DE GRUYTER Green Processing and Synthesis 2022; 11: 385–395

Research Article

Jun Li*, Na Li, Xiaoxi Wan, Shihong Tian, Jianhua Liu, Lei Xu, Qin Wang, and Shaohua Ju*

Preparation of the micro-size flake silver powders by using a micro-jet reactor

https://doi.org/10.1515/gps-2022-0040
received December 03, 2021; accepted March 09, 2022

Abstract: The micro-size flake silver powders were prepared through wet-chemical reduction method by using a micro-jet reactor. Herein ascorbic acid was used as a reducing agent, and sulfuric acid was used as a stabilizer. And the lauric acid was used as a dispersing agent to prevent particles' agglomeration. The micro-jet reactor collides the two solutions together and uniformly mixes outside the reactor, to avoid the problem of clogging in the microchannel. The effects of dispersant addition and micro-jet flow rate on the morphology, particle size, and other parameters of silver powder is investigated in the present work. Interestingly, the addition of dispersant agent and stabilizer have a significant impact on the morphology and parameter of the silver particles. Under the conditions of micro-jet flow rate of 50 $\text{mL}\cdot\text{min}^{-1}$, sulfuric acid addition amount of 2%, and lauric acid addition amount of 0.8% by the weight of silver nitrate, a kind of flake silver powders with 4.40–4.70 μm can be prepared. The volume resistivity of the silver paste prepared from the obtained flake silver powders is in the range of $1.4\text{–}1.6 \times 10^{-4}\ \Omega\cdot\text{cm}^{-1}$, which meets the application test requirements of conductive silver paste.

Keywords: micro-jet reactor, flake silver powder, micro-size, sulfuric acid, lauric acid

1 Introduction

The silver nanoparticles (NPs) are widely used in catalysis [1], chemical sensing [2], biosensing [3], environment [4], and pharmaceuticals [5]. Meanwhile, because of the excellent electrical and thermal conductivity, the ultrafine silver powders are widely used in various conductive functional materials in conductive paste. The morphologies of the ultrafine silver powder are spherical (or quasi-spherical), flake, dendritic, and microcrystalline [6,7], which has a great influence on the electrical properties of the conductive paste [8].

The conductivity of the spherical powders in the conductive paste mainly relies on the point contacting between the particles, and usually requires a higher content of silver powders to effectively reduce the resistivity. In a system with the same amount of silver fillings, the contact area between silver particles with small average particle size is relatively small, so the resistivity of the microcrystalline silver powder with small particle size is usually higher than big ones. Due to the large particle size and contact area between the silver particles, the dendritic and flake silver powders have low resistivity even in the conductive silver paste with low silver content. At present, the flake silver powders are widely used in conductive silver paste due to their easy processing and stable properties [6]. When using flake kind of silver powders, the particles will form surface contact and line contact, and the upper and lower silver particles will overlap repeatedly to form a conductive coating. In general, densely connected silver conductive paths have higher electrical conductivity, so they are widely used

---

*** Corresponding author: Jun Li,** Faculty of Metallurgical and Energy Engineering, Kunming University of Science and Technology, Kunming, Yunnan 650093, China; Key Laboratory of Unconventional Metallurgy, Ministry of Education, Kunming, Yunnan 650093, China; National Local Joint Laboratory of Engineering Application of Microwave Energy and Equipment Technology, Kunming, Yunnan 650093, China, e-mail: 350349326@qq.com
*** Corresponding author: Shaohua Ju,** Faculty of Metallurgical and Energy Engineering, Kunming University of Science and Technology, Kunming, Yunnan 650093, China; Key Laboratory of Unconventional Metallurgy, Ministry of Education, Kunming, Yunnan 650093, China; National Local Joint Laboratory of Engineering Application of Microwave Energy and Equipment Technology, Kunming, Yunnan 650093, China, e-mail: jushaohua@kust.edu.cn
Na Li, Xiaoxi Wan, Shihong Tian, Jianhua Liu, Lei Xu: Faculty of Metallurgical and Energy Engineering, Kunming University of Science and Technology, Kunming, Yunnan 650093, China; Key Laboratory of Unconventional Metallurgy, Ministry of Education, Kunming, Yunnan 650093, China; National Local Joint Laboratory of Engineering Application of Microwave Energy and Equipment Technology, Kunming, Yunnan 650093, China
Qin Wang: Kunming Yinke Electronic Materials Co., LTD, Kunming, Yunnan 650114, China

in the touch screens, carbon film potentiometers, LED chip packaging, and other fields [9,10].

The preparation methods of flake silver powder are mainly divided into chemical reduction method and physical ball milling method. First, the silver powder precursor is obtained through chemical reduction followed by mechanical ball milling for the synthesis of flake silver powder in the physical ball milling method. The problems associated with this process are; long processing time, high energy consumption, and purity of silver powder being affected by ball milling aids in the grinding process [11]. The chemical reduction method directly involves in reduction of metallic silver salt to controllable size, shape, and less surface coating flake silver powder. In the process of preparing nano or micron particles by chemical reduction, the reduction method and surfactants have an important effect on the size, morphology, and dispersion characteristics of the particles [12]. Huan-Zhen et al. [6] used silver nitrate as the precursor, hydrogen peroxide as the reducing agent, and PVP as the protective dispersant in ethylene glycol medium to control the preparation of dispersed spherical single particles and hexagonal flake silver powder with a thickness of less than 100 nm and a maximum surface length of 200–500 nm. Cai et al. [13] used sulfate as a protective agent in the solution and reduced silver nitrate with ascorbic acid as a reducing agent to prepare flake silver powder. The results showed that the concentration of sulfate has a greater influence on the morphology of the silver powder. Chen et al. [14] discovered that triangular silver nano-prisms were first grown in a solution mixed with silver seed crystals and cetyltrimethylammonium bromide, and silver nano-disc particles were prepared after aging. Yang et al. [15] reported a simple and environmentally friendly method for preparing the micron-sized ultra-thin flake silvers. The prepared flake silver powder has a particle size of 2–3 μm and a thickness of about 50–100 nm. They also studied the pH value of the solution and the speed of silver nitrate addition, and the influence of factors such as the amount of polyvinyl alcohol and polyvinyl alcohol on the microstructure of ultra-thin flake silvers.

