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Identification of a source of size polydispersity and its solution in Brust–Schiffrin metal nanoparticle synthesis[†]

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The co-presence of thiol *vs.* disulfide in the well-known Brust–Schiffrin two-phase synthesis has been identified as a source of size polydispersity in nanoparticles synthesized and a procedure has been proposed to address this long outstanding issue.

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 organochalcogenates^{10–13} 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's 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 outstanding issue.⁹ Consequently, laborious fractionalization³ has been frequently employed to achieve homogeneously distributed Au NPs and for the same purpose a novel size-focusing method was developed recently.⁹ Despite its clear practical importance, few pertinent studies are available in the literature to shed light on the (molecular) cause of the polydispersity simply because detailed mechanistic information on the BSM has been too sketchy to enable well-targeted research.

A recent thought-provoking work by Goulet and Lennox led to a rethinking of the long-held belief.¹⁵ Specifically, instead of confirming the long-held belief that polymeric (AuSR)_n species were the intermediate Au(1)-ion precursors, their results have shown that tetraoctyl-ammonium metal(1) halide complex *i.e.*, $[TOA]^+[M(1)X_2]^-$, was actually the Au(1)-ion precursor in the BSM, which was generated by reducing the $[TOA]^+[M(11)X_4]^$ complex with thiol:

 $[\text{TOA}][\text{M}(\text{III})\text{X}_4] + 2\text{RSH} \rightarrow [\text{TOA}][\text{M}(\text{I})\text{X}_2] + \text{RSSR} + 2\text{HX}$ (1)

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Our own recent work¹⁶ 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 the $[TOA]^+[M(i)X_4]^-$ complex or this complex mixed with polymeric (AuSR)_n species as reaction intermediates in the BSM.¹⁷ 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 adaptation¹⁸ of the original BSM in which no separation of the 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 the [TOA]⁺[M(I)X₂]⁻ complex, polymeric (AuSR)_n species, residual thiols, and reduction-generated disulfide.¹⁷ Although the mixed presence of the [TOA]⁺[M(I)X₂]⁻ complex and polymeric (AuSR)_n species was identified as a source of polydispersity,¹⁷ 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 the bulk gold surface.^{19–21} It has been demonstrated that disulfide had a much slower SAM formation kinetics than thiols.²⁰ On the other hand, disulfide also showed a similar activity in the ligand-exchange reaction of thiolate-protected Au NPs as thiol.²² 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 NaBH₄ in the original BSM,¹⁶ enables us to design experiments to address the source of polydispersity specifically and this communication reports the results of such a study.

For a thiol/Au ratio of 3:1, reaction (1) predicts that one equivalents of RSH will not be consumed. This inference has been confirmed by the ¹H NMR spectra of the intermediates[‡] in the BSM, where the peaks indicated the existence of thiol ($\delta_{\rm H}$ (300 MHz; C₆D₆; C₆D₆) 2.17 (2H, m, CH₂S)), disulfide ($\delta_{\rm H}$ (300 MHz; C₆D₆; C₆D₆) 2.58 (4H, t, CH₂SSCH₂)), and the [TOA][AuBr₂] complex ($\delta_{\rm H}$ (300 MHz; C₆D₆) 3.11 (8H, br, N⁺CH₂)) shown in Fig. S1 (see the ESI[†]). In order to

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distinguish the effect of thiolate precursors (*i.e.* thiol vs. disulfide), revised BSM procedures were adapted in which the synthesized $[TOA][Au(I)Br_2]$ or $[TOA][Au(III)Br_4]$ complex was used as the starting Au source.

We first discuss the results of using $[TOA][AuBr_2]$ as a starting material. Specifically, 0.025 mmol $[TOA][AuBr_2]$ 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 h, a fresh NaBH₄ aqueous solution (0.25 mmol NaBH₄ in 0.5 mL H₂O) was poured in and stirred for another 3 h, leading to a dark brown solution. The NPs could be collected in the solid state with ethanol.

