

A Novel Way for Preparing Cu Nanowires

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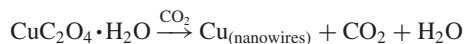
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Copper nanowires with lateral dimensions of 50–200 nm were successfully synthesized by the pyrolysis of copper oxalate hydrate in the presence of CO₂ at 220 °C. The phase and morphology of the products were analyzed by X-ray powder diffraction (XRD) and transmission electron microscopy (TEM). The possible mechanism and future application were proposed.

One-dimensional (1D) nanostructures of metals are thought to play a significant role in future nanosensors, electron emitters, and many other fields.^{1–4} Among all 1D metal wires, copper nanowires have attracted much attention because of its high electrical conductivity and its possible applications such as interconnect.⁵ Up to now, copper nanowires are mainly fabricated by template-directed methods involving electrochemical deposition and the reduction of Cu compounds in the channels of the template.^{6–11} The main disadvantage of the template synthesis is its complicated procedures, as well as its low yield and defects in the products. Recently, some templateless approaches, such as vacuum vapor deposition (VVD),¹² complex-surfactant-assisted hydrothermal reduction process,¹³ and vapor–solid reaction growth (VSRG)¹⁴ have also been developed to fabricate copper nanowires.

Herein we show a novel method for preparing copper nanowires. The new method is a one-step procedure that only involves the pyrolysis of copper oxalate hydrate under supercritical CO₂. CO₂ controls the pyrolysis rate of oxalate precursors, which leads to the formation of 1D nano copper. We denote this approach the Slowly Orientational Growth (SOG), in which process rate plays a significant role in the determination of the morphology of final products. The reaction was carried out in an autoclave and can be described as follows:



In a typical reaction, copper oxalate hydrate was prepared by mixing toluene, 0.299 g of copper acetate hydrate, 0.195 g of oxalic acid dihydrate, 3.00 g of DBS (dedecylbenzenesulfonic acid sodium salt) and 6.0 mL of alcohol in 30.0 mL of toluene, and then the solution was refluxed for 5 h. Then, 0.100 g of copper oxalate dihydrate and 5 g of dry ice were placed a 10-mL autoclave, which was maintained at 220 °C, 100 atm for 8 h. The pressure was autogenic depending on reaction conditions. The resulting red solid product was washed with absolute ethanol, and dried in vacuum at 60 °C for 6 h.

The X-ray diffraction (XRD) analysis was performed using a Rigaku D/max-γA X-ray diffractionmeter equipped with graphite monochromatized Cu Kα radiation ($\lambda = 1.54178 \text{ \AA}$). The TEM images were recorded on a Hitachi H-800 transmission electron microscope performed at 200 kV.

Figure 1 shows the XRD pattern of the sample. All peaks

can be indexed as face-centered cubic copper with lattice constant $a = 3.613 \text{ \AA}$, which is in good agreement with the reported data (JCPDS 4-836, $a = 3.615 \text{ \AA}$). No characteristic peaks of oxides were obtained under current synthetic conditions from XRD pattern. But the sample partly converted to copper oxide after one day.

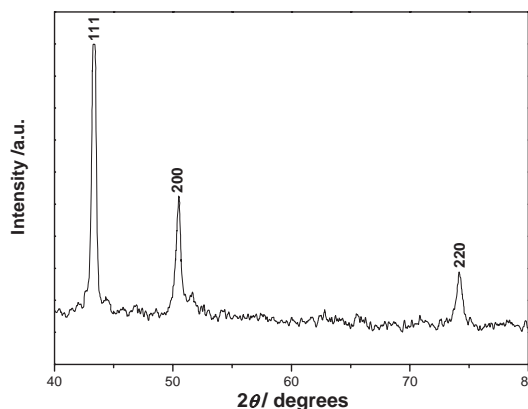


Figure 1. XRD pattern of the as prepared sample.

The morphology and dimension of the as-prepared products were examined by TEM. The TEM images of the synthesized nanowires are shown Figures 2a and 2b. It can be seen that the sample consists of nanowires with lateral dimensions of 50–200 nm. The corresponding selected-area electron diffraction (SAED) pattern shown in Figure 2c confirms that these nanowires are of single crystals of face-centered cubic Cu. The diffraction spots other than Cu may due to copper oxides.

