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Research paper

Rapid synthesis of irregular sub-micron flaky silver with high flake-particle ratio: Application to silver paste

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HIGHLIGHTS

- Irregular sub-micron flaky silver was rapidly synthesized at room temperature.
- The conductive pastes doped with irregular sub-micron flaky silver revealed a good conductivity of 3.1×10^{-4} Ω·m.
- The possible formation mechanism of irregular sub-micron flaky silver was discussed.

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ABSTRACT

In this paper, irregular sub-micron flaky silver has been rapidly synthesized at room temperature. The product was detailedly characterized by X-ray diffraction (XRD), transmission electron microscopy (TEM), scanning electron microscopy (SEM), and ultraviolet visible (UV–Vis) spectroscopy. The average diameter and thickness of the irregular sub-micron flaky silver were 200–600 nm and ~70 nm, respectively, and the flake-particle ratio of product was over 95%. Further, the possible formation mechanism of the irregular sub-micron silver flakes was discussed. The conductive pastes doped with irregular sub-micron flaky silver revealed a good conductivity of 3.1×10^{-4} Ω·m, indicating its potential applications in the electronic materials.

1. Introduction

In recent years, noble metal particles have been widely studied for their excellent properties and their potential applications in optical, microelectronics, magnetic devices, electronic, and catalyst [1–7]. Among various metal nanostructured materials, silver (Ag) has drawn much attention due to its excellent electrical conductivity and thermal conductivity. Currently, silver nanostructures with different morphologies have been synthesized, such as nanospheres [8], nanocubes [9], nanodisks [10], nanoplates [11–13], and nanowires [13,14]. Especially, two-dimensional, anisotropic nanostructures of silver commonly have drawn much attention due to their fascinating electrical properties. Compared to spherical powder, flake powder has good electrical conductivity and rheological properties. The formation of surface contact and line contact between the flake powder contribute to the lower contact resistance [15], meanwhile because of its special two-dimensional structure, the flake powder slurry has excellent shielding effect, slurry stability and adhesion strength [16,17]. In addition, when the flake powder takes the place of the spherical powder, the rheology of the conductive paste is better [18]. Therefore, silver flakes are widely used in the electronic materials.

At present, the synthesis of silver flakes with controlled radius-thickness ratio has developed a series of methods, such as mechanical ball milling method [19], liquid phase reduction method [20], ultrasonic assisted method [21], and light induced method [22]. The sizes of silver flakes prepared are mostly within 100 nm or over 3 μm. The particle size of flaky silver in the 0.1–1.0 μm is sub-micron, which has nano thickness and micron diameter and thus have the dual effect of nano and micron flakes. However, the type of flaky silver still remains largely unexplored.

Here we report the one-step synthesis of irregular sub-micron flaky silver and its possible formation mechanism was proposed. Further, the conductive pastes doped with irregular sub-micron flaky silver exhibited a good conductivity of 3.1×10^{-4} Ω·m, indicating its potential applications in the electronic materials.

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2. Experimental

2.1. Synthesis of irregular sub-micron flaky silver

In a rapid synthesis of irregular sub-micron flaky silver, 1.0 g of silver nitrate ($AgNO_3$, 99.99%) and 0.2 g of PVP (MW = 40000) were dissolved in 100 ml of deionized (DI) water hosted in a 200 ml vial at room temperature. 2.5 g of ferrous sulfate ($FeSO_4{\cdot}7H_20$, 99.99%) was dissolved in 25 ml of deionized water. Then, ferrous sulfate solution was added as one portion into the silver nitrate solution with vigorous magnetic stirring at room temperature.

The obtained reaction mixture was centrifuged at 3000 rpm for 3 min. The precipitate was washed with ethanol and deionized water for several times, and was re-dispersed in ethanol for further characterization.

2.2. Preparation of conductive pastes

To prepare the conductive pastes, a mixture of polyurethane, aliphatic dibasic esters (DBE) and isocyanic with a weight ratio of 1:0.8:0.05 was first prepared as organic carrier. Then, the irregular sub-micron flaky silver at weight ratio of 70% was added into the vehicles. The suspensions were processed with full agitation, followed by dispersion of these pastes with a standard three-roller mill to generate the conductive pastes.

Screen printing tests were performed using a screen printer on polyethylene terephthalate (PET) substrates. The thick film patterns were screen printed onto PET films by using nylon mesh of mesh-size 325. After screen printing, the PET films with printed patterns were put into the drum wind dryer at 160 °C for 20 min. After cooling down, the electrical properties of the printed circuit were further tested by multimeter.

2.3. Characterization

The resultant products were characterized by scanning electronic microscope (SEM) (Sirion 200), X-ray diffraction (XRD) (Philips X'pert-PRO), ultraviolet visible spectroscopy (UV–Vis) (TU-1901), and transmission electron microscope (TEM) (JEM-2010). The electrical properties of conductive pastes doped with irregular sub-micron flaky silver were measured by multimeter (FLUKE-15B).

