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Synthesis of silver nanoparticles with flake-like shapes

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Abstract

Flake-like silver nanoparticles have been synthesized in large quantity by simply aging the aqueous solution of silver and urotropine in the presence of poly-(vinylpyrrolidone) (PVP). Silver nanoflakes of different shapes from circular to polygonal could be obtained in different reaction stages. PVP molecules play an important role in the anisotropic growth of silver nanoflakes. The as-synthesized silver colloidal solution remained stable for at least 1 month. Electron diffraction analysis showed that the nanoflakes are well crystallized. The UV-VIS absorption properties have also been studied.

Keywords: Solution synthesis; Silver; Nanoflakes; Metals

1. Introduction

Silver particles have been investigated extensively in recent years because of their potential applications in catalysis [1] and photographic process [2] as well as surface-enhanced Raman scattering detection [3]. It is accepted that the properties are strongly dependent on the size and shape of the particle, and therefore tremendous research effort has been devoted to the synthesis and characterization of silver nanoparticles with different morphologies.

Size-controlled spherical silver nanoparticles have been obtained in micelle or reverse micelle solutions [4], by a simultaneous polymerization–reduction approach [5], through a Tollens process [6], laser ablation method [7], microwave irradiation [8], photo-reduction method [9], and solvothermal method [10,11]. The synthesis of silver nanorods or wires has been carried out through a wide range of routes including the polyol process [12] and the seed-mediated approach [13]. Attempts have also made to control other morphologies such as prism [14], cube and box [15], and dendrite [16]. The synthesis of silver nanodisks has been reported through a seed-mediated growth and aging process [17], using polystyrene mesospheres as templates [18], or in reverse micelle solutions [19].

Although silver nanoparticles of different shapes and size have been successfully obtained through various methods, the concentrations of nanosilver were extremely low or/and the reaction solution was always in microliter volumes in most of the procedures. Recently, concentrated dispersions of silver nanoparticles were prepared by reducing silver nitrate solutions with ascorbic acid in the presence of Daxad 19 as stabilizing agent [20]. However, the synthesis of well-dispersed silver nanoparticles in high yield is still a challenge. Herein, we report a mild solution route to synthesize flake-like silver nanoparticles in high concentration by simply aging an aqueous solution containing silver nitrate, urotropine, and poly-(vinylpyrrolidone) (PVP). By varying the aging time we could easily control the size and shape of the nanosilver under mild conditions.

2. Experimental

In a typical procedure, 30 ml of aqueous solution containing 0.025 mol/l of $AgNO_3$, 5.0 g/l of poly-(vinylpyrrolidone) (PVP), and 0.125 mol/l of urotropine was aged for 30 min to 3 h in capped test tubes at 80 °C. The colloidal suspension was cooled to room

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temperature, centrifuged, and washed with water before characterization.

XRD patterns of the products were recorded by employing a Philips X'pert X-ray diffractometer with Cu K-Alpha radiation (λ=0.154187 nm). TEM images of the samples were taken on a Hitachi-800 transmission electron microscope. SEM images were obtained on a JSM-6700F field emission scanning electron microscope. UV-VIS spectra were recorded on a Shimadzu UV-2401PC UV-VIS spectrophotometer in the range of 200–800 nm.

3. Results and discussion

The formation of metal silver in the present process was confirmed by powder X-ray diffraction (XRD) analysis. Fig. 1 shows typical XRD pattern of an as-obtained silver sample. The broadening of the diffraction peaks reveals the nanoscale structure of this sample. Three diffraction peaks can be indexed as (111), (200), and (220) planes of the cubic structured metallic silver (JCPDS cards NO. 4-783). The strong and sharp peaks suggest the formation of highly crystalline silver nanoparticles.

The evolution of the particle size and morphologies of silver samples is clearly revealed by TEM images in Fig. 2. Well-dispersed silver nanoparticles are observed in each sample. As shown in Fig. 2a, the overlapped silver nanoparticles are nearly transparent, which reveals the thin flake characteristic of silver nanoparticles obtained in the initial stage. For most of the particles, outlines of round circle can be clearly defined and diameters are in the range of 37–50 nm. As the reaction proceeded (1 h), silver nanoflakes grow in the thickness, but remain slightly transparent based on the overlapped silver nanoflakes observed under TEM (Fig. 2b). It can also be seen that circular flakes tend to show polygon shapes, and the size distribution of silver nanoflakes became even narrow and is centered at 70 nm. At the end of the reaction procedure (3 h), more silver nanoparticles tend to show polygon or prism-shaped morphologies. Fig. 2c shows TEM images of silver nanoparticles obtained in this stage. The sample is well-dispersed and the size is relatively uniform and the size distribution is centered at 120 nm (Fig. 2e), although several larger flakes (~240 nm) can also be observed. The flake-like morphology was further characterized using SEM. As shown in Fig. 2d, most of the silver nanoparticles tend to exhibit more or less regular polygon shapes. The thickness of the nanoflakes is determined to be 30 nm on average from the edge width shown in Fig. 2d. It is interesting that the well-dispersed silver nanoparticles synthesized via this procedure exhibited good stability. The colloids were preserved at least 1 month with no obvious precipitates.

