

Preparation of Highly Stabilized Silver Nanopowders by the Thermal Reduction and Their Properties

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Received August 10, 2012, Accepted September 6, 2012

Silver nanopowders were prepared from silver 2-ethylhexylcarbamate (Ag-EHCB) complexes by simple thermal reduction at 85 °C without any reducing agent in organic solvent. 2-Ethylhexylammonium 2-ethylhexylcarbamate (EHAHC) was investigated in terms of their abilities to stabilize the silver nanoparticles (Ag-NPs) and its subsequent effects on the preventing aggregation between Ag-NPs. Conditions (concentration of stabilizer and reaction time) used to reduce Ag-EHCB complex were systematically varied to determine their effects on the sizes of Ag-NPs. The formation of the stabilized Ag-NPs were easily monitored by UV-vis spectroscopy and characterized by TGA, TEM, SEM and XRD. When EHAHC was used as a stabilizer, Ag-NPs of 10-30 nm in diameter were easily obtained in high yield. Silver patterns were obtained from a silver nano-paste by heat treatment at 200 °C in air and were found to have resistivity values of $2.9 \times 10^{-8} \Omega\cdot\text{m}$.

Key Words : Silver 2-ethylhexylcarbamate, Nanopowders, Thermal reduction, Silver nano-paste

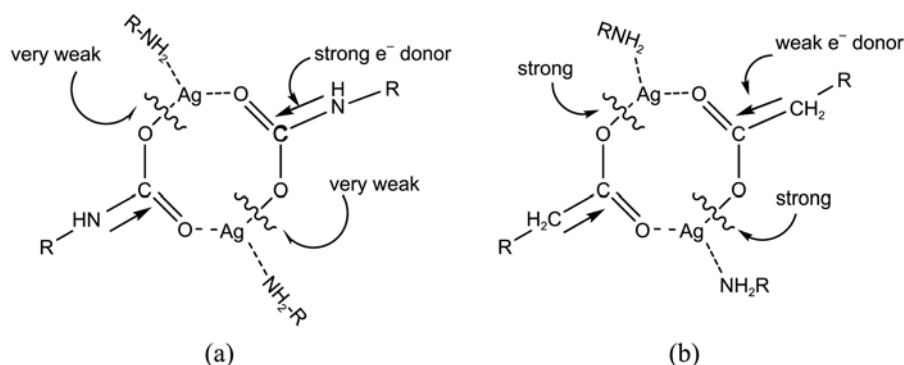
Introduction

Various chemical methods have been used to synthesize silver nanoparticles (NPs) dispersions. The most common of these approaches uses a strong reducing agent such as sodium borohydride, sodium citrate, ascorbic acid, hydrogen gas, or others.¹⁻⁶ However, these reactions are difficult to apply to large-scale synthesis, due to high dilutions and the highly exothermic nature of the reduction reaction. Thermal reduction has great advantages for large-scale synthesis at the industrial level and offers the advantage of producing essentially 'clean' Ag-NPs, that is, Ag-NPs free of inorganic ions.⁷⁻¹³

Several silver precursors have been used to synthesize Ag-NPs. AgNO₃ is the most common source of silver ions, but the sulfate, carbonate, oxide, perchlorate, and carboxylate of silver have also been used.¹⁴⁻²⁰ In particular, silver carboxylate and amine complexes are reduced to silver metal by

heating at acceptable temperatures, and the freed carboxylic acid and alkyl amine entity stabilize the Ag-NPs produced.²¹⁻²⁵ This method also offers the advantage of producing the Ag-NPs capped by alkyl carboxylate ligand. However, high boiling, long chain carboxylic acid and amine remain in the colloidal solution produced.^{25,26} Ag-NPs with different sizes and shapes were prepared by facile reduction of silver alkylcarbamate complex using various reducing agents and stabilizers.²⁷⁻³²

The controlled thermal reduction of silver carbamate complex in common organic solvents is one of the simplest methods of synthesizing Ag-NPs. Because the ionic bond between the silver and carbamate is weakened by the coordination of alkyl amine with the silver atom.³³ Thus Ag-EHCB complex is able to decompose at ~120 °C immediately.^{34,35} Moreover, thermal decomposition to silver metal can occur at 85 °C within 1 h. The chemistry between CO₂ and amines is essentially an acid-base equilibrium. Two mole-



Scheme 1. Schematic structure of silver (a) alkyl carbamate and (b) alkyl carboxylate.

cles of an amine, in the presence of CO₂, react to form a carbamic salt, presumably by way of the corresponding carbamic acid. Carbamate is thermally unstable and equilibrated between CO₂ and corresponding amine upon heating.^{19,36,37} This can be useful for the capping of growing Ag-NPs with carbamic acid as a stabilizer. Therefore, 2-ethylhexylammonium 2-ethylhexylcarbamate (EHAHEC) reacted with the surfaces of Ag-NPs during thermal reduction.

