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Growth of La_2CuO_4 nanofibers under a mild condition by using single walled carbon nanotubes as templates

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Abstract

La_2CuO_4 nanofibers (ca. 30 nm in diameter and 3 μm in length) have been grown in situ by using single walled carbon nanotubes (SWNTs; ca. 2 nm in inner diameter; made via cracking CH_4 over the catalyst of $Mg_{0.8}Mo_{0.05}Ni_{0.10}Co_{0.05}O_x$ at 800 °C) as templates under mild hydrothermal conditions and a temperature around 60 °C. During synthesis, the surfactant poly(ethylene glycol)–block–poly(propylene glycol)–block–poly(ethylene glycol) and H_2O_2 were added to disperse SWNTs and oxidize the reactants, respectively. The structure of La_2CuO_4 nanofibers was confirmed by powder X-ray diffraction (XRD) and their morphologies were observed with field emission scanning electron microscope (FESEM) at the hydrothermal synthesis lasting for 5, 20 and 40 h, respectively. The La_2CuO_4 crystals grew from needle-like (5 h) through stick-like (20 h) and finally to plate-like (40 h) fibers. Twenty hours is an optimum reaction time to obtain regular crystal fibers. The La_2CuO_4 nanofibers are probably cubic rather than round and may capsulate SWNTs.

Keywords: La_2CuO_4 nanofibers; Single walled carbon nanotubes; Templates; Hydrothermal synthesis

1. Introduction

La_2CuO_4 is a well-known milestone in high-T_c superconductive materials. It has been extensively studied on account of its relative simplicity in structure. Generally, the multi-crystal La_2CuO_4 powder is made by calcining the mixture of lanthanide and cupric salts at temperatures around 1000 °C [1]. The single-crystal La_2CuO_4 is expected to be applicable in high-speed microelectronic switches and large current switches [2]. Bulk La_2CuO_4 single crystal has previously been grown by the traveling solvent floating zone (TSFZ) method [3]. But the TSFZ apparatus is quite complicated and the reaction temperature is as high as 1200 °C. The single-crystal La_2CuO_4 film has been prepared by infrared-heated liquid-phase epitaxial technique [4]. The growth of single-crystal nanofibers of La_2CuO_4 or other cupric one-dimensional (1D) superconductive materials is considered the most desirable in practical applications such as in the processing and development of micro/nano-electronic devices, but we have not encountered any known successes of such synthesis in the literature.

The discovery of carbon nanotubes (CNTs) has aroused great research enthusiasms in the scientific community due to their many anticipated peculiar mechanical, electronic and optical properties [5]. At present, the synthesis of CNTs seems no longer a secret, whereas their real applications are still a challenge [6]. The intrinsic 1D superconductivity has been experimentally observed either in the ultrasmall-radius (0.4 nm) CNTs [7] or in ropes of CNTs [8] and the rope was prospected to show better superconductive behavior than the individual tube after a theoretical analysis [9]. In the proximity effect, the superconducting pair amplitude appears in a region where the pair interaction is zero. The mesoscopic structures comprising two macroscopic superconducting electrodes and a normal metallic wire in between have been investigated [10]. The superconductor–ferromagnetic hybrid structure was studied and was found that in this structure the pair amplitude showed decaying oscillations with alternating

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sign inside the ferromagnetic layers [11]. The single walled carbon nanotubes (SWNTs) with diameter of 1–2 nm are ideal systems to study transport properties of 1D conductors. The superconductor–SWNT–superconductor junctions have been investigated and proximity-induced superconductivity was observed [12,13]. Due to the strong 1D character the temperature and magnetic field dependence on the critical current showed an unusual feature.

Based on the above facts, we think to make either La_2CuO_4 1D nanofibers or the hybrid La_2CuO_4–CNT nanofibers is of great significance in the superconductor manufacture. Hutchison et al. have employed SWNTs as templates for the growth of 1D KI crystals [14]. This paper reports a hydrothermal synthesis method to produce aligned La_2CuO_4 single-crystal nanofibers by using our home-made SWNTs as templates under a very mild synthesis condition, where the reaction temperature is as low as 60 °C.

