NEW CARBON MATERIALS
Volume 30, Issue 1, Feb 2015
Online English edition of the Chinese language journal

Available online at www.sciencedirect.com
ScienceDirect

Cite this article as: New Carbon Materials, 2015, 30(1): 19–29

RESEARCH PAPER

Transformation of carbon black into carbon nano-beads and nanotubes: the effect of catalysts

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Abstract: Structural transformation of carbon black (CB) into carbon nano-beads and nanotubes was achieved at 1000 °C using ferrocene and nickelocene as catalyst precursors using a simple and single step chemical vapor deposition method. The samples were characterized by XRD, SEM, TEM, HR-TEM and Raman spectroscopy. Results indicate that different morphological and high quality nano carbon structures were obtained using different weight ratios of catalyst to precursor. The use of bimetallic catalysts provides many different morphologies and a higher degree of crystal order of the carbon nanostructures than the use of mono-metallic catalysts. The nanotubes were mostly filled with metal nanoparticles and the degree of metal-filling is dependent on the weight ratio of catalyst precursor to CB. Metal–filled multi-walled carbon nano-bead structures with a high degree of crystalline order are also obtained at weight ratios of CB: ferrocene: nickelocene of 1:2:2.

Key Words: Carbon black; Carbon nano-beads; Nanotubes; Catalytic transformation; CVD

1 Introduction

Carbon nanotubes (CNTs) have been considered as a promising material for many applications owing to their unique mechanical, optical and electronic properties[1]. Various techniques such as pyrolysis, chemical vapor deposition (CVD), plasma enhanced chemical vapor deposition (PECVD), laser vaporization, and arc-discharge have been used for the synthesis of CNTs[2-6]. Each of these methods has its own merits and demerits and nanotube morphology and structure varies with the particular synthesis method.

Compared to techniques mentioned above, CVD is found to be the most advantageous in nanotube synthesis compared to other techniques mentioned above and also a powerful method for large-scaled production of nanotubes[4]. In CVD methods, CNTs are obtained either by catalytic decomposition of CO, or, pyrolysis of hydrocarbons in the presence of transition metal nanoparticles such as iron, cobalt or nickel. The type and size of the metal nanoparticles formed during the process is considered to be important as they control both the formation process and the diameter of the nanotubes.

In addition to traditionally used aromatic/aliphatic hydrocarbons, solid carbon (such as C60, graphite), CO[2-6], or amorphous carbon such as carbon black (CB)[7-13] have also been reported as carbon source in the synthesis of CNT and other nanostructures. Transformation of CB into nanotubes without catalysts is not feasible using thermal chemical vapor deposition techniques [7], but it has been shown to be possible in an arc-discharge process, where a solid-state transformation mechanism leads to CNT formation[8,9]. In ref. [9] it is proposed that the defects in the CB graphene layers are the key element for the growth of nanotubes. Further, the authors add that the growth is achieved by the migration of pentagon, heptagon and other defects present in CB to the stem of a nanotube.

So far, the transformation of CB into nano-graphitic structure has been carried out either at high temperature without catalyst as reported in [8, 9] or it has required oxygen as the key element in the reaction[7, 11, 13]. In the current research, the transformation of CB was carried out at relatively low temperature compared to the work reported in references [8-10] and in a simple approach using a single stage furnace. To the best of our knowledge, for the first time a bimetallic catalyst has been used in the structural transformation of CB to multi-walled carbon nanotubes (MWCNT) and multi-walled carbon nanobeads (MWCNB) via a simple and single step heating process.

We also studied the effect of catalysts in the transformation process. In nanotube synthesis via hydrocarbon synthesis, role of bimetallic alloy particles of transition and other metals, such as Ni–Fe, Fe–Co, M–Cu and M–Al (where M represents the transition metal), have been extensively studied[14-16]. These bimetallic catalysts have been found to show excellent catalytic properties in the synthesis of nanocarbon products than the mono-metallic catalyst. In particular, the use of Ni-Fe alloy catalysts for nanotube synthesis leads to a larger yield compared to the case when either pure Fe or Ni is used[17]. We investigated here the role of both mono-metallic and bi-metallic catalysts in the structural transformation of CB into graphitized nanocarbon products. It is interesting to note that the range of crystallinity

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Received date: 28 Sep 2014; **Revised date:** 01 Feb 2015

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DOI: 10.1016/S1872-5805(15)60172-X

and the rate of yield varied with the amount of bimetallic catalysts.

