

Poly(vinylpyrrolidone)-Free Multistep Synthesis of Silver Nanoplates with Plasmon Resonance in the Near Infrared Range

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Herein, a poly(vinylpyrrolidone) (PVP)-free method is described for synthesizing Ag nanoplates that have localized surface plasmon resonance in the near-infrared (NIR) range. Citrate-capped Ag spherical nanoparticles are first grown into small Ag nanoplates that resonate in the range of 500–800 nm. The small Ag nanoplates are used as seeds to further grow into large Ag nanoplates with a lateral dimension of 100–600 nm and a plasmon resonance wavelength of 800–1660 nm and above. The number of growth steps can be increased as desired. Without introducing additional citrate into the solutions of small Ag nanoplate seeds, large Ag nanoplates can be synthesized within minutes. The entire synthesis is completely PVP free, which promotes the nanoparticle growth along the lateral direction to form large Ag nanoplates. The multistep growth and the minimum usage of citrate are essential for the fast growth of high-aspect-ratio Ag nanoplates resonating in the NIR range.


Plasmonic nanoparticles are important building-block materials that have vast potential in applications including sensing,^[1,2] imaging,^[3,4] catalysis,^[5,6] photovoltaics,^[7] memory storage,^[8] and microelectronics.^[9] Particularly, plasmonic nanoparticles with plasmon resonance in the near-infrared (NIR) range have been used in cell imaging,^[10] photothermal therapy,^[3,11,12] and optical communication^[12–14] because of their excellent capability of penetrating tissues and other barriers. To prepare plasmonic nanoparticles in the NIR range, nanoparticles of various shapes have been synthesized including nanoplates,^[15,16] nanorods,^[17] nanoshells,^[18] nanocrescents,^[19] and nanocages.^[20] Among them, Ag nanoplates are most attractive because they have a wide range of tunable plasmon resonance wavelengths and can be synthesized via a variety of methods.^[16,21–26] Most of the methods, however, require long

hours to finish the synthesis and involve poly(vinylpyrrolidone) (PVP), which has to be removed to facilitate the growth along the lateral direction of the seeds. Herein, we describe a PVP-free method for synthesizing Ag nanoplates that resonate in the NIR range. The new method is simple, easy, and fast. It requires no complicated post-synthesis purification.

The currently available methods for seed-mediated synthesis of Ag nanoplates are either thermal^[22–24,26] or photo-induced.^[16,21,22,27,28] Nanoplates, which means that the nanoparticles have a platelet-like shape, include triangular nanoprisms, rounded nanodisks, and hexagonal plates. All these 2D nanoplates follow a similar synthesis mechanism. The surface capping agent plays a key role in the growth of spherical seeds into nanoplates.^[24,25] Previously, PVP was typically used to prepare Ag seeds and nanoplates.^[15,24,26] For example, Xia and co-workers used PVP to prepare Ag nanoplates resonating in the visible and NIR range.^[15] In this synthesis reaction, PVP served as both a surface capping agent and a mild reducing agent for AgNO₃. By using PVP as a polymer ligand, Liz-Marzán and co-workers reported a photoinduced method^[16] to prepare large Ag nanoplates with plasmon resonance in the NIR range. Both methods, however, required long hours (≈24–96 h) to complete the synthesis reaction or the plasmon resonance of the nanoparticles would not reach the NIR range. Later work by Xia and co-workers showed that the absence of PVP was essential for synthesizing high-aspect-ratio Ag nanoplates. PVP blocked the Ag{100} surfaces and promoted the growth along the Ag<111> directions, resulting in thick Ag nanoplates. On the contrary, citrate binded strongly to the Ag{111} surfaces and facilitated the crystal growth along the lateral direction, leading to thin Ag nanoplates with high aspect ratios.^[24] To minimize PVP usage and speed up the synthesis process, Yin and co-workers exchanged the capping agent of Ag seeds from PVP to citrate and synthesized large Ag nanoplates via multiple growth steps. The exchange of PVP with citrate, however, required laborious purification steps.^[26] In addition, although the amount of PVP molecules in colloidal solutions of Ag nanoparticles can be minimized by centrifugation, those adsorbed on the nanoparticle surfaces can be challenging to be removed. The adsorbed PVP molecules contribute to a significant polymer layer around the nanoparticles, as seen under

