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High yield polyol synthesis of round- and sharp-end silver nanowires with high aspect ratio

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HIGHLIGHTS

- Long silver nanowires with high aspect ratio of 130 were produced.
- More than 95% nanowires were produced in products.
- The produced nanowires had round- and sharp-ends with pentagonal cross section.
- Additives were needed neither for high yield synthesis nor for round-end nanowires.
- Melting and etching of MTPs in high energy borders resulted to round-end nanowires.

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ABSTRACT

Long silver nanowires (average length of 28 μm, average aspect ratio of 130) with uniform diameter along their length were produced by polyol synthesis of $AgNO_3$ in ethylene glycol in the presence of PVP as preferential growth agent. Nanowires were produced with no addition of chloride salts such as NaCl or $CuCl_2$ (or other additives such as Na_2S) which are usually used for lowering reduction rate of Ag ions by additional etchant of O_2/Cl^-. Lower reduction rate was obtained by increasing the injection time of PVP and $AgNO_3$ solutions, which was the significant factor in the formation of nanowires. Therefore, there was enough time for reduced Ag atoms to be deposited preferentially in the direction of PVP chains, resulting in high yield (the fraction of nanowires in the products) of nanowires (more than 95%) with high aspect ratio. The produced nanowires had both round- and sharp-ends with pentagonal cross section. Higher energy level of Ag atoms in borders of MTPs, which increases the dissolution rate of precipitated atoms, in addition to partial melting of MTPs at high synthesis temperatures, leads to the curving of the surfaces of exposed (111) crystalline planes in some MTPs and the formation of round-end silver nanowires.

1. Introduction

Liquid phase synthesis is widely used for production of silver nanowires because of the advantages including homogenous reaction, wide range of usable solvents, simple monitoring of the reactions, low cost and the possibility of scaling up the process [1]. Polyol method is a highly attractive synthesis route among liquid phase synthesis methods. Polyol synthesis is defined as heating a polyol with a salt precursor and a polymeric capping agent, which in the case of silver nanostructures, it can be ethylene glycol (EG), silver nitrate ($AgNO_3$), and poly(vinyl pyrrolidone) (PVP), respectively [2]. In some researches, nanowires were grown using initial seeds of silver nuclei produced from an initial seeding step [3,4]. Sun et al. [5] stated that a seeding step is the key to the formation of uniform silver nanowires. Moreover, some additives such as ammonium carbonate [6], sodium sulfide [7–9], copper chloride [10] or sodium chloride [11–15] were used as the key factor for producing uniform silver nanowires. Schuette and Buhro [13] presented a polyol method for the production of silver nanowires in the presence of NaCl. NaCl accelerated the formation of nanocubes which served as the seeds for the subsequent formation of nanowires. These nanocubes introduced some inhomogeneity in the shape of nanowires by attaching to one end of nanowires. Coskun et al. [14] showed, using SEM micrographs, that in their typical synthesis, addition of NaCl was essential for the production of nanowires and in the absence of NaCl, only Ag nanoparticles were

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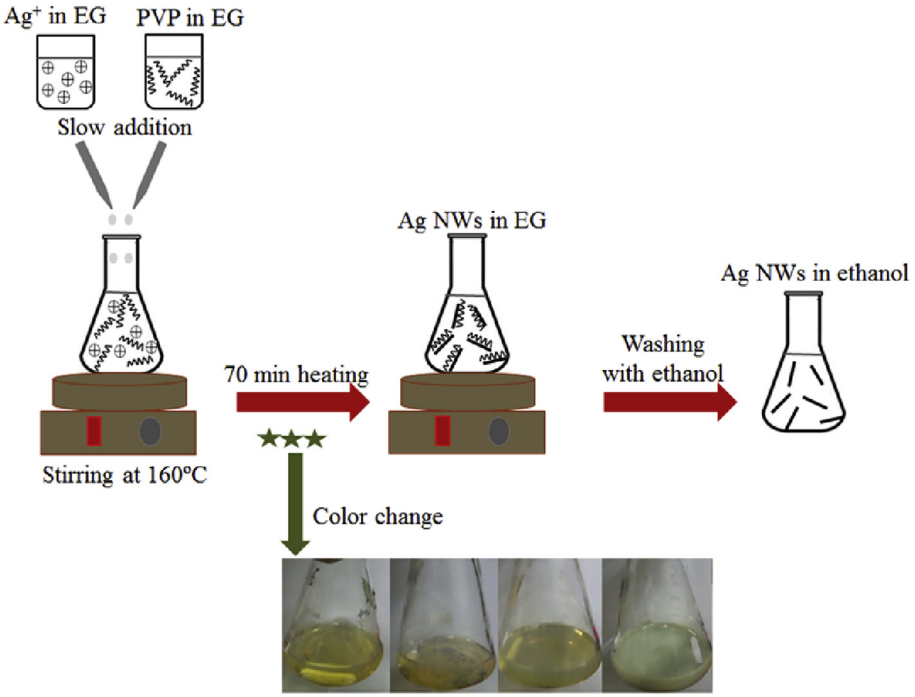