2. Experimental

2.1. SWNTs synthesis

SWNTs were home-made by cracking CH_4 over a mixed-oxide catalyst $Mg_{0.8}Mo_{0.05}Ni_{0.10}Co_{0.05}O_x$. The catalyst was prepared according to the following processes: (i) dissolving the starting chemicals of $MgNO_3$, $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$, $Ni(NO_3)_2\cdot 6H_2O$ and $Co(NO_3)_2\cdot 6H_2O$ (Mg/Mo/Ni/Co = 0.8:0.05:0.10:0.05) together with citric acid into distilled water; (ii) heating and stirring the mixed solution at 80 °C until a slurry was formed; (iii) baking the slurry at 110 °C for 2 h and followed by calcining at 900 °C for 10 h.

The steps to synthesize SWNTs are: (i) holding the catalyst $Mg_{0.8}Mo_{0.05}Ni_{0.10}Co_{0.05}O_x$ in a stainless-steel tubular reactor (i.d. 15 mm); (ii) pre-reducing the catalyst at 800 °C in diluted hydrogen (H_2/He = 1/9) for 6 h; (iii) cracking diluted CH_4 (CH_4/H_2/He = 1/1/8) through the reactor at 800 °C for 8 h for SWNTs production. The SWNTs sample was purified by nitric-acid washing repeatedly in an ultrasonic bath.

2.2. La_2CuO_4 nanofibers synthesis

The procedures to hydrothermally synthesize La_2CuO_4 single-crystal microfibers by using SWNTs as templates were: (i) the surfactant of poly(ethylene glycol)–block–poly(propylene glycol)–block–poly(ethylene glycol), $La(NO_3)_3\cdot 6H_2O$ and $Cu(NO_3)_2\cdot 6H_2O$ (according to the stoichiometric composition of La_2CuO_4) were mixed in distilled water. The weight concentration of surfactant in the solution was 0.5%. (ii) The solution was heated at 50 °C with stirring for 30 h. (iii) SWNTs (weight concentration in solution was 0.005%) and 2 mL H_2O_2 were added into the solution and dispersed in an ultrasonic bath for 1 h. The addition of H_2O_2 is to help further dispersion of CNTs and oxidization of the La–Cu precursor during hydrothermal processes ($2H_2O_2 = 2H_2O + O_2$). The agglomeration of CNTs in water or even in an organic solvent is one of the major problems hindering their further manipulation. We found that the addition of surfactant and H_2O_2 dispersed the CNTs thoroughly and homogeneously. (iv) The mixture was put into an autoclave for hydrothermal synthesis at 60 °C for desired hours. We observed that during synthesis, the pressure inside the autoclave automatically reached 35 bar ($2H_2O_2 = 2H_2O + O_2$).

After hydrothermal synthesis, a black precipitate was generated in the solution. By filtering and washing the precipitate with distilled water repeatedly, we got the product. The product was then dried at 110 °C for 1 h; eventually a black powder was obtained.

2.3. Characterization

Crystallographic information of La_2CuO_4 fibers was investigated with powder X-ray diffraction (XRD) (Shimadzu 6000) using filtered Cu$K\alpha$ radiation as the X-ray source ($\lambda = 1.5406$ Å). The morphologies of SWNTs and La_2CuO_4 fibers were observed under transmission electron microscope (TEM) (JEOL, JEM 2010) and field emission scanning electron microscope (FESEM) (JEOL, JSM 7600F).

