Chemical Vapor Deposition

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Synthesis of Carbon Nanotubes from Propane**

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Since their discovery, there have been extensive developments in various methods for producing carbon nanotubes (CNTs), including laser ablation, arc discharge, pyrolysis, and CVD.[1] CVD is currently the most popular and widely used of these techniques, owing to its low cost, good yield, and simple scalability.

Among many CVD growth conditions for CNTs, the carbon precursor is likely to play a crucial role in determining the structural properties of the final material. Many gaseous precursors, such as methane, acetylene, carbon monoxide, and others, are widely used for high-quality CNT synthesis.[1,2] Simpler and thermodynamically more stable precursors, such as CH_4, are preferred for synthesizing high-purity single-walled (SW)CNTs.[1,2] Higher hydrocarbons (e.g., propane) are less controllable during the synthesis process and are thus less commonly used. For instance, propane has been used for CVD growth of multi-walled (MW)CNTs.[3,4] Other related work considers the complex topic of aerosol particle formation from the pyrolysis of $C_3H_8 + Fe(CO)_5$ mixtures, where CNTs have been seen as a link between Fe_3C particles.[5] To the best of our knowledge, there is no work reporting temperature-dependent transition from SW- to MWCNT growth using propane.

We demonstrate CNT growth via a catalytic CVD technique using pure propane (C_3H_8) as the carbon source. We study the influence of the synthesis temperature ($600 - 1100\,^{\circ}C$) on the grown material, and demonstrate the possibility of selectively synthesizing SWCNTs and MWCNTs. In particular, we show that a low precursor flow rate ($<5\,mL\,min^{-1}$) and moderate processing temperature ($800\,^{\circ}C$) promote high-quality SWCNT growth, with MWCNTs favored at higher temperatures. This work may shed some light on the growth mechanism for CNTs using propane as the carbon precursor. Another advantage of using propane, in comparison to commonly used methane, is the lower cost of the gas and lower temperature of the stable reaction zone.

In our study, we use a catalytic CVD. Figure 1a is a brief illustration of our thermal CCVD system. This system is based on a modified Lindberg/BlueM furnace and consists of a quartz reaction tube (inner diameter of 25 mm and length of 100 cm) embedded in two heating coils. The central part of the reactor (where the sample is kept) can maintain a stable temperature up to $1100\,^{\circ}C$. The growth process was performed via the catalytic decomposition of propane (purity 99.999%) on a SiO_2 substrate with a previously prepared catalyst. The procedure of catalyst preparation is described in the Experimental section. The role of the catalyst is not discussed in this report, however we note that catalysts used in this work have also been used before in a CVD process with methane as a carbon source for production of high-quality SWCNTs,[6] and further used in many applications.[7–9]

A typical growth procedure (Fig. 1b) involves an initial preheating step under an argon atmosphere ($500\,mL\,min^{-1}$) to the growth temperature, followed by a 10 min annealing under an argon and hydrogen atmosphere (500 and $400\,mL\,min^{-1}$, respectively). Propane was then introduced into the gas stream for 15 min at a fixed flow rate of $1\,mL\,min^{-1}$ (which is much lower than rates reported in the literature [3,10]). At the same time, the flow rate for argon and hydrogen was fixed at 500 and $100\,mL\,min^{-1}$, respectively. The growth temperature was set to a fixed value for a given process (e.g., $800\,^{\circ}C$). The procedure was finished with a cooling step, and at $500\,^{\circ}C$, the hydrogen feed was switched off. See the diagram in Figure 1b for a graphical representation of the growth procedure using a target temperature of $800\,^{\circ}C$. In general, the synthesis was performed across a wide range of temperatures from $600\,^{\circ}C$ to $1100\,^{\circ}C$, under atmospheric pressure. The flow rates ranged from 1 to $15\,mL\,min^{-1}$. In addition, the growth procedure was tested on a bare substrate without any catalysts to confirm no carbon material deposition occurred when the catalysts were absent.

