Preparation of Silver Dendritic Nanoparticles Using Sodium Polyacrylate in Aqueous Solution

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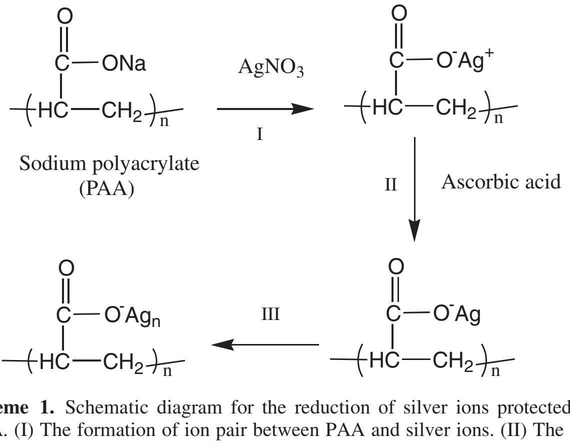
Silver dendritic nanoparticles of uniform size and morphology have been prepared at room temperature using ascorbic acid as a reducing agent and sodium polyacrylate (PAA) as a protective agent in aqueous solution.

Nanoscale materials are of great interest because of their unique optical, electrical, and magnetic properties. These properties are strongly dependent on the size and shape of the particles[1] and therefore it is very important to be able to finely control the morphology of the nanomaterials. However, shape control has been much more difficult to be achieved.

Metal nanoparticles of various morphologies such as cubics,[2,3] rods,[4] triangulars,[5,6] disks,[6,7] and prisms[8] have already been synthesized. Recently, dendritic nanostructures are interesting to synthesize and study because of their attractive structures and applicable possibilities in catalysis. Gold dendritic nanostructures[9] have been prepared by vapor phase polymerization of pyrrole onto solution-cast films of polystyrene-block-poly(2-vinylpyrolidine). Chen and co-workers[10] reported an UV irradiation photoreduction technique for the preparation of silver dendritic supramolecular nanostructures at room temperature using poly(vinyl alcohol) as a protective agent. Zhu and co-workers[11] reported that silver nanoparticles with spheres, rods, and dendritic shapes had been prepared by a pulse sonoelectrochemical technique from the electrolysis of a solution of $AgNO_3$ with nitrilotriacetate (NTA). Recently, Chujo and co-workers[12] reported preparation of silver dendritic nanostructures with assistance of electron transfer from tetrathiafulvalene (TTF) to silver ions in acetonitrile.

In this study, silver dendritic nanoparticles were prepared by the chemical reduction technique at room temperature using ascorbic acid as a reducing agent and PAA as a protective agent in aqueous solution. It was found that concentration of PAA has a significant effect on the formation and growth of dendritic nanoparticles. The reduction of silver ions protected by PAA is schematically illustrated in Scheme 1.



Scheme 1. Schematic diagram for the reduction of silver ions protected by PAA. (I) The formation of ion pair between PAA and silver ions. (II) The formation of silver nucleation. (III) Small particles rearrange and rotate.

Into the 20 mL aqueous solution containing sodium polyacrylate (PAA, average M_w ca. 5100) and 0.25 mM $AgNO_3$, the 100 μL of 0.1 M freshly prepared aqueous ascorbic acid solution was injected under the vigorous agitation at room temperature. Here, ascorbic acid is a weak reducing agent. To accelerate the reduction rate by ascorbic acid, finally 50 μL of 1 M NaOH solution was added. Within 1 min, color of the solution was changed to bluish gray. The solution was allowed to sit at room temperature for about 2 h. After the reaction was completed the samples were centrifuged at 3000 rpm for 10 min. In order to remove PAA, the silver nanoparticles obtained by centrifugation were washed with distilled water and absolute ethanol several times. The morphology of the final particles was characterized with the TEM.

Figure 1A shows the TEM image of the silver nanoparticles prepared in the solution containing 0.1 wt % PAA and 0.25 mM $AgNO_3$. The nanoparticles seem to grow homocentrically. It shows that Ag nanoparticles are about 400–500 nm in diameter and display dendritic nanostructures. Silver nanoparticles put out the thick branch from center and the relatively fine branch from thick branch. Size distribution and morphology of silver dendritic nanoparticles were very uniform. The surface area of silver dendritic nanoparticles was investigated through the BET measurements. The surface area of silver dendritic nanoparticles was found to be 18.0785 m^2/g. Figure 1B is the en-

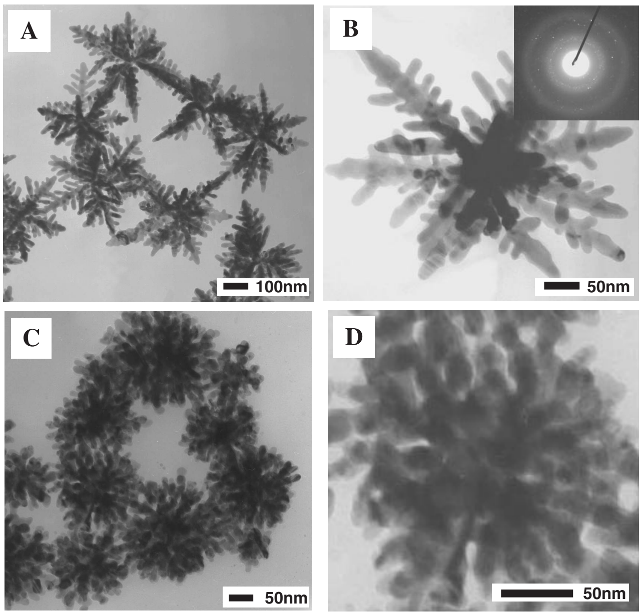


Figure 1. TEM images of the silver nanoparticles obtained by reducing the solution containing (A,B) 0.1 wt % PAA and 0.25 mM $AgNO_3$ (C,D) 0.5 wt % PAA and 0.25 mM $AgNO_3$. The inset of Figure b is electron diffraction (ED) pattern of silver dendritic nanoparticles. PAA($M_w = 5100$).

