Use of Saccharides as Solid-state Precursors for the Synthesis of Carbon Nanotubes

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ABSTRACT

Saccharides, ranging from simple table sugar (sucrose) to lactulose were successfully used as solid-state precursors for the synthesis of multi-walled carbon nanotubes (MWCNT). Dehydrated saccharide residues mixed with catalyst powders were subjected to pyrolysis at high temperatures (up to 1300°C) under flowing Argon atmosphere. Pyrolysis products were investigated using TEM, SEM, Raman spectroscopy and EDS. Images taken using the S/TEM and bright field mode of TEM showed the presence of helical multi-walled carbon nanotube (H-MWCNT) and regular MWCNT formation. More than two or three catalyst particles were observed to be present inside the hollow core of some of the nanotubes synthesized, suggesting a high level of capillary activity inside the tubes during synthesis.

INTRODUCTION

Since, carbon nanotubes (CNT) were discovered[1], they continue to attract more and more attention of scientists from diverse fields of science because of their unique structural, mechanical, and electronic properties[2]. Potential applications of CNTs range from semiconductors, chemical sensors to structural composites[3]. Presently, there are three main techniques being used as synthesis methods for CNTs; these are arc discharge[4], laser ablation[5] and chemical vapor deposition (CVD) [6]. Although, CNTs can be easily synthesized by these techniques and their variants in a laboratory environment, scaling up the CNT synthesis for high volume manufacturing utilizing these does pose some disadvantages, such as upfront capital costs, running costs, process/quality control and yield[7]. For instance, for the arc discharge method necessary precursor purity and quantity are high[8].

Small amount of sulfur presence has been suggested to promote CNT growth and enhance yield of synthesis process used in some studies[9,10]. In an earlier study, Katsuki et al[11] reported higher carbon fiber yields for cases when sulfur and iron were used together in comparison to runs where only one was used. Sulfur can be introduced to the synthesis reactor through the use of sulfur containing gas (e.g. H_2S) [12], sulfur powder [13], metal compound (e.g. CdS) [14], or as a part of the floating catalyst[15].

While the exact role of sulfur or the mechanism through which it influences the CNT growth is not very well understood, sulfur has been found to lower the surface tension of metal/carbon interface and improve the growth of carbon nanotube as the metal catalyst flows inside the tube by the capillarity[16]. Another proposed mechanism through which sulfur may influence CNT growth mechanism is that sulfur aiding the graphitization of carbon below 1700 ^{0}C [16]. Hence, there are also cases where with addition of sulfur to catalysts lead to the observation of changes in the CNT shapes[10], diameter and number of layers of multi walled carbon nanotubes (MWCNT) [17, 18]. Y-shaped CNTs (YCNTs) and helical CNTs (HCNTs) were observed in material synthesized with sulfur compounds[17]. Also, the presence of sulfur was considered essential for the formation of double walled carbon nanotubes (DWCNT) [19].

In this study, we report a novel method for synthesis of carbon nanotubes from a low-cost, abundant, non-hazardous, environmentally friendly solid-state precursor family; saccharides. We have used various compounds of saccharide family, ranging from simple table sugar to lactulose, successfully as solid-state precursors for the synthesis of MWCNT through a modified pyrolysis process where powdered Fe, Ni and $FeSO_4$ are used as catalysts. We have investigated the relationship between the precursor type used and the size and shape of the MWCNTs synthesized. Also, we have scrutinized the role of sulfur for the synthesis of CNTs through this new technique of production.

