Carbon 126 (2018) 313–318

Contents lists available at ScienceDirect

Carbon

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

Substrate-anchored solid solution catalysts for high density SWNTs growth

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ARTICLE INFO

Article history:
Received 8 July 2017
Received in revised form
8 September 2017
Accepted 26 September 2017
Available online 15 October 2017

Keywords:
Substrate-anchored
Solid solution
Fresh
Active
High density
SWNTs

ABSTRACT

A novel substrate-anchored catalyst, solid solution, was developed, which experienced the annealing treatment of the single crystal MgO substrates with Co species deposited. The formation of specific structure on MgO surface and sub-surface makes Co catalysts anchored. Subsequent H_2 reduction treatment continuously released fresh active catalysts from this anchored special structure for SWNTs nucleation and growth. This gradual releasing behavior provides more catalytic opportunities to nucleate and realizes high density SWNTs growth.

1. Introduction

Single-walled carbon nanotubes (SWNTs) have been the star materials due to their extraordinary mechanical, electronic, and thermal properties and potential applications in high tensile composites [1], energy storage [2], biotechnology [3], thermal interface materials [4], *etc*. especially in the nanoelectronics [5–7]. However, the main obstacle for nanoelectronics application is the lack of SWNTs structure controlling, such as density, diameter and chirality. It is generally accepted that the catalysts activity performance directly affects the growth of SWNTs in density and yields [8]. During the chemical vapor deposition (CVD) process for SWNTs growth, the traditional metal catalytic nanoparticles tend to thermal coalescence and aggregation on the single crystal substrate because of the Ostwald ripening [9,10], which results in non-uniform diameter distribution [10] and low density growth of SWNTs [11]. Although rapid and numerous progresses have been made on the surface growth of high density of SWNTs during past two decades [8,12–19], how to succeed in loading the fresh and active catalysts is still challenging and difficult. In order to push forward this problem, recently, the typical Trojan catalysts were developed undergoing sequence thermal annealing dissolving into substrate, gradually releasing from the substrate via H_2 reduction, thus grew high density SWNTs eventually [20–22]. However, the further development of this typical Trojan catalysts is still in its infancy. Trying new substrates with formation of specific structures via chemical reaction, changing of growth ambient atmosphere and utilizing other catalysts are all possible and potential ways.

It is well known that the structures (face-centered cubic, fcc) and the cation radiuses (72.0 p.m. and 74.5 p.m. for Mg^{2+} and Co^{2+}, respectively) of MgO and CoO share very similar lattice parameters (Figs. S1 and S2), namely which is reasonable for Co ions migrating into the lattice structure of MgO crystal and Co would be anchored. Thus it leads to the formation of the eutectic crystals, solid solution on MgO substrate surface. Once they can be reduced gradually under H_2 treatment, Co nanoparticles will be continuously released and form the excellent catalysts for the growth of

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https://doi.org/10.1016/j.carbon.2017.09.096
0008-6223/

high density SWNTs due to providing more fresh opportunities to nucleate.

Herein, we report a novel and potential Trojan catalyst system, substrate-anchored solid solution, to directly grow high density SWNTs. The single crystal MgO is applied as the substrates and Co species are deposited as the potential Trojan catalysts. Specific structure is expected to form on the surfaces and sub-surfaces (inner section) of the MgO substrate after high temperature annealing, where the Co ions are anchored. Subsequent H_2 reduction treatment will continuously release active catalysts from this anchored special structure and for the nucleation and growth of high density SWNTs. Remarkably, our study further developed the Trojan catalyst system and proved them to be highly efficient for growing high density SWNTs, which will broaden potential nanoelectronics applications of SWNTs.

2. Experimental section

2.1. Materials

The MgO substrates (single-side polished, miscut angle of 0.5°, surface roughness of 5 Å) were purchased from Hefei Kejing Materials Technology Co., China. Ethanol (Analytical Reagent, AR), acetone (AR), isopropanol (AR), and other chemical reagents (AR) were obtained from Aladdin Industrial Inc.

2.2. Preparation of the substrate-anchored solid solution Trojan catalysts

In general, the MgO substrates were used as the substrates. Cleaning with acetone, isopropanol and acetone sonication for 15 min in sequence (avoiding from water), and further needing to be blown dry with argon. After cleaning, the substrates underwent the necessary temperature-programmed annealing process (at 1000 °C in air for 8 h) for better crystallization [23]. Then, 0.05 mmol/L $CoCl_2 \cdot 6H_2O$ catalysts precursors ethanol solution was dispersed onto the MgO substrates by spin-coating method (2500 r/min, 60 s). Another annealing process was followed (at 1000 °C in air for another 8 h as described above) to fill the Co into the substrate to form Trojan catalysts.

