EFFECTS OF SYNTHESIS CONDITIONS ON THE FORMATION AND MORPHOLOGY OF SILVER NANOWIRES

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ABSTRACT

Silver nanowires with one-dimensional structures have attracted much research interest due to their potential applications in several areas. It is well-known that their properties strongly depend on the size and morphology of the silver nanostructures. Therefore, in our work, silver nanostructures were prepared using a polyol process and the effects of synthesis conditions on the formation and morphology of silver nanowires were investigated. The structure and morphology of the synthesized silver nanostructures were characterized using transmission electron microscopy (TEM) and X-ray powder diffraction (XRD). The results showed that the morphology of the silver nanowires can be effectively controlled via adjusting parameters of the synthesis process.

Keywords: silver, nanowires, one-dimensional, morphology control, polyol process.

1. INTRODUCTION

One-dimensional (1D) nanostructures have received much attention due to their different properties compared to bulk structures [1]. Due to the high electrical and thermal conductivity of silver (Ag) compared to other metals, their 1D structures attracted considerable attention. There have been several attempts to synthesize Ag nanowires. For instance, Sun et al. synthesized Ag nanowires with diameters about 30-50 nm, using PtCl₂ as the mediated agent [2]. Apart from PtCl₂, different mediated agents such as NaCl, CuCl₂, FeCl₃, KBr have been investigated for Ag nanowire synthesis [3-7]. Polyol method is often used for nanoparticle preparation due to its low cost, effectiveness and simplicity [8].

It is well-known that the morphology, shape and size of nanoparticles strongly affect their properties. Therefore, in this work, a polyol process was used to synthesize Ag nanowires and the effects of synthesis conditions, i.e. silver nitrate (AgNO₃) and poly(vinyl)pyrrolidone (PVP)
concentration, temperature and reaction time on the formation and morphology of the Ag nanowires were investigated.

2. METHODOLOGY

2.1. Chemicals

Silver nitrate (AgNO₃, 99.0 %), ethylene glycol (EG, 99.5 %), sodium chloride (NaCl, 99.5 %), potassium bromide (KBr, 99.0%) and ethanol (99.5 %) were purchased from Sigma Aldrich. Polyvinylpyrrolidone (PVP) was purchased from BDH Prolabo Chemicals.

2.2. Experimental

Firstly, 10 mL of EG and a certain amount of PVP were added to a three necked flask (equipped with a condenser, a thermometer and a magnetic stirring bar). The mixture was heated to 140-180 °C until the temperature was steady. After 3 min, 0.1 mL of a 0.1 mM KBr solution in EG was injected into the flask. The mixture was stirred for 3 min, then 0.1 mL of a 0.1 mM NaCl solution in EG was added into the solution. Then, a certain amount of 0.4 M AgNO₃ was added dropwise into the flask for about 6 min to avoid rapid supersaturation. The reaction temperature 140-180 °C was maintained throughout the process. After 60-150 min, the flask was cooled down to room temperature. Then, to remove the solvent, the sample was diluted with ethanol (at a volume ratio of 1:10) and centrifuged several times at 3000 rpm for 20 min to obtain the nanoparticles.

2.3. Characterization

The samples were characterized by transmission electron microscopy (TEM, JEOL 2010, at an acceleration voltage of 200 keV) and X-ray powder diffraction (XRD, D8 Bruker AXS X-ray diffractometer, CuKα radiation, 40 kV, 20 mA).

3. RESULTS AND DISCUSSIONS

3.1. Effect of PVP concentration

In the polyol method for the synthesis of silver nanowires, PVP is used as a polymeric capping agent which makes silver particles be confined and directed to grow into nanowires with uniform diameters. This process can be illustrated in Figure 1 [9].
In order to investigate the influence of PVP on the morphology of the obtained silver products, a series of experiments was proceeded at 160 °C with a fixed AgNO₃ concentration of 0.3M and various PVP concentrations of 0.4, 0.5, 0.6, 0.65, 0.7 and 0.75 M for 120 min. TEM results of all synthesized samples are shown in Figure 2 (a2 - f2), respectively.

Nanowires are defined as materials have the diameter in range of 10 - 200 nm, and the length in range of 5 – 100 μm [10]. According to this definition, the TEM results shown in Figure 2b2 and c2 indicate that the products are almost silver nanowires with 1D structures. When PVP amount is 0.5 or 0.6 M, the synthesized nanowire diameter is around 112 and 40 nm with the length from 1.5 to 5.0 μm and from 1.7 to 7.0 μm, respectively. Besides, the nanowire density displayed in Figure 2c2 (0.6 M) is higher than that in Figure 2b2 (0.5 M). On the other hand, Figures 2a2, d2 and f2 display only nanoparticles. The possible reason is that conducting the reaction at suitable PVP concentrations (0.5-0.6 M) leads to the formation of nanowires because PVP is absorbed on the (100) planes of Ag seeds. As a result, the anisotropic growth develops along only the (110) direction. Meanwhile, the lower concentration (0.4 M) or higher ones (0.65, 0.7, 0.75 M) generate only particles. When the PVP amount is inadequate, the (100) facets of Ag seeds cannot be totally covered, making them develop along both (100) and (110) facets. Meanwhile, the excessive PVP amount will cover all facets, blocking the anisotropic growth.

