Synthesis and Simulation Study of Right Silver Bipyramids via Seed-Mediated Growth cum Selective Oxidative Etching Approach

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In this study, a simple method to synthesize right silver bipyramid (AgBP) nanostructures via the seed-mediated growth cum oxidative etching approach in aqueous solution is developed. The key strategy of this method is to control the growth and etching process by careful adjustment of the reactants concentration. Ascorbic acid (AA) is used to reduce silver precursor while cetyltrimethylammonium bromide stabilizer is used to direct the preferential growth of (100) facets. The presence of Cu²⁺ and AA in the reaction mixture also enable in-situ generation of H₂O₂, leading to selective etching of (111) facets, which is crucial to the formation of anisotropic AgBPs. The structure-properties of AgBPs is systematically investigated through a series of experiments and theoretical simulations. Transmission electron microscope images and X-ray diffraction patterns of the as-synthesized AgBPs show the formation of single crystalline twined nanostructures with a relatively high yield. These results suggest the important role of the excitation of electric dipole in enhancing the electric field at the six sharp corners of AgBPs, making them especially promising for a wide range of technological applications including surface-enhanced Raman scattering with a significant enhancement factor of 1.50 x 10⁵ as demonstrated herein.

1. Introduction

Noble metal nanoparticles such as gold (Au) and silver (Ag) exhibit unique optical, electronic and catalytic properties that are not found in their bulk form,¹ which are useful for many technological applications.² For example, excitation of light to the plasmonic metal nanostructures not only gives them the color for far-field imaging, but also enhances the electric field near their surface dramatically.³ This enhanced electric field can be used to develop different optical devices and sensing probes for biomedical diagnostics⁴ and theranostics.⁵ Due to the high surface to volume ratio, these nanoscale metals, particularly platinum (Pt) and palladium (Pd), are also effective catalysts for various chemical reactions.⁶ To dates, various types of metal nanoparticles (e.g., triangular Au nanoplates,⁷ Ag nanocubes,⁸ and Pt nanoboxes⁹) with tunable size and shapes have been successfully synthesized.⁷,⁹,¹⁰ Among them, anisotropic silver nanostructures with sharp corners (e.g., bipyramid) and polyhedral nanocrystals with defined crystallographic facets (e.g., (111) and (100)) are of great importance due to their lower energy loss and stronger electric field,¹¹ which are well suited for metal-enhanced fluorescence (MEF),¹² metal-enhanced singlet oxygen generation (ME-SOG),¹² and surface-enhanced Raman scattering (SERS).¹³,¹⁴ There are several challenges to synthesize anisotropic metal nanostructures, in particular silver, with high yield and well-distributed size and shapes. This is because silver is more reactive and tends to interact (or get oxidized) easily with the existing ions and charged molecules present in the reaction mixture during synthesis.¹⁵ The synthesis is also highly sensitive to the reaction conditions such as temperature, pH as well as the stabilizing agents used to control the morphology and growth of anisotropic silver nanostructures with certain crystallographic facets.¹⁶ Recently, synthesis of nanoscale silver bipyramids (AgBPs) has attracted more attention than the other polyhedral nanostructures due to their unique optical properties.
However, there are only a few reported synthesis procedures for AgBPs over the last decade. Typically, the synthesis of AgBPs requires long reaction time, involving the use of specialty chemicals, organic solvent and high temperature to grow the anisotropic single crystalline nanostructures high yield. For example, Xia’s group has developed the polyol approach to form the twinned seeds in the presence of Br\textsuperscript{-} ions for the synthesis of right AgBPs.\textsuperscript{[17]} However, the polyol approach usually requires the use of ultrapure ethylene glycol with low content of iron and chloride for the synthesis of AgBP nanostructures.\textsuperscript{[18]} In addition, high-temperature synthesis conditions and multiple washing steps with organic solvent make the polyol synthesis more expensive and less environmentally friendly. In another study, Mirkin’s group has reported a photo-mediated approach based on the sodium citrate reduction of Ag\textsuperscript{+} ions in the presence of phenylphosphine dihydrate dipotassium salt (BSPP) by controlling the pH, Ag\textsuperscript{+} to phenylphosphine BSPP ratio and wavelength of irradiation light. However, such synthesis requires a relatively long irradiation time (i.e., 8 h using 150 W halogen lamp) to form the AgBPs.\textsuperscript{[17b,c]}

