Preparation of Thiol-Capped Gold Nanoparticles by Chemical Reduction of Soluble Au(I)–Thiolates

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A novel preparation method of thiol-stabilized gold nanoparticles is described. Soluble Au(I)–thiolate complexes were prepared, isolated, and reduced with Superhydride (lithium triethyl borohydride) in suitable inert solvents. The dimensions of the resulting gold nanoparticles were compared to those prepared using conventional methods (i.e., that use a mixture of Au(III) salts and thiols as the initial reagents). The sizes (and size dispersity) of the thiol-capped gold nanoparticles synthesized here are comparable to those prepared by the conventional methods used.

Introduction

Ligand-capped gold nanoparticles are very stable metal colloids with a number of fascinating properties. Au nanoparticles are typically prepared by the Brust[1,2] or the Ulman[3] techniques, where a Au(III) chloride salt is mixed with a thiol in a suitable solvent, and subsequently reduced with sodium borohydride or Superhydride, respectively. Before the reduction step, the thiols reduce some of the Au(III) salt into Au(I). However, with the typical thiol:Au ratios being less than 3:1 in the conventional methods, only a small fraction of the Au(III) is reduced to Au(I).[4] After the reduction step, these preparation methods mainly yield nanoparticles of a particular size range and distribution, independent of the nature of the thiol. An important exception to this generalization is the case of very bulky ligands such as polystyrene–thiol or poly(ethylene glycol)–thiol, which produce slightly larger nanoparticles and also larger dispersion in size.[5,6] Variation in the initial thiol:Au ratio also has an effect on nanoparticle sizes in the conventional preparation methods.[7–9]

There have been suggestions[10,11] that in situ formed Au(I)–thiolates are precursors to the gold nanoparticles made via these solution-based syntheses. This is an intriguing possibility, because, if valid, it creates opportunities to directly control the nanoparticle synthesis. The generality of Au(I)–thiolates being precursors has not however been definitely demonstrated in the literature. This report thus summarizes our efforts to synthesize soluble Au(I)–thiolates and to then introduce them into nanoparticle syntheses as well-characterized entities (Figure 1).

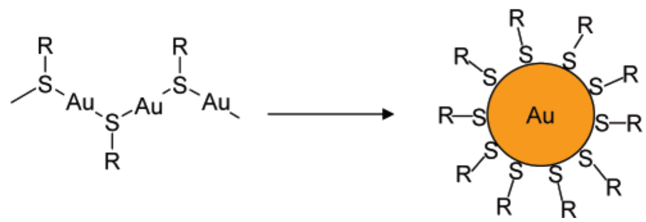

Figure 1. Schematic representation of our gold nanoparticle synthesis route.

There are several preparation methods of gold(I)–thiolate complexes.[12–14] In this study, Au(I)–thiolate complexes via Au(I)–chlorothioether complexes (thiodiglycol and tetrahydrothiophene) were prepared. There was no discernible difference between the resulting Au(I)–thiolate complexes when each technique was used to prepare the same complex. We attempted to isolate and characterize the intermediate Au(I) complexes that form in the Brust and Ulman techniques (i.e., before the reduction step).[15] However, these compounds are unstable in solution and/or the complexity of the reaction mixtures rendered their characterization difficult.

Metal–thiolate complexes have been the subject of numerous studies.[16] Organothiolate anions (RS^-) are important ligands, and their ligand properties are quite comparable to those of the halide ligands Cl^-, Br^-, and I^-. Because

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thiolates are strong electron-releasing ligands with high polarizability, the resulting metal complexes tend to be two- or three-coordinate. Most gold(I) complexes are in fact linear two-coordinate.[17,18] Gold(I) and gold(III) are soft Lewis acids and prefer to form complexes with large polarizable ligands.[18] Thiolate ligands are typically terminal, or doubly bridging.[16] Consequently, metal(I)−thiolate structures are predominantly zigzag strands or rings of {-(μ-SR)−M−(μ-SR)−M} segments. Such strands can associate into lamellar structures via van der Waals forces,[19,20] or intertwine to form one-dimensional nonmolecular structures.[21] Silver(I)−thiolates, in particular, have this tendency.[19−21]

