Preparation of Ultrafine Silver Powder Using Glycerol as Reducing Agent

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Abstract

The production of silver nanoparticles and sub-micron particles can be achieved by silver alkoxide from silver sulfate and subsequently reducing with glycerol. To reduce the particle size of silver sulfate precursors, ball milling was employed to reduce particle sizes down to 0.81 microns. However, silver sulfate without grinding provided smaller particle sizes of silver particles as opposed to ground specimens. Stirring silver alkoxide simultaneously was efficient to provide for uniform distribution of silver powder. The silver powder thus produced had brain-like shape consisted of very fine aggregate silver particles. The yield of silver powder was in the range of 95-99 %. Silver powder had fcc crystal structure by X-ray diffraction (XRD). The average particle size and powder cluster sizes were in the range of 60 to 250 nanometers and from 6 to 30 microns, respectively. The surface areas were approximately 1.1-2.9 m^2/g and apparent densities were from 0.6 to 1.2 g/cm^3.

Introduction

Nowadays the chemical syntheses to control uniform size and distribution of silver particles have been attractive because ultrafine particles can be widely used in catalysts, electronics, bactericidal action and the jewelry industry. Silver powder can be produced through various methods such as chemical reduction, [1-3] physical process (atomization and milling), electrochemical and thermal deposition. Among the various preparative methods employed, chemical processes offer distinct advantage over the others in terms of powder morphology as well as efficient scale-up for mass production. The polyol process including glycerol reducer[4] has also been successfully used to obtain reduced metal powder in a finely dispersed form.

The objective of this paper is to study appropriate initial silver sulfate size, reaction temperature, time and condition for controlling silver powder sizes which were produced from silver sulfate reduced with glycerol as reducing agent.

Materials and Experimental Procedures

All chemicals of reagent grade quality were used without further purification. Silver sulfate was produced by reaction of silver metal with 98% concentrate sulfuric acid (AR). Silver sulfate, used as a precursor, was ground by ball milling for 5, 10 and 20 h. in order to reduce silver sulfate size. Each of the precursors containing 10 g of Ag_2SO_4 was brought to react with sodium alkoxide in absolute ethanol (Carlo, AR) for 1 h thus silver alkoxide was completely obtained. No protective agent in the form of PVP or seed particle (nucleating agent) was used. Then the sample of silver alkoxide was reduced by glycerol with magnetic stirring (800 rpm) at constant temperatures of 150°C and 180°C for 30 min and 1 h, respectively. The reaction temperature was measured using a thermometer submerged in the solution through a glass port. Silver powder was obtained by reaction of silver alkoxide with glycerol. The metallic silver powder was recovered from the solution, washed and dried at 110°C for 1 h.

The crystal structure of silver powder was characterized by using X-ray diffraction (XRD) method on an X'pert, model PW3810 (Phillipe) to ensure that the metallic silver powder was completely and successfully produced.

Direct observation of the silver powder cluster and particle morphology was made by scanning electron microscope (SEM) on a JEOL (model JSM-6400) to reveal the shape, size and size distribution. The average sizes and the

standard deviation were directly measured from SEM image using SemAfore program.

