J|A|C|S
COMMUNICATIONS

New Insights into Brust−Schiffrin Metal Nanoparticle Synthesis

Paul J. G. Goulet and R. Bruce Lennox*

*Department of Chemistry and Centre for Self-Assembled Chemical Structures (CSACS), McGill University,
801 Sherbrooke Street West, Montreal, Quebec, Canada, H3A 2K6*

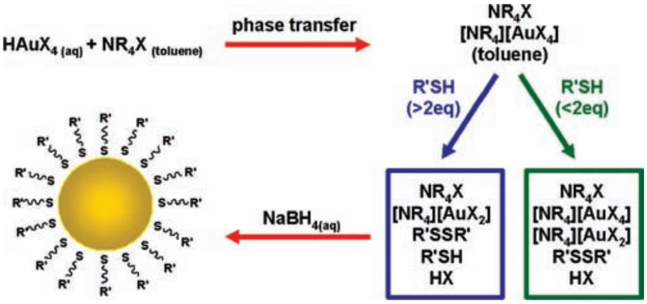
Received May 10, 2010; E-mail: bruce.lennox@mcgill.ca

Abstract: A revised view of Brust−Schiffrin metal nanoparticle syntheses is presented here. Precursor species of these reactions are identified and quantified for Au, Ag, and Cu systems. Contrary to the assumptions of previous reports, tetraalkylammonium metal complexes are shown to be precursors of the two-phase reactions, whereas M(I) thiolates are shown to be precursors of the one-phase reactions. A new scheme is outlined for the two-phase synthesis, and the implications of this scheme are discussed. A new synthetic strategy employing well-defined precursors is also introduced. Finally, M(I) thiolate formation, and its impact on nanoparticle synthesis, is discussed. It is expected that the results presented here will lead to modifications in the manner in which these important syntheses are conducted.

The two-phase Brust−Schiffrin method[1] for the synthesis of thiolate-protected gold nanoparticles has been tremendously influential in nanomaterials chemistry. It has inspired a number of related approaches and remains widely employed more than 15 years after its initial publication.[2,3] It reliably produces large quantities of relatively monodisperse samples of small nanocrystals (1−6 nm). These readily undergo ligand exchange and can be conveniently dried, purified, and redissolved. Brust et al.[4] also developed a related one-phase method that is carried out in polar solvent and shares the positive attributes of the two-phase approach. Both of these approaches have since been successfully applied to other metals, including Ag and Cu.[5−11] Although these reactions have been studied extensively by many groups, and their products have been thoroughly characterized,[7,8,10,12,13] there remain significant questions regarding their detailed mechanisms. In particular, there is little definitively known regarding the precursor species present in solution prior to reduction with $NaBH_4$. When the precursor question has been addressed, researchers have generally assumed the formation of M(I) thiolate polymers in both the one- and two-phase reactions (where M = Au, Ag, or Cu). Given that the size and properties of the products of these syntheses are dependent upon the reaction conditions,[12,14] and thus implicitly upon the reaction intermediates, it is necessary to establish clearly the composition of precursor solutions.

We report here the identification and quantification of the precursor species of Au, Ag, and Cu Brust−Schiffrin nanoparticle syntheses. A particular focus is placed upon the two-phase Au synthesis, as it is the most widely employed variant. We conclude that, contrary to the assumptions of previous reports, Au(I) thiolate ($[AuSR]_n$) is not a measurable (^1H NMR) precursor in this reaction when it is performed under typical conditions.[1,12] Rather, Au(I)- and Au(III)- tetraalkylammonium complexes are the relevant Au species in solution prior to reduction with $NaBH_4$. The intermediate step in this method is shown to follow reaction 1 rather than the oft-stated reaction 2.[3,15] In accordance with this, a revised view of the two-phase Brust−Schiffrin reaction is outlined (Scheme 1), and its implications are discussed. This general reaction motif is shown to also apply to two-phase syntheses employing Ag and Cu, as well as to those where the phase-transfer agent or thiol have been substituted. This information is utilized toward the development of a new synthetic strategy employing well-defined precursor species. A discussion is presented regarding the formation of M(I) thiolate species and the potential impact of this on nanoparticle syntheses.

