Letter

Preparation and characterization of core/shell structure of HMX/NTO composite particles

Guangcheng Yang[†] and Fude Nie

Institute of Chemical Materials, CAEP, Mianyang, 621900, CHINA
[†]Corresponding address: ygcheng@hotmail.com

Abstract

This paper reports the preparation and characterization of a new type of composite particles with a core/shell structure. A tetrahydrofuran suspension containing 3-nitro-1,2,4-triazol-5-one(NTO) and Octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine (HMX) was injected into a spray dryer. After solvent evaporation, the NTO crystallized in the shape of small particles on the surface of the ultrafine HMX particles. Through this process the core/shell structure of HMX/NTO composite particles was obtained. Scanning Electron Microscopy (SEM) images (20 kV) of these composite particles revealed that extensive flaws existed in the external shell layer. Atomic Force Microscopy (AFM) revealed that the surface of the composite particles were "potholed" while those of the HMX particles were smooth. The nitrogen 1s spectrum of X-ray Photoelectron Spectroscopy (XPS) indicated that, on the surface of composite particles, the content of NTO was much higher than that of HMX. Thermogravimetry and Differential Scanning Calorimetric (TG-DSC) curves revealed that thermolysis of NTO in the core/shell composite particles occurred with a slight shift toward the lower temperature region compared with that of HMX/NTO physical mixture at the same ratio. Friction and impact sensitivity of the HMX/NTO core/shell composite explosive were significantly reduced in comparison with that of the physical mixture with an equivalent composition.

1. Introduction

A decrease in the sensitivity of high explosives such as Hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX) and Octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine (HMX) under mechanical and thermal stimuli would lead to the increase of safety in handling, storage and production of those materials. The reduction in sensitivity of high explosives can be attained by coating the crystal with an inert material such as a polymer. Lei Liangfang, Akhavan J., Voigt H. et al have conducted a significant amount of research on this subject. The impact, friction and shock sensitivity of HMX and RDX were lowered to some extent by coating with acrylonitrile-1,3-butadiene-styrene copolymer, polyvinyl pyrrolidone, polyethyl acrylate, etc.[1]~[6]. However, the performance of the explosive was decreased at the expense of an increase in inert polymer. Additional investigations were conducted on this subject in order to obtain an optimal improvement in sensitivity with only a minimal amount of inert material.

In this paper, we introduced another technique to lower the mechanical sensitivity of molecular explosives. A high explosive was coated with another safer explosive. As a result, a composite particle with a core/shell structure was prepared. In the process of preparation, only a minimal amount of inert polymer (≈ 0.1 % by mass) was used as an adhesive to conglutinate the shell layers and the core particles. It was reported that the composite particles with this core/shell structure reveal many properties of shell material even the content of the shell material is much lower than that of core material. Additionally this structure can effectively prevent the conglomeration of ultrafine particles[7],[8]. 3-Nitro-1,2,4-triazol-5-one (NTO) is a high explosive with low sensitivity, and many low sensitive formulations employ NTO as an insensitive component, such as B2214, B2248 [9]. In this paper, NTO was used to coat HMX by a spray drying method and the properties of an explosive with a core/shell structure were studied.

2. Experimental

2.1 Materials

Ultrafine HMX with a mean size of ≈ 7 μm was prepared with an F. C. bond ball mill at 140 RPM in a medium of purified water. The original NTO crystalline shape was rod-like. Polyoxyethylene (10) alkylphenol ether (OP-10) was obtained from Shanghai Auxiliaries Manufactory CO., LTD. Tetrahydrofuran (THF), 99 %, was purchased from Lyondell Chemical Company. Polymethyl methacrylate (PMMA), w. M. = 350000, was obtained from Atohaas.

2.2 Instrument and apparatus

Spray drying was carried out by employment of a Bütch Mini Spray Dryer-B191 instrument. The experimental temperature at the inlet was set at 50 °C , while the feedback from outlet was 45 °C and the working pressure was 6~8 atm.

A SK8200LH Ultrasonic cleaning instrument, from KUDOS (China), was used to disperse ultrafine HMX particles at a frequency of 40 kHz. With Scanning electron microscopy (SEM), studies were conducted by Stereoscan Leo440s analyzer (ambridge) with an acceleration voltage of 20 kv and scanning rate of 20 fram sec^{-1}. A SPA300HV Atomic Force Microscope (AFM) was used to read the morphologic information of particles in a tapping mode. X-ray photoelectron spectroscopy (XPS) was accomplished using a VG ESCALAB 250 instrument equipped with a dual X-ray anode (Mg and Al). Data was obtained with Mg Ka radiation at 200W. Thermogravimetry and Differential Scanning Calorimetric (TG-DSC) characteristics were determined by employment of a NTEZSCH STA 449C instrument at a heating rate of 10 °C min^{-1} and using argon at a flow rate of 2 ml min^{-1} and a sample amount of 1.4 mg. The impact sensitivity was determined with a WL-1 drop weight impact machine. About 50 mg of sample was subjected to an impact of a 10 kg mass dropped from a height of 25 cm. A WM-1 friction apparatus was used to determine the friction sensitivity. Approximately 30 mg of sample was subjected to a pressure of 3.92 MPa, then friction tested at a pendulum angle of 90°.

2.3 Preparation of core-shell structure of HMX/NTO composite particles

NTO (0.51 g) and PMMA (0.02 g) were added to tetra-