A scanning electron microscope (SEM) system (Raith eLine plus) and a standard tapping mode atomic force microscope (AFM) (NT-MDT) were used to examine the orientation and the length of produced CNTs, and dispersion of the catalyst. Micro Raman spectroscopy (RS) (Renishaw inVia, 514 nm excitation line, objective $\times 100$ with

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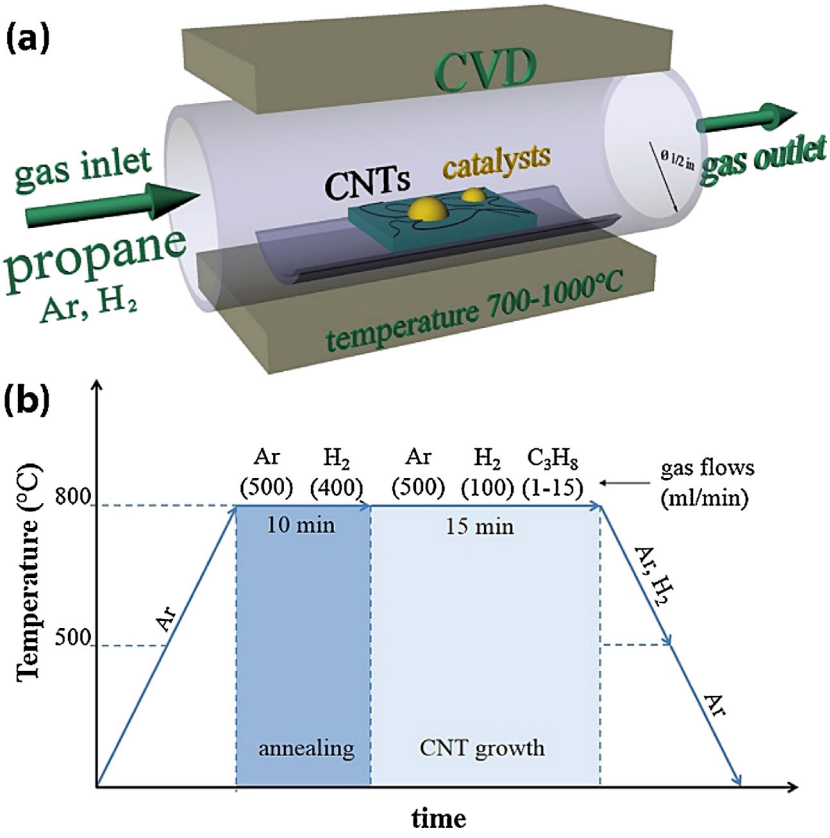

Fig. 1. a) Schematic of our catalytic CVD set-up using propane as the carbon feeding gas. b) An example growth procedure (here for 800 °C growth temperature) showing the timing, gas flow rates, and temperature during the various steps.

NA = 0.85) was used to structurally characterize the CNTs and supporting surface. High resolution transmission electron microscope (HRTEM) (JEOL JEM-2100) was used to image the morphology and the structure of the grown material.

The highest quality individual SWCNTs were grown directly on the SiO_2/Si substrate at a temperature of 800 °C. Figure 2a shows an example SEM image of individual and straight nanotubes on a SiO_2 substrate. Figure 2b shows three typical Raman spectra for nanotubes collected using the above growth conditions. All spectra contain three common Raman bands characteristic of SWCNTs. The G band shown in black consists of two peaks located at approximately 1600 cm^{-1} and is typical for semiconducting CNTs. The G band shown in green has a shoulder at 1555 cm^{-1}, which is indicative of metallic CNTs. The D band has very low intensity, suggesting low defectiveness of the carbon material. The radial breathing modes (RBMs) shown in Figure 2b range between 145 cm^{-1} and 188 cm^{-1} (overall up to 226 cm^{-1}; data not shown here). Using the conventional formula:[10] $\omega_{RBM} = 227/d_t$, where ω_{RBM} is the peak position and d_t is the tube diameter, we obtained d_t for the range 1.09–1.56 nm. These results agree well with the AFM study, which yielded diameters from 0.6 nm to 1.5 nm.[11] An example AFM image is shown in Figure 2c, where a series of CNTs grow from the catalyst agglomeration (left-bottom black area). Finally, the quality of individual SWCNTs is confirmed by TEM images, shown in Figure 2d. We note that all of the above measurement techniques show a clean sample surface, indicating the lack of other material deposition.

