100nm RANGE SHORT TUBE PRODUCTS OF NANO CARBON FROM SOLID PHASE SYNTHESIS PROCESS WITHOUT SHORTENING EFFORT

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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 additives (TCA) and metal catalyst.* It is discovered from this synthetic process that TCA is the key component producing tube shape of nano carbon products from the process. It is also observed that relatively short tube length products (60 - 100nm) can be obtained without any effort to shorten them. The small scale of the raw material precursor is believed to be the key of the short tube products when a suitable baking condition (sudden heating or gradual heating) is practiced. Short tube of nano carbon products is desired for multiple applications, firstly, improving polarity and compatibility with other media in nano composites , then tip for AFM, electronic device,

Keywords: *60-100nm sort tube, shortening, sudden heating, Solid phase synthesis*, *solid raw materials*, t*ube control additives (TCA)*,

1 INTRODUCTION

The carbon nanotube (CNT) products from catalytic growth process, generally, are long tube ranging from um to mm. The in situ products are very hard to use for multiple applications, especially, for dispersing in certain medium to form nano composite. A lot of efforts had been made to shorten carbon nano tube products. The shortening of carbon nano tube had been known by thermally assisted field evaporation [1] , by electron bombardment [4] (100nm short tube) for AFM tip applications , by ball milling [2], by E beam for transistor applications (20nm short nanotube) [3], by steam [5] , by oxidation with sulfuric acid [6], by electric arc [7] for tube functionalization . The post shortening process easily causes the tube damage.

Recent years, we have investigated the solid phase process to produce CNT using precursor as admix of solid carbon source, tube control additive (TCA), metal catalyst and found that the TCA plays a significant role in providing tube shape for nano carbon products. The solid phase process, also provides several advantages over the conventional gas phase catalytic support growth process for examples, a) good mix between carbon source (CS) and metallic catalyst source (MS) for better control of CS/MS ratio and thus, better control of compatibility between CS and MS, better control of CS adsorption on suitable amount of MS b) products having better uniformity in terms of tube length and tube diameter. The reaction can occur in a very simple oven containing non oxidizing gas feeder, heater and temperature controller. The technology had been published in the proceeding of Nanotech 2007, 2008, 2009.

As continuing efforts to develop single walled nanotube (SWNT) with solid phase process, we had investigated several factors including the scale and shape of raw material sources. We discovered that very short, small tubes were able to achieve when much finer particle of carbon source is used with specific baking condition.

2 REACTOR

In the present study, the CNT was prepared by the pyrolysis of solid CS in a furnace equipped with high heat resistant ceramic materials including oven cover, heat resistant layer, heat resistant ceramic tube, coil heater, heat controller and a Pyrex glass reactor tube. 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 . Another connector neck can be used to remove the gaseous waste from the reactor. The gas feeding is controlled by a gas flow meter supplied by Kobold, USA. The reactor chamber is a Pyrex glass tube with variable diameter for different quantity of solid raw material feeding. The larger diameter the higher product throughput. The present furnace can provide up to 3 kg CNT product for each reaction batch taking place between 1 to 3 hrs. The heating system (heater and controller) can provide a well controlled temperature to the reactor chamber up to 1200C.

3 MATERIAL SET

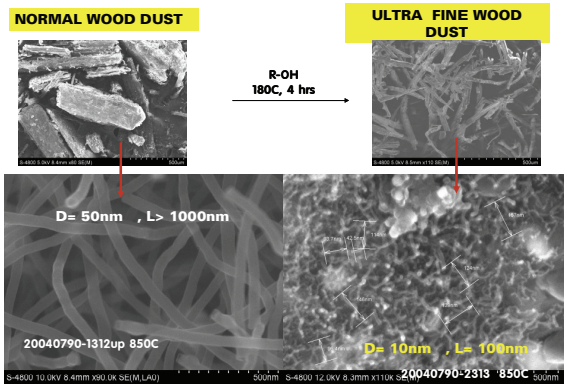

Fig. 1A Effect of raw material size scale on the shape of solid phase nano tube (SPNT) product

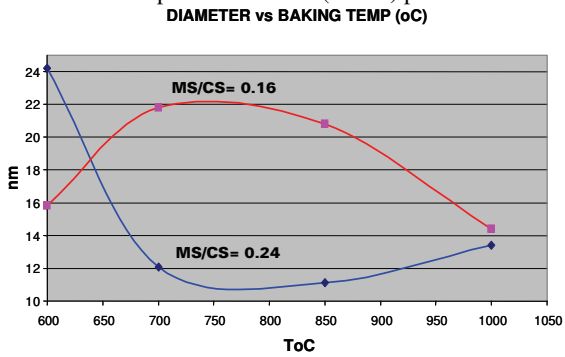

Fig. 1B indicates the effect of baking temperature on the diameter of the SPNT products fabricated with sudden heating process having different MS/CS ratio

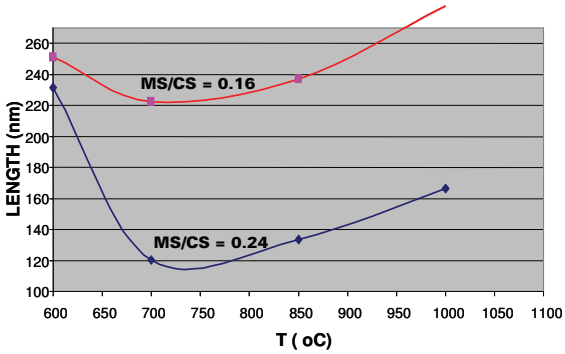

Fig 1C shows the relationship between baking temperature and tube length in a sudden heating mode

Solid carbon source is selected from flammable solid having high C content such as natural tree products

Catalysts are selected from the compounds containing transition metal elements of Ni, Fe, Co

TCA are proprietary of the present study, which is selected from wide range of low molecular weight and high molecular weight molecules having specific functionalities such as –OH, -NR,

The full solid precursor of the solid phase process is prepared by mixing powder of solid carbon source with catalyst and TCA in solvents followed with the evaporations of solvent.

