

Simple Large-Scale Synthesis of Monolayer-Protected Silver Nanocrystal

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ABSTRACT

In this study, we attempted to present a direct synthesis of narrowly dispersed silver nanoparticles in highly concentrated organic phase (> 2 M) without use of a size-selection process. The fully organic phase system contains silver nitrate as a silver precursor, alkyl ligand as a media dissolving silver salt, alkanolic acid as a capping molecule, hydrocarbon solvent as a media, and reducing reagent. Even using only generic chemicals, monodispersed silver nanocrystals with size of 7 nm were easily synthesized at 100 gram-scale in 1 liter reactor. Also, systematic studies revealed that the as-synthesized silver nanocrystals were stabilized through bidentate bridging of carboxyl group in alkanolic acid.

Keywords: silver; nano; ligand; complex;

1 INTRODUCTION

Over the past decade, metallic nanoparticles have drawn intense interest due to their potential applications in microelectronics [1], catalysis [2] and optics [3]. The metallic nanoparticles show unique properties different from bulk and atomic species because of their peculiar electronic structure and extremely large surface area with high percentage of surface atom [4]. For examples, gold nanoparticle with 5 nm exhibit a drastic decrease in melting point over 500 °C compared to the bulk [5]. The metallic nanoparticles with various cores including Au, Ag, Cu, and Pd have been investigated. Especially, silver nanoparticles have been of interest due to their size-dependent optical and surface plasmon properties including surface-enhanced Raman effects. Recently, silver nanoparticles have been further explored in printed electronics that are related to their low sintering temperature, high electric conductivity and chemical inertness [6,7]. In the printed electronics, direct writing technologies for metallic patterning on various substrates including glass, ITO, and polymer require stable and concentrated dispersions of metallic nanoparticles [8,9]. Monodispersity of the silver nanoparticles is very important in many of these cases.

Silver nanoparticles are mostly synthesized through various colloidal processes of surfactant-stabilized silver nanoparticles in liquid phases through chemical reductions of silver salts in aqueous solutions. With some exceptions, most of the chemical synthetic approaches are based on the reduction of water-soluble silver salt precursors, AgNO₃

and its derivatives reduced by boron hydrides, alcohols, citrates, and alkyl sulfates. The size distributions of the nanoparticles synthesized are often broad and the stability of these colloids has been problematic, as they aggregate and precipitate out over time in aqueous solution.

Since the preparation of alkanethiolate-stabilized gold nanocrystals [10-14], there have been intense research efforts on various aspects of soluble metal particles and their aggregates. Recently, other capping molecules such as alkylamines [15-17] and carboxylates [18-20], which are weakly anchored to Ag particle cores compared to alkanethiols, have been studied and reported.

However, silver nitrate as a silver precursor has not been used directly in organic phase due to its low solubility although it had some advantages such as low cost and chemical stability. Therefore, silver precursors used in organic phase have been (i) expensive but labile silver salts (such as silver perchlorate, silver triflate, or etc.) or (ii) silver nitrate derivatives such as silver-alkanate complex (RCO₂-Ag, R: alkyl group), which is synthesized by below schemes:



where R, Y, X are hydrocarbon (such as alkyl), cation (such as NH₄⁺, Na⁺, K⁺), and anion (such as OH⁻), respectively. The synthesized silver-alkanate complex can be dissolved into organic phase above 130 °C due to its stable solid-state and then resulted in alkanate-stabilized silver nanoparticle by thermal decomposition above 300 °C

In this paper, we attempted to synthesize monodispersed silver nanocrystals for low temperature-metallized electrode for printed electronics. Also, these silver nanocrystals have to satisfy low cost and stable dispersability. The former may be achieved through synthesis of narrowly dispersed silver nanocrystals in highly concentrated organic phase using only cheap generic chemicals. The latter is the key point of application to printed electronics and may be achieved through controlling structure of capping molecules. Furthermore, we attempted to investigate coordinative interactions and then make metallic patterns at low temperature through direct writing technology.

