Journal of Colloid and Interface Science 531 (2018) 109–118

Contents lists available at ScienceDirect

Journal of Colloid and Interface Science

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

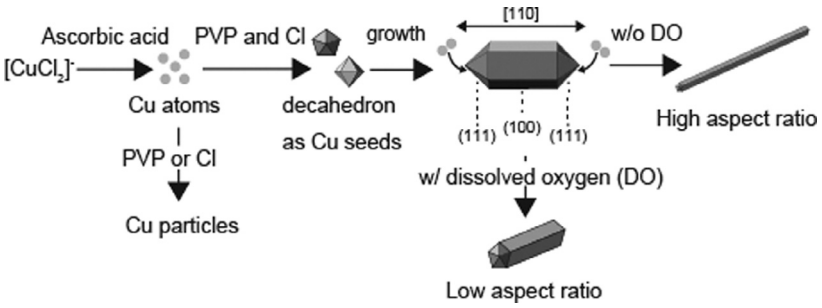
Regular Article

Environmentally friendly synthesis and formation mechanism of copper nanowires with controlled aspect ratios from aqueous solution with ascorbic acid

Shun Yokoyama [a,*], Kenichi Motomiya [a], Balachandran Jeyadevan [b], Kazuyuki Tohji [a]

[a] Graduate School of Environmental Studies, Tohoku University, 6-6-20, Aramaki, Aoba-ku, Sendai 980-8579, Japan
[b] Department of Material Science, University of Shiga Prefecture, 2500 Hassaka-cho, Hikone City, Japan

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 22 May 2018
Revised 29 June 2018
Accepted 11 July 2018
Available online 12 July 2018

Keywords:
Ascorbic acid
Aqueous chemical reduction
Cu nanowires
Aspect ratio
Dissolved oxygen
Surface oxidation
Capping agents

ABSTRACT

Copper (Cu) nanowires (NWs) were synthesized by the reduction of Cu–chloride complexes using ascorbic acid (AA) as a mild reducing agent, polyvinylpyrrolidone (PVP) as a capping agent, and NaCl as an additive under atmospheric conditions at 80 °C. Surface analyses revealed that both Cl ions and PVP were required for the synthesis of Cu NWs. Together, the Cl ions and PVP capped the Cu (1 0 0) side faces, leading to anisotropic growth of Cu NWs along the [1 1 0] direction. To obtain Cu NWs with high aspect ratios, we evaluated the synthetic mechanism under different reaction conditions. The results indicated that the presence of dissolved oxygen (DO) was the dominant factor affecting aspect ratio of Cu NWs. DO and hydrogen peroxide resulting from the reaction between DO and AA oxidized the surfaces of the growing Cu NWs, preventing further growth. Decreasing the amount of oxides on the Cu NW surfaces and removing DO increased the aspect ratios of the Cu NWs. The results indicated that DO should be removed from the reaction solution to obtain high-aspect-ratio Cu NWs in aqueous solutions containing AA.

1. Introduction

Networks of copper (Cu) nanowires (NWs) have shown promise as an alternative to indium tin oxide (ITO) films in the production of flexible, transparent, and conductive films. Unlike expensive and brittle ITO films, Cu NWs have low cost and flexibility along with high conductivity. Generally, to create high-performance films using Cu NWs, the NWs must have high aspect ratios [1]. Cu NWs are usually synthesized via chemical reduction as this method is low-cost and can be used for large-scale NW production [2]. However, these chemical syntheses often require high temperature (above 100 °C), high pressure, organic solvents, and toxic reducing agents such as N_2H_4 [3–13], which increase the cost of Cu NW production. For practical applications, it is desirable to

* Corresponding author.
E-mail address: shun.yokoyama.c2@tohoku.ac.jp (S. Yokoyama).