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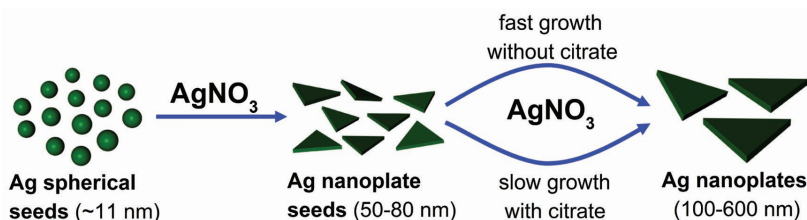


Figure 1. Schematic illustration of the multistep growth of large Ag nanoplates with plasmon resonance in the NIR range. Ag spherical seeds are first grown into small Ag nanoplates resonating in the visible light range, which are used as seeds to further grow into large Ag nanoplates resonating in the NIR range. The growth rate can be modulated by citrate. The numbers in the parentheses are nanoparticle sizes.

high resolution transmission electron microscopy (TEM).^[16] The layer of PVP is detrimental and prevents the nanoparticles from subsequent ligand exchange and surface functionalization. Therefore, a method that is completely PVP free and solely based on citrate is highly desirable for easy and fast synthesis of Ag nanoplates with high aspect ratios and plasmon resonance wavelengths in the NIR range.

To avoid using PVP as a surface directing agent, Kelly and co-workers^[23] have developed a thermal method based on citrate for synthesizing Ag nanoprisms via one-step growth. This method is fast and only requires a few minutes to finish the synthesis, however, it is challenging to synthesize large Ag nanoplates that resonate in the NIR range. Herein, we propose that large Ag nanoplates can be synthesized via multistep growth from citrate-capped Ag spherical seeds, similar to the synthesis of high-aspect-ratio Au nanorods reported by Murphy and co-workers.^[29] Through the multistep seed-mediated synthesis, we can prepare large Ag nanoplates that resonate in the NIR range. The synthesis is completely free of PVP and the Ag spherical seeds can be prepared in an aqueous solution of citrate. We have investigated the effect of citrate on the growth rate of Ag nanoplates. Without capping the Ag nanoplate seeds with additional citrate, the entire synthesis reaction can be finished within minutes.

The synthesis procedure of large Ag nanoplates is as follows (**Figure 1**). First, small Ag spherical seeds were prepared by reducing AgNO₃ using a strong reducing agent NaBH₄ in the presence of trisodium citrate and poly(sodium 4-styrenesulfonate) (PSSS). PSSS is known to play a key role in controlling the defective structures in Ag spherical seeds. As suggested by Kelly and co-workers, Ag spherical seeds that were produced without PSSS led to polydisperse nanoprisms and nanospheres.^[23] Since PSSS was only used in the synthesis of Ag seeds and no PSSS was added in the subsequent growth steps, the concentration was low and decreased with additional growth steps. The Ag spherical seeds were then grown into small Ag nanoplate seeds of different sizes by adding AgNO₃ and a weak reducing agent ascorbic acid (AA). Finally, the small Ag nanoplate seeds were grown into large Ag nanoplates resonating in the NIR range. The number of growth steps from the small Ag nanoplates to the large Ag nanoplates can be increased as needed. The small Ag nanoplate seeds may or may not be capped with additional citrate, which determines the rate of the subsequent growth steps. It is expected that the subsequent growth steps are fast and can be finished within

minutes if the small Ag nanoplate seeds are not capped with additional citrate. Otherwise the growth rate is slow and it takes hours to finish the synthesis of nanoplates.

To evaluate the feasibility of growing large Ag nanoplates via multisteps, we first tested the synthesis of Ag nanoplates via two-step growth (**Figure 2**). The Ag spherical seed solution appeared yellow [**Figure 2A(a)**] and had a localized surface plasmon resonance wavelength (λ_{LSPR}) of 394 nm [**Figure 2B(a)**]. The Ag spherical seeds were then grown into small Ag nanoplate seeds. The solution appeared blue [**Figure 2A(b)**] and had a λ_{LSPR}

