

Controlled Synthesis of Uniform Silver Nanowires via a Simple Polyol Process

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Abstract. Uniform silver nanowires were synthesized via a simple polyol process. Different aspect ratio of silver nanowires was obtained by regulating the concentration of ferric chloride and polyvinyl pyrrolidone, the maximum aspect ratio of synthesized silver nanowires is 570. The silver nanowires film with the aspect ratio of 240 was prepared and its conductivity was measured by four probe method. Controlled synthesis of uniform silver nanowires is crucial, silver nanowires will be the most promising material in the optical, electrical and photonic fields.

1. Introduction

Metal nanostructures have received considerable attention due to their unique optical, electrical, catalytic and photonic properties in the past years [1]. Silver nanowires (AgNWs), as a kind of one-dimension (1D) metal nanostructures, not only have the excellent electrical and thermal conductivity, but also have large specific surface area, high transparency, excellently flexible and bendable properties, it is one of the most promising materials in transparent conductive films (TCFs), conductive silver adhesive, nanowelding technology, solar cell and touchscreens, etc [2]. It is known that the excellent properties of nanostructures depend on their size, shape, composition and sequence. Therefore, it is necessary to explore a method which can effectively and controllably synthesize uniform AgNWs.

Many approaches to AgNWs have been explored, including the polyol process [3-5], microwave-polyol method [6], electrochemical technique [7], solvothermal process [8], ultraviolet irradiation [9], template technique [10]. Ilie et al. selected single-wall carbon nanotube as template and synthesized the AgNWs with ultra-low diameter of 1 nm [11]. Lee et al. used successive multistep growth (SMG) method and prepared the AgNWs with the maximum length of 400~500 μm in high concentration ion solution [12]. Polyol reaction solution was irradiated with MW microwaves, 1D nanostructures can be formed within minutes [13]. Most of these synthesis methods still have some limits in controllability and uniformity, and the process is relatively hard to operate.

Our group developed a controllable and convenient approach to the uniform AgNWs with different aspect ratio. AgNWs with different length and diameter were synthesized by a simple polyol process by adding different concentration of ferric chloride (FeCl_3) and polyvinyl pyrrolidone (PVP) into the reaction solution. A mechanism for regulating the structures of AgNWs has been proposed. The AgNWs film has been prepared and its conductivity was measured by the four probe method.



2. Experimental

2.1. Materials

Ethylene glycol (EG, analytical reagent (AR)) was purchased from Tianjin Yongda Chemical Reagent Company Limited. FeCl₃ and PVP (K88-96, Mw 1,300,000) were provided by Aladdin Industrial Corporation. Silver nitrate (AgNO₃, (purity 99.9%)) was purchased from Shanghai Fine Chemical Industry Material Research Institute. All chemicals and reagents are used without further purification. Deionized water was used throughout entire experiment.

2.2. Methods

0.2 g PVP was dissolved in 25 ml EG and 0.25 g AgNO₃ was added into PVP/EG solution to obtain solution A. 3.5 ml FeCl₃/EG (600uM) solution was poured into solution A under continuously vigorous magnetic stirring. Then the solution was added to a 250 ml round bottom flask and heated at 130°C for 5 hours in a silicon bath. The faint yellow solution changed to brownish red and then turned to milk white. The mixture was allowed to be cooled to room temperature in air for 1 hour. To acquire purified AgNWs, the mixture was diluted with acetone, deionized water and ethanol, washed and centrifuged 3 times to remove excess of EG and other reaction products. In the whole reaction, the EG acts as both reducing agent and solvent, surfactants such as PVP could control the growth rates of various faces of silver by coordinating to the surfaces, lead silver to grow into uniform nanowires, FeCl₃ as mediated and nucleation agent can react with and remove the adsorbed atomic oxygen from silver surfaces.

3. Results and Discussions

The controllable synthesis of uniform AgNWs was realized by regulating different concentrations of FeCl₃ and PVP. Figure 1 shows a series of SEM images of AgNWs with different concentrations of FeCl₃. There is no FeCl₃ in reaction solution, the product is sphere-like nanoparticles and no nanowires exist (see Fig. 1a). Adding FeCl₃ (0.3 mM) into the reaction solution, the product is AgNWs with diameter of 70~80 nm and length of 10 μm (shown in Fig. 1b). Increase the concentration to 1.2 mM, as shown in Fig 1c, horizontal and vertical dimensions of the product improve a little comparing to the AgNWs in the case of lower concentration, diameter is up to 80~90 nm and length increases by 2 μm. When the concentration of FeCl₃ increases to a higher level (2.4 mM), as shown in Fig. 1d, the growth of AgNWs is greatly promoted, its length reaches to 40 μm and diameter is up to 150 nm. In the entire concentration range, the aspect ratio of AgNWs varies from 250 to 533.