Herein, we report a new strategy to synthesize the single crystalline AgBPs in aqueous solution based on the seed-mediated growth approach, coupled with the simultaneous oxidative etching of the (111) facets at a much lower heating temperature (80 °C) and shorter reaction time (2 h). This method is simpler and does not need any special chemicals (e.g., BSPP and ultrapure ethylene glycol) or light with a specific wavelength. Therefore, the presented synthesis protocol is more controllable and reproducible. The as-obtained Ag nanostructures are found to have a narrow size distribution of 87 ± 3 nm (edge length), exhibiting two strong distinct electric dipole resonances located at the 466 nm and 542 nm wavelength, respectively. Detailed characterizations (including X-ray diffraction [XRD], transmission electron microscopy, and selected area electron diffraction) and finite-element simulation studies (e.g., absorption, scattering and extinction cross-sections, electric field, and surface charge distribution) have been conducted to understand the structure-properties of the AgBP nanostructures. Results show that the as-synthesized AgBPs possess single crystalline nanostructures with strongly enhanced electric field at their sharp corners, which has been successfully employed for SERS application with a considerable enhancement factor as demonstrated in this study.

2. Results and Discussions

In this study, we have developed a simple and efficient seed-mediated approach to synthesize silver right BP nanostructures (AgBPs) in aqueous solution using cetyltrimethylammonium bromide (CTAB) as the stabilizer and ascorbic acid (AA) as the reducing agent, while the Cu\textsuperscript{2+} ion/AA pair is used to produce hydrogen peroxide as the oxidizing agent. This new synthesis protocol combines the concept of seed-mediated growth with simultaneous chemical etching of the edges and corners of the growing nanocrystal to form anisotropic AgBPs. It has been well reported that the halide ions have a shape-driven role in the synthesis of anisotropic silver nanostructures.\textsuperscript{[19]} For instance, bromide ions, either in the form of NaBr salt or CTAB surfactant, could be employed for the synthesis of Ag nanocubes.\textsuperscript{[20]} In addition, Cu\textsuperscript{2+} ion has been used for morphological evolution of metal nanoparticles in the presence of AA and cetyltrimethylammonium chloride (CTAC) in an aqueous medium.\textsuperscript{[21]} Therefore, it inspired us that co-existing of a shape-driven agent and etchant might lead to form a new shape of particle with (100) facets.

As shown in Figure 1a, Ag seeds (2–5 nm) were first prepared by using NaBH\textsubscript{4} to reduce silver nitrate in the presence of CTAC as a surfactant (see extinction spectra of Ag seeds in Figure S1, Supporting Information). Then, the seed-mediated growth approach is employed to synthesize the AgBPs by adding the as-prepared Ag seeds to a growth solution containing CTAB, AA, Cu\textsuperscript{2+} and silver nitrate. After 2 h of reaction, an orange-reddish color solution is obtained (inset of Figure 1c). As shown in transmission electron microscope (TEM) image (Figure 1b), the main product is silver right BP (AgBP) with high uniformity in both shape (>90%) and size (87 ± 3 nm edge length and an 85 ± 4 nm base). The extinction spectra of the AgBPs showed two distinct peaks at 466 nm and 542 nm wavelength, corresponding to the transverse and longitudinal resonances, respectively (Figure 1c). The as-obtained AgBPs are positively charged with a zeta potential value of 26.8 ± 3.36 mV, suggesting the presence of CTAB molecules as the capping agent. This is further confirmed by the elemental mapping results, showing the elemental Br on the surface of AgBPs (Figure 1d).

