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Synthesis of mono-dispersed fine spherical silver powders by chemical reduction method

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Abstract The synthesis of spherical silver powders by chemical reduction method was investigated. Conductive metal pastes to have good properties in adhesion, stability, and conductivity, it is very important to control the purity, size, and shape of metal particles. In the present study, proper methods to control the properties of micron sized metal powders for conductive pastes are investigated. Chemical reduction method in aqueous solution was adapted to produce silver powder. The effects of reaction time, concentration of reductant and additives, and stirring speed were investigated, in experimental. Fine spherical silver powder of 0.5 to 3 ㎛ were synthesized from silver nitrate solution with hydroquinone as a reducing additive by liquid phase method, and some variables and reaction mechanism in conjunction with the particle morphology and size were studied.

Introduction

Fine metal powders of high purity are widely used for electronic products as conductive inks and pastes, contact materials, and so on. Electronic industry of Korea needs to secure the raw materials to meet its annual growth of over 20 % [1]. According to the 2002 statistics of the Korea customs service office [2], about 28 million dollars equivalent metal pastes were currently imported.

In order for conductive metal pastes to have good properties in adhesion, stability, and conductivity, it is very important to control the purity, size, and shape of metal particles. There are little manufacturers to be able to produce such micron sized high purity metal powders in Korea. Even though numerous studies on the synthesis for metal powders have been reported [3], it is hardly found in relation to morphology controlled metal powders for the use of conductive pastes. Since the transfer of the powder making technologies from abroad is not expectable, they should be developed for Korea's continued growth.

In the present study, proper methods to control the properties of micron sized metal powders for conductive pastes are investigated. Liquid phase reduction method in aqueous and organic solutions is adapted to produce silver powder. An objective of the study was to establish synthesizing technologies of high purity silver and copper powders of 99.9 % and over. Fine spherical silver powder of 0.5 to 3 ㎛ was synthesized from silver nitrate solution with hydroquinone as a reducing additive by chemical reduction method, and some variables and reaction mechanism in conjunction with the particle morphology and size were studied.

Experimental

The experimental was carried out at room temperature and under atmospheric pressure using the solution of silver nitrate as source of silver powder, hydroquinone as reductant and NH_4OH as

complex agent with agitation by a stirrer with 2 blades. All following chemicals of reagent grade were used in a typical experiment without more purification: $AgNO_3$ (Junsei Chemicals Co., Japan), NH_4OH (Junsei Chemicals Co., Japan), hydroquinone ($C_6H_6O_2$, 1, 4-Benzenediol, Sigma-Aldrich chemical Co., USA).

In order to silver-NaOH complex solution, 10 ml of NH_4OH solution was mixed to 100 ml of $AgNO_3$ solution. Reduction of silver ion from the silver-NH_4OH complex solution was carried out with 99 % hydroquinone. To reduce of silver ion in the solution to metallic silver, the temperature was kept at 18 ^oC for 10 min. to carry out the reaction. The metallic silver powder was obtained from the solution, washed and vacuum dried. The Experimental conditions for preparation of spherical silver powder is shown in Table 1.

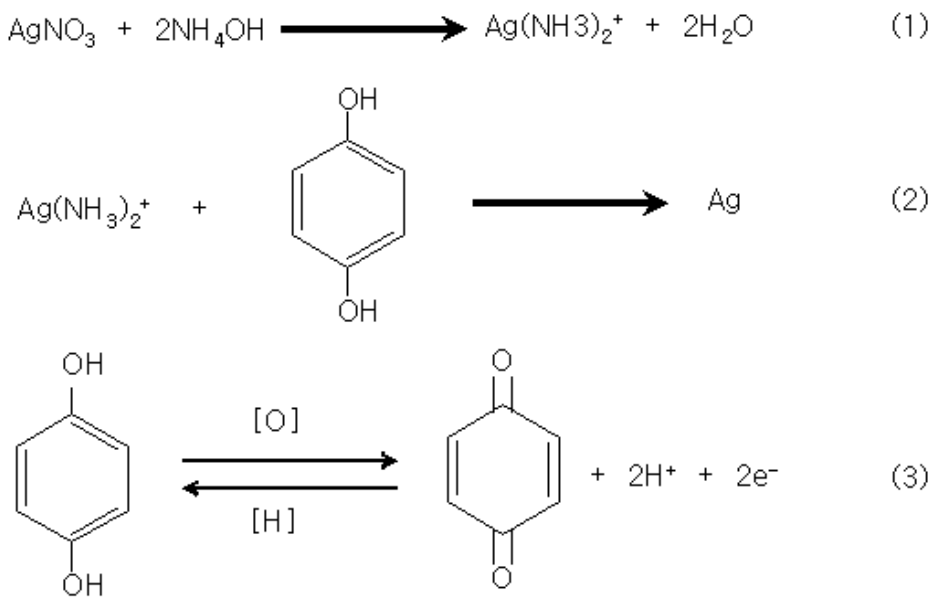
The observation of the powder was made by scanning electron microscopy (SEM) on a JSM 6380LA (Jeol, Japan) to reveal the shape and agglomeration of particle. The mean particle size and the standard deviation were estimated by Laser Particle Size Analyzer-BIC (LPSA). The crystal structure was characterized by X-ray diffractometor (XRD, RTP 300RC, Rigaku, Japan) with Cu Kα radiation.