Microfluidic reaction technology adopts micro-size reaction microchannels. The mixing and diffusion of two fluids in the microchannels are easier to control. It has the advantages of high mass and heat transfer efficiency, uniform material mixing, and easy modular amplification. As a reaction enhancement technology, it has been widely used in medicine, chemical industries, materials, and other fields [16]. However, there are certain gears to focus during the preparation of micro-nano particles via microfluidic reaction because the microchannel is at risk of being blocked by precipitated particles, which depends on particle synthesis conditions, type of micro-reactor, and size of microchannel [17]. Gao et al. [18] studied the micro-mixing efficiency of a T-type closed impinging jet reactor (CIJR) by using an iodine reaction system. The results showed that the closed impinging jet reactor has better micro-mixing performance than the conventional stirred tank. The annular multilayer micro-reactor proposed by Nagasawa is an annular five-layer structure, which is located inside the cylinder in the center of the micro-reactor [19]. The annular multilayer micro-reactor is used to study the crystallization process of nanosilver halide particles, which effectively avoided the blockage of microchannels, and encouraged the possibility of using this technology in the field of the NP production industry. Katayama et al. [20] developed a micro-reactor system including a pressure sensor and ultrasonic generator. It is reported that the reactor system can effectively prevent the blockage of NPs and prepare AgCl NPs with a size of 86 nm. Baber et al. [21] studied the preparation of silver NPs in an impinging jet reactor. The reactor has the problem of efficient mixing and no channel wall blockage. Silver NPs were prepared at room temperature by reducing silver nitrate with sodium borohydride in the presence of sodium hydroxide. However, most of the research focuses on the preparation of nanoscale flake silver powders by chemical reduction. Due to the high production cost and preservation requirements of nanoscale silver powder, it is difficult to meet the large-scale use requirements of high-performance conductive silver paste. Therefore, it is necessary to develop a process based on chemical reduction, which can quickly and effectively prepare micro-size flake silver powder.

The micro-jet reactor would focus the reaction solution outside the reactor, which can mix the solution uniformly and perform a micro-reduction reaction. It would effectively control the mixing and reduction conditions of the reaction liquid, and avoid the problem of clogging of precipitates in the microchannel. In this study, a simple, rapid, and environment-friendly micro-jet reaction method was used. The two reactant solutions were evenly mixed on a micro-scale at a temperature of 25°C. In addition, fewer protective agents, and dispersants were used for continuous and rapid reduction to prepare micro-size flake silver powder. The effects of the micro-jet flow rate and the amount of dispersant added on the morphology and particle size of the prepared flake silver powder under the conditions of the micro-jet reaction were experimentally studied.

2 Materials and methods

2.1 Materials and instruments

The instruments, materials, and reagents used in the experiment are shown in Table 1.

2.2 Preparation of silver powders

The chemical reduction reaction between ascorbic acid and silver nitrate is as follows:

$$2AgNO_3 + C_6H_8O_6 = 2Ag\downarrow + C_6H_6O_6 + 2HNO_3 \quad (1)$$

Solutions A and B were prepared as follows; 0.1 mol·L^{-1} silver nitrate solution was prepared by dissolving silver nitrate in deionized water and sulfuric acid (2.0% of the weight of silver nitrate) was added to it as a stabilizer, and stirred to obtain reactant solution A; 0.05 mol·L^{-1} ascorbic acid solution was prepared by dissolving ascorbic acid in deionized water and lauric acid (0.2–1.0% of the weight of silver nitrate) was added to it as a dispersant, and stirred well to obtain reducing solution B. The temperature of the reactant solutions A and B were maintained at 25°C by using an electric thermostatic water bath.

The reactant solutions A and B were controlled by a flat flow pump to a certain flow rate and were injected into the two internal channels of the micro-jet mixing reactor, respectively, as shown in Figure 1. The micro-jet reactor is made of photosensitive resin 3D printing. There are two microchannels with an inner diameter of 0.5 mm, corresponding to inlet 1, inlet 2, outlet 3, and outlet 4. The direction of the two outlets is inclined inward, and the outlet spacing, $d = 10$ mm. The liquid ejected from outlet 1 and outlet 2 converges at a point outside the micro-jet reactor, and the included angle of the jet mixing point is 70°. Reactant A and reactant B were mixed and reacted immediately from the beginning of contact. The mixed solution flows vertically into a beaker containing 200 mL of deionized water, and the solution was stirred at 200 rpm. The two reactant solutions were continuously sprayed for 1 min and then the mixed solution in the beaker was continuously stirred for 1 min. The solution gradually precipitates in layers. The supernatant was added to 10% NaCl solution without white flocculent precipitation which indicates that silver nitrate is completely reduced. The reacted solution was filtered and the precipitate was washed 3–4 times with deionized water until the conductivity of the washing water fell below 5 μs·cm^{-1}, and then dried at 60°C for 4–6 h to obtain a silver powder product.

2.3 The volume resistivity test of conductive silver paste

0.75 g silver powder and 0.25 g organic carrier (the organic carrier is composed of epoxy resin, curing agent, solvent,

Table 1: The experiment equipment and reagents

Experimental instruments and material reagents	Specification/model	Brand/manufacturer
$AgNO_3$	Analytical purity	Tongbai Hongxin New Material Co., Ltd
H_2SO_4	Analytical purity	Tianjin Zhiyuan Chemical Reagent Co., Ltd
$C_6H_8O_6$	Food grade	Zhengzhou Tuoyang Industrial Co., Ltd
$C_{12}H_{24}O_2$	Analytical purity	Shanghai Macklin Biochemical Technology Co., Ltd
C_2H_6O	Analytical purity	Chengdu Kelong Chemical Co., Ltd
NaCl	Analytical purity	Chengdu Kelong Chemical Co., Ltd
Deionized water	Eco-Q30	Shanghai Hetai Instrument Co., Ltd
Field emission scanning electron microscope	Nova Nano SEM450	American FEI Company
X-ray diffractometer	Xpert Powder	PANalytical, Netherlands
Laser particle sizer	Rise-2002	Jinan Runzhi Technology Co., Ltd
BET surface area measurement	DX400	Beijing Jingwei Gaobo Science and Technology Co., Ltd
DC low resistance tester	TH2511	Changzhou Tonghui Electronics Co., Ltd
Advection pump	2PB type	Beijing Xingda Technology Development Co., Ltd. (Shenzhou micro)
Magnetic stirrer	85-2 type	Jintan Dadi Automation Instrument Factory
Electric constant temperature water bath	XMTD-7000	Beijing Yongguangming Medical Instrument Co., Ltd
Electric blast drying oven	101 type	Beijing Yongguangming Medical Instrument Co., Ltd