To further optimize the synthesis, a series of experiments were conducted to investigate the effect of Ag seeds to AgNO\textsubscript{3} precursor ratio. It was found that initial amount of Ag seeds is critical to the formation of AgBPs. As shown in Figure 2a, at lower Ag seeds volume (e.g., 25 µL), different Ag nanostructures were formed including cube, BP, and sphere, where the extinction spectra of the sample exhibited multiple localized surface plasmon resonance (LSPR) peaks indicating the formation of Ag nanoparticles mixture with different morphology. A slight increase in the volume of seeds (i.e., 80 µL) results in the formation of AgBPs with high yield (Figure 2b). Further increase in the seeds led to the formation of spherical Ag nanoparticles as shown by the disappearance of LSPR peak at a longer wavelength (Figure 2a), which is mainly due to the less charge separation caused by high symmetry of spherical shape.\textsuperscript{[22]}

On the other hand, the amount of AgNO\textsubscript{3} in the growth step was also varied to study its effect on the morphology control of the final product. It was found that 40 µL of AgNO\textsubscript{3} led to the formation of various Ag nanostructures, including cube, sphere, and BPs in the sample mixture (Figure 3b). TEM images show that the AgBPs were formed with 80 µL of AgNO\textsubscript{3} added in the synthesis (Figure 1b) while further increase in AgNO\textsubscript{3} results in the formation of Ag nanowires and other irregular shapes (Figure 3c,d).

As illustrated in Scheme 1, Cu\textsuperscript{2+} and AA were added to the Ag seeds to facilitate the chemical etching process in forming anisotropic AgBPs. To evaluate the role of Cu\textsuperscript{2+} in the synthesis of AgBPs, the extinction spectra and TEM images of the samples synthesized using different amounts of Cu\textsuperscript{2+} were obtained (Figure S2a,b, Supporting Information). It was found that an optimum amount of Cu\textsuperscript{2+} (i.e., 40 µL of CuSO\textsubscript{4} solution) is essential for the production of AgBPs with high yield. In the
absence of Cu$^{2+}$, a mixture of nanocubes and nanowires were formed. At high concentrations of Cu$^{2+}$ (i.e., >40 µL of CuSO$_4$ solution), chemical oxidation becomes dominant, leading to the formation of spherical Ag nanoparticles.\cite{23} To demonstrate the role of Cu$^{2+}$ in producing oxidizing H$_2$O$_2$ (see Equation 1-4), similar experiment was conducted using Fe$^{2+}$ and Fe$^{3+}$ ions. The extinction spectra of these two samples were very similar to that obtained without Cu$^{2+}$ (Figure S2c, Supporting Information), indicating that no H$_2$O$_2$ is produced.\cite{24} This observation suggests that Cu$^{2+}$ is irreplaceable in the chemical etching reaction with AA. Furthermore, control experiment was carried out in the N$_2$ environment (Figure S2d, Supporting Information). Results show that oxygen plays a crucial role to enable the efficient chemical etching process to form

Figure 1. a) Proposed formation mechanism of AgBP via seed-mediated growth coupled with selective oxidative etching approach, b) TEM image, c) extinction spectra, and d) elemental mapping of the as-synthesized AgBPs. The inset of 1c shows the color photographs of AgBPs solution.
the anisotropic AgBPs. The possible reactions involved in the Cu$^{2+}$/AA-induced chemical etching process are proposed below:[25]

Step 1: H$_2$O$_2$ production in the presence of Cu$^{2+}$ and AA.

Cu$^{+}$ + ascorbate $\rightarrow$ Cu$^{2+}$ - ascorbate Complex $\rightarrow$ Cu$^{+}$ - ascorbyl

(1)

Cu$^{+}$ + O$_2$ $\rightarrow$ Cu$^{2+}$ + O$_2^-$

(2)

Cu$^{+}$ + O$_2$ + 2H$^+$ $\rightarrow$ H$_2$O$_2$ + Cu$^{2+}$

(3)

2O$_2$ + 2H$^+$ $\rightarrow$ H$_2$O$_2$ + O$_2$

(4)

Step 2: Oxidative etching of Ag atoms in the presence of CTAB.