of 596 nm. To further grow large Ag nanoplates of various sizes, solutions of a constant amount of AgNO₃ were introduced into a series of reactors containing various amounts of the Ag nanoplate seeds (0.5–1.4 mL). To allow for a fast growth rate, no additional citrate was added to the Ag nanoplate seed solution. After the second growth, the resulting solutions contained large Ag nanoplates and had light colors [**Figure 2A(c–f)**]. The corresponding UV–vis–NIR spectra confirmed that the large Ag nanoplates had in-plane dipole resonance wavelengths of 796, 914, 1014, and 1160 nm, respectively [**Figure 2B(c–f)**]. Although the in-plane dipole resonance peaks were in the NIR range, the in-plane quadrupole resonance peaks were still in the visible light range but had comparatively low intensities, similar to the Au nanoprisms.^[30,31] The light colors are attributed to the in-plane quadrupole resonance of the nanoparticles. Regardless of the size, all Ag nanoplates had a characteristic peak at ≈ 330 nm, which corresponded to the out-of-plane quadrupole resonance of the Ag nanoplates.^[28]

The Ag nanoparticles were imaged by TEM. Most Ag nanoplates had a prismatic shape, but other shapes such as hexagon, rounded disk, and truncated prism were also present, especially when the nanoplates were small in size (**Figure 2C** and **Figure S1**, Supporting Information). As determined with dynamic light scattering (DLS) (**Figure S2**, Supporting Information), the size distribution of the Ag nanoplates became broader as the size increased, in agreement with the UV–vis–NIR spectra which had broader LSPR peaks (**Figure 2B**). For typical nanoparticle synthesis, the size dispersity is expected to increase with the nanoparticle size. Using citrate to cap the Ag nanoplate seeds can slightly decrease the size distribution. However, since DLS can only estimate the approximate size of the nanoparticles, especially anisotropic nanoplates, we cannot obtain the growth mechanism based solely on the DLS data. The average diameter of the Ag spherical seeds was 11 nm as determined with DLS. High-resolution TEM images revealed that the spherical seeds had polycrystalline structures with twin defects (**Figure S3**, Supporting Information). As reported previously,^[16,23,25,32] the twin defects were required for the crystal to grow along the lateral direction and form Ag nanoplates. The twin defects acted as self-propagating sites for adding Ag atoms.^[25,33] Although no additional citrate was introduced to the growth solution, there were sufficient citrate molecules to bind strongly onto the Ag{111} surfaces and weakly to the others,^[25] and thus facilitated the growth along the lateral direction to generate large Ag nanoplates.

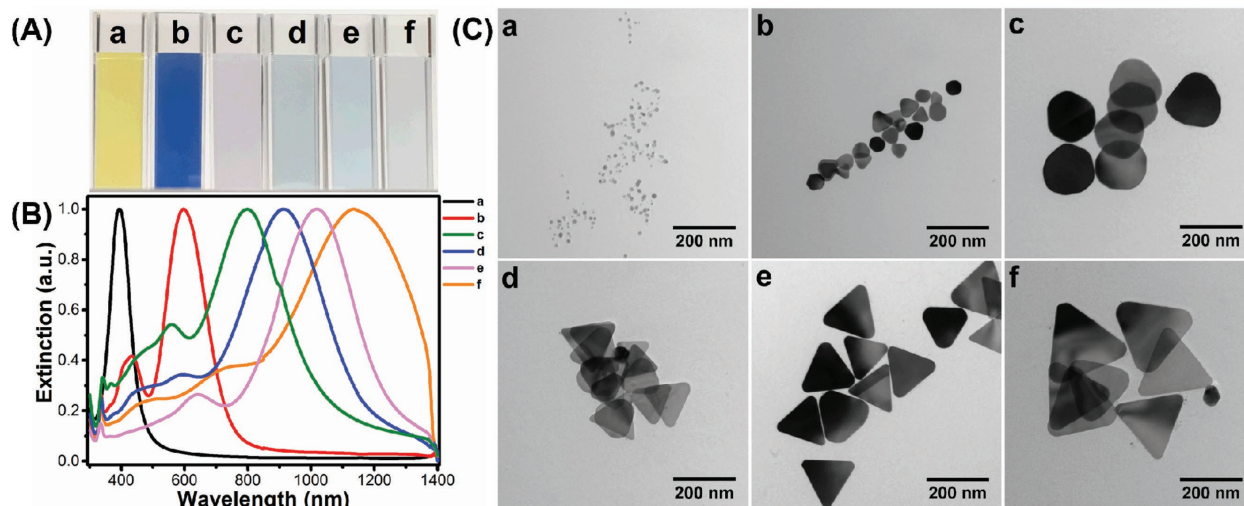


Figure 2. Two-step growth of large Ag nanoplates without introducing additional citrate after the first growth step. A) Optical graph of the Ag nanoparticles at various growth steps. a) Ag spherical seeds stabilized by citrate and b) small Ag nanoplate seeds after the first growth. No additional citrate was added. Large Ag nanoplates further grown from various amounts of the small Ag nanoplate seeds: c) 1.4 mL, d) 1.0 mL, e) 0.7 mL, and f) 0.5 mL. After the second growth, citrate was added to stabilize the Ag nanoplates. B) The corresponding UV-vis-NIR extinction spectra of the Ag nanoparticles. C) The corresponding TEM images of the Ag nanoparticles.