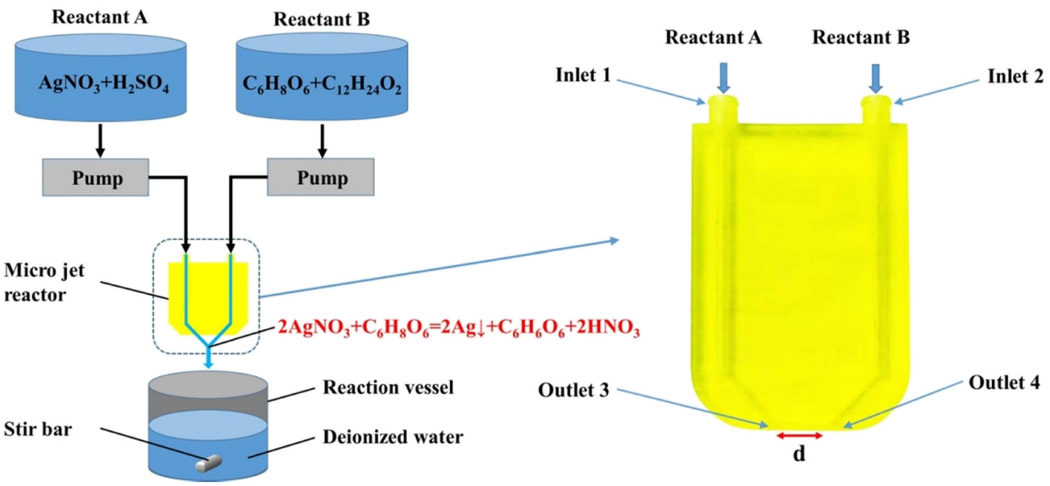

Figure 1: Schematic diagram of the micro-jet reactor.

etc., in a certain proportion, which is provided by Kunming Norman Electronic Materials Co., Ltd.) were ground in agate grinding for 30 min to ensure that the silver powder and carrier were mixed evenly. Afterward, the silver powder was completely wetted by the carrier, to obtain conductive silver paste. The conductive silver paste was uniformly printed on the glass slide by screen printing with a stainless-steel scraper to form a 10 mm × 60 mm rectangular strips. The printed glass slide was dried at 150°C for 30 min to obtain a thickness of 8–10 μm conductive film. The resistance was measured using DC low resistance tester and volume resistivity is calculated as follows:

$$\rho = RS/L \tag{2}$$

where L (cm) is the length of the conductive line and S (cm^2) is the cross-sectional area (width) of the conductive line × thickness; R (Ω) is the surface resistance of the conductive line and the unit of volume resistivity is $\Omega{\cdot}\mathrm{cm}^{-1}$.

2.4 Characterization

The surface morphology of the silver powder was characterized by a Nova Nano SEM450 field emission scanning electron microscope (SEM). The phase of silver powder was characterized by X-ray diffractometer (XRD; Xpert Powder, PANalytical). The particle size distribution of silver powder was detected by Jinan Runzhi Rise-2002 laser particle sizer. The specific surface area of flake silver powder was tested by BET surface area measurement (DX400). The volume resistivity of the prepared flake silver powder was tested after printing, drying, and curing.

3 Results and discussion

3.1 Effect of micro-jet flow on the morphology of silver powder

The silver powders were prepared using reactant solutions (A and B), with the addition amount of stabilizer, sulfuric acid, was 2% and the addition amount of dispersant, lauric acid, was 0.8% (other conditions were consistent with the description of the test process in Section 2.2). According to the previous reports, the flow rate of the micro-jet reactor has a significant impact on the mixing strength of the two reactant solutions and affect the morphology and particle size of the micro-and nanoparticles prepared by the chemical reduction [17]. The flow of the two solutions could not form effective injection convergence when the flow rate was lower than 50 $\mathrm{mL{\cdot}min^{-1}}$, hence the flow of the micro-jet reactor is controlled to be 50 and 70 $\mathrm{mL{\cdot}min^{-1}}$, respectively. The convergence images of the front view and side view at different micro-jet flow rates were visualized using optical cameras, as shown in Figure 2a and c, and the SEM images of the prepared silver powder at different micro-jet flow rates are shown in Figure 2b and d.

It can be seen that the flow pattern at the convergence point changes under the two micro-jet flow conditions of 50 and 70 $\mathrm{mL{\cdot}min^{-1}}$. At the flow rate of 50 $\mathrm{mL{\cdot}min^{-1}}$, the two micro-jets converge and form a confluence. The two solutions participating in the reaction in this area can be quickly mixed, fall vertically for a certain distance and gradually form dispersed droplets. When the micro-jet flow is increased to 70 $\mathrm{mL{\cdot}min^{-1}}$, the two streams collide together and form an elliptical liquid film area at the

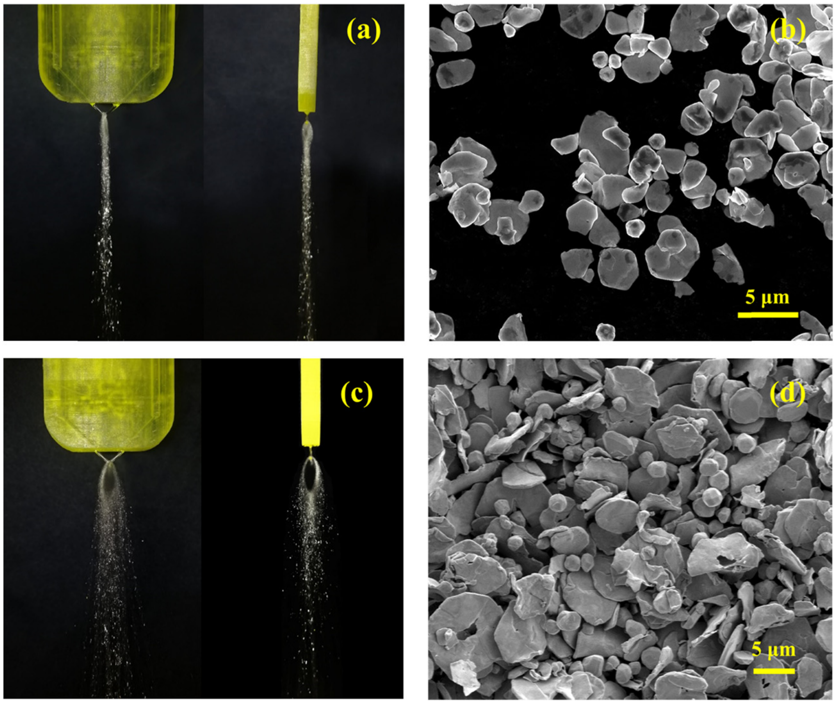

Figure 2: Images of the micro-jet flow and SEM of the prepared silver powder: (a) a front view and side view at 50 mL·min^{-1}; (b) prepared silver powder at 50 mL·min^{-1}; (c) a front view and side view at 70 mL·min^{-1}; (d) prepared silver powder at 70 mL·min^{-1}.

convergence point. However, due to the increase in the momentum when the micro-jet collides, more droplets scatter rapidly and forming the liquid edge of the film.

