

Synthesis of Large Bumpy Silver Nanostructures with Controlled Sizes and Shapes for Catalytic Applications

Ju-Hwan Oh, Do Yeon Kim, and Jae-Seung Lee*

Department of Materials Science and Engineering, Korea University, Seoul 136-713, Korea. *E-mail: jslee79@korea.ac.kr
Received August 26, 2013, Accepted October 7, 2013

We have synthesized disc-like large silver nanomaterials that have nanostructured bumps on the surface using smaller nanoplate seeds. The size and shape of the bumpy nanostructures are rationally controlled by changing the concentrations of nanoplate seeds, silver ion, reductant, and citrate ion. Importantly, the synthetic mechanism of these bumpy nanostructures is remarkably similar to that of the conventional seed-mediated growth based on tiny seeds. We have further investigated the catalytic properties of the bumpy nanostructures for the reduction of 4-nitrophenol, which is associated with a concomitant color change from yellow to colorless.

Key Words : Seed-mediated growth, Silver, Nanostructure, Microstructure, Catalysis

Introduction

Seed-mediated growth methods have been widely utilized to synthesize metallic nanoparticles with various shapes and sizes.¹⁻³ These methods rely on the synthesis of tiny ‘seed’ nanoparticles whose diameter is typically less than 5 nm, and their subsequent growth into larger nanoparticles. During the seed formation or growth, (1) structure directing reagents such as polymers or anions play a crucial role in determining the shapes of the nanoparticles, and (2) the concentration of the seeds controls their sizes. Based on these seed-mediated growth methods, a variety of silver nanoparticles have been synthesized, whose shapes include plates,^{4,5} polyhedrons,^{6,7} rods,⁸ wires,⁹ and more complicated structures.¹⁰⁻¹³ Importantly, such enormous attention on the synthesis of the silver nanoparticles is due to their distinctive optical properties, surface tailorability, catalytic activity, and biological functionalities.¹⁴⁻¹⁶ In contrast to the nanosized silver materials, however, larger silver materials have been far less investigated, mainly owing to the synthetic problems to control the shapes and sizes of the resultant materials.

For the recent few years, our group and others have intensively investigated the synthesis of larger silver nanostructures (diameter > 100 nm), particularly in consideration of the key parameters that determine their structures and sizes.^{10,11,17,18} In this work, we present the synthesis of large bumpy silver nanostructures (diameter = 246 ± 23 nm, thickness = 20 nm). This synthetic strategy consists of two stages: the preparation of nanoplate seeds (diameter = 116 ± 18 nm, thickness = 5 nm) grown from the tiny seed particles (diameter = ~ 5 nm) in the first stage, and the synthesis of the large bumpy silver nanostructures grown from the nanoplate seeds that were prepared in the first stage (‘nanoplate seeds’) (Figure 1(a)). Importantly, this synthesis can be considered as an advanced version of the conventional seed-mediated growth method, where our new ‘nanoplate seeds’ play a significant role in controlling the shapes and sizes of the nanostructures. These

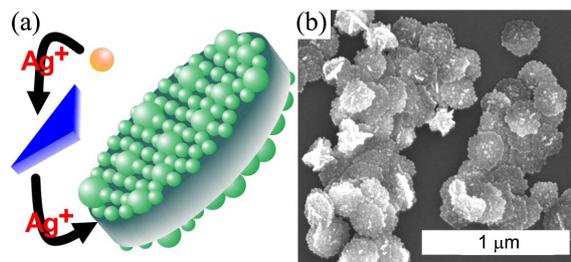


Figure 1. (a) A scheme representing the synthesis of the large bumpy nanostructures, and (b) an SEM image of the ones obtained under standard conditions.

novel structures exhibit highly catalytic surface nature.

Experimental

Materials. Silver nitrate (Cat. # 204390), sodium borohydride (Cat. # 480886), poly(sodium 4-styrenesulfonate) (PSSS, Cat. # 434574), trisodium citrate dihydrate (Cat. # S4641), 4-nitrophenol (Cat. # 241326) and L-ascorbic acid (Cat. # A5960) were purchased from Sigma-Aldrich (Milwaukee, WI, USA). Ultrapure water from a Millipore Direct-Q3 system (18.2 M Ω -cm) was used. All chemical solutions were freshly prepared before usage.

