Nanostructures

Precise Control of the Lateral and Vertical Growth of Two-Dimensional Ag Nanoplates

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Abstract: Tuning localized surface plasmon resonance (LSPR) is crucial for practical applications of two-dimensional Ag nanoplates (AgNPs) and relies on the precise control of their lateral length or/and thickness. In the present seed-mediated synthetic method, by taking advantage of underpotential deposition (UPD) of Cu on the (111) surfaces of AgNPs, a solely lateral growth of AgNPs was achieved when Cu(NO$_3$)$_2$ was employed, while a vertical growth of AgNPs could be attained by introducing CuCl$_2$ into our growth solutions. The lateral length and the vertical thickness of the AgNPs could be tuned in the ranges of 115 to nearly 300 nm and 13.4 to around 200 nm, respectively. Along with control of the dimensional size of AgNPs, LSPR could also be tuned in the visible to near-infrared range. Plausible growth mechanisms for the precise control of the lateral and vertical growth of AgNPs were proposed.

Having tunable LSPR (localized surface plasmon resonance) bands ranging from the visible to near-infrared region, Ag and Au nanocrystals have found many practical applications in photonics,[1] sensing,[2] catalysis,[3] and biomedicine.[4] Their optical property shows a strong dependence to their shape and dimensional size.[5] Up to date, tremendous efforts have been made to prepare Ag and Au nanoscale products with various shapes and dimensional sizes, including plates,[6] cubes,[7] octahedron,[8] rods,[9] and their hybrid structures as well.[10] Among these, Ag nanoplates (AgNPs) have a tunable LSPR in a wide range and play vital roles in biomedical applications.[4a] Therefore, the precise control of the lateral size or/and thickness of the AgNPs have been intensively pursued.

When using thermal reduction synthesis in solution, the anisotropic growth of AgNPs has been dictated by their inner defect structure with planar orientation (stacking faults).[11] Further tuning of the dimensional sizes of AgNPs could be achieved through the control of the lateral and vertical growth with the help of organic additives.[8a,12] In the presence of citrate, a reagent that tends to be selectively adsorbed on the top and bottom (111) faces of AgNP, the growth rate along the vertical direction was slowed down, while the lateral growth rate remained relatively unchanged.[64] When polyvinylpyrrolidone (PVP) was used, thicker AgNPs could be obtained as a result of suppressing lateral growth due to the preferential adsorption of PVP on the (100) facet at the lateral sides.[12] However, in both cases, the control over one of these two growth dimensions (lateral and vertical) is usually accompanied with the lack of control of the other.[12]

In addition to organic additives, foreign inorganic ions have been also used for the same purpose.[13] The most classical example is the synthesis of gold nanorods through a seed-mediated method.[14] By introducing Ag$^+$ and cetyltrimethylammonium bromide (CTAB), it is easy to realize the controllable synthesis of Au nanorods with tunable longitudinal and transverse dimensions. Although the CTAB surfactant was proposed to play the role of a soft template or surface passivation agent, more and more evidences revealed that the underpotential deposition (UPD) of Ag on the side facets of gold nanorods hindered the transvers growth and led to a longitudinal growth.[14c] Furthermore, as demonstrated by Mirkin et al.,[14e] the role of UPD could be modulated by introducing various halides, leading to the suppression or enhancement of specific face growth. Taking advantage of this strategy, a series of gold nanoparticles such as concave cubes, tetrahedra, and trioctahedra have been produced. Besides Ag UPD, Cu UPD has also been proven to be efficient for the surface-controlled growth of Pd and Pt nanoparticles.[13c, e, 4]

Herein, we demonstrate efficient approaches to maintain an either solely lateral growth of AgNPs under the Cu UPD or purely vertical growth of AgNPs with the presence of Cl$^-$ by the seed-mediated method. The only difference that lies between the two processes is the use of different copper salts. The validity of these two methods could be further confirmed by switching between lateral and vertical growth in several successive growth steps by selecting either Cu(NO$_3$)$_2$ or CuCl$_2$ as inorganic additive. The lateral size of the Ag triangular nanoplates could be precisely controlled in the continuous range of 115 to nearly 300 nm through controlling the amounts of AgNO$_3$ and ascorbic acid solutions. Meanwhile, the
vertical growth mode of Ag nanoplates can be exclusively achieved until the formations of complete bipyramidal and cubic nanostructures. In addition to these, the success in controlling their dimensional sizes allows us to tune their corresponding LSPRs.

