

Oleylamine Assisted Synthesis of Ultralong Copper Nanowires

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Abstract. This paper reports the hydrothermal synthesis of smooth and ultralong copper nanowires (Cu NW) prepared using oleylamine (OM), oleic acid (OA), and Cl⁻ ion as coordinating and etching agents respectively. Cu nanowires with mean diameters around 82.3 nm and lengths exceeding 300 μm were synthesized using 2 % vol. OM and 1.8 mM OA at 120°C after 12 h. The Cu NWs exhibit five-fold twinning and growth along the [110] direction. The morphological evolution of the products were also observed and discussed. Without Cl⁻, octahedral crystals instead of nanowires were formed. The addition of oleic acid as coordinating agent resulted to fewer particles and smoother nanowires which exhibit excellent mechanical stability. This method provides a simple, low-cost and high yield synthesis of Cu NWs for applications such as gas sensors and transparent conducting electrodes.

1 Introduction

Copper nanowire (Cu NW) research has attracted considerable attention because of its wide range of applications such as electrical interconnects, photodetectors, field emission devices, microheaters, gas sensors, and as a potential low-cost alternative to indium tin oxide for use as a transparent conducting electrode [1-3]. Its excellent electrical and thermal conductivity coupled with its abundance makes it a very viable alternative. Among the various methods for Cu NW production, a solution-based process allows for a simple, low-cost, and large scale synthesis of free standing Cu NWs which can be easily collected. Aqueous or organic solvents such as HDA, ODA, SDBS, or CTAB have been used to promote nanowire growth. Morphological control over the nanowires can easily be achieved by simply varying the concentrations of reactants, temperature, and time

Some of the earliest studies of Cu NWs grown via aqueous synthesis was first reported in 2003 by Liu et. al. using sodium dodecyl benzenesulfonate (SDBS) as the structure directing agent and phosphate (HPO₃²⁻) as the reducing agent [4]. In 2005, a synthesis method was developed by a Zeng et. al. using a Cu precursor and ethylene diamine (EDA) in a highly basic solution [5]. They were able to synthesize Cu NWs with diameters around 90-120 nm and lengths of 40-50 μm after 1 h of reaction. Since then, a number of synthesis methods have been reported to produce Cu NWs. While the aqueous synthesis route is proven to be low cost, common problems such as oxidation and long term storage have limited the process from producing it on a large-scale [5,

6]. Moreover, the some have reported tapering along the wires and rough morphologies. These were found to have a significant impact in increasing the electrical resistivity of the Cu NW [7]. In this study, we present an aqueous synthesis route for producing smooth, ultralong, and oxidation stable Cu NWs using oleylamine and oleic acid as coordinating agents.

2 Experimental

In a typical synthesis, a copper solution containing 0.68 g (40 mM) of CuCl₂ salt and 0.792 g (40 mM) of anhydrous glucose are added into a 250 mL beaker containing 80 mL of deionized H₂O. The solution was stirred until the metal salt and glucose were completely dissolved. In a separate 500 mL Erlenmeyer flask, 8 mL (2 % vol.) of oleylamine (OM), 14 mL (3.5 % vol.) of ethanol, and varying amounts of (0.60-1.8 mM) of oleic acid (OA) were mixed together. Then, the copper solution was quickly added. Finally, the solution was diluted to 400 mL using deionized H₂O and was heated at 50°C for 12 hrs. After ageing, 100 mL of the precursor solution was transferred into a Teflon lined autoclave reactor and heated to 120°C for varying times.

The morphologies, structure and composition of the obtained products were characterized using high resolution transmission electron microscope (HRTEM, JEOL JEM-ARM200F), scanning electron microscope (SEM, JEOL 5300) and X-ray diffraction (XRD, Cu K α , Shimadzu XRD-7000) respectively. The reported diameters were taken from measurements of more than 300 wires.

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3 Results and discussion

Figure 1 shows the SEM images of Cu NWs formed at 120°C and under high pressure using 2 % vol. OM and 0.6 mM OA, taken at different reaction times. After 4 h of reaction, rectangular-pyramid-like microstructures and very thin nanowires having average diameters of 43 nm were formed. The pyramidal microstructures are tapered at the ends and have an average base diameter of 3-5 μm as shown in Fig 1a. When the reaction is allowed to

proceed further to 8 h, thicker nanowires with an average diameter of 229 nm were formed together with irregular-shaped precipitates as shown in Fig 1b. However, the amount of rectangular-pyramid structures across the solution gradually decreased. After 12 h, only nanowires with average diameters of 82.3 nm and lengths exceeding 300 μm were present in the solution. The wires also exhibit mechanical strength as seen in their ability to withstand bending even at angles greater than 90°.