In this paper, we report the facile preparation of highly stabilized and size controlled silver nanopowders produced only by the thermal reduction of silver 2-ethylhexylcarbamate (Ag-EHCB) in alcoholic solvents without reducing agent. In addition, silver paste using nano-sized silver nanopowders was prepared. Microstructures and related specific resistivity of the silver thin films with sintering temperatures were investigated.

Experimental

Chemicals and Instruments. Silver 2-ethylhexylcarbamate (Ag-EHCB) complex (C₈H₁₇NHCOO)₂Ag₂·2C₈H₁₇NH₂) was prepared as previously described.³³ 2-Propanol (Aldrich Chem. Co.) and 2-methoxyethanol (Aldrich Chem. Co.) were used as received. Oleic acid-protected Ag-NPs were prepared by the method reported by M. Nakamoto.²⁶

Isolated organic compounds were characterized by GC-MS, which was conducted by GC/MSD (Varian 4000). XRD patterns of the Ag-NPs produced were measured using a Shimadzu XD-D1 X-ray diffractometer and Cu K α radiation ($\lambda = 1.54056 \text{ \AA}$) at a scanning rate of 2 degrees per second in a 2θ range from 30° to 90°. TEM images were obtained using a JEOL electron microscope (JEM-2000EXII). TEM samples were prepared by dropping a small amount of silver colloid solution onto a carbon-coated copper grid. UV-vis spectra (from 200 to 800 nm) were obtained using a Shimadzu UV-1601PC spectrometer. Silver nanocolloid solutions were diluted with 2-propanol and placed in the cell of a quartz cuvette. Conductivity of Silver pastes was checked by using four point probe (2420 3A Source Meter) method.

Preparation of Ag Nanocolloid by Thermal Reduction. A round bottomed flask (1000 mL) was charged with 2-propanol (600 mL) and Ag-EHCB complex solution (4.0 g, $2.48 \times 10^{-2} \text{ mol/L}$). The reaction mixture was stirred at room temperature for 5 min, and then the flask was placed in the oil bath preheated at 85 °C for 10, 30 and 60 min. The resulting colloidal solution was cooled immediately to room temperature and the samples for UV-vis were prepared.

Preparation of Silver Nanopowders Stabilized with 2-Ethylhexylammonium 2-Ethylhexylcarbamate (EHAHEC). A solution of Ag-EHCB complex (10.0 g) and EHAHEC (3.0 g) in 2-propanol (500 mL) was stirred in a round bottomed flask (1 L). The flask was placed in an oil bath heated at 85 °C. Heating the solution at that temperature for 1 h caused gradual decomposition to produce a brown dispersion with metallic luster. The reaction mixture was cooled to 20 °C and then methanol was added. The resulting colloidal solution was centrifuged and collected by filtration,

washed with methanol, and dried under vacuum (85% yield based on silver).

Preparation of Silver Nano-Paste. The silver nano-paste with 40 wt % of Ag-NPs, which were synthesized by the above-mentioned thermal reduction process, was prepared. The amount of vehicle is fixed for the preparations. The vehicle contains ethyl cellulose (3 wt %) and polyurethane acrylate (EB-230, 7%) binders, and PEGMEA solvent. After sonication and degassing process, spin coating was applied on the surface of glass substrates ($2.5 \times 2.5 \text{ cm}^2$). Annealing process was done under 150 °C for 30 min in air.

