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Preparation of copper coated carbon nanotubes by decomposition of Cu(II)acetylacetonate in hydrogen atmosphere

Guo Wenli · Zhang Yue · Liang Tongxiang

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Abstract In this paper, copper coated carbon nanotubes (CNTs) was synthesized by decomposition of Cu(II) acetylacetonate (Cu(acac)$_2$) in hydrogen atmosphere at 300 °C. The thickness of the copper coating was in nanoscale according to scanning electron microscopy (SEM) and transmission electron microscopy (TEM) images, and Raman spectra indicated that certain intermediate bonds were formed between copper and the template CNTs. The crystalline structure of copper and its growth orientation were determined by X-ray diffraction (XRD) and selected area electron diffraction (SAED). The copper coating on CNTs had a face-centered cubic structure and its growth orientation was parallel to $(\bar{1}11)$ planes. The method developed in this paper had the advantages of simplicity in both process control and experiment equipments, so that it might provide a possibility of large-scale production.

Introduction

One-dimensional nano-structures, like nanorods, nanowires and nanoscale coatings are drawing more and more attentions owing to their unique physical, chemical and electrical properties and their potential applications in the new generation of nanodevices [1–4]. Copper is a good conductor of electricity (secondly to silver) that has been widely used as interconnection materials. Copper nanorods and copper coated carbon nanotubes have been reported to be good catalysts [5, 6] and negative electrodes in Li ion batteries [7] (after doped with Li$^+$).

Preparation of copper nanorods or copper coated carbon nanotubes through various approaches has been successfully carried out [8–14]. Among them, template-method is one of the most popular methods due to its simplicity and easy control in achieving various nanostructures. Commonly used template materials include CNTs, porous alumina and silica, DNA, polymers, such as potentiostatic electrochemical deposition (ECD) within the nanochannels of porous anodic alumina templates to form copper nanotubes [15], eletroless plating method to form copper coated CNTs [16] and polycarbonates as template to form copper nanowires [17]. Materials served as copper source include copper powders [18], Cu^{2+} solutions (CuSO$_4$, Cu(NH$_3$)$_4^{2+}$) etc. [19]. However, most of the above approaches rely on either high vacuum or advanced equipments, they have relatively complex processes, low deposition rate, and meanwhile the quantity of the products is not large. It is necessary to develop a more simple and effective method for synthesizing copper with one-dimensional nanostructures.

In this paper, copper coated carbon nanotubes were synthesized by decomposition of Cu(II) acetylacetonate (Cu(acac)$_2$) using Mult-walled CNTs (MWCNTs) as template, this process is very simple and large scale production may be realized.

Experimental

The whole process included three steps: (1) pretreatment of CNTs, (2) adsorption of the copper precursors on CNTs,

G. Wenli · L. Tongxiang (✉)
Institute of Nuclear Energy Technology, Tsinghua University,
Beijing 100084, P. R. China
e-mail: txliang@mail.tsinghua.edu.cn

Z. Yue
Forschungszentrum Karlsruhe GmbH, Institut fur
Nanotechnologie, D-76021 Karlsruhe, Germany

and (3) decomposition of the precursors in hydrogen atmosphere.

Pretreatments of CNTs

MWCNTs were fabricated by catalytic pyrolysis of the propylene-hydrogen (C_3H_6:H_2 = 2:1) mixture at about 750 °C with Ni particles as catalyst. First, the as-prepared MWCNTs were washed in dilute nitric acid to remove the catalyst particles, then they were activated by heating at 500 °C for 20 min in air to remove the amorphous carbons, finally, MWCNTs were immersed in concentrated nitric acid and boiled for 60 min. After filtered with a ceramic filter and washed with distilled water, the MWCNTs were dried at 60 °C. After this process, some function groups such as >C=O, –OH and –COOH were introduced on the outer wall of MWCNTs [20, 21], which improved the adsorption ability of the surface of MWCNTs and might provide a better adhesion between copper atoms and MWCNTs.

Adsorption of Cu precursors

1.5 g Cu(acac)$_2$ (Aldrich company, 97%) was dissolved into 50 mL acetyl acetone to form a saturated solution, then 1 g MWCNTs (after pretreated in 2.1) were added and the mixture was ultrasonic vibrated for 1 h. Finally, the mixture solution was filtrated and dried at 60 °C. After this process, Cu precursors were adsorbed on the surface of MWCNTs.

