Novel Solid Phase Synthesis with Tube Control Agent for Large Volume Production of Carbon Nano Tube & Fiber

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ABSTRACT

We have studied a solid phase synthetic process of carbon nano tube using full solid raw materials blended with the *tube control agent (TCA)*. It is discovered that the particular tube control agent plays a significant role in the tube shape forming mechanism and product uniformity. Without the tube control agent or when the concentration of metal sources (MS) exceeds certain levels in the feed stock of the raw material, the carbon nano fiber is formed, instead. The solid state raw materials can form thin or thick solid film prior to the reaction, showing capability of controlling tube length, tube diameter through the thickness.

1. INTRODUCTION

Since the first report of Ijima [1] on single walled carbon nano tube (SWCNT) in 1991, there are a lot of efforts to discover new applications including electronic devices, nano composites having superior mechanical strength, biomedical, chemical and energy technology. So far, gas phase reaction using acetylene gas as carbon sources in plasma CVD or thermal CVD (pyrolysis) becomes the most popular process of scaling up CNT products. The advantages of gaseous and liquid carbon sources are the relatively fast forming of free carbon radicals but the tradeoff can be seen in the difficulties of controlling the ratio of carbon sources (CS) and metal sources (MS) , especially in a heterogeneous phase which can affect the purity and also the uniformity of the products. This issue can be one of the biggest concerns, especially, for the electronic device and nano composite applications; long tubes do need to be cut using E beam or X-Ray techniques [2]. Besides the issues of non-uniformity in terms of tube length and tube diameter, the cost due to the poor yield in gas phase reaction is still remained as other issues which continue to prevent application product developments.

Regarding reaction yield improvement, first of all, it is necessary to consider a harmonically compatibility between transitional MS which can provide pure metals as catalyst and CS which can effectively generate free radicals of carbon absorbing on the metallic landing sites to growth the tube. If the pure metal element was formed prior to the arrival of free carbon radicals, then it can stack together into large particles or big bundle where free radical adsorption occurs randomly into tubes having various diameters; thus small and uniform diameter tubes needs stable metal nucleation in the nano scale. On the other hand, if the free radicals of carbon can be quickly formed prior to the generation of metal particles, then they can easily convert into amorphous carbon black or non-tube products. Overall, the incompatibility between carbon sources and metal sources will harm the tube uniformity. In general, the feed stock of MS can be achieved in solid state or liquid state which is eventually converted into the gas phase under high heat condition of the reactor. The CS can be found in a gas phase, liquid phase and solid phase. The best choices for best control of (CS / MS) ratio are full solid precursors. It is no doubts that full solid precursors are more easily handled in the reaction chamber inquiring high heat and unoxidizing environment.

It is no doubt the solid phase reaction can offer many advantages over the gas phase reaction in terms of

a) well controlled impurities by a selection of compatible (MS/CS) combination
b) solid precursor for CNT can offer excellent uniformity of thin or thick film on a substrate where the CNT can grow with well controlled length and tube diameter
c) Solid phase raw materials are more easily handled than gas or liquid phase.

The suitable combination of (MS/CS) having harmonically compatibility in solid state can be found in a material set in which metal element somehow is connected to the carbon sources by sigma bonds as seen in most of organo-metallic compounds [3], by coordinated bond as seen in a metal chelates and by ionic bond as seen in several metal organic salts. Any above mentioned material set can form CNT products under right condition of heat and unoxidizing environment. The disadvantage of utilizing organo-metallic compound as CS itself can be related to the large portion of metal left behind to form metallic impurities. Removal of metallic impurities by condensed sulfuric acid may result in the tube deform. Also, again, organometallic compounds could not be used as CS as it is not a low cost material for large scale production.

We have studied a novel solid phase synthetic process of carbon nano tube using full solid raw materials blended with the *tube control agent (TCA).* The reaction occurs by the pyrolysis of solid phase raw materials in a non-oxidizing environment. It is discovered that the particular tube control agent plays a significant role in the tube shape forming mechanism and product uniformity. Without the tube control agent or when the concentration exceeds certain levels in the feed stock of the raw material, the carbon nano fiber, and amorphous carbon are formed, instead. The solid state raw materials can form thin or thick solid film prior to the reaction, showing capability of controlling tube length, tube diameter through the thickness.

