

Low-Temperature Growth of Carbon Nanotubes from the Catalytic Decomposition of Carbon Tetrachloride

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Since the discovery of carbon nanotubes (CNTs) by Iijima,¹ the scientific world has been fascinated with perhaps the most elegant allotrope of carbon. Of the variety of methods used to synthesize CNTs, catalyzed chemical vapor deposition (CVD) represents the current method of choice.² Although CVD offers the benefit of significantly lower deposition temperatures than arc-based techniques, the common temperature range of 600–1000 °C precludes the use of temperature-sensitive substrates. Hence, there is much current interest in lowering the growth temperature, while maintaining high yields and controllable morphology. To date, the lowest-reported temperature for growth of MWNTs is 200 °C, from benzene-thermal-reduction-catalysis (BTRC), which uses chloride-containing precursors with in situ alkali metal-facilitated reduction.³

Although the exact mechanism involved in nanotube growth is not completely understood, it has been demonstrated that the diameters of catalytically grown CNTs may be altered through changing the diameter and/or nature of the catalytic sites.⁴ Metal-encapsulated dendrimers represent a particularly attractive catalyst for nanotube growth, as the size of the entrained metal may be easily manipulated through changes in the core/periphery structure of the dendrimer.⁵ To date, there is only a single report of utilizing a dendritic host to control nanotube diameters.⁶ However, direct dendrimer–CNT linkages did not remain intact, as the polymeric matrix was removed through pyrolysis prior to high-temperature CNT growth. The benefits of synthesizing CNT–dendrimer nanocomposite materials are intriguing, possibly allowing CNTs to be solubilized in organic solvents, and extending the applications for nanotubes beyond the “dry world” into the “wet world”.

For such nanocomposite growth, our synthetic strategy has been to find a method to control the size and distribution of the catalyst seed particle, as well as to develop a low-temperature, nonreactive means of carbon production, to best preserve the structure of temperature-sensitive dendrimers. As an initial step toward this goal, we present the use of supercritical carbon dioxide as a medium for the decomposition of CCl₄ using iron-encapsulated polypropyleneimine (PPI) dendrimers as a catalyst for MWNT growth (Figure 1).

The most rational method to decrease the growth temperature is to substitute traditional hydrocarbon-based precursors with carbon halides, featuring weaker C–X bonds. The literature reveals only a few recent reports where chlorinated hydrocarbons were used as carbon feedstock for CNT synthesis.^{7,8} However, these reactions involved metathesis reactions, requiring the use of alkali metals or lithium acetylide to aid in the decomposition of the precursor. Our procedure does not require the use of co-reactants, featuring only the controlled decomposition of CCl₄ within a medium of supercritical CO₂.

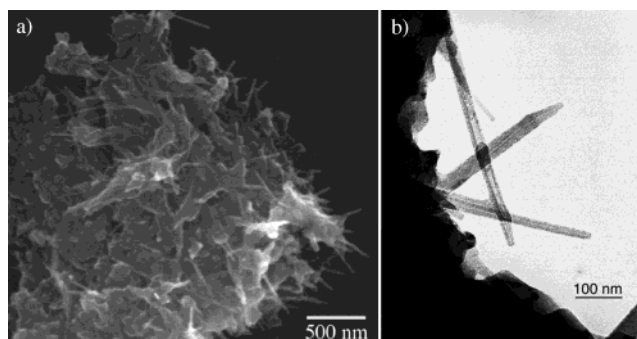


Figure 1. FESEM and TEM images of MWNTs grown on an Fe@dendrimer catalyst at 175 °C.

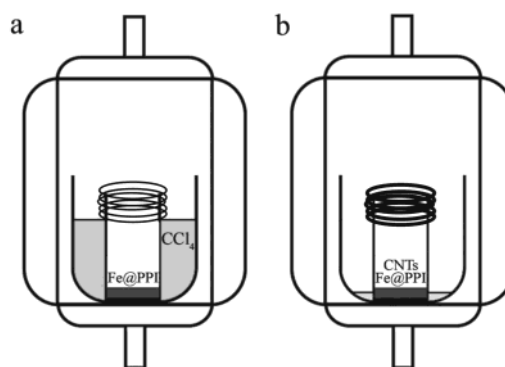


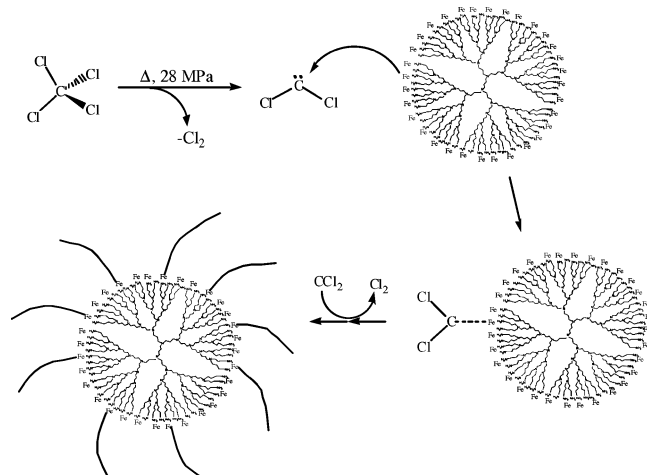
Figure 2. Schematic of the supercritical fluid reactor contents before (a) and after (b) the experiment. Spirals of copper wire, used to sacrificially remove the Cl_{2(g)} byproduct, are shown.