2 EXPERIMENTAL

The fully organic phase system contains silver nitrate as a silver precursor, alkyl ligand as a media dissolving silver salt, alkanolic acid as a capping molecule, hydrocarbon solvent as a media, and reducing reagent. Silver nitrate (AgNO_3 , +99.8%, Junsei Chemical Co.), alkanolic acid (RCO_2H , GR grade, Junsei Chemical Co.), alkyl ligand (GR grade, Junsei Chemical Co.), reductant (GR grade, Junsei Chemical Co. and Fluka Co.), and solvents (EP grade) was used as received without further purification.

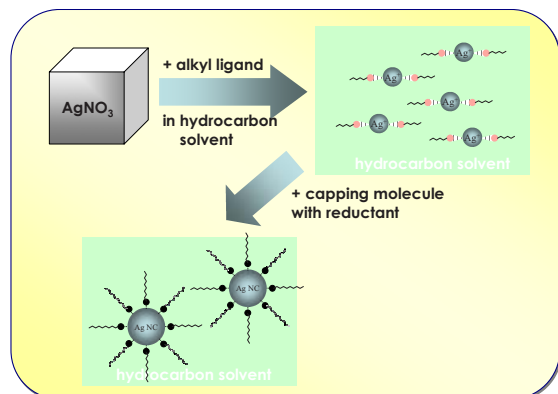


Figure 1: Experimental schemes for synthesis of silver nanocrystal in organic phase

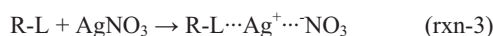
Silver nitrate (1 mol) was dissolved into alkyl ligand (2 mol) completely and then hydrocarbon solvent (300 ml) was poured into the above solution, which resulted in molar concentration ($[\text{Ag}]$) above 2 M. After addition of alkanolic acid (0.03 mol) and equimolar reductant, the solution became dark brown and then was refluxed for 1 hr. After completion of reaction, products were precipitated by addition of acetone/methanol mixture. The precipitates were collected through glass funnel filter and then washed several times by methanol and acetone.

Formation of silver nanoparticle was observed through GBC Cintra40 UV-Visible (UV) spectroscopy, which shows surface plasmon peaks in the range between 380 ~ 450 nm, and Rigaku Rint2000 X-ray Diffractometer, which shows typical cubic structure. Size and size distribution of the silver nanoparticles were investigated through FEI Technai G2F20S-Twin filed-emission transmission electron microscopy (FE-TEM) and Microtac Nanotracer250 particle size analyzer, respectively. Furthermore, molecular structure and bonding origin of capping molecules were studied through Bio-Rad FTS65A FT-IR spectroscopy, JEOL 300 MHz NMR, and Ulvac-Phi PHI Quantetra SXM XPS.

3 RESULTS AND DISCUSSION

3.1 Complex formation between silver ion and amino group

The silver nitrate can be dissolved in hydrocarbon solvent if there are some ligands which can dissociate lattice of silver nitrate. In this study, alkyl ligand was used in order to dissolve silver nitrate through coordinative interaction, as shown in below reaction:



Coordinative interaction was related to electron donation from ligand group to metal atom and electron back-donation from metal atom to ligand. Usually, ligand groups include some atoms such as O, N, S, or P, which donate those lone pair electrons to metal atom, and π -bond, which have so high electron density to donate electron to metal atom. FT-IR spectroscopy was used in order to investigate coordinative interaction between silver atom and alkyl ligand. The alkyl ligand consisted with hydrocarbon chain and functional group. Figure 2 showed some peaks for hydrocarbon (C-H) and other peaks for functional group of alkyl ligand. After adding silver nitrate to alkyl ligand, the peaks related with functional group shifted to lower wavenumber. This shift was attributed to electron donation from functional group to silver atom, which decreased electron density of functional group and resulted in lower wavenumber. Therefore, it could be summarized that the lattice of silver nitrate was dissociated by coordinative interaction with alkyl ligand and then dissolved into hydrocarbon solvent.

