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Preparation and characterization of dendritic silver nanoparticles

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Dendritic silver nanoparticles have been prepared by a soft solution technique from the aqueous solution of silver nitrate and poly (vinyl pyrrolidone) (PVP) in the presence of ethanol used as a reducing agent. The resultant silver nanoparticles were characterized by using scanning electron microscopy (SEM), transmission electron microscopy (TEM), X-ray diffraction (XRD), energy dispersive analyses of X-ray (EDX), and UV-Visible absorption spectroscopy. It was found that the well-defined dendritic silver nanoparticles which had the length 0.5–1 μm and the width of 100–200 nm.

In recent years, nanostructured and shaped noble metal particles have been the subject of much intensive research due to their potential applications in microelectronics, optical, electronic, magnetic devices [1]. These applications are strongly dependent on the sizes and shapes of the nanoparticles. Silver nanoparticles with different shapes seem to be particularly interesting to synthesize and study because bulk silver exhibits the highest electrical and thermal conductivities among all metals. Several methods involving micelle, Langmuir-Blodgett film (LB), zeolite, two-phase liquid-liquid and organometallic techniques have been used in recent years for controlling the sizes and shapes of the nanoparticles [2]. For example, El-sayed and his coworkers demonstrated a successful example of controlling the shape and size of platinum nanoparticles by changing the ratio of the concentration of the capping polymer material to the concentration of the platinum cations used in the reductive synthesis of colloidal particles [3]. The produced platinum display tetrahedral, cubic, irregular-prismatic, icosohedral and cubic-octahedral particle shapes. Xia and co-workers have prepared silver nanowires by polyol process [4].

Since a dentritic structure has many special characteristics, such as its large surface area, excellent connectivity etc., it will be of great benefit to prepare and to introduce dentritic nanoparticles into materials manufacturing. Many efforts have been made to prepare dentritic silver nanoparticles [5]. Here we describe a novel soft solution method for preparing dendritic silver nanoparticles using polyvinylpyrrolidone (PVP) as protective agent. This method requires no complex apparatuses and any templates.

Experiment and results

In a typical synthesis, 5 ml ethanol was injected into a 100 ml round-bottom flask that equipped with a condenser, thermcontroller, and magnetic stirring bar, and the solution then was stirred constantly with a magnetic stirrer at 120°C. The dendritic silver nanoparticles were produced by slowly adding 5 ml aqueous solution of $AgNO_3$ (0.1 mol/l) and 5 ml aqueous of PVP (0.1 mol/l in repeating unit, $M_w \approx 30{,}000$), which resulted in a turbid mixture with an orange or brown color after 10 min. The solution was allowed to react for 90 min. Vigorous stirring was maintained throughout the entire process.

The SEM and TEM images of the as-prepared silver nanoparticles are shown in Fig. 1A and B. The particles have clear outline and are mainly dendritic structures. The dendritic silver nanostructures have the length of 0.5–1 μm and the width of 100–200 nm. The exact mechanism for the formation of dendritic silver nanostructures via this solution-phase approach is still not yet known. The conventional model adopted for the explanation of the growth of treelike structure of silver nanoparticles is known as DLA (diffusion-limited aggregate model) [6]. At the beginning of the reaction, silver ions are reduced to atoms from the solution during a very short period. The silver atoms aggregate, rapidly forming wirelike and rodlike nanoparticles, in which one particle after another is formed and then diffuses, and adheres to the growing structure. Moreover, it is found that the molar ratio of the PVP repeating unit to $AgNO_3$ also effects the formation of silver nanoparticles. The relatively low molar ratio of PVP to $AgNO_3$ might cause low coverage of PVP on all faces of the

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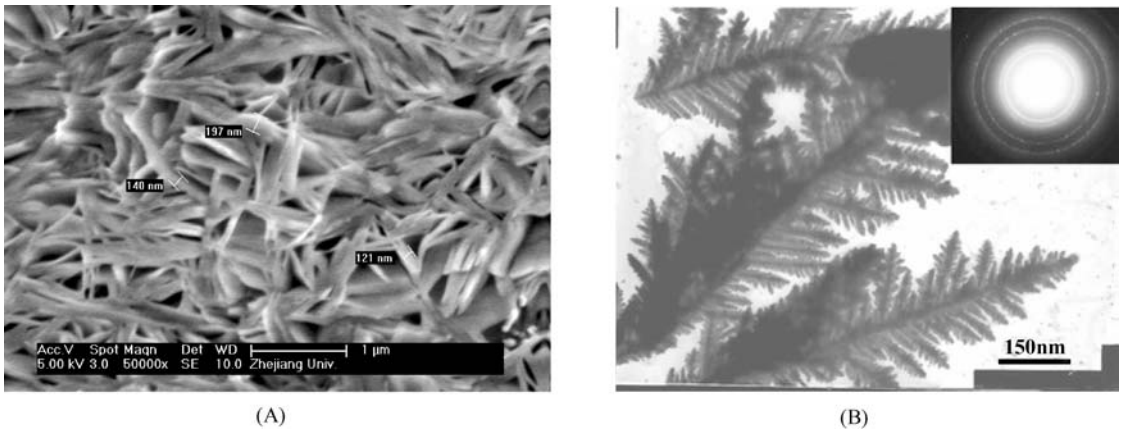

Figure 1 SEM (A), TEM (B) and selected area electron diffraction (SAED) (inset in B) images of the as-prepared dendritic silver nanoparticles.

