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Fast deflagration to detonation transition of energetic material based on a quasi-core/shell structured nanothermite composite

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ABSTRACT

Nanothermites (also called metastable intermolecular composites), composed of nanoscale metals and metal oxides, have drawn increasing interests as energetic materials over the past two decades. Nanothermites have twice the energy density of 2,4,6-trinitroluene, and their nanostructures, functions, energy release, and reaction performance are continuously being improved. However, these materials suffer from low pressure because of low gas expansion from the reaction and incapability of deflagration to detonation transition (DDT). Fast DDT is necessary to substantially improve the reaction velocity and output pressure not only of nanothermites but also of other monomolecular organic energetic materials, such as cyclotrimethylene trinitramine (RDX) and octogen. Accordingly, this study aims to produce energetic composites material that are safe, green, and free from heavy metals. A strategy of rapid DDT acceleration is proposed by fabricating quasi-core/shell structured materials of RDX@Fe_2O_3–Al based on Fe_2O_3–Al nanothermites. A surface modifying and ultrasonic synthesis technology is also demonstrated. Scanning electron microscopy and X-ray photoelectron spectroscopy characterizations prove that the material comprises an RDX core and an Fe_2O_3–Al nanothermite shell. Results of closed vessel combustion tests show that the RDX@Fe_2O_3–Al combustion velocity accelerates to an average pressurization rate of 2.527 MPa/μs. DDT tube tests further confirm that DDT accelerates to a primer explosive level in which the run-to-detonation distances of DDT is below the test-condition limitation (<15 mm). Sensitivity tests also reveal that the RDX@Fe_2O_3–Al composite has low sensitivity to impact, friction, and electric spark. Therefore, the RDX@Fe_2O_3–Al composite with a quasi-core/shell structure is a potential green and safe fast DDT energetic material that is easy to synthesize and applicable to other quasi-core/shell structures.

1. Introduction

Nanothermites (also known as metastable intermolecular composites, MIC), composed of a metal fuel and a metal oxide in nanoscale, are attracting significant interest over the last two decades. The reaction kinetics of nanothermite could be significantly improved because of the drastic heat reduction and mass transfer distances in the nanoscale level, leading to several attractive properties, such as low ignition/onset-reaction temperature, high combustion velocity, and self-propagation in the microscale [1–4]. Several potential MIC applications [5–10] have been proposed using nanothermites as energetic materials. In the recent two years, increasing number of studies on nanostructures, such as hollow nanosphere [11], nanowire [12], core/shell nano-arrays [13], and assembly nano-particles [14,15] have been demonstrated to improve the MIC performances, especially the various designs that have been proposed to improve the MIC combustion velocity or pressurization [16–19]. However, to the best of our knowledge, the attained MIC combustion wave speeds are not significantly high and only exhibit a maximum value of 2500 m/s for Bi_2O_3–Al MIC [20]. One key reason causing this limitation is that minute gas products are generated during MIC combustion, which is the key role of mass and heat transfer under turbulent flow [21]. Evidently, the lack of high pressure during an MIC reaction is a key limitation that could be used for various applications, such as initiation, deflagration to detonation transition (DDT), and driving metal. Compared with MIC, several monomolecular organic energetic materials, such as cyclotrimethylene trinitramine (RDX) and octogen (HMX), are superior because of the resulting high

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pressure gases during combustion or detonation. RDXs have been the most commonly used high explosives in mining and military applications. However, their combustion velocities are considerably slow (less than 10 m/s) despite of their detonation velocity of more than 8000 m/s. Moreover, realizing DDTs is difficult unless intense confinement and large amounts of charge are available.

For energetic materials use, DDT is the key process to improve the reaction velocity and output pressure because of the difference between combustion and detonation. The former only offers the weak pressures and combustion waves, and the latter offers extremely high pressures and shock waves. To initiate the high explosive charge, primer explosives (PEs), such as lead azide, lead styphnate, and cadmium carbohydrazide perchlorate, are generally used to attain a rapid DDT and output shock wave. These PEs contain lead or other heavy metal elements, and therefore are mostly hypertoxic and cause substantial harm to the environment and human health [22]. For example, a survey showed that lead in the blood of an employee working in an FBI shooting range in America was ten times that of the U.S. Federal Government standard [23]. In recent years, several green explosives, such as high-nitrogen [24,25], azides [26], nitrogen-rich heterocyclic compound, and their salts [27–30] have been synthesized as potential PEs. However, organic wastewater and other pollutant are still difficult to mitigate during the manufacture of these materials. Furthermore, most of these materials are extremely sensitive to random stimulations, such as impact, friction, and electro-static discharge, which may easily cause accidental explosion and severe damage during manufacturing, transport, and usage. Compared with PEs, several high explosives (RDX and HMX) and MIC are more environment-friendly and less sensitive to impact, friction, and electric spark (ES). These characteristics make them attractive candidates for PEs. However, significant challenges in DDT acceleration must be overcome to realize the transition by themselves.

