



Control of product nature and morphology by adjusting the hydrogen content in a continuous chemical vapor deposition process for carbon nanotube synthesis



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ABSTRACT

Floating catalyst chemical vapor deposition (FCCVD) is commonly considered as one of the most attractive processes for the production of carbon nanotubes (CNTs). Understanding the phenomena occurring during the FCCVD synthesis of CNTs is critical to improve the process selectivity and scalability. The present work correlates information on gas chemistry and structural characteristics of the carbonaceous products, and show how both are strongly related to the hydrogen content in the reactor. Hydrogen plays different roles in the CNT growth process whose contributions depend on the synthesis conditions. Its presence induces an augmentation in carbon supply by promoting the decomposition of hydrocarbon vapors into more reactive byproducts, and by serving as an activation agent for the dissociation of physisorbed hydrocarbons on the surface of catalyst particles. However, high hydrogen content can induce catalytic hydrogenation of carbon and lead to surface modification of CNTs. Hydrogen also interferes with the decomposition of catalytic precursors, thus influencing the size and availability of catalyst nanoparticles. As a result, the mean and core diameters, crystallinity of the graphene walls, and length of CNTs are greatly influenced by the hydrogen flow, which offers the possibility to tune the CNT properties in a very simple, yet efficient way.

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1. Introduction

Comprised of one or several sheets of hexagonally packed carbon atoms rolled into concentric seamless cylinders, carbon nanotubes (CNTs) exhibit extraordinary properties that make them highly desirable for a wide range of applications from energy storage [1,2] to environmental remediation [3,4] and structural composites [2,5]. The properties of CNTs, such as conductivity, thermal stability, stiffness, and surface area are determined by their length, diameter, wall numbers and how the carbon atoms are arranged within the graphene wall [6]. However, the ability to produce CNTs with specific and uniform properties at a large scale still remains an unsolved challenge and often requires several post-

treatment steps [7].

Among the different synthesis methods, floating catalyst chemical vapor deposition (FCCVD) is an easily-scalable, one-step, continuous technique which has already been adopted by several companies [8]. This process involves the simultaneous injection of hydrocarbon and catalytic precursors into a reactor at temperatures ranging from 800 to 1200 °C in a reducing atmosphere [9,10]. Ferrocene is one of the most commonly used catalytic sources due to its good stability, low cost and non-toxicity [11]. Thermal decomposition of ferrocene leads to the nucleation of iron particles, where decomposed carbon can diffuse, precipitate and assemble into tubular structures. As CNTs begin to grow, they preferentially bundle due to attractive Van der Waals forces, forming aligned CNT arrays [12]. Numerous parametric studies have been reported in the past few years and the carbon and catalyst feeding rates are widely accepted as the most influential factors on the resulting CNT properties [13–15]. However, the control of both carbon and catalytic feeding rates often requires the fine tuning of multiple parameters, such as the reaction temperatures, synthesis time, and

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nature and ratio of carbon and catalyst sources. For instance, the size of catalyst particles can be modulated by the catalyst precursor feeding rate via the ferrocene concentration in the feed solution or the evaporation temperature [16–18].

The control of both carbon and catalytic feeding rates may be achieved by the accurate regulation of hydrogen, which would open up a simple and versatile method for the selective synthesis of various types of CNTs. In addition, since hydrogen is almost always present in CVD processing systems, either directly as a feedstock or indirectly as a byproduct of the reaction, a thorough understanding of its role in the formation of carbon nanomaterials is critical. In conventional CVD systems, hydrogen is mainly used to reduce the oxidized catalyst particles as a pre-treatment step. However, very limited studies have reported the effect of hydrogen in FCCVD synthesis of CNTs, whereas its presence is known to have a strong influence on the decomposition kinetics of both catalytic and hydrocarbon species [12,13]. Previous works on the CVD growth of CNTs using pre-deposited catalysts showed that the CNT morphology and crystalline structure can be greatly influenced by hydrogen flow rates [19]. Some studies revealed synergistic effects between hydrogen and carbon precursor in the CNT growth process [20], while other reports indicated that hydrogen can etch pyrolytic carbon from the catalyst surface, thus prolonging the catalyst activity [21]. These observations motivate a detailed investigation of the role of hydrogen on the FCCVD synthesis of CNTs. In particular, the precise structural control of CNTs by the sole regulation of hydrogen has not been explored entirely and more efforts are required to determine whether there is a link between the gas chemistry and the CNT growth process [22].

In this paper, the influence of hydrogen on the properties of CNTs synthesized on quartz and alumina micro-particles ($\mu\text{Al}_2\text{O}_3$) by FCCVD was investigated. The CNT growth was carried at 650 °C with the ratio of hydrogen to total gas ranging from 0 to 50 vol%. Lower synthesis temperature was achieved compared to other FCCVD systems (*i.e.* typically above 800 °C), which could increase the growth lifetime and make the CNT synthesis more practical for various applications [23]. The evolutions in the gas phase composition during the CVD process was recorded in real time by mass spectrometry. The analysis of the decomposition species synthesized from reactant inputs was correlated with the CNT yield, length, diameter, wall number, and crystallinity to provide new insights into the role of hydrogen in the formation of CNTs by FCCVD.

