Preparation of Sliver Nanoparticles by Liquid Chemical Reduction Method

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Abstract

The development of printing electronics technology promotes the application of conductive ink, and nano-silver conductive ink is a hot research. Sliver particles are the main conductive component in conductive ink, so nano-silver particles are very important for the ink conductivity. In this paper, silver nano-particles were reduced from silver nitrate solution by liquid chemical reduction method, with Sodium hypophosphite as reductant, PVP as surface-protection reagent, and sodium hexametaphosphate as dispersant. Orthogonal test with 4 factors and 3 levels is designed in which the effect of reducing agent dosage, protective agent dosage, dispersant content and reaction temperature on the nano-particle size and morphology of silver is investigated. The size distribution of nano-silver powder is measured by nano-size potential analyzer, and the morphology of silver particles is characterized with the SEM. The experiment results showed that the minimum average size of sliver particles can reach 23.87nm, and the dispersed spherical nano-particles with the average size is about 60nm can be obtained。

Introduction

The development of printing electronics technology promotes the application of conductive ink, and nano-silver conductive ink is a hot research. Sliver particles are the main conductive component in conductive ink, so nano-silver particles are very important for the ink conductivity. Thus, it is important to synthesize nano-sized silver dispersions with small sizes and narrow distribution. The preparation methods of nano-silver particles contain direct ball milling, physical reduction, chemical reduction and biological reduction, etc [1, 2, 3]. Chemical reduction method is the mainstream method of nano-silver preparation, with low cost, simple process, short production cycle and large production capacity, etc. In this paper, nano-sliver particles were obtained by liquid chemical reduction with silver nitrate and sodium hypophosphite as reactants，PVP as protective agents, and sodium hexametaphosphate as dispersant. The chemical reaction equation is shown as (1)

$$4Ag^{+} + NaH_2PO_2 + H_2O = 4Ag\downarrow + PO_4^{3-} + 6H^{+} \quad (1)$$

Experimental

Experimental materials and instruments

Experimental materials: Silver nitrate, AR, Sinopharm Chemical Reagent Co., Ltd. Sodium hypophosphite, AR, Tianjin Bodi Chemical Co., Ltd. PVP, K30, Boao Biotechnology Co. Ltd (Shanghai, China). Sodium hexametaphosphate, AR, Mettler - Toledo Instruments Co., Ltd. Sulfuric acid, AR, Guangzhou Dong-Hong Chemical Factory.

Experimental instruments: precision by force electric mixer (JJ-1), Changzhou Aohua Instrument Co., Ltd. Constant temperature water bath (HH-1), Changzhou Aohua Instrument Co., Ltd. Electric centrifuge (800), Changzhou Aohua Instrument Co., Ltd. Electronic Balance (AL204), Mettler-Toledo Instruments Co., Ltd. Scanning electron microscope (S-550), Hitachi, Japan. Ultrasonic cell pulverizer， JY98-□DN， Ningbo Xin-zhi Biotechnology Co., Ltd. Nano-particle size and potential analyzer, ZEN3600, malvern instruments.

Experimental methods and steps

1) Silver solution preparation. 3.40g ANgO3 weighed is dissolved in 20mL deionized water, and silver nitrate solution with the concentration of 1.0mol / L would be prepared

2) Orthogonal test design [5]. The orthogonal test with 4 factors and 3 levels was used to investigate the best preparation conditions. The molar ratio of $NaH_2PO_2 \cdot H_2O/AgNO_3$, the molar ratio of PVP/ $AgNO_3$, the molar ratio of (NaPO3)6/ $AgNO_3$, and the reaction temperature are seen as 4 factors which is named A, B, C, and D respectively, seen as Table 1. Every factor would be given 3 levels under the fixed other conditions of stirring speed, dropping speed, and reaction time. The design of factors and levels is shown in Tab.3. According to the orthogonal test design, there are nine experiments, and the orthogonal table is shown as Table 2.

Table 1: Factors and levels

Level	Factor			
	A	B	C	D/ (^{0}C)
1	1.5 : 1	1 : 1	0.0005 : 1	30
2	2.5 : 1	1.5 : 1	0.0007 : 1	40
3	3.5 : 1	2 : 1	0.001 : 1	50

3) In every experiment, sodium hypophosphite is instilled into the mixture solution of silver nitrate and PVP at the speed of 20 drops per minute under stirring conditions with the speed of 300r/min in a water bath.

4) After the reaction is finished, stirring is continued for 30 minutes.

5) The reaction solution would be treated by ultrasonic dispersion in ultrasonic cell pulverizer, in which the duration is set as 10 minutes, and it will be terminated for 5 seconds when dispersion is continued foe 4 seconds.

6) Obtaining the nano-silver size distribution by Nano-particle size and potential analyzer.

7) Obtaining the micrograph of silver particles by Scanning electron microscope.

