A novel approach for the synthesis of carbon nanotubes and carbon nanoparticles using a newly developed catalytic-blast technology

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Abstract
Since the discovery of carbon nanotubes (CNTs), this kind of carbon nanostructures 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. Muti-walled carbon nanotubes (CNTs) and carbon nanoparticles have been successfully synthesized by a self-heating detonation process using an energetic explosive of HMX 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, SEM, EDX and TEM techniques. The systematic experiments carried out indicate that catalysts can be selected to improve the yield of CNTs in the product distributions. These data experimentally show that it is possible for a cheaper process to produce CNTs under catalytic detonation conditions used in this study. The systematic experiments carried out indicate that mixture of HMX/nickelcene as a molecular precursor can be employed to produce Ni 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 nanotubes, Catalyst, Blast, Explosive

1. Introduction
The synthesis of carbon-encapsulated metal nanoparticles has attracted much attention for their wide promising applications, especially in information technologies and biomedicines [1]. 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]. 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.

Pyrolysis of transition-metal compounds has been well proved to be a promising way towards not only multi-wall nanotubes, single-wall nanotubes, but also carbon-encapsulated metal nanoparticles [8-10]. Distinct from other approaches, transition-metal compounds such as nickelcene can furnish both nickel and carbon sources in the synthetic strategy. In the current technique for the transformation of nickelcene to the carbon-encapsulated iron nanoparticles, however, it is necessary to pre-vaporize nickelcene, 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 nickelocene to carbon-encapsulated nickel nanoparticles. This detonation approach, previously used to effectively synthesize carbon nanotubes and nanobulbs [11–17], 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 pyrolysis of nickelocene and the formation of the target structures. For the experiments described here we used the energetic compound of cyclotetramethylenetetranitramine (HMX) 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.

2. Experimental

All of the chemical reagents used were of analytical grade without further pre-treatment. HMX compound (octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine) is one the powerful commercially available explosive and has a detonation rate of 9110 m/s, with a density of 1.89 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 HMX explosive (Fig. 1).

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 HMX explosive. After the detonation, the vessel was cooled in air to ambient temperature. The as-synthesized samples were examined using a scanning electron microscopy (SEM) carried out operated at 30 kV and a transmission electron microscopy (TEM) operated at 100 kV. High-resolution TEM imaging 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 Ka radiation and a Ni filter at 30 kV and 100 mA anode current.

3. Results and discussion

The obtained solid materials are black voluminous powder, exhibiting strong nickel magnetic property. TEM analyses show that the detonation of the mixture of HMX and nickel with a molar ratio of 2:1 generates uniform spheroidal Ni nanoparticles, which have a narrow diameter distribution of 5–20 nm (Fig. 2) and are separately embedded in the carbon matrix. A limited amount of amorphous carbon particles and small graphite debris are also evident. The detonation of the 5:1 HMX–nickelocene mixture yields similar products. The spheroidal nanoparticles are dominant, with diameters in an order of 10 nm. In the two cases, tubular objects are not found in the products. When the molar ratio of HMX to nickelocene shifts to 10:1, majority of products are still Ni spheroidal nanoparticles showing similar diameter distribution, however, a small quantity of carbon nanotubes with a content of about 10% are formed (Fig. 3). The nanotubes exhibit very wide channels and show continuously hollow or bamboo-shaped morphologies. The diameters of the nanotubes are 40–100 nm, compared to the diameters of the nickel particles located at tube ends, but significantly larger than the diameters (5–20 nm) of the abundant nickel spheroids. High-resolution TEM (HRTEM, Fig. 2 insert spherical figures) 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 9-12 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 of 0.20 nm (Fig. 3-insert spheres), related to the (110) plane of the Ni crystal. The feedstock (nickelocene) 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. In this way, uniform nickel nanoparticles well encapsulated within graphitic shells can be obtained, with size of 5–20nm and body-centered cubic (bcc) crystalline structure of parent nickel. The content of carbon nanomaterials 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 outside 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.4 displays a typical HR TEM image of the resulted material, showing that the Ni–C core–shell structures are remained after the HNO₃ treatment. It is well known that Ni is a nice catalyst for the carbon nanotube synthesis, however, Ni–C core–shell structure can be formed selectively in the present approach via simply controlling the ratio of HMX/nickelene. The similarity of the iron particle size at different HMX:nickelene ratios excludes the possible effect of nickel particle size on the formation of carbon nanotubes. The residue found inside the cartridge primarily consisted of carbon (>95 wt%), with small amounts of nitrogen (2.9 wt%) and oxygen (<1.7 wt%) as well as hydrogen (0.4 wt%) as determined by combustion analysis and energy dispersive X-ray (EDX) analysis. In the present process, HMX not only serves as heat source by exothermic decomposition but also provides additional carbon source for the formation of carbon nanotubes. The residue found inside the cartridge primarily consisted of carbon (>95 wt%), with small amounts of nitrogen (2.9 wt%) and oxygen (<1.7 wt%) as well as hydrogen (0.4 wt%) as determined by combustion analysis and energy dispersive X-ray (EDX) analysis. In the present process, HMX not only serves as heat source by exothermic decomposition but also provides additional carbon source for the formation of Ni–C core–shell structure or carbon nanotubes although most of the carbon atoms involved in HMX molecular would be converted into Cox gases during the detonation. 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.

