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Communications

A Propylene Glycol Route to Silver Metal Particles

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In our previous researches, the nanometer sized transition metal oxides with ferromagnetic and dielectric functions have been successfully prepared with the wet chemical methods like sol-gel process and coprecipitation in an aqueous solution.¹ And we extended our interests to the fine metal particles, which are also expected to be possibly synthesized in a non-aqueous solution, and in the present communication, an attempt has been made to propose a new, simple and economical route to prepare the fine silver particles.

Silver metal particles with uniform size and shape have been needed in preparing the conductive pastes and adhesives for the application of electronic parts. In order to prepare such fine particles, several preparative methods have been studied like evaporation,² irradiation,³ pyrolysis of precursor materials,⁴ and reductive method using boron compounds.⁵ But the chemical reduction of metal salts has been known to be one of the widely used technique to prepare homogeneous and monodisperse metal particles, since such an approach in solution has several advantages compared to the other synthetic techniques in the view point of narrow particle size distribution, small particle size, monodispersity and chemical flexibility.

Among those chemical reduction methods, silver metal particles have been prepared through the reduction of silver salts in organic medium, especially in ethylene glycol or in alcoholic media such as ethanol and propanol.⁶ Ethylene glycol can play an important role as a reducing and dispersive agent, and also in the nucleation and growth of metallic nuclei by oxidizing itself to diacid or aldehyde. Although the polyol process using the boiling ethylene glycol is known to be a relatively easy method to prepare the me-

tal particles with a given shape and size by adjusting some reaction factors such as molar ratio, reaction temperature, and time, etc., a significant problem arises due to the aging of metal particles or too much reactants are needed to prepare fine silver particles.⁶ Since propylene glycol is even cheaper in price and lower in boiling point (bp=189 °C) than the ethylene glycol (bp=197 °C), which leads to higher reactivity, an attempt has been made to suggest a new propylene glycol route for preparing the nanosize and monodisperse silver particles.

At higher temperature, the propylene glycol can be easily oxidized to aldehyde and acid type, and subsequently decomposed to CO, CO₂ and H₂O. Thus silver ions can be reduced to the corresponding metal particles, whose nucleation and crystal-growth in the propylene glycol could be controlled under well-designed condition. For the best reaction condition, the reaction temperature and the weight ratio of polyvinyl pyrrolidone (PVP) to silver nitrate were optimized, but the reaction time was fixed to 10 minutes in the whole experiments.

Preparation of silver metal particles was undertaken as follows. Silver nitrate (99.8%, 1.70 g) was dissolved in propylene glycol (PG) of 20 mL. And PVP (MW=40,000) of 1, 1.5, 2 (henceforth *x*) weight times to silver nitrate were dissolved in 15 mL of propylene glycol. In air, each solution was simultaneously added dropwisely to the boiling (150 °C, 175 °C) propylene glycol taken as 50 molar times to silver nitrate. Refluxing the solution for 10 minutes with vigorous stirring gave a clear brown to beige solution of silver metals, that is, a colloidal dispersion of silver. After cooling down to room temperature, the resulting colloidal silver particles were washed with acetone and water several times to remove the excess reactants. In order to confirm silver me-

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tal phase, the powder X-ray diffraction (Ni filtered Cu K- α radiation, $\lambda=1.54184$) analyses were performed. Primary particle size was determined by using Scherrer's equation⁸ with X-ray line broadening of some reflections. Transmission electron microscopy was also used to determine particle size and morphology by using CM 30 Philips TEM operating at 200 kV.

After the reaction, the homogeneous dispersion of colloidal silver particles indicated the maintenance of Brownian motion in solution. It is thought that the formation of silver metal proceeds through the coordination of PVP to silver (I) ion and the reduction of silver (I) ion by oxidizing propylene glycol to acid or aldehyde.

According to Lamer's model,^{6,9} as the nucleation proceeds, the metal concentration in organic solution increases and as a consequence the supersaturated solution could be formed, leading to spontaneous nucleation. Particle growth occurs on those nuclei. So in order to control the size and uniformity of particles, it is necessary to prevent their aggregation during the crystal growth, which was in practice realized by using protective polymer (PVP) and by controlling the reaction conditions (concentration and temperature).

PVP with the formula of $(-[\text{CH}-\text{CH}(\text{NCH}_2\text{CH}_2\text{CH}_2\text{CO})]_n-)$ is an acetylene derivative, and is known to prevent the aggregation of metal particles by steric stabilization, and therefore disperses them homogeneously in a liquid media.¹⁰ The amount of PVP (x) as a protective agent was varied as 1-2 weight times to AgNO_3 to examine the effect of surface coverage on particle sintering.

