Self-organized Synthesis of Silver Chainlike and Dendritic Nanostructures via a Solvothermal Method

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Well-defined silver chainlike and dendritic nanostructures with fractal features were self-organized via a simple solvothermal method using poly(vinyl pyrrolidone) (PVP) as an adsorption agent and architecture soft template. The branching fractal morphology was reasonably explained by using the Cayley tree model. There is no obvious boundary observed at necks between continuous Ag particles. With prolonging reaction duration, the necks disappear, and the growth of the chainlike silver leads to the formation of the Ag dendritic nanostructure and nanowires. The formation of the Ag dendritic nanostructure can be explained as a process of initial reduction−nucleation−adsorption−growth−branching−growth.

I. Introduction

Nanomaterials of noble metals have drawn considerable attention due to their unique magnetic, optical, electrical, and catalytic properties.[1−3] They have been widely exploited for use in photography,[4] catalysis,[5] biological labeling,[6] optoelectronics,[7] and surface-enhanced Raman scattering (SERS).[8] It is well-known that catalytic reactivity depends on the size and shape of the metal nanoparticles and that the size could be critical for their properties and applications.[9] In particular, the formation, evolution, and consequences of fractal structures in metal systems, including metal−polymer composites, have been the subject of fruitful research for a long time.[10−13] Fractals are generally observed in a nonequilibrium growth process, and studies of such materials instabilities have important technological applications concerning the formation and control of materials systems with the desired properties (e.g., nanojets,[14] nanowires,[15] thin films, and other surface-supported structures).

Because the performance of silver in most of the applications ranging from electronics and catalytics to photonics[16] could be significantly enhanced by processing silver into nanostructures with well-controlled dimensions,[17] a few methods have been devoted to the preparation of silver nanostructure with fractal morphologies. For example, single-crystal silver dendritic supramolecular nanostructures have been prepared via an ultraviolet irradiation photoreduction technique at room temperature using poly(vinyl alcohol) (PVA) as a protecting agent;[18] Xiao et al. have synthesized silver dendritic nanostructures with ultrasonically assisted hard-templating technology;[19] and most recently, through the deposition of silver clusters on graphite, the room-temperature fragmentation instability of fractal islands is formed and governed by the ratio of the length to the width of the silver fractal arms.[20] In this paper, we report a novel chainlike and dendritic nanostructure of silver with fractal features, synthesized via a simple solvothermal method in the presence of poly(vinyl pyrrolidone) (PVP) and propose a possible growth-branching mechanism for the formation of such a self-organized Ag nanostructure.

II. Experimental Section

All chemicals are analytical grade and used without further purification. Appropriate amounts of ethylene glycol (EG) solution (0.1 M) of silver nitrate and EG solution (0.001 M) of

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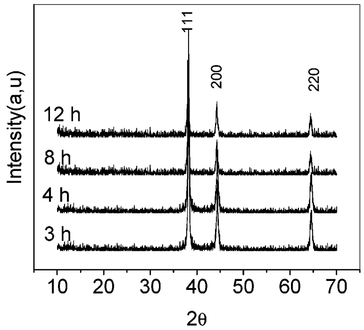

Figure 1. XRD patterns of as-prepared nanostructured silver grown at 180 °C for 3, 4, 8, and 12 h.

PVP (M_w = 49000 and $n \approx 445$) were put into a Teflon-lined autoclave. The autoclave was filled with ethylene glycol up to 90% of its capacity, maintained at 180 °C for 3, 4, 8, and 12 h and then cooled to room temperature naturally. The products were filtered and washed with water and absolute ethanol in sequence. Finally, the products were dried at 70 °C. Powder X-ray diffraction (XRD) was used to characterize the samples. Data were collected on a Bruker D8 Advance X-ray diffractometer with Cu Kα radiation (λ = 1.54178 Å). The morphology and size were examined by scanning electron microscopy (SEM) and transmission electron microscopy (TEM). The TEM images were recorded on a JEOL JEM-200CX TEM, using an accelerating voltage of 200 kV. Further structural and elemental analyses were performed using high-resolution TEM (JEOL, JEM-2010 at 200 kV), selected area electron diffraction (SAED), and energy-dispersive X-ray spectroscopy (EDS).