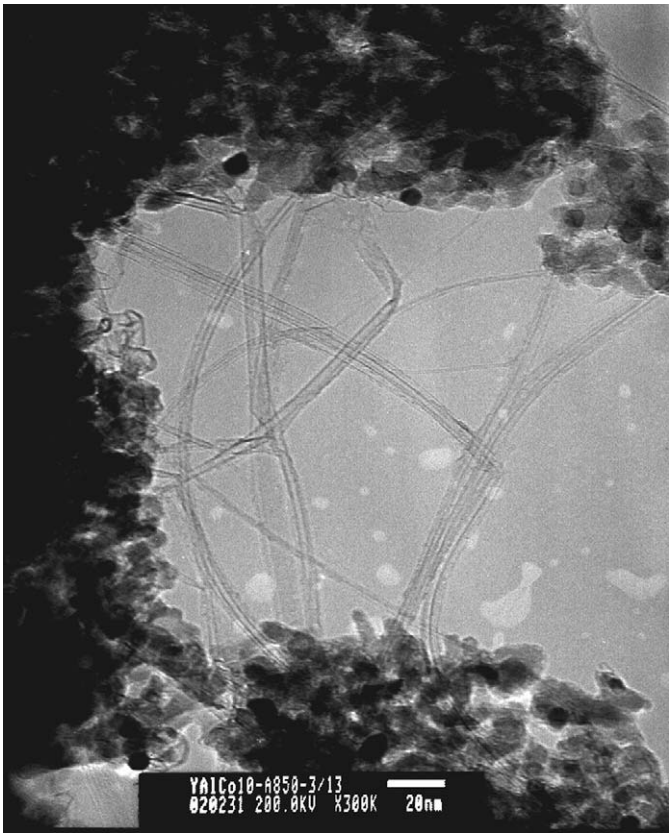

Fig. 1. Transmission electron microscopy image (TEM) (× 300,000) of single walled carbon nanotubes (SWNTs) together with catalyst.

3. Results and discussion

Fig. 1 is the TEM image of harvested carbon tubes together with catalyst, showing that the CNTs are single walled with a 2 nm in-average inner diameter. In the catalyst of $Mg_{0.8}Mo_{0.05}Ni_{0.10}Co_{0.05}O_x$, nickel and/or cobalt are the essential components to crack methane. SWNTs grow on the nanosized particles of nickel/cobalt (or Ni/Co–Mo). The MgO matrix is to stabilize the nanoparticles from agglomeration [15].

Figs. 2–4 are the FESEM images of the powder products obtained after hydrothermal synthesis lasting for 5, 20 and 40 h, respectively. In Fig. 2a, we observed groups of aligned needle (or grass-leaf)-like fibers created after reaction for 5 h. We have not yet observed SWNTs again. We assume that the SWNTs have involved in the synthesis. In other words, in the beginning step, La–Cu oxide may grow around the SWNTs. Fig. 2b is the enlarged FESEM image of one bundle of the needle fibers. The fibers are quite straight but gathered in several hundreds together, indicating that during hydrothermal processes the SWNTs were stretched but still not completely separated from each other. In Fig. 3a (hydrothermal reaction for 20 h), we observed groups of aligned microfibers. The fibers were highly orientated and uniform in diameter. The length of fiber is close to 3 μm. The pattern style (fiber direction) in Fig. 3a is similar as that in Fig. 2a. This means that Fig. 2a has transformed to Fig. 3a after 15 more hours' growth of the fibers. In Fig. 3a, we also observed some single-crystal cubes. We deduce that the long fibers come from the long SWNTs, whereas the small cubes may be the result from those very short SWNTs. To synthesize very homogeneous SWNTs, particularly in length, is still a challenge. Fig. 3b is the enlarged FESEM image for the individual fibers. The

