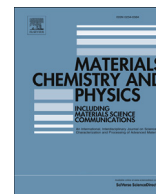




Contents lists available at ScienceDirect

Materials Chemistry and Physics

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

The effects of a cationic surfactant on copper nanowires and their dimensions

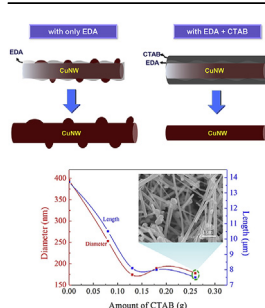
Yange Luan, Yeaji Park, Jin-Seo Noh*

Department of Nano-Physics, Gachon University, 1342 Seongnamdaero, Sujeong-gu, Seongnam-si, Gyeonggi-do 461-701, South Korea

HIGHLIGHTS

- CTAB can effectively decrease the dimensions of copper nanowires.
- A combination of CATB and EDA can improve the surface quality of copper nanowires.
- CTAB can also accelerate the nanowire growth rate.
- The combined use of HDA and CTAB leads to copper nanoparticles.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:

Received 30 September 2015

Received in revised form

1 September 2016

Accepted 17 September 2016

Available online xxx

Keywords:

Nanostructures

Metals

Chemical synthesis

Crystal growth

ABSTRACT

Copper nanowires were synthesized using a solution method with varying the amount of a cationic surfactant, CTAB. It was revealed that CTAB can effectively decrease the dimensions of copper nanowires and improve the nanowire surface quality. At a small CTAB concentration of 0.0169 M, the diameter and the length of copper nanowires were reduced by 55% and 43%, respectively, with respect to the nanowires grown without CTAB. This is discussed based on the interplay between CTAB and EDA. A series of syntheses with varying reaction time confirmed that CTAB can also accelerate the nanowire growth rate. When HDA was used as a replacement of EDA, copper nanoparticles were formed with few nanowires, indicating that a combination of HDA and CTAB functions in a way different from the combination of EDA and CTAB.

© 2016 Elsevier B.V. All rights reserved.

1. Introduction

Transparent conductors are essential components for many optoelectronic devices such as touch screens, photovoltaic cells, organic light emitting diodes (OLEDs) [1–3]. Traditionally, Indium tin oxide (ITO) has been most widely used as a transparent conductor due to its low sheet resistance of approximately $10 \Omega \text{ sq}^{-1}$ at a high transmittance of 90% [4–7]. However, indium, which

is a main element of ITO, becomes exhausted, and vapor phase ITO film deposition is not still efficient enough, leading to an almost 10-fold increase of ITO film price in the past decade [8–10]. Furthermore, ITO is not suitable for flexible applications because it is brittle. For these reasons, many research groups have been motivated to find out flexible and low-cost alternatives. Graphene, single-walled carbon nanotubes (SWNTs) networks, metal nanowires, doped zinc oxide (ZnO) films, and poly(3,4-ethylenedioxythiophene) doped with poly(styrene sulfonate) (PEDOT:PSS) are typical candidates that have been intensively investigated [11–17].

* Corresponding author.

E-mail address: jinseonoh@gachon.ac.kr (J.-S. Noh).

Metal-nanowires-networked films have attracted great attention thanks to their unique structures, good performance, and the easy processibility. Films coated with silver nanowires (AgNWs) showed a sheet resistance of $20 \Omega \text{ sq}^{-1}$ at a transmittance of 95%, which is close to the performance of ITO films [18,19]. The performance of copper nanowires (CuNWs) films are known to be slightly inferior to AgNWs films. For instance, the conductivity of CuNWs films is approximately 6% lower than AgNWs films at a similar transmittance. However, copper is 100 times cheaper than silver, and CuNWs can be synthesized more quickly than AgNWs, which can drastically reduce the fabrication cost of metal-nanowires-based transparent conductors [20–22]. Large-scale synthesis of high-quality CuNWs would be of critical importance for the practical application of CuNWs. In a previous report, it was demonstrated that 1.2 g of crystalline CuNWs could be synthesized within an hour from a 3 L of reaction flask [20]. Although ethylenediamine (EDA) was reported to play a crucial role in the determination of nanowire size, however, the control over nanowire dimensions was not enough: CuNWs with a diameter of $90 \pm 10 \text{ nm}$ and a length of $10 \pm 3 \mu\text{m}$ were obtained, which are thicker and shorter than values reported for AgNWs.

Herein, we report a CuNW solution synthesis assisted by a cationic surfactant, cetyltrimethyl ammonium bromide (CTAB). This study demonstrates that CTAB can efficiently decrease the dimensions of CuNWs with saturation phenomena at a certain concentration. Time-dependent CuNW growth with and without CTAB will be discussed. We also present the effect of another additive, hexadecylamine (HDA) on copper nanostructures.

2. Experimental

2.1. Materials

Copper nitrate [$\text{Cu}(\text{NO}_3)_2$], EDA [$\text{C}_2\text{H}_4(\text{NH}_2)_2$], hydrazine monohydrate [$\text{N}_2\text{H}_4 \cdot \text{H}_2\text{O}$], and HDA were purchased from Sigma-Aldrich; CTAB and sodium hydroxide [NaOH] were purchased from Daejung Chem. These chemicals were used with no further treatment. All Cu nanostructures were synthesized using deionized water (DI water) as the solvent.

