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# Shape controlled synthesis of $Cu_2O$ and its catalytic application to synthesize amorphous carbon nanofibers

Fanglin Du [a,*], Jungang Liu [b], Zhiyan Guo [a]

[a] *Key Laboratory for Nanostructured Materials, Qingdao University of Science and Technology, Qingdao 266042, China*
[b] *Technical development center, Laiwu Steel Corp. Ltd., Laiwu 271104, China*

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ABSTRACT

Octahedral $Cu_2O$ particles and $Cu_2O$ nanowires were synthesized by a simple solution-phase route using $N_2H_4{\cdot}H_2O$ as reducing agent at room temperature. Amorphous carbon nanofibers were synthesized using octahedral $Cu_2O$ particles and an acetylene gas source at atmospheric pressure. The samples were characterized by X-ray diffraction (XRD), transmission electron microscopy (TEM), scanning electron microscopy (SEM), Fourier transform infrared (FT-IR) spectroscopy and thermogravimetric (TG) analysis. SEM and TEM images indicated that most of the obtained octahedral $Cu_2O$ particles had an edge length of 400–700 nm. The obtained nanowires had uniform diameters of about 15 nm, and the length of the nanowires ranged from 5 to 10 μm. The XRD result revealed the amorphous feature of the nanofibers. IR spectrum revealed that the nanofibers consist of –CH, $-CH_2$, –C=C– and $-CH_3$ groups. The concentrations of $N_2H_4{\cdot}H_2O$ and NaOH played important roles in controlling the geometric shape of the $Cu_2O$.

## 1. Introduction

It is important to control the size, shape and structure of particles because of the tight correlation between these parameters and optical, electrical and catalytic properties [1]. Metal and semiconductor nanoparticles have been widely studied in various fields such as electronics devices [2] and catalysis [3,4]. Over the past several decades, cuprous oxide ($Cu_2O$) has attracted much interest because of its potential applications in catalysis, biosensors, and micro/nanoelectronics [5–7]. Nanostructured $Cu_2O$ with different morphologies has been synthesized using solution routes [8–13] and electrodeposition method [14].

Carbon nanofibers and nanotubes can be synthesized by metal powders such as nickel, cobalt and iron [15–17]. Qin et al. [18] reported the growth of helical nanofibers on copper nanoparticles by using acetylene as a gas source. Helically shaped multiwalled carbon nanotubes were obtained as main products in large quantities by using co-pyrolysis of $Fe(CO)_5$ as floating catalyst precursor and pyridine or toluene as carbon source [19]. Carbon nanofibers were synthesized by using alumina-supported Ni catalyst [20]. However, there are few reports on the synthesis of amorphous carbon nanofibers using cuprous oxide particles as catalyst.

Herein we reported a simple solution-phase route to control the morphology of cuprous oxide at room temperature and its catalytic applications to synthesize amorphous carbon nanofibers.

## 2. Experimental

All of the chemical reagents used in this experiment were analytical grade. In a typical synthesis, 0.250 g $Cu(NO_3)_2{\cdot}3H_2O$ and 0.250 g polyethylene glycol (PEG; Mw 20000) were dissolved in 200 ml $H_2O$, which was stirred with a magnetic stirrer for 10 min. Then, 1.2 ml of 4 M NaOH solution was slowly dropped into the $Cu(NO_3)_2$ solution. After stirring for 10 min, 2.4 ml of 1.5 M $N_2H_4{\cdot}H_2O$ solution was slowly dropped into the mixed suspension. The solution was kept for 10 min under constant stirring. The resulting products were collected, washed several times using absolute ethanol and distilled water and dried in a vacuum oven at 80 °C for 2 h.

Acetylene was used as the only carbon source and the as-synthesized octahedral $Cu_2O$ particles were used as catalyst in our experiment. The reaction tube of quartz was used as a reactor, which was heated by an electric furnace. After the reactor was pumped to vacuum, the acetylene gas was introduced into the reaction room. The reaction began at 265 °C and this temperature was kept constantly until the reaction finished.

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* Corresponding author. Tel.: +86 532 84022870; fax: +86 532 84022870.
*E-mail address:* dufanglin@qust.edu.cn (F. Du).

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## 3. Characterization

X-ray powder diffraction (XRD) patterns of the samples were obtained on a XB-3A instrument using monochromatic Cu Kα radiation ($\lambda = 0.15418$ nm). The experimental conditions correspond to step width of 0.02° and scan speed of 7°/min. Transmission electron microscopy (TEM) was carried out on a JEM-1200EX operating at an accelerating voltage of 60 kV. The overview morphology of the samples was measured by field emission scanning electron microscopy (FESEM), performed on a JSM-6700F. The samples for characterization were prepared by dripping the precipitate onto a silicon wafer. FT-IR spectrum was performed on a Nicolet Fourier transform infrared (FT-IR) spectroscopy. The nanofibers were characterized by a thermogravimetric analysis (TG) at a heating rate of 10 °C/min.

