

Flame-assisted chemical vapor deposition for continuous gas-phase synthesis of 1-nm-diameter single-wall carbon nanotubes

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ABSTRACT

Flame synthesis enables the mass-production of carbon black and fullerene but not of carbon nanotubes (CNTs) due to the narrow window for producing CNTs while preventing tar generation. We report a flame-assisted chemical vapor deposition method, in which a premixed flame is used for the instantaneous generation of floating catalysts, the heating of the gas, and the growth of single-wall CNTs (SWCNTs) using a furnace at the downstream of the flame. This method yields high quality SWCNTs with a small average diameter of 0.96 nm, a small diameter deviation of 0.21 nm, and a high carbon purity of ~90 wt%. Multiple parameters affect the SWCNT production significantly, which are investigated systematically and optimized carefully. The effects and possible mechanisms of the key parameters are discussed.

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1. Introduction

To fully realize the various potential applications of single-wall carbon nanotubes (SWCNTs), the ability to produce them on large scales and with low costs is essential. To this day, various methods have been studied and developed, most of which can be categorized into two groups of techniques: physical vapor deposition (PVD), which includes techniques such as arc discharge [1] and laser oven [2] methods, and chemical vapor deposition (CVD), which uses either floating [3–6] or supported catalysts [7–10]. Among these methods, CVD processes using fluidized beds [8–10] and rotary kilns with catalysts supported on powders hold great advantages in productivity; multi-wall carbon nanotubes (MWCNTs) of 5–20 nm in diameter are now produced and sold by several companies at low prices of ~100 USD/Kg or less [11,12] with annual production yields of several hundred tons or more. By using CVD with floating catalysts, the large-scale production of vapor-grown carbon fibers (VGCFs which are MWCNTs with large diameter of ~150 nm) were realized [13]. However, SWCNT production at

such scales has yet to be realized, because the small catalyst particles used to synthesize SWCNTs aggregate and coarsen more easily than the large catalyst particles used for VGCFs; SWCNTs are also much lighter than VGCFs. The price of SWCNTs thus remains 2–4 orders of magnitude higher than the price of MWCNTs and VGCFs.

Flame synthesis is an efficient method for the production of spherical carbon nanomaterials such as carbon black and fullerenes [14]. Howard and coworkers applied this method to the synthesis of carbon nanotubes (CNTs) [15–17], and various groups followed, as reviewed in Ref. [18]. In contrast with the non-catalytic synthesis of spherical carbon nanomaterials, catalysts are essential for the efficient synthesis of CNTs, although some MWCNTs have been found in carbon nanostructures that were formed from flames in the absence of catalysts [15]. Some studies have implemented flame synthesis for catalysts supported on substrates, but the advantages of flame synthesis over CVD were limited, because the gas conditions could not be widely varied (O₂ must be fed at high concentrations), and the catalysts had to be used in a limited temperature range (~800 °C) on timescales (from minutes to hours) similar to that of CVD. Other studies fed catalyst source vapors to either diffusion or premixed flames, and yielded floating catalyst particles; this yields SWCNTs in a mechanism similar to that

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occurring in CVD using floating catalysts [3–6]. Height et al. for example, used $\text{Fe}(\text{CO})_5$ as a catalyst source and fed it to a premixed $\text{C}_2\text{H}_2/\text{O}_2/\text{Ar}$ flame; they confirmed the production of SWCNTs in a narrow fuel equivalent ratio window of $1.6 \leq \phi \leq 1.8$ [16]. A startup company, Nano-C, also reported the continuous production of SWCNTs at 5 g/h using a “large burner” [17]. From these reports, it is evident that flame synthesis is a promising technology, and still has plenty of room for further development.

When we consider the future scale-up of the process, premixed flame is attractive, because it enables rapid self-heating in milliseconds, via passing through a flame plane of ~ 1 mm [19] at a laminar burning velocity of ~ 1 m/s [20], regardless of the reactor size. The time constant for gas heating by an external furnace is a few seconds for lab-scale reactors that are only a few centimeters in diameter, and the time constant increases with the second power of the reactor diameter. However, flame has a disadvantage in the gas composition; the resulting gas inherently yields H_2O and/or CO_2 at high concentrations. There is a narrow window for the fuel equivalent ratio [16] in producing CNTs while preventing tar generation. Therefore, we combine the premixed flame with the conventional floating catalyst CVD method; using the premixed flame for the instantaneous catalyst generation and gas heating, followed by the growth of SWCNTs using the carbon source gas added downstream of the flame in the furnace. We report the continuous synthesis of 1-nm-diameter, highly-crystalline SWCNTs by the flame-assisted CVD (FACVD) method.