Now, we will further discuss the effect of temperature on the grown carbon material. At 900 °C (low propane flow rate < 5 mL min^{-1}), both SW- and MWCNTs are present in the grown material as is clearly seen in the SEM and TEM images shown in Figure 3a and 3b, respectively. We estimate that the amount of SWCNTs is lower than MWCNTs. In addition, spring-like MWCNTs were also present in the grown material (inset in Fig. 3a). It seems that further increase of the temperature (to 1000 °C) promotes low quality MWCNTs and shows no evidence of the presence of SWCNTs (see Fig. 3c and d), which is further supported by the Raman study. At 1100 °C only a few, short, and strongly defective MWCNTs can be observed (Fig. 3e and f).

We note that the decomposition of propane at higher temperature leads to deposition of additional carbonaceous compounds besides nanotubes. These compounds are barely visible in Figure 3c (1000 °C) and are more pronounced in

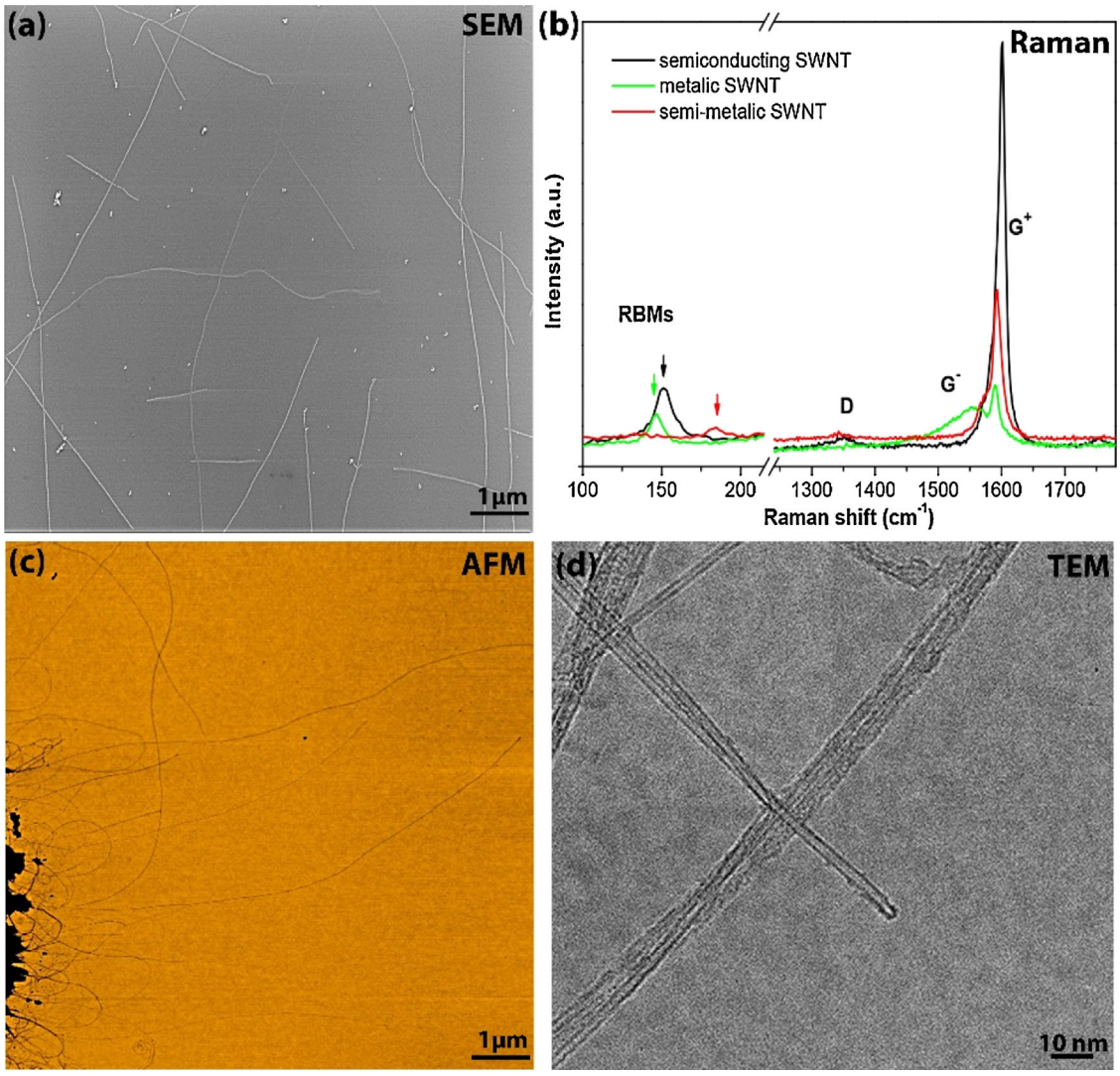

Fig. 2. Nanotube grown at 800 °C. a) SEM image of the individual tubes on a SiO_2 substrate. The scale bar is 1 μm. b) Typical Raman spectra showing three main bands (G, D, RBMs), which suggest the presence of different CNT types, both metallic and semiconducting. c) Typical AFM image of nanotubes with diameters ranging from 0.6 to 1.5 nm (extracted from cross-section plots). Scale bar is 1 μm. d) TEM image.

Figure 3e (1100 °C). Notably, the increased deposition of various carbonaceous compounds was amplified by increasing the rate flow (over 5 mL min^{-1}) but this deposition was negligible at lower temperatures.

The Raman spectral evolution for samples processed at different temperatures is shown in Figure 4. The lowest I_D/I_G ratio is seen for tubes grown at 800 °C. The spectra at temperatures above 800 °C are more typical for MWNTs. The I_D/I_G ratio increased significantly with the growth temperature, which suggests an increased formation of disordered carbon material.[12] The spectrum for 700 °C shows a single nanotube signature with lower quality compared to the material grown at 800 °C (see intensity ratio). At 600 °C and below, no CNT presence has been observed (confirmed further by AFM).

In general, low-temperature CVD using most hydrocarbons yields MWNTs, whereas higher temperature processes favor SWCNT growth.[13] Our results suggest that, for propane, this trend is rather reversed. This behavior could originate from the thermodynamic equilibrium of the precursor decomposition that, in our case, is reached for temperatures ~800 °C (taking into account the vapor pressure, flow rate, and precursor concentration).[14] It is likely to be due to the fact that, for higher temperatures, saturated hydrocarbons undergo a series of gas-phase reactions leading to the formation of a complex mixture of e.g., hydrogen and other hydrocarbons.

In summary, we grew high-quality CNTs using propane as a carbon source. The SWCNT and MWCNT volumes in the grown material can by tuned using the growth temperature.

