

Synthesis of nano-sized Ag metal particles protected by adsorbed 3-mercaptopropionic acid

Masanori Tomonari^{a,b}, Hitomi Sadohara^b, Tetsu Yonezawa^c, Kohsuke Mori^a and Hiromi Yamashita^{a,*}

^aDivision of Materials and Manufacturing Science, Graduate School of Engineering, Osaka University, 2-1 Yamada-oka, Suita, Osaka 565-0871, Japan

^bFunctional Materials R&D Division, R&D Strategy Headquarters, Ishihara Sangyo Kaisha, Ltd., Yokkaichi, Mie, Japan

^cDepartment of Chemistry, Graduate School of Science, The University of Tokyo, Bunkyo-ku, Hongou, Tokyo, Japan

Nano-sized Ag metal particles can be synthesized by the addition of sodium borohydride as a reducing agent into an aqueous solution of AgNO₃ mixed with 3-mercaptopropionic acid as a protective agent. Using this method the synthesis of an aqueous Ag colloid system with a high density became possible, because the surfaces of synthesized nano-sized Ag metal particles were covered and protected by the adsorbed 3-mercaptopropionic acid. The strong electrostatic repulsion of the negative charge of the carboxylate anion of the adsorbed 3-mercaptopropionic acid disturbed the aggregation of metal particles in the solution with a high pH value (pH > 5), but the aggregation occurred in a solution of low pH value (pH < 2) because of the neutral surface of particles. Using simple coating and baking processes with this aqueous Ag colloid system, an Ag membrane can be formed on glass plate by the partial welding between the nano-size Ag particles. This Ag membrane exhibited a very low electrical resistivity even after baking at a low temperature such as 423 K.

Key words: nano-sized Ag particle, Ag colloid, mercaptopropionic acid, Ag membrane.

Introduction

Nano-sized metal particles are very attractive materials which can perform various unique phenomena [1-5]. A simple wet-process is acceptable to synthesize large amount of nano-sized metal particles at low cost. The control of particle size is very important to increase their usefulness, because the stability of nano-sized metal particles is not so high and they aggregate easily. The development of a technique to design stable functionalized nano-sized metal particles is very attractive. Using metal colloid solutions, a metal membrane could be synthesized by lip-coating or spin coating methods. This membrane is attractive material and can be applied in various electrical devices [6, 7].

In the present study, the synthesis of nano-sized Ag metal particles has been carried out using sodium borohydride as the reducing agent and 3-mercaptopropionic acid as a protective agent for the metal particles. The surfaces of nano-sized Ag metal particles should be protected by the adsorbed 3-mercaptopropionic acid in order to realize a unique aqueous colloid system with a high density of metal particles. Using this aqueous Ag colloid solution, an Ag membrane has been produced on a glass plate by a spin coating technique. The appli-

cation of the Ag membrane as an electrically conductive membrane has been also carried out. The characterization of samples was carried out using XRD, XAFS, TEM, SEM and Zeta-potential measurements.

Experimental

The nano-sized Ag particles and their aqueous colloid solution were synthesized by the procedure shown in Fig. 1. AgNO₃, NaBH₄, and 3-mercaptopropionic acid were used as the source of the Ag metal, reductant agent and protective agent, respectively. As the Ag precursor solution [A], a mixture of AgNO₃ (0.1 mol), 14 mol/l aq.NH₄OH (26.0 ml), 3-mercaptopropionic acid (8×10^{-3} mol) and H₂O (15 ml) was prepared. As the reduction solution [B], a mixture of NaBH₄ (0.02 mol), 14 mol/l aq.NH₄OH (2.0 ml), and H₂O (15 ml) was prepared. For the reduction of Ag ions into the nano-sized Ag metal particles, the solution A and B were added to H₂O (300 ml) solvent [C] (H₂O) slowly over 30 minutes at room temperature. The mixture was stirred for 30 minutes and filtered and washed with pure water to obtain the nano-sized Ag metal particles. Using the aqueous Ag colloid solution, the Ag membrane was synthesized as follows. The aqueous Ag colloid solution (5.4 mol/l, 10 g) was mixed and stirred with the solvent mixture of 2-propanol (5 g) and ethylene-glycol-monoethyl-ether (5 g). Using this solution, the Ag membrane was produced on a glass plate by a spin coat method and baking at various temperatures. The characterization