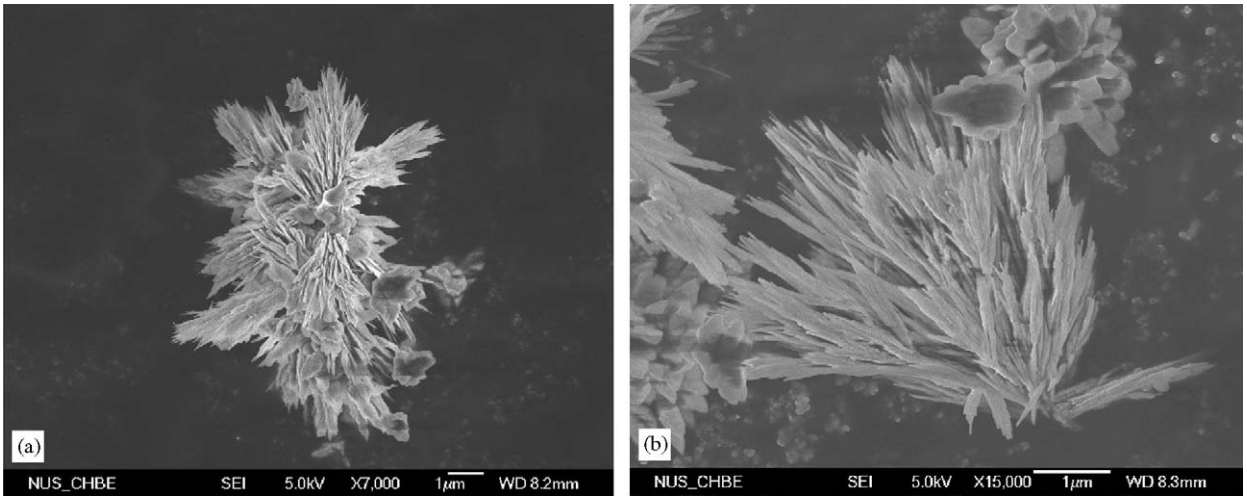

Fig. 2. Field emission scanning electron microscopy (FESEM) images of La_2CuO_4 single-crystal fibers after hydrothermal synthesis lasting for 5 h. (a) (× 7000) Groups of aligned needle-like fibers are evident; (b) (× 15,000) an enlarged view of one bundle of such fibers.

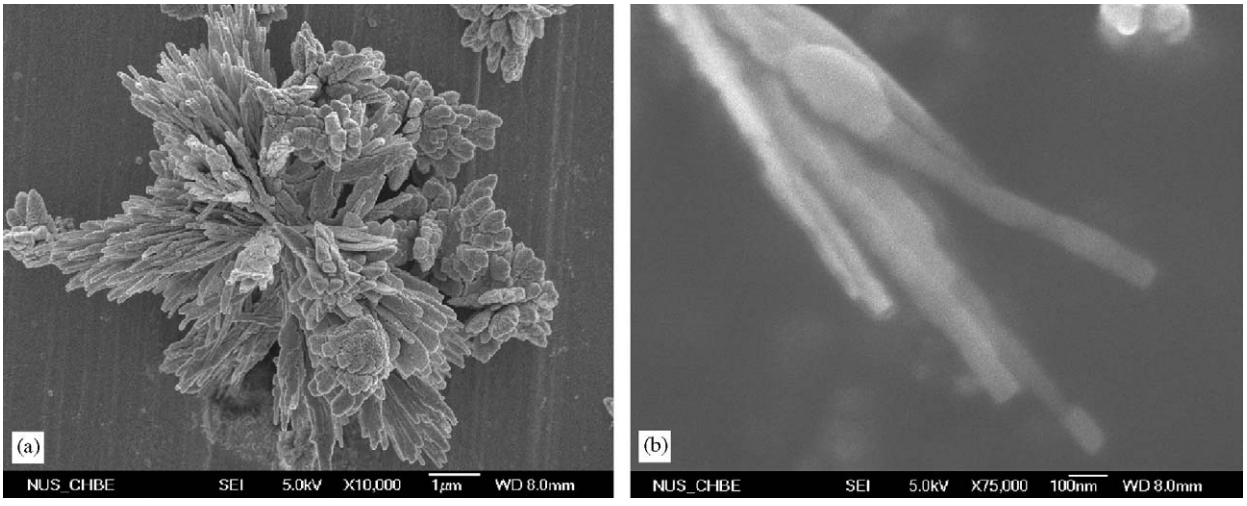

Fig. 3. Field emission scanning electron microscopy (FESEM) images of La_2CuO_4 single-crystal fibers obtained after hydrothermal synthesis lasting for 20 h. (a) (× 10,000) Groups of highly oriented and uniform-diameter fibers are evident; (b) (× 75,000) an enlarged image of some individual fibers.

