An Novel Approach for the Assembly of Bio-nanocapsules by Detonation Process

[1]Yeuh-Hui Lin,* and [2]Sheau-Long Lee

[1] Department of Greenergy Science and Technology, Kao Yuan University, Kaohsiung 840, Taiwan, ROC
[2] Department of Chemistry, Chinese Military Academy, Kaohsiung 830, Taiwan, ROC
*Corresponding Author's E-mail: lin@cc.kyu.edu.tw

Abstract: Carbon bio-nanocapsules, a graphitic structure of nanoparticles with a hollow core, have been synthesized via an enhanced detonation process using a Trinitrotoulene (TNT) explosive with parts of toulene as carbon sources and solvent in the presence of titanium dioxide (TiO_2) powder as starting mixtures. Titanium nanoparticles, in stu formed from a detonation-assisted decomposition and rapid reduction of titanium dioxide, show good metal-induced activity for nanocapsule nucleation and for disproportionation reaction of from the TNT detonation. The products of hollow carbon nanocapsules are characterized by XRD, TGA, TEM and EDX techniques. The results shows that surface of hollow carbon bio-nanocapsules displays multilayer wall in structure with 0.35 nm space between the layers and the external diameter of the hollow carbon nanocapsules is 20-90 nm with the thickness of the wall is about 3-10 nm. The method is capable of assembling of the carbon nanocapsules without the participaation of a catalyst. This novel method can be as an alternative technique and may give great potential for the cost-effective ptroduction of hollow carbon nanocapsules.
[Yeuh-Hui Lin, and Sheau-Long Lee. **An Novel Approach for the Assembly of Bio-nanocapsules by Detonation Process.** Life Sci J 2012;9(3):171-174]. (ISSN: 1097-8135). http://www.lifesciencesite.com. 25

Keywords: Synthesis; Nanocapsules; Explosives; Nanoparticles; Detonation; Nanocapsules.

1. Introduction

Nano-structured materials have an area of intense research recently due to novel structure-related physical and chemistry properties as well as variety of significant potential applications [1-3]. Carbon nanocapsules are basically constituted by sp2 C-C covalent bonds as in graphite planes. Their syntheses have been highly successful following various routes, such as laser evaporation or arc-discharge of graphite, catalytic chemical vapor deposition, and decomposition of organic explosives [4;5]. These methods are based on a common key process: the assembly of small carbon species (C*n*) generated at high temperatures. The presence of discontinued defects in the tube structures means that an individual tube could be actually viewed as an assembly of small grapheme sheets and that they could be directly synthesized from the graphene sheets under mild conditions if proper organization technology is available. Although the intrinsic high-energy consumption and intensive hardware of these techniques are mainly responsible for the high cost, the studies on the structures of carbon nanostructures have shown that the practically obtained carbon nanomaterials are highly defective and have a local structure similar to that of turbostratic graphite [6-8]. In the synthesized carbon nanostructured samples, graphitic impurity nanocapsules are always present. Using detonation chemistry for peaceful purposes is an interesting and challenging issue, especially for nanostructure constructions due to simple processing and low production cost. This process has been developed industrially over 15 years to produce flexible graphite for the application of sealing gaskets. In the synthesized carbon nanocapsule samples, graphitic impurity nanoparticles are always present. They seriously hamper the accurate characterization of the bulk properties of nanocapsules and affect their practical applications. To remove these impurities, various purification methods have been developed. Although the graphitic nanoparticles intrinsically contain richer sub-stable nonhexagonal rings and thus are more reactive than carbon nanocapsules, the presence of defects in the tube structures renders the purification difficult. Hence, carbonaceous impurities are also frequently present in the inner voids of tubes. These internal impurities are more resistant and survive even under purification-purposed deep oxidation that causes severe damage to the tubes. How to use these impurity graphitic nanoparticles as a valuable carbon sources is of great interest but, to our knowledge, has not yet been achieved. The synthesis generally employs high-energy explosives and operates at very high loading densities to reach a detonation state with extremely high pressures and temperatures, typically a few tens GPa and thousands degrees [9]. In this paper, the detonation of a TNT explosive was used for the first time to synthesize carbon nanocapsules at HP and HT reaction conditions by introducing metal catalyst (Ti) with some content of carbon source of wax (10 wt %) into the detonation system.

