Synthesis and spectroscopic characterization of gold nanobipyramids prepared by a chemical reduction method

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Abstract
Gold nanobipyramids (NBPs) have attracted much attention because they have potential for applications in smart sensing devices, such as medical diagnostic equipments. This is due to the fact that they show more advantageous plasmonic properties than other gold nanostructures. We describe a chemical reduction method for synthesizing NBPs using conventional heating with ascorbic acid reduction and cetyltrimethylammonium bromide (CTAB) + AgNO₃ as capping agents. The product was characterized by ultraviolet–visible spectroscopy (UV–vis), Fourier transmission infrared spectroscopy (FTIR), transmission electron microscopy (TEM), x-ray powder diffraction (XRD). The results showed that gold nanoparticles were formed with bipyramid shape (tip-to-tip distance of 88.4 ± 9.4 nm and base length of 29.9 ± 3.2 nm) and face-centered-cubic crystalline structure. Optimum parameters for preparation of NBPs are also found.

Keywords: gold nanobipyramids, seed mediated, chemical reduction method, high aspect ratio
Classification numbers: 4.02, 5.00

1. Introduction
Noble metal nanoparticles possess physical and chemical properties that are different from their corresponding bulk material [1, 2]. They have potential for applications in optics [3], catalysis [4], sensor [5], medicine [6] etc. The progress in developing methods for preparation of metal nanoparticles and understanding the optical properties of these nanoparticles has been performed. However, there are still some problems and ambiguous questions that might not to be addressed.

One of the challenges in the design and preparation of metal nanoparticles is that how to control their shape and size, which not only affect the optical properties but also the plasmonic properties [7]. In some cases, sharp and edgy nanostructures can be of great interest since they provide a very high sensitivity to local changes in the dielectric environment, as well as larger enhancements of the local electric field [8, 9]. Recently, many synthetic techniques have been used to fabricate nanospheres [10], nanorods [11], nanocubes [12] and nanostars [13]. However, preparation of nanobipyramids and understanding of their properties are still rare.

In this work we perform the preparation of gold nanobipyramids (NBPs) by chemical reduction method in high yield through the seed-mediated growth process and
purification of NBPs. Effects of seed particles, ascorbic acid and AgNO₃ on the formation of gold nanobipyramids are also discussed.

2. Experimental

2.1. Material and reagents

Chloroauric acid (HAuCl₄ · 3H₂O, 99.9%), cetyl-trimethylammonium bromide (CTAB, 99%), sodium borohydrate (NaBH₄, 99%), silver nitrate (AgNO₃, 99%) were obtained from Sigma-Aldrich, ascorbic acid and sulfuric acid (H₂SO₄, 99%) were purchased from Prolabo Company. Deionized (DI) water was used throughout experiments. All chemical materials were GR grade.

2.2. Method for preparation of NBPs synthesis of the seeds solutions

The preparation of CTAB-stabilized gold nanoparticles (seeds) was modified from the method of Wei et al [14]. 50 μl of aqueous HAuCl₄ (10⁻² M) was mixed with a CTAB solution (0.2 M, 1 ml) and 950 μl DI water under stirring at ambient temperature. 200 μl of freshly prepared cold 0.1 M NaBH₄ solution (4 °C) was added immediately. The solution color changed from orange to brownish yellow, indicating the seed particle formation. This solution was kept at room temperature for 24 h before using it in the experiment.

2.3. Preparation and purification of NBPs

NBPs were prepared as follows: 250 μl of aqueous HAuCl₄ (10⁻² M) was added to the solution of CTAB (2.5 ml, 0.2 M) and 2.25 ml DI water under stirring. The solution turned brownish yellow. After that, 37.5 μl of ascorbic acid (AA) 0.1 M was added, making it change from brownish yellow to colorless. 50 μl of aqueous AgNO₃ (0.1 M) was dissolved in the solution with pH about 3 (using H₂SO₄ (20%) for changing pH). Then, this solution was dissolved in 17.5 μl of the seed solution at room temperature for about 5 h. After that, this solution was purified in order to remove the excess CTAB and gold nanospheres using centrifugation with 9000 cycles min⁻¹ for 15 min and 10 ml DI water (three times). The spectroscopic behaviors for NBPs were recorded by using UV–vis spectrophotometer Jasco V-600 and Fourier transform infrared (FTIR) spectrometer Bruker Tensor 27. A transmission electron microscope (TEM) JEM1010-JEOL and an x-ray diffractometer (XRD) Bruker D5005 using Cu radiation were employed to characterize the gold nanoparticles.

3. Results and discussion

3.1. Synthesis and characterization of NBPs

NBPs were prepared by a two step synthesis process (also known as seed-mediated growth). First, CTAB-protected nano gold seeds were obtained by the reduction of a gold salt with NaBH₄ in the presence of the surfactants. Second, this solution was injected into a growth solution of HAuCl₄, AgNO₃, CTAB and ascorbic acid at pH = 3. The produced NBPs were stabilized by a bilayer of cetyl-trimethylammonium bromide [15]. The UV–vis spectrum and TEM pictures of nano gold bipyramid suspensions are presented in figures 1 and 2.

