Materials Letters 213 (2018) 23–26

Contents lists available at ScienceDirect

Materials Letters

journal homepage: www.elsevier.com/locate/mlblue

Behind the role of bromide ions in the synthesis of ultrathin silver nanowires

Pei Zhang [a,b,c,d], Yanlong Wei [a,b,d], Ming Ou [a,b,d], Zhenzhu Huang [a,b,d], Shudong Lin [a,b,d], YuanYuan Tu [a,b,d], Jiwen Hu [a,b,c,d,*]

[a] Guangzhou Institute of Chemistry, Chinese Academy of Sciences, Guangzhou 510650, PR China
[b] Key Laboratory of Cellulose and Lignocellulosics Chemistry, Chinese Academy of Sciences, Chinese Academy of Sciences, 510650, PR China
[c] The University of the Chinese Academy of Science, Beijing 100039, PR China
[d] Guangdong Provincial Key Laboratory of Organic Polymer Materials for Electronics, 510650, PR China

ARTICLE INFO

Article history:
Received 28 August 2017
Received in revised form 18 October 2017
Accepted 30 October 2017

Keywords:
Electronic materials
Nanocrystalline materials
Nanoparticles

ABSTRACT

The bromide-mediated polyol method has been widely used to synthesize ultrathin silver nanowires, however, the reason why the addition of bromide ions can reduce the diameter of silver nanowires is unclear. To elucidate this mechanism, we have conducted a series of experiments in which the amount of halide ions is kept constant while the ratio of Cl^- to Br^- ions is varied, to investigate how the halide ions influence the morphology of AgNWs. Based on these experiments and previous studies, we propose herein that the bromide ions fulfill three roles: (i) facilitating the formation of AgBr cubes as nucleation events, (ii) limiting the lateral growth of AgNWs and (iii) enabling the formation of more stable AgBr complexes. Our current study should be useful for enabling size-controlled synthesis of silver nanowires via the bromide-mediated polyol method.

1. Introduction

Silver nanowires (AgNWs) have attracted much attention due to their unique electronic conductive properties and their potential use in wearable devices, solar cells, touch panel screens, medicine and novel nanofluids for thermal heating efficiency [1–5]. The polyol method developed by Xia's group has been the most successful route to produce AgNWs both at large scales and of high quality [6]. The size of the AgNWs, such as the diameter, length and aspect ratio, have a crucial influence on the performance of AgNW-based transparent conductive films [7]. Transparent conducting films incorporating AgNWs with smaller diameters exhibit high transmittance, low sheet resistance and haze. Efforts have been devoted to controlling the morphology of AgNWs by tuning the reaction parameters such as the temperature, the ratio of poly(vinylpyrrolidone) (PVP) to $AgNO_3$, the injection rate, the stirring rate and the type of salt, etc. [8]. In order to fabricate transparent conductive films with high light transmittance and low sheet resistance, the diameter of the AgNWs must be very thin. The AgNWs synthesized via the common polyol method usually have diameters in the range of 30–80 nm. The addition of bromide ions has been found to promote the formation of AgNWs with narrow diameters in recent years. Wiley et al. reported that AgNWs with diameters of 20 nm and aspect ratios of up to 2000 were obtained through the addition of NaBr to the polyol reaction medium [9]. Zhang et al. have synthesized AgNWs with an average diameter of 26 nm and an aspect ratio exceeding 800 by using KBr as a co-nucleant [10]. AgNWs with an average diameter of 30 nm and a high aspect ratio of over 1300 were synthesized through NaCl- and KBr-mediated polyol reactions by Kim et al. [11]. Meanwhile, Xia et al. have synthesized AgNWs with diameters below 20 nm and an aspect ratio exceeding 1000 [12].

All of these reported bromide-mediated polyol methods have demonstrated that the presence of bromide ions can effectively reduce the diameters of AgNWs. However, the reason why the addition of bromide ions can reduce the diameter of nanowires remains unclear. To achieve a high degree of control over the length and diameter of AgNWs, a deep understanding of the "role" of bromide ions in the bromide-mediated polyol methods is important. As described herein, we have investigated the role of bromide ions in the one-pot polyol synthesis process. In the one-pot polyol synthesis method, both the AgCl and AgBr serve by accommodating the nucleation events [9,10,13]. We kept the total amount of halides constant, and by tuning the ratio of Cl^- to Br^-, we investigated

* Corresponding author at: Guangzhou Institute of Chemistry, Chinese Academy of Sciences, Guangzhou 510650, PR China.
E-mail address: hjw@gic.ac.cn (J. Hu).

https://doi.org/10.1016/j.matlet.2017.10.128
0167-577X/

how the bromide ions influence the morphology of AgNWs. The diameter and length distributions of the AgNWs synthesized under different conditions were statistically counted. We proposed a plausible mechanism to explain the role of bromide ions in the synthesis process on the basis of statistical data. Our current study should be helpful for enabling the production of AgNWs with well-controlled lengths and narrow diameters via bromide-mediated polyol methods.

2. Experimental

All chemicals and solvents were purchased from Aladdin Reagent Company of China and used without further purification. We used a polyol synthesis that has been modified compared to those that have previously been reported [7]. In each synthesis, 30 mL of pure ethylene glycol (EG), 15 mL of $AgNO_3$ (0.1 M EG solution), 15 mL of PVP (0.2 M EG solution) and varying concentrations of NaCl and KBr were added into a two necked round-bottom flask and stirred at room temperature. The mixtures were then heated in an oil bath set at 75 °C for 30 min and subsequently heated to 120 °C with stirring for 8 h before they were finally cooled down to room temperature. During heating, nitrogen gas was bubbled through the reaction solution. TEM images were collected using a JEM-100CX II microscope operated at 80 kV. Optical microscope images were collected using an optical microscope (Weiscope-US500).

