MECHANISTIC INSIGHT INTO THE BRUST–SCHIFFRIN TWO-PHASE METHOD FOR ORGANOCHALCOGENATE-PROTECTED METAL NANOPARTICLES

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MECHANISTIC INSIGHT INTO THE BRUST–SCHIFFRIN TWO-PHASE METHOD FOR ORGANOCHALCOGENATE-PROTECTED METAL NANOPARTICLES

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ABSTRACT

The primary objective of this thesis research was to explore the mechanism of the Brust–Schiffrin two-phase method, which has been widely used for preparing the thiolate-protected metal nanoparticles with the core diameter less than 5nm; to synthesize and characterize the ligand-protected gold nanoparticles using dialkyl ditelluride with different alkyl chain length as ligand precursor; and to develop a new synthetic route for obtaining ultra-small (< 2 nm) gold nanoparticles covered by tellurium-anchoring ligands.

Since the Brust–Schiffrin two-phase method was first reported in 1994, many groups have tried to identify the precursors of metal ions prior to the addition of NaBH₄. The widely accepted assumption has been that the addition of thiol reduces Au(III) to Au(I) and forms [AuSR]ₙ-like polymers. Recently Lennox and coworkers have demonstrated that the metal precursor before the addition of the reductant is TOA metal(I) halide complex [TOA][MX₂], and not [MSR]ₙ-like polymers. Our Raman spectroscopic investigations showed that, in a typical BSM synthesis, no metal(M)–sulfur(S) bonds were formed after thiol addition. These observations provide independent spectroscopic confirmation of the recent work by Lennox and co-workers. On the basis of Raman, NMR, and surface plasmon resonance characterizations, we found that before the formation of any metal–chalcogen bonds, metal nucleation centers/NPs were first formed inside the inverse micelles of the tetrabutylammonium bromide in the organic solvent, where the
metal ions were reduced by NaBH\textsubscript{4}. The ensuing formation of the metal–chalcogen bonds between the naked metal NPs inside the micelles and the organochalcogen ligands in the organic solvent is the mechanism by which the further growth of the metal core can be controlled. This proposed mechanism has been further examined in the formation of Ag and Cu nanoparticles.

This new mechanistic understanding enabled the design of some specifically targeted experiments to address the size polydispersity problem frequently observed in the traditional Brust–Schiffrin two-phase syntheses. We identified that the co-presence of the residual thiol and reduction-generated disulfide as found in a typical Brust–Schiffrin two-phase synthesis is a source of the observed size polydispersity. We also found that in the presence of H\textsubscript{2}O, thiol acted as a better ligand than disulfide for smaller and more homogenous Au nanoparticles while in a water-deprived situation bisulfide was superior.

In addition, the critical role of water and structure of inverse micelles in a typical Brust–Schiffrin two-phase synthesis of gold nanoparticles were further investigated. We found that the presence of a certain amount of water was a key factor that determined whether the Au(I) precursor was a [TOA][AuX\textsubscript{2}] complex or a mixture of [TOA][AuX\textsubscript{2}] complex and polymeric [AuSR]\textsubscript{n} species. The water encapsulated in the inverse micelles of [TOA]\textsuperscript{+} also hosting metal ions formed a hydrophilic microenvironment that acted as a reaction-enabling proton accepting medium for the thiol protons (RS–H). We also discovered that not only the presence but also the amount of water in the reaction medium has profound effect on the reduction of Au(III) by thiols and on the formation of uniform small gold nanoparticles.

Using dialkyl ditelluride with different alkyl chain lengths as ligand precursors, air-stable gold nanoparticles protected by tellurium-containing ligands were successfully obtained by the Brust–
Schiffrin two-phase synthetic route. The capping monolayers were studied in details by $^1$H, $^{13}$C, and $^{125}$Te NMR, IR, and XPS. The chemical behaviours of dialkyl ditelluride in the formation of ligand-protected nanoparticles were also investigated by $^1$H NMR and Raman spectroscopies. More importantly, during the aforementioned mechanistic study, we developed a new synthetic route, by which homogenous tellurium-containing ligand-protected Au nanoparticles with the sizes less than 2 nm were obtained.
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TEM images with size distribution and UV-visible spectra of (a) C₆Se–Au NPs, (b) C₈Se–Au NPs, (c) C₁₂Se–Au NPs, (d) C₆Te–Au NPs, (e) C₈Te–Au NPs, and (f) C₁₂Te–Au NPs.

Figure 7.9
¹H NMR spectra of NPs for (a) Se and (b) Te system; ¹³C NMR spectra of NPs for (c) Se and (d) Te systems (R: C₆ - black, C₈ - red, and C₁₂ - blue), all in C₆D₆.

Figure 7.10
(a) Bonding energies of Au 4f in RS–Au NPs, RSe–Au NPs, and RTe–Au NPs; (b) Se 3d XPS spectra of RSe–Au NPs; and (c) C 1s XPS spectra of RSe–Au NPs (R: C₆ - black, C₈ - red, C₁₂ - blue).
1.1 Background

Molecular electronics is drawing more attention worldwide as a result of the rising costs and physical limits involved in the continual downsizing of microelectronics and the requirements of Moore’s law. The fundamental research of molecular electronics is based on the donor-molecular wire-acceptor model (see Figure 1.1). The conductivity along a molecular wire is mainly through bond quantum tunneling and for a small bias potential the conductance $G$ follows an exponential law: $G = G_0 \exp(-\gamma L)$, where $G_0$ is the contact conductance determined by the metal-ligand bonding, $\gamma$ is the inverse dampening length determined by ligand’s internal electronic structure, and $L$ is the ligand length.

Quantum calculations by Dr. Di Eentra and Dr. Lang investigated the conductance of a molecular device with different chalcogen (i.e., S, Se, and Te) as an anchoring element to connect the molecule wire to the gold electrodes (see Figure 1.2). They found that the Fermi levels in the case of S and Se terminations falled in the gap between the highest occupied and lowest unoccupied molecular orbitals (HOMO-LUMO), while the HOMO of Te-anchoring groups is nearly exactly at the position of the Fermi levels (see Figure 1.3). In the case of S, transport occurs via the tails of the LUMO orbitals giving the molecular region a natural “n doping”; on the other hand, the HOMO of the molecules ending with Se is very close to the Fermi levels and the charge transfer occurs from the molecule to the electrodes, which provides a slight “p doping” to the molecular region; while Te as anchoring element makes an even larger charge
transfer from the molecular region to the electrodes, pushing the HOMO practically into resonance with the Fermi level. These findings are important for understanding the interaction between molecule wires and electrodes. However, whether these predictions work in practice or not is still a question.

Murray’s group has found that alkanethiolate-protected Au nanoparticles (NPs) can be considered nanometer-sized electrodes. So the organochalcogen-protected gold NPs, where S, Se, or Te is to be used as anchoring element, will be good models to study the interaction between the ligands and Au.

The studies on gold NPs can be dated back to mid-nineteen century. In 1857, Michael Faraday successfully obtained gold colloid solution (Figure 1.4), which is very stable and still exhibited in Royal Institution of Great Britain, London, UK. A lot of research has been done on gold NPs, because of their applications, as building blocks to assemble macroscopic structures, drug delivery, imaging labels, etc. Among them, most common capping monolayers were bound to metal cores by using sulfur as an anchoring element. However, few published studies exist for the metal NPs protected by the ligands containing other chalcogen (i.e., RSe–Au NPs, RTe–Au NPs). It is probably because of the air-instability of alkanechalcogenol (i.e., RSeH, RTeH) and the commercial unavailability of dialkyl dichalco-genide (i.e. R₂Se₂, R₂Te₂), which is considered an alternative of alkanechalcogenol. To the best of our knowledge, except our published results, only Brust and co-workers have attempted to synthesize metal NPs using tellurium as an anchoring element. Unfortunately they did not provide any further characterizations other than Langmuir isotherm plot due to the instability of their obtained NPs.
There have been only a few studies about the self-assembled monolayers (SAMs) of alkane/aromatic telluride on oriented single-crystal metal surface.\textsuperscript{14-18} Tohru Nakamura and co-workers found that the dioctylditelluride-derived thin films on Au (111) exhibited insulating properties compared with the disulfide and diselenide films.\textsuperscript{15} Starting with the dialkyl ditelluride with different alkyl chain length (i.e. C4, C8, and C16), they found that the ditellurides have been auto-oxidized when adsorbed onto Au(111).\textsuperscript{16} The X-ray photoelectron spectroscopy (XPS) results of SAMs from dioctyl disulfide, dioctyl diselenide, and dioctyl ditelluride on Au(111) suggested that dichalcogenides dissociatively adsorbed on Au(111) surfaces to form the corresponding monolayers having chalcogen-gold covalent bonds.\textsuperscript{17} Weidner and co-workers’s studied the SAMs formed from bis(4'-methylbiphenyl-4-yl) ditelluride on Au(111) and Ag(111) substrates by high-resolution XPS and found that such SAMs were not stable under ambient conditions but underwent rapid autoxidation, which affected exclusively the tellurolate headgroups.\textsuperscript{18}

1.2 Brust–Shiffrin Two-Phase Method (BSM)

There are several synthetic routes to synthesize Au NPs. Among them, Brust–Shiffrin two-phase method\textsuperscript{19}, abbreviated herein as BSM for simplicity, is the most popular for preparing chalcogenate-protected metal NPs,\textsuperscript{11,13,20,21} in particular thiolate-protected Au NPs\textsuperscript{9,13,22-39}. Their synthetic procedures are easy-to-follow. The average size of the obtained NPs can be easily controlled by adjusting the ratio of thiol to gold\textsuperscript{26,28}. These NPs are very stable, can be isolated, stored for a long term, redissolved in common organic solvent,\textsuperscript{28,39} just like commercial shelf chemicals. The surface of these NPs can also be further functionalized.\textsuperscript{37,40} Although these NPs
are polydisperse\textsuperscript{39}, this method has been widely used to synthesize metal NPs with the size of less than 5 nm.

BSM was first reported in 1994.\textsuperscript{19} Its mechanistic details of the synthesis are still unclear so far. It has generally been accepted that a typical BSM synthesis consists of three steps:

(i) Phase transfer of Au(III) ions from aqueous layer to organic layer (i.e. toluene or benzene) with the help of phase transfer agent TOAB (tetrabutylammonium bromide);

\[
\text{HAuCl}_4 \text{ (aq)} + \text{TOAB (toluene)} \rightarrow \text{TOA}^+ \text{AuCl}_4^- \text{ (toluene)}
\]

(ii) Reduction of Au(III) to Au(I) by the added thiols;

(iii) Reduction of Au(I) to Au(0) by NaBH\textsubscript{4} in the presence of thiols and/or other sulfur-containing ligands that leads to the formation of Au NPs.

In the paper, Brust and co-workers suggested to slowly add fresh NaBH\textsubscript{4} aqueous solution with vigorous stirring at Step (iii), and proposed the reaction as follows, happening at Step (ii) and (iii):

\[
m \text{AuCl}_4^- \text{ (toluene)} + n \text{RSH} + 3m \text{e}^- \text{ (from NaBH}_4) \rightarrow 4m \text{Cl}^- \text{ (aqueous layer)} + (\text{Au}_m \text{RSH})_n \text{ (toluene)}.19
\]

Due to earlier papers by Whetten et al,\textsuperscript{6,23,24} a long-held belief concerning the metal precursor produced at Step (ii) until recently was that polymeric metal-thiolate species, [M(I)SR\textsubscript{n}]\textsubscript{m}, is the metal-ion precursor of metal NPs\textsuperscript{12,41}. In 1997, Whetten group suggested that the gold cluster growth process was the solution-phase decomposition of [AuSR\textsubscript{n}]\textsubscript{m}-like polymer: [AuSR\textsubscript{n}] \rightarrow \text{Au}_x \text{(SR)}_y + \text{RSSR}, 1.6 < x/y < 2.7, which process was stimulated reductively under mild conditions (i.e. room temperature) by adding a reducing agent to the mixture of HAuCl\textsubscript{4} aqueous solution and TOAB toluene solution.\textsuperscript{24} They suggested the following crucial points for the formation of smaller NPs by BSM, which were consistent with principles of crystallite nucleation and multistage growth: (i) polymeric AuSR precursor, which had only modest
solubility in toluene (depending on R) and was obtained with a S:Au molar ratio of 3:1 by the precise stoichiometric reaction \[ 3RSH + \text{AuCl}_4^- \rightarrow \text{AuSR} + \text{RSSR} + (\text{acid and salt}); \] (ii) adding the aqueous NaBH\textsubscript{4} all at once with great molar excess to the vigorously stirred mixture, which resulted in a rapid color change (~10s) from colorless to opaque-brown-black; (iii) temperature effect on NP’s size, i.e. that increasing (or decreasing) temperature would produce higher abundance of larger (or smaller) NPs; (iv) reaction time, i.e. halting the reaction at \(~10^3\) s would get higher yields of the smallest cores compared to the terminal state at \(10^4\sim10^5\) s.\textsuperscript{24} Although it was also found that larger thiol: gold molecular ratios give smaller average NPs’ core sizes,\textsuperscript{28} [AuSR]\textsubscript{n}-like polymer has been widely accepted as gold precursor species in BSM (Figure 1.5).\textsuperscript{28,37,39}

The most recent, thought-provoking results from Lennox and co-workers\textsuperscript{41} have shown otherwise. On the basis of a quantitative \textsuperscript{1}H NMR study of the solutions after adding thiols with different S: Au ratios to the organic layer of the mixture of H\textsubscript{AuCl}_4 aqueous solution and TOAB toluene solution, they have demonstrated that the metal precursor species before adding the reductant (i.e. NaBH\textsubscript{4}) is TOA metal(I) halide complex [TOA][AuX\textsubscript{2}], and not [AuSR]\textsubscript{n}-like polymers. By monitoring the UV peak of the intermediate of BSM with different amounts of thiols, they determined only 2 equiv of thiols were needed to reduce all Au(III) in [AuX\textsubscript{4}]\textsuperscript{−} to Au(I) (i.e. [AuX\textsubscript{2}]) as the following: \[ [\text{TOA}][\text{AuX}_4] + 2\text{RSH} \rightarrow [\text{TOA}][\text{AuX}_2] + \text{RSSR} + 2HX.\textsuperscript{41}\] Therefore, what is the correct metal precursor species in BSM, [TOA][AuX\textsubscript{2}] complex or [AuSR]\textsubscript{n}-like polymer? Since the former does not involve a metal (M)–sulfur (S) bond, what happens and at what stage the Au–S bond is formed after the addition of NaBH\textsubscript{4} during MSM? These questions remained largely unresolved. In addition, polydispersity in the obtained metal
NPs has been an remaining issue of BSM.\textsuperscript{39} Consequently, laborious fractionalizations\textsuperscript{23} have been frequently employed and a novel size-focusing method\textsuperscript{39} was recently developed to achieve homogeneously distributed Au NPs. Despite its clear practical importance, few pertinent studies are available in the literature to shed the light on the (molecular) cause of the polydispersity simply because detailed mechanistic information on the BSM has been unelaborated, which makes the well-targeted research very difficult.

1.3 Research Purpose

The research presented here is in the field of nanomaterial synthesis. Our studies focus on the mechanism of the BSM (Brust–Schiffin two-phase method), that was widely used for preparing thiolate-protected metal NPs (nanoparticles), as well as on the synthesis and characterization of metal NPs with new type of anchoring element, i.e., using Te to replace S.

The term \textit{nanomaterial} refers to the materials with the dimensions in the range of 1~100 nm (1 nm = 10\textsuperscript{-9} m). Considering that atoms have a size around 1 Å, a nanoparticle consists of tens to hundreds of atoms. Sometimes the metal nanoparticles with the core diameter less than 3 nm are called as nanoclusters (or clusters for short), which is believed to contribute an important intermediate size regime between localized atomic states and delocalized band structure (Figure 1.6).\textsuperscript{39} Chalcogenate-protected gold NPs have been considered good model systems for self-assembly, biolabeling, electron-transfer theories, etc., because of their unusual optical properties and size-dependent electrochemistry. Even though most of the current investigations are on thiolate-protected metal NPs, the primary objective of this research is to obtain the metal NPs, on which the capping monolayers are bound to metal cores by using Te as an anchoring elements.
The synthesis, purifications, and characterization (including $^1$H, $^{13}$C, and $^{125}$Te NMR spectroscopy, Raman spectroscopy) of ligand precursors, i.e., dialkyl ditelluride with different alkyl chain lengths (C6, C8, C12, and C16) are present in Chapter II and VII. The synthesis of the Au NPs protected by Te-containing ligands, are present in Chapter II, followed either a typical BSM or our reversed synthetic route. The chemical behaviors of dialkyl ditelluride in the synthesis of ligand-protected Au NPs by BSM are also studied in details (see Chapter III and VII). The capping monolayers of such NPs and their effects on the obtained NPs are investigated in Chapter III.

Although BSM has been widely used to synthesize thiolate-protected metal NPs especially for the NPs with the core diameter of less than 5 nm, the correct metal precursor species before the addition of the reductant are still unclear. The Raman spectroscopic investigations on the intermediates give some indications to figure out the state of metal-ion precursors in BSM, which are shown in Chapter IV and V. The $^1$H NMR spectra of the intermediates together with the DLS study results stimulated us to propose a general metal NPs formation mechanism applicable to the typical BSM in Chapter IV. That is, a typical BSM is basically an inverse micelle-based synthetic procedure, which enables the design of some specifically targeted experiments to address the size polydispersity problem frequently observed in the traditional BSM (see Chapter VI). In addition, the critical role of the encapsulated water and structure of inverse micelles in a typical BSM is further studied in Chapter V.

The work of this project is to bring new mechanistic insight into the popular BSM, to open a door for preparing the fascinating ligand-protected metal NPs with homogeneous sizes, to enrich
the ligand-protected metal NPs by using a new type of anchoring element, and to envision novel exciting materials for the future.
Figure 1.1 Schematic of Donor-Bridge-Acceptor Systems\(^2\) (Note: \(^a\) “molecule” can include complex enzyme system; \(^b\) Single molecule spectroscopy; \(^c\) scanning probe microscopy.)
Figure 1.2 Schematic of (a) two bare electrodes (represented by the unperturbed Hamiltonian $H_0$) kept at a certain external potential difference; (b) the total system, i.e. sample (a molecule or any set of atoms) plus electrodes; (c) the three molecular structures investigated.\textsuperscript{5}
Figure 1.3 Difference between the density of states of the two semi-infinite electrodes with and without the molecules (see Figure 1.2) in between. (Note: The Fermi level of the semi-infinite electrodes without the molecule in between has been chosen as the zero of energy. The Fermi of the semi-infinite electrodes with the molecule in between is at 10 meV.)^5
Figure 1.4 Faraday’s gold colloid (on the right of each pair) and a pink solution (on the left of each pair). (Left Panel: in ambient light; Right Panel: Faraday-Tyndall effect)
Figure 1.5 Scheme for gold nanoparticle synthesis by BSM.\textsuperscript{37}
Figure 1.6 Scheme of metal nanoclusters, bridging organometallic complexes and nanocrystals (Scale bar = 5 nm).
1.4 References


(8) Tweney, R. D. Perspectives on Science 2006, 14, 99-121.


2.1 Chemicals

Tellurium (200 mesh, 99.85%), sodium borohydride (powder, 98%, NaBH₄), bromine (Br₂), silver nitrate (AgNO₃), 1-bromooctane (OctBr, 99%), 1-bromohexane (C₆H₁₃Br), 1-bromododecane (C₁₂H₂₅Br), and 1-bromoocdecane (C₁₈H₃₇Br) were purchased from Aldrich. Sodium sulfite (Na₂SO₃) was from EM Science. Copper(II) chloride dehydrate (CuCl₂·2H₂O) was from Acros. Tetra-n-octylammonium bromide (TOAB, 98%), lithium perchlorate (LiClO₄), tetra-n-butylammonium perchlorate (Bu₄NClO₄), and potassium tetrabromoaurate(III) dihydrate (KAuBr₄·2H₂O) were from Alfa Aesar. Hydrogen tetrachloroaurate hydrate (HAuCl₄, 49 wt % Au) and ferrocene (99%) were from Strem Chemicals. Organic solvents, dimethyl formamide (DMF), dichloromethane (CH₂Cl₂), chloroform (CHCl₃), hexane, toluene, methanol (MeOH), methanol (EtOH), acetonitrile (ACN), and tetrahydrofuran (THF) were of analytical grade. They were all used as received. Milli-Q water (18.2 MΩ·cm) was used. All glassware was cleaned in sulfuric acid with Nochromix and rinsed with a large amount of water before use.