4 PROCESS

The dried full solid precursors were carefully weighed into a quartz (Pyrex) tube then the air in the tube was evacuated followed with the purging of unoxidizing gases (N2 or Ar). The reactor tube must be inserted into the furnace where the heating occurs to form carbon nano tube products. There is several heating process which were practiced in the present study. In the ***sudden heating process***, the quartz tube filled with precursor was inserted into a preheated chamber and keeps heating temperature constant during baking process. On the other hand, the quartz tube containing the raw material is inserted into the reactor fist set at room temperature the slowly raise the reactor to the set temperature and keep it constantly during baking time . This is called as ***gradual heating process***. This process does show the effect on controlling the tube length as well as tube diameter.

At the reaction end, the heat was slowly removed under unoxidizing environment and the product was taken out at normal atmosphere environment.

5 TESTING

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

ii) *TEM measurement* was carried out with Hitachi TEM

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

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

6 RESULTS

Effect of raw material size scale As indicated in Fig1.A a normal wood dust (CS) having average particle size of 500nm long and 150nm wide was treated with long alkyl chain alcohol at high temperature (180C) for 4 hours yielding ultra fine wood fibril with average width of 30-50nm , 3-5X reduction in size . For comparison purpose, these materials were used to formulate the precursor containing TCA and catalyst and baked the same way (850C, 1 hr,). As result, the normal wood dust yields products having average diameter D= 50nm with average length > 1000nm, while the ultra fine wood dust gives rise to product having average diameter of 10nm and average length of 100nm. So, changing the size

scale of the carbon source would be the way to narrow down the tube size. Fig 1B indicates the effect of baking temperature on the average diameter for two different MS/CS ratios. It should be noted that (MS= metallic catalyst source, CS= carbon source) the (MS/CS) ratio does show some effect on tube diameter in ***the sudden heating mode***. The MS/CS ratio = 0.24 shows smaller diameter tube in a scale of 2X compared to smaller MS/CS ratio=0.16.

Fig 1C shows the relationship between baking temperature and tube length in ***a sudden heating mode*** for two different (MS/CS) ratios. Again, the larger (MS/CS) exhibits shorter length compare to the larger one.

In another study, we calculated the volume V (nm^3) of the tube based on the formulae $V= \pi R^2 L$. The value of V indicates how small the tube is. Fig 1D exhibits the

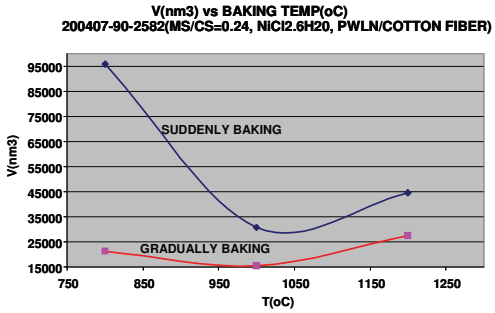

Fig. 1 D Relationship between baking temperature and tube volume (nm3) in two different heating modes: sudden and gradual

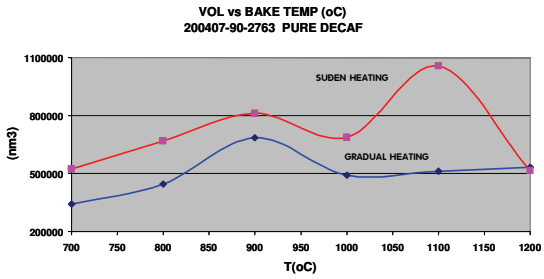

Fig. 1E shows the relationship between baking temperature and tube volume (nm^3) for coffee precursor baked at different mode of heating: sudden and gradual

relationship between V (nm3) and baking temperature for comparing the effect of ***sudden heating mode*** and ***gradual heating mode***. The precursor is made out of ***cotton*** as CS, PWLN as TCA and NiCl2 as MS. It is found that sudden bake process gives rise to much large size tube (volume) than gradual bake no matter what the baking time is the same for both.

Fig. 1E shows the effect of baking temperature on tube volume for two different baking modes using ***coffee precursor*** .Again, the similar results was obtained; sudden heating mode gives larger volume tube (bigger size) than gradual heating mode .

7 CONCLUSIONS

It can be concluded that in the solid phase synthesis of CNT utilizing TCA

1. Reduction of size scale of the raw material can reduce the diameter , the length and the overall tube volume at well
2. Larger MS/CS ratio gives rise to smaller diameter and length
3. Gradual heating mode always gives smaller tube than sudden heating mode

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