Single-Phase Synthesis of Functionalized Gold Nanoparticles

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A single-phase synthesis of thiolate monolayer-protected gold clusters (MPCs) is described. This method avoids the problem of persistent ionic contamination from residual phase-transfer catalyst while retaining the versatility associated with the commonly used two-phase Brust synthesis. MPCs having alkyl, diphenylacetylene, ether, amide, or ester functionalities were prepared by this single-phase synthesis and characterized via ^{1}H NMR, FT-IR, and UV–vis absorption spectroscopy, TGA, STM, and TEM. Comparisons of products synthesized by this method and by existing methods are made for a subset of MPCs. Results are considered in the context of using MPC thin films as chemically sensitive interface layers in chemiresistor vapor sensors.

Introduction

The unique properties of thiolate monolayer-protected gold clusters (MPCs) make them excellent candidates for use in a variety of advanced technologies. Current applications include vapor sensing,[1–7] nonlinear optics,[8] and catalysis.[9,10] MPCs are also used in the fabrication of nanostructured arrays[11,12] and nanocomposite materials.[13,14] The prevalent method for synthesizing MPCs, reported by Brust and co-workers,[15] offers control of both the monolayer composition and the size of the gold core through a two-phase reaction involving the reduction of a gold salt in the presence of a thiol. Briefly, $HAuCl_4$ and the phase-transfer catalyst, tetraoctylammonium bromide (TOAB), are dissolved in water and vigorously stirred with a toluene solution of the thiol. Aqueous $NaBH_4$ is added to reduce the gold, and the MPCs form spontaneously. This two-phase method provides a simple means of producing stabilized nanoparticles with diverse functionalities and has contributed significantly to the recent proliferation of research on these materials.[16]

One reported shortcoming of the Brust method is the persistent contamination of isolated MPC products with residual TOAB.[17] The influence of this impurity on the electrical characteristics of MPCs has not been explored until the present study. Such contamination may be particularly problematic in vapor-sensing applications employing thin MPC films cast on interdigital electrodes that rely on changes in electron tunneling currents arising from reversible vapor sorption. Eliminating trace ionic impurities is critical for achieving stable and reproducible baseline resistances as well as ensuring that vapor selectivity is dictated by the MPC ligand structure and not by interactions with ionic charge carriers.

Two different single-phase syntheses of MPCs that avoid the use of phase-transfer catalyst have been known for several years.[18–20] In one the gold salt is reduced in the presence of the passivating ligand using a water/methanol solution. Originally demonstrated

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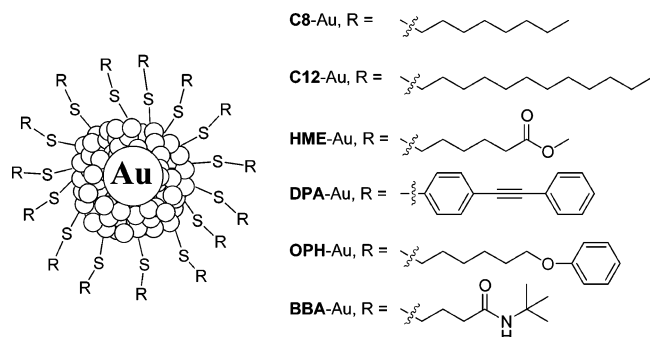
C8-Au, R =

C12-Au, R =

HME-Au, R =

DPA-Au, R =

OPH-Au, R =

BBA-Au, R =

Figure 1. Thiolate monolayer-protected gold nanoparticles synthesized in this study.

with 4-mercaptophenol,[18] this method has since been used to produce MPCs with a variety of water-soluble ligands.[21,22] Another single-phase synthesis uses THF as the solvent and thereby permits incorporation of a wider range of ligands (i.e., not just water-soluble ligands),[19] but it employs the very strong reducing agent lithium triethylborohydride (Super-Hydride), which reduces esters, amides, and other potentially desirable ligand functional groups[23] that survive the milder reducing conditions used in the two-phase Brust method.

A homogeneous MPC preparation that accommodates such readily reducible ligands would be useful. We initiated this study by investigating the single-phase synthesis of MPCs with 1-octanethiol ligands (C8−Au). Screening different combinations of reducing agents (i.e., $NaBH_4$ and $LiBH_4$) and solvents (i.e., ether, THF, and acetonitrile) under a variety of reaction conditions (i.e., reducing agent addition rate, reaction time, equivalents of reducing agent, and concentration of reaction solution), we discovered that treatment of $HAuCl_4$ and the thiol with an excess of $LiBH_4$ in THF under ambient conditions produces gold nanoparticles in high yield. We then went on to explore its use for synthesizing MPCs encapsulated with alkyl, diphenylacetylene, phenyl ether, amide, and ester moieties (see Figure 1). Following a description of the method, we present data characterizing the various products and illustrating the advantages of this synthetic approach over those described above.