2.2 Dialkyl Ditelluride

Originally for the capping monolayers of Te-containing ligand-protected gold nanoparticles (NPs), dialkyl ditelluride was used. Dialkyl ditelluride was used as a Te-containing ligand source because both alkanetellurol and dialkyl telluride are unstable.¹ Because of its commercial unavailability, the dialkyl ditelluride used in this study was synthesized in the laboratory.
2.2.1 Synthesis and Purification of Dihexyl/Dioctyl Ditelluride

Both dihexyl ditelluride and dioctyl ditelluride (Oct$_2$Te$_2$) are deep-red oily liquid at the room temperature. Their preparation methods are the same except the use of 1-bromohexane to replace 1-bromoocctane as a chemical reagent to control the alkyl chain length of ditelluride in the synthesis. The following are the procedures of the synthesis and purification taking Oct$_2$Te$_2$ as an example.

Tellurium (200 mesh, 99.85%), sodium borohydride (powder, 98%, NaBH$_4$), bromine (Br$_2$), 1-bromoocctane (OctBr, 99%), 1-bromohexane were purchased from Aldrich. Sodium sulfite (Na$_2$SO$_3$) was from EM Science. Tetra-$n$-octylammonium bromide (TOAB, 98%) was from Alfa Aesar, and hydrogen tetrachloroaurate hydrate (49 wt % Au, HAuCl$_4$) was from Strem Chemicals. Organic solvents, dimethyl formamide (DMF), dichloromethane (CH$_2$Cl$_2$), hexane, toluene, methanol, ethanol, and tetrahydrofuran (THF) were of analytical grade. They were all used as received. Milli-Q water (18.2 MΩ·cm) was used. Note that all solvents were degassed by bubbling with nitrogen or argon before use and all glassware was cleaned in sulfuric acid with Nochromix and rinsed with a large amount of water before use.

Oct$_2$Te$_2$ was synthesized via the intermediate sodium ditelluride (Na$_2$Te$_2$), which was prepared by refluxing a mixture of 3.0 g of tellurium powder and 0.71 g of NaBH$_4$ in 30 mL of DMF at 85°C under argon gas for 20 min$^2$. The resulting mixture was deep purple in color, indicating the formation of Na$_2$Te$_2$. A molar equivalent of OctBr DMF solution (4.9 mL of OctBr in 10 mL of DMF) was then added to the solution at room temperature and stirred for about 3h. The chemical reactions for the steps mentioned above are as followsg.
The obtained mixture was filtered to remove unreacted tellurium and the filtrate was separated with 125 mL of hexane and 100 mL of water. The red organic layer was collected and the solvent was evaporated to give dark red oil (5.82 g), producing crude Oct₂Te₂. Because of the possible side reaction shown below and the residual OctBr, the purification of the crude product was indispensable.

\[
\text{(1) } 2\text{Te} + 2\text{NaBH}_4 + 6\text{DMF} \xrightarrow{\text{DMF, } 85^\circ\text{C}} \text{Na}_2\text{Te}_2 + 2\text{B(CON(CH}_3)_2}_2 + 7\text{H}_2
\]

\[
\text{(2) } \text{Na}_2\text{Te}_2 + 2\text{RBr} \xrightarrow{\text{DMF, N}_2, \text{room T}} \text{R-Te-Te-R} + 2\text{NaBr}
\]

In order to purify the product, the oil was dissolved in 50 mL of CH₂Cl₂ and then three molar equivalents of Br₂ (5.81 g) were added dropwise into the solution, which was placed in an ice bath. After the overnight reaction, the solution was evaporated to remove the solvent and then solidified in an ice bath. The solid was recrystallized twice in a mixture of 30 mL of hexane and 70 mL of CH₂Cl₂ to give yellow needle crystals of octyl tellurium tribromide (OctTeBr₃). In order to reduce OctTeBr₃ crystals to Oct₂Te₂, Na₂SO₃ aqueous solution (3.32 g of Na₂SO₃ in 10 mL of H₂O) was added dropwise to a 25 mL of methanol solution of the OctTeBr₃ crystals (6.37 g), and hexane (30 mL) was added to extract the Oct₂Te₂ product. The occurrence of the reduction was indicated by the color of the hexane layer changing from colorless to deep red. The resulting two-phase mixture was separated. The top red layer was collected and the solvent
was removed by rotary evaporation at room temperature. The obtained dark red oil ran through a silica gel/hexane column. The first band contained the pure desired product. Note that all solvents were degassed by bubbling with nitrogen or argon before use. The following are the reactions involved in the steps of purification.

\[
\begin{align*}
(1) \quad & \text{R}_2\text{Te}_2 + 3\text{Br}_2 \xrightarrow{\text{CH}_2\text{Cl}_2, \text{room T}} 2\text{RTeBr}_3 \\
(2) \quad & 2\text{RTeBr}_3 + 3\text{Na}_2\text{SO}_3 + 3\text{H}_2\text{O} \xrightarrow{\text{MeOH, Hexane}} \text{R-Te-Te-R} + 3\text{H}_2\text{SO}_4 + 6\text{NaBr}
\end{align*}
\]

2.2.2 Synthesis and Purification of Didodecyl/Dihexyldecyl Ditelluride

The synthetic routes of didodecyl ditelluride and dihexyldecyl ditelluride ((C\(_{12}\)H\(_{25}\)Te)\(_2\), (C\(_{16}\)H\(_{33}\)Te)\(_2\)) are the same as those for Oct\(_2\)Te\(_2\) except that C\(_{12}\)H\(_{25}\)Br or C\(_{16}\)H\(_{33}\)Br is used to replace OctBr in the starting materials. Since both (C\(_{12}\)H\(_{25}\)Te)\(_2\) and (C\(_{16}\)H\(_{33}\)Te)\(_2\) are deep-red needle-like crystals at the room temperature, their purification methods are different from those for Oct\(_2\)Te\(_2\). The following are the purification procedures.

After obtaining the crude product by removal of the solvent, ~100mL of hexane was added to re-dissolve all crude product and then ~30mL of MeOH was added. The two-layer mixture was filtered with vacuum and the filtrate was then transferred to separatory funnel. After shaking vigorously, the top deep-red solution was collected. Another ~60mL of hexane was added to the bottom yellowish solution. After shaking, the bottom layer was almost colorless and the top layer was mixed with the top phase after the 1\(^{st}\) separation. The solvent was removed from the mixed top layers via rotoevaporation. The deep-red slurry was re-dissolved with ~10mL of hexane and
then went through a silica gel/hexane column. The first band was collected. After the removal of all solvent by rotoevaporation, the desired deep-red crystals were obtained.

2.2.3 Stability and Storage

Didodecyl ditelluride and dihexyldecyl ditelluride are stable solids at room temperature. After the two-year storage of \((C_{12}H_{25}Te)_2\) in the air, all crystals can be re-dissolved well in toluene with no impurity observed in the NMR spectra. However, the stabilities of dihexyl ditelluride and dioctyl ditelluride are not as good as that of \((C_{12}H_{25}Te)_2\). Even after a couple of days (shorter than one week) in a freezer, some yellowish insoluble precipitate was observed around the side of the Teflon tube where the \((C_6H_{13}Te)_2\) after the purification and removal of the solvent was stored. The stability of \(\text{Oct}_2\text{Te}_2\) is much better than that of \((C_6H_{13}Te)_2\). After the pure \(\text{Oct}_2\text{Te}_2\) was stored in Teflon tube in a freezer for several months, yellowish insoluble precipitate was also observed. This kind of yellowish insoluble precipitate is considered as polymeric tellurium oxide species, which can not be dissolved in the common organic solvent and water, but can be removed from the ditelluride toluene solution by centrifugation. Table 2.1 lists the stabilities of \(\text{Oct}_2\text{Te}_2\) and \((C_{12}H_{25}Te)_2\) (~6.0 mg) in different common solvents (3.0 mL).

2.3 Synthesis of Organochalcogenate-Protected Metal Nanoparticles (NPs)

2.3.1 Alkanetelluroxide-Protected Au NPs by BSM

Dihexyl ditelluride, dioctyl ditelluride, and didodecyl ditelluride were used respectively as ligands to synthesize alkanetelluroxide-protected gold NPs by the modified Brust–Schiffrin two-phase method. The detailed procedure, where the preparation of octanetelluroxide-protected Au NPs is taken as an example, was as the following: A mixture of 1.5 mmol of HAuCl₄ in 10 mL
of H₂O and 4.5 mmol of TOAB in 300 mL of toluene was vigorously stirred with a magnet for 30 min. The top, clear wine-red layer was separated and collected, and then 0.5 mmol of Oct₂Te₂ in 3 mL of toluene was added dropwise, which led to a stable colorless solution. After another 20 min of stirring, 15 mmol of fresh NaBH₄ in 10 mL of H₂O was poured in quickly, and a dark-brown solution was obtained immediately. The dark-brown solution was vigorously stirred for another 3 h (30-min stir when (C₆H₁₃Te)₂ was used as ligands; overnight stir for (C₁₂H₂₅Te)₂). The toluene phase was separated, rinsed three times with a large amount of water, and then filtered through a fritted glass filter. The filtrate was collected and dried by rotary evaporation with a pump at room temperature. The resulting black slurry was re-dissolved with 2 mL of toluene and then covered with 250 mL of ethanol. After standing overnight in a freezer, the dark-brown precipitate was collected on a micropore filter apparatus and stored in air.

Acetonitrile also could be used to crush out Au NPs protected by Te/Se-contained ligands. We found that the re-dissolvability of the Au NPs crushed out with ACN in toluene were much better than with EtOH. In order to get narrow size distribution, centrifugation at 14.5k rpm for 1 hour was performed twice and the top solution after centrifugation was collected.

2.3.2 Chalcogenate-Protected Au NPs via Reversed Synthetic Route⁶

0.70 mL of 0.1421M HAuCl₄ (0.10 mmol) aqueous solution was mixed with 10 mL of TOAB (0.30 mmol) toluene solution. After 30-min vigorous stirring, 1 mL of fresh NaBH₄ (1 mmol) aqueous solution was added. In around 10 second or shorter time, the ligands dissolved in 1~2 mL of toluene (0.30 mmol C₁₂H₂₅SH, 0.05 mmol (C₁₂H₂₅S)₂, 0.05 mmol (C₈H₁₇Se)₂, or 0.05 mmol (C₁₂H₂₅Te)₂) were poured in. After stirring for some time (overnight for S-contained ligands, 1 hour for diselenide, and 10 min for ditelluride), the solution was measured with UV-
vis spectroscopy. The nanoparticles could be collected following the same procedures as mentioned above in 2.3.1 Brust Method.

2.3.3 Alkanethiolate-Protected Ag NPs

The same two recipes (Brust method and our reversed synthetic route) were used as those for Au nanoparticles in 2.3.1 and 2.3.2, except the procedures for the phase transfer of Ag cation and the ratio of thiol to Ag (S: Ag = 1.5: 1). The following procedures were used to make all of Ag\(^+\) transfer from aqueous to organic phase. 0.1 mmol AgNO\(_3\) was dissolved in ~5 mL water and then mixed with 10 mL of TOAB (0.3 mmol) toluene solution. The mixture was stirred vigorously overnight or longer until all precipitate disappeared and a clear colorless two-layer solution was obtained.

2.3.4 Alkanethiolate-Protected Cu NPs

Because of the low efficiency of phase transfer of Cu cation via the traditional method which was used for Au and Ag ions\(^7\), a reported approach\(^8\)\(^9\) was followed. CuCl\(_2\)·H\(_2\)O (0.1 mmol) and TOAB (0.2 mmol) were mixed in 50-mL anhydrous ethanol. The mixture was heated in water bath to 80\(^\circ\)C. After 30-min stirring at 80\(^\circ\)C, the solvent was removed from the clear dark red solution by rotary evaporation with pump. The obtained dark red solid, [TOA]\(_2\)[Cu((II)X\(_4\))], was used as the Cu source of the synthesis. The same procedures except the phase transfer as those used for Au and Ag nanoparticles (2.3.1~2.3.3) were followed (S: Cu = 3: 1).
2.4 Chemical Methods

2.4.1 Nuclear Magnetic Resonance (NMR)

The solution $^1\text{H}$, $^{13}\text{C}$, and $^{125}\text{Te}$ NMR spectra were recorded on a Bruker AM 300 MHz spectrometer that was interfaced with Tecmag DSPect acquisition system. Some solution $^{125}\text{Te}$ NMR spectra (in Chapter IV) were obtained via a 400 MHz Varian Unity spectrometer. Solution heteronuclear multiple quantum coherence (HMQC) NMR was carried out on a 500 MHz Varian Unity spectrometer. When deuterated benzene was used as a solvent, its $^1\text{H}$ (7.16 ppm) and $^{13}\text{C}$ (128.39 ppm) peaks were used as references. When deuterated chloroform with TMS was used as a locking agent, TMS $^1\text{H}$ (0 ppm) and CDCl$_3$ $^{13}\text{C}$ (77.23 ppm) peaks were used as references. Solid-state $^{125}\text{Te}$ NMR was performed on a Tecmag Libra acquisition system interfaced with a homemade Oxford active-shielded 400MHzwide-bore superconducting magnet. The peak of tellurium hexahydroxide in deuterium oxide at 707 ppm$^{10}$ was used as a reference for the $^{125}\text{Te}$ NMR spectrum.

2.4.2 Raman Spectroscopy

The spectra were obtained using a confocal microprobe Raman system (Renishaw RM1000) equipped with a deep depletion CCD peltier cooled down to -70°C. The microscope attachment was based on an Olympus BH2-UMA system and a 50x-long working-length objective (8 mm) was used. A holographic notch filter was used to filter the exciting line and two selective holographic gratings (1200 g/mm and 2400 g/mm) were employed with respect to the required spectral resolution. The exciting wavelength was 785 nm from diode laser with a max power of 27 mW and a spot of ca. 3 μm on the surface. The spectroscopy was calibrated with the peak at
520 cm\(^{-1}\) of clean Si wafer. Liquid sample was measured in 5-mm NMR tube. Solid or slurry sample was measured on clean microscope slide.

2.4.3 UV-Vis Spectroscopy

Solid samples were first dissolved in toluene to make a dilute solution. Then they were transferred into a 1-cm path length quartz cuvette, and the measurements were made on an HP 8453 diode array UV-vis spectrometer. A typical experiment scanned the wavelength range from 300 to 800 nm. Background adjustments were made using a toluene blank.

2.4.4 Infrared (IR) Spectroscopy

The IR spectra were obtained using a Bruker Vector-22 infrared spectrometer. For the liquid ligands, the liquid sample was dropped onto a KBr pellet and covered with another KBr pellet. For the solid samples such as NPs, a small amount of powder was mixed with KBr powder as a solid support and ground to an even mixture with a pestle. The mixture was pressed into a wafer for IR measurement. All measurements were performed in the transmittance mode at 2 cm\(^{-1}\) resolution. The spectra were background subtracted with respect to KBr and subjected to baseline correction and smoothing.

2.4.5 Transmission Electron Microscopy (TEM)

The TEM characterization was performed on JEOL JEM-2100 LaB6 transmission electron microscope at 100 kV. Some TEM images (in Chapter III) were obtained with a JEOL JEM-1010 transmission electron microscope at 60 kV. The samples were prepared by placing two or three drops of the dilute nanoparticle dispersion in toluene on carbon-coated copper grids (400 mesh, Electron Microscopy Science). Nanoparticle sizes were measured using ImageJ.
2.4.6 Thermogravimetric Analysis (TGA)

The measurements were carried out on a TA Instruments TGA Q50. About 4 to 5 mg of Au NPs were put into a ceramic pan, and the temperature was ramped from room temperature to 1000 °C at a heating rate of 10 °C/min.

2.4.7 X-ray photoelectron spectroscopy (XPS)

The Au NPs (in Chapter III) were analyzed with a Kratos Axis Ultra X-ray photoelectron spectrometer using a monochromatic Al X-ray source at 75 W (5 mA, 15 kV). The samples were mounted using conductive copper-backed double-sided adhesive tape (3M 1182). Data were collected at a takeoff angle of 90°. The calibration and charge correction were made in two separate steps. Calibration of the binding-energy scale was done using a Cu–Au film co-deposited on Si with Cu 2p3/2 = 932.7 eV and Au 4f = 84.0 eV. Charge correction was done by referencing to C 1s = 285.0 eV.

2.4.8 Dynamic Light Scattering (DLS)

DLS measurements were performed using a 632.8nm HeNe laser excitation and a single mode optical fiber collection, which is coupled to an avalanche photodiode detector (Perkin Elmer SPCM CD22882). The collected signals were input to and analyzed by ALV-5000 Multiple Tau Digital Correlator software.
Table 2.1 Solubility and stability of liquid dialkyl ditellurides in common solvents

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Dipole Moment</th>
<th>At the beginning</th>
<th>after one-day storage</th>
</tr>
</thead>
<tbody>
<tr>
<td>Toluene</td>
<td>/</td>
<td>clear yellow solution</td>
<td>no change</td>
</tr>
<tr>
<td>Hexane</td>
<td>/</td>
<td>clear yellow solution</td>
<td>no change*</td>
</tr>
<tr>
<td>CHCl₃</td>
<td>/</td>
<td>clear yellow solution</td>
<td>no change*</td>
</tr>
<tr>
<td>CH₂Cl₂</td>
<td>1.60</td>
<td>clear yellow solution</td>
<td>no change*</td>
</tr>
<tr>
<td>THF</td>
<td>1.63</td>
<td>clear yellow solution</td>
<td>colorless solution</td>
</tr>
<tr>
<td>EtOH</td>
<td>1.69</td>
<td>partly dissolved</td>
<td>milky solution with black precipitate</td>
</tr>
<tr>
<td>MeOH</td>
<td>1.70</td>
<td>little dissolved</td>
<td>milky solution with black precipitate</td>
</tr>
<tr>
<td>H₂O</td>
<td>1.80</td>
<td>insoluble</td>
<td>no change</td>
</tr>
<tr>
<td>Acetone</td>
<td>2.88</td>
<td>clear yellow solution</td>
<td>milky solution with black precipitate</td>
</tr>
<tr>
<td>DMF</td>
<td>3.82</td>
<td>mostly dissolved</td>
<td>milky bottom layer w. black precipitate</td>
</tr>
<tr>
<td>ACN</td>
<td>3.92</td>
<td>partly dissolved</td>
<td>milky solution with black precipitate</td>
</tr>
<tr>
<td>DMSO</td>
<td>3.96</td>
<td>partly dissolved</td>
<td>pale milky solution</td>
</tr>
</tbody>
</table>

Notes:
* After one month, black precipitate was present in ditelluride CHCl₃ or hexane solution, while ditelluride CH₂Cl₂ solution turned to white.
2.5 References


CHAPTER III
ALKANETELLUROXIDE-PROTECTED GOLD NPs

Reproduced with permission from Li, Y.; Silverton, L. C.; Haasch, R.; Tong, Y. Y., Alkane-telluroxide-Protected Gold Nanoparticles. *Langmuir* 2008, 24, 7048-7053. Copyright 2008 American Chemical Society. It was the result of my research effort under the direct guidance of my mentor, Prof. YuYe J. Tong. Dr. Haasch from Frederick Seitz Materials Research Laboratory at University of Illinois at Urbana–Champaign helped us doing the XPS measurements on the samples. Ms. Silverton, an undergraduate student, worked under my direction.

