supposedly imaged with their ligand shell) and irregularly packed, giving the surface a cauliflowerlike appearance. This contrasts previous findings of hexagonal close-packed superlattices of monothiol-stabilized Au particles, which are obtained even from preparations with a considerable size distribution^{2d} and can be observed by STM.⁹ The use of dithiols as a covalent linking agent probably reduces drastically the mobility of the individual particles and hinders the formation of well-ordered superlattices.

Electron-Transport Properties. The electron-transport mechanism in the 1,9-nonanedithiol-linked thin film material was probed by measuring the temperature dependence of its electronic conductivity. For a system in which the metal particles are in direct contact with each other, a metallic conduction mechanism should be expected (i.e., the conductivity should increase linearly with decreasing temperature). Nonmetallic conduction is generally characterized by an often complicated decrease in conductivity with decreasing temperature. The percolation transition in systems containing metallicly

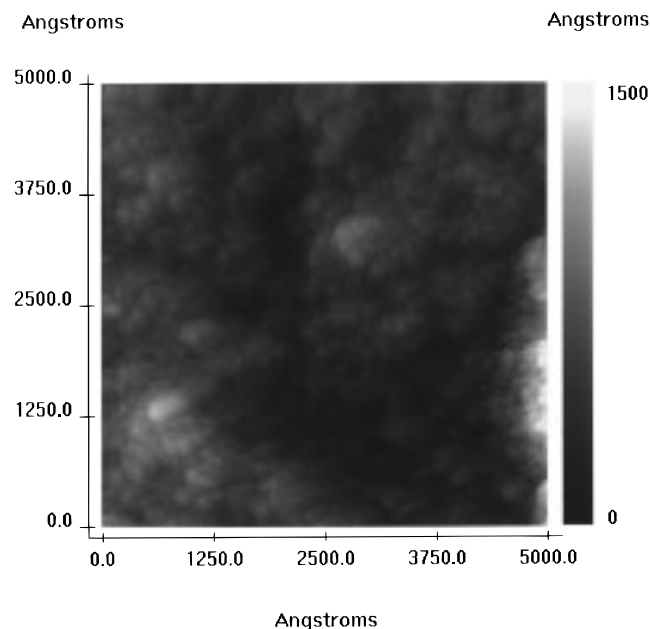


Figure 5. STM image of a sample of 20 layers of 1,9-nonanedithiol-linked Au nanoparticles on a glass substrate. Bias voltage 250 mV (substrate positive), set point current 1.2 nA. The surface is dithiol-terminated to prevent particle fusion in the top layer.

conductive particles has been studied in detail using ultrathin metal island films ($\sim 2\text{--}8\text{ nm}$) in which an abrupt change in the conduction mechanism from activated electron hopping to metallic conductivity is observed as soon as the first continuous path across the film is established.¹⁰ The temperature dependence of the conductivity in discontinuous films below the percolation threshold can be described by a simple Arrhenius-type formula implying activated charge transport

$$\sigma = (\sigma_0 \exp[-E_a/(RT)]) \quad (1)$$

where σ_0 is a constant and E_a is the electrostatic activation energy for charge transport.^{10a} As demonstrated previously, the conductivity of pressed pellets of dithiol cross-linked Au nanoparticles can be described by eq 1, giving activation energies dependent on particle size and spacing³ whose experimental values can be predicted reasonably well by an electrostatic model developed by Abeles et al. to describe activated electron transport in cermets:¹¹

$$E_a = (1/2)e^2[r^{-1} - (r + s)^{-1}]/4\pi\epsilon\epsilon_0 \quad (2)$$

where r is the radius of the particles, s is the interparticle spacing, and ϵ is the dielectric constant of the embedding medium.¹¹ Figure 6 shows the logarithmic plot of eq 1 for the thin film material comprising 38 layers of Au particles. In the temperature range of the experiment, the conductivity of the material decreases exponentially with decreasing temperature which is in agreement with activated electron hopping. An activation energy of $E_a = 0.02 \pm 0.002\text{ eV}$ is obtained from the slope of the graph in Figure 6 in agreement with eq 2 and previous studies of bulk materials.³ Murray and co-workers have reported similar studies of monothiol-stabilized Au clusters in the solid state.^{2c} The electron-hopping mechanism prevalent in