2. Experimental

The detonation of TNT was performed in a sealed stainless steal pressure vessel, induced by rapid heating to its's ignition temperature. TNT/Titanium dioxide /Wax mixture was prepared in desired ratios, serving as catalyst precursor and additional carbon source, respectively. When the detonation occurs, high pressure of shock wave and temperature are produced inside the vessel. After the detonation, the vessel was cooled in air and emptied of gaseous products, and then the solid products were collected. TNT was used as the explosive to generate the high temperature required and to provide part of carbon species for assembling nanocapsules [10]. A small quantity of the as-prepared carbon nanomaterials has been dispersed in ethanol and dispersed onto copper grids in order to perform detailed observations on individual carbon nanostructures by TEM and high resolution TEM (HR-TEM). Energy-dispersive X-ray (EDX) analyses were coupled to TEM observations to determine the nature of the products.

3. Results and Discussion

In this research, the detonation synthetic system (Fig. 1.) can provide a unique environment, which ensures a survival of the pre-fed catalyst and simultaneously a ready generation of the Cn species. This advantage of the detonation system enables us to give an insight into the self-catalysis of carbon nanostructures under the conditions. From the SEM image and TGA results of detonation products using TNT with the mixture of Nickelocene/$C_{14}H_{10}$, it can be seen that copper from the cartridge wall melted and solidified to lumps of different size, ranging from several hundred nanometers to over a micron (Fig. 2).

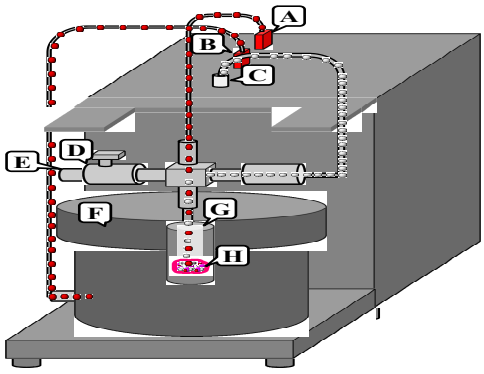


Figure 1. Schematic diagram of catalytic detonation of TNT to form nanomaterials.

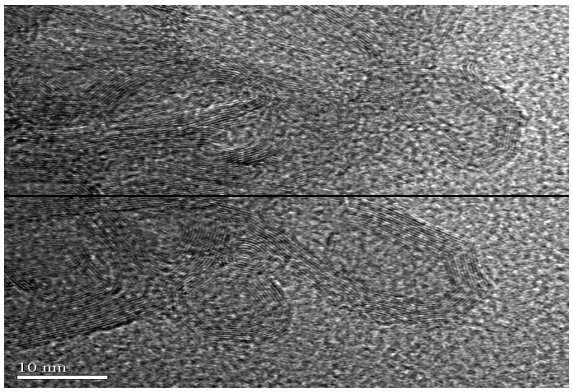


Figure 2. TEM image for the detonation of TNT to synthesis nanocapsules using Ti catalyst.

In addition to the elemental metal catalyst (Ti), agglomerates of carbon nanoparticles can be seen as well. The carbon nanocapsules exhibit outer diameters of 100–120 nm. mixture are virtually stressed that simply mixing TiO_2 with 20% wax. While metal complex reaction is clearly essential, there appears to be pronounced specificity with respect to precursor structure, suggesting perhaps the necessity for certain molecular or packing features conducive to closed shell carbon construction.