3.1 Introduction

Monolayer-protected gold nanoparticles (NPs) with cores in the nanometer size range have attracted a remarkable amount of research because of their intriguing optical and electronic properties.\(^1\)\(^2\) It is well known that capping monolayer can be varied and have a dramatic influence on the physical and chemical functionalities of NPs, and their solubilities in diverse solvents that range from aqueous and nonaqueous (organic) to fluorous phases can thus be tuned.\(^3\)\(^4\) Most capping monolayers were bound to metal cores by using sulfur as an anchoring element. However, sulfur anchoring has been known to be prone to oxidation and results in a large mismatch between metallic and molecular energy levels.\(^5\) It is therefore highly desirable to have alternatives. Quantum calculations have shown that other chalcogens such as Se and Te may possess better characteristics as anchoring elements and are therefore worthy of being researched.\(^6\) Nevertheless, they have been much less investigated than their sulfur counterparts. For Te, there have been only a few studies focusing on the packing of alkane/ aromatic telluride...
on oriented single crystal metal surfaces.\textsuperscript{7-11} Even fewer published studies exist for metal NPs. To the best of our knowledge, only Brust and coworkers\textsuperscript{6} have attempted to synthesize metal NPs using tellurium as an anchoring element. However, they failed to obtain stable NPs, and no further characterizations other than Langmuir isotherm were carried out.\textsuperscript{12}

Following our previous study on octaneselenolate-protected Au NPs,\textsuperscript{13} we report here the successful synthesis of the first long-term air-stable Te-containing ligand-protected Au NPs and their rather detailed characterizations.\textsuperscript{14} Using dioctyl ditelluride (Oct\textsubscript{2}Te\textsubscript{2}) as the starting ligand, the synthesis of NPs was conducted by a modified Brust method.\textsuperscript{15} The average particle size of the formed Au NPs measured by transmission electron microscopy (TEM) was 2.7 nm. \textsuperscript{1}H, \textsuperscript{13}C, and \textsuperscript{125}Te NMR spectroscopy, infrared spectroscopy (IR), and X-ray photoelectron spectroscopy (XPS) were used to investigate the composition and structure of the capping monolayers and the formed Au NPs. Similar patterns of the \textsuperscript{1}H and \textsuperscript{13}C spectra to those of the alkanethiolate-protected Au NPs indicated that the capping monolayer contained an intact octyl group similar to that of alkanethiolate. Solid-state \textsuperscript{125}Te NMR further confirmed that the anchoring element was Te. The IR spectra of the formed NPs also showed a dominant Te-C trans vibrational band, which was in great contrast to that of free Oct\textsubscript{2}Te\textsubscript{2} where only a Te-C gauche vibrational band was observed. This observation strongly suggested that the Te-Te bond of the starting ligand was broken. However, the O 1s and Te 3d XPS spectra strongly suggested that the capping ligands were alkyl telluroxide. Furthermore, the Au 4f XPS spectrum showed that the binding energy (BE) of the Au 4f\textsubscript{7/2} was shifted to lower energy, which indicated charge transfer from ligands to Au. This is in great contrast to octanethiolate-protected Au NPs, for which an opposite trend was observed. The thermogravimetric analysis (TGA) on the formed Au NPs gave a two-step weight
loss process at about 300 and 800°C. The former probably corresponded to the loss of the octyl group accompanied by C-Te bond breaking, and the latter was due to the loss of residual telluroxide. The calculated stoichiometry of the formed NPs was \( \text{Au}_{607}(\text{Te}(=\text{O})\text{C}_8\text{H}_{17})_{133} \) with about 53% monolayer coverage. Equally interesting is the observation of the intriguing reducing power of Oct\(_2\)Te\(_2\). Proper handling of Oct\(_2\)Te\(_2\) seemed to be the key for synthesizing air-stable alkanetelluroxide-protected Au NPs.

3.2 Starting Ligand

The capping monolayers of Te-containing ligand-protected Au NPs were originally from Oct\(_2\)Te\(_2\). Oct\(_2\)Te\(_2\) was used as a Te-containing ligand source because both octanetellurol and dioctyltelluride are unstable.\(^1\) Because of its commercial unavailability, the Oct\(_2\)Te\(_2\) used in this study was synthesized in the laboratory. The synthesis and ensuing purification followed Scheme 3.1. (See Chapter II 2.1.1 Synthesis of Dialkyl Ditelluride for details.) The yield of the synthesis was about 47%. The purification procedures, which aimed at removing the residual OctBr and possible dioctyltelluride side product, were integral to ensuring the quality of the final product. The purity of the product was assayed by \(^1\)H, \(^{13}\)C, and \(^{125}\)Te NMR as well as by IR.

The \(^1\)H, \(^{13}\)C, and \(^{125}\)Te NMR spectra of the purified product and the assignments of the peaks are shown in Figure 3.1. The peak positions in the \(^1\)H NMR spectrum (Figure 3.1a) were in good agreement with the published data for dialkyl ditelluride.\(^7\)-\(^{11}\) In particularly, the triplet peak at ~3.10 ppm (~2.95 ppm in \( \text{C}_6\text{D}_6 \), see Figure 3.4a) was from the protons attached to the carbons directly bonding to the two Te atoms, which could be used as an indicator of Oct\(_2\)Te\(_2\). The absence of the peak at ~2.6 ppm\(^{18,19}\) supported the absence of dioctyltelluride. In the \(^{125}\)Te NMR
spectrum (Figure 3.1b), compared with the peak of tellurium hexahydroxide in deuterium oxide at 707 ppm\textsuperscript{16} which is often used as a reference for the \textsuperscript{125}Te NMR spectrum, a single peak at \~111 ppm (\~104 ppm in C\textsubscript{6}D\textsubscript{6}) was observed, proving that a pure Te-containing product (i.e., Oct\textsubscript{2}Te\textsubscript{2}) was obtained. The observed slight splitting of the peak was possibly due to a small isotope shift of Te in the ditelluride bond.\textsuperscript{20,21} However, the peak position appeared to be more upfield than the published value (138 ppm),\textsuperscript{22} which might be caused by using a different reference. The \textsuperscript{13}C NMR spectrum (Figure 3.1c) showed eight well-resolved peaks corresponding to the eight carbons in the two equivalent octyl groups of the molecule. The peak at 4.90 ppm (4.72 ppm in C\textsubscript{6}D\textsubscript{6}, see Figure 3.5a) was assigned to the carbon directly connected to Te, according to the heteronuclear multiple quantum coherence (HMQC) NMR spectrum in Figure 3.2. However, for dialkyltelluride such as (C\textsubscript{5}H\textsubscript{11})\textsubscript{2}Te, the two C\textsubscript{\alpha}’s peak was observed at 2.70 ppm\textsuperscript{23}. Compared with the respective values of dioctyl disulfide and dioctyl diselenide, the C\textsubscript{\alpha} peak of ditelluride was also unusually upfield shifted. This can be understood by the much higher electron-donating tendency of Te and is consistent with the observed unusual reductive power of Oct\textsubscript{2}Te\textsubscript{2} (vide infra).

The transmission IR spectra of Oct\textsubscript{2}Te\textsubscript{2} are shown in Figure 3.3a, c. In a normal IR spectrum, dioctyldisulfide has a (S-\textsuperscript{12}C)\textsubscript{\textit{trans}} stretching band at 723 cm\textsuperscript{-1} that overlaps with the methylene rocking band at 722 cm\textsuperscript{-1} and a (S-\textsuperscript{12}C)\textsubscript{\textit{gauche}} stretching band at 641 cm\textsuperscript{-1}.\textsuperscript{21} Hooke’s law, which stated the relationship among frequency of oscillation, atomic masses and force constant of a bond, could be used to approximate the stretching frequencies by treating the connecting bond as a simple harmonic oscillator consisting of two masses jointed by a spring.\textsuperscript{37} Assumed \(f_{\text{Te-C}} = f_{\text{S-C}}\), the frequencies of Te-C stretching vibration could be estimated by the following equation, where,
\[ \bar{v} = \frac{1}{2\pi \cdot c} \left| \frac{f}{(M_x M_y)/(M_x + M_y)} \right|^{1/2} \]

The calculated frequencies of (Te-\(^{12}\)C\(_{\text{trans}}\)) and (Te-\(^{12}\)C\(_{\text{gauche}}\)) were 645 cm\(^{-1}\) and 572 cm\(^{-1}\), respectively. In the IR spectrum of Oct\(_2\)Te\(_2\) (Figure 3.3c), the peak at 721 cm\(^{-1}\) could be identified as \(v_{\text{rocking}}(\text{CH}_2)\), the peak at 548 cm\(^{-1}\) was from the stretching vibration of (Te-C)\(_{\text{gauche}}\). Interestingly, only a gauche band of the Te-C vibration at 548 cm\(^{-1}\) was observed in free Oct\(_2\)Te\(_2\) (Figure 3.3c). Besides methylene rocking vibration, no (Te-C)\(_{\text{trans}}\) vibration was observed in the IR spectrum of pure Oct\(_2\)Te\(_2\). We inferred that there was a strong interaction between KBr and the Te, which has a strong electron donating tendency, that would push the two octyl chains aligned in the same direction, inducing a dominant gauche conformation, as observed on metal surfaces.\(^{24, 25}\) In details, the supporting substrates for IR measurement were made of KBr, a polar compound, which would push non-polar hydrophobic ends away, lead to the aggregation of the alkyl chains, and consequently make pure Oct\(_2\)Te\(_2\) exhibit gauche-conformation (Scheme 3.2). This confirmed again that the ligand that we synthesized was Oct\(_2\)Te\(_2\).

3.3 Capping Monolayers of the Formed Au NPs

The TEM picture of the formed Au NPs, the corresponding size distribution histogram (total 200 counts), and the UV-vis spectrum of the freshly prepared NP toluene solution are shown in Figure 3.4. An average NP size of 2.70 nm (± 0.68 nm) in diameter was calculated on the basis of the measured size distribution. The UV-vis spectrum gave a well-formed surface plasmon
resonance band centered at 506 nm, which is blue-shifted and more intense as compared to that of thiolate-protected Au NPs with similar sizes (\(~515\) nm). We believe that the blue shift and large intensity resulted from the strong electron donation of tellurium that enriched the charge of the Au NPs (\textit{vide infra}).

We compare the $^1$H (Figure 3.5) and $^{13}$C (Figure 3.6) NMR spectra of the Te-containing ligand-protected Au NPs with those of the octanethiolate-protected Au NPs (i.e., OctS-Au NPs). Many similarities were obvious: the three $^1$H peaks at about 0.97, 1.40, and 2.38 ppm and the four $^{13}$C peaks at 14.7, 23.5, 30.8, and 32.8 ppm closely overlap in their respective spectra. These similarities strongly suggested that the Te-containing capping monolayers of the Au NPs would have similar chemical components and structures to octanethiolate. Moreover, the disappearance of the $^{13}$C$_\alpha$ peak at 4.72 ppm and the peak of the protons attached to C$_\alpha$ at 2.95 ppm in the respective $^{13}$C and $^1$H NMR spectra indicated that no free Oct$_2$Te$_2$ existed in the NP solution and the capping ligands were bound to the Au core via Te. The latter was further corroborated by the preliminary solid-state $^{125}$Te NMR of the formed Au NPs as shown in Figure 3.7. The large positive shift of the resonance with respect to that of the pure Oct$_2$Te$_2$ (Figure 3.1b) and the extremely broadened line width also indicated that tellurium, as the anchoring element of the capping ligands, was bound directly to the Au NP surface.

The IR spectra of the formed Au NPs (Figure 3.3b, d) showed red-shifted $\nu_{as}$(CH$_2$) and $\nu_{s}$(CH$_2$) stretching bands as compared with those of the free Oct$_2$Te$_2$ (Figure 3.2a, c) and a strong broad band in the Te-C stretching region centered at 653 cm$^{-1}$, which corresponds to the expected Te-C trans stretching wavenumber via Hooke’s calculation discussed above. The former indicated a more ordered octyl chain arrangement on the Au NP surface, which has also been observed on
alkanethiolate-protected Au NPs. The latter, however, was in great contrast to the IR spectrum of the pure Oct$_2$Te$_2$ where only a gauche stretching band was observed, indicating that the Te-Te bond was broken, thus enabling dominant trans (Scheme 3.2(b)) packing of the capping ligands on the Au NP surface. Furthermore, the unusual broadness as compared with that of the alkanethiolate-protected Au NPs implied a different local molecular composition/structure. Indeed, the XPS measurements (vide infra) showed strong evidence that octane-telluroxide was formed on the Au NP surface.

The O 1s and Te 3d and 4d XPS spectra are shown in Figures 3.8 and 3.9, respectively. The strong O 1s peak at 530.85 eV, a value that agrees with the O 1s BE of the dialkyl ditelluride autooxidized monolayers on Au(111), strongly suggests the existence of some tellurium oxide-like species. Because the atomic ratio of O to Te obtained from the XPS measurements was ~1, we concluded that the capping monolayers were composed of octanetelluroxide (i.e. OctTe(=O)-Au NPs). Accordingly, we believed that it was the local surface heterogeneity in the O=Te-Au moiety that caused the broadening of the Te-C stretching band in the IR spectra (Figure 3.3d).

The Te 3d spectrum in Figure 3.9a exhibited a dominant Te 3d$_{5/2,3/2}$ doublet at 576.52 eV (3d$_{5/2}$) and 586.85 eV (3d$_{3/2}$), and both showed a positive shift of ~3.4 eV with respect to the BEs of the Te metal: 573.1 eV for 3d$_{5/2}$ and 583.5 eV for 3d$_{3/2}$ electrons. This value is much larger than the combined BE positive shift of 1.73 eV expected for a Te bound to an alkyl group (~0.4 eV) and an oxygen (=O, ~1.33 eV). Because the atomic ratio of O/Te being close to 1 dictated the stoichiometry of the oxide to be telluroxide, the remaining 1.67 eV positive shift should have to do with a significant charge redistribution induced by the strong Te-Au NP bonding as implied by the TGA results. Similar results were also found in the Te 4d spectrum (Figure 3.9b) that
showed a partially overlapped doublet at \( \sim 43.54 \text{ eV} \) \((4d_{5/2})\) and \( \sim 44.93 \text{ eV} \) \((4d_{3/2})\). Compared with the bulk Te 4d BEs\(^{29}\), the shift of the Te 4d level was \( \sim 3.0 \text{ eV} \), also larger than what would be expected for a lonely Oct-Te=O moiety, which again pointed to a strong effect of Te-Au NP bonding.

The interaction (i.e., charge redistribution) between anchoring elements and Au cores can be investigated by looking at Au 4f XPS spectra. In Figure 3.10, we compared the Au 4f XPS spectrum of the OctTe(=O)-Au NPs with that of the OctS-Au NPs. The vertical dashed line indicated the BE of the bulk Au 4f\( _{7/2}\) level \( (84.0 \text{ eV}) \).\(^{30}\) As can be seen, the BE of Au 4f\( _{7/2}\) in the OctTe(=O)-Au NPs \( (83.88 \text{ eV}) \) is more negative whereas that in the OctS-AuNPs \( (84.05 \text{ eV}) \) is more positive than the reference value \( (84.0 \text{ eV}) \). The latter observation is in agreement with the literature.\(^{31}\) Although small, the shifts were in the opposite direction, indicating different directions of charge redistribution. In particularly, the relatively large negative shift observed in the OctTe(=O)-Au NPs \(-0.12 \text{ vs. } +0.05 \text{ eV}\) may indicate a stronger charge transfer from Te to Au, which explains the observed larger positive BE shifts in the Te 3d and 4d levels (vide supra). The observed difference in the direction of charge redistribution, as discussed above, is also in agreement with the theoretical calculations.\(^6\)

It is interesting that on the single-crystal bulk gold substrate a different chemical structure of RTeO\(_2\)H has been proposed for the Te-containing ligands based on both the XPS-determined atomic ratio and the positively shifted BE of the Te 3d level.\(^9, 11\) The different structure highlights again that the surface chemistry of Au NPs can be very different from that of bulk Au, a noticeable example of which is the high catalytic activity frequently observed on Au NPs\(^{32}\) as compared to the chemical inertness of bulk Au.
3.4 Conditions for Synthesizing Stable Au NPs

In the only paper known to us that dealt with the Te-containing ligand-protected Au NPs, Brust and co-workers failed to produce stable Au NPs.\(^{12}\) By trial and error, we found that certain conditions needed to be met in order to form stable OctTe(=O)-Au NPs, which included the amount of TOAB and the molar ratio of Te to Au.

Research on alkanethiolate-protected Au NPs suggested that the highly ordered structure of the Au(I)-SR polymer\(^{33}\) was one of the key factors in the preparation of monodisperse Au NPs.\(^{34}\) We found that a similar intermediate of Au(I)-TeR might also play the same crucial role in the formation of stable octanetelluroxide-protected Au NPs. In Figure 3.11-13, we show the UV-vis spectra of toluene solutions of (a) surfactant TOAB, (b) TOAB plus Au(III)Cl\(_4^-\), and (c-e) TOA\(^+\)Au(III)Cl\(_4^-\) plus Oct\(_2\)Te\(_2\) as a function of the Te/Au molar ratio. As the Te/Au ratio increased, the UV absorption peak corresponding to TOA\(^+\)Au(III)Cl\(_4^-\) at ~360 nm decreased and finally disappeared at a molar ratio of (Te/Au ) 1:1.5. At this point, the solution became colorless and was very stable. Such a transition was the same as that observed in the alkanethiol/Au system (Figure 3.13f-h), where the colorless state was reached at a molar ratio of S/Au = 1.8:1. Three drops of such a colorless intermediate solution (i.e. the solution before adding NaBH\(_4\) to produce OctTe(=O)-Au NPs) was dropped on the carbon-coated copper grid and then irradiated by the electron beam in TEM, which was similar as the treatment of Au(I)-SC\(_{18}\)H\(_{37}\) polymer in the literature\(^{34}\). Some spherical NPs were found in the TEM image (see Figure 3.14). Since there was no surface plasmon resonance band in the UV-Vis spectrum of the colorless intermediate (Figure 3.12(e)), no NP existed in the colorless intermediate solution before radiation. It was concluded that the observed nanoparticles were formed by the irradiation of the electron beam in
TEM. This phenomenon confirmed that the chemical state of Au in the intermediate state could be +1. Therefore, the color change after the addition of Oct₂Te₂ implies that Au(III) was reduced gradually to Au(I) by ditelluride and the reduction of the Au(III) was highly likely to be accompanied by Te-Te bond breaking and Te being oxidized to telluroxide. However, once the Te/Au ratio was increased beyond 1:1.5, the color of the solution turned to light yellow and then to brown under stirring. The brown solution exhibited a surface plasma peak at 519 nm, indicating the formation of Au NPs. Further overnight stirring led to a colorless solution but with the appearance of a golden precipitate on the stir bar. These phenomena suggested that Au(I) was further reduced to Au(0) by the extra Oct₂Te₂. In other words, stable OctTe(=O)-Au NPs could be formed only when NaBH₄ was added to the solutions of TOA⁺AuCl₄⁻ + Oct₂Te₂ with a Te/Au ratio ≤ 1/1.5. For Te/Au = 1:1.5, the synthesis produced the highest yield of NPs with the narrowest size distribution. In contrast, further addition of thiol beyond S/Au = 1.8:1 in the alkanethiol/Au system and continuous stirring did not lead to the formation of Au NPs or a golden precipitate. However, if Oct₂Te₂ was added to the colorless solution (i.e., Au(I)-SR polymer) in the octanethiol/Au system, then Au NPs were formed at first, and golden precipitates were finally obtained. These phenomena indicated that Oct₂Te₂ did have a much stronger reducing ability than octanethiol.

The amount of TOAB used also turned out to be very important for the formation of the colorless intermediate state. No colorless intermediate state was formed when the TOAB/Au ratio was less than 1.8:1. Consequently, no stable Au NPs could be made. This was again in great contrast to the thiol/Au system where the formation of the colorless intermediate state depended much less on the amount of TOAB. We believe that the existence of TOAB with the right
amount would homogenize the reduction of Au(III) to Au(I) and at the same time prevent the overreduction of Au(I) in the ditelluride/Au system, which was the key step in forming the important colorless intermediate state. This conclusion was corroborated by the observation that if THF instead of toluene was used as Lee and co-workers did \(^{34}\) (no TOAB was needed because the HAuCl\(_4\) aqueous solution was readily miscible with THF) then no colorless intermediate could be obtained and only a golden precipitate was formed at the end.

We found that once it was synthesized by following the optimized procedure as discussed above, the octanetelluroxide-protected Au NPs were stable for a long time in air. We have checked a sample that had been stored in air for more than 9 months, and it re-dissolved well in toluene and gave a similar UV peak to that of the toluene solution of the freshly synthesized NPs. Therefore, the longevity of octanetelluroxide-protected Au NPs is comparable to that of octanethiolate-protected Au NPs.

Additionally, we found that the octanetelluroxide-protected Au NPs were less stable in CHCl\(_3\) than in toluene. The initial solubility of the Au NPs in CHCl\(_3\) was very high, but as time went on, a black solid was gradually precipitated out until the solution became colorless. The precipitate was insoluble in common organic solvents. This observation might explain why Brust and co-workers\(^{12}\) failed to obtain stable Te-containing ligand-protected Au NPs.

3.5 Thermogravimetric Analysis

The TGA curves of the OctTe(=O)-Au and OctS-Au NPs are compared in Figure 3.15. A distinct two-step weight loss process was observed for the OctTe(=O)-Au NPs (Figure 3.15a), which was significantly different from the roughly one-step-like weight loss process observed on
the OctS-Au NPs (Figure 3.15b). The first weight loss of ~11.0% was observed in the temperature range from ~100 to ~270 °C, and the second weight loss of ~11.2% occurred between ~605 and ~800 °C. Shiny gold pieces were observed only after the second weight loss. Thus, the first weight loss was probably due to the destruction of the alkyl chains of ligands, and the second was probably due to the remaining tellurium oxide leaving the surface of Au NPs. In other words, the C-Te bond was broken in the first step, and Te-Au bond breaking occurred in the second step. In contrast, the OctS-AuNPs showed a dominate weight loss (25%) from ~100 to ~220°C, followed by a small additional 3% weight loss that ended at ~500°C. That is, all ligands of OctS-Au NPs were gone before the temperature reached 500°C. After comparing the temperature of Te-Au bond breaking with that of S-Au, it could be concluded that the Te-Au NP bond is stronger than the S-Au bond.