*Corresponding author:
Tel : +81-6-6879-7457
Fax: +82-2-2271-7395
E-mail: yamashita@mat.eng.osaka-u.ac.jp

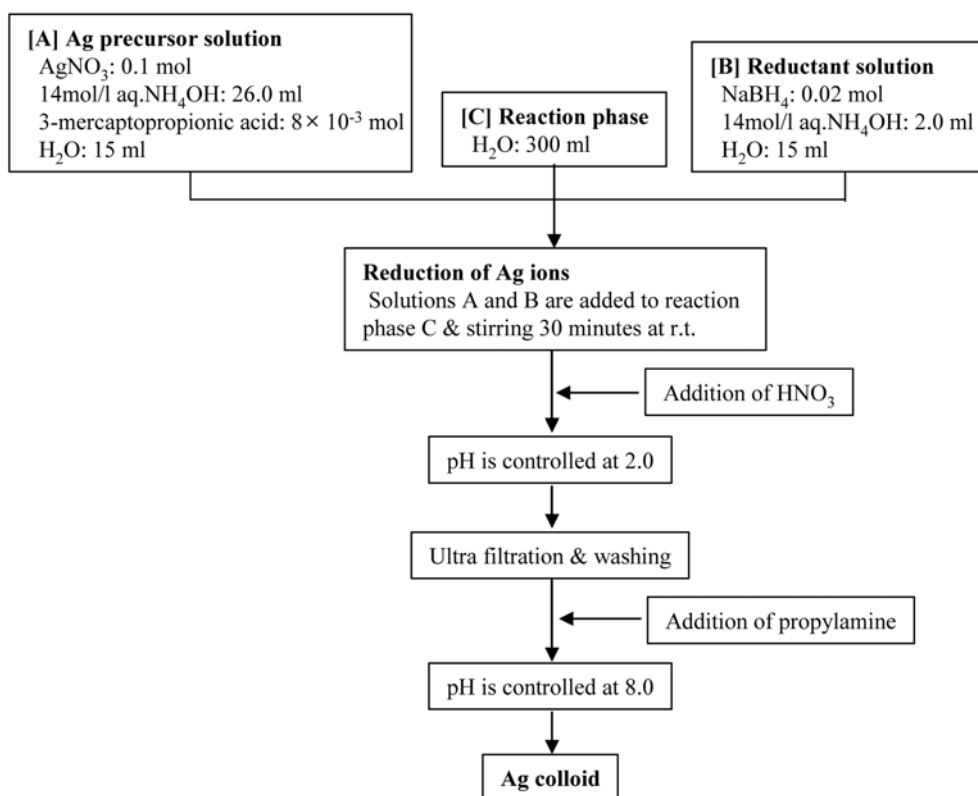


Fig. 1. Scheme for the synthesis of Ag colloids.

of samples was carried out using XRD, XAFS, TEM, SEM, Zeta-potential and electrical resistivity measurements. XAFS spectra for the Ag K-edge absorption were recorded in the transmission mode at BL01B1 of Spring-8 [8, 9].

Results and Discussion

Preparation of nano-sized Ag metal particles

With the optimized content of the protective agent 3-mercaptopropionic acid against Ag, the synthesis of an aqueous Ag colloid solution system with a very high density of Ag metal and superior stability could be realized. The synthesized aqueous Ag colloid solution displayed a red-rust color which is characteristic of the absorption by the plasmon vibration of Ag nano-sized particles. In the XRD measurements with the powder obtained by the evaporation of the colloid solvent under vacuum, only peaks due to crystalline Ag metal were observed. The formation of Ag metal as a single phase also could be confirmed by the XAFS measurement at the Ag K-edge. A transmission electron microscope (TEM) image of the synthesized Ag colloid is shown in Fig. 2. The Ag metal particles are in a spherical form of spherical with a well-controlled particle size. The analysis of TEM images on the distribution of particle size was carried out and the result is shown in Fig. 3. The distribution of particles size of Ag metal is very narrow and the average particle size is about 10 nm.