The Fe-encapsulated dendrimer catalyst was prepared by encapsulating various concentrations of Fe³⁺ ions inside a fourth-generation (G4) PPI dendrimer, within an ethanol solution. The iron cations were then reduced with NaBH₄, resulting in the precipitation of the Fe@dendrimer catalyst as a dark-brown precipitate. The product was concentrated in a centrifuge and air-dried.

Subsequent production of CNTs was accomplished using an SFT-150 system with a 200-mL supercritical reactor purchased from Supercritical Fluid Technologies, Inc. Figure 2 illustrates the setup that was used inside the high-pressure reactor. The dried Fe@dendrimer powder was placed within a 15-mL vial, surrounded with a 50-mL beaker that contained 5 mL of CCl₄. Initial runs revealed the formation of a yellow product of iron chloride, formed through the reaction of chlorine gas with the catalyst particles. As shown in Figure 2, the problem of quenching the chlorine gas evolved in the thermolysis was circumvented through using a “sacrificial anode” of copper wire that was wrapped around the mouth of the vial. Prior to heating, the reactor was charged with 8.3 MPa of CO₂, which increased to 27.6 MPa after reaching a

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Scheme 1. Representation of a Proposed Mechanism, Showing Nanotube Formation onto Individual Fe@Dendrimer Catalyst Particles



final temperature of 175 °C. After 24 h, the reactor was slowly vented and the product removed for analysis.

The average diameter of the resultant nanotubes was 20–25 nm, much smaller than those reported through other low-temperature methods.^{3,8} Two Raman peaks were observed at 1338 and 1579 cm^{-1} , confirming the presence of the graphitic carbon architecture of MWNTs.⁸ It should also be noted that branched and bent nanotube morphologies were commonly observed, analogous to the Y-junction CNTs recently reported by Wang et al.³ The increased number of such occurrences in our system may indicate a more complex growth mechanism involving our Fe@PPI-G4 catalysts, where encapsulated and peripheral iron atoms would each exhibit different catalytic rates for nanotube growth.

Since the diameter of the G4-PPI is ca. 2.3 nm, the formation of MWNTs with diameters an order of magnitude larger indicates that nanotube growth emanated from an agglomeration of Fe@dendrimer catalyst nanoparticles (Figure 1a). A variety of iron concentrations were investigated, with no observable change in resultant nanotube diameters. Through nitric acid digestion and subsequent quantification, our average yield is 15% relative to starting materials, which is low compared to high-temperature methods but consistent with other recently reported low-temperature methods.^{3,8}

For our initial study, we used amine-terminated PPI dendrimers. Hence, it is likely that the metal is mostly entrained along the periphery of the dendritic sphere, rather than encapsulated within the inner voidspace. Scheme 1 illustrates a generalized mechanism for the growth of CNTs from our catalyst. The decomposition of CCl_4 and subsequent CNT growth likely proceeds through a dichlorocarbene intermediate,⁹ initially forming an iron carbene transient species. We are currently attempting to trap dichlorocarbene in our reactor with electron-rich alkenes, in the absence of the Fe@dendrimer catalyst. Although we have found no precedent for the reaction of dichlorocarbene with carbon dioxide, such a side-reaction may partially explain our low overall yield.

It has been recently suggested that small-diameter CNTs are formed more efficiently at higher temperatures.¹⁰ We are currently

investigating the use of hydroxyl-terminated dendrimers to position the catalyst nanoparticles further within the dendritic structure, to assess whether our extremely low-temperature regime is able to yield CNTs with smaller diameters.

The role of carbon dioxide for nanotube formation is most likely three-fold. First, this medium serves to simply purge the reactor of oxygen and water, which would result in the formation of oxychloride species from the decomposition of CCl_4 , rather than graphitic carbon. Second, the high-pressure exerted by the CO_2 assists in the decomposition of CCl_4 . It should be noted that no nanotube growth was observed with an analogous experimental setup, in the absence of CO_2 . Hence, this medium is needed to deliver the intermediate species to the encapsulated iron surface for nucleation and growth of CNTs. The gas/liquid behavior of SCFs should also allow the use of higher-generation dendrimers, with fully encapsulated metals.

In summary, we have successfully synthesized MWNTs at the lowest-reported temperature to date via the decomposition of CCl_4 in supercritical CO_2 . This is the first reported use of CCl_4 as a precursor for CNT growth, as well as the first use of metal-encapsulated dendrimers as catalysts for low-temperature growth. The temperature and pressure used in our system for CNT growth is far below the conditions we observed for decomposition of the G4-PPI dendrimer itself, suggesting the presence of nanotube–dendritic linkages.

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Supporting Information Available: A representative Raman spectrum of our carbon nanotubes. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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