Temperature Activated BN Substitution Of SWCNT

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Abstract. A promising recipe for the production of single wall boron nitride nanotubes (BNT) is the so-called substitution reaction. We used SWCNT (HiPCo) as a starting material, B_2O_3 and N_2 gas as boron and nitrogen sources respectively. An important complication arises due to the presence of the reacted variants in the final product. We performed optical and multi frequency Raman measurements to identify the phonon modes of BNSWNT and unwanted side-products.

INTRODUCTION

Boron nitride nanotubes, where electronic properties are independent of helicity [1] have been synthesized using almost the same methods as for the production of carbon nanotubes. Arc discharge [2, 3], high preassure laser heating [4] and oven-laser ablation result in low yields with respect to the amount and purity of the final product. Later on, a new method was presented the so-called "synthesis of boron nitride nanotubes (BNT) by a substitution reaction" [5]. Using carbon nanotubes (CNT) as a template for this chemical reaction, one could produce considerable amounts of BN-nanotubes as well as mixed systems like BC or BCN nanotubes [6]. In this work, we tried to investigate the conditions in which the reaction takes place and to identify the unwanted side-products which play a significant role in the optical response of the final material.

EXPERIMENTAL

The substitution of carbon atoms in SWCNTs by B and N atoms can be represented formally in the following way:

$$B_2O_3 + 3C \text{ (nanotubes)} + N_2 \rightarrow 2BN \text{ (nanotubes)} + 3CO$$
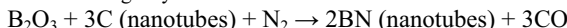
In the above reaction B_2O_3 vapor generatet from molten B_2O_3 reacts with CNTs and N_2 gas. Pure single wall carbon nanotubes (SWCNT) produced by Carbon Nanotechnologies, Inc (Houston, USA) by the HiPCo process were heated gradually together with B_2O_3 in a flowing nitrogen atmosphere at 1150-1270 °C, held at this temperature for 2-4 hours and then cooled down to room temperature over 2 h. The heating was carried out in a horizontal tube furnace, in a quartz tube and the B_2O_3 powder was placed on an Al_2O_3 crucible covered with SWCNTs. The N_2 gas flows continuously at ambient preasure. After the heat treatment the reaction product was

extracted from the crucible and samples in the form of pellets were prepared with KBr powder for IR and multi-frequency Raman spectroscopy.

IR, FT-Raman and visible Raman spectra of the final product were recorded in an BRUKER IFS-66V spectrometer, FT 106 (λ = 1064, resolution = 4 cm^{-1}) spectrometer and Dilor *xy* triple monochromator (λ = 514.5 nm, resolution = 1.5 cm^{-1}) with a liquid cooled CCD detector, respectively.

RESULTS AND DISCUSSION

Substitution reaction below 1200 °C: IR spectra (Fig. 1b,c) taken from samples from the substitution reaction at 1150 °C show differences from initial SWCNT (which have no IR activity). The modes at around 800 cm^{-1} are also shifted by 10-15 cm^{-1} compared to the hexagonal BN, h-BN (Fig. 1a), which is a stable form of boron nitride and a side product of the reaction. Similarly for the high frequency part of the spectra the response from the reacted material is shifted by 15 cm^{-1} as compared to h-BN. The question rises whether this IR activity comes from boron substituted SWCNT or it is due to nano-crystalline BN phase. Nano-crystalline BN may have different IR response from h-BN.
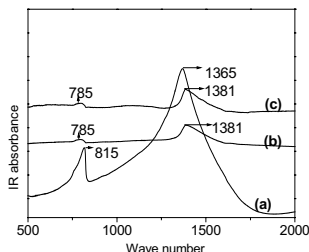

Figure 1. IR spectra of **(a)** h-BN, **(b)** substituted SWCNT at 1150 °C, 2h, **(c)** substituted SWCNT at 1150 °C , 4h
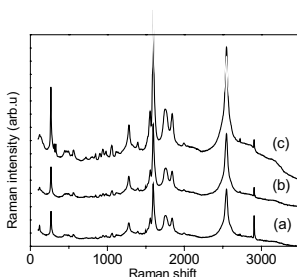
Figure 2. Raman spectra of **(a)** substituted SWCNT at 1150°C , 4h. **(b)** substituted SWCNT at 1150 °C, 2h. **(c)** pure SWCNT (HiPCo)

Fig. 2a, b show FT-Raman spectra of substituted SWCNTs at 1150 °C in 4 and 2 hours, respectively. The low resolution, 4 cm^{-1} , of the experiment did not allow the detection of any differencies in the Raman shift between untreated and substituted SWCNTs sample. Fig. 2c. shows untreated SWCNTs.
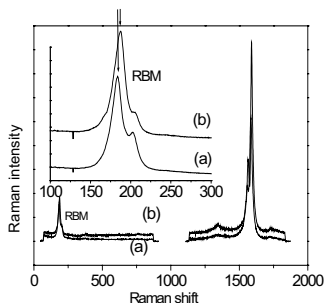
371

Figure 3. Raman spectra of **(a)** B-substituted SWCNT at 1150°C, 2h. **(b)** pure SWCNT (HiPCo)

   The better resolution, 1.5 cm^{-1}, of the multichannel Raman apparatus allowed the detection of differencies in Raman shift Fig. 3 shows the Raman shift at λ = 514.5 nm for the treated (Fig. 3a.) and non treated (Fig. 3b.) SWCNTs. We observe a change in the Raman shift of the radial breathing modes, RBM, in the order of 3 wave numbers An explanation for that can be found by the breaking of the C≡C symetry from boron substitution.

   Substitution above 1200 °C: When the substitution reaction is done above 1200 °C the resulting material has a rich IR activity (Fig. 4a.). Modes detected for materials with this reaction temperature can not be immediately attributed to BN nanotubes. This is evidenced by a control experiment where the same IR active modes were detected when no SWCNT material was used: $B_2O_3 + N_2$, at 1270 °C for 4 hours (Fig. 4b.). The material (b) was therefore investigated by Transmission Electron Microscopy (TEM) and no tubes were detected.
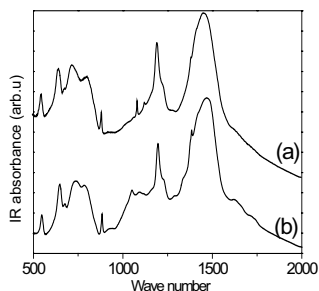

Figure 4. IR spectra of **(a)** the resulting material: SWCNT at 1270 °C, 4h. **(b)** heat treated B_2O_3 at 1270 °C / 4h in N_2

372

CONCLUSIONS

We have shown that the substitution process is rather complex and the final material is contaminated from side products which have several IR active modes. Below 1150 °C no reaction takes place between the starting materials. Between 1150 °C and 1270 °C reaction temperature, a weak shift in the heat treated tubes indicates some substitution reaction. A better understanding of the process to determine the right temperature in which the reactions take place and trying other sources of boron as well as other carrier gases is the ongoing work. Raman characterization of the substitution level seems to be more useful than infrared as the final material has a complex IR response that strongly depends on the reaction temperature.

ACKNOWLEDGMENTS

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