Obtaining ultra-long copper nanowires via a hydrothermal process

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Abstract

Ultra-long and uniform copper nanowires with controllable diameters of 30–100 nm, length up to several millimeters (aspect ratio \( > 10^5 \)) and tunable crystallinity were obtained by hydrothermal processing the complex emulsion of copper (II) chloride and ODA at 120–180 °C. Both XRD pattern and EDX spectrum indicated that the products were pure copper without any observable impurities. It is observed by FESEM that the diameters and aspect ratios of the synthesized copper nanowires were influenced by the concentration of ODA and reaction temperature. HRTEM images and SAED patterns revealed that the crystallinity of copper nanowires were strongly dependent on the synthesis temperatures. Poly- and single-crystal copper nanowires were obtained at 120 °C and 180 °C, respectively.

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1. Introduction

Gold, silver and copper nanowires have drawn large attention in recent years owing to their unusual physical properties and potential applications in chemical and biological sensors and as interconnectors for nanoscale electronic and optoelectronic devices [1–5]. In particular, many efforts have been devoted to the preparation of copper nanowires because bulk copper exhibits higher thermal and electrical conductivity than many other metals and has been commonly used as interconnector in electronic circuits [6,7]. Nanoscaled copper wires may be used as an essential component in the future generation of nanodevices. Long copper nanowire with high aspect ratio may be used as building blocks in constructing macroscopic micro- and nano-devices, and may also present an ideal 1D nano-material for fundamental research on its mechanical and electrical properties [6,8]. Therefore, facile synthesis of copper nanowires with large aspect ratio and controllable diameter is of significant meaning in both nanotechnologies and material sciences.

Although several physical and chemical methods have been developed for preparing copper nanowires, those approaches always need tedious procedure to remove the matrix [9–12], or require complex apparatus and rigorous processing conditions [13–15]. The aspect ratio of the produced nanowires is limited and the yield rate is relatively low. Developing a new method to obtain ultra-long and uniform copper nanowires in large-scale is still a challenge. Recently, Qian and co-workers have reported a complex-surfactant-assisted hydrothermal reduction process to prepare copper nanowires [7]. In their report, copper nanowires are prepared through the reduction of complex copper (II)-glycerol by HPO$_3^{2-}$ in a high concentration of NaOH and glycerol aqueous solution with the assistance of sodium dodecyl benzene sulfonate (SDBS). Herein, we present a novel hydrothermal route to obtain ultra-long copper nanowires with uniform diameters and controlled crystallinity by the reduction of copper chloride aqueous solution using octadecylamine (ODA).

This method does not need any other surfactants or organic solvents to direct the anisotropic growth of copper nanowires. On the other hand, ODA has long been used as a nonionic surfactant for building Langmuir-Blodgett films [16,17] and a ligand-assisted template for preparing mesoporous materials [18] and vanadium oxide nanotubes [19,20]. To our knowledge, little attention has been focused on the reducibility of ODA, and the reduction of copper (II) to elemental copper by amines has never been reported before. It is well known that primary amines are easily attacked by oxidizing agents [21], and copper (II) is a useful...
oxidizing agent for a wide range of organic substances [22]. However, aliphatic amines are generally inert towards copper (II) at normal atmosphere. We find that under hydrothermal conditions, ODA can reduce copper (II) completely to metallic copper and such a simple chemical reaction provides a novel approach to obtain ultra-long copper nanowires.

2. Experimental procedure

2.1. Synthesis process

In a typical process for synthesizing copper nanowires, 2 mmol octadecylamine (ODA) was added to 80 mL of copper (II) chloride (12.5 mmol L\(^{-1}\) aqueous solution and vigorously stirred for 5 h forming a blue emulsion. Then the solution was transferred into a Teflon-lined autoclave of 100-mL capacity and heated at 120–180 °C for 48 h. After the autoclave was cooled down to room temperature naturally, the supernatant was decanted and the final product was obtained after washing the solid part with n-hexane, deionized water and ethanol, respectively.