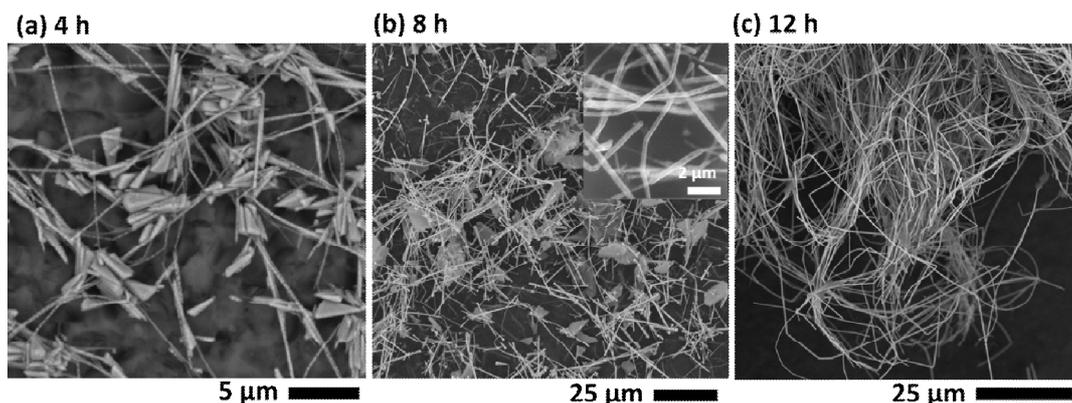


Figure 1. SEM images of Cu NWs prepared by hydrothermal method using 0.6 mM OA at 120°C at 4, 8, and 12 h respectively.

Figure 2 shows the XRD patterns of the synthesized products. At 4 h, peaks at 42.5, 61.5, and 74° correspond to the 200, 220 and 311 plane of Cu_2O (JCPDS card no. 05-0667). A shoulder peak at 43.5 is observed at 4 h, indicating the formation of metallic copper. After 12 h, only peaks at 43.5, 51, and 74.5 which correspond to 111, 200, and 222 planes of copper (JCPDS card no. 85-1326) are observed. Using Scherrer's equation, the crystallite size was determined to be 3.51 nm for Cu_2O using the 200 plane, and 8.94 nm for Cu using the 111 plane.

Figure 3 shows the SEM images of Cu NWs prepared using varying amounts of oleic acid. At 0.6 mM oleic acid, very thin nanowires (~72.33 nm) were present. However, these were combined with tetragonal and spherical nanoparticles even after 12 h. Increasing the oleic acid concentration to 1.2 mM led to the formation of smooth wires that are able to withstand torsion (Fig. 3b, inset). Further addition of oleic acid produced faceted wires with rigid sides. All the Cu NW products easily exceed 200 μm in length and do not exhibit tapering along the entire length.

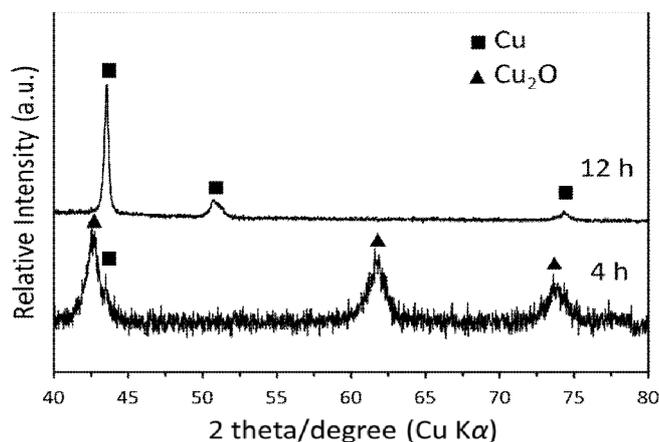


Figure 2. XRD patterns of Cu nanowires prepared by hydrothermal synthesis using .6 mM oleic acid at 120°C after 4 and 12 h respectively.

