Korean J. Chem. Eng., 32(12), 2468-2472 (2015)
DOI: 10.1007/s11814-015-0084-0

pISSN: 0256-1115
eISSN: 1975-7220

A solid control strategy for preparation of silver nanoparticles in aqueous medium

Daechul Cho*,† and Sung-Hyun Kwon**

*Department of Energy & Environmental Engineering, Soonchunhyang University, Asan 336-745, Korea
**Department of Marine Environmental Engineering/Institute of Marine Industry,
Gyeongsang National University, Tongyong 650-160, Korea

(*Received 5 April 2015 • accepted 21 April 2015*)

Abstract−Uniformly distributed, spherically shaped, mild concentrated silver nanoparticles with single-digit to hundreds nm size have been prepared by reducing silver nitrate with popular reducers like sodium borohydride or hydrazine in the presence of ordinary stabilizers such as SDS, PVP, Polysorbates and ultrasonication. Uv-visble spectroscopic analysis, particle size analysis, and particle-imaging through transmission electron microscopy (TEM) were used for nanoparticle characterization. Higher temperature accelerated the reduction rates, which follows the typical autocatalytic kinetics. Particularly, ultrasonication helped to facilitate the crucial stage of reduction phase to result in excellent quality of nanosolution, such as narrow distribution of particles and size uniformity. We found that initial location or arrangement of silver ions in clouds of stabilizers and 'effectve mixing' in the stage of reduction were vital for successful preparation of silver nanosolution. Also, reagent/stabilizer ratio, reducer input, solution environment such as pH, temperature, and stabilizer properties were optimized and discussed in detail. Proper selection of stabilizer and molar ratio to reagent and effective 'mixing' for preventing grain growth needs to be investigated more in the future work.

Keywords: Silver Nanosolution, Reductive Chemical Method, Dispersant, Stabilizer, Reaction Control Strategy

INTRODUCTION

Silver is a valuable multi-function material that is anti-bacterial, with high thermal and electrical conductivities, and of great reflectivity. In addition, its nano form also has several strong advantages such as material saving out of exceptional specific surface area, sophisticated structures, formation of useful composites, and so on [1]. Recently, silver nano forms have been applied to home appliances, personal wearware, decorative material, windows, and medical device and material.

Silver nano forms can be prepared using three different routes [2]: vapor deposition, ion implantation and wet chemistry. The first two methods include particle formation or growing on a specific substrate; meanwhile the last one guarantees sole formation of nanoparticles in powder or in suspension regardless of any substrates. To synthesize sliver nanoparticles silver nitrate is normally used as starting reagent with reducing agents such as sodium borohydride, hydrazine in the presence of colloidal stabilizer. Polyvinyl alcohol, poly(vinylpyrrolidone), bovine serum albumin, and cellulose are known to be suitable stabilizers for stable colloidal solution. Also, organic solvent processes including the polyol or alcohol process [3-8], the microemulsion method [9], and seed-mediating process [10,11] have been reported so far.

Some basic research on silver nanoparticles can be found in [12, 13]. Huang et al. [12] stated that silver particles would spontaneously form in the presence of strong base and a protecting agent against molecular aggregation. They also found silver particles could exist in the forms of cluster, and proposed a well-known catalytic kinetics for metallic small particles. Chou and Ren [13] researched on finding suitable protecting agent which could be a crucial factor to control the particle-grain growth. In this work, PVP/PVA and formaldehyde/sodium carbonate were chosen for controlling the quality of nanoparticles. Recently, Yang et al. [14] proposed a quicker and higher productive method using aniline as the reductant and dodecylbezenesulfonic acid (DBSA) in a strong alkaline solution. In their system, DBSA along with aniline formed a DAA mesoscopic structure (a kind of surfactant-reagent complex), which later were supposed to be readily reduced by aniline even in highly concentrated silver nitrate solution. Intentional slow reactions by choosing a weaker reductant were explored in order to trace their hypothetical mechanics of reduction. Because the chemical reduction methods are believed to be the most versatile, and convenient to form stable, controllable, and economical nanoparticles or dispersed solution, it has still a great opportunity to investigate further and in depth.

