Rapid Synthesis of Silver Nanowires

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Abstract

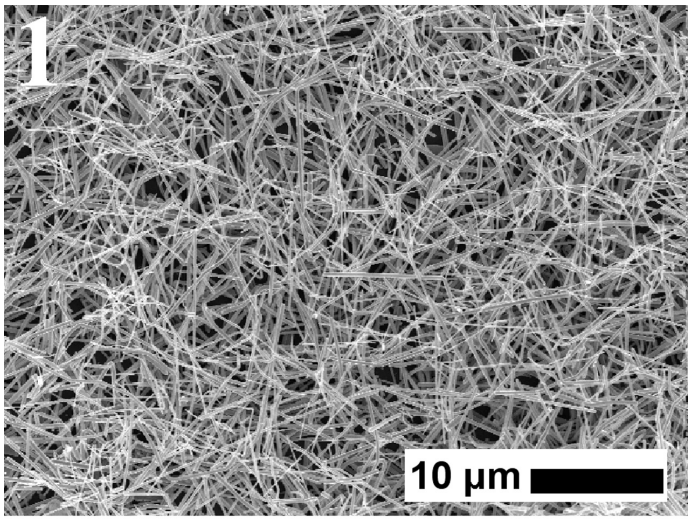
The presence of either copper(I) or copper(II) chloride in the polyol reduction of silver nitrate facilitates the production of silver nanowires. Silver nanowires have applications in many areas, including electronics and catalysis. These wires are produced quickly (in approximately one hour), with the synthesis being easily performed in disposable glass vials, using only pipettes to deliver reagents. Specifically, silver nitrate is reduced by ethylene glycol in the presence of poly(vinylpyrrolidone) (PVP) and copper(II) chloride. PVP acts as a stabilizing agent, while the copper chloride likely controls the rate of silver(I) reduction and initial seed formation. Our results indicate that both the copper and chloride ions are necessary to synthesize the wires; otherwise, ill-defined silver particles are formed. Scanning electron microscopy (SEM) has been used to characterize the wires.

Introduction

Metallic nanostructures have a wide range of properties and applications. These properties and applications are determined by the shape, size, structure, and composition of the nanostructures. The presence of various ions has been shown to influence the shape and size of metallic nanostructures produced via the polyol method. For example, previous research done by the Xia group has shown that the presence of iron(II) or iron(III) ions in the polyol synthesis facilitates the growth of silver nanowires or cubes, depending on the concentration of the iron ions [1]. A study of copper salts has shown that the presence of copper(I) or copper(II) chloride in the polyol reduction of silver nitrate allows for the production of silver nanowires, which can be used in many areas, including electronics and catalysis [2].

Experimental Procedure

The polyol method involves the reduction of a metal salt precursor by a polyol, a compound containing multiple hydroxyl groups. The polyol used in this synthesis, ethylene glycol, served as both the reducing agent and solvent. 5 mL of ethylene glycol was heated at 150°C for one hour with stirring (260 rpm). This pre-heating was done in disposable glass vials placed in an oil bath. 40 μL of a 4 mM $CuCl_2 \cdot 2H_2O$/ethylene glycol solution was added, and the solution was allowed to heat for 15 minutes. 1.5 mL 114 mM PVP/ethylene glycol was then added to each vial, followed by 1.5 mL 94 mM $AgNO_3$/ethylene glycol. All reagents were delivered by pipette. The reaction was stopped when the solution became gray and wispy, after approximately one hour. The reaction was stopped by submerging the vials in cold water. The product was washed once with acetone and three times with deionized water.



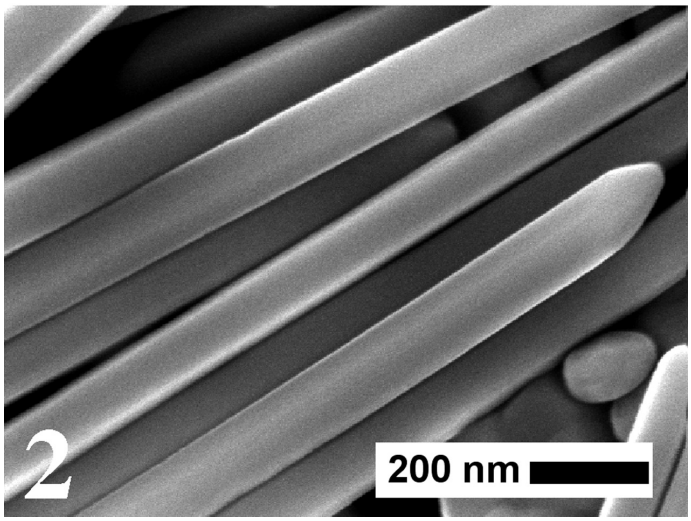


Figure 1: SEM of silver nanowire.

Figure 2: Higher magnification SEM of silver nanowires.

Results and Conclusions:

The produced wires were relatively uniform in shape and size. They had a pentagonal cross-section, as determined by scanning electron microscope (SEM), and were, on average, approximately 10-50 μm in length.