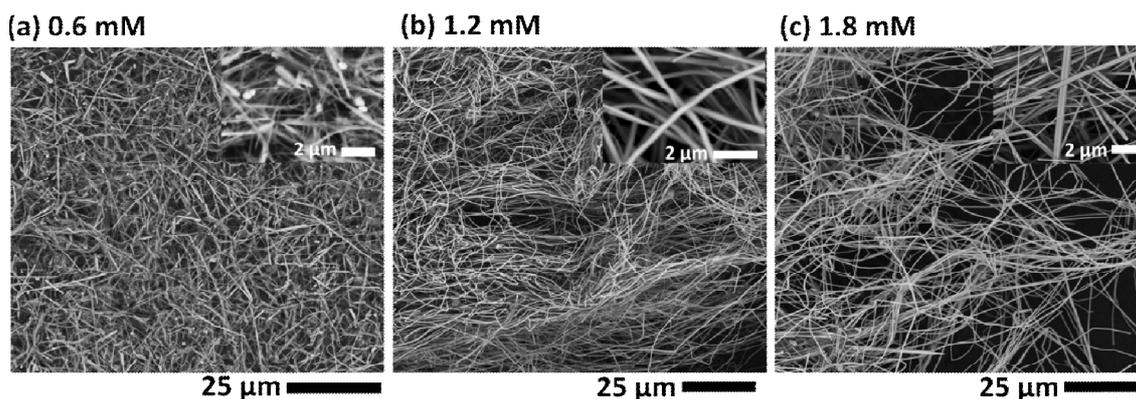


Figure 3. SEM images of the Cu NWs prepared by hydrothermal synthesis for 12 h at 120°C using (a) 0.6, (b) 1.2, and (c) 1.8 mM oleic acid.

High resolution TEM (HRTEM) images indicate that the Cu NWs appear to be very smooth and uniform in diameter as shown in Fig 4a (inset). The measured diameter was found to be 76.8 nm which corresponds well to the average diameter taken from SEM images. The preferred growth direction was found to be along the [1-10] as shown in Fig 4a. The selected area electron diffraction (SAED) pattern obtained from the Cu NW indicates two sets of diffraction patterns which can be assigned to the [110] and [111] zone axes of face-centered cubic (fcc) structure as shown in Fig. 4b. The superimposed pattern signifies a five-fold twinned pentagonal structure which was found to be a significant factor in the nanowires' ability to withstand torsion and bending [8].

The presence of Cl⁻ ions was found to be critical in promoting anisotropic growth. The absence of Cl⁻ leads to the formation of faceted octahedron and spherical crystals with a large variation in the sizes ranging from 500 nm to

2 μm as shown in Fig 4d. The facets may be due to planar defects on the surface of the crystals. The initial ageing of the precursor solution at 50°C for 12 h was found to be a necessary step in the reaction process. During ageing, the OM complexes with the Cu²⁺ ion. Initially, the OM was immiscible in the solution, but as the solution was heated, and vigorous stirring was employed, the color changed from royal blue to avocado green after about 6 h as shown in Fig 4c and inset. The royal blue color at the beginning of the reaction indicates the presence of free Cu²⁺ in the mixture. After 12 h, the OM became fully soluble in the solution and the change in color may indicate complexation of OM with the Cu²⁺ ion. In this system, the OM selectively binds at the {111} plane, which has the highest surface energy among fcc planes. As a result, the presence of OM restricts further addition of Cu atoms along the [111] plane and subsequent Cu reduction occurs along the [110] direction.