Surface area was measured with BET surface analyzer on a Micromeritics. Figure 1 illustrates the flow chart of the process used for producing the very fine silver particles using glycerol as reducing agent.
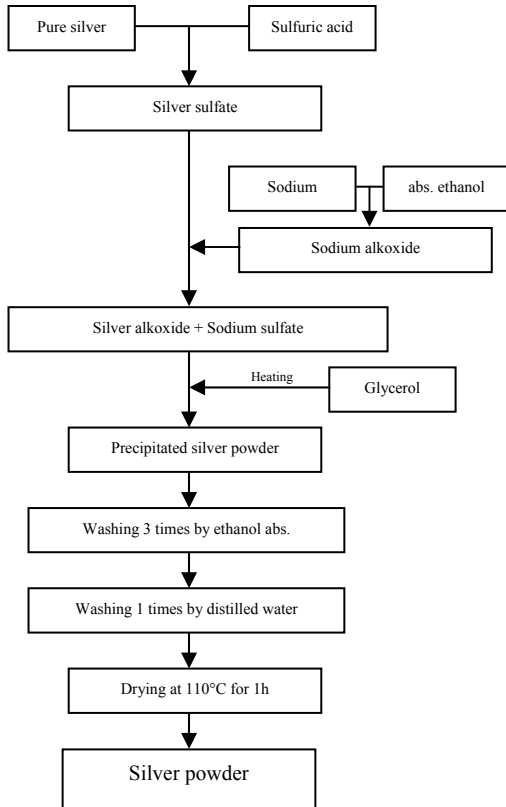
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┌──────────────┐        ┌──────────────┐
│ Pure silver  │────────│ Sulfuric acid│
└──────────────┘        └──────────────┘
        │
┌──────────────────┐
│  Silver sulfate  │
└──────────────────┘
        │           ┌──────────┐   ┌──────────────┐
        │           │  Sodium  │───│  abs. ethanol│
        │           └──────────┘   └──────────────┘
        │              ┌──────────────────┐
        │◄─────────────│  Sodium alkoxide │
        │              └──────────────────┘
┌──────────────────────────────────┐
│ Silver alkoxide + Sodium sulfate │
└──────────────────────────────────┘
        │      Heating   ┌──────────┐
        │◄───────────────│ Glycerol │
        │                └──────────┘
┌──────────────────────────────┐
│ Precipitated silver powder   │
└──────────────────────────────┘
        │
┌──────────────────────────────┐
│ Washing 3 times by ethanol abs.│
└──────────────────────────────┘
        │
┌──────────────────────────────┐
│ Washing 1 times by distilled water│
└──────────────────────────────┘
        │
┌──────────────────────────────┐
│ Drying at 110°C for 1h       │
└──────────────────────────────┘
        │
┌──────────────────────────────┐
│       Silver powder          │
└──────────────────────────────┘
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Figure 1. Flow chart of the production process

Results and discussion

To obtain uniformly small silver sulfate particles, ball milling was used. The scanning electron micrographs of silver sulfate precursors after grinding for 0-20 h are shown in Figure 2a-d.

Measurement according to[5] in ASTM standard E20 was used to measure the sizes of irregularly shaped particles. An initial average size of silver sulfate (4.35 μm) can be reduced to 2.88, 1.35 and 0.81 μm by ball milling for 5, 10 and 20 h, respectively.

After stirring and heating the silver alkoxide for 1 h, white silver sulfate powder became blackish silver alkoxide. The shape and size of silver alkoxide were similar to those of the initial silver sulfate.

Stirring silver alkoxide during the reaction with glycerol offers the uniform powder cluster as shown in Figure 3a-d. The unstirred system results in very huge powder cluster sizes due to more agglomeration which occurs at the bottom of the beaker. It was found that metallic silver particles in the range of nanometer to sub-micron occurred due to the reduced silver alkoxide powder. Silver particles started to join each other to form silver clusters which had a brain-like or coral structure.
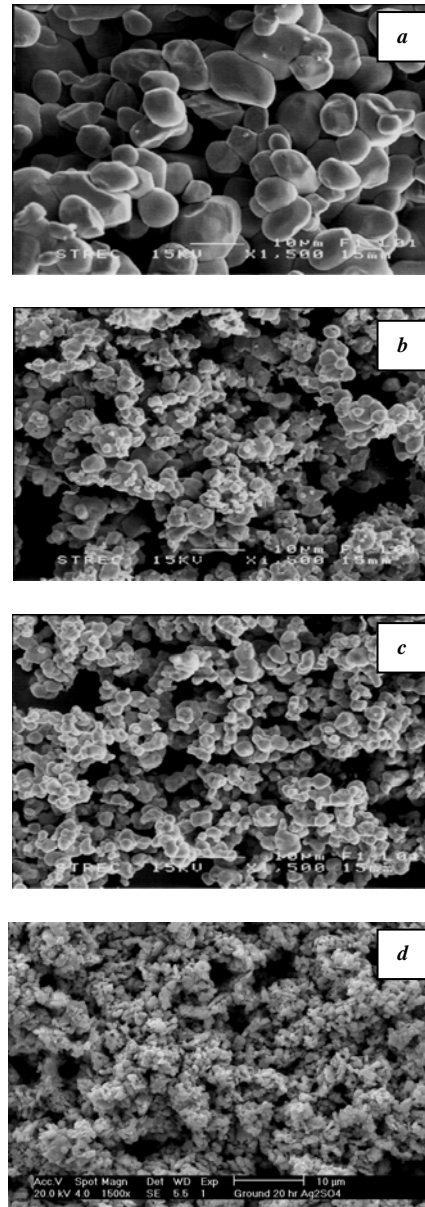
Figure 2. SEM of silver sufate prepared from ball milling with various grinding time (a) 0, (b) 5, (c) 10 and (d) 20 hr.