Decomposition of Cu precursors

The MWCNTs were put in an alumina crucible and placed into a tube furnace to perform the decomposition process. The atmosphere was hydrogen with a flux of 200 mL/min at atmospheric pressure. The decomposition temperature was 300 °C and the decomposition time was 30 min.

X-ray diffraction (XRD, DMAXIII, Rigaku), scanning electron microscopy (SEM, Amray-1910) transmission electron microscopy (TEM, H-800), and Raman spectrum measurements (Renishaw, RM100) were performed to determine the chemical compositions and structures of the products.

Results

Figure 1 is the TEM image of copper coated MWCNTs with a diameter of about 40 nm, the selected area electron diffraction (SAED) patterns demonstrate that the copper coating on MWCNTs has a face-centered cubic (FCC) structure and its growth orientation is parallel to $(\bar{1}11)$ planes.

Figure 2 is the XRD spectrum of the copper coated MWCNTs, which confirm that the products contain copper and little carbon (from MWCNTs), and copper has a cubic structure.

Figure 3 is the SEM image of the product, the EDAX measurement is performed at the surface area of the observed copper nanorods. It shows that copper distributed on MWCNTs and formed a coating on it. The average diameter of the products was closed to the original MWCNTs (about 30–40 nm), which indicates that the coatings are very thin. The qualitative analysis of EDAX shows that the atom percentage of copper and carbon is 40% and 60%, respectively, which indicates that the copper coatings of the selected local area are compact.

Discussions

Decomposition process of Cu(acac)$_2$

In order to get a understanding of the decomposition process, the TG/DTG analysis of Cu(acac)$_2$ was performed in Hydrogen atmosphere with a flux of 200 mL/min. In Fig. 4, the TG curve shows that the decomposition temperature of Cu(acac)$_2$ begin at about 180 °C and end at about 250 °C. According to the DTG curve, the decomposition reaches its highest velocity at the range of about 220–250 °C.

Analysis of the intermediate products

Figure 5 is the Raman spectra of the MWCNTs (curve A) and the products after decomposition of Cu(acac)$_2$ at