2.2. Characterizations

The X-ray diffraction (XRD) pattern was recorded on a Rigaku D/max 2500 diffractometer, using Cu K\(_\alpha\) radiation. SEM images were taken with a field emission scanning electron microscope (XL-30 S-FEG). TEM images, HRTEM images, selected area electron diffraction (SAED) patterns and EDX analysis spectra were performed on a Philip Tecnai F30 transmission electron microscope with an accelerating voltage of 300 kV. Samples for the transmission electron microscope were prepared by ultrasonic dispersion for 0.5 h of 0.01 g of the as-prepared sample with 4 mL of ethanol in a 5 mL centrifugal tube. Then, the suspension was dropped onto a conventional carbon-coated copper micro grid for TEM observation.

3. Results and discussion

3.1. Phase and composition

As-obtained red textile-like products show the characteristic color of metallic copper. Phase and chemical compositions were detected using XRD and energy dispersive X-ray spectroscopy (EDX). All recorded peaks in the XRD pattern (Fig. 1(A)) can be assigned to the face-centered cubic phase of copper (JCPDS file No. 04-0836) and no impurities can be observed. EDX spectrum (Fig. 1(B)) of the fresh sample also confirms that only copper exists and no oxygen appears. Therefore, copper (II) has been completely reduced to pure copper metal under the present synthesis conditions. Other samples obtained at different temperatures have XRD patterns similar to that in Fig. 1(A).

3.2. Morphology

Fig. 2 presents FESEM images of the product obtained at 160 °C with different magnifications. The product is composed of a large quantity of uniform nanowires without any other morphology and many of them bundle together. Low magnification SEM images show the nanowires have a remarkable length up to several millimeters. High magnification micrographs reveal that they are straight with uniform diameters of 50–100 nm (aspect ratio >10\(^5\)). Interestingly, reaction temperature has been found to be a key factor that could affect the diameters of the copper nanowires. It is shown that the sample prepared at 120 °C has uniform diameters of 30–50 nm and an extraordinary length of millimeter magnitude. At an elevated temperature (180 °C), the diameters of the nanowires show a wide diameter distribution (50–10\(^3\) nm) and the aspect ratio decrease to the range of 10\(^3\)–10\(^5\). Besides, the synthesis temperature, concentration of ODA in the reaction system also influences the diameters of the nanowires. Ultra-long nanowires with uniform diameters of 50–100 nm are also obtained at 180 °C by increasing the concentration of ODA (Fig. 3(B)).

![Fig. 1. XRD pattern (A) and EDX spectrum (B) of the as synthesized sample at 120 °C. (The weak peak of carbon comes from copper grid).](image-url)
3.3. Crystallinity

Crystallinity of the synthesized copper nanowires is strongly dependent on the reaction temperature. Fig. 4 shows the TEM images and high-resolution TEM images of the nanowires obtained at different temperatures. The copper nanowire synthesized at 180 °C is a single crystal. HRTEM image (Fig. 4(B)) of a single nanowire shows the lattice fringe distances are 2.08 Å, consistent with Cu (111) interplanar spacing. The angle between the (111) planes and the axis direction of the nanowire is around 55°. The spot feature of the corresponding SAED pattern (inset of Fig. 4(A)) also confirms that the copper nanowire is a single crystal with face-centered cubic structure. While the crystallinity of the sample synthesized at 120 °C is obviously low. Both HRTEM image (Fig. 4(D)) and SAED pattern (inset of Fig. 4(C)) indicate the nanowire is polycrystalline. Copper nanowire obtained at 160 °C shows obviously improved crystallinity (Fig. 5). All the lattice planes have the same spacing and direction as those of the nanowire obtained at 180 °C, but some defects still exist in the HRTEM micrograph.

3.4. Discussion

The reaction apparently proceeded via a reduction mechanism, in which metallic copper nanowires formed spontaneously and no additional reductant or surfactant was added. The reducing power of ODA can be readily ascertained by mixing the copper (II) salt octadecylamine complexes under hydrothermal conditions for a period of time. Reduction of cupric is complete as indicated by the disappearance of blue color, which is associated with copper (II) [23]. In the case of preparing copper nanowires, copper

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Fig. 2. FESEM images of the ultra-long copper nanowires obtained at 160 °C.