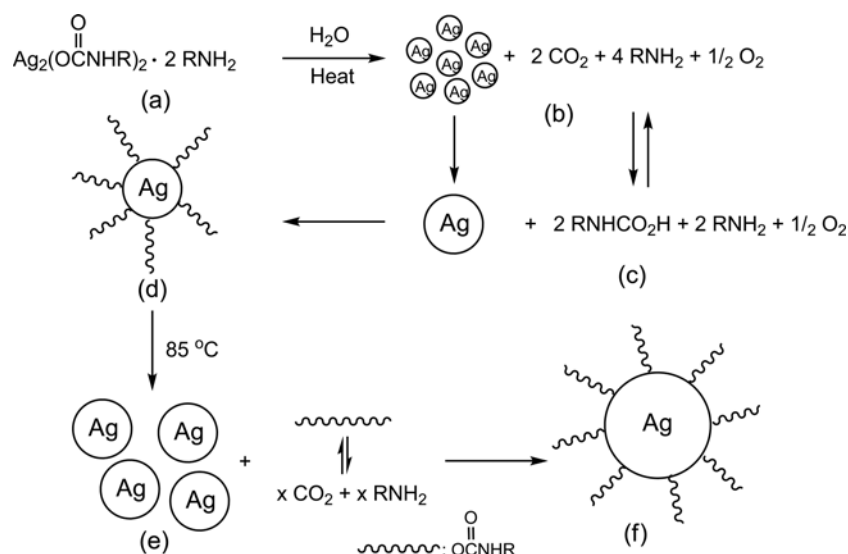
Results and Discussion

Silver 2-ethylhexylcarbamate (Ag-EHCB) complex was prepared by reacting silver oxide with 2-ethylhexylammonium 2-ethylhexylcarbamate (EHAHEC). The ionic bond between silver and carbamate anion is weakened considerably by coordination between alkyl amine and the silver. Thus, the silver to oxygen bond energy was low enough to allow decomposition at 85 °C within 1 h.³⁴

The concentration of Ag-EHCB complex has an effect on the formation of Ag-NPs in organic solvent by thermal reduction at 85 °C without stabilizer. When concentration reached at $1.24 \times 10^{-2} \text{ mol/L}$, stable UV absorption spectra of the resulting silver plasmon resonance absorption of Ag-NPs around 410 nm were obtained. In addition, the time was found to be the most important considerations. The initially formed silver nuclei were found to form a fixed number of seeds during early stage of the reaction, and then these nuclei grew by diffusion-driven silver deposition. The CO₂ and 2-ethylhexylamine generated during the reaction reacted to produce 2-ethylhexylcarbamic acid, which then reacted with the surfaces of Ag-NPs (Scheme 2).

Rates of reduction were estimated using UV-vis spectra. Figure 1 shows the UV-vis spectra of Ag nanocolloid solutions prepared by heating Ag-EHCB complex at 85 °C. In the case of thermal reduction for 10 min, the maximum wavelength remained around 410 nm, which characteristically is the silver plasmon spectroscopic region. However, other peak appeared at over 470 nm and increased to 510 nm steadily with heating time up to 1 h, indicating that steady aggregation took place during thermal reduction without stabilizer. Nevertheless, the Ag particles obtained retained sizes in the nano range. It would appear that the surfaces of Ag-NPs produced were hydrophobic due to presence of absorbed 2-ethylhexylcarbamic acid. In fact, these surface-modified Ag-NPs were easily dispersed in organic solvents (Scheme 2(b)-(d)).

Stabilizer of Ag-NPs was expected to influence particle size, distribution, and stability markedly. EHAHEC was selected as a stabilizer for the dispersion of Ag-NPs in 2-propanol. To determine the optimal conditions required to prepare stable silver nanocolloids with different sizes and distributions, several experiments were conducted at different concentrations of EHAHEC. On heating the precursor solution at 85 °C for 1 h, the solution turned to greenish



Scheme 2. Schematic view of formation of stable silver nanopowders by thermal reduction of Ag-EHCB complex in the presence of EHAHHC: (a) Ag-EHCB 2-ethylhexylamine complex, (b) products produced after thermal reduction, (c) formation of aggregated Ag-NPs and 2-ethylhexylcarbamic acid, (d) modification of Ag-NPs with 2-ethylhexylcarbamic acid, (e) gradual thermal decomposition of surface-protected Ag-NPs, (f) growth of Ag-NPs and formation of stable nanopowders.

