# Preparation of Silver Nanoparticles for Electro-conductive Inkjet Inks

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## Abstract

*This paper describes a new method to prepare silver nanoparticles being useful for printing electronic circuits. We have tried to develop a silver nitrate reduction method, where a certain reducing agent has played an important role in the reduction of silver ions in an aqueous solution. The reduction has occurred rapidly at room temperature and the silver particles have been separated very easily from the solution in a short time. In this process, any organic solvent has not been used and separation of silver nanoparticles has not been complicated. All chemicals used in this study have been water-soluble. Small and relatively uniform particles of a diameter lower than 10 nm can be obtained with high purity, high yield and low cost.*

## Introduction

Since an inkjet print-head can put an ink droplet of a fixed volume at a decided place, inkjet printing technology can be applied to the manufacturing of printed electronic circuits. It has a number of benefits. (1) Fine images are printed even on a curved surface. (2) Various size things can be used as printing media. (3) Beautiful color images are easily printed without any prepress plates required in a conventional printing industry. (4) High throughput is possible. Therefore it has been applied to producing display, device and 3D printing etc. It is possible to produce flexible electronic circuits at low cost by using this technology (1-3).

Many studies of this kind of application have been reported in recent years. It is important to develop inks for this application. We have an interest in inkjet inks dispersing nano-size metal particles that are useful to produce electronic circuits from the following view points: uniformity of small metal particles dispersed in the inks and cost reduction to manufacture the inks (4-6). The nano-size metal particles have been used in various fields due to their unusual optical, physical and chemical properties which differ from their bulk properties.

Several methods have been used to prepare silver nanoparticles including chemical and physical methods. It is well known that silver nanoparticles can be produced as a result of chemical reaction at low cost and high yield. The chemical reaction includes commonly reduction process of silver ions. However, there still remain the problems such those a mass of organic solvent is needed in many cases, the reduction process proceeds at relatively high temperature, and the complete separation of silver particles is not easy due to the existence of other compounds in the same reaction vessel (7-13).

In this study we have tried to find a new method to prepare silver nanoparticles where any organic solvent is not used and separation of silver nanoparticles is not complicated. We also characterized the obtained product of silver colloids by using various measurements such as UV-Vis spectro-photometer, X-ray diffractometer (XRD), transmission electron microscope (TEM) etc. It has been indicated that small and relatively uniform particles of a diameter lower than 10 nm have been obtained. The silver nanoparticles samples were characterized by casting them on polyimide film and sintering, showing low volume resistivity.

## Experimental

### *Materials*

Silver nitrate ($AgNO_3$), sodium citrate hydrate, and dimethylaminoethanol were obtained from Wako Pure Chemicals Co. Polyvinylpyrrolidone (PVP) (molecular weight ~10,000) was obtained from Tokyo kasei Co. LTD.

### *Preparation of silver nanoparticles*

1g of Polyvinylpyrrolidone (PVP) was dissolved in 20ml de-ionized water with stirring for 10min at room temperature. To this solution, 0.50g of $AgNO_3$ was added and the solution was kept stirring for 10min in order to dissolve the $AgNO_3$, then an aqueous solution of sodium citrate hydrate (0.88g dissolved in 20ml de-ionized water) was added drop by drop by using a micro pump. After the dropping of the solution was finished, an aqueous solution of dimethylaminoethanol (0.027g in 0.5 ml de-ionized water) was added to the reaction mixture. Then the mixture was kept stirring for 1hour at room temperature.
After the reaction, the silver particles were separated from the solution by centrifugation (5000 rpm), and washed with 20ml de-ionized water twice, then were dispersed again into de-ionized water (10ml).

### *Samples to measure volume resistivity*

The samples were prepared to measure volume resistivity by casting the silver nanoparticles suspension on polyimide film surface. Then the samples were sintered in an oven for 1 h at 200, 250, 300°C, respectively.

