

Synthesis of Nanoparticles by Metallic Catalyzed-blast Technology

Ming-Zen Chang¹, Chao-Chin Chan², Yi-Qi Huang², Yeuh-Hui Lin^{2,*}

Abstract—Since the discovery of carbon nanostructures, this kind of carbon nanoparticles (CNPs) have attracted extensive attention due to their novel properties and potential applications such as in high-performing nano-materials, nanoelectronics, high-efficiency energy storage, cold field emitter. Carbon nanoparticles have been successfully synthesized by a self-heating detonation process using an energetic explosive of RDX to provide the need of high temperatures, high shock waves, and parts of carbon sources in the presence of various metallic-containing catalysts. The products of carbon nanotubes and nano-scale catalyst particles are characterized by XRD, EDX and TEM techniques. The systematic experiments carried out indicate that catalysts can be selected to improve the yield of CNPs in the product distributions. These data experimentally show that it is possible for a cheaper process to produce CNPs under catalytic detonation conditions used in this study. The systematic experiments carried out indicate that mixture of RDX/Zr(Ac)₄ as a molecular precursor can be employed to produce metal Zr core-shell nanoparticles encapsulated in concentric layers of graphitic carbon. Various pure carbon or metal nanostructures can be simply obtained from the detonation of the desired molecular precursors. The approach used in this study involving bottom-up nanotechnology is universal and low-cost, and especially it has the potential ability to convert waste explosives to form highly valuable materials, as well as providing the suitable alternatives to reuse the energetic explosive further..

Keywords—Carbon Nanoparticles, Blast, Explosive

I. Introduction

The synthesis of carbon-encapsulated metal nanoparticles has attracted much attention for their wide promising applications, especially in information technologies and biomedicines [1]. The intrinsic high energy consumption and intensive hardware of these techniques are mainly responsible for the high cost of manufacturing carbon-encapsulated nanoparticles and thus limit their practical applications.

^{2,*}Yeuh-Hui Lin, PhD, * Corresponding author.

Department of Greenery & Institute of Chemical and Biochemical Engineering, Kao Yuan University
Kaohsiung, Taiwan, ROC

¹Ming-Zen, Chang, PhD
Department of Applied Foreign Languages, Kao Yuan University
Kaohsiung, Taiwan, ROC

Chao-Chin Chan, PhD
Department of Greenery, Kao Yuan University
Kaohsiung, Taiwan, ROC

Pyrolysis of transition-metal compounds has been well proved to be a promising way towards not only multi-wall nanotubes, single-wall nanotubes [8,10], but also carbon-encapsulated metal nanoparticles [8,9]. So far, various techniques have been developed to synthesize carbon encapsulated metal nanoparticles, including standard [2] and modified [3] carbon arc techniques, tungsten arc technique [4], magnetron and ion-beam co-sputtering [5], high-temperature annealing of the mixtures of carbon-based materials and metal precursors [6], catalytic carbonization process [7], catalytic chemical vapor deposition [8] and pyrolysis of organometallic compound [9].

Distinct from other approaches, transition-metal compounds such as metallic compounds can furnish both metal and carbon sources in the synthetic strategy. In the current technique for the transformation of RDX/cerium acetate/ wax to the carbon-encapsulated ZrO₂ nanoparticles, however, it is necessary to pre-vaporize Zr(Ac)₄, to carry the feedstock into reactor by high-pure nitrogen that can also prevent the feedstock from burning, to heat the reactor to high temperatures by external heating source. These careful-control-needed steps are critically responsible for operational complexity and high-production cost. In this article, we report a highly simple detonation-induced pyrolysis process for the transformation of the nickelcene to carbon-encapsulated nickel nanoparticles. This detonation approach, previously used to effectively synthesize various carbon nanostructures and nanomaterials [11–15], exhibits a self-heating characteristic. The huge thermal energy transformed from the chemical energy of explosive compounds allows the reaction systems to reach high temperature and to support the detonation of Ce metallic compound and the formation of the target structures. For the experiments described here we used the energetic compound of RDX explosive and investigated the influence of transition metal surfaces and the degree of confinement of the explosive charge on the formation and morphology of the carbon nanostructures and other carbonaceous products.

