Carbon 102 (2016) 181–197

Contents lists available at ScienceDirect

Carbon

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

Review article

Epitaxial growth of single-wall carbon nanotubes

Feng Zhang [1], Peng-Xiang Hou [1], Chang Liu*, Hui-Ming Cheng

Shenyang National Laboratory for Materials Science, Institute of Metal Research, Chinese Academy of Sciences, Shenyang 110016, People's Republic of China

ARTICLE INFO

Article history:
Received 11 December 2015
Received in revised form
26 January 2016
Accepted 8 February 2016
Available online 9 February 2016

ABSTRACT

Single-wall carbon nanotubes (SWCNTs) have been a focus of nanomaterial research over the past two decades, due to their wide range of potential applications in micro- and nano-electronics, energy storage, solar cells, sensors, drug delivery, and neuronal interfaces. Structurally-uniform and chirality-pure SWCNTs are highly desired and essential for both fundamental studies and many applications such as electronics, optoelectronics, and biomedical imaging. Great efforts have been devoted to the controllable synthesis of SWCNTs with defined helicities by investigating and understanding the parameters involved in their growth. In recent years, epitaxial growth has been found to be a powerful strategy in growing uniform SWCNTs using low-dimensional nanocarbons, organic macromolecules and metal nanoparticles as growth seeds or templates to control their nucleation. This article summarizes recent progress on the epitaxial growth of SWCNTs, and then outlines the challenges remaining in this field.

Contents

1. Introduction

The single-wall carbon nanotube (SWCNT) is an allotrope of carbon having the form of a hollow cylinder that can be seen as formed by a rolled-up graphene sheet, which is an extended planar hexagonal lattice of purely sp^2-bonded carbons. A SWCNT can be completely described, except for its length, by an intrinsic geometrical property, $\boldsymbol{C}_h$, known as the chiral vector [1,2]. The chiral vector is defined by the equation $\boldsymbol{C}_h = n\boldsymbol{a}_1 + m\boldsymbol{a}_2$ where the integers (n, m) are the numbers of steps along the zig-zag carbon bonds and $\boldsymbol{a}_1$, $\boldsymbol{a}_2$ are the graphene lattice basic vectors in real space (Fig. 1a).

* Corresponding author.
E-mail address: cliu@imr.ac.cn (C. Liu).
[1] These authors are equal major contributors.

http://dx.doi.org/10.1016/j.carbon.2016.02.029
0008-6223/

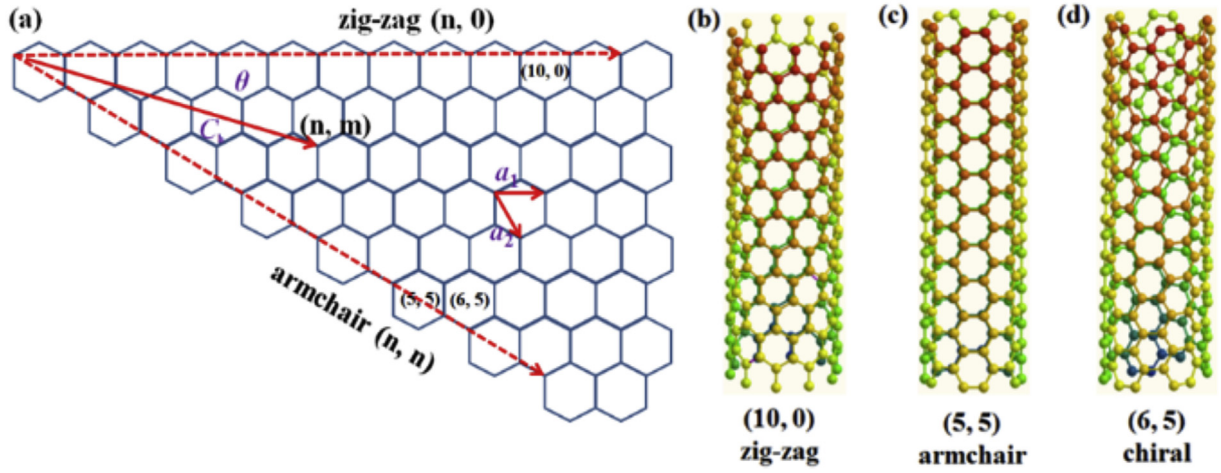

Fig. 1. (a) Unrolled single layer graphene sheet showing the geometry of the SWCNT. (b–d) Examples of the three types of nanotube sidewall; zig-zag, armchair, and chiral. (A color version of this figure can be viewed online.)