It is necessary to confirm the morphology and composition of the synthesized products by means of characterization. Mahmood et al. used UV-Vis spectroscopy to characterize silver NPs synthesized in liquid phase, and the result showed that the formed NPs were uniformity and had a certain degree of monodispersity [22]. For the micro-size silver particles synthesized in this study, the SEM and XRD can be used to verify the silver powders [6,23].

The flake silver powders prepared at different micro-jet flow rates were characterized by SEM and the results of the two samples are shown in Figure 2b and d. Different micro-jet flow leads to different shapes of the collision mixing region and droplet scattering degree, which affect the mixing effect of the liquid flow, and then affects the morphology and aggregation of the flake silver particles. At the flow rate of 50 mL·min^{-1}, the two liquids, reactant A and B, merge within a certain distance after convergence to form a confluence area. The two solutions can be evenly mixed and react in the confluence. The mixed solution falls vertically for a certain distance and gradually forms dispersed droplets. These droplets dispersed after uniform mixing are independent of each other, the microenvironment in the droplet is conducive to the uniform nucleation and growth of the silver particles. It can also be seen from the SEM that the morphology of the prepared silver particles is highly uniform and have flake like structure. On increasing the micro-jet flow to 70 mL·min^{-1}, due to the increase in the momentum during a micro-jet collision, more droplets are rapidly scattered at the edge of the liquid film areas formed by the convergence of the two solutions A and B, and some splashed droplets are directly scattered due to strong collision. The contact time of the droplets in the relatively effective film area is very small, and due to a large number of sprayed droplets, the mixing efficiency is affected. After falling into the beaker, the nucleation and growth reaction of silver particles may occur at the same time, and the sulfuric acid stabilizer may not be evenly mixed, which affects the induced crystallization process of the particles, resulting in both flake and spherical silver particles.

The flake silver powders were prepared with the flow rate of 50 and 70 mL·min^{-1}, when the addition amount of stabilizer, sulfuric acid, was 2% and the addition amount of dispersant, lauric acid, was 0.8% (other conditions were consistent with the description of the test process in Section 2.2). The samples were characterized by XRD, as shown in Figure 3.

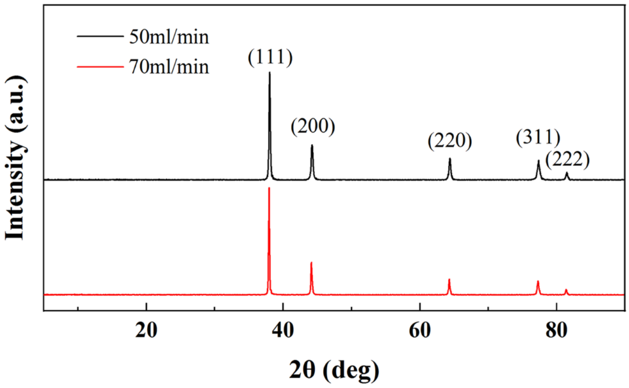

Figure 3: XRD of the flake silver powders prepared at different flow rates (50 and 70 mL·min^{-1}).

The images show that a sharp diffraction ray was observed at 2θ = 38.1°, and the other four relatively weak peaks were 44.2°, 64.4°, 77.4°, and 81.5°, respectively, corresponding to the (111), (200), (220), (311), and (222) crystal planes of face-centered cubic silver. In addition, no peaks of impurities were observed, indicating that the purity of the silver products in both the flow rates were high. Similar results were also reported in earlier studies [13], when sulfuric acid was used as the protective agent, the adsorption capacity of sulfate on different crystal faces of the silver core was different, and the (111) crystal face was most obviously adsorbed by the protective agent sulfuric acid. A large number of sulfate ions are deposited on the (111) crystal face of the silver core, thus limiting the growth of other crystal faces, forming flake silver powder dominated by (111) crystal face.

3.2 Effect of dispersant addition on morphology and particle size of silver powder

The dispersant can be adsorbed on the surface of the nucleated silver particles in the process of solution reaction, which affects the growth and aggregation of the silver particles. The flake silver powders were prepared using the reactant solutions (A and B) with 50 mL·min^{-1} flow of the micro-jet reactor and the addition amount of dispersant is 0.4%, 0.6%, 0.8%, and 1.0%. Other conditions are consistent with the description of the test process in Section 2.2. The flake silver powder prepared with different addition amounts of dispersant were characterized by SEM, as shown in Figure 4.

From Figure 4, it can be seen that different dispersant addition has a significant effect on the dispersion of flake silver powder. When the addition amount of dispersant is 0.4%, most of the prepared flake silver powders aggregate with each other. When the addition amount of dispersant is increased to 0.6%, the aggregation of flake silver powder is improved and the particle size is reduced

