Single-step synthesis of hierarchical flower-like silver structures with assistance of gallic acid

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Abstract

We synthesize hierarchical flower-like silver microspheres with tunable size and shape, using ascorbic acid as reducing agent and gallic acid as structure-directing agent. The chemical nature of the gallic acid plays a vital role in the process of assembling silver particles into Chinese rose hierarchical structures. By changing the amount of gallic acid or silver nitrate solution (AgNO\textsubscript{3}), it is easy to adjust the anisotropic morphologies of as-synthesized silver structures and promote the preferential growth, resulting in a complete, clear, and stable multi-layered floral silver structure. This single-step wet-chemical synthesis method provides a new synthetic strategy for the anisotropic growth and morphology control of flower-like silver particles.

1. Introduction

Silver particles have been the most intensively studied metallic particles in recent years because of their unique optical and electrical properties \cite{1, 2}. Various investigations are focused on the influencing factors of size, shape and topography, or synthesis of specific nanostructures \cite{3–5}. Among these structures, the flower-like Ag have complex morphology and high surface roughness, which could generate more hot spots and are likely to exhibit higher surface-enhanced Raman scattering (SERS) activity \cite{6–8}. For synthesizing flower-like Ag, many categories have been reported include using different organics as structure-directing agent \cite{7}, seed-mediated approach \cite{9}, two-step wet-chemical approach \cite{3}, hot precipitation method \cite{10}, synthesis on graphene \cite{11} and so on. On this basis, the reduction, synthesis and optimization of the silver substrate through the use of environmentally friendly reducing agents and structure-directing agents have become the main breakthrough point in the current green chemical application. For example, C. Nichita \cite{12} used plant extract gallic acid to biological reduce silver ions, green synthesis of silver nanoparticles, and applied them in the exploration of biomedicale fields. Using ascorbic acid as reducing agent and green extract (oxalic acid, malic acid and citric acid) as structure guiding agent, Zhang \cite{7} prepared hierarchical flower-like silver with controllable size and morphology, which is expected to be applied in sensor field. Here, we report for the first time an eco-friendly method to synthesize flower-like silver using gallic acid as structural guide agent. The flower-like Ag particles with uniform particle size and stable performance were synthesized in one step. The formation mechanism was also analyzed. This research has promising potential to solve the problems existing in the preparation methods of silver nanomaterials, such as harsh reaction conditions, complicated methods and poor environmental compatibility, and greatly expanded the properties and application fields of silver particles.

2. Materials and methods

2.1. Materials

AgNO\textsubscript{3} (>99%, Sigma-Aldrich), gallic acid (AR, Macklin), ascorbic acid (AA, 99%, Sigma-Aldrich), polyvinylpyrrolidone (PVP, Mr = 10 000, Macklin) were commercially purchased. Deionized water was homemade.
2.2. Methods
In a typical synthesis of flower-like Ag particles, room temperature, 1 mol l\(^{-1}\) AgNO\(_3\) solution, 1 mol l\(^{-1}\) ascorbic acid solution, 1 mol l\(^{-1}\) PVP solution and 0.1 mol l\(^{-1}\) gallic acid solution were respectively configured. Under the condition of ice water bath, different volume (0.2–0.4 ml) of AgNO\(_3\) solution and 2 ml PVP solution were added into a 25 ml beaker with 10 ml ultra-pure water with magnetically stirring. Then, different amount of gallic acid solution was added and continuously stirred for 5 min. After the 0.2 ml ascorbic acid solution was rapidly injected, and the solution quickly changed from colorless to black gray. Finally, the reaction solution was removed and centrifuged with ultrapure water for 3 times (2000 rpm, 5 min), and the flower-like Ag particles were obtained.

3. Result and discussion
As shown in figures 1(a)–(c), without the addition of gallic acid, the spherical Ag particles with an average diameter of 1.5 \(\mu m\) were obtained, consisting of many irregular plates. With the assistance of gallic acid, hierarchical Ag microparticles which resemble Chinese rose shapes were perfectly assembled by numerous secondary or tertiary branch nanosheets (figures 1(d)–(e)). The results show that gallic acid could exert exquisite control in the surface morphologies of Ag particles, changing from lumpy aggregates to sheet-like assembly hierarchical structures.