3. Results and discussion

Fig. 1 shows the TEM images of AgNWs synthesized using various NaCl and KBr concentrations (see the corresponding optical microscope images in Fig. S1). With an increasing amount of bromide ions, more particles were generated, and the quantity of AgNWs decreased constantly. Fig. 2a-f shows the diameter distribution of the as-synthesized AgNWs. The amount of ultrathin wires (<30 nm) had increased with an increasing KBr concentration, and it reached a maximum when the concentration of KBr was 0.084 mM. When the concentration of KBr was increased further, the amount of ultrathin wires had decreased slightly, and the smallest amount of ultrathin AgNWs were observed when the chloride ions were absent.

The plots of the average AgNW diameter and length vs. KBr concentration are shown in Fig. 2g. The average diameter decreased when the concentration of KBr increased, and it reached the lowest value when the KBr concentration was 0.084 mM. However, in contrast with the results from other studies [9–11], the average diameter increased when the KBr concentration was increased further, possibly due to the availability of sufficient bromide ions to passivate both the {100} facets and the {111} facets. The average length steadily decreased when the concentration of KBr increased, which was consistent with previous studies [9].

Fig. 3 illustrates the process through which the AgNWs grow. AgCl and AgBr cubes are formed during the preheating stage, as have been observed via TEM and SEM images by Wiley and Buhro [9,13], and the AgCl cubes are much larger than the AgBr cubes that were observed via TEM by Wiley [9]. When the temperature is increased to 120 °C the silver ions are reduced to Ag atoms, and multiply twinned particles (MTPs) as well as nanoparticles are formed on the nanocube surfaces [6,13]. During the growth stage, the MTPs grow into silver nanorods and continuously grow into nanowires with the assistance of PVP, which is similar to other metal nanowires synthesized by slightly different approach [14]. The PVP macromolecules interact more strongly with the {100} facets than with the {111} facets [6], and bromide ions have been demonstrated to exhibit a similar effect. This is consistent with the Xia's finding that the bromide ions can bind to the surfaces of Ag nanocrystals and thus promoted anisotropic growth [12,15]. In comparison with PVP, the bromide ions can more effectively passivate the {100} facets and limit lateral growth, due to their smaller size [12]. Moreover, Schuette et al. proposed that the larger cubes promoted the growth of AgNWs with larger diameters [13]. Since the AgBr cubes are much smaller than the AgCl cubes, the formation of AgBr cubes promotes the formation of thinner AgNWs. This is the reason why the average diameter decreased steadily when the KBr concentration was increased from 0 to 0.08 mM (Fig. 2g), and the amount of AgNWs with diameters under 30 nm increased steadily (Fig. 2b –d). As is the case with PVP, upon increasing the

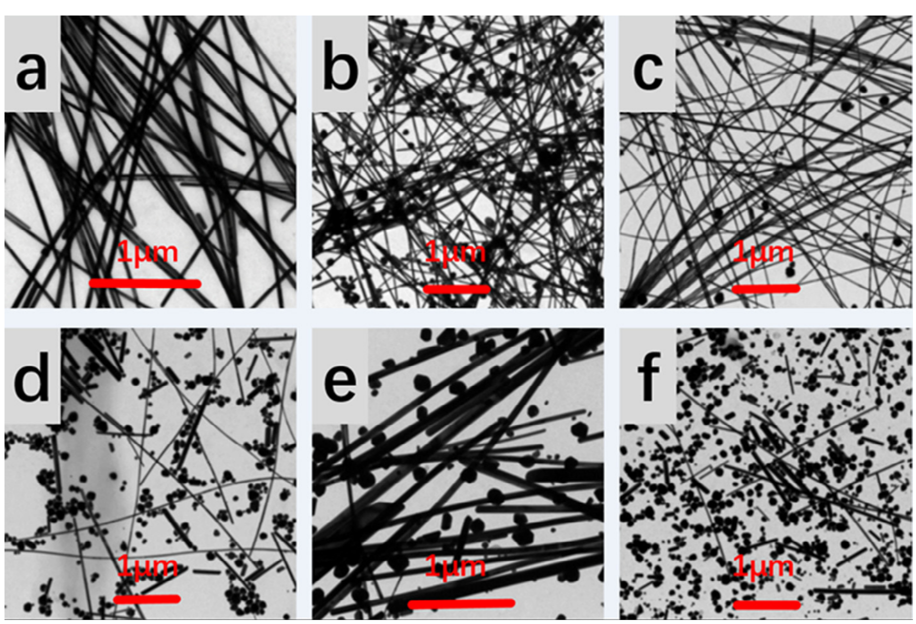

Fig. 1. TEM images of AgNWs synthesized using (a) 0.125 mM NaCl, (b) 0.1 mM NaCl and 0.025 mM KBr, (c) 0.084 mM NaCl and 0.041 mM KBr, (d) 0.041 mM NaCl and 0.084 mM KBr, (e) 0.025 mM NaCl and 0.1 mM KBr, and (f) 0.125 mM KBr.