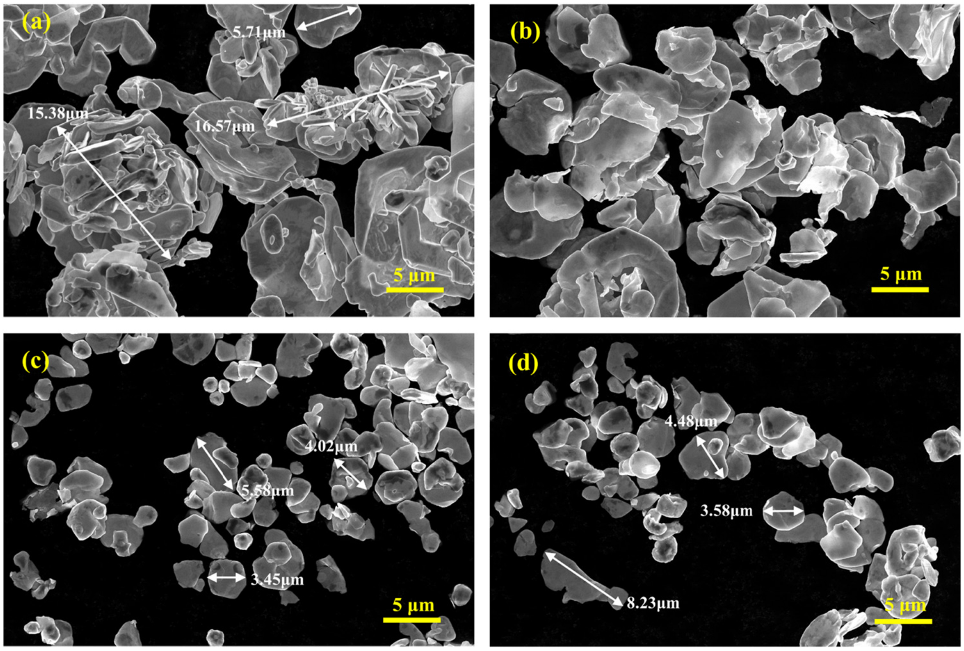

Figure 4: SEM of the silver powder prepared with different dispersant addition: (a) 0.4%, (b) 0.6%, (c) 0.8%, and (d) 1.0%.

accordingly. When the addition amount of dispersant is increased to 0.8%, the silver particles become monodispersed. When the addition amount of dispersant increased to 1.0%, the morphology and dispersion of flake silver particles changed moderately. During the wet-chemical reduction reaction of silver powder, the formation of silver particles needs to go through the nucleation and growth processes. The dispersant in the solution will usually be adsorbed on the surface of the nucleated particles. Under the action of steric hindrance and electrostatic repulsion, the mutual contact between the nucleated particles is limited, to control the growth and aggregation process of the nuclei [23].

This shows that when less dispersant makes the silver particles aggregate with each other, resulting in aggregation and growth of flake silver powder. Because the two reaction solutions can be mixed more evenly under the condition of micro-jet mixing, the addition amount of dispersant of 0.8% can effectively coat the generated silver particles and prevent the silver particles from growing and gathering, and the average flake silver particle size with 4.5 μm was obtained. Continuing to increase the dispersant addition has no obvious effect on the particle size of flake silver powder, but may cause excessive residual dispersant on the surface of silver powders, which may harm the conductivity of the conductive silver paste. Therefore, it is considered that the dispersant addition amount of 0.8% is appropriate.

3.3 Effect of dispersant addition on the parameters of flake silver powder

The effect of dispersant addition on the parameters of flake silver powder prepared by using the micro-jet reactor was investigated. The two prepared reactant solutions A and B were used with controlled addition of stabilizer, sulfuric acid = 2%, and dispersant, lauric acid of 0.8%, where the flow of the micro-jet reactor is controlled at 50 mL·min^{-1}. Other conditions are consistent with the description of the test process in Section 2.2.

3.3.1 Effect of dispersant addition on the density of silver powder

When flake silver powder is applied to the conductive adhesive, its apparent density and tap density have an important impact on the added content of silver. Under the condition of meeting the requirements of viscosity, printability, and electrical properties of conductive adhesive, the lower apparent density and tap density can reduce the added amount of flake silver powder and reduce the material cost [24]. The apparent density of the flake silver powder was tested by loose density meter and the tap density was tested by tapping apparatus, respectively, and the results are shown in Figure 5.

It can be seen from the test results that the apparent density of flake silver powder obtained by adding different ratios of dispersants is in the range of 1.2–1.5 g·cm^{-3}, and the tap density is in the range of 2.4–3.0 g·cm^{-3}. When the amount of dispersant was 0.8%, the apparent density of flake silver powder was 1.20 g·cm^{-3} and the tap density was 2.42 g·cm^{-3}. On increasing the amount of the dispersant to 1.0%, the apparent density slightly increased to 1.28 g·cm^{-3} and the tap density to 2.58 g·cm^{-3}. The apparent density and tap density increased again when the amount of dispersant was increased from 0.8% to 1%, the main reason may be due to more dispersants made the silver particles disperse better and the particles were packed more tightly. The particle morphology, particle size distribution, and dispersion of flake silver powder are the main factors affecting the apparent density and tap density of the silver powders [7]. For the same weight of silver powders, the spherical silver powders are packed more tightly into each other than flake silver powders. So, the flake silver powder has lower apparent density and tap density than spherical silver powder. As shown in Figure 5, the smallest apparent density and tap density were obtained when the amount of dispersant was 0.8%. The lower apparent density and tap density of flake silver powders can effectively reduce the amount of silver powders in the conductive

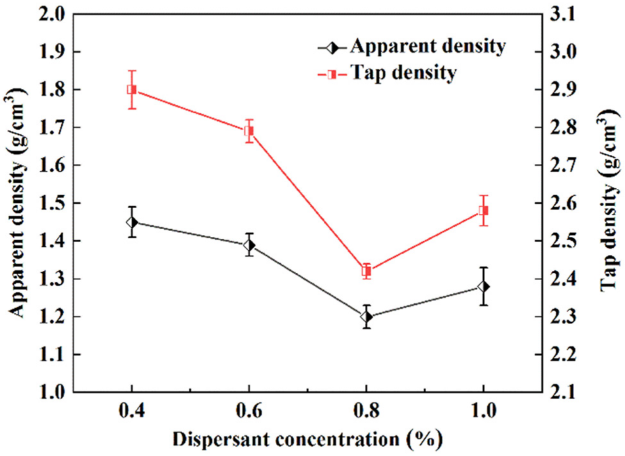

Figure 5: Apparent density and tap density of silver powder prepared with different dispersant addition.

silver paste while meeting the requirements of electrical conductivity.

3.3.2 Effect of dispersant addition on the specific surface area of silver powder

The specific surface area of flake silver powder is an important parameter to be referred when applying in conductive silver paste, which has a great influence on the viscosity and printing performance of the silver paste. The variation in specific surface area of flake silver powder prepared in the presence of different amounts of dispersant was detected, and the results are shown in Figure 6.

With the increase in the amount of dispersant, the specific surface area of flake silver powder increased, as shown in Figure 6. When the amount of the dispersant is 0.4%, the specific surface area is 0.58 $m^2 \cdot g^{-1}$, and when the amount of dispersant is 0.8%, the specific surface area increases to 0.74 $m^2 \cdot g^{-1}$. As can be seen from the SEM pictures of silver powder in Figure 4, with the increase in the dispersant addition, the aggregation of large particles of flake silver powder gradually decreases. The monodispersed flake silver powder with a small particle size is obtained, and its specific surface area increases accordingly. On continuing to increase the amount of the dispersant to 1.0%, the specific surface area increases slightly to 0.76 $m^2 \cdot g^{-1}$. Because the particle size of the flake silver powder does not further decrease, the specific surface area changes little.