2. EXPERIMENTAL PROCEDURE

2.1) CNT forming reactor

In the present study, the CNT was prepared by the pyrolysis of solid CS in a reactor described in Fig .1. The reactor is an oven 1 equipped with high heat resistant ceramic materials including oven cover 1.1, heat resistant

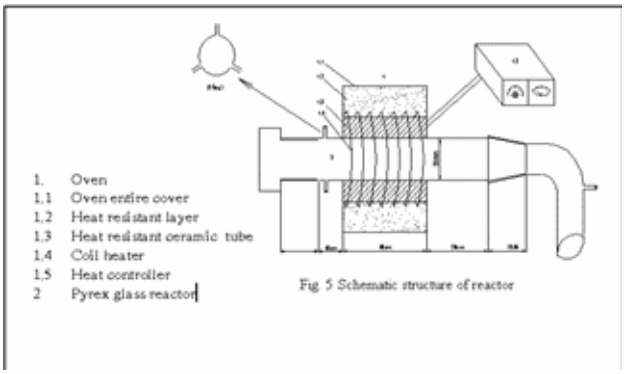


Fig.1 Schematic diagram of the reactor for solid phase synthesis of CNT using TCA

layer 1.2, heat resistant ceramic tube1.3 , coil heater 1.4 , heat controller 1.5 and a Pyrex glass reactor tube 2 . The Pyrex glass tube is connected with 3 neck connector in one end where suitable inert gases can be fed in or the air can be succeed out to form unoxidizing environment in the reaction chamber . The diameter of the Pyrex glass tube is about 25mm, active heating length is about 40 cm and the entire length of the tube is about 70cm. The heating system (heater and controller) can provide a well controlled temperature to the reactor chamber up to 1000C. There is several heating process which can be used with the reactor in the present study. For example, the heating was started first to reach maximum temperature detected then a sealed sample holder containing raw solid material can be inserted right into the center of the reactor chamber . Or the sample holder can be fed into the reactor chamber first then the evacuation, inert gas feeding and heating can be started afterward. Depending on the chemistry of the solid precursor, the heating time at maximal temperature can vary between few minutes to few hours.

2.2) Solid phase synthesis material set

CS is selected from flammable solid having high C content. Acetylene gas is known as highest C content (> 92%wt) CS but it doesn't exist in a solid state. Other solid CS having high C content can be found in a series of unsaturated and saturated hydrocarbon and its derivatives.

MS are selected from variety of organo-metallic compounds and metal salts from inorganic and organic acids.

TCA are proprietary of the present study, which can be selected from wide range of hydroxylated compounds. The full solid precursor of the present study is prepared by a mixing between CS, MS and TCA using sol-gel process followed with the evaporations of solvent.

2.3) Preparation of CNT

The dried full solid precursors were inserted into the reactor chamber filled with unoxidizing gas and heated up above 1000C. At the reaction end, the heat was slowly removed under unoxidizing environment and the product was taken out at RT at normal atmosphere environment.

2.4) Testing procedure

I) FE-SEM measurement was carried out using Hitachi S4800.

ii) *TEM measurement* was carried out with JEM-1010 (Jeol)

iii) *XRD measurement* was carried out with Siemens 5000

IV) *Raman Spectroscopy* measurement was done with Model LabRam-1B (Jobin Yvon)

3. RESULTS AND DISCUSSION

3.1) FE-SEM image of solid phase synthesized CNT

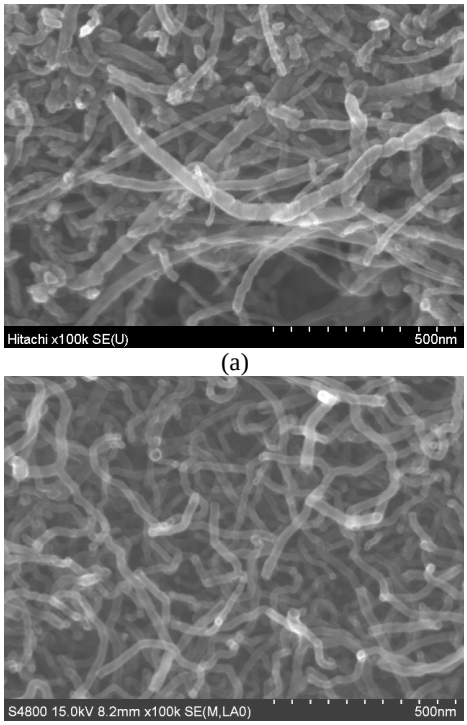
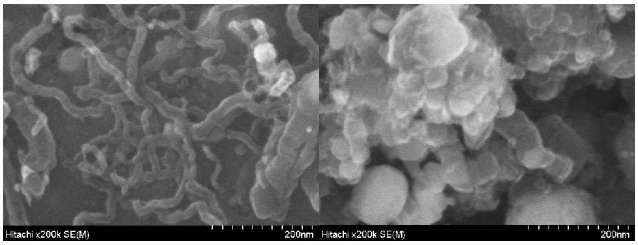


