

# Aggregation-based growth of silver nanowires at room temperature

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## Abstract

We describe an aggregation-based growth mechanism for formation of silver nanowires at room temperature. It is found that the pH of solution and the concentration of L-cysteine capping molecules have an important effect on the formation and growth of nanowires. Characterization by atomic force microscopy (AFM) and UV–vis spectroscopy recorded as time clearly shows that the silver nanowires are grown at the expense of nanoparticles.

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## 1. Introduction

The controlled synthesis of one-dimensional (1D) nanostructures such as nanowires, nanorods, nanobelts and nanotubes has attracted much attention because of their importance in both fundamental and potential applications in nanodevices [1–3]. In particular, 1D nanostructures of silver play an important role because silver exhibits the highest electrical conductivity in the bulk and novel optical properties that depend on nanoparticle size and shape [4–9]. Recently, solution-based synthesis of 1D silver nanostructures are of great interest because of their low cost, high yield and simplicity. For example, silver nanowires and nanorods have been successfully synthesized by chemical reduction in the presence of surfactants or polymers [10–12] or with use of citrate as both reductant and capping agent in the absence of a surfactant or polymer [13,14]. It is generally accepted that organic agents, such as surfactants or capping reagents, play an important role in directing the 1D growth [14–16]. A good understanding of the process and parameters controlling the silver nanowires formation in solution method is important for designing novel nanostructures for desired

properties. However, despite so many studies have been focused on the preparation of the silver nanowires by solution method, it is still a challenging research area to investigate common mechanisms underlying the 1D nanostructures formation.

There is a well-known mechanism for the formation of nanostructure in a solution, which involves the fast nucleation of primary particles and the following growth: Ostwald ripening [17–19]. Ostwald ripening means that the larger particles grow at the cost of smaller ones, which is most accepted process for the crystal growth. However, recent studies on the growth of nanocrystals have suggested that this model is unable to explain the growth of many semiconductor nanorods, nanowires [20–22]. A distinct aggregation-based growth model has been proposed recently by Banfield et al. [23] to interpret their interesting findings in the natural iron oxyhydroxide. In their work, the nanoparticles whose inter-distance is 2 or 3 nm can spontaneously aggregate and finally grow into bulk crystals in a way so-called “oriented attachment”. They found that perfect single crystals are formed when the neighboring nanoparticles’ crystallography are parallel oriented, otherwise dislocations are resulted from slight misorientation between them. However, to our best knowledge, there is few report on the formation of silver nanowires based on the aggregation-based mechanism.

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In this work, we demonstrated an aggregation-based mechanism for the formation of silver nanowires. Atomic force microscopy (AFM) and UV–vis spectroscopy characterizations of such nanowires accompanying interaction time clearly reveal that the aggregation-based attachment of nanoparticles is a primary process during the formation of silver nanowires.

## 2. Experimental

### 2.1. Materials

Silver nitrate (A.R.) and sodium borohydride (A.R.) were purchased from Beijing Chemical Co. (Beijing, China). L-Cysteine ( $\text{NH}_2\text{-CH}_2\text{-CH(SH)-COOH}$ , 99%) was purchased from Fluka. Reagent-grade HCl and NaOH were used to adjust the pH values. All chemicals were used as received. Ultrapure water ( $\geq 18.2 \text{ M}\Omega \text{ cm}$ ) was used through all the experiments. All of the glassware and the magnetic stirring beads coated by Teflon were cleaned with aqua regia, followed by repeated rinsing with tap water, ultrapure water and dried in air.

### 2.2. Synthesis of silver nanowires

Silver nanowires were readily synthesized by reducing silver nitrate with sodium borohydride in presence of L-cysteine at room temperature (ca.  $20^\circ\text{C}$ ). In a typical synthesis, 10 mL 0.25 mM silver nitrate solution was mixed with 0.1 mL 10 mM L-cysteine. No color change was observed during this procedure. After 5 min, a freshly prepared aqueous sodium borohydride solution (10 mM) was added dropwise to above mixed solution under vigorous stirring. The solution was allowed to stand for 90 min, leading to the gradual formation of nanowires. The final pH of the mixture was about 5.1. The reacting solutions initially became yellow brown, indicating the appearance of Ag nanoparticles, and then turned to suspension with dark brown precipitates.

