

A novel wet-chemical method for preparation of silver flakes

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Abstract: A novel wet-chemical method for the preparation of silver flakes was studied. The well-defined particles were prepared by directly adding FeSO_4 solution into AgNO_3 solution containing citric acid at an agitation speed of 150 r/min at room temperature. The products were characterized by scanning electron microscopy (SEM) and X-ray diffraction (XRD). The results show that particles are irregular thin silver flakes. And the sizes of them range from 2 to 10 μm . It is found that citric acid plays an important role in the formation of silver flakes. There is an optimum amount of citric acid for the preparation of silver flakes by this method. It is also found that high reduction rate is favorable for the formation of silver flakes.

Key words: silver flake; wet-chemical method; $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$; citric acid

1 Introduction

The ultrafine metallic powders are used extensively in light, electricity, magnetism, heat and catalysis areas. And the silver powders had attracted considerable attention during the past few years for their many advantages, such as high electrical and thermal conductivity, high inoxidizability, excellent solderability and reasonable price. Among many preparation methods of silver particles, the wet-chemical method is often preferred for its advantage of the size and shape controlling. Nowadays, people have made many progresses in the wet-chemical synthesis of silver nanostructures with different shapes, such as nanocubes [1,2], nanodisks [3,4], nanoprisms [5–7], nanoplates [5,8–10], nanorods [11,12], and nanowires [1,13,14]. And people also succeeded in the synthesis of micro-sized silver particles with different shapes, such as micro-sized sphere [15,16] and micro-sized dendrites [17–19], by wet-chemical methods. They also developed some approaches for the preparation of micro-sized silver flake. DU et al [20] presented another thermal method to prepare silver sheets at 250 °C via decomposition of the silver nitrate in ethanol in the

presence of ammonia. The lateral dimension of the silver sheets was up to 15 μm . And LIANG et al [21] synthesized silver flakes by reducing the tollen reagent with hydrogen peroxide under the catalysis of chloroplatinic acid in ethylene glycol. The size of the silver flakes could reach 30 μm . Obviously, the methods mentioned above for the preparation of micro-sized silver flakes need to be carried out in a thermal process or need seeds to catalyze and promote the anisotropic growth of silver nucleus. In our previous work [22], the micro-sized hexagonal and triangular silver plates were prepared by mixing of $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ solution with silver nitrate solution in the presence of different modifiers at room temperature. The mean edge lengths of resulting products were 2 and 3 μm , respectively. But the product yield was very low. To promote the preparation of the silver flakes with the simple wet-chemical methods and enhance the understanding of the formation mechanism of silver crystals during these preparation processes, a simple approach to prepare the micro-sized silver flakes still needs to be demonstrated. In this work, a novel simple wet-chemical method for the preparation of micro-sized silver flakes is presented. It is carried out by directly adding the $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ into silver nitrate solution at the presence of citric acid at room temperature.

2 Experimental

2.1 Materials

In this study, silver nitrate (AgNO_3 , analytical reagent, Shanghai Chemical Reagent Co., Ltd), Iron (II) sulfate heptahydrate ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$, analytical reagent, Sinopharm Chemical Reagent Co., Ltd), citric acid ($\text{C}_6\text{H}_8\text{O}_7 \cdot \text{H}_2\text{O}$, analytical reagent, Shanghai Chemical Reagent Co., Ltd), absolute ethanol ($\text{C}_2\text{H}_5\text{OH}$, analytical reagent, Shanghai Chemical Reagent Co., Ltd) and de ionized water were used as the raw materials without further purification.

2.2 Method

In a typical process, 1 g AgNO_3 and 4.4 g $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ were dissolved in 50 mL de ionized water to prepare the solutions of them, respectively. And 0.15 g $\text{C}_6\text{H}_8\text{O}_7 \cdot \text{H}_2\text{O}$ was added in the AgNO_3 solution. Then the $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ solution was added in AgNO_3 solution immediately with an agitation speed of 150 r/min at room temperature. When the color of the mixed solution did not change, the reaction was ceased. After separated from the mixed solution, the precipitation was washed by de ionized water for 3–4 times and then by ethanol for 2–3 times. Then the powders were obtained after the precipitation was desiccated in the vacuum-desiccator at 50 °C for 30 min.

