

Seedless and Electroless Plating of Silver on Silica Particles by Using Microreactor

San San Maw^{1,2}, Takeshi Watanabe¹, Minoru T. Miyahara¹, and Satoshi Watanabe^{*1}

¹ Department of Chemical Engineering, Kyoto University, Katsura, Nishikyo, Kyoto 615-8510, Japan

² Green Myanmar Environmental Services Co., Ltd., Hlaing Thar Yar Township, Yangon, The Republic of the Union of Myanmar

^{*}nabe@cheme.kyoto-u.ac.jp

ABSTRACT

Synthesis of silver nanoshells is still a challenge especially in the absence of surface modification of core particles and/or metal seed decoration on core surfaces. In this study, we applied a microreactor to seedless and electroless plating of silver on bare silica particles, and investigated the effects of reaction temperatures and silver ion concentrations on the morphology and surface coverage of silver on the core particle surface. Our experiments demonstrated that the use of the microreactor enabled the one-step direct deposition of silver with a morphology close to complete shells and that silver ion concentrations from 0.2 to 0.5 mM at a moderate temperature of 50 °C produced high coverage and yield. Besides, the mixing sequence of NH_3 and HCHO in the synthesis procedure was found to be a key factor to achieve the high silver coverage. In addition, we demonstrated that the addition of polyvinylpyrrolidone (PVP) after the silver shell growth reaction increases the stability without decreasing the reaction rate.

Keywords: Silver nanoshells, Direct deposition, Heterogeneous nucleation, Microreactor, Suspension stability

1. INTRODUCTION

Silver nanoshells, which comprise dielectric core particles such as silica or polystyrene covered with a thin silver layer, have been widely explored over the decades since the first successful synthesis in 2001 [1]. Due to their unique chemical, optical, and surface plasmon resonance properties, silver nanoshells show great promise in a wide field of application such as catalysis [2], photonics [3], sensing [4], and solar technologies [5]. Several synthetic approaches have been proposed to synthesize silver nanoshells, including seed-mediated growth [1, 5-13] and layer-by-layer deposition [14, 15]. In the seed-mediated growth technique, core particle surface is typically functionalized with either metal ions such as Sn^{2+} or alkoxysilanes, followed by attaching small metal nanoparticles (mostly gold or silver) as seeds on the core surface and then growth of silver shells. As for the layer-by-layer deposition, shell growth process is repeated for obtaining complete nanoshells with a desired shell thickness. These two methods inherently require many steps for complete nanoshells and accordingly the reaction period for the shell growth step is relatively long from 30 min to 7 h. Besides, in some cases with metal nanoparticle seeding, those nanoparticles are separately synthesized [9, 13, 14], which takes an additional time and effort. Seed-mediated growth and layer-by-layer deposition methods are thus generally time-consuming even though complete nanoshells are successfully synthesized. In our previous studies, we applied a microreactor to the seed-mediated growth process and greatly shortened reaction times required both for the seeding and shell growth steps by taking advantage of excellent mixing ability of the microreactor [16-18]. By using the microreactor flow process, we successfully synthesized complete silver nanoshells with a thickness of approximately 10 nm [19, 20]. However, multiple synthetic steps are still involved in the microreactor flow process, and it would be more favorable if we could synthesize complete nanoshells without the functionalization of silica core particles and the

seeding of metal nanoparticles, allowing direct deposition of silver on bare silica particles so that time and effort are further diminished.

Although direct deposition (template-free) approaches to coat silica particles with silver have been reported [21-29], the synthesis of complete silver nanoshells with those single step processes is still a challenge. Typical resultant morphology was not complete shells but inhomogeneous deposition of silver, which demonstrates that uniform shell growth in the seed-mediated growth methods was largely assisted by metal seeds as nucleation sites. Another difficulty would come from poor attraction of silver ions and the core surface, and accordingly the core particle surface was functionalized in some works to intensify the attraction. Organic solvents, such as water/ethanol solution, ethylene glycol, ethanol, and triethanolamine aqueous solution were also used to enhance the reaction. However, the surface functionalization requires additional synthesis steps and the use of organic solvents is not environmentally friendly. Besides, even though the synthesis was conducted with a single step reaction, the reaction period was still long from 30 min to 12 h at temperatures ranging from 5 °C to 100 °C. This long reaction period would be attributed to the use of mild reducing agents, such as octylamine, polymers (polyvinylpyrrolidone (PVP) and polyethylenimine), and glucose. Because heterogeneous nucleation is less favored in the absence of seed metal particles than the case with seeds, the use of a strong reducing agent could have resulted in the formation of silver nanoparticles in the bulk phase, which is a possible reason for the use of mild reducing agents. In principle, however, heterogeneous nucleation must be favored over self-nucleation as long as silver ions are accumulated in the vicinity of the core particle surface and, more importantly, the reaction field (concentration and temperature) is uniform. Therefore, it would be possible to realize direct coating of silver on silica particles by using a microreactor because excellent mass and heat transfer characteristics in a microreactor enable the creation of a uniform reaction field [30, 31]. To the best of our knowledge, almost no studies have been

conducted along this line except the direct deposition of silver by using a continuous flow T-mixer [32, 33], which however produced patchy particles, and direct deposition of silver into complete shells has not yet been achieved.