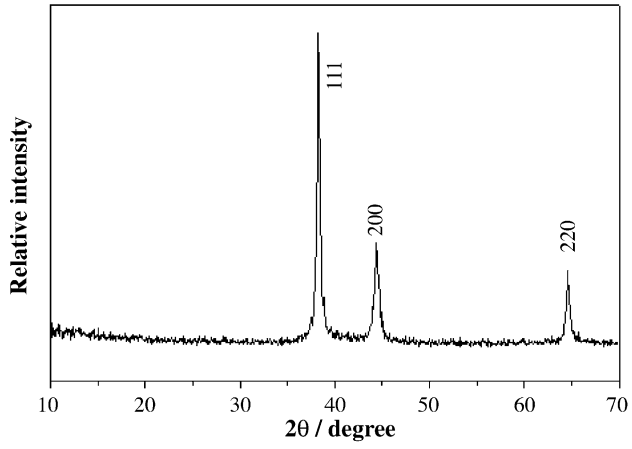

Fig. 1. Typical XRD pattern of an as-obtained silver sample.

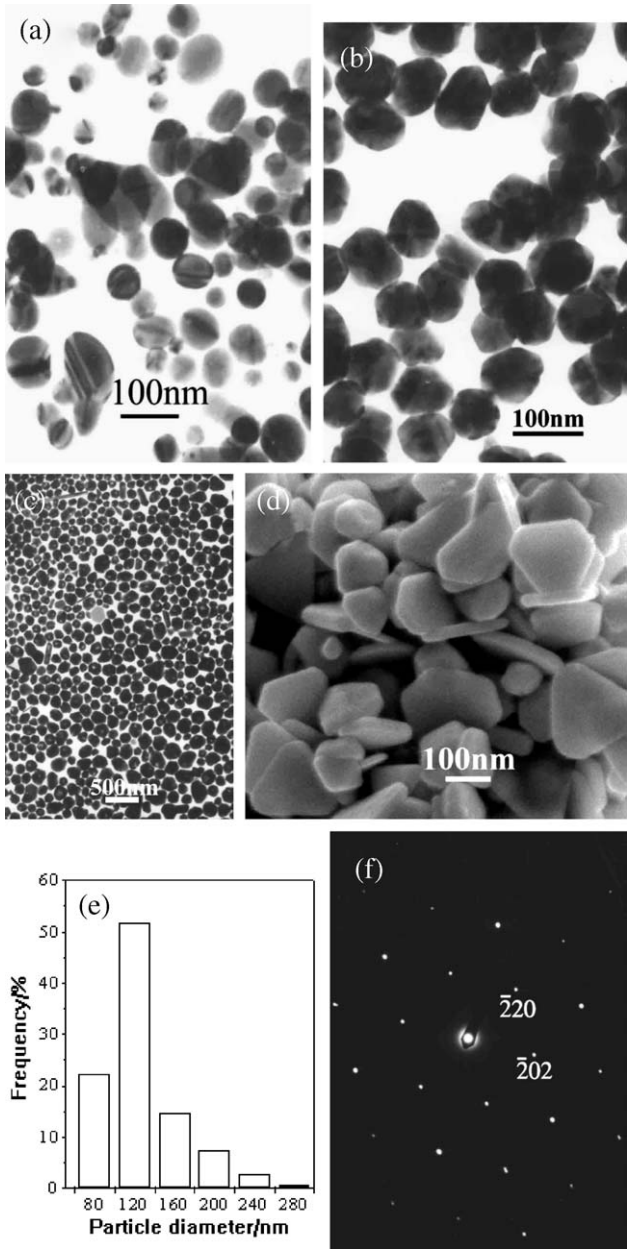

Fig. 2. TEM and SEM images of silver samples obtained after reaction of: 30 min (a), 1 h (b), and 3 h (c, d), and size distribution histogram (e) and ED pattern (f) of silver nanoflakes shown in panel (c).