### *Characterization*

The UV-Visible spectra of silver suspensions were obtained with a Hitachi U-4100 UV-VIS spectro-photometer. The transmission

electron microscope (TEM) pictures of silver nanoparticles were obtained with a JEOL JEM2010 operating at 200kV. The samples were prepared by placing a drop of the silver suspension on a carbon-coated Formvar film on copper grids, and drying at room temperature. The Diameter distribution of silver particles was measured with Zetasizer Nano Series (Malvern Instruments). The Energy Dispersive x-ray Spectroscopy measurement (EDS) were made with the emission scanning electron microscope (SEM, Hitachi S-5000) equipped with an EDS instrument. The X-ray diffraction (XRD) experiment was carried out with Rigaku D/MAX-IIIV X-ray Diffractometer using Cu-Kα radiation. The volume resistivity was measured with Loresta-GP MCP-T610 resistivity meter (Mitsubishi chemical Analytech CO.LTD). A four-probe method was used for measuring the volume resistivity.

## Results and Discussion

Figure 1 shows the UV-Vis absorption spectra of silver nanoparticles. They have the characteristic absorption bands with a peak at 420-430 nm caused by the silver nanoparticles that is similar to the literature values (11).

Figure 2 shows the result of EDS analysis. The peak at around 3KeV shows a high intensity of silver signal without other metal ion impurities. The SEM pictures are shown in Figure 3. This fact indicates that all reagents used have not remained. Because chemicals used in this study are water-soluble, the final product can be separated easily from the reaction mixture. The silver nanoparticles prepared in this process can be used to print electronic circuits with inkjet printers.