As for control experimental conditions, the pH of the solution was adjusted to 3.9 and 8 using HCl and NaOH

solution; the concentration of silver nitrate solution was altered to 0.1 and 0.5 mM with other conditions unchanged.

### 2.3. Instruments

Tapping mode AFM imaging was performed on a Digital Instrument Multimode AFM controlled by Nanoscope IIIA (DI, Santa Barbara, CA) equipped with an E scanner. Scan rate is 1–1.5 Hz. UV–vis absorption spectra were measured by a Cary 500 UV–vis spectrophotometer. TEM images of the sample were taken at 100 kV using JEOL-1000 TEM. For FTIR measurements a Nicolet 730 FTIR spectrometer was used. It is noted that the production was not washed before analysis for AFM and UV–vis spectra.

## 3. Results and discussion

### 3.1. L-Cysteine stabilized silver nanowires formed at room temperature

Fig. 1a shows an AFM image of silver nanowire prepared by the simple reduction of the silver ions with sodium borohydride in the presence of L-cysteine at room temperature. It clearly indicates that the products are the mixture of nanowires and nanoparticles. The nanowires seem like needle and extend along different directions. When we measure the length and diameter of the nanowires, the tip broadening must be considered. As reported by Liao and Hafner [24], the tip broadening can be determined by subtracting the measured height (the true diameter) from the width (diameter plus broadening), and this value for the tip broadening can then be subtracted from length measurements to determine the true length. The average length and diameter of the silver nanowires in Fig. 1a are about  $1.3 \mu\text{m}$  and 27 nm, as indicated in Fig. 2a and b, respectively. It is estimated that the aspect ratio (AR) for the silver nanowires in Fig. 1a is about 50. It is also found that the size of the nanoparticles in the products is usually smaller than the diameter of the nanowires by section analysis. The

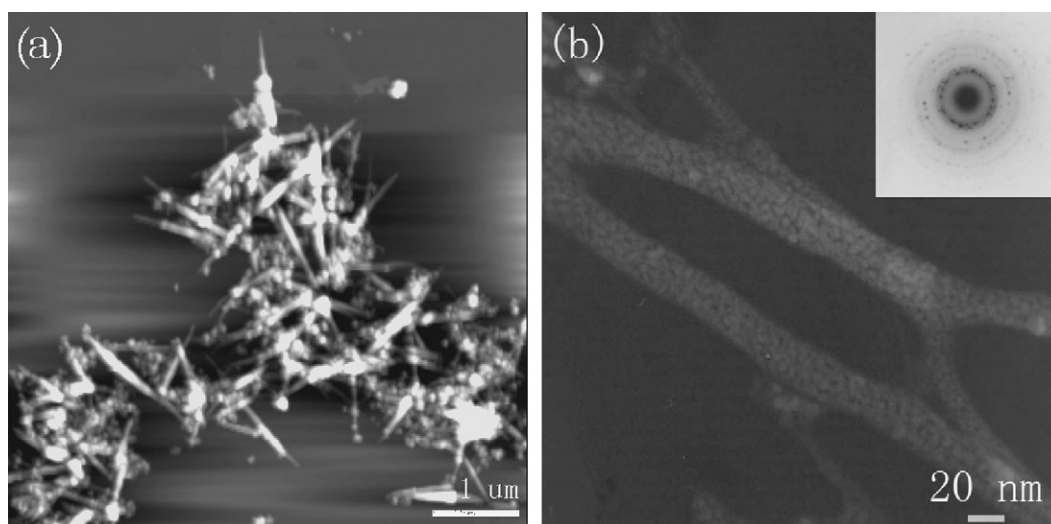


Fig. 1. (a) Tapping mode AFM image of silver nanowire after staying for 90 min (b) TEM images of silver nanowires, inset is the electronic diffraction pattern.

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