Table 1. Experimental conditions for preparation of spherical silver powder

Parameters	Conditions
$AgNO_3$ (g/L)	50, 100, 150, 200
Hydroquinone (g/L)	10, 13.2, 15, 18, 19.8, 26.4, 33, 39.6, 49.2
NH_4OH(ml)	0, 2.5, 5, 10, 20
Stirring speed(R. P. M.)	50, 100, 200, 300, 400, 500, 600

Results and discussion

Chemical reduction reaction by hydroquinone Silver nitrate was used in the chemical reduction in aqueous solutions of the most common silver compound to prepared monodispersed, non-agglomerated silver powder. The process mainly produces the following chemical reactions with silver ion, ammonia and hydroquinone [4]:



The formation of spherical silver particles could proceed through a two stage mechanism [4]. At first, silver ion is combined with ammonia and then formatted silver-ammonia complex ion shown in Eq. 1. In two stage, reduction of silver-ammonia complex ion is occurred shown Eq. 2. Eq. 3 is shown the decomposition of hydroquinone act as donor of electron in solution. The primary particles are produced which is easy of agglomeration but ammonia which is absorbed in the surface of silver powder could be prevent the agglomeration of particles. Fig. 1. shows the XRD pattern of the product prepared by the solution containing $AgNO_3$ and hydroquinone. From this pattern, it is known that the diffraction pattern shows the characteristic peaks of crystalline metallic silver powder, respectively which is very close to that given by Wu [5].

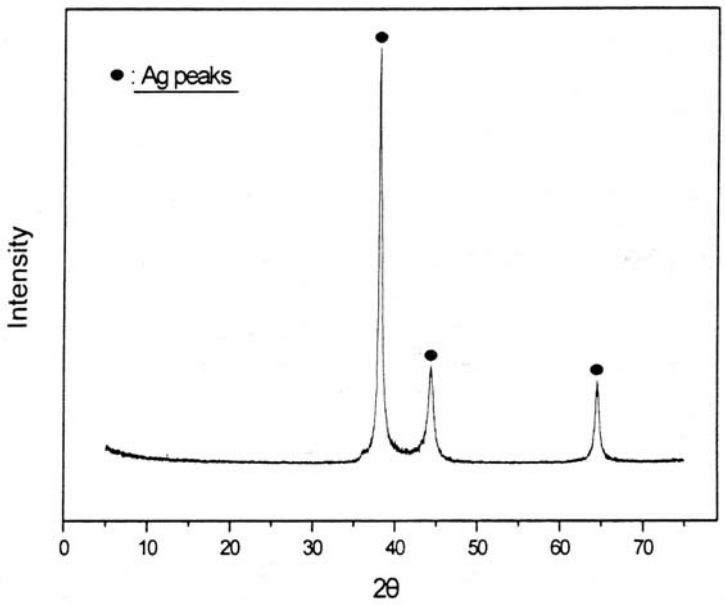


Fig. 1 XRD diffraction of silver powder

Effect of hydroquinone concentration Reduction reactions of silver with hydroquinone through Eq. 1 to 3 are strongly dependent on the concentration of reductant. The effect of hydroquinone concentration on the mean particle size and morphology of silver by varying the hydroquinone concentration from 13.2 g/l to 50 g/l was shown in Fig. 2.

Fig. 2 shows that the morphology of particles are seen spherical, respectively and well dispersed and the particle size of particles are about 1 μm. But the particles of 13.2 g/l hydroquinone concentration, were shown more agglomerated and coarse than the condition of 32.5 g/l hydroquinone concentration. This is why diffusion of reductant is controlled reaction in the case of low reductant concentration and then the growth of particle is occurred. From these results, the optimum condition of hydroquinone concentration is 32.5 g/l in this experiment.

