# Synthesis and Formation Mechanism of Silver Nanowires by a Templateless and Seedless Method

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Silver nanowires in large quantities can be obtained through a simple method in the absence of a surfactant or polymer and without addition of external seeding nanocrystallites. A plausible mechanism was proposed to elucidate the formation mechanism of silver nanowires based on TEM studies.

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Recently, one-dimensional (1D) nanostructures, such as nanowires and nanobelts have been received considerable attention because of their potential applications in nanoelectronic and biological devices.[1–4] In addition, exploration of the formation mechanism of nanostructures for further understanding the detailed chemical and physical properties of these nanomaterials is also an important issue of materials research in nanometer regime. Long metallic nanowires, especially silver nanowires, have been synthesized with different approaches.[5–10] Among them, most of the synthetic methods resort to hard templates such as silica gels or single-walled carbon nanotubes to guide the growth of nanowires,[6,10] or require seeds or soft templates such as polymers or surfactants for helping the formation of nanowires.[11,12] Here we present a nontemplate, seedless process to make high-quality silver nanowires in large quantities. TEM observations provided a clear evidence for the 1D formation process of silver nanowires, indicating that the initially aggregated silver nanoparticles with irregular shapes slef-assemble to form oriented nanostructures and then fuse each other to produce silver nanowires.

All the reagents including *N*,*N*-dimethylformamide (DMF), tetrabutyl titanate (TBT), acetylacetone (AcAc), and silver nitrate ($AgNO_3$) purchased from Shanghai Chemicals Co., were analytical grade and used without further purification. The preparation procedure is as follows. At first, a solution (referred to as A) of 0.017 g $AgNO_3$ dissolved in 20-mL of DMF and a mixture (referred to as B) of 1 mL of TBT and 1 mL of AcAc were prepared, respectively. Subsequently, B solution was introduced into A under mild magnetic stirring and the silver ions were reduced by DMF progressively. Then the reaction solution was heated up to ≈373 K and kept at this temperature for 8 h. The synthesized products were separated from the final reaction solution by means of centrifugation and washed with ethanol and distilled water for several times until the precipitates were essentially free of spherical nanoparticles.

The composition, microstructure and purity of the product were characterized by X-ray diffraction (XRD, D8-ADVANCE X-Ray diffractometer), scanning electron microscopy (SEM, LEO 1530VP field emission scanning electron microscope), transmission electron microscopy (TEM, JEOL JEM-2011 transmission electron microscope) and energy dispersive spectroscopy (EDS).

Figure 1 shows the XRD pattern of the silver nanowires dried at 343 K in vacuum, indicating the presence of diffraction peaks corresponding to the silver crystal planes of fcc structure (JCPDS, File No. 04-0783), and there are no characteristic peaks of impurities, such as $TiO_2$ in the product. This result indicates that the chelate complex consisting of TBT and AcAc does not hydrolyze in DMF solution and the products can be easily separated from the solution. It also can be clearly seen from the EDS result (see the inset in Figure 1) that no other impurities could be found in the silver nanowires.

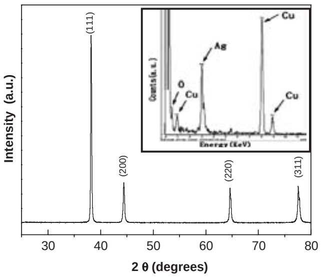

**Figure 1.** XRD pattern of the silver nanowires. The EDS elemental analysis of silver nanowires shown in the inset confirms that the product is composed of pure silver.

Figure 2 exhibits representative SEM and TEM images of the collected product. From the TEM image and the inset shown in Figure 2a, one can see that most of the silver nanowires have uniform morphology and diameters are in the range of 10–70 nm. By virtue of the HRTEM image shown in Figure 2b, it clearly indicates that the wires are highly crystalline and the interplanar spacing is about 0.236 nm, suggesting that the nanowires was preferentially grown along the *c* axis, or the {011} crystallographic direction. This observation is also supported by the experimental results obtained from the SAED pattern (see inset in Figure 2b).

Figure 3 shows the optical absorption spectra of the samples with different reaction time lengths. It can be clearly seen that before reaction, the appearance of a resonance peak at ≈410 nm indicates the formation of silver colloids,[12] and at $t = 0$ min, the plasmon band splits into two peaks located at ≈400 and ≈570 nm, respectively. As the reaction goes on, it is also found that the resonance at ≈410 nm corresponding to the main resonance of silver nanoparticles is strongly damped after 8 h reaction. The transverse plasmon band at ≈350 nm (see curve e in Figure 3) shows the typical characteristic of silver nanowires.[13] As the length of these nanowires grows with time, the intensity of the transverse plasmon peak increases.[5] Nevertheless, a shoulder at ≈450 nm indicates that silver nanoparticles still co-existed in the final product before centrifugation and the peak slightly shifts to longer wavelength as the particles grow in size progressively.