https://doi.org/10.1016/j.jcis.2018.07.036
0021-9797/

develop low-cost and environmentally friendly methods for Cu NW synthesis. Recently, Cu NWs were successfully synthesized in aqueous solution at temperatures below 100 °C and without high pressure using ascorbic acid (AA) in place of the commonly used toxic reducing agents [14,15]. However, the synthetic mechanism associated with this new procedure remains unclear. Furthermore, the use of organic co-solvents is required to obtain Cu NWs with high aspect ratios, and other factors affecting the aspect ratio are not well understood. Previously, we reported the green synthesis of Cu nanoparticles (NPs) via the reduction of aqueous Cu complexes using AA as a mild reducing agent at near-room temperature and atmospheric conditions [16]. In this synthesis, Cu NWs were partially synthesized in the presence of chloride (Cl) ions as an additive and polyvinylpyrrolidone (PVP) as a capping agent. Based on this finding, we attempted to develop an environmentally friendly procedure for synthesizing high-aspect-ratio Cu NWs for use in low-cost and high-performance transparent films with flexibility and conductivity. In this study, we demonstrate the selective synthesis of Cu NWs under 80 °C and atmospheric conditions using AA as a reducing agent and PVP and Cl as capping agents. We then show that the lengths and diameters along with the crystal structures of the Cu NWs can be controlled by varying several experimental factors such as K values of PVP, solution volume, and reaction atmosphere. We also evaluate the growth mechanism based on the results obtained from a careful investigation of the Cu NW surfaces. Finally, we discuss the formation mechanism and main factors affecting the aspect ratio of Cu NWs during synthesis.

2. Experimental methods

2.1. Synthesis of Cu NWs

All chemicals used in this study were obtained from Wako Pure Chemical Industry, Ltd. (Japan). Deionized water (18 MΩ) obtained from a water purifier system (WT101UV; Yamato Scientific Co., Ltd., Japan) was used in all experiments. Cu NWs were synthesized using Cu chloride dehydrate ($CuCl_2{\cdot}2H_2O$; purity ≥ 99.5%) as the source of Cu, sodium chloride (NaCl; purity ≥ 99.0%) as an additive, PVP K25, K30, and K90 as capping agents, and L(+)-AA ($C_6H_8O_6$, purity ≥ 99.6%) as the reducing agent. $CuCl_2$ and AA solutions were prepared by separately dissolving $CuCl_2$ and AA in deionized water under ultrasonication. PVP and NaCl were added into the AA solution in a glass vial (LABORAN SCREW VIAL No.8, 110 ml obtained from AS ONE Corp.) under stirring. The $CuCl_2$ solution was then poured into the glass vial. Subsequently, the solution pH was adjusted to 2.5–4.5 by adding NaOH. The final volume and reagent concentrations were as follows: volume, 30–90 ml; $CuCl_2$, 0.10 mol/l; NaCl, 0.00–0.35 mol/l; PVP, 0.30–2.4 wt%; and AA, 1.5 mol/l. The reaction temperature was controlled at 80 °C using a water bath. The reaction solution was stirred at 500 rpm under air or N_2 atmosphere at a flow rate of 50 ml/min. For N_2 atmosphere, a water-cooled reflux condenser was used to avoid excess loss of reaction solution resulting from the N_2 flow.

