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Synthesis of dendritic silver nanostructures by means of ultrasonic irradiation

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ABSTRACT

In this paper, a simple and effective route for the synthesis of silver dendritic nanostructures by means of ultrasonic irradiation has been developed. Well-defined silver dendritic nanostructures were obtained by sonicating the aqueous solution of 0.04 mol/L silver nitrate with 4.0 mol/L isopropanol as reducing agent and 0.01 mol/L PEG400 as disperser for 2 h. The effects of the irradiation time, the concentration of Ag^+ and the molar ratio of PEG to $AgNO_3$ on the morphology of silver nanostructures were discussed. The structures of the obtained samples were characterized by transmission electron microscopy (TEM), selected area electron diffraction (SAED) and X-ray powder diffraction (XRD), and the chemical composition of the dendrites was examined by energy-dispersive X-ray spectrum (EDS).

1. Introduction

In recent years, nanostructured and shaped noble metal particles have been widely studied due to their excellent properties and their potential applications as advanced materials with electronic, magnetic, optical and catalytic properties [1–4]. As we know, the intrinsic properties of a noble metal nanoparticle strongly depend on its sizes and shapes. There have been several reports on promising attempts to create various shaped nanoparticles, e.g., controlling the shapes and particle sizes of noble metal nanoparticles [5–7], producing one-dimensional (1D) nanostructured noble metal materials [8,9] and fabricating self-organized nanostructures for metal particles [10,11]. Sun et al. [12] synthesized silver nanowires by reducing $AgNO_3$ with ethylene glycol in the presence of seeds and poly(vinyl pyrrolidone). Chen and Gao [13] reported the preparation of silver nanorods by PVP-directed polyol processing. The scanning tunneling microscopy (STM) technique has been applied to fabricated metallic nanowires and a single gold atom wire [14,15].

There is an increasing interest in the synthesis of dendritic fractals because of their attractive supramolecular structures that can not only provide a framework for the study of disordered systems, but can also be used as catalysts whose activity and selectivity are strongly dependent on the morphology of the structures. Silver nanoparticles with dendritic structures seem to be particularly interesting to synthesis and study because bulk silver exhibits the hightest electrical and thermal conductivities among all metals. There are some reports about synthesis of silver nanoparticles with fractal and dendritic structure, such as electrochemical deposition [16], γ-irradiation route [17,18], ultraviolet irradiation [19], template approach [20] and electron transfer reduction [21].

Sonochemical processing has proved to be a useful technique for generating novel materials with unusual properties [22–29]. The chemical effects of sonication arise from acoustic cavitation, namely the formation, growth, and implosive collapse of bubbles in a liquid which produces unusual chemical and physical environments. The collapse of bubbles generates localized hot spots with transient temperature of about 5000 K, pressures of about 1000 atm, and cooling rates in excess of 109 K/s [30–32]. It was reported that fractal and dendritic structures are generally observed in far-from equilibrium growth conditions [33,34]. Sonochemical process just provides such conditions. Zhu et al. [35] reported a preparation of shaped silver nanoparticles with spheres, rods, and dendrites by using electrochemical deposition with ultrasonic irradiation. Xiao et al. [36] have reported the synthesis of palladium and silver dendritic nanostructures using Reney nickel as the template with the assistance of ultrasonic waves. In present paper we report a preparation of well-defined silver dendritic nanostructures from $AgNO_3$ aqueous solution by using ultrasonic irradiation without any template and any other assistant means.

2. Experiment

All the reagents used in our experiments including silver nitrate, isopropanol and poly(ethylene glycol) purchased from Shanghai Chemicals Co., were analytical grade and used without further purification. A typical synthesis of the silver dendritic nanostructures was carried out as follows. 100 mL 0.04 mol/L aqueous solutions of $AgNO_3$ and 4.0 mol/L isopropanol in the

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presence of 0.01 mol/L PEG400 in a 150 mL glass reactor cell were sonicated for 2 h. A Model JCS-204 Ultrasonic Reactor with a 6-mm-diameter titanium probe operating at 20 kHz was used for ultrasonic irradiation experiments. The power transferred to the solution was 0.76 W measured by means of the calorimetric method [37]. The reaction temperature was controlled for 25 ± 1 °C with the help of condensation water surrounding the reactor cell. The obtained samples were characterized by X-ray powder diffraction (XRD) analysis performed on a Japan Rigaku D/MAX-γA diffractometer with Cu Kα radiation. Transmission electron microscopy (TEM) and selected area electron diffraction (SAED) were performed on a JEOL Model JEM-100CXII transmission electron microscope with an accelerating voltage of 200 kV. EDS analysis was performed on a EDAX 9100 energy disperse spectroscopy.

3. Results and discussion

Fig. 1 showed a typical TEM image of the silver dendritic nanostructures obtained by sonicating the aqueous solutions of 0.04 mol/L $AgNO_3$ and 4.0 mol/L isopropanol in the presence of 0.01 mol/L PEG400 for 2 h. It is clearly seen that the side branches are well-symmetric and the angles of them to the main branches are all about 60°, which implies that all side branches grow along the same direction. From the Fig. 1 it can be seen that the side branches of the dendritic silver are constructed by lots of well-crystallized small nanorods. The selected area electron diffraction (SAED) image of dendritic silver nanostructures from a side branches(Inset in Fig. 1) reveals that the silver dendrite has single crystal nature with cubic phase and the side branch direction assembles along <011> direction. Fig. 2 is the typical XRD patterns of the as-prepared sample, in which four peaks can be indexed to diffraction from the (111), (200), (220) and (311) of face-centered cubic (fcc) Ag (JCPDS No. 420783). The chemical composition of the dendrites was also examined by energy-dispersive X-ray spectrum (EDS). Fig. 3 is the EDS of the silver dendritic nanostructures dropped on a copper grid. The peak of Ag at about 3.0 showed that the dendrite is only consists of Ag atoms.