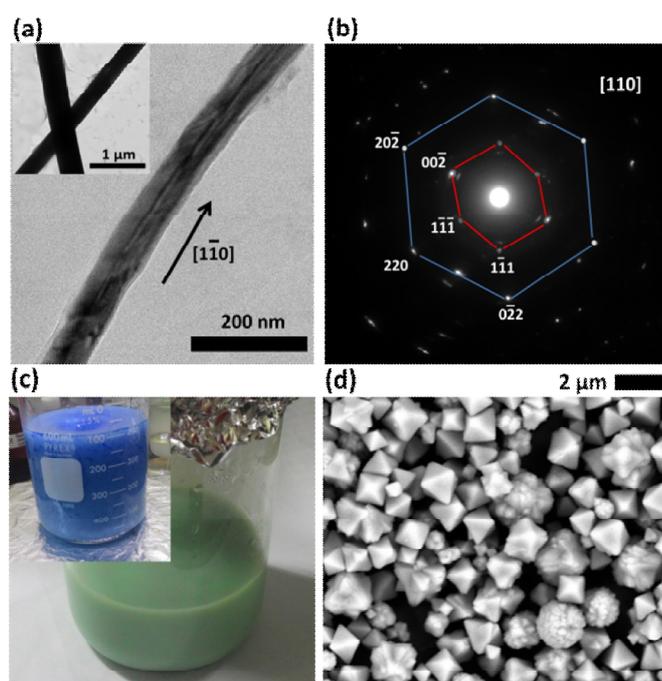


Figure 4. (a) HRTEM images showing smooth and uniform NWs produced using 1.8 mM OA at 120°C for 12 h and its growth direction along the [1-10] plane. (b) Corresponding SAED pattern shows a five-fold twinned pentagonal structure. (c) Precursor solution before (inset) and after 12 h of stirring at 50°C showing a change in color. (d) Cu microcrystals products formed when CuCl₂ was replaced with Cu(NO₃)₂ salt using 1.2 mM OA at 120°C for 12 h.

At the start of the reaction, the Cu²⁺ ion is oxidized to Cu₂O seeds in the presence of water at high pressure and temperature as evidenced by corresponding Cu₂O peaks in the XRD (Fig. 2a). However, the presence of an etchant such as Cl⁻ ions, selectively etches the oxide seeds present in the solution through a process known as oxidative etching [9]. In order to ascertain the role of Cl⁻, the CuCl₂ precursor was replaced with equal molar Cu(NO₃)₂. When Cu(NO₃)₂ was used, Cu octahedral crystals were formed instead of Cu NWs. As such, in the absence of an etchant, the seed crystals will continue to grow to form faceted crystals as shown in Fig 4d.

As the reaction continues, the octahedral Cu₂O seeds are etched back to form Cu²⁺ ions. These ions are then preferentially reduced in the presence of glucose along the [110] direction. However, when the amount of OA required to coordinate with the freed Cu²⁺ is insufficient, the ions are eventually reduced by glucose and form spherical and irregular shaped particles instead, as shown in Fig 3a. Regardless, only metallic Cu products remain after 12 h reaction suggesting that the presence of glucose will eventually reduce the Cu₂O seeds even in the absence of an etchant.

The complementary etching and reducing reactions take place simultaneously during the process. This is further shown in the decrease of tetragonal structures found in Fig. 1a and subsequent formation of more wires in Fig. 1b,c. With sufficient coordination, all the initial Cu₂O seeds are completely etched and only Cu wires remain after 12 h. This XRD patterns also agrees well with the proposed formation mechanism.

The OA increases the coordination of the Cu along the [111] plane. The OA has a similar alkyl chain with OM, but the amine at the end is replaced with a hydroxyl functional group. This allows it to selectively bind with Cu²⁺ without being an electron donor. As such, it can increase the coordination of the ions without affecting the overall reduction kinetics. As more OA is added, the wires become cylindrical (Fig 3b, inset) and cubic (Fig 3c, inset) due to the increase in the overall coordination.

4 Summary

In summary, Cu NWs with lengths exceeding 200 μm and an average diameter of 82.3 nm were synthesized through an oleylamine-assisted, hydrothermal method for 12 h at 120°C. XRD peaks at 4 and 12 h confirmed that the Cu²⁺ was initially oxidized to Cu₂O before being fully reduced to metallic copper. The wires easily reach an aspect ratio >1000 and can withstand bending and torsion. In the absence of Cl⁻, crystal growth was observed, which indicates the importance of Cl⁻ as an etchant for anisotropic growth.

Acknowledgment

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References

1. D. Zhang, R. Wang, M. Wen, D. Weng, X. Cui, J. Sun, H. Li, Y. Lu, *Journal of the American Chemical Society* **134**, 14283-14286 (2012)
2. Y. Won, et al., *NPG Asia Materials* **6**, (2014)
3. I. Stewart, A.R. Rathmell, L. Yan, S. Ye, P. Flowers, W. You, B. Wiley, *Nanoscale* **6**, 5980-5988 (2014)
4. Z. Liu, Y. Yang, et. al., *Journal of physical Chemistry B* **107**, 12658-12661 (2003)
5. Y. Chang, M. Lye, H. Zeng, *Langmuir* **21**, 3746-3748 (2005)
6. B. Wiley, *Chemical Communications* **50**, (2014)
7. R.L. Graham, et al., *Applied Physics Letters* **96**, 2116 (2010)
8. H.J. Yang, S.Y. He, H.Y. Tuan, *Langmuir* **40**, 602-610 (2014)
9. R. Long, et al., *Chemical Society Review* **43**, 6288-6310 (2014)