In this study, we conducted template-free direct coating of silver on bare silica surfaces by in-situ reduction of silver ions in the absence of surface modification and seed nanoparticles by using a microreactor. We investigated the effects of reaction temperatures and silver ion concentrations on the resultant morphology and surface coverage of silver on core silica particles. In addition, we examined the stability of resultant suspensions and found that the addition of PVP after the shell growth reaction increased the stability without decreasing the reaction rate. This study paves a way for the synthesis of complete nanoshells through seedless and electroless plating of silver on bare silica particles.

2. EXPERIMENTAL SECTION

2.1. Materials

An aqueous suspension of silica particles with 120 nm diameter (Spherica slurry 120) was purchased from Catalysts & Chemicals Industrial Co., Ltd. (Japan). Silver nitrate (AgNO_3 , $\geq 99\%$ purity), PVP (molecular weight $M_w = 55\,000$), formaldehyde (HCHO , 37 wt% in aqueous solution), and ammonium hydroxide solution (28 wt% in aqueous solution) were purchased from Sigma-Aldrich Co. LLC. (USA). Hydrochloric acid (HCl , 0.1 mol L^{-1}) was purchased from Kishida Chemical Co., Ltd. (Japan). All chemicals were used as received without further purification. Solutions and suspensions with desired concentrations were prepared by dissolving or diluting the original chemicals with ultrapure water (resistivity $> 18\text{ M}\Omega\cdot\text{cm}$, Arium mini, Sartorius, Germany).

2.2. Electroless plating of silver on bare silica particles

The electroless plating of silver on bare silica particles was conducted by using a central collision type microreactor [19], which comprises three plates (inlet, mixing, outlet plates) as illustrated in Fig. 1A, to achieve quick and homogeneous mixing of the two inlet fluids with an estimated mixing time of less than 1 ms [18]. In the experiments, we prepared a mixed suspension of bare silica particles, silver nitrate, and ammonia and put the mixed suspension into Syringe A as in Fig. 1B. Then we initiated the reaction by mixing the premixed suspension with a reducing agent, HCHO, set in Syringe B by pumping the two syringes into the microreactor with a flow rate of 10 mL min⁻¹ for each syringe (a total flow rate of 20 mL min⁻¹ from the outlet), and collected the reaction suspension in a vial. The collected suspension was kept stationary for 1h. We varied the reaction temperature by immersing the microreactor and vial in a water bath set at a desired temperature ranging from 40 to 80 °C. The typical concentration set after mixing in the synthesis was as follows: 0.012 g L⁻¹ of SiO₂, 16 mmol L⁻¹ of NH₃, and 0.1 mmol L⁻¹ of HCHO. The concentration of AgNO₃ was varied from 0.15 to

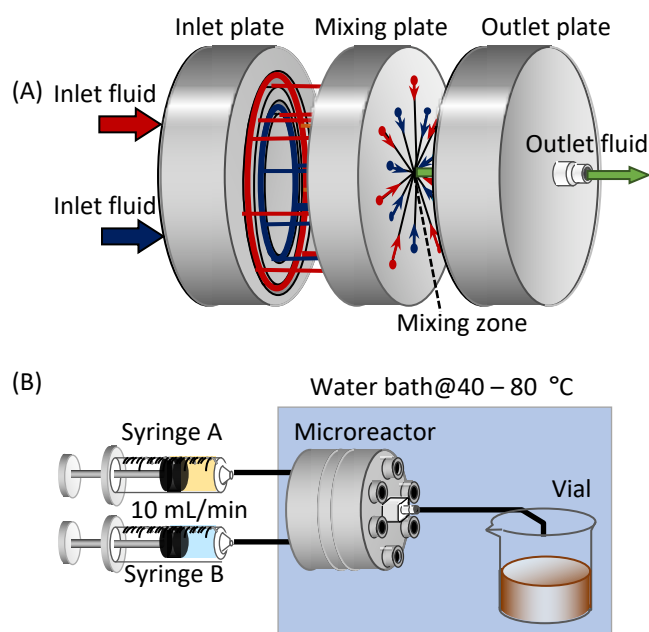


Figure 1. Schematic illustrations of (A) central collision-type microreactor (disassembly image) and (B) experimental set up for seedless and electroless plating of silver on silica particles using the microreactor.

2.5 mM. In separate experiments, we added PVP either in Syringe B or in the collected suspension with a concentration after mixing of 0.3 μ M.

2.3. Characterization

The extinction spectra of the resultant colloidal suspensions were measured with a UV-visible spectrophotometer (UV-1800, SHIMADZU Corp., Japan). The morphologies of the synthesized particles were observed with a transmission electron microscope (JEM-1010, JEOL Ltd., Japan). Samples for TEM observations were prepared by putting a droplet of the as-obtained colloidal suspension on a carbon coated copper grid and drying them in a vacuum oven overnight.