The direction-controlled growth of AgNPs was achieved by using three consecutive seed-mediated methods as shown in Scheme 1. In the first seeded process, round Ag nanoplate seeds with lateral size around 22 nm (Figure S1 in the Supporting Information) were allowed to grow into triangular AgNPs, which will be used as secondary seeds for subsequent direction-controlled growth processes. The details for the synthesis of the round Ag nanoplate seeds as well as the secondary larger triangular AgNPs seeds are provided in the Supporting Information. Although some hexagonal nanoplates and few irregular nanoparticles coexisted, the dominant products for the secondary seed reaction are triangular AgNPs, which have an average lateral size of 133 nm and a thickness of 13.4 nm given from the SEM images and AFM analysis (Figure 1a–c and Figure S2a–b in the Supporting Information). The obtained AgNPs are rather uniform and have a narrow size distribution resulting from the size focusing effect\(^\text{[15]}\) in the subsequent overgrowth process. After redispersing the secondary triangular AgNP seeds into 6.0 mL ultrapure water, 1.0 mL of sodium citrate (25 mM) and 1.0 mL of PVP (25 mM for repeat unit) were added to the secondary seeded solution to form a growth solution. Further simultaneous additions of 2.0 mL AgNO\(_3\) (5.0 mM) and 2.0 mL ascorbic acid (AA, 5.0 mM) solutions to the growth solution using a peristaltic pump with the presence of 0.3 mL of CuX\(_2\) (X = NO\(_3\) or Cl) (25 mM) would yield different AgNPs as a result of different growth modes.

For the growth using Tri-AgNP seeds as secondary seeds with the presence of Cu(NO\(_3\))\(_2\), similar triangular AgNPs as the major product with larger lateral length were obtained (Figure 1d). The average lateral length was increased to 230 nm, while their thickness remained nearly unchanged (Figure 1e–f and Figure S2c–d in the Supporting Information). When Cu(NO\(_3\))\(_2\) was substituted by CuCl\(_2\), the overall morphology was hexagonal (truncated triangular). The average lateral size of the hexagonal nanoplate is 115 nm, less than that of the triangular AgNP seeds due to the truncation of the corners of Tri-AgNPs (Figure 1g). Along with this truncation, the thickness was increased up to 23.5 nm (Figure 1h–i and Figure S2e–f in the Supporting Information). For the sake of clarity, the two products obtained with the presence of Cu(NO\(_3\))\(_2\) and CuCl\(_2\) were

Scheme 1. Schematic illustration showing the growth processes of silver nanoplates. The triangular AgNPs (Tri-AgNPs) grew from the 1st seeds (round Ag nanoplate seeds), and then served as secondary seeds for the growth of AgNP-LG (lateral growth) and AgNP-VG (vertical growth). Subsequently, AgNP-VG served as the third seeds for following lateral and vertical growth processes. The green and blue arrows denote lateral and vertical growth processes, respectively.

Figure 1. a, d, g) SEM, and b, e, h) AFM images with corresponding height profiles (c, f, i) for Tri-AgNPs, AgNPs-LG, and AgNPs-VG, respectively.
termed as AgNP-LG and AgNP-VG, respectively, in which the LG and VG denote lateral growth and vertical growth accordingly. Accompanying with the increases of the dimensional sizes of the two products after growth, the main LSPR bands show a redshift from 990 to 1150 nm for AgNP-LG and a blue-shift from 990 to 685 nm for AgNP-VG (Figure S3).

TEM was also used to characterize these two products, which was supported on molybdenum grids covered with an ultrathin carbon film. For AgNP-LG, most of the particles are triangular nanoplates with lateral length about 230 nm (Figure 2a). As to AgNP-VG, the nanoplates nearly exclusively show a hexagonal morphology (Figure 2c). The lateral size of the hexagons is about 115 nm. Both shapes and dimensional sizes are consistent with those observed from SEM measurements (Figure 1d,g). The lattice fringe with a spacing of 2.5 Å for both samples could be obtained in the high-resolution TEM (HRTEM) images (insets in Figure 2a,c) and forbidden 1/3(422) spots were discernible in their selected area electron diffraction (SAED) patterns (Figure S4). These suggest the presence of stacking faults (or planar defects) in both nanoplates.[6a,11] Elemental analysis was also carried out by scanning transmission electron microscopy energy-dispersive X-ray spectroscopy (STEM-EDX) elemental mapping (Figure 2b,d). Signals of Ag and Cu were found to be evenly distributed on both nanoplates, but the intensity of Cu was much lower than that of Ag. Such distribution was also observed from the side of a hexagonal AgNP-VG nanoplate standing on the supported membrane (Figure S5). On the basis of these analyses, the uniform distribution of Cu throughout the two kinds of nanoplates suggests that Cu would enter into the Ag crystal lattice to form an AgCu alloy. The occurrence of metallic Cu on both samples was also confirmed from XPS measurement (Figure S6). Additionally, XPS results indicated that Cl⁻ was adsorbed on AgNP-VG. However, neither Cu nor Cl could be found in the two samples using inductively coupled plasma atomic emission spectroscopy (ICP-AES), which indicates that their contents in the samples are extremely low.