EXPERIMENTAL

We used a high temperature atmosphere controlled tube furnace for the pyrolysis of saccharide based precursors for the synthesis of MWCNTs. Figure 1 shows a simple schematic of the experimental set-up used for the pyrolysis synthesis process for MWCNTs. First, a mixture of a saccharide (i.e. simple table sugar, lactulose, agarose etc) and catalyst powders (nickel (Ni), iron (Fe) or $FeSO_4$) is prepared. Then, this mixture is dehydrated by adding some amount of concentrated sulfuric acid (H_2SO_4) to the mixture. After the dehydration process, the carbonized mixture is placed into a graphite crucible. Pyrolysis of the carbonized mixture (precursor) is done in the high temperature tube furnace (Protherm – PTF 15 / 75/ 450). This process takes approximately 4 hours to complete under flowing argon atmosphere (180ml /min) and during the process the temperature of the tube furnace is kept at around 1300° C. The same procedure has been followed for rest of the experiments with different carbon sources; molasses, glucose, lactulose and agarose.
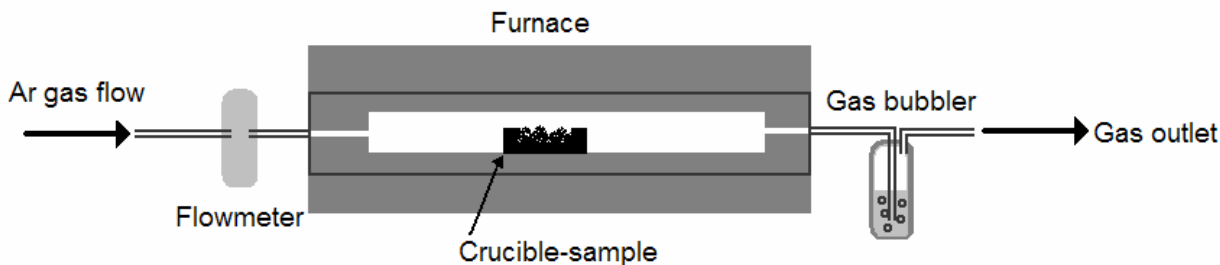

Figure 1. A schematic of experimental set up used for the pyrolysis of solid state precursors for MWCNT formation.

At the end of the process, the remaining residue left inside the graphite crucible is recovered. This recovered residue is then analyzed for the presence of MWCNTs first by using scanning electron microscopy (Carl-Zeiss EVO 40) inspection. We used oxidation by air at 500° C as a purification step to get rid of the non-tubular carbonaceous by-products to isolate single MWCNTs and allow for easy inspection in later stages. Purified MWCNTs were then, characterized using transmission electron microscope (JEOL 2100FX). We also have employed Raman spectroscopy (Jobin-Yvon MicroRaman) and FT-IR for the analysis of chemical bonding in the MWCNTs synthesized.

RESULTS

SEM pictures from the MWCNTs synthesized using saccharides are presented in figure 2(a)-(e). The sizes of the tubes (length and diameter) also observed to vary with the type of the saccharide that is used during the process, while temperature and the catalyst type and size are kept constant. From the SEM investigation on the pyrolysis products, it is found that the length of the MWCNTs range from several hundred nanometers to 20 μm, while the diameter ranges from 500 nm to 20 nm. Further analysis in a TEM using the high-angle annular dark field (HAADF) technique, as shown on figure 3, we observed that some of the MWCNTs produced indicated a helical structure with multiple metal catalyst particles trapped through the length of the nanotube.
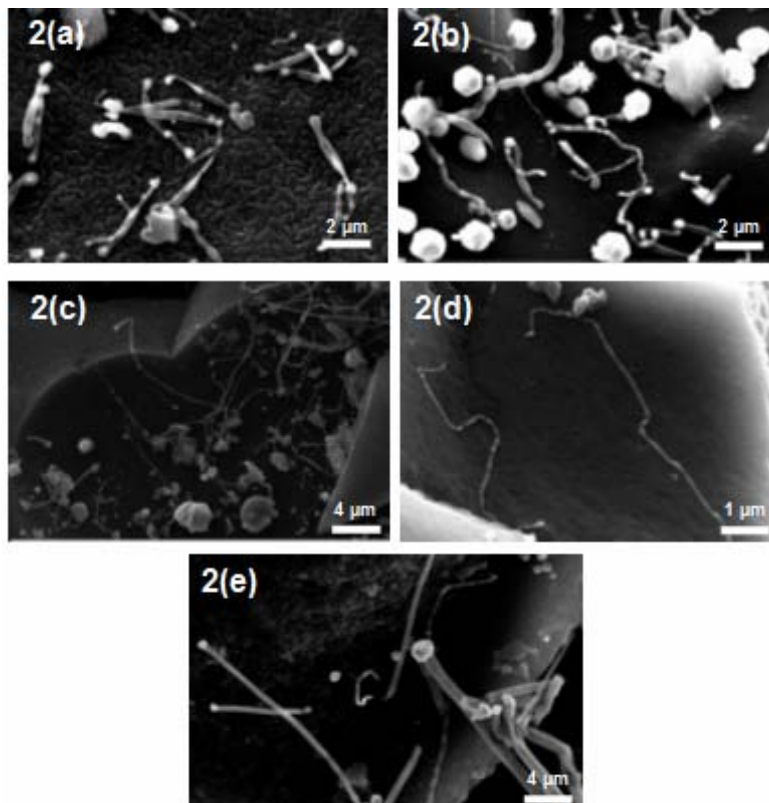

