A Method to Prepare Silver Nanoparticles for Inkjet Inks Capable of Sintering at Low Temperature

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Abstract

We have been studying a method to prepare silver nanoparticles. At NIP26 we reported a new method to prepare silver nanoparticles of a diameter less than 10 nm with no organic solvent and complicated separation, in which amine compounds have the effect on the growth process of silver nanoparticles. In this study, the effect of dispersing agents such as sodium gluconate is investigated. We have tried to prepare the silver nanoparticles by using dispersing agents of low molecular weight compound instead of polymer. Similarly, nanoparticles of a diameter less than 10 nm can be obtained. This procedure of producing silver nanoparticles leads to a fall in sintering temperature. It is expected that the manufacturing of electronic circuits can be achieved at relatively low temperature with inks prepared in this study.

Introduction

Inkjet printing technology has a number of benefits: fine images are printed even on a curved surface; various size things can be used as printing media; beautiful color images are easily printed without any prepress plates required in a conventional printing industry; operation and maintenance are easy. Since an inkjet print-head can put an ink droplet of a fixed volume at a decided place, 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].

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.

Chemical and physical methods have been well known to prepare silver nanoparticles. The chemical method includes commonly reduction process of silver cations. Although such the chemical method becomes popular, there still remain several problems such as 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].

Furthermore, sintering process is necessary to obtain high electric conductivity. In usual method, the polymeric compounds are used as dispersing agent to prevent aggregation of silver nanoparticles. These polymeric compounds cause the problem that high temperature is required in sintering process.

We reported at NIP 26 a new method to prepare silver rnanoparticles of a diameter less than 10 nm with no organic solvent and complicated separation [14, 15]. In this study, we have tried to prepare the silver nanoparticles by using dispersing agents of low molecular weight compound instead of polymer. It is expected that the sintering process can be performed at relatively low temperature.

We will characterize the obtained product of silver particle colloids by using various measurements such as UV-Vis spectro-photometer, X-ray diffractometer (XRD), transmission electron microscope (TEM) etc. We will also measure the volume resistivity of these samples prepared by coating silver nanoparticles suspension on polyimide film and sintering with Loresta-GP MCP-T610 resistivity meter.

Experimental

Materials

Silver nitrate ($AgNO_3$), sodium citrate hydrate (Na_3Ct), dimethylaminoethanol (DMAE), triethylamine, imidazole, DL-malic acid disodium salt and sodium gluconate were obtained from Wako Pure Chemicals Co. Ltd.

Preparation of silver nanoparticles

As reported at NIP26, silver nanoparticles **A** were prepared using polyvinylpyrrolidone (PVP) as dispersing agent.

By the similar procedure, silver nanoparticles **B** were prepared as follows: sodium gluconate (1 g) was dissolved in de-ionized water (20 ml) by stirring for 10 min at room temperature. Into this solution, $AgNO_3$ (0.50 g) was added and the solution was kept stirring for 10 min in order to dissolve completely the $AgNO_3$, then an aqueous solution of sodium citrate hydrate (0.88 g) in de-ionized water (20 ml) was added drop-wise using a micro pump. After all of the solution was added, an aqueous solution of dimethylaminoethanol (0.027 g) in de-ionized water (0.5 ml) was added to the reaction mixture. Then the mixture was kept stirring for 1 hour at room temperature.

After the reaction, the silver particles were separated from the solution by centrifugation (5000 rpm), and washed with 20 ml de-ionized water twice, then dispersed again into de-ionized water (10 ml). The same reaction procedure described above was used to prepare other silver nanoparticles by varying the kinds of reactants.

Samples to measure volume resistivity

To measure volume resistivity, samples were prepared by coating the silver nanoparticles suspension on polyimide film surface. Then the silver nanoparticles **A** samples were sintered in an oven for 1 hour at 150, 200, and 250°C, respectively. On the other hand, when sodium gluconate was used as dispersing agent, the resulting silver nanoparticles **B** samples were sintered at 140, 150, and 250°C, respectively and soaked in water or 0.1M KOH solution and dried at room temperature after sintered.

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 200 kV. 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

The structure of sodium gluconate and PVP are shown in Figure 1, and imaging figures of silver nanoparticles **A** and **B** prepared using these dispersing agents are shown in figure 2.