Now combining the TGA and TEM data, the percentage of surface coverage of the ligands on the NP surface could be calculated.\(^35,36\) A 2.7 nm diameter NP as determined by the TEM image (Figure 3.4) contained about 607 Au atoms. A \(~22.2\%\) weight loss in TGA corresponded to 53% ligand monolayer coverage on the Au\(_{607}\) core. These estimates led to a stoichiometry of Au\(_{607}(\text{Te}(=\text{O})\text{C}_8\text{H}_{17})_{133}\).

3.6 Conclusions

We have reported the synthesis and characterization of the first stable tellurium-containing ligand-protected Au NPs. The key to synthesizing stable octanetelluroxide-protected Au NPs was to realize a homogeneous reduction of Au(III) to Au(I) by Oct2Te2 before the addition of another reducing agent (NaBH\(_4\)) to form the Au NPs. It was found that the right amounts of
TOAB and Oct$_2$Te$_2$ were required in the synthesis: TOAB/Au g 1.8:1 and Te/Au e 1:1.5. The $^1$H, $^{13}$C, and $^{125}$Te NMR and IR results on the NPs strongly indicated that the Te-Te bond of the initial dioctylditelluride was broken in forming the capping monolayers. The O 1s and Te 3d and 4d XPS spectra suggested that the capping monolayers were composed of alkane telluroxide. The TEM and TGA data showed that the formed NPs had a stoichiometry of Au$_{607}$(Te(=O)C$_8$H$_{17}$)$_{133}$. The Au 4f XPS data suggested a charge-enriched Au core, and TGA implied that the Te-Au bond is stronger than the S-Au bond. We believe that the successful synthesis of long-term stable alkyl telluroxide-protected Au NPs, as demonstrated in this letter, opens a promising venue to investigate the alternative attachment chemistry of anchoring elements other than the prevailing sulfur.
**Scheme 3.1** Preparation and purification of Oct$_2$Te$_2$ (Note: fill colors are for the corresponding chemicals)
Figure 3.1 NMR spectra of Oct$_2$Te$_2$ in CDCl$_3$: (a) $^1$H NMR, (b) $^{13}$C NMR, and (c) $^{125}$Te NMR.
Figure 3.2 HMQC NMR spectrum of Oct₂Te₂ in C₆D₆.
Figure 3.3 IR spectra of the Oct$_2$Te$_2$ (red) and the octanetelluroxide-protected Au NPs (black): (a & b) methylene and methyl stretching regions, respectively, and (c & d) Te-C stretching regions.
Scheme 3.2 Schematic representation of the conformations of (a) Oct$_2$Te$_2$ and (b) ligand part of OctTe(=O)-Au NP.
Figure 3.4 Octanetelluroxide-protected Au NPs: (a) TEM image, (b) UV-vis absorbance spectrum (in toluene), and (c) size distribution histogram.
Figure 3.5 $^1$H NMR spectra of (a) Oct$_2$Te$_2$, (b) octanetelluroxide-protected Au NPs, and (c) octanethiolate-protected Au NPs, all in C$_6$D$_6$. 
Figure 3.6 $^{13}$C NMR spectra of (a) Oct$_2$Te$_2$, (b) octanetelluroxide-protected Au NPs, and (c) octanethiolate-protected Au NPs, all in C$_6$D$_6$. 
Figure 3.7 Solid-state $^{125}\text{Te}$ NMR spectrum of the octanetelluroxide-protected Au NPs.
Figure 3.8 O 1s XPS spectrum of the octanetelluroxide-protected Au NPs.
Figure 3.9 Te 3d and 4d XPS spectra of the octanetelluroxide-protected Au NPs.
Figure 3.10 Au 4f XPS spectra of (a) octanetelluroxide-protected Au NPs and (b) octanethiolate-protected Au NPs.
Figure 3.11 UV-vis absorbance spectra of (a) TOAB in toluene, (b) the toluene layer after adding HAuCl₄ to the TOAB toluene solution.
Figure 3.12 UV-vis absorbance spectra of adding the Oct$_2$Te$_2$ to the mixture of TOAB and HAuCl$_4$ with the ratio of Au: Te = (c) 1: 1/3, (d) 1: 1/1.7, and (e) 1: 1/1.5.
Figure 3.13 UV-vis absorbance spectra of adding octanethiol to the mixture of TOAB and HAuCl₄ with the ratio of Au: thiol = (f) 1: 1.5, (g) 1: 1.6, and (h) 1: 1.8.
Figure 3.14 TEM image of Au NPs formed by irradiating Au(I)-TeR with electron beam in TEM.
Figure 3.15 TGA analyses of (a) the octanetelluroxide-protected Au NPs showing a two-step weight loss process corresponding to 22.2% organic content in total and (b) of the octanthiolate-protected Au NPs showing a roughly one-step-like weight loss corresponding to 27.8% organic content.
3.7 References


(23) SDBS database (http://riodb01.ibase.aist.go.jp/sdbs/cgi-bin/direct_frame_top.cgi), SDBS No.: 16475.


(27) Octanethiolate-protected gold nanoparticles were synthesized by the Brust’s two-phase method. The preparation was done in toluene with HAuCl₄: TOAB: Octanethiol: NaBH₄ = 1: 2: 5: 10 and overnight stir.


CHAPTER IV
MECHANISTIC INSIGHTS INTO BSM

Reproduced with permission from Li, Y.; Zaluzhna, O.; Xu, B.; Gao, Y.; Modest, J. M.; Tong, Y.Y. J., Mechanistic Insights into the Brust–Schiffrin Two-Phase Synthesis of Organo-chalcogenate-Protected Metal Nanoparticles. J. Am. Chem. Soc. 2011, 133, 2092-2095. Copyright 2011 American Chemical Society. It was the result of my research effort under the direct guidance of my mentor, Prof. YuYe J. Tong. Ms. Zaluzhna took all of TEM images on the samples. Some contributive discussions on the experiment design were with Dr. Xu. Mr. Gao (an exchange undergraduate student from Fudan University) and Mr. Modest (an undergraduate student) worked under my direction.

4.1 Introduction

Since the first synthesis of thiolate-protected Au NPs reported in 1994¹, the Brust–Schiffrin two-phase method (BSM) has become the most widely used synthesis of small Au NPs²-⁵ as well as Ag, Cu, and other metal NPs⁶-¹¹. Since it was showed by quantum calculations that other chalcogens-metal contacts might achieve better conductance than S¹², the Au NPs with Se or Te as anchoring element have also been prepared by the revised BSM¹³-¹⁶. In order to obtain uniform metal NPs with size control, extensive efforts have been devoted to the stepwise investigation of the BSM. Many groups¹⁷-²⁰ tried to identify the precursors of metal ions prior to the addition of NaBH₄, but their exact form remains debatable. The widely accepted assumption has been that the addition of thiol reduces Au(III) to Au(I) and forms [AuSR]ₙ-like polymers.⁴,⁵

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Yet the most recent thought-provoking results from Lennox and coworkers have shown otherwise. Based on quantitative solution $^1$H NMR study of the metal salts, the phase transfer agent TOAB, and the thiol, they have demonstrated that the metal precursor before the addition of the reductant is TOA metal(I) halide complex [TOA][AuX$_2$], and not [MSR]$_n$-like polymers. However, since the former does not involve metal–sulfur (M–S) bond, what happens and at what stage is the Au–S bond formed after the addition of NaBH$_4$ during the BSM synthesis remain largely unresolved.

We report here detailed Raman, NMR, and surface plasmon resonance (SPR) spectroscopic studies of the reaction solutions after the sequential additions of thiols (or ligands in general) and NaBH$_4$ post the phase transfer and separation. Since our systematic Raman study showed no M–S bond formation in the reaction solutions before the NaBH$_4$ addition, we confirmed that the [MSR]$_n$-like polymers in which M–S bond is expected are not the metal-ion precursors. While this observation renders a strong support to the Lennox’s proposition, it nonetheless raises an intriguing but also fundamentally important question, as to when the M–S bond is formed, because this is the key step by which the metal NP growth and size are controlled. To answer this question, a reversed synthetic route in which reduction by NaBH$_4$ takes place before the addition of thiols (or other ligands) was devised and employed. This reversed (with respect to that of the original BSM synthesis) procedure was inspired by the $^1$H NMR observation of possible existence of inversed micelles in the reaction solutions (vide infra). A time variable between the NP formation right after the reduction and the subsequent binding of the ligand was thus introduced and expected to help delineate the process. Based on the careful analysis of the comparative spectroscopic results obtained in both the reversed and the BSM syntheses of metal
NPs, we propose a general metal NP formation mechanism for the latter, as outlined in Scheme 4.1. Its salient point is that the M–S bond is formed after the formation of the metal NPs in the inverse micelles. This general mechanism is shown to also apply to the formation of the Ag and Cu NPs. As we will show below, unraveling this mechanism makes it possible to use the stirring time prior to the addition of thiol to control the sizes of metal NPs. The reversed synthetic route also works with Se- and Te contained ligands.

4.2 Absence of M–S Bond

Whether or not the M–S bonds were formed in the reaction solution of a typical BSM reaction before the addition of NaBH₄ was monitored by Raman spectroscopy. The typical procedures to get the mixture of all precursors were as follows: a hydrogen tetrachloroaurate (HAuCl₄, 0.05 mmol) aqueous solution (0.35 mL) was mixed with a TOAB (0.15 mmol) toluene solution (5.0 mL) and stirred until the color of the aqueous phase disappeared. The bottom colorless layer was then discarded and dodecanethiol (C₁₂SH, 0.10 mmol) added to the separated wine-red toluene (or benzene) layer. After being stirred for 1 hr, a clear colorless solution was obtained, even in the cases of higher RSH/Au(III) ratios (such as RSH/Au = 3 or 5), which is different from Whetten's procedure in which no phase separation was done before the addition of thiols and NaBH₄. Before the Raman measurement, most solvent was removed by rotary evaporation under vacuum. The Raman spectrum of the fresh mixture, i.e., the concentrated organic solution of HAuCl₄, 3 equiv of TOAB, and 2 equiv of dodecanethiol, is compared with those of relevant reference materials in Figure 4.1. The absence of the peak at ~327 cm⁻¹, which is a manifestation of the Au–S bond formation as demonstrated clearly in Figure 4.1(c) of the self-assembled
dodecanethiol on the rough Au electrode and Figure 4.1(d) of the [AuSR]_n-like polymer obtained by following Lee's one-phase method\textsuperscript{22} respectively, demonstrates convincingly that the addition of thiol to the separated Au(III)-plus-TOAB solution did not form any Au–S bond. The disappearance of the S–H vibration at 2568 cm\textsuperscript{-1} and the new tiny peak at 525 cm\textsuperscript{-1} of C12S–SC12 (Figure 1e), together with the new peak at 2.57 ppm in the \textsuperscript{1}H NMR spectrum (Figure 4.2(a)), indicates that the reduction of Au(III) by RSH did occur as suggested in Whetten’s early work\textsuperscript{18}. The peak at 209 cm\textsuperscript{-1} can be assigned to the [Au–Br\textsubscript{2}]\textsuperscript{+} stretching vibration.\textsuperscript{23} Since no Au–S vibrational peak was observed (also see Figure 4.3 & 4.4 for the Ag and Cu systems respectively), it confirms that the metal-ion precursor after the addition of thiol was not [MSR]_n-like polymers, but [TOA][MX\textsubscript{2}] complex\textsuperscript{20}.

4.3 Inverse Micelle Structure

The \textsuperscript{1}H NMR spectra of the TOAB-plus-Au(III) solutions with different TOAB/Au(III) ratios were also recorded (Figure 4.5) to provide further structural information of the solutions. The large down-field shift of the H\textsubscript{2}O peaks in spectra (c) to (f) as compared to the free H\textsubscript{2}O peaks (spectra (a) and (h)) was indicative of the encapsulation of H\textsubscript{2}O in the inverse micelle structures formed by TOAB. In addition, the peaks observed in the DLS spectra of the TOAB-plus-Au(III) solutions before and after the addition of thiols (Figure 4.6) are consistent with the existence of the inverse micelle structures, although these peaks were usually assigned to [MSR]_n-like polymers in literature\textsuperscript{19}.
4.4 Possible Mechanism

Now the questions become at what stage in the BSM synthesis are the Au–S bonds formed and how are they formed? Just as some previous literature showed\textsuperscript{24,25}, we have observed that the addition of NaBH\textsubscript{4} to the mixture of TOAB and HAuCl\textsubscript{4} without the presence of any ligand can also form metal NPs due to the presence of micelles\textsuperscript{26}, despite lack of long-term stability. Therefore, the observation of micelle-encapsulated water in the \textsuperscript{1}H NMR spectra (Figure 4.5) in the separated organic phase led us to hypothesize that the following may happen stepwise in the BSM synthesis after the addition of NaBH\textsubscript{4}. As shown above, the organic layer after the phase separation and the thiol addition contains the TOAB micelles of [TOA][MX\textsubscript{2}] complex. The subsequent addition of NaBH\textsubscript{4} first reduces the metal ions that form the “naked”, micelle-encapsulated (but not TOAB directly capped) Au NPs. The ligands (the thiolate generated from the reduction of disulfide and the unreacted thiol) in the organic solvent then diffuse through the TOA shell and form the Au–S bonds at the water/organic solvent interface by which the ligand-protected metal NPs are formed, as illustrated in Scheme 4.1.

4.5 Reversed Synthetic Route

To test the above hypothesis, we employed a reversed synthetic route for the metal NPs formation as follows. A HAuCl\textsubscript{4} (0.1 mmol) aqueous solution (0.7 mL) was first mixed with a TOAB (0.3 mmol) toluene solution (10 mL) and stirred until the aqueous phase became colorless. As shown in Figure 4.5, micelles were formed in this mixture. A fresh NaBH\textsubscript{4} aqueous solution (1 mL) was then poured into the mixture. After 10-second stirring, as the color of the mixture changed from the initial wine red to red brown that indicated the formation of the micelle-
encapsulated Au NPs. A C12SH (0.3 mmol) toluene solution (2 mL) was added quickly into the solution to form the final stable, ligand-protected ultra-small Au NPs with good size distribution (1.7 ± 0.3 nm), as confirmed by the SPR spectrum and the TEM image (Figure 4.7(a)). We notice that when the BSM was followed with exactly the same amounts of materials, Au NPs with the same size were obtained (Figure 4.8), strongly suggesting that they follow the same NP formation mechanism.

If the proposed mechanism is correct, then increasing the stirring time before the thiol addition while keeping other parameters constant is expected to increase the probability of collision between micelles\(^{26}\) in which the initially-formed smaller Au NPs would grow larger. This was indeed observed when the stirring time was increased from 10 s to 10 min and 24 hrs, larger Au NPs (2.5 ± 0.7 nm and 4.8 ± 1.1 nm respectively) were formed as shown by the corresponding SPR spectra and TEM images (Figures 4.7(b) and 4.7(c)). The same procedure was also applied to forming the Ag and Cu NPs (Figure 4.9). As observed for the Au NPs, the UV-vis spectra of Ag and Cu NPs also showed the same SPR peaks as those prepared via the typical BSM synthesis (Figure 4.10), suggesting strongly again the same NP formation mechanism in both synthetic routes. The NP size controlling effect of the thiol/Au ratio that has been widely used in the BSM synthesis\(^{2,18}\) can also be achieved in the reversed route as illustrated in Figure 4.11 and 4.12.

Additionally, it was observed that disulfide could also be used as ligands in both synthetic routes and produced Au NPs of similar size (Figure 4.13), which was different from that using thiol as ligands and with the same S/Au ratio. Consequently, the fact that thiol and disulfide co-exist before the reduction with NaBH\(_4\) in a typical BSM synthesis\(^{20}\) is probably one of the
reasons why the size distribution of the fresh NPs synthesized by the BSM method is not narrow and post-synthetic treatment is needed\textsuperscript{4,5}. Moreover, since disulfide can not reduce Au(III), these results showed that Au(I) is not a necessary precursor for forming Au NPs.

We next compared the Au NPs formation processes using dialkyl diselenide (RSeSeR) and dialkyl ditelluride (RTeTeR) as ligands in the BSM and the reversed synthetic routes. The \textsuperscript{1}H NMR spectra of the reaction solution after adding RSeSeR or RTeTeR were recorded (Figure 4.14). The disappearance of the triplet peak at 2.75 (or 2.95) ppm due to the proton in –CH\textsubscript{2}Se– (or –CH\textsubscript{2}Te–) suggested strongly that the RSe–SeR (RTe–TeR) bond was broken via reacting with Au(III). Although the exact chemical state of the organo-chalcogen species after the bond breaking is currently under investigation, the similar proton NMR spectra (Figure 4.14(c), (e), and (g)) of the respective reaction solutions after the addition of the ligands suggest all of them had a similar precursor species of Au ions, i.e., [TOA][AuX\textsubscript{2}]. It has also been observed that the BSM generally fails to produce less-than-2nm Au NPs and the size distribution is usually poor for diselenide (Figure 4.15(a), 3.4±0.5 nm and 4.15(c), 3.1 ± 1.2 nm). On the other hand, the reversed synthetic route shows a superior performance in these cases and can easily produce less-than-2 nm Au NPs with good size distribution (Figure 4.15(b), 1.4 ± 0.3 nm and 4.15(d), 1.5 ± 0.2 nm).