In our experiment, the control of the amount of CO₂ as well as the temperature is very important. CO₂ controls the reaction rate and prevents copper from being oxidized by oxygen. Temperature also controls the reaction rate. Copper oxalate hydrate begins to pyrolyze at 220 °C. With the reaction temperature elevating, the reaction rate becomes much faster, resulting in larger diameter, and finally the disappearance of nanowires. At 280 °C, some of the copper nanowires synthesized reach a diameter of about 250 nm (Figure 2f), which were not found in the products at 220 °C. What is more, at high temperature copper may react with CO₂, leading to the formation of copper oxides.

Then we conclude that the morphology of the products is highly dependent on the reaction rate. Only at a relatively slow rate could the pyrolysis lead to the formation of nanowires. So the copper nanowires is not formed by the assembly of smaller particles, which could be seen in Figures 2a and 2b. Instead, it follows a slow but one-step and orientational approach. That could explain the result of the SAED pattern, which shows that the as-prepared copper nanowires are single crystalline. This is also in agreement with the presence of variously shaped copper

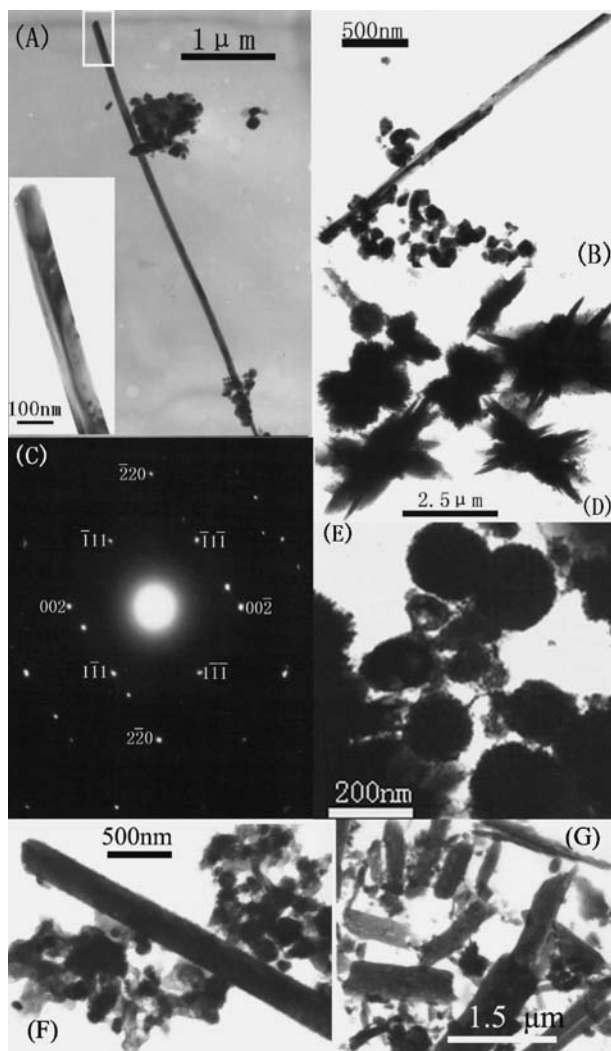


Figure 2. TEM images of the products. (A), (B) copper nanowires. (C) SAED pattern taken from the nanowires shown in (A). (D) Flowerlike metallic copper, (E) quasisphere metallic copper in the products, (F) copper nanowires synthesized at 280 °C, (G) the as-prepared precursor: copper oxalate dihydrate.

in the products. Other than nanowires and nanoparticles, copper could form flowerlike (Figure 2d) and quasisphere (Figure 2e) shapes, which suggests that the precursor might have a great effect on the reaction. As a matter of fact, the morphology of the copper oxalate hydrate was 3D (1–4 μm) when prepared in water, resulting the three-dimensional final products. So the morphology of the products highly depends on that of the precursors, in which case high quality and large-scale nanowires could be

synthesized by choosing appropriate methods of preparing 1D oxalates. While according to the image of the precursors shown in Figure 2g, there is no strict relationship between the morphology of precursors and that of the synthesized copper nanowires: the copper nanowires are much longer and thinner than the precursors. So both the slow reaction rate and the morphology of precursors are crucial, and only by combining both conditions, could we get long and thin copper nanowires. More detailed and exact mechanism is under study in order to prepare large scale of copper nanowires.

In conclusion, copper nanowires with a diameter of 50–200 nm have been synthesized by the pyrolysis of copper oxalate hydrate. We propose SOG as possible mechanism. By controlling the morphology of the precursor, the morphology of the final products could be controlled to some extent. What is more, the methods could be extended to the growth of metal (such as Ni, Co, Pb, Ag, etc.) nanowires or metal oxide (such ZnO, MnO, CrO, Al₂O₃, etc.) nanowires at different temperature.

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