Core/shell structure has been an effective means to improve performance of the composites materials by combining the unique characteristics of core materials and shell materials in recent years [31–33]. In this study, a strategy was proposed by fabricating a novel quasi-core/shell structure material RDX@Fe_2O_3–Al based on Fe_2O_3–Al nanothermites to accelerate the DDT of MIC and high explosives. The main underlying principle of these methods is that RDX particle surfaces are enwrapped with Fe_2O_3–Al nanothermites, forming a quasi-core/shell structure. Thus, the RDX surface in the core could be ignited to burn through the fast MIC combustion, thereby accelerating the RDX. In addition, the high pressure and gases produced through RDX would accelerate the MIC heat and mass transfer in shell, thereby accelerating the RDX. To obtain the abovementioned quasi-core/shell structure material (RDX@MIC), a surface modifying and ultrasonic process are demonstrated. In addition, further combustion, DDT, and sensitivity tests are performed to prove the superiorities of the synthesized materials.

2. Experimental section

2.1. Materials, synthesis, and characterization

To determine the particle size effect, two types of RDXs were used in the present study. Recrystallized RDX (R-RDX) particles and fine RDX (F-RDX) were purchased from Yinguang Chem. Co., Ltd. Al nanoparticles with an average diameter of 100 nm, having a ~5 nm oxide shell and active metal content of 65.0 wt.% were purchased from Wuhan Nanoparticle Co., Ltd.

For green purpose and nanothermite use, Fe_2O_3 nanoparticles were synthesized through sol–gel method and low-temperature CO_2 supercritical extraction (SCE) process as describe in Ref. [34]. About 10.0 g of $Fe(NO_3)_3 \cdot 9H_2O$ was dissolved in 10.0 g of anhydrous ethanol to give a clear red–orange solution. Upon adding 2.0 g of propylene oxide into the solution with stirring, the solution color changed to dark red–brown. By maintaining the solution at 45 °C, gelation occurred in less than 5 min. After aging the gel at 45 °C for 24 h, anhydrous ethanol was then added in the solution and replaced every 24-h period for 3–5 times. The CO_2 SCE process was subsequently performed in a vessel where the liquid in the pores were exchanged with liquid CO_2. After CO_2 exchanging, the vessel temperature increased to 45 °C and its pressure reached 15 MPa. The aerogel was obtained by maintaining the temperature and pressure for 1 h followed by depressurization. To remove the organic impurity, the aerogel was heated in a muffle furnace at 350 °C for 3 h, and then the Fe_2O_3 nanoparticles were obtained.

Fig. 1 shows that the RDX@Fe_2O_3–Al quasi-core/shell structure was synthesized via a similar surface modification and ultrasonic approach. In addition, this method is similar to that reported in the literature [35]. First, R-RDX or F-RDX raw materials were modified using estane. About 0.512 g of Estane was dissolved in 20 mL of dichloroethane ($C_2H_4Cl_2$) at 50 °C to form a colorless transparent solution. After allowing the solution to naturally cool to room temperature, 20 g of R-RDX (or F-RDX) was added to the and the mixture was stirred for 30 min. The modified R-RDX or (or F-RDX) microparticles were obtained through vacuum filtration and dried in an oven at 60 °C for 6 h. Second, the modified R-RXD (or F-RDX), Al, and Fe_2O_3 nanoparticles were ultrasonicated to form quasi-core/shell structures. Exactly 3.84 g of Al and 6.16 g of Fe_2O_3 were dispersed into 100 mL of isopropanol with ultrasonic irradiation at output acoustic power of 240 W and frequency of 40 kHz (Jeken Ultrasonic Cleaner PS-40, China) for 60 min. Moreover, a given quality of estane-modified R-RDX (or FRDX) particles were dispersed into 40 mL of isopropanol, facilitated by using the other ultrasonic apparatus (Model KQ-500VDE, 100 kHz, 500 W, and 40% power intensity, purchased from Kunshan Ultrasonic Instrument Co., Ltd.) for 30 min. The hot suspension of sonicated Al-Fe_2O_3 nanothermite was then immediately added to the above estane-modified RDX suspension and ultrasonicated for 15 min. Afterward, the resulting brown product was filtered and vacuum-dried in an oven at 60 °C for 2 h.

The morphologies and surface appearances of the samples were characterized using field emission scanning electron microscopy (FESEM, Ultra-55, Carl Zeiss). The element distribution on the surface of the quasi-core/shell structure was characterized using X-ray photoelectron spectroscopy (XPS, VG ESCALAB 250).

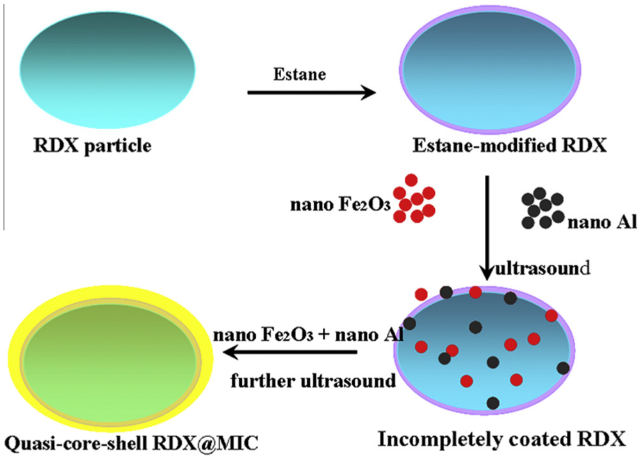

Fig. 1. Schematic for formation of quasi-core/shell structured RDX@Fe_2O_3–Al microparticle.