Ag + H$_2$O$_2$ + 2H$^+$ + Br$^-$ $\rightarrow$ AgBr + 2H$_2$O

(5)

In the presence of dissolved oxygen, Cu$^{2+}$ ions could catalyze the oxidation process of AA molecules, where H$_2$O$_2$, a strong etchant, is being produced. It is well reported that H$_2$O$_2$ could etch the Ag atoms.[30,31] On the other hand, it has been reported that O$_2$ molecules have high affinity to be adsorbed on different facets of silver nanostructures including (100), (110), and (111) facets.[27] However, the molecular oxygen only exists on (111) facets as the adsorbed oxygen molecules on both (100), and (110) facets will be chemically dissociated into an atomic form via the interaction with Ag surface atoms.[28] Hence, it might lead to the in-situ formation of H$_2$O$_2$ in (111) facets[29] and therefore, selective etching of these crystallographic facets led to the anisotropic growth of AgBPs. The importance of in-situ formation of H$_2$O$_2$ on (111) facets was further examined by the replacement of Cu$^{2+}$ ions with H$_2$O$_2$ (i.e., equivalent to molar Cu$^{2+}$) in the reaction, which resulted in the formation of spherical Ag nanoparticles due to etching all facets (Figure S3a, Supporting Information).[23] Moreover, it was found that no reaction occurred at room temperature (Figure S3b, Supporting Information), which could be due to the low reduction potential of the as-formed AgBr in the growth solution to Ag atoms (AgBr$^-$ + e$^-$ $\rightarrow$ Ag + Br$^-$, $E_0 = 0.071$ V).[30] In addition, the absence of CTAB resulted in the formation of large pellets precipitated out from the solution as shown in Figure S3c, Supporting Information. Both experimental[20a] and theoretical[31] studies have shown that Br$^-$ ions could stabilize the (100) facets, thus making them the ideal capping agent for the exclusive formation of AgBPs nanostructures enclosed by (100) facets (Figure 1a).

The XRD pattern was obtained to assess the crystal structure of the as-synthesized AgBPs. As can be seen in Figure 4a, the (111), (200), and (222) diffraction peaks are the characteristics of face-centered-cubic silver [JCPDS file no. 04-0783] owing to the random orientation of the AgBPs on the substrate.[17] The XRD pattern gives further evidence that AgBPs preferentially orient with their (111) plane parallel to the substrate. To further confirm the twinned nature of the as-synthesized AgBPs, the selected area electron diffraction (SAED) patterns of a single BP.
was investigated at different angles (Figure 4b). Assuming that AgBPs contain two pyramids (called part 1 and part 2), at an angle of 0°, the observed diffraction indicates highly crystalline structure of the as-synthesized AgBPs when the beam is tilted along the [100] zone axis and perpendicular to the substrate. The spot array is the characteristic of [100] zone axis, indicating that the AgBP lies with a (100) facet flush with the substrate, where part 1 is the main contributor to the diffraction. At the angle −19.6°, the main contributor to the diffraction pattern is part 2. When tilted to +35.3°, both twins are along the [211] zone axis. The tilting angle between [100] and [211] zone axis of crystal 1 is 35.3°, and that between [211] and [011] zone axis of crystal 2 is 54.9°. Both are very close to the theoretical values, that is, 35.26° for the former and 54.47° for the latter. These results are consistent with the previously reported data for AgBP, indicating the twinned structure of the as-synthesized AgBP in this study, where two right pyramids are attached with their (111) facet and six (100) facets are exposed in the structure of AgBP.

After investigation of the morphology evolution process, we further studied the optical properties of AgBPs, by simulating the extinction spectra, electric field, and surface charge distribution through solving Maxwell’s equations using the finite-element method. Figure 5a shows the simulated extinction spectra for the AgBPs. According to the results, the simulation accurately predicts the main features (two LSPR peaks) of the extinction spectra in the visible region using Johnson and Christy (J&C) dielectric function. For comparison, the extinction spectrum was simulated using Palik dielectric function as well. Interesingly, Figure S4, Supporting Information reveals that only the simulated extinction spectra based on J&C data could resolve peaks sharpness due to the lower optical loss of J&C function. This simulation further verifies the high crystalline quality of the as-obtained AgBPs and the consequent lower optical losses. Such highly crystalline structure with low optical losses renders the as-synthesized AgBPs a promising candidate for plasmonic applications where high-quality factor resonances are crucial. It should be highlighted that as AgBPs have random orientations with respect to the light source, three main orientations were considered and averaged (according to Figure S5, Supporting Information) in producing the extinction spectra. To identify the origin of the two main resonance peaks, a multipole decomposition approach was applied to the simulated extinction spectra of the AgBP based on the orientations in Figure S5, Supporting Information. These results indicate that the two resonance peaks at 445 and 550 nm are mainly determined by the formation of electric dipoles (Figure 5b). The surface electric field and surface charge distributions for the different orientations of incident light further confirm the formation of dipoles along the polarization axis.

