

Overview of Solid Phase Synthesized Carbon Nano Tube; revealing of the regional affects

*Khe C. Nguyen, *Anh T. N. M., *Thy N. N., *Phat T. H., *Hieu T. Le, * Doanh T. Tieu
*Saigon Hi Tech Park Research Laboratories, HoChiMinh City, Viet Nam , Kng3328196@aol.com

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 metallic catalyst* .. It is discovered that the particular tube control agent plays a significant role in the tube shape forming mechanism and product uniformity. 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.

Keywords : solid phase synthesis, *solid raw materials*, *tube control additives (TCA)*, solid precursor, purity, uniformity

INTRODUCTION

After being firstly discovered by Masanobu Endo [1] in 1976, carbon nano tube (CNT), the most typical nano material had been revisited by Ijima in 1991[2] when many nano particle observing tools such as STM, AFM, FE-SEM etc had successfully been developed . So far, plasma process associated with gas phase reaction including catalytic growth CVD, PECVD seem to be the most popular in the fabrication of MWNT and SWNT in the world , lab scale or industrial scale . Gas phase reaction utilizes hydrocarbon gases including acetylene, methane, ethanol, etc.. as carbon source (or raw materials) and metallic compounds as catalyst . It is assumed that the carbon free radicals need to adsorb on the surface of catalytic elements to grow the tube. In conventional set up condition (gas feeding rate in the range of several hundred sccm, and vacuum rate of a few 10^{-2} torr) , the gas phase reaction occurs very fast no matter how the plasma CVD reactor or the thermal CVD reactor , and ends up with CNT products mixed up with non tubular products. The tube products could be very long and contain varied tube diameter even in a single tube or in different tubes . The impurities of the gas phase reaction process are likely amorphous carbon which might be due to free carbon radicals having no landing sites on the metal catalyst elements, and it can be easily detected by TGA or it can be easily removed with oxygen annealing at as high temperature as 1000C . The major causes for the generation of amorphous carbon is believed due to the mismatched adsorption between carbon sources and metal sources in the gas phase reaction . Efforts have been made to improve the uniformity of the gas phase reaction products by using catalyst vapor of $\text{Fe}(\text{CO})_5$ iron pentacarbonyl in the high-pressure CO conversion (HiPCO)[3] process aiming at the increased compatibility between carbon sources and metal sources . Even though, the HiPCO process still leaves behind the issue of how to precisely control the ratio of carbon source versus metallic catalyst sources. The difference between catalyst decomposing temperature and tube forming temperature can be the key affecting the

generation of impurities and the uniformity . These combined factors actually make gas phase reaction mechanism more complicated to achieve industrial scale products with desired properties . Efforts have also been focused on producing ideally uniform SWNT by experiencing different kinds of catalysts or by reducing gas feeding rate down to a few sccm including carbon source gases, inert gases as well as aqueous gaseous additives . However it still ends up with a very low yield products, not suitable for large volume production .

We have investigated solid phase process in the purpose of achieving 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 c) products having higher purities d) products having good yield for large volume production .

The solid phase process of CNT in the present study utilizes solid carbon sources instead of gaseous carbon sources . Besides solid carbon sources, other important components for this process are tube control additives (TCA) and metallic catalyst . These components must be well compatible to each other when TCA likely works as a hook to link carbon source to catalyst . In order to guaranty the strong adsorption of the TCA onto the surface of carbon source, the solid carbon source must be formed into a nano scale somehow by a physical process, a chemical process or even by a bio-chemical process . The solid phase process producing CNT products can be carried out in a furnace , a thermal CVD or in a plasma CVD equipment ...

It should be noted that the concept of solid phase reaction had been known through the arc discharge and laser ablation technique of graphite .

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 1000C.

