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Glycerol and ethylene glycol co-mediated synthesis of uniform multiple crystalline silver nanowires

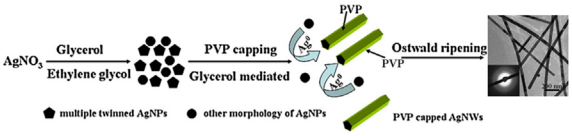
Changchao Jia, Ping Yang*, Aiyu Zhang

Shandong Provincial Key Laboratory of Preparation and Measurement of Building Materials, Key Laboratory of Inorganic Functional Materials of Shandong Universities, School of Material Science and Engineering, University of Jinan, 250022 Jinan, PR China

HIGHLIGHTS

- Multiple crystalline uniform silver nanowires created by a facile one-pot polyol-thermal method.
- The silver nanowires were fabricated using glycerol together with ethylene glycol.
- The yield of the silver nanowires dependent on the volume ratio of ethylene glycol and glycerol.
- V-shaped silver nanostructure was obtained through adjusting parameters.

GRAPHICAL ABSTRACT



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ABSTRACT

The large scale synthesis of multiple crystalline silver nanowires (NWs) with uniform diameter were carried out by using glycerol and ethylene glycol (EG) as co-mediated solvents in the presence of poly(vinyl pyrrolidine) (PVP). Experimental results and structural characterizations reveal that Ag NWs are evolved from the multiple crystalline seeds initially generated by the reduction of $AgNO_3$ with EG and glycerol. Owing to the different reduction ability and viscosity of EG and glycerol, which play an important role for controlling the nucleation at the beginning of reaction, glycerol with high viscosity slows down the migration velocity of Ag^0 in favor of forming the uniform Ag NWs with small diameter (40 nm) in the presence of PVP molecules selectively adsorbed on the surface of Ag seeds. The yield of the Ag NWs is dependent on the volume ratio of EG and glycerol. In the absence of EG, large amount of Ag nanoparticles (NPs) and few Ag NWs were created. In contrast, Ag nanorods and polyhedral particles are prepared in the case of no glycol added. This paper provides a new approach for the large scale synthesis of Ag NWs with uniform diameter by simply adjusting the solvent components. Furthermore, V-shaped Ag nanostructure was obtained and the possible growth mechanism was discussed.

1. Introduction

Over the past few decades, metallic nanomaterials have received intensive attention owing to their unique physical and chemical properties compared to the bulk solid [1–3]. One-dimensional (1D) metallic nanomaterials in which carrier motion is restricted in two directions exhibited significant electron-transport properties [4,5]. Among the metals, the synthesis of silver nanowires (NWs) has been widely investigated due to the high electrical and thermal conductivities of bulk silver. In addition, Ag NWs have exhibited important applications in various fields such as optical sensing, plasmonics, catalysts, as well as in biomedical and chemical sensors via surface-enhanced Raman scattering (SERS) and surface-enhanced fluorescence [6–10]. In recent years, Ag NWs with a high aspect ratio are used to fabricate transparent conductive electrodes for touch panel display because of their excellent electrical conductivity (6.3×10^5 S cm^{-1}) [11]. In addition, Ag NWs have been used as unique template to synthesize Au and TiO_2 nanotube [12,13].

* Corresponding author. Tel.: +86 531 89736225; fax: +86 531 87974453.
E-mail address: mse_yangp@ujn.edu.cn (P. Yang).

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To promise the applications of Ag NWs, it is critical to synthesize uniform NWs with high quality and yield to realize practical requirements. A number of methods have been exploited to synthesize nanostructures. These methods can be classified into mainly several categories: template, seed-mediated, electrochemical, photochemical reduction, ultraviolet irradiation, microwave-assisted, and solvothermal method. The template method with a lot of disadvantages such as the preparation and removal of template is costly and troublesome, as well as the yield and size are restricted by the template. A seed-mediated growth method is consisted of two steps: the preparation of crystal seeds and the growth process from seeds to NWs. It is necessary for a photochemical reduction method to control many experimental parameters. In terms of cost, yields and simplicity, a polyol method, by which nanoproducts are produced by the reduction of precursors with the help of anisotropic growth directed by surfactant and polyol served as reductant and solvent, seems promising.

A polyol synthesis as an excellent method for the synthesis of metallic nanostructures was reported by Fievet et al. [14] for the first time. Subsequently, the method was developed by researchers to synthesize the nanostructures with various morphologies through changing experimental parameters. Xia et al. [15] synthesized Ag NWs with high aspect ratios through controlling the injection rate of an $AgNO_3$ and PVP solution using ethylene glycol (EG) as solvent and reductant. For the formation of Ag NWs with high yield, low precursor concentration and slow addition rate are crucial. Multiple-twined particles formed at the initial stage through slowing addition rate, and then served as seeds for the growth of Ag NWs, which is the so-called self-seeding process. In this case, an injection pump was used during preparation for precisely controlling the injection rate.

