Fabrication and Characterization of Porous Copper Nanorods with Rectangular Cross Sections

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Porous copper nanorods with rectangular cross sections have been successfully prepared in high yield via a hydrothermal reduction process at a relative low temperature. The phase and morphology of products were analyzed by X-ray powder diffraction (XRD) and field-emission scanning electron microscopy (FE-SEM). An interesting red shift was observed in the optical absorption measurement and attributable to the porous nanorod with rectangular cross sections.

One-dimensional (1D) nanostructures of metals are thought to play a significant role in future nanosensors, electron emitters, SERS, and many other fields.[1–5] Among all metals, the conductive copper with a high electrical conductivity has been used in a wide variety of commercial applications and its properties can be enhanced by processing it into various nanostructures with well-controlled dimensions and aspect ratio. Up to now, copper nanowires and nanorods are mainly fabricated by template-directed methods involving electrochemical deposition and reduction of copper compounds in the channels of the template.[6–10] Recently, some templateless approaches, such as vacuum vaper deposition (VVD)[11] and vapor–solid reaction growth (VSRG)[12] have also been developed to fabricate copper 1D nanostructure.

Here, we report a new method of the fabrication and characterization of porous copper nanorods with rectangular cross sections. The preparation was performed using a hydrothermal reduction process at a relative low temperature.

All of the chemical reagents used were of analytical grade. In a typical synthesis process, 0.24 g of $Cu(NO_3)_2$ 0.37 g of trisodium citrate dihydrate, and 0.2 g of ascorbic acid were mixed with 40 mL of distilled water. After stirring for 5 min, 0.5 g of poly(vinylpyrrolidone) (PVP) was added into the stirred solution. The mixture was stirred vigorously to homogeneity and then transferred into a 60-mL steel autoclave. The clave was sealed, maintained at 120 °C for 4 h and then cooled to room temperature. The product was washed with distilled water and ethanol for several times to remove the impurities before characterizations.

XRD of the samples was recorded at a scanning rate of 0.05°/s with the 2θ range from 10 to 80° using an X-ray diffractometer with high-intensity Cu Kα radiation ($\lambda = 0.154178$ nm). FE-SEM was used JEOL JSM-6700 FESEM (operated at 10 kV).

Figure 1 was a typical XRD pattern of the sample. Three peaks at $2\theta = 43°$, $50°$, $74°$ could be indexed to the face-centered cubic copper with lattice constant $\alpha = 0.3614$ nm, which is very close to the reported data (JCPDS 85-1326, $\alpha = 0.3615$ nm). No characteristic peaks of the of oxides can be detected. This indicated that metal copper products were obtained under current synthetic conditions.

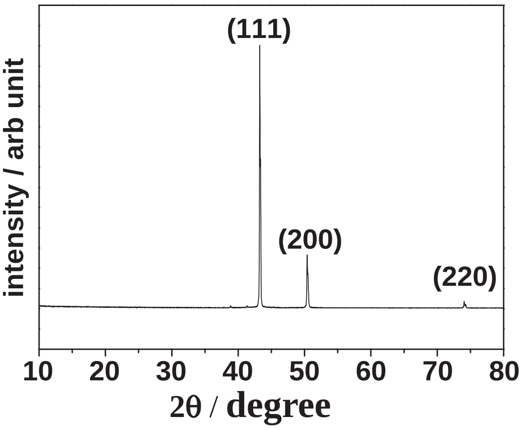

Figure 1. XRD pattern of the porous copper nanorods with rectangular cross sections.

Morphology and size of the product were studied by SEM. Figure 2a shows a representative SEM image and illustrates that the reaction produces predominantly straight nanorods with well-defined facets. From the Figure 2a, it is clearly showed that the yield of copper nanorods is about 80%. Cross-sectional SEM images, such as that shown in the inset of the Figures 2c and 2d, have further revealed that these porous nanorods exhibit clear rectangular cross sections. Imaging of the reaction products from multiple reaction runs shows that the average width of typical Cu