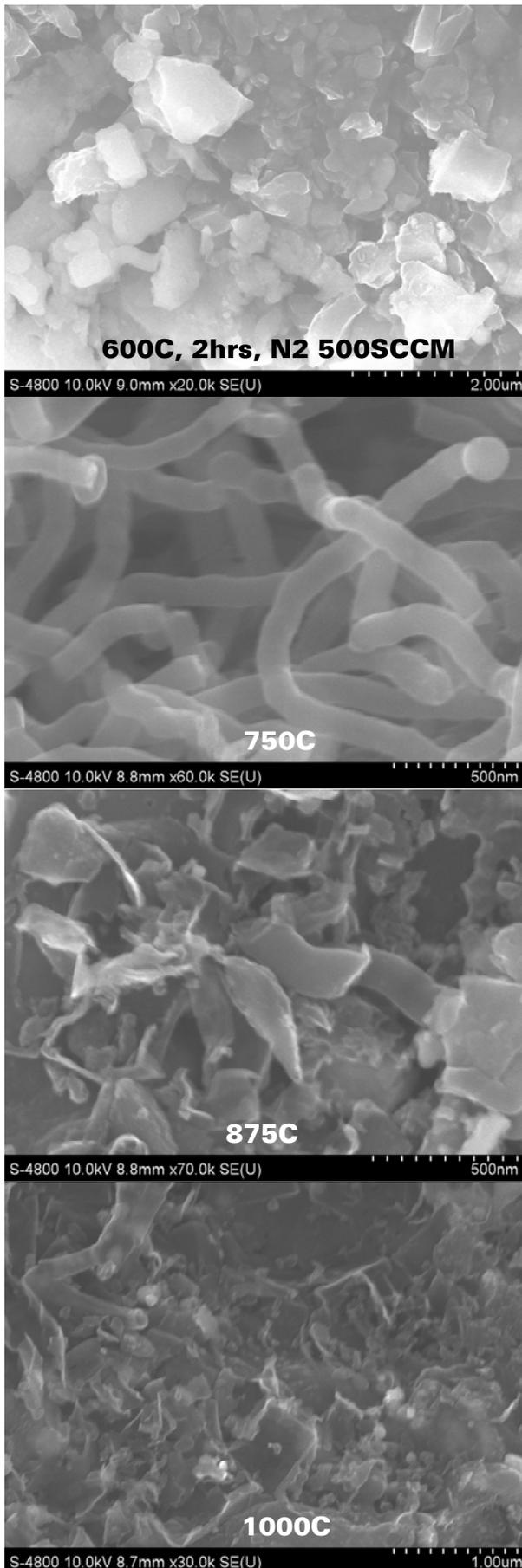


Fig 1 indicates FE-SEM images of products coming out from wood precursor baked at various temperature .
Tube shape products were observed only at 750C

MATERIAL SET

Solid carbon source is selected from flammable solid having high C content, which can be synthetic polymers, natural rubbers and woods

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

TCA are proprietary of the present study, which can be 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 nano powder of solid carbon source with catalyst and TCA in solvents followed with the evaporations of solvent. The solid additives are already added into the solid precursor components. The gas phase additives can be added during the solid precursor burning process.

The nano format of the solid carbon sources can be achieved by physical process or by bio-chemical process .

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 can be practiced in the present study. For example, the furnace heating was started first to reach targeted temperature then the reactor tube will be inserted right into the center of the furnace. In another process, the reactor tube is inserted into the furnace first at room temperature then the furnace heating slowly starts to reach targeted temperature. These two process aiming at the good timing for the generation of heat induced free radicals of carbon sources and for the generation of catalytic metal element . The heating time at targeted temperature can vary upon the chemistry of carbon sources, the chemistry of catalytic precursor as well as TCA and additives .

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

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)

RESULTS

As indicated in Fig1 A solid precursor comprised of wood powder, tube control additive TCA1 and ionic catalyst only shows tubular shape product with average diameter of about 100nm when the baking temperature is 750C

The effect of catalyst amount, catalyst chemistry and CS was shown in Fig. 2 where one can see the tube diameter, tube length can be controlled . In this Fig, QN wood is a natural product from Quang Nam Province, and LD wood is a natural wood product from Lam Dong Province in Viet Nam . TCA1 and TCA2 are two separated set of TCA