3. RESULTS AND DISCUSSION

3.1. Direct silver coating of bare silica particles

Figure 2 shows typical TEM images of resultant particles synthesized at different temperatures under a fixed concentration of silver ions of 0.2 mM. At a reaction temperature of 40 °C, although some silica particles are covered with silver, bare silica particles are also observed (Fig. 2A). This is because the reaction temperature was so low that the silver

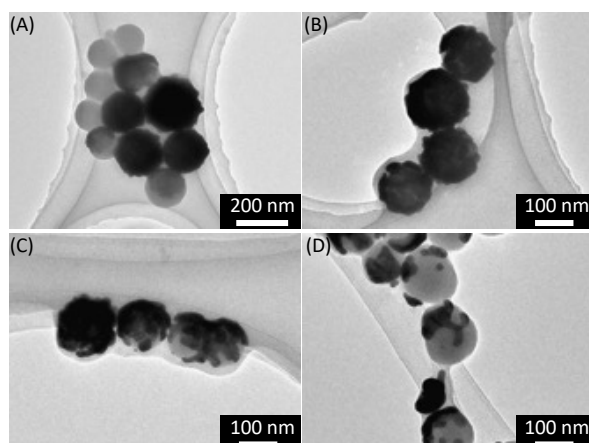


Figure 2. Typical TEM images of resultant particles synthesized at different reaction temperatures of (A) 40 °C, (B) 50 °C, (C) 60 °C, and (D) 80 °C under a fixed concentration of silver ions of 0.2 mM.

deposition reaction did not fully proceed. At higher temperatures of 50 °C and 60 °C, a larger number of silica particles are covered with silver (Figs. 2B and 2C). However, the reaction at a temperature of 80 °C produced free silver nanoparticles as well as partially-covered silica particles (Fig. 2D), which is possibly because the energy barrier for the self-nucleation was easily overcome in a high temperature condition. Resultant particles were further characterized by UV-vis measurements. As shown in Fig. 3, the intensity of extinction spectra increased when the temperature increased from 40 °C to 60 °C, indicating higher silver coverage at higher temperatures. The maximum intensity between the spectra of 50 °C and 60 °C was almost the same, although two broad peaks observed at ~550 nm and ~ 800 nm in the 50 °C spectrum merged into a single peak at 60 °C. Because a theoretical spectrum of silica@silver core-shell particles with shell thickness of 10 nm based on Mie theory [34] has similar peak wavelengths

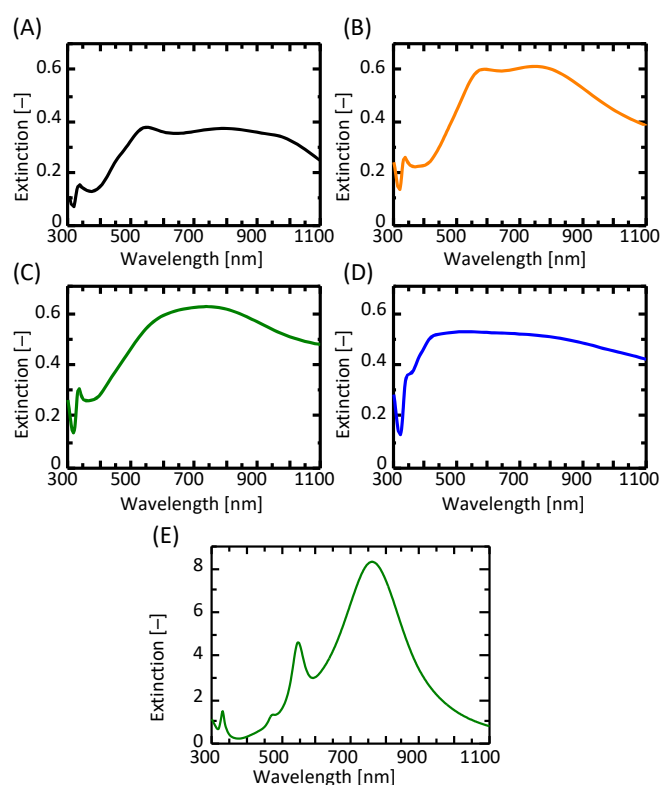


Figure 3. UV-vis spectra of resultant suspensions synthesized at different temperatures of (A) 40 °C, (B) 50 °C, (C) 60 °C, and (D) 80 °C under a fixed concentration of silver ions of 0.2 mM. (E) Theoretical UV-vis spectrum of a silver nanoshell with a core size of 120 nm and shell thickness 10 nm calculated by using MieLab software [31].

to those of 50 °C (Fig. 3E), these results indicate that the morphology of deposited silver at 50 °C is close to complete shells while that at 60 °C is rather patchy. Further increase to 80 °C increased the intensity around 400 nm, indicating the formation of silver nanoparticles, and also increased the extinction in the near-infrared region relative to the visible region, indicating the deposition of small silver patches.

We then investigated the effects of the silver ion concentration at a reaction temperature of 50 °C as shown in Fig. 4. The increase in the silver ion concentration to 0.5 mM increased the intensity of resultant spectra, which indicates increased deposition of silver on core silica particles (Fig. 4A). This trend is also confirmed in TEM images shown in Fig. 4B. However, further increase to 1.5 and 2.5 mM resulted in flattened spectra (Fig. 4A) and nonuniform