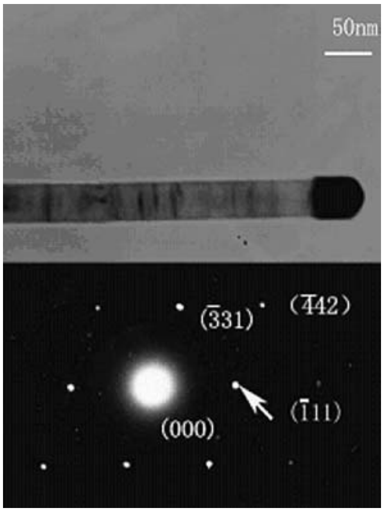

Fig. 1 TEM image and SAED patterns of the copper coated CNTs

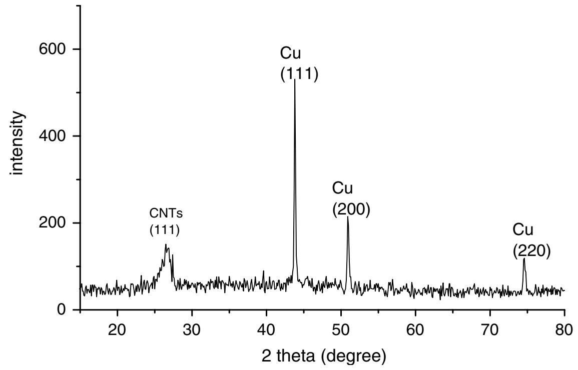

Fig. 2 XRD spectrum of the copper coated CNTs

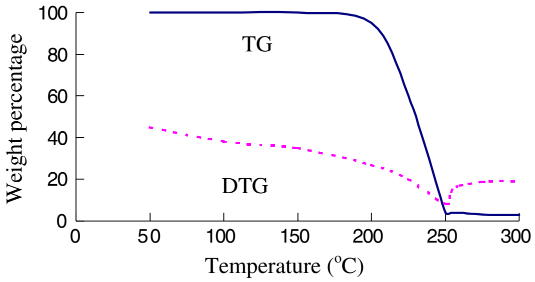

Fig. 4 TG/DTA curves of $Cu(acac)_2$

280 °C (curve B) and 300 °C (curve C) in Hydrogen atmosphere, respectively. The characteristic Raman shifts of MWCNTs are at 1,345 and 1,574 cm^{-1} (as shown in curve A). In the spectra curve B and C, the Raman shift at 818–819 cm^{-1} is the characteristic of copper carbide, which indicated that certain intermediate bonds were formed between copper and the template CNTs. The Raman shift was considered as the characteristic spectrum of copper, for the template is carbon. Above the wave number of 900 cm^{-1}, there are hardly any differences between the products and single MWCNTs in the spectrum. As shown in curve B, besides the characteristic copper carbide Raman shift at 818 cm^{-1}, there are several other Raman shifts at 244, 291, 338, 379, 667 cm^{-1}. In curve C, after $Cu(acac)_2$ decomposes at 300 °C under hydrogen to produce copper coated CNTs, no other Raman shifts except the characteristic Raman shifts of MWCNTs and a low copper carbide shift (818 cm^{-1}) appears, it indicates that there are some intermediate products or some intermediate combination chemical bonds such as Cu–O (its characteristic shifts are at 292, 237 cm^{-1}) are formed during the decomposition process.

Figure 6 is the XRD spectrum of the sample after decomposed at 280 °C, it demonstrates that copper oxide (CuO) exits in the intermediate products, and the crystalline structure is monoclinic.

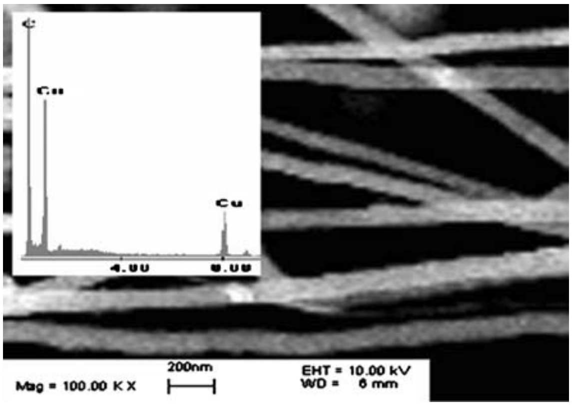

Fig. 3 SEM image and EDAX diagram of the copper coated CNTs

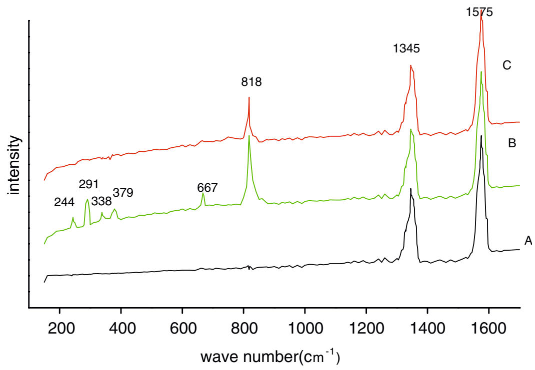

Fig. 5 Raman spectra of the MWTNTs (**A**) and sample after decomposition at 280 °C (**B**) and at 300 °C (**C**)

Possible decomposition mechanism

$Cu(acac)_2$, whose molecular structure is shown in Fig. 7, is a metallic ligand, which has been used to form copper thin films [22, 23]. The decomposition mechanism of $Cu(acac)_2$ is still unclear. Here, we propose a possible decomposition route by which copper is produced from $Cu(acac)_2$. As

