Synthesis of Cu Nanowires via Solvothermal Reduction in Reverse Microemulsion System

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Abstract: Copper nanowires with high aspect ratios were synthesized by solvothermal reduction of Cu^{2+} in H_2O/CTAB/n-butanol/n-hexane reverse microemulsion system with a water to surfactant molar ratio (ω) = 40. The synthesized products were studied by XRD, SEM, and TEM respectively. The phase structure of the products was cubic face-centered Cu as straight nanowires with an average diameter of ~20 nm and lengths up to 2 μm. It was found that higher water content (ω=40) favored the formation of nanowires with high aspect ratios. The evolution of the nanowires was unidirectional with constant diameters. In aqueous solution experiments, flower-like microspheres consisted of short nanorods were obtained, which indicated that the microemulsion system was a crucial prerequisite for the formation of nanowires with high aspect ratios. A tentative formation mechanism of the nanowires is proposed, which involves unidirectional crystal growth as a consequence of irreversible micellar fusion, micellar longitudinal exchange and coalescence of micelles.

1. Introduction

In recent years researches on one-dimensional (1D) nanomaterials with unique magnetic, optical, electrical and catalytic properties in nanometer scale [1-5], have been the subject of much interest. Tremendous efforts have been made to tailor the morphology and aspect ratio of 1D nanostructure, which are highly attractive building blocks for electronic, optoelectronic, electrochemical and electromechanical devices [6-8] due to their inherent anisotropies and efficient transport of electrons and excitons within dimensions of nano-scale.

Among all the 1D nano-materials under research, special attentions have been paid on copper and related materials in the past few years. Metallic copper with a high electrical conductivity and cheap price has been used in a wide variety of commercial applications. Various nanostructures of copper with desirable properties can be used as a wide variety of potential applications such as chemical sensors [9], catalyst [10], interconnects [11], solid lubricant and etc. A number of approaches have been actively explored to synthesize 1D copper nanostructures [12, 13]. Up to now, the fabrication of copper nanostructures is mainly achieved by template-directed methods. A variety of templates have been successfully demonstrated for use by this method, and they can be classified into hard templates and soft templates. Typical hard templates include alumina membrane [14], carbon nanotubes [15, 16], CaCO_3 [17], silicas [18] etc. Although hard templates are effective in preparing nanowires with uniform and controllable dimensions, they usually lead to complicated processes and furthermore they are hard to remove. Whereas soft templates such as organic surfactants [19], block copolymers [20],...
and biomacromolecules including DNA [21] and viruses [22] seem to be better choice for synthesizing 1D nanostructures without the problems of hard templates.

As effective colloidal templates or nanostructure reaction media, reverse micelles and microemulsions have been widely used for the controlled synthesis of inorganic nanocrystals with specific size and shape [23, 24]. A variety of one dimensional nanosized materials including metals [25], oxides [26], sulfides [27], sulfate [28], tungstate [29] and etc [30-34] have been successfully synthesized in the reverse micelle or reverse microemulsion system. Especially Pileni [24] synthesized cylindrical Cu nanoparticles in AOT/water/isoctane reverse micelles. However the aspect ratios of the cylindrical nanoparticles synthesized by him were low, and there were a lot of spherical nanoparticles in the products.

Very recently, solventthermal method has been widely used to synthesize nano-scale materials because it can provide a unique reaction environment, which facilitates the formation of products that are hard to obtain in normal conditions. In this paper, we demonstrated that Cu nanowires with aspect ratios as high as 100 could be synthesized by solventthermal reaction in the reverse microemulsion system. The diameters and lengths of the nanowires can be tuned by adjusting water to surfactant molar ratio (\(\omega\)). With the reduction of \(\omega\) (from 40 to 10), the nanowires turned thicker and shorter and finally transformed into crinkly nanoflakes. Based on the results of time-controlled experiments at a series of growth time and the experiment in aqueous solution, a tentative formation mechanism of the nanowires is proposed, which involves unidirectional crystal growth as a result of irreversible micellar fusion, micellar longitudinal exchange and coalescence of micelles.