In this study, we present a modified chemical reduction method, characterized as quick formation of silver nanoparticles of noble quality. Conventional reagents like silver nitrate, sodium borohydride and several dispersants including sodium dodecyl sulfate, and poly(vinylpyrrolidone) were used to form well-characterized silver dispersion. During the trials the procedure and ingredients were optimized for 10-100 nm of silver nano particles in solution that should have a long, stable shelf life.

EXPERIMENTAL

1. Preparation of Silver Nano Colloid

A dispersant was dissolved in 45 mL of triple-distilled purified

---

[†] To whom correspondence should be addressed.

E-mail: daechul@sch.ac.kr

Table 1. Reagent composition in this work

Dispersant	Reducing agent
Poly(vinylpyrrolidone)(PVP) (to [Ag+]=10 : 1, or 5 : 1 in molar ratio)	$(NH_2)_2\ H_2O$ 5 mM $NaBH_4$
Tween20 (to [Ag+]=10 : 1, or 5 : 1 in molar ratio)	$(NH_2)_2\ H_2O$ 5 mM $NaBH_4$
Sodium dodecyl sulfate (SDS) (to [Ag+]=10 : 1, or 5 : 1 in molar ratio)	$(NH_2)_2\ H_2O$ 5 mM $NaBH_4$

water at 50-60 °C for 20 min. Five mL of 0.44 M silver nitrate (99.8%, Sigma-Aldrich, USA) solution was added to the suspension under vigorous agitation for 10 min. The reducing agent (5 mM) was dropped into the solution by 50 µL using a micropipette (Epfendorf, Germany) until the solution turned to transparent yellow, which was supposed to signal nano ranged size distribution of reduced silver. Reducers and dispersants used in this work are listed in Table 1. Also, a sonicator (Q700, Qsonica, USA) was used for complete homogenization of the mixture during the reductive reaction.

Stability of suspensions was determined in terms of color of a suspension and its turbidity. The stability was checked every week up to two months.

2. Particle Size Measurement and Image Development

Nanotrac 150 (Microtrac, Japan) was used to analyze the size distribution of silver nanoparticles in solution. Size distribution and mean size (in triplet) were determined for each sample. A transparent electron microscope (TEM, JEOL 100-CX, Germany) was used to photograph all images of the nano suspensions.

RESULTS AND DISCUSSION

1. Specification and Stability of Prepared Nano Suspension

Basically, high concentration of PVP showed strong stability and yellow color. Insufficient amount of PVP failed to prevent "autocatalytic agglomeration," which resulted in a darker color. For SDS (sodium dodecyl sulfate) or Tween20, like PVP, a well dispersed colloid of silver was kept for a couple of months. Excessive reduction (overdose of reducing agents) would cause to transform reduced atomic particles into silver complexes (a certain ionic form), thus resulting in turbid solution or silver deposition on glass surfaces. Reaction end point was presumed to be the time when the solution color turned to from bright yellow to dark reddish depending on initial silver concentration.

In general, with PVP addition, relatively uniform and larger particle sized suspension was made. Particle size could be controlled via choice of stabilizers and/or reductants; for example, stronger reductant hydrazine and medium sized surfactant, Tween20 resulted in smaller particles like 5-16 nm. Hydrazine (pKa=28 at room temperature) has an advantage of governing initial stage of reduction if the following agglomeration among nucleated atomic particles is terminated or interfered. Unlike to the bulky PVP, Tween20, the smaller surfactant may produce the smaller cluster of particles (we assume surfactant bound particles shown in TEM images). However, too many surfactant molecules in suspension are likely to cause larger cluster of silver particles. Consequently, we propose two critical factors - stabilizer and reductant - need to be wisely used to prepare nano suspension with required specification.