Fig. 3 shows a TEM image of the obtained materials with the change of composition to Ti metal, indicating dramatic changes in composition and morphology. Carbonaceous impurities are significantly reduced for both the materials external to the tubes and the materials in the cavities of the tubes. The newly formed tube walls are the consequence of the assembly of the functionalized graphene sheets. The nanostructures are well constructed, with uniform wall thickness along full tube and large interval spaces between the outer and inner tubes. The tube ends are normally open, which facilitates further intuitional observations of the perfect structures. Moreover, TEM image of an individual nanostructures assembly at its open end. Both the outer and inner tube moieties are clearly observable, confirming the encased tubular structures.

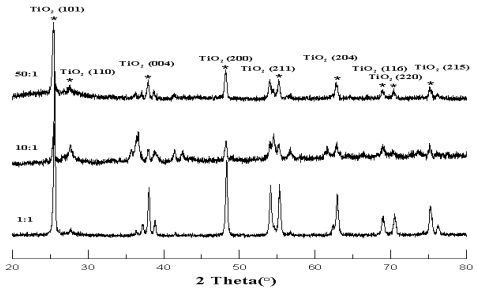


Figure 3. XRD spectrum of the as-synthesized product using TNT/TiO_2/Wax mixture.

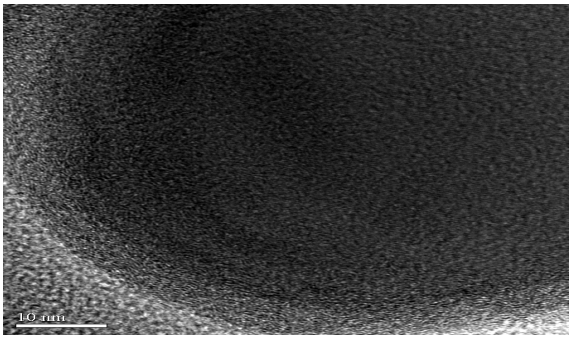
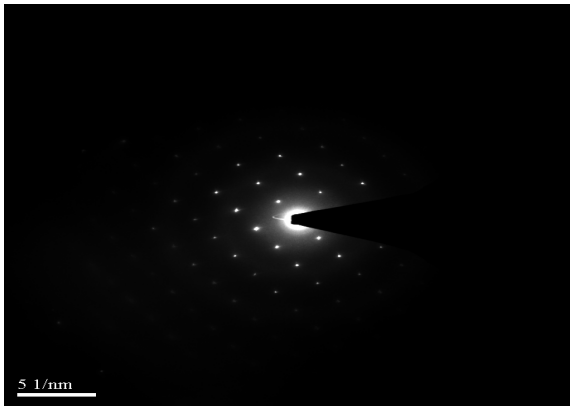


Figure 4. HRTEM image for metallic detonation of TNT to form Ti induced carbon nanostructures.

The high-yield formation of nanostructures other than re-integrated carbon particles indicates that the functionalized grapheme sheets have a preference to assemble in the direction of the pristine tubes. Combined with the uniformity of the wall thickness of the newly formed tube moieties, it also suggests that the graphene layers have very strong self-managing and self-tailoring abilities, even in the used mild wet chemical environment. Fig. 4 presents the high-resolution TEM image of the walls of a tube assembly. The wall of the inner tube shows a fishbone-like graphitic structure with interlayer distances of 0.34 nm, which is similar to the structure of pristine tubes. The outer tube is clearly the newly assembled moiety. It exhibits pre-graphitic short-rangeordered structure, with larger interlayer distances of about 0.35 nm and many discontinued and dislocated defects. Such a structure is a reflection of the soft chemical characteristic of the assembling process involved linkage mode of the small graphene segments. Tailoring the structures into well-ordered graphitic structures is possible by annealing treatments at high temperatures, which could clip off the involved oxygen-containing groups and weld the small graphene sheets together by forming C-C bonds. Fabrication of nanostructures has been accomplished before. The present method is based on a soft chemical technology and it should be easier to rationally control the tubular structures and to produce them. The multisurface and multichannel characteristics of the tube nanostructures should be greatly beneficial for the improvement or tuning of nanocapsule properties and for wide potential applications in catalysis, gas storage and sensing, electrode materials, and so on, like the conventional single-channel nanocapsule.



