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Communication

Getting rid of $NaBH_4$: Gold seeds reduced by air-stable agents for synthesizing *quasi* one-dimensional gold nanoparticles

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ABSTRACT

Herein, we have presented a novel and easy to operate seed-mediated system for fabricating gold bipyramids (AuBPs) with 85% yields without any separation/purification processes. The used gold seeds are reduced by tannin and citrate, two kinds of air stable ligands, and conventionally employed unstable $NaBH_4$ are thoroughly cast off. In addition, the as-proposed gold seeds can also be employed for AuNRs fabrication with rather larger diameters (22.2–60.3 nm), which is difficult to be achieved by conventional seed mediated fabrication system.

Quasi one-dimensional (1D) gold nanoparticles (AuNPs), such as gold bipyramids (AuBPs) and gold nanorods (AuNRs), have attracted considerable attention ranging from fabrication strategies to localized surface plasmon resonance (LSPR) properties to various applications [1]. In 2001, Murphy *et al.* have reported a seed-mediated growth approach for colloidal fabrication of rod-like AuNPs [2]. Then, El-Sayed and co-workers have proposed an alternative synthesis system for well-defined AuNRs with high yields (>90%) [3]. In 2005, Liu and Guyot-Sionnest found that AuBPs could be formed based on Murphy's synthesis system as the pH value of the growth solution was tuned by HCl [4]. Because AuBPs possess superior optical properties (sharper LSPR band, stronger electric field) and higher stability as compared with AuNRs, they have become a special interest of material scientists and chemists [5]. One of big challenges is how to enhance AuBPs' yields. In 2007, Wang and co-workers presented an improved synthesized system. They employed CTBAB (cetyltributylammonium bromide) to replace CTAB (hexadecyltrimethylammonium bromide) molecules; at the same time, the incubation temperature for the growth solution was raised from 30 °C to 65 °C. As a result, the AuBPs' yields were well enhanced from 30% to 50%–60% [6]. For a rather long period of time, ~60% yield seems to be difficult to be exceeded. As a result, various separation and purification processes have accordingly been reported [7]. Until recently, Liz-Marzán group adopted thermal treated gold seeds, and the AuBP yields were well enhanced to about 90% [8].

Despite these substantial achievements, there are still a few issues and even problems should be well concerned. In terms of the reported seed-mediated synthesis strategies, we note that almost all the used gold seeds are fabricated by using $NaBH_4$ as reducing agents. In fact, in addition to *quasi* 1D products, the seed-mediated approaches can be employed for fabricating various gold nano polyhedrons. Also, the used gold seeds are reduced by $NaBH_4$ agents [9]. As we know, $NaBH_4$ is highly active and unstable at ambient conditions. To decrease its decomposition, the operation of ice-water bath is commonly essential. In addition to cumbersome and tedious processes, such synthesis systems inevitably suffer from reproducibility concern due to the mutability of $NaBH_4$. Thus, in terms of the seed-mediated growth approach, the exploration of the gold seeds prepared by air-stable reducing agents is not only fundamentally significant but helpful for promoting nano-fabrication and corresponding applications.

Herein, for the first time, we present that both AuBPs and AuNRs synthesis can be well achieved by using the proposed modified seed-mediated system, which is easier to be operated as compared with previous ones [4,6]. AuNPs in 3.81 nm sizes [10] are first synthesized by the reduction of tannin and citrate, two kinds of air-stable ligands. The obtained AuNPs are then simply treated by heat incubation in the presence of CTAB molecules and gold seeds are obtained. The AuBPs fabrication can reach about 85.0% yields without any separation/purification, which rather closes to the present record value [8]. In addition to completely getting rid of unstable $NaBH_4$ agents, the AuBPs' parameters, such as size and

