Rapid synthesizing of gold nanobipyramids

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Abstract

We report on a rapid method to synthesize gold nanobipyramids that utilizes a hexagonal liquid crystal as a frame, suggesting a liquid crystal accelerated growth process. The method represents an improvement in processing time as compared to previously reported methods. Furthermore, as the bulk of the total processing time is required by a purification step, the method presented in this paper holds the promise of an order of magnitude improvement of processing time by further optimization of the growth process that would eventually eliminate the need for purification.

1. Introduction

The ability to prepare gold nanorods (GNRs) \cite{1,2} has enabled its use in a wide variety of nanotechnology applications such as in phototherapy \cite{1} and as bio-probes \cite{3}. Recently it has been shown that the edge of gold nanobipyramids (GBPs) are sharper than those of GNRs, which can yield local electric-field enhancements of GBPs 3 times larger than those of GNRs \cite{4}. Thus substituting GNRs for GBPs should be beneficial in some applications \cite{5,6}, e.g. for photodynamic and photothermal therapies \cite{7} probes for bio-applications \cite{8}, detection of influenza virus \cite{9}, surface-enhanced Raman scattering detection \cite{10}, as well as cancer cell imaging and photodynamic therapies \cite{11}.

Synthesizing GBPs remains time consuming. A commonly used procedure \cite{12} typically takes more than 12 h to complete, though recent publications have reported on improved synthetization times. Using a method in which GBPs were induced using chloroplatinic acid, GBPs were synthesized in 5 h with a yield of 85\% \cite{13}. In another method, which employed thermal treatment of the seeds, the total time to time to synthesize was 3.5 h (90 min thermal treatment and 2 h of growth) \cite{14} and had a yield of 85\%–90\%. By contrast, in this paper we report on a new method by which synthetization is achieved in only 10 min. The as-prepared yield of 40\% is so far rather low and thus a subsequent purification step is required to achieve a total yield of 90\%–95\%, resulting in a total process time of about 2 h. Crucially however, careful optimization of the synthetization conditions should enable an elimination of the need for the purification step thus promising a true rapid method for synthetization of GBPs. Our method utilizes a hexagonal liquid crystal (40\% CTAB solution) as a template growth frame \cite{15}, which suggests that the formation of bipyramids is the result of a liquid crystal accelerated growth process. Several reports of synthesis of gold NPs using CTAB water solution, with typical processing times of the order of 12 h, exist \cite{16–18}, however the method of synthesizing GBPs as presented here has to our knowledge previously not been reported.

2. Experimental

2.1. Chemicals and materials

Hydrogen tetrachloroaurate trihydrate (HAuCl\textsubscript{4} · 4H\textsubscript{2}O, 99.9\%), purchased from Sigma-Aldrich; hexadecyl trimethyl ammonium bromide (CTAB, 99.0\%), purchased from Sino Chemical Reagent Co., Ltd; silver nitrate...
(AgNO₃, 99%), sodium borohydride (NaBH₄, 99%), sodium citrate (99%), the latter three all purchased from Aladdin Reagent Co. In addition, deionized (DI) water was used in all of the experiments.

2.2. Instrumentation
Absorption spectra were obtained using a PerkinElmer Lambda 950 UV–vis-NIR spectrophotometer; transmission electron microscopy (TEM) images of the obtained gold nanoparticles were acquired using a JEOL JEM-2100HR transmission electron microscope; scanning electron microscopy (SEM) images and EDX spectrum of GBPs were acquired using a ZEISS Ultra 55 scanning electron microscope; and particle size distribution histograms of gold was obtained using a D8 Advance Bruker x-ray diffractometer.

2.3. Synthesis of GBPs
Prior to synthesis we prepare a seed solution as follows: 50 μl of 50 mM sodium citrate and 50 μl of 50 mM HAuCl₄ are added into 9.9 ml of DI water, after which 100 ml of 0.03 M NaBH₄ are added at 1500 rpm. The seed solution was stored at room temperature before use.

A growth solution is prepared by stirring 10 ml of 40% CTAB (hexagonal liquid crystal) at 1000 rpm (heated to 90 °C) and adding 200 μl of 25 mM HAuCl₄, 80 μl of 16 mM AgNO₃, and 90 μl of 80 mM ascorbic acid in sequence.

The GBPs are then synthesized by adding 15 μl of the seed solution to the growth solution and leaving the mixture undisturbed for 10 min after which the color of the solution turns to burgundy, indicating that GBPs with absorption wavelengths of 900 nm were acquired.

2.4. Purification of GBPs
We follow the approach of Zhou et al [18]; 10 ml of the as-prepared GBPs solution were centrifuged at 10000 rpm for 5 min two times in succession, after which it was added into 10 ml of 0.28 M CTAB solution. The mixtures were then deposited for 2 h at 70 °C. Purification is achieved as depletion interaction between two nanoparticles results in preferential aggregation and sedimentation of GBPs [19]. The sediments were subsequently dispersed in DI water.