4.6 Conclusions

In summary, we have reported above several observations of general importance in understanding how metal NPs are formed in the popular BSM synthesis. First, our Raman spectroscopic investigation (Figure 4.1) showed that after thiol addition no M–S bonds were
formed. This was demonstrated by the control experiment of Raman measurement on the synthesized [MSR]ₙ-like polymers. Notably, the Raman measurement showed that the [MSR]ₙ-like polymers did involve the M–S bonds (Figure 4.1d). These observations provide independent spectroscopic confirmation of the recent work by Lennox and co-workers²⁰ in which they elegantly showed that the metal precursors before the NaBH₄ reduction in the BSM is not the generally believed [MSR]ₙ-like polymers but the [TOA][MX₂] complex. Second, based on the observation of the micelle-encapsulated water that hosts the metal ion complex (Figure 4.5 and 4.6) and the success of the reversed synthetic route (Figure 4.7 and 4.15), we have proposed a general metal NPs formation mechanism applicable to the BSM as illustrated in Scheme 4.1. In other words, it is basically an inverse micelle based synthetic procedure. Third, we have also shown that the reversed synthetic route generally offers better control in forming different metal (Au, Ag, and Cu) NPs with different organo-chalcogen ligands as the stabilizers. A similar process was reported previously but digestive ripening was necessary to obtain the homogenous larger (~ 5 nm) Au NPs.²⁷ The emergence of these new mechanistic insights will help synthesize organo-chalcogens-stabilized metal NPs with better control.
Scheme 4.1 Scheme for chalcogenate-protected metal NP synthesis mechanism by the Brust–Schiffrin method.
Figure 4.1 Raman spectra of (a) dodecanethiol, (b) didodecyl disulfide, (c) dodecanethiol self-assembled on rough Au electrode, (d) synthesized [AuSR]ₙ-like polymer, (e) the concentrated C₆H₆ layer of HAuCl₄ and 3 equiv of TOAB after the addition of 2 equiv of dodecanethiol, (f) synthesized [TOA][AuBr₂] complex, (g) TOAB, (h) C₆H₆.
Figure 4.2 $^1$H NMR spectra of (a) the intermediate obtained after the addition of 2 equiv of dodecanethiol to TOAB-plus-Au(III) (TOAB: Au = 3:1) C₆D₆ layer, (b) synthesized [TOA][AuBr₂] complex, (c) TOAB, (d) dodecanethiol, and (e) synthesized didodecyl disulfide, all in 0.80 mL C₆D₆.
Figure 4.3 Raman spectra of (a) dodecanethiol, (b) didodecyl disulfide, (c) synthesized \([\text{AgSR}]_n\) polymer, (d) the mixture of \(\text{AgNO}_3\) aqueous solution and 3 equiv of TOAB toluene after removing most solvent, (e) adding 3 equiv of dodecanethiol to the benzene layer of \(\text{AgNO}_3\) and 3 equiv of TOAB and removing most solvent, and (f) TOAB.
Figure 4.4 Raman spectra of (a) dodecanethiol, (b) didodecyl disulfide, (c) synthesized [CuSR]$_n$ polymer, (d) synthesized [TOA]$_2$[CuX$_4$], (e) the mixture of [TOA]$_2$[CuX$_4$] and 3 equiv of dodecanethiol in toluene after removal of most solvent, (f) CuCl$_2$·H$_2$O, (g) CuBr, and (h)TOAB. (X: Cl or Br).
Figure 4.5 $^1$H NMR spectra of (a) [TOA][AuBr$_4$] complex (0.025 mmol) in C$_6$D$_6$; the organic layer of TOAB (0.03 mmol) in C$_6$D$_6$ mixed with (b) HAuCl$_4$ (0.03 mmol) aqueous solution (0.21 mL), (c) HAuCl$_4$ (0.015 mmol) aqueous solution (0.105 mL H$_2$O), (d) HAuCl$_4$ (0.01 mmol) aqueous solution (0.07 mL), and (e) HAuCl$_4$ (0.006 mmol) aqueous solution (0.042 mL); (f) the organic layer of TOAB (0.03 mmol) in C$_6$D$_6$ mixed with 0.105 mL H$_2$O; (g) TOAB (0.03 mmol) in C$_6$D$_6$; and (h) the organic layer of C$_6$D$_6$ mixed with 0.105 mL H$_2$O. (Note: 0.80-mL C$_6$D$_6$ for each sample and 0.1421 M of the stock HAuCl$_4$ aqueous solution was used).
Figure 4.6 DLS spectra of (a) the toluene layer of HAuCl₄ and 3 equiv of TOAB, (b) the clear colorless solution obtained after adding 2 equiv of octanethiol to the toluene layer of HAuCl₄ and 3 equiv of TOAB.
Figure 4.7 TEM images with size distribution and UV-visible spectra of the dodecanethiolate-protected Au nanoparticles obtained through our reversed synthetic route with the stirring time of (a) 10 s, (b) 10 min, and (c) 24 hrs before the addition of thiols.
Figure 4.8 TEM image of dodecanethiolate-protected gold nanoparticles (1.8 ± 0.4 nm) by Brust–Schiffrin two-phase method.
Figure 4.9 TEM images of dodecanethiolate-protected (a) Ag (2.9 ± 0.4 nm) and (b) Cu (1.8 ± 0.3 nm) nanoparticles by our reversed synthetic route.
Figure 4.10 UV-vis spectra of dodecanethiolate-protected (a) & (b) Au, (c) & (d) Ag, and (e) & (f) Cu nanoparticles by the Brust–Schiffrin two-phase method (dot line) vs. our reversed synthetic route (solid line).
Figure 4.11 UV-vis absorption spectra of dodecanethiolate-protected Au nanoparticles by our reversed synthetic route with (a) 1, (b) 2, (c) 3, (d) 0 equiv of dodecanethiol in toluene.
Figure 4.12 TEM images of dodecanethiolate-protected Au nanoparticles through our reversed synthetic route with (a) 1 (3.9 ± 0.6 nm), (b) 2 (2.5 ± 0.5 nm), (c) 3 (1.7 ± 0.3 nm), and (d) 0 (i.e. without any ligand, also named as “naked” TOA-stabilized Au nanoparticles, 5.30 ± 0.94 nm) equiv of dodecanethiol.
Figure 4.13 UV-vis spectra and TEM images of Au nanoparticles formed using didodecyl disulfide as ligands by (a) Brust–Schiffrin two-phase method (1.8 ± 0.3 nm) vs. (b) our reversed synthetic route (2.0 ± 0.3 nm).
Figure 4.14 $^1$H NMR spectra of (a) TOAB, (b) dioctyl disulfide, (c) adding 3 equiv octanethiol to the organic phase of HAuCl$_4$ and 3 equiv of TOAB (i.e. HAuCl$_4$ + 3TOAB), (d) dioctyl diselenide, (e) adding 0.5 equiv dioctyl diselenide to HAuCl$_4$ + 3TOAB, (f) dioctyl ditelluride, and (g) adding 1/3 equiv dioctyl ditelluride to HAuCl$_4$ + 3TOAB in C$_6$D$_6$. 
Figure 4.15 TEM images with size distributions and UV-vis spectra of Au nanoparticles protected with (a) & (b) Se-contained ligands, and (c) & (d) Te-contained ligands by Brust–Schiffrin two-phase method (dot line) vs. our reversed synthetic route (solid line). (Note: (c) after centrifugation.)
4.7 References


CHAPTER V
CRITICAL ROLE OF WATER AND STRUCTURE OF INVERSE MICELLES IN BSM

Reproduced with permission from Li, Y.; Zaluzhna, O.; Tong, Y. J., Critical Role of Water and Structure of Inverse Micelles in the Brust-Schiffrin Synthesis of Metal Nanoparticles. submitted to Langmuir 2011. It was the result of my research effort under the direct guidance of my mentor, Prof. YuYe J. Tong. Ms. Zaluzhna took all of TEM images of the samples.

5.1 Introduction

The Brust–Schiffrin two-phase method (BSM)\(^1\) is a highly popular synthetic route for preparing chalcogenate-protected metal nanoparticles (NPs)\(^2\)\(^-\)\(^10\), in particular thiolate-protected Au NPs\(^11\)\(^-\)\(^21\). This is due to their easy-to-follow synthetic procedures, good shelf stability of the products and their re-dissolvability in organic solvent.\(^11\)\(^,\)\(^14\) Although mechanistic details of the synthesis are still sketchy, it has generally been accepted that a typical BSM synthesis consists of three steps: (i) the phase transfer of Au(III) ions from aqueous layer to organic layer (i.e. toluene or benzene) with the help of phase transfer agent TOAB (tetrabutylammonium bromide), (ii) the reduction of Au(III) to Au(I) by the added thiols, and (iii) the reduction of Au(I) to Au(0) by NaBH\(_4\) in the presence of thiols and other sulfur-containing ligands that leads to the formation of Au NPs. A long-held belief concerning the metal precursor in the BSM synthesis of metal NPs, probably due to earlier papers by Whetten et. al.\(^16\),\(^22\), had been until recently\(^23\),\(^24\) that the metal-thiolate polymer, \([\text{M(I)SR}]_n\), is the metal-ion precursor of metal NPs. Yet, a recent thought-provoking paper by Goulet and Lennox has made a different claim, providing evidence that the metal-TOAB complex, \([\text{TOA}][\text{M(I)X}_2]\), is the correct metal-ion precursor, which was confirmed
by our recent work\textsuperscript{23}. Which of the two (polymer or complex) is the correct metal-ion precursor naturally becomes a question of broad interest in terms of figuring out the detailed mechanism of the BSM method and achieving better control of the NP size and size homogeneity. There are also other unanswered, fundamentally important questions in the BSM synthesis, such as what is the structure of the inverse micelles that have been identified recently\textsuperscript{23} as a critical ingredient of the BSM synthesis? What is the fate of the thiol hydrogen? And what is the role of water? Herein, we report a study that addresses all of the questions above.

Two key advances in our general understanding of the BSM synthesis of metal NPs achieved recently form the basis and motivation of the current study. The first is the recent discovery\textsuperscript{24} that the phase transfer in the BSM synthesis led to the formation of [TOA][M(III)X\textsubscript{4}] complex and the subsequent reduction by thiols produced [TOA][M(I)X\textsubscript{2}] complex instead of long-believed polymeric [M(I)SR\textsubscript{n}] species. The second is the realization\textsuperscript{23} that the BSM synthesis of monolayer-protected metal NPs was basically an inverse-micelle based synthesis and the metal–sulfur bond didn’t form until the formation metal nuclear centers. These two advances have put us on track of a detailed mechanistic investigation of how different ingredients of reaction medium influence the final formation of metal NPs and guided us in formulating specific experimental measurements that combined principally Raman and \textsuperscript{1}H NMR spectroscopies with controlled synthetic steps. These measurements were expected to improve substantially our mechanistic understanding of the BSM synthesis of metal NPs by which an optimal synthetic procedure for synthesizing homogenously distributed metal NPs may be established.

For facilitating ensuing discussions, we name the mixture solution (aqueous plus organic layers) right after the phase transfer as Sol-0, the separated organic phase of Sol-0 with added
thiols as Sol-I, and Sol-0 (no phase separation) with added thiols as Sol-II. Raman spectra (Figure 5.1) confirmed the formation of \([\text{TOA}][\text{AuX}_4]\) complex in the organic phase of Sol-0. Once a proper amount of thiols (e.g., \(S: \text{Au} = \sim 3\)) was added to the solutions under stirring, the initial wine red color of \(\text{Au}(\text{III})\) turned colorless within 30 minutes, indicating a reduction of \(\text{Au}(\text{III})\) to \(\text{Au}(\text{I})\). For Sol-I, it remained colorless and crystal clear even after being stirred for > 1hr. But for the Sol-II, the solution became cloudy white (Figure 5.2a) and formed three well-separated layers after being still for a while (Figure 5.2b). The top (Sol-II-T) and bottom (Sol-II-B) layers were clear and colorless while the middle layer (Sol-II-M) was opaque white. Notice that no middle opaque-white layer was formed if thiol: \(\text{Au}\) ratio was less than 2.

5.2 State of the Metal-Ion Precursors

We show in Figure 5.3 the Raman spectra of the different reaction solutions and the relevant reference materials. Spectrum 5.3(a) was of the pure dodecanethiol with the RS–H vibration\(^{25}\) at 2568 cm\(^{-1}\) as indicated. Spectrum 5.3(b) was of didodecyl disulfide with the RS–SR vibration\(^{26}\) at 525 cm\(^{-1}\) as indicated. Spectrum 5.3(c) was of the dodecanethiol self-assembled on a highly roughened \(\text{Au}\) electrode. The peak at 327 cm\(^{-1}\) was the characteristic vibration of the \(\text{Au}–\text{SR}\) bond\(^{23,26}\) whose appearance is accompanied by the disappearance of the RS–H vibrational band. Spectrum 5.3(d) is of the synthesized \([\text{AuSR}]_n\) polymer. The appearance of the peak at 327 cm\(^{-1}\) indicates the formation of an \(\text{Au}–\text{SR}\) bond whose exact frequency depends slightly on the alkyl chain length (Figure 5.4). Spectrum 5.3(e) was of the Sol-II-M and shows identical spectral features to those of Spectrum 5.3(d), including the \(\text{Au}–\text{SR}\) vibration at 327 cm\(^{-1}\). The appearance of the latter peak is a strong evidence showing that the Sol-II-M contained the polymeric
[AuSR]ₙ species in which Au–SR bonds are expected. Spectrum 5.3(f) was of the synthesized [TOA][AuBr₂] complex solid with the Au–Br vibration band at 209 cm⁻¹ as indicated, which agrees with the literature value²⁷. Spectrum 5.3(g) was of the freshly concentrated Sol-I. The appearance of a peak at 209 cm⁻¹, the absence of a peak at 327 cm⁻¹, and the overall similarity to the Spectrum 5.3(f) (the strong peak at 991 cm⁻¹ in the former was from the benzene solvent) indicate that the [TOA][AuBr₂] complex was formed in Sol-I. The appearance of the RS–SR vibration at ~520 cm⁻¹ is consistent with the observations by Goulet and Lennox that reduction of Au(III) by thiols led to the formation of disulfide²⁴. Spectrum 5.3(h) was of the freshly concentrated Sol-II-T. That it is identical to the Spectrum 5.3(f) shows that the [TOA][AuBr₂] complex was also formed in Sol-II-T. When the concentrated (slurry) Sol-II-T was exposed to air for ~24 hrs, the Spectrum 5.3(h) turned into Spectrum 5.3(i). The appearance of the peak at 327 cm⁻¹ implies strongly that the moisture in the air facilitated the formation of the polymeric [AuSR]ₙ species in the concentrated reaction solution where the polymeric species did not exist initially. Spectrum 5.3(j) is of pure TOAB for comparisons.

Similar phenomena were observed when Ag(I) was used as the metal source in the BSM synthesis. Although no redox reaction occurred between thiols and Ag(I)²⁴, the Ag-S vibration band (at ~320 cm⁻¹) was still observed in the Raman spectra (Figure 5.5) when the mixture of [TOA][AgBr₂] and 3 equiv of dodecanethiol was stirred overnight or longer in the presence of water (like Sol-II above). Altogether, the above observations strongly suggest that the amount of water plays a major differentiating role in the formation of the polymeric species.
Thus, the reactions that took place upon the addition of thiols in the BSM synthesis were as follows. If the reaction solution is Sol-II (i.e., no phase separation), then Reaction (1) occurs (Figure 5.3e and 5.3h):

\[
[\text{TOA}][\text{AuX}_4] + \text{RSH} \rightarrow [\text{TOA}][\text{AuX}_2] + [\text{AuSR}]_n + \text{RSSR} + \text{HX} \quad (1)
\]

The appearance of polymeric species is in agreement with Whetten and coworkers’ observations.\textsuperscript{16, 22} But if the reaction solution is the Sol-I (i.e., aqueous phase being removed), then Reaction (2) occurs (Figure 5.3g), which is in agreement with the observations by Goulet and Lennox\textsuperscript{24}:

\[
[\text{TOA}][\text{AuX}_4] + \text{RSH} \rightarrow [\text{TOA}][\text{AuX}_2] + \text{RSSR} + \text{HX} \quad (2)
\]

We have discovered that the reaction media before the addition of thiols and the ratio of thiol to Au determine the chemical state of the Au(I) precursor species in the BSM synthesis. The correct answer to the question as to which of the two (polymeric [AuSR]\textsubscript{n} vs. complex [TOA][AuX\textsubscript{2}]) is the correct Au-ion precursor, is therefore that both Reactions (1) and (2) can be correct, depending on the specific reaction medium (i.e. with or without aqueous phase) before the addition of thiols and the ratio of thiol to Au. If the aqueous layer was removed after the phase transfer of the Au(III) (i.e., AuCl\textsubscript{4}–) with TOAB from aqueous to the organic phase and only to the latter thiols were added (Sol-I), the precursor species was the [TOA][AuX\textsubscript{2}] complex. On the other hand, if thiols were added to the mixture of aqueous and organic phases (Sol-II) and the thiol: Au ratio was larger than 2, the precursor species was a mixture of the [TOA][AuX\textsubscript{2}] complex and the polymeric [AuSR]\textsubscript{n} species. When the ratio of thiol to Au was less than 2, no matter whether the aqueous layer was removed or not, the precursor species was always the [TOA][AuX\textsubscript{m}] (m = 2 or 4) complex.
The effect of the different Au(I) precursors on the final formation of Au NPs was studied by adding 1-mL NaBH₄ aqueous solution to the 10-mL toluene solutions of Sol-I, Sol-II, and synthesized polymeric [Au(I)SR]ₙ (the same type of species as contained in Sol-II-M) respectively, with Au (0.025 mmol): [TOA]⁺: S: NaBH₄ of 1: 1: 3: 10. The respective Au NPs so-obtained are shown in Figure 5.6(a) through 5.6(c). Their corresponding sizes and size distributions are $1.16 \pm 0.17$ nm, $1.48 \pm 0.23$ nm, $2.26 \pm 0.39$ nm. Notice that Sample 5.6(a) (Sol-I) contained only [TOA][AuX₂] complex, Sample 5.6(b) (Sol-II) a mixture of [TOA][AuX₂] complex and polymeric [AuSR]ₙ species, and Sample 5.6(c) only polymeric [AuSR]ₙ species together with 1 equiv of TOAB (the addition of TOAB ensured that all three reaction media contained the same amount of surfactant). The above results show that among the three samples, Sample 5.6(a) produced the smallest, Sample 5.6(c) the largest, and Sample 5.6(b) in-between size of Au NPs, with the breadth of size distribution in the same order. Thus, polymeric [Au(I)SR]ₙ is in general not a good metal precursor species to form homogeneous ultra-small Au NPs and a mixture of Au complex and polymeric species increases the polydispersity of the synthesized Au NPs.

5.3 Structure of the Inverse Micelles

It is well known that inverse micelles can be formed when the surfactants are dissolved in organic solvents with or without water. In the presence of water, some water can be solubilized in the polar core together with the polar head of surfactants and form a “water pool” or encapsulated water (en-H₂O). This indeed happened when an organic solution of TOAB was mixed with water as shown in our recent study. A detailed illustration is shown in Panel A of Figure 5.7 where the ¹H NMR spectra of the organic layer separated after mixing (with 1-hr
stirring) 16.4 mg (0.03 mmol) TOAB dissolved in 0.8 mL C_6D_6 with different amount of water are presented (the separated benzene phase was used for NMR measurements): 5.7(a), 0.210 mL; 5.7(b), 0.105 mL; 5.7(c), 0.070 mL; 5.7(d), 0.0425 mL; and 5.7(e), 0 mL. For reference, the Figure 5.7 (f) is the ^1H NMR spectrum of 0.8 mL C_6D_6 mixed with 0.070 mL H_2O whose peak position at 0.44 ppm is very close to the tabulated value (0.4 ppm).^29

The appearance of a peak at ~2.44 ppm in Figure 5.7(a) to 5.7(e) indicates the formation of the en-H_2O by the surfactant TOAB.^30 This becomes clearer by comparing Figure 5.7(c) with 5.7(f). Both have the same initial C_6D_6: H_2O volumetric ratio (80: 7) for mixing and stirring but the former has the additional 16.4 mg TOAB that can form inverse micelles in C_6D_6 in the presence of water but not the latter which was TOAB free. The accompanying appearance of a peak at 2.43 ppm and the disappearance of the water peak in C_6D_6 at 0.44 ppm provide the direct experimental evidence of the formation of the en-H_2O in the inverse micelles of TOAB, with the peak position determined by the fast exchange between water dissolved in C_6D_6 and encapsulated in inverse micelles (vide infra). Notice that there existed a trace amount of water even in the pure TOAB C_6D_6 solution whose peak shows up at 2.33 ppm (Figure 5.7(e)). Also notice that both peak positions of the \( \alpha \)-protons (i.e., \( \text{H}_2\text{C}^-\text{N}^+ \)) at ~3.34 ppm and the (fast exchanging) \( \text{H}_2\text{O} \) is independent of the initial water amount during the mixing. This indicates that the amount of water up-taken by the benzene solution of TOAB was rather constant, implying a constant formation of the inverse micelles.

When the Au salt was added, it became quite different story, which is illustrated by the \(^1\text{H} \) NMR spectra collected in Panel B of Figure 3 where the \(^1\text{H} \) NMR spectra of 16.4 mg TOAB in 0.8 mL C_6D_6 mixed with different volumes (the same values as in Figure 5.7(a) to 5.7(e)
respectively) of aqueous solution of HAuCl₄ (0.1421 M) are shown (the separated benzene phase was used for NMR measurements): 5.7(g), 0.210 mL; 5.7(h), 0.105 mL; 5.7(i), 0.070 mL, and 5.7(j), 0.0425 mL. The corresponding TOAB: Au ratios were 1: 1, 2: 1, 3: 1, and 5: 1. For comparison, the ¹H NMR spectra of the synthesized [TOA][AuBr₄] complex (0.0125 mmol) in 0.8 mL C₆D₆ with (0.09 mL) and without H₂O mixing are shown in Figure 5.7(k) and 5.7(l).

Contrary to the constant peak positions as seen in Figure 5.7(a) to 5.7(e), the water and α-protons peaks became dependent of the amount of mixing water, i.e., of the Au(III) ions. The pair (H₂O/α-protons) peak values are now 0.70/ 2.97 ppm, 2.36/ 3.18 ppm, 2.63/ 3.22 ppm, and 2.69/ 3.26 ppm for TOAB: Au ratios of 1: 1, 2: 1, 3: 1, and 5: 1 respectively. That the peak position of the α-protons in the TOAB: Au = 1: 1 case (Figure 5.7(g)) is the same as that of the synthesized [TOA][AuBr₄] complex (Figure 5.7(k) and 5.7(i)) indicates strongly that one [TOA]⁺ cation was associated with one [AuX₄]⁻ anion where X could be either Br⁻ or Cl⁻ (see Figure 5.1(d)). As the TOAB: Au ratio increases, more and more [TOA]⁺ cations can be associated with halogen anions (for instance Br⁻ or Cl⁻) other than the Au(III) complex. Yet, that only one α-proton peak was observed in all cases is a sign of fast exchange between the Au(III) complex unit and the halogen anion in the inverse micelles.

Now taking 2.97 ppm (Figure 5.7(g), 5.7(k), and 5.7(l)) and 3.34 ppm (Figure 5.7(a) to 5.7(d)) as the peak positions of the α-protons in two extremities (all Au(III) units vs. all halogen anions), we calculated the expected peak position using the fast-exchange model: δₓα-proton = y × 2.97+ (1 - y) × 3.34 (in ppm), where y is the fraction of the Au(III) units among the total anions (i.e. [AuX₄]⁻ and X⁻). 3.16, 3.22, and 3.27 ppm were found for TOAB: Au ratios of 2: 1, 3: 1, and 5: 1 respectively. These should be compared with 3.18, 3.22, and 3.26 ppm, the experimentally
observed values (Figure 5.7(h) to 5.7(j)). That the calculated values are in excellent agreement with the experimentally observed ones indicates strongly that the partition of the Au(III) units and the halogen anions in a given inverse micelle follows the nominal stoichiometry.