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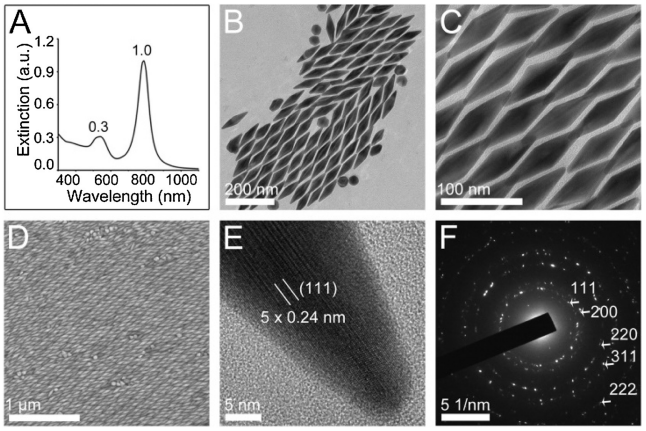

Fig. 1. Extinction spectrum (A), large scale TEM (B), small scale TEM (C), SEM (D), HRTEM (E) and SAED pattern (F) of the as-prepared AuBPs synthesized by using the gold seeds treated by 80 °C heat treatment for 24 h in the presence of 100 mmol/L of CTAB molecules. In Fig. 1A, the two bands at 540 and 788 nm come from transverse and longitudinal resonance, respectively.

aspect ratio can be well tuned (diameter: from 20.2 nm to 50.4 nm; length: from 52.7 nm to 210.4 nm) by experimental conditions. In addition, the as-proposed gold seeds can also be employed for AuNRs fabrication as Ag^+ cations do not be introduced into the growth solution [2,8]. The obtained AuNRs possess rather larger diameters (22.2–60.3 nm), which is difficult to be achieved by conventional seed mediated fabrication system reported by El-Sayed group [3].

Fig. 1A shows the LSPR spectrum of the typical fabricated AuBPs from the proposed gold seeds without any separation/purification. The short and longer wavelength bands locate at 540 and 788 nm, which come from transverse and longitudinal resonance, respectively [1d,8]. For simplicity, the two bands are named as $LSPR_{Trans}$ and $LSPR_{Long}$. In terms of them, several points should be noted. First, the intensity ratio of $LSPR_{Long}/LSPR_{Trans}$ can be adopted for roughly estimating AuBPs' yields, which is expected to be larger for highly purified products. Then, similar to AuNRs, larger aspect ratio of AuBPs corresponds to longer wavelength of $LSPR_{Long}$. Third, the values of full width at half maximum (FWHM) of AuBPs are positively related to their aspect ratios. Namely, the AuBPs with larger aspect ratio possess intrinsic wider FWHM value. Finally, for certain AuBPs, a narrower FWHM often signifies better uniform and monodisperse products. As shown in Fig. 1A, The FWHM is 69.2 nm, which is even narrower than that of the purified AuBPs (green curve in Fig. S1 in Supporting information [11]). Furthermore, the intensity ratio of $LSPR_{Long}/LSPR_{Trans}$ is as high as 3.3. In terms of the un-separated AuBPs, the intensity ratios of $LSPR_{Long}/LSPR_{Trans}$ are commonly about 1.7–2.1 [6,12]; as far as we know, only one literature reports that this ratio exceeds 3.0 [8]. Herein, the narrow FWHM and large $LSPR_{Long}/LSPR_{Trans}$ ratio indicate the as-prepared AuBPs have uniform shape and high yields.

Fig. 1B shows a large scale TEM image of the as-prepared AuBPs. Most of the NPs possess well-defined bi-pyramidal shape. The AuBPs' yield are about 85.0% by random statistics of 1000 NPs, which rather closes to the best result so far, as reported by Liz-Marzán group [8]. Their length and diameter are 110.3 nm and 30.1 nm, respectively. Almost all the AuBPs possess symmetrical structure and sharp tips. Because of high uniformity and monodispersity, the as-prepared AuBPs can well self-assemble at TEM grids and form long-range order superstructures (Fig. 1C). As the substrate is changed from hydrophobic carbon film to hydrophilic SiO_2, the self-assembly of the AuBPs is still easily to be achieved (Fig. 1D). Such AuBPs' self-assembly substrates have application potentials for surface enhanced Raman scattering study. Figs. 1E and F are high resolution (HR) TEM image and selected area electron diffraction (SAED) pattern of the AuBPs. They show that the NPs are both crystalline with face-centered-cubic structure and standard lattice parameters. Based on literature, the as-prepared AuBPs probably possess pentatwinned crystalline structure [4,13].