Figure 2(a) – (e). SEM images of the pyrolysis products from different saccharides; table sugar (a), molasses (b), agarose (c), lactulose (d), glucose (e). Enhanced capillary activities of metal particles are observed inside MWCNTs.

Majority of the pyrolysis products is a carbonaceous support material that the tubes grow on. Raman spectra of the pyrolysis products suggest that this major component of the pyrolysis products carry more resemblance to activated carbon as shown in figure 4. In order to isolate single MWCNTs, we have developed a useful routine for purification. Intensity ratio of the G band the D band as a function of oxidation time at 500° C was used a reference and control parameter for the purification process. Chemical analysis of the MWCNTs during SEM and TEM analysis using EDS indicated significant amounts of sulfur to be present in the catalyst particle at the tip region of the tube, as shown in the EDS mapped image presented in figure 5. In this elemental analysis map, it clearly indicates that sulfur is present together with Ni particle located at the tip region of the MWCNT.
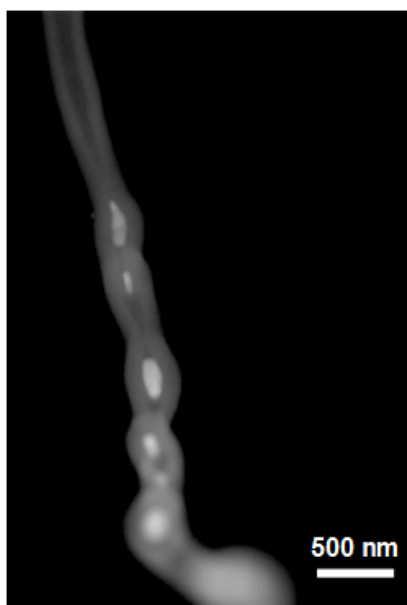
Figure 3. High-angle annular dark field (HAADF) image of a MWCNT. Multiple metal catalyst particles are visible at each "knot".
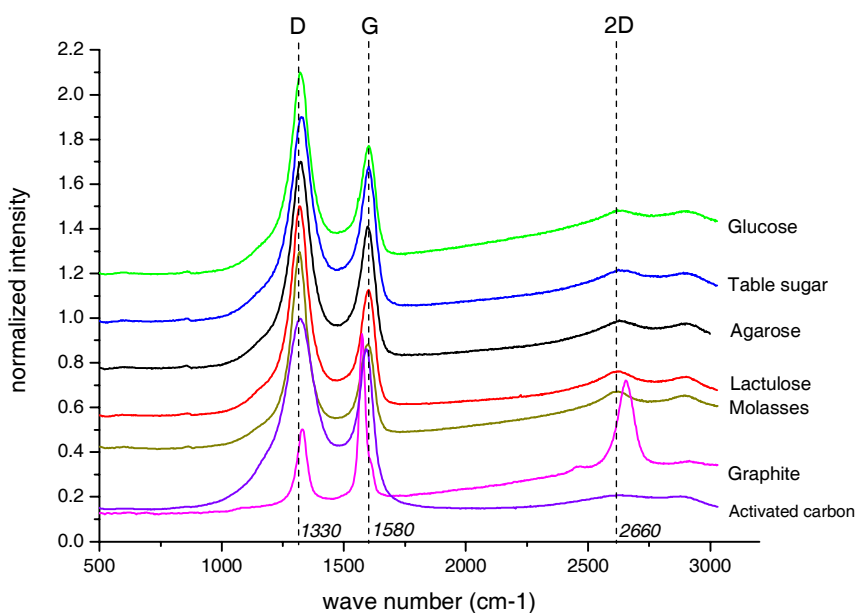

Figure 4. Raman spectra of the pyrolysis products from various saccharide precursors are clearly distinctive and display more resemblance to the spectrum obtained for activated carbon than graphite.