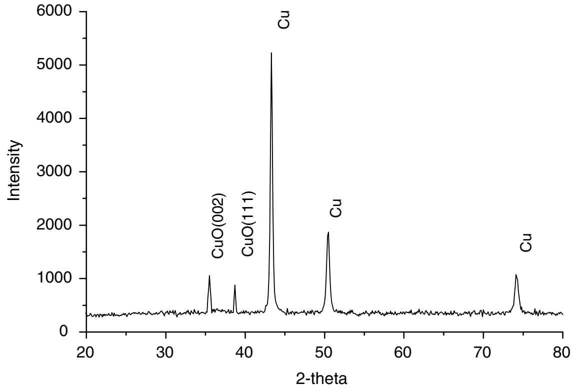

Fig. 6 XRD spectrum of the sample after decomposition at 280 °C

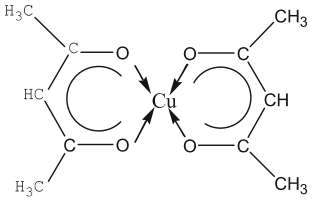

Fig. 7 molecular structure of Cu(acac)2

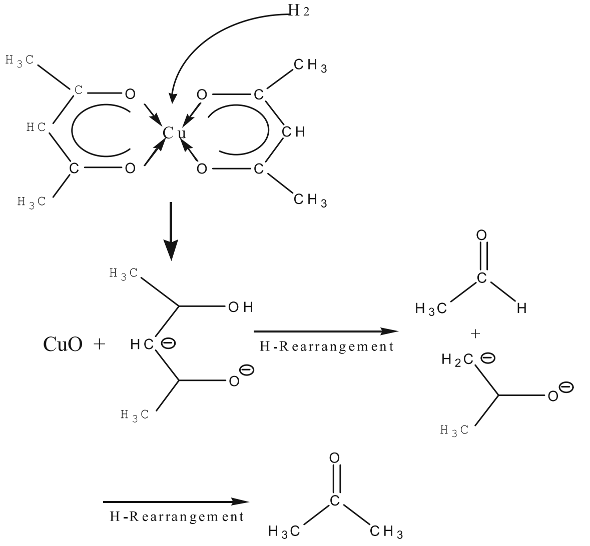

Fig. 8 Mechanism proposed for the decomposition of the ligand $Cu(acac)_2$

shown in Fig. 8, the decomposition contains four stages: (1) after adsorption of Hydrogen, Cu–O bonds are replaced with O–H bonds and meanwhile copper oxide is formed; (2) with the H-rearrangement reaction acetaldehyde is formed; (3) Hydrogen reacted with the enol-like intermediate and acetone is formed; and (4) copper oxide is reduced to copper in the presence of Hydrogen and CNTs. The complete reactions are:

$$\mathrm{Cu(acac)_2{+}2H_2 \rightarrow CuO + CH_3CHO + (CH_3)_2C = O}$$

$$\mathrm{CuO + H_2 \rightarrow Copper + H_2}O \tag{1}$$

$$\mathrm{CuO + CNTs \rightarrow Copper + CO} \tag{2}$$

$$\mathrm{CuO + CNTs \rightarrow Copper + CO_2} \tag{3}$$

Since there are three reducing reactions available, their reaction thermodynamics and kinetics are calculated to prove its feasibility. The enthalpy difference (ΔH) and the Gibbs free energy change (ΔG) are obtained from:

$$\Delta G_m = \Delta H_m - T\Delta S_m \quad \text{(Gibbs function)}$$

$$\Delta H_m(T) = \Delta H_m(298\,\mathrm{K}) + \int_{298}^{\mathrm{T}} \sum v_B C_{p,m}(B)\,\mathrm{d}T$$
$$\text{(Kirchhoff's Equation)}$$

$$\Delta S_m(T) = \Delta S_m(298\,K) + \int_{298}^{T} \sum v_B C_{p,m}(B)\,\mathrm{d}\ln T$$

The ΔH, ΔG and the equilibrium constant K of the three reactions at 573 K are calculated and listed in Table 1, which shows that the three reactions are feasible in kinetics. Except reaction (2) they are feasible in thermodynamics.

In summary, the whole decomposition process could be described as the following steps: (1) the solvent acetyl acetone is adsorbed on the surface of CNTs, it vaporizes at about 78 °C (its boiling point) and escapes from the reaction system; (2) $Cu(acac)_2$ is decomposed by reaction with hydrogen and meanwhile copper oxide is formed on the surface of CNTs; and (3) copper oxide is reduced to copper due to its reduction reactions with Hydrogen and CNTs. As a reult, the copper coated nanotubes are formed.

Conclusions

Copper coated CNTs was synthesized by the decomposition of $Cu(acac)_2$ in hydrogen atmosphere under atmospheric pressure at 300 °C, there were certain bonds formed between copper and the surface of CNTs. The copper coating on CNTs had a face-centered cubic structure and its growth orientation was parallel to $(\bar{1}11)$ planes. Being different to other reported approaches, the method developed in this paper had the advantages of simplicity in both process control and experiment equipments, so that it might provide a possibility of large-scale production.

Table 1 The results of thermodynamics and kinetics calculation

Reaction	ΔH (kJ/mol)	ΔG (kJ/mol)	K
CuO + H_2 → copper + H_2O (1)	–98.49	–148.72	3.67×10^{13}
CuO + CNTs → copper + CO (2)	36.44	–52.72	6.43×10^{4}
CuO + CNTs → copper + CO_2 (3)	–53.51	–118.93	7.03×10^{10}

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