Similarly to silver nanoparticles **A**, silver nanoparticles **B** shows the characteristic absorption bands with a peak around 400 nm caused by the silver nanoparticles (11) in UV-Vis absorption spectra; the silver nanoparticles **B** prepared in this process show high purity by EDS analysis.

Silver nanoparticles **B** examined with an X-ray diffractometer show the fcc (111), (200), (220), and (311) planes which are in accordance with the standard data, indicating that silver nanoparticles are well crystallized.

Figure 3 shows TEM pictures of silver nanoparticles **B**. It is clear that these silver nanoparticles have spherical shape of a diameter less than 10 nanometer in size.

As shown in Table 1, the particle size of silver nanoparticles **B** changes with various combinations of reaction agents. However, by comparison with silver nanoparticles **A** using PVP as dispersing agent, there is no great influence on the particle size in silver nanoparticles **B** using α-hydroxy acids compounds of low molecular weight as dispersing agents, and small and relatively uniform particles of a diameter less than 10 nm can be obtained in different experimental conditions.

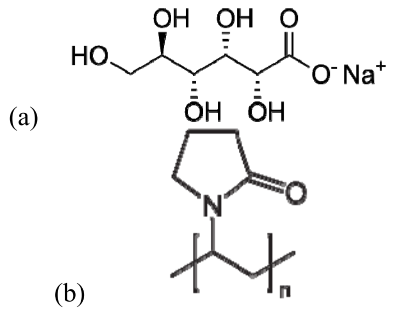

Figure 1. *The structure of sodium gluconate (a) and polyvinylpyrrolidon (PVP) (b).*

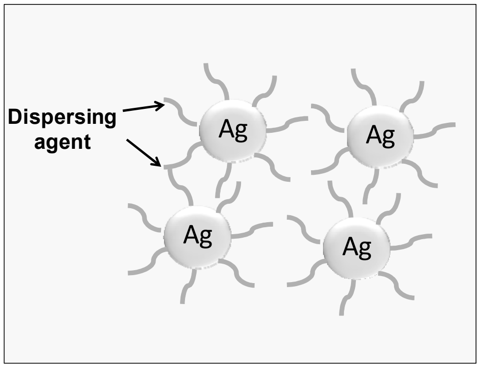

Figure 2. *The schematic diagram of silver nanoparticles in solution. Silver nanoparticles **A**: dispersing agent is PVP; silver nanoparticles **B**: dispersing agent is sodium gluconate.*

Table 1. Comparison of different agents in the formation of silver nanoparticles B samples.

Amine	Reduction Agent	Dispersing Agent	Average Particles Size (nm)
DMAE	Na_3Ct	Sodium gluconate	5
Et_3N	Na_3Ct	Sodium gluconate	5
Imidazole	Na_3Ct	Sodium gluconate	10
Imidazole	Ammonium hydrogen citrate	Sodium gluconate	4
DMAE	Na_3Ct	DL-Malic acid disodium salt	5

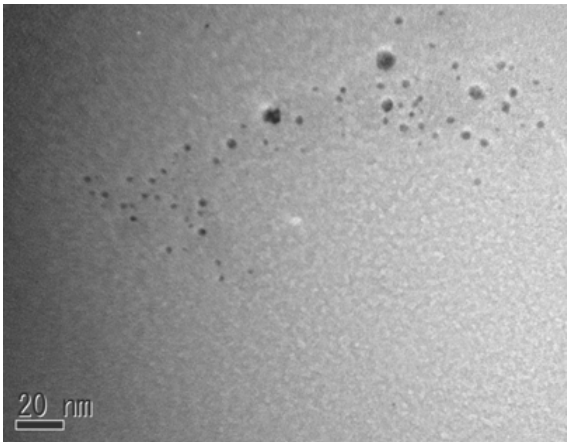

Figure 3. *TEM micrographs of silver nanoparticles **B**.*

Figure 4 shows an example of change in volume resistivity of the silver nanoparticles **A** samples with rising temperature. It is observed that the volume resistivity decreases with increasing temperature. The value of volume resistivity drops to a low extent when the ink is sintered at 250°C. This can be explained that the silver particles contact or fuse each other because the polymer has been removed, which results in high conductivity. In general, metallic silver shows a volume resistivity of 1.6×10^{-6} Ω·cm. The silver nanoparticles **A** samples prepared in our work show 1.6×10^{-4} Ω·cm at 200 °C, 1.7×10^{-5} Ω·cm at 250 °C, and 6.9×10^{-6} Ω·cm at 300 °C, which is close to that of metallic silver. However, the sample does not show electrical conductivity under 200 °C.