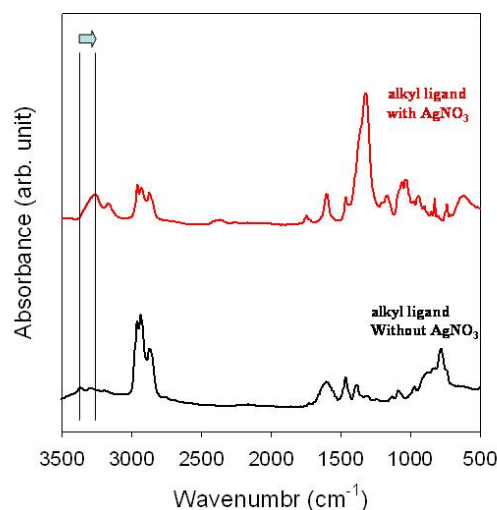


Figure 2: FT-IR spectra for alkyl ligand with or without silver nitrate

3.2 Synthesis of silver nanocrystals

The as-synthesized powder was re-dispersed in toluene and then those particle size and size distribution were characterized through transmission electron microscopy (TEM). Figure 3 illustrates TEM images of the silver nanocrystals obtained from the single-phase approach. A plausible control over the size and size distribution of the nanocrystals is evident. The nanoparticles showed a significantly narrow size distribution with average 7 nm.

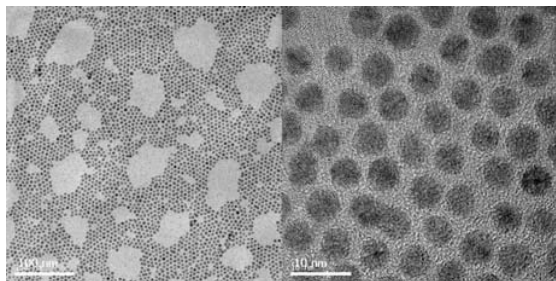


Figure 3: TEM images for as-synthesized silver nanoparticles

This monodispersity of silver nanoparticles was possible to control chain structure of capping molecule and crystal growth kinetics. In the case of crystal growth kinetics, fast nucleation and slow growth process is useful to make nanoparticles monodisperse [21]. Usage of reductant could make fast nucleation possible and resulted in monodispersed nanoparticles. Also, linear structured capping molecule can form crystal layer and therefore be useful for monodispersity of nanoparticle. Therefore, monodispersed nanocrystals could be made using linear structured fatty acid and reductant.

Also, it could be assured that the synthesized nanoparticles were silver nanocrystals from surface plasmon peak at 420 nm from UV-Visible spectroscopy and X-ray diffraction pattern for face-centered cubic structure of silver crystal. Therefore, it could be concluded that the monodispersed silver nanocrystals could be synthesized through one-step reaction in fully organic phase, even though silver nitrate was used as a silver precursor. This could be obtained by the coordinative interaction between silver atom and alkyl ligand. The concentration of the capping molecule and the reducing agent as well as temperature played a key role in determining nucleation and growth of silver nanocrystals in the solution. Usage of reducing agent can accelerate reduction of silver nitrate at low temperature and result in high yield for silver nanocrystals.

3.3 Bonding origin between silver nanocrystal and capping molecule

Alkanoic acid, silver-alkanate complex and silver nanocrystals were investigated through FT-IR in order to investigate complexation behavior of silver with carboxyl group. Figure 4 showed that alkanolic acid had some peaks for hydrocarbon (C-H) and other peaks for carboxylic acid. Especially, peaks for carboxylic acid consisted of C=O stretch peak at 1690 cm^{-1} , out-of-plane O-H stretch peak at 930 cm^{-1} and O-H stretch peak at $3500 \sim 2500\text{ cm}^{-1}$. In silver-alkanate complex, two peaks related with O-H stretch disappeared and the C=O stretch peak shifted from 1690 to 1523 cm^{-1} . This may be associated with the complexed C=O bond attributable to the coordination between Ag^+ and carbonyl oxygen. In silver nanocrystals, there were also disappearance of the O-H stretch peak and red shift of the C=O stretch peak. FT-IR showed that capping molecule stabilizing silver nanocrystal is not carboxylic acid form (CO_2H) but carboxylate form (CO_2^-). Also, wave number separation for C=O stretch peak ($\Delta: 1690 - 1523 = 167\text{ cm}^{-1}$) can be ascribed to bridging bidentate, where the interaction between the CO_2 group and the Ag atom is covalent [22,23].