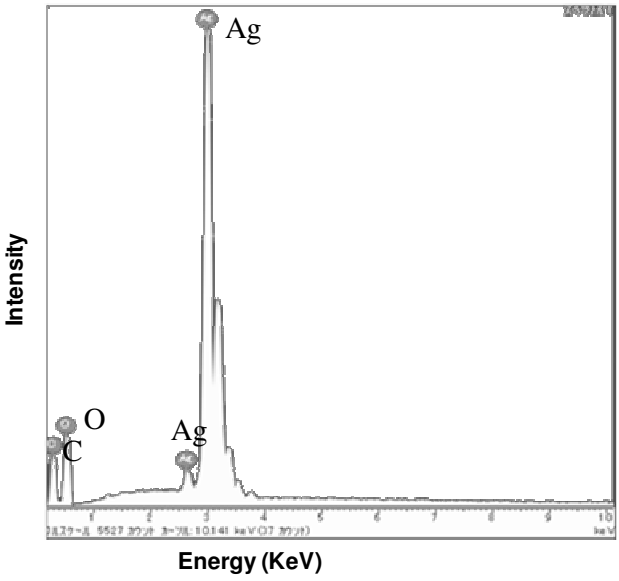


***Figure 2.*** *EDS spectra of Ag nano-particles*

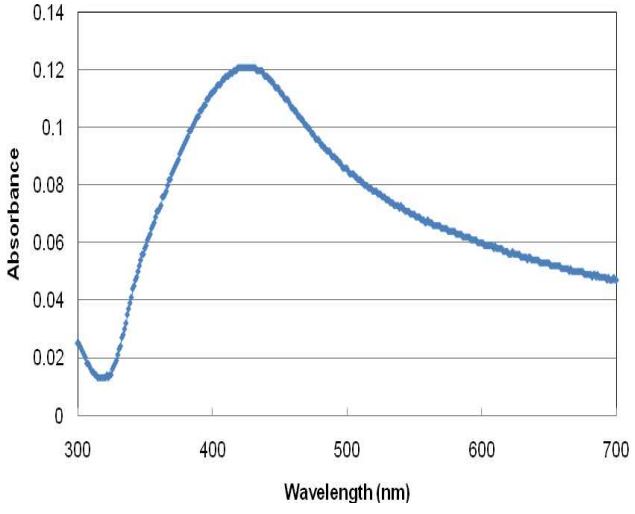


***Figure 1.*** *UV-Vis absorption spectra of silver nanoparticles suspension*

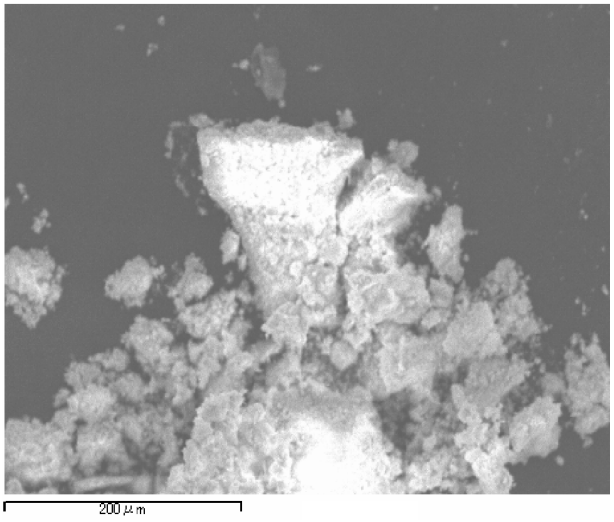


***Figure 3.*** *SEM micrographs of silver nanoparticles*

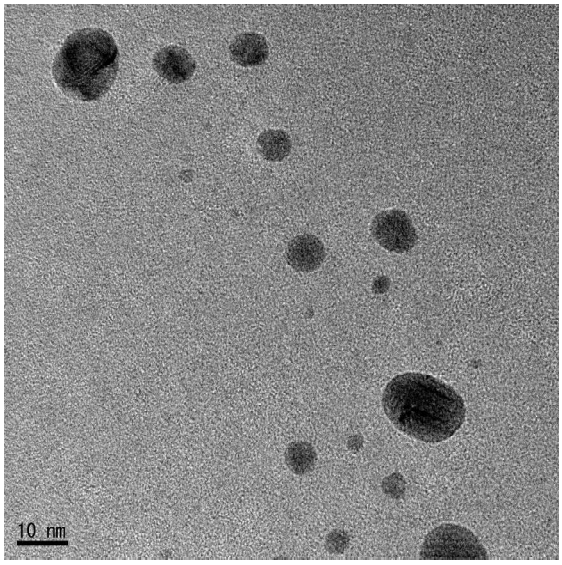


***Figure 4.*** *TEM micrographs of silver nanoparticles*

**Table 1. Details of the reaction parameters used in the silver nanoparticles synthesis, corresponding size of the particles measured from TEM**

| $AgNO_3$ (g) | $Na_3Ct$ (g) | DMAE (g) | PVP (g) | Average particles size (nm) from TEM |
|---|---|---|---|---|
| 0.5 | 0.88 | 0.027 | 1.0 | 5 |
| 0.5 | 0.44 | 0.027 | 1.0 | 20 |
| 0.5 | 2.64 | 0.027 | 1.0 | 30 |
| 0.5 | 0.88 | - | 1.0 | 40 |
| 0.5 | 0.88 | 0.027 | 0.5 | 40 |
| 0.5 | 0.88 | 0.027 | 2.0 | 20 |

Figure 4 shows TEM pictures. It is clear that these silver nanoparticles have spherical shape of a diameter lower than 10 nanometer in size.

The nanoparticles have been examined with an X-ray diffractometer. The XRD pattern is shown in Figure 5. The reflection peaks are indexed as the fcc (111), (200), (220), and (311) planes which are in accordance with the standard data, indicating that silver nanoparticles are well crystallized.

Figure 6 shows a diameter distribution of the silver nanoparticles, indicating a narrow distribution.

Figure 7 shows the change of the volume resistivity of the ink with temperature. It is observed that the volume resistivity decreases with increasing temperature. The value of volume resistivity drops largely when the ink is sintered at 250°C. This can be explained that the silver particles contact or fuse each other because the polymer was removed, which results in good conductivity. Therefore, the silver nanoparticles can be expected to have high electrical conductivity.

We have also investigated the factors affecting the particles size. It is found that the dropping rate of reduction agent solution is very important. When the reduction agent solution was added quickly, the size of particles has grown larger.

As shown in Table 1, the concentration of PVP as stabilizer and reduction agent has also affected the particle size. Furthermore, the amine has played an important role in the reduction of silver ions in an aqueous solution. When the amine did not been added, silver particles have grown larger and the separation of silver nanoparticles from the reaction mixture has been difficult.