According to the X-ray diffraction analysis as shown in Figure 1, all the peaks are characteristic of metallic silver with the face centered cubic phase and its cell parameter is determined to be $a=4.084$ Å. Particle sizes were estimated from the X-ray line broadening of (111) and (200) reflections by using Scherrer's equation,⁸ and their values are represented in Table 1, and compared to those observed by the transmission electron microscopy in Figure 2 and those of previous report.⁶

When the reaction was performed at 175 °C, the particle

shape became spheroidal and polydisperse, and many of the crystals seemed to be composed of smaller microcrystals as shown in Table 1 and Figure 2(a). The average particle size was about 110 nm. For $x=2$, quite satisfactory results could be obtained at 150 °C, since the silver metal particles were monodisperse without any remarkable aggregation, whose average diameter was determined to be 50 nm as shown in Figure 2(b). This is one of the small particle size reported for the silver particles with very narrow size distribution. In this way, the problems of polyol process⁶ using the boiling ethylene glycol like monodispersity, particle size, and economic reaction condition could be improved by replacing ethylene glycol with propylene glycol. In addition, we have found that the aggregation of silver particles prepared at higher temperature increased remarkably due to the

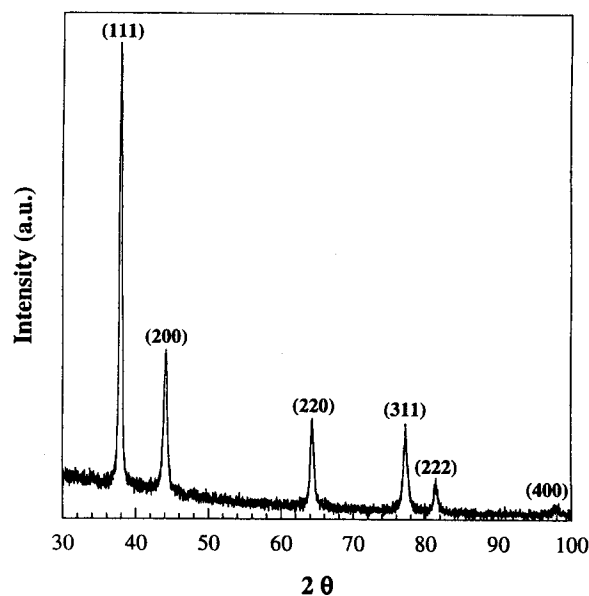


Figure 1. Powder X-ray diffraction pattern for silver metal particles prepared by the propylene glycol route.

Table 1. The particle sizes (nm) and shapes of silver metal particles prepared from the propylene glycol method under various reaction conditions

Temp.(°C)	Weight ratio of PVP/Ag (=x)	TEM ^a	XRD ^b	Shape	Polyol process ^c (based on ethylene glycol)
175	1	180±10	75	distorted spheroidal	at 180 °C, $x=1$, 300~1300 nm, aggregated
"	1.5	120±10	75	"	at 180 °C, $x=1.2$, 300~1300 nm, aggregated
"	2	110±10	78	"	at 180 °C, $x=1.6$, 800 nm, monodisperse
150	1	110±10	70	distorted spheroidal	at 160 °C, $x=1$, 370 nm, monodisperse
"	1.5	100±10	78	spheroidal	at 160 °C, $x=1.2$, 300~1000 nm, aggregated
"	2	50±10	63	sphere	at 160 °C, $x=1.2$, 300~1000 nm, aggregated

^a sizes determined from transmission electron micrographs, ^b sizes estimated from the Scherrer's equation in XRD,⁸ and ^c sizes and shapes reported from the conventional polyol process (15 minutes of reaction time, and 0.025 AgNO_3 /ethylene glycol molar ratio are same for all reaction).⁶

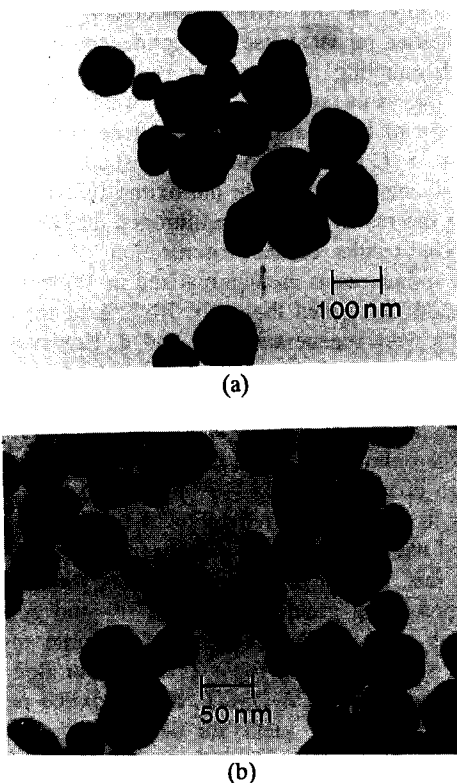


Figure 2. Transmission electron micrographs of silver metal particles prepared under various conditions of (a) $x=2$ at 175 °C and (b) $x=2$ at 150 °C.

higher probability of particle collisions and adhesion, and those have led to lowering the surface area of particles.⁶

The silver particles of 50 nm prepared in this work is thought to be polymeric silver metal clusters consisted of 3.8×10^6 number of silver atoms, which was calculated by using the silver atomic radius of 2.9 Å, and the packing fraction of *ccp* array, 0.74. In the face-centered cubic structure, a silver atom is coordinated by twelve neighboring silver atoms, which could be assumed as the first metal cluster. Such small clusters can be aggregated together to form

large particles through many steps, which accounts for the difference of particle sizes in between XRD and TEM.

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3-Nitrobenzophenone Oxime Resin-A New Reliable Polymer Support for Solid Phase Peptide Fragment Synthesis

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Kaiser oxime resin (4-nitrobenzophenone oxime resin) has been one of the useful polymer supports in solid-phase peptide fragment synthesis.¹ However, from our previous ex-

periences, a few but critical handicaps have been found. First, the peptide-resin linkage was not sufficiently stable that no little portion of the anchored peptide moiety was