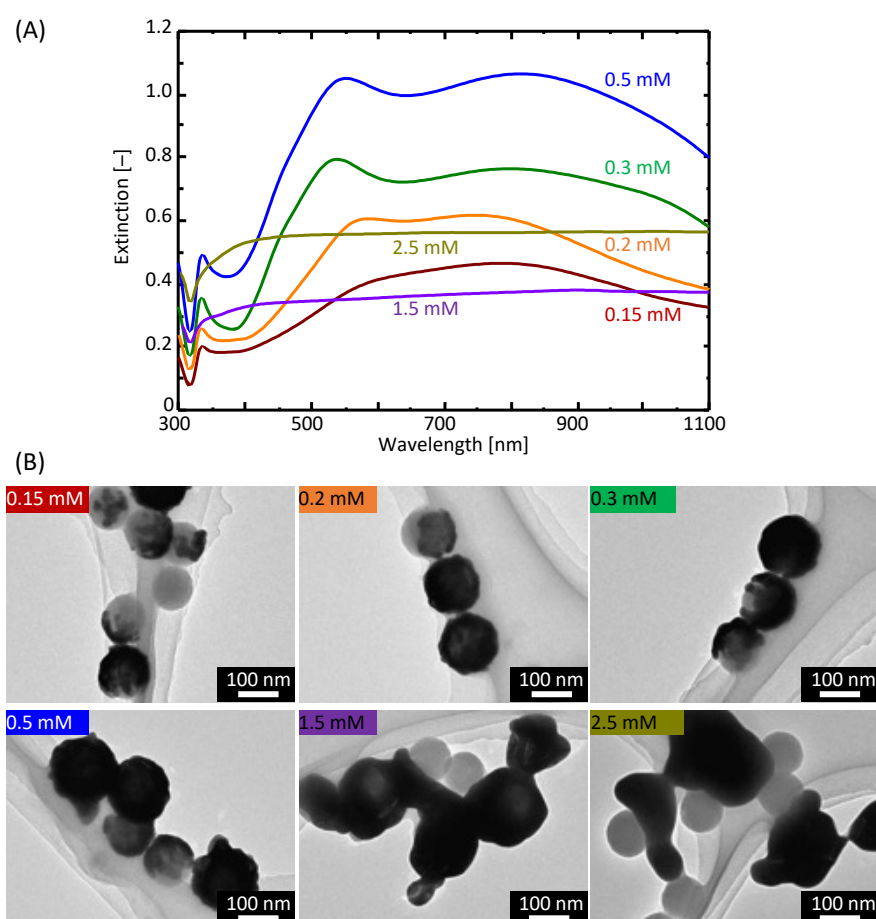


Figure 4. Synthetic results with different concentrations of silver ions (0.15, 0.2, 0.3, 0.5, 1.5, and 2.5 mM) at 50 °C: (A) UV-vis spectra of obtained suspensions and (B) TEM images of resultant particles.

deposition on silica particles as well as the formation of silver nanoparticles in the bulk phase (Fig. 4B). These results indicate that the coverage and yield of silver-coated particles through the synthesis process using the microreactor are improved by promoting the heterogeneous nucleation on the core particle surface and by suppressing the self-nucleation in the bulk phase; too low temperature and/or concentration does not drive the deposition reaction, while too high temperature and/or concentration results in the formation of silver nanoparticles. Under the experimental conditions in this study, silver ion concentrations from 0.2 to 0.5 mM at 50 °C are found to produce silver-coated particles with high coverage that have morphologies and UV-vis spectra similar to complete silver nanoshells. The rather high intensity above 900 nm in the spectra of 0.3 and 0.5 mM is possibly due to increased roughness of silver shell surface [35]. Therefore the successful synthesis of silver-coated particles through direct deposition of silver on bare silica particles is attributable to the excellent mixing performance of the microreactor to enhance heterogeneous nucleation on core particle surfaces.

Another key factor is the order of addition of HCHO and NH_3 for achieving silver coating with high coverage. In our typical procedure, we premixed silica particles, silver ions, and NH_3 , and then mixed the premixed suspension with HCHO. However, when we swapped HCHO and NH_3 in the synthesis procedure, the intensity of a resultant spectrum was lower than that from the typical procedure and the morphology of silver was rather dendritic as shown in Fig. 5. This is in accordance with the works by Klupp Taylor and co-workers [32, 33, 36],

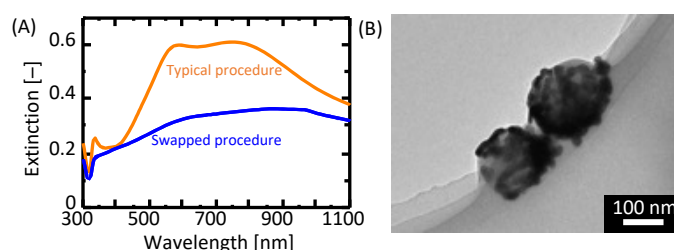


Figure 5. Comparison of the results from the swapped procedure with those from the typical one: (A) UV-vis spectra of obtained suspensions and (B) TEM image of resultant particles. The syntheses were conducted at 50 °C and silver ion concentration of 0.2 mM.

in which a premixed suspension of silica particles, silver ions, and HCHO was mixed with NH_3 (i.e. same as the swapped procedure) to result in the formation of patchy particles. These results would be attributable to the reaction sequence of silver ions. In this silver deposition reaction, silver ions first react with NH_3 to form silver-ammonia complex ions, and then the complex ions are reduced by HCHO, which is so-called the silver-mirror reaction. In our typical procedure as illustrated in Fig. 6A, silver-ammonia complex ions form in the premixing step and get adsorbed on or crowd around the core silica surface because of the electrostatic attraction (A-i). Homogeneous mixing with HCHO in the microreactor thus promotes uniform reaction between silver-ammonia complex ions and HCHO around the core particles, leading to preferential nucleation on the core silica surface (A-ii), and consequently produces silver-coated particles with high surface coverage (A-iii, Fig. 3B). In the swapped procedure (Fig.

