A facile and "green" chemistry method of synthesis of Micro-scale noble metals (Au, Ag, Cu)

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Abstract. This paper reports a facile and environmental method of synthesizing highly dendrite silver microstructure and flower-like gold, copper microstructure. By reducing $AgNO_3$ $CuSO_4{\cdot}5H_2O$, $HAuCl_4{\cdot}4H_2O$ with L-ascorbic acid in an ethyl alcohol solution without any dispersing agent, their morphology was formed in a few minutes. A mechanistic study of the growth process revealed that the silver branches grew from a bulbous seed formed through aggregation, and that by changing the concentrations of the reagents, the degree of particle branching could be altered. As we all know , the copper, silver and gold are possess of outstanding conductivity, and the dendrite silver have more contact spots than silver nanowires. So we prepare the dendrite silver for substituting the silver nanowires in flexible conducting device applications.

1. Introduction

Due to their excellent electrical conductivity properties and plentiful applications such as physics, chemical, material, biology, medical science and electron, noble metal nanostructures have attracted plenty of interest and have been extensively excavated [1-4]. The chemical and physical properties of metal nanometer materials is closely related to their size and morphology [5-8]. So, it has great significance to control their size and morphology. Because of the noble metal crystal highly symmetrical face-centered cubic lattice structure, anisotropic noble metals nanomaterial grow in the solution of the isotropic has a huge challenge and there is no rule that can follow [9-13]. It has also been well-existed that the size and morphology of noble metal nanostructures are profitable for their characterization and applications, and therefore the design of Nan crystals with well-defined sizes and morphologies has received public attention [14-17]. The methods of synthesizing noble nanometer metal are electrochemical, physical vapor deposition and pyrolysis, etc. Xia had synthesis various morphology of Ag, Au, Pt, Pd, etc.by polyol process [18]. We tried to find a facile and green method to obtain various morphology of noble mental.

2. Experimental Section

Materials: $AgNO_3$ (99 + %), L-AA (99 + %), C_2H_5OH (99 + %), $CuSO_4{\cdot}5H_2O$, $HAuCl_4{\cdot}4H_2O$ were all purchased from Sinopharm Chemical Reagent Co., Ltd. All the reagents are pure analytical.

2.1. Preparation and Characterization of Silver Dendritic Micro-structures

In a typical synthesis, 0.1g AgNO3 was solved in 10ml ethanol. Next, 0.1g L-AA was solved in 10ml ethanol. Then add the AgNO3 ethanol solution to the L-AA ethanol solution slowly. The final concentration of silver nitrate and ascorbic acid were 0.06M and 0.06 M, respectively. The reaction was experimented at room temperature with stirring and additions were made by micropipette. The originally colorless ascorbic acid solution turned gray as soon as the addition of AgNO3 ethanol solution. With the addition of all the AgNO3 ethanol solution, the color of solution did not turn any more. The dendritic nanostructures were separated and purified by centrifugation at 4000 rpm after 5 min of reaction for 5 min, washing with ethanol and water respectively by 3 times.

2.2. Preparation and Characterization of gold flower-like Structures

In a typical synthesis, 1g $HAuCl_4 \cdot 4H_2O$ was solved in 100ml ethanol. Next, 0.1g L-AA was solved in 10ml ethanol. Then add 10ml $HAuCl_4 \cdot 4H_2O$ solution to the ascorbic acid ethanol solution slowly. The concentrations of $HAuCl_4 \cdot 4H_2O$ and ascorbic acid were 0.024M and 0.06 M, respectively. The reaction was experimented at 40℃ by the use of water bath heating with stirring. The initially colorless L-AA ethanol solution turned yellow within 10 minutes of $HAuCl_4 \cdot 4H_2O$ ethanol solution addition. The flower-like structures were separated and purified by centrifugation at 4000 rpm after 20 min of reaction for 20 min, washing and centrifuging with ethanol and water 3 times respectively.