Fig. 1. Schematic representation of the polyol synthesis of Ag nanowires.

produced. Li et al. [15] described that the presence of NaCl is essential due to the formation of silver chloride (AgCl) which consumes the silver ions and decreases the rate of nucleation which let the silver atoms to deposit preferentially along the PVP chains. Nghia et al. [16] suggested that the chloride ions are necessary in the synthesis of silver nanowires in order to control the reduction rate of silver and to form initial seeds. Liu and coworkers [6] reported that in the synthesis of silver nanowires, the additives such as $(NH_4)_2CO_3$ could also control the relative concentration of Ag^+ and Ag^0 atoms with dissociation of CO_3^{2-} ions and NH_3 which react with Ag^+ to form Ag_2CO_3 and Tollens reagent, respectively. Chen et al. [8] and Tang et al. [9] synthesized silver nanowires in the presence of sodium chloride. They mentioned that Ag_2S, produced in the initial stage of the formation of silver seeds, reduces the concentration of free Ag^+ ions and hence, silver nanowires are grown preferentially due to slow reduction of silver atoms. Dodecylamine is another additive which acts as complexing, reducing and capping agent in the preferential synthesis of silver nanowires in ethanol-based medium [17]. Although in the mentioned researches, using seeds or additives, other than PVP, was mentioned to be critical for the formation of nanowires, there are also valuable researches that did not use them [18–21]. In these researches, by varying different synthesis parameters such as injection rate, $AgNO_3$ concentration, PVP to $AgNO_3$ molar ratio, synthesis temperature, molecular weight of PVP, etc., silver nanowires were produced as the major product.

Using initial seeds and additives or not, It is widely accepted that multiply twinned particles (MTPs) are essential for the formation of nanowires [5,20,22]. In the growth criteria, in addition to MTPs, the existence of a surfactant such as PVP is necessary for the formation of nanowires with preferential growth of (111) facets. Growth of (111) facets in MTPs in the presence of PVP results in the formation of nanowires [1]. The most famous mechanism for the growth of nuclei to any shape of product is Ostwald ripening which is the dissolution of fine particles and redeposition of the dissolved species on the surfaces of larger particles [20]. The presence of MTPs and PVP are essential for the formation of nanowires. The synthesis of AgNWs was widely investigated considering these two essentials. Although MTPs are the seeds that result in the formation of nanowires, it is hard to prevent the formation of single-twinned particles (STPs) which results in the formation of nanoparticles. Therefore, the formation of nanoparticles in the polyol synthesis of nanowires is inevitable [6]. Synthesis of nanowires by very high yield process is essential in order to prevent wasting initial materials as byproducts.

Regarding the shape of nanowires, it was highly mentioned in the previous researches [5,20,22–24] that decahedral MTPs result in sharp tips with pentagonal shape in cross sections of the nanowires. Liu et al. [6] have shown that these nanowires have round-end shape due to the partial melting of the MTPs and the presence of additions of NH_3 and CO_3^{2-} other than etchant of NO_3^- in an $(NH_4)_2CO_3$-mediated polyol medium.

In the present work, it was shown that there is no need for additives other than PVP for production of silver nanowires. Uniform nanowires with high aspect ratio were synthesized via high yield polyol process. The growth of nanowires was investigated during synthesis using SEM micrographs. The end shapes of nanowires were analyzed using SEM to show their round- or sharp-ends. The effects of synthesis parameters on the yield and aspect ratio of produced nanowires were also investigated.

2. Materials and methods

The statistical method of response surface methodology (RSM) was used for analyzing the best synthesis condition to receive the maximum length of nanowires and the highest synthesis yield. Using RSM, polyol synthesis was performed at different conditions by varying the initial concentration of $AgNO_3$ from 0.07 to 0.1 M and the molar ratio of PVP/$AgNO_3$ from 1.5 to 4.5 at different temperatures of 150–170 °C. The results of this method were reported in another paper (unpublished work). The best synthesis condition obtained at the temperature of 160 °C, 0.085 M $AgNO_3$ and PVP/

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