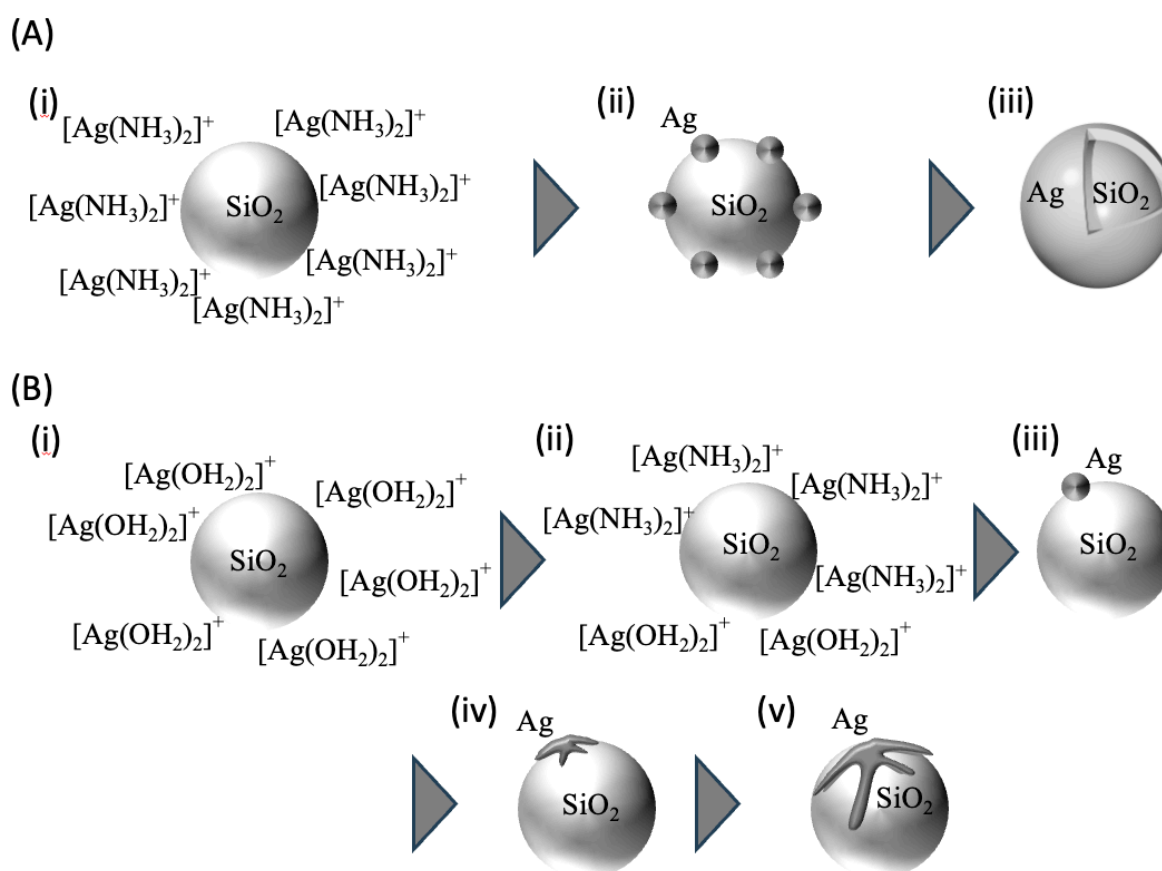


Figure 6. Schematic illustration of the reaction of silver ions (A) in the typical procedure and (B) in the swapped procedure.

6B), by contrast, the silver-ammonia complex formation and reduction reaction are assumed to sequentially proceed after the mixing in the microreactor (B-i, B-ii). Hence the nucleation on the core surface would not occur simultaneously but rather locally to produce a small number of nuclei (B-iii). Once a nucleus is formed, the growth of the nucleus is preferred to the formation of a new nucleus (B-iv). Because the growth reaction is thought to be diffusion-limited, reduced silver readily deposits on the growth front, which results in the dendritic morphology (B-v, Fig. 5B). In this manner, optimizing reaction temperature, concentration, and mixing sequence enables the direct coating of silver with high coverage on bare silica particles.

3.2. Increasing Stability of Resultant Suspension

Figure 7A shows the time course of extinction spectra of a resultant suspension synthesized with the typical procedure under the condition of 50 °C and a silver ion concentration of 0.2 mM. As the time elapsed after the synthesis, the intensity decreased and