II. Experimental

All of the chemical reagents used were of analytical grade without further pre-treatment. RDX explosive is one the powerful commercially available explosive and has a detonation rate of 8700 m/s, with a density of 1.81 g/cm. Before the detonation experiments, the starting materials were mixed mechanically in desired ratios. The detonation was performed in a sealed stainless steel pressure vessel induced with an external heating to ignition temperature of RDX compound. Before the detonation experiments, the starting

materials were mixed in desired ratios. The detonation was performed in a sealed stainless steel vessel connected with vacuum and inert gas control system, and induced external heating to ignition temperature. When the detonation occurs, pressure and temperature were generated inside the vessel, varied with the loading density of RDX. After the detonation, the vessel was cooled in air to ambient temperature. The as-synthesized samples were examined using a transmission electron microscopy (TEM) operated at 100 kV. High-resolution TEM images were performed operated at 200 kV, which is equipped with energy dispersive X-ray spectrometer (EDX) for elemental analysis. For TEM analyses, the samples were prepared by sonicating in ethanol for 10 min, followed by depositing one drop of the resulted suspension on thin carbon film supported on holey copper grid. X-ray diffraction (XRD) patterns of the products were recorded using a Rigaku X-ray diffractometer operated at a step size of 0.02 with Cu K α radiation and a Ni filter at 30 kV and 100 mA anode current.

III. Results and Discussion

The obtained solid materials are black voluminous powder, exhibiting strong cerium dioxide property. TEM analyses show that the detonation of the mixture of RDX and Zr metallic compound with a weight ratio of 10~50:1 generates uniform spheroidal ZrO₂ nanoparticles, which have a narrow diameter distribution and are separately embedded in the carbon matrix. A limited amount of amorphous carbon particles and small graphite debris are also evident (Fig. 1).

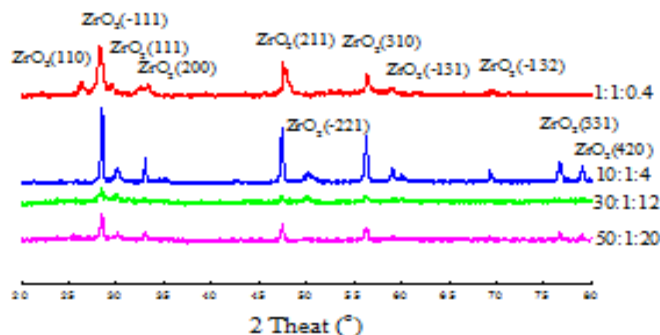


Fig. 1. XRD spectrums of the as-synthesized product using catalytic detonation of RDX/ZrO₂/Wax mixture.

TEM (Fig. 2) analyses reveal that all of the spheroidal nanoparticles have a core-shell structure with a nickel core and carbon shells. The carbon shells tightly surround the core nanoparticles, no obvious voids can be observed between the core and the shell. The shells are uniform in thickness and usually consist of 6–20 layers. The spacing of the lattice fringes is about 0.34 nm, which is close to that of the graphite (002) planes. The nickel cores are crystal and have lattice fringe spacing related to the plane of the ZrO₂ crystal. The further identification of the phase can be realized in virtue of XRD measurements. XRD characterization is performed to

further validate the corresponding structure of the core and shell. The feedstock can be mixed physically with the explosive compounds in solid state, and the detonation is carried out in a sealed vessel, so, any carrier gas is unnecessary.