Figure 5 shows an example of change in volume resistivity of the silver nanoparticles **B** samples sintered at 150°C for 1 hour and soaked in 0.1 M KOH solution for 1 hour. It is clear that the volume resistivity decreases with increasing soaking time, showing a volume resistivity of 3.7×10^{-3} Ω·cm at 150 °C after soaked for 1 hour. But there is no great change in volume resistivity with increasing soaking time over 1 hour.

As shown in Table 2, within same sintering temperature (150 °C) and soaking time (0.5 hour), volume resistivity of silver nanoparticles **B** samples decreases with rising temperature. However, there is no great difference between 150 and 250 °C. This means that the silver nanoparticles **B** samples can be sintered even at relatively low temperature of 150 °C. This results from low melting point of sodium gluconate.

Table 3 shows an example of change in volume resistivity of silver nanoparticles **B** samples with soaking time when the samples were sintered at 150 °C for 1 hour. When the samples were soaked in water, the volume resistivity is very high in a period of time shorter than 10 min, meaning the electrical conductivity is low. However, the volume resistivity decreases greatly after the samples were soaked in water over 30 min, then it does not change so greatly after soaked in water over 1 hour.

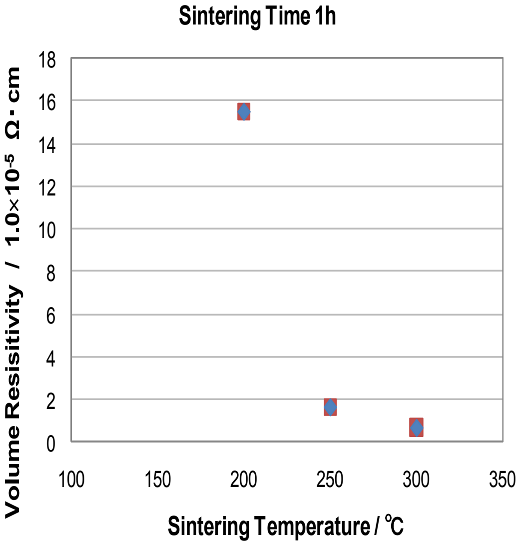

Figure 4. *Change in volume resistivity of silver nanoparticles **A** with rising temperature (this figure was described again for reference).*

On the other hand, when the samples were soaked in 0.1 M KOH solution, the volume resistivity decreases immediately, then it does not change so greatly after soaked over 30 minutes.

As a result, the silver nanoparticles **B** samples show high electrical conductivity when treated with either 0.1 M KOH solution or water. In particular, the samples show higher electrical conductivity when treated with water than 0.1 M KOH solution. This indicates that it is better to treat the samples with water because of the high electrical conductivity and protection for environment from the industrial manufacturing point of view.

By comparison with silver nanoparticles **A** prepared using PVP as dispersing agent, silver nanoparticles **B** prepared using dispersing agents of low molecular weight compound can be sintered at relatively low temperature.

Conclusions

A new practical route to form stable silver nanoparticle colloids of small size has been described. The process has the following features: short reaction time; small and relatively uniform particles of a diameter less than 10 nm; room temperature treatment through all process; no use of any organic solvent; easily separation process. These will be able to result in low cost, safe treatment and protection for environment, those are important from the industrial manufacturing point of view. Furthermore the silver nanoparticles **B** show high conductivity and can be sintered at low temperature. Therefore, these advantages make the present method practically useful and potentially applicable to large-scale industrial manufacturing process for stable colloids of silver nanoparticles, and the fabrication of electronic circuits can be achieved at relatively low temperature with inks dispersing the silver nanoparticles prepared by this method.