III. Results and Discussion

On the basis of the reaction of silver nitrate and PVP in EG at 180 °C for 3 h, the silver chainlike nanostructure with fractal geometry was synthesized. When the reaction time was prolonged to 4, 8, and 12 h in the same solvothermol system, the silver nanostructures with different morphologies, especially dendritic nanostructures, were also prepared. The typical powder XRD patterns of the products are shown in Figure 1. The three diffraction peaks can be respectively indexed to the (111), (200), and (220) planes of face-centered-cubic (fcc) silver, with a lattice constant of a = 4.080 Å, which is in agreement with the reported values a = 4.086 Å (JCPDS 04-0783). X-ray energy-dispersive analysis patterns for the products showed the presence of only Ag peaks. The reaction temperature plays an important role in the synthesis of the silver fractal nanostructures. For example, no silver was produced when the solvothermal reaction was performed at 120, 140, and 160 °C for 12 h.

To investigate the morphology of the resultant products when the reaction time is short, for example, 3 h, TEM images are presented in Figure 2, indicating that all the particles contact each other to form a chainlike network with fractal features. The chainlike network consists of chains of Ag nanoparticles with branches. The sizes of the Ag particles range from 100 to 150 nm in diameter. The branches lead to the formation of the network. Parts b and c of Figure 2 show more details of the local chainlike structure. The SAED pattern shown in the inset of Figure 2b gives the microdiffraction pattern recorded by focusing an electron beam on the A neck between contiguous Ag particles, and it consists of two sets of spots corresponding to each conjoint

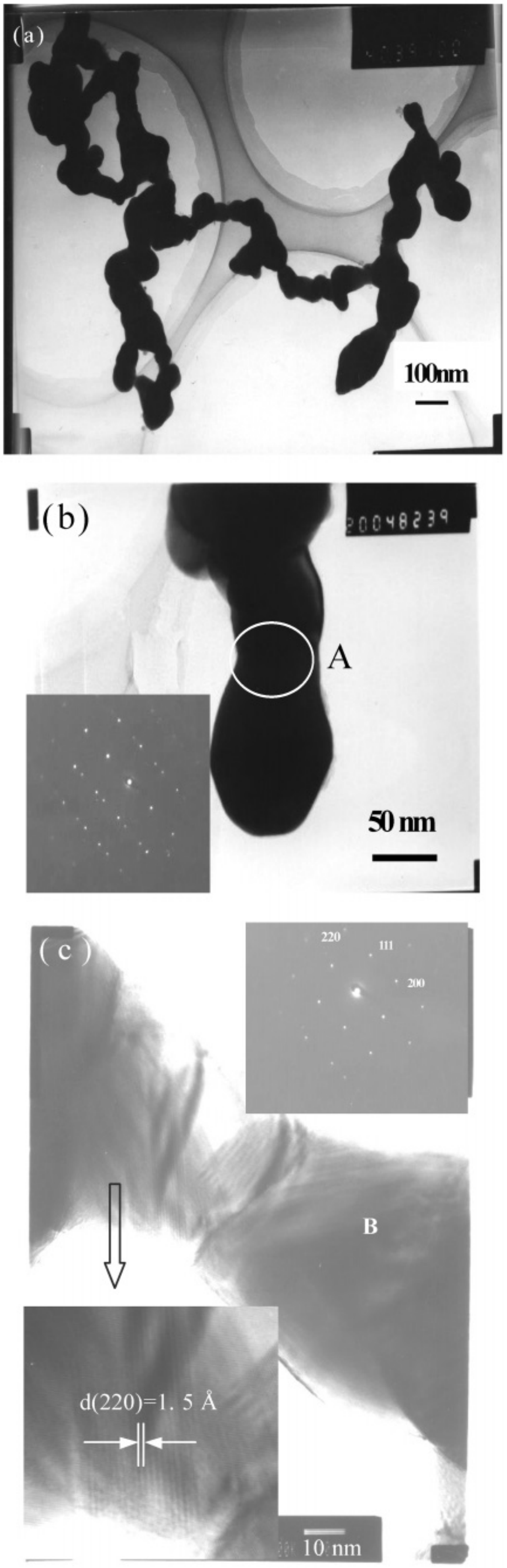

Figure 2. TEM images of as-prepared nanostructured silver at 180 °C for 3 h: (a) the local structures of the fractal network; (b) more details of the local chainlike structure, where the inset is a SAED pattern recorded by focusing an electron beam on the A neck; and (c) HRTEM image taken from the A neck, where the inset is a SAED pattern for the B area as indicated.