It is known that AuBPs possess pentatwinned crystal structure. Conceivably, if the used gold seeds have corresponding crystalline structure and suitable surface chemical properties, the fabrication of AuBPs would be feasible in theory. In these regards, $NaBH_4$ regents seem to be not indispensable. Based on literature, pentatwinned crystalline AuNPs tend to be formed in the presence of citrate [4]; furthermore, if using tannin as reducing agents, AuNPs with small and tunable size (3.5–10 nm) can be obtained [10]. On the other hand, it has been an open question what surface properties of gold seeds are appropriate for AuBP fabrication. Obviously, "suitable surface chemical properties" is rather subtle, which needs to be checked by experiments. As described by the light green curve in Fig. S2A (Supporting information), in terms of the untreated AuNPs synthesized by (tannin + citrate), it is rather not ideal for AuBPs fabrication. Instead, as the as-prepared AuNPs are treated by combination of CTAB and heat incubation, AuBPs dominated products can be well obtained (black curve in Fig. S2A). Interestingly, if the AuNPs are only treated by CTAB or heat incubation, AuBPs' fabrication also cannot be well achieved. Furthermore, if CTAB is replaced by CTAC (hexadecyltrimethylammonium chloride), the yields of AuBPs drastically decreases (Fig. S3 in Supporting information). Herein, in terms of the gold seeds, the treatment of CTAB and heat incubation can well affect their sizes, shapes, as well as surface chemistry, which will profoundly influence shape modulation of the synthesized AuNPs.

Then, the heat incubation temperature of the gold seeds was studied. Based on the black curve in Fig. S2B (Supporting information), at 30 °C heat incubation, the products possess high $LSPR_{Trans}$ intensity, indicating that AuBPs' yields are rather low. As the heat incubation temperature increases to 60 °C, the yields of the AuBPs are obviously increased (red curve in Fig. S2B). Based on the experiments, 80 °C seems to be an optimal temperature for the highest yields. Furthermore, as the gold seeds are incubated at higher temperature, the obtained products have longer wavelength of $LSPR_{Long}$. Then, the effects of CTAB concentrations on the gold seeds treatment have been investigated. As shown in Fig. S2C (Supporting information), as 100 mmol/L of CTAB is used, the products have the highest ratio of $LSPR_{Long}/LSPR_{Trans}$. Furthermore, higher concentrations of CTAB correspond to larger aspect ratios of the obtained AuBPs.

Based on above, for obtaining high yields of AuBPs, it is essential that the gold seeds are heat treated in suitable temperature (80 °C) in the presence of 100 mmol/L of CTAB molecules. In the following, the effects of heat incubation time (at 80 °C) for the gold seeds were investigated, as shown in Fig. 2. Fig. 2A shows a series of LSPR bands of the products, which are fabricated using the gold seeds by heat incubation for 6, 12, 24, 36, 48 and 60 h, respectively. Overall, all the products exhibit rather typical rod-like LSPR properties. Furthermore, with the increase of heat incubation time, the $LSPR_{Long}$ gradually shifts to longer wavelength. At 24 h incubation, the products possess the largest value of $LSPR_{Long}/LSPR_{Trans}$. Then, the products were characterized by TEM technique. As shown in Figs. 2A and B, well-defined AuBPs products are observed using 6 h heat treated gold seeds. The diameter and length of the AuBPs are 20.2 nm and 52.7 nm, and their yields are about 67.3%. As the heat incubation time increases to 24 h, the yields of the AuBPs can reach about 85.0% (Figs. 2I and J), which is well in agreement with that of the LSPR band (Fig. 2A). Furthermore, in addition to the increase in their sizes and aspect ratios, the AuBPs (Figs. 2I and J) possess sharper tips. As the incubation time further increases to 36, 48 and 60 h, the AuBPs' yields

