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Synthesis of spherical silver particles with micro/nanostructures at room temperature

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ABSTRACT

Spherical silver micro/nanoarchitectures were synthesized via a facile and environmentally benign route in the presence of poly(vinyl pyrrolidone) and ascorbic acid at room temperature. The prepared spherical microstructures were composed of nanorods of 50 nm in diameter and 300 nm in length. The products were characterized with X-ray diffraction, scanning electron microscopy, and transmission electron microscopy techniques. The growth mechanism of spherical silver micro/nanoarchitectures involves the three stages of seeds formation, primary subunits formation, and aggregation of primary subunits. Some crucial factors affect the growth of micro/nanoarchitectures, such as initial pH value of solution and poly(vinyl pyrrolidone) content. In this article, the results of examinations of these factors are presented and discussed.

1. Introduction

Silver powders with micro/nanostructures have gained growingly attention due to their special morphologies, structures, and particle size effects [1,2]. They are widely applied in catalysts, sensors, and in optical and electronic systems [3,4]. Nanoparticles (NPs), nanorods, and nanoplates as building blocks can spontaneously aggregate into spherical [5], flower-like [6], dendritic [7], and other different structures. It is generally accepted that the micro/nanostructures form under nonequilibrium growth conditions, thus, can be used as a natural framework for the investigations on disordered systems [8]. Therefore, studying the reaction parameters and process for controlling the formation of micro/nanostructures is really important.

The formation of micro/nanostructures in solution involves two steps: Burst nucleation of the primary particles and formation of the secondary particles through their aggregation [9]. Meanwhile, a large number of experimental and theoretical works have been performed and reported in literature. Wiley et al. reported the preparation of silver nanoparticles with different shapes and proposed four steps in their formation process: (I) Formation of silver clusters, (II) nucleation of seeds, (III) growth of seeds, and (IV) formation of metal clusters and seeds with different cystallinities [10]. Ostwald ripening led to the production of starfish-like rhodium nanocrystals; a processes in which larger particles grow at the expense of smaller ones [11]. However, this "burst-nucleation" mechanism is not suitable for larger particles than 100 nm. Many experimental examinations have confirmed the fact that most microstructures are formed by small crystalline subunits [12–15]. Actually, the final structures are formed through aggregation of primary particles; a process that is called "formation of the secondary particles by aggregation". But, currently the study about spherical silver microparticles is not enough, especially on their morphology controlled by several complex experimental parameters.

Here, a simple method is proposed to prepare spherical, well-dispersed silver microstructures using poly(vinyl pyrrolidone) (PVP) as dispersing agents in an amount of 5% by mass of silver nitrate. In this article, the whole silver nanoparticles growth process producing microstructure from silver ions to eventually spherical microstructures is discussed. The effects of PVP content and the initial pH value on the particle size and morphology in different stages of production process are discussed.

2. Experimental procedure

Silver nitrate (pure pa) was provided by Tianjin Damao Chemical Reagent Factory. Ascorbic acid was purchased from Aldrich and used as the reducing agent. Poly(vinyl pyrrolidone) (PVP) was provided by Tianjin Damao Chemical Reagent Factory and used as stabilizers. Deionized water was used for preparation of mixture solutions.

In the experiments, we used homemade deionized water to prepare 50 mL silver nitrate solution (0.15 mol/L) and 50 mL ascorbic acid solution (0.09 mol/L). Then, added PVP up to 5 wt% to the prepared ascorbic acid and stirred thoroughly for 5 min to mix well at 25 °C. Finally, 50 mL of silver nitrate solution was rapidly poured into the ascorbic acid solution to react under continuous stirring. Ten minutes

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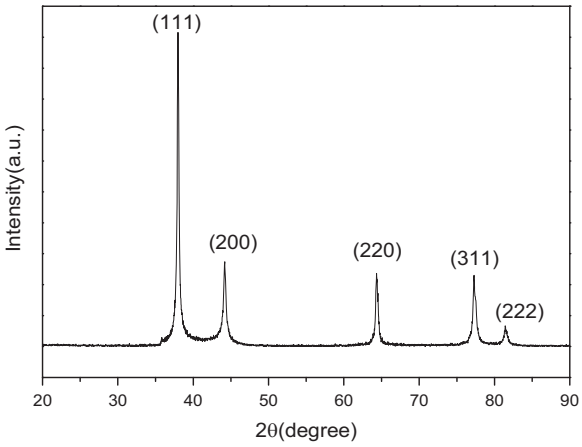

Fig. 1. XRD pattern of silver powders samples containing up to 5% PVP.

later, the above mixture turned from colorless to yellow. After several hours, the resulting precipitates were collected and washed with deionized water and ethanol respectively for several times. The final products were dried under vacuum conditions for 4 h.

Morphological observation was achieved with a field-emission scanning electron microscope (FE-SEM , Zeiss , German) and a field-emission transmission electron microscope (TEM, Philips TECNAI-F20). X-ray diffraction (XRD) analysis was conducted using X-ray diffractometer (D8, Bruker) at room temperature. The scanning angle was from 5° to 90° and a scanning speed of 10°/min with 40 kV voltages and 15 mA. current.