The most extensively studied gold(I)−thiolate complexes are those involved in the treatment of rheumatoid arthritis (chrysotherapy).[22−34] Sodium gold(I) thiomalate (Myochrisin) and gold(I) thioglucose (Solganol), for example, are both amorphous solids that are only water-soluble. A complete structure determination of these complexes has been elusive.[25−29] Such metal−thiolate complexes, including Myochrysin and Solganol, are presumed to have nonmolecular (i.e., "polymeric") structures. Whether these nonmolecular structures are cyclic or open chain remains open to debate.[16,22,25,26,29−31]

Thus far, only a few gold(I)−thiolate structures have been confirmed by X-ray crystallography, due to the difficulty in obtaining X-ray diffraction quality crystals. Related solution characterization is also problematic in part because of poor solubility and/or poor crystallinity, especially when the R group of the thiolate RS^- anion is not bulky. Intermolecular interactions between adjacent polymer units in the solid may be a factor determining the insolubility of the Au(I)−thiolate complexes. These interactions probably depend on the size and polarity of the thiolates.[26] This parallels the situation of other metal−thiolate complexes such as silver(I)−cyclohexanethiol,[35] but seems to be a particular problem in the case of gold(I)−thiolate complexes.[23] Depending on the thiolate, Au(I)−thiolate structures with rings varying from 4 to 6 "repeat units" have been reported.[36−40] Gold(I)−thiolate catenanes with two interpenetrating pentagons or hexagons have recently been reported with ortho and para *tert*-butylthiophenol.[37] The existence of such structures is attributable to the maximization of the number of strong Au···Au interactions within the catenane.[37] Such aurophilic Au···Au interactions have an estimated energy of 5−10 kcal/mol for a Au−Au distance of 3.05 Å.[41] This is comparable to the energy of a hydrogen bond. Aside from the ligand bulkiness, the electronic structure of the ligand is almost certainly another factor governing the ultimate structure of the gold(I)−thiolate complex obtained. With so little information available in the literature on the structure of gold(I)−thiolate complexes, one of our goals was to synthesize new soluble gold(I)−thiolate complexes, eventually amenable to crystallization, to elucidate their structure.

Our use of gold(I)−thiolate complexes as gold nanoparticle precursors parallels a very recent study of the preparation of iron oxide nanoparticles, which uses an iron oleate precursor.[42] Highly monodiperse samples (size variation < 5%) were prepared, and tuning of the nanoparticle size by altering the experimental conditions was possible.

Experimental Section

Reagents. Thiocholesterol, 8-mercaptomenthone (80%), cyclohexanethiol (97%), tetrahydrothiophene (99%), and thiodiglycol (99%) were purchased from Sigma-Aldrich. All thiols were used as received. Triisopropylthiophenol (TRIP) was synthesized following the procedure by Blower et al.[43] and characterized by solution ^{1}H and ^{13}C NMR. PS_{19}−SH (a thiol-terminated polystyrene (PS) oligomer with 19 units of PS) was synthesized by anionic polymerization as previously published.[5,6] $KAuBr_4$ was purchased from Precious Metals Online (Australia), and gold acetate was from Alfa. $HAuCl_4 \cdot 3H_2O$, sodium borohydride, and lithium triethylborohydride ("Superhydride") were obtained from Sigma-Aldrich.

Tetrahydrofuran (THF) and diethyl ether were distilled from sodium/benzophenone and collected prior to use. All other solvents were used as received. All glassware was rinsed with aqua regia, then several times with MilliQ water, and finally oven-dried overnight at 160 °C. The spatulas used for transfer were coated with Teflon to avoid any potential reduction of the Au(I)−thiolates by their metallic surface.

Synthesis and Characterization of Au(I)−Thiolate Complexes. The Au(I)−thiolates were prepared by two published routes.[12−14] The Au(I)−thiolate complexes were characterized by thermogravimetric analysis (TGA) and X-ray photoelectron spec-

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Table 1. Characterization Data and Physical Properties of the Au(I)−Thiolate Complexes Studied

thiol	Au/thiol mol ratio[a]	Au/S atomic ratio[b]	C/S atomic ratio[b]	solubility[c]	crystallization
thiocholesterol(I)	1.07	1.10	29.7	THF, $CHCl_3$	inconclusive
cyclohexanethiol(II)	1.0	1.1	6.3	$CHCl_3$, toluene	no
PS_{19}−SH(III)	1.14	n.a.	n.a.	THF, $CHCl_3$, toluene	no
triisopropylthiophenol(IV)	1.0	1.1	15.1	ether, toluene	yes (ether/THF)
8-mercaptomenthone(V)	0.8	n.a.	n.a.	THF, $CHCl_3$, toluene	no