These wires were also present in high yield (approximately 90% relative to other structures) and were produced in approximately one hour after the addition of all reagents. Figures 1 and 2 show SEM images of the wires produced.

One of the advantages of this particular synthesis is its simplicity. To avoid supersaturation of the reaction media and thus particle formation, typically a syringe pump is required to controllably add reagents. Here, we are able to prepare silver wires in high yield without a syringe pump, which may not be available in all laboratories due to costs. The vial setup allows the reaction to be scaled up by simply running the reaction in additional vials. This setup of vials also allows a range of variables, such as concentration or temperature, to be tested at once.

To elucidate the role of copper(II) chloride, several controls were run. Sodium chloride and copper(II) nitrate were used to test the effect of each ion on this synthesis (sodium and nitrate ions are spectators and should have no effect on this synthesis). As shown in Figure 3, when only copper(II) nitrate is present, only particles are produced. Similarly, as shown in Figure 4, when only sodium chloride is present, only particles are produced. However, when both copper(II) nitrate and sodium chloride were added, wires were produced, indicating that both ions are necessary for wire growth.

Previous reports indicate that chloride ions can help stabilize initial silver seeds, preventing agglomeration, while Cl^-/O_2 has been shown to etch seeds [3]. To further investigate the function of copper(II) in this synthesis, further experiments were performed using copper(I) chloride. As with copper(II) chloride, copper(I) chloride facilitates silver wire formation. This result suggests that the redox behavior of the copper additives helps to control the reduction of silver nitrate and avoid initial supersaturation.

Future Work

To better understand this proposed mechanism, trials run in an inert atmosphere are now underway to determine the role of oxygen in this synthesis.

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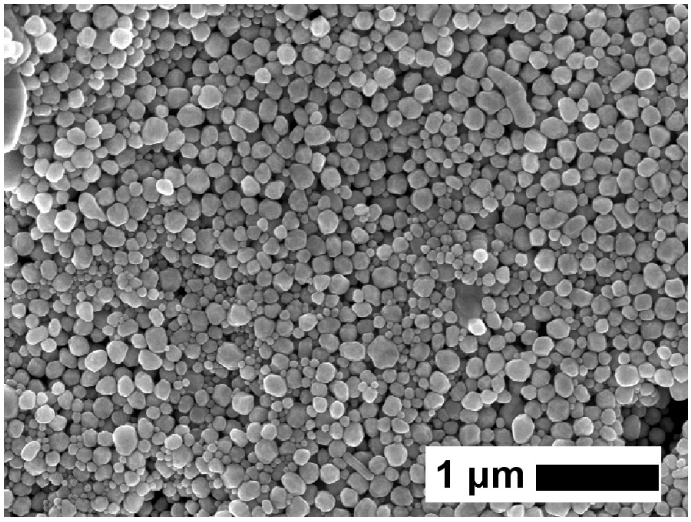
References

[1] Wiley, B., et al; "Polyol Synthesis of Silver Nanostructures: Control of Product Morphology with Fe(II) or Fe(III) Species"; Langmuir, 21, 8077-8080 (2005).

[2] Xia, Y., et al; "One-Dimensional Nanostructures: Synthesis, Characterization, and Applications"; Advanced Materials, 15, 353-389 (2003).

[3] Wiley, B., et al; "Polyol Synthesis of Silver Nanoparticles: Use of Chloride and Oxygen to Promote the Formation of Single-crystal, Truncated Cubes and Tetrahedrons"; Nano Letters, 4, 1733-1739 (2004).



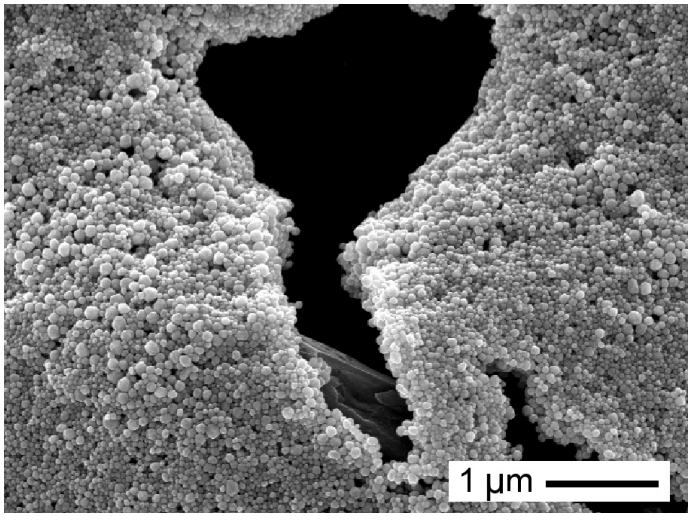


Figure 3, top right: SEM of sample produced in the presence of copper(II) nitrate (no Cl present).

Figure 4, bottom right: SEM of sample produced in the presence of sodium chloride (no Cu present).