Scheme 1. Revised View of the Two-Phase Brust−Schiffrin Au Nanoparticle Synthesis



$$[NR_4][AuX_4] + 2\,R'SH \rightarrow [NR_4][AuX_2] + R'SSR' + 2\,HX \quad (1)$$

$$[NR_4][AuX_4] + 3\,R'SH \rightarrow [AuSR']_n + R'SSR' + NR_4X + 3\,HX \quad (2)$$

The stoichiometry of the reduction of $[NR_4][AuX_4]$ to $[NR_4][AuX_2]$ (Au^{3+} to Au^{1+}) was confirmed by monitoring the disappearance of the 402 nm absorption band of the Au^{3+} upon addition of alkanethiol (with the solution going from intense orange to colorless). As in a typical two-phase Brust−Schiffrin reaction, tetraoctylammonium bromide (TOAB, 3 equiv) in toluene was rapidly stirred with hydrogen tetrachloroaurate ($HAuCl_4$, 1 equiv) in water until all Au^{3+} was transferred to the organic phase. The $[TOA][AuX_4]$ complex formed, likely with a mix of Cl^- and Br^- ions. After discarding the aqueous phase, aliquots of dodecanethiol were titrated into the isolated toluene phase. After each addition, the solution was stirred until reaction was complete, and its UV−visible absorption spectrum was recorded. Complete reduction from Au^{3+} to Au^{1+} occurs with the addition of 2 equiv of dodecanethiol (Figure S1). This is consistent with reaction 1 and inconsistent with Au(I) thiolate formation proceeding via reaction 2. Further addition of alkanethiol produces no additional change in color or apparent precipitation.

The species present during this reaction were quantitatively monitored by ^1H NMR spectroscopy. A solution of TOAX and $[TOA][AuX_4]$ was prepared by phase transfer of $AuCl_4^-$ (1 equiv) into deuterated toluene with TOAB (2.5 equiv). After sufficient

10.1021/ja104011b

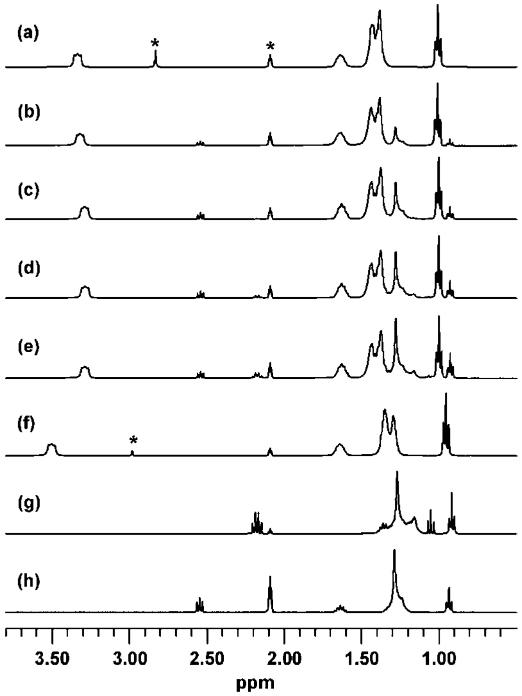


Figure 1. ^{1}H NMR spectra of TOAX + [TOA][AuX_4] solutions with (a) 0, (b) 1, (c) 2, (d) 3, and (e) 4 equiv of dodecanethiol added. Also shown, for comparison, are the ^{1}H NMR spectra of pure solutions of (f) TOAB, (g) dodecanethiol, and (h) dodecyl disulfide. * indicates water and solvent peaks.