DISCUSSION

Dehydration of table sugar using an acid catalyst is a well-known chemical reaction. In this study, we have used a very strong dehydrating agent, sulfuric acid, to carbonize various sugars. Sugars, or saccharides, are a member of organic compounds commonly termed as "carbohydrates" with the general chemical formula $C_n(H_2O)_m$. Hence, dehydration of these

compounds leaves behind a large carbonaceous backbone. In this study, the dehydration process after mixing saccharides with the catalyst particles is used to completely encapsulate these metallic particles with carbon. A similar approach has been employed by Yu et al[20] for the preparation of meso-porous activated carbon using nano-sized silica beads as pore templates. Hence, the source of the sulfur found in the catalyst particles is the sulfuric acid used for dehydration.
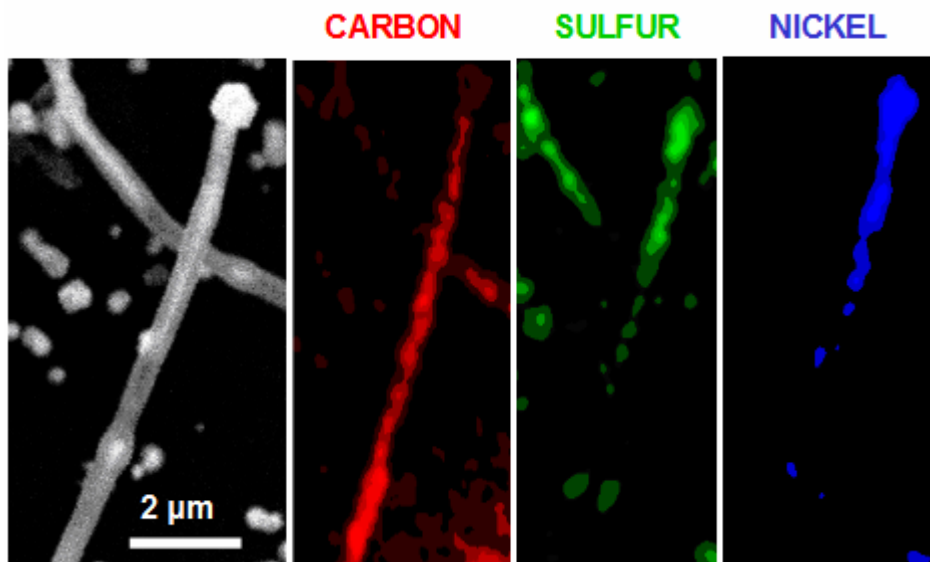

Figure 5. EDS elemental map of a MWCNT showing the distribution of carbon, sulfur and nickel across the length of the MWCNT. Sulfur and nickel maps match closely suggesting significant amounts of sulfur in the nickel matrix.

In order to understand the role of sulfur in the nanotube formation process, after the dehydration process, the carbonized saccharide precursor was washed 18 hours at room temperature in a dilute acetic acid solution in order to induce ion exchange of the acetate anion (CH_3COO^-) with the sulfate anion (SO_4^{2-}). SEM investigation of the pyrolysis products of the solid carbonized precursor after ion-exchange procedure did not result in any MWCNT observations. This result may suggest that presence of sulfur is a stronger factor for the MWCNT nucleation and growth than the encapsulation of catalyst with carbon. However, in another experiment, sucrose was dehydrated by phosphoric acid (H_3PO_4). Pyrolysis of the carbonized precursor prepared by phosphoric acid did result in the formation of MWCNT. This result suggests a possible replacement to sulfur for the formation of CNTs. Furthermore, it may help explain the enhancement of CNT growth and yield due to sulfur.

CONCLUSION
In this conclusion, we have successfully attained the synthesis of CNTs using pyrolysis of various different saccharides as solid-state precursors under controlled atmosphere. Most of the sulfur which enters the process during the dehydration process while the solid-precursor is prepared is found to end up in the catalyst metal. We have also found that while the presence of sulfur is shown essential for the synthesis of CNTs, it could be replaced by phosphorus.

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