3.3.3 Effect of dispersant addition on the loss on ignition (LOI) of silver powder

The application of silver powder in the conductive silver paste not only depends on the particle size distribution, particle morphology, and dispersion of silver powder but is also highly influenced by its purity. The LOI was usually used to reflect the residue of impurities in the silver powder. The higher the LOI, the more impurities coated on the surface of the flake silver powder. In general, excessive impurities on the surface of silver powder will adversely affect the wettability and printing performance of silver powder in the paste. The calculation formula of the LOI is as follows:

$$\mathrm{LOI} = \frac{(G_1 - G_2)}{G_1} \times 100\% \tag{3}$$

where G_1 is the mass before burning, and G_2 is the mass after burning.

1 g flake silver powder prepared at different dispersant addition was kept in a muffle furnace for heating at 550°C for 60 min, then the LOI of the original samples was calculated and the results are shown in Figure 7.

Figure 7 shows that the addition amount of dispersant has a significant effect on the ignition loss of the flake silver powder. When the addition amount of dispersant was increased from 0.4% to 0.6%, the LOI of flake silver powder increased slightly. Increasing the dispersant amount to 0.8%, the LOI was slightly lower than the measured value, and when the addition amount of dispersant was increased to 1.0%, the LOI of the flake

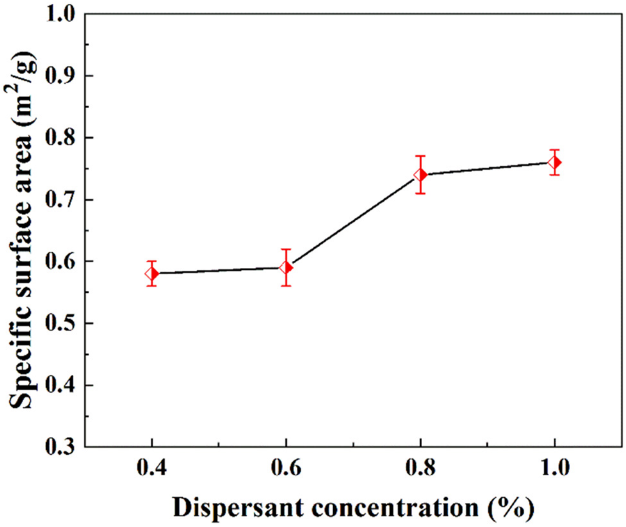

Figure 6: Specific surface area of the silver powder prepared with different dispersant addition.

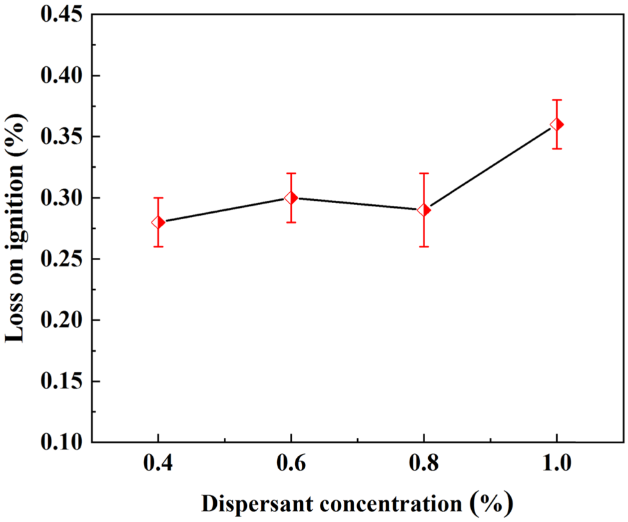

Figure 7: LOI of the silver powder prepared with different dispersant addition.

silver powder increased rapidly to 0.36%. Clearly, too much dispersant in the solution could coat on the surface of the silver powder or between the agglomerated particles of the silver powder, for the high surface energy and microstructure of flake silver powder particles. It would affect the purity of the silver powder and its corresponding properties in the conductive silver paste. It can also be seen from the SEM of silver powder in Figure 4. when the addition amount of dispersant is low, although few dispersants are entering the solution, the LOI of silver powder has insignificant or very less difference than when the addition amount of dispersant was 0.8%. It is mainly due to that more reductants or dispersants that do not react in time may be wrapped in the aggregated particles, which is difficult to remove in the subsequent cleaning process. When the addition amount of dispersant is 0.8%, the flake silver powder has good dispersion, the reduction of agglomeration makes the organic impurities coated in the agglomerated particles relatively less, so the LOI is also lower than 0.3%. However, with the increase in the dispersant up to 1.0%, the LOI of the flake silver powder increases obviously. This is mainly because too much dispersant is coated on the surface of the silver particles, resulting in the obvious increase in the ignition loss of the silver powder.

3.3.4 Effect of dispersant addition on the volume resistivity of silver paste

The conductive silver paste with 75% silver content was prepared, and its volume resistivity by addition of different amounts of dispersant was tested. The results are shown in Figure 8.

The volume resistivity of flake silver powder prepared with the addition of different amounts of dispersant is less than $3.5 \times 10^{-4}\ \Omega\cdot\text{cm}^{-1}$ (Figure 8). When the amount of dispersant is 0.4% and 0.6%, the volume resistivity of silver powder is 2.4×10^{-4} and $2.3 \times 10^{-4}\ \Omega\cdot\text{cm}^{-1}$, respectively. At 0.8%, the volume resistivity of the silver powder decreases to $1.6 \times 10^{-4}\ \Omega\cdot\text{cm}^{-1}$ but on further increase in the dispersant amount to 1.0%, the volume resistivity increases to $3.3 \times 10^{-4}\ \Omega\cdot\text{cm}^{-1}$. In the abovementioned experiment, when the amount of the dispersant is 0.8%, the morphology of the silver particles is flake silver powder with good dispersion. Under the same silver content, the flake silver powder in silver paste has better overlapping and conduction ability, but too much dispersant leads to the increase in the LOI of silver powder, and its electrical conductivity will be adversely affected.

