Self-assembled Silver Dendritic Nanostructure on the Surface of AAO Template

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Silver dendritic hierarchical structures have been prepared using a simple, surfactant-free method by carrying out the silver mirror reaction on the surface of a porous anodic aluminium oxide (AAO) template. The surface of the AAO template has a guiding effect in the formation process of silver dendritic hierarchical structures.

Anodic aluminum oxide (AAO) template-based synthesis has been proved to be an elegant approach to synthesize nanostructure materials owing to its several unique structural properties, such as controllable pore diameters, extremely narrow pore size distribution and their intervals, and ideally cylindrical shape of pores.[1,2] The applications of AAO templates, such as filters for separation, catalysts, magnetic recording media, and electrodes[3] have been previously reported. Nanowires and nanotubes of metals,[4–6] semiconductors,[7–9] carbon,[10] and other solid materials have been fabricated within the pores of AAO using a variety of methods.

The main difference between AAO template and other templates is that the surface of AAO is unique owing to its uniform and parallel pore structure, which makes it possible to grow some special structures on its surface. The potential energy of the pores is lower than that in the other parts of the surface. Therefore, there is a fluctuation in potential energy on the surface of the AAO template. Some special structures can be formed on the surface of the AAO template under appropriate conditions. Here, we describe a simple, low-cost, and green-chemical solution-phase approach to fabricate silver dendritic nanostructures by carrying out the silver mirror reaction on the surface of an AAO template.

Silver dendritic nanostructures are traditionally formed on electrode surfaces in electrochemical deposition.[11] Such metallic nanodendrites, as a complex of one-dimensional (1D) nanostructures, have a hierarchical structure and may have potential applications in plasmonics, biosensors, and catalysis.[12] Silver dendritic nanostructure on the surface of metal matrix has been reported,[13] and many efforts have been made to prepare dendritic silver nanostructures.[14–17]

Through-hole AAO templates were prepared using high-purity aluminum foil in 0.3 mol/L $H_2C_2O_4$ under 40 V at 0–5 °C via a two-step anodization process as described in literature.[18] In a typical procedure, a through-hole AAO template was immersed into a freshly prepared mixed solution containing silver complex (5 mL of 1 mol/L $Ag(NH_3)_2{}^+$ and 10 mL of 0.56 mol/L glucose), and then the bubbles were pumped out within the nanochannels of the AAO template for about 15 min. Then, the AAO template was taken out of the solution, washed with distilled water, and dried in air. The above procedure was repeated several times at regular intervals. After that, the AAO template was immersed into the solution again, heated in a water bath at about 100 °C for 30 min under magnetic stirring, and then slowly cooled down to room temperature. After reaction, the AAO template was immersed into distilled water to remove the residual reactants and then dried in air at 60 °C for 4 h.

X-ray diffraction (XRD) measurements of the products were performed on an X-ray diffractometer (Rigaku, D/MAX-γA) with Cu Kα radiation ($\lambda = 0.15418$ nm) in the range of $20^\circ \le 2\theta \le 80^\circ$. The morphology of as-prepared samples was observed using a field emission scanning electron microscope (FE-SEM, JSM-6700F).

X-ray diffraction pattern of the as-prepared product is shown in Figure 1. It can be seen from Figure 1 that all of the diffraction peaks can be indexed as the face-centered cubic (fcc) Ag [space group: $Fm\bar{3}m$ (225)] with a lattice constant ($a = 0.4091$ nm) which is in agreement with the reported data in literature (JCPDS Card No. 04-0783). The four diffraction peaks can be attributed to the (111), (200), (220), and (311) planes, respectively.

Typical FESEM images of the surface of the as-prepared product with different magnifications are presented in Figure 2. The top view of the sample clearly shows that large-scale dendritic hierarchical structures with fractal geometry are formed with a high yield. In the dendritic hierarchical structures, several leaves with different lengths and widths connect to the main branch. The length of the main branch is several tens of

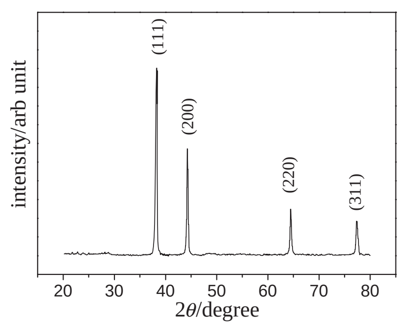

Figure 1. XRD pattern of the as-prepared product.