Synthesis of the Silver Nanoplate Seeds. Silver nanoplate seeds were prepared by the seed-mediated growth method following a literature procedure.⁴ In brief, a yellow seed solution was obtained by continuous injection of the AgNO₃ solution (5 mL, 0.5 mM) to an aqueous mixture containing trisodium citrate (5 mL, 2.5 mM), PSSS (0.25 mL, 500 mg/L), and NaBH₄ (0.3 mL, 10 mM) at a rate of 2 mL/min with stirring. The freshly synthesized seeds (0.06 mL), ascorbic acid (0.075 mL, 10 mM) and pure water (5 mL) were mixed to prepare a growth solution. The silver nanoplate seeds were finally obtained by injecting the AgNO₃ (3 mL, 0.5 mM) solution at a rate of 2 mL/min to the growth solution

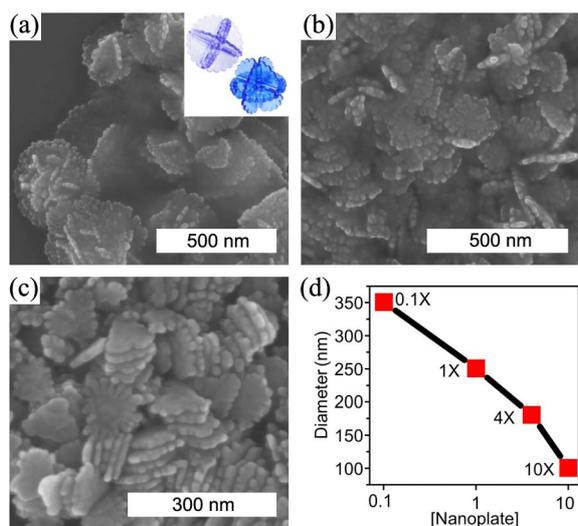


Figure 2. SEM images of large bumpy nanostructures synthesized at various nanoplate seed concentrations: (a) 0.1X, (b) 4X, and (c) 10X. Note that laundry ball-like structures were obtained (a, inset). As the concentration of silver nanoplate increased, less bumpy structures were obtained, and (d) The size of bumpy nanostructures was plotted as a function of the of nanoplate concentration in a logarithmic scale.

with stirring. The as-synthesized final mixture was washed with a 4.4 mM citrate solution three times by repeated centrifugation and redispersion.

Synthesis of the Large Bumpy Nanostructures. The standard large bumpy nanostructures were prepared by gradual addition of the AgNO_3 solution (3 mL, 50 mM) at a rate of 2 mL/min to an aqueous mixture containing silver nanoplate seeds (2 mL), ascorbic acid (1 mL, 9 mM) with stirring. The final mixture was washed with the 4.4 mM citrate solution three times by repeated centrifugation and redispersion.

Catalytic Activity. The large standard bumpy nanostructures (diameter = 246 ± 23 nm, 0.1 mL) were combined with a 4-

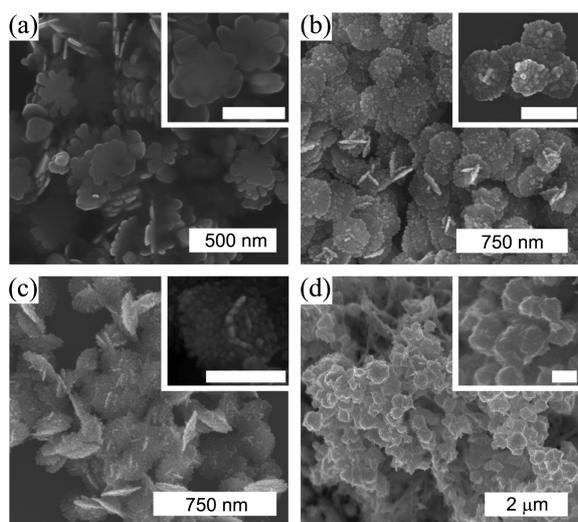


Figure 3. SEM images of large bumpy nanostructures synthesized at various Ag^+ concentrations, and their magnified images (insets): (a) 5 mM, (b) 17 mM, (c) 300 mM, and (d) 500 mM. Scale bars in the insets are corresponding to 250 nm.

nitrophenol solution (0.9 mL, 250 μM). Subsequently, a freshly prepared sodium borohydride solution (0.1 mL, 88 mM) was injected. The color change of the mixture from yellow to colorless was monitored by UV-vis spectroscopy every minute using Agilent 8458 spectrophotometer (Agilent Technologies, Inc.).