[a] From TGA measurements and subsequent calculations. [b] From XPS measurements. [c] Solvents assessed include tetrahydrofuran (THF), chloroform ($CHCl_3$), toluene, acetone, diethyl ether, dimethyl sulfoxide (DMSO), hexanes, benzene, and *N*,*N*-dimethyl formamide (DMF).

troscopy (XPS). The complexes were tested for solubility in a variety of solvents, and the soluble complexes were assessed for purity by ^{1}H and ^{13}C solution NMR in deuterated solvents.

Thermogravimetric Analysis. TGA confirmed the presence of gold in the complexes (in the form of a gold colored residue at the end of the run). Assuming that all of the organics are removed under the TGA conditions, the thiol/Au mass ratio of a sample can be determined. These mass ratios were then used to calculate the thiol/Au mol ratio in the complexes. TGA analyses were performed at a heating rate of 10 °C/min on a Q500 thermogravimetric analyzer (TA Instruments, USA) equipped with a Pt pan. The experiments were performed under an N_2 atmosphere. The feeder gas was switched to air for 10 min at the end of the cycle at 700 °C to ensure complete combustion of the organic material. N_2 and air gases were introduced at a rate of 50 mL/min.

X-ray Photoelectron Spectroscopy. XPS experiments were performed on a VG ESCALAB 220i-XL spectrometer equipped with a monochromatic Al Kα X-ray source ($h\nu = 1486.6$ eV) and a hemispherical electrostatic analyzer. The analysis chamber was maintained under high vacuum, less than 10^{-9} Torr. A constant analyzer pass energy scan of 20 eV was used in the case of the high-resolution scans (Au 4f, S 2p, and C 1s). A flood gun was used to minimize the charging in all of the runs. The CasaXPS software (version 2.2.29) was used for the spectral curve fittings. Binding energies were referenced to the C 1s of alkyl chains or alkyl contaminants at 284.6 eV. The peaks were fitted with a Gaussian−Lorentzian function. A Shirley background was subtracted from all curves.[44] The 3.67 eV spin−orbit splitting of Au $4f_{5/2}$ and Au $4f_{7/2}$ was maintained, as well as the 3:4 intensity ratio of the splitting. Moreover, the 1.18 eV spin−orbit splitting ratio was maintained for S $2p_{1/2}$ and S $2p_{3/2}$, as well as the 1:2 intensity splitting ratio. The number of atoms of element A probed was proportional to the intensity of the normalized corresponding peak (I_A) divided by the relative sensitivity factor of the element A for the corresponding transition. As a result, the A to B elemental ratio was obtained using:

$$n_A/n_B = (I_A.S_B)/(I_B.S_A)$$

where S_A is the relative sensitivity factor of the element A for the main peak. S_A is the product of the Scofield photoionization cross-section (σ_A) and the transmission function of the pass energy analyzer (T_A) of the element A.[45,46]

The XPS spectrometer used in this study is capable of high-resolution measurements (i.e., full-width half-maximum value of 0.6 eV for Ag) enabling one to accurately obtain small shift differences. However, relatively large shifts in the binding energy values were observed from run-to-run for the same sample. C 1s and S 2p spectra were obtained twice for each sample, at the beginning and the end of a measurement. Shifts in the peak position were detected before and after the 20-min runs. Moreover, two different Au species were discernible after deconvolution under each Au 4f peak. Beam damage and spectrometer-mediated chemical transformations (i.e., reduction of Au(I) to Au(0)) likely occurred. This type of beam damage has been reported in bioinorganic-complex studies[47,48] and is a concern in RS/Au SAM studies.[49,50] Charging at the surface of the sample, despite the use of the electron flood gun, was probably the source of the large time-dependent shifts. To counteract the charging and decomposition issues, samples were prepared by grinding carbon graphite and Au(I) complex (10% by mass) and pressing this mixture into pellets. In this case, the binding energies were referenced to the C 1s of graphite at 284.7 eV. This only slightly improved the charging and decomposition problems. Beam damage and/or charging were not encountered in previous studies from our group[51] and others[4,52] on similar Au(I)−thiolate species.