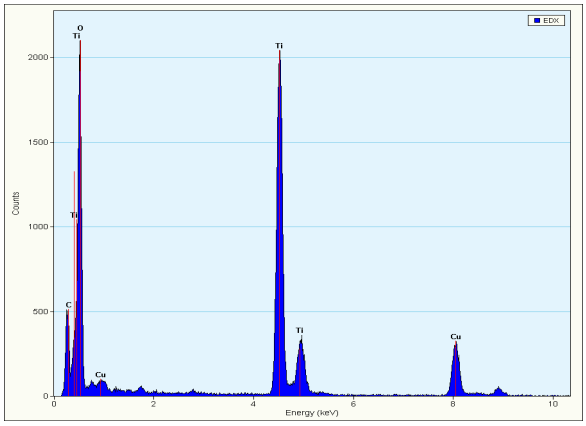


Figure 5. ED patterns and EDX mapping results of the catalytic detonation of TNT to form metallic core-shell nanoparticles

In Fig. 5, a crystalline metal particle can be seen. EDX investigation showed that it is TiO_2 particles containing small amounts of copper (from the ignition wall). Most of the nanocapsules in this sample ended in such spherical crystalline Ti particles which are not transparent to the TEM electron beam. The outer layers are not entirely parallel, indicating some degree of turbostratic disordering. In addition to the metal, the carbon nanomaterials formation was influenced by the experimental set-up, especially the method of sealing. This indicates that the pressure and temperature versus time changes need to be considered in order to fully understand or describe the nanocapsule formation by detonative decomposition techniques. A very high Ti content of nearly 100% of these lumps, was verified using EDX. Additionally, the TEM micrograph shows that the length of the tubes can reach more than a dozen microns and that they are segmented. A detailed and quantitative studies of the influence of nitrogen incorporation on the morphology of carbon nanostructures remains to be conducted in the future. In the experiments without any gasket between the steel plates, a very fast pressure decline can be assumed, as the detonation was loudly audible. The solid carbon yield in these cases was small and no tubes, only nanocapsules were found. The graphitization was not very distinct, as observed by TEM. However, no attempts were made to measure the maximum pressure or its decline as a function of time, and the conclusions of this work hence must remain qualitative.

4. Conclusion

In this paper, a very common CHNO explosive, TNT, is employed with a Ti metal as a catalyst with sufficient carbon sources introduced into the detonation system. Such a catalytic detonation process is chemically much different from that for pure explosives and facilitates practical operation. Compared to the other processes for the syntheses of carbon nanocapsules, the in-stui method used in the current work is characterized by high-density and high-pressure conditions, which experimentally shows that carbon nanostructures can grow in such an environment and provides an alternative process for producing nanostructures and a potential route for carbon bio-nanocapsule formation, especially in high density environments with the existing carbon species with the presence of Ti metal compounds.

References

1. Bethune, D. S., Kiang, C. H., de Vries, M. S. Nature, 605-607, 363 (1993) 6430.
2. Feng, Z., Brown, I. G., Ager, J. W., J. Mater. Res., 10, 1585 (1995) 1585.
3. Monthioux, M. Carbon, 40 (2004) 1809.
4. Globerg, D., Bando, Y. Appl. Phys. A, 76(2003)479.
5. Ajayan, P. M. Chem. Rev., 99 (1999) 1787.
6. Dai, H. J. Top. Appl. Phys. 80 (2001) 29.
7. Kang, F.; Zheng, Y. P.; Wang, H. N.; Nishi, Y.; Inagaki, M. Carbon, 40 (2002) 1575.
8. Ebbesen, T. W.; Ajayan, P. M.; Hiura, H.; Tanigaki, K. Nature, 367(1994) 519.
9. Hiura, H.; Ebbesen, T. W.; Tanigaki, K. AdV. Mater. 7 (1995) 275.
10. Lu, Y.; Zhu, Z. P.; Wu, W. Z.; Liu, Z. Y. Chem. Commun.21 (2002) 2740.

5/5/2012