Experimental Section

All commercial reagents were used without further purification. Solvents were purchased from Fisher Scientific, and uninhibited THF was dried by passing through activated alumina columns. $HAuCl_4 \cdot 3H_2O$ was obtained from Strem. 1-Octanethiol, 1-dodecanethiol, $LiBH_4$, benzene-d_6, and chloroform-d were purchased from Acros, and Super-Hydride in THF was purchased from Aldrich. *N-tert*-Butyl-4-mercaptobutyl-amide,[24] 4-mercaptodiphenylacetylene,[25] 1-mercapto-6-phenoxy-

hexane,[26] and methyl 6-mercaptohexanoate[27] were prepared by published procedures.

All single-phase syntheses were conducted under ambient conditions. The general procedure is as follows: $HAuCl_4$ (0.125 g, 0.317 mmol) was dissolved in anhydrous THF (10 mL). The thiol was then added to this solution (0.25 equiv vs gold salt for all MPCs discussed here). $LiBH_4$ in anhydrous THF (2.96 mL, 0.311 M, 2.9 equiv vs gold salt) was added at a constant rate (1.15 mL/min) to the stirring reaction solution. Immediately following reducing agent addition, the product was diluted with toluene (2 mL) and then concentrated under reduced pressure to ca. 2 mL to remove the THF. The solution was diluted with additional toluene (50 mL) and washed with water (3 × 85 mL). The toluene was removed under reduced pressure and the crude product suspended in acetonitrile (15 mL) with sonication, isolated on a fritted-glass funnel, and washed with ethanol (2 × 250 mL) to remove unbound ligand.[28] The purified product was finally collected from the funnel by dissolution in toluene (87% mass recovery of gold and thiolate as MPCs in the C8−Au synthesis). This method can be conveniently scaled and produces gram quantities of C8−Au in 82% yield.

All MPCs were characterized spectroscopically (¹H NMR, FT-IR, UV−vis absorption), by TGA, and with TEM (Table 1). The ¹H NMR spectra (400 MHz) of C8−Au, C12−Au, and OPH−Au were collected in benzene-d_6 and those of DPA-Au, BBA-Au, and HME-Au were collected in chloroform-d. FT-IR spectra were recorded from MPC samples pressed in KBr pellets. All UV−vis absorption spectra were collected from solutions of MPCs in toluene. TGA was performed in air at 40 °C/min and temperatures required for loss of all volatile material were recorded. Samples for TEM analysis were prepared from a 1 mg/mL solution of the MPCs in toluene. A single drop of this solution was deposited on a holey carbon-coated copper grid (200 mesh) resting on filter paper. Bright field images were obtained using a JEOL 2010F Analytical Electron Microscope operating at 200 keV using a field emission filament. Representative areas of each sample at 300000 magnification were used for particle size and distribution measurements, each of which entailed analyzing at least 350 particles. Electronic images were analyzed using Scion Image 4.0.2 to measure nanoparticle diameters.

STM imaging of drop-cast thin film samples deposited on freshly cleaved highly oriented pyrolytic graphite (HOPG) was performed under ambient conditions with mechanically cut Pt/ Ir tips. These films were formed by evaporation of a 1 mg/mL solution of the MPCs in toluene. MPCs did not show significant change in position during image acquisition. Typical measurements employed 200−300 pA of current and 800−1000 mV of bias (sample positive).

Conductivities were determined of MPC films spray-coated from toluene solutions onto interdigital Au/Cr electrode arrays on quartz substrates (Microsensor Systems, Inc., Bowling Green, KY). Each array consisted of 50 pairs of electrodes spaced by 15 μm and having an overlap length of 4.8 mm. All coated electrodes were stored under identical conditions prior to measurement. The in-phase and out-of-phase current components for each film were determined with a lock-in amplifier from 1 to 1000 Hz at an applied potential of 100 mV.