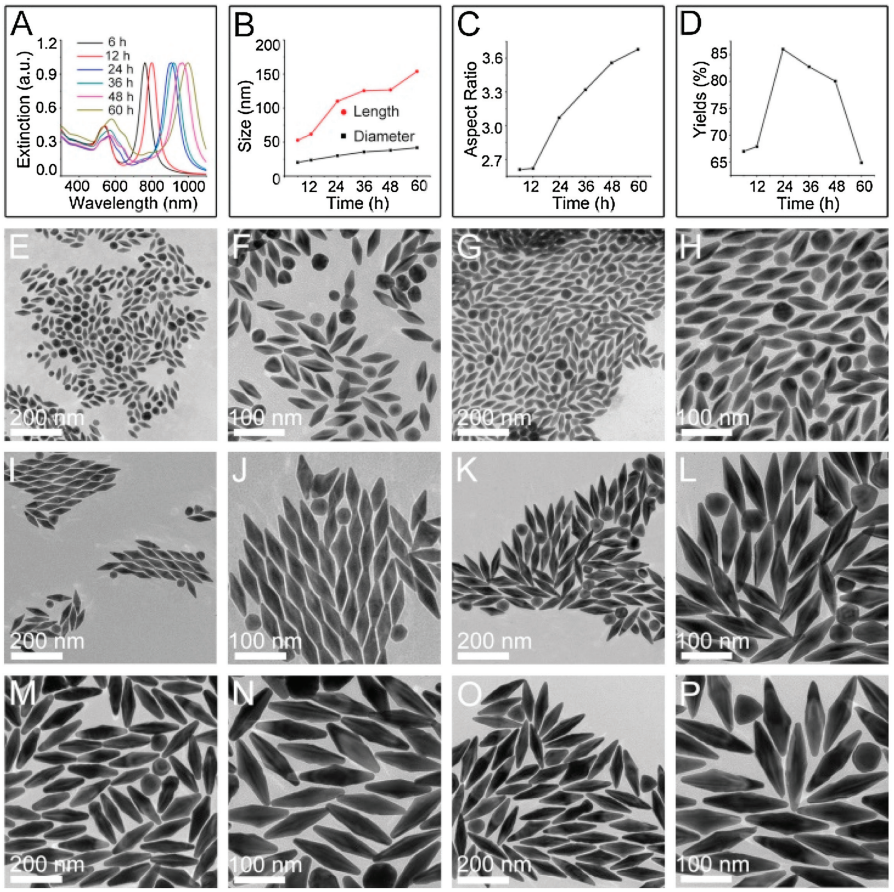

Fig. 2. The AuBPs synthesized by using the gold seeds obtained by 80 °C heat incubation for different time in the presence of 100 mmol/L of CTAB. (A) Extinction spectra of six products synthesized using the gold seeds by different heat incubation time. (B) Length and diameter of the AuBPs *vs.* gold seeds heat incubation time. Aspect ratio (C) and yields (D) of the AuBPs *vs.* gold seeds heat incubation time. TEM images of the products synthesized using the gold seeds by heat treatment for 6 h (E, F), 12 h (G, H), 24 h (I, J), 36 h (K, L), 48 h (M, N), and 60 h (O, P), respectively.

gradually decrease to 82.7%, 80.0% and 64.9%, respectively. At the same time, both the sizes and aspect ratios of the obtained products continuously increase (Figs. 2B and C).