Results and Discussion

Overview of the Synthesis. The synthesis begins with the preparation of the nanoplate seeds which are grown from the tiny seed particles (diameter < 5 nm). The prepared nanoplate seeds exhibit a strong plasmonic band at 800 nm, a diameter of 116 ± 18 nm and a thickness of 5 nm (see Supporting Information). These nanoplate seeds have the planar and side crystal surfaces that are Ag (111) and Ag (100), respectively.⁴ The nanoplate seeds are protected by citrate anions which preferentially bind to Ag (111) and are allowed to further grow on the side in the presence of Ag^+ under reductive conditions using ascorbic acid. The effect of nanoplate seeds, Ag^+ , ascorbic acid, and citrate anions are investigated as key parameters to control the shape and size of the resultant nanostructures. Under standard synthetic conditions, typically much larger, bumpy discoidal nanostructures (diameter = 246 ± 23 nm, thickness = 20 nm) are obtained (Figure 1(b)).

Nanoplate Seed Concentration. We first investigated the capability of our method to control the size of the bumpy nanostructures. In the conventional seed-mediated growth method, the size of the grown structures is controlled by varying the concentration of the tiny nanoparticle seeds. In our work, similarly, we observed controlled variations of sizes and structures upon varying the concentration of the nanoplate seeds. For example, at a lower nanoplate concentration (0.1X), the diameter of bumpy nanostructures increased to 376 ± 72 nm, forming laundry ball-like structures (Figure 2(a)). In contrast, at a higher nanoplate concentration (4X), much smaller sized (diameter = 167 ± 28 nm, thickness = 21 nm) and less bumpy structures were formed (Figure 2(b)). Moreover, when the concentration of the nanoplates was the highest (10X), the growth of the silver nanoplates was much less observed (diameter = 113 ± 25 nm, thickness = 21 nm), because of the limited amount of Ag^+ per nanoplate seed (Figure 2(c)). The size of the bumpy nanostructures is plotted as a function of the nanoplate concentration (Figure 2(d)).

Silver Ion (Ag^+). The effect of silver ion (Ag^+) on the morphology of the final structure was investigated with various Ag^+ concentrations at 5, 17, 300, and 500 mM. Because citrate ions act as a capping agent which preferentially binds to Ag (111) facets (the planar surface of nanoplates), they hinder the reduction of Ag^+ on the Ag (111) facets and induce crystal growth along Ag (100) facets (the side surface of nanoplates).^{19,20} Therefore, at a lower Ag^+ concentration (5 mM), Ag^+ would less likely penetrate the citrate ion layer on the Ag (111), and is supposed to be less rapidly, and thus more evenly reduced on the Ag (111), simply increasing the

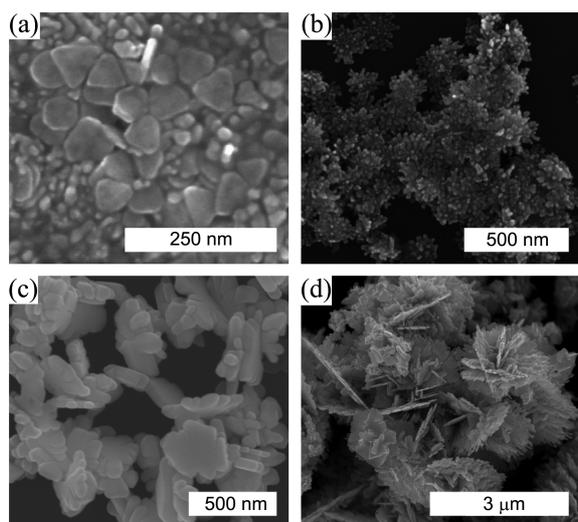


Figure 4. SEM images of large bumpy nanostructures synthesized at various AA concentrations: (a) 0.3 mM, (b) 1.5 mM, (c) 30 mM, and (d) 60 mM.