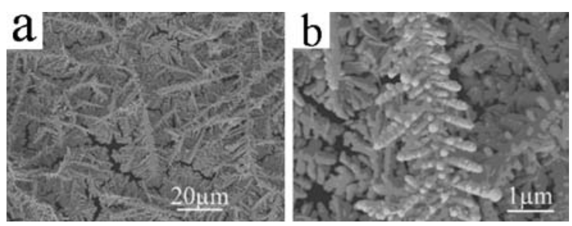

Figure 2. Typical FESEM images of the silver dendrites: (a) magnified FESEM image of the as-prepared product, (b) higher magnifications FESEM image of Figure 2a.

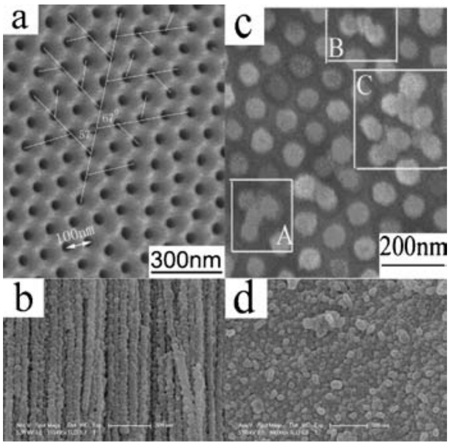

Figure 3. Schematic formation diagram of silver dendrites: (a) empty AAO template and schematic formation diagram of silver dendrites. (b) Cross-section SEM image of the nucleation of silver nanoparticles inside the nanopores. (c) Silver nanoparticles grow up to the surface (the framed area indicates the adjacent nanoparticles growing close to each other). (d) AAO template covered with a layer of silver film when the reaction is long enough.

micrometers; that of each leaf is about 0.5–4 µm with a width ranging from 100 to 300 nm. Interestingly, close inspections of the nanostructure surface under higher magnifications clearly show that each leaf connecting to the main branch also acts as a secondary main branch to be connected with some smaller leaves, as shown in Figure 2b. It is clear that the dentrites have symmetric structure, and the angles between the stem and the breaches are mostly about 50–70° which are consistent with the reported result.[12] These leaves are composed of a large number of pyramid-like leaf-tip nanoparticles and self-assembled into a 3D hierarchical structure.

The growth of silver dendritic supramolecular nanostructure is usually explained by a diffusion-limited aggregation (DLA) model.[19] In our system, the AAO template has an important effect on the formation of the silver dendritic nanostructure. Figure 3a is an empty AAO template, from which it can be seen that the angle between the adjacent intersectant ordered pores is about 50–70°, and the adjacent pore distance is about 100 nm. This is consistent with the structure of as-prepared silver dendrites. Most likely, silver nanoparticles first nucleate in the nanopores of the AAO template because of low potential energy on the pore walls as shown in Figure 3b. After the particles grow up to the surface, the adjacent nanoparticles will grow close to each other to form the main branch via local oriented attachment along the same ordered pore array. Then, the leaves will grow along the adjacent intersectant pore array with a similar process (see Figure 3c). If the reaction time is long enough (about 45 min), the surface will be covered with a layer of silver film (see Figure 3d), and the dendritic nanostructures will not be seen. In the initial stage, high concentrations of the silver salt and the reduction agent lead to reduction–nucleation–growth of silver nanoclusters to form a chain-like network. As the reaction time increases, the growth is mainly driven by a decrease of surface energy because of the greatly decrease of the concentrations of the silver salt and reduction agent, and thus the dendritic silver nanostructures are formed. The schematic formation diagram is shown in Figure 3. This nanostructure material might have great potential to be building blocks for assembling minifunctional devices of the next generation. However, the exact mechanism for formation of the silver dendritic nanostructure is not yet known.

In summary, silver dendritic hierarchical structures have been prepared using a simple, surfactant-free method by carrying out the silver mirror reaction on the surface of a porous anodic aluminium oxide (AAO) template. The symmetric structure of silver dendrites is promising for applications in optoelectronics and as building blocks for assembling mini-functional devices of the next generation. Our experiment has demonstrated that we can use the surface of AAO templates to grow some special structures under appropriate conditions. This will extend and throw a new light on the use of the AAO template to synthesize new nanostructure materials.

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