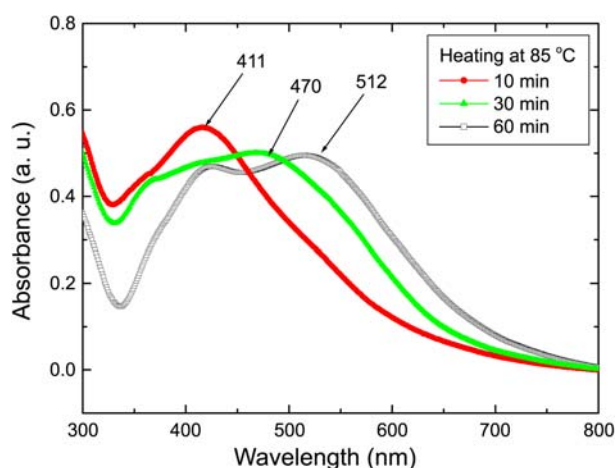


Figure 1. UV-vis absorption spectra of silver colloidal solutions obtained by thermal reduction at 85 °C in 2-propanol.

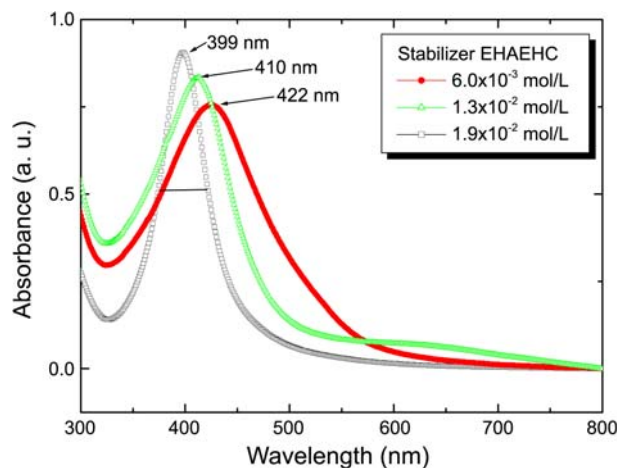


Figure 2. UV-vis absorption spectra of silver colloidal solutions obtained from Ag-EHCB in the presence of various amounts of EHAHHC by heating at 85 °C for 1 h.

brown instantly and the significant changes in the shapes and intensities of UV-vis absorption bands were observed. The completeness of Ag-EHCB complex reduction was followed by UV-vis spectroscopy by monitoring the appearances of the absorption bands of the silver surface plasmon around 400–420 nm. As the concentration of EHAHHC was increased from 6.0×10^{-3} to 1.9×10^{-2} mol/L in 2-propanol, the maximum wavelength of the silver plasmon peak was shifted from 399 to 422 nm and the full width at half maximum of the absorption band decreased from 101 to 52 nm as shown in Figure 2. This result suggests that the particle size distribution was narrowed by the presence of EHAHHC stabilizer. However, the strongest intensity and a relatively narrow particle size distribution were obtained at an EHAHHC concentration of 1.9×10^{-2} mol/L and heating at 85 °C. The reduction by heating resulted in very stable samples without precipitation after several months.

Figure 3 shows a typical TEM photograph of the silver nanocolloid prepared from EHAHHC concentrations of 6.0×10^{-3} to 1.9×10^{-2} mol/L at 85 °C. The smallest sized (5–15 nm) Ag-NPs were obtained using high EHAHHC concentrations. Most Ag-NPs were well-dispersed and sphere and polygon-shaped, which was in-line with UV-vis absorption findings.

The silver colloidal solutions produced were centrifuged to precipitate Ag-NPs, which were isolated as deep greenish brown powders. These powders were stable for several months at room temperature and dispersed easily in both polar and nonpolar solvents, such as, 2-propanol and toluene, respectively.

Shown in Figure 4(a) is the SEM picture of nano-sized Ag-NPs prepared in this work. Roughly, for the nano-sized Ag-NPs, their shape appeared irregular and also contained a