The above experimental results imply that Cu or/and Cl could exert dramatic influence on the growth mode of Ag nanostructures. By substituting Cu(NO₃)₂ by CuSO₄ or Cu(CH₃COO)₂, nearly identical extinction spectra were obtained as shown in Figure S7 in the Supporting Information. If no copper salt was added to the secondary seed solution, an AgNP sample with a main LSPR band blueshift to 930 nm (Figure S7) was obtained, which implies that a vertical growth leading to increasing thickness might be involved.[16] These observations suggest that Cu²⁺ favors lateral and suppresses vertical growth of the AgNPs. To unveil the effect of Cl⁻ on the growth of triangular AgNPs, a NaCl solution with the same amount of Cl⁻ to that of CuCl₂ was added into the growth solution. However, the formation of a AgCl precipitate (Figure S8) made our control experiment toward studying this effect infeasible. This implies that the reduction of Ag⁺ could be accelerated with the coexistence of Cu²⁺ and Cl⁻ in our reaction system, otherwise a AgCl precipitate would be formed. A similar phenomenon was observed for Pd nanocubes, in which the growth rate was significantly increased with the presence of RuCl₃.[17]

An additional experiment was carried out through the standard procedure but in the absence of Ag seeds and without adding AgNO₃. No Cu particles were observed, indicating that Cu²⁺ cannot be reduced directly by ascorbic acid. It is reasonable that the standard reduction potential of Cu²⁺ (Cu²⁺ + 2e⁻ → Cu with E° = 0.34 V) is much lower than that of Ag⁺ (Ag⁺ + e⁻ → Ag with E° = 0.80 V). The formation of a AgCu alloy in our experiments could be interpreted using the well-known underpotential deposition (UPD) mechanism.[13c,d] UPD allows the reduction of metal ions to occur at a lower redox potential than its standard reduction potential. During the UPD controlled growth, a thin layer of AgCu alloy can be formed on the surface and has a profound effect on the nanocrystal growth kinetics and subsequent morphology.[13d,e,14b] This is similar to early reported works for the preparation of Au nanorods using Ag UPD, in which the deposition of Au at the transvers sides was suppressed as a result of Ag UPD.[14] When CuCl₂ was introduced into our growth solution, the lateral growth was changed into vertical growth. Based on our findings here and understanding toward this process, we propose plausible growth mechanisms for the two growth modes. During the lateral growth process, the stacking faults have higher surface energy and are believed to be responsible for such growth. Cu UPD makes the surface energy of (111) lower and favors the lateral growth. The presence of Cl⁻, which tend to be absorbed by the defect sites on the stacking faults as well as (100) faces, reduces their surface energies and results in the surface energy of them even lower than that of the (111) surface. The lateral growth was then suppressed and the verti-

![Figure 2. a) TEM image of AgNP-LG. b) HAADF-STEM image and corresponding STEM-EDX elemental mappings of AgNP-LG. c) TEM image of AgNP-VG. d) HAADF-STEM image and corresponding STEM-EDX elemental mappings (including line scanning) of AgNP-VG. The insets in (a) and (c) are the corresponding HRTEM images (scale bars for both samples are 2.0 nm).](image-url)
cal growth became dominant. This is similar to previous studies in which halides had a profound effect on the Ag UPD directed growth of Au nanocrystals. On the contrary, in the growth of Au nanocubes, the introduced Br destabilized the Ag UPD layer and favored Au deposition, leading to the formation of convex nanocubes.