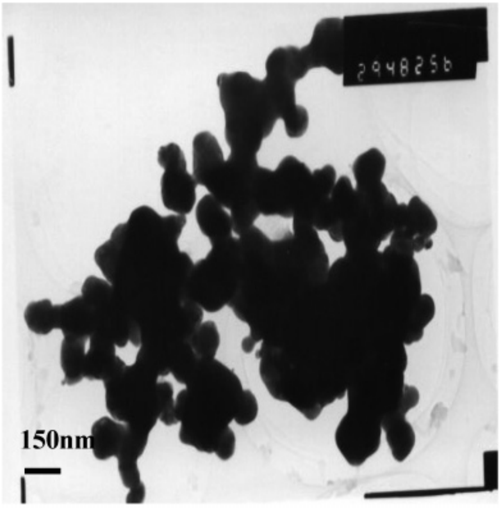

Figure 3. TEM image of the chainlike silver particles synthesized at 180 °C for 4 h.

particle. Each set could be independently indexed to reveal the corresponding (111), (200), and (220) planes of fcc silver. We have observed the high-resolution transmission electron microscopy (HRTEM) image (Figure 2c) of the neck part (indicated by A) of the chainlike silver nanostructure in Figure 2c at higher magnification, though the image is not so clear for the whole neck area due to its large thickness. All the lattice planes in the chainlike silver nanostructure have the same spacing and direction where the singular fringe spacing is about 1.50 Å, which is nearly consistent with the (220) reflection plane spacing of the cubic Ag phase in the XRD pattern. The [220] direction was parallel to the axis of the chainlike nanostructure, indicating that the [220] direction is the growth direction for the cubic silver. The SAED patterns of the single particle (e.g., as indicated by B in Figure 2d) confirm it is a single crystal. The present observation shows that there seems no obvious boundary at the neck between contiguous Ag particles as shown in Figure 2d. Grain boundaries could be formed at some necks between the particles. Selected area EDS measurement was used to characterize the chemical composition of different parts of the chainlike nanostructure (A in Figure 2b and B in Figure 2c) at room temperature. The results showed that only element silver exists.

Our experiment demonstrates that the morphology of the nanostructured Ag is dependent on the reaction duration in the solvothermal process. To investigate the evolution of the morphology of the nanostructured silver with time, the solvothermal reaction was also conducted under a few different durations, for example, 4, 8, and 12 h, respectively. When the reaction duration is prolonged to 4 h, the majority of the products remain to be the chainlike morphology with an average particle diameter of 100 nm, as shown in Figure 3. With the reaction time increasing to 8 h, the silver nanoparticles with chainlike features partly grow into dendritic nanowires and nanorods with about 100 nm in diameter

