Investigation of freshly prepared AgCl for high yield silver nanowires under polyol method

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Abstract. Silver nanowires (Ag NWs) have attracted much interest in academics and industries because of their potential applications in electronic devices such as flexible displays, pressure sensors, temperature sensors, and conductive layers. Generally, silver nanowire synthesized by the polyol method is the most common and promising chemical reaction. However, its by-products, a mixture of Ag NWs and silver nanoparticles, reduced Ag NWs performance. In this work, we reported the chemical method that is a fast and straightforward synthesis of Ag NWs by using freshly prepared silver chloride to avoid its degradation. The result showed that the freshly prepared silver chloride plays an essential role in promoting the formation of Ag NWs. The by-product was lower compared to using commercial silver chloride. We also found that avoiding boiling bubbles in flask via controlling temperature and reaction time by injecting ethylene glycol, resulting in decreased nanowires degradation. Furthermore, instantaneously decreasing temperature after finishing the cooking time helps reduce its by-product. A high yield of Ag NWs is noticeable under the observed synthetics.

1. Introduction

Silver nanowires (Ag NWs) are an inexpensive and flexible component of transparent conductive layers with a wide range of applications, including nanoelectronics with low optical extinction [1, 2], temperature sensors [3], strain and pressure sensors [4], substrates for surface-enhanced Raman [5]. Silver nanowires are commonly made using the polyol synthesis method, which involves dissolving silver nitrate in ethylene glycol with PVP as a stabilizing agent and a metal halide [6]. A wet chemical technique is the most promising method for generating Ag NWs. On the other hand, by-products might occur during the process, lowering Ag NWs performance. Although this technique has several advantages, it frequently produces a mixture of Ag NWs and silver nanoparticles as by-products, which cannot be ignored [7]. This study aims to use freshly prepared silver chloride to reduce the development of by-products during the synthesis of Ag NWs. We also investigated the different amounts of freshly prepared silver chloride and the injection rate of ethylene glycol to maintain the constant temperature. These two factors are crucial in improving Ag NWs while drastically reducing their by-products.
2. Experimental

Chemicals and Materials. Commercial Silver chloride (AgCl, 99.9%) and silver nitrate (AgNO₃, 99.9%+) were purchased from Alfa Aesar. Sodium chloride (NaCl, 99%+) was purchased from Acros Organics. Polyvinylpyrrolidone (PVP, Mw ≈ 55000, powder) and ethylene glycol (anhydrous, 99.8%) were purchased from Sigma-Aldrich. Acetone (99.5%) was purchased from LOBA Chemical and iso-propyl alcohol (IPA, ≥99.8%) was purchased from Fisher Scientific. All the chemicals were used without any purification step.

Synthesis of AgCl. This synthesis is performed in the dark due to the photosensitivity of AgCl. Silver nitrate aqueous solution (1 mL, 0.5 M) is mixed with sodium chloride aqueous solution (1 mL, 0.5 M) then silver chloride immediately precipitated. The silver chloride was clean by DI water several time and then store in acetone before using.

Synthesis of Ag NWs. A modified polyol method was used to synthesized Ag NWs. In briefly, 0.217 g of PVP (Mw ≈ 55000) was added to 60 mL of ethylene glycol in a 100 mL three-neck round-bottom flask. The solution was heated to 168 °C under stirring at 510 rpm. At the same time, AgNO₃ 0.3 g was dissolved by EG 0.6 mL in a separated vial. Once the solution has a stable temperature, the freshly prepared AgCl was added and then the solution turned from transparent to light yellow. After 20 min, the prepared AgNO₃ solution was injected to the flask. Ag NWs appeared as gray color and was cooked for a designed time before quickly cooling the solution to room temperature.

Measurements. The UV-VIS Spectrophotometer (UV-vis) and Scanning electron microscopy (SEM).