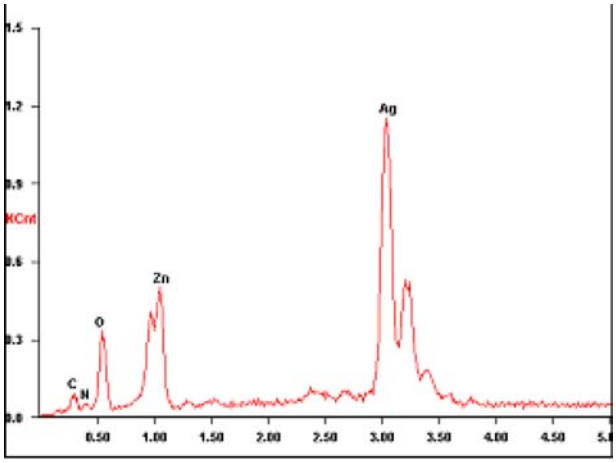

Figure 2 EDX spectrum of silver nanoparticles dropped on a cupper pillar.

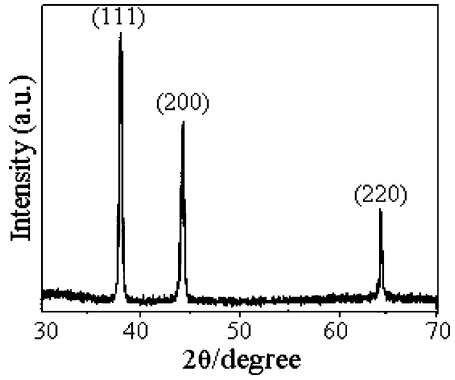

Figure 3 XRD patterns of the final particles.

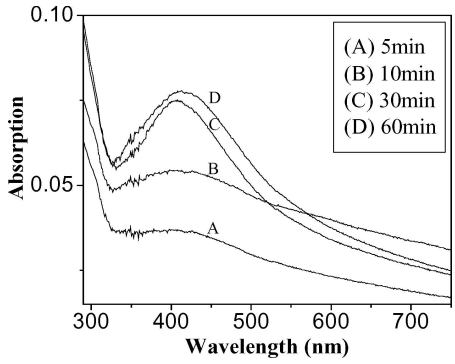

Figure 4 The UV-visible absorption spectra obtained from the reaction mixture at various times.

silver nanoparticles, leading to an aggregation of silver nanoparticles. When the molar ratio of PVP to $AgNO_3$ further increased to 10, no dendritic nanostructures are formed. The resultant particles are ~200 nm in diameter. In this case, the high molar ratio of PVP to $AgNO_3$ cause high coverage of PVP on all faces of the silver nanoparticles, leading to an isotropic growth mode [7]. The selected area electron diffraction (SAED) pattern (inset in Fig. 1B) shows the presence of distinct diffraction rings, confirming the crystalline nature of the particles.

The composition of a typical silver nanostructure was further probed by energy dispersive analyses of X-ray (EDX) analysis (Fig. 2). Strong signals from the silver atoms in the nanoparticles are observed, while the signals from the substrate materials and weaker signals from C, N and O atoms were also recorded. The C, N, and O signals are likely to be due to X-ray emission from PVP. These data gave the clue that the particles were nanocomposites consisting of Ag and PVP.

X-ray diffraction (XRD) was used to examine the crystal structure of the sample. A typical XRD pattern of as-prepared silver dendrites (Fig. 3) shows the three diffraction peaks can be indexed to (111), (200) and (220) planes, indicating that the sample is of high crystallinity and the face centered cubic (fcc) structure [8].

Fig. 4 shows the UV-visible spectra of solutions sampled from the reaction mixture of 5 ml (0.1 mol/l) $AgNO_3$ aqueous solution and 5 ml (0.5 mol/l) PVP aqueous solution at various times. The broad band with a long tail obtained at reaction time around 5 min, implying that the wide distribution of particles in the colloidal solution peak. The intensity of the peak at around 420 nm grew greatly with the reaction proceeding for 30 min, while the longitudinal plasmon resonance essentially disappeared. This large change in the spectra may imply the decrease of the particles polydispersion. The intensity of this plasmon peak changed very little from 30 to 60 min, indicating the reaction has alomst completed. Moreover, the peak slightly shifted to the red, possible to show an increase in size for the silver nanoparticles [9].

In summary, we have achieved the first preparation of well-defined dendritic silver nanoparticles with the length 0.5–1 μm and the width of 100–200 nm using a soft solution technique from the aqueous solution of $AgNO_3$ and PVP using ethanol as a reducing agent. It is found that the molar ratio of $AgNO_3$/PVP has a significant effect on the formation and growth of these novel dendritic nanoparticles. The shaped dendritic silver nanoparticles may have many important applications especically in conductive adhesive. This present technique may also be extended to prepare other mental nanoparticles. This work also demonstrates that the solution-phase approach provides an effective and simple way for preparation metal nanomaterials with well-defined shapes providing advantages in certain applications. The further research is proceeding.

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