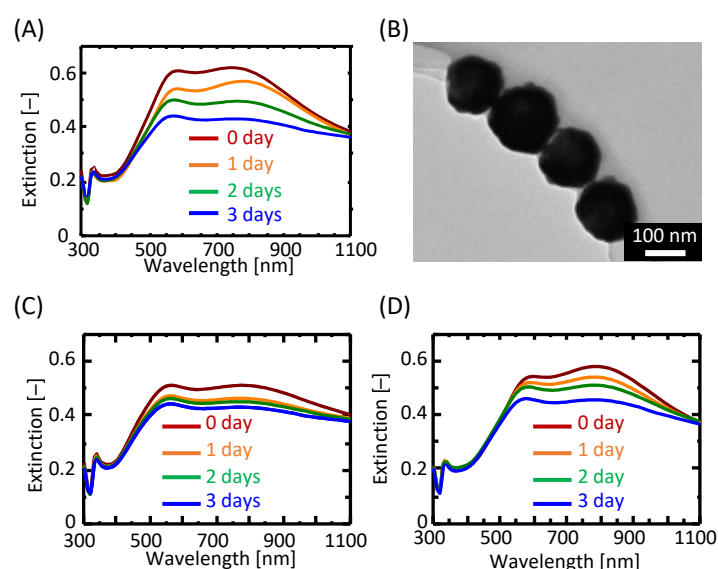


Figure 7. Effect of PVP on the stability of resultant suspensions: (A) time course of extinction spectra of a suspension without PVP addition, (B) TEM image of resultant particles and (C) time course of UV-vis spectra of the suspension with PVP addition in Syringe B, and (D) time course of UV-vis spectra of the suspension with PVP addition into the reaction suspension 5 min after being collected. All the syntheses were conducted at a temperature of 50 °C with silver ion concentration of 0.2 mM.

the peak at 700~800 nm shifted to longer wavelengths. These results would be because of the aggregation of obtained particles, and accordingly the addition of stabilizers is required to increase the stability of resultant suspensions. We thus used PVP as a possible stabilizer by premixing PVP with HCHO so that PVP molecules were not adsorbed on the core silica surface but adsorbed the silver surface after the reaction. This process produced particles with high silver coverage (Fig. 7B) and suppressed the degradation with time in the extinction intensity (Fig. 7C) compared to the case without the PVP addition. However, a problem is that the intensity immediately after the synthesis with PVP (labeled as 0 day in Fig. 7C) is lower than that without PVP (labeled as 0 day in Fig. 7A). This would be because PVP molecules which existed close to the surface inhibited the silver deposition reaction to lower the reaction rate. To solve this problem, we modified the synthesis procedure as follows: we conducted a silver coating experiment with the typical synthesis procedure (without PVP), and added PVP into the reaction suspension 5 min after collecting it into a vial. 5 min was assumed to be long enough to complete the silver deposition reaction. This modified procedure successfully yielded a suspension with a similar UV-vis spectrum to that from the typical procedure (Fig. 7D). In addition, the stability of the suspension was improved as the decay in the spectra intensity was slowed down possibly because PVP molecules simply served as stabilizers by adsorbing on the surface of resultant particles. Although the timing to add PVP molecules further has to be optimized, we demonstrated that it is possible to stabilize resultant particles without lowering the reaction rate by adding PVP molecules after the synthesis.

4. CONCLUSIONS

The template-free electroless plating of silver on bare silica particles has been investigated by using the central collision type microreactor in the absence of surface modification of core particles and seeding metal nanoparticles. The experimental results

demonstrated that a moderate temperature of 50 °C is suitable for achieving high coverage and yield of silver on silica particles possibly because this temperature promotes the heterogeneous nucleation on the core particle surface and, at the same time, suppresses the self-nucleation in the bulk phase. The silver ion concentrations from 0.2 to 0.5 mM at 50 °C are demonstrated to result in silver coating close to complete shells on silica particles. Besides, the mixing sequence in the synthetic process plays an important role; NH_3 has to be premixed with silver ions for uniform reaction to result in high coverage of silver on bare silica particles, while premixing of HCHO instead of NH_3 resulted in a dendritic morphology of deposited silver. Furthermore, we investigated the stability of resultant suspensions, and found that the addition of PVP molecules as a stabilizer into a reaction suspension 5 min after being collected from the microreactor outlet improved the stability of resultant particles. In this way, we have successfully demonstrated that the microreactor enabled direct coating of silver on bare silica particles by taking advantage of its excellent mixing performance.

FIGURE CAPTIONS

Figure 1. Schematic illustrations of (A) central collision-type microreactor (disassembly image) and (B) experimental set up for seedless and electroless plating of silver on silica particles using the microreactor.

Figure 2. Typical TEM images of resultant particles synthesized at different reaction temperatures of (A) 40 °C, (B) 50 °C, (C) 60 °C, and (D) 80 °C under a fixed concentration of silver ions of 0.2 mM.

Figure 3. UV-vis spectra of resultant suspensions synthesized at different temperatures of (A) 40 °C, (B) 50 °C, (C) 60 °C, and (D) 80 °C under a fixed concentration of silver ions of 0.2 mM. (E) Theoretical UV-vis spectrum of a silver nanoshell with a core size of 120 nm and shell thickness 10 nm calculated by using MieLab software [34].

Figure 4. Synthetic results with different concentrations of silver ions (0.15, 0.2, 0.3, 0.5, 1.5, and 2.5 mM) at 50 °C: (A) UV-vis spectra of obtained suspensions and (B) TEM images of resultant particles.

Figure 5. Comparison of the results from the swapped procedure with those from the typical one: (A) UV-vis spectra of obtained suspensions and (B) TEM image of resultant particles. The syntheses were conducted at 50 °C and silver ion concentration of 0.2 mM.

Figure 6. Schematic illustration of the reaction of silver ions (A) in the typical procedure and (B) in the swapped procedure.