Results and Discussion

Samples of the C8−Au MPC were synthesized by this single-phase method and by the Brust method using the same metal-to-ligand ratio. After purification by literature procedures,[15,28] both methods yielded similar black waxy materials soluble in toluene, benzene, and meth-

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Table 1. MPC Characterization Data

MPC encapsulating ligand	^{1}H NMR (ppm)	FT-IR (cm^{-1})	UV–vis (λ_{max}, nm)	TGA (°C, % mass loss)	MPC diameter[a] (nm)
1-octanethiol (C8–Au)	1.38 (bm) 0.97 (bm)	2954, 2920, 2851, 1462, 1163, 720	517	224, 16%	4.3 ± 0.9
1-dodecanethiol (C12–Au)	1.41 (bm) 0.98 (bm)	2955, 2917, 2849, 1465, 1455, 719	521	290, 23%	4.2 ± 1.2
methyl 6-mercaptohexanoate[b] (HME–Au)	3.66 (bs) 2.33 (bm) 1.82 (bm) 1.68 (bm)	2925, 2854, 1736, 1435	516	414, 20%[c]	4.7 ± 1.1
4-mercaptodiphenylacetylene (DPA–Au)	7.14 (bm)	3044, 3017, 2210, 1580, 1490	522	743, 24%[d]	3.4 ± 0.8
1-mercapto-6-phenoxyhexane (OPH–Au)	6.84 (bm) 3.63 (bm) 1.89 (bm)	3027, 2917, 2850, 1244	515	324, 17%	3.9 ± 1.2
N-tert-butyl-4-mercaptobutylamide (BBA–Au)	1.25 (bs) 0.88 (bm)	3308, 1646, 1540	515	240, 35%	3.4 ± 0.8

[a] All MPC diameters were measured from TEM images. [b] HME–Au was synthesized following the general single-phase method substituting cold 2-propanol for ethanol in the final wash. [c] HME–Au decomposes with two losses in the TGA; 13% of the total mass was volatized by 247 °C followed by another loss of 7% by 414 °C. [d] DPA–Au shows a mass loss over a broad temperature range of 203–743 °C, with half the volatile material volatized by 485 °C, and differs from the relatively sharp mass loss observed with the other MPCs.
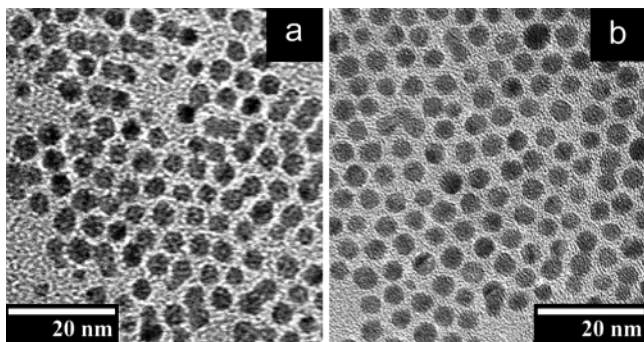
Figure 2. (a) TEM image of C8–Au prepared by the two-phase route. (b) TEM image of C8–Au prepared by the single-phase route.

ylene chloride. Measurements from TEM images gave average particle diameters of 4.1 ± 0.8 and 4.3 ± 0.9 nm, respectively, for the two-phase and single-phase methods (Figures 2a and 2b). Both products form films in which the individual MPCs spontaneously order in a hexagonal array, as is commonly seen in the packing of nanometer-scale particles.[29] FT-IR and ^{1}H NMR analyses of these two C8–Au samples were in close agreement, with the prominent exception of a broad multiplet at 3.1 ppm (benzene-d_6) in the ^{1}H NMR spectrum of the two-phase product. This resonance corresponds to residual TOAB. The characteristic FT-IR stretches of the two C8–Au products differed by <2 cm^{-1}.[30] The single-phase synthesis reported here thus produces 1-octanethiol encapsulated gold nanoparticles with a size distribution comparable to that from the Brust synthesis but with no ionic contamination from the phase-transfer catalyst. Furthermore, the former method requires only a 3-min reaction time, compared to 3 h for the latter method.[15]

Samples of the C12–Au MPC were then prepared by both routes using 1-dodecanethiol. The ac electrical characteristics of C12–Au films are shown in Figure 3. A strong dependence of the current upon the fre-
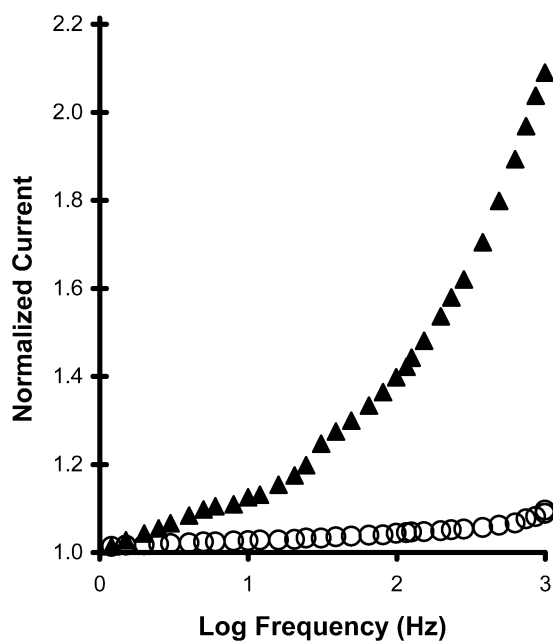