2. Experimental methods

2.1. Synthesis of carbon nanotubes

Vertically aligned CNTs were synthesized under atmospheric pressure in a horizontal CVD reactor using a 1,200 mm long quartz tube with an inner diameter of 45 mm and argon as the reactor and carrier gas (Fig. 1a). The reactor was heated by a three-zone electrical furnace (CARBOLITE HZS) to 650 °C under 1 L min⁻¹ argon flow. The temperature profile along the heated zone is shown in Fig. 1b. Hydrogen was introduced and the system was stabilized for 15 min. To eliminate possible side effects from impurities in the gas composition, high purity hydrogen (99.99%) was utilized with levels of O₂ and H₂O as low as 0.1 and 0.5 ppm, respectively. The precursor solution consisted of a liquid feedstock of carbon source (*i.e.* ortho-xylene, 98.5% Alfa Aesar) with dissolved ferrocene (0.01 g mL⁻¹), which was injected into the reactor at a rate of 0.2 mL min⁻¹ using a syringe system fitted with a liquid flow meter (Razer Science, R99-E). Acetylene was also provided to the system at a rate of 0.02 L min⁻¹ to serve as a second carbon precursor. The addition of acetylene in a gas/liquid carbon source mixture was

found to accelerate the FCCVD synthesis of CNTs [24]. Digital mass flow meters (Bronkhorst, France) were used to control the gas flow such that the total flow rate was kept constant at 1 L min⁻¹, as detailed in Table 1. After 10 min the injection of all carbon and catalytic sources was stopped and the reactor was cooled down to room temperature under argon and hydrogen atmospheres. CNTs were synthesized onto two different substrates: quartz plates and micro-spherical alumina particles ($\mu\text{Al}_2\text{O}_3$, size ranging in 3–10 μm , with 99.8% purity including 800 ppm SiO₂, 600 ppm Na₂O, purchased from Performance Ceramic company, Peninsula, OH, USA). The $\mu\text{Al}_2\text{O}_3$ particles exhibited a multiphase crystallographic structure, containing mostly the thermodynamically stable hexagonal α -Al₂O₃, and to a lesser extent metastable tetragonal δ and monoclinic θ phases. It is also worth noting that no evident phase-transformation occurred when the $\mu\text{Al}_2\text{O}_3$ particles were heated at temperatures up to 800 °C [25]. The CNT growth was located at a fixed position in the middle of the heated zone (20–30 cm) where the temperature was constant, as depicted in Fig. 1b.

2.2. Characterization

The evolution in the gas phase composition during the CVD process was recorded in real time by mass spectrometry (MS, Pfeiffer Vacuum Thermostar GSD 301 T3). The gas exhaust at the end of the heated zone (40 cm) was probed using a metallic stainless steel capillary of 0.3 mm diameter. Thermogravimetric analyses (TGA) were conducted in air on a Netzsch analyzer (STA 449 F3 Jupiter) using a thermo-program between 50 and 900 °C at a heating rate of 10 °C/min. The oxidation temperatures for the as-synthesized CNTs were in the range of 400–650 °C, while the weight loss at 350 °C was associated to the non-crystalline carbonaceous structures and used to estimate the amount of amorphous carbon [26]. Raman spectra were recorded over the range of 1000–2000 cm⁻¹ with a spectral resolution of 1 cm⁻¹ by a LabRAM Horiba Raman spectrometer using the 632.8 nm emission of a He–Ne laser source. Samples were analyzed by registering the spectra for each specimen randomly on three different positions. All recorded curves were baseline and fitted using Lorentzian line shapes, and the D- and G-peak intensities were used for the calculation of the I_G/I_D ratios. Electron microscopy observations were used to investigate the morphology of the as-prepared materials. Transmission electron microscopy (TEM) was performed using a FEI Titan instrument equipped with an aberration-corrected condenser operating at 200 kV, and scanning electron microscopy (SEM) was conducted on a ZEISS LEO 1530 Gemini FEG instrument with an accelerating voltage of 5 kV. A thorough statistical analysis of over 50 tubes (from SEM and TEM micrographs) was conducted for each synthesis condition. The results were subjected to one-way analysis of variance (ANOVA) followed by Tukey tests to ensure statistical significance. CNT length and diameter were analyzed based on 5% alpha level (*i.e.* 95% confidence). Statistical differences in CNT length and diameter were determined with p-values <0.05.

3. Results and discussion

3.1. Influence of hydrogen on the decomposition of reactant inputs

The decomposition species from reactant inputs was recorded by *in situ* mass spectrometry for different hydrogen flow rates. As shown in Fig. 2a, a fast decline in total hydrocarbon concentration with increasing hydrogen flow is first observed. The ion intensities representing the amounts of xylene and acetylene respectively decrease by 45% and 36% at 0.1 L min⁻¹ hydrogen when compared to hydrogen-free synthesis. The reduction of all hydrocarbon quantities in the gas phase can be attributed to the conversion of

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