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Single-walled carbon nanotubes prepared in small $AlPO_4$-5 and CoAPO-5 molecular sieves by low-temperature hydrocracking

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ABSTRACT

Single-walled carbon nanotubes (SWNTs) were prepared in the channels of small $AlPO_4$-5 and cobalt-incorporated $AlPO_4$-5 (CoAPO-5) crystals (4–6 μm in diameter and 10–30 μm in length), by hydrocracking at 350 °C. The effects of Co content in the precursor gel and carbon density of the structure-directing agent on the resulting SWNTs were investigated. The results of high-resolution transmission electron microscopy and polarized Raman scattering indicated that SWNTs formed in the channels of $AlPO_4$-5 and CoAPO-5 crystals, after hydrocracking for 10 h at 350 °C. The SWNTs were 0.4 nm in diameter, and possessed well-defined symmetry. When the Co/Al ratio of the precursor gel was 0.075, the relative intensity ratio of Raman D to G band (I_D/I_G) was 0.286, and the weight loss (500–700 °C) of the SWNTs formed in CoAPO-5 was 3.27 wt%. This Co/Al ratio yielded the lowest obtained I_D/I_G value and the highest weight loss of SWNTs, which indicated the lowest amorphous carbon density and the highest SWNT quantity. The density and quantity of SWNTs in the $AlPO_4$-5 crystals increased when the structure-directing agent was changed from triethylamine to tripropylamine, because of the higher carbon content of the latter's unit cell. Low-temperature hydrocracking can be used to prepare SWNTs in the channels of $AlPO_4$-5 and CoAPO-5 crystals, even for small low-quality crystals.

1. Introduction

The discovery of carbon nanotubes [1] has offered new prospects to fundamental and applied nanotechnology [2]. Many properties of carbon nanotubes depend on their diameter [3], and ultra-small single-walled carbon nanotubes (SWNTs) have attracted much attention. SWNTs can be prepared by electric arc-discharge [4], laser ablation [5], and chemical transformation of carbon precursors [6]. A common feature of these techniques is that the SWNTs grow in free space, which makes it difficult to control their size and structure. Much effort has been focused on synthesizing SWNTs with well-controlled directions and lengths [7–10]. The SWNTs with pre-designed tube structure can also be grown in host materials. Tang et al. prepared SWNTs with 0.4 nm uniform diameters in the pores of $AlPO_4$-5 molecular sieves [11], and many similar studies have since been reported [12–16]. Such SWNTs exhibit exciting properties such as one-dimensional superconductivity fluctuation, interesting electrochemistry and high adsorption capacities [17–19].

AFI is a crystalline microporous aluminophosphate ($AlPO_4$-n) that contains parallel open channels in a hexagonal arrangement, and $AlPO_4$-5 is a representative AFI [20]. There are various ways to improve the density and quality of SWNTs formed within the channels of $AlPO_4$-5 crystals. The adsorption of the organic precursor to the channel walls can be enhanced by introducing local dipoles, through doping with alternative metals [13,21]. Exploiting structure-directing agents with high carbon densities has also been shown to be effective [14]. An additional carbon source such as CO or ethylene can also be introduced into the channels of $AlPO_4$-5 [22]. The effect of different metals on the formation of SWNTs in AFI channels has been reported. However, the effect of varying metal contents of AFI hosts on the resulting SWNTs has not. Problems with the thermal cracking process also remain. The carbon nanotubes in the channels of AFI crystals could only be synthesized at 450–800 °C by the traditional thermal cracking [11], so AFI crystals had usually been treated at ≥550 °C under vacuum for several hours. A significant amount of hydrocarbon guest molecules escape from the channels, because their adsorption to the AFI molecular

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sieve is weaker at high temperature. The remaining carbon content is often insufficient to form continuous SWNTs, and the resulting crystals usually contain low SWNT densities. AFI crystals exceeding 80 μm in diameter and 400 μm in length have been hand selected from crystal mixtures in reported papers, to ensure sufficient carbon within single crystals to form SWNTs during thermal cracking [11–14,21,22]. And this requires the addition of HF to the precursor gel. The limitations of traditional processes hinder research on, and applications of, the resulting SWNTs.

Herein, low-temperature hydrocracking is used to prepare SWNTs in the channels of AFI molecular sieves, thus reducing carbon escape during heating. Small $AlPO_4$-5 and CoAPO-5 crystals (4–6 μm in diameter and 10–30 μm in length) are employed as hosts. The effects of Co content in the precursor gel and the density of carbon atoms within the crystals are investigated. The structure of the 0.42-nm-diameter SWNTs is confirmed by transmission electron microscopy (TEM) and Raman spectroscopy. This method is efficient even for small AFI crystals, so is suitable for preparing SWNTs in the channels of AFI molecular sieves at low temperature.

2. Experimental

2.1. Materials

All chemical reagents were of analytical grade, and were used without further purification. Aluminum isopropoxide (AIP, 99.5%), orthophosphoric acid (H_3PO_4, 85%), tripropylamine (TPA, 99.5%) and triethylamine (TEA, 99%) were purchased from Tianjin Chemical Reagent Co., Inc. (Tianjin, P.R. China). Cobalt acetate [$Co(CH_3COO)_2 \bullet 4H_2O$, 99.5%] was supplied by Tianjin GuangFu Chemical Reagent Co. (Tianjin, P.R. China). Distilled water was used throughout this study.