stirring, the phases were allowed to separate (ca. 2 min). The toluene phase was then transferred to a new reaction vessel using a Pasteur pipet, and the water phase was discarded. Dodecanethiol was added to each of five equal aliquots of the toluene solution (0, 1, 2, 3, or 4 equiv relative to the Au in each aliquot). These samples were stirred until reaction was complete, and ^{1}H NMR spectra were obtained (Figure 1). Comparison with spectra of pure samples of TOAB, dodecanethiol, and dodecyl disulfide reveals that the spectrum of the mixture of TOAX and [TOA][AuX_4] (Figure 1a) is similar to that of pure TOAB (Figure 1f). There are, however, significant shifts of all the resonance peaks due to the association with the AuX_4^- anion. TOA^+ peaks are not observed for each of the anions, but rather a single averaged peak is observed for each of the different chemical environments of the cation. This is consistent with a fast anion exchange process.

After the reaction of 1 equiv of dodecanethiol (Figure 1b), 0.5 equiv of dodecyl disulfide is generated through complete oxidation of the added thiol. Correspondingly, 0.5 equiv of [TOA][AuX_2] is produced, leading to further shifts of the TOA^+ peaks. Addition of 2 equiv of dodecanethiol to TOAX and [TOA][AuX_4] (Figure 1c), on the other hand, generates 1 equiv of dodecyl disulfide. All of the Au^{3+} is reduced to Au^{1+}, again producing shifts in the peaks of the TOA^+ cation and leaving a colorless solution. Finally, addition of 3 and 4 equiv of the thiol (Figure 1d and 1e, respectively) results in all of the [TOA][AuX_4] being converted to [TOA][AuX_2] with the associated generation of 1 equiv of the disulfide. However, in these cases, 1 and 2 equiv of free thiol, respectively, are also observed (α CH_2 at ca. 2.18 ppm and SH at ca. 1.06 ppm as per pure dodecanethiol). These results clearly show that polymeric Au(I) thiolate species are not generated in measurable quantities (i.e., reaction 2 is not operative). Rather, the intermediate step of the Brust−Schiffrin synthesis proceeds via reaction 1, where Au(I) and Au(III) tetraalkylammonium complexes are the relevant Au precursors.

With this information, the complications associated with the phase transfer step of the Brust−Schiffrin synthesis can be avoided by simply carrying out these reactions with pure samples of [TOA][$AuBr_4$] and [TOA][$AuBr_2$]. These are readily prepared via a modified literature approach.[16] Addition of 3 equiv of dodecanethiol to 1 equiv of [TOA][$AuBr_4$] in deuterated toluene generates a single equivalent of dodecyl disulfide (Figure S2). All [TOA][$AuBr_4$] is reduced to [TOA][$AuBr_2$], and 1 equiv of thiol remains unreacted. Furthermore, when 3 equiv of dodecanethiol are added to 1 equiv of [TOA][$AuBr_2$], no reaction occurs and 3 equiv of free thiol are observed. These experiments reinforce the fact that the intermediate step in the two-phase Brust−Schiffrin reaction indeed proceeds via reaction 1. Importantly, they also suggest a new synthetic strategy with control over well-defined precursor species.

When Ag and Cu are used in the Brust−Schiffrin reaction, as [TOA][$AgBr_2$] and $[TOA]_2[CuBr_4]$ respectively, similar behavior to the Au case is observed (Figures S3 and S4). [TOA][$AgBr_2$] is prepared by codissolving TOAB (5 equiv) and $AgNO_3$ (1 equiv) in toluene, without signs of AgBr precipitate formation. No reaction occurs when this complex, with Ag already in a +1 oxidation state, is mixed with dodecanethiol. On the other hand, the reaction of $[TOA]_2[CuBr_4]$, prepared according to a modified literature procedure,[17] with dodecanethiol, leads to a one-electron reduction via reaction 3. As in the Au case, the formation of Ag(I) and Cu(I) alkanethiolate polymers[18−21] is prevented by the stabilization afforded by the TOA^+ cation.

$$[TOA]_2[CuBr_4] + RSH \rightarrow 1/2\ RSSR + [TOA][CuBr_2] + TOAB + HBr \quad (3)$$