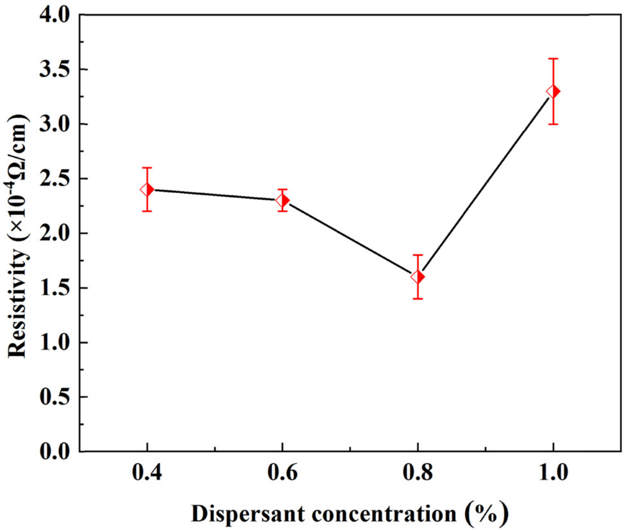

Figure 8: Effect of different dispersant addition on volume resistivity of flake silver powder.

3.4 Preparation of micro-size flake silver powders

Five parallel experiments were carried out in order to verify the stability and recovery rate of micro-size flake silver powders prepared by using micro-jet reactor [25–28]. The experimental conditions are as follows: the concentration of silver nitrate solution is $0.1\ \text{mol}\cdot\text{L}^{-1}$, the concentration of ascorbic acid solution is $0.05\ \text{mol}\cdot\text{L}^{-1}$, both solutions A and B are 50 mL, 0.017 g sulfuric acid (2.0% of the weight of silver nitrate) is used as stabilizer and 0.007 g lauric acid (0.8% of the weight of silver nitrate) as a dispersant, the micro-jet flow is $50\ \text{mL}\cdot\text{min}^{-1}$, and other conditions are consistent with the description of the test process in Section 2.2 test process. And the volume resistivity of conductive silver paste is tested according to Section 2.3. The results are shown in Table 2.

As shown in Table 2, the flake silver particles with an average particle size of 4.40–4.70 μm were prepared.

Table 2: Characterization of as-synthesized micro-size flake silver particles

Experiment no.	Particle size (μm)	Recovery rate (%)	Volume resistivity ($\Omega\cdot\text{cm}^{-1}$)
E_{01}	4.60	97.2	1.5×10^{-4}
E_{02}	4.40	96.3	1.6×10^{-4}
E_{03}	4.70	96.8	1.6×10^{-4}
E_{04}	4.70	97.4	1.4×10^{-4}
E_{05}	4.50	96.6	1.6×10^{-4}

In this process, the reactant solution is mixed quickly inside the micro-jet reactor followed by mixing of solution (stirring for 1 h), whereas the conventional drip reaction usually takes several hours of reaction time [29]. According to the previous reports, the conductive silver paste with micro-size flake silver particles as conductive material generally requires the volume resistivity of orders of magnitude not higher than $10^{-4}\,\Omega\cdot\text{cm}^{-1}$ [8,30]. The volume resistivity of the conductive silver paste prepared from the obtained flake silver powders is in the range of $(1.4\text{–}1.6) \times 10^{-4}\,\Omega\cdot\text{cm}^{-1}$, which meets the application test requirements of the conductive silver paste. And the recovery rate of flake silver powders is in the range of 96.3–97.4%.

4 Conclusion

1. In this piece of research, silver flake powder was prepared by reducing silver nitrate with ascorbic acid in the presence of sulfuric acid as protective agent and lauric acid as dispersant and the effects of different parameters on the morphology and dispersion of silver powder have been successfully demonstrated. The simple and rapid wet-chemical reduction method via micro-jet reaction was assisted to synthesize the desired structured silver particles.
2. The effects of dispersant addition and micro-jet flow on the morphology, particle size, and other parameters of the flake silver powder were studied. Upon investigation it was found that the average particle size of the prepared flake silver powder is 4.40–4.70 µm, and the volume resistivity is in the range of $(1.4\text{–}1.6) \times 10^{-4}\,\Omega\cdot\text{cm}^{-1}$, which meet the requirements towards conductive materials application for conductive silver paste.
3. Compared with the conventional stirred reactor, the micro-jet reactor can mix the reactant solution quickly and effectively avoid the problem of deposition or blockage of synthetic products in the microreactor channel. The results of this work concluded that the proposed micro-jet reactor has potential application in the controlled synthesis of nano-micron silver particles, and can be scaled up appropriately by increasing the size of microchannels or modularization of reactors.

Funding information: The financial support was provided by the National Scientific Foundation of China (no. 51964032).

Author contributions: Jun Li: writing – original draft, investigation, and conceptualization; Na Li: investigation; Xiaoxi Wan: investigation; Shihong Tian: resources; Jianhua Liu: writing – review and editing; Lei Xu: funding acquisition; Shaohua Ju: methodology, formal analysis, and project administration.

Conflict of interest: Authors state no conflict of interest.

References

[1] Deng H, Yin J, Ma J, Zhou J, Zhang L, Gao L, et al. Exploring the enhanced catalytic performance on nitro dyes via a novel template of flake-network Ni-Ti LDH/GO *in-situ* deposited with Ag_3PO_4 NPs. Appl Surf Sci. 2021;543:148821. doi: 10.1016/j.apsusc.2020.148821.

[2] Ma JM, Zhu JQ, Ma P, Jie Y, Wang ZL, Cao X. Fish bladder film-based triboelectric nanogenerator for noncontact position monitoring. ACS Energy Lett. 2020;5(9):3005–11. doi: 10.1021/acsenergylett.0c01062.

[3] Ren XL, Meng XW, Chen D, Tang FQ, Jiao J. Using silver nanoparticle to enhance current response of biosensor. Biosens Bioelectron. 2005;21(3):433–7. doi: 10.1016/j.bios.2004.08.052.

[4] Jiao TF, Zhao H, Zhou JX, Zhang QR, Luo XN, Hu J, et al. Self-assembly reduced graphene oxide nanosheet hydrogel fabrication by anchorage of chitosan/silver and its potential efficient application toward dye degradation for wastewater treatments. ACS Sustain Chem Eng. 2015;3(12):3130–9. doi: 10.1021/acssuschemeng.5b00695.

[5] Kumar A, Vemula PK, Ajayan PK, John J. Silver-nanoparticle-embedded antimicrobial paints based on vegetable oil. Nat Mater. 2008;7:236–41. doi: 10.1038/nmat2099.