The powders were characterized by scanning electron microscopy (SEM, S-3000, Hitachi) and X-ray diffraction (XRD, X'Pert PRO, PANalytical B.V, Holland).

3 Results and discussion

3.1 Formation of silver flakes

The silver particles prepared in the typical process mentioned above were characterized by SEM and XRD. The SEM results are shown in Fig. 1. It shows that silver microcrystals mostly consist of irregular flakes (Fig. 1(a)). The flakes have smooth surfaces. And they are so thin that look like frangible. And the sizes of them range from 2 to 10 μm (Fig. 1(b)).

Figure 2 shows the XRD pattern of the particles. It reveals that the significant diffraction peaks locate at 38.3° , 44.4° , 64.6° , and 77.6° , which correspond to the characteristic peaks of (111), (200), (220), and (311) crystal planes of silver metal, respectively, indicating that the powders consist of pure crystalline silver.

The reduction of Ag^+ by Fe^{2+} can be formulated as follows:



The formation process of silver microcrystals

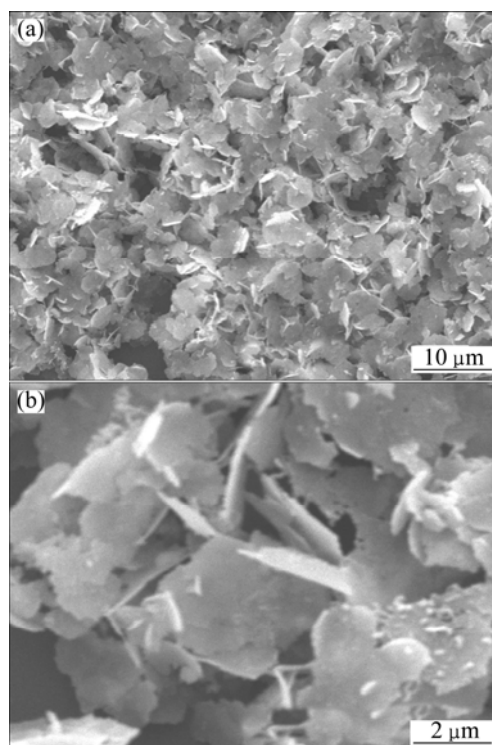


Fig. 1 SEM images of silver flakes with low magnification (a) and high magnification (b)

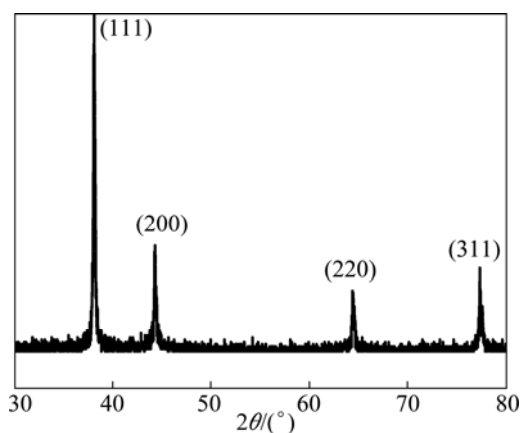


Fig. 2 XRD pattern of silver powders

commonly includes the production of silver nucleus and the growth of silver crystals. And the growth process of silver crystals is often affected by the diffusion rates of components in the mixed solution [23]. It is found that the (111) plane of silver possesses the lowest surface energy, and it can absorb some suitable additives, such as citrate [4,9] and sulfate ion [24], which can further lower the surface energy and stabilize the silver plates with the (111) plane as the basal plane. Then the growth rate of silver crystals along the {111} facets is the fastest. As mentioned above, the growth rate is also affected by the diffusion rate of the silver atoms, which is decided by the reduction rate. According to Eq. (1), when the reduction

rate is high, the new silver atoms will be produced instantly. It is easy for them to diffuse to the formed nucleus. The anisotropic growth of silver crystals will happen under the regulation of sulfate ion and citric acid. Then the silver flakes will be produced. If the reduction rate is low, the concentration of silver atoms will decrease. And the diffusion rate of silver atoms to the silver nucleus will decrease too, which will lead to the decrease of anisotropic growth rate of silver crystals. In this typical process, the mole ratio of $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ to AgNO_3 is much bigger than the theoretical value. It leads to a high reduction rate and a big concentration of silver atoms. Then under the regulation of sulfate ion and citric acid, the silver nucleus grow into flakes.