thickness of the final flat structures (diameter = 283 ± 24 nm, thickness = 18 nm; Figure 3(a)). At higher Ag^+ concentrations (17 and 300 mM), however, sufficient Ag^+ could arrive at Ag (111) and induce spotty nucleation on the Ag (111) surface sporadically, forming densely packed nanobumps (at $[\text{Ag}^+] = 17$ mM, diameter = 250 ± 48 nm, thickness = 23 nm; at $[\text{Ag}^+] = 300$ mM, diameter = 261 ± 47 nm, thickness = 30 nm; Figures 3(b) and 3(c)). Interestingly, when the Ag^+ concentration reached 500 mM, the nucleation occurred not only on the nanoplates but also in the reaction mixture, finally building up networked structures (Figure 3(d)). Therefore, the selective formation of nanobumps on the flat surface (Ag (111)) of the nanoplate seeds could be attributed to the uneven and rapid Ag^+ reduction on Ag (111), which is achieved by controlling the Ag^+ concentration. In fact, we have already reported the formation of other isotropic bumpy silver nanostructures, indicating the favorable formation of bumps under similar seed-mediated synthetic conditions.¹⁷

Ascorbic Acid (AA). The concentration of the reductant in the seed-mediated growth method contributes to both kinetics and thermodynamics of the growth, which could lead to the formation of different shapes and sizes. Considering that the AA concentration used for the bumpy nanostructure in Figure 1(b) was 3 mM before the addition of Ag^+ , we first decreased the AA concentration down to 0.3 mM, and obtained only the original nanoplate seeds (Figure 4(a)). Interestingly, much smaller nanoparticles with irregular shapes were also observed, which possibly formed owing to the reduction of Ag^+ regardless of the nanoplate seeds in the mixture solution. As the AA concentration increased to 1.5 mM, however, the growth of the nanoplate seeds obviously took place, resulting in an increase in both size and thickness of the bumpy nanostructures up to 159 ± 32 nm and 14 nm, respectively. We also observed the formation of many ‘bumps’ both on the edges and faces of the structure at this point (Figure 4(b)). When the AA concentration further

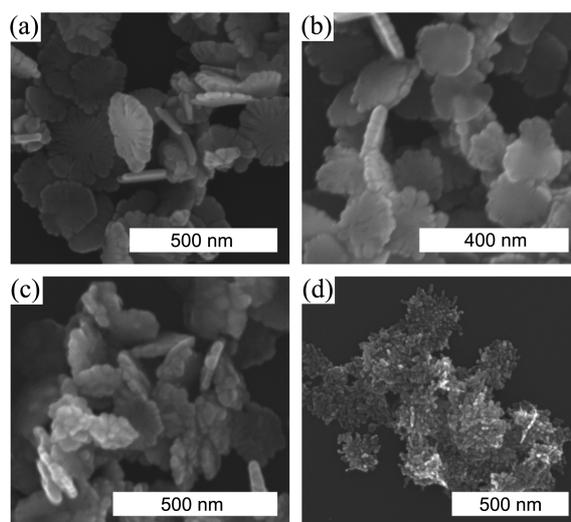


Figure 5. SEM images of large bumpy nanostructures synthesized at various citrate concentrations: (a) 7.3 μM , (b) 29.3 μM , (c) 293 μM , and (d) 7.3 mM.

increased to 30 and 60 mM, the overall diameter of the structures kept increasing to 377 ± 31 nm and 2.16 ± 0.15 μm , respectively (Figures 4(c) and 4(d)). The resultant structures at 30 mM of AA are flat on the faces, but still are bumpy on the edges, indicating that the bump formation occurs preferentially on the edges. At the highest concentration of AA (60 mM), the final structures transformed from 2-dimensional structures to rather 3-dimensional ones. This observation indicates that the facet-selective growth of the structures owing to the different surface potentials is almost negligible under highly reductive conditions.