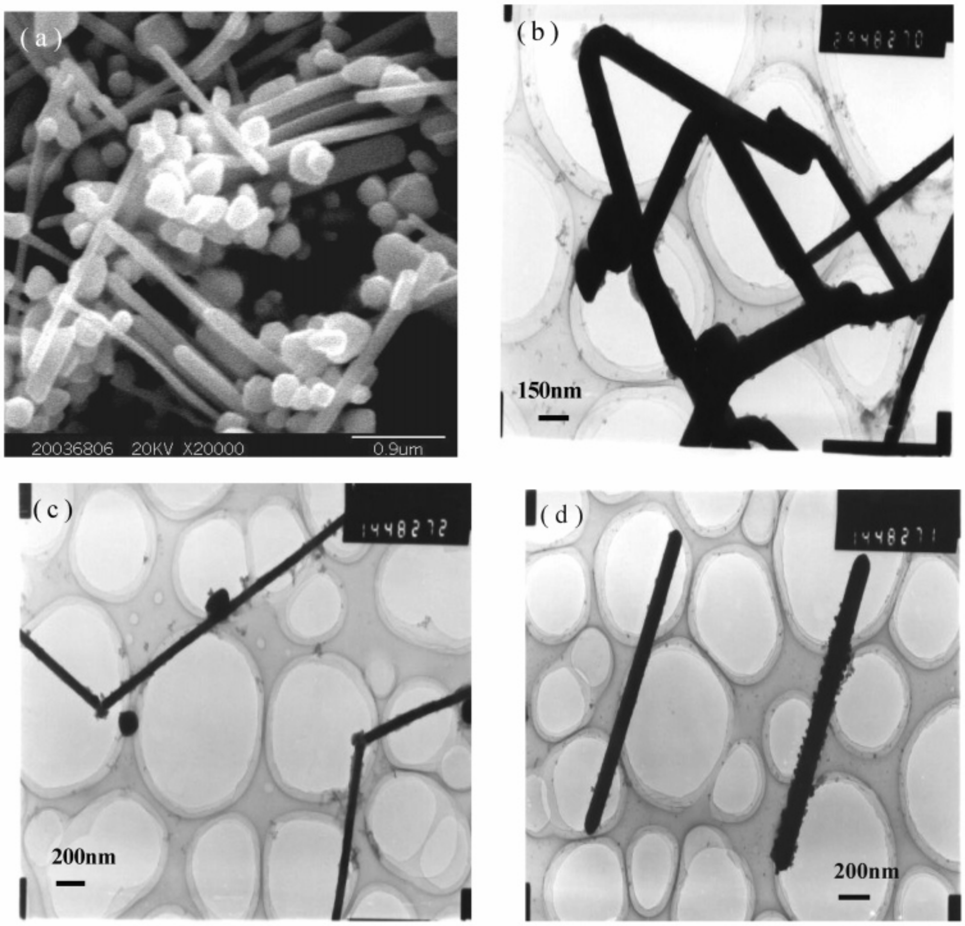

Figure 4. SEM and TEM images of the as-prepared nanostructured silver at 180 °C for 8 h: (a) SEM image, (b) novel dendritic network, (c) branched nanowires with V morphology, and (d) silver nanorods.

