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New developments in the growth of 4 Angstrom carbon nanotubes in linear channels of zeolite template

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ABSTRACT

We report new developments on the chemical vapor deposition growth of 0.4 nm single-walled carbon nanotubes (SWCNTs) inside the linear channels of the aluminophosphate zeolite, $AlPO_4$-5 (AFI), single crystals (0.4 nm-SWCNT@AFI). Ethylene (C_2H_4) and carbon monoxide (CO) were used as the feedstock. Polarized Raman spectroscopy was used to analyze the structure and quality of SWCNTs, both the radial breathing mode and G-band are much clearer and stronger than the samples grown by the old process which used template tripropylamine molecules for growing SWCNT@AFI. From the Raman spectra, it is clearly seen that the RBM is composed of two peaks at 535 and 551 cm^{-1}. By using the pseudopotential module in Material Studio to calculate the Raman lines, the 535 cm^{-1} peak is attributed to the (5,0) SWCNTs and the 551 cm^{-1} peak to the (3,3) SWCNTs. The abundance of (4,2) is relatively small. Thermal gravity analysis showed that while the samples grown by CO display less than 1 wt% of carbon, for the samples heated in C_2H_4 atmosphere the weight percentage of SWCNTs is around 10%, which implies ~30% of the AFI channels are occupied with SWCNTs, a significant increase compared with the previous samples.

1. Introduction

Carbon nanotubes (CNTs) have been intensively studied since their discovery [1,2]. Owing to their unique physical properties and the one-dimensional character, they are regarded as one of the basic materials of the nanotechnology industry [3–6]. Much effort has been devoted to the synthesis of desirable chirality (n,m) single-walled carbon nanotubes (SWCNTs) at a given location, with well-controlled direction and length [7–11]. Compared with large-sized SWCNTs, ultra-small SWCNTs have aroused special interests because of the strong curvature effect that can lead to a significant hybridization between the sigma (σ^*) and pi (π^*) orbitals [12]. The curvature effect enriches the electronic properties by redistributing the energy in the electronic states, and opens new channels for electron–phonon coupling which can lead to special transport characteristics. However, SWCNTs with very small diameter can become unstable, as the system energy increases

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rapidly with decreasing diameter [13]. Theoretical calculations predicted the existence of SWCNTs with diameter as small as 0.4 nm [14]. Later it was reported that the ultra-small SWCNTs can be produced inside the channels of aluminophosphate, $AlPO_4$-5 (AFI), zeolite single crystals [15], and the diameter was determined to be 0.4 nm by high resolution transmission electron microscopy [16]. With such a small diameter and extreme curvature, these well-aligned and mono-sized SWCNT arrays showed interesting physical properties, e.g. superconductivity has been observed in this system [17–21].

The host AFI zeolite crystal is a type of microporous aluminophosphate zeolites. It is widely used in the host–guest chemistry because of its thermal stability up to 1200 °C, optical transparency over the broad range ultraviolet to near infrared, and electrically insulating characteristic [22–26]. Fig. 1 shows the structure of the AFI crystal viewed along the [001] (c-axis) direction. The framework is composed of alternating tetrahedral $(AlO_4)^-$ and $(PO_4)^+$ units, forming parallel open channels that are arranged in a triangular lattice structure [27]. The inner diameter of the channel is 0.734 nm and the center-to-center distance between two neighboring channels is 1.374 nm. The tripopylamine $[(CH_3CH_2CH_2)_3N$ (TPA)] molecules are aligned head-to-tail along the c-axis, serving as the precursor template while synthesizing the AFI crystals. In the old method of producing the 0.4 nm CNTs, the SWCNTs were obtained by pyrolyzing the TPA molecules [15]. The AFI crystals were heated to 580 °C in vacuum for several hours, leading to the decomposition of the TPA molecules that are encapsulated inside the AFI channels, with a small fraction forming the SWCNTs. There are limitations for this process: In Raman spectroscopy the intensity of the radial breathing mode (RBM) is weak and the peaks are broad; the thermal gravity analysis (TGA) data showed the weight percentage of carbon over the total mass of SWCNT@AFI crystal to be ~1.5 wt%, translating into a filling factor of SWCNTs inside the AFI channels of ~4.5%. This is a relatively small number, indicating that the samples are not uniform and only a small fraction of AFI channels are occupied with SWCNTs. In this approach, the carbon atoms that formed the SWCNTs came from the pyrolysis of the TPA molecules inside the AFI channels. Since the total amount of TPA molecules are limited in quantity and some of them may escape during the heating process (the AFI crystals were heated in vacuum), the low filling factor is understandable.