3. Results and discussions

An X-ray diffraction technique was utilized to characterize the phase purity and crystal structure. Fig. 1 shows a typical powder XRD pattern of the as-prepared flaky silver. One sharp and strong diffraction line together with four weak diffraction lines are observed at 2θ = 38.12°, 44.30°, 64.45°, 77.41° and 81.55°, respectively, which can be assigned to the (1 1 1), (2 0 0), (2 2 0),(3 3 1) and (2 2 2) reflections of the face-centered cubic (fcc) structure of metallic silver (JCPDS No. 4-0783) [23]. In addition, no peaks of any impurities are observed, indicating that the products are composed of pure silver. It is worth noting that the ratio between the (1 1 1) and other diffraction peaks is much higher than the conventional value, suggesting that the products are primarily dominated by (1 1 1) facets. All these observations reveal that the flaky silver basal plane is the (1 1 1) plane, which is consistent with previous studies on silver nanocrystals bounded by atomically flat surfaces.

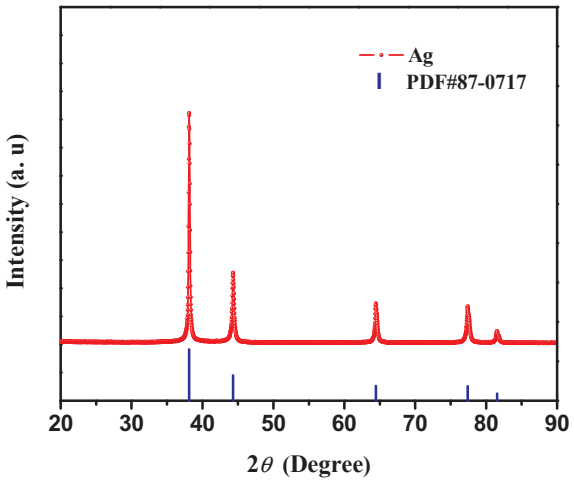

Fig. 1. XRD pattern of irregular sub-micron flaky silver.

Fig. 2a–d shows a typical SEM image of the as-synthesized irregular sub-micron flaky silver. The overall morphology of as-synthesized sample is shown in Fig. 2a and b. It can be seen that the product consists of thin flakes with an irregular shape and smooth surface. The flake-particle ratio of the product formed was estimated to be over 95%. For the flakes, the average lateral size was 200–600 nm, and the thickness was approximately 70 nm (Fig. 2c and d). Fig. 2e shows the EDS results of irregular sub-micron flaky silver. It can be clearly seen that the product consists of pure silver without any other impurities.

To investigate the morphological evolution of silver nanostructures during the synthesis, we performed UV–Vis spectroscopy analysis. Fig. 3 shows UV–Vis spectra recorded at different reaction time of the synthesis (5 s, 30 s, 180 s, 600 s). After 5 s, a peak at around 350 nm is the out-of-plane quadrupole resonance, a weak and broad peak at around 480 nm is the in-plane quadrupole resonance of the silver nanoplates [24]. As the reaction proceeded, the intensity of 480-nm peak gradually enhanced and the peak at 350 nm gradually became a shoulder band at the same time. In addition, it is clearly seen that the peak shape and position were not significantly changed with the increasing intensity of the 480-nm peak. It indicates that the formation and growth of irregular sub-micron flaky silver are likely to be completed in a very short time.

In order to further comprehend the structure and the growth mechanism of the irregular sub-micron flaky silver, TEM was used to monitor the morphology of the nanostructures. Fig. 4a shows TEM image of irregular sub-micron flaky silver, we can see that the structure of products is flaky and the morphologies of silver flakes are irregular. A detailed analysis of the high resolution lattice image (Fig. 4b) shows that there is a 0.235 nm period in the lattice image (2d = 0.47 nm). The high resolution Fourier transform pattern of Fig. 4c indicated the structures of single crystal and the diffraction of silver ⟨1 1 1⟩ zone axis, further confirming that the structure is silver flake and the exposed surface of the nanoflake is (1 1 1) plane [25].

In order to explore the possible growth mechanism of silver sub-micron flakes, SEM images of silver sub-micron flakes at different reaction times (5 s, 600 s) was obtained. As shown in the Fig. 5a and b, small silver nanoflakes are obtained after 5 s and further grew into sub-micron flakes after 600 s. Fig. 5c shows the possible growth mechanism of irregular sub-micron flaky silver. In this system, silver ions were reduced by Fe^{2+} and formed nucleus. In the adsorption of PVP on (1 1 1) plane, silver ions gathered to nucleus, which lead to produce small silver nanoflakes. As the reaction progressed, silver nanoflakes further grew into sub-micron flakes. It is found that the (1 1 1) plane of silver possesses the lowest surface energy, and it can adsorp some groups and protective agents, such as sulfate ion [26] and PVP [27]. PVP was commonly used as the surfactant. It is generally acceptable that PVP molecules can chemically adsorp onto the surface of silver nanoparticles and thus can kinetically control the growth rates of various crystal planes by interacting with these planes through adsorption and desorption [28]. In the formation of irregular sub-micron flaky silver, the reduction rate will influence concentration of silver atoms. It is found that the crystal growth rate of silver nucleus along the {1 1 1} facets is the fastest. But it is inevitable of growth of outshoots on the