UV–vis spectroscopy is useful to tracking the morphological evolutions and optical properties because gold nanostructures exhibit surface plasmon resonance depending on various shapes and sizes at different frequencies. Curve (a) in figure 1 shows the visible absorption of NBPs before purification of NBPs. Our results show that the UV–vis spectrum presents two clearly distinct peaks: a broad absorption band ranging from 450–575 nm referred to the base of the bipyramid (and a 40% sphere contribution) and the absorption wavelengths in the range of 600–900 nm referred to the elongation of the tips (a mixture of nanobipyramids and nanorod) as shown in curve (a) of figure 1. In addition, purification of NBPs using centrifugation allowed us to obtain the desired bipyramids geometry, with only two absorption bands in the range of 500–550 nm and 625–750 nm (curve (b) in figure 1). These results are similar to those reported by Parola et al [16].

The TEM image shows the formation of NBPs with a general tip-to-tip distance of 68 nm and a base length of 12 nm. In addition, more than 60% of the nanoparticles observed by TEM are bipyramids, the rest (spherical nanoparticles or nanorods) are pseudo-spherical nanoparticles or nanorods (figure 2(a)). After the purification of NBPs using centrifugation, NBPs occupy more than 95% (see figure 2(b)). Counting over 100 nanoparticles in the TEM image, we obtain a size distribution of 88.4 ± 9.4 nm and 29.9 ± 3.2 nm for NBPs.

Figure 3 shows the FTIR spectra for NBPs before and after purification. Two peaks at 2925 and 2850 cm⁻¹ observed in NBPs-CTAB may refer to –C–H group of CTAB.
After the purification, these peaks disappear, indicating that NBPs solution was purified by removing the excess CTAB.

XRD was employed to identify the crystallinity of the as-synthesized NBPs (figure 4). The recorded XRD pattern exhibits peaks at $38^\circ$, $45.2^\circ$, $64.9^\circ$, $77.5^\circ$ and $82^\circ$ in the $2\theta$ range which are corresponding to (111), (200), (220), (331) and (222) planes of gold with face-centered-cubic crystalline structure. Lattice constant determined from XRD pattern ($a = 4.08 \text{ Å}$) is in good agreement with the standard diffraction pattern of cubic gold metal [18].
3.2. Effect of seed particles to NBPs

UV–vis of various seeds after 24, 48, 72 and 168 h were shown in figure 5(a). The visible peaks increase from 525 to 546 nm indicated the average diameters increase in proportion to the storage time of seeds. NBPs were prepared with different seeds (24–168 h) to investigate the effect of seed particles. Figure 6 shows the UV–vis of NBPs synthesized with different seeds.

Figure 6. UV–vis of NBPs synthesized with different seeds.

Figure 7. UV–vis spectra of NBPs synthesized with different concentrations of AgNO₃.

Figure 8. TEM images of NBPs synthesized with different concentrations of AgNO₃: (a) 0.8 µmol, (b) 1.0 µmol and (c) 1.1 µmol.

Figure 9. (a) UV–vis of NBPs synthesized with different concentrations of ascorbic acid (AA). (b) NBPs obtained after 30 min with different concentrations of AA: (1) 3.25 µmol, (2) 3.50 µmol, (3) 3.75 µmol; (4) 4.00 µmol and (5) 4.25 µmol.
different seeds. As it can be seen, the absorption bands are 525–575 nm and 660–900 nm meaning that seeds with large diameter are not suitable for NBPs preparation. However, the smaller seed particles, which have the optimal diameters of about 10 nm, are the better for NBPs preparation (figure 5(b)).

3.3. Effect of the concentration of AgNO₃ and ascorbic acid

Figure 7 shows the UV–visible spectra of NBPs suspension produced with different concentrations of silver nitrate (0, 0.8, 1.0 and 1.1 μmol) in identical growth solutions as previously described [19].

It can be seen that the relative silver nitrate quantity plays an important role in the Au-BP formation. For low AgNO₃ concentrations (below 0.4 μmol), the absorbance wavelength localized at 525 nm is similar to the absorption band of spherical gold nanoparticles. By increasing the silver nitrate concentration (0.8–1.1 μmol), the absorption bands localized in the range 530–550 and 758–773 nm attributed to the longitudinal mode of the bipyramids. The optimization of silver nitrate concentration for producing NBPs structure was found to be 1.0 μmol. These results demonstrate the fact that with an appropriate silver nitrate concentration, we can control the formation of NBPs as shown in figure 8.

Figure 9(a) shows the absorption spectra of NBPs suspension synthesized with different reductant concentrations. For low ascorbic acid concentration (3.5 μmol), ascorbic acid was not enough to reduce Au³⁺ to Au⁺, leading to the disappearance of NBPs (figure 9(b)). With a high ascorbic acid concentration (larger than 3.75–4.25 μmol), the longitudinal plasmon band (corresponding to the tip-to-tip elongation) is redshifted from 755 to 775 nm when reductant concentration increases.

As previously reported [20], the ascorbic acid concentration directly affects the object structure. The optimum ascorbic acid concentration for producing NBP struture was found to be 3.75 μmol (figure 10).

4. Conclusion

In conclusion we reported a simple way to prepare NBPs with ascorbic acid reduction and cetyltrimethylammonium bromide (CTAB) + AgNO₃ as capping agents. The obtained nanoparticles are homogeneous with bipyramid shape (tip-to-tip distance of 88.4 ± 9.4 nm and base length of 29.9 ± 3.2 nm). Optimum AgNO₃ and ascorbic acid concentration for producing gold nanobipyramidal structure are 1.0 and 3.75 μmol, respectively. The successful preparation of NBPs is expected to open the way for biomedical applications.

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