A suitable condition to obtain the smallest cluster (Figure 3c) with average cluster size of 6.5 μm is silver sulfate with initial size of 1.35 μm

(ball milling for 10 h). Although the smallest initial size of silver sulfate (0.81 μm) was prepared by using the condition after milling for 20 h, but very large silver clusters were obtained as shown in Figure 3d. This might be due to high surface energy of the small particles while there was no protective reagent added.
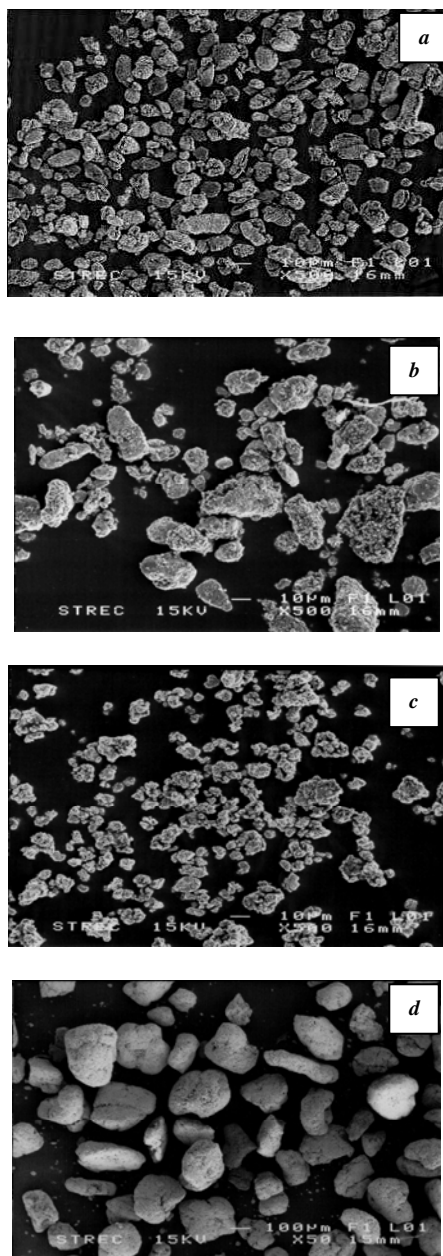
Figure 3. Silver powder was produced at 150°C for 30 min by using precursors with (a) no grinding, with grinding time of (b) 5, (c) 10 and (d) 20 hr.

Reaction temperature at 150°C-180°C and holding time of 30 mins-1h during the reduction with glycerol insignificantly affect the size and shape of the silver cluster. Only the initial size of

silver sulfate affects the morphology of silver particles in the cluster.

The conversion of silver sulfate to silver powder in all tested conditions was 95-99%. The powder was collected and analyzed by XRD. The XRD patterns of silver powders prepared through glycerol route in all conditions are shown in Figure 4. The patterns reveal the diffraction peaks corresponding to *fcc* silver phase and no other elements and compound occur.