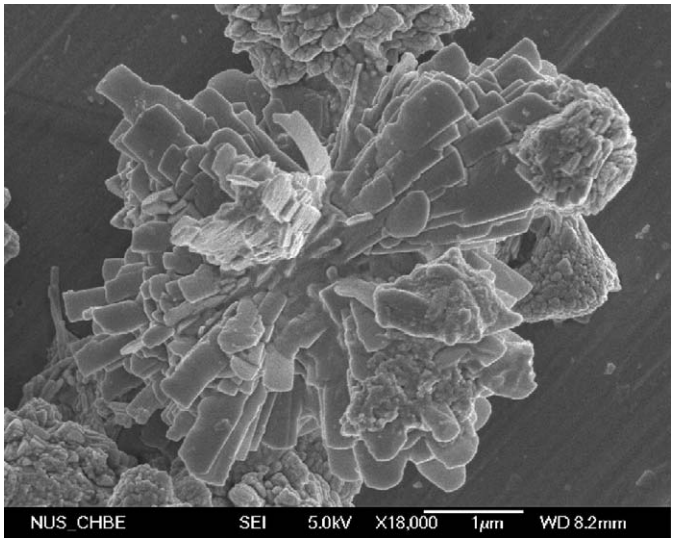

Fig. 4. Field emission scanning electron microscopy (FESEM) images ($\times$18,000) of La_2CuO_4 single-crystal fibers after hydrothermal synthesis lasting for 40 h. Plate-like single crystals are evident.

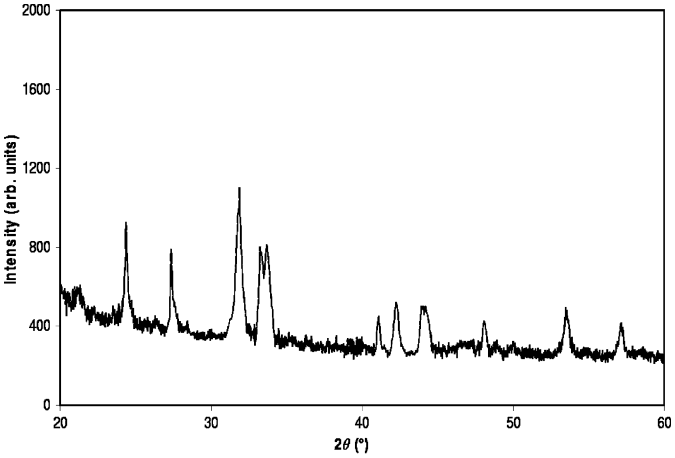

Fig. 5. Powder X-ray diffraction (XRD) pattern of 20-h-hydrothermal-synthesized single-crystal La_2CuO_4.

diameter of fibers is around 60 nm. The fibers seem in cubic style rather than in round. This is reasonable as the La_2CuO_4 crystal is in cubic structure. When the hydrothermal reaction was prolonged to 40 h, we obtained a FESEM image as in Fig. 4. The fibers have already grown to be like plates. This observation supports the assumption that the fibers in Fig. 3 are cubic while not round. The XRD pattern of the powder obtained after 20 h hydrothermal synthesis is shown in Fig. 5. By comparing with the La_2CuO_4 standard XRD pattern and those in the literature [4], we confirmed that these single-crystal fibers were of La_2CuO_4 crystal structure. Of course, the relative intensities of diffraction peaks are a little bit different from those in standard powder XRD pattern as La_2CuO_4 fibers grew almost in one direction. We could not detect the XRD diffraction peaks of SWNTs. The reason may be that the concentration of SWNTs in the powder is too low to be detected by XRD. We did not detect the diffraction peaks of $La(OH)_3$, La_2O_3, $Cu(OH)_2$, CuO and Cu_2O. An elemental analysis of the liquid solution of the dissolved synthesized material also confirmed that the atomic ratio of La/Cu of the synthesized material was indeed 2:1. Thus, we could say that we had synthesized La_2CuO_4 nanofibers.