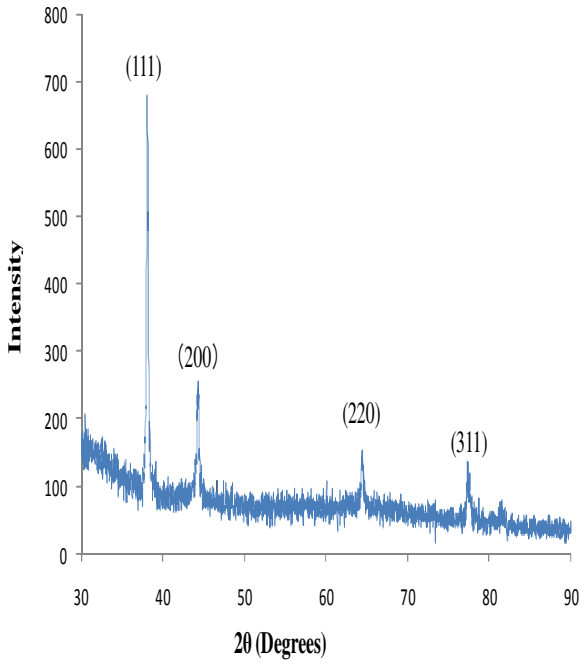


***Figure 5.*** *XRD pattern of silver nanoparticles suspension*

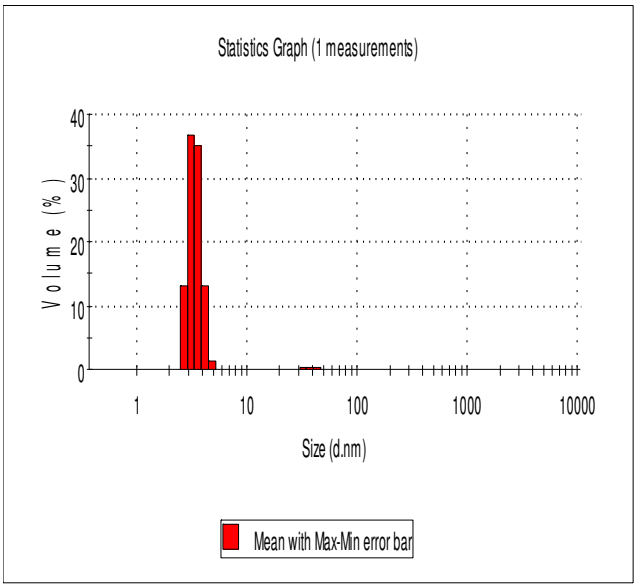


***Figure 6.*** *Diameter distribution of sample (Ag particles)*

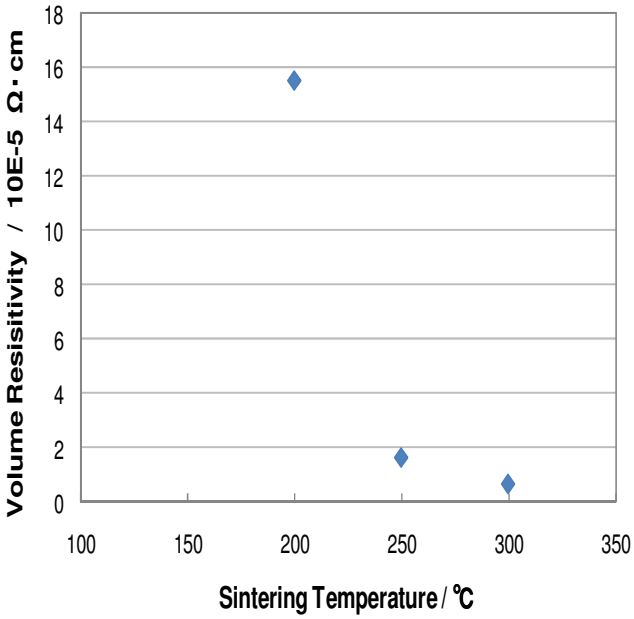


***Figure 7.*** *Change of the volume resistivity of the ink with temperature*

## Conclusions

The present study suggests a simple, low cost chemical synthetic route to form silver nanoparticle colloids. The process of this study has the following features; (1) short reaction time, (2) small and relatively uniform particles of a diameter lower than 10 nm, and (3) room temperature treatment through all process. All chemicals have been water-soluble in this study and any organic solvent has not been used. So the process to separate silver nanoparticles is not complicated. These can result in low cost, safe treatment and protection for environment, those are important from the industrial manufacturing point of view. The silver nanoparticles in this study are basically pure and show high conductivity; therefore they can be used for electronic application.

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