2.2. Synthesis of Cu nanostructures

A precursor solution consisting of EDA (0.15 mL), NaOH (15 M, 20 mL), and $\text{Cu}(\text{NO}_3)_2$ (0.2 M, 1 mL) were mixed in a 50 mL vial with or without CTAB [20]. The solution was stirred at 200 rpm for 3 min at 80°C before N_2H_4 (35 wt%, 0.025 mL) was added. The mixed solution was then heated to 80°C and stirred at 200 rpm for 60 min. The amount of CTAB was varied from 0 to 0.26 g to examine its effect on Cu nanostructures. After the reaction, the suspension was centrifuged at 5000 rpm for 5 min, and the supernatant was decanted from the nanostructures. The nanostructures were then dispersed in a 3 wt% aqueous solution of hydrazine by vortexing for 30 s. These centrifugation and decanting processes were repeated 3 cycles. The final Cu nanostructures were stored in a 3 wt% hydrazine solution at room temperature.

In another sets of experiments, different amounts of HDA (0.0416 g, 0.208 g) were mixed with a fixed amount of CTAB (0.13 g) in a 50 mL vial and stirred at 200 rpm for 3 min at 80°C . Then, NaOH (15 M, 20 mL), $\text{Cu}(\text{NO}_3)_2$ (0.2 M, 1 mL), and N_2H_4 (35 wt%, 0.025 mL) were successively added to the solution of HDA and CTAB. The mixed solution was then heated to 80°C and stirred at 200 rpm for 60 min at that temperature. The Washing and centrifugation steps were same as the above description. The experimental conditions for the synthesis of various Cu nanostructures are summarized in Table 1.

2.3. Characterization

Solution color changes caused by any chemical reactions in the solution were visually inspected. The morphology and dimensions of Cu nanostructures were analyzed using a field emission scanning electron microscope (FE-SEM, JEOL JSM-7500F). The crystal structure and crystal quality of Cu nanowires were evaluated using X-ray diffraction (XRD, Rigaku D/Max 2200) with Cu K_α radiation of $\lambda = 0.154178 \text{ nm}$. The optical absorbance spectra of the deep blue precursor solution were measured to confirm the formation of a $[\text{Cu}(\text{OH})_4]^{2-}$ complex, using a UV–Vis spectrophotometer (Shimadzu UV-2550). The optical transmittance of CuNW films on the polyethylene terephthalate (PET) substrate was tested using the same UV–Vis spectrophotometer.

3. Results and discussion

Fig. 1 shows the SEM images of CuNWs synthesized with varying amounts of CTAB (samples A1–A5 in Table 1). All other experimental conditions were kept constant. Similar to the previous report [20], CuNWs are found to be grown from spherical seeds irrespective of the use of CTAB. In the absence of CTAB (Fig. 1(a)), the average diameter and length of CuNWs were measured at $\sim 400 \text{ nm}$ and $\sim 14 \mu\text{m}$, respectively, which indicate an increase in both dimensions from the literature values, presumably due to the use of less amount of EDA. Most notably, the diameter of CuNWs apparently decreases with an increase in the amount of CTAB (Fig. 1(a) – (d)). This reduction in nanowire diameter was accompanied with the shortening of nanowire length. In Fig. 1(e), the average diameter and length of CuNWs are plotted against the amount of CTAB added to the solution. Both the diameter and the length of CuNWs substantially decrease with increasing the CTAB amount until they almost saturate at a critical amount. In this study, the critical amount of CTAB was 0.13 g (0.0169 M), and the average diameter and length of CuNWs at this critical value were approximately 180 nm and 8 μm , which represent 55% and 43% reduction in diameter and length with respect to CuNWs grown without CTAB. This substantial reduction in nanowire dimensions may be attributed to the dynamic interplay between CTAB and EDA. It has been reported in several literature [23–25] that EDA, which has end groups with negative polarity, is preferentially absorbed onto high-energy {100} side surfaces of Cu crystals, leaving behind low-energy {111} planes for the adsorption of incoming Cu atoms. This is why CuNWs become thinner at higher EDA concentrations. CTAB is a typical amphiphilic surfactant consisting of a long alkyl chain and a cationic headgroup ($-\text{N}^+(\text{CH}_3)_3$). The cationic headgroup of CTAB is likely to be electrostatically attracted to the polar group of EDA, which has already been absorbed on the side surfaces of the growing CuNWs. This may lead to the passivation of nanowire side surfaces by higher concentrations of CTAB molecules as compared to the tips of the nanowire, resulting in the significant suppression of the nanowire radial growth. This effect of CTAB will be saturated above a critical concentration, where the side surfaces are fully passivated by CTAB. Both EDA and CTAB can also be absorbed on the tips of CuNWs, contributing to the reduction of nanowire length. As another positive effect of CTAB, surface morphology of CuNWs becomes smoother with increasing the concentration of CTAB (Fig. 1(a) – (d)). This may be because more perfect surface passivation at a higher CTAB concentration can effectively suppress the local and random radial growth. The reduction in nanowire dimensions and the improved surface quality, which resulted from the cooperative action of EDA and CTAB, are schematically shown in Fig. 2 with a comparison to the case of using only EDA.

XRD measurements were performed to check any potential change in the crystal structure and crystallinity caused by the

Download English Version:

<https://daneshyari.com/en/article/5448413>

Download Persian Version:

<https://daneshyari.com/article/5448413>

[Daneshyari.com](https://daneshyari.com)