[6] Huan-Zhen L, Dong-Jin K, Hun S. C, Jie Z, Ke-Ning Y, Shao-Hua L, et al. Mechanism for the formation of flake silver powder synthesized by chemical reduction in ethylene glycol. Acta Phys Chim Sin. 2003;19(2):150–3. doi: 10.3866/PKU.WHXB20030212.

[7] Yu LG, Zhang YH. Preparation of nanoflake silver by chemical reduction. Rare Met Mater Eng. 2010;39(3):0401–4. doi: 10.1016/S1875-5372(10)60088-4.

[8] Xiong SH, Yang RC, Wu DJ, Zheng DF, Tian MB. Effects of morphologies and size of Ag particle on electrical performance of conductive adhesive. Electron components&materials. 2005;24(8):14–6. doi: 10.3969/j.issn.1001-2028.2005.08.005.

[9] Cui HW, Kowalczyk A, Li DS, Fan Q. High performance electrically conductive adhesives from functional epoxy, micron flake silvers, micron silver spheres, and acidified single-wall carbon nanotube for electronic package. Int J Adhes Adhesives. 2013;44:220–5. doi: 10.1016/j.ijadhadh.2013.03.004.

[10] Yan FC, Gan GY, Teng Y, Kang KY, Yan JK, Yi JH. Research progress and the prospect of the conductive silver paste for solar cell. Mater Rep. 2016;30(2):139–43. doi: 10.11896/j.issn.1005-023X.2016.03.027.

[11] Ju W, Yi XB, Zhang J, Wang QC, Mu QH, Fan HL. Affecting factors of planetary ball milling the flake silver powders. China Powder Sci Technol. 2016;22(6):46–9. doi: 10.13732/j.issn.1008-5548.2016.06.011.

[12] Najeeb J, Farwa U, Ishaque F, Munir H, Rahdar A, Nazar MF, et al. Surfactant stabilized gold nanomaterials for environmental sensing applications – A review. Environ Res. 2022;208:112644. doi: 10.1016/j.envres.2021.112644.
[13] Cai YK, Chen C, Pang FF, Geng X, Han GZ. Controlled synthesis of silver particles with different reaction system. Chin J Inorg Chem. 2014;30(6):1339–44. doi: 10.11862/CJIC.2014.194.
[14] Chen SH, Carroll DL. Silver nanoplates: size control in two dimensions and formation mechanisms. J Phys Chem B. 2004;108(18):5500–6. doi: 10.1021/jp031077n.
[15] Chao Y, Yang H, Li Y, Guo S, Wang C, Wang C. Synthesis and formation mechanism of micron-size flake silvers with high radius-thickness ratio: application to silver paste. J Mater Sci Mater Electron. 2017;70(8):183–7. doi: 10.1016/j.cplett.2018.08.021.
[16] Zhao CX, He LZ, Qiao SZ, Middelberg AP. Nanoparticle synthesis in microreactors. Chem Eng Sci. 2011;66(7):1463–79. doi: 10.1016/j.ces.2010.08.039.
[17] Schoenitz M, Grundemann L, Augustin W, Scholl S. Fouling in microstructured devices: A review. Chem Commun. 2015;51(39):8213–28. doi: 10.1039/c4cc07849g.
[18] Gao ZM, Han J, Bao YY, Li ZP. Micromixing efficiency in a T-shaped confined impinging jet reactor. Chin J Chem Eng. 2015;23(2):350–5. doi: 10.1016/j.cjche.2014.11.024.
[19] Nagasawa H, Mae K. Development of a new microreactor based on annular microsegments for fine particle production. Ind Eng Chem Res. 2006;45(7):2179–86. doi: 10.1021/ie050869w.
[20] Katayama E, Togashi S, Endo Y. Production of AgCl nanoparticles using microreactors. J Chem Eng Jpn. 2010;43(12):1023–8. doi: 10.1252/jcej.10we106.
[21] Baber R, Mazzei L, Thanh N, Gavriilidis A. Synthesis of silver nanoparticles using a microfluidic impinging jet reactor. J Flow Chem. 2016;6(3):268–78. doi: 10.1556/1846.2016.00015.
[22] Mahmood M, Abid M, Nazar MF, Zafar MN, Raza MA, Ashfaq M, et al. Wet chemical synthesis of surfactant-capped quasi-spherical silver nanoparticles with enhanced antibacterial activity. Mater Adv. 2020;1:2332–8. doi: 10.1039/D0MA00408A.
[23] Wu SP, Meng SY. Preparation of ultrafine silver powder using ascorbic acid as reducing agent and its application in MLCI. Mater Chem Phys. 2005;89(2–3):423–7. doi: 10.1016/j.matchemphys.2004.09.026.
[24] Kaviya S, Santhanalakshmi J, Viswanathan B. Biosynthesis of silver nano-flakes by Crossandra infundibuliformis leaf extract. Mater Lett. 2012;67(1):64–6. doi: 10.1016/j.matlet.2011.09.023.
[25] Duester L, Fabricius AL, Jakobtorweihen S, Philippe A, Weigl F, Wimmer A, et al. Can cloud point-based enrichment, preservation, and detection methods help to bridge gaps in aquatic nanometrology? Anal Bioanal Chem. 2016;408:7551–7. doi: 10.1007/s00216-016-9873-5.
[26] Nazar MF, Shah SS, Eastoe J, Khan AM, Shah A. Separation and recycling of nanoparticles using cloud point extraction with non-ionic surfactant mixtures. J Colloid Interface Sci. 2011;363(2):490–6. doi: 10.1016/j.jcis.2011.07.070.
[27] Myakonkaya O, Hu Z, Nazar MF, Eastoe J. Recycling functional colloids and nanoparticles. Chem – A Eur J. 2010;16:11784–90. doi: 10.1002/chem.201000942.
[28] Nazar MF, Myakonkaya O, Shah SS, Eastoe J. Separating nanoparticles from microemulsions. J Colloid Interface Sci. 2011;354(2):624–9. doi: 10.1016/j.jcis.2010.11.017.
[29] Liang HZ, Kim DJ, Yu KN, Chung HS, Zhang J, Li SH, et al. Synthesis of hexagonal flake silver powder. Powder Metall Techonol. 2003;21(4):218–23. doi: 10.3321/j.issn:1001-3784.2003.04.006.
[30] Gan WP, Luo J, Guo GQ, Xiang F, Liu H. Preparation of ultra-fine silver powder used in electronic paste by chemical reduction. Electron Components Mater. 2010;29(11):15–8. doi: 10.3969/j.issn.1001-2028.2010.11.005.