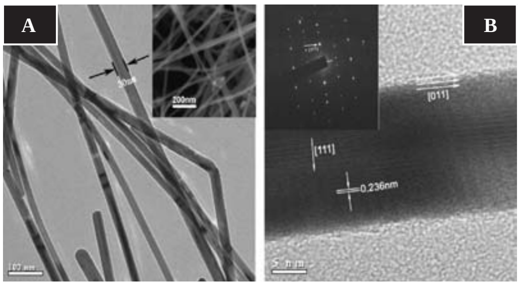

**Figure 2.** Typical TEM (a) and high resolution TEM (b) images of the as-prepared silver nanowires. The inset in A is the FESEM image of silver nanowires. The inset in B is the SAED pattern of the corresponding wire.

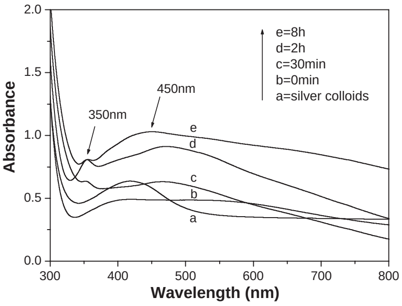

**Figure 3.** UV–vis absorption spectra of the samples at different stages of nanowire growth: (a) silver colloids, (b) silver aggregates, and (c)–(e) correspond to the reaction mixture heated for 30 min, 2 and 8 h, respectively.

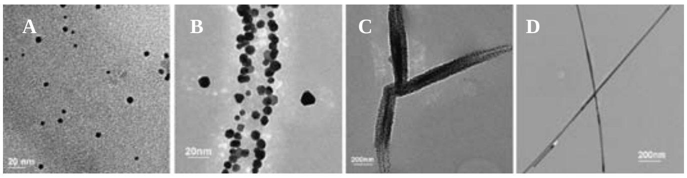

**Figure 4.** TEM images of various intermediates during the formation of silver nanowires from silver nanoparticles. (a) initial silver colloids, (b), (c) chain-like silver aggregates, (d) silver nanowires.

To substantially understand the formation mechanism of the nanowires accurately, it is necessary to visually investigate the morphology of the intermediates involved in their different growth stages. TEM studies were used to check the samples spanning silver colloids and the final nanowires. It is shown in Figure 4 that the initial silver colloids in DMF are composed of small silver nanoparticles, which spatially direct aggregation along preferred crystallographic axes once the mixture of TBT and AcAc is introduced into the silver colloids. This coalescence from nanoparticle to chain-shaped nanostructure can be observed in our TEM images, as shown in Figures 4a and 4b. The presence of the particle chains suggests that the nanowires form, not through a point-initiated epitaxial growth process but rather by the oriented alignment, fusion and crystallization of nanoparticles with the support of silver ions, which are reduced between closed nanoparticles facing each other and linked the particles together, as shown in Figure 4c.

The reconstruction of silver nanostructures from particle aggregates to rods and wires, and finally rearrange the crystallographic planes to yield long and single crystalline nanowires, as shown in Figure 4d. This demonstration is similar to the formation of 2D networked gold nanowires through a solidification and crystallization process.[14]

Two important questions that remain here are why the aggregation of the initial nanoparticles takes place and why 1D nanostructures rather than other branched or fractal aggregates are the most usual occurrences. The further details will be discussed elsewhere. Here it is proposed that the Van der Waals forces thus make these nanoparticles aggregate through the so-called depletion flocculation.[15] For the silver nanocrytals, as is known already, the surface free energies of the crystallographic planes decrease in the order $\gamma_{\{110\}} > \gamma_{\{100\}} > \gamma_{\{111\}}$,[13,16] suggesting that the bonding ability and chemical reactivity of the {110} plane are greater than those of {100} and {111}, giving rise to nanoparticle-to-nanowire transition along the preferential {110} facet from short-range orientation to long-range arrangement.

In conclusion, we have successfully prepared single crystalline silver nanowires through a templateless, seedless method in a mild condition. Introduction of the mixture of acetylacetone and tetrabutyl titanate into silver colloids dispersed in *N*,*N*-dimethylformamide initiates the aggregation of silver nanoparticles by depletion flocculation. Subsequent attachment and merging of adjacent nanoparticles with different polarizability and reactivity on the irregular crystallographic surfaces may give rise to nanoparticle-to-nanowire transition in DMF solution, resulting in the formation of silver nanowires through rearrangement and recrystallization of nanostructures along the preferred orientation. This novel demonstration of controlled nanocrystal aggregation growth points the way toward the possibility of "down-top" assembly of other metallic nanoparticles into one-dimensional nanostructures in solution.

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