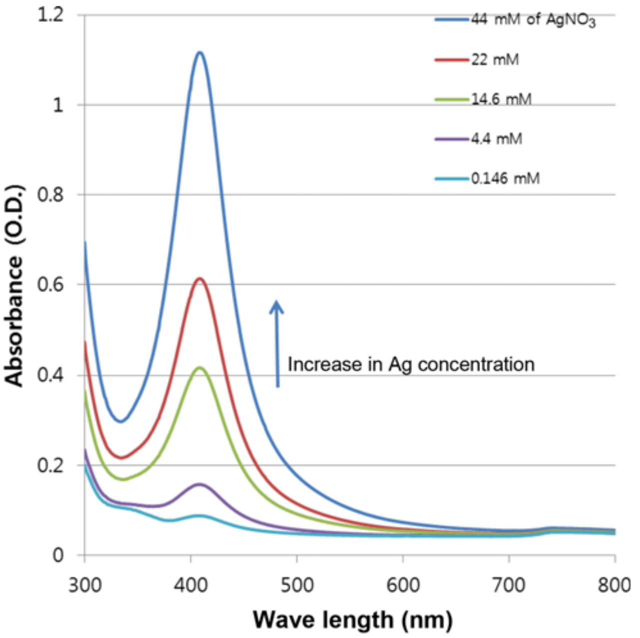

Fig. 1. UV-visible spectra of silver nano solutions. Reaction conditions: molar ratio of Ag to stabilizer (SDS)=0.1; T=55 °C. Maximum peak was observed at 408 nm. 44 mM of Ag, 10/1 (stabilizer/Ag) and T=55 °C are denoted as standard conditions.

2. UV-vis Spectroscopic Analysis

We carried out a UV-visible spectroscopic analysis to confirm whether our solutions were properly manufactured or not. Fig. 1 shows some spectrometric plots, where the experimental conditions are described in the captions. The scanned spectra clearly show the maximum absorbance at 408-409 nm of wavelength, which is well matched with other published results. Depending on the classes of stabilizers the peak absorbance was shifted by 1-2 nm. The details will be discussed in another section. Also, the absorbance was found to be affected by the density and size of the nanoparticles according to our preliminary tests on calibration (not shown here).

3. Kinetic Analysis: Autocatalytic Reduction and Agglomeration

Kinetic analysis was executed according to Huang's autocatalytic assumption [12]. Reaction conditions were set under overdose of a stabilizer, which guarantees all silver ions are fully captured in swamp of the stabilizer. In general, the reduction rate at room temperature was very fast, and a part of the kinetics experiments was done in a cool chamber, sustained below 5 °C. The spectral distribution over time was shown in Fig. 2. At the chosen wavelength of 408 nm, the reductive reactions at different experimental conditions were plotted over time (Fig. 2(b)). Absorbance leveled off after the continual growth, symbolizing nucleation of silver nanoparticles out of silver ionic complex. Based on Fig. 2 data we plotted 'ln (a/1−a) versus time' under the autocatalytic reaction regime (Fig. 3). From that figure we determined the reaction rates over initial silver concentration. The calculation considered the average agglomeration number and initial silver nitrate concentration. The curve fit was very good; the correlation constants were nearly 1.0. The resul-

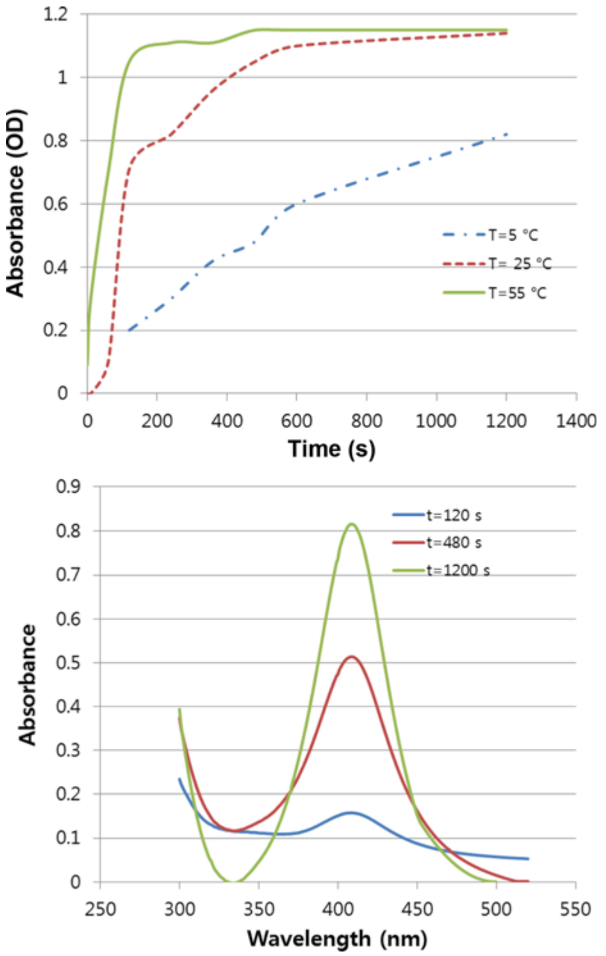

Fig. 2. Reaction rates vs. time at different reaction temperature under standard conditions (top). Absorbance spectra over time at T=5 °C (the slowest reaction) (bottom).

