

NANO STRUCTURE OF CARBON NANO TUBE PRODUCTS SYNTHESIZED IN SOLID PHASE

KC Nguyen*, S.T.Do*

*Saigon Hi Tech Park Research Laboratories, Hochiminh City, Vietnam **KTube Technology LLC, San Jose CA, USA

ABSTRACT

Solid phase synthetic process of carbon nano tube using solid precursor comprised of solid state carbon source, metallic catalyst and tube control agent has been reported in the last Nanotech 2007 (Santa Clara).

In the present study, we discovered that a tube control agent molecule having carbonitrile -CN functionality, is an effective hook which links carbon source molecule to metallic atoms to form tube shape products in the pyrolysis process. Certain carbonitrile compounds show adequate interaction with specific carbon sources to give rise to unique tube structure and eliminate non-tube components in the product. A harmonica precursor with above mentioned 3 components can give rise to various tube shapes including fat tubes (outside diameter \approx 600nm, inside diameter \approx 400nm), thin tubes (diameter \approx 20-30nm), ultra thin tube (diameter \approx 1nm), twisting tubes etc. These tubes are suitable for applications in nanofiltration, nanocomposites for EM shielding, nanocomposites for light structural materials and even for energy devices.

Keywords: solid phase synthesis, solid precursor, tube control agent

5. INTRODUCTION

We have reported in Nanotech 2007 a novel solid phase synthetic process of carbon nano tube [1]. In this process, the tube growing process is controlled by a tube control agent mixed together with a solid carbon source instead of gas phase raw material conventionally utilized in catalytic growth process [2]. It is likely that somehow the tube control molecule must play a role of a connector slightly linking carbon source molecule with metallic atoms. The need of a chemical link between carbon source and metallic element has been report in a polymer template technique [3] utilized for the synthesis of SWCNT. In this technique, a copolymer of vinyl pyridine capable of forming complex with metal element becomes polymer template for synthesis of CNT using ethanol as carbon source. In the present study, we found that a molecule carrying carbonitrile -CN group even in a polymeric format or in a non-polymeric molecule can enhance the formation of tube shape products in our solid phase synthetic process. Furthermore, specific additives can dramatically change the tube geometry such as tube length, tube diameter as well as tube shape. Straight CNT, coiled CNT, Y-form CNT, zigzag CNT products also obtained from this process.

2. EXPERIMENTAL PROCEDURE

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 layer 1.2, heat resistant ceramic tube 1.3, 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. For the larger scale production, larger diameter ($\phi=100$ mm) and longer length tube will be used. The heating system (heater and

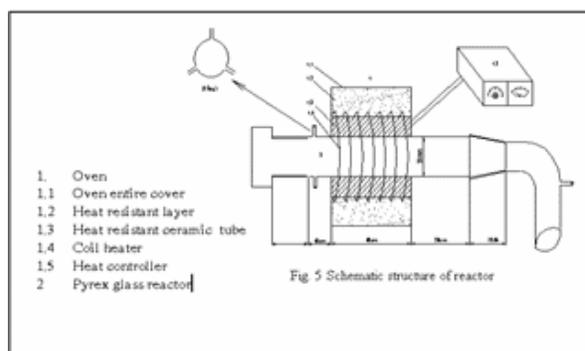


Fig 1 General schematic of reactor using electric stove for the synthesis of carbon nanotubes in solid phase

controller) can provide a well controlled temperature to the reactor chamber up to 1000C.

