DETERMINING THE EFFECTS OF PRECURSOR GEOMETRY AND CHEMISTRY ON CNT GROWTH IN A CVD PROCESS

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Introduction

Multi-walled carbon nanotubes (MWCNTs) consisting of graphene sheets wrapped in concentric tubes have been explored for a number of applications. An established method of producing these CNTs is through a chemical vapor deposition (CVD) process where xylene is decomposed and used as a carbon source. The xylene used is a mixture of three isomers: ortho-, meta-, and para-xylene.

A previous study reported growing bulk MWCNT sponges capable of significant recoverable deformation using 1,2-dichlorobenzene as a precursor. It was suggested that these sponges were formed due to the high degree of asymmetry of the precursor. This investigation sought to determine whether the degree of asymmetry has such an influence, or if the high electronegativity of the chlorine groups affected the bond breaking and led to the formation of sponges.

Procedure

To determine the effects of symmetry on CNT formation, ortho-, meta-, and para-xylene were used as precursors in solution with a ferrocene catalyst (50 mL solvent, 5 g ferrocene). To test the effects of the chemistry of the side groups, 2-chloro- and 3-chlorotoluene were also explored to compare with the xylenes.

In all CVD reactions, 10 mL of precursor/catalyst solution was decomposed in a hydrogen/helium carrier gas at 680°C.

Results and Discussion

CNTs produced from o- and m-xylene are shown in figure 1. Those made from o-xylene show a lack of alignment, while m-xylene led to CNTs with a considerably more aligned structure. Also evident in the o-xylene sample is a large amount of impurity particles which are not present in the m-xylene sample. Both samples, however, showed a wide distribution of tube diameters.

Samples produced from 2-chlorotoluene and 3-chlorotoluene are shown in figure 2. The CNTs produced from 2-chlorotoluene (an o-xylene analog) showed a similar degree of misalignment, but did not contain the impurities found in the previous sample, and had a much more uniform size distribution than all three xylene samples.

3-chlorotoluene as a precursor produced unexpected results. Rather than CNTs, this sample contains carbon ribbons of very uniform size (approx. 1.5 µm width and 200 nm thickness). These will be examined further in the future.

These results provide strong evidence that the geometry of the precursor chemical has a significant effect on the product. The xylenes, which vary only by the location of a CH₃ group, produced more aligned CNTs from more symmetrical isomers. In samples where a CH₃ group was replaced with a chlorine atom, geometry had an even more significant impact. 2- and 3-chlorotoluene have the same chemical formula, yet the difference in placement of the chlorine atom determined the production of CNTs versus carbon ribbons.

There is also evidence that the electronegativity of the side groups affects the product formed. O-xylene and 2-chlorotoluene have identical geometries, yet replacing the CH₃ group with a Cl atom led to CNTs with significantly less impurities and a narrower size distribution. Likewise, between m-xylene and 3-chlorotoluene the chemistry due to the electronegativity difference determined whether CNTs or ribbons were formed.

Conclusions

There is strong evidence to show that both molecular geometry and side group electronegativity have an influence on CNTs produced in this process. Attempts to reproduce sponges have not been successful, but it is possible that those reported were produced due to the high degree of asymmetry of the precursor and the increased electronegativity of the two chloro groups.