Phosphonium salts demonstrate chemical behavior analogous to that of ammonium salts. Tetraoctylphosphonium cation (TOP^+) is thus substituted for TOA^+ in a modified Brust−Schiffrin reaction. [TOP][$AuBr_4$] is readily synthesized according to a modified literature procedure,[16] dissolved in deuterated toluene (1 equiv), and reacted with 3 equiv of dodecanethiol. As expected, this leads to the production of 1 equiv of dodecyl disulfide, while 1 equiv of thiol remains unreacted (Figure S5). Correspondingly, all [TOP][$AuBr_4$] present is reduced to [TOP][$AuBr_2$], leading to significant shifts of the TOP^+ peaks and a complete loss of the solution's intense orange color. Thus, TOP^+ behavior clearly parallels that of TOA^+ in modified Brust−Schiffrin reactions.

Finally, reaction 1 is also operative when phenylethanethiol (PET) is used in the Brust−Schiffrin reaction (Figure S6).[22−24] Reaction of [TOA][$AuBr_4$] (1 equiv) in deuterated toluene with PET (5 equiv) yields 1 equiv of disulfide, and 3 equiv of thiol remain unreacted. [TOA][$AuBr_4$] is quantitatively reduced to [TOA][$AuBr_2$], with a corresponding color loss. There is no evidence of Au(I) thiolate formation, even when this reaction is carried out following the low temperature procedure of Zhu et al.[23] The method of Zhu et al.[23] is reported to generate Au(I) thiolate intermediates that, upon further reduction, produce Au_{25} clusters in high yield. This discrepancy may be explained by water remaining in the reaction, which promotes the generation of thiolate aggregates (vide infra).

The identification and quantification of precursor species provide key information for understanding and controlling these reactions. The thiol-to-metal ratio influences the size and properties of the products.[8,12,14] However, the mechanistic origins of this effect remain unclear. Here, we have shown explicitly how altering the thiol-to-metal ratio also alters the ratios of different metal precursors and adsorbates. These ratios may be important determinants of the kinetics of nanoparticle formation. The new synthetic strategy presented here, with well-defined precursors, provides a key tool for disentangling these two factors (i.e., the redox and passivation kinetics).

The intermediate step in two-phase Brust-Schiffrin reactions was previously believed to involve the generation of *soluble* M(I) alkanethiolate species. However, these materials have been studied by several groups[18,19,25,26] and have been shown to be *insoluble* in common solvents, including toluene. In fact, the poor solubility of M(I) thiolates, in general, is well-known, and has been attributed to intermolecular interactions between adjacent polymer units, including metallophilic interactions[20,21,25,27−30] Accordingly, in these reactions, precipitation should be viewed as an important indicator that polymeric M(I) thiolate species are forming. Correspondingly, a lack of precipitate is an indicator that it is unlikely that they are forming.

M(I) thiolate species form in significant amounts in the intermediate step of the two-phase Brust-Schiffrin reaction when larger quantities of water are present (though typical conditions, with small amounts of water present, do not lead to measurable quantities of M(I) thiolates). This occurs both with and without a quaternary cation being present. M(I) thiolates also form (as white precipitates) if the precursor M(I) solutions are exposed to water, or if toluene is removed. Other polar solvents (methanol, ethanol) are also capable of promoting the formation of M(I) thiolate polymers. This is attributed to the breaking or absence of the metal anion-quaternary cation ion-pairs that form in nonpolar solvents, including toluene. Drying toluene solutions prior to thiol addition could prove useful in minimizing M(I) thiolate formation in two-phase reactions. One-phase Brust-Schiffrin reactions carried out in polar solvents (THF, ethanol, methanol) without phase transfer agents also generate M(I) thiolate precipitates. These results suggest that M(I) thiolate formation is likely to occur when Au, Ag, or Cu salts are exposed to thiols in the presence of highly polar solvents where ion-pairs are not prevalent. This general conclusion is supported by observations reported in the literature.[25,31−34]