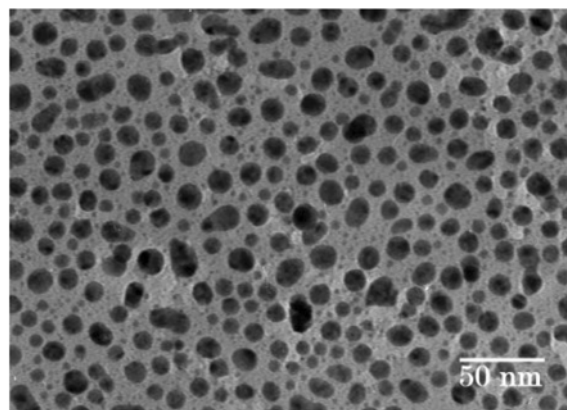


Fig. 2. A TEM image of the Ag colloid.

These results indicated that using 3-mercaptopropionic acid as the protective agent, nano-sized Ag particles with a well-controlled particle size can be synthesized by the simple wet-process.

The effect of the pH of the colloid solution on the dispersed state of Ag metal particles has been studied by the addition of the HNO₃ and NH₄OH aqueous solutions to the colloid solution which originally showed a pH=6.2. The stable colloid state having a red-rust color characteristic of the presence of Ag nano-sized particles was retained while the pH of the colloidal solution was adjusted on alkaline side by the addition of NH₄OH aqueous solution. In the pH region for the colloidal solution of less than 5 formed by the addition of HNO₃

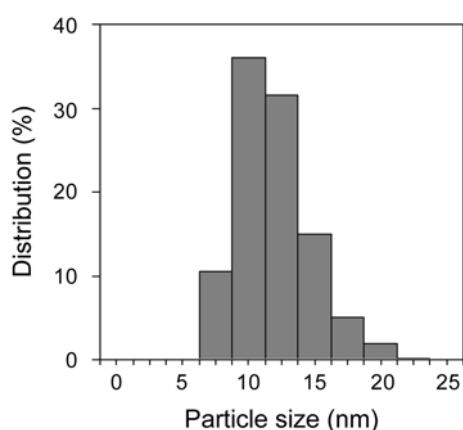


Fig. 3. The particle size distribution for a Ag colloid.

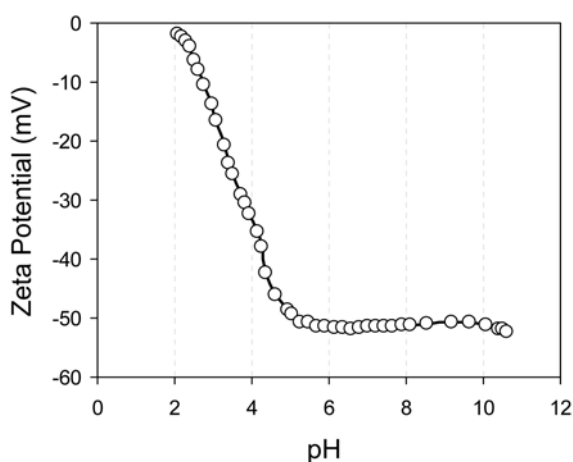


Fig. 4. The pH dependence of the Zeta-potential for Ag colloids.

aqueous solution, the aggregation and precipitation of Ag particles occurs and the color of the colloidal solution changed from red purple to black. The aggregation

of Ag metal particles became serious at a pH less than 3 and the aggregated Ag particles grew to become completely separated from solution. However, the Ag particles were dispersed again to make a colloid state with the original red-rust color by the addition of NH_4OH aqueous solution to increase the pH again.

To estimate the electrical charge at the surface of Ag metal particles, the effect of pH values of the solutions on the Zeta electric potential of the Ag colloid has been investigated and the results are shown in Fig. 4. As shown in Fig. 4, the surface of Ag metal particles in the solution was charged negatively in the region with the pH larger than 5, but the electric charge decreased in the region with the pH less than 5 and became zero at $\text{pH}=2$.