Effect of reaction time The influence of reaction time on the reduction ability of hydroquinone is important because the reaction behavior of hydroquinone is known very fast. The effects of reaction time in conjunction with SEM images were represented by varying the reaction time from 30 second to 10 min. in Fig. 3. As seen Fig. 3, the particles are spherical, well dispersed, and have uniform size and narrow particle distribution and the particle sizes of particles are about 1 to 2 μm but in the case of 10 min., it is known that more agglomerated particles is obtained.

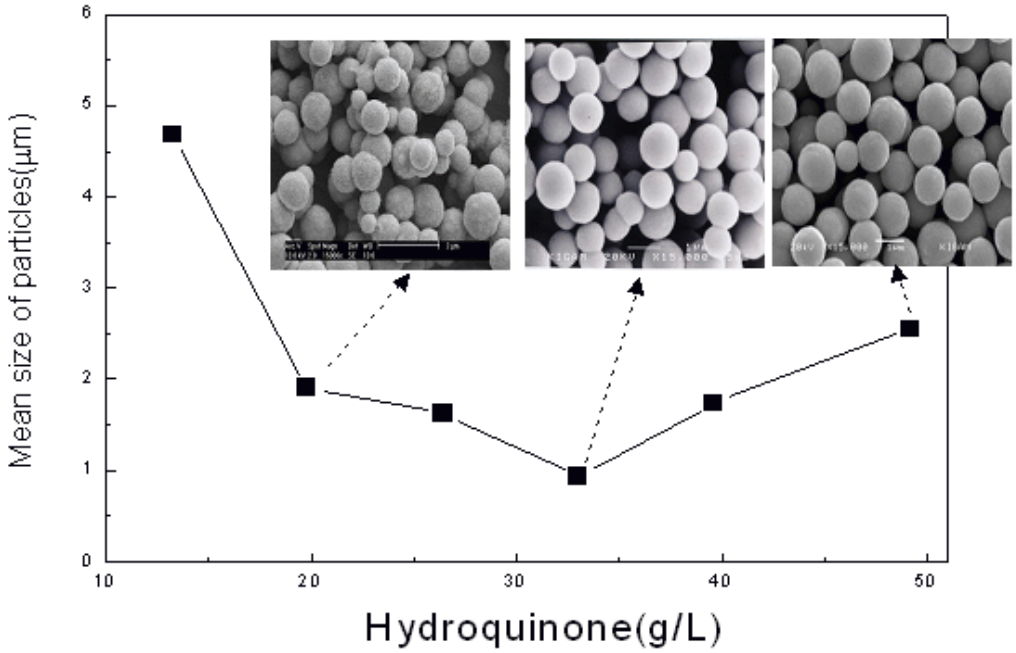


Fig. 2 Effect of hydroquinone as reductant on the variation of mean particle size of silver at 20 ℃ (100 g/l $AgNO_3$ and 10 ml NH_4OH).

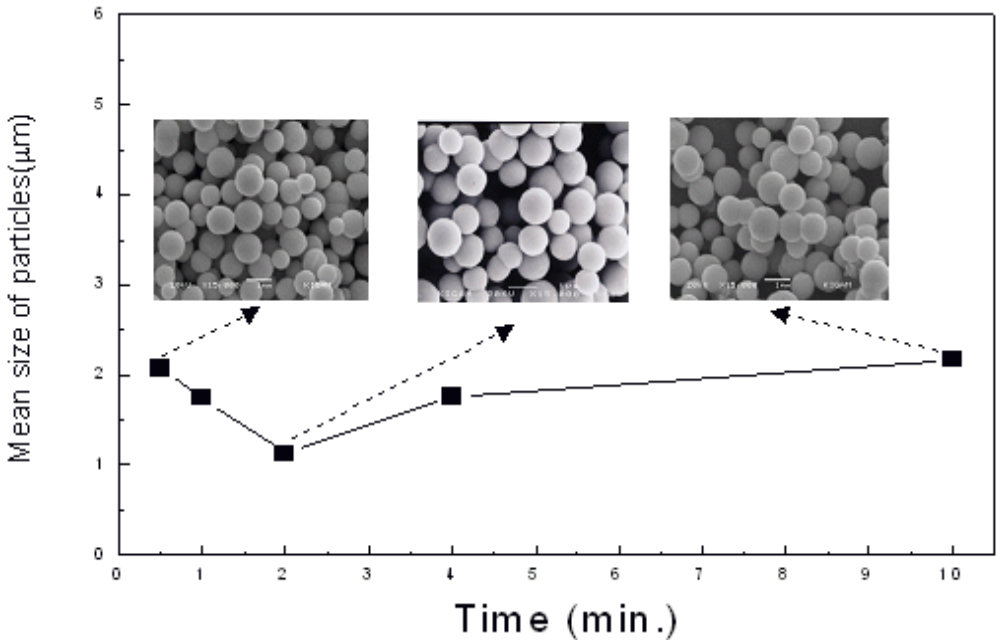


Fig. 3 Effect of reaction time on the variation of mean particle size of silver at 20 ℃ (100 g/l $AgNO_3$ and 10 ml NH_4OH)