2.2. Synthesis of $AlPO_4$-5 and CoAPO-5 molecular sieves

$AlPO_4$-5 molecular sieves contain one-dimensional channels of 0.73 nm in diameter, and are suitable hosts for SWNTs. $AlPO_4$-5 crystals are relatively inert and have a very weak local dipole moment. Many metal elements can reportedly exist in its framework besides aluminum and phosphorus [23], which destroys its electrically neutral structure and gives rise to acidic sites. In this report, $AlPO_4$-5 and CoAPO-5 crystals were synthesized hydrothermally. AIP and H_3PO_4 were used as the aluminum and phosphorus sources, respectively. TPA and TEA were used as structure-directing agents. The gel composition was $1.0Al_2O_3$:1.3-P_2O_5:2.4TPA or TEA:$xCo(CH_3COO)_2 \bullet 4H_2O$:$150H_2O$, where x is the Co/Al molar ratio.

AIP was first hydrolyzed by heating with an oil bath at 150 °C for 5 h in distilled water under stirring, to obtain a translucent alumina sol. H_3PO_4 and $Co(CH_3COO)_2 \bullet 4H_2O$ were added sequentially into the synthesized alumina sol under stirring, and then TEA or TPA was added, followed by vigorous stirring for 2 h. The formed gel was sealed in a polytetrafluoroethylene-lined stainless steel autoclave, aged for 10–12 h, and heated at 180 °C under stirring for 24 h. The autoclave was then cooled to room temperature in water. The solid products were collected by filtration, washed with distilled water, and dried at 110 °C overnight.

2.3. SWNTs preparation

SWNTs were prepared using the above synthesized $AlPO_4$-5 and CoAPO-5 crystals as hosts. The low-temperature hydrocracking procedure is shown schematically in Fig. 1. Approximately 0.5 g of template samples were placed in a temperature programmable atmosphere furnace, and pretreated at 110 °C for 60 min under a N_2 atmosphere to remove water and air. Then, 50% H_2–50% N_2 (v/v) was introduced into the furnace in place of N_2, at a flow rate of 150 ml/min. Samples were heated to 350 °C, at a rate of 3 °C/min. The furnace was under a pressure of 0.01 MPa throughout the entire 600 min process.

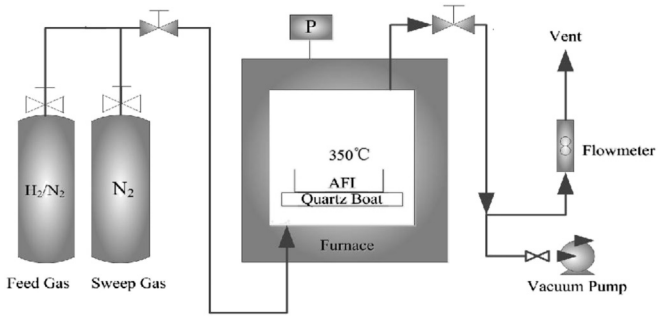

Fig. 1. Schematic diagram of the apparatus for SWNTs preparation via low-temperature hydrocracking.

2.4. Sample characterization

X-ray diffraction (XRD) spectra were recorded on an X' Pert Pro MPD diffractometer (Holland), and Co contents were determined by X-ray fluorescence (XRF) using an AxiosmAX Petro elemental analyzer (Holland). Optical images were collected using a Nikon SMZI500 stereoscope. Raman spectra of SWNTs formed in the channels of the samples were measured using a Horiba JY Labram HR800 micro-Raman spectrometer (France), using the 514 nm line of the Ar laser as the excitation source. High-resolution TEM images were collected using a JEOL 2010 microscope (Japan), operated at 200 kV. Samples were first dissolved in 30% (mass fraction) HCl for 30 min, to discharge the SWNTs from the channels of the AFI crystals. The SWNT-containing solution was concentrated, and dispersed on a copper film for TEM observation. The acidities of the samples with different Co contents were determined by NH_3-temperature programmed desorption (TPD), using a Quantachrome ASIQACIV200-2 chemical adsorption instrument (America). The SWNT contents of the samples were determined using a Netzsch STA409C/PC thermal analyzer (Germany), by heating from 28 to 900 °C in air (20 mL/min), at a rate of 10 °C/min.

3. Results and discussion

XRD patterns of the $AlPO_4$-5 and CoAPO-5 molecular sieves are shown in Fig. 2. When the Co/Al molar ratio was 0–0.1, the samples exhibited typical AFI structures without other diffraction peaks, suggesting that they were pure phase. When the Co/Al molar ratio was 0.15, the peak of the chabazite (CHA) structure was observed at $2\theta = 21.4°$. This indicated that some AFI crystals transformed to molecular CHA crystals, because the structure became unstable owing to excess Co [24]. The compositions of the gel precursors, the Co contents and crystallinities of the prepared samples are shown in Table 1. The Co contents of the CoAPO-5 crystals were similar to those of the starting gels, indicating that most Co substituted with elements of $AlPO_4$-5, and became incorporated into the molecular skeleton. The crystallinities of the prepared samples decreased with increasing Co/Al ratio, which was expected to affect the density of the resulting SWNTs.

High-resolution TEM was used to identify the morphology of SWNTs removed from the channels of $AlPO_4$-5 crystals. A typical TEM image of the SWNTs is shown in Fig. 3, in which more than ten SWNTs (indicated by arrows) are observed. The paired dark fringes