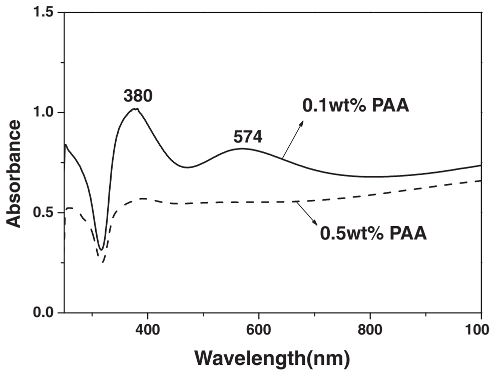


Figure 2. UV–vis absorption spectra of silver colloid corresponding to the Figure 1A (0.1 wt % PAA) and Figure 1C (0.5 wt % PAA).

larged image of Figure 1A. The surface area of these silver dendritic nanoparticles is much larger than general spherical nanoparticle of the same size. The inset in Figure 1B is electron diffraction (ED) pattern corresponding to the Figure 1A. The electron diffraction pattern of silver dendritic nanoparticles showed the presence of diffraction rings corresponding to the (111), (200), (220), and (311) planes, indicating the formation of metallic silver.

Figure 1C shows the TEM image of the silver particles prepared in the solution containing 0.5 wt % PAA and 0.25 mM AgNO$_3$. Figure 1D is the enlarged image of Figure 1C. The diameter of silver nanoparticles is about 160–200 nm. As can be seen from Figures 1A and 1C, the two-as-synthesized particles obtained at different PAA concentrations appeared different morphology except that have numerous protuberances. Compared with silver nanoparticles synthesized at 0.1 wt % PAA, silver nanoparticles synthesized at 0.5 wt % PAA appeared spherical shape that has numerous protuberances homocenterically. It was found that concentration of PAA has a significant effect on morphology of silver nanoparticles. The effect of the concentration of PAA on the shape of the Ag nanoparticles is very similar to reported one that ratio of the concentration of the capping polymer material to the concentration of the metal salts can influence the shapes and sizes of metal nanoparticles.[2,10] In order to confirm effects of molecular weight on the formation of silver dendritic nanoparticles, we applied various molecular weights ($M_w = 2100, 15000$) of PAA to preparation of dendritic nanoparticles. In result, the morphologies of these silver dendritic nanoparticles were independent of the molecular weight of PAA.

It is well known that the size and shape of nanoparticles may influence the position and the width of plasmon bands. Figure 2 shows the UV–vis absorption spectra of silver colloid corresponding to the Figures 1A (solid curve) and 1C (dashed curve). The silver colloid synthesized at 0.1 wt % PAA exhibited two distinctive peaks located at 380 and 574 nm. The absorption spectrum of the silver dendritic nanoparticles synthesized at 0.1 wt % PAA is similar to that of silver nanorods.[13] On the other hand, silver colloid synthesized at 0.5 wt % PAA exhibited a very broad plasmon band due to silver aggregates.

In order to investigate the effects of structure of PAA on the formation of dendritic nanoparticles, several other water-soluble polymers (poly (sodium 4-styrenesulfonate) (PSSS), poly (vinyl pyrrolidone) (PVP), poly(acrylamide) (PAM)) were added in this system instead of PAA. The morphologies of particles using other water-soluble polymers are different from those of using PAA. In case of PSSS and PVP, general spherical nanoparticles appeared. When PAM was used as a protective agent, resulting nanoparticles were aggregated by small primary particles in the polymer matrix. This result implies the importance of the molecular structure of PAA in forming silver dendritic nanoparticles. Also, PAA was frequently used to stabilize metal nanoparticles and control sizes and shapes of them at the synthesis of nanopaticles through the reduction of metal salt.[2,14,15] Recently, silver nanoclusters protected by PAA were prepared by UV irradiation of an alcohol–water solution of silver perchlorate in the presence of PAA.[15] However, dendritic structures were not observed. Consequently, fomation of silver dendritic nanoparticles has relation to not only structure of PAA but also reducing method.

The growth of silver dendritic nanoparticles may be based on an aggregation mechanism. The first step was the formation of ion pair between PAA and silver ions (Scheme 1-I). Second, the complex promotes silver nucleation, which tends to produce small silver particles (Scheme 1-II). Next, small silver nanoparticles rearrange and rotate to find a place to minimize the surface energy (Scheme 1-III). Finally, after recrystallization, silver dendritic nanoparticles form. However, the exact mechanism for formation of silver dendritic nanoparticles is not yet known.

In summary, nanoscale (<500 nm) silver dendritic nanoparticles of uniform size and morphology have been prepared by chemical reduction of AgNO$_3$ at room temperature using PAA as a protective agent and ascorbic acid as a reducing agent in aqueous solution. It was found that concentration of PAA has a significant effect on the morphology of silver dendritic nanoparticles. These silver dendritic nanoparticles with unusual nanostructures may have important applications especially in catalysis, and this method may be extended to prepare nanoparticles of other noble metals. With this method, uniform dendritic nanoparticles can be prepared. This method is relatively simple and does not require the high temperature.

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