2.2. Characterization of Cu NWs

The crystal structure of the Cu NWs was analyzed by X-ray diffraction (XRD; Smart Lab., Cu Kα, Rigaku Corp., Japan). NW morphology was assessed using field-emission scanning electron microscopy (FE-SEM; S-4200 or S-4800, Hitachi High-Technologies Corp., Japan) and scanning transmission electron microscopy (STEM; HD-2700, Hitachi High-Technologies Corp., Japan). The chemical states of the Cu NWs were analyzed by X-ray photoelectron spectroscopy (XPS; K-Alpha, Thermo Fisher Scientific Inc., USA) with a monochromatic Al Kα X-ray source. The elemental distributions of the Cu NWs were obtained using FE-SEM or STEM equipped with energy-dispersive X-ray spectroscopy (EDX) module (Noran System 7, UltraDry 30 SDD from Thermo Fisher Scientific Inc., USA or APOLLO XLT SDD system from EDAX, USA). A 200-eV Ar ion beam was used to collect the XPS depth profiles of the Cu NWs. The metal complexes formed in the mixture of deionized water, $CuCl_2$, PVP, NaCl, and AA at 80 °C were identified using electrospray ionization time-of-flight mass spectrometry (ESI-TOFMS; Bruker Daltonics Inc.; micrOTOFII) in the m/z range of 50–3000. A detailed description of the MS analysis is given in Ref. [17]; in this study, the temperature of dry gas was 80 °C in negative mode for identification of metal complexes. ESI-TOFMS was also used to identify oxidation products of AA in the reaction solutions. The temperature of dry gas was 35 °C in positive mode for the oxidation products. To determine the Cu NW yield, Cu in the reaction solution was quantitatively analyzed using inductively coupled plasma (ICP-AES; AMETEK Co., Ltd.; SPECTRO ARCOS). The concentrations of dissolved oxygen (DO) in the reaction solutions after Cu NW syntheses were determined using a multi-function meter (MM-60R, DKK-TOA Corp. Japan) equipped with a DO electrode (OE-270AA, DKK-TOA Corp. Japan).

3. Results

3.1. Synthesis of Cu NWs

Since AA can reduce Cu ions or Cu complexes to Cu metal, the shape of the resulting Cu metal depends strongly on the pH of the aqueous solution [15,16]. Thus, we synthesized Cu NWs at various pH values. Fig. 1 shows the XRD profiles and SEM micrographs of samples obtained via the reduction of $CuCl_2$ by AA in the presence of PVP (0.3 wt%) between pH 2.5 and 4.5. At all tested pH values, the color of the mixture of $CuCl_2$, deionized water, and PVP changed from blue-green to white after the addition of AA. All the XRD profiles confirmed the formation of CuCl; AA immediately reduced $CuCl_2$ to CuCl, causing the precipitation of white-colored CuCl [18]. CuCl was not reduced to Cu metal at pH 2.5; as the pH increased above 2.5, CuCl was reduced to Cu metal, and the reaction speed increased with the increase in pH [Fig. 1(a–c)]. The redox potential of AA varies with pH, whereas the reduction potential of CuCl does not. Thus, increasing the pH enhances the driving force for reduction [19,20]. As a result, AA reduced CuCl to Cu metal at higher pH. However, the precipitate contained Cu NPs only at pH values above 4.5 [Fig. 1(e)]. At pH 3.5, AA reduced CuCl to both Cu NWs and Cu NPs [Fig. 1(d)]. Based on these results, pH 3.5 was selected for the subsequent synthesis of Cu NWs via the reduction of $CuCl_2$ by AA in aqueous solution.

The concentrations of PVP and NaCl were varied to achieve the selective synthesis of Cu NWs. While increasing the PVP concentration facilitated the generation of Cu NWs, it also resulted in the partial formation of Cu particles [Fig. 2(a–c)]. Increasing the concentration of NaCl as an additive significantly increased the ratio of Cu NWs to Cu NPs, and Cu NWs were the main synthetic product at NaCl concentrations greater than 0.35 M. In this case, the solution containing white precipitate (CuCl) changed into a clear solution during the initial synthetic stage (Fig. S1), indicating that CuCl formed stable complexes with Cl^-. The ESI-TOFMS results indicated the formation of $[CuCl_2]^-$ (Table S1). Thus, at NaCl concentrations above 0.35 M, CuCl was completely converted to $[CuCl_2]^-$, resulting in a clear solution. At low NaCl concentrations, $CuCl_2$ was reduced to a mixture of Cu NPs and Cu NWs via insoluble CuCl (Eqs. (1) and (2)). At NaCl concentrations above 0.35 M, $CuCl_2$ was primarily reduced to Cu NWs via soluble $[CuCl_2]^-$ (Eqs. (3) and (4)). The reduction of $[CuCl_2]^-$ to Cu required more time (approximately