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Original article

Fabrication of flower-like silver nanoparticles for surface-enhanced Raman scattering

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ABSTRACT

The flower-like silver nanoparticles have been synthesized by reducing silver nitrate ($AgNO_3$) with ascorbic acid (AA) as the reductant and polyvinyl pyrrolidone (PVP) as the capping agent under vigorous stirring. Such flower-like nanoparticles are aggregates of small nanoplates and nanorods. They were tested as substrates for the surface-enhanced Raman scattering (SERS), showing high sensitivity for detecting Rhodamine 6G (R6G) at a concentration as low as 10^{-7} mol/L. It has been found that replacing mechanical stirring with ultrasound sonication would drastically change the particle morphology, from flower-like nanoparticles to well-dispersed smaller nanoparticles. Furthermore, when trace amounts of NaCl were added into the reagents, well-dispersed Ag nanoparticles formed even in vigorous stirring. These phenomena can be explained with the diffusion and reactant supply during nucleation and growth of Ag nanoparticles.

1. Introduction

In recent years, silver nanomaterials have received great interest due to their potential applications in catalysis [1], biology [2], electronics [3,4], and optoelectronics [5,6]. A great deal of effort has been put into the research of the synthesis of silver nanostructures. Xia's group [7–9] has explored the polyol synthesis method to produce controllable Ag nanostructures. Based on numerous studies, they have concluded that the final shape of a nanocrystal is closely related to the internal structure of the seed and the capping agent. They also found that the oxidative etching of Cl^- can result in the dissolution of twinned seeds, and that Br^- only can selectively remove the multiply twinned seeds. Manzano-Ramírez [10] has also confirmed that silver nanowires could be obtained with short-chain PVP as the capping agent. In this process, it was found that a longer stirring time could lead to the formation of acicular particles. Shaban prepared Ag nanoparticles by a green and rapid method using sunlight and cationic surfactants [11]. Also some green synthesis methods have been developed to produce Ag nanoparticles, such as synthesis with the aqueous extracts of Enteromorpha flexuosa as the reductant [12].

Here we study the effect of mechanical agitation, either stirring or sonication, on the morphology of nanoparticles when synthesizing Ag nanoparticles by reducing $AgNO_3$ with AA as the reductant and PVP as the capping agent. With vigorous stirring, flower-like Ag nanoparticles formed. However, trace amounts of Cl^- could drastically change the nanoparticle morphology. When the sonication was used for the agitation, only dispersed nanoparticles were produced. Flower-like Ag nanoparticles have a highly roughed surface which gives rise to a good performance as the substrate for SERS.

2. Experimental

The flower-like Ag nanoparticles were synthesized by chemical reduction of $AgNO_3$, with AA as the reductant. In a typical synthesis process, $AgNO_3$ aqueous solution (0.06 mol/L, 9 mL) and PVP (0.06 mol/L, 9 mL) aqueous solution were added into beaker with magnetic stirring at room temperature. The PVP concentration was calculated in terms of the repeating units. After 30 min magnetic stirring, AA (0.2 mol/L, 2 mL) was quickly injected into the mixture.

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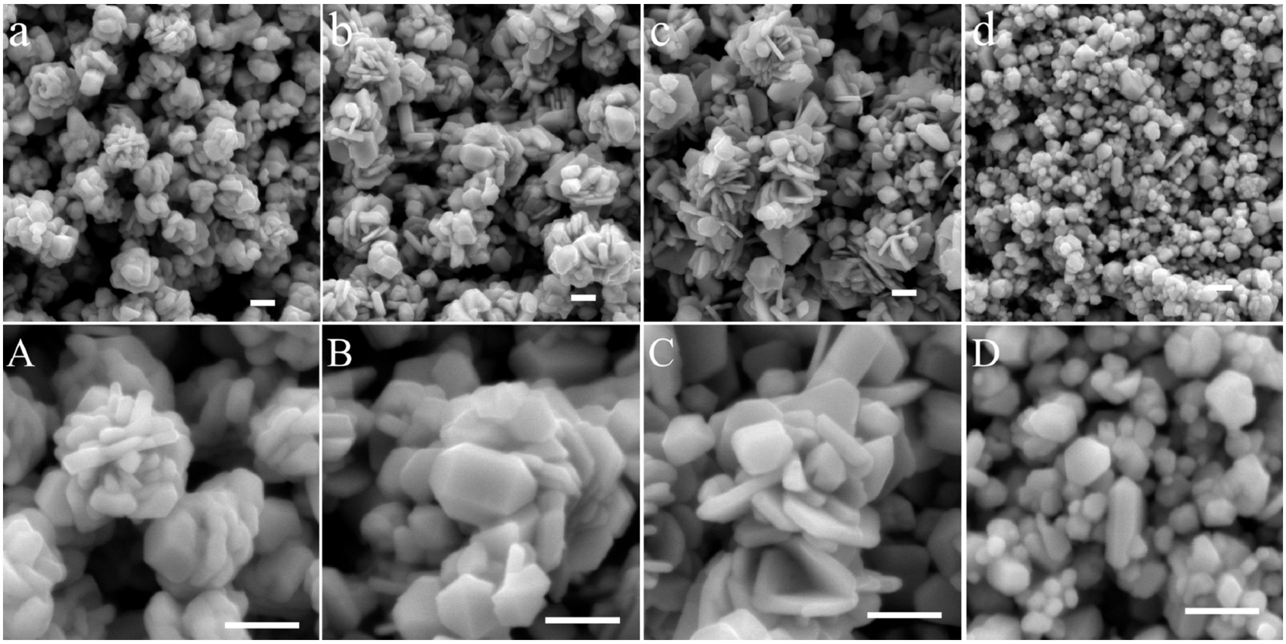