Solution ^{1}H and ^{13}C NMR. ^{1}H and ^{13}C NMR solution spectra of the gold(I)−thiolate complexes, dissolved in $CDCl_3$, were performed on a 400 MHz Varian Mercury spectrometer operated with VNMR 6.1B software on a SUN Ultra 5 workstation. Typically 32 scans were acquired.

Solubility and Crystallization of the Au(I)−Thiolate Complexes. A series of common organic solvents (THF, toluene, $CHCl_3$, DMSO, acetone, hexanes, etc.) was used to test the solubility of the complexes at room temperature. Low intensity sonication or warming of the solutions (50 °C maximum) was used. Heating of the complexes above 50 °C usually resulted in their decomposition. Some soluble complexes decomposed after 5 min in solution at room temperature.[53]

Crystallization attempts were performed on the soluble complexes, by classical techniques of slow solvent evaporation (with one or binary solvents) and solvent vapor diffusion.

X-ray Crystallography. A colorless needle crystal of Au(I)−TRIP having approximate dimensions of 0.25 × 0.07 × 0.05 mm was mounted on a glass fiber. All measurements were made on a Nonius Kappa CCD area detector diffractometer (University of Zurich, Dr. A. Linden) with graphite monochromated Mo Kα radiation and a sealed tube generator. The data were collected at a temperature of −113 ± 1 °C using the ω-2θ scan technique to a maximum 2θ value of 50.0°.

Table 1 summarizes the characterization data of the Au(I)−thiolate complexes.

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Solution Synthesis and Characterization of Gold Nanoparticles. *Synthesis of Au Nanoparticles by One-Phase Superhydride Reduction of Au(I)−Thiolate Complexes.* Prior to use, the components of the reaction vessel were flamed-dried under vacuum and then maintained in an ultrapure nitrogen atmosphere. The Au(I)−thiolate complexes were dissolved either in THF or in diethyl ether, depending on their solubility. In a typical synthesis, 60 mg of Au(I)−cyclohexanethiol was dissolved in 5 mL of freshly distilled THF. Superhydride (1.0 M) was added, first in a 1 mL aliquot, then in 0.5 mL aliquots over ca. 2 h, until there was no more gas evolution. The color of the solution instantly became dark brown after the first Superhydride addition. The solution was stirred overnight under an N_2 atmosphere.

Synthesis of Au Nanoparticles by Two-Phase $NaBH_4$ Reduction of Au(I)−Thiolate Complexes without Phase-Transfer Catalyst. The Au(I)−thiolate complexes (e.g., 20 mg of TRIP−Au(I)) were dissolved in toluene (e.g., 4.5 mL) in the reaction flask. $NaBH_4$ (e.g., 21 mg) was dissolved in MilliQ water (e.g., 3 mL), and the solution was added to the reaction flask. The reaction mixture was stirred overnight. No color change was observed after addition of the reducing agent for any of the Au(I)−thiolate complexes studied.

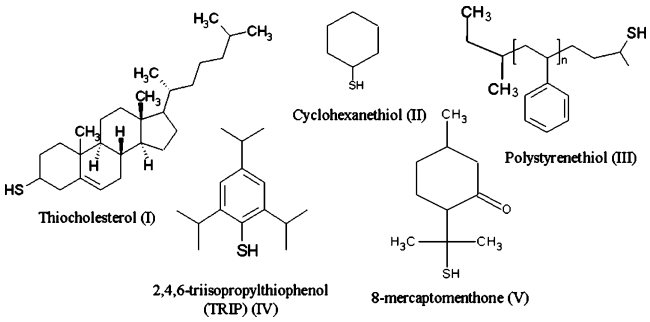
Synthesis of Au Nanoparticles by Two-Phase $NaBH_4$ Reduction of Au(I)−Thiolate Complexes with Phase-Transfer Catalyst. The Au(I)−thiolate complexes (e.g., 10 mg of TRIP−Au(I)) were dissolved in toluene (e.g., 1 mL) in the reaction flask. Tetraoctylammonium bromide (TOAB) (58 mg) was dissolved in toluene (e.g., 2 mL) and added to the reaction flask. $NaBH_4$ (e.g., 10 mg) was dissolved in MilliQ water (e.g., 2 mL), and the solution was added to the reaction flask. The toluene solution changed from colorless to orange to dark red/purple within a few seconds. The reaction mixture was stirred overnight.