Fig. 5 presents the profile of the as-synthesized products from 5:1 HMX–nickelene mixture. The peaks at 43.76°, 51.06° and 76.36° can be identified as the Ni (111), Ni (200) and Ni (220) planes of bcc-Ni. Although it is difficult to completely rule out the presence of very small oxide and carbide particles from the XRD pattern 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 bcc-Ni. The diffraction peak can be assigned to the planes of hexagonal graphite structure with an interlayer spacing of 0.34nm, 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. 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.

As shown in Fig. 6, a schematic diagram of mechanistic routes for the catalytic detonation to form various nanomaterials has been proposed. In this article, the variety of HMX:nickelene ratio leads to a significant change of the C:Fe atomic ratio in the reaction system. The C:Ni atomic ratio is likely responsible for the nanotube formation. This result strongly supports the speculation that C:Ni atomic ratio plays a key role in the controllable formation of carbon nanotubes and carbon-encapsulated iron nanoparticles. The above data show that the detonation-induced nickel pyrolysis is able to controllably produce well-constructed Ni–C core–shell nanostructures. In this process, since the detonation of HMX is induced by temperature-programmed heating and occurs at about 250℃. The hot gases generated from the detonation collide with the gaseous nickelene molecules and make latter quickly decompose into small carbon (Cn) and Ni species, which subsequently condense into solid materials when cooling. The simultaneous condensation of the Ni clusters and the Cn species leads to the likely formation of a (Fe, C) alloy, whose carbon content varies with the system temperature. When the carbon dissolution in the Ni nanoparticles reaches saturation, a precipitation of pure carbon around the nanoparticles would start in the form of graphite.
4. Conclusions

Uniform carbon-encapsulated Ni nanoparticles are successfully synthesized through the detonation of HMX and nickelocene mixture. A key factor for the controlling formation of carbon-encapsulated Ni nanoparticles and carbon nanotubes is C:Ni ratio in the starting materials, which is very easily adjusted to obtain pure encapsulated Ni 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 HMX detonation.

The self-heating together with other characteristics such as the fast reaction and the less hardware should make this technique applicable for large-scale syntheses of the carbon-encapsulated metal nanoparticles and other related nanomaterials. It is concluded that catalytic detonation of carbon-rich explosives can be designed as a useful method and with the potential application for the production of nano-structured materials of graphitic carbon-encapsulated nanoparticles and carbon-nanotubes.

References


Fig 1. Schematic diagram of catalytic detonation of HMX explosive to form nanomaterials.

Fig 2. TEM and HRTEM images of the catalytic detonation product using HMX to nickelocene = 2:1.

Fig 3. TEM and HRTEM images of the catalytic detonation product using HMX to Nickelocene = 10:1.

Fig 4. EDS images of the detonation product using HMX/C_{14}H_{10}/nickelocene mixture.

Fig 5. XRD images of the detonation products using HMX to nickelene for (A) 2:1, (B)5:1 and (C)10:1.

Fig 6. Schematic diagram of mechanistic routes for the catalytic detonation to form various nanomaterials.