As we can see from Fig. 1, AgNWs were formed with the assistance of FeCl₃. Molecular oxygen is known to adsorb and dissociate to atomic oxygen on a silver surface, and Fe³⁺ can react with atomic oxygen indirectly to remove it. Therefore, multiple crystalline seeds can be produced in large numbers and existed. In addition, Ag seeds are selectively adsorbed by PVP molecules and grow up gradually. As for increase of the aspect ratio of AgNWs, it is proposed that the catalytic oxidation of Fe³⁺ decreases the number of Ag seeds, causing the increasing of concentration of free Ag atoms. In this way, probability of Ag atoms growing to the formed seeds increased, the horizontal and vertical growth of AgNWs is promoted.

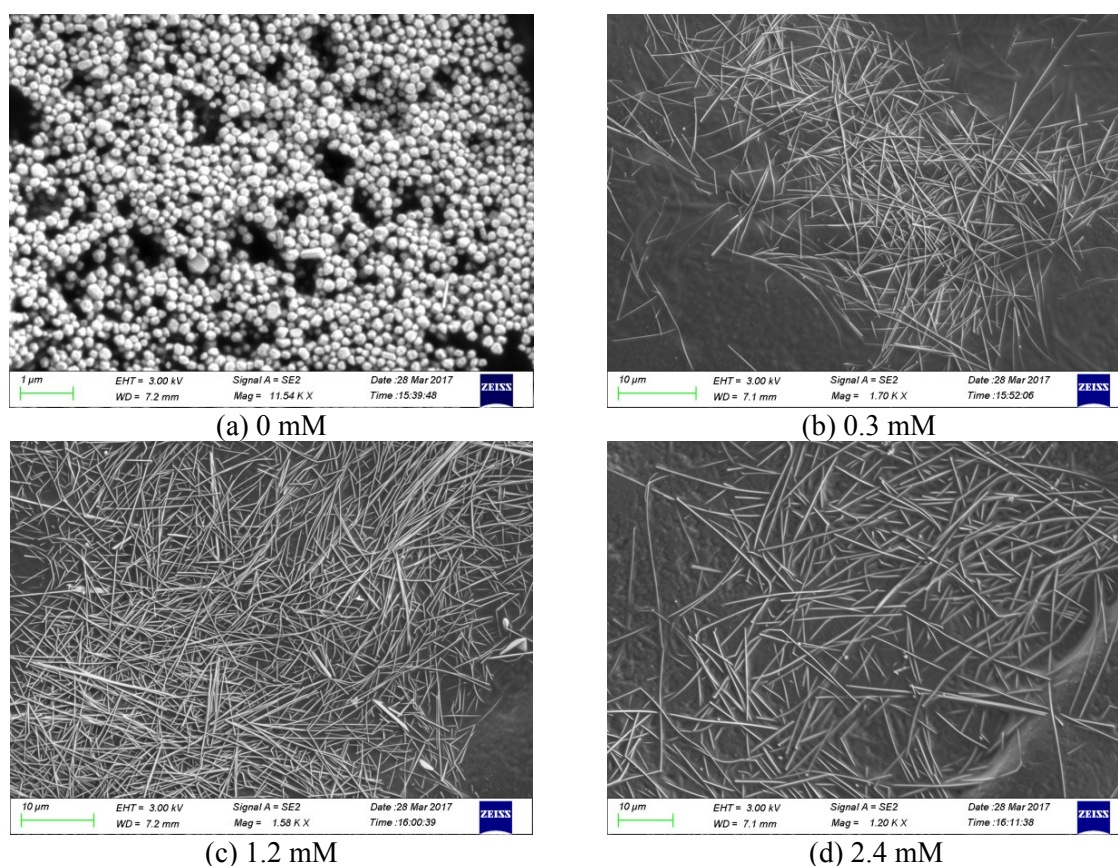
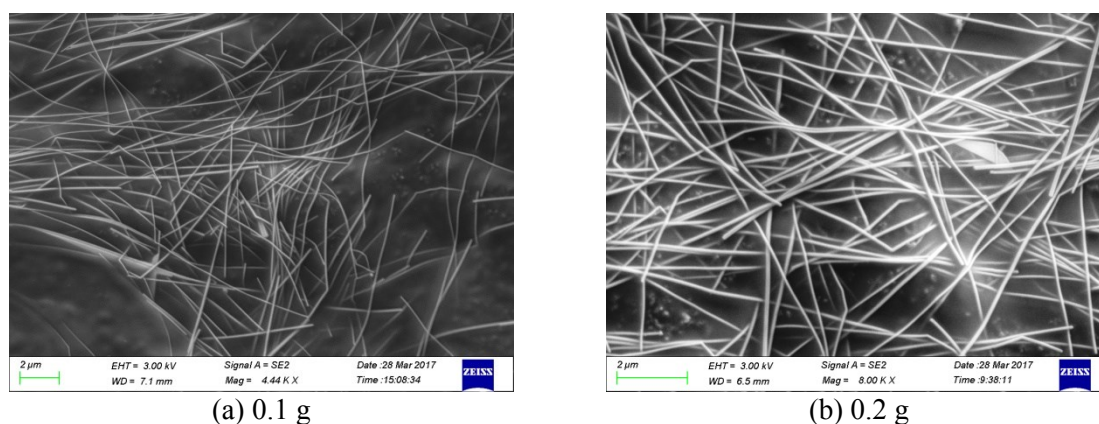