In recent years, control agents have been widely investigated to synthesize Ag NWs with simple manipulation. The addition of a trace of amount of salts, such as Fe (II) or Fe (III) salts or $CuCl/CuCl_2$, has been used to synthesize Ag NWs. It has been found that these salts played a same role. The investigations of mechanism elucidated that these variable valency metal ions with low valence can remove oxygen from the solvent preventing twinned seeds dissolved by oxidative etching during initial formation of seeds and scavenging absorbed atomic oxygen from the surface of the seeds, and formation of AgCl colloid resulted in slow releasing Ag^+ to the solution, which facilitates the formation of Ag NWs.

Recently, a new method for the synthesis of Ag NWs has been studied by An and co-workers [16]. They provided a way to produce single crystalline Ag NWs using insoluble salts (AgCl nanocubes) via a glycerol-mediated solution route. To prepare uniform Ag NWs, a reaction temperature (220 °C) is normally necessary, owing to the redox potential of AgCl/Ag ($\varphi^{\theta}_{AgCl/Ag} = 0.22$ V) is much lower than that of Ag^+/Ag ($\varphi^{\theta}_{Ag+/Ag} = 0.80$ V). Herein, uniform multiple crystalline Ag NWs were prepared by a facile and new method using glycerol and EG co-mediated in the presence of PVP. It is for the first time to prepare Ag NWs with a high yield and uniform diameter in the mixed solvents (glycerol and EG) without addition of any exotic seeds and salts using a facile method. EG and glycerol play an important role for controlling the nucleation at the beginning of reaction, subsequently, glycerol with high viscosity slows down the migration velocity of Ag^0 in favor of forming the uniform Ag NWs. Furthermore, V-shaped Ag NWs were also obtained by adjusting the preparation parameters.

2. Experimental

2.1. Synthesis of Ag NWs

All chemicals were used as received without any further purification. For a typical synthesis, PVP (K-30, $M_w \sim 40{,}000$) was dissolved in the solution of 10 mL glycerol and definite amount of EG. Meanwhile, 0.034 g of $AgNO_3$ was dissolved in 5 mL of glycerol solution. Two kinds of solution as then mixed together. The mixed solution was further stirred for uniformity and then transferred into a 100 mL Teflon-lined autoclave and then put in an oven at 200 °C for 5 h. The resulting sample were rinsed with deionized water ($\rho \sim 18$ MΩ·cm) and centrifuged at 4000 rpm to remove PVP and polyols. As prepared samples were then redispersed in water for further characterization. In our synthesis, the amount of $AgNO_3$ and glycerol were set as 0.034 g and 15 mL, respectively, unless stated especially, and the amount of EG was changed from 0 to 5 mL. The preparation conditions of samples are demonstrated in Table 1.

2.2. Characterization

The morphology observation of samples was carried out using a field emission scanning electron microscope (FESEM, QUANTA 250 FEG, FEI, America). The transmission electron microscopy (TEM) observation and selected area electron diffraction (SAED) pattern of samples were taken using a JEM-2010 electron microscope. The absorption spectra of samples were recorded using a conventional spectrometer (Hitachi U-4100) at room temperature with a quartz cell. The crystal structures and phase composition of samples were identified using an X-Ray Diffraction (XRD) meter (Bruker D8-Advance, Germany).

3. Results and discussion

Fig. 1a shows the SEM image of Ag NWs synthesized at 200 °C with reaction time for 5 h. It is clearly shown that Ag NWs with a length up to 10 μm have been created with high yield. The color of as-prepared sample in the inset of Fig. 1a is gray. Further detailed structure was investigated using TEM observation and SAED analysis. As shown in Fig. 1b, the diameter of Ag NWs is about 40 nm. According to the SAED pattern shown in the inset of Fig. 1b, Ag NWs are multiple crystalline. Fig. 1c shows the typical XRD pattern of Ag NWs. The diffraction peaks occurring at 38.1°, 44.3°, 64.5°, 77.5°, and 81.6° are indexed as (111), (200), (220), (311), and (222) facets, being consistent well with a face-centered-cubic (fcc) Ag crystalline structure (lattice constants $a = b = c = 4.086$ Å, JCPDS 04-0783). No peaks for other crystal types are observed. The sharp diffraction peaks indicated the sample having a high crystallinity. Furthermore, the relative high intensity ratio of the (111) to (200) peaks indicates as prepared samples are Ag NWs.

In our experiments, EG and glycerol were mixed as solvents for the synthesis of Ag NWs. The volume ratio of EG and glycerol is crucial for the formation of uniform Ag nanostructures. For

Table 1
Preparation conditions of Ag NWs.

Sample	$AgNO_3$ (g)	PVP (g)	EG (mL)	Glycerol (mL)	Temperature (°C)	Reaction time (min)
1	0.034	0.067	N/A	15	200	300
2	0.034	0.067	0.5	15	200	300
3	0.034	0.067	1	15	200	300
4	0.034	0.067	3	15	200	300
5	0.034	0.067	5	15	200	300
6	0.034	0.067	15	N/A	200	300
7	0.034	0.067	3	15	200	3
8	0.034	N/A	3	15	200	300
9	0.034	0.044	3	15	200	300
10	0.034	0.088	3	15	200	300
11	0.034	0.066	0.25	15	200	180
12	0.034	0.044	0.25	15	200	180