

SYNTHESIS AND GROWTH MECHANISMS OF MULTIWALLED CARBON NANOTUBES

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INTRODUCTION

In a recent publication we have described the synthesis of multiwalled carbon nanotubes (MWNTs) by the reaction of a hydrocarbon vapor over a dispersed iron catalyst that is deposited *in situ* on quartz substrates¹. Our system configuration involves entraining a mixture of xylene and ferrocene into an inert gas stream. Decomposition of the ferrocene at temperatures in the range 625-775 °C, and at atmospheric pressure, produces a coating of iron nanoparticles on the quartz surfaces, and these metal sites function as catalysts for the formation and growth of MWNTs. In this study, we report the influence of operating conditions on MWNT purity and yield. These parameters include the feed injection temperature, furnace temperature, hydrocarbon partial pressure, reaction time, space velocity, and iron to carbon ratio in the feed. We observed that the quality of the MWNTs depend sensitively on the growth parameters and a window for the operating conditions is identified for the growth of high purity aligned MWNTs. Characterization of the MWNTs by electron microscopy has shown that there is a relationship between metal particle size and MWNT diameter. The low temperature synthesis process¹ is an attractive synthesis route since (i) selectivity of the intermediate products can be controlled to generate high purity MWNTs; and (ii) the process is readily scaleable for large scale production of carbon nanotubes.

EXPERIMENTAL

Briefly, the nanotube synthesis reactor system consists of a quartz tube reactor inside a tube furnace. A syringe pump allows the continuous injection of the xylene-ferrocene liquid (~1-3 ml/h) into a preheater section that is operated at ~200 °C, i.e., at a temperature above the sublimation temperature (~175 °C) of ferrocene and the boiling point of xylene liquid (~140 °C). The xylene-ferrocene vapors are carried from the preheater into the relatively hotter zone of the furnace by an Ar/H₂ (10%) carrier gas which also controls the partial pressure inside the quartz tube reactor. Standard operating procedure is as follows: the quartz tube and additional quartz substrates are installed into the furnace and then purged with Ar gas. The preheater and furnace heaters are ramped up to achieve the desired stable temperatures. The liquid and gas feeds are started and run for the desired reaction times. On quartz plates that are placed inside the quartz tube reactor to provide additional surface area for growth, the MWNTs grow perpendicular to the plates in parallel alignment, forming thick mats that can be readily harvested. After completion of a run, the preheater and furnace are cooled to room temperature, dismantled and the products are recovered for scanning electron (SEM) and transmission electron (TEM) microscopy studies. Several systematic runs were carried out with a view towards determining which of the synthesis parameters had the greatest influence on the purity and production rate of MWNTs.

RESULTS AND DISCUSSION

In Fig. 1, we present the MWNT production rates obtained from the products deposited on the quartz substrates as a function of the furnace temperature. Clearly, in the temperature window of 725 - 775 °C, MWNT production rates as high as 0.5 mg/m²/s were achieved. Outside this temperature window, a concomitant increase in the conversion of carbons into amorphous carbon was detected from the HRSEM and TEM images.

Interestingly, high furnace temperature also leads to the growth of larger catalyst particle that control the outer tube diameters. We arrive at this conclusion based on the data depicted in Fig. 2. A systematic TEM study of MWNTs synthesized at different furnace temperatures finds that the nanotube outer diameter is directly correlated to the catalyst particle size². High resolution TEM images of MWNTs showed the presence of the metal catalyst at the tip of the MWNTs. Predominately, the root ends of the MWNTs were found to be open¹. In the runs which used metal to carbon ratios in excess of 0.075, HRTEM indicated the presence of Fe within the core of the MWNTs. In an independent study, after initiation of MWNT growth using xylene-ferrocene mixture, we found that the MWNT continue to grow even in the absence of ferrocene in the feed stock.

CONCLUSIONS

In this study, we have found that the operating parameters such as furnace temperature, space velocity and carbon partial pressure impact nanotube production and quality. Data indicated that an increase in production rate is accompanied by an increased co-production of carbon nanofibers (> 100 nm diameter) or amorphous carbon. HRTEM images obtained on several individual MWNTs revealed a correlation between the outer tube diameter with the size of the catalyst particle at the tip.

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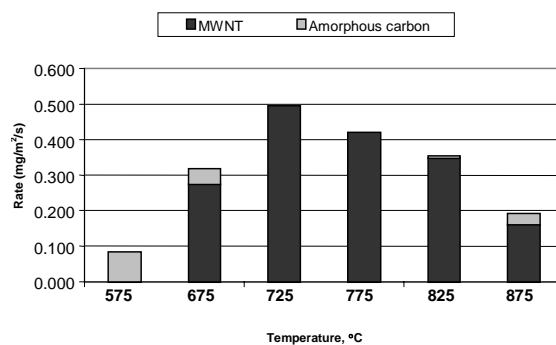


Figure 1. Production of MWNT on substrate has maximum at 725 °C furnace temperature.

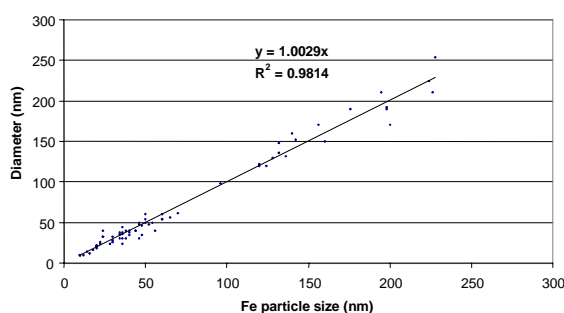


Figure 2. Nanotube diameter corresponds to Fe particle size.