Purification of Silver Nanoparticles via Solvent Extraction at Different Temperatures

Nopphon Weeranoppanant, Kanokporn Sritawong and **Noppakao Pankaew**

Department of Chemical Engineering, Faculty of Engineering,
Burapha University, Chonburi, 20131 Thailand
Email: nopphon.we@eng.buu.ac.th

Manuscript received August 8, 2018
Revised October 16, 2018

ABSTRACT

Synthesis of nanoparticles or nanocrystals often required excess amount of reducing agents for completion of reaction and stabilization of the nanoparticles. However, these agents remaining after the synthesis are considered impurities as they can affect subsequent processing steps such as shell growth and ligand exchanges. Therefore, it is important to remove these agents from the synthesized nanoparticles. Conventional purification methods are centrifugation, chromatography and electrophoresis, but they all have some limitations. In this work, we examine the possibility of using solvent extraction as a way to remove the impurities or excess ligands. The case study was the extraction of free oleylamine from synthesized silver nanoparticle solution (in hexane). Dimethyl formamide was used as extraction solvent. The extraction was considered as mild because the shapes and particle sizes of the silver nanoparticles were maintained even after the extraction, according to TEM images. The extraction was experimented at 30, 40 and 50 ºC. The samples were characterized with UV-Vis spectrometer and TGA. Increasing extraction temperature was found to be effective in promoting the extraction.

Keywords: *Silver nanoparticles, Solvent Extraction, Oleylamine, Purification, Liquid-liquid Extraction*

1. INTRODUCTION

Nanoparticles (NPs) has been widely studied for their unique properties such as catalytic and antibacterial activities. In general, the NPs be produced by three methods: chemical, biological, and physical. For the chemical and biological methods, they require starting ions and reducing agents. The reducing agents are normally added in excess to stoichiometry so as to drive the reaction to completion. After the synthesis, some of the reducing agents will be adsorbed onto the NPs'surface, and they are termed as surface ligands. These surface ligands prevent the NPs to aggregate, maintaining colloidal properties of the NPs. The rest of the reducing agents, which are not bound to the NPs' surface, will remain in the crude solution, and they are termed as free ligands.

The free ligands are considered as impurities of the reaction. They may have adverse effects on subsequent processing such as shell growth and ligand exchange steps [1]. Therefore, it is crucial to remove these residual free ligands from the solution. There are different methods for purification of NPs such as centrifugation [2], filtration [2], electrophoresis [3], extraction [4] – [5] and gel chromatography [6]. However, each of the methods has its own limitations. For example, centrifugation is commonly used as a post-synthesis step to separate out byproducts and impurities from the synthesized NPs. It relies on different densities between the free ligands (light, molecular) and the NPs (heavy, particulates). However, centrifugation may induce aggregation [1]. Gel chromatography relies on a similar principles of size exclusions. In the chromatography, the gels have specific porosity through which only small molecules can diffuse. On the other hand, large molecules or particles (e.g. NPs) will be excluded from the pores, and elute from a column first. However, the gel chromatography is a discontinuous, time-consuming, and labor-intensive method. Electrophoresis is very efficient, but it can be employed only for small quantity of the sample.

Liquid-liquid extraction (LLE) holds a great promise for the purification of NPs as it is easy-to-operate, and can be transformed to continuous mode. Based on polarity, the LLE allows different molecules to partition

into different layers of immiscible liquids. Yu and Peng used methanol to extract impurities from the solution of CdSe and CdTe [4]. In some studies, co-extractants were added to enhance the extraction efficiency [7] – [8]. Recently, Shen and Weeranoppanant [5] demonstrated the LLE to purify CdSe and gold nanoparticles via a multistage countercurrent setup, improving and the extraction efficiency significantly.

In this work, we investigated the LLE for the purification of NPs by using colloidal silver nanoparticles (AgNPs) solution as a case study. The morphology and particle size distribution of the AgNPs were obtained via transmission electron microscopy (TEM). To our knowledge, process parameters of the solvent extraction have been rarely studied. Here, we varied the temperature during which the LLE took place. The thermogravimetric analysis (TGA) was used to qualitatively indicate the amount of the ligands before and after the extraction. The AgNPs recovery was estimated using UV-Visible spectroscopy (UV-Vis).

2. MATERIALS AND METHODS

2.1 Materials

Silver acetate (AR grade, CARLO ERBA), oleylamine (nitrogen-flushed, C18-content 80-90%, ARCOS), and hexane (AR grade, Qrec) were used for AgNPs synthesis. Dimethyl formamide (AR grade, QReC) was purchased. All solvents were used without any prior purification. Before any experiment, all glassware was cleaned with deionized water, and then rinsed with hexane three times.