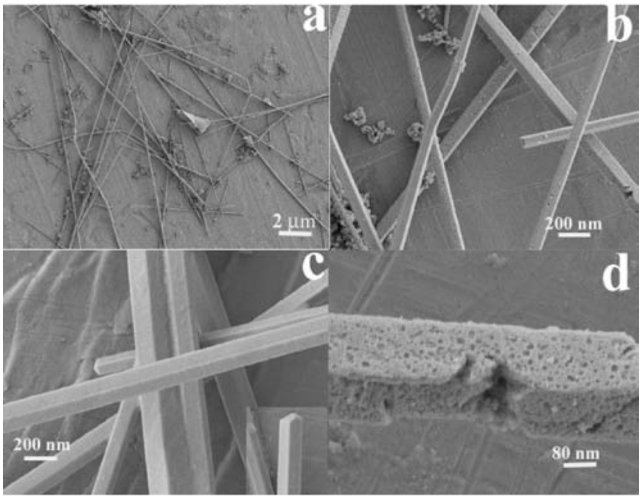

Figure 2. a) SEM image of the sample. b) Low-magnification view about porous copper nanorods. c) SEM image of the copper nanorods without porous. d) Typical porous copper nanorods with rectangular cross sections.

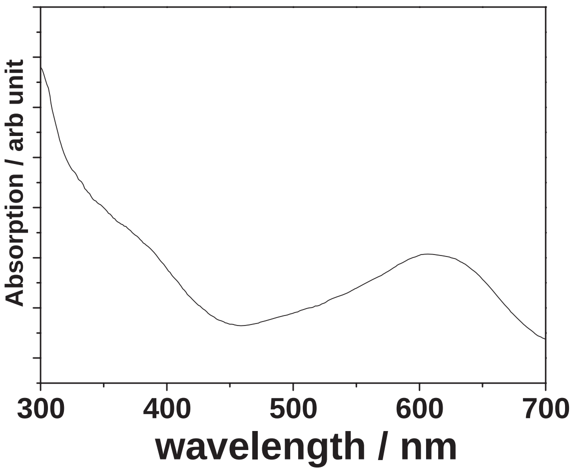

Figure 3. UV–vis spectra of the as-prepared porous copper nanorods.

nanorod is about 50–100 nm with lengths reaching >10 µm.

We found that the trisodium citrate dihydrate played a crucial role on the porous copper nanorods growth. In order to study the role of trisodium citrate dihydrate, the experiments were carried out in aqueous solution without trisodium citrate dihydrate, and the concentrations of reactants and temperatures were kept constant. SEM image indicated that imperforate copper nanorods with rectangular cross sections were obtained (Figure 2c). However, the reason why the trisodium citrate dihydrate we added produced porous shape was still unclear while the related research was under way. In the reaction, the ascorbic acid acted as ligand and reducer as well, which played an important role in the growth of nanorods. We found that the ascorbic acid was unique for the formation of Cu nanorods with rectangular cross sections in the present preparation. When other reducing agents, such as sodium hypophosphite and $N_2H_4 \cdot H_2O$, were used instead of ascorbic acid, no nanorods with rectangular cross sections were produced. In the reaction mixture, PVP was also a important factor in determining the morphology of the final product. With the assistance of PVP, these copper nanoparticles were able to grow into rod-shaped structures. It could be believed that the surfactant PVP was to kinetically control the growth rates of various faces by interacting with these faces through selectively adsorbing on these facets. The roles of PVP on the formation of Cu nanorods were similar to these of formation of Ag and Pb nanowires.[13,14] In the absence of PVP the reaction only produced very irregular nanoparticles.

Figure 3 shows the UV–vis absorption spectrum taken from the as-prepared copper nanorods dispersed in ethanol. The curve for the sample exhibits a UV–vis absorb peak around 635 nm ascribed to the porous copper nanorods. It is surprising that its red shift extends about 70 nm compared with that of a system composed of simple nanorods.[15,16] We presume that the key factor is likely to be the unique morphology of the product. This is due to the fact that the surface area of copper nanorods with rectangular cross sections is larger than that with normal shape. And we also think that there may be some oxides on the surface of copper nanorods, and something may be adhibited inside the aperture. As a result, the UV–vis light absorbance of the copper nanorods with rectangular cross sections is more than that of the normal copper nanorod.[15] This may be the reason of red shift, while the main reason of red shift of porous copper nanorods is still under research.

We have successfully prepared nanoscale porous copper rods with rectangular cross sections using a hydrothermal reduction process at a low temperature. The results obtained from SEM measurements indicate that the trisodium citrate dihydrate and PVP has a significant influence on the formation of porous copper nanorods with rectangular cross sections. The resultant porous copper nanorods may provide interesting possibilities for further applications in catalyzing because of the large surface area. The related research was under way.

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