Figure 3. In-phase current through films of C12–Au, normalized to the in-phase current value at 1 Hz ac frequency, as a function of the frequency of the applied voltage. In-phase current measurements were collected over a 1-kHz range where the parasitic effects of the out-of-phase current are negligible. (Filled triangles: C12–Au prepared by the Brust method. Open circles: C12–Au prepared by the single-phase method.)

quency of the applied voltage is evident in the two-phase C12–Au film, consistent with ionic conduction involving residual TOAB.[31] This behavior is not observed with the film of single-phase material, which exhibits behavior indicative of tunneling-dominated conduction. The presence of ionic conduction in sensor films designed to rely on changes in tunneling current accompanying vapor sorption is clearly an undesirable complicating factor.[32]

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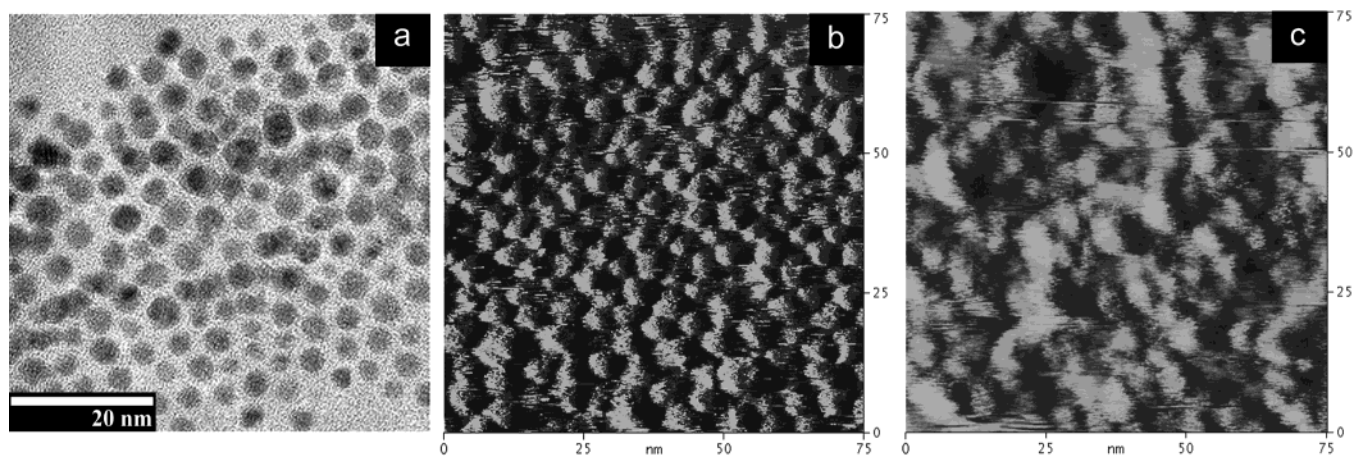
Figure 4. (a) TEM image of DPA−Au. (b) STM image of closely packed C12−Au demonstrating well-defined particle boundaries. (c) STM image of DPA−Au showing blurred particle boundaries.

Films of C12−Au gave resistances in the high-MΩ range. Lower film resistances are favored for vapor-sensing applications because they afford lower baseline noise levels and allow simpler measurement circuitry. It was reasoned that, without alteration of the particle size or ligand length, unsaturated ligands would lower film resistance by reducing the tunneling barrier between gold particles. A related strategy has been employed successfully by others; diphenylacetylene thiol ligands incorporated into two-dimensional self-assembled monolayers exhibit a reduced tunneling barrier compared to alkane thiol monolayers of similar thickness.[33] The single-phase synthesis of DPA−Au gave particles with an average diameter of 3.4 ± 0.8 nm by TEM (see Figure 4a and Table 1) that were soluble in toluene and methylene chloride.[34] Consistent with expectations, DPA−Au films exhibit lower resistances than C8−Au or C12−Au films of similar mass.[35]