The electric field enhancement at the interface of the metal nanoparticle and surrounding environment is of great importance for different plasmonic applications including MEF, ME-SOG, and SERS. Therefore, we simulated the electric field distribution around the AgBPs under the plane-wave light with three different orientations as depicted in Figure 6. As can be observed, the hot spots are formed along the light source polarization direction on the AgBPs corners. The amplitude of the enhanced electric field for the AgBPs when it is irradiated...
by light at both resonance peaks is higher than other silver nanostructures such as sphere, cube, and prism (Figure S6, Supporting Information).[13,38] These results reveal that AgBPs could be used as the effective plasmonic enhancers for MEF, ME-SOG, and SERS applications. To confirm this ability, we obtained the Raman spectra of 1,4-benzenedithiol (1,4-BDT) as Raman probe in the presence of the as-synthesized AgBPs under excitation at 532 nm (Figure S7, Supporting Information). Results show a dramatic enhancement in the Raman peaks of 1,4-BDT when they were adsorbed onto the surface of AgBPs. The SERS enhancement factor (SERS EF) was calculated by the following equation.

\[
\text{SERS EF} = \frac{I_{\text{SERS}}}{I_{\text{Ref}}} \times \frac{N_{\text{Ref}}}{N_{\text{SERS}}}
\]

where \(I_{\text{SERS}}\) and \(I_{\text{Ref}}\) is the intensity of the same peak in the Raman spectra of SERS and reference sample. \(N_{\text{Ref}}\) and \(N_{\text{SERS}}\) refer to the concentration of Raman probe in the reference and SERS sample, respectively. The intensity of peak at 1562 cm\(^{-1}\) was used to calculate the SERS enhancement factor, which gave

![Figure 4](image1.png)

Figure 4. a) XRD pattern of the as-synthesized AgBPs. b) TEM images of a AgBP tilted around [0 1–1] direction and the corresponding SAED patterns showing its single crystalline nanostructure.

![Figure 5](image2.png)

Figure 5. a) Experimental versus simulated extinction spectra of rounded-corner AgBPs. AgBPs dimensions are extracted from the TEM image. Each right triangular pyramid has an 87 nm edge length and an 85 nm base. A radius fillet of 10 nm was used to decrease the sharpness of edges and corners. b) Multipole decomposition of simulated extinction spectra. ED: Electric dipole; MD: Magnetic dipole; EQ: Electric quadrupole; MQ: Magnetic quadrupole. c) Surface electric field and charge distribution of the AgBP under irradiation of plane-wave light with three different propagation and polarization directions.
a value of $1.50 \times 10^5$, which is higher than that reported SERS enhancement by the Ag nanocubes.\cite{8d,39} This study shows that the highly crystalline structure and multiple sharps ends of AgBPs may result in a dramatic enhancement in the electric field, leading to a higher SERS enhancement factor.

3. Conclusion

In summary, a simple and effective strategy has been developed for the synthesis of AgBPs in aqueous solution. This approach relies on the simultaneous growth of silver nanostructure and selective etching of the (111) facets via in-situ generation of $\text{H}_2\text{O}_2$ molecules on the surface of Ag nucleic, leading to the formation of single crystalline AgBPs. The proposed formation mechanism of the AgBPs through the seed-mediated growth coupled with oxidative etching has been evaluated through a series of control experiments. The twinned structure of the single crystalline AgBPs nanostructures were confirmed by the finite-element method simulation of extinction spectra using J&C data and XRD, as well as the analysis of SAED patterns of the AgBPs at different angles.