To validate the above proposed growth mechanism, further lateral and vertical growth experiments were carried out on AgNP-VG after the secondary seeded growth by adding different volumes of 5.0 mM AgNO₃ with the presence of, again, Cu(NO₃)₂ or CuCl₂. The volumes of 5.0 mM AgNO₃ that were added to the growth solution were 0.5, 1.0, 1.5, and 2.0 mL. When Cu(NO₃)₂ was present, the growth mode of AgNP-VG was changed back into lateral growth. The SEM images in Figure 3 show that the plate-like shape is maintained and the lateral sizes change to 180, 220, 262, and 300 nm, respectively. The final thickness of the largest Ag nanoparticles after lateral growth is close to the original AgNP-VG (Figure 3e). For comparison, when no Cu²⁺ was added to the growth solution, both lateral and vertical growth could be observed for AgNP-VG (Figure S9). Along with this, small particles originating from new nucleation events were produced. This again suggests that Cu UPD plays an important role for the lateral growth. With a large ratio of lateral length to thickness, AgNPs exhibit extraordinary optical properties. As shown in Figure 3f, AgNP-VG have four LSPR bands (black line) with peaks at 685, 493, 400, and 343 nm, which are indexed to in-plane dipole resonance, in-plane quadrupole resonance, out-of-plane dipole resonance, and out-of-plane quadrupole resonance, respectively. With increasing lateral size after lateral growth, both the in-plane dipole and quadrupole resonance peaks of the AgNPs tend to redshift from 680 nm to 780, 890, 1015, and 1230 nm and from 493 nm to 513, 558, 620, and 735 nm, respectively (Figure 3f). The other two LSPR bands remain nearly unchanged as a result of the similar thickness. In this lateral growth, the changes of the lateral size along with the LSPR bands indicate that controlling the lateral size is an efficient way to tune the LSPR bands in a broad region.

With increasing volume of AgNO₃ to be added for the growth of AgNP-VG in the presence of CuCl₂, the vertical growth of the nanoparticles could be maintained and the thickness gradually increased from 48 nm to 67, 99, and 200 nm, while the lateral size remained nearly unchanged (Figure 4 and Figure S10 in the Supporting Information). More interesting, it was found that the particles eventually evolved into two kinds of polyhedral nanostructures, namely, cubes and bipyramids. To fulfill a complete growth of the polyhedral particles, the reaction with 4.0 mL of a 5.0 mM AgNO₃ solution was also inves-
tigated (Figure 4d). Panoramic SEM images of all five samples were provided in Figure S10. As illustrated by geometric models (Figure 4e–h, i–l), the bipyramids evolved from triangle nanoparticles, while the cubes originate from hexagonal nanoparticles. According to Kitaev et al., the number of stacking faults in the AgNPs determines the final shape. It has been demonstrated that odd-numbered stacking faults is the prerequisite to form bipyramids and even-numbered stacking faults result in the formation of nanocubes. From a random point of view, the occurrence of either even-numbered or odd-numbered stacking faults should be 50%, which is close to our observations of those two shapes in Figure 4 and Figure S10 in the Supporting Information. Although twinned silver nanocubes were also prepared by a plasmon-mediated process, however, as far as we know, it is the first time that truncated octahedron (Figure S11) are captured as the intermediate during the shape evolution from hexagonal nanoparticles to nanocubes. The lattice spacing calculated from HRTEM results is 0.20 nm (Figure S12) parallel to the surface face of the bipyramid, which is indexed to the (100) face of fcc Ag. Therefore, both polyhedral nanoparticles obtained here were enclosed by (100) faces.

The LSPR bands also varied along with the continuous vertical growth. As shown in Figure 4t, with increasing volume of the AgNO₃ solution from 0.5 to 2.0 mL, the in-plane dipole resonance was firstly blueshifted to 648 nm and then changed marginally. Further increasing the volume to 4.0 mL moves the redshift to 755 nm, which might be due to the increase of the edge length of nanocubes and nanobipyramids. The out-of-plane dipole resonance band was redshifted from 370 nm to 377, 398, 410, 419, and 450 nm with increasing thickness. Furthermore, its intensity also increased and eventually it became dominant in the mixture of the two polyhedral particles. Also the in-plane quadrupole resonance band gradually blueshifted in the range from 500 to 450 nm and nearly vanished in the polyhedral mixture of particles. The vertical growth of AgNPs demonstrated that a precise control of the thickness is vital for manipulating the resonance modes and relative intensities.

In summary, we precisely controlled the lateral or vertical growth of AgNPs using a seed-mediated strategy with the presence of different copper salts. An exclusive lateral growth of AgNPs was attained under Cu UPD conditions, in which copper salts other than CuCl₂ were present in the reaction systems. With the presence of CuCl₂, the lateral growth mode was completely changed to vertical growth as a result of adsorption of Cl⁻ by stacking defects. The two growth modes could be switched by changing the two copper salts in the growth solution. Two dimensional AgNPs could completely evolve into nanoscale Ag bipyramids and cubes, depending on the number of stacking faults in the AgNPs. The success in precisely controlling the lateral length of the AgNP under the Cu UPD process makes the fine tuning of the LSPR bands of AgNPs possible.

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Conflict of interest

The authors declare no conflict of interest.

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