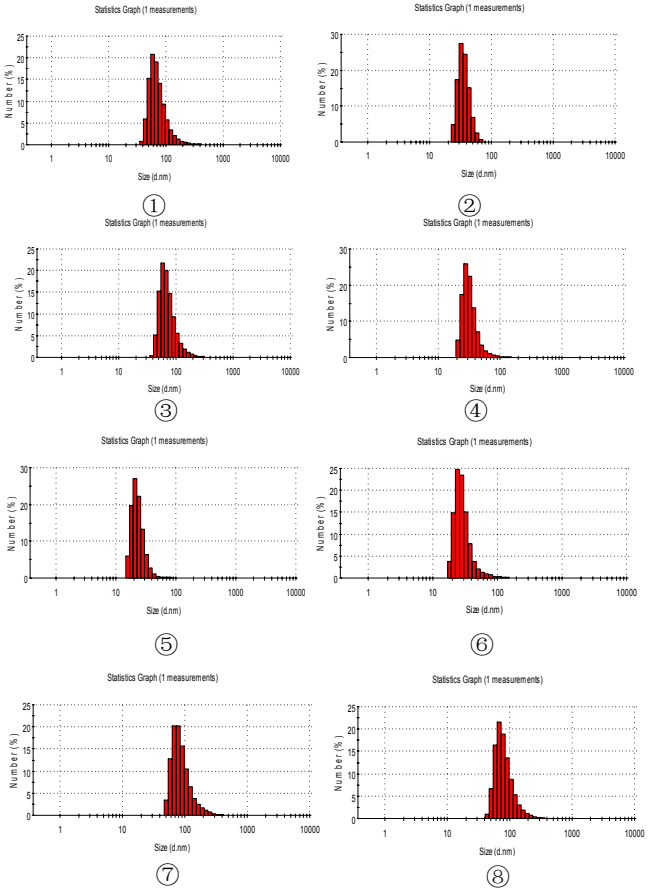
Table 2: Orthogonal table

No.	A	B	C	D
1	1	1	1	1
2	1	2	2	2
3	1	3	3	3
4	2	1	2	3
5	2	2	3	1
6	2	3	1	2
7	3	1	3	2
8	3	2	1	3
9	3	3	2	1

Experimental results and discussion

Particle size distribution

The nine samples were tested by nano-particle size and potential analyzer, and particle size distribution would be obtained, as shown in Figure1. In Figure 1, ①~⑨ is corresponding to 1~9 in Tab.2.



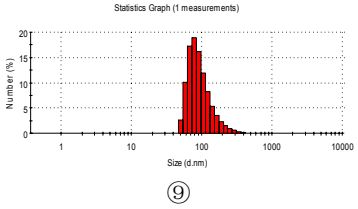
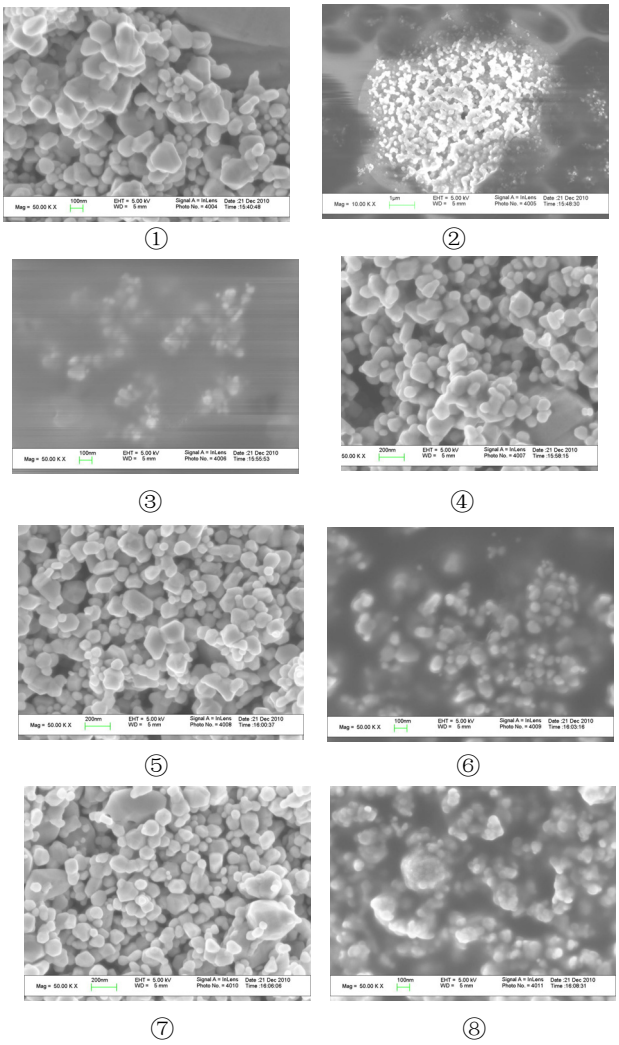


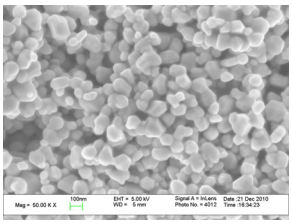
Figure 1. Size distribution of nano-silver particle

From Figure 1, we can find that, silver particles reduced from silver nitrate solution by sodium hypophosphite are in nanoscale, and most particles size is less than 100 nm.