3. Results and discussion

3.1. Characterization of spherical silver microarchitectures

XRD method was used to characterize the phase and the crystallographic structures of the products. The observations (Fig. 1) reveal obvious diffraction peaks for the prepared silver powders at 38.2°, 44.3°, 64.5°, 77.5°, and 81.6° angels, corresponding to (111), (200), (220), (311), and (222) facets of silver, respectively. The peaks were indexed to the face-centered cubic (fcc) structure of Ag crystal. The sharp diffraction peaks are evidence of a high degree of crystallinity for the silver powders.

The morphology, size and structure of the as-prepared Ag nanoarchitectures were examined with FESEM technique. The micrograph exhibited in Fig. 2(a) clearly shows walnut-shaped spherical structure silver particles with size in the range of 0.5–1.5 μm. The magnified image (Fig. 2(b)) shows that the spherical structures are composed of nanorods of 50 nm in diameter and 300 nm in length.

3.2. Formation process and growth mechanism of micro/nanoarchitectures

3.2.1. Formation process of silver nanoparticles

The chemical reaction that occurs in the conducted process can be described as below:

$$C_6H_8O_6 + 2Ag^+ \rightarrow 2Ag + C_6H_6O_6 + 2H^+ \quad (1)$$

In the first stage, the process consists of seeds formation (Fig. 3(I), (II)). In the liquid phase and presence of ascorbic acid as a reducing agent, silver ions are reduced to silver atoms. Then, these silver atoms rapidly nucleate and form seeds [16], which include single and multiply twinned single crystals. Different kinds of seeds maybe exist together in the system, so it is the key issue to control the number of other seeds whose structures are different from the desired seeds in order to obtain the single morphology nanoparticles. The formation of seeds can be controlled via kinetics and thermodynamic properties of the system [17,18].

In the second stage of the process, primary subunits are formed (Fig. 3(III)). These seeds, through adsorption of silver atoms or atom clusters, grow into primary subunits, which are also called crystals (see Fig. 2(b), Fig. 4(b), (c)) [19]. The formation of the primary subunits is affected by selective adsorption of protective agents, structural defects, and crystals overgrowth [20].

Finally, due to the high free energy of the system at this stage, these primary subunits cannot be stable all the time; as a result, they are accumulated into micro/nanostructures silver particles (Fig. 2(a), Fig. 4(a), (c)).

3.2.2. Effects of PVP as protective agent on silver powders microstructures

In the experiments, PVP was added as protective agent to influence the morphologies and particle sizes of the primary subunits [21–23]. When the mass content of PVP was smaller than 5%, as shown in Fig. 2(b), the primary subunits appeared as elongated nanorods, whereas at PVP content of 8%, the primary subunits were observed as irregular lumps and flakes (Fig. 4(b)). When the PVP content was increased to 10%, the primary subunits were observed as shorter nanorods and spherical nanocrystals (Fig. 4(d)). These observations indicate that the mass content of PVP has an important effect on the morphologies of the primary subunits. With increase in the PVP content, there was a tendency for morphologies of particles changing from elongated nanorods to spherical nanocrystals.

This behavior is because when the amount of PVP is at the appropriate level of 5%, Ag {100} facets are wrapped by PVP and metal atoms would be deposited on {111} facets, inducing growth of nanorods. When the mass content of PVP is excessive (for instance, 10%), no facets could grow preferentially, the primary subunits will thermodynamically be more stable as spherical particles. Meanwhile, we found that the microparticles were smaller (Fig. 4(c)) when the PVP content was at the greatest amount. The reason for this observation is

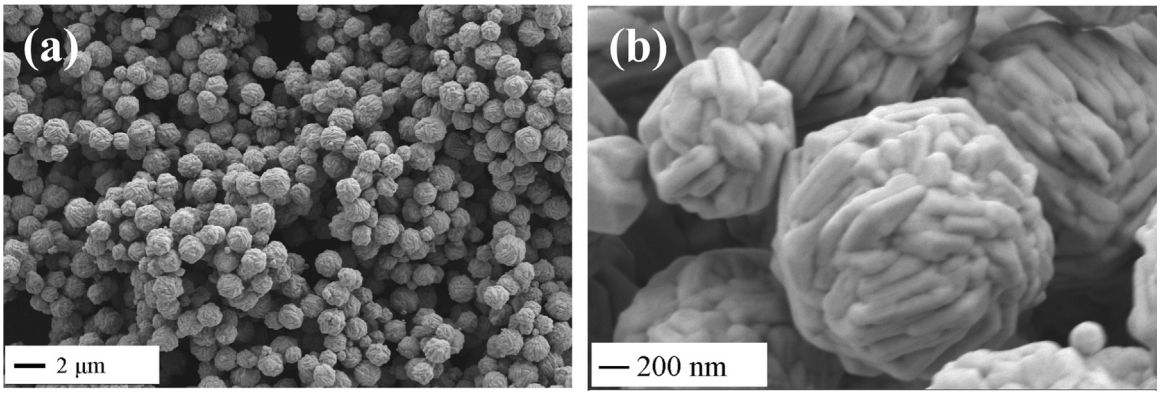

Fig. 2. (a) Low magnification FESEM image of sample containing 5 wt % PVP, (b) high magnification FESEM image of micrograph shown in (a).