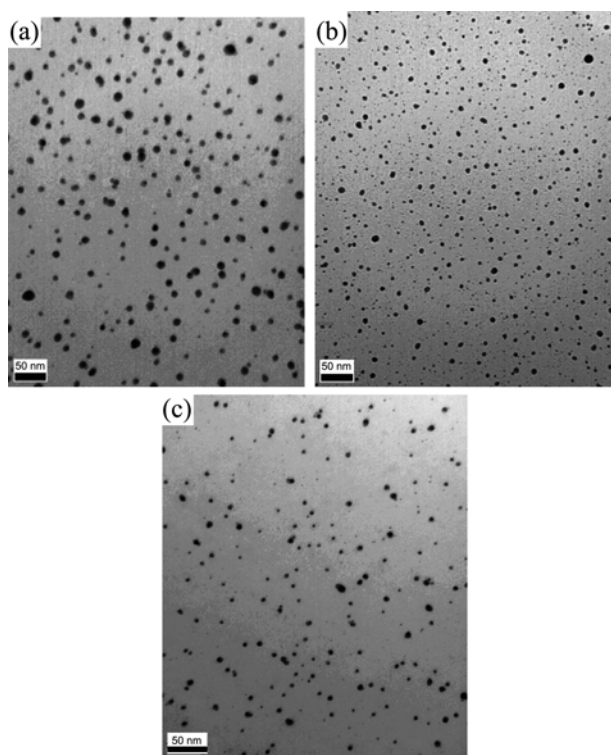


Figure 3. TEM images of silver colloidal solutions obtained from Ag-EHCB in the presence of EHAHC (a) 6.0×10^{-3} , (b) 1.3×10^{-2} and (c) 1.9×10^{-2} by heating at 85 °C.

few small particles. They were spherical in shape and had a size range between 10 and 30 nm with an average of 25 nm, which is also crystalline based on XRD data. Figure 4(b) shows typical transmission electron microscopic (TEM) images of Ag-NPs prepared by dispersing silver nanopowders in toluene. TEM image showed the controlled growth of spherical Ag-NPs. According to the histogram depicted in Figure 4(c), these spherical Ag-NPs displayed a narrow size distribution ranging from 20 to 25 nm. The aggregation of silver nuclei was suppressed and the growth of silver was limited to an average diameter of 25 nm despite the thermal procedure.

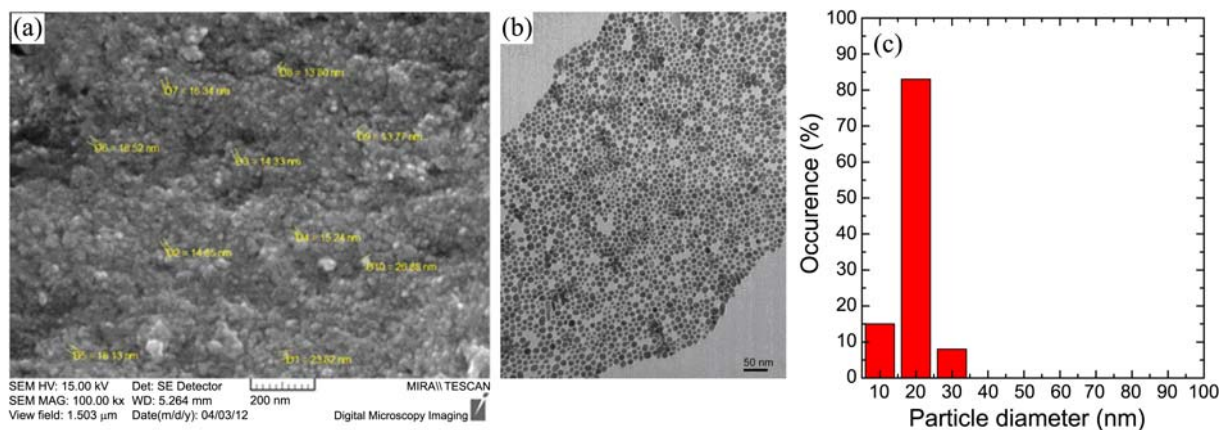


Figure 4. (a) SEM image of silver nanopowders, (b) TEM image of silver nanopowders redispersed in toluene and (c) histogram of size distribution of silver nanopowders.

