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Two-step process for synthesizing flower-like silver nanoparticles by wet-chemical method

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ABSTRACT

Flower-like silver nanoparticles (F-AgNPs) are facilely synthesized with two-step wet-chemical method. In the first step, ho leaf extracts reduce $AgNO_3$ to form spherical AgNPs. In the second step, F-AgNPs are synthesized from spherical particles. The effect of gum arabic and HNO_3 on morphology of F-AgNPs is intensively investigated. The reduction and oxidation provide a trade-off between aggregation and detachment of Ag atoms on the surface, while the structure-directing agent boosts preferential growth, contributing to formation of F-AgNPs with different shapes. Our results pave an alternative way for synthesizing AgNPs with specific shapes and advancing applications.

1. Introduction

Silver nanoparticles (AgNPs) have become a subject of intense interest in recent years due to their broad-acting activities and potential applications in chemical, biological and environmental fields. Unique properties are highly sensitive to size and shape of AgNPs. Various investigations are focused on influencing factors of size, shape and topography, or synthesizing specific nanostructures including nanowires, nanoprisms, nanooctahedra, nanosheet-assembled micro-hemispheres, nanocubes, nanospheres, hierarchical dendrites and flower-like nanopaticles [1–10]. For synthesizing flower-like AgNPs (F-AgNPs), reported categories include using different organics as structure-directing agents [2], utilizing marine sponge or leaf extract of Rosa damascena as reducing agent [3], seed-mediated approach [4], single-step wet-chemical approach [5,6], hot precipitation method [7], double-potentiostatic method [8], synthesis on graphene [9] and self-assembly method [10]. Here, we develop an eco-friendly approach by employing reducing solution originated from ho leaf extracts. We introduce two-step process which is different from documented methods in that the shape and size of AgNPs can be finely tuned by simply sticking reduced Ag atoms (in the second step) to already-formed spherical AgNPs (in the first step). With the assistance of structure-directing agent of gum arabic (GA), a novel class of F-AgNPs with low-cost and scalable manufacturing are demonstrated. The formation mechanism is also analyzed.

2. Materials and methods

HNO_3, GA (AR grade), ascorbic acid (Vc) and $AgNO_3$ were commercially purchased. Ho leaves were collected from camphor trees.

Step 1. Preparation of spherical AgNPs

Ho leaves were cleaned, dried, baked (at 60 °C for 12 h) and smashed to 100 meshes with high speed disintegrator. 5 g ho leaf powders were added into 250 mL H_2O and oscillated at 50 °C for 12 h, then cooled to room temperature. Insoluble biomass was removed by centrifugation, and the supernatant ho leaf extracts were preserved at 4 °C. Next, 20 mL 0.01 M $AgNO_3$ and 20 mL ho leaf extracts were reacted for 24 h on bath shaker at 60 °C, then cooled to room temperature. $AgNO_3$ was reduced by ho leaf extracts and formed Ag clusters/nanocrystals with typical spherical shape, as shown in the scanning electron microscopy (SEM, JEOL JSM-6700F) image in Fig. 1(a). The transmission electron microscopy (TEM, JEOL JEM-2100EX) image (Fig. 1(b)) displays that

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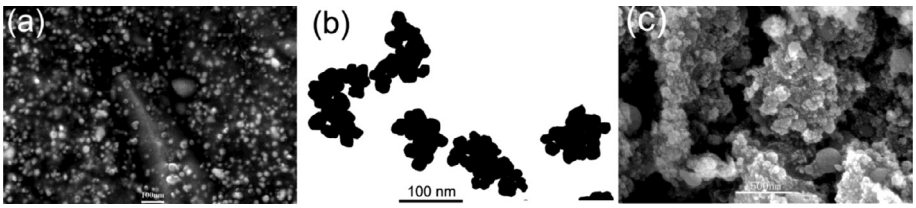

Fig. 1. (a) SEM and (b) TEM images of synthesized spherical AgNPs. (c) AgNPs prepared by RF-induction-plasma.

AgNPs feature an average size of ~25 nm. The as-prepared spherical AgNPs aqueous solution denotes as **Solution S**. For comparison, spherical AgNPs prepared by RF induction plasma system are shown in Fig. 1(c).