STM images of C12−Au and DPA−Au nanoparticles are shown in Figures 4b and 4c, respectively. These images represent close-packed structures spontaneously formed from evaporated solutions. As noted by previous investigators, STM does not resolve individual ligands.[36,37] However, since tunneling occurs through the protecting monolayer, STM images represent the shapes of nanoparticles including some contribution from the ligands. This differs from TEM imaging where only the high-contrast metal cores are observed (Figure 4a). The STM image of C12−Au (Figure 4b) shows a closely packed array with well-resolved boundary regions between particles. The average apparent particle diameter in this image is 5.3 ± 0.9 nm, which is 26% larger than the diameter measured by TEM. The STM image of DPA−Au shows poorly resolved boundaries between particles when compared to C12−Au under the same imaging conditions (Figure 4c). This is ascribed to greater tunneling through the thiolate monolayer of the nanoparticles due to the conjugated ligands. This effect makes DPA−Au appear larger in the STM experiment and leads to blurred edges between nanoparticles. The diameter of the DPA−Au measured by STM is 5.4 ± 0.8 nm, a value 59% larger than that measured by TEM. This greater increase in apparent particle diameter for the STM image of DPA−Au, relative to C12−Au, supports the interpretation that such conjugated monolayers present a reduced barrier to tunneling.

Additional MPCs were synthesized with ether, amide, and ester functionalities to investigate the versatility of this synthetic method. MPCs with an ether moiety (OPH−Au) were made using 1-mercapto-6-phenoxyhexane. This MPC was chosen as a model synthetic target because of the range of possible ether-containing ligands that can be easily produced from the large supply of commercially available phenols. An MPC with an amide moiety (BBA−Au), which has previously been made by the Brust method,[24] provides an example of how reducible functional groups can be accommodated in this single-phase MPC preparation. The characteristic FT-IR amide stretches from the *N-tert*-butyl-4-mercapto-butylamide ligands, 1646 and 1540 cm^{-1}, are identifiable in the single-phase product.[38]

Preparation of HME−Au, which contains a much more readily reduced methyl ester group, was then explored. This MPC was prepared by the single-phase method described here as well as by the single-phase method employing Super-Hydride.[19] Analyses of the HME−Au nanoparticles synthesized with our single-phase synthesis indicate that the ester groups survive without being reduced. The FT-IR spectrum of HME−

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(38) Although the FT-IR spectrum is consistent with the published data, the ^{1}H NMR spectrum (CDCl$_3$) of the single-phase prepared BBA−Au lacks the 3.34 and 1.66 ppm peaks of the two-phase product reported in the literature.[24] We attribute these extra peaks in the ^{1}H NMR spectrum of BBA−Au prepared by the two-phase method to residual TOAB.

Au contains a characteristic ester peak at 1736 cm^{-1} and the methyl group of this ester gives rise to a broad singlet at 3.66 ppm in the ^{1}H NMR spectrum. Digestion of HME−Au with iodine to liberate the passivating monolayer as the disulfide was used to probe for possible reduction of the ligands.[39] The major products of HME−Au−iodine digestion are the same as those resulting from iodine treatment of methyl 6-mercaptohexanoate, as determined by gas chromatography with a flame ionization detector (GC-FID). In both cases the disulfide derived from methyl 6-mercaptohexanoate is the prominent species. Furthermore, chromatographic analysis verified that 6-mercaptohexanol−iodine reaction products are not produced with this preparation. The correspondence between the major HME−Au and methyl 6-mercaptohexanoate ligand decomposition products and an absence of 6-mercaptohexanol decomposition species indicates that reduction of the gold salt is favored over that of the ligand ester functionality.

In contrast, attempts to synthesize MPCs with this ester functionality using the Super-Hydride single-phase method were unsuccessful. Conditions that smoothly afforded C8−Au with the Super-Hydride single-phase synthesis led to extensive ester reduction products in the HME−Au case. This was determined by both the solubility behavior of the nanoparticles produced and comparison of freed ligand, by GC-FID and ^{1}H NMR, to an authentic sample of the disulfide derived from 6-mercaptohexanol.

Conclusions

The reduction of HAuCl$_4$ in THF by LiBH$_4$ in the presence of a thiol is a simple and expedient means of synthesizing pure monolayer-protected gold nanoparticles with a broad range of ligand functionalities. It can be conveniently scaled to produce gram quantities of MPCs with size distributions similar to those prepared by the two-phase route. Notably, amide and ester functionalities survive the synthetic conditions without being reduced. The absence of ionic contamination will facilitate further studies of the inherent electrical properties and device applications of MPCs. Presently, the electronic noise and conduction properties of MPCs produced via our synthetic method are being explored.[32] These materials are also showing promising results as interfacial films on integrated chemiresistor sensors arrays in microanalytical systems.[40−42]

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