3.2 Effect of amount of citric acid on formation of silver flakes

According to the mentioned formation mechanism, citric acid may be the key role in the formation of silver flakes. In order to investigate the effect of the amount of it on the morphologies of prepared silver powders, the silver powders were prepared at the cases of 0.07 and 0.3 g citric acid, respectively. And other conditions were identical to the description in section 2.2. The results are shown in Fig. 3.

It is clear that the shape of silver particles does not change much when the amount of citric acid decreases to 0.07 g from 0.15 g. The silver particles prepared at different conditions both consist of flakes. But the particle size decreases. It ranges from 1 to 5 μm when the amount of citric acid is 0.07 g. But when the amount of citric acid increases to 0.3 g, there are some flower-like silver crystals among the silver flakes. And the particle size decreases, too. The average size of them is about 3 μm . It can be concluded that citric acid plays an important role and there is an optimum value of it in the formation of big silver flakes.

In the formation of silver flakes, a low reduction rate will lead to a low concentration of silver atoms. And the growth of outshoots on the (111) planes or in other crystal facet directions is inevitable although the crystal growth rate along the {111} facets of silver nucleus is the fastest. The outshoots can act as new silver “nucleus” during the growth process of silver crystals. When the concentration of silver atoms is low, the diffusion rate of silver atoms to the silver nucleus, which grows into a silver flakes along the {111} facets, will decrease greatly. But at this time, the diffusion rate of silver atoms to the new silver nucleus can not be ignored for the shorter diffusion distances. And the silver atoms do not need to diffuse to the special spots to promote the anisotropic growth. Then newly arriving silver atoms can easily diffuse onto the surfaces of the new silver “nucleus”. Then they incorporate into these silver “nucleus” in an

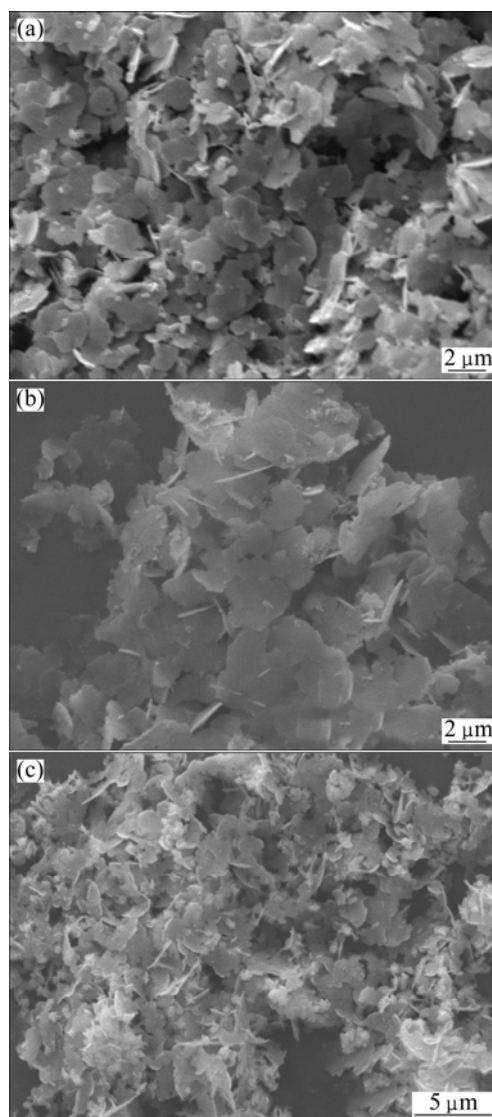


Fig. 3 SEM images of silver flakes obtained at citric acid of 0.07 g (a), 0.15 g (b) and 0.3 g (c)

oriented direction that the (111) plane also serves as the basal plane under the regulation of citric acid and sulfate ion. Then secondary flakes with {111} facet terminations are formed and the hierarchical structures terminating with {111} facets are roughly developed. The mentioned growth processes are repeated. The third and the higher level flakes are also formed. Finally, the flower-like silver particles are produced. This formation process is similar to that of the silver and gold flower-like nano architectures with electrochemical approach [23,25].

