Carbon 118 (2017) 485–492

Contents lists available at ScienceDirect

Carbon

journal homepage: www.elsevier.com/locate/carbon

Diameter-specific growth of single-walled carbon nanotubes using tungsten supported nickel catalysts

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ARTICLE INFO

Article history:
Received 24 January 2017
Received in revised form
20 March 2017
Accepted 26 March 2017
Available online 26 March 2017

ABSTRACT

We developed a W/WO_x-supported Ni catalyst for the diameter-controlled growth of single-walled carbon nanotubes (SWNTs) by chemical vapor deposition (CVD) valid for different substrates and broad growth conditions. The Ni nanoparticles anchored on W/WO_x are well dispersed and show superior stability to high temperature. Under broad CVD windows of temperature and carbon feedstock supply conditions, SWNTs with narrow diameter distribution of ~1.3 ± 0.1 nm can be steadily synthesized. This strategy also works well in the growth of surface lattice oriented SWNT arrays. The aligned SWNTs grown on ST-cut quartz show similar diameters to those obtained on silicon wafers.

1. Introduction

Single-walled carbon nanotubes (SWNTs) have attracted great attentions in the past 25 years. Their outstanding performances in different applications, such as nanoelectronics [1–3], photovoltaic process [4–6], and bioimaging [7,8] benefit from the unique electronic band structures, which are directly related to their diameter and helicity [9]. The diameter control is a basic step toward the structure-controlled synthesis of SWNTs.

Chemical vapor deposition (CVD) has been regarded as one of the most promising methods for structure-controlled growth of SWNTs. It is generally accepted that SWNTs nucleate and grow from the active catalyst nanoparticles in the CVD process. The structure of catalyst nanoparticles, including size [10–14], composition [14–21], and morphology [22,23] directly affects the diameter selective growth of SWNTs [24]. Various catalyst supports, including metal [19,21] and metal oxides or carbide [23,25–28] have been utilized owing to their high temperature stability, strong interaction with the catalysts, which will be propitious to the size and structure control of the catalyst nanoparticles and therefore further contributes to the diameter control of SWNTs in CVD process. Resasco et al. synthesized SWNTs with a (6, 5) content of 55% using CoMo catalyst [16,17]. They attributed this selectivity to the uniform size of Co nanoparticles stabilized by the molybdenum oxide/carbide, which prevent Co nanoparticles from aggregation in high-temperature sintering. A similar mechanism was also evident in FeCu [19] and CoCu [21] bimetallic catalysts, in which the metallic Cu serves as the support, while Fe and Co nanoparticles can only exist and be anchored on the surface of Cu. Those highly dispersed Fe and Co nanoparticles enable the structure selective growth of sub-nanometer-diameter SWNTs. He et al. used MgO-supported Co catalysts to grow (6, 5) enriched SWNTs. An epitaxial relationship between the MgO matrix and the Co nanoparticle stabilizes the Co catalysts, while a mismatch of ~16% in the lattice constants leads to the formation of smaller Co nanoparticles. Therefore, SWNTs with small diameter and narrow chirality distribution were produced [28].

Besides the catalyst nanoparticles, the CVD conditions are also important [13,29–34]. The change of growth conditions will directly affect the carbon supply and the catalyst activity, thus significantly affect the growth of SWNTs. For a certain catalyst, a high structure selectivity of SWNTs produced is always based on a strict and specific growth condition. Therefore, the growth of uniform SWNTs under a broad growth condition window is no doubt of high interest. Here we proposed a new supported catalyst system, W/WO_x-supported Ni nanoparticles (NiWCAT). The good wet

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http://dx.doi.org/10.1016/j.carbon.2017.03.083
0008-6223/

ability and strong interaction between Ni and W [35,36] would prevent the evaporation, migration, and aggregation of Ni nanoparticles on W/WO_x support through high temperature treatment. Using the stable NiWCAT, we achieved highly preferential growth of SWNTs with a narrow diameter distribution of ~1.3 ± 0.1 nm under a broad CVD growth condition window.

2. Experimental

2.1. Catalyst preparation and SWNT growth

Nickel acetate ($C_4H_6O_4Ni{\cdot}4H_2O$, AR, Beijing Shiji) and phosphotungstic acid ($H_3O_{40}PW_{12}{\cdot}xH_2O$, AR, Beijing TongGuang Fine Chemical) (with Ni/W molar ratio of 3: 24 and Ni concentration of 0.3 mmol· L^{-1}) were dissolved in ethanol/H_2O (v/v = 9: 1) and served as the catalyst precursor solution.

