CARBON 50 (2012) 4588–4595

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Catalytic metal-free formation of multi-walled carbon nanotubes in atmospheric arc discharge

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ARTICLE INFO

Article history:
Received 21 December 2011
Accepted 18 May 2012
Available online 26 May 2012

ABSTRACT

Metallic-impurity-free, nano-sized, short multi-walled carbon nanotubes (MWCNTs) in the form of a tape have been synthesized using stabilized arc discharge under atmospheric conditions. The long, thin tape consisted of crystalline MWCNTs exhibiting indiscernibly blurred interior lattice images and a narrow, hollow core, as well as small and large nanoparticles. The disordered interior regions of the tubes were enlarged into hollow cores by thermal treatment at 2000 °C, suggesting that the elongated tubes crystallize via a supercooling process. The proposed macroscopic model for the growth process of the tubes in the arc resembles the fiber formation of a recently reported electrospinning process; thermally activated carbon ion and vapor create viscous carbon clusters, and the built-up charge in the clusters leads to the elongation into tubules.

1. Introduction

Tiny but fascinating one-dimensional carbon nanotubes consisting of rolled-up graphene sheets built from sp^2-carbon units have attracted the imagination of scientists as an ideal nanomaterial [1–3]. Thus, there has been intense study of synthetic techniques (e.g., arc discharge [4–9] and catalytic chemical vapor deposition (CCVD) [10–12]) for producing high purity multi-walled carbon nanotubes (MWCNTs) at relatively low cost. Among such techniques, the CCVD method has been adopted as one of the most suitable for industrial-scale production of carbon nanotubes due to its superior controllability and scalability [13–15]. Unfortunately, arc-based techniques for producing highly pure MWCNTs on a large scale have not yet been accomplished due to the difficulty in controlling the experimental conditions (e.g., the stabilized arcing point) in a high-energy plasma environment, and there have been only limited studies regarding the mechanism of catalyst-free nanotube growth compared to catalytically grown carbon nanotubes.

In contrast to catalytically grown nanotubes, nanotubes grown using arc discharge exhibits two distinctive merits: (1) higher structural order, which is known to be a key factor for fully exploiting their physical and transport properties [16], and (2) higher biocompatibility due to their short length and the absence of any byproducts. Catalytically grown tubes, on the other hand, are very long (up to 20 μm), [17] and contain entrapped metallic impurities and aromatic hydrocarbons, which are known to be responsible for the toxic nature of carbon nanotubes [18]. Therefore, considering the promising versatility of their applications, including recently reported bio and medical field [19,20], the arc technique must be further developed based on a clear understanding of its growth mechanism.

In this study, we have demonstrated the ability to produce highly pure, relatively short MWCNTs with a high abundance

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0008-6223/$ - see front matter
http://dx.doi.org/10.1016/j.carbon.2012.05.044

of nanotubes relative to nanoparticles in the form of a tape using stabilized arc discharge under *atmospheric* conditions, using a movable, hollow graphite anode and rotating, highly resistive carbon cathode. Our optimally designed arc apparatus employs a simple, highly efficient and economical process for producing highly crystalline MWCNTs in a semi-continuous system. In addition, the proposed growth model for nucleation and growth of catalyst-free MWNT resembles the fiber formation of an electrospinning system, where the built-up charge on the viscous carbon clusters acts as the driving force for the elongation into tubes. The proposed model is able to explain qualitatively most of the known experimental results related to tube nucleation and growth in the absence of a metal catalyst.

2. Experimental

Relatively highly pure (ca. 73%) carbon nanotubes relative to nanoparticles in the form of a tape were fabricated by the atmospheric arc discharge method under optimized conditions. As shown in Fig. 1(a), in order to achieve the stabilized arc discharge, which is known to be a critical factor for obtaining high-purity carbon nanotubes [8], we used a movable hollow graphite anode (outer diameter = 10 mm, inner diameter = 4 mm) with a speed of 170 mm per minute, and a rod-type carbon cathode (diameter = 35 mm) having a high specific resistivity above 4000 μΩ-cm with a rate of rotation of 155 rpm. The cathode and anode were made of pure graphite (or carbon) with a purity of 99.99%. Then, by precisely controlling the gap between the electrodes (ca. 1 mm), applying a constant current of 100 A (voltage = 20 V), and using argon gas at a flow rate of 1 L/min along the hollow tube of the graphite cathode, we were able to deposit grey tape spirally on the outer surface of the cathode (width = 3–5 mm, thickness = ca. 175 μm) largely comprised of carbon nanotubes. Finally, cooling gas was used to easily detach the deposited thin tape from the cathode without disrupting the tape morphology. The arc system for producing carbon nanotubes does not need both a sealed chamber and a cooling system, which are requisites for conventional arc discharge method [8]. All of the experiments were carried out in an atmospheric condition. As a post-treatment, we used high-temperature thermal annealing at various temperatures (2000, 2300, 2500 and 2800 °C) for 30 min using a graphite-resistance furnace operating in a high-purity argon atmosphere, in order to understand the structural changes (or evolutions) of the arc-grown pristine tubes.