Fig. 3. FESEM images of the ultra-long copper nanowires obtained at: (A) 120 °C with 25.0 mmol L⁻¹ ODA; (B) 180 °C with 37.5 mmol L⁻¹ ODA.
(II) is completely reduced to copper element by ODA at more than 120 °C.

Besides serving as a reducing agent, the nonionic surfactant should play a ligand-assisted template role in the formation of nanowires during hydrothermal process. As we know, it is difficult to dissolve ODA into pure water. However, it is found that ODA can be partially dissolved in the copper (II) chloride solution under vigorous stirring. Because the lone pair of electrons on the nitrogen atom results in both basicity and nucleophilicity of amine, it is supposed that ODA molecules would coordinate with copper (II) cations in aqueous solution, which results in a transfer of copper (II) cations from aqueous phase to the interface between ODA and aqueous phase [24]. At elevated temperatures, the head groups of ODA molecules self-assemble into lamellar phase structure with the increasing of dissolved ODA [25]. The interlayers of ODA micelle may serve as microreactors and are responsible for the formation of nanowires, which is analogous to the formation of tungsten, cobalt and copper nanowires from lamellar composite precursors, because lamellar structures favor the formation of wires under some conditions [26–28].

In comparison with the mechanism of other solution-phase method employed to fabricate 1D metal nanowires [29–30], i.e. using surfactant as soft template to organize into rod-shaped inverse micelles, the growth mechanism in our case is different. The basicity (pH = 10) of the solution after hydrothermal reaction implies that ODA molecules are partially hydrolyzed. Therefore, we assume that the protonized ODA\(^+\) would adsorb onto the surface of copper particles and the interaction between metal surfaces and surfactants lessens the surface energy of copper nanoparticles. The absorbed cationic surfactant of ODA\(^+\) prevent the reduced copper clusters from aggregating into large entities in the nucleation stage, and the capped nanoparticles would prefer to grow anisotropically into wire-like structure. The growth mechanism is similar to the formation of lead nanowires using poly(vinyl pyrrolidone) (PVP) [31]. Hence, the reactant concentration of ODA may play an important role in regulating the shapes and morphologies of the products. Copper nanowires with larger diameter size come out concomitantly at higher temperature, due to higher reducing reaction rate. However, the increased temperature provides better crystallinity via thermodynamic diffusion. Only poly-crystal copper nanowires can be obtained when the reaction temperature is lower than 160 °C and well crystallized single crystal copper nanowires are obtained at 180 °C in our reaction system.

Detailed mechanisms of the redox reaction and the growth of nanowires need further investigation. It is worth noting that ODA employed in our reaction system played multiple roles in the formation of copper nanowires, serving at least as both a soft reducing agent and an adsorption agent. We expect that the reductant of ODA in the present system may expand to other long chain alkylamines, and this new kind of redox reaction can be used to grow 1D and other morphology interesting nanomaterials.

4. Conclusions

In summary, reduction of copper (II) to metallic copper with ODA is a simple chemical reaction for synthesizing ultra-long copper nanowires in large-scale with controllable diameters and tunable crystallinity. The aspect ratio of the copper nanowires is up to 10\(^5\). The diameters, aspect ratios and crystallinities of the as-obtained copper nanowires are strongly dependent on the synthesis temperatures. The concentration of ODA also dramatically influences the diameter distributions and aspect ratios of the nanowires. The nonionic surfactant of ODA played multiple roles in...
the synthesis of copper nanowires, serving at least as both a soft reducing agent and an adsorption agent. We expect that the multifunctional reagent of ODA in the present system may be expanded to other long chain aliphatic alkylamines, and this new kind of redox reaction can be used to grow 1D and other morphology interesting nanomaterials. The obtained nanowires could be used as building blocks for constructing micro- and nano-devices, and interesting 1D materials for fundamental research on their specific physical properties.

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