The H$_2$O peak position is also no longer constant, neither is its amplitude. Particularly, the presence of the [TOA][AuX$_4$] complex seems to suppress significantly the amount of en-H$_2$O, as evidenced by comparing Figure 5.7(g) with 5.7(a). To be more quantitative, we integrated the relevant proton peaks and normalized them by the peak integral (set to be 8 for the 8 protons in 4 α-CH$_2$ group per [TOA]$^+$ cation (pTc)) of the α-CH$_2$ since the same amount of TOAB (16.4 mg) was used in all samples (see Table 5.1 to 5.3). The numbers so-obtained are the numbers of protons pTc. As can be calculated from the data in Table 5.1 through 5.3, the average values for the –CH$_3$ group and the residual proton in C$_6$D$_6$ (0.8 mL) were 11.4 ± 0.4 and 7.2 ± 0.4 respectively. The closeness of the former to the expected value of 12 and the excellent reproducibility of the both values (i.e., very small standard deviations) justify well our choice of the α-CH$_2$ peak as the internal reference and accuracy of the measurements.

As expected, the amount of H$_2$O in Figure 5.7(a) through 5.7(d) was a constant: 5.1 ± 0.2 (~2.5 H$_2$O pTc, Table 5.1). So is the saturated free water in C$_6$D$_6$ shown in Figure 5.7(f) and 5.7(k) (1.68 ± 0.04, or ~0.8 H$_2$O pTc, Table 5.1). It is reasonable to assume that there only existed two types of water in the benzene solution: the H$_2$O dissolved in benzene (resonant at 0.44 ppm) and the en-H$_2$O in inverse micelles. Since a discernible water layer was always formed after the mixing in all experiments, the amount of water used should be high enough to saturate the C$_6$D$_6$ solvent and micelles. Thus, the absence of the peak at 0.44 ppm indicates that these two types of water must experience a fast exchange on the NMR time scale. By subtracting the amount of
water dissolved in C₆D₆, one can find that the amount of en-H₂O is ~ 1.74 H₂O pTc. Now assuming (ad hoc) that a stoichiometry of 1:1 between [TOA]⁺ of a given inverse micelle and surface water molecules of the en-H₂O, a dispersion (number of surface H₂O over total en-H₂O) of 0.57 can be calculated. Using this dispersion and molecular volume of room-temperature bulk H₂O (~ 0.03 nm³), we estimate that the size of a spherical volume of the inverse micelle has a diameter of ~2.5 nm and each micelle consisted of ~156 [TOA]⁺ cations that encapsulated ~273 H₂O molecules.

The following strategy was used to estimate the core size of inverse micelle formed by TOAB. According to Table 5.1, the average number of protons from the H₂O in Sample (a~d) is 5.11 per TOAB. After subtracting the number of protons from the H₂O saturated in C₆D₆ (i.e. 1.63 per TOAB (Sample (f)), the number of protons from the H₂O encapsulated in the inverse micelles formed by TOAB is 3.48, which means that the ratio of the encapsulated H₂O to TOAB is 1.74. Assuming that one molecule of TOAB is surrounded by one molecule of H₂O, 57% of the encapsulated H₂O might locate the outer layer of the inverse micelle core. Together with the fact that the H₂O volume per molecule is 0.03 nm³ at 20°C (density of H₂O: 0.998 g/mL), the diameter of the inverse micelle core, i.e. the part of the H₂O encapsulated in the inverse micelle of TOAB, is 2.53nm.

In contrast, the amounts of H₂O in Figure 5.7(g) through 5.7(j) were 1.32, 3.75, 3.90, and 4.91 (Table 5.2) as the amount of Au(III) decreased. At a TOAB: Au(III) ratio of 1:1, the H₂O peak position was at 0.7 ppm, which is very close but not equal to that of H₂O dissolved in C₆D₆ (0.44 ppm). Additionally, the amount of water (1.32) was even lower than that of the saturated water dissolved in C₆D₆ (1.68). Therefore, we believe that there was only a very tiny amount of en-
H₂O in this sample. As the TOAB: Au ratio increased from 1: 1, to 2: 1, 3: 1, and 5: 1, increasing number of [TOA]⁺ cations were free from being associated with the Au(III) complex. Consequently, the amount of en-H₂O increased, from almost zero to 1.04, 1.11 and 1.62 pTc. Notice that the last value is quite close to the value (1.74 pTc) of the Au(III)-free micelles. Assuming (ad hoc again) that the size of the micelles did not change in the presence of the Au(III) complex, the numbers of Au(III) cations in a given micelle would thus be ~156, 78, 52, and 31 for TOAB: Au(III) ratio of 1: 1, 2: 1, 3: 1, and 5: 1, respectively. However, mixing water with synthesized [TOA][Au(III)Br₄] complex did not produce en-H₂O as evidenced by comparing Figure 5.7(k) with 5.7(f) of which the latter did not contain TOAB. The same peak position and water amount were observed in both samples.

5.4 Fate of the Thiol Protons

Once the organic (benzene or toluene) phase is separated in a BSM synthesis, the next step is to add thiols to the separated organic layer and Reaction (2) is expected to happen. Since the reaction happens in an organic (hydrophobic) medium, understanding the processes involving hosting the reaction-generated hydrophilic proton is fundamentally important. For instance, we have observed that the reduction of the synthesized [TOA][AuBr₄] complex to [TOA][AuBr₂] by thiols in an anhydrous organic (toluene or benzene) solvent was extremely slow, but happened almost instantaneously in the presence of H₂O.

In order to find what happens to the –H after the S–H bond of thiol is broken during the reduction of Au(III), ^1H NMR spectra of the samples prepared by adding dodecanethiols (2S: 1Au) to solutions of Figure 5.7(g) to 5.7(j)) were recorded. These spectra are shown in Panel C
of Figure 5.7, together with those of relevant reference materials. The appearance of the disulfide peak and the residual thiol peak in Figure 5.7(m) to 5.7(p), as indicated by the arrows, demonstrates clearly that the reduction of Au(III) by thiols did occur. Quantitative reaction stoichiometry can be calculated from the data in Table 5.3. The calculated S (i.e. thiol and disulfide): Au ratios are 1.9: 1, 2.0: 1, 2.1: 1, and 2.3: 1 for the 4 samples (5.7(m) to 5.7(p)) respectively. These values are very close to the nominal ratio of 2: 1, indicating the reliability of this quantitative analysis.

The most striking difference between Figure 5.7(m) to 5.7(p) and their respective parent spectra (Figure 5.7(g) to 5.7(j)) is the large positive shift of the water peak, from 0.7 ppm in 5.7(g) to 4.16 ppm in 5.7(m), 2.34 ppm in 5.7(h) to 5.56 ppm in 5.7(n), 2.63 ppm in 5.7(i) to 4.69 ppm in 5.7(o), and 2.69 ppm 5.7(j) to 3.96 ppm in 5.7(p), respectively. We attribute such positive shifts to the acidification of the original water by the reduction-produced proton. In other words, the existing inverse micelles-encapsulated water or/and organic solvent-dissolved water provided a receiving medium to the reaction-generated protons, enabling Reaction (2) to proceed forwards readily. Although the H$_2$O saturated in C$_6$D$_6$ made the reduction of Au(III) happen when thiols added into the organic solution of [TOA][AuBr$_4$] (sample 5.7(k)), no acidified en-H$_2$O (i.e. H$_3$O$^+$) was observed (Figure 5.7(q)) because the generated protons were not encapsulated in the inverse micelles and could not observed by NMR. On the other hand, no reduction neither en-H$_2$O was observed when disulfide (Figure 5.7(r)) or thiol (Figure 5.7(s)) was added to the organic solution of [TOA][AuBr$_2$].
5.5 Role of Water

With the detailed discussions presented above, the state of the Au(I) precursors and their influence on the formation of Au NPs, the structure of the inverse micelles, and the state of the en-H$_2$O involved in a typical BSM synthesis have been largely clarified. However, how the presence or absence of water affects the formation of NPs is not yet to be answered, which will be the theme of the following discussion.

The effect of water on the formation of NPs in the BSM synthesis was studied by using the synthesized [TOA][AuBr$_4$] complex as Au source for the NP synthesis because the starting material (the complex) can be made anhydrous. When the anhydrous [TOA][AuBr$_4$] complex was dissolved in 10-mL toluene and then thiol was added, it was in a stage of Sol-I but without any en-H$_2$O. By directly adding a 1-mL NaBH$_4$ to this solution, Au NPs shown in Figure 5.8(a) were synthesized. As can be seen, the Au NPs shown in Figure 5.8(a) had a larger average NP size and a much wider size distribution (1.79 ± 0.49 nm) than those in Figure 5.8(a) (1.16 ± 0.17 nm). Yet, the only difference between the two syntheses was that the latter contained en-H$_2$O (Figure 5.8(m)), highlighting the important role that water plays in the BSM synthesis.

It turns out that not only the presence of water but also the amount of water is equally important. To illustrate the latter, we compared two syntheses that were all identical but the amount of water involved. For synthesis A (syn-A), 0.175-mL water and 1.6-mL [TOA][AuBr$_4$] toluene solution was first mixed and stirred for 30 min. Then the organic phase of the mixture was separated out and diluted to 10 mL with toluene. Although water solubility in toluene is about 4 times smaller than in benzene$^{32}$, a tiny amount of water was still expected to exist in the separated organic phase. For synthesis B (syn-B), no separation of the organic phase was carried
out. The remaining synthetic steps (adding thiols and NaBH₄) were the same. So the only difference between syn-A and syn-B was the amount of water (much more water in syn-B). Yet, the resulting Au NPs were very different. The syn-A-produced Au NPs are shown in Figure 5.8(b) (2.11 ± 0.31 nm) and syn-B in Figure 5.8(c) (1.27 ± 0.18 nm). Clearly, Au NPs made by syn-B (i.e., with more water present) had smaller average size and better size distribution.

5.6 Conclusions

In summary, we have clarified that the Au(I) precursor in a BSM synthesis is either [TOA][AuX₂] complex or a mixture of [TOA][AuX₂] complex and polymeric [AuSR]ₙ species, which depends on the reaction condition (i.e. with or without aqueous phase) before the addition of thiols, as illustrated by Scheme 5.1. We have shown (by ¹H NMR spectra) where the thiol proton (RS–H) goes when disulfide is formed after the redox reaction between Au(III) and thiol. More importantly, our data have clearly shown that the inverse micelles of [TOA]⁺ encapsulating metal ions together with water are reaction microenvironment in a typical BSM synthesis. Not only the presence but also the amount of water in the reaction medium has profound effect on the reduction of Au(III) by thiols and on the formation of uniform small NPs. Additionally, the extremely small size (~2.5 nm) of the inverse micelles is probably the main reason why the BSM synthesis does not work very well for synthesizing >5 nm metal NPs. It is expected that these new insights will help achieve better size and size distribution control in metal NPs synthesis.
Table 5.1 Proton Numbers of intermediates per [TOA]$^+$ in Figure 5.7A.

<table>
<thead>
<tr>
<th>Sample $^a$</th>
<th>Ratio</th>
<th>C$_6$D$_6$</th>
<th>cn-H$_2$O</th>
<th>$\alpha$-CH$_2$-N$^+$</th>
<th>CH$_3$</th>
<th>H$_2$O in C$_6$D$_6$</th>
</tr>
</thead>
<tbody>
<tr>
<td>(a) TOAB + 0.21-mL H$_2$O</td>
<td></td>
<td>6.61</td>
<td>4.97</td>
<td>$8^\dagger$</td>
<td>11.65</td>
<td>/</td>
</tr>
<tr>
<td>(b) TOAB + 0.105-mL H$_2$O</td>
<td></td>
<td>7.38</td>
<td>4.91</td>
<td>8</td>
<td>11.00</td>
<td>/</td>
</tr>
<tr>
<td>(c) TOAB + 0.07-mL H$_2$O</td>
<td></td>
<td>7.11</td>
<td>5.14</td>
<td>8</td>
<td>10.66</td>
<td>/</td>
</tr>
<tr>
<td>(d) TOAB + 0.0425-mL H$_2$O</td>
<td></td>
<td>7.86</td>
<td>5.43</td>
<td>8</td>
<td>12.03</td>
<td>/</td>
</tr>
<tr>
<td>(e) TOAB</td>
<td></td>
<td>6.96</td>
<td>0.37</td>
<td>8</td>
<td>11.49</td>
<td>/</td>
</tr>
<tr>
<td>(f) 0.07-mL H$_2$O</td>
<td></td>
<td>7.18$^\dagger$</td>
<td>/</td>
<td>/</td>
<td>/</td>
<td>1.63</td>
</tr>
</tbody>
</table>

Note: $^a$ 0.8 mL C$_6$D$_6$ and/or 0.03 mmol TOAB were used.  
$^\dagger$ The number of protons in $\alpha$-CH$_2$-N$^+$ from TOA$^+$ was assigned as 8.  
$^\ddagger$ The proton number from C$_6$D$_6$ in Sample (f) was the average of proton numbers of Sample (a~e), Sample (g~j), and Sample (m~p).
Table 5.2 Proton Numbers of intermediates per [TOA]$^+$ in Figure 5.7 B.

<table>
<thead>
<tr>
<th>Sample(^*)</th>
<th>Ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>C(_6)D(_5)</td>
</tr>
<tr>
<td>(g) TOAB + 0.21-mL HAuCl(_4) aq</td>
<td>7.30</td>
</tr>
<tr>
<td>(h) TOAB + 0.105-mL HAuCl(_4) aq</td>
<td>7.46</td>
</tr>
<tr>
<td>(i) TOAB + 0.07-mL HAuCl(_4) aq</td>
<td>7.05</td>
</tr>
<tr>
<td>(j) TOAB + 0.0425-mL HAuCl(_4) aq</td>
<td>7.08</td>
</tr>
<tr>
<td>(k) [TOA][AuBr(_4)] + 0.09-mL H(_2)O</td>
<td>7.18(^{\ddagger})</td>
</tr>
<tr>
<td>(l) [TOA][AuBr(_4)]</td>
<td>7.18(^{\ddagger})</td>
</tr>
</tbody>
</table>

Note: * Sample (g-j): organic layer of 0.03 mmol TOAB in 0.8mL C\(_6\)D\(_5\) and HAuCl\(_4\) (0.1421 M) aqueous solution were used; 0.0125 mmol (for Sample (k)) or 0.025 mmol (for Sample (l)) [TOA][AuBr\(_4\)] was used.

\(^{\dagger}\) The number of protons in \(\alpha\)-CH\(_3\)-N\(^+\) from TOA$^+$ was assigned as 8.

\(^{\ddagger}\) The proton number from C\(_6\)D\(_5\) in Sample (k-l) was the average of proton numbers of Sample (a-e), Sample (g-j), and Sample (m-p).
**Table 5.3** Proton Numbers of intermediates per [TOA]$^+$ in Figure 5.7C.

<table>
<thead>
<tr>
<th>Sample$^*$</th>
<th>Ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>C$_6$D$_6$</td>
</tr>
<tr>
<td>(m) Sample (g) + C$<em>{12}$H$</em>{25}$SH</td>
<td>7.10</td>
</tr>
<tr>
<td>(n) Sample (h) + C$<em>{12}$H$</em>{25}$SH</td>
<td>6.96</td>
</tr>
<tr>
<td>(o) Sample (i) + C$<em>{12}$H$</em>{25}$SH</td>
<td>7.28</td>
</tr>
<tr>
<td>(p) Sample (j) + C$<em>{12}$H$</em>{25}$SH</td>
<td>7.25</td>
</tr>
<tr>
<td>(q) Sample (k) + C$<em>{12}$H$</em>{25}$SH</td>
<td>7.18$^\ddagger$</td>
</tr>
<tr>
<td>(r) [TOA][AuBr$<em>2$] + (C$</em>{12}$H$_{25}$S)$_2$</td>
<td>7.18$^\ddagger$</td>
</tr>
<tr>
<td>(s) [TOA][AuBr$<em>2$] + C$</em>{12}$H$_{25}$SH</td>
<td>7.18$^\ddagger$</td>
</tr>
</tbody>
</table>

Note: * Sample (m-p): the ratio of S to Au was 2: 1; Sample (q-s): the ratio of S to Au was 3: 1; 0.011 mmol (for Sample (r)) or 0.025 mmol (for Sample (s)) [TOA][AuBr$_2$] was used.

$^\dagger$ The number of protons in $\alpha$-CH$_2$-N$^+$ from TOA$^+$ was assigned as 8.

$^\ddagger$ The proton number from C$_6$D$_6$ in Sample (q-s) was the average of proton numbers of Sample (s-e), Sample (g-j), and Sample (m-p).
Figure 5.1 Raman spectra of (a) KAuBr₄, (b) synthesized [TOA][AuBr₄], (c) synthesized [TOA][AuBr₂], (d) concentrated organic phase of Sol-0 containing 2 equiv of TOAB and 1 equiv of HAuCl₄ by removing most solvent by rotoevaporation, (e) HAuCl₄ (0.1421 M) aq solution, and (f) TOAB.
Figure 5.2 Photos of Sol-II after stirring with thiols for 1h and then being still for 2 hrs.
Figure 5.3 Raman spectra of (a) dodecanethiol, (b) didodecyl disulfide, (c) dodecanethiol self-assembled on a roughened Au electrode, (d) synthesized $[\text{AuSR}]_n$ polymer, (e) Sol-II-M collected by centrifugation, (f) synthesized $[\text{TOA}][\text{AuBr}_2]$ complex, (g) freshly concentrated Sol-I, (h) freshly concentrated Sol-II-T, (i) concentrated Sol-II-T exposed to air for 24 hrs, and (j) pure TOAB.
Figure 5.4 Raman spectra of (a) dodecanethiol, (b) octanethiol, (c) synthesized \([\text{AuSC}_{12}\text{H}_{25}]_n\) polymer, and (d) synthesized \([\text{AuSC}_{8}\text{H}_{17}]_n\) polymer.
Figure 5.5 Raman spectra of (a) dodecanethiol, (b) didodecyl disulfide, (c) synthesized [AgSC\textsubscript{12}H\textsubscript{25}]\textsubscript{n} polymer, (d) the white precipitate of Ag-Sol-II-M after centrifugation, (e) concentrated Ag-Sol-II-T, (f) concentrated organic phase of Ag-Sol-0, and (g) TOAB.
Figure 5.6 TEM images with size distribution histograms and UV-visible spectra of dodecanethiolate-protected Au NPs synthesized from the toluene solution (a) Sol-I, (b) Sol-II, (c) \([\text{AuSC}_{12}\text{H}_{25}]_n\) with TOAB. (Note: 0.025 mmol Au originally from 0.175 mL of 0.1421 M HAuCl₄ aqueous solution, 10-mL toluene, and 1-mL NaBH₄ aqueous solution were used in all cases. Au: [TOA]⁺: thiol: NaBH₄ = 1: 1: 3: 10).
Figure 5.7 Panel A. $^1$H NMR spectra of the organic layer separated after mixing (with 1-hr stirring) 16.4 mg (0.03 mmol) TOAB dissolved in 0.8 mL C$_6$D$_6$ with different amount of water: (a) 0.21 mL, (b) 0.105 mL, (c) 0.07 mL, (d) 0.0425 mL, and (e) 0 mL; (f) of a solution the same as (c) but without TOAB; Panel B. $^1$H NMR spectra of the organic layer separated after mixing 16.4 mg (0.03 mmol) TOAB in 0.8 mL C$_6$D$_6$ with different amounts of HAuCl$_4$ aqueous solution (0.1421 M): (g) 0.21 mL, (h) 0.105 mL, (i) 0.07 mL, (j) 0.0425 mL; (k) of [TOA][AuBr$_4$] (0.0125 mmol) in 0.8 mL C$_6$D$_6$ mixed with 0.09 mL H$_2$O; (l) of [TOA][AuBr$_4$] (0.025 mmol) in 0.8 mL C$_6$D$_6$; Panel C. $^1$H NMR spectra (m~g) of the samples prepared by adding dodecanethiol (2S: 1Au) to sample (g~j); (q) of the sample prepared by adding dodecanethiol (3S: 1Au) to sample (k); of [TOA][AuBr$_2$] (0.025 mmol) mixed with (r) didodecyl disulfide, and (s) dodecanethiol (3S: 1Au).
Figure 5.8 TEM images with size distribution histograms and UV-visible spectra of dodecanethiolate-protected Au NPs synthesized from the toluene solution: (a) [TOA][AuBr₄] complex, (b) [TOA][AuBr₄] complex with the water dissolved in 1.6-mL toluene, (c) [TOA][AuBr₄] complex with 0.175-mL H₂O. (Note: 0.025 mmol Au(III), 10-mL toluene, and 1-mL NaBH₄ aqueous solution were used in all cases. Au: [TOA]⁺: thiol: NaBH₄ = 1: 1: 3: 10).
Scheme 5.1 Revised pathways of the precursor species of Au ions in a Brust–Schiffrin two-phase synthesis.
5.7 References


CHAPTER VI

IDENTIFICATION OF A SOURCE OF SIZE POLYDISPERSITY IN BSM

Reproduced with permission from Li, Y.; Zaluzhna, O.; Tong, Y. J., Identification of a source of size polydispersity and its solution in Brust–Schiffrin metal nanoparticle synthesis. Chem. Commun. 2011, DOI: 10.1039/C1CC11642H. Copyright 2011 Royal Society of Chemistry. It was the result of my research effort under the direct guidance of my mentor, Prof. YuYe J. Tong. Ms. Zaluzhna took all of TEM images of the samples.