Table 2. Change in volume resistivity of silver nanoparticles B samples with rising temperature

Sintering temperature (°C)	Sintering time (h)	Soaking time (min.)	Volume resistivity (Ω•cm)
140	0.5	45	1.7×10^{0}
150	0.5	45	2.6×10^{-2}
250	0.5	45	0.1×10^{-2}

Table 3. Change in volume resistivity of silver nanoparticles B with soaking time when their samples was sintered at 150 °C for 1 hour.

Soaking time (min.)	Volume resistivity (Ω•cm)	
	soking in H_2O	soaking in 0.1 M KOH
5	2.3×10^{2}	3.7×10^{-2}
10	1.2×10^{1}	1.2×10^{-2}
30	2.0×10^{-3}	
45	6.4×10^{-4}	6.7×10^{-3}
60	4.6×10^{-4}	3.7×10^{-3}
75	2.9×10^{-4}	2.9×10^{-3}
90	3.0×10^{-4}	

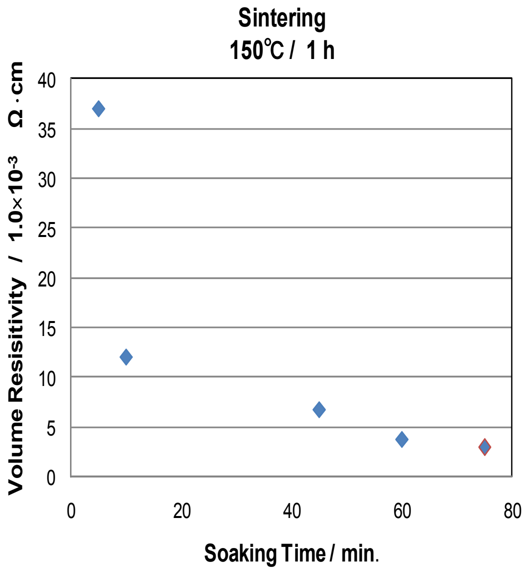

Figure 5. *Change in volume resistivity of silver nanoparticles* ***B*** *with soaking time.*

Acknowledgements

This research was supported by Program for Fostering Regional Innovation in Nagano, granted by MEXT, Japan.

References

[1] A. lennon, R. Utama, A. Ho-Baillie, M. Lenio, N. Kuepper, S. Wenham, Proceedings of the Digtal Fabrication conference, 882-885 (2007).

[2] R. Utama, A. lennon, M. Lenio, N. Borojevic, A. Ho-Baillie, S. Wenham, Proceedings of the 23rd European Photovoltaic Solar Energy conference, (2008).

[3] S. Tsuruga and T. Abe, Proceedings of the Pan-Pacific Imaging Conference (2008).

[4] H. H. Lee, K. S. Chou, Nanotechnology 16, 2436 (2005).

[5] B. c. Gates, Chem. Rew. 95, 511 (1995).

[6] N. R. Jana, T. K. Sau, T. J. Pal, j. Phys. Chem., B 103 (1), 115 (1999).

[7] K. Torigoe, Y. Nakajima and K. Esumi. J. Phys. Chem. 97, 8304 (1993).

[8] Y. Zhu, Y. Qian, M. Zhang and Z. Chen. Mater. Lett. 17, 314 (1993).

[9] Japan patent, 2009-155674 A

[10] Japan patent, 2007-84930 A

[11] Kan-Sen Chou, and Chiang-Yuh Ren, mater. Chem. Phys. 64, 241 (2000).

[12] Y. Tan, X. Dai, Y. Li and D. Zhu, J. Mater. Chem., 13, 1069 (2003).

[13] I. Sondi, D.V. Goia, E. Matijevic, J. Colloid Interface Sci. 260, 75 (2003).

[14] J. Natsuki and Takao Abe, J. Colloid Interface Sci. 359, 19 (2011).

[15] J. Natsuki and Takao Abe, Proceedings of NIP 26 and Digital Fabrication 2010, 127-130 (2010).

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J. Natsuki, received her B.S. in Chemical Engineering from Beijing University of Chemical Technology, China in 1986. She received her M.S. and PhD degrees in organic chemistry from Kyoto University, Japan in 1991 and 1994, respectively. She has worked as a research scientist at R&D sections of some companies and universities since 1997. Her main activity has been in the field of analytical chemistry, material chemistry and biochemistry. Her current interest is in the development of electro-conductive inkjet inks useful for digital fabrication.