2 Experimental

The CB used in the following experiments was ENSACO 350G provided by Timcal Graphite & Carbon. Ferrocene and nickelocene compounds were purchased from Sigma-Aldrich (98% in purity) and toluene used was chemical grade. Ferrocene, nickelocene and CB were used in the prescribed weight ratio presented in Table 1.

The experiments were all conducted as follows: A known quantity of CB, ferrocene and/or nickelocene were put into a beaker and 20 mL of toluene was added. The mixture was subjected to ultrasonic vibration for about 15 min to form a homogenous suspension. Next the mixture was loaded into an open alumina boat (8 cm long and 4 cm height). The boat was then placed at the center of an alumina tube single stage MXITL horizontal furnace of 80 mm in diameter and 1000 mm in length at room temperature. Afterwards, the furnace was heated to 1 000 °C at rate of 10 °C/min set and the furnace was maintained at this temperature for 6 h. Then the furnace was set to cool at a rate of 5 °C/min. The whole reaction was carried out under flowing nitrogen.

Samples finally collected from the boat were characterized using transmission electron microscopy, TEM (JEOL 1011), high-resolution transmission electron microscopy, HR-TEM (JEOL 2100) and X-ray diffraction, XRD (Bruker D8 Advance diffractometer) and Raman analysis (Horiba-Jobin Labram 800 HR Raman spectrometer). Samples were mixed with ethanol, ultrasonicated and dropped on a copper grid prior to TEM and HR-TEM analysis and bright field images were obtained. The XRD patterns were recorded in the 2θ range of 10-80°, using a Cu Kα source (where λ was equal to 0.154 nm).

Raman spectra were obtained as follows: The powder samples were dispersed on glass slides and directly mounted under an Olympus BX41 petrographic microscope. Measurements were made with a 100 mW argon ion laser (514 nm excitation wavelength, 1-2 μm spot size, and a 1800 lines/mm grating). A density filter was used to diminish the light intensity to approx. 0.5 mW. Spectra were obtained for 2×10 seconds over a range of 150-4000 cm^{-1} on a Peltier-cooled (-70 °C) 1024 × 256 pixel CCD array detector. Raman peak characteristics were obtained by peak de-convolution using a Gauss-Lorentzian function with 100 iterations per fit, using the program Labspec version 5.58.25.

3 Results and discussion

Fig. 1 displays XRD patterns of samples CN1- CN5 and parental carbon (Timcal 350G). It is clear that all 5 samples (CN1-CN5) show (002) reflections at $2\theta \approx 26°$, which corresponds to the graphitic peak. The narrower and high intensity peak for CN1 and CN4 indicates a higher degree of crystallinity in these samples than those in the samples CN2, CN3 and CN5. It gives a clear indication that the samples CN1 and CN4 possess higher graphitic crystal order than the other samples.

The other peaks obtained from the samples CN1-CN3 at around 43.9°, 51.1° and 75° correspond to (111), (200) and (220) respectively of Fe-Ni alloy [18]. There are no peaks that correspond to other structures such as pure Fe, pure Ni, or FeC3 (cementite). Other peaks obtained from sample CN4 at $2\theta \approx 43.60°$, 50.86° and 74.78° arising from iron carbide indicate the formation of metal carbide structures in CN4 [13]. XRD pattern of CN5 displays a peak $2\theta \approx 43.7°$ which corresponds to the (100) planes of graphitic structure. The peaks at 50.80° and 74.84° corresponds to (2 0 0) and (2 2 0) reflections of γ-FeNi alloy respectively. Only CN5 displays a strong peak corresponding to the (1 0 0) planes of graphitic structure. For Timcal Ensaco 350G CB (parental carbon in this work), a rather wide and shallow (002) peak is observed in its XRD pattern at $2\theta \approx 26°$, implying that the parental carbon is an amorphous carbon material with small regions of crystallinity.

The interlayer spacing d_{002} in CN1, CN2, CN3, CN4, and CN5 is found to be around 0.341, 0.344, 0.347, 0.344, and 0.344 nm respectively while the parental CB shows an interlayer spacing d_{002} around 3.66 nm. The interlayer spacing of the samples CN1-CN5 is found to match with the inter-planar distance in a graphitic structure (0.335 nm) [19].

Table 1 Catalyst weight ratio, L_c values of the samples obtained from XRD result and I_D/I_G values obtained from Raman analysis.

Sample	CB : Ferrocene : Nickelocene(weight ratio)	XRD L_c (nm)	Raman I_D/I_G
CN1	1:5:5	7.732	0.51
CN2	1:5:2	6.962	0.80
CN3	1:2:5	3.733	0.85
CN4	1:10:0	7.193	0.52
CN5	1:2:2	5.558	1.41
Timcal 350G	-	2.184	-