Figure 7. Effect of PVP on the stability of resultant suspensions: (A) time course of extinction spectra of a suspension without PVP addition, (B) TEM image of resultant particles and (C) time course of UV-vis spectra of the suspension with PVP addition in Syringe B, and (D) time course of UV-vis spectra of the suspension with PVP addition into the reaction suspension 5 min after being collected. All the syntheses were conducted at a temperature of 50 °C with silver ion concentration of 0.2 mM.

REFERENCES

- [1] J.B. Jackson, N.J. Halas, Silver Nanoshells: Variations in Morphologies and Optical Properties, *J. Phys. Chem. B*, 105 (2001) 2743-2746.
- [2] J. Lee, D.-J. Jang, Highly Efficient Catalytic Performances of Eco-Friendly Grown Silver Nanoshells, *J. Phys. Chem. C*, 120 (2016) 4130-4138.
- [3] J. Zhang, J. Liu, S. Wang, P. Zhan, Z. Wang, N. Ming, Facile Methods to Coat Polystyrene and Silica Colloids with Metal, *Adv. Funct. Mater.*, 14 (2004) 1089-1096.
- [4] L. Huang, J. Wan, X. Wei, Y. Liu, J. Huang, X. Sun, R. Zhang, D.D. Gurav, V. Vedarethinam, Y. Li, R. Chen, K. Qian, Plasmonic silver nanoshells for drug and metabolite detection, *Nat Commun*, 8 (2017) 220.

- [5] S. Caliskan, J.K. Kim, G.S. Han, F. Qin, I.S. Cho, H.S. Han, J.-K. Lee, Enhancing Solar Water Splitting of Textured BiVO₄ by Dual Effect of a Plasmonic Silver Nanoshell: Plasmon-Induced Light Absorption and Enhanced Hole Transport, *ACS Appl. Energy Mater.*, 3 (2020) 11886-11892.
- [6] X. Ye, Y. Zhou, J. Chen, Y. Sun, Deposition of silver nanoparticles on silica spheres via ultrasound irradiation, *Appl. Surf. Sci.*, 253 (2007) 6264-6267.
- [7] T. Liu, D. Li, D. Yang, M. Jiang, An improved seed-mediated growth method to coat complete silver shells onto silica spheres for surface-enhanced Raman scattering, *Colloids Surf. A*, 387 (2011) 17-22.
- [8] T. Liu, D. Li, D. Yang, M. Jiang, Preparation of echinus-like SiO₂@Ag structures with the aid of the HCP phase, *Chem. Commun.*, 47 (2011) 5169-5171.
- [9] A.M. Britto-Silva, R.G. Sobral Filho, R. Barbosa-Silva, C.B. Araujo, A. Galembeck, A.G. Brolo, Improved Synthesis of Gold and Silver Nanoshells, *Langmuir*, 29 (2013) 4366-4372.
- [10] G. Ren, W. Wang, M. Shang, H. Zou, S. Cheng, Using a Macroporous Silver Shell to Coat Sulfonic Acid Group-Functionalized Silica Spheres and Their Applications in Catalysis and Surface-Enhanced Raman Scattering, *Langmuir*, 31 (2015) 10517-10523.
- [11] C. Wang, M. Li, Q. Li, K. Zhang, C. Wang, R. Xiao, S. Wang, Polyethyleneimine-mediated seed growth approach for synthesis of silver-shell silica-core nanocomposites and their application as a versatile SERS platform, *RSC Adv.*, 7 (2017) 13138-13148.
- [12] R.G. Sobral-Filho, A.M. Brito-Silva, M. Isabelle, A. Jirasek, J.J. Lum, A.G. Brolo, Plasmonic labeling of subcellular compartments in cancer cells: multiplexing with fine-tuned gold and silver nanoshells, *Chem Sci*, 8 (2017) 3038-3046.
- [13] L. Lermusiaux, L. Roach, M. Lehtihet, M. Plissonneau, L. Bertry, V. Buissette, T. Le Mercier, E. Duguet, G.L. Drisko, J. Leng, M. Treguer-Delapierre, Silver Nanoshells with Optimized Infrared Optical Response: Synthesis for Thin-Shell Formation, and

Optical/Thermal Properties after Embedding in Polymeric Films, *Nanomaterials* (Basel), 13 (2023).

[14] A.G. Dong, Y.J. Wang, Y. Tang, N. Ren, W.L. Yang, Z. Gao, Fabrication of compact silver nanoshells on polystyrene spheres through electrostatic attraction, *Chem. Commun.*, 2 (2002) 350-351.

[15] Z.-j. Jiang, C.-y. Liu, Y. Liu, Z.-y. Zhang, Y.-j. Li, Fabrication of Silver Nanoshell on Functionalized Silica Sphere through Layer-by-Layer Technique, *Chem. Lett.*, 32 (2003) 668-669.

[16] S. Watanabe, T. Hiratsuka, Y. Asahi, A. Tanaka, K. Mae, M.T. Miyahara, Flow Synthesis of Plasmonic Gold Nanoshells via a Microreactor, *Part. Part. Syst. Charact.*, 32 (2015) 234-242.

[17] S. Watanabe, Y. Asahi, H. Omura, K. Mae, M.T. Miyahara, Flow microreactor synthesis of gold nanoshells and patchy particles, *Adv. Powder Technol.*, 27 (2016) 2335-2341.