3. Results and discussion

Freshly synthesized AgCl was used instead of commercial AgCl to create Ag NWs. Figure 1 shows SEM images of Ag NWs created with commercial AgCl and freshly synthesized AgCl. Figure 1a showed a mixture of nanowires and nanoparticles of various sizes and shapes when Ag NWs were made by commercial AgCl. In contrast, the by-products of Ag NWs created with freshly synthesized AgCl (Figure 1b) are barely visible.

Figure 1. Scanning electron microscopy images of Ag NWs comparison by using (a) commercial AgCl and (b) freshly prepared AgCl.

Moreover, UV–vis spectra of Ag NWs made commercial AgCl and freshly prepared AgCl are conducted as seen in Figure 2. The results show the peak of Ag NWs using freshly generated AgCl is narrower than the peak of Ag NWs using commercial AgCl. This indicated that Ag NWs using freshly prepared AgCl have a low yield of by-products than Ag NWs using commercial AgCl.
Although freshly prepared AgCl can reduce nanoparticles, AgCl concentration is also crucial for Ag NWs formation. The amount of freshly prepared AgCl was investigated, including 1.7 mg, 10 mg, 15 mg and 20 mg. Figure 3 shows the SEM images of Ag NWs prepared at different concentrations of AgCl. Numerous nanoparticles are formed as by-products when 20 mg of AgCl is used (Figure 3d). The lowest concentration of AgCl 1.7 mg (Figure 3a), on the other hand, barely observed the by-products. The results are also confirmed by UV-vis spectra in Figure 4 as comparative spectra for various conditions. Figure 4a shows that Ag NWs synthesized with freshly prepared AgCl 1.7 mg has the narrowest peak compared to the others.

Figure 2. Absorbance of UV vis spectra of commercial AgCl (dash line) and freshly prepared AgCl (solid line).

Figure 3. SEM images of Ag nanowires grown with the polyol process by various amounts of freshly prepared AgCl, which are 1.7 mg (a), 10 mg (b), 15 mg (c) and 20 mg (d).

Figure 4. a. UV vis spectra of various freshly prepared AgCl concentration 1.7 mg (solid line), 10 mg (dot line), 15 mg (dash dot line) and 20 mg (dash line), b. UV vis spectra of varying EG injection rate 0.25 mL/min (dash dot dot line), 0.5 mL/min (dot line) and 0.75 mL/min (dash line), c. Comparison of UV vis spectra between AgCl 10 mg (dot line) and 1.7 mg (solid line) at the similar EG injection rate.
In addition to the AgCl study, we investigated injecting ethylene glycol to maintain a steady temperature in the process to avoid a boiling bubble. With the same amount of AgCl, multiple rates of injecting ethylene glycol are investigated, including 0.25 mL/min, 0.5 mL/min, and 0.75 mL/min. As seen in Figure 4b, the high-rate injection of ethylene glycol produces the lowest amount of by-products while the low-rate injection produces a higher amount of by-products. Therefore, the injection rate plays a role in minimizing the by-products of Ag NWs. We also compare the similar injection rate with different amounts of AgCl. Both UV curves are not much different at a similar injection rate around 0.75 mL/min with a high different amount of AgCl 1.7 mg and 10 mg (Figure 4c). By adjusting another parameter, we can compare the effects of the EG injection rate (Figure 4b) and the amount of AgCl (Figure 4a). Surprisingly, the data suggest that the rate of EG injection has a more significant impact than the amount of AgCl. It may also be demonstrated by setting the amount of AgCl and altering the EG injection rate (Figure 4b), resulting in UV curve broadening. Furthermore, immediately lowering the temperature after the cooking period helps reduce by-products.

4. Conclusions

In this experiment, we present a simple and fast one-pot method to synthesize a high yield of silver nanowires along with reducing its by-products. The result showed that the freshly prepared silver chloride plays an essential role in reducing by-products compared to commercial silver chloride. In addition, we also found that avoiding boiling bubbles in reaction through maintaining temperature by injecting ethylene glycol will lower the by-products.

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