To examine the effect of citrate on the growth rate, the small Ag nanoplate seeds were capped with additional citrate and then used for growing large Ag nanoplates under similar reaction conditions. Due to an excess of citrate molecules on the Ag nanoplate seeds, a much longer time was required for the small Ag nanoplates to grow into large Ag nanoplates. **Figure 3** shows the optical graph and UV-vis-NIR spectra of the seeds and nanoplates. The small Ag nanoplate seeds used here were grown from a different batch of Ag spherical seeds and the size was slightly larger than those in Figure 2. Typically, 10 μ L of Ag spherical seeds were used to prepare Ag nanoplate seeds in the first growth step, but the concentration of Ag spherical seeds differed slightly from batch to batch. Therefore, the concentration of the Ag nanoplate seeds differed from batch to batch and different amounts of Ag nanoplate seeds were used in the subsequent growth steps. Regardless of the exact concentrations, the spherical or nanoplate seeds grew into large Ag nanoplates follows the same trend. As a result, the solutions of large Ag nanoplates had similar light colors (Figure 3A). The in-plane dipole resonance peaks of the large Ag nanoplates redshifted from the visible to the NIR range, and the in-plane quadrupole resonance peaks redshifted as the nanoplate size increased (Figure 3B). The plate-like shape of the nanoparticles was confirmed by TEM (Figure S4, Supporting Information). A variety of 2D plate-like nanoparticles were observed, including discs, hexagonal plates, and truncated prisms. To get an estimated size of the nanoplates, we diluted the nanoplate solutions and obtained the size statistics using DLS (Figure S5, Supporting Information). The size distributions were relatively narrow in comparison with those synthesized from nanoplate seeds without introducing additional citrate (Figure S2, Supporting Information), suggesting that the fast growth rate and the narrow size distribution were trade-off factors. If the nanoplate

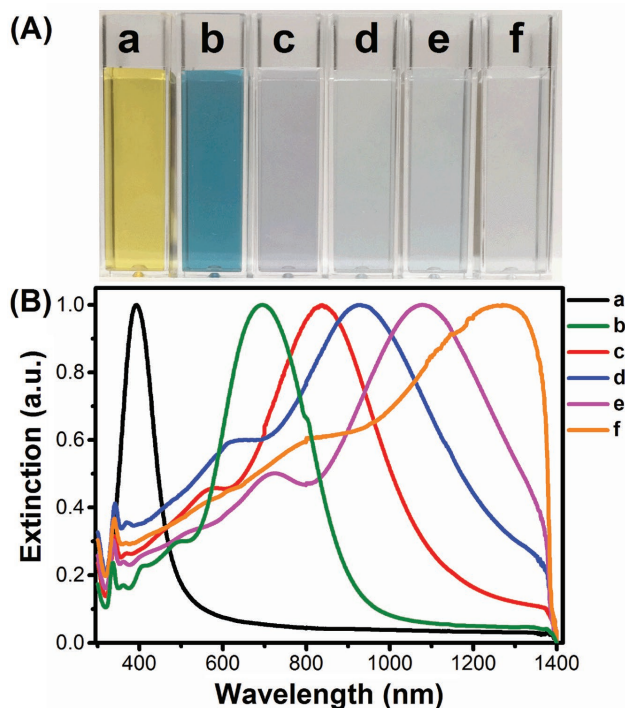


Figure 3. Two-step growth of large Ag nanoplates. The small Ag nanoplate seeds were capped with additional citrate after the first growth step. A) Optical graph of Ag nanoparticles at various growth steps. a) Ag spherical seeds stabilized by citrate and b) small Ag nanoplate seeds after introducing additional citrate. c-f) Large Ag nanoplates grown from various amounts of the small Ag nanoplate seeds. The amount of Ag nanoplate seeds ranged from (c) 2.0 to (f) 0.5 mL. B) The corresponding UV-vis-NIR extinction spectra.