The as-synthesized La_2CuO_4 nanofibers sample (20 h hydrothermal synthesis) was exposed to air at 700 °C for 1 h for purification. The FESEM image was shown in Fig. 6. The fiber's quality in Fig. 6 looks better than that in Fig. 3a. The diameter of fibers in Fig. 6 is around 30 nm, about half of that in Fig. 3a. The La_2CuO_4 lattice parameters are $a = b = 0.53$ nm, $c = 1.30$ nm [16]. So we

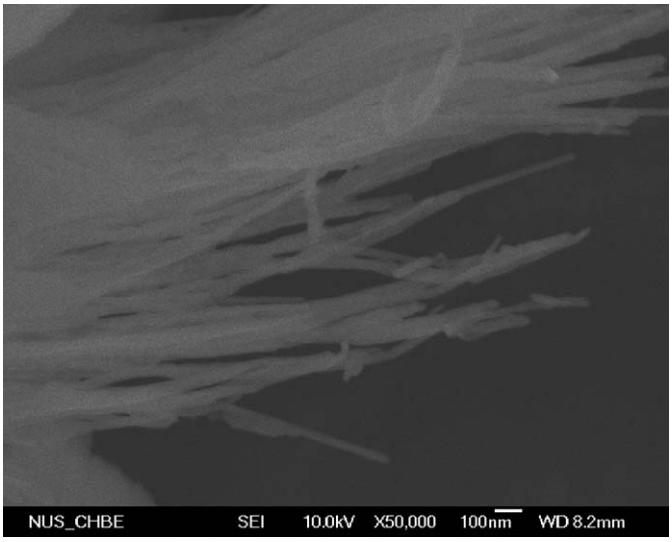

Fig. 6. Field emission scanning electron microscopy (FESEM) image ($\times$50,000) of La_2CuO_4 fiber after being oxidized in air at 700 °C for 1 h.

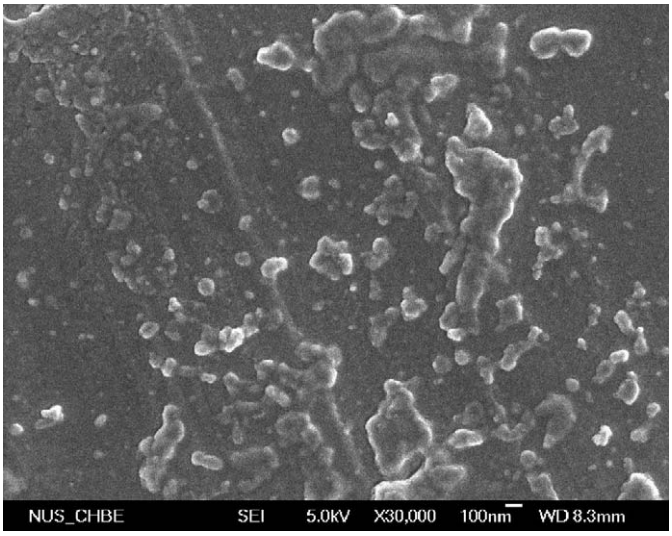

Fig. 7. Field emission scanning electron microscopy (FESEM) image ($\times$30,000) of 20-h-hydrothermal-synthesized product without SWNT template.

image that in the cross-section of the cubic fiber there are about 100 La_2CuO_4 molecule units. We are not sure if the CNTs inside the La_2CuO_4 fibers have been burnt out completely after 700 °C oxidation in air.

In order to clarify the putative role of SWNTs as templates, we studied the hydrothermal synthesis only without SWNTs. The FESEM image of product obtained after 20 h synthesis is shown in Fig. 7, in which we could not find either crystal fibers or cubes. This result indicates that SWNTs material actually plays a template role during the growth of La_2CuO_4.

A nanofiber structure of La_2CuO_4 or La_2CuO_4[SWNT] has been created. We are not sure whether or not there is La_2CuO_4 inside the SWNTs. May be it is possible if the SWNTs are tip-opened. Hutchison et al. [17] have successfully synthesized the simple binary 1D structures such as MI (M = Li, Na, K, Rb, Cs) and $ThCl_4$ by filling the molten halides or iodides into the SWNTs.

4. Conclusion

The hydrothermal synthesis method by using SWNTs as templates may be a novel technique to induce the growth of single-crystal complex oxide nanofibers. For example, using this hydrothermal synthesis assisted by SWNTs templates, $YBa_2Cu_3O_7$ superconductive single-crystal nanofibers may also be synthesized by only changing lanthanide nitrate to yttrium and barium nitrates. We expect that such hybrid nanofibers would show unique properties in superconductivity due to its 1D (or quasi-1D) and juncture structure.

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