The SEM observation with higher magnification (15000x) on the silver powder cluster from completed reaction is shown in figure 5a-d. Aggregated silver nanoparticles and sub-micron particles were produced on the surface of silver clusters.
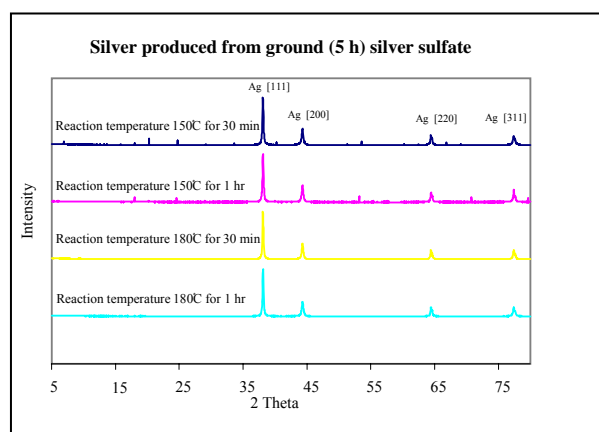
Figure 4. XRD patterns of silver powder after reduction under various conditions.

The silver particles were in the form of irregular shape and joined together as a brain-like shape or coral structure. The agglomeration of silver particles is due to the high surface energy of silver particles. The excess surface energy[6] is released and converted to thermal energy. Besides, it was found that grinding, reaction temperature and holding time during the reduction with glycerol affected the average particle size. Table 1 indicates that silver particles produced from silver sulfate without ball milling had smaller average size in a range of 60-130 nm while those silver sulfates with ball milling provided a larger size (100-240 nm)

Reaction temperature and time tended to increase the particle size of metallic silver due to a higher quantity of reactions occurring at a higher temperature and over a longer time span. At a

temperature of 150°C the particle sizes reduced from silver sulfate without grinding were about 60-70 nm while the particles reduced at 180°C had an average of 110-140 nm in size. However, there is no clear evidence to determine the relationship among particle size, temperature and time in the condition of the ground silver sulfate experiments due to the fluctuation of measured silver particle size at elevated temperature which may resulte from ball milling as shown in Table 1.
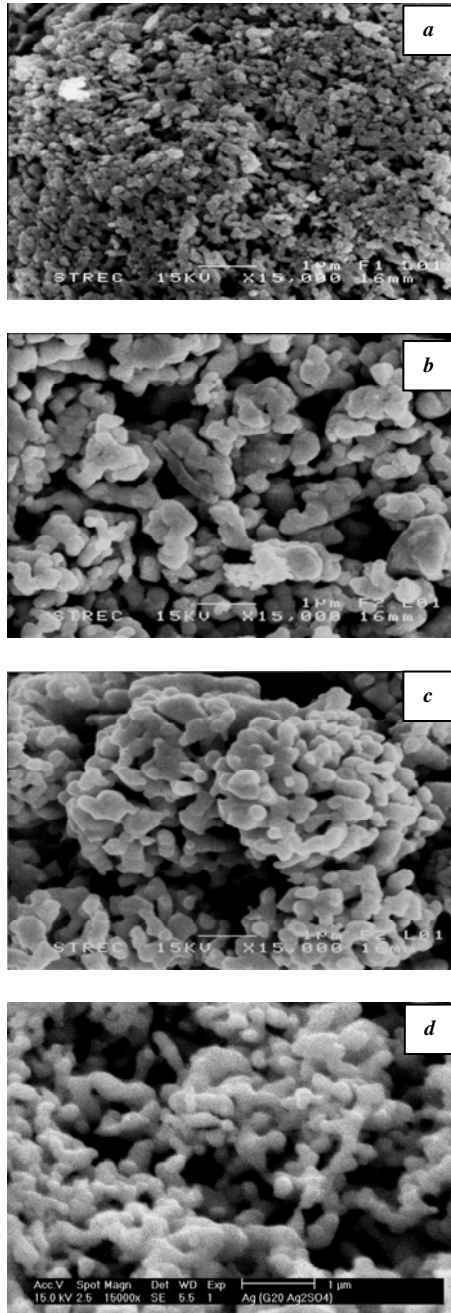
Table 1. Average particle size of silver reduced with glycerol in various conditions.