2.2 Methods

The AgNPs were synthesized, in similar to the reported procedure [9]. 10 mL oleylamine was added to 0.2 g of silver acetate. The mixture was sonicated for 30 minutes before it was transferred to a round-bottom flask containing 200 mL of hexane. The synthesis was operated under reflux for 2 days, during which the mixture turned from light yellow to dark brownish solution, indicating the presence of AgNPs. The AgNPs solution was kept in a glass vial, covered with aluminum foil, and stored at 10 ºC.

The extraction solvent used in this study was dimethyl formamide (DMF), which was immiscible to hexane. To perform the extraction, the AgNPs solution and DMF were mixed in a 50 mL tube. The mixing ratio was 1:1 by volumes. The tube was immersed in water bath for temperature control. The extraction temperatures studied in this work were 30, 40, and 60ºC. The temperature was not increased above 60ºC owing to significant evaporation of solvent (i.e., hexane). During the first 12 hours, the mixture was mixed and stirred using a magnetic bar. After that, the mixture was allowed to settle into two layers for another 6 hours. The top and bottom layers contained mainly hexane and DMF, respectively. As for nomenclature, the samples from the top and bottom layers will be called raffinate and extract, respectively.

The samples before and after extraction were analyzed with three different methods: TEM, TGA, and UV-Vis. First, the AgNPs solution (before extraction) and the raffinate samples were characterized with TEM to determine the change in morphology such as particle size distribution and particle shape. In this characterization, only sample from the experiment at 30ºC was tested. The samples for TEM were prepared by dropping onto formvar coated grid and allowing the solvent to evaporate overnight. The TEM module was Phillip Techni 20 at an accelerated voltage of 120 kV. The particle size distributions were obtained through an image analysis in ImageJ.

Then, the AgNPs solution (before extraction) and the raffinate samples were measured with TGA (module: Mettler Toledo TGA/DSC3+). The TGA was programmed with initial and final temperatures of 30 and 700ºC, with ramping at rate of 10ºC/min, using 30 mL/min N_2 flow. Using TGA, the weight loss at different temperatures represent the amount of different components in the samples. The possible components were AgNPs, solvent (mainly hexane), the adsorbed ligands (i.e., adsorbed oleylamine), the free ligands (i.e., free oleylamine), acetic acid (byproducts of the reduction), silver acetate (residue from the reaction). The AgNPs would not be decomposed at temperatures lower than 550ºC. Also, solvent (hexane) was likely to undergo complete phase transition at temperature lower than 100ºC. The amount of acetic acid and silver acetate in the samples were considered negligible as the silver acetate was a limited agent. Therefore, the weight loss at temperatures between 100 and 550ºC indicated the amount of the adsorbed and free oleylamines – the impurities.

Lastly, it was crucial to ensure that the AgNPs did not leach out with the extract. Therefore, the extract samples were analyzed with UV-Vis to determine the presence of AgNPs. The spectrometer was operated at 200-800 nm with resolution of 1 nm.

3. RESULTS AND DISCUSSIONS

After the extraction, the top layer had a brownish color, likely because of the presence of AgNPs, while the bottom layer was colorless (Fig. 1). This provided us a preliminary indication that most of AgNPs were retained with the top layer (raffinate).

Fig.1 *Photograph of Two Immiscible Layers After the Extraction.*

To prove that the extraction is a mild method, the samples were characterized with TEM to determine if the extraction affected the morphology of the AgNPs. Note that only the samples from the extraction at 30ºC were characterized. Other samples obtained with 40ºC and 60ºC experiments were not characterized with TEM. The TEM images (Fig. 4) show that the AgNPs before and after the extraction with DMF at 30ºC were similar in shape.

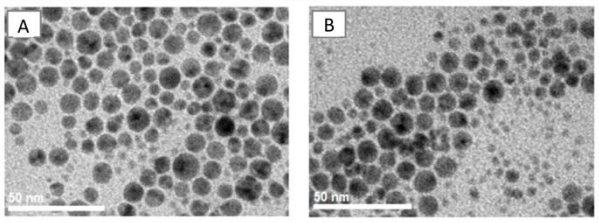

Fig. 2 *TEM images of AgNPs before (A) and after (B) the extraction with DMF at 30ºC (scale bar: 50 nm)*

The TEM images from Fig. 2 were then plotted to exhibit particle size distribution (Fig. 3). This demonstrated that the extraction had a negligible effect on the morphology of AgNPs.