Some M(I) thiolate formation is likely to commonly occur when excess water is not removed, or when aqueous NaBH$_4$ solutions are added very slowly, or at low concentration, in two-phase Brust−Schiffrin syntheses. This also occurs when one-phase nanoparticle syntheses are carried out with thiols.[24,32,34] The consequences of this are not yet fully understood for the wide variety of synthetic methods that exist. However, it can be reasonably expected to produce poor synthetic outcomes in some cases. Partial M(I) thiolate formation generates unknown mixtures of multiple metal precursors with different redox potentials and states of aggregation. It also produces mixtures of ligands with different adsorption properties. The heterogeneous reaction of insoluble M(I) thiolates with reductants can be very slow and, in some cases, may not occur at all. These factors are likely to lead to higher polydispersity, reduced yields, and insoluble metal and M(I) thiolate byproducts.[22,24,34,35]

In summary, a revised view of Brust−Schiffrin nanoparticle syntheses has been detailed here. Precursor species of these reactions have been identified and quantified. Tetraalkylammonium metal complexes are shown to be precursors of two-phase reactions, while M(I) thiolates are shown to be precursors of one-phase reactions conducted in polar solvents. A new synthetic strategy employing well-defined precursors was introduced. M(I) thiolate formation, and its impact on nanoparticle synthesis, was also discussed. Strategies for avoiding the production of these insoluble species were suggested. It is expected that the results presented here will lead to modifications in the way that these important syntheses are conducted.

Acknowledgment. The Natural Sciences and Engineering Research Council of Canada (NSERC) and the Centre for Self-Assembled Chemical Structures (CSACS) are gratefully acknowledged for financial support.

Supporting Information Available: Experimental and synthetic details, UV−visible absorption, and ^{1}H NMR data. This material is available free of charge via the Internet at http://pubs.acs.org.