Ag_2SO_4 grinding time	Temp (°C),	Time (min)	Average particle size (nm) (measured)	Crystalline size (nm) (calculated)
0	150	30	63.3	35.9
5			167.9	37.2
10			220.7	44.2
20			180.1	34.8
0		60	74.8	35.7
5			172.0	35.0
10			200.0	40.3
20			164.7	33.2
0	180	30	136.3	37.7
5			104.1	37.9
10			166.2	42.5
20			141.6	34.8
0		60	111.2	37.2
5			241.9	40.9
10			186.4	41.5
20			166.1	39.1

The crystalline size can be determined by Debye-Scherrer equation[7] from diffraction peak of XRD results. The calculated average crystalline sizes were in the range from 30 to 45 nm as shown in Table 1 and then plotted (graph is shown in Figure 6). Although the results of crystalline size from calculation do not meet the actual size, they show linear relation between measured actual particle size and calculated crystalline size. When crystalline size is large, particle size is large, too.
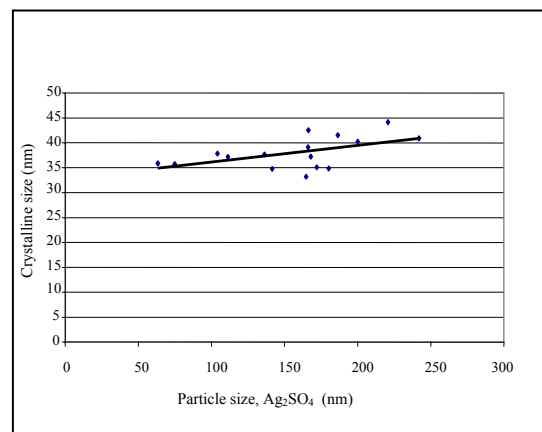

Figure 5. SEM of silver particles produced from Ag_2SO_4 at 150°C for 30 min with various grinding conditions ; (a) without grinding, grinding time for (b) 5, (c) 10 and (d) 20 h

Figure 6. Shows a linear relationship between actual particle size and calculated crystalline size.

Surface areas measured by BET surface area analysis are shown in Figure 7. Surface area of silver powder from this process is in a range of 1.1-2.9 m^2/g. It was found that surface area strongly depends on the particle size rather than

silver cluster. Therefore high surface area with more than 2 m^2/g can be achieved in the specimens without grinding in which a small average particle size exists (Figure 5 a), whereas the lower surface area resulted from the large particle size. Apparent density was measured in the range of 0.6-1.2 g/cm^3
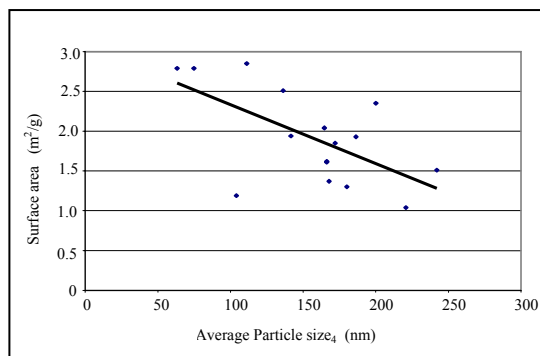

Figure 7. Shows linear trend of relationship between average size of silver particles and surface area measured by BET method

Conclusions

In conclusion, the synthesis of very fine silver powder by the reaction of silver alkoxide and glycerol were achieved. The size of precursor, silver sulfate, can be successfully reduced by ball mill grinding technique. When using a milling time of 20 h, silver sulfate size was reduced from 4.35 to 0.81 microns. Stirring silver alkoxide during glycerol reduction is essential for avoiding the agglomeration of particles which leads to unexpectedly large silver clusters. The silver powders in this technique have *fcc* crystal structure and can have a process yield of about 95-99 %. The average particle size produced from silver sulfate without grinding has been found to be smaller than 100 nm and also depends on reaction temperature and holding time.

Surface area was measured in the range of 1.1-2.9 m^2/g. and depended on the average particle size of silver powder produced.

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