The as-produced AgBPs showed two distinct resonance peaks with a strong enhanced electric field at their corners due to the formation of electric dipoles. The structure-properties of the as-synthesized AgBPs were confirmed by both the experimental and simulation studies. Last, we have demonstrated the SERS application of the as-synthesized AgBPs with a significant enhancement factor (i.e., $1.50 \times 10^5$). We believe the successful synthesis of these single crystalline anisotropic AgBPs with high yield will find various technological applications, especially in the field of optical sensing and plasmonic enhancement such as MEF, ME-SOG, and SERS for analytical and biomedical purposes.

4. Experimental Section

Chemicals: Silver nitrate (99.9%), CTAB, NaBH$_4$, AA, (CTAC, 25% solution in water), copper(II) sulfate pentahydrate (CuSO$_4$·5H$_2$O), iron(II) chloride tetrahydrate (FeCl$_2$·4H$_2$O), iron(III) chloride hexahydrate (FeCl$_3$·6H$_2$O), and 1,4-benzenedithiol were purchased from Sigma, Germany. All the reagents were used without further purifications. Ultrapure water (>18.0 MΩ) was used in all the experiments.
Synthesis of AgBP Nanostructures: The AgBPs were synthesized via a seed-mediated growth approach. First, the Ag seeds were synthesized according to the literature. Briefly, 10 mL of 0.5 mm CTAC solution was prepared. Then, 25 μL of AgNO₃ solution (100 mM) was added to the above solution followed by the addition of 450 μL of ice-cold NaBH₄ (20 mM). After 1 min, the yellow color solution was further stirred for 40 min at 30 °C to decompose the excess NaBH₄. The as-prepared Ag seeds were used freshly for the synthesis of AgBPs. Next, 50 μL of Ag seeds was added to 7.42 mL of CTAB solution (containing 36 mg CTAB). Then, 80 μL of AgNO₃ (100 mM) and 40 μL of CuSO₄ solution (1 mM) were added to the reaction solution, and the vial was shaken gently. Finally, 4 mL of AA (50 mM) was injected into the reaction solution and the vial was capped and put in 80 °C bath under continuous stirring for 1000 rpm. The AgBPs were obtained after 2 h of reaction and washed with water (centrifugation at 10 000 g) to remove the excess CTAB and unreacted chemicals.

Instrumentation: The UV–visible spectra of the samples were measured using the Tecan microplate reader (Infinite M200, Switzerland). The JEOL JEM-2100 TEM was used to obtain the TEM images and SAED patterns. Zeta potential of the colloidal solution was measured by the Malvern Zetasizer. XRD pattern was collected on the Bruker D8 Advance diffractometer with CuKα radiation (λ = 1.54 Å). The Raman spectra were recorded using a Renishaw inVia Raman spectrometer coupled with a Leica microscope using a 100× objective.

SERS Measurements: The Raman spectra of different samples were measured using a protocol reported in the literature. Briefly, 1 mL of the as-synthesized AgBPs was mixed with 1.4-BDT (final concentration of 1.5 × 10⁻³ mM) and stirred for 1 h before SERS measurements. The 1.4-BDT (0.05 mL) in cooled 12 mL aqueous NaOH solution was used as reference. The excitation wavelength, collection time, and laser power were 532 nm, 30 s, and 50 mW, respectively. The holographic notch filter with a grating of 2400 lines mm⁻¹ was used to collect the data.

Simulation: Finite element method simulations were carried out in COMSOL Multiphysics software package (www.comsol.com) to calculate the electric field, magnetic field, surface charge distribution, absorption, scattering, and extinction cross-sections. The complex refractive index of Ag was taken from the values reported by J&C. Water is used as the surrounding environment (index of refraction, n = 1.33). A linearly polarized plane wave in the wavelength range of 300–800 nm is set as the source. The absorbance, scattering, and extinction spectra were calculated by averaging the values of different orientations of particle X-ray diffractometer with CuKα radiation (λ = 1.54 Å). The Raman spectra were recorded using a Renishaw inVia Raman spectrometer coupled with a Leica microscope using a 100× objective.

Supporting Information
Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest
The authors declare no conflict of interest.

Keywords
anisotropic morphology, controlled crystal growth, oxidative etching, seed-mediated growth, silver nanostructures, surface-enhanced Raman scattering

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