To confirm that the AgNPs were not leached out with the extract, the extract phase was taken to measure with UV-Vis spectrometer. The original AgNPs solution (before extraction) showed a surface plasmon resonance (SPR) band at 440 nm. The extract samples after the extraction showed very low intensity as shown in Table 1. This verified that nearly 100% of AgNPs were recovered, and did not leached out with the extract phases.

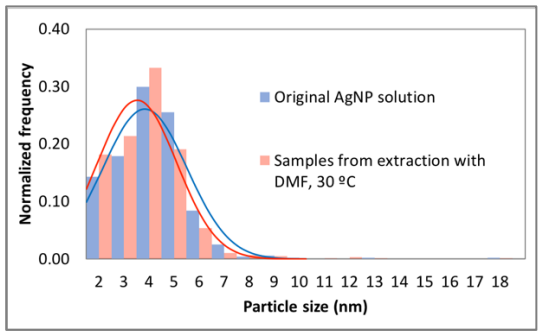

Fig. 3 *Particle Size Distribution of the Original AgNP Solution and the Samples Collected from the Extraction with DMF at 30 ºC.*

Table 1 *Absorbance of the SPR Band at 440 nm*

Samples	Experiment	Absorbance
Original solution	Before extraction	1.44
Extract phase	After extraction at 30 ºC	0.05
Extract phase	After extraction at 40 ºC	0.05
Extract phase	After extraction at 60 ºC	0.05

As discussed previously, the amount of impurities remaining in the raffinate phase were determined via the thermogravimetric analysis. Fig. 4 shows that the weight loss for the samples collected from the extraction of the original AgNPs solution with DMF at different temperatures. In all three experiments, the weight loss happened between 100 and 500 ºC. The weight loss during these temperatures was mainly due to the thermal degradation of oleylamine [10]. The TGA curve remained flat at temperature higher than 500 ºC as the inorganic component (i.e. AgNPs) was not decomposed.

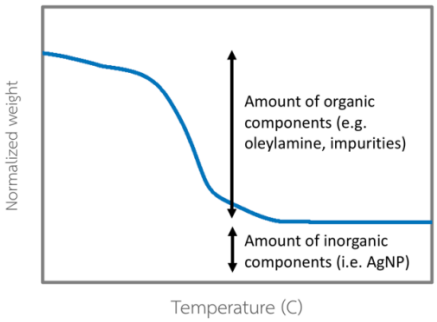

Fig. 4 *TGA Curve Showed the Weight Loss Due to Organic and Inorganic Components*

As shown in Fig. 5, the amount of organic components in samples after extraction at different temperatures were all lower than that in original AgNPs solution. These results indicated that DMF was able to extract a fraction of oleylamine from the original AgNPs solution.

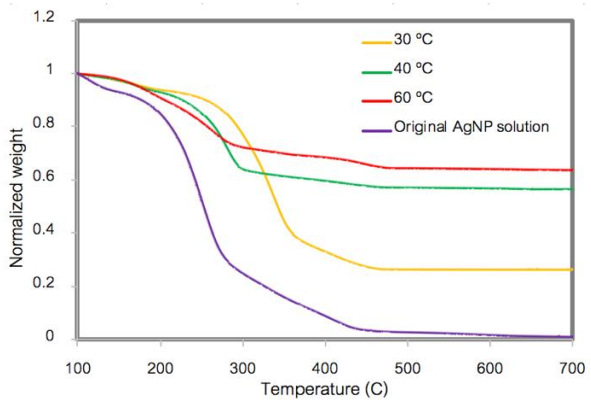

Fig.5 *TGA Curves of Original AgNPs Solution and Samples Collected from the Extraction with DMF at 30ºC, 40ºC, and 60ºC*

Increasing the extraction temperature appeared to enhance the amount of impurities that were extracted. The percent of extracted organic component were approximated to be 25.3%, 56.6%, and 70.7% for the experiment at 30ºC, 40ºC, and 60ºC, respectively. The TGA curves were slightly different in shape for different temperatures, probably due to the natures of oleylamine, either adsorbed or free, in the solution.