When the amounts of citric acid are 0.07 and 0.15 g, the reduction rates are high for the low concentrations of citric acid. The complexation of citrate between Ag^+ can happen, which can affect the reduction rate. The less citric acid is, the weaker the complexation is and the higher the reaction rate is. Then the effect of diffusion of silver atom can be ignored. Under the regulation of sulfate ions and citric acid, the silver nucleus grows into

bigger silver flakes (Figs. 3(a) and (b)). And when the amount of citric acid decreases to 0.07, from 0.15 g, the complexation between the citrate and silver ions decreases. Then the reduction rate is higher, and more silver nucleus are produced at the initial reaction stage, which causes the size of silver flakes decreased (Fig. 3(a)). When the amount of citric acid increases to 0.3 g, the reduction rate decreases. And the concentration of silver atoms decreases. Then, the effect of the diffusion of silver atoms becomes apparent. It is beneficial for the formation of flower-like silver microcrystals (Fig. 3(c)).

3.3 Effect of concentration of $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ solution on morphologies of silver particles

To clarify the behavior of the silver crystals growth at different concentrations of the reductant solution, systematic experiments were carried out at different concentrations of $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ solution. The silver particles were synthesized at the concentrations of $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ solution of 2.0 and 1.0 g per 50 mL deionized water, respectively. And other conditions are the same as those described in Section 2.2. The results are shown in Fig. 4.

It is obvious that the concentration of $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ solution has a huge impact on the morphologies of silver powders. With the decreasing of the concentration of FeSO_4 , the amount of silver flakes and the flake size both decrease. And there are more flower-like microcrystals. When the concentration of $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ solution decreases (Figs. 4(b) and (c)), the reduction rate decreases. And the mediation of sulfate ions on crystal growth also decreases. It is beneficial for the formation of the flower-like silver microcrystals. And the more the concentration of $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ solution decreases, the more the proportion of flower-like silver microcrystals is. It is similar to the results caused by the increase of amount of citric acid from 0.15 to 0.3 g. And it implies that it is favorable to obtain big silver flakes at high concentration of $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ solution by this proposed method.

3.4 Effect of adding method of $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ solution on morphologies of silver particles

In order to investigate the effect of the adding method of $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ solution into AgNO_3 solution on the morphologies of silver powders, two kinds of particles were prepared when $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ solutions were poured in and dripped in AgNO_3 solution, respectively. That is, one kind of powder was prepared according to the method described in Section 2.2, and the other was prepared when the $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ solution was added into the AgNO_3 solution drop by drop in 20 min. The other conditions were identical. The results are

shown in Fig. 5.