5. SOLID PRECURSOR AND TUBE FORMING PROCESS

The solid precursor is mainly composed of a) flammable solid carbon source b) hooks or tube control

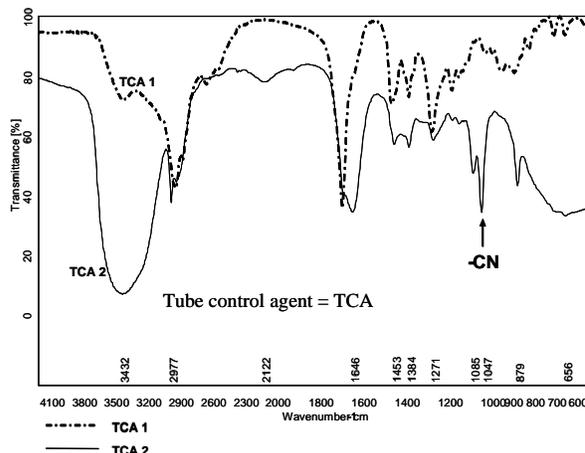


Fig. 2 FtIR chart of two different TCA in which TCA2 shows absorption peak due to the-CN group

agent having specific chemical functional groups of carbonitrile derivatives c) metal salts as metal source.

Fig.2 exhibits FTIR data of two different kinds of tube controls agents (TCA) (1) and (2) and one can see that only the additive (2) does contain carbonitrile -CN group but the first one doesn't.

Fig.3 exhibits FE-SEM image of the product of the solid precursor containing additive (1) and no tube shape product was achieved besides round shape particle

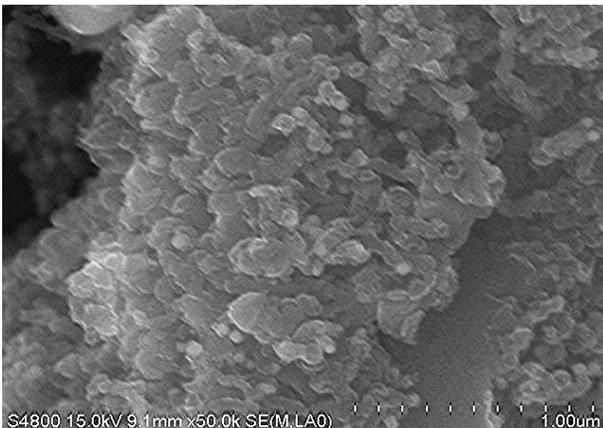


Fig.3 FE-SEM image of product using TCA 1 containing no-CN group. Absolutely, there is no tube observed.

agglomerate .

On the other hand, Fig. 4 shows the FE-SEM image of the product of the solid precursor containing additive (2). It is obvious that the tube shape product was successfully formed, confirming the role of the precursor carbonitrile -CN in the solid synthetic process. In this case, the tube is relatively straight with uniform diameter. This is the proof of carbonitrile -CN additives in the tube forming mechanism.

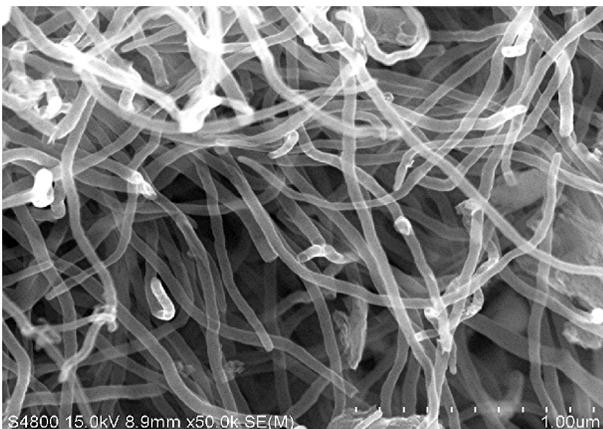


Fig. 4 FE-SEM image product using TCA2 containing CN group. Absolutely, tube shape product is obtained.

Next, Fig. 5, 6, 7 are FE-SEM image of solid phase synthesized products at three different process (A), (B), (C) showing three different shapes : fiber like (process A) , fat tube (process B) and coiled tube (process C) . It should be noted that fiber like product (process A) was made at high level of metal (carbon source CS/metal source MS > 0.5) showing tube diameter in the range of a few nm . On the other hand , the fat tube (outer diameter \cong 600nm, inner

diameter \cong 400nm) was formed when the unpurified carbon nano tube product in the solid phase , was used as catalyst. The fat tube product can be used as membrane for nanofiltration of waste water, blood The coiled product is achieved by a combination of process B with gaseous additive during burning period. The coiled product seems to be adequate for nano composite.