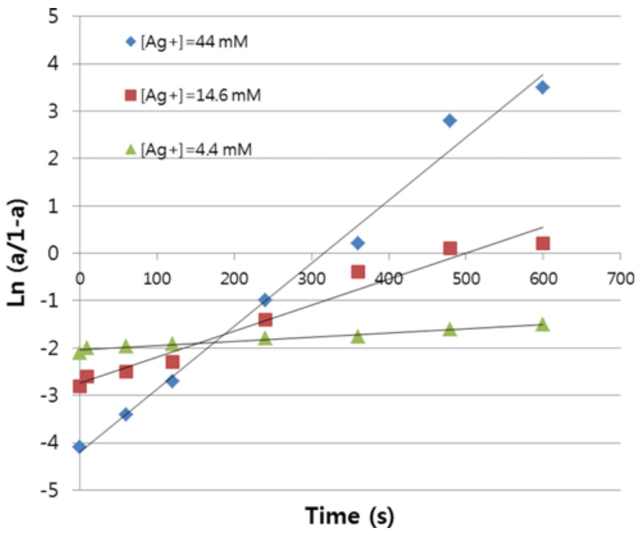

Fig. 3. Kinetics plot based on the presumed autocatalytic reaction for different Ag concentrations. The other conditions denote standard. The observed kinetic rate constants can be calculated from the regression fitting. The correlation coefficients, r^2 were 0.996-0.998.

tant rate constants were found to be 0.302/s, 0.0976/s and 0.025/s in decreasing concentration order.

On the other hand, agglomeration is likely to occur instantly at the very early stage of reduction. We used ultrasonication to disperse the reagent as much as we could along with a stabilizer. Ordinary agitation during the whole reaction would cause 'agglomerated clumps of silver particles' whereas added ultrasonication effected