3.2. Effect of AgNO₃ concentration

The AgNO₃ concentration is considered one of the most crucial parameters in preparing nanowires by polyol method. Figure 3 (a3- f3) show the TEM images of samples synthesized with AgNO₃ concentrations of 0.1 M, 0.2 M, 0.3 M, 0.4 M, 0.45 M and 0.5 M at 160 °C with a PVP amount of 0.6 M and a reaction time of 120 min.
It can be observed in Figures 3c3 and 3d3 that the products are mostly silver nanowires with the diameter around 110 nm and 50 nm, the length from 1.3 to 4.0 µm and from 1.7 µm to 9.0 µm, respectively. Moreover, the density of wires in Figure 3d3 is extremely higher than the other. Other samples consist of only silver particles. Thus, AgNO₃ concentration of 0.4 M was applied to prepare all of the following samples.

![Image](image_url)

Figure 3. TEM images of silver nanowires synthesized with different concentrations of AgNO₃:
(a3): 0.10 M; (b3): 0.20 M; (c3): 0.30 M; (d3): 0.40 M; (e3): 0.45 M; (f3): 0.50 M.

### 3.3. Effect of reaction temperature

The reaction temperature plays an important role in the formation and morphology of silver nanowires. The reason is that this factor has a deeply effect on the reduction of seeding step which is one of the two most crucial steps during the process.

Figure 4 (a4 - e4) describes TEM images of prepared samples at different temperatures (140, 150, 160, 170 and 180 °C). It can be seen that the density of nanowires is changed due to the temperature variation. When the reaction temperature is 140 or 170 °C, the obtained products were mixtures of short silver wires and large aggregated particles. While the sample synthesized at 180 °C consist of only particles with size about 50 nm.

In contrast, TEM images of the samples at 150 °C and 160 °C (Figure b4 and c4) show almost nanowires. Especially, conducting this reaction at 150 °C resulted in the highest yields of nanowires with a diameter about 120-130 nm which is smaller than the value in Ma’s report (235 nm) [4] and 4.5 – 42.7 µm in length. Based on this data, the suitable temperature for silver nanowire synthesis is 150-160 °C. This is because of the conversion of ethylene glycol to glycolaldehyde, which served as a reducing agent, occurred above 140°C with the presence of oxygen in the air as shown in the reaction below.

\[
2\text{HOCH}_2\text{CH}_2\text{OH} + \text{O}_2 \rightarrow 2\text{HOCH}_2\text{CHO} + 2\text{H}_2\text{O}
\]
When operating the reaction system at 150 or 160 °C, the reducing agent is produced at a proper rate. As a result, the silver seeds are formed with an appropriate rate, the most significant factor facilitating the development of nanowires. Meanwhile, lower reaction temperature (140 °C) or higher temperature (170, 180 °C) caused the unfavorable thermal energy to the formation of nanowires, leading to a lot of particles in products.

*Figure 4.* TEM images of silver nanowires synthesized at different temperatures: (a4): 140 °C; (b4): 150 °C, (c4): 160 °C, (d4): 170 °C, (e4): 180 °C.

### 3.4. Effect of reaction time

*Figure 5.* TEM images of silver nanowires synthesized for different reaction time: (a5): 60 min, (b5): 90 min, (c5): 120 min.
TEM images in Figure 5 (a5, b5 and c5) demonstrate the development of silver wires prepared at 150 °C for 60, 90 and 150 minutes while maintaining the concentrations of PVP and AgNO₃ at 0.6 and 0.4 M, respectively. It can be seen that the longer reaction is, the longer length is achieved, from 6.7 to 42.7 μm. There is not so much difference in nanowire length between sample a5 and b5. However, the yield of nanowires in b5 is higher than a5. Adjusting reaction time to 120 minutes makes a significant rise in product’s length in c5.

3.5. XRD pattern of the silver nanowires

![XRD pattern of the silver nanowires](image)

*Figure 6. XRD pattern of the silver nanowires.*

After centrifuging several times for cleaning, the synthesized silver nanowire sample was dried at 70 °C in nitrogen atmosphere for XRD testing. The XRD pattern in Figure 6 shows that the sample has the FCC structure of silver. The peak positions are in coherence with a standard spectrum of silver metal (JCPDS file No. 04-0783) at 2θ of 38.3; 44.4; 64.5 and 77.5°.

4. CONCLUSIONS

The silver nanowires were synthesized via a polyol process with ethylene glycol. The effects of synthesis parameters (PVP concentration, AgNO₃ concentration, reaction temperature and time) on the formation and morphology of silver nanowires were studied in details. The results showed that the formation and morphology of the silver nanostructures can be effectively controlled via adjusting the synthesis conditions.

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