Fig. 2 FE-SEM images of MWCNT (a) prepared by gas phase reaction (commercial product) (b) prepared by novel solid phase reaction using TCA (in-house)

Fig. 2 respectively shows FE-SEM image of MWCNT synthesized by (a) conventional gas phase reaction and by (b) solid phase reaction using TCA. One can see that the solid phase product using solid CS (A) exhibits some Y-form with better uniformity in diameter than gas phase commercial product. In the Fig. 2(b), it is also observed that the tube diameter is determined by the size of initial metal particle where the radicals absorbed.

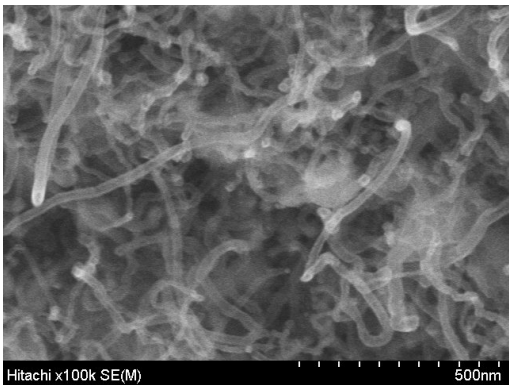
In another experiment utilizing different solid CS (B), the effect of TCA can be seen in Fig. 3 as shown below (a) solid precursor containing TCA and (b) solid precursor containing no TCA. It is also very clearly indicated in this case that the TCA gives rise to tube shape while the solid precursor containing no TCA shows irregular shape or round particle shape.



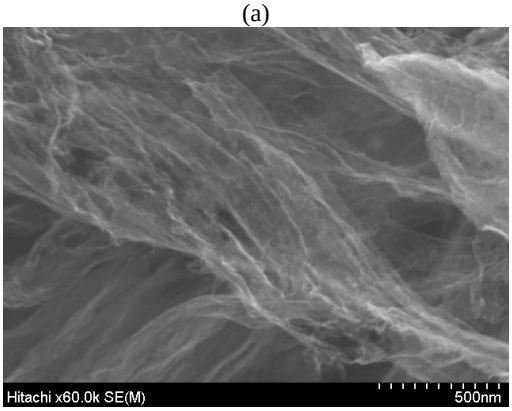
(a) (B)

Fig.3. FE-SEM images of CNT product from solid precursor using CS (B) (a) with TCA and (b) without TCA

Fig. 4 indicates the effect of (CS/MS) ratio in a solid precursor containing TCA using CS (A) (a) (CS (A) +TGA)=96%wt and (b) (CS (A) +TGA = 60% wt).



(a)



(b)

Fig.4 FE-SEM images of product made out of solid precursor having (a) CS (A) +TCA = 92% wt and (b) CS (A) +TCA = 60% wt

It is interesting to observe that the carbon nano fiber was formed when the (CS (A) +TCA) content goes down below 60%wt in the solid precursor. Thus, the tube forming mechanism is also depending on (CS/MS) ratio.