3. Results and discussion
In preparation for analysis, the product was dispersed in DI water to dilute the liquid crystal solution concentration. The gold nanoparticles were extracted by centrifugation at 10000 rpm for 5 min and the precipitate was then dispersed in DI water for measurements.

Figures 1(a) and (b) show SEM and TEM images of the gold nanoparticles in which it can clearly be seen that the product indeed includes GBPs with a length about 120 nm as well as byproducts consisting of spherical nanoparticles. A possible reason for the existence of the byproduct is difficulty to control the nucleation and growth due to the nucleation occurring continuously throughout the entire growth process [12]. Figure 1(c) shows particle size distribution histograms of the gold nanoparticles where we see that the GBP lengths are in the 110–140 nm range, and the spherical nanoparticle diameter is in the range of 50–90. The measured EDX spectrum of figure 1(d) only exhibits characteristic Au peaks, suggesting that the constituent of the GBPs is indeed pure Au.

The measured UV-NIR absorption spectrum of the as-prepared GBPs (red line in figure 2(a)) shows two surface plasmon resonance bands centered at 560 and 900 nm indicating that the mixture contains two separate types of nanoparticles. The measured UV-NIR absorption spectrum of the purified solution (shown as the black line in figure 2(a) shows a strong reduction of the 560 nm peak, and thus we can make a straightforward assumption that the absorption peak at 900 nm can be attributed to the GBP, while the first peak at 560 nm can be attributed to the spherical nanoparticles. This is confirmed by the TEM image of the gold nanoparticles shown in figure 2(b) in which it can be seen that nearly all remaining nanoparticles are GBPs having an average length of 120 nm.

We confirm the synthesis time by inspection of the dynamic UV-NIR absorption spectra of the GBPs shown in figure 3(a). We can find that the UV-NIR absorption spectra of 5 min and 10 min are very close in shape and the UV-NIR absorption spectra of 10 min and 15 min are near-identical from which we conclude that the synthesis procedure of GBP is completed after 10 min.

The pH value is an important factor for the proportion of GBPs and to study the extent of this we prepared three growth solutions having pH 6, 7, and 8 respectively. The products were diluted in DI water and gold nanoparticles extracted in the same manner as discussed above, after which UV-NIR spectra was measured. As can be seen in figure 3(b), the three absorption spectra have the same ordinate values at 900 nm, whereas the
ordinate values differ at 560 nm. A lower ordinate value of 560 nm indicates a higher proportion of GBPs and so we confirm pH 7 of the growth solution to be the most favorable.

A speculation on the mechanism of the rapid formation of GBPs is merited. With increasing concentration, the phase of CTAB in water changes first from free molecules to micellar phase and then to a hexagonal array liquid crystal as can be seen in the phase diagram in figure 4 [20]. As can further be seen in figure 4, at the growth conditions used in the method presented in this paper (40% CTAB, 90 °C), the hexagonal structure is the equilibrium phase. In this phase the gap between CTAB clusters is such that only slender spaces exist, which enables rapid growth of GBPs by means of liquid crystal templating [15]. As shown by e.g. Canbek et al silver(I)-assisted growth will favor the formation of pentatwinned bipyramids [16] and, as furthermore explained by Liu et al during the formation of GBPs, the absorption of Br⁻ on certain facets of gold seeds inhibits the growth in the corresponding direction [21]. In the present work, we synthesize GBPs with a CTAB concentration of 40%, in which hexagonal liquid crystal is the major phase. In this situation, Br⁻ will distribute predominantly on the side of gold seeds, thus accelerating the growth of the gold seeds in the perpendicular direction, which in turn enables GBPs to grow faster than in previously reported methods.

Figure 1. (a) SEM image of GBPs. (b) TEM image of the GBPs. (c) The corresponding particle size distribution histograms of gold nanoparticles. (d) EDX spectrum of GBPs.

Figure 2. (a) UV-NIR absorption spectra of the as-prepared GBPs (red) and purified GBPs (black). (b) TEM image of purified GBPs.
4. Summary

In summary, we have developed a novel method for rapid synthesis of gold nanobipyramids using a hexagonal liquid crystal system as an accelerated frame, the experimental verification of which has been presented in this letter. The method reduces the time to synthesize GBPs to just 10 min, highly pure GBPs can be obtained by purification following the synthesis. While the purification step undoubtably increases the total processing time, this still represents a clear improvement as compared to previous reports and further optimization of the synthetization conditions that would eliminate the need for the subsequent purification step would enable a truly very rapid process of GBP fabrication.

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