Comprehensive SEM (JEOL JSM-6335Fs) and TEM observations (JEOL JEM-2010FEF, 200 kV) were carried out in order to characterize the macro-morphology and micro-texture of the nanotube tape. Raman spectra were recorded with a Kaiser HoloLab 5000 system using a 532 nm Ni-Yag laser line as the excitation source. X-ray diffraction (JEOL-JDX3532, CuK_α (λ = 1.54056 Å)) was used to measure changes in crystallinity. In addition, we measured the nanotube purity relative to

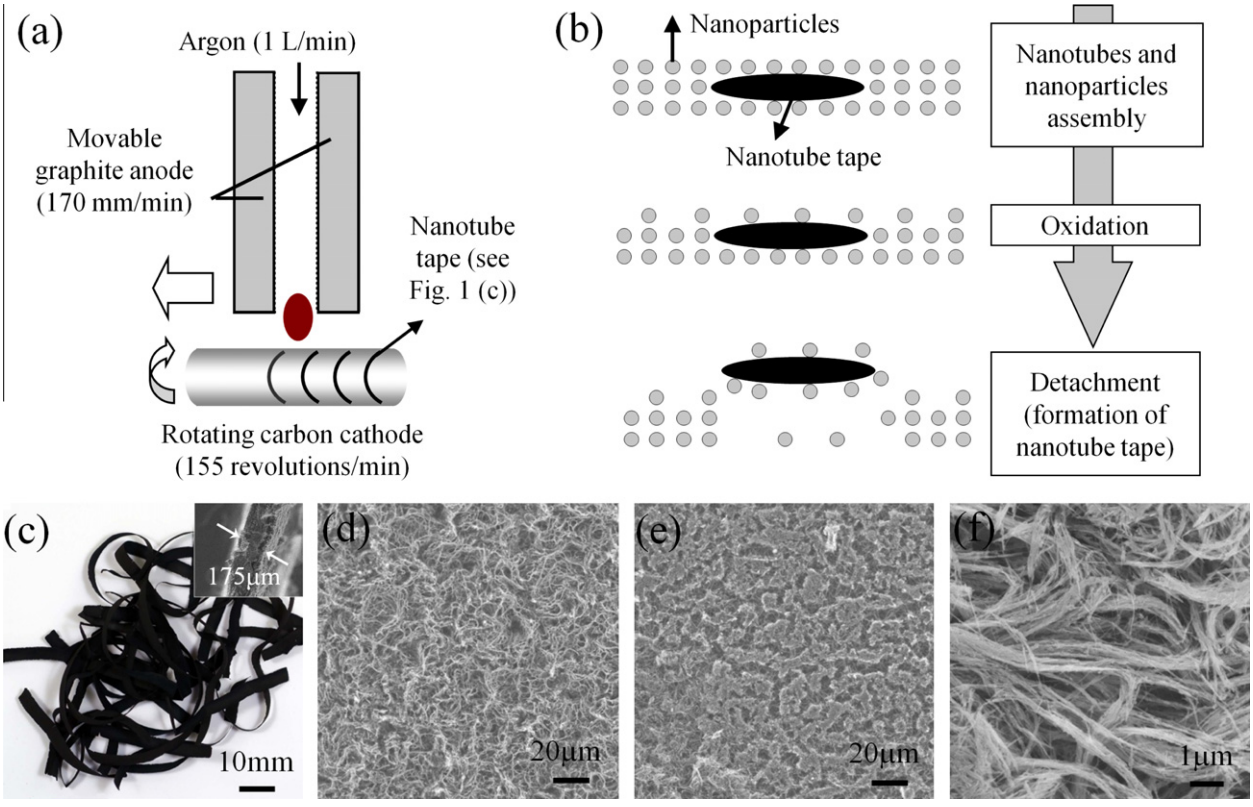

Fig. 1 – (a) Schematic diagram of the arc apparatus for producing carbon nanotubes, (b) schematic model of nanotube tape formation, oxidation and detachment, (c) photograph of long carbon nanotube tape (inset is low resolution SEM image of tape thickness), SEM images on the upper side (d) and the bottom side of the tape (e), and (f) SEM images showing long, large nanotube bundles.