6.1 Introduction

Since the seminal 1994 paper by Brust and co-authors on synthesizing alkanethiolate-protected gold (Au) nanoparticles (NPs)¹, this synthetic method, abbreviated here as BSM (Brust–Schiffrin method) for simplicity, has probably become the most widely used method for synthesizing < 5 nm metal NPs² stabilized by thiolates³⁻⁹ in general and by other organo-chalcogenates¹⁰⁻¹³ in particular. Although thiols are originally used for NP synthesis in the BSM, the thiol–gold bond is commonly described as a surface bound thiolate.¹⁴ After Whetten group achieved the synthesis of <2-nm Au NPs,³ a thiol to Au molar ratio of 3:1 has become a routine reaction condition of the BSM.⁹ However, polydispersity in the synthesized Au NPs has been an ongoing issue.⁹ Consequently, laborious fractionalization³ has been frequently employed and a novel size-focusing method was developed recently to achieve homogeneously distributed Au NPs.⁹ Despite its clear practical importance, few pertinent studies are available in the literature to elucidate the (molecular) cause of the polydispersity simply because detailed mechanistic information on the BSM has been too unelaborate to enable well-targeted research.
A recent thought-provoking work by Goulet and Lennox became a breakthrough. Specifically, instead of confirming the long-held belief that polymeric \([\text{AuSR}]_n\) species were the intermediate \(\text{Au(I)}\)-ion precursors, their results have shown that tetraoctyl-ammonium metal(I) halide complex i.e., \([\text{TOA}]^+\text{[M(I)X}_2^-]\), was actually the \(\text{Au(I)}\)-ion precursor in the BSM, which was generated by reducing \([\text{TOA}]^+\text{[M(III)X}_4^-]\) complex with thiol:

\[
[\text{TOA}][\text{M(III)X}_4] + 2\text{RSH} \rightarrow [\text{TOA}][\text{M(I)X}_2] + \text{RSSR} + 2\text{HX}
\]  

(1)

Our own recent work has not only confirmed Goulet and Lennox’s findings but also shown that the BSM is in principle an inverse-micelles based synthesis. We have further clarified and differentiated the reaction conditions that lead to either \([\text{TOA}]^+\text{[M(I)X}_4^-]\) complex or this complex mixed with polymeric \([\text{AuSR}]_n\) species as reaction intermediates in the BSM. These progresses put us in a position to address the aforementioned polydispersity issue.

Generally speaking, there are two main variants of the BSM. The first is the original BSM in which the organic phase is separated out after the phase transfer of the metal (Au) ions and thiols are added to the separated organic phase. The second is the Whetten adaptation of the original BSM in which no separation of organic phase is carried out and thiols are added to the mixed aqueous and organic phases. At a thiol/Au ratio of 3:1, the latter leads to a mixture of \([\text{TOA}]^+\text{[M(I)X}_2^-]\) complex, polymeric \([\text{AuSR}]_n\) species, residual thiols, and reduction-generated disulfide (Reaction (1)). Although the mixed presence of \([\text{TOA}]^+\text{[M(I)X}_2^-]\) complex and polymeric \([\text{AuSR}]_n\) species was identified as a source of polydospersity, it is still unclear what is the effect of the co-presence of thiol and disulfide.

Numerous studies have observed that both thiols and disulfides can form self-assembled monolayers (SAMs) on bulk gold surface. It has been demonstrated that disulfide had a much
slower SAM formation kinetics than thiols.\textsuperscript{19} On the other hand, disulfide also showed a similar activity in ligand-exchange reaction of thiolate-protected Au NPs as thiol.\textsuperscript{21} These observations indicate that the action by thiol and disulfide are highly reaction-environment dependent. Now our improved mechanistic understanding of the BSM, particularly the observation that the Au–S bonds do not form until the last reduction step by NaBH$_4$ in the original BSM,\textsuperscript{16} enables us to design experiments to address this question specifically and this chapter\textsuperscript{21} reports the results of such a study.

6.2 Results and Discussion

For a thiol/Au ratio of 3:1, Reaction (1) predicts that one equivalence of RSH will not be consumed. This inference has been confirmed by the $^1$H NMR spectra of the intermediates in the BSM, where the peaks indicated the existence of thiol ($\delta_H$ (300 MHz; C$_6$D$_6$; C$_6$D$_6$) 2.17 (2H, m, CH$_2$S)), disulfide ($\delta_H$ (300 MHz; C$_6$D$_6$; C$_6$D$_6$) 2.58 (4H, t, CH$_2$SSCH$_2$)), and [TOA][AuBr$_2$] complex ($\delta_H$ (300 MHz; C$_6$D$_6$; C$_6$D$_6$) 3.11 (8H, br, N$^+$CH$_2$)) shown in Figure 6.1. The intermediate solutions monitored with $^1$H NMR spectroscopy were prepared as follows. A hydrogen tetra-chloroaurate (HAuCl$_4$, 0.025 mmol) aqueous solution (0.21 mL) was mixed with a TOAB (0.050 mmol) C$_6$D$_6$ solution (0.8 mL) and stirred until the color of the aqueous phase disappeared. The bottom colorless layer was then discarded. 1, 2, or 3 equiv of dodecanethiol (C$_{12}$H$_{25}$SH) was added to the separated wine-red C$_6$D$_6$ layer. After the solution was stirred for 1 hr, $^1$H NMR spectra were obtained. In order to distinguish the effect of thiolate precursors (i.e. thiol vs. disulfide), revised BSM procedures were adapted in which synthesized [TOA][AuBr$_2$] or [TOA][AuBr$_4$] complex was used as the starting Au source.
We first discuss the results of using [TOA][AuBr₂] as a starting material. Specifically, 0.025 mmol [TOA][AuBr₂] was dissolved in 10-mL toluene and mixed with 0.21-mL H₂O. Then 0.075 mmol of dodecanethiol, 0.0375 mmol didodecyl disulfide, or a mixture of 0.025 mmol of dodecanethiol and 0.025 mmol of didodecyl disulfide was added to the solution. After the colorless solution was stirred for 1 hr, a fresh NaBH₄ aqueous solution (0.25 mmol NaBH₄ in 0.5-mL H₂O) was poured in and stirred for another 3 hrs, leading to a dark brown solution. The NPs could be collected in solid state with ethanol.

The IR spectra of the Au NPs protected by the ligands originated from thiol and disulfide respectively were shown in Figure 6.2. Both samples showed similar IR patterns (ν_max/cm⁻¹ 2954 (CH₃), 2920 and 2850 (CH₂), 721 (CH₂ and S–C trans)), in agreement with the literature observations⁵, ²³. The absence of vibrational bands at 2575 cm⁻¹ of ν(S–H) and at 575 cm⁻¹ of ν(S–S) indicates the breakage of the S–H bond of dodecanethiol or the S–S bond of the didodecyl disulfide had occurred during the formation of BSM metal NPs. In other words, thiolate-protected Au NPs were formed in both cases no matter if thiol or disulfide was added as the ligand precursor. This is similar to the absorption of thiol or disulfide on bulk gold substrate where both thiol and disulfide were observed to produce thiolate-like species when being self-assembled.¹⁹

The TEM images and corresponding surface plasmon resonance (SPR) spectra of the thiolate-protected Au NPs originated from the thiol (1.36 ± 0.19 nm), the mixture of thiol and disulfide (1.68 ± 0.21 nm), and the disulfide (2.58 ± 0.33 nm) respectively are shown in Figure 6.3. They clearly show that thiol produced smaller and more homogeneous thiolate-protected Au NPs than disulfide. This observation is more consistent with the reference of thiol exhibiting stronger
preference comparing to disulfide in forming SAMs on bulk Au substrate, than with the one of disulfide showing similar exchange reaction activity as thiol. The former was explained by the smaller steric hindrance of approaching Au substrate and a lower activation entropy of adsorption for thiol, although the bond dissociation energy of RS–H is higher than that of RS–SR. Similar preference for thiol during the formation of thiolate-protected Au NPs to that in the thiolate SAM on bulk gold strongly supports our previously reported BSM mechanism, in which thiolate bonding to Au occurs after Au(0) nuclei are formed. When only disulfide was used, larger and less homogeneous (2.58 ± 0.33 nm) Au NPs were produced, indicating a presence of disulfide led to higher size dispersity in the synthesized Au NPs.

Remarkably, opposite ligand effect was observed when no water was added before the reduction with NaBH₄. In this case in which the step of adding 0.21-mL water was omitted, using didodecyl disulfide made smaller and more homogeneous Au NPs (1.93 ± 0.36 nm) than thiol (2.81 ± 0.42 nm), as shown by the TEM images in Figure 6.4. The absence of H₂O exclude an excellent receiving medium for accepting hydrophilic protons that would be generated from the the breakage of thiols’ S–H bond and therefore increases substantially the reaction barrier. Yet no such barrier is expected to exist for the breakage of disulfide (RS–SR) bond; therefore it easier to break. Consequently, using disulfide produces better results than using thiol in a water deprived situation.

We now discuss the results of using synthesized [TOA][AuBr₄] as starting material. In a typical BSM synthesis with the organic phase separated (the original BSM), [TOA][AuBr₄] complex is formed after the phase transfer with TOAB but before the addition of thiols. For the purpose of comparison, Figure 6.5(a) shows the results of a normal BSM synthesis (0.025
mmol of HAuCl₄ aqueous solution and 0.025 mmol of TOAB toluene solution) with a thiol: Au ratio of 3: 1. Au NPs of 1.70 ± 0.22 nm were obtained, which is the typical result of such synthesis. If 1.5 equivalence of disulfide was used instead of the thiol above, Au NPs of 2.24 ± 0.28 nm were obtained, as shown in Figure 6.5(b). Notice that in former case, reduction of [TOA][AuBr₄] to [TOA][AuBr₂] took place after the addition of thiols that led to a mixture of residual thiol and reduction-generated disulfide (Reaction (1)). In the latter case, no reduction of [TOA][AuBr₄] happened after the addition of disulfide. When the synthesized [TOA][AuBr₄] was used directly as the starting material to synthesize NPs with thiol and disulfide respectively, the phase transfer step was no longer needed. The reaction medium was thus a 10-mL toluene solution of the [TOA][AuBr₄] complex plus 0.021-mL H₂O with the amount of ligands (thiol or disulfide) giving a S/Au ratio of 3: 1. TEM images and corresponding SPR spectra of the resulting Au NPs are shown in Figure 6.5(c) for thiol (1.50 ± 0.19 nm) and (d) for disulfide (2.14 ± 0.43 nm). While Figure 6.5(b) and (d) show the same results which are somewhat expected because they were basically the same synthesis, using thiol as the sole source of ligand improved the quality of Au NP synthesis.

6.3 Conclusions

In summary, the recently improved mechanistic understanding of the BSM¹⁵-¹⁷ enabled us to have designed some specifically targeted experiments to address the size polydispersity problem frequently observed in the traditional BSM syntheses. We were able to identify that the co-presence of the residual thiol and reduction-generated disulfide as found in typical BSM syntheses is a source of size polydispersity observed. We also found that in the presence of H₂O,
thiol was a better ligand than disulfide for obtaining smaller and more homogenous Au NPs. But in a water deprived situation, opposite results were obtained, which suggested bisulfide better. Based on the observations discussed above, we believe that the organic (toluene or benzene) solution of synthesized [TOA][AuBr₂], thiols, a small amount of water, plus the subsequent reduction of Au(I) by NaBH₄ is important to achieve the optimal reaction medium for a BSM synthesis that can minimize the size polydispersity frequently observed in typical BSM syntheses.
Figure 6.1 $^1$H NMR spectra of the intermediate obtained after the addition of (a) 1, (b) 2, (c) 3 equiv of dodecanethiol to TOAB-plus-Au(III) (TOAB: Au = 2: 1) $C_6D_6$ layer, (d) of synthesized [TOA][AuBr$_2$] complex, (e) TOAB, (f) dodecanethiol, and (g) synthesized didodecyl disulfide, all in 0.80 mL $C_6D_6$. (Note: en-H$_2$O means the water encapsulated by the inverse micelles of TOAB.)
Figure 6.2 IR spectra of (a) pure didodecyl disulfide, (b) Au NPs protected with the ligands originally from didodecyl disulfide, (c) Au NPs protected with the ligands originally from dodecanethiol, (d) pure dodecanethiol.
Figure 6.3 TEM images with corresponding size distributions and UV-visible spectra of the Au nanoparticles formed from a mixture of [TOA][AuBr₂] toluene solution and water with (a) 3 equiv of dodecanethiol, (b) a mixture of 1 equiv of dodecanethiol and 1 equiv of didodecyl disulfide, (c) 1.5 equiv of didodecyl disulfide. (Au: S = 1: 3)
Figure 6.4 TEM images with size distribution and UV-visible spectra of the Au nanoparticles formed from [TOA][AuBr₂] toluene solution (no addition of 0.2-mL water) with (a) 3 equiv of dodecanethiol (2.81 ± 0.42 nm), (b) a mixture of 1 equiv of dodecanethiol and 1 equiv of didodecyl disulfide (2.11 ± 0.38 nm), (c) 1.5 equiv of didodecyl disulfide (1.93 ± 0.36 nm).
Figure 6.5 TEM images with corresponding size distributions and UV-visible spectra of the Au nanoparticles formed by a typical BSM from the organic layer of 0.025 mmol of HAuCl₄ aqueous solution and 0.025 mmol of TOAB toluene solution (10 mL) together with (a) 3 equiv of dodecanethiol and (b) 1.5 equiv of didodecyl disulfide; formed from a mixture of [TOA][AuBr₄] toluene solution and 0.21-mL water together with (c) 3 equiv of dodecanethiol and (d) 1.5 equiv of didodecyl disulfide. (Au: S = 1: 3)
6.4 References


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CHAPTER VII
CHEMICAL BEHAVIOUR OF DIALKYL DICHALCOGENIDES IN BSM

Reproduced with permission from Zaluzhna, O.; Li, Y.; Zangmeister, C.; Allison, T. C.; Tong, Y. J., Chemical behaviour of dialkyl dichalcogenides in the Brust–Schiffrin synthesis of gold nanoparticles. To be submitted. It was the result of combined research efforts of Ms. Zaluzhna (a graduate student) and myself under the direct guidance of my mentor, Prof. YuYe J. Tong. My contribution to the work was the studies involved with tellurium, \(^1\)H NMR and Raman measurements of two-phase BSM intermediates, and the syntheses and characterizations of the gold nanoparticles prepared with the ligand precursor of ditelluride as well as a portion of the written text. Ms. Zaluzhna was to be credited with a portion of the part of organoselenium, all of TEM images on the samples, and organization of the written text. Dr. Zangmeister and Dr. Allison from NIST performed the XPS measurements and theoretical calculations respectively.

7.1 Introduction

Since Brust and Schiffrin discovered the two-phase\(^1\) and one-phase\(^2, \text{ }^3\) procedures for gold nanoparticles (NPs), abbreviated here as BSM (Brust–Schiffrin method), an enormous amount of studies have taken to prepare thiolate-protected metal NPs.\(^3-\text{ }^9\) Although BSM has become primary synthetic route for many groups, its mechanism was not clear until recently. The long-held assumption has been that the addition of thiol reduces Au(III) to Au(I) and forms polymeric [AuSR]\(_n\) species in both one-phase and two-phase BSM. A recent thought-provoking work by Goulet and Lennox showed that [TOA]\(^+\)[AuX\(_2\)]\(^-\) complex (tetraoctyl-ammonium gold(I) halide), which was formed from the reduction of [AuX\(_4\)]\(^-\) by thiol, was actually the Au precursor in the
two-phase BSM. Our recent work has not only confirmed Goulet and Lennox’s findings, but also proposed a mechanism for two-phase BSM, where the BSM is in principle inverse-micelles based synthesis.

The quantum calculations demonstrated that heavy chalcogens (i.e., Se and Te) are promising candidates as anchoring elements with better conductance than S. Several groups have investigated self-assembled monolayers of dichalcogenides (i.e. R₂Se₂ and R₂Te₂) being adsorbed on Au or Ag substrates. However, there are few studies on the metal NPs protected by Se/Te-containing ligands. Brust and co-workers were first who attempted to prepare such Au NPs by two-phase BSM, yet they did not provide any characterization results except Langmuir isotherm. Later, Ulman’s group synthesized and characterized Au NPs with didodecyl diselenide ((C₁₂H₂₅Se)₂) as a ligand precursor by one-phase BSM. Based on their observations, they concluded the following: no reaction between Au(III) and (C₁₂H₂₅Se)₂ occurred, THF replaced Cl⁻ to coordinate with Au³⁺, and as a surfactant, THF stabilized the formed Au NPs. Furthermore, in our previous work we showed that dioctyl diselenide and dioctyl ditelluride as ligand precursors were able to form stable Au NPs by two-phase BSM. In this Communication, we address how R₂Se₂ and R₂Te₂ are chemically involved in the formation in one- and two-phase BSM of metal NPs. Furthermore, alkyl chain length effect on average size of Au NPs obtained by both methods are shown, when R₂Se₂ or R₂Te₂ with different alkyl chains (C₆, C₈, and C₁₂) are used as ligand precursors. Even though, some investigations on alkylthiolate-protected Au NPs have shown that the average particle size increased as the ligand length was changed from C₆ to C₈ and C₁₂, no studies demonstrated how the alkyl chain length influence NPs’ size in Se or Te systems.
7.2 Results and Discussion

Due to the commercial unavailability, dialkyl dichalcogenides, i.e., \((\text{C}_6\text{H}_{13}\text{–Se/Te})_2\), \((\text{C}_8\text{H}_{17}\text{–Se/Te})_2\), and \((\text{C}_{12}\text{H}_{25}\text{–Se/Te})_2\) were first synthesized and characterized by \(^1\text{H}\) (Figure 7.1), \(^{13}\text{C}\) (Figure 7.2), \(^{77}\text{Se}\) or \(^{125}\text{Te}\) NMR (Figure 7.3), and Raman spectroscopy. (Figure 7.4) To investigate the chemical behaviours of dialkyl dichalcogenides in the synthesis of Au NPs, the intermediate solutions were prepared. For two-phase BSM, the mixture of hydrogen tetrachloroaurate (HAuCl₄, 0.05 mmol) aqueous solution (0.35 ml) was mixed with a TOAB (0.15 mmol) toluene solution (5.0 ml). The aqueous layer was then discarded, and \((\text{C}_8\text{H}_{17}\text{Se})_2\) (0.025 mmol) or \((\text{C}_8\text{H}_{17}\text{Te})_2\) (0.017 mmol) was added to toluene layer. After addition of \(\text{R}_2\text{Se}_2\), no color change of the solution was observed. \(\text{R}_2\text{Te}_2\) though, just as in thiol case,

![Figure 7.1](image1.png)

![Figure 7.2](image2.png)

![Figure 7.3](image3.png)

![Figure 7.4](image4.png)

![Figure 7.5](image5.png)

![Figure 7.5(a)](image6.png)

![Figure 7.5(b)](image7.png)

no colorless, which suggested that Au (III) has been reduced to Au (I). For one-phase BSM, the mixture of HAuCl₄ (0.05 mmol) aqueous solution (0.35 ml) was mixed with \((\text{C}_8\text{H}_{17}\text{Se})_2\) (0.025 mmol) in THF (5.0ml). After the addition of \(\text{R}_2\text{Se}_2\), no color change yet again was noted, while \(\text{R}_2\text{Te}_2\) additions lead to immediate formation of the precipitate. After overnight stirring, the goldish precipitate was obtained, indicating that \(\text{R}_2\text{Te}_2\) reduced Au (III) to Au (0) in THF. The concentrated intermediate solutions after removing the solvent by rotary evaporation were used for Raman and NMR measurements.