Step 2. Growth of F-AgNPs

Firstly, the effect of GA was investigated. 2 mL 14.4 M HNO_3 and 20 mL GA with concentrations of 0.1, 0.2, 0.3, 0.5 and 1 M were added into **Solution S**. The mixture was stirred and heated to 40 °C for reaction of 5 min. Then 5 mL 1 M Vc was quickly injected into the mixture and stirred for 15 min. The resulting samples were centrifuged at 20,000 rpm for 20 min and dispersed in H_2O. Secondly, the effect of HNO_3 was investigated. 20 mL 0.02 M GA and 2 mL HNO_3 with concentrations of 1, 5, 10 and 14.4 M were added into **Solution S**. The mixture was stirred and reacted for 3 min at 15 °C. The resulting samples were centrifuged at 20,000 rpm for 20 min and dispersed in H_2O.

3. Results and discussions

Fig. 2 shows the morphology change of F-AgNPs with increasing GA concentration. At lower concentration, spherical particles and small amounts of flower-like particles are observed (Fig. 2(a)). Increasing concentration to 0.2 M, large-diameter F-AgNPs are assembled (Fig. 2(b)). High concentration of GA also results in flower-like Ag microspheres growing in three directions (Fig. 2(c)). The microspheres change from flake to laminated shape with the concentration reaches 0.5 M (Fig. 2(d)), and finally become a compact laminated structure (Fig. 2(e)). It is deduced that GA concentration plays a vital role in confining shapes of F-AgNPs. The probable reason may associated with the bonding between the functional groups of GA and surface of Ag ions/clusters. X-ray diffraction (XRD, Philips PW 1140) patterns in Fig. 2(f) exhibit four peaks around 38.0°, 44.0°, 64.0° and 77.1°, corresponding to (1 1 1), (2 0 0), (2 2 0) and (3 1 1) planes, respectively, which are assigned

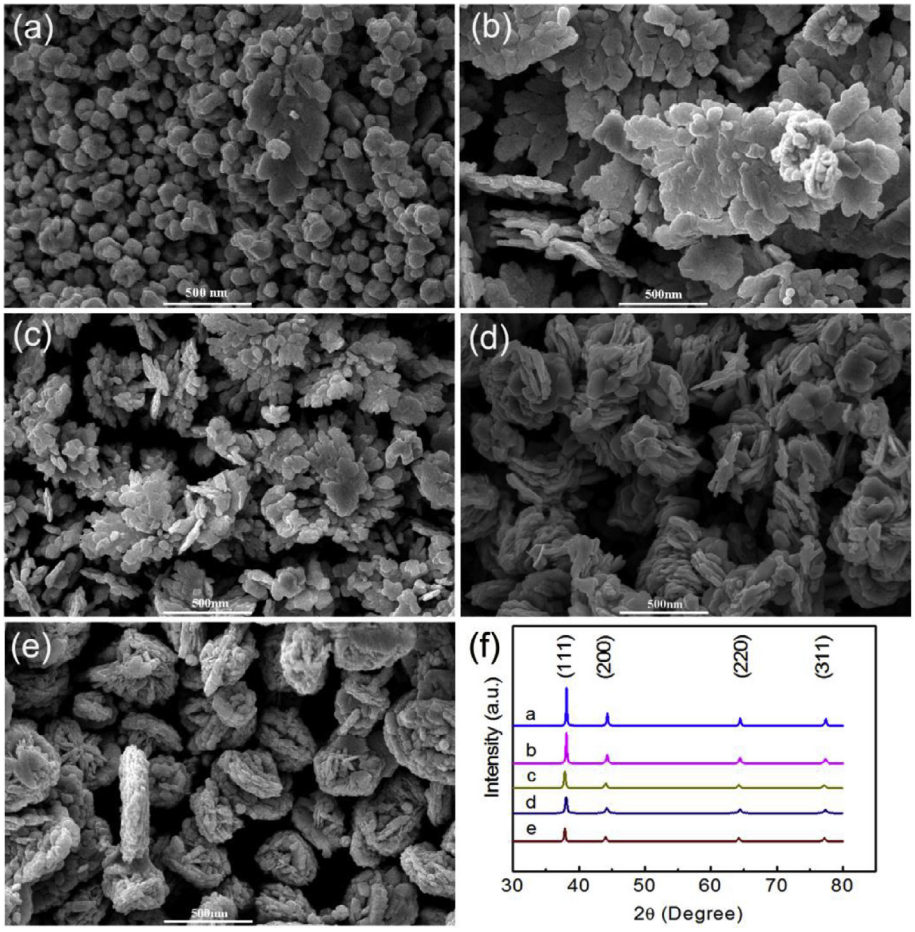

Fig. 2. SEM images and XRD patterns of F-AgNPs synthesized under conditions of different GA concentrations: (a) 0.1, (b) 0.2, (c) 0.3, (d) 0.5 and (e) 1 M.