It is found that the morphology of silver crystal is strongly dependent on reaction period (Fig. 4). At the beginning of the reaction only silver spheroidal nanoparticles were obtained (Fig. 4a). With prolonging of ultrasonic irradiation time the silver nanoparticles aggregated together to assemble a silver dendrites, but some single Ag particles were found near the dendrites (Fig. 4b). Defined silver dendrites and few single particles near the clusters were observed with 1 h sonication (Fig. 4c). It can be seen from Fig. 1 that the aggregation has finished after 2 h ultrasonic irradiation, a well-defined silver dendritic nanostructures was obtained and no single silver particle was found near the dendrites. Then these dendritic nanostructures transform to compact crystals if they are irradiated for a sufficient period of time. About 6 h later, only hexagonal compact crystals were observed (Fig. 4d).

The morphology of silver crystal is also strongly dependent on the concentration of Ag^+. Fig. 5 showed the TEM image of silver nanoparticles from Ag^+ aqueous solution at different concentrations. It can be seen from the figure that the hexagonal compact crystals were observed at higher Ag^+ concentration (Fig. 5a). Well-symmetric silver dendrites nanostructures were obtained from 0.01–0.04 mol/L $AgNO_3$ (Fig. 5b and c). When Ag^+ was complexed with NH_3, only silver spheroidal nanoparticles were observed because of very low free Ag^+ concentration (Fig. 5d).

Furthermore, it is found that the molar ratio of disperser to $AgNO_3$ also effects the formation of silver dendrites. The relatively

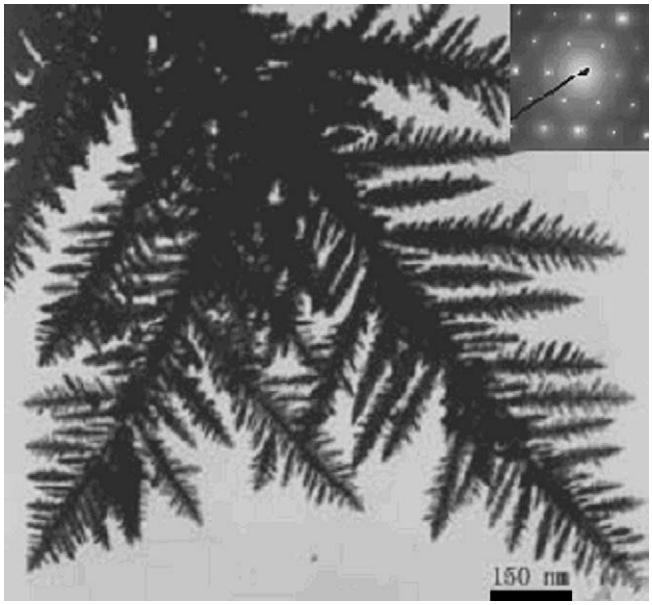

Fig. 1. A typical TEM image of a silver dendritic nanostructures obtained by sonicating the aqueous solutions of 0.04 mol/L $AgNO_3$ and 4.0 mol/L isopropanol in the presence of 0.01 mol/L PEG400 for 2 h and inset corresponding SAED pattern.

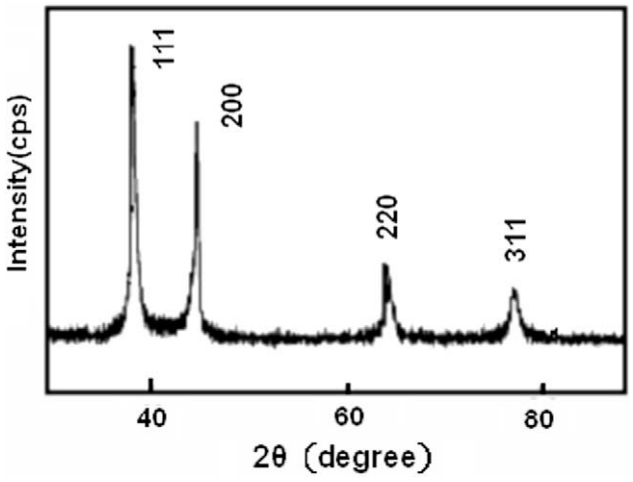

Fig. 2. XRD patterns of the silver dendritic nanostructures.

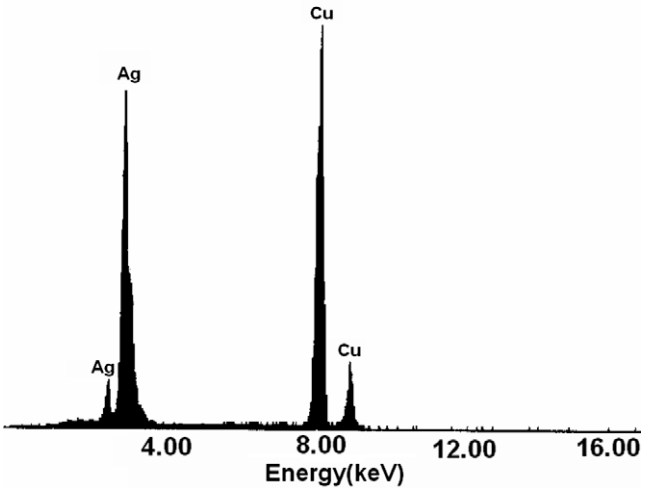

Fig. 3. EDS of the silver dendritic nanostructures dropped on a copper grid.