From the observations of the Zeta potential, the mechanism of dispersion and aggregation of Ag particles depending on the pH value can be proposed and a suggested scheme is shown in Fig. 5. The 3-mercapto-propionic acid having a thiol group adsorbs on Ag particles by forming Ag-S bonds as a protective agent. In the solution at pH values higher than 5, the proton of the carboxyl group at the end opposite to the thiol group becomes electrolytically dissociated to form a carboxylate anion and a negative electrical potential is formed on the surface of Ag metal particles. The Ag nano-particles having a negative surface charge can demonstrate a highly dispersed state without aggregation because of the electrostatic repulsion between the Ag metal particles. At a pH less than 2, the Ag surface becomes electrostatically neutral to lose the driving force of dispersion and lead to the aggregation of Ag particles, because the proton of the weak acid carboxyl group of 3-mercapto-propionic acid adsorbed on metal particles can not be ionized.

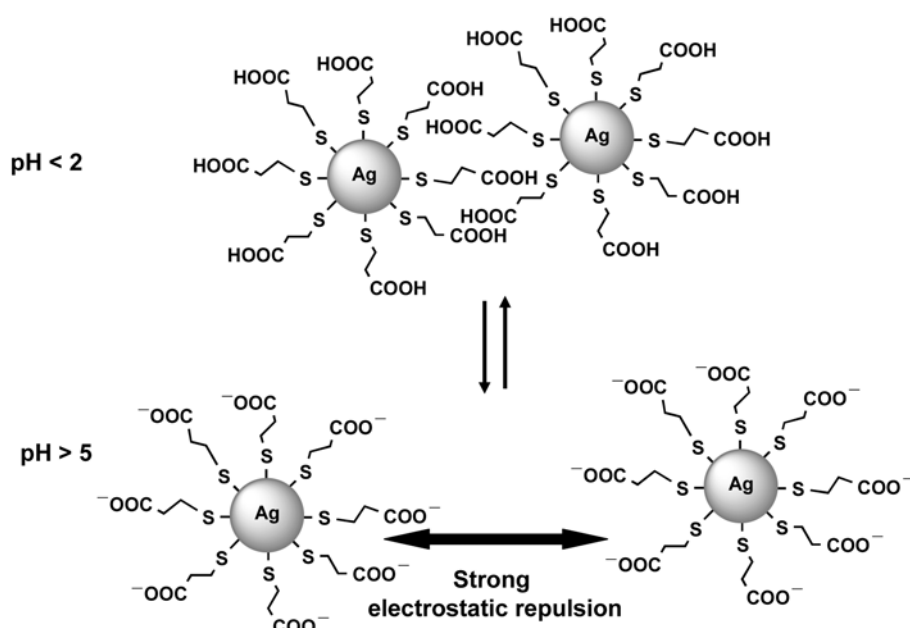


Fig. 5. The mechanism for the dispersion-aggregation of the Ag colloids.

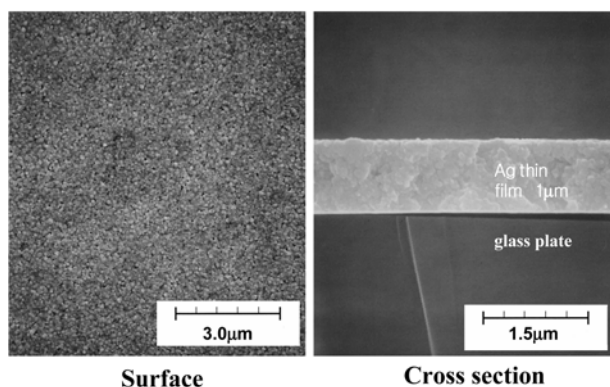


Fig. 6. SEM images of the Ag membrane.

Preparation of Ag Membrane

In order to decrease the boundary tension of the synthesized Ag colloidal aqueous solution, 2-propanol and ethylene-glycol-mono-ethyl-ether were added. Using this mixed solution, a Ag membrane was produced on a glass plate by a spin coating and baking method. The thickness of the Ag membrane could be controlled by changing the number of spin coating processes and a membrane with a thickness of 1 μm could be prepared. Fig. 6 shows SEM images of the surface (the left) and the cross section (the right) of the Ag membrane obtained by this method. The surface of membrane is very smooth and the thickness of membrane is well-controlled. It can be proposed that the Ag particles have a welded state at the connection of the particles to aggregate with each other and make a smooth membrane even at a temperature as low as 423 K. Because the Ag particles were well-controlled with a small size of 10 nm, the surface energy of particles is very high, the molten state of the surfaces can be formed easily even at a low temperature at the point of contact between the particles.