Effect of pH and ammonia concentration The oxidation/reduction potential of hydroquinone represented to Eq. 4 and 5.

$C_6H_6O_2 = C_6H_4O_2 + 2H^+ + 2e^-$

$E^0 = -0.54$ V [6] (4)

$E = E^0 + 0.059$ pH (5)

The existing state of silver ion depends on the pH value in aqueous solution. The influences of pH and ammonia on the powder particles were investigated. The pH values of silver nitrate solution were controlled by aqueous ammonia. In this experimental, aqueous ammonia was added into reductive solution to control certain stable pH value. The influences of pH value and ammonia on the spherical silver powder prepared at different ammonia concentration is given to Fig. 4, it is seen that mean particle size reduces as ph value and ammonia concentration. The obtained particle without ammonia at 9 pH value is shown agglomerated bar-type shape but particle was change to spherical with increasing of ammonia. In the condition of 10 ml ammonia, the size of particle is about 1 μm and well-dispersed.

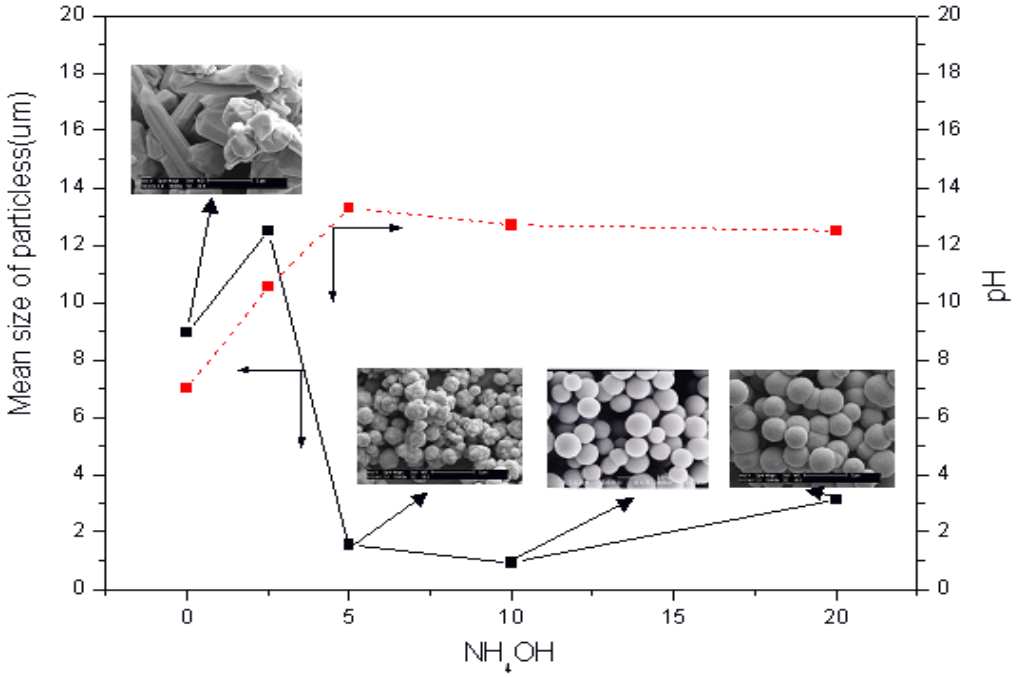


Fig. 3 Effect of NH4OH concentrations on the variation of mean particle size of silver at 20 ℃($AgNO_3$ 100 g/l and H. Q. 32.5 g/l).

Summary

Silver nitrate as a silver source, ammonia as a pH control agent, and hydroquinone as a reducing additive were used, and spherical silver powders of 0.9 to 3 μm were able to be synthesized.

An optimum condition for the synthesis was found to be at 45.5 g/ℓ of $AgNO_3$, 10 Mℓ of NH_4OH, and 15 g/ℓ of hydroquinone at 20℃ for 2 minutes, resulting in having an average particle size of 1 μm.

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