Synthesis of Au Nanoparticles via the Ulman method.[3] The components of the reaction vessel were flamed under vacuum and maintained under an ultrapure nitrogen atmosphere. In a typical synthesis, 5 mL of freshly distilled THF was used to dissolve 200 mg of $HAuCl_4 \cdot 3H_2O$ in a round-bottom flask, resulting in a pale yellow color. A solution of 0.125 mL of $C_{14}SH$ in 5 mL of THF was then added to the flask. The solution became slightly orange, with greenish undertones for the first few minutes. The orange solution was stirred overnight in the dark. The reduction was initiated with a 1 mL one-shot addition of Superhydride (lithium triethylborohydride, Aldrich, 0.1 M in THF), at which point the solution developed a very dark, deep red Bordeaux color. Superhydride was subsequently added in increments of 0.5 mL over several hours until gas evolution ceased. The solution was stirred overnight in the dark. We also employed $KAuBr_4$ in the Ulman-type synthesis trials, and the molar ratios used were RSH:Au 1:1.1 (i.e., Au was in 10% excess) in all cases.

Purification of the Gold Nanoparticles. The nanoparticle samples were cleaned by successive precipitation in selected solvents.[6]

TEM Characterization of the Gold Nanoparticles. The nanoparticles were dissolved in a suitable organic solvent (typically THF, toluene, or chloroform). A drop of dilute solution of Au nanoparticles was deposited directly onto a 400 mesh copper grid covered with a thin carbon film (Electron Microscopy Sciences), and the solvent was allowed to evaporate at ambient pressure and temperature. A JEOL 2000FX transmission electron microscope was used at the 80 kV setting. Digital pictures were obtained using a Gatan Bioscan CCD camera (model 792). The CCD camera was interfaced with a PC running DigitalMicrograph software (Gatan). The TEM images were analyzed using SigmaScan Pro 4.0 (SPSS Inc.). Calibrated areas of approximately 300 nanoparticles per image were measured, and the diameters were estimated (assuming sphericity of the gold cores). Histograms of the populations of diameters were constructed using SigmaPlot 8.0 (SPSS Inc.).

Chart 1. Structures of the Thiols Used To Make Soluble Au(I)−Thiolate Complexes in This Study



Results and Discussion

Synthesis, Characterization, and Properties of Au(I)−Thiolate Complexes. Two preparation procedures of Au(I)−thiolate complexes were used. Each procedure yielded apparently similar Au(I)−SR complexes for a given thiol ligand. A large number of Au(I)−SR complexes was prepared, anticipating that those prepared from bulky thiol ligands would more likely be soluble.[26,36,38] It was reasoned that Au(I)−thiolates, which have bulky ligands that do not interact well, will be unable to have close packing in the solid state. The overall solubilization in such a material would therefore be more facile. Chart 1 shows the structures of the thiols that yielded soluble complexes in this study.

PS_{19}−SH is the bulkiest thiol ligand used in this study, and Au(I)−PS_{19} is indeed soluble in a variety of the organic solvents tested (e.g., toluene, THF, $CHCl_3$). TGA measurements yield a 1.1:1 Au/thiol mole ratio (using an average molecular weight of 2000 g/mol for PS_{19}−S), consistent with two-coordinate Au.[16] Given the propensity for two-coordinate Au, all of the Au(I)−SR materials prepared here (soluble and insoluble) are expected to have a Au/thiol mole ratio of 1:1. This was experimentally confirmed by TGA and XPS measurements (Table 1).

Au(I)−TRIP is also a soluble gold(I)−thiolate complex (e.g., in diethyl ether) and was the only one studied here that formed crystals in our hands. The crystal structure as determined here conforms to that reported by Leblanc et al. and corresponds to a ring composed of 6 gold atoms and 6 sulfur atoms.[34,36] The solvent of crystallization in the complex was diethyl ether as per LeBlanc et al.[34] The same Au(I) complex, solvated by THF, was reported by Schröter et al.[36]

Solution ^1H NMR of the Au(I)−TRIP confirms the decreased mobility of the thiol molecules bound to the complexes by a broadening of the peaks. The difference in chemical shift of the −CH signals, between the free thiols and the Au(I)−thiolate complexes, further confirms the binding of the thiolate to a Au atom (Supporting Information).