Figure 7 shows the electrical resistivity values of the Ag membrane after baking under various conditions (temperature and time). In a comparison with the electrical resistivity value ($1.59 \mu\Omega \text{ cm}$) of a bulk Ag foil, a one order higher value was observed with the membrane after baking at 403 K for 180 minutes. The electrical resistivity decreased to a value several times higher than the Ag foil after baking at 473 K for 30 minutes. This Ag membrane can exhibit a high performance with a very low electrical resistivity even after baking at low temperatures.

Conclusions

Using sodium borohydride as the reducing agent and 3-mercaptopropionic acid as the protective agent of metal particles, nano-sized Ag metal particles can be synthesized from an aqueous solution of AgNO_3 . The 3-mercaptopropionic acid adsorbed on the surfaces of

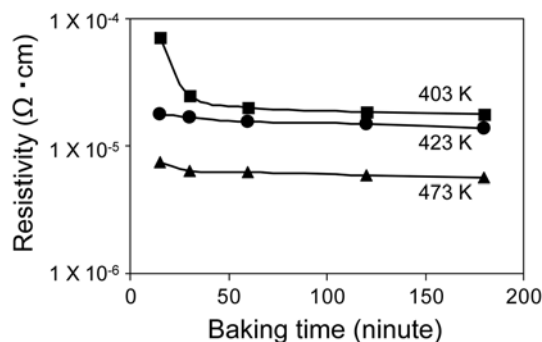


Fig. 7. The effect of baking time and temperature on the electrical resistivity of the Ag membrane.

nano-sized Ag metal particles protected the aggregation of Ag metal particles and controls their particle size. The negative charge of the carboxylate anion of the adsorbed 3-mercaptopropionic acid disturbed the aggregation of metal particles in a solution of high pH value ($\text{pH} > 5$), but the aggregation occurred in solutions of low pH values ($\text{pH} < 2$). Using this Ag colloidal aqueous solution, a Ag membrane could be produced on a glass plate by a spin coating method. This Ag membrane can exhibit a low electrical resistivity even after baking at low temperatures because of the formation of welds at the connection of particles.

Acknowledgement

The present study is supported by the Grant-in-Aid for Scientific Research (KAKENHI) in the Priority Area "Molecular Nano Dynamics" from Ministry of Education, Culture, Sports, Science and Technology (No. 1865238). This work is partly performed under a project of collaborative research at the Joining and Welding Research Institute (JWRI) of Osaka University. The X-ray adsorption experiments were performed at the Spring-8 (2006A1278, 2006A1279).

References

1. A. Badia, S. Singh, L. Demers, L. Cuccia, and G.R. Brown, *Chem. Eur. J.* 2 (1996) 359-365.
2. K. Mori, T. Hara, T. Mizugaki, K. Ebitani, and K. Kaneda, *J. Am. Chem. Soc.* 126 (2004) 10657-10663.
3. D. Astruc, F. Lu, and J.R. Aranzaes, *Angew. Chem. Int. Ed.* 44 (2005) 7852-7858.
4. T. Yonezawa, H. Matsune, and N. Kimizuka, *Adv. Mater.* 15 (2003) 499-505.
5. M. A. El-Sayed, *Acc. Chem. Res.* 34 (2001) 257-263.
6. I. Tanahashi, M. Yoshida, Y. Manabe, T. Tohda, S. Sasaki, T. Tokizaki, and A. Nakamura, *Jpn. J. Appl. Phys.* 33 (1994) L1410-L1416.
7. I. Tanahashi, H. Inoue, and A. Mito, *Res. Chem. Intermed.* 29 (2003) 939-945.
8. F. Montilla, E. Morallon, and H. Yamashita, *J. Phys. Chem. B.* 108 (2004) 5044-5050.
9. H. Yamashita, M. Matsuoka, K. Tsuji, Y. Shioya, and M. Anpo, *J. Phys. Chem.* 100 (1996) 397-403.