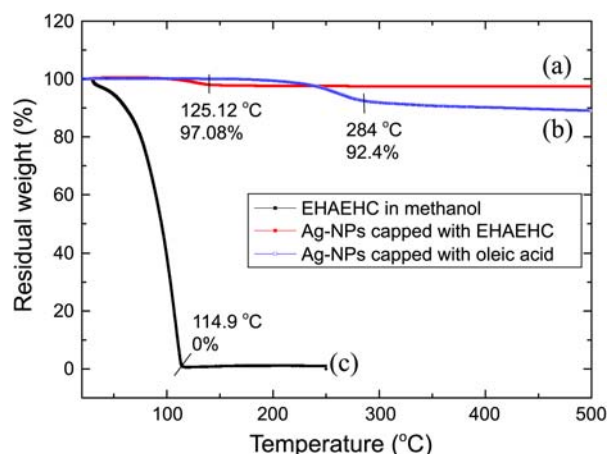


Figure 5. TGA thermograms of (a) silver nanopowders obtained by thermal reduction of Ag-EHCB at 85 °C, (b) silver nanopowders obtained by thermal reduction of silver oleate in the presence of 2-ethylhexyl amine and (c) EHAHC in methanol solution.

The metal contents of Ag-NPs were determined by thermogravimetric analysis, and were found to contain 97.08% silver and 2.92% organic stabilizer and to lose its weight at 125 °C, as shown in Figure 5. On the other hand, The Ag-NPs stabilized with oleic acid showed > 7.6% organic content. Moreover the stabilized Ag-NPs lose its weight more than at 284 °C.^{22,26} Yields were also confirmed by weight and by adjusting for the metal contents of isolated Ag-NPs. The GC-MS analysis of the organic components of Ag-NPs produced at 150 °C for 3 min, revealed 2-ethylhexylamine and carbon dioxide derived from of 2-ethylhexylcarbamic acid as illustrated in Scheme 2(e) and Figure 5(c). The precipitated Ag-NPs were also subjected to powder X-ray diffractometry. The XRD pattern of the Ag-NPs exhibited peaks at 2θ values of 38.00 (111), 44.4 (200), 64.5 (220), and 77.5° (310), which correspond to the face-centered cubic (fcc) structure of silver (Figure 6).

The silver electrodes were examined by SEM in order to determine microstructural features before and after heat treatment. The micrographs shown in Figure 7 are typical

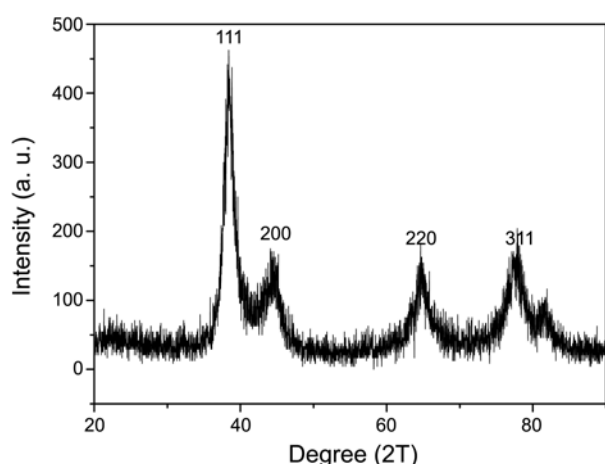


Figure 6. XRD pattern of silver nanoparticles obtained by thermal reduction of Ag-EHCB in the presence of EHAEHC at 85 °C.

examples of silver electrodes, which have a granular appearance on higher magnification. It is a nano-crystalline with a mean grain size of approximately 20-30 nm. There are some voids and an even coating has formed as a result of the deposition and heat treatment process. High resolution SEM images of these nano-sized silver grains, demonstrates their

dense packing and narrow size distribution (Figure 7(a) and (b)). The rapid evaporation of solvent would also limit mobility of silver, therefore resulting in localized crystal growth within the forming electrode microstructure (Figure 7(c)). In this study, silver nanoparticles protected with EHAEHC did not render the by-product in the conductive silver electrode after sintering. The fine grain size (0.3-0.8 μm) is thought to be consistent with the low conversion temperature (150 °C), which would introduce multiple nucleation events (Figure 7(d)). A mean resistance figure of $38.2 \pm 0.4 \text{ m}\Omega/\square$ was obtained using the four-way contact probe technique for track lengths of 2.5 cm on all substrates. From this the resistivity of the coated silver paste is in the range $2.9 \times 10^{-8} \Omega\text{-m}$, which corresponds to 1.8 times the resistivity of bulk silver. The silver thin layer with 1 μm thickness without polymeric binder shows $1.6 \times 10^{-8} \Omega\text{-m}$ of resistivity, which is comparable to bulk silver.