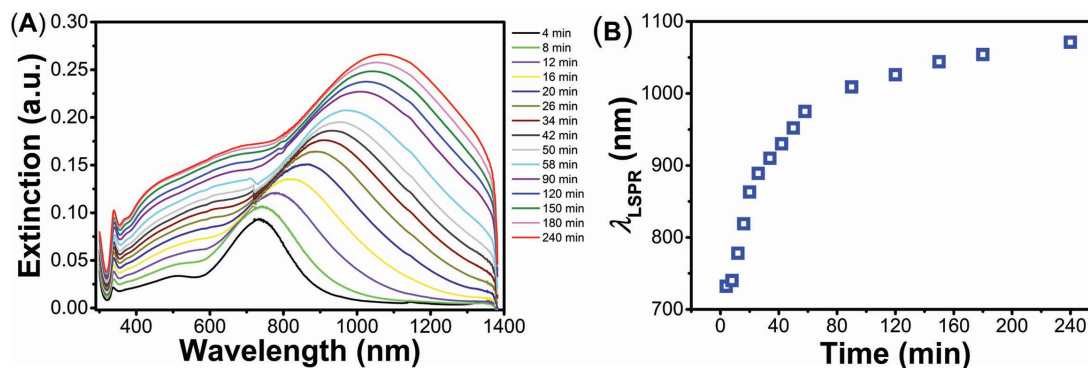


Figure 4. A) Evolution of the extinction spectra from small Ag nanoplates to large Ag nanoplates. The small Ag nanoplates were stabilized by adding citrate to slow down the growth so that there was sufficient interval time to collect the UV-vis-NIR spectra. B) λ_{LSPR} as a function of growth time.

seeds were not capped with additional citrate, the growth rate was fast but the resulting nanoparticles had a relatively broad size distribution. On the contrary, if the nanoplate seeds were capped with additional citrate, the growth rate was slow but the resulting nanoparticles had a relatively narrow size distribution.

The introduction of additional citrate to the Ag nanoplate seeds did not have a prominent effect on the final shape of the nanoparticles, but it allowed for investigating the spectral evolution during the growth of large Ag nanoplates. UV-vis-NIR spectra were taken at intervals (Figure 4). The λ_{LSPR} shifted fast within the first hour, then it stabilized and did not shift much after ≈ 3 –4 h. The slow growth of the Ag nanoplates is attributed to the interaction between the Ag nanoplate surfaces and the citrate molecules. Although the interaction between citrate and Ag{100} is weaker than that between citrate and Ag{111},^[34–36] an excess of citrate in the growth solution results in a dense layer of citrate on the Ag{100} surfaces. Only when the citrate molecules intermittently desorb from the Ag{100} surfaces, incoming Ag atoms can be adsorbed onto the nanoplate lateral edges and continue the nanoplate growth to achieve a high aspect ratio. The slow spectral evolution (Figure 4) suggests that, at a high concentration of citrate, the desorption rate of the citrate from the Ag nanoparticle surfaces was slow, which induced a slow nanoparticle growth rate. Therefore, a sufficient but minimum amount of citrate is required for the fast growth of Ag nanoplates with a high aspect ratio and a long λ_{LSPR} in the NIR range.

We further investigated the effect of the aging time of the Ag spherical and nanoplate seeds on the growth of large Ag nanoplates. We observed that the synthesis of Ag nanoplate seeds strongly depended on the aging time of the Ag spherical seeds. The Ag spherical seeds aged for a short time produced larger Ag nanoplate seeds than those aged for a long time did (for example, 5 and 10 min vs 120 min) (Figures S6 and S7, Supporting Information). Similarly, the growth of the large Ag nanoplates strongly depended on the aging time of the Ag nanoplate seeds when they were not capped with additional citrate. As the aging time of the Ag nanoplate seeds increased, the λ_{LSPR} of the large Ag nanoplates blueshifted (Figure S6, Supporting Information). In contrast, when the Ag nanoplate seeds were capped with additional citrate, the aging time was not as

critical and λ_{LSPR} of the large Ag nanoplates did not blueshift significantly (Figure S7, Supporting Information).