For SWNT growth, the catalyst precursor solution was spin coated on SiO_2/Si wafers (SiO_2 thickness: 400 nm) or ST-cut quartz, annealed in air at 700 °C for 4 min and then reduced with H_2 from 850 °C to 1000 °C for 7 min to prepare the NiWCAT. Afterwards, a flow of Ar through an ethanol bubbler (in ice bath) and another flow of H_2 (40 sccm) were introduced to the system to grow SWNTs for 10 min. Different flow rates of Ar (from 200 to 500 sccm) were used to carry ethanol vapor and vary the carbon feedstock supply.

As a control, we also prepared mono-metallic W and Ni catalysts by using nickel acetate and phosphotungstic acid as precursors, respectively. The SWNT growth conditions are exactly the same as described above.

2.2. Characterizations

The X-ray diffraction (XRD) patterns, X-ray absorption (XAS), X-ray photoelectron spectroscopy (XPS), and high resolution transmission electron microscope (HRTEM) were used to characterize the structure of NiWCAT. Scanning electron microscopy (SEM), Raman spectroscopy, and HRTEM were used to characterize SWNTs.

The SiO_2 microspheres were used instead of SiO_2/Si wafers as

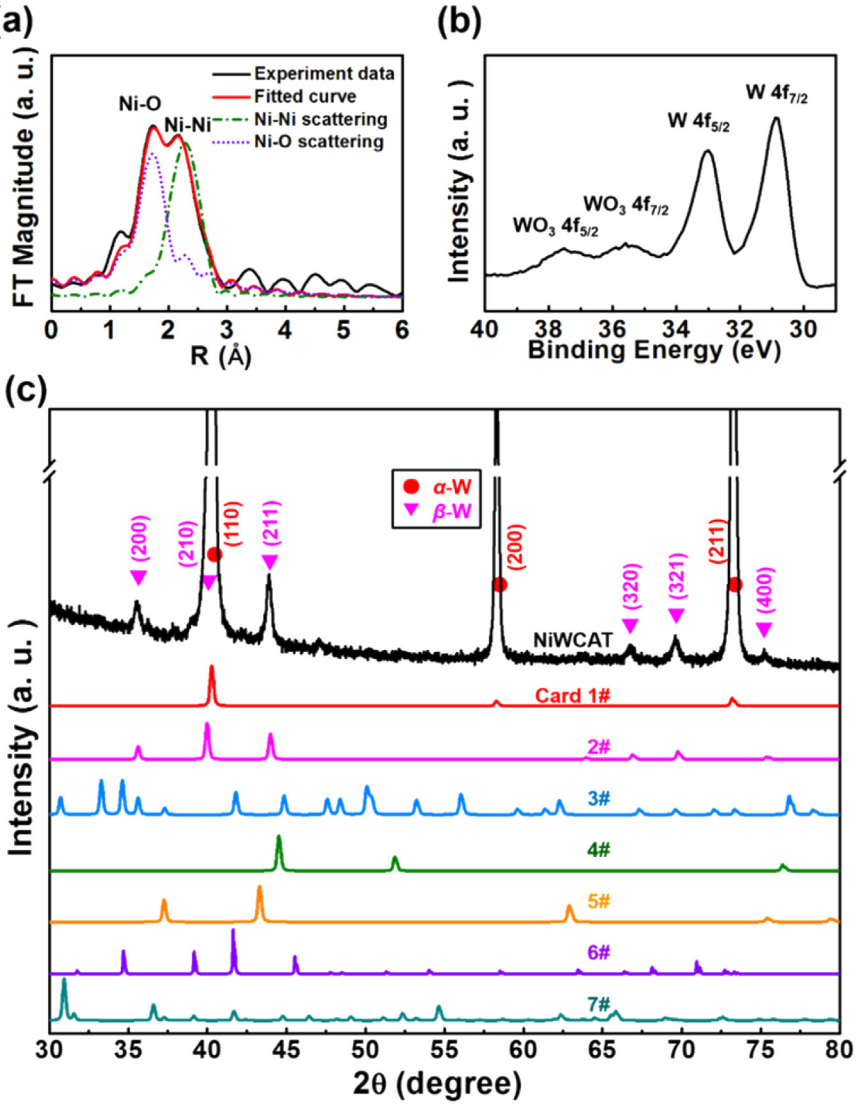

Fig. 1. (a–c) Characterizations of NiWCAT. (a) Fourier transforms of the *K*-edge extended XAS fine structure data of Ni obtained on NiWCAT (without phase shift). Here *R* is the distance between two adjacent atoms. (b) XPS of W core level line of NiWCAT. (c) XRD pattern obtained on freshly reduced NiWCAT (black line). Standard cards from the JCPDS database are included for comparison: α-W (1#, JCPDS 89-3012), β-W (2#, JCPDS 65-6453), WO_3 (3#, JCPDS 2-310), Ni (4#, JCPDS 4-850), NiO (5#, JCPDS 47-1049), Ni_2W_4C (6#, JCPDS 20-796) and $NiWO_4$ (7#, JCPDS 15-755). (A colour version of this figure can be viewed online.)