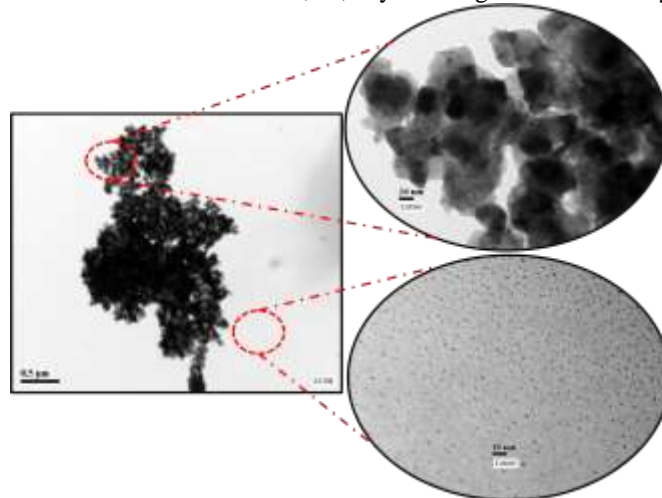


Fig. 2. TEM images for the catalytic detonation of RDX to synthesis various nano-sized nanoparticles.

In this way, uniform iron nanoparticles well encapsulated within graphitic shells can be obtained, with size of crystalline structure of parent Zr(Ac)₄ compound. The content of carbon nanostructures is estimated as the volume ratio of carbon nanostructures to the whole carbonaceous products based on systematic TEM and SEM investigations using the random sampling and repeated observations. According to the hydrodynamic theory of detonation, a pressure amplitude of >10 GPa was estimated with a more than 200 K temperature increasing observed out the reactor by the furnace thermocouple. However, nanostructures are supposed to nucleate and grow in a supersaturated zone behind the shock wavefront and at time scales larger than that corresponding to the detonation rate. Therefore, the static pressure inside the detonation reactor, just after the whole charge has decomposed, might be the more important parameter. Fig. 3 presents the profile of the as-synthesized products from 30:1 RDX/Zr(Ac)₄/wax mixture.

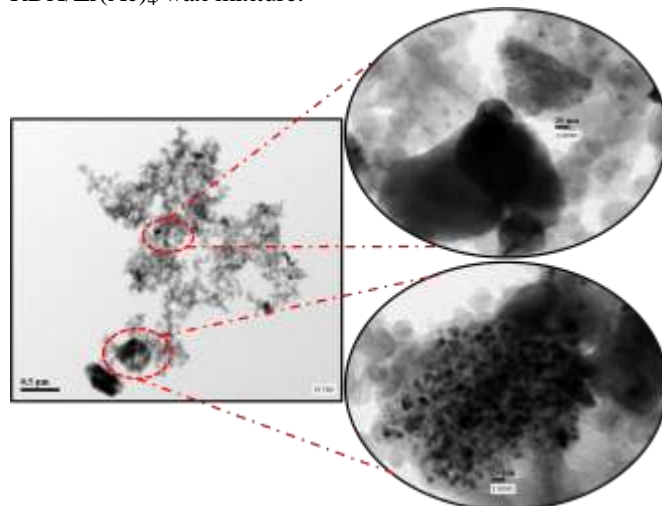


Fig. 3. TEM images for the as-synthesized products by detonation of RDX:ZrO₂:Wax = 1:1:0.4 of weight ratio.

Although it is difficult to completely rule out the presence of very small oxide and carbide particles from the XRD pattern obtained from Fig. 1 because the particles possessing a scattering region smaller than 2nm cannot be registered with the X-ray technique. TEM observation shows that the size of the particles are larger than 5nm, suggesting the cores should be ZrO₂ crystal. The diffraction peak can be assigned to the (002) planes of hexagonal graphite structure with an interlayer spacing of 0.34 nm, corresponding to the encapsulating carbon shells. The peak is rather asymmetry, broader and lower than that of the well-crystallized graphite, indicating a relatively small crystalline dimension.

