Controllable Synthesis of Copper Nanowires by Hydrothermal Method

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Abstract: In this paper, copper nanowires with different aspect ratios were synthesized by hydrothermal method at 150 ℃, using environmentally friendly and inexpensive reagents such as chloride dihydrate ($CuCl_2 \cdot 2H_2O$), tetradecylamine (TDA), and glucose. Moreover, the effects of different reaction times and reactant ratios on the synthesis were investigated to obtain copper nanowires with different aspect ratios spanning from 150 to 500.

1 INTRODUCTION

Copper nanowires are becoming increasingly popular due to their advantages of good electrical conductivity, low cost and abundant crustal content. The applications of copper nanowires mainly depend on their different aspect ratios. For example, copper nanowires with low aspect ratio can be used for catalytic reactions(He et al., 2014) and antimicrobial applications(Jiang et al., 2015). High aspect ratio copper nanowires can be used as transparent electrodes(Guo et al., 2013) and they are also applied in solar cells(Yu et al., 2016), organic light emitting diodes(Eritt et al., 2010), and smart windows(Runnerstrom et al., 2014). Therefore, it is necessary to control the aspect ratio of the synthesized copper nanowires. Zhang et al. synthesized ultrathin semicircle-shaped copper nanowires with the aspect ratio of around 2000, which can be used in optical devices(Zhang et al., 2018). Deshmukh et al. obtained high aspect ratio copper nanowires which were used to fabricate copper nanowire films with a sheet resistance of 24.5 Ω/sq, and a transmittance of T = 71%(Deshmukh et al., 2018). Wang et al. successfully prepared copper nanowires by hydrothermal method with aspect ratio of approximately 2500(Wang et al., 2018). In this paper, we prepared copper nanowires by a hydrothermal method in an environmentally friendly approach and investigated the effects of different parameters in order to achieve controllable synthesis of copper nanowires.

2 EXPERIMENTAL

2.1 Materials

Chloride dihydrate (Aladdin, AR), tetradecylamine (Aladdin, 96%), and glucose (Aladdin, AR) were used for the synthesis of copper nanowires. Trichloromethane (Aladdin, 96%), ethanol (Aladdin, 99.7%), and hexane (Aladdin, 97%) were used as solvents in centrifugal purification.

2.2 Synthesis of Copper Nanowires

Firstly, 0.34 g of copper chloride dihydrate, 0.36 g of glucose and 1.6 g of tetradecylamine were dissolved in 80 ml of deionized water. Then, the mixture was stirred magnetically for half an hour. Secondly, the solution was poured into a 100 ml reaction tank, then charged into the reaction vessel, and reacted at 150 ° C for 4 hours. Finally, after the resulting solution was cooled down, the supernatant was poured off, and the remaining red fibrous material was collected. The fibrous material was purified by centrifugation with deionized water, n-hexane and chloroform, respectively. Finally, a pure red material was obtained and stored in n-hexane.

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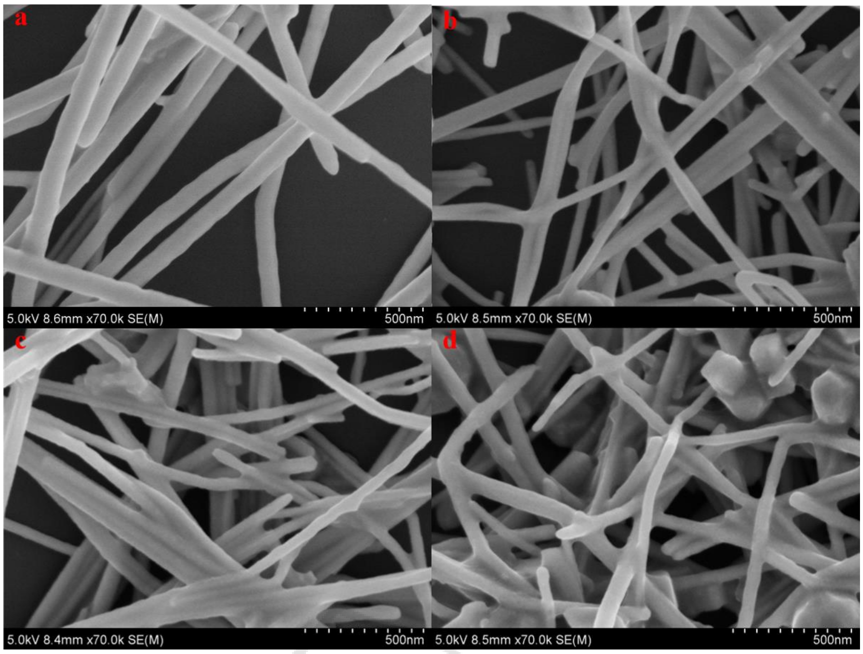