Other soluble Au(I)−thiolates prepared include Au(I)−thiocholesterol (which forms a turbid gel in solution after a few minutes), Au(I)−triphenylmethanethiol (which decomposes rapidly in solution), Au(I)−cyclohexanethiol, Au(I)−8-mercaptomenthone, Au(I)−4-methoxybenzenethiol (de-

Table 2. Syntheses of Thiol-Stabilized Gold Nanoparticles from Au(I)−Thiolates and from $HAuX_4$ via the Ulman Method

thiol	synthesis conditions	diameter distribution (nm)
thiocholesterol(I)	$NaBH_4$ reduction of Au(I)−thiocholesterol in toluene/water without TOABr	no reaction
thiocholesterol(I)	Superhydride reduction of Au(I)−thiocholesterol in THF	1.2 ± 0.2 + a few large ones (3−6 nm)
thiocholesterol(I)	Ulman synthesis with $HAuCl_4$	2.8 ± 0.6
thiocholesterol(I)	Ulman synthesis with $KAuBr_4$ + HBr	2.4 ± 0.6 + large ones + precipitate
cyclohexanethiol(II)	Superhydride reduction of Au(I)−cyclohexanethiol in THF	2.9 ± 0.8 + precipitate
cyclohexanethiol(II)	Ulman synthesis with $HAuCl_4$	3.3 ± 0.7 + precipitate
PS_{19}−SH(III)	Superhydride reduction of Au(I)−PS_{19} complex in THF	2.9 ± 0.9
PS_{19}−SH(III)	Ulman synthesis with $HAuCl_4$	4.4 ± 1.2
TRIP(IV)	$NaBH_4$ reduction of Au(I)−TRIP in toluene/water without TOABr	no reaction
TRIP(IV)	$NaBH_4$ reduction of Au(I)−TRIP in toluene/water with TOABr	3.7 ± 0.8
TRIP(IV)	Superhydride reduction of Au(I)−TRIP in ether	3.1 ± 0.8
TRIP(IV)	Ulman synthesis with $HAuCl_4$ in ether	2.2 ± 0.6
TRIP(IV)	Ulman synthesis with $KAuBr_4$ in ether/THF	2.2 ± 0.6
mercaptomenthone(V)	Superhydride reduction in THF of Au(I)−mercaptomenthone	2.6 ± 0.7 + a few large nonspherical ones
mercaptomenthone(V)	Ulman synthesis with $HAuCl_4$	2.1 ± 0.5 + large nonspherical ones (4−5 nm)

composes rapidly), and Au(I)−4-methoxy-α-toluenethiol (partially soluble in warm DMSO with sonication). Au(I)−2-furanmethanethiol immediately decomposes in solvents tested (i.e., THF or chloroform). It should be noted that the soluble Au(I)−thiolates tend to become less soluble after long-time storage in the solid state in a cold and dark environment. This may be due to slow decomposition or to slow formation of more stable polymorphs.