Figure 1. SEM images of AgNWs synthesized with different concentration of FeCl_3 .

Figure 2 shows several SEM images of AgNWs with different concentrations of PVP. Adding 0.1 g PVP into the reaction solution, as shown in Fig. 2a, AgNWs with diameter of 75 nm and length of 10 μm were produced. Increase the amount of PVP to 0.2 g, length of the products increases to 12 μm (see Fig. 2b). When the concentration of PVP is 0.3 g, AgNWs continue to grow, length is up to 17 μm , but diameter did not change (shown in Fig. 2c). When the amount of PVP is higher (0.4 g), as shown in Fig. 2d, AgNWs grow up constantly to a length of 20 μm and a diameter of 70 nm. In the whole experiment, slightly smaller size occurs in the diameter of the synthesized AgNWs, but its length increases from 10 μm to 20 μm gradually and the maximum aspect ratio increases by 1 times.



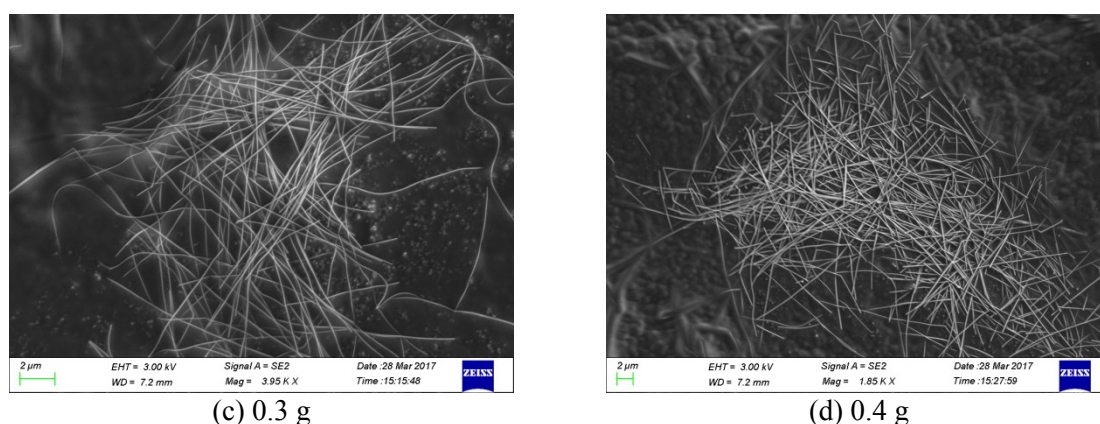


Figure 2. SEM images of AgNWs synthesized with different concentration of PVP.

PVP, as a polymeric surfactant, can selectively adsorb on the (100) facets of silver nanocrystals through O-Ag banding, in the way of absorption and desorption with different crystalline faces, it can kinetically control the growth rates. Analysis of the experimental results from Fig. 2, we propose that increase of the amount of PVP can slightly decrease the diameter of AgNWs due to the increase of PVP coverage of silver crystal surface, in this way, horizontal growth is promoted.

For the AgNWs product in Fig. 2b, we prepared an AgNWs films and measured its conductivity by four probe method. We poured the AgNWs ethanol solution into a glass groove with 4 cm×1.5 cm×1 cm. According to the silver density (10.6 g/cm³) and the mass of AgNWs film, the thickness of the film can be calculated as 10 μm. In order to obtain accurate film conductivity, we use FT-341 four probe devices which measurement error is less than 0.3%. Conductivity of the film is 2.21×10³ S/cm, lower than the standard silver (6.67×10⁵ S/cm), it is possible that contact resistance between adjacent AgNWs forming conductive lap is the cause.

4. Conclusions

Uniform AgNWs have been synthesized by a simple polyol process. Regulating the concentration of FeCl₃ and PVP can effectively control the morphologies of the products. In the entire experiment, the aspect ratio of AgNWs varies from 250 to 570. A possible growth mechanism of AgNWs was proposed. Four probe method was used to measure the conductivity of AgNWs film, test result show that its conductivity is 2.21×10³S/cm. AgNWs with different structure have potential applications in optical and electrical fields.

5. References

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