To understand such AuBPs' parameter modulation, the gold seeds properties *vs.* heat incubation time were then investigated (Fig. 3). As shown in Fig. S4 (Supporting information), for the AuNPs synthesized in the presence of tannin and citrate, their diameter is about 3.81 nm. In addition to non-uniform size, a few elliptical and even short rod-like particles are observed. Due to their polydispersity, their LSPR band (472–586 nm) is rather wide (black curve in Fig. S5 in Supporting information). As CTAB molecules are introduced, the ζ-potential values change from −29.8 mV to +61.7 mV. At the same time, the LSPR spectrum exhibits an overall elevation (red curve in Fig. S5), probably due to

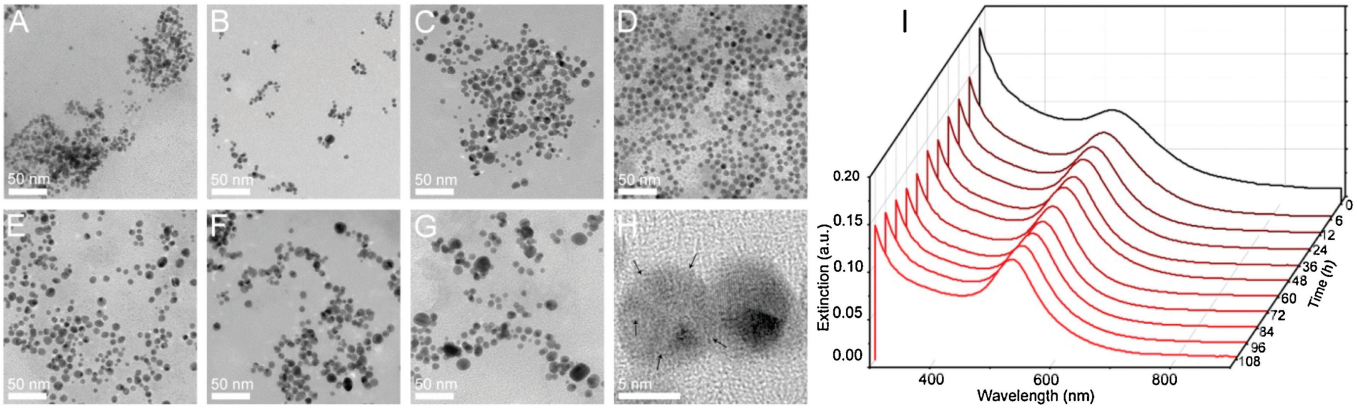

Fig. 3. Effects of heat (80 °C) incubation time on the gold seeds in the presence of 100 mmol/L of CTAB molecules. (A–G) TEM images of the AuNPs at different heat treatment time: 0 h (A), 6 h (B), 12 h (C), 24 h (D), 36 h (E), 48 h (F), 60 h (G). (H) HRTEM image of the AuNPs for 24 h heat incubation. (I) Extinction spectra of the AuNPs at different heat incubation time.

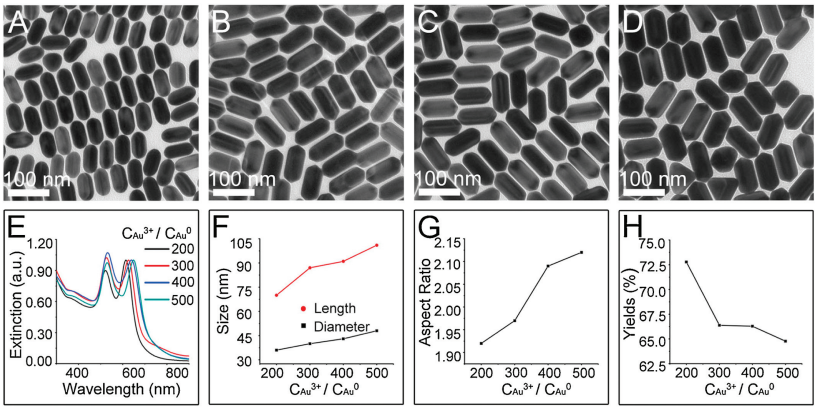

Fig. 4. Effects of the amounts of the gold seeds on the AuNRs' synthesis (the gold seeds were obtained by 80 °C heat treatment for 24 h in the presence of 100 mmol/L of CTAB molecules). (A) Extinction spectra of the products synthesized by using different amounts of the gold seeds. (B) Length and diameter of the AuNRs *vs.* the amounts of the gold seeds. Aspect ratio (C) and the yields (D) of the AuNRs *vs.* the amounts of the gold seeds. (E–H) TEM images of the four products synthesized by different amounts of the gold seeds. From E to H, the used gold seeds gradually decreases, which corresponds to that shown in Fig. 4A.