The IR spectra of the Au NPs protected by the ligands originated from thiol and disulfide, respectively, are shown in Fig. S2 (ESI[†]). 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 observations.^{5,23} 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 were observed to produce thiolate-like species when being self-assembled.²⁰

The TEM images and corresponding surface plasmon resonance (SPR) spectra of the thiolate-protected Au NPs originated from the thiol $(1.36 \pm 0.19 \text{ nm})$, the mixture of thiol and disulfide $(1.68 \pm 0.21 \text{ nm})$, and the disulfide $(2.58 \pm 0.33 \text{ nm})$, respectively, are shown in Fig. 1. They clearly show that using thiol made smaller and more homogeneous thiolate-protected Au NPs than using disulfide did. This observation is more consistent with the observation of thiol exhibiting stronger preference than disulfide in forming SAMs on bulk Au substrate²⁰ than with the one of disulfide showing similar exchange reaction activity as thiol.²² The former was explained by the smaller steric hindrance

Absorbance (AU)

(b)

300 400

10 nr %

15

5

500 600

2.5 3.3

Wavelength (nm

(a)

(b) (c)

700

Fig. 1 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).

of the approaching Au substrate and a lower activation entropy of adsorption for thiol,²⁰ although the bond dissociation energy of RS–H is higher than that of RS–SR.^{24,25} 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.¹⁶ When only disulfide was used, even larger and less homogeneous (2.58 ± 0.33 nm) Au NPs were produced, indicating that the presence of disulfide led to wider 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 using thiol did (2.81 ± 0.42 nm), as shown by the TEM images in Fig. S3 (ESI†). The absence of H₂O precludes an excellent receiving medium for accepting hydrophilic protons that would be generated from the breakage of thiol's S–H bond and therefore increases substantially the reaction barrier.¹⁷ Yet no such barrier is expected to exist for the breakage of the disulfide (RS–SR) bond and becomes easier to be broken. Consequently, using disulfide produces better results than using thiol in a water deprived situation.

We now discuss the results of using synthesized $[TOA][Au(III)Br_4]$ as the starting material. In a typical BSM synthesis with the organic phase separated (the original BSM),¹ the [TOA][Au(III)Br₄] complex is formed after the phase transfer with TOAB but before the addition of thiols.^{15,16} For the purpose of comparison, Fig. 2(a) shows the results of a normal BSM synthesis (0.025 mmol of HAuCl₄ aqueous solution and 0.025 mm 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 (see the ESI[†]). If 1.5 equivalents of disulfide was used in lieu of the thiol above, Au NPs of 2.24 \pm 0.28 nm were obtained, as shown in Fig. 2(b). Notice that in the former case, reduction of $[TOA][Au(III)Br_4]$ to $[TOA][Au(I)Br_2]$ 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][Au(III)Br₄] happened after the addition of disulfide. When the synthesized [TOA][Au(III)Br₄] was used



Fig. 2 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][Au(III)Br₄] 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).

10 nm

%

15

5

15

nm 1.3

08

10 nm

1.6 nm

1.9

2.5

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][Au(III)Br₄] 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 Fig. 2(c) for thiol (1.50 \pm 0.19 nm) and (d) for disulfide (2.14 \pm 0.43 nm). While Fig. 2(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.

In summary, the recently improved mechanistic understanding of the BSM^{15-17} 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 making smaller and more homogenous Au NPs but in a water deprived situation bisulfide was better. Based on the observations discussed above, we believe that the organic (toluene or benzene) solution of synthesized [TOA][AuBr₂] and thiols plus a small amount of water consist the optimal reaction medium before the addition of NaBH₄ for a BSM synthesis that minimized the size and size polydispersity from 1.70 ± 0.22 nm of a typical BSM to 1.36 ± 0.19 nm.

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Notes and references

[‡] The intermediate solutions monitored with ¹H NMR spectroscopy were prepared as follows: a hydrogen tetra-chloroaurate (HAuCl₄, 0.025 mmol) aqueous solution (0.21 mL) was mixed with a TOAB (0.050 mmol) C₆D₆ 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 (C₁₂H₂₅SH) was added to the separated wine-red C₆D₆ layer. After the solution was stirred for 1 h, ¹H NMR spectra were obtained.

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