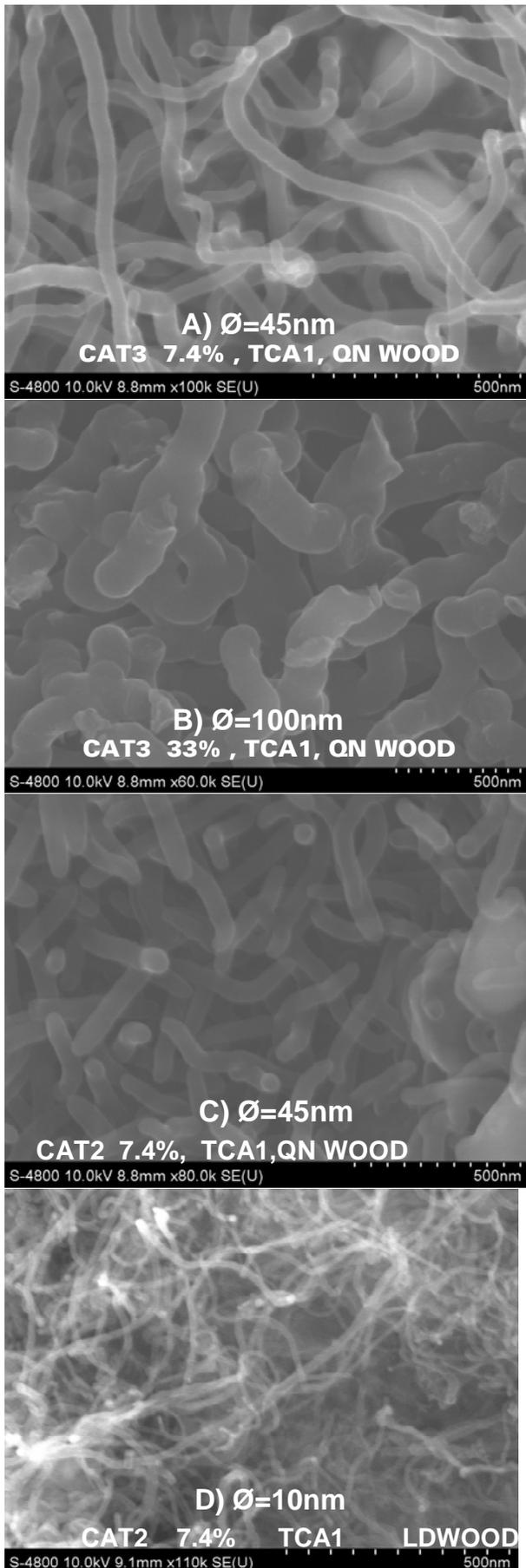


Fig. 2 FE-SEM images of CNT products as effect of CS, catalyst and catalyst loading

CAT2 and CAT3 are respectively catalysts to test out the process. As a result, one can see that tubes with different diameter from 100nm to 10nm are obtained with different set of CS, TCA and catalyst, revealing the possibility of producing desired products, just by changing these parameters. When QN wood, TCA1, CAT3 are used, higher catalyst concentration gives rise to larger tube diameter. However, with CAT2 and LD wood, smaller diameter tube of about 10nm is obtained. The effect of catalyst can also be seen in sample A) and C) in which CAT 2 tends to give rise to shorter tube than CAT3. It should be noted that all of the samples was prepared at 750C for 2 hours.

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. CS can be found from natural sources which needs to be converted into nano format before the reaction to form tube shape of nano carbon. There should be many knobs such as temperature, CS/MS ratio, CS, MS, TCA chemistry to achieve desired CNT products from large diameter from 500nm down to a few nm. SWNT should be on the way of the solid phase process

REFERENCES

- [1] Endo Masanobu, Carbon Conference 2008
- [2] S. Iijima, Nature, 354, 56-58, 1991
- [3] Gökçen T, Dateo CE, Meyyappan M.J Nanosci Nanotechnol. 2002 Oct;2(5):535-44
- [4] Guo et al, J. Phys. Chem., **99**, 10694-10697
- [5] Philip G. Collins and Phaedon Avouris (2000), Nanotubes for Electronics - Scientific American December 2000, page 67