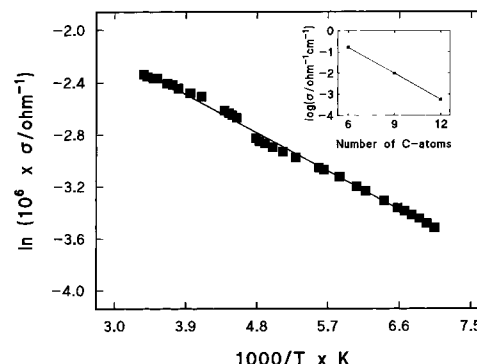


Figure 6. Logarithmic plot of the temperature dependence of the electronic conductivity for a sample of 38 layers of 1,9-nonanedithiol-linked Au nanoparticles on glass. The graph indicates electron-hopping conductivity with an activation energy of 0.02 eV (see eq 1). Inset: Specific conductivity of Au nanoparticle thin film materials at room temperature as a function of the aliphatic hydrocarbon chain length of the dithiol linker molecule. The samples comprised 20 layers giving $\sim 150\text{-nm}$ film thickness. The addition of three carbon atoms leads to a decrease of conductivity by approximately 1 order of magnitude.

these materials provides additional strong evidence for the individual character of the particles, which are isolated from each other by their dithiol ligand shell. The room temperature conductivity of the thin film materials depends strongly on the length of the dithiol linker molecule employed (see inset Figure 6). This dependence has also previously been found for bulk nanocomposites and illustrates possibilities of tuning the electronic properties of the materials by the variation of linker molecules.³ All films prepared show an exponential temperature dependence of the conductivity in accordance with eq 1.

Optical Properties. The complex refractive index $N = n - ik$ of the thin film material linked with 1,9-nonanedithiol has been measured by ellipsometry. To obtain a first estimate of the values for n and k , a film of sufficient thickness was grown (~ 20 layers) to make the contribution of the glass substrate vanishingly small (i.e., the addition of further layers did not lead to appreciable changes in the measured ellipsometric angles Δ and Ψ). In this case, the optical constants can be readily calculated from the ellipsometric data employing a model that regards the surface as a pure substrate. The optical constants obtained were $n = 2.34$ and $k = 1.72$. These values were then used to simulate the expected $\Delta\text{--}\Psi$ signatures for film growth. They were subsequently modified slightly until the best fit in comparison with the experimental data was obtained for two different angles of incidence (70° and 50°). The optical constants giving the best fit were $n = 2.63$ and $k = 1.55$. The main reason these values have not been obtained also from the 20-layer sample could be the influence of surface roughness and the presence of voids in the material (see also the STM image in Figure 5) which will become more critical with increasing film thickness. It has also been assumed that the optical constants do not depend on the film thickness which is an oversimplification as can be concluded from the slight shift of the absorption maximum upon deposition of the first few layers (Figure 3). The aim of this investigation has not been to determine the optical properties of this new material with high accuracy, but rather to demonstrate that they are dramatically different from those of bulk metal and give a reliable estimate of their values. For comparison, the optical constants of bulk gold at $\lambda = 632.8$

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nm are $n = 0.197$ and $k = 3.45$,¹² further reinforcing the conclusions from the conductivity results, *showing that these films are indeed nanostructured, retaining the individual properties of the nanoparticles.*

Conclusions

It has been demonstrated that thin film materials obtained by successive self-assembly of Au nanoparticles linked with organic dithiol molecules exhibit nonmetallic optical and electronic properties. The electronic conductivity of the thin films resembles that of nanostructured bulk materials of similar composition which have been described previously. On the basis of a simple electrostatic model the temperature dependence of the conductivity can be predicted quantitatively, indicating an electron-hopping mechanism of charge transport. The optical

constants have been measured and confirm qualitatively the nonmetallic character of this new material. An analysis of the optical function of the films in terms of an effective medium theory will be presented elsewhere.¹³ The results give strong evidence that the individual particles do not fuse to form bulk gold. They also suggest that it should be possible to control the physical properties of the materials by variation of particle size and spacing, and by the introduction of chemical functionalities as part of the linker units. Such systems are currently under detailed investigation in our laboratory.

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