To further examine the effect of aging on Ag spherical and nanoplate seeds, UV-vis spectra were taken every 15 min for the first 3 h after seed preparation (Figure S8, Supporting Information). The position of the extinction peaks of the Ag spherical seeds, which were capped with citrate, remained constant but the intensity increased slightly with time. For Ag nanoplates seeds capped with additional citrate, the plasmon resonance peak blueshifted and the intensity decreased slightly. For Ag nanoplate seeds not capped with additional citrate, the plasmon resonance peak blueshifted slightly but the intensity increased. The increase in extinction peak intensity indicates that the concentration of the nanoplate seeds increased with time. The unreacted Ag^+ ions were probably reduced slowly which eventually led to an increase in nanoparticle concentration. For Ag nanoplate seeds either capped or not capped with additional citrate, λ_{LSPR} blueshifted and the nanoplate seeds tended to reach an equilibrated state that had a slightly smaller nanoparticle size. The absence of additional citrate shortened the time to reach the equilibrium and decreased the barrier for further growth into large nanoplates.

After demonstrating the feasibility of two-step growth, we continued to synthesize large Ag nanoplates via multiple steps (Figure 5). As shown in Figure 5A, small Ag spherical seeds (a) were first grown into Ag nanoplates (b); then (b) was used as seeds to grow into (c); (c) was used to grow into (d); lastly, (d) was used to grow into (e). To make sure the Ag nanoplate seeds can be immediately used in the next growth step, all nanoplates were not capped with additional citrate until the last step, that is, when (e) was synthesized. Each growth step required ≈ 3 –4 min, and a four-step growth of nanoplates from (a) to (e) cost a total time of ≈ 16 min, which was faster than any methods reported before. The corresponding optical graph, UV-vis-NIR spectra, and TEM images of the nanoplates are shown in Figure 5B–D, respectively. As the number of growth steps increased, the color of the nanoplate solutions faded, the in-plane dipole resonance peak redshifted, and the size of the nanoplates increased. To further increase the final Ag nanoplate size, we can increase the number of growth steps (Figure S9, Supporting Information) or maximize the growth in each step by adding slightly

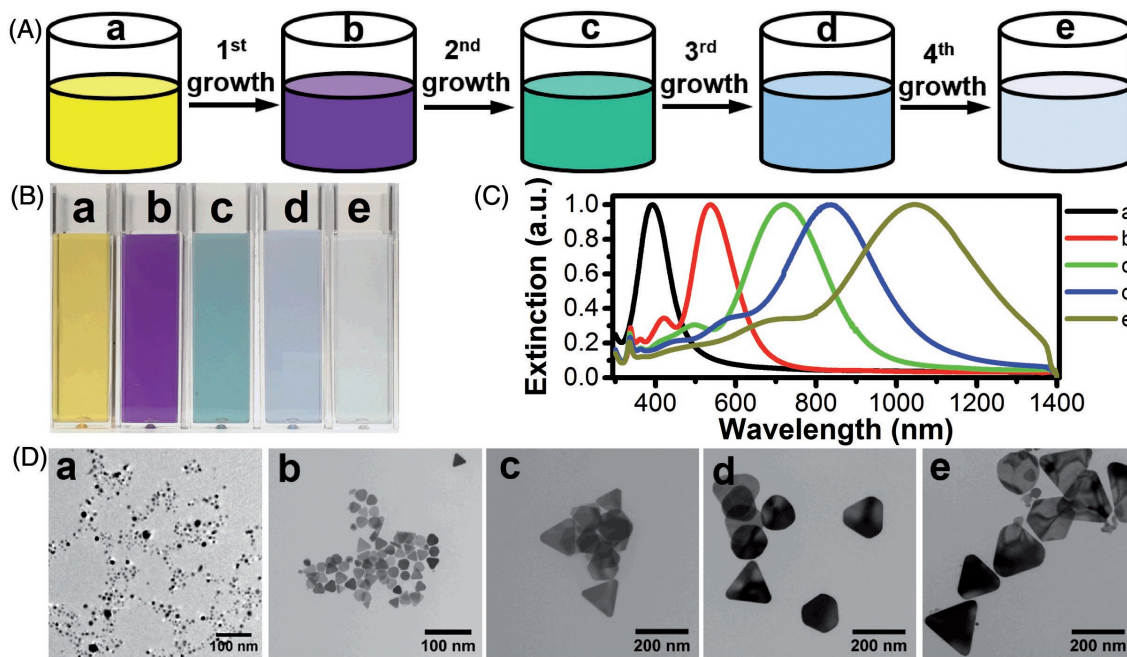


Figure 5. A) Schematic illustration of the multistep growth of large Ag nanoplates. Nanoplates (b)–(e) were synthesized through one, two, three, and four growth steps, respectively. B) Optical graph, C) UV–vis–NIR extinction spectra, and D) TEM images of the Ag nanoparticles.