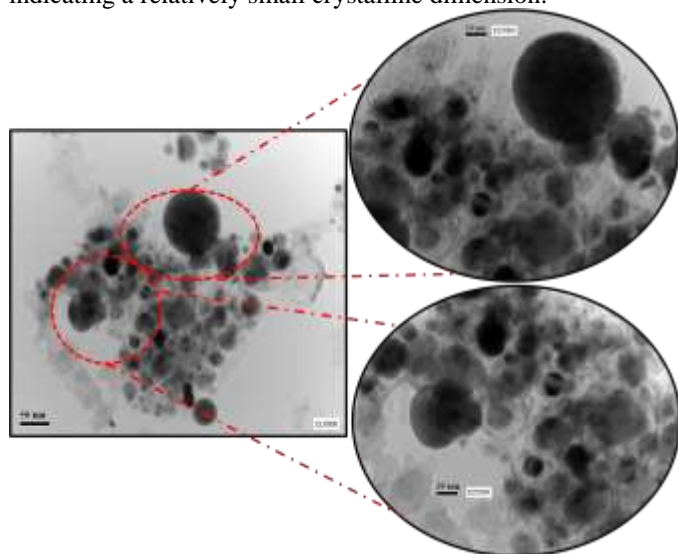


Fig. 4. TEM images for the as-synthesized products by detonation of RDX:ZrO₂:Wax = 10:1:4 mixture.

Amorphous carbon background in the products contributes to the broad diffraction peak in proximate to the graphite peak. Further information about the structure of the carbon shell was obtained from Raman investigation. Fig.4-6 displays some typical TEM images of the resulted material, showing that the ZrO₂-C core-shell nanoparticles are remained after the detonation reaction. The similarity of the iron particle size at different HMX:nickelcene ratios excludes the possible effect of nickel particle size on the formation of carbon nanotubes. In the present process, RDX not only serves as heat source by exothermic decomposition but also provides additional carbon source for the formation of ZrO₂-C core-shell structure or carbon nanocapsules although most of the carbon atoms involved in RDX molecular would be converted into volatile gases during the detonation. Therefore, the variety of RDX of E: metal compound of M: carbon source of C ratio leads to a significant change of the C:M atomic ratio in the reaction system. The E:M:C atomic ratio is likely responsible for the nanostructure formation. To further validate this speculation, we have carried out a comparative experiment, in which appropriate amount of carbon-rich compound of

anthracene (C₁₄H₁₀) is introduced into the 10:1 explosive and metallic compound mixture to increase C:M atomic ratio. The detonation product, greatly distinct from the others, contains numerous carbon nanocapsules (Fig. 5).

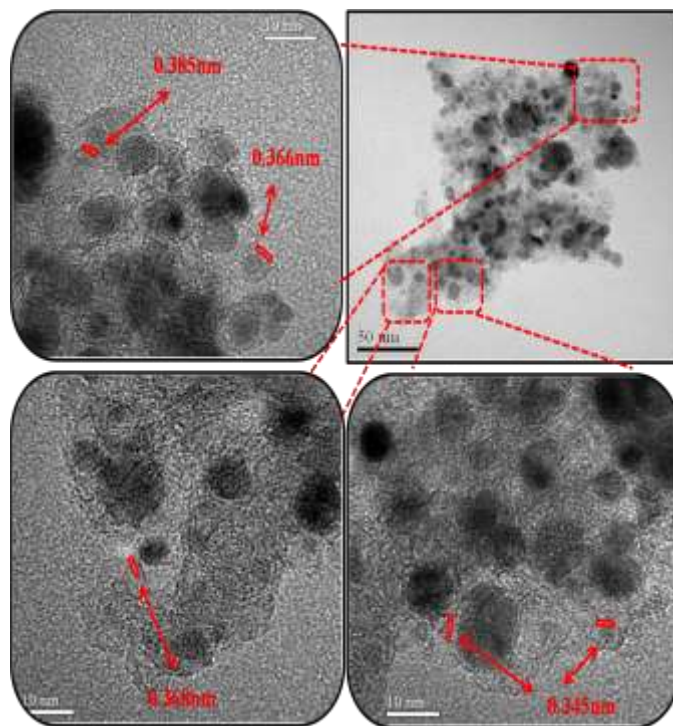


Fig. 5. TEM images for the nanoparticles of metallic core-shell in weight ratio of RDX:ZrO₂:Wax = 30:1:12.