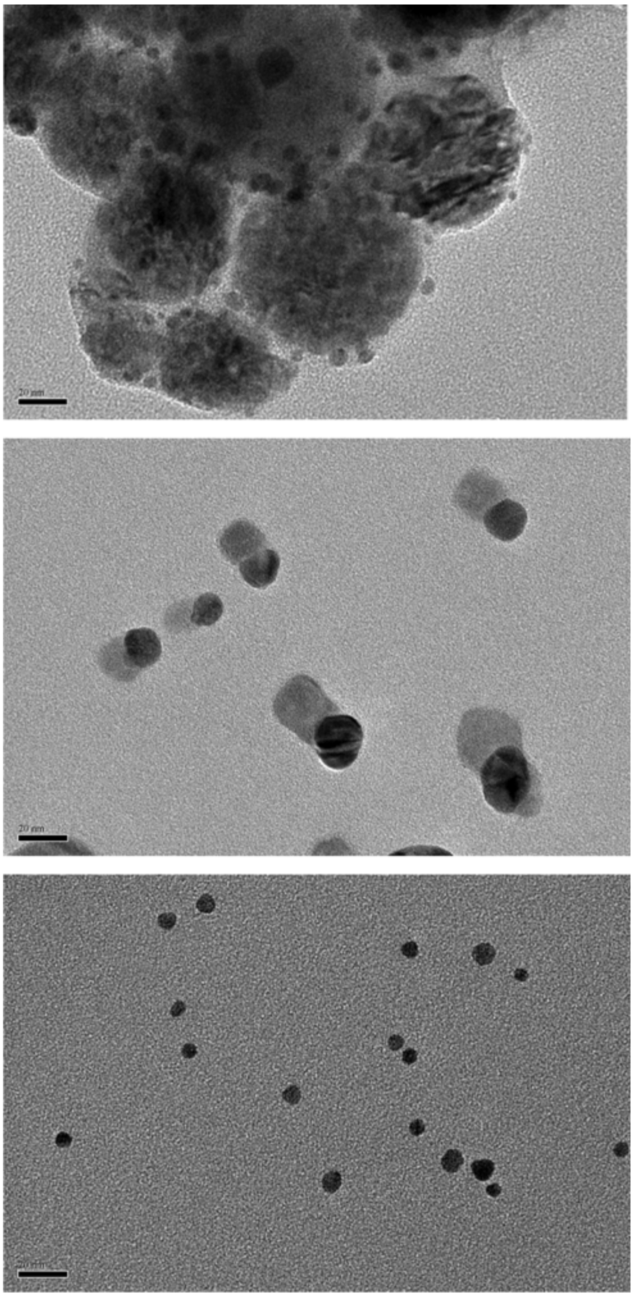

Fig. 4. TEM images taken from nano dispersions: (top) random sized nanoparticles mingled with insufficient or overdosed stabilizers and unreacted residues (may form the clouds). (mid) 8-20 nm sized nanoparticles when SDS was used as stabilizer. (bottom) 3-6 nm nanoparticles when PVP and ultrasonication were used as stabilizer. All magnification was 100,000 folds.

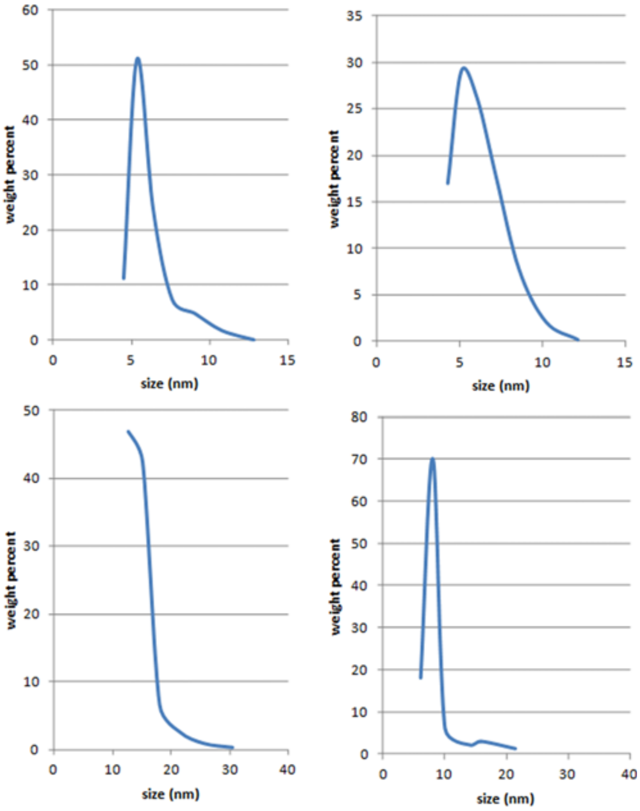

Fig. 5. Particle distributions for different stabilizing effects: (a) using PVP (b) Tween20. For (c) SDS only was used meanwhile for (d) SDS and ultrasonication were applied. All samples were prepared under standard conditions.

better segregation between particle clusters as shown in Figs. 4 and 5. Even the smallest silver cluster ranged 3-15 nm, which implies about 20 to 100 silver atoms in a cluster (silver atom is estimated to be 0.14 nm in actual size but gets larger because of hydration effect and the surrounding surfactant molecules). In fact, it seemed to be extremely difficult to control the very early times in which silver ions are rapidly reduced with electrons donated by nearby hydroxide ions or equivalent at the moment of reducer injection. Thus freshly nucleated, closely neighboring silver atoms attract each other by inherent van der Waals interaction, resulting in diverse forms of agglomerated clusters.

