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A SIMPLE WAY OF PREPARING NANOCOPPER POWDERS AND ITS CATALYTIC APPLICATION TO SYNTHESIZE CARBON NANOFIBERS

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In this paper, copper nanorod and nanoparticles have been synthesized by a fast microwave-assisted method. The samples were characterized by X-ray diffraction, transmission electron microscopy, scanning electron microscopy and thermogravimetric analysis. The result indicated that the ethylenediamine played a crucial role in the formation of copper microstructures. With the as-prepared nanoparticles as catalyst, carbon nanofibers (CNFs) were synthesized by catalytic polymerization of acetylene at a lower temperature. The effects of the catalyst particle sizes on the morphologies of the CNFs were studied.

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1. Introduction

During past years, synthesis of high-quality, nanostructured copper attracts much attention because of its application span over catalyst, electron conduction slurry, microelectronics, metal alloy, solid lubricant, and so on [1-3]. Beyond all doubt, it is crucial to control nano-copper size, size distribution, external shape, internal structure for the synthesis process. However, several critical problems such as solvent re-dispersed of copper nanoparticles, easily oxidized, high-cost and complex synthetic method has restrained its further application [4]. Therefore, it is very important to develop some other fast methods for the preparation of copper powders with controlled size, morphologies and properties in mild reaction conditions.

Carbon nanofibers (CNFs) and carbon nanotubes (CNTs) are important materials because of their novel physical and chemical properties, and versatile applications [5]. CNFs and CNTs can be synthesized by metal powders such as nickel, cobalt, copper and iron [6-9]. Here, we describe a fast microwave-assisted method for fabricating nanocopper powders with different shapes and size. The catalytic property of the as-prepared copper nanoparticles was tested in the synthesis of carbon CNFs by polymerization of acetylene at a lower temperature.

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2. Experimental

All chemicals were of analytical grade reagents and used as received without any further purification. In a typical experimental procedure, 1 mmol of $CuSO_4 \cdot 5H_2O$ was added into 10 mL NaOH (4 mol/L) and 5 mL ethylenediamine (EDA) to form a uniform solution and then a mass of 0.6 g $N_2H_4 \cdot H_2O$ (80 wt%) solution was added dropwise to the solution. After that, the mixture was microwave-heated at intermediate fire level (400 W) for 6 min. Then, the microwave heating was terminated, and the solution was cooled to room temperature. The products were separated centrifugally and washed with ultrapure water and absolute ethanol three times, and dried under vacuum at 45 °C for 12 h.

X-ray powder diffraction (XRD) analysis was performed on a BRUKER AXS D8 Advance diffractometer with Cu Kα radiation (λ=1.54178 Å) using a 40 kV operation voltage and 40 mA current. The transmission electron microscopy (TEM) images were collected on a JEOL JEM 2100 transmission electron microscope operating at an accelerating voltage of 200 kV. Scanning electron microscopy (SEM) images were obtained using a HITACHI S-3000N microscope. Thermogravimetric analysis (TGA) was carried out on a Q600 thermal analyzer with a heating rate of 10 °C min^{-1} in flowing air.

3. Results and discussion

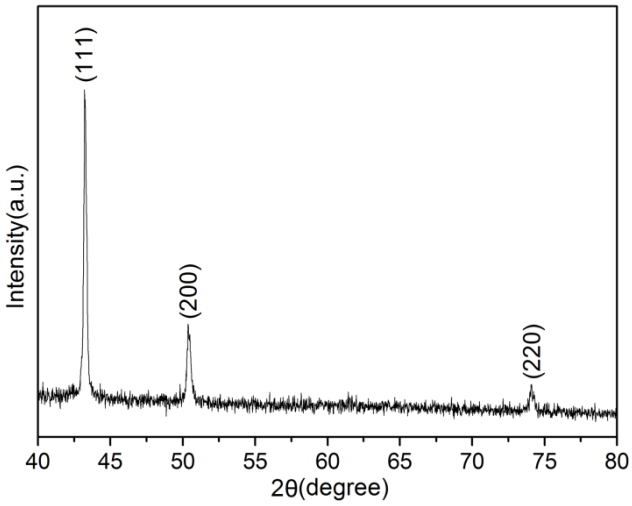

Fig. 1. XRD pattern of as-prepared nanocopper powders

Fig. 1 shows the XRD pattern of the synthesized rodlike nanocopper sample. From the XRD pattern, it can be found that the rodlike nanocopper sample has the major characteristic peaks for pure metallic Cu at 2θ values of 43.38, 50.48, and 74.18 assigned to (111), (200) and (220) planes of copper and no other peaks are observed. The result indicates that there were no copper oxides or other crystalline materials formed and only pure Cu powders were obtained under given experimental conditions.