4. CONCLUSIONS

Metal nanoparticles are mostly produced with excess ligands, which are considered impurities as they can affect post-synthesis steps such as ligand exchanges. Conventional methods including centrifugation, filtration, and chromatography have some limitations. In this work, we explored an alternative method, solvent extraction by showcasing the extraction of oleylamine from the silver nanoparticles (AgNPs) solution that used hexane as solvent. Here, oleylamine served as the reducing agent as well as capping agent. However, significant amount of oleylamine stayed free and detached from the AgNP. Dimethyl formamide was found to be an effective solvent for this system. The extraction was considered as mild because it did not damage the shapes and sizes of AgNPs as characterized by TEM images of the samples from the extraction at 30ºC. UV-Vis results confirmed negligible amount of AgNPs were leached out with the extraction. In other words, percent recovery of AgNPs were close to 100%. In addition, the TGA results showed that increasing extraction temperatures were found to enhance the percent of extraction.

5. ACKNOWLEDGMENT

The research grant VJP. 10/2560 from Faculty of Engineering, Burapha University is acknowledged.

REFERENCES

[1] Y. Shen, M. Y. Gee, and A. B. Greytak "Purification technologies for colloidal nanocrystals," *Chemical Communications*, vol. 53, no. 5, pp. 827-841, 2017.

[2] J. Hühn, C. Carrillo-Carrion, M. G. Soliman, , C. Pfeiffer, D. Valdeperez, A. Masood, I. Chakraborty, L. Zhu, M. Gallego, Z. Yue, M. Carril, N. Feliu, A. Escudero, A. M. Alkilany, B. Pelaz, P. D. Pino, and W. J. Parak "Selected standard protocols for the synthesis, phase transfer, and characterization of inorganic colloidal nanoparticles", *Chemistry of Materials*, vol. 29, no. 1, pp. 399-461, 2016.

[3] W. J. Parak, T. Pellegrino, C. M. Micheel, D. Gerion, S. C. Williams, and A. P. Alivisatos, "Conformation of oligonucleotides attached to gold nanocrystals probed by gel electrophoresis", *Nano Letters*, vol. 3, no. 1, pp. 33-36, 2003.

[4] W. W. Yu, and X. Peng "Formation of high-quality CdS and other II–VI semiconductor nanocrystals in noncoordinating solvents: tunable reactivity of monomers", *Angewandte Chemie International Edition*, vol. 41, no. 13, pp. 2368-2371, 2002.

[5] Y. Shen, N. Weeranoppanant, L. Xie, Y. Chen, M. R. Lusardi, J. Imbrogno, M. G. Bawendi and K.F. Jensen. "Multistage extraction platform for highly efficient and fully continuous purification of nanoparticles" *Nanoscale*, vol. 9, no. 23, pp. 7703-7707, 2017.

[6] Y. Shen, A. Roberge, R. Tan, M. Y. Gee, D. C. Gary, Y. Huang, D. A. Blom, B. C. Benicewicz, B. M. Cossairt, and A. B. Greytak "Gel permeation chromatography as a multifunctional processor for nanocrystal purification and on-column ligand exchange chemistry", *Chemical Science*, vol. 7, no. 9, pp. 5671-5679, 2016.

[7] W. Nan, Y. Niu, H. Qin, F. Cui, Y. Yang, R. Lai, W. Lin and X. Peng "Crystal structure control of zinc-blende CdSe/CdS core/shell nanocrystals: synthesis and structure-dependent optical properties" *Journal of the American Chemical Society*, vol. 134, no. 48, pp. 19685-19693, 2012.

[8] Z. Li, Y. Ji, R. Xie, S. Y. Grisham, and X. Peng "Correlation of CdS nanocrystal formation with elemental sulfur activation and its implication in synthetic development" *Journal of the American Chemical Society*, vol. 133, no. 43, pp. 17248-17256, 2011.

[9] H. Hiramatsu and F. E. Osterloh "A simple large-scale synthesis of nearly monodisperse gold and silver nanoparticles with adjustable sizes and with exchangeable surfactants" *Chemistry of Materials*, vol. 16, no. 13, pp. 2509-2511, 2004.

[10] M. Seyhan, W. Kucharczyk, U. E. Yarar, K. Rickard, D. Rende, N. Baysal, S. Bucak, and R. Ozisik "Interfacial surfactant competition and its impact on poly (ethylene oxide)/Au and poly (ethylene oxide)/Ag nanocomposite properties" *Nanotechnology, science and applications*, vol. 10, pp. 69, 2017.

N. Weeranoppanant, photograph and biography not available at the time of publication.

K. Sritawong, photograph and biography not available at the time of publication.

N. Pankaew, photograph and biography not available at the time of publication.