References

(1) Brust, M.; Walker, M.; Bethell, D.; Schiffrin, D. J.; Whyman, R. *J. Chem. Soc., Chem. Commun.* **1994**, 801–802.
(2) Daniel, M. C.; Astruc, D. *Chem. Rev.* **2004**, *104*, 293–346.
(3) Sardar, R.; Funston, A. M.; Mulvaney, P.; Murray, R. W. *Langmuir* **2009**, *25*, 13840–13851.
(4) Brust, M.; Fink, J.; Bethell, D.; Schiffrin, D. J.; Kiely, C. *J. Chem. Soc., Chem. Commun.* **1995**, 1655–1656.
(5) Murthy, S.; Bigioni, T. P.; Wang, Z. L.; Khoury, J. T.; Whetten, R. L. *Mater. Lett.* **1997**, *30*, 321–325.
(6) Heath, J. R.; Knobler, C. M.; Leff, D. *J. Phys. Chem. B* **1997**, *101*, 189–197.
(7) Kang, S. Y.; Kim, K. *Langmuir* **1998**, *14*, 226–230.
(8) Bauer, C. A.; Stellacci, F.; Perry, J. W. *Top. Catal.* **2008**, *47*, 32–41.
(9) Garitaonandia, J. S.; Insausti, M.; Goikolea, E.; Suzuki, M.; Cashion, J. D.; Kawamura, N.; Ohsawa, H.; Gil de Muro, I.; Suzuki, K.; Plazaola, F.; Rojo, T. *Nano Lett.* **2008**, *8*, 661–667.
(10) Ang, T. P.; Wee, T. S. A.; Chin, W. S. *J. Phys. Chem. B* **2004**, *108*, 11001–11010.
(11) Dong, T.-Y.; Wu, H. H.; Song, J. M.; Chen, I. G.; Kao, T. H. *Appl. Surf. Sci.* **2009**, *255*, 3891–3896.
(12) Hostetler, M. J.; Wingate, J. E.; Zhong, C.-J.; Harris, J. E.; Vachet, R. W.; Clark, M. R.; Londono, J. D.; Green, S. J.; Stokes, J. J.; Wignall, G. D.; Glish, G. L.; Porter, M. D.; Evans, N. D.; Murray, R. W. *Langmuir* **1998**, *14*, 17–30.
(13) Templeton, A. C.; Wuelfing, W. P.; Murray, R. W. *Acc. Chem. Res.* **2000**, *33*, 27–36.
(14) Leff, D.; Ohara, P. C.; Heath, J. R.; Gelbart, W. M. *J. Phys. Chem.* **1995**, *99*, 7036–7041.
(15) Alvarez, M. M.; Khoury, J. T.; Schaaff, T. G.; Shafigullin, M.; Vezmar, I.; Whetten, R. L. *Chem. Phys. Lett.* **1997**, *266*, 91–98.
(16) Braunstein, P.; Clark, J. H. *J. Chem. Soc., Dalton Trans.* **1973**, 1845–1848.
(17) Gill, N. S.; Taylor, F. B.; Hatfield, W. E.; Parker, W. E.; Fountain, C. S.; Bunger, F. L. *Inorg. Synth.* **1967**, *9*, 136–142.
(18) Dance, I. G.; Fisher, K. J.; Banda, R. M. H.; Scudder, M. L. *Inorg. Chem.* **1991**, *30*, 183–187.
(19) Voicu, R.; Badia, A.; Lennox, R. B.; Ellis, T. H. *Chem. Mater.* **2000**, *12*, 2646–2652.
(20) Duncan, W. E.; Ott, E.; Reid, E. E. *Ind. Eng. Chem.* **1931**, *23*, 381–384.
(21) Eller, P. G.; Kubas, G. J. *J. Am. Chem. Soc.* **1977**, *99*, 4346–4351.
(22) Donkers, R. L.; Lee, D.; Murray, R. W. *Langmuir* **2004**, *20*, 1945–1952.
(23) Zhu, M.; Lanni, E.; Garg, N.; Bier, M. E.; Jin, R. *J. Am. Chem. Soc.* **2008**, *130*, 1138–1139.
(24) Wu, Z.; Suhan, J.; Jin, R. *J. Mater. Chem.* **2009**, *19*, 622–626.
(25) Cha, S.-H.; Kim, J.-U.; Kim, K.-H.; Lee, J.-C. *Chem. Mater.* **2007**, *19*, 6297–6303.
(26) Sandhyarani, N.; Pradeep, T. *J. Mater. Chem.* **2001**, *11*, 1294–1299.
(27) Al-Sa'ady, A. K. H.; Moss, K.; McAuliffe, C. A.; Parish, R. V. *J. Chem. Soc., Dalton Trans.* **1984**, 1609–1616.
(28) Corbierre, M. K.; Lennox, R. B. *Chem. Mater.* **2005**, *17*, 5691–5696.
(29) Schmidbaur, H. *Gold Bull.* **2000**, *33*, 3–10.
(30) Hermann, H. L.; Boche, G.; Schwerdtfeger, P. *Chem.*−*Eur. J.* **2001**, *7*, 5333–5342.
(31) Al-Sa'ady, A. K. H.; McAuliffe, C. A.; Parish, R. V.; Sandbank, J. A. *Inorg. Synth.* **1985**, *23*, 191–194.
(32) Schaaff, T. G.; Knight, G.; Shafigullin, M. N.; Borkman, R. F.; Whetten, R. L. *J. Phys. Chem. B* **1998**, *102*, 10643–10646.
(33) Susha, A. S.; Ringler, M.; Ohlinger, A.; Paderi, M.; LiPira, N.; Carotenuto, G.; Rogach, A. L.; Feldmann, J. *Chem. Mater.* **2008**, *20*, 6169–6175.
(34) Reilly, S. M.; Krick, T.; Dass, A. *J. Phys. Chem. C* **2010**, *114*, 741–745.
(35) Templeton, A. C.; Chen, S.; Gross, S. M.; Murray, R. W. *Langmuir* **1999**, *15*, 66–76.

JA104011B