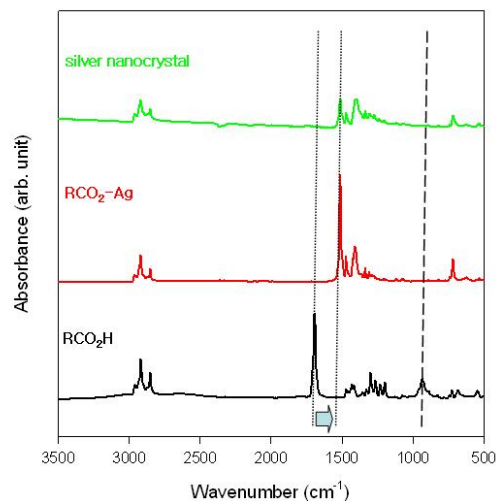


Figure 4: FT-IR spectra for alkanolic acid, silver alkanate, and silver nanocrystal

The binding energy obtained in X-ray photoelectron spectra (XPS) were corrected for specimen charging by referencing the C 1s peak to 284.8 eV, as shown in Figure 5. The binding energy for Ag $3d_{5/2}$ is 368.4 eV. The above FT-IR results can be supported from XPS results, which showed monovalent O 1s peak around 530 eV. Furthermore, XPS results showed that degree of electron donation from carboxylate to silver is higher in silver-dodecanate complex (C 1s: 288.3 eV, O 1s: 531.5 eV) peak than in silver

nanoparticles (C 1s: 287.8 eV, O 1s: 530.9 eV). This is attributed from the state of silver, i.e. silver ion (in silver-alkanate) vs. silver atom (in silver nanoparticle).

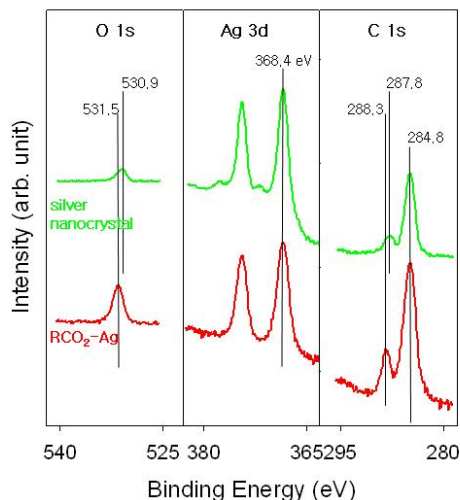


Figure 5: XPS spectra for silver alkanate and silver nanocrystal

It can be summarized from FT-IR and XPS analysis that silver nanocrystals were stabilized through bidentate bridging of carboxyl group in fatty acid, as shown in Figure 6.

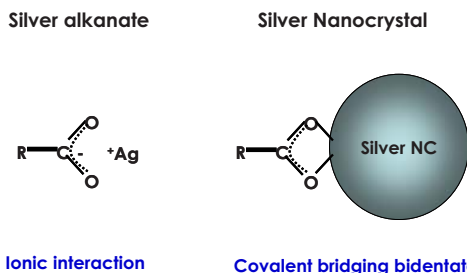


Figure 6: Interaction modes of silver alkanate and silver nanocrystal

4 CONCLUSION

In summary, the size and size distribution control of silver nanocrystal was found to be feasible by adopting single-phase and one-pot approaches using generic chemicals. The key to the success to the single-phase approaches is the alkyl ligand dissociating silver nitrate in hydrocarbon, the structure of capping molecule and the reducing agent. Ultimately, we could synthesize 100 gram of the monodispersed silver nanocrystals using 1 liter reactor with much lower material cost (<1/10), compared to commercial products. Furthermore, the as-synthesized silver nanocrystals were stabilized through covalent

bidentate bridging of carboxylic in fatty acid and therefore had lower thermal decomposition temperature than silver alkanate with ionic interaction. Also, the as-synthesized silver nanocrystals also showed sufficient electrical conductivity even though sintered at 250 °C and therefore may be applicable to printed electronics such as printed circuit board.

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