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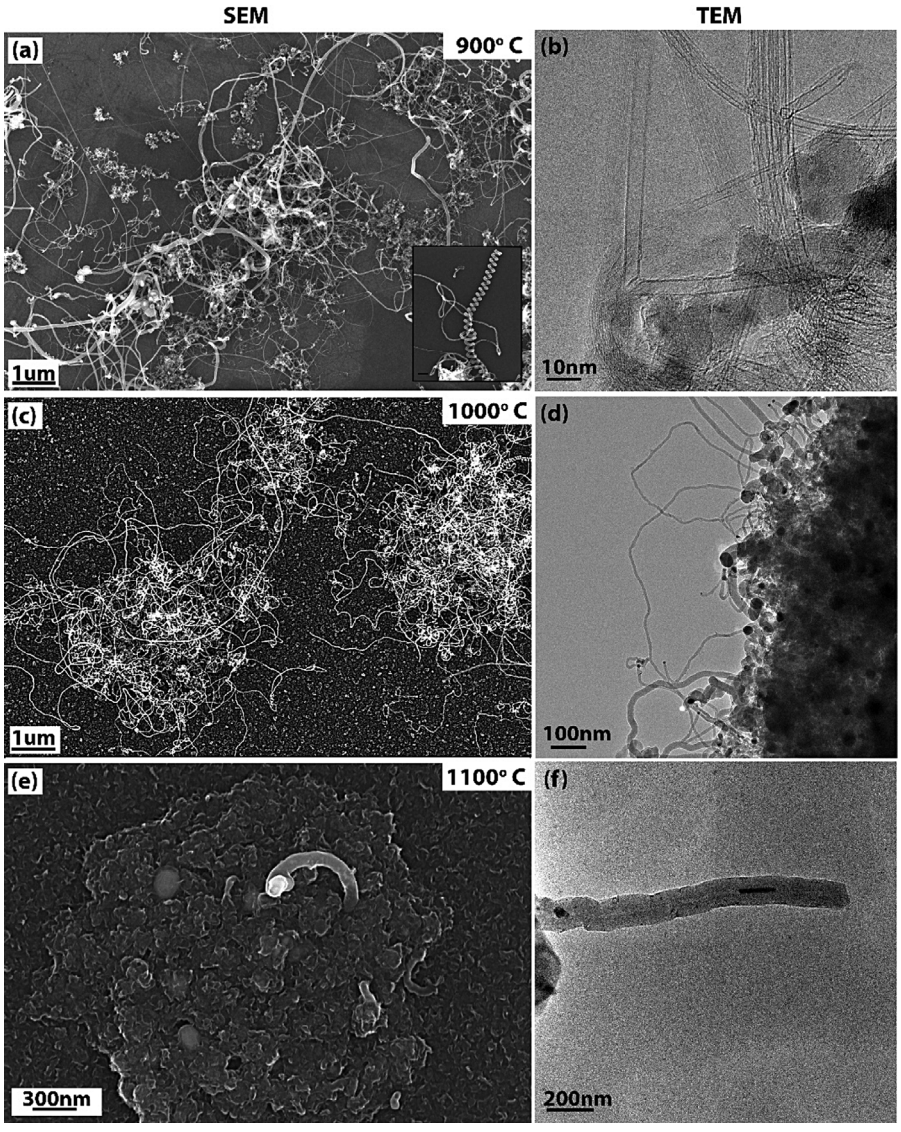

Fig. 3. a) SEM and b) TEM images of CNTs grown at 900 °C with both SWCNTs and MWCNTs visible. Inset in a): image of a helical MWCNT. c) SEM and d) TEM image of CNTs grown at 1000 °C. e) SEM and f) TEM image of CNTs grown at 1100 °C.

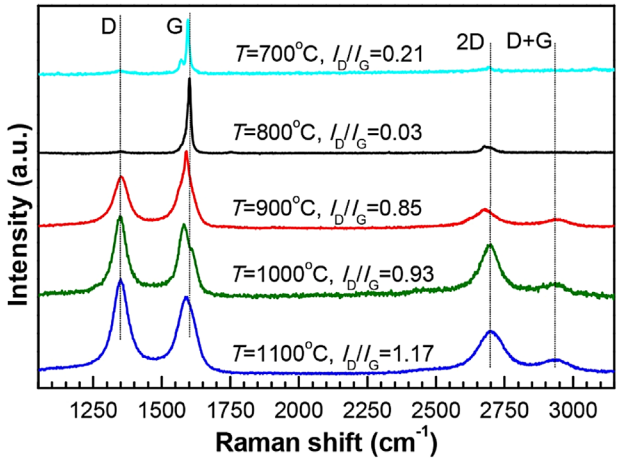

Fig. 4. The Raman spectral evolution with the nanotube growth temperature. The increased I_D/I_G ratio confirms the lower structural quality.

We emphasize the low propane flow rates in this process. Further study of other growth conditions, such as pressure, flow rates, and the role of the catalysts is needed.

Experimental

The growth process was performed via the catalytic decomposition of propane (C_3H_8, purity 99.999%) on a SiO_2 substrate with a previously prepared catalyst. Briefly, the catalysts were prepared with the following ingredients (from Sigma Aldrich): 80 mg of iron ($Fe(NO_3)_3$ nonahydrate), 4 mg of bis(acetylacetonato)dioxomolybdenum(VI), 60 mg of aluminum oxide, all in 60 mL of methanol (HPLC). Next, all components were mixed together and ultrasonicated for one hour before using. Finally, 10 μL of the catalysts solution was dropped onto the substrate and dried by the nitrogen stream. Directly after, catalysts deposition samples were introduced into the furnace. This procedure is based on the work of Kong et al.[6]

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