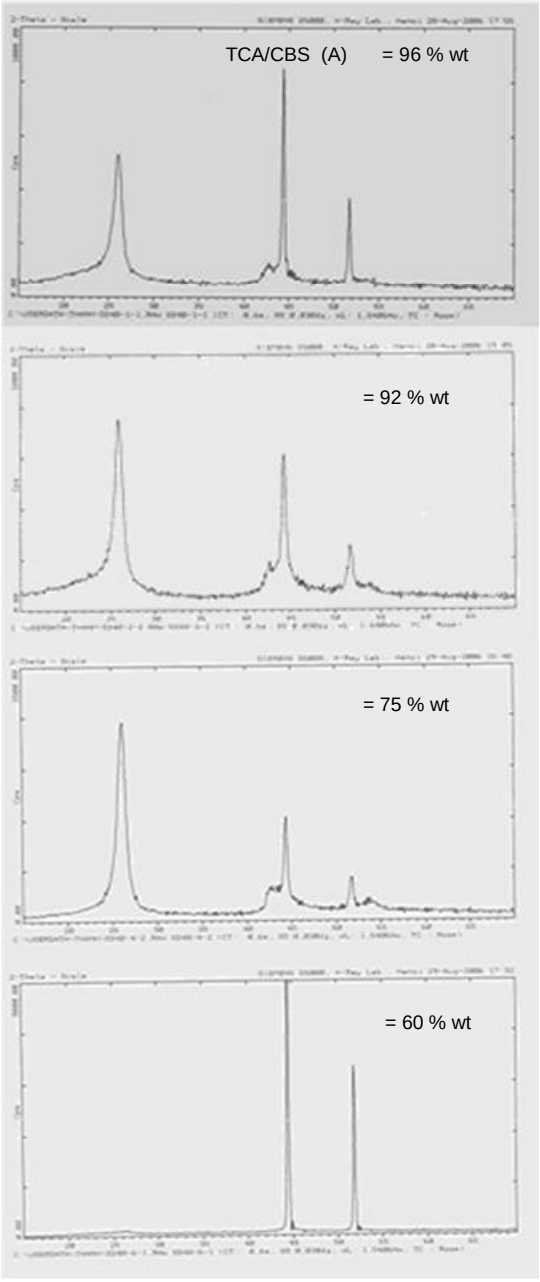


Fig. 5 XRD data of varied (CS (A) +TCA) content

For further investigations, the X-Ray Diffraction (XRD) measurements were carried out with the CNT products having various (CS (A) +TCA) content and the result is illustrated in Fig. 5. One can see the major diffraction peak at two theta = 26 degree representing CNT structure appears always through from 96%wt down to above 60%wt. Carbon nano fiber products shows two sharp peaks at two theta = 44.5 degree and 52 degree, confirming a change from tube shape into fiber shape.

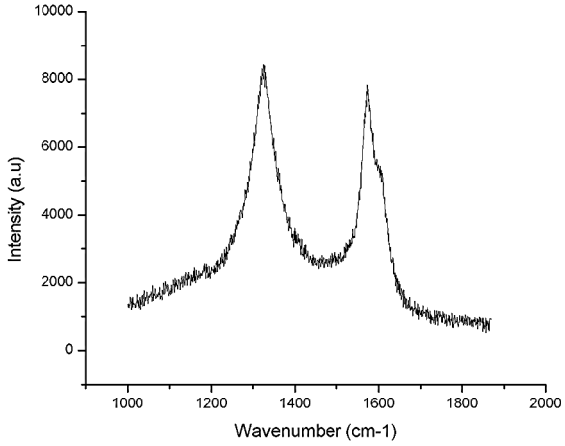


Fig. 6 RAMAN spectroscopy of solid phase synthesized CNT using TCA

Fig.6 exhibits RAMAN spectroscopy chart of a typical solid phase synthesized CNT. The structure of CNT was confirmed by strong peak at 1600(cm-1).

Fig 7 exhibits TEM image of typical MWCNT (a) using organo-metallic as CS and (b) CS (A) with TCA in solid phase synthesis. One can see the hollow tubes exist in both cases. However, the TCA process can give rise to smaller tube diameter

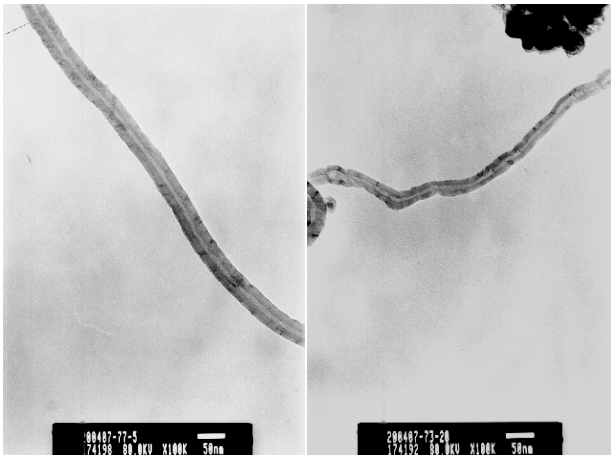


Fig.7 TEM images

4. CONCLUSION

It can be concluded that the solid phase synthesis of CNT utilizing TCA is a novel process as it is different from laser ablation technique [4] and arc discharge technique [5] which do not produce large quantities. TCA is a tube forming nucleation for large quantities and different chemistry of CS. TCA can be used as CS itself but it can be blended with different CS chemicals due to chain transfer mechanism between TCA and CS . The tube diameter can be controlled with TCA contents . Also, again, the yield of CNT product with solid phase synthesis using TCA has been achieved up to 55% while the gas phase with good handling condition only gives rise to a yield of 8%. Thus the solid phase synthesis using TCA can be available for large quantities production.

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