[18] S. Watanabe, S. Ohsaki, A. Fukuta, T. Hanafusa, K. Takada, H. Tanaka, T. Maki, K. Mae, M.T. Miyahara, Characterization of mixing performance in a microreactor and its application to the synthesis of porous coordination polymer particles, *Adv. Powder Technol.*, 28 (2017) 3104-3110.

[19] S.S. Maw, S. Watanabe, M.T. Miyahara, Flow synthesis of silver nanoshells using a microreactor, *Chem. Eng. J.*, 374 (2019) 674-683.

[20] S.S. Maw, S. Watanabe, M.T. Miyahara, Multiple Roles of Polyethylenimine during Synthesis of 10 nm Thick Continuous Silver Nanoshells, *Langmuir*, 36 (2020) 4511-4518.

[21] Y. Kobayashi, V. Salgueiriño-Maceira, L.M. Liz-Marzán, Deposition of Silver Nanoparticles on Silica Spheres by Pretreatment Steps in Electroless Plating, *Chem. Mater.*, 13 (2001) 1630-1633.

- [22] C. Tian, B. Mao, E. Wang, Z. Kang, Y. Song, C. Wang, S. Li, Simple Strategy for Preparation of Core Colloids Modified with Metal Nanoparticles, *J. Phys. Chem. C*, 111 (2007) 3651-3657.
- [23] M.S. Peterson, J. Bouwman, A. Chen, M. Deutsch, Inorganic metallodielectric materials fabricated using two single-step methods based on the Tollen's process, *J. Colloid Interface Sci.*, 306 (2007) 41-49.
- [24] D. Chen, H.-Y. Liu, J.-S. Liu, X.-L. Ren, X.-W. Meng, W. Wu, F.-Q. Tang, A general method for synthesis continuous silver nanoshells on dielectric colloids, *Thin Solid Films*, 516 (2008) 6371-6376.
- [25] J.C. Flores, V. Torres, M. Popa, D. Crespo, J.M. Calderón-Moreno, Variations in morphologies of silver nanoshells on silica spheres, *Colloids Surf. A*, 330 (2008) 86-90.
- [26] H. Kang, J.-K. Yang, M.S. Noh, A. Jo, S. Jeong, M. Lee, S. Lee, H. Chang, H. Lee, S.-J. Jeon, H.-I. Kim, M.-H. Cho, H.-Y. Lee, J.-H. Kim, D.H. Jeong, Y.-S. Lee, One-step synthesis of silver nanoshells with bumps for highly sensitive near-IR SERS nanoprobe, *J. Mater. Chem. B*, 2 (2014) 4415-4421.
- [27] J.K. Yang, H. Kang, H. Lee, A. Jo, S. Jeong, S.J. Jeon, H.I. Kim, H.Y. Lee, D.H. Jeong, J.H. Kim, Y.S. Lee, Single-Step and Rapid Growth of Silver Nanoshells as SERS-Active Nanostructures for Label-Free Detection of Pesticides, *ACS Appl. Mater. Interfaces*, 6 (2014) 12541-12549.
- [28] K. Wang, X. Zhang, C. Niu, Y. Wang, Template-activated Strategy towards One-step Coating Silica Colloidal Microspheres with Silver, *ACS Appl. Mater. Interfaces*, 6 (2014) 1272-1278.
- [29] H. Chang, E. Ko, H. Kang, M.G. Cha, Y.-S. Lee, D.H. Jeong, Synthesis of optically tunable bumpy silver nanoshells by changing the silica core size and their SERS activities, *RSC Adv.*, 7 (2017) 40255-40261.

- [30] K. Mae, Advanced chemical processing using microspace, *Chem. Eng. Sci.*, 62 (2007) 4842-4851.
- [31] X. Yao, Y. Zhang, L. Du, J. Liu, J. Yao, Review of the applications of microreactors, *Renew. Sustain. Energy Rev.*, 47 (2015) 519-539.
- [32] T. Meincke, H. Bao, L. Pflug, M. Stingl, R.N. Klupp Taylor, Heterogeneous nucleation and surface conformal growth of silver nanocoatings on colloidal silica in a continuous flow static T-mixer, *Chem. Eng. J.*, 308 (2017) 89-100.
- [33] T. Meincke, J. Walter, L. Pflug, T. Thajudeen, A. Volkl, P. Cardenas Lopez, M.J. Uttinger, M. Stingl, S. Watanabe, W. Peukert, R.N. Klupp Taylor, Determination of the yield, mass and structure of silver patches on colloidal silica using multiwavelength analytical ultracentrifugation, *J. Colloid Interface Sci.*, 607 (2022) 698-710.
- [34] O. Peña-Rodríguez, P.P. González Pérez, U. Pal, MieLab: A Software Tool to Perform Calculations on the Scattering of Electromagnetic Waves by Multilayered Spheres, *Int. J. Spectrosc.*, 2011 (2011) 583743.
- [35] M.G. Cha, H. Kang, Y.S. Choi, Y. Cho, M. Lee, H.Y. Lee, Y.S. Lee, D.H. Jeong, Effect of Alkylamines on Morphology Control of Silver Nanoshells for Highly Enhanced Raman Scattering, *ACS Appl. Mater. Interfaces*, 11 (2019) 8374-8381.
- [36] H. Bao, W. Peukert, R. Klupp Taylor, One-Pot Colloidal Synthesis of Plasmonic Patchy Particles, *Adv. Mater.*, 23 (2011) 2644-2649.