Comparison of Nanoparticle Synthesis via Direct Reduction of Au(I)−Thiolate Complexes and via the Ulman (Superhydride) Procedure. The preparation of gold nanoparticles by the reduction of soluble Au(I)−thiolate complexes has not, to our knowledge, been previously reported. Typical syntheses of gold nanoparticles involve the reduction of Au(III) salts in the presence of thiols, amines, or ions. Reduction of Au(III) salts in the presence of thiols principally takes place in a two-phase synthesis method, where a phase-transfer catalyst (usually tetraoctylammonium bromide, TOABr) is necessary to transfer the Au(III) salt from the aqueous phase to the toluene phase. It is likely that the thiol also reduces some of the Au(III) salt to yield the Au(I)−thiolate complex. Because a 1:3 Au:RSH ratio for complete reduction of Au(III) to Au(I) is necessary, the thiol is the limiting reagent for typical reactions run under 1:1 conditions. Addition of $NaBH_4$ further reduces the Au(I) (and the remaining Au(III)) to form thiol-stabilized Au(0) nanoparticles. A previous study by Murray et al. suggests that the reducing agent causes fragmentation of the Au(I) intermediate en route to gold nanoparticles.[11] A one-phase preparation method on the other hand involves the reduction of a Au(III) salt in the presence of a thiol in THF. These preparation methods consistently yield nanoparticles of similar diameters (1−4 nm).[1,3,6] The choice of gold(I)−thiolate used for nanoparticle preparation was based on solubility. Au(I)−thiocholesterol, Au(I)−TRIP, Au(I)−cyclohexanethiol, Au(I)−mercaptomenthone, and Au(I)−PS_{19} were thus used as starting reagents to prepare gold nanoparticles. For comparison purposes, nanoparticles capped with the same thiols were prepared using the one-phase (Ulman) synthesis method and $HAuCl_4$ and $KAuBr_4$ as starting gold(III) salts. Table 2 summarizes the resulting gold nanoparticle diameters (with associated standard deviations) as a function of reaction conditions. The Au(I)−thiolates isolated here do not react with $NaBH_4$ in two-phase reaction conditions in the absence of a phase-transfer catalyst such as TOABr. However, when the same two-phase experiment was performed in the presence of TOABr, the Au(I)−thiolate complexes were reduced into gold nanoparticles. This confirms that the role of TOABr in the two-phase Brust reaction is not only to transfer the gold(III) salt from the aqueous to the toluene phase, but also to transfer the borohydride anions from the aqueous to the toluene phase. Reduction of the Au(I) intermediate into Au nanoparticles thus occurs. Because the two-phase system is more complex, due to the necessary presence of a phase-transfer catalyst, we concentrated on one-phase Superhydride reduction of the Au(I)−thiolates.

The Superhydride reduction of Au(I)−thiocholesterol in THF predominantly yields very small and monodisperse gold nanoparticles (ca. 1.2 ± 0.2 nm), as well as a small quantity of larger nanoparticles (in the range 3−6 nm) (Figure 2). Conventional Ulman synthesis of thiocholesterol-capped gold nanoparticles yields significantly larger nanoparticles, with diameters 2.8 ± 0.6 nm when starting with $HAuCl_4$, and 2.4 ± 0.6 nm when starting with $KAuBr_4$ plus HBr. The differences in nanoparticle product between the two starting gold salts are not significant, although a small amount of insoluble material was obtained when using the $KAuBr_4$ salt. However, the diameters are significantly larger when the nanoparticles are made from the Au(III) salts rather than from the Au(I)−thiocholesterol complexes (Figure 2).

Similar experimental conditions were applied to the Au(I)−TRIP materials. Larger nanoparticles were obtained than in the case of thiocholesterol (with diameters ranging from 2.1 ± 0.6 to 3.1 ± 0.8 nm), but overall, the diameters are not significantly different from one another when the nanoparticles are made from the Au(I)−TRIP or the Au(III) salts.

The PS_{19}-stabilized gold nanoparticles prepared from the Superhydride reduction of Au(I)−PS_{19} and the conventional Ulman synthesis did provide significantly different nanoparticle sizes, with smaller diameters in the former case (2.9 ± 0.9 vs 4.4 ± 1.2 nm). Similarly, slightly smaller nanoparticles were obtained from the Superhydride reduction of