The Raman spectra of the concentrated two-phase BSM intermediate solutions together with those of the relevant reference materials are shown in Figure 7.5. Dioctyl diselenide spectrum is presented in Figure 7.5(a), where peak at 287 cm\(^{-1}\) corresponds to the Se–Se vibration. Figure 7.5(b) represents concentrated intermediate obtained with \(\text{R}_2\text{Se}_2\). The disappearance of the peak at 287 cm\(^{-1}\) indicates that Se–Se bond in \(\text{R}_2\text{Se}_2\) broke and reacted with Au (III), although no
obvious color change was observed. The new peak at 290 cm\(^{-1}\) can be assigned to the RSe–Br bonding, according to our theoretical calculations (283.6 cm\(^{-1}\)). The appearance of this peak also strongly supports the occurrence of the reaction between R\(_2\)Se\(_2\) and [AuX\(_4\)]\(^-\), which was produced after phase transfer of HAuCl\(_4\) with TOAB. The peak at \(~209\) cm\(^{-1}\) was assigned to Au–Br\(_2\) stretching vibration (Figure 7.5(e)).\(^{11,24}\) Figure 7.5(c) shows the spectra of the dioctyl ditelluride with the peak at 194 cm\(^{-1}\), which corresponds to the Te–Te vibration in R\(_2\)Te\(_2\), while Figure 7.5(d) corresponds to intermediates obtained by adding R\(_2\)Te\(_2\). The similar change as in Figure 7.5(b) was observed, where the peak due to chalcogen bond disappeared and a new peak was formed at \(~280\) cm\(^{-1}\). With respect to our computational study (243.9 cm\(^{-1}\)) and the literature result,\(^{25}\) the peak was assigned to RTe–Br vibration, which was produced when R\(_2\)Te\(_2\) reduced Au (III). Figure 7.5(e) ~ (g) were the spectra of the synthesized [TOA][AuBr\(_2\)] complex, TOAB, and benzene for reference.

In one-phase BSM, the reaction between R\(_2\)Se\(_2\) and Au (III) also occurred (Figure 7.6), although once again, no color change was observed. Comparing with the spectra of the starting materials, such as R2Se2 with peak of the RSe–SeR bond at 287 cm\(^{-1}\) (Figure 7.6(a)) and HAuCl\(_4\) with splitted peaks\(^{24}\) at 327 and 351 cm\(^{-1}\) (Figure 7.6(c)), the spectrum for the one-phase intermediate (Figure 7.6(b)) indicates the breakage of Se–Se and AuCl\(_4\)\(^-\). The new peaks represent new products of the reduction of Au (III) by R\(_2\)Se\(_2\), where peak at 230 cm\(^{-1}\) can be assigned to the Au–Se\(^{26}\) and the splitted peaks at 315 cm\(^{-1}\) and 332 cm\(^{-1}\) to the Se–Cl bonds.\(^{27,28}\)

Thus, these Raman results suggest that dichalcogen bonds were broken when R\(_2\)Se\(_2\) or R\(_2\)Te\(_2\) was added to the solution containing [AuX\(_4\)]\(^-\), which has also been confirmed by the \(^1\)H NMR of the intermediate solutions (Figure 7.7). Although no change in peak position for \(\alpha\)-protons was
observed for R₂S₂ intermediate,²⁹ the peak of α-protons in R₂Se₂ (δH (300 MHz; C₆D₆; C₆D₆) 2.8 (4H, t, CH₂Se), Figure 7.7(d)) or in R₂Te₂ (δH (300 MHz; C₆D₆; C₆D₆) 2.9 (4H, t, CH₂Te), Figure 7.7(f)) was absent after mixing with Au (III) (Figure 7.7(e) and (g)). Therefore, due to formed peaks from the Se/Te–X bonding observed in the intermediates, it is concluded that R₂Se₂ or R₂Te₂ does react with [AuX₄]⁻ in both one-phase and two-phase BSM.

Furthermore, aqueous NaBH₄ solution was added to the aforementioned intermediate solutions, and the Au NPs (i.e., RSe–Au NPs or RTe–Au NPs) were formed. The TEM images with size distribution diagrams and the surface plasmon resonance (SPR) spectra are presented in Figure 7.8. For the Se system, two-phase method did not produce homogenous NPs; therefore one-phase BSM was used instead, obtaining NPs with the average sizes of 2.60 nm (± 0.72 nm) for C₆Se–Au NPs (Figure 7.8(a)), 2.00 nm (± 0.56 nm) for C₈Se–Au NPs (Figure 7.8(b)), and 1.54 nm (± 0.33 nm) for C₁₂Se–Au NPs (Figure 7.8(c)). The toluene solution of C₆Se–Au NPs showed SPR band at ~ 510 nm, but no noticeable bands were observed for C₈Se–Au NPs and C₁₂Se–Au NPs, due to small NPs.³⁰ When R₂Te₂ was used in two-phase BSM as ligand source, the average size produced 3.92 nm (± 0.50 nm) for C₆Te–Au NPs (Figure 7.8(d)), 3.76 nm (± 0.69 nm) for C₈Se–Au NPs (Figure 7.8(e)), and 3.44 nm (± 0.51 nm) for C₁₂Se–Au NPs (Figure 7.8(f)). All of these NPs showed a SPR band at ~ 508 nm. For both system, Se and Te, the obvious chain length effect was noted as the sizes of the NPs decreased with increasing the alkyl chain length of the protected ligands (C₆, C₈, and C₁₂).

¹H NMR of R₂Se₂ (Figure 7.1(a) ~ (c)) and R₂Te₂ (Figure 7.2 (a) ~ (c)) demonstrated the peak of α-proton in R₂Se₂ at ~2.8 ppm and R₂Te₂ at ~2.9 ppm slightly downfield shifted with the increasing alkyl chain. Furthermore, ¹³C NMR spectra of α-carbon diselenides at ~31 ppm
(Figure 7.1(d)–(f)) and ditellurides at ~5 ppm (Figure 7.2(d)–(f)) showed very different chemical shifts. The $^{125}\text{Te}$ peak of $\text{R}_2\text{Te}_2$ (Figure 7.3) at ~110 ppm showed a clear chain length dependence, which was not seen for $^{77}\text{Se}$ peak of $\text{R}_2\text{Se}_2$ at ~310 ppm. We believe that different shift values imply different electron donating ability among chalcogens. As for the obtained NPs, the disappearance of the peak from $\alpha$-protons and $\alpha$-carbons in methylene bound to chalcogens in their NMR spectra (Figure 7.9) indicated that the alkyl chains were connected to Au via Se or Te, including XPS (Figure 7.10) analysis that indicated that Se or Te acted as anchoring elements.

7.3 Conclusions

In summary, we showed chemical behaviours of dialkyl dichalcogenides in the synthesis of Au NPs. In both, one-phase and two-phase BSM, the dichalcogen bonds were broken prior to the addition of NaBH$_4$. Furthermore, we demonstrated the effect of the alkyl chain lengths on the final NPs sizes. In a word, when Se and Te were used as anchoring elements, the sizes of NPs decreased as the alkyl chain length increased.
Figure 7.1 $^1$H and $^{13}$C NMR spectra of (a) & (c) $(\text{C}_{12}\text{H}_{25}\text{Se})_2$, (b) & (d) $(\text{C}_{8}\text{H}_{17}\text{Se})_2$, and (c) & (f) $(\text{C}_{6}\text{H}_{13}\text{Se})_2$, all in C$_6$C$_6$. 
Figure 7.2 $^1$H and $^{13}$C NMR spectra of (a) & (c) (C$_{12}$H$_{25}$Te)$_2$, (b) & (d) (C$_8$H$_{17}$Te)$_2$, and (c) & (f) (C$_6$H$_{13}$Te)$_2$, all in C$_6$C$_6$. 
Figure 7.3 Top: $^{77}$Se NMR spectra of (C$_6$H$_{13}$Se)$_2$, (C$_8$H$_{17}$Se)$_2$, and (C$_{12}$H$_{25}$Se)$_2$; Bottom: $^{125}$Te NMR spectra of (C$_6$H$_{13}$Te)$_2$, (C$_8$H$_{17}$Te)$_2$, and (C$_{12}$H$_{25}$Te)$_2$, all in C$_6$C$_6$. 
Figure 7.4 Raman spectra of (a) \((C_{12}H_{25}S)_{2}\), (b) \((C_{6}H_{13}Se)_{2}\), (c) \((C_{8}H_{17}Se)_{2}\), (d) \((C_{12}H_{25}Se)_{2}\), (e) \((C_{6}H_{13}Te)_{2}\), (f) \((C_{8}H_{17}Te)_{2}\), and (g) \((C_{12}H_{25}Te)_{2}\).
Figure 7.5 Raman Spectra of (a) dioctyl diselenide, (b) concentrated organic phase of HAuCl₄, 3 equiv of TOAB, and 0.5 equiv of dioctyl diselenide, (c) didodecyl ditelluride, (d) organic phase of HAuCl₄, 3 equiv of TOAB, and 0.33 equiv of dioctyl ditelluride, (e) synthesized [TOA][AuBr₂] complex, (f) TOAB, and (d) benzene.
Figure 7.6 Raman spectra of (a) dioctyl diselenide, (b) the slurry of HAuCl₄ and 0.5 equiv of dioctyl diselenide after removing THF, and (c) aqueous HAuCl₄ aqueous solution.
Figure 7.7 $^1$H NMR spectra of (a) TOAB, (b) dioctyl disulfide, (c) adding 3 equiv octanethiol to the organic phase of HAuCl$_4$ and 3 equiv of TOAB (i.e., HAuCl$_4$ + 3 TOAB), (d) dioctyl diselenide, (e) adding 0.5 equiv dioctyl diselenide to HAuCl$_4$ + 3 TOAB, and (f) dioctyl ditelluride, and (g) adding 1/3 equiv dioctyl ditelluride to HAuCl$_4$ + 3 TOAB, all in C$_6$D$_6$. 
Figure 7.8 TEM images with size distribution and UV-Vis spectra of (a) C6Se–Au NPs, (b) C8Se–Au NPs, (c) C12Se–Au NPs, (d) C6Te–Au NPs, (e) C8Te–Au NPs, and (f) C12Te–Au NPs.
Figure 7.9 $^1$H NMR spectra of (a) RSe–Au NPs and (b) RTe–Au NPs; $^{13}$C NMR spectra of (c) RSe–Au NPs and (d) RTe–Au NPs (R: C6 - black, C8 - red, and C12 - blue), all in C6D6.
Figure 7.10 (a) Bonding energies of Au 4f in RS–Au NPs, RSe–Au NPs, and RTe–Au NPs; (b) Se 3d XPS spectra of RSe–Au NPs; and (c) C 1s XPS spectra of RSe–Au NPs (R: C6 - black, C8 - red, C12 - blue).
7.4 References


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Organochalcogenate-protected metal nanoparticles (NPs) represent a novel class of nanomaterials with fascinating properties, which distinguish them from bulk metals and atoms. These metal NPs stabilized by thiolate or tellurium-containing ligands can be obtained by the Brust–Schiffrin two-phase method (BSM). However, the knowledge of the mechanism of this popular method is minimal, making the well-controlled nanoparticle synthesis with the desired size and homogeneous size distribution much more difficult.

This research concentrated on the mechanistic investigation of the widely used BSM for thiolate-protected metal NPs and the synthesis and characterization of gold NPs with new type of anchoring element, i.e. using tellurium to replace sulfur. The contributions of this research to the nanomaterial chemistry (in particular nanoparticle synthesis) can be summarized as follows:

**Precursor species of metal-ion in BSM.** Our Raman spectroscopic investigations showed that in a typical BSM synthesis no metal(M)–sulfur(S) bonds were formed after thiol addition. This was demonstrated by the control experiment of Raman measurement on the synthesized [M(I)SR]ₙ-like polymers. Notably, the Raman measurement showed that the [M(I)SR]ₙ-like polymers did involve the M–S bonds. These observations provide independent spectroscopic confirmation of the recent work by Lennox and co-workers, that the metal precursor before the addition of the reductant is TOA metal(I) halide complex [TOA][MX₂], and not [MSR]ₙ-like polymers. Moreover, we found that a certain amount of water present was a key factor that determined whether the Au(I) precursor was a [TOA][AuX₂] complex or a mixture of [TOA][AuX₂] complex and polymeric [Au(I)SR]ₙ species. When the aqueous layer was removed
after the phase transfer of the Au(III) (i.e., AuCl₄⁻) with TOAB from aqueous to the organic phase, proceeded with the addition thiols, then the precursor species was the [TOA][AuX₂] complex. On the other hand, if thiols were added to the mixture of aqueous and organic phases and the thiol/Au ratio was larger than 2, the precursor species was a mixture of the [TOA][AuX₂] complex and the polymeric [AuSR]ₙ species. When the ratio of thiol to Au was less than 2, no matter whether the aqueous layer was removed or not, the precursor species was always the [TOA][AuXₗ] (l = 2 or 4) complex.

_BSM as an inverse-micelle based synthetic route._ On the basis of the ¹H NMR observation of the micelle-encapsulated water, that hosts the metal ion complex and the success of the reversed synthetic route, we have proposed a general metal NPs formation mechanism applicable to the typical BSM. Before the formation of any metal-chalcogen bonds, metal nucleation centers/NPs were first formed inside the inverse micelles of the tetrabutylammonium bromide in the organic solvent, where the metal ions are reduced by NaBH₄. The ensuing formation of the metal-chalcogen bonds between the naked metal NPs inside the micelles and the organochalcogen ligands in the organic solvent is the mechanism by which the further growth of the metal core can be controlled. In other words, it is basically an inverse micelle-based synthetic procedure, which not only worked for Au, but also for the formation of thiolate-protected Ag or Cu NPs.

_Polydispersity source of the formed NPs by BSM._ This new mechanistic understanding of the BSM enabled us to design specifically targeted experiments to address the size polydispersity problem. We identified that the co-presence of the residual thiol and reduction-generated disulfide as found in a typical BSM synthesis is a source of size polydispersity. It was found that in the presence of H₂O, thiol was a more superior ligand than disulfide in producing smaller and
Critical role of water and structure of inverse micelles in BSM. Besides the effect on the state of metal-ion precursors in BSM, water encapsulated in the inverse micelles of [TOA]⁺ also hosting metal ions formed a hydrophilic microenvironment that acted as a reaction-enabling proton accepting medium for the thiol protons (RS–H). The presence and the amount of water in the reaction medium has a profound effect on the reduction of Au(III) by thiols and on the formation of uniform small metal nanoparticles. A quantitative analysis of the ¹H NMR of the intermediates before and after the addition thiols to the solution with different Au: TOAB ratios enabled an estimation of the size and composition of the involved inverse micelles.

Tellurium-containing ligand-protected gold NPs. The first air-stable tellurium-containing ligand-protected gold nanoparticles (NPs) were synthesized using dialkyl ditellurides followed by the BSM. The ¹H and ¹³C NMR spectra, as well as infrared spectra (IR) of the formed Au NPs, indicated that the Te–Te bond in the starting ligand was broken but the alkyl chain was intact. This was further corroborated by the solid-state ¹²⁵Te NMR spectrum that displayed a very broad and significantly downfield-shifted peak, indicating that tellurium was directly bound to the Au core. Furthermore, the O 1s and Te 3d XPS spectra of the Au NPs indicated that the capping ligands were alkanetelluroxide. Additionally, dialkyl ditelluride demonstrated an intriguing reductive power that led to a more sophisticated chemistry of the NP formation in BSM. The chemical behaviors of dialkyl ditelluride were further investigated by Raman and ¹H NMR spectroscopies, where the results showed that ditelluride could reduce Au(III) at the same time as the Te–Te was broken. Interestingly, using the dialkyl ditelluride with longer alkyl chains
resulted in a smaller gold NPs. Moreover, ultra small (< 2 nm) tellurium-containing ligand-protected gold nanoparticles were successfully obtained by the developed “reversed synthetic route”.

The next challenging step is to control the sizes of the inverse micelles, by which the numbers of metal ions encapsulated in the inverse micelles can be adjusted to control the sizes of metal NPs. In addition, it is important to explore the properties of metal NPs stabilized by tellurium-containing ligands. The research presented here demonstrates new mechanistic insights into the synthesis of homogeneous nanoparticle, and opens a door for the new studies of ligand-protected metal nanoparticles with new type of anchoring element.
APPENDIX A
SYNTHESES OF REFERENCE CHEMICALS

A.1 Didodecyl Disulfide

Dialkyl disulfide was synthesized according to a modified literature approach.\textsuperscript{1,2} 15 mg NaI was added to the solution of 2.4-mL C\textsubscript{12}H\textsubscript{25}SH and 30-mL ethyl acetate. After the addition of 1.1 mL of 30 wt\% H\textsubscript{2}O\textsubscript{2}, the mixture was stirred at room temperature for 30min, which led to a clear yellowish solution. 15-mL Na\textsubscript{2}S\textsubscript{2}O\textsubscript{3} (3.13 g) aqueous solution was then poured in. The color of the solution then faded. The two-phase mixture was transferred to a separatory funnel. After removing the solvent from the top solution, the desired product was obtained as white crystal powder.

A.2 [TOA][Au(III)Br\textsubscript{4}] Complex

[TOA][Au(III)Br\textsubscript{4}] was prepared following the reported approach.\textsuperscript{2-4} TOAB (1.26 g) and KAuBr\textsubscript{4}·2H\textsubscript{2}O (1.37 g) were mixed with 60 mL of anhydrous EtOH. After 1-h stir and 10-min sonication, the mixture was stored in a freezer overnight. The expected product was collected through vacuum filtration.

In order to purify the product, the following procedures were performed. The crude product was dissolved in toluene with sonication. The wine-red solution was transferred to several 1-mL centrifuge tubes and then centrifuged at 14.5K rpm for 1h. The top clear wine-red solution was collected. After the removal of the solvent by rotary evaporation, EtOH was added to dissolve the deep-red solid with sonication. The wine-red suspension was transferred to a clean vial and
then put in a freezer overnight. The pure product was the deep-red crystals formed in the solution and collected through vacuum filtration.

A.3 [TOA][Au(I)Br₂] Complex

[TOA][Au(I)Br₂] was synthesized according to a revised literature approach.²⁻⁴ The mixture of [TOA][AuBr₄] (0.88 g) and 8.8-mL anhydrous EtOH was heated in water bath up to 70°C, by which [TOA][AuBr₄] was completely dissolved in EtOH. Once the temperature of water bath reached 70°C, 0.88-mL acetone was added. After that, the solution turned to white cloudy in a short time and then heating was stopped. When the mixture was cooled down, vacuum filtration was performed to remove the white insoluble byproduct. The clear colorless filtrate was stored in a freezer overnight. The expected product was collected through vacuum filtration as colorless crystals.

[TOA][Au(I)Br₂] toluene solution should be colorless. Sometimes the yellowish color was shown, which indicated that the product was not pure enough. In order to get the pure product, the following procedures were taken. The crude product was dissolved in EtOH with sonication and then put in a freezer overnight. The colorless crystals were collected via vacuum filtration.

A.4 [M(I)SR]ₙ-like Polymer

[M(I)SR]ₙ-like polymer was prepared directly following the reported approach.²⁻⁵ 0.1 mmol metal salt (i.e. HAuCl₄, AgNO₃, and CuCl₂·H₂O) was dissolved in 1.0 mL H₂O, then mixed with 20-mL THF, and 0.10-mL C₁₂H₂₅SH was added. After an overnight stir, the precipitate, which was the desired product, was collect with vacuum filtration.
A.5 Dodecanethiol Self-Assembled on Rough Au Electrode

A commercial gold rod electrode (Bioanalytical, 2 mm²) was used. The Au electrode was first roughened by square wave oxidation-reduction cycles (SWORC) method devised by Dr. Bolian Xu in our group. In details, the Au electrode was subject to square wave cycling that had a frequency of 166 Hz and upper and lower switching potentials at +2.4 V and -0.2 V respectively in a supporting electrolyte of 0.5 M H₂SO₄ for 30 min. The electrode was held at +1.4V and then -0.25 V for 5~10 min respectively until a decay curve was observed in the Raman spectra of the electrode surface after holding at -0.25V. The clean rough Au electrode was immersed into 1 mL of 10 mM C₁₂H₂₅SH EtOH solution overnight, and then rinsed with EtOH.

A.6 Dioctyl Diselenide

Dioctyl diselenide was synthesized directly following the previously reported work of our group with the additional purification step, where the silica/hexanes column (60 cm in length and 6 cm in diameter) was run to purify the product.
A.7 References