5. DISCUSSION

In the art of making carbon nano tube, the solid phase process reveals major advantages over the gas phase process such as a) well handled feed stock raw material (well controlled CS / MS ratio) b) suitable for large scale production c) better uniformity and higher purity d) more easily handled products ; for example, 100g of gas phase product has to be packed in a 100,000ml volume bag while solid phase products are easily contained in a 500 ml plastic jar e) well controlled morphologies with various additives .

In general, the solid phase synthesized products exhibit shorter length than gas phase products. Thus, it is ready to use and there is no need to cut long tubes into short tube using expensive and complicated tools such as E-beam or X-ray which may cause the damages for the tube. The short tube tends to show more porous than the very long tube produced in gas phase process. This unique feature of solid phase synthesized products makes it more compatible with polymeric binders in nano composite process.

In the solid phase synthetic process, the raw materials which are solid precursors need to have some hooks which can effectively generate the chemical links between free radicals generated in early stage of heating. We found that the effective hook is selected from group of chemicals having carbonitrile -CN substituents such as phthalonitrile, polymeric molecules containing -CN such as poly acrylonitrile and its copolymers including ABS resin (copolymer of acrylonitrile, butadiene, and styrene). Phthalonitrile has been known as precursor for metal chelates such as metal phthalocyanine pigments synthesis. Using a mixture of phthalonitrile and transitional metallic salts as a solid precursor in a oxygen free chamber of a furnace heated up at 1000C shows the formation of multiwalled carbon nano tube (MWCNT) and singlewalled carbon nano tube (SWCNT) upon the variation of (CS/MS) ratio. In the solid phase synthetic process, TGA data shows that the pure carbon nano tube content occupies up to 75% wt in the product in-situ. The impurities mainly are metals and non tubular carbon including amorphous carbon and the like. Re-heating the product in-situ in ambient at 1000C will eliminate the non tubular products. Otherwise the non-tubular products can be also eliminated by chemical process.

5. CONCLUSION

MWCNT product has been achieved with solid phase synthetic process using additive containing carbonitrile -CN functionality group .Changing the chemistry and the amount of additive (or tube control agent) will change the tube shape . Further works will be done with SWCNT in future .

REFERENCES

- [1] K.C. Nguyen, S.T. Do T.V.Le, S.T. Nguyen, Nanotech 2007 Proceeding, and p. 61
- [2] Jos-Yacamn, M. (1993). "Catalytic growth of carbon microtubules with fullerene structure". *Appl. Phys. Lett.* 62: 657
- [3] J.Lu, Q.Fu, C.Lu, and J. Liu, Nanotech 2007 Proceeding, p.25

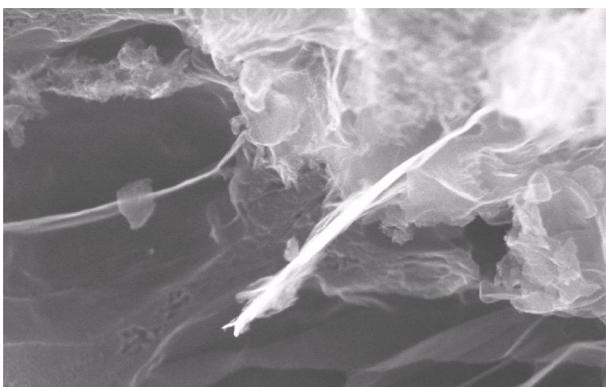


Fig.6 FE-SEM image of process (B)'s product
(Unpurified CNT product was used as catalyst)



Fig.7 FE-SEM image of process (C)'s product
(Process B + gaseous additive)