The chiral vector makes an angle, θ, known as the chiral angle, with the zig-zag or $\boldsymbol{a}_1$ direction. This angle determines the amount of "twist" in the nanotube and there are two limiting cases, where the chiral angle is 0° and 30°, that are named zig-zag and armchair (Fig. 1b–c). All other conformations in which the C–C bonds lie at angles $0° < \theta < 30°$ are known as chiral (Fig. 1d). Because the (n, m) integers completely describe the nanotube chirality, they also determine the electronic band structure. Thus, it is the chirality that has the most impact on the optical and electronic properties of carbon nanotubes. In particular, a slight change of the chiral angle leads to SWCNTs that are conductors, small bandgap or large bandgap semiconductors [3]. Therefore, the electronic, magnetic, and optical properties of SWCNTs are all determined by their chiralities [4–9]. For electronic applications, when the (n, m) indices satisfy the relationship $n - m = 3j$, where j is an integer, the SWCNTs are metallic, and they can work as conductive wires; in contrast, SWCNTs are semiconducting with different bandgaps when $n - m = 3j + 1$ or $3j + 2$, and they can be used as channel materials in transistors [10–12]. SWCNTs within specific diameter ranges with suitable bandgaps have revealed excellent performance as a transistor [13–17]. For biomedical applications, SWCNTs with helicity show much brighter photoluminescence, leading to lower SWCNT doses and fewer toxicity concerns [18–20]. For photovoltaic applications, SWCNTs with the same helicity show better performance than mixed metallic and semiconducting SWCNTs [21,22]. With these advantages, it has been a long-standing goal to selectively prepare SWCNTs with the same chirality for their wide-ranging potential applications [16,23–25]. This is considered the ultimate and the hardest goal in the field of SWCNT production.

To achieve this goal, significant research efforts have been devoted to both chirality selective synthesis and the post-synthesis sorting of SWCNTs [26–30]. In particular, post-synthesis sorting has made significant progress in the last few years. Currently, it is possible to obtain high purity individual (n, m) species from SWCNT mixtures by using several techniques, such as density gradient ultracentrifugation of surfactant-wrapped SWCNTs [26,27], size exclusion chromatography [31], ion-exchange chromatography [28], gel-based chromatography [30,32], and selective polymer wrapping [33,34]. Despite the fascinating developments in SWCNT sorting, the yield, scalability and cost of these sorting methods, as well as the properties of the sorted SWCNTs, such as the shortened lengths and the addition of surface functionality, are great obstacles to their practical applications. Although challenges remain with the direct helicity-selective growth of SWCNTs, it has great promise. In recent years, SWCNTs with selected type electrical of conductivity, narrow-distribution helicity, or even single (n, m) have been synthesized by *in-situ* selective etching [35–40], design of the supporting catalyst [41–46], and epitaxial growth [47–51]. Among these strategies, epitaxial growth, the use of a template molecule or high melting point metal nanoparticle to unambiguously dictate the diameter and helicities of the resulting SWCNTs, appears to have a potential of obtaining SWCNTs with uniform structures and properties.

Epitaxial growth is widely used in synthesizing low dimensional nanomaterials such as nanowires and two dimensional materials [47–51]. It has been demonstrated that it is a powerful and useful approach to obtain materials with controlled structures from specific seeds and templates [52]. However, not all materials can be obtained by this method, especially SWCNTs which grow at high temperatures. In this review, we define the "epitaxial growth" as follows: SWCNTs nucleate from crystalline catalyst by a lattice-matched way, or SWCNTs grow from seeds/templates with inherited structures. In consequence, the key point of this technology is how to design and prepare seeds or templates with a suitable crystalline structure, matching plane, and high thermal stability. Since first proposed by Smalley et al. in 2005 [53,54], researchers have developed different seeds and templates for the epitaxial growth of SWCNTs. In this article, we summarize the progress in the epitaxial growth of SWCNTs aimed at controlling their structures, and the challenges and the future trend of this approach are then discussed.

2. Epitaxial growth of SWCNTs from nanocarbons

2.1. Synthesis of SWCNTs from 0 dimensional fullerenes

It has been proposed that the structure of a SWCNT is determined by the "cap" formed during the nucleation process, and it is possible to control the helicity of SWCNTs by controlling the cap formation [55]. However, when using metal nanoparticles as the catalyst, the structures of the carbon caps formed on the particle surface is stochastic due to inevitable thermal vibrations at high growth temperatures, which make it difficult to control the structure of the SWCNTs [56]. Fullerenes are typical zero dimensional nanocarbons, and the cap of SWCNTs can be imagined to be half of a fullerene molecule. It is therefore reasonable to use opened