2.3. Preparation and Characterization of copper flower-like Structures

The same way as previous as flower-like gold, the concentration of $CuSO_4 \cdot 5H_2O$ and L-AA is 0.02M and 0.03M respectively. In order to prevent the oxidation of micro-copper, the reaction was needed to proceed in the protected of Ar. The reaction was experimented at 60℃ for 10 minutes. When the colorless L-AA turned red, the reaction was over. The separation and purification is the same as above.

2.4. Characterization

The shape of the silver, gold and copper microstructures was detected by a JSM-6390LA scanning electron microscope (SEM) operated at an accelerating voltage of 20kV. Powder X-ray diffraction (XRD) was performed with an X' Pert Pro MPD diffract meter using Cu KR with a resolution of 0.02° in 2θ.

3. Results and Discussion

This paper have found that within a specific range concentrations of L-AA and $AgNO_3$,L-AA and $HAuCl_4 \cdot 4H_2O$, L-AA and $CuSO_4 \cdot 5H_2O$, dendritic silver particles, flower-like copper and gold were generated. Figure 1(A-F) shows SEM images of the product extracted from a typical synthesis. As can be seen from figure 1 A, Ag powder is mainly composed of dendritic Ag crystals. The length of single dendritic Ag crystals is 5~10 um, and the bilateral symmetry of the branches is distributed like the secondary structure of leaves and branches. As we can see SEM images from (Figure 1D), the copper particles have a near spherical micro-structure about 1um.We can see that the gold particles seems composed by many small pieces of gold from (Figure 1 F).

Figure 2(A-C) shows an XRD pattern of the Ag micro-dendrites, flower-like gold and Cu particles. All the diffraction peaks observed can be correspond to the cubic Ag, Cu and Au with unit cell parameter. The diffractive peaks at 2theta are 43.4 50.56 and 74.02, 89.2 respectively correspond to the copper crystal phase (111) (200) (220) and (222) of the core cubic copper crystal, which is consistent with the standard card JCPDS card (No.4-0836). On the dendritic Ag powder obtained by XRD characterization (figure 2) (b), 38.3, 44.4, 64.6, 77.6, and 81.7 the peaks correspond to the Ag metal (111), (200), (220), (311) and (222) crystal plane.

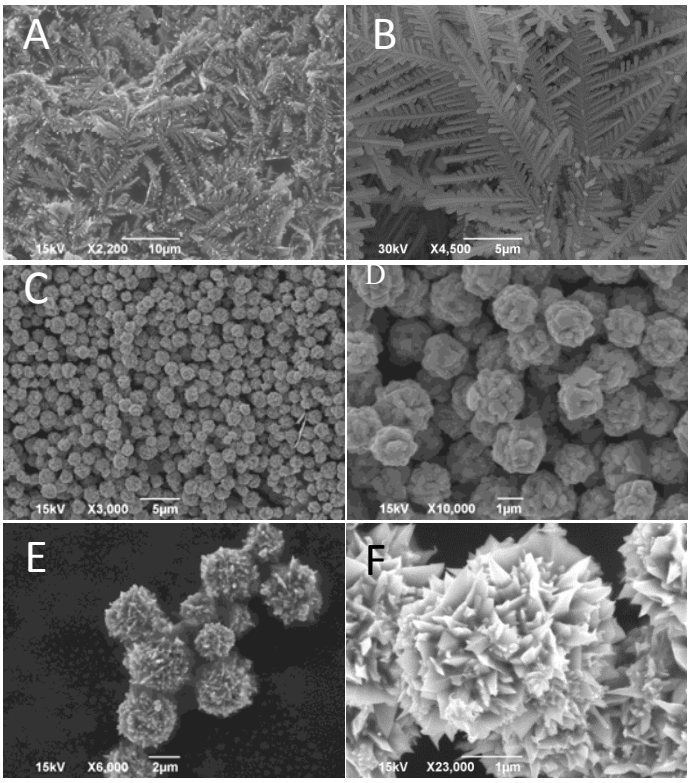

Figure 1. SEM image of branch-like silver particles, flower-like copper particles and gold particles.