Figure 1: SEM images of CuNWs. a. nCu : nglucose = 1:2; b. nCu : nglucose = 1:1; c. nCu : nglucose = 3:2; d. nCu : nglucose = 2:1.

3 RESULTS AND DISCUSSION

3.1 Effect of Reactant Ratio

The effect of reactant ratios on the reaction was investigated, especially the ratio between copper chloride dihydrate and glucose. The amounts of tetradecylamine and copper chloride dihydrate were kept constant while the amount of glucose was changed. The copper nanowires were obtained at the same reaction time and reaction temperature.

Figure 1 exhibits the SEM images of CuNWs synthesized with different reagent ratios. The different reactant ratios caused the copper nanowires to exhibit different morphologies. As seen from the images in Figure 1, copper nanowires were formed as the amount of glucose decreased, but several copper crystals were also observed in Figure 1d. The reason for this behaviour could be that： the presence of five hydroxyl groups in one glucose molecule, and the ratio of Cu^{2+} to glucose molecules should be 1:0.4 in theory. The amount of steric hindrance agents remained constant, so the directional growth of copper crystals was limited. As a result of decreasing ratio of glucose, less copper nanoparticles were obtained and they were not fully elongated along the [110] direction(Jin et al., 2011) to generate CuNWs conforming to the Ostwald ripening process. This also explained why addition of less glucose resulted in the formation of thinner and shorter CuNWs (as described below). In order to study the difference in morphology, 50 to 100 copper nanowires with different reactant ratios were measured, their length was tested, and finally their aspect ratio was calculated, as shown in Figure 2. Figure 2 illustrates the effect of different reactant ratios on the diameter of copper nanowires. As the amount of glucose decreased, there was an overall trend of decreasing diameter, which was because less CuNPs led to incomplete growth. Therefore, the copper nanowires with different aspect ratios can be obtained.

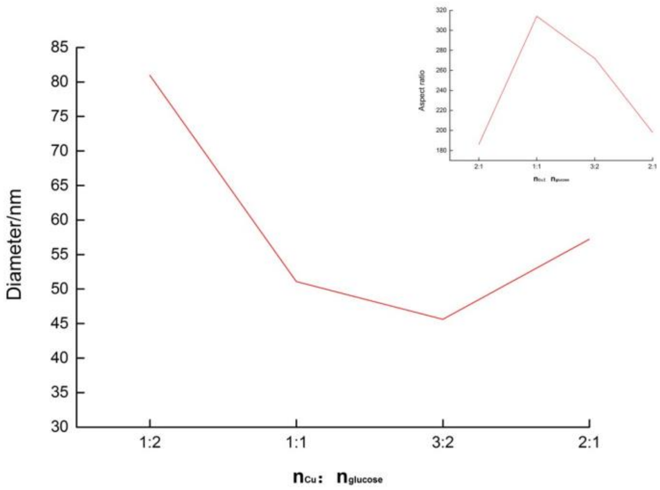

Figure 2: Change in diameter of copper nanowires with different reactant ratios. The inset is a line chart indicating the relationship between the reactant ratio and the aspect ratio.

3.2 Effect of Reaction Time

The effect of reaction time on the synthesis was also investigated, by keeping the ratio of reactants the same, and changing the reaction time to 4h, 8h, 16h, 24h, and 32h.

Figure 3 shows the scanning electron micrographs of copper nanowires prepared at different reaction times. CuNPs grew in a particular orientation due to the selective binding of steric agent TDA to {100} facets of Cu (Jia et al., 2013). The amount of TDA was constant, indicating limited steric effects, and a prolonged reaction time led to a more complete growth of CuNPs. In theory, the purity of CuNWs should be better with increase in reaction time. However, a small of amount of CuNPs were observed in Figure 3b, Figure 3c and Figure 3d, which could be due to an insufficient purification process.