2. Experimental

2.1. Synthesis of SWCNTs by FACVD

The schematic of the FACVD apparatus is shown in Fig. 1. The reactor was made out of a coaxial double tube (quartz glass, inner diameter of the inner tube of 40 mm) with an external electric furnace (heating zone length of 260 mm), and a small stainless-

steel burner (2 mm in inner diameter) set upward at the bottom. The reactor had three gas inlets. A slightly fuel-rich mixture ($\text{C}_2\text{H}_4/\text{O}_2/\text{Ar}$, fuel equivalence ratio of 1.05) was fed from the inner inlet to generate the premixed flame. Ferrocene, a popular catalyst source [3], was also fed through the inner gas by sublimation of its powder with Ar (0.206 SLM) at 80°C . Ar gas was fed from the middle inlet to cool down the flaming gas and nucleate Fe particles. Sulfur vapor was also supplied as a co-catalyst [21] by sublimation at 110°C by flowing the middle Ar (1.2–2.7 SLM) through its powder. A carbon source gas (CH_4 , C_2H_4 , or C_2H_2) was also fed from the middle gas to nucleate SWCNTs from the as-nucleated Fe particles. In some experiments, instead of supplying ferrocene and sulfur separately, they were fed simultaneously by bubbling their melted mixture (ferrocene/sulfur = 1/20 wt/wt, 120°C) with Ar (0.040 SLM) through the inner or middle inlet. CVD gas (CH_4/Ar), which was preheated while flowing down the outer tube, was fed from the outer inlet through 8 small holes ($\phi 2$ mm) radially to the center, and was mixed with the inner and middle gases to grow the SWCNTs in the furnace. The resulting SWCNTs were collected on a membrane filter (ADVANTEC Y008A047A, Tokyo, Japan) set at the outlet of the reactor.

2.2. Characterization of SWCNTs and their films

The microstructure of the as-produced SWCNTs was characterized by scanning electron microscope (SEM; Hitachi S-4800, Tokyo, Japan), scanning transmission electron microscope (STEM; S-4800), and transmission electron microscope (TEM; JEOL JEM-2100F, Akishima, Japan), their elemental composition was examined using energy dispersive X-ray spectroscopy (EDS; Ametek EDAX Genesis, Elancourt, France) equipped to the SEM, and their quality was assessed using Raman scattering spectroscopy (Horiba HR-800, Kyoto, Japan) with excitation wavelengths of 488 and 633 nm. Thermogravimetry-differential thermal analysis (TG-DTA; Rigaku TG8120, Akishima, Japan) was also conducted for an as-synthesized SWCNT sample to evaluate the inclusion of amorphous carbon. The sheet resistance of the SWCNT film as collected on the membrane filter was analyzed by the four-point-probe method to evaluate the relative amount and quality of the SWCNTs.

3. Results and discussion

3.1. Typical SWCNTs synthesized by the FACVD method

Fig. 2 shows the typical SWCNTs synthesized by the FACVD method. The condition was 8.6 vol% $\text{C}_2\text{H}_4/24.6$ vol% O_2/Ar at 0.7 SLM with ferrocene and sulfur vapors (by bubbling) for the inner inlet, 3.4 vol% $\text{C}_2\text{H}_4/\text{Ar}$ at 1.8 SLM for the middle inlet, and 20 vol% CH_4/Ar at 2.5 SLM for the outer inlet. The furnace temperature was $T = 950^\circ\text{C}$, the synthesis time was $t = 10$ min, and the burner position was the same as Fig. 3c. The SEM image in Fig. 2a shows the small-diameter CNTs with small Fe particles attaching on their surface. The yield was 2.38 mg and the Fe/C weight ratio was 0.11 (EDS). The TEM image in Fig. 2b shows that the products were small diameter SWCNTs. The wall number and diameter were analyzed for 134 CNTs using multiple TEM images. All of them were SWCNTs with an average diameter of $D_{\text{ave}} = 0.96$ nm and a standard deviation of $\sigma = 0.21$ nm. Raman spectra in Fig. 2d show the characteristic peaks for SWCNTs; a strong G-band peak at ~ 1590 cm^{-1} , a weak D-band peak at 1300 – 1350 cm^{-1} , and clear radial breathing mode (RBM) peaks at 150 – 300 cm^{-1} . The diameter d calculated from the Raman shift ω using the relationship, $d = 248/\omega$ [22], agrees well with the diameter distribution acquired by the TEM in Fig. 2c. We then compared the diameter distribution of our SWCNTs with those of the SWCNTs by the floating catalyst CVD method

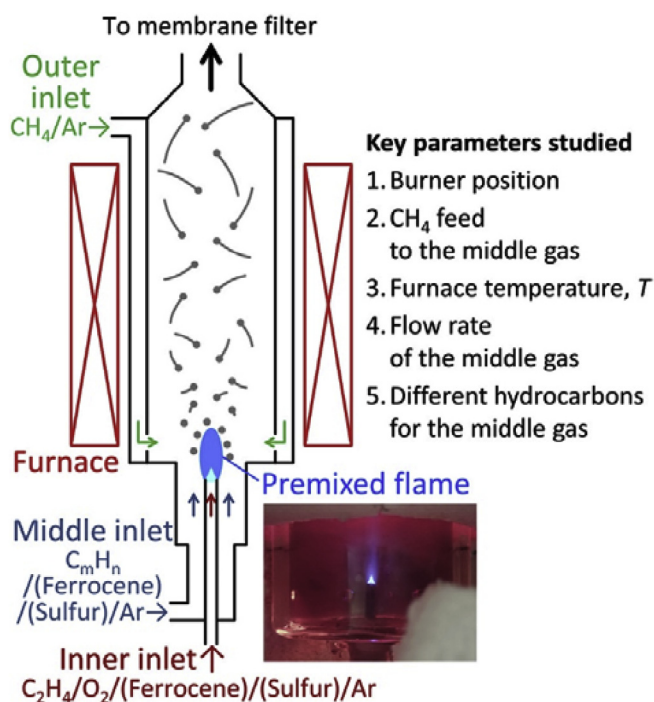


Fig. 1. Schematic of the FACVD apparatus developed and used in this work. Inset photo shows the premixed flame. (A colour version of this figure can be viewed online.)

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