2. Experimental Section

All the chemicals were analytic grade reagents used without further purification. A typical synthesis of Cu nanowires was as follows: Two types of water /cetyltrimethyl ammonium bromide (CTAB)/1-butanol /n-hexane microemulsion solution were prepared by solubilizing 1 ml of 0.6 mol/L CuCl₂·2H₂O solution (1 ml of 1.2 mol/L NaBH₄ solution in another microemulsion solution), 1 ml 1-butanol into 30 ml CTAB n-hexane solution with a surfactant to oil concentration of 0.087 M. The final \([H_2O]/[surfactant]\) molar ratio of the two microemulsion solution was 40. The two different microemulsion solutions were vigorously stirred until they were optically transparent. And then they were mixed rapidly and magnetically stirred for another 15 min. Afterwards the mixture was transferred into an 80 ml Teflon-lined autoclave, sealed, heated and reacted at 180 °C for 12 h. Then the Teflon-lined autoclave was cooled to room temperature naturally. The obtained precipitate was separated, washed several times with distilled water and absolute ethanol, and then dried in a vacuum at 45 °C for 5 h.

The phase structure of the as-prepared products was characterized by X-ray powder diffraction (XRD) using a D/max-2500 X-ray diffractometer with Cu Kα radiation (\(\lambda = 1.5418 \text{ Å}\)). The morphology and microstructure of the products were characterized using a JEOL JSM-6700F field-emission scanning electron microscopy (FESEM) operated at 5.0 kV, and a JEM-2000EX transmission electron microscope (TEM) an acceleration voltage of 160 kV.

3. Result and Discussion

3.1. The phase structure of the products.

The phase structure of the as-synthesized products was determined from the XRD pattern shown in Figure 1. The main reflection peaks can be indexed to cubic face-centered Cu which is very close to the reported data (JCPDS 04-0836) with a lattice parameter \(a=3.615 \text{ Å}\). Additional peaks marked with triangle can be indexed into a cubic structure of Cu₂O (JCPDS 5-667). As is known, metallic copper can be slowly oxidized in the atmosphere. When its size reduces into nanometers, the surface energy is enhanced with the increase of specific surface area and oxidization is accelerated. Liu et al [35] have studied the oxidation process by exposing copper nanowires without oxides in atmosphere and after 24 h Cu₂O appeared. In our experiment, the products had been exposed to air after vacuum drying.
before XRD test, so we can speculate that the as-obtained nanowires were copper nanowires with surface oxidized. Further methods to prevent the products from oxidizing need to be developed.

![Figure 1. XRD pattern of the nanowires.]

3.2. The morphology of the products.
The morphology of the products synthesized above was examined by FESEM. SEM images (Figure 2a) demonstrate that the final products were straight nanowires with diameters of 20 nm±10nm and typical lengths of 1-2 μm. The diameter of a typical nanowire was uniform along the axial direction (Figure 2b) and no bent of large radian was observed.

![Figure 2. FESEM images(a)and TEM image(b) of as-prepared Cu nanowires.]

3.3. The effect of water content on the morphology of the products.
Keeping other reaction conditions constant, controlled experiments were carried out at four different ω values (30, 20, 10, 5). Nanowires with diameters about 20 nm were still obtained when ω = 30, but the aspect ratios turned low since their lengths reduced to less than 500 nm (Figure 3a). Only short nanorods with diameters about 40-50 nm and aspect ratios of about 3 were obtained when ω was reduced to 20 (Figure 3b). Crinkled nanoflakes were obtained when ω=10 (Figure 3c). And when ω was reduced to 5, the morphology of the products was polydisperse without uniformity. This controlled experiment demonstrated that the selected water content (ω=40) is beneficial to the formation of nanowires with high aspect ratios.
3.4. Investigation on the formation mechanism of the nanowires.