To improve this situation, we have developed a new chemical vapor deposition (CVD) process by first burning off the TPA molecules in oxygen atmosphere, and then introducing carbon-containing gas as the feedstock. Two gases were tested: C_2H_4 and CO. In this approach, continuous carbon source can enter the empty channels of the AFI crystals. Compared with the traditional CVD method for growing CNTs, no catalyst is used in the present process. The fact that CNTs can still be formed suggests that the framework of AFI crystal must play a weak catalytic role in the pyrolysis and conversion of ethylene, or CO, to SWCNTs.

2. Experimental

The AFI zeolite crystals are synthesized by the conventional hydrothermal method. In the synthesis procedure, aluminum tri-isopropoxide $[(iPrO)_3Al$ 99 wt%] and phosphoric acid (H_3PO_4 85 wt%) were used as aluminum and phosphorus sources, respectively. The TPA molecules served as the template during the synthesis process. The details are described in reference [28]. The as-grown AFI crystals, with TPA molecules capsulated in the channels, are optically transparent with a typical dimension of 300 μm in length and 100 μm in diameter.

The as-made AFI crystals are first heated in a flowing oxygen atmosphere at 900 °C, to remove the organic template TPA molecules through oxidization. Raman spectroscopy of the AFI crystals after this step showed no RBM or G band, which means that the channels of the AFI crystals are mostly empty and ready for the growth of SWCNT. Subsequently, a

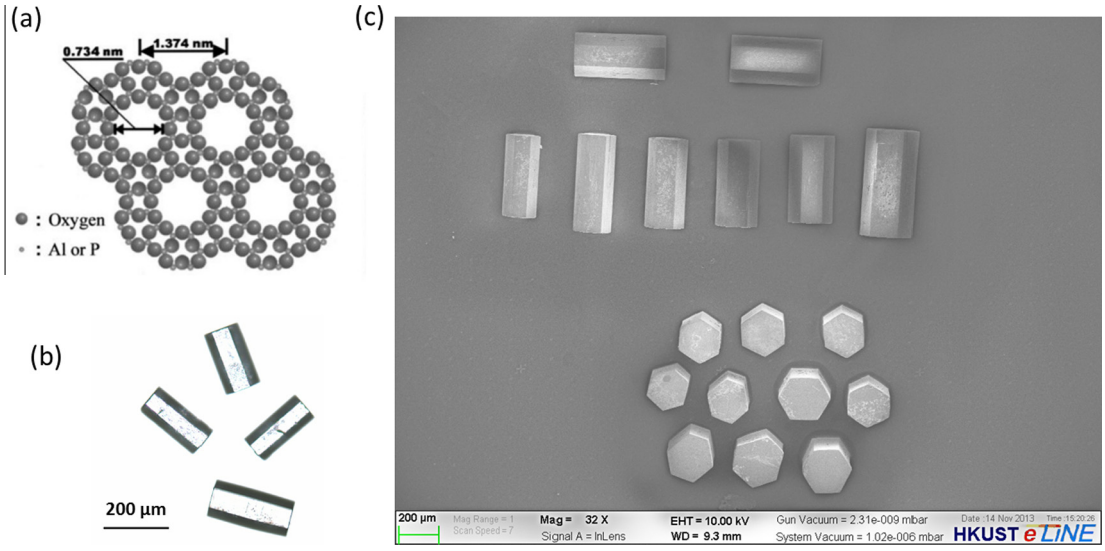

Fig. 1 – The (a) framework, (b) optical and (c) SEM images of AFI zeolite crystals. (A color version of this figure can be viewed online.)

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