As seen in Figure 4, as the reaction time increased, the diameter of the copper nanowires decreased and the aspect ratio increased. When the reaction time increased, the time of oriented growth became longer. As a result, the length of copper nanowires increased, and the diameter decreased as the amount of reactants remained constant, which is consistent with Ostwald ripening.

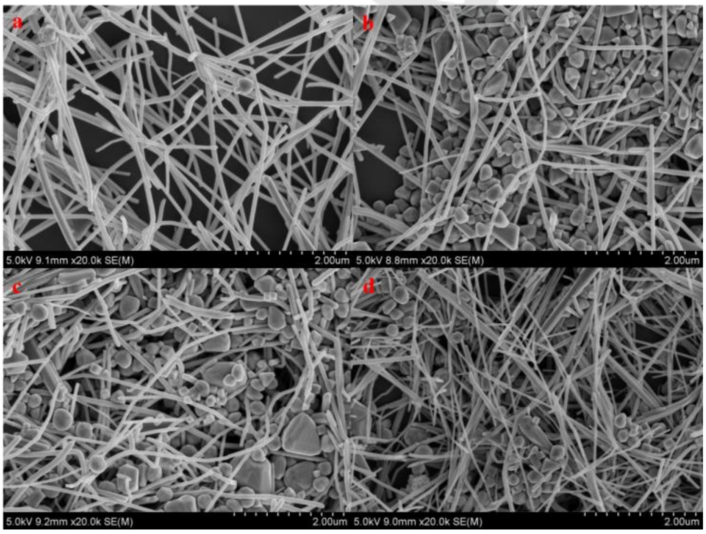

Figure 3: SEM images of CuNWs prepared with different reaction times. a. 8h; b. 16h; c. 24h; d. 32h.

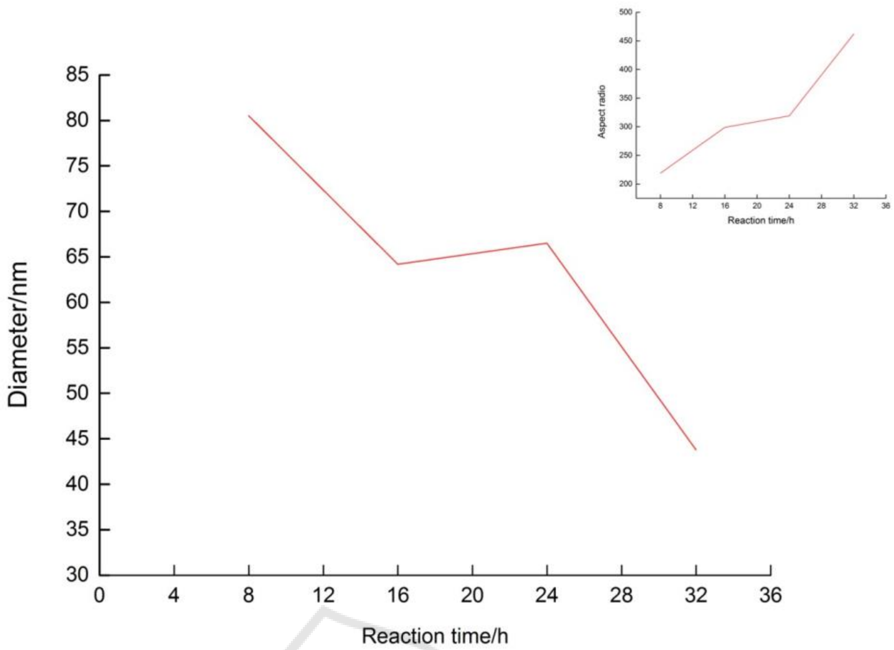

Figure 4: Change in diameter of copper nanowires with different reaction times. The inset is a line chart indicating the relationship between the reaction time and the aspect ratio.

4 CONCLUSIONS

In this work, copper nanowires were controllably prepared by a TDA-assisted hydrothermal method. Moreover, the effects of different reactant ratios and reaction times on the morphology of the resulting copper nanowires were investigated. By varying the above reaction parameters, CuNWs were obtained with different aspect ratios ranging from 150 to 500. When the amount of glucose decreased and reaction time increased, thinner CuNWs were obtained. Thus, the results of this work could help guide the production of suitable CuNWs for different applications such as sensors and solar cells.

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