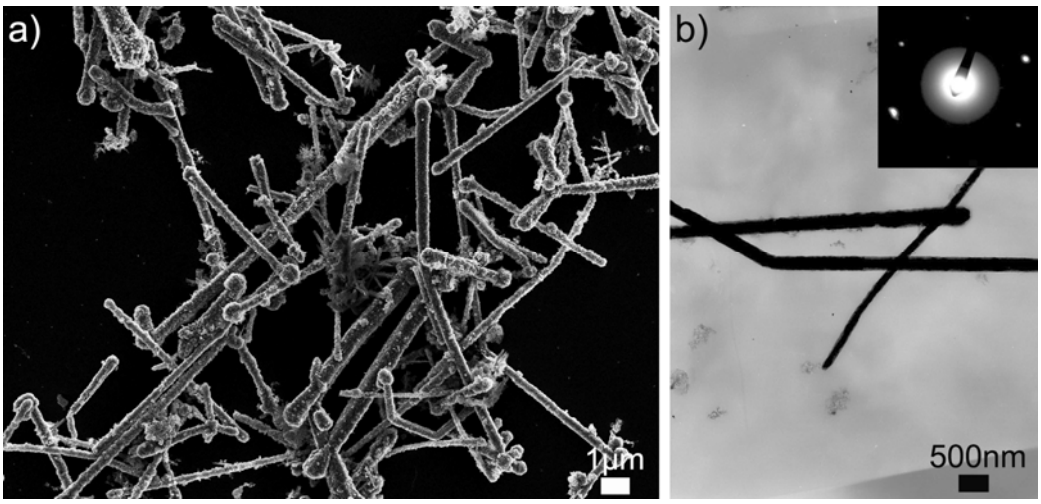

Fig. 2. (a) SEM and (b) TEM images of the as-synthesized rodlike nanocopper powders.

Fig. 2a shows a typical SEM image of the as-prepared nanocopper powders. It is clear that a uniform copper rodlike structure can be obtained under the present experimental conditions and the rodlike copper crystal has a length of ca. 10 μm and a spherelike structure in one end with a diameter of ca. 500 nm in the center. The rodlike shape of copper crystal was further confirmed by a TEM image (Fig. 2b). The selected area electron diffraction (SAED) pattern (inset to Fig. 2b) taken from an individual rodlike crystal is indexed to a cubic-phase copper, indicating that it is a single crystal.

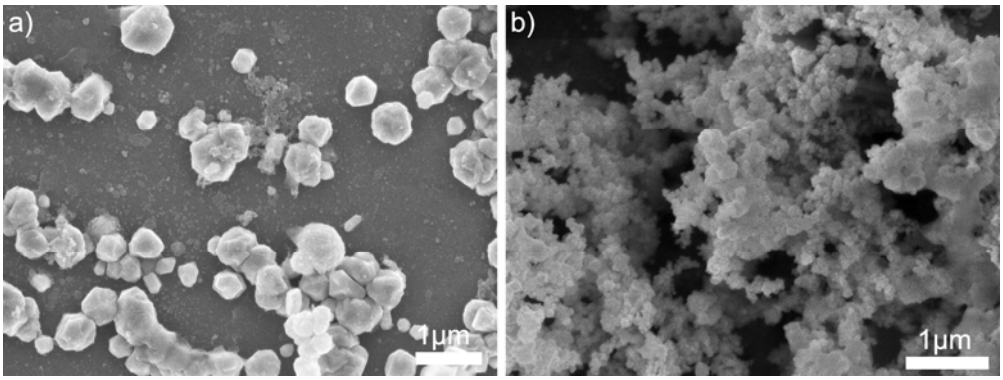

Fig. 3. SEM images of nanocopper powders with different amounts of EDA (a) 2 ml and (b) 1 ml.

In the preparation processing, the amount of EDA has a significant effect on the shape of products. Fig. 3 shows SEM images of nanocopper powders synthesized at various amounts of EDA while the other conditions were the same. As the amount of EDA decreases from 5 to 2ml, the shape of the sample changes from rod to particle. As shown in Fig. 3a, all the particles appear spherical and the average size of these particles is about 520 nm. When the amount of EDA further decreases from 2 to 1ml, Fig. 3b shows the samples are uniform nanoparticles with an average size of about 50 nm. This result indicated that the EDA played a crucial role in the formation of copper microstructures.

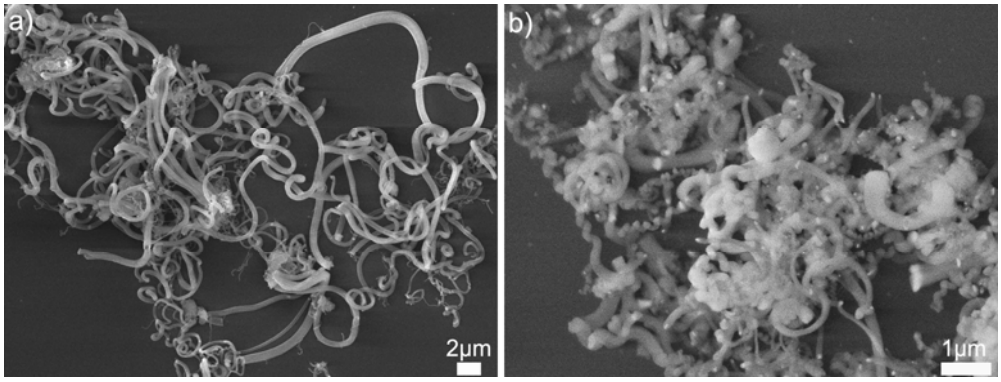

Fig. 4. SEM images of CNFs catalyzed by copper nanoparticles prepared using (a) 2 ml and (b) 1 ml of EDA.

The catalytic property of the as-prepared copper nanoparticles was tested also in the synthesis of CNFs by polymerization of acetylene. Fig. 4a shows the SEM image of the CNFs synthesized with copper nanoparticles (2ml EDA) as catalysts. We can see that the diameter of most of CNFs is about 1.0 μm and the length of these CNFs is up to dozens of micrometers. Most of them are linear and few coil CNFs could be found. When copper particles with a lesser size were used as catalyst, more coil CNFs with an average diameter of 150 nm were synthesized (Fig. 4b). From these SEM images, we can infer that the diameter and shape of CNFs was influenced by the size of copper nanoparticles. The reason for the helical growth of these coiled fibers is not clear at present and requires further investigation.

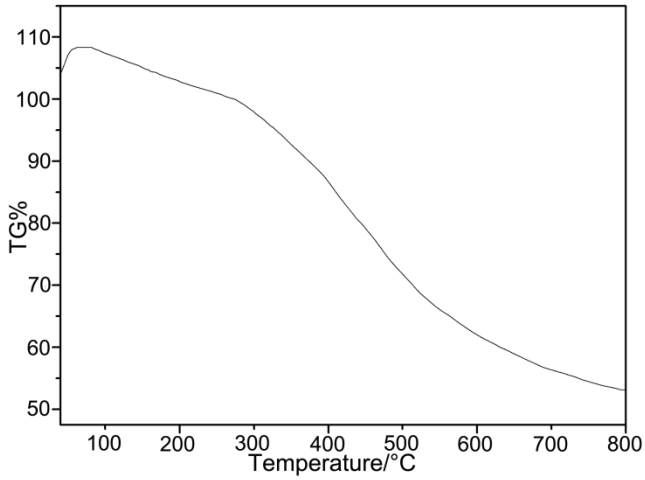

Fig. 5. TGA of the CNFs.

The thermal stability of CNFs was determined by TGA. As shown in Fig. 5, with the increase of the temperature, obvious weight loss was observed. The weight loss of CNFs indicated that the products released small hydrocarbon molecules because of the C-H cleavage and structural reconfiguration of the nanofibers.

4. Conclusions

In this work, we used a simple microwave-assisted method for fabricating copper powders with different shapes. With a high concentration of EDA, rodlike copper powders were major products. When the amount of EDA was decreased, the shape of the sample changes from rod to particle. The catalytic property of the as-prepared copper nanoparticles was tested in the synthesis of CNFs by polymerization of acetylene. The diameter and shape of CNFs was influenced by the size of copper nanoparticles. When copper particles with a lesser size were used as catalyst, more coil CNFs with an average diameter of 150 nm were synthesized.

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