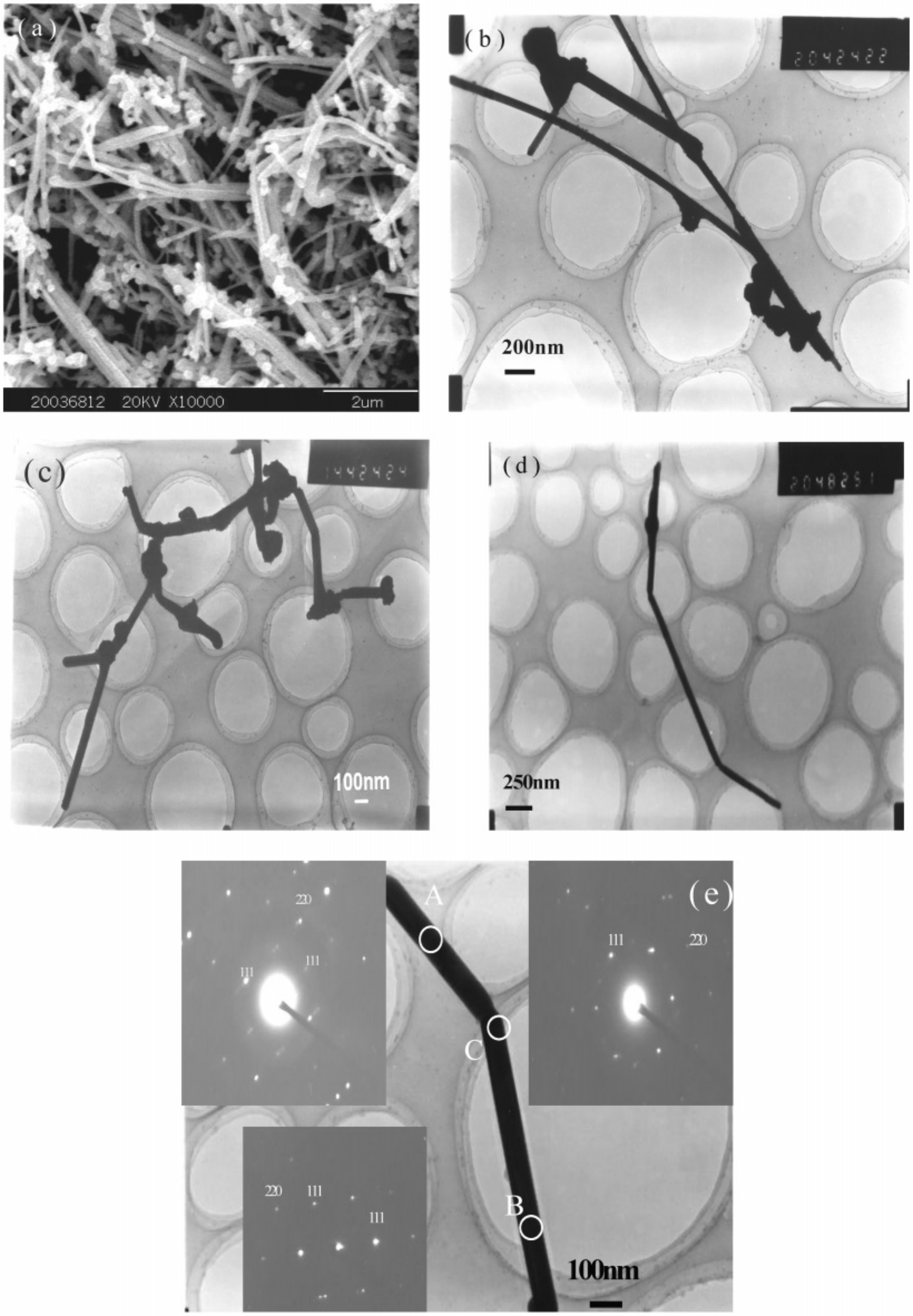

Figure 5. SEM and TEM images of as-prepared silver at 180 °C for 12 h: (a) SEM image of large-scale silver dendrites, (b) single silver dendrite, (c) chainlike dendrite, (d) a multinode structure, and (e) dendritic silver with V morphology, where the inset shows the SAED patterns measured at the A, B, and C positions.

and 5 μm in length as shown in Figure 4. Of particular interest to note is that the chainlike network (Figures 2 and 3) with a closed ring has grown into a novel dendritic network (Figure 4a,b), branched nanowires with V morphology (Figure 4c), and silver nanorods (Figure 4d).

As the reaction time is further prolonged, say, to 12 h, a well-defined nanoscale silver dendritic form (see Figure 5), and especially silver nanowires with about 20−100 nm in diameter and 15 μm in length, are obtained (Figure 5a,b), some of which exhibit the fractal structure with chainlike features (Figure 5c) or multinode structure (Figure 5d). Furthermore, the single-crystalline nature of the silver dendrites is confirmed by the SAED measured on different positions of the nanowire, that is, A, B, and C as indicated in Figure 5e. The reflections correspond to the (111) and (220) planes of the fcc Ag.

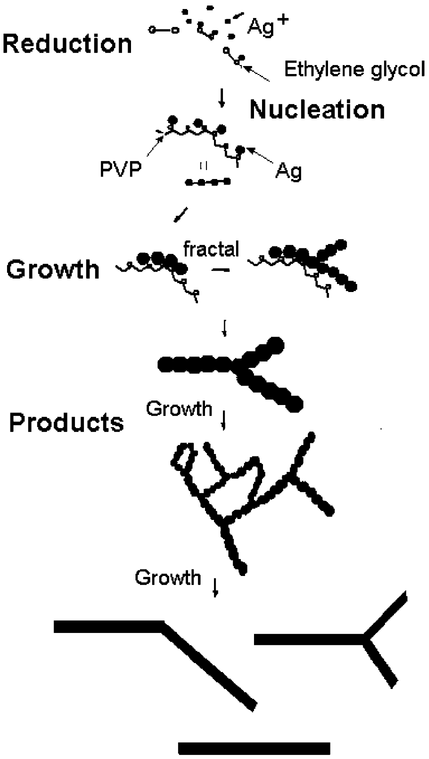

Figure 6. Schematic illustration of the growth process of Ag chainlike and dendritic nanostructures.