4. Use of Stabilizers

Fig. 5 explains how particle size distribution (PSD) changes with different experimental conditions which were set under our control strategy. Three different type of surfactants - sodium dodecyl sulfate (SDS) and Tween20 as ionic ones and poly(vinylpyrrolidone) as nonionic one - were used to determine the behavior of particle size distribution when the reaction was complete. With predetermined (optimal) doses of the stabilizers, three distinctive PSDs were obtained: PVP and SDS exhibited relatively narrow population of the particles, on average 5.6±1.1, 15±5.8, respectively. Meanwhile, Tween20 revealed a broader particle distribution, corresponding to 11±6.2 nm. This difference might originate from discrete structural forms of the three 'ionic complexes.' That is, SDS may embrace silver ions by interaction between its negative sulfate ion and the positive charge of the silver ion, and then letting each cluster apart away. This initial positioning would not be affected that much by following reduction to result in a uniform and dispersed nanosolution. PVP could also form a coordinative complex of silver ions in aqueous environment owing to its loan pair electrons of oxygen and nitrogen atoms to the outer orbital of silver ions [3,8]. In other words, the silver ions-PVP complex has favorable electronic clouds so that electrons are more easily transferred rather than non-PVP water. These complexes thus prohibit particle aggregation and further growth of the agglomerates. Unlikely to the bulky PVP, Tween20 is a long chain polysorbate, being hard to form a stable complex with the smaller silver ions. This structural unfitting may cause a 'loose cluster' so that random, localized growth of the grains happens, which was often found under uncontrolled reaction regime as seen in Fig. 4(a). In addition, when ultrasonication was applied with SDS we observed a dynamic shift of PSD, which meant smaller size but uniform distribution probably due to the mixing effect, preventing the earlier agglomeration of Ag ions or Ag atoms (see Fig. 5(c) and 5(d)).

CONCLUSIONS

Uniformly distributed, spherically shaped, mild concentrated silver nanoparticles with 3-15 nm size have been prepared by reducing silver nitrate with popular reducers like sodium borohydride or hydrazine in the presence of ordinary stabilizers such as SDS, PVP, Polysorbates and ultrasonication. Particularly, ultrasonication helped to facilitate the crucial stage of reduction phase to result in excellent quality of nanosolution. We found that initial location or arrangement of silver ions in clouds of stabilizers and 'effective mixing' in the stage of reduction were vital for successful preparation of silver nanosolution. Also, reagent/stabilizer ratio (1/10), reducer input, solution environment such as pH, temperature, and stabilizer properties was optimized and discussed for future research.

ACKNOWLEDGEMENT

This work was supported by the Soonchunhyang University Research Fund (20110000). The authors are grateful for that support.

REFERENCES

1. N. H. Nersisyan, J. H. Lee, H. T. Son, C. W. Won and D. Y. Maeng, *Mater. Res. Bull.*, **38**, 949 (2003).
2. M. Montazer, F. Alimohammadi, A. Shamei and M. K. Rahimi, *Carbohydr. Polym.*, **87**, 1706 (2012).
3. J. S. Kim, *J. Ind. Eng. Chem.*, **13**(4), 566 (2007).
4. B. Wiley, Y. Sun and Y. Xia, *Acc. Chem. Res.*, **40**, 1067 (2007).
5. Y. Xia, Y. Xiong, B. Lim and S. E. Skrabalak, *Angew. Che. Int. Ed.*, **48**, 60 (2009).
6. Z. Li, H. Huang, T. Shang, F. Yang, W. Zheng, C. Wang and S. K. Manohar, *Nanotechnology*, **17**, 917 (2006).
7. Y. Sun and Y. Xia, *Science*, **298**, 2176 (2002).
8. S. E. Skrabalak, B. J. Wiley, M. Kim, E. V. Formo and Y. Xia, *Nano Lett.*, **8**, 2077 (2008).
9. W. Zang, X. Qiao and J. Chen, *Mater., Sci. Eng. B*, **142**, 1 (2007).

10. Y. Sun, Y. Yin, B. T. Mayers, T. Herricks and Y. Xia, *Chem. Mater.*, **14**, 4736 (2002).
11. L. M. Huang, W. H. Liao, H. C. Ling and T. C. Wen, *Mater. Chem. Phys.*, **116**, 474 (2009).
12. Z. Y. Huang, G. Mills and B. Hajek, *J. Phys. Chem.*, **97**, 11542 (1993).
13. K. S. Chou and C. Y. Ren, *Mater. Chem. Phys.*, **64**, 241 (2000).
14. J. Yang, H. Yin, J. Jia and Y. Wei, *Langmuir*, **27**, 5047 (2011).