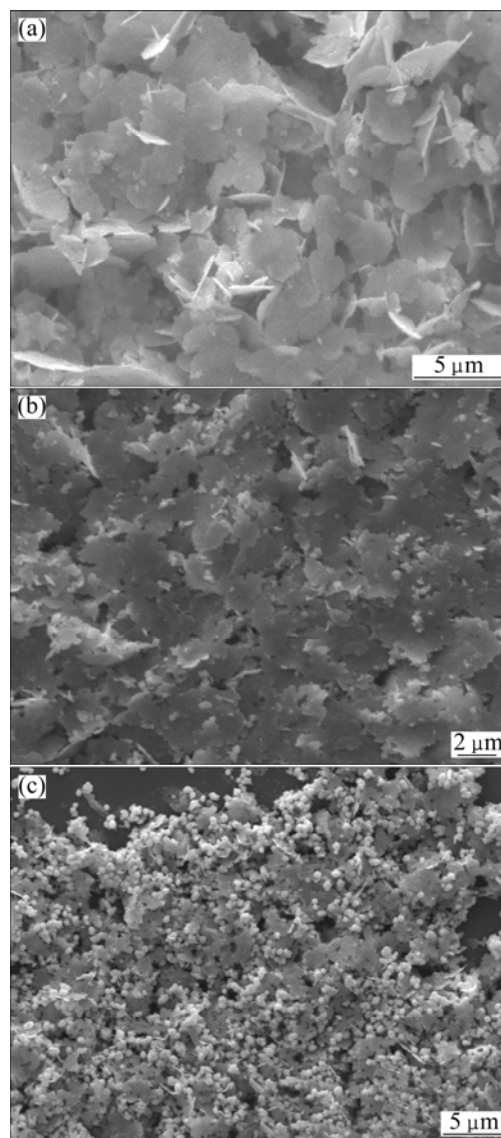


Fig. 4 SEM images of silver flakes obtained at $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ solution of 4.4 g (a), 2.0 g (b) and 1.0 g (c)

It is clear that the morphologies of microcrystals change greatly. When the $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ solution is dripped in AgNO_3 solution, the powders consist of flower-like silver crystals. And there are a few silver flakes. The diameter of flower-like silver crystals is about 1 μm . And many of them agglomerate together. When the $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ solution is added into the AgNO_3 solution by dripping, the concentration of $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ is lower than that by pouring method. So the reduction rate decreases and the concentration of silver atoms also decreases. And similar to the description in Section 3.3, the crystal-growth mediation of sulfate ion becomes weaker for its low concentration. So it is favorable for the formation of silver flower-like microcrystals. And it is similar to the case that the concentration of $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ solution is 1.0 g.

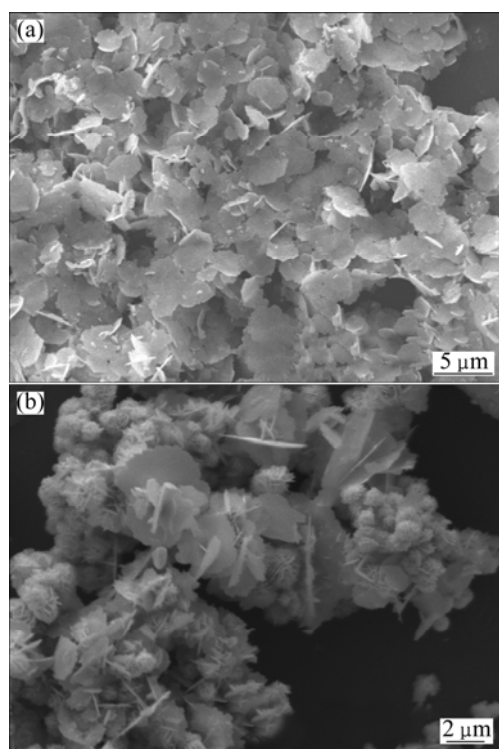


Fig. 5 SEM images of silver microcrystals obtained with $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ solution by pouring in (a) and dripping in (b) AgNO_3 solution

4 Conclusions

1) The silver flakes were prepared by directly adding $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ solution into AgNO_3 solution containing citric acid at ambient temperature.

2) It was found that the citric acid promoted the anisotropic growth of the silver nucleus into flakes through its capping and cooperation mediation with sulfate ion on silver nucleus growth and complexation between Ag^+ . There was an optimum value of it in the formation of big silver flakes.

3) The flower-like silver particle could be obtained when the reduction rate was enough low in this proposed method, which was caused by the low diffusion rate of silver atoms during the growth of silver crystals.

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一种新颖的制备片状银粉的湿化学法

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摘 要: 提出一种片状银粉的湿化学制备方法。在室温下, 搅拌速度为 150 r/min 时, 把 $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ 溶液倒入含有柠檬酸的 AgNO_3 溶液中制备银微晶体。采用扫描电镜(SEM)和 X 射线衍射仪(XRD)对制备的银微晶体进行表征。结果表明: 制备的银微晶体主要由大量的不规则形状的片状银粉组成, 其尺寸为 2~10 μm ; 柠檬酸在片状银粉的形成过程中起关键作用, 其用量对片状银粉的形成存在一个最佳值; 当体系的还原速率较大时, 更有利于片状银粉的形成。

关键词: 片状银粉; 湿化学法; 硫酸亚铁; 柠檬酸

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