Scanning electron microscope results

The SEM of nine samples is shown in Figure 2, and ①~⑨ is corresponding to 1-9 in Tab.4. In these figures, ③, ⑥, and ⑧ are not clear, for PVP amount is too much in these experiments which affect the scanning electron microscope results. In ②, the particles flocculation has occurred , for the PVP amount is too less ,and it will not play a well dispersion role. The others show that silver particles are spherical in nanoscale, and most particles size is less than 100 nm.





⑨

Figure 2. SEM image of nano-silver

Orthogonal experimental results

According to the orthogonal experimental program with 4 factors and 3 levels, the 1-9 samples of experiments are designed shown in Table 3. After preparation experiments, the morphology of silver nano-particles was characterized by SEM, and the SEM results are shown in Figure 2. The effect of different factor on the experimental results can be judged by intuitionistic analysis on the average size of nano-particles, and the intuitionistic analysis results are shown in Table 4.

Table 3: Projects and results of orthogonal design of L9(3^3)

Run NO.	A	B	C	D	Mean Size/nm
1	1	1	1	1	74.37
2	1	2	2	2	37.50
3	1	3	3	3	76.67
4	2	1	2	3	33.88
5	2	2	3	1	23.87
6	2	3	1	2	30.59
7	3	1	3	2	91.97
8	3	2	1	3	85.67
9	3	3	2	1	98.85

Table 4: Results of the intuitionistic analyse

Factors	Mean size of silver nanoparticles/nm			
	Level	Level 2	Level 3	R
A	62.847	29.447	66.462	37.015
B	66.74	56.743	68.703	11.96
C	63.543	56.743	64.17	7.427
D	65.697	53.353	65.407	12.344

From Table 4, we can infer that A is the most important factor in the selected three factors, followed by D and B, and finally C. That is, the effect of four factors on experimental results is A>D>B>C. According to the analysis of orthogonal experimental results, taking into account particle size, dispersion and reagent amount, we can select $A_2B_2C_2D_2$ to be the best preparation program. $A_2B_2C_2D_2$ means that the molar ratio of $NaH_2PO_2{\cdot}H_2O/AgNO_3$ is 2.5, the molar ratio of PVP and silver nitrate is 1.5, the molar ratio of (NaPO3)6/ $AgNO_3$ is 0.007 and the temperature is 40^0C. The scanning electron micrograph of nano-silver prepared under the best condition of $A_2B_2C_2D_2$ is shown in Figure 3. The nanosize particles of spherical, better dispersion, narrow size distribution are seen in Figure 3, and Figure 4 shows its size distribution. We can obtain that the particles size mainly concentrated in between 50-70nm from Fig.21.

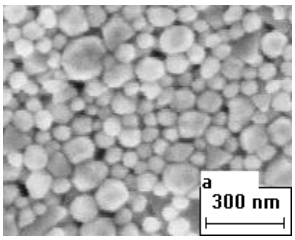


Figure 3. SEM image of nano-silver particles in A2B2C2D2

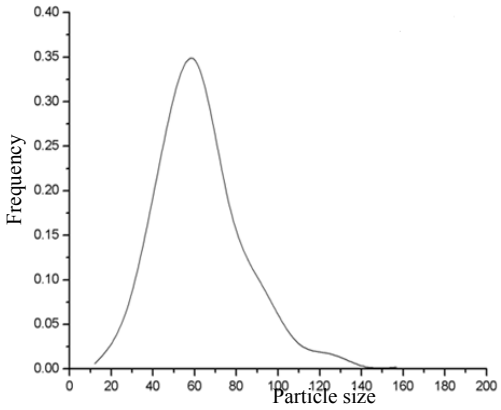


Figure 4. Nano silver particle size distribution

Conclusion

Nano-silver is a new functional material with high surface area and surface activity, which is widely used in catalyst, antistatic materials, low-temperature superconducting materials, electronic paste, biosensor, and pharmaceutical chemical. Therefore, many researchers pay attention to the preparation and properties of nano-silver. In this paper, we developed a simple way to synthesize nanosized silver by liquid chemical reduction method with Sodium hypophosphite as reductant and PVP as surface-protection reagent. In the experimental design, orthogonal test L9(43) with four factors and three levels is adopted which investigated the effects of The sodium hypophosphite amount, the PVP amount, the sodium hexametaphosphate amount and the reaction temperature on the size and morphology of silver nano-particle. Through the orthogonal experimental design, the best conditions for nano-silver preparation is determined, in which the molar ratio of NaH2PO2·H2O/AgNO3 is 2.5, the molar ratio of PVP and silver nitrate is 1.5, the molar ratio of (NaPO3)6/ AgNO3 is 0.007 and the temperature is 400C. Scanning electron microscopy was used to characterize the morphology of silver nano-particles, and the results show that the dispersed spherical nano-particles with the average size is about 60nm can be obtained in this work.

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