To investigate the formation mechanism of Cu nanowires, samples at different growth times were studied by FESEM. Figure 4 shows FESEM images of the products obtained slovenothermal at 180°C for 0.5h, 1h, 2h and 4h respectively, which clearly exhibits the evolution process form nanoparticles to high aspect ratio nanowires. Subsphaeroidal nanoparticles with average diameter of 20 nm were obtained after slovenothermal growth for 0.5h (Figure 4a). Nanorods with diameters about 20nm and lengths about 100nm appeared after slovenothermal treating for 1h (Figure 4b). With diameters unchanged, the lengths of the nanorods were grown to about 200nm when the slovenothermal time reached 2h (Figure 4c). The nanorods turned into nanowires at 4h of slovenothermal growth (Figure 4d) since the aspect ratio exceeded 20 at this time. To sum up, the growth process of the nanowires can be included as a longitudinal equant growth process with the aspect ratio increases with time.

![Figure 3](image1)

**Figure 3.** FESEM images of the products obtained at different water content: (a)30; (b)20; (c)10; (d)5.

![Figure 4](image2)

**Figure 4.** FESEM of the products at different growth times: (a)0.5h; (b)1h; (c)2h; (d)4h.

![Figure 5](image3)

**Figure 5.** FESEM of the products obtained in aqueous solution at 180°C for 12h.

![Figure 6](image4)

**Figure 6.** FESEM images of the products formed at room temperature in reverse microemulsion.

It is found that the microemulsion system is a crucial prerequisite for the formation of high aspect ratio nanowires. If the reaction is conducted in aqueous solution keeping other experiment parameter unchanged (reactant concentration based on the total volume, the amount of surfactant used, reaction
temperature and time). Flower-like microspheres consisted of nanorods with diameters of about 100nm were obtained (Figure 5).

3.5. The formation mechanism of Cu nanowires.

On the basis of experimental results discussed above, a tentative formation mechanism of the Cu nanowires is proposed as follows: When two microemulsion solutions containing Cu\(^{2+}\) and BH\(^{-}\) are mixed in the previous stage, the dimers formed by micelle droplet collision break down again as the Cu nucleation rate is comparatively low at room temperature. The contents from one micelle can be transferred into the other uniformly and the products obtained after 12h were spherical nanoparticles (Figure 6).

![Figure 7](image)

**Figure 7.** Schematic illustration of the proposed mechanism for the formation of Cu nanowires in reverse microemulsions.

When the mixed microemulsions were transferred into solvothermal condition in which the Cu nucleation was very fast, irreversible micellar fusion would occur because surfactants could be adsorbed onto the surface of previously formed rodlike nucleus in the center of a dimer, which would form a cylindrical micelle. The surfactants in the central region of the dimer became fixed and immobile while at the end of the cylindrical micelle, where water was enriched, the surfactant molecules were relatively free. Thus, the cylindrical microemulsion micelle may dynamically exchange content with other micells at both ends forming a equant cylindrical micelle which grew simultaneously with the rodlike nucleus along the axial direction. This process (shown in Figure 7) may result in the formation of one-dimensional Cu nanowires whose diameters are constant and lengths are the function of growth time.

4. Conclusion

Cu nanowires with diameters of ~20nm and lengths up to 2\(\mu\)m have been synthesized in a cationic surfactant CTAB microemulsion system under solvothermal conditions. Higher water content (\(\omega=40\)) favored the formation of nanowires with high aspect ratios. The evolution of the nanowires was unidirectional with constant diameters. The microemulsion system is a crucial prerequisite for the formation of nanowires with high aspect ratios. The formation mechanism of the nanowires involves unidirectional crystal growth as a result of irreversible micellar fusion, micellar longitudinal exchange and coalescence of micelles.

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