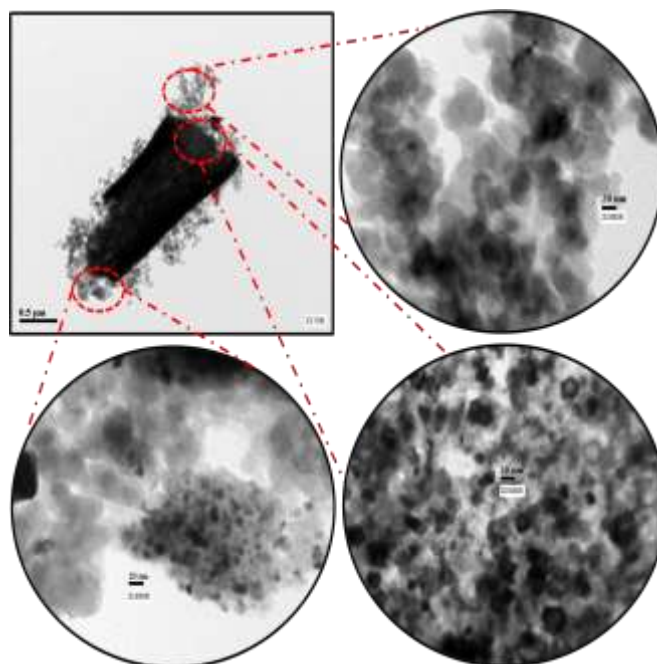


Fig. 6. TEM images for the as-synthesized products in weight ratio of RDX:ZrO₂:Wax = 50:1:20 mixture.

This result strongly supports the speculation that C:Zr atomic ratio plays a key role in the controllable formation of carbon nanocapsules and carbon-encapsulated metal nanoparticles. The simultaneous condensation of the metal clusters and the C_n species leads to the likely formation of a (ZrO₂, C) alloy, whose carbon content varies with the system temperature. When the carbon dissolution in the ZrO₂ nanoparticles reaches saturation, a precipitation of pure carbon around the nanoparticles would start in the form of graphite. The above data show that the detonation-induced ZrO₂ pyrolysis is able to controllably produce well-constructed Mi - C core - shell nanostructures. In this process, the detonation of RDX is induced by temperature-programmed heating and occurs at about 210 °C. The hot gases generated from the detonation collide with the gaseous metallic molecules and make latter quickly decompose into small carbon (C_n) and metal species, which subsequently condense into solid materials when cooling.

IV. Conclusions

Carbon-encapsulated ZrO₂ metallic-nanoparticles are successfully synthesized through the detonation of RDX/Zirconium acetate/wax mixture. A key factor for the controlling formation of carbon-encapsulated ZrO₂ nanoparticles and carbon nanotubes is C: metal ratio in the starting materials, which is very easily adjusted to obtain pure encapsulated ZrO₂ nanoparticles without the formation of carbon nanotubes. This method represents a simple and low cost process towards metal-carbon encapsulating structures, in which the needed high-temperature environment is self-provided by the energy emitted from the RDX detonation. It is concluded that can be designed as a useful method and with the potential application for the synthesis of core-shell-like metal-induced carbon-nanoparticles.

The self-heating together with other characteristics such as the fast reaction and the less hardware should make this technique applicable. Results might also help in the development of an efficient method for the production of graphitic carbon-encapsulated metallic nanoparticles, since understanding bottom-up self-assembly system uptake within metallic-catalyzed conversion of a carbon-rich explosive matrix into nanostructures is a key aspect in developing suitable syntheses of the carbon-encapsulated metal nanoparticles and other related advanced nanostructures.

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