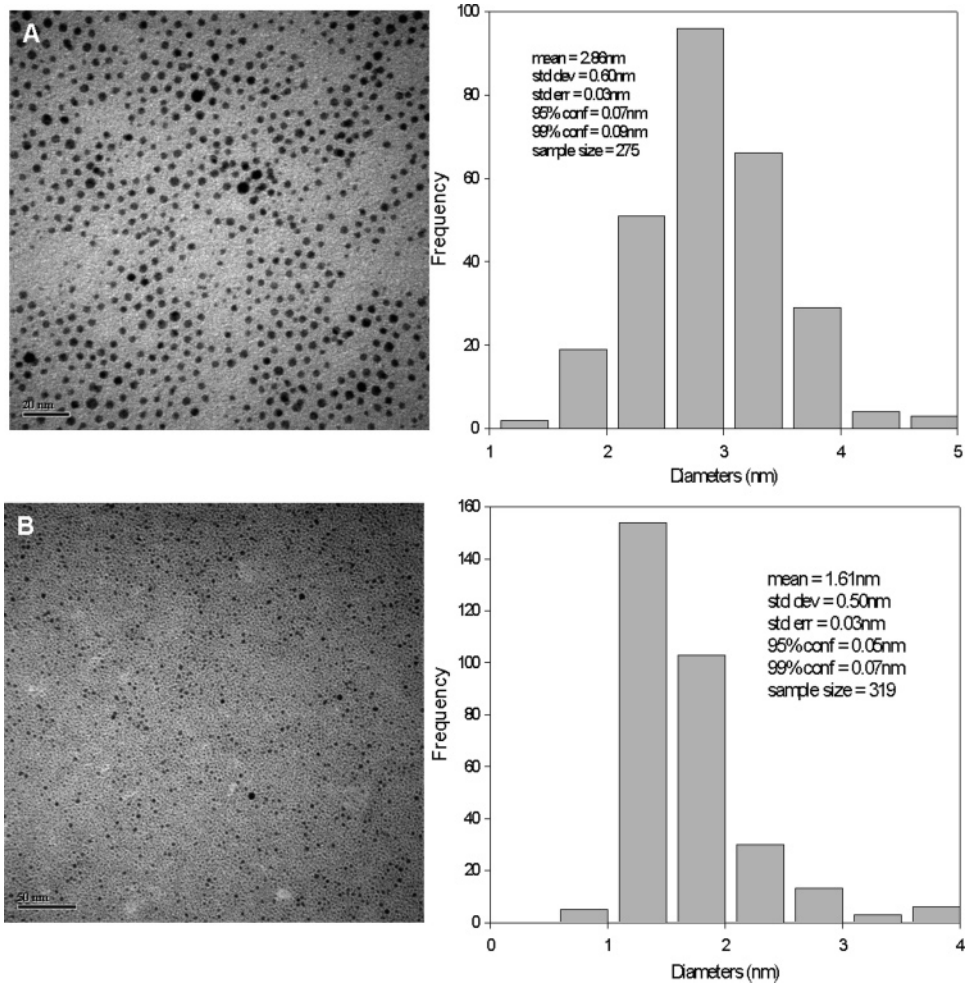


Figure 2. TEM images of thiocholesterol−Au nanoparticles prepared (A) by conventional Ulman synthesis with $HAuCl_4$, and (B) by Superhydride reduction of Au(I)−thiocholesterol. Micrograph scale bars = 20 nm (A) and 50 nm (B).

Au(I)−cyclohexanethiol as compared to the Ulman procedure (2.9 ± 0.8 vs 3.3 ± 0.7 nm). Mercaptomenthone-stabilized gold nanoparticles of similar sizes were obtained via each method (2.6 ± 0.7 vs 2.1 ± 0.5 nm).

In general, the gold nanoparticles prepared from the Superhydride reduction of soluble Au(I)−thiolate materials are similar in diameter to those prepared by conventional methods. This is an indication that the nonisolated intermediate Au(I) complexes in the standard methods[1,3] may be the same as the pre-prepared Au(I)−thiolates used here.

The nanoparticles prepared using the Ulman synthesis range from 2.1 to 4.4 nm. This is consistent with other reports.[1−23,7,9] A bulky thiol group such as PS_{19}−SH does not have a marked effect on the size of the nanoparticle as compared to a smaller thiolate ligand such as cyclohexanethiol.[6]

Conclusion

We have thus demonstrated the ability to control the solubility of the gold(I)−thiolate materials with the use of bulky thiolate ligands. In this way, the potential of attractive intermolecular Au···Au interactions, and their potential to cause insolubility, is avoided. Clearly, the synthetic process of gold nanoparticles is a complex one, and several factors are at play. The solution synthesis of gold nanoparticles from the reduction of soluble Au(I)−thiolate complexes yields small nanoparticles, with core diameters within the usual range obtained by conventional methods using thiolates as ligands. We have thus confirmed that isolated Au(I)−thiolates are indeed rational precursors to the preparation of gold nanoparticles and that a range of nanoparticles are accessible using these complexes as starting materials.

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Supporting Information Available: ^{1}H NMR spectra of TRIP and Au(I)−TRIP (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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