more metal precursors (Figure S10, Supporting Information). For example, Ag nanoplates with an in-plane dipole resonance peak at 1660 nm were obtained (Figure S10, Supporting Information). High-resolution TEM images confirmed that the large Ag nanoplates were highly crystalline (Figure S11, Supporting Information). The nanoparticles retained the 2D shape through the multiple growth steps, as shown by the TEM images (Figure 5D and Figures S9 and S10, Supporting Information).

The mean diameter of the Ag nanoplates varied from 77 to 600 nm. The thickness of the nanoplates was determined using TEM by stacking the nanoplates on the side edges or using atomic force microscopy. Based on the diameter and thickness measurements, the aspect ratio of the nanoplates ranged from 4.5 to 50. The upper bound of our aspect ratio is among the highest values of all reported methods that use citrate as a capping agent.^[1,23,37] For example, the aspect ratio of Ag nanoprisms by Charles et al. ranged from 2.1 to 13.3. The synthesis protocol is highly reliable given good-quality Ag spherical and nanoplate seeds. For best results, the Ag spherical and nanoplate seeds should be used within 5–20 min after seed preparation. The high yield and purity of the nanoplates were evident by the UV–vis–NIR spectra of the solutions and no fractionation was necessary to purify the nanoparticles (Figure S12, Supporting Information). Each spectrum had a single in-plane dipole peak in the visible or NIR range. To quantify the purity, the final nanoparticles were not subject to any purification after synthesis and were imaged directly by TEM. Statistical analysis showed a high purity of >90% for the as-synthesized Ag nanoplates. Ag spherical seeds and small nanoplates constituted <10% of the final product. As the number of growth step increased, the amount of spherical nanoparticles and small

n nanoplates increased, probably due to homogeneous nucleation of small Ag spheres in later growth steps.

We note that multiple growth steps are required for synthesizing large Ag nanoplates with a high aspect ratio and a long λ_{LSPR} . If one growth step was used, simply increasing the amount of AgNO_3 could not produce Ag nanoplates with a high aspect ratio and a long λ_{LSPR} . Instead, small nuclei appeared and the nanoplates agglomerated to form particles of undesired shapes (Figure S13, Supporting Information). The extinction spectrum of the product solution spanned across 300–1400 nm, suggesting a poor control over the nanoparticle shape during the one-step growth of high-aspect-ratio Ag nanoplates resonating in the NIR range. Therefore, multistep growth is required to avoid the defective structures and produce large Ag nanoplates with well-controlled shapes.

In summary, we have demonstrated a PVP-free method for synthesizing large Ag nanoplates via multistep seed-mediated growth. The resulting Ag nanoplates had high aspect ratios and long λ_{LSPR} in the NIR range. During the synthesis, if the Ag nanoplate seeds were capped with additional citrate, the subsequent growth had a slow rate and it required hours to finish the growth. Without capping the Ag nanoplate seeds with additional citrate, however, the subsequent growth was completed within minutes. Via multiple steps and maximized growth in each step, we synthesized nanoplates with a lateral dimension of up to 600 nm. Since the synthesis was solely based on citrate and free of PVP, the final Ag nanoplate products had no polymer coating, which may adversely alter the nanoparticle properties and prevent the reactants from reaching the nanoparticle surfaces in catalysis. Lastly, the Ag nanoplates resonating in the NIR range can find broad applications in chemical sensing, biological imaging, photothermal heating, and optical communication.

Experimental Section

Materials: Silver nitrate ($\geq 99.9999\%$), sodium citrate tribasic dihydrate ($\geq 99.0\%$), sodium borohydride ($\geq 99.99\%$), poly(sodium 4-styrenesulfonate) (PSSS, average $M_w \approx 1000$ kDa), and ascorbic acid (AA, $\geq 99.0\%$) were purchased from Sigma-Aldrich and used as received. Ultrapure water with a resistivity of $17 \text{ M}\Omega \text{ cm}$ was obtained from a Thermo Scientific Barnstead GenPure Pro. All experiments were performed at room temperature and ambient atmosphere.