The formation mechanism of these silver chainlike and dendritic nanostructures observed can be schematically described in Figure 6. The PVP molecules play a key role in the formation of such silver chainlike and dendritic nanostructures with fractal features as an adsorption agent and architecture soft template since only silver nanoparticles were prepared in the same solvothermal reactive system without the presence of PVP. PVP is a protective polymer and it was usually used for stabilization of nanoparticles in solution, via adsorption of polymer units on growing nanoparticles.[21] In the solvothermal process, the EG acts as both solvent and reducing agent. Thus, nucleation first occurs in EG solution, and when particles start growing, PVP is adsorbed on the nanoparticle surfaces. Then chains of crystalline seeds would form in the next nucleation process, which finally yields chainlike products. Fractal silver nanostructures are generated with high yields via a self-organized process that uses the PVP as the adsorption reagent.[22] The formation of the chainlike and dendritic structures with fractal features could be well-represented by the Cayley fractal tree model.[23] In the case of fractal growth, growing fractal aggregates instead of uniform crystals form, and Cayley trees are always trimmed and some of the branches have dead ends.[24] When two growing branches encounter each other at their ends, they stop growing and gradually form closed rings. One of the key steps in building up the Cayley fractal tree is the branching from the tips of the growing chains.[25] With prolonging reaction duration, the surface of particles in the silver chainlike structure continues to grow and becomes a dendritic nanostructure as schematically shown in Figure 6. Furthermore, the change of the growth mode from a Witten-Sander type fractal aggregate structure[10] to a dendritic growth mode with the prolonging reaction duration seems to be not only a result of the enlarged size of the aggregate but also a result of epitaxial growth along a certain crystal plane such as the (220) plane, as confirmed by the HRTEM image in Figure 2c and TEM images in Figure 5e. The change observed in the crystal morphology could be also due to the change in the relative concentration of the silver salt with time. During the initial stage, high concentration of the silver salt and reduction agent lead to reduction−nucleation−growth of Ag nanoparticles simultaneously at a lot of positions to form a chainlike network. With prolonging reaction duration, the concentration of the silver salt and reduction agent greatly decreases, the growth is mainly drived by decreasing surface energy, and thus the necks disappear to form the dendritic silver structure.

Thus, the possible formation process of the chainlike and dendritic nanostructures can be summarized in the following five steps. First, silver ions are partly reduced to silver nanoparticles by EG. Second, nucleation occurs in EG solution, and PVP is adsorbed on the nanoparticle surfaces as a chain template when particles begin growing. Third, the chains continue to grow to form chainlike products. Fourth, some chainlike products branch from the growing chains and form fractal trees. The formation of the chainlike network with fractal nature in this solvothermal process is mainly due to an initial nucleation, growth, and then branching process. Fifth, the branches of the chainlike trees with fractal features continue to grow, and the necks between continuous Ag particles disappear, thereby leading to the formation of the dendritic trees with prolonging reaction duration; meanwhile, the dendritic trees might break at some nodes, and as a result, single- or multinode silver nanowires are obtained. It can be seen that the silver chainlike network is a precursory process of the formation of the silver dendritic nanostructure (for example, see Figure 2a and Figure 4b). And the formation of the silver dendritic structure with fractal nature can be explained as a continuous process of initial reduction−nucleation−adsorption−growth−branching−growth.

IV. Conclusions

Well-defined silver chainlike and dendritic nanostructures have been self-organized via a simple solvothermal process in the presence of PVP. During the initial reaction process, a chainlike network that consists of chains of Ag nanoparticles with branches forms, and the nanoparticles contact each other without obvious boundary to form a crystal. The branching fractal morphology has reasonably been explained by using the Cayley tree model. When the reaction duration is prolonged, the growth of the chainlike silver leads to the formation of the dendritic nanostructure and silver nanowires of

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about 20−100 nm in diameter and 15 μm in length. The formation of the final Ag dendritic structure with fractal nature can be explained as a process of initial reduction−nucleation−adsorption−growth−branching−growth. The solvothermal synthetic approach could be extended to other metals to obtain novel nanostructures.

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