Figures 1(c), (f) present the x-ray diffraction (XRD) patterns of the flower-like silver without and with the addition of gallic acid. The XRD patterns clearly reveal five sharp intense peaks at \(2\theta = 38.1^\circ, 44.2^\circ, 64.4^\circ, 77.3^\circ\) and \(81.3^\circ\), corresponding to (111), (200), (220), (311) and (222) planes of pure face-centered cubic (FCC) Ag structure. It is worth noting that the intensity of dominant peak of (111) is much higher than that of other peaks, implying these hierarchical structures have the preferential growth orientation parallel to the (111) direction.

3.1. Influence of amount of gallic acid
Figure 2 shows the morphology evolution of Ag nanostructures with increasing gallic acid amount. At initial step, the gallic acid with functional groups were able to easily capture Ag\(^+\) to form relatively stable complexes. With the amount of gallic acid solution increased from 0.05 to 0.1 ml, more silver ions were prone to be coordinated to form stable complexing agent, inducing the kinetics-controlled anisotropic growth. Equilibrium was attained when the amount of gallic acid reached 0.1 ml, Ag particles becoming a compact laminated flower-like structure. After that, with the further increase of gallic acid, flowers began to collapse due to the silver petals being etched by excess gallic acid. This phenomenon could be seen more clearly in figures 2(g)–(h) when the amount of gallic acid solution was 0.125 ml. It can be inferred that there are more active functional groups in gallic acid and the interaction with silver ion surface clusters is strong, which is easy to form stable complexes. And the surface morphology of silver particles can be carefully controlled by changing the amount of gallic acid.
3.2. Influence of amount of Ag
In order to study the role of AgNO₃ dosage in the nucleation and growth process of hierarchical Ag particles, a series of experiments in the absence of gallic acid were carried out with varying AgNO₃ amounts. As the amount reached 0.2 ml, a flower-like Ag microstructure can be formed by assembly of numerous complete and distinct multilevel nanosheets (figures 3(a)–(b)). Future increase did not change the flower shapes, but the nanosheets became broken and the densely packed stripes on the surface gradually changed into loosely packed protuberances (figures 3(c)–(d)). Then, increasing the dosage to 0.4 ml, most of the nanosheets broke into pieces and the petals collapsed (figures 3(e)–(f)). This experiment indicated that a flower-like Ag structure with well-defined morphology can be obtained just by controlling the amount of AgNO₃ solution, proper precursor monomer concentration favors the formation of kinetically controlled anisotropic shapes, which is also confirmed by Zhang et al [13].

3.3. Growth mechanism
A growth mechanism of hierarchical Ag nanostructures was proposed. As shown in figure 4, gallic acid’s functional groups, carboxyl and hydroxyl, captured Ag⁺ from the solution easily and coordinated with Ag⁺ ions to form relatively stable complexes. When ascorbic acid was added, Ag⁺ ions trapped in complexes were gradually released and reduced to Ag atoms. Under the suppress effect of gallic acid-silver complexes on the reducing rate, the initial seeds started to aggregate into primary Ag crystals. With the incorporation of gallic acid, Subsequently, Ag particles grew preferentially in certain directions, which favors to forming flower-like structure. Gallic acid was added, and free Ag atoms were deposited continuously, forming hierarchical Ag particles with different surface roughness. Accordingly, gallic acid played a role of structure-directing agent and paved a way for confining shapes of growing Ag particles.

4. Conclusions
In summary, we developed a single-step synthetic method for the preparation of flower-like Ag using gallic acid as structure-directing agent. The addition of gallic acid could effectively control the diffusion of Ag⁺ and consequently suppress the reduction rate, which induced the anisotropic growth of flower-like Ag under a
kinetically controlled regime. The morphologies of flower-like Ag were affected significantly by the amount of gallic acid and Ag precursor.

**Data availability statement**

All data that support the findings of this study are included within the article (and any supplementary files).

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