Conclusion

In summary, silver nanoparticles with a narrow size distribution were synthesized successfully via thermal reduction of a novel silver alkylcarbamate complex. The proper reaction temperature (85 °C) and heating time (< 1 h) are critical

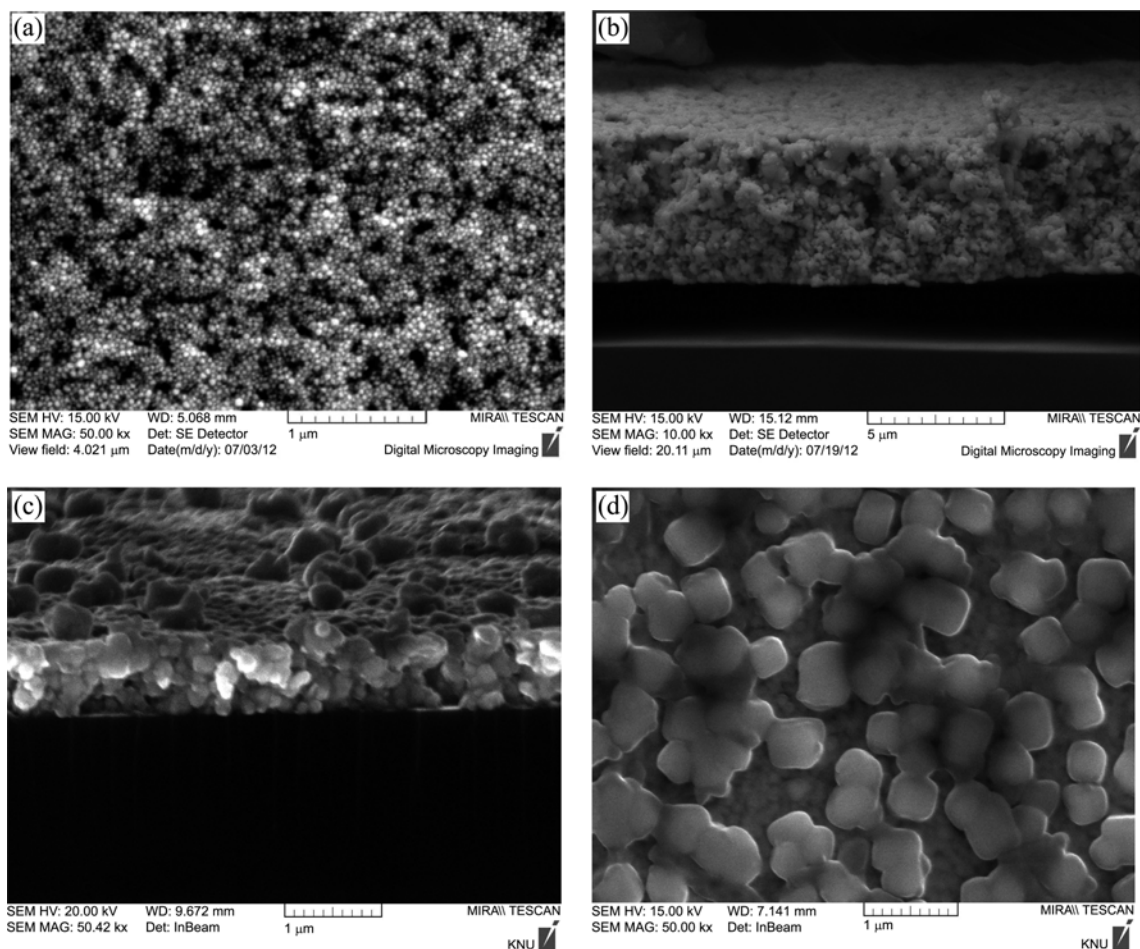


Figure 7. SEM images of electrode printed with silver nano-paste before heating; (a) surface and (b) cross section and after heating at 150 °C; (c) cross section and (d) surface.

requirements for the synthesis of highly stabilized nano-sized silver powders by thermal reduction. When EHAHC was used as a stabilizer, silver nanopowders of 10-30 nm in diameter were easily obtained. Nano-sized silver powders can be easily dispersed in various organic solvents. Conductive path with 40% of silver nanopowders and 10% polymeric binder can achieve very high conductivity. This study shows that silver alkylcarbamate complexes are promising candidates for the production of the Ag-NPs for future application in printing of conductive line.

Acknowledgments. The present research was conducted by the research fund of Dankook University in 2010.

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