Citrate Ion. Citrate ion is known to play an essential role in determining the structure of silver nanomaterials.^{19–21} In our synthetic method, the presence of citrate ion is inevitable owing to their initial role to protect the nanoplate seeds.⁴ To investigate the effect of the citrate ion on the final structure, we lowered the citrate concentration to 7.3 μM and observed plate-like flat and thick structures that were, however, branched on the side edges (Figure 5(a), diameter = 226 ± 34 nm, thickness = 21 nm). As the citrate concentration increased to 29.3 μM , the trenches between the branches were rather filled, leading to suppression of the bumps on the side edges (Figure 5(b), diameter = 163 ± 16 nm, thickness = 31 nm). This flat surface formation would be attributed to the energetically stable Ag (111), which is the flat surface of silver nanoplate. The Ag (111) interacts more preferentially with citrate anions and becomes energetically more stable than other facets; forming Ag (111) is a spontaneous reaction in the presence of citrate anions. When the concentration of citrate increased further to 293 μM , however, bumps on Ag (111) also started to form (Figure 5(c), diameter = 142 ± 44 nm, thickness = 18 nm). Moreover, at a higher citrate concentration (7.3 mM), highly bumpy and irregularly sized nanostructures were observed, which suggests that the citrate anions play an important role in both surface properties and size distribution of the bumpy silver nanostructures (Figure 5(d),

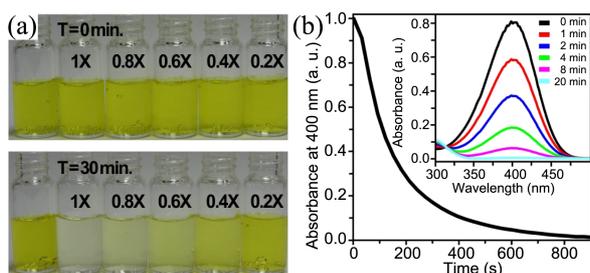


Figure 6. (a) Catalytic reduction of 4-nitrophenol using the silver bumpy nanostructures as heterogeneous catalysts. The picture of the reaction mixtures containing the bumpy nanostructures at different concentrations were taken before and after the reaction. Note that the color changes that are indicative of the reduction progress take place more significantly at higher nanostructure concentrations. (b) Absorbance changes (at 400 nm) of the 4-nitrophenol solution containing the silver nanostructures under reductive conditions as a function of time. The UV-vis spectra of the solution were obtained as the catalytic reactions proceeded (inset).

diameter = 150 ± 88 nm, thickness = 13 nm).

Catalytic Applications. We finally evaluated the catalytic activity of the bumpy nanostructures for the reduction of 4-nitrophenol to 4-aminophenol. In the presence of the standard bumpy nanostructures, 4-nitrophenol is catalytically reduced by NaBH_4 , which is associated with a concomitant color change from yellow to colorless (Figure 6(a)). The spectral change of the reduction as a function of time was monitored by a UV-vis spectrophotometer (Agilent 8453) at 400 nm, where the maximum extinction was obtained (Figure 6(b)). As the reduction proceeded, the plasmonic band at ~ 400 nm decreases gradually, indicating the effective reduction of 4-nitrophenol in the presence of the bumpy structures. Considering the amount of NaBH_4 is in huge excess (final [4-nitrophenol] = $205 \mu\text{M}$, and final $[\text{NaBH}_4]$ = 8 mM), we assumed the first order reaction with respect to 4-nitrophenol, and obtained the rate constant based on the following equation,

$$\ln [4\text{-nitrophenol}]_t = -kt + [4\text{-nitrophenol}]_0$$

where t is the reaction time and k is the rate constant. Using the kinetic data of the catalytic reaction in Figure 6(b), k is determined to be $3.8 \times 10^{-3} \text{ s}^{-1}$. The amount of the total silver used to obtain this rate constant is 2.70×10^{-4} g. While such catalytic applications of noble metal nanoparticles are mostly reported with rather smaller particulated nanomaterials (diameter < 100 nm),²²⁻²⁴ it is notable that several larger silver nanostructures (diameter > 200 nm) also exhibit similar catalytic properties as demonstrated in this work.^{18,25,26} In particular, the large surface area of the bumpy nanostructures would be highly attractive as efficient heterogeneous catalyst.

Conclusion

A general synthetic route has been developed for the large silver nanomaterials based on the growth of nanoplate seeds. This method is rapid, convenient, and rational, whose

mechanism is similar to that of the conventional seed-mediated growth method. Further development of the synthesis based on different types and materials of nanoparticle seeds, such as gold or silver polyhedrons, rods, and wires, would provide substantially promising advanced nano- and microstructures with controlled shapes for various applications.