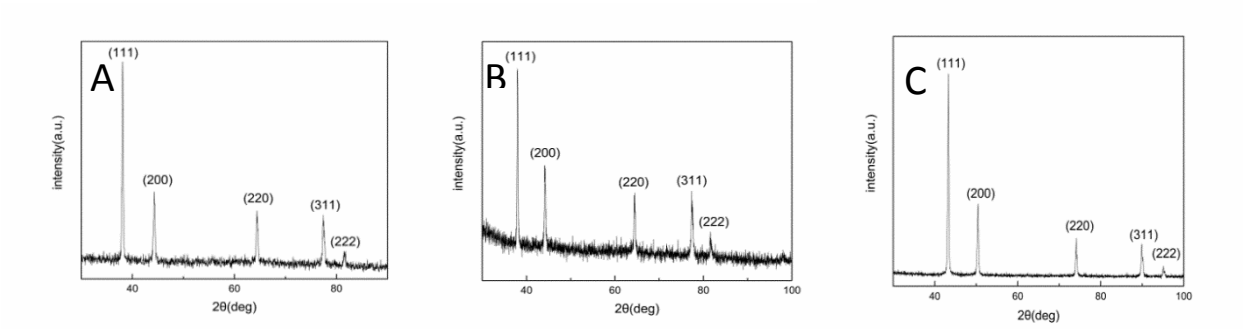

Figure 2. XRD pattern of the bulk dendrites Ag, copper and flower-like gold, respectively.

In order to study the growth mechanism and process of dendritic silver, SEM images of different reaction times have been collected. As Figure 3A depicts the beginning of reaction ($t < 3$ s), Ag seed were formed. Then, as the reaction proceeded to 5-10 s, Ag particles gathered around the core (Figure 3B), silver ions are continuously diffused form body solution to supplement. The formation of the silver nucleus has the effect of accelerating the reaction speed of the oxidation reduction, so the new silver particles are constantly rising around the nucleus. After 5 minutes, the micro- structure of the silver particles did not change any more. The process seems nucleate-germinate-branch-germinate.

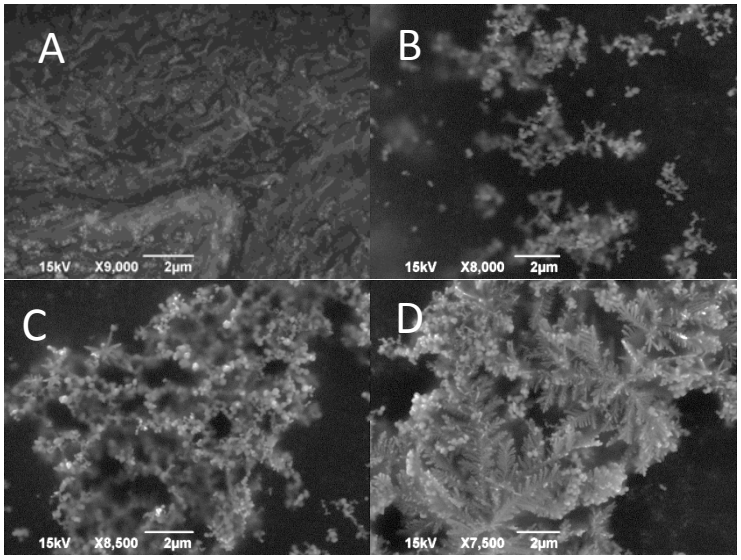

Figure 3. SEM images of the silver particles sampled at different reaction times : (A) 3-5 s, (B) 5-10 s, (C) 10-15 s, and (D) 20-25 s.

4. Conclusion

This paper demonstrated a facile and "green" synthetic route to dendrite particles of silver, flower-like particle copper and gold. These highly branched, flower-like micro-structures are easily formed through the reduction of AgNO3, $CuSO_4 \cdot 5H_2O$, $HAuCl_4 \cdot 4H_2O$ with L-AA in ethanol. On account of the surfuce tension of ethanol is relatively smaller than water, ethanol acts as a dispersant and a certain degree of reductant. Dendritic growth may be preferred to form the mechanism of Ag core Ag particles gathered around the core, under nonequilibrium grain of diffusion controlled by kinetics, converged into a highly ordered dendritic structure.

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