the increased scattering intensity. With the heat incubation, the AuNPs show gradual size increase; meanwhile, their LSPR bands become sharper (Fig. 3I). As shown in Fig. 3D, the AuNPs exhibits the best monodispersity (mean size 8.16 nm) for 24 h heat incubation. Furthermore, the corresponding AuNPs possess distinctly pentatwinned crystalline structure (Fig. 3H). As heat incubation time further proceeds, a few rather larger gold particles (>10 nm) are observed (Figs. 3E–G) due to Ostwald ripening effects. As a result, the monodispersity of the AuNPs correspondingly decrease again. Generally, the ζ-potential values of the AuNPs decrease with the enhancement of heat incubation time, although there is a litter fluctuation (Fig. S6 in Supporting information). The decrease in their ζ-potential values probably correspond to the reduction of the adsorbed CTAB molecules on the particles' surface. Based on these inspections, the gold seeds modulated AuBPs' fabrication can be qualitatively understood as follows: With the increase of the heat incubation time, the AuNPs' size becomes larger and larger on the whole (Fig. S7 in Supporting information), which causes the concentration decrease of the gold seeds. So, the gold seeds with longer heat incubation time are employed, the AuBPs with larger sizes are obtained. On the other hand, due to the gold seeds with 24 h incubation time are highest monodisperse, the corresponding AuBPs have the best yields.

Then, the effects of the amounts of the used gold seeds on AuBPs' fabrication have been investigated. As shown in Fig. S8A (Supporting information) as the volumes of the added gold seeds are 3.665, 1.830, 1.220 and 0.960 mL, respectively, the $LSPR_{Long}$ peaks of the obtained AuBPs are 864, 940, 1004 and 1060 nm. In terms of the four obtained AuBPs, their aspect ratios are 3.67, 3.88, 4.39 and 4.60. Overall, the AuBPs' yields are ~79.3%–84.6%. As shown in Figs. S8E–H (Supporting information) all the AuBPs possess well-defined symmetrically pyramidal shape with sharp tips, indicating the effective tunability of the proposed fabrication system.

In addition to AuBPs, the proposed gold seeds could also be employed for the synthesis of AuNRs. Figs. 4A–D shows four kinds of products fabricated by different amounts of the gold seeds, in the absence of Ag^+ cations. All the AuNPs exhibit distinct rod shape. As shown in Figs. 4E–H, as the Au^{3+}/Au^0 ratios increase from 200 to 500, the aspect ratios of the AuNRs correspondingly increase from 1.92 to 2.12 (length: from 70.2 nm to 101.1 nm, diameter: from 36.2 nm to 48.3 nm). It is noted that the AuNRs obtained by the "standard" fabrication system proposed by El-Sayed group often possess 18 nm in width. If using the seed-mediated system by dramatically increasing the amount of the seed solution, the widths of the obtained AuNRs are below 10 nm [14]. In contrast, it is rather difficult to synthesize AuNRs with larger width (>18 nm) by the seed-mediated approach. To solve this problem, Murray group employed another stabilizer, namely oleic acid [15].

In summary, the synthesis of AuBPs and AuNRs has been well achieved by using the gold seeds reduced by air-stable agents. The conventionally employed unstable $NaBH_4$ is completely replaced. The preset contribution, on the one hand, is promising for simplifying AuBPs/AuNRs processes, on the other hand, provides a paradigm for better understanding morphology modulation of the synthesis of NPs.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary material related to this article can be found, in the online version, at doi:https://doi.org/10.1016/j.cclet.2019.12.037

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