Fig. 1. SEM images of Ag nanoparticles obtained by changing the concentration of $AgNO_3$ (PVP kept the same with $AgNO_3$) in reaction solution and the vigorous stirring reacting. (a) and (A) 0.06 mol/L, (b) and (B) 0.08 mol/L, (c) and (C) 0.1 mol/L; (d) and (D) 0.06 mol/L (mixing the reaction solution in ultrasonic field). All scale bars are 300 nm.

Immediately, the color of solution turned into dark grey, indicating the formation of a large quantity of Ag nanoparticles. After 30 min magnetic stirring, the reaction liquid was centrifuged at 13,000 rpm for 15 min, followed by alternately washing with water and ethanol 3 times. Finally, Ag nanoparticles were dispersed in 5 mL ethanol.

UV–vis spectra was recorded on a Unico UV4802 UV/vis spectrometer. Scanning electron microscopy (SEM) analysis was performed on Tescan MIRA 3LMH scanning electron microscope. The crystal structures of the silver nanoparticles were analyzed by the powder X-ray diffraction (XRD) with Cu-$K\alpha$ source (Siemens D500) with patterns recorded in the range of 30–80° (2θ). Raman spectra was obtained from Raman spectroscopy HR800 (Jobin-yvon).

3. Results and discussion

Fig. 1 shows the morphology of the products. It clearly shows that mechanical agitation can cause very different morphologies. When the solution was vigorously stirred using a magnetic stirrer, the flower-like Ag nanoparticles were produced (Fig. 1a–C). With the concentrations of $AgNO_3$ and PVP increased from 0.06 mol/L to 0.1 mol/L, the size of flower-like Ag nanoparticles are increased from 500 nm to 1000 nm. The petal of flower-like nanoparticles gradually changed from nanorods to nanosheets. The transformation can be clearly found from Fig. 1A, B and C. It is well known that the growth of flower-like silver nanoparticles can be attributed to the outgrowth process [13,14]. After the quick injection of AA, the color of the solution was immediately turned into dark grey, indicating a rapid reaction. With vigorous stirring, the transportation of the reactants became faster to raise the growth rate of the silver nanostructures [13]. As the increasing of concentration, the rate of production and growth of seed crystals increases. The number of flake-like Ag nanoparticles has significantly increased, which might be explained from the fact that a higher rate is conducive to produce seeds with stacking faults.

When ultrasonic agitation was used, dispersed nanoparticles with a wide size distribution can be observed (Fig. 1d and D). Mechanical stirring can offer shear forces and significantly accelerate the transfer of mass [15], but ultrasonic agitation accelerate the Brownian movement of Ag colloid. Ultrasound radiation resulted in the homogenously dispersion of PVP in solution and the production of stable spherical micelles [16]. Spherical nanoparticles could be produced by the reduction of silver ions inside these micellar templates. In addition, these dispersed nanoparticles may result from the dissociation from the flower-like silver nanoparticles [17]. Moreover, mass transport with stirring is favorable for isotropic and compact growth, which may result in the aggregation of Ag nanoparticles from some smaller nanoparticles [10].

Fig. 2 shows the XRD patterns of these Ag nanoparticles. It indicates the formation of highly pure silver nanoparticles with perfect crystallization. The intensity ratio of the (1 1 1) to (2 0 0) peak is higher than that of the standard card of silver (PDF#87-0720

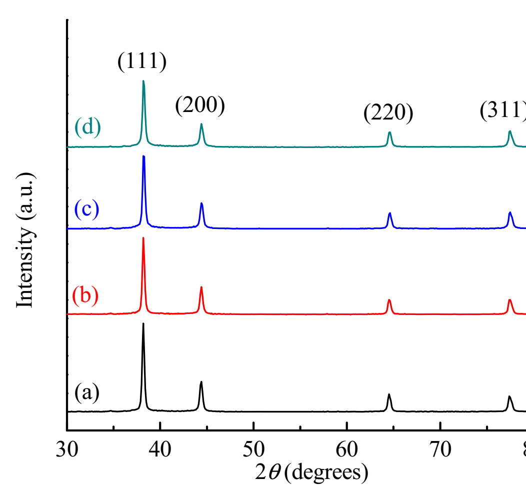

Fig. 2. XRD patterns of Ag nanoparticles obtained by changing the concentration of $AgNO_3$ (PVP kept the same with $AgNO_3$) in reacting solution and vigorous stirring the reacting solution. (a) 0.06 mol/L, (b) 0.08 mol/L, (c) 0.1 mol/L; (d) 0.06 mol/L (mixing the reacting solution in ultrasonic field).