Acknowledgments. This work was supported by a Korea University Grant, and Basic Science Research Program through the National Research Foundation of Korea (NRF) funded by the Ministry of Education, Science and Technology (Grant No. NRF-2012R1A1A2A10042814). We thank Dr. Hionsuck Baik at the Korea Basic Science Institute (KBSI; Seoul, Republic of Korea) for his help with the electron microscopic analysis.

References

- Jana, N. R.; Gearheart, L.; Murphy, C. J. *Adv. Mater.* **2001**, *13*, 1389.
- Nikoobakht, B.; El-Sayed, M. A. *Chem. Mater.* **2003**, *15*, 1957.
- Zhang, Q.; Li, W.; Moran, C.; Zeng, J.; Chen, J.; Wen, L.-P.; Xia, Y. *J. Am. Chem. Soc.* **2010**, *132*, 11372.
- Aherne, D.; Ledwith, D. M.; Gara, M.; Kelly, J. M. *Adv. Funct. Mater.* **2008**, *18*, 2005.
- Kim, B.-H.; Oh, J.-H.; Han, S. H.; Yun, Y.-J.; Lee, J.-S. *Chem. Mater.* **2012**, *24*, 4424.
- Tao, A.; Sinsermsuksakul, P.; Yang, P. *Angew. Chem., Int. Ed.* **2006**, *45*, 4597.
- Sun, Y.; Xia, Y. *Science* **2002**, *298*, 2176.
- Han, S. H.; Lee, J.-S. *Langmuir* **2012**, *28*, 828.
- Sun, Y.; Mayers, B.; Herricks, T.; Xia, Y. *Nano Lett.* **2003**, *3*, 955.
- Wang, Y.; Camargo, P. H. C.; Skrabalak, S. E.; Gu, H.; Xia, Y. *Langmuir* **2008**, *24*, 12042.
- Han, S. H.; Park, L. S.; Lee, J.-S. *J. Mater. Chem.* **2012**, *22*, 20223.
- Liang, H.; Li, Z.; Wang, W.; Wu, Y.; Xu, H. *Adv. Mater.* **2009**, *21*, 4614.
- Aizawa, M.; Cooper, A. M.; Malac, M.; Buriak, J. M. *Nano Lett.* **2005**, *5*, 815.
- Willems, K. A.; Van Duyne, R. P. *Annu. Rev. Phys. Chem.* **2007**, *58*, 267.
- Wiley, B.; Sun, Y.; Xia, Y. *Accounts Chem. Res.* **2007**, *40*, 1067.
- Rycenga, M.; Cobley, C. M.; Zeng, J.; Li, W.; Moran, C. H.; Zhang, Q.; Qin, D.; Xia, Y. *Chem. Rev.* **2011**, *111*, 3669.
- Kim, G. A.; Han, S. H.; Lee, J.-S. *Mater. Lett.* **2012**, *68*, 118.
- Oh, J.-H.; Lee, J.-S. *J. Nanosci. Nanotechnol.* **2014**, *14*, 3735.
- Zeng, J.; Tao, J.; Li, W.; Grant, J.; Wang, P.; Zhu, Y.; Xia, Y. *Chemistry-an Asian Journal* **2011**, *6*, 376.
- Zhang, Q.; Li, N.; Goebel, J.; Lu, Z.; Yin, Y. *J. Am. Chem. Soc.* **2011**, *133*, 18931.
- Jana, N. R.; Gearheart, L.; Murphy, C. J. *Chem. Commun.* **2001**, 617.
- Gangula, A.; Podila, R.; M. R.; Karanam, L.; Janardhana, C.; Rao, A. M. *Langmuir* **2011**, *27*, 15268.
- Liang, M.; Wang, L.; Su, R.; Qi, W.; Wang, M.; Yu, Y.; He, Z. *Catal. Sci. Technol.* **2013**, *3*, 1910.
- Ai, L.; Jiang, J. *Bioresour. Technol.* **2013**, *132*, 374.
- Xu, B.-B.; Zhang, R.; Liu, X.-Q.; Wang, H.; Zhang, Y.-L.; Jiang, H.-B.; Wang, L.; Ma, Z.-C.; Ku, J.-F.; Xiao, F.-S.; Sun, H.-B. *Chem. Commun.* **2012**, *48*, 1680.
- Jiang, Z.-J.; Liu, C.-Y.; Sun, L.-W. *J. Phys. Chem. B* **2005**, *109*, 1730.