2.3. Growth of SWNTs on MgO substrates

The general CVD growth was conducted under atmospheric pressure in 1 inch quartz tube which was heated by a horizontal tube furnace (TF55035C-1 Lindberg/Blue M). The MgO substrates with catalysts were put into the tube and heated in air to the expected temperature. Briefly, after sintering at 850 °C in air for sufficient oxidation sustained 30 min, then the system was purged with 300 sccm (standard-state cubic centimeter per minute) argon and 300 sccm hydrogen for catalysts reduction, with the oxidation and reduction treatment, it can improve the catalyst activity. Later, 100 sccm argon (through an ethanol bubble) were introduced for the growth of SWNTs at 850 °C for 20 min, finally cooling down to room temperature with 300 sccm argon. For comparison, we also tried growing SWNTs without undergoing long time annealing treatment and kept the others same.

2.4. Characterizations for the as-grown SWNTs

The as-grown SWNTs were analyzed with the scanning electron microscopy (SEM, Hitachi S4800 field emission, operated at 1 kV), atomic force microscopy (AFM, Veeco NanoScope IIIA, Veeco Co.) and Raman spectroscopy (Horiba HR800 Raman system). X-ray photoelectronic spectroscopy (XPS, ESCALab250, Thermo Scientific) and AFM were used to confirm the chemical composition of catalysts and morphology of the MgO substrates surface, respectively. X-ray diffraction (XRD, Bruker, operated at the generator voltage of 40 kV and generator current of 200 mA) was performed for the MgO support structure. Transmission electron microscope (TEM) and high resolution transmission electron microscope (HRTEM) were used to characterize the micro-nano structures.

3. Results and discussion

Fig. 1 schematically illustrates the substrate-anchored solid solution Trojan catalysts preparation and SWNTs growth process. Briefly, the Co precursors were deposited on the annealed MgO substrates. Then, the substrates ware annealed at 1000 °C in air for 8 h to fulfill Co species into the MgO substrates. After the annealing treatment, a special structure was formed on the MgO surface and sub-surface and the Co ions were successfully anchored in this process. Later, the active catalysts, Co nanoparticles, were gradually released from the anchored structure under the H_2 reduction treatment. Finally, high density SWNTs film could be grown by the modified Trojan catalysts. Depending on the anchored process and subsequent releasing of catalysts, much more active opportunities were provided for SWNTs nucleation to improve the density.

The scanning electron microscopy (SEM) images of SWNTs grown on the MgO substrate by this novel Trojan catalysts as shown in Fig. 2(a,b). It is obvious that high density SWNTs covered on the whole substrate surface. Fig. 2(d) shows a statistical analysis of the diameter of SWNTs obtained from the atomic force microscopy (AFM) characterization measurement in Fig. 2(c). The diameter distribution ranges from 0.7 nm to 2.0 nm, with an average diameter of 1.23 nm according to Gauss linear fitting analysis pattern. Raman is used to characterize the properties of SWNTs based on their radial breathing mode (RBM) band frequencies and the excitation wavelength. Fig. 2(e) shows the clear RBM peaks in the low-frequency region. In addition, the as-grown SWNTs showed excellent qualities without noticeable defect-induced D band at ~1350 cm^{-1}, namely the low D/G ratio.

The MgO substrates were systematically characterized to explore the anchored and releasing processes of Trojan catalysts. For better crystallization, the original MgO substrates underwent the necessary temperature-programmed annealing process at

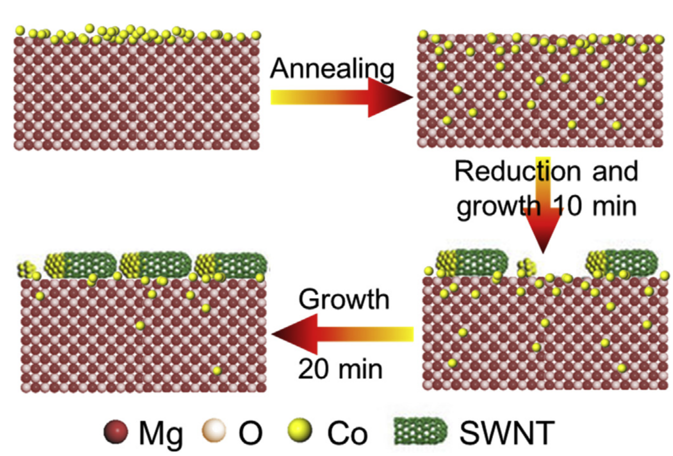

Fig. 1. Schematic illustration for the process of novel substrate-anchored solid solution catalysts preparation and high density SWNTs growth. (A colour version of this figure can be viewed online.)