Ag Spherical Seeds Synthesis: Small spherical Ag seeds (11 nm in size) capped with citrate were prepared following a previous report.^[23] Aqueous solutions of PSSS (0.25 mL , 0.5 mg mL^{-1}) and NaBH_4 (0.3 mL , $10 \times 10^{-3} \text{ M}$, ice-cold) were sequentially added to an aqueous solution of sodium citrate (5 mL , $2.5 \times 10^{-3} \text{ M}$) under vigorous stirring. Afterward, AgNO_3 (5 mL , $0.5 \times 10^{-3} \text{ M}$) was added to the mixture at a rate of 2 mL min^{-1} . After the synthesis, the Ag spherical seeds were aged for various lengths of time (t_1) and then used for preparing Ag nanoplate seeds.

Synthesis of Large Ag Nanoplates Using Nanoplate Seeds not Capped with Additional Citrate: To prepare Ag nanoplate seeds, an aqueous solution of AA ($75 \mu\text{L}$, $10 \times 10^{-3} \text{ M}$) was added to H_2O (10 mL). Various amounts of Ag spherical seeds ($5\text{--}40 \mu\text{L}$) were added to the growth solutions, followed by the addition of AgNO_3 (3 mL , $0.5 \times 10^{-3} \text{ M}$) at a rate of 1 mL min^{-1} . The color of the growth solutions changed from yellow to red, and to blue, indicating that Ag nanoplates were grown. Once the Ag nanoplates finished the growth, the stirring was stopped and the Ag nanoplates were ready for the growth in the next steps.

To further grow the Ag nanoplate seeds into large Ag nanoplates, various amounts of the Ag nanoplate seeds ($0.5\text{--}1.4 \text{ mL}$) were added to the subsequent growth solutions containing H_2O (10 mL) and AA ($75 \mu\text{L}$, $10 \times 10^{-3} \text{ M}$). Then, AgNO_3 (3 mL , $0.5 \times 10^{-3} \text{ M}$) was injected into the growth solution at a rate of 1 mL min^{-1} . The color of the growth solutions changed as the growth continued. Once the synthesis of large Ag nanoplates was completed, an aqueous solution of trisodium citrate (0.5 mL , $25 \times 10^{-3} \text{ M}$) was added to the final product. If multiple steps were used for the growth, no citrate was added until the last growth step was completed.

Synthesis of Large Ag Nanoplates Using Nanoplate Seeds Capped with Additional Citrate: Small Ag nanoplate seeds were synthesized similar to the above procedure, but the small Ag nanoplates were capped with trisodium citrate (0.5 mL , $25 \times 10^{-3} \text{ M}$) immediately after the first growth. During the subsequent growth steps, various amounts of citrate-capped Ag nanoplate seeds ($0.5\text{--}2.0 \text{ mL}$) were added to the growth solutions containing H_2O (10 mL) and AA ($75 \mu\text{L}$, $10 \times 10^{-3} \text{ M}$). Afterward, 3 mL of AgNO_3 was injected at a rate of 1 mL min^{-1} . Once all AgNO_3 was added, there was no apparent change in the color of the solution, suggesting that the growth was incomplete. UV-vis-NIR spectra were taken at different intervals to reveal the evolution of λ_{LSPR} during the growth of large Ag nanoplates. The plasmon resonance peaks stabilized after $3\text{--}4 \text{ h}$ and then trisodium citrate (0.5 mL , $25 \times 10^{-3} \text{ M}$) was added to stabilize the large Ag nanoplates.

Characterization: DLS measurements were performed on a DynaPro NanoStar (Wyatt Technology) to provide an estimation of the nanoparticle size. The nanoparticle solutions were diluted by a factor of 1000 times before the DLS measurements. TEM was performed on a Philips EM420 or a JEOL 2100 TEM at an accelerating voltage of $120\text{--}200 \text{ keV}$. To prepare the TEM samples, aliquots of concentrated nanoparticle solutions ($6\text{--}8 \mu\text{L}$) were drop casted onto TEM grids and left overnight for complete drying. A total of ≈ 350 nanoparticles from each sample were used to determine the purity of the nanoparticles. UV-vis-NIR spectroscopy was performed on an Agilent Cary 5000 spectrophotometer.

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

Ag nanoplate, multistep growth, near infrared, plasmon resonance

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