## 4. Results and discussion

Fig. 1 shows the XRD pattern of the as-prepared octahedral $Cu_2O$ particles. The diffraction peaks in this pattern can be indexed to cubic structure of octahedral $Cu_2O$ with lattice constants of $a = 4.26$ Å. This is in good agreement with the literature values (JCPDS05-0667). The peaks with $2\theta$ values of 29.59°, 36.52°, 42.36°, 61.56°, 73.70° and 77.60° correspond to the crystal planes of 1 1 0, 1 1 1, 2 0 0, 2 2 0, 3 1 1 and 2 2 2 of crystalline $Cu_2O$, respectively.

Fig. 2 shows the overall morphology of $Cu_2O$ prepared under different conditions. As shown in Fig. 2(a), when 2.4 ml of 1.5 M $N_2H_4{\cdot}H_2O$ solution was added into the suspension, the major products were nanowires. Few octahedral $Cu_2O$ particles were observed. Most nanowires had uniform diameters of about 15 nm and length from 5 to 10 μm. When 2.4 ml of 5 M $N_2H_4{\cdot}H_2O$ solution was added into the suspension with other conditions unchanged, only octahedral $Cu_2O$ particles were obtained, which is shown in Fig. 2(b). Most of the octahedral particles had an edge length of 1 μm. All of the particles had a mean edge length of 400–700 nm and smooth surface. To investigate the effects of concentration of NaOH, 1.2 ml of 24 M NaOH solution was slowly dropped into the suspension with other conditions unchanged. As shown in Fig. 2(c), only octahedral $Cu_2O$ particles were observed. Different concentrations of PEG were also investigated in this experiment. As shown in Fig. 2(d), when 0.500 g PEG was added into the suspension, octahedral $Cu_2O$ particles and $Cu_2O$ nanowires were observed. We can conform that the concentration of PEG is not the crucial factor to control the morphology of $Cu_2O$. All the results above suggested that it was possible to tune the morphology of $Cu_2O$ by controlling the experimental conditions.

Fig. 3(a) shows the typical transmission electron microscopy (TEM) image of octahedral $Cu_2O$ particles prepared with 2.4 ml of 1.5 M $N_2H_4{\cdot}H_2O$, 1.2 ml of 24 M NaOH and 0.250 g PEG. Bulk quantities of octahedral particles were formed with symmetrical

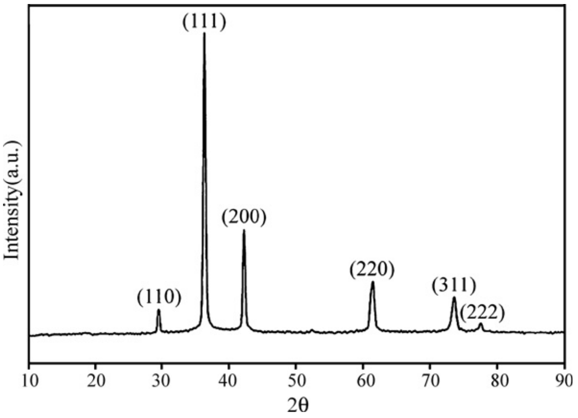

**Fig. 1.** XRD pattern of the as-synthesized octahedral $Cu_2O$.

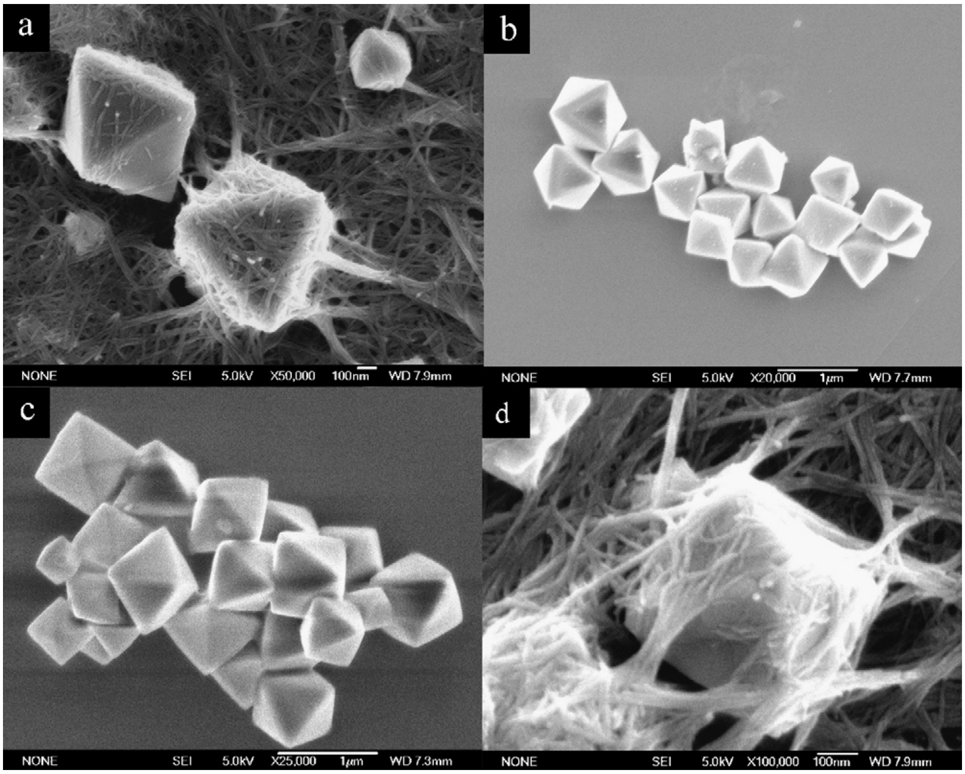

**Fig. 2.** SEM images of products prepared under different conditions.

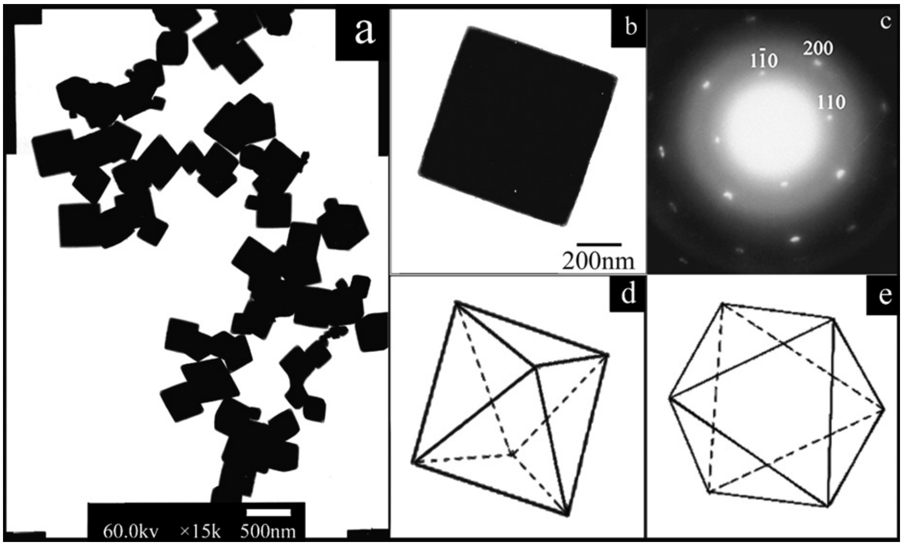

**Fig. 3.** (a) TEM image of octahedral $Cu_2O$ particles, (b) single octahedral $Cu_2O$ particle, (c) the corresponding SAED pattern, (d) and (e) schematic illustrations of octahedral $Cu_2O$ particle.

morphology. Fig. 3(b) shows a typical octahedral particle. The size and morphology were in good agreement with the results of SEM images. Fig. 3(c) shows the selected area electron diffraction (SAED) pattern of the particle. This pattern indicates the single crystal nature of the octahedral $Cu_2O$ particles.

In the experiment, hydrazine hydrate was used as the reducing agent. $Cu_2O$ with different morphologies was obtained by following reactions:

$$Cu(NO_3)_2 + 2NaOH \rightarrow Cu(OH)_2 + 2NaNO_3 \quad (1)$$

$$4Cu(OH)_2 + N_2H_4 \rightarrow 2Cu_2O + 6H_2O + N_2 \quad (2)$$

Bulk $Cu_2O$ was a cubic structure. Choi [14] reported that it was possible to modify the growth ratio, *R*, which was defined as the growth rate along the $\langle 1\,0\,0\rangle$ direction to that along $\langle 1\,1\,1\rangle$ direction. In our experiment, we hypothesized that copper(II) coordinated to the oxygens of the PEG initially in water. The observed $Cu_2O$ nanowires suggested that the capping groups of PEG on the $Cu_2O$ surface led to anisotropic shapes. Since there was a small quantity of $N_2H_4{\cdot}H_2O$ and NaOH, the reaction rate was also slow. $Cu_2O$ crystals grew to nanowires because of the surfactant. As the concentration of $N_2H_4{\cdot}H_2O$ and NaOH was increased, the growth ratio *R* was also increased above 1.73. As a result, relatively faster growing $\{1\,0\,0\}$ facets were eliminated in the final morphology forming octahedral $Cu_2O$. This hypothesis was in good agreement with our experiment.

The XRD pattern of nanofibers is shown in Fig. 4. The broad diffraction peaks of amorphous nanofibers can be observed. No diffraction peak of graphitic carbon appears, revealing an amorphous feature of the nanofibers. The other diffraction peaks at higher diffraction angles can be indexed to cubic structure of Cu with lattice constants of $a = 3.615$ Å. This is in good agreement with the literature values (JCPDS04-0836). No peaks due to impurities were found. Jiang [18] synthesized amorphous carbon nanofibers and reported that about 6% hydrogen was released from the acetylene precursor. In our reaction, the heat treatment led to the cleavage of acetylene. The C–H cleavage process produces atomic hydrogen which was in an adsorbed state. After $Cu_2O$ was reduced by the atomic hydrogen, the deposition reaction of acetylene occurs on the surfaces of copper obtained. In our study, we can formulate the main reaction process as follows:

$$C_2H_{2(a)} \rightarrow C_{2(a)} + 2H_{(a)} \quad (3)$$

$$2H_{(a)} + Cu_2O \rightarrow 2Cu + H_2O \quad (4)$$

Fig. 5 shows typical SEM and TEM images of the fibers catalyzed by octahedral $Cu_2O$ particles. Fig. 5(a) shows that all of the fibers had a ribbon-like shape. It can be seen that most fibers have diameters of 400–500 nm and length from 10 to 20 μm. Fig. 5(b) shows that the catalyst particles seemed to have a regular projected faceted shape, such as rhombic and triangular after the fibers grew. The changes of the catalyst particles' shape were found in Fig. 5(b). Fig. 5(c) shows that the fiber diameter was approximately equal to the size of the single catalyst particles. From Fig. 5(b) and Fig. 5(c), we can conclude that the fiber diameter was determined on the size of the single catalyst particles and the shape of catalyst particles was not a crucial factor to control the morphology of the fibers. Helical carbon nanofibers were synthesized with a copper catalyst [21] as a catalyst. It can be noted that the size of copper catalyst in their experiment was about 50 nm, which was much smaller than the $Cu_2O$ particles in our experiment. We can conclude that the size of the catalyst was a crucial factor to control the morphology of the fibers.

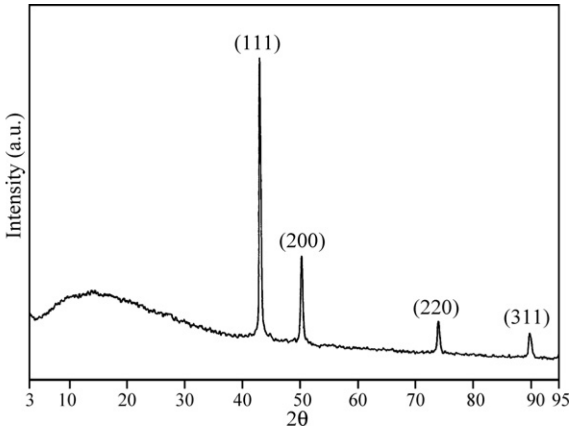

**Fig. 4.** XRD pattern of the carbon fibers.

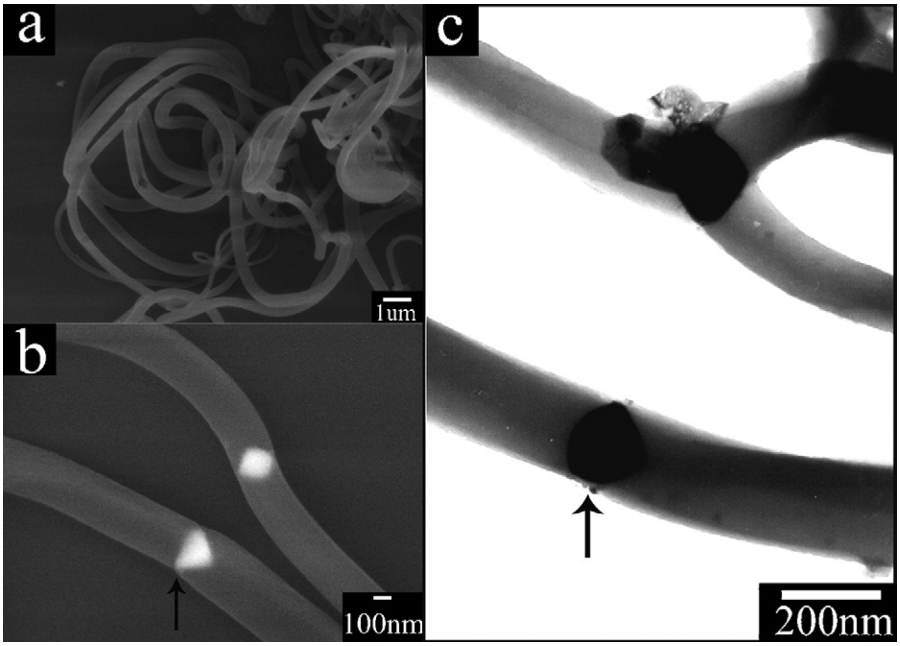

**Fig. 5.** (a and b) SEM images of carbon nanofibers. (c) TEM image of the fibers catalyzed by $Cu_2O$.

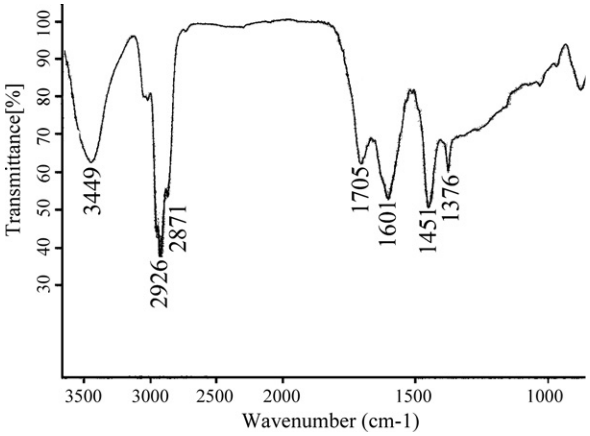

**Fig. 6.** IR spectrum of nanofibers.

Fig. 6 shows the infrared (IR) spectrum of the nanofibers. The peaks at 3449 $cm^{-1}$ and 1705 $cm^{-1}$ are ascribed to the stretching vibrations of –O–H and –C═O, indicating the slight oxidation of the product when the nanofibers were took out from the reactor. The peaks ascribed to the –C–H vibration in $-CH_2$ or –CH were observed at 2926 $cm^{-1}$, 2871 $cm^{-1}$ and 1451 $cm^{-1}$, respectively. The peak at 1601 $cm^{-1}$ was ascribed to the –C═C– stretching vibration. The peak at 1376 $cm^{-1}$ could be assigned to –C–H deformation in $-CH_3$ induces. The IR spectrum indicated the high hydrogen content in the nanofibers.

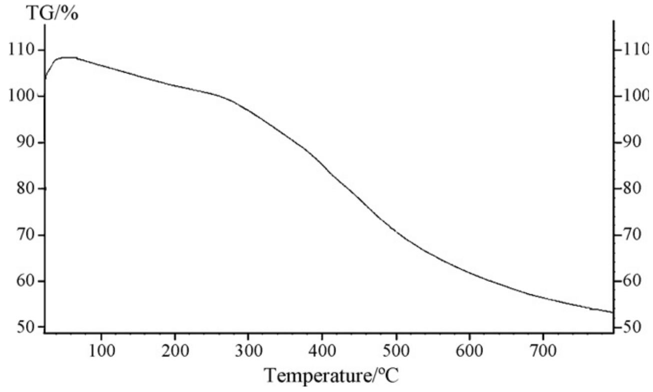

**Fig. 7.** TG analysis of the nanofibers.

The thermal stability of the nanofibers was determined by thermogravimetric (TG) analysis. As shown in Fig. 7, with the increase of the temperature, obvious weight loss was observed. The weight loss of nanofibers indicated that the products released small hydrocarbon molecules because of the C–H cleavage and structural reconfiguration of the nanofibers.

## 5. Conclusions

In conclusion, $Cu_2O$ with different morphologies had been synthesized by controlling the experimental conditions. With low concentration of $N_2H_4{\cdot}H_2O$ and NaOH, $Cu_2O$ nanowires were major products. When the concentration of $N_2H_4{\cdot}H_2O$ and NaOH was increased, only octahedral $Cu_2O$ particles were obtained. The concentration of PEG was not the crucial factor to control the morphology of $Cu_2O$. In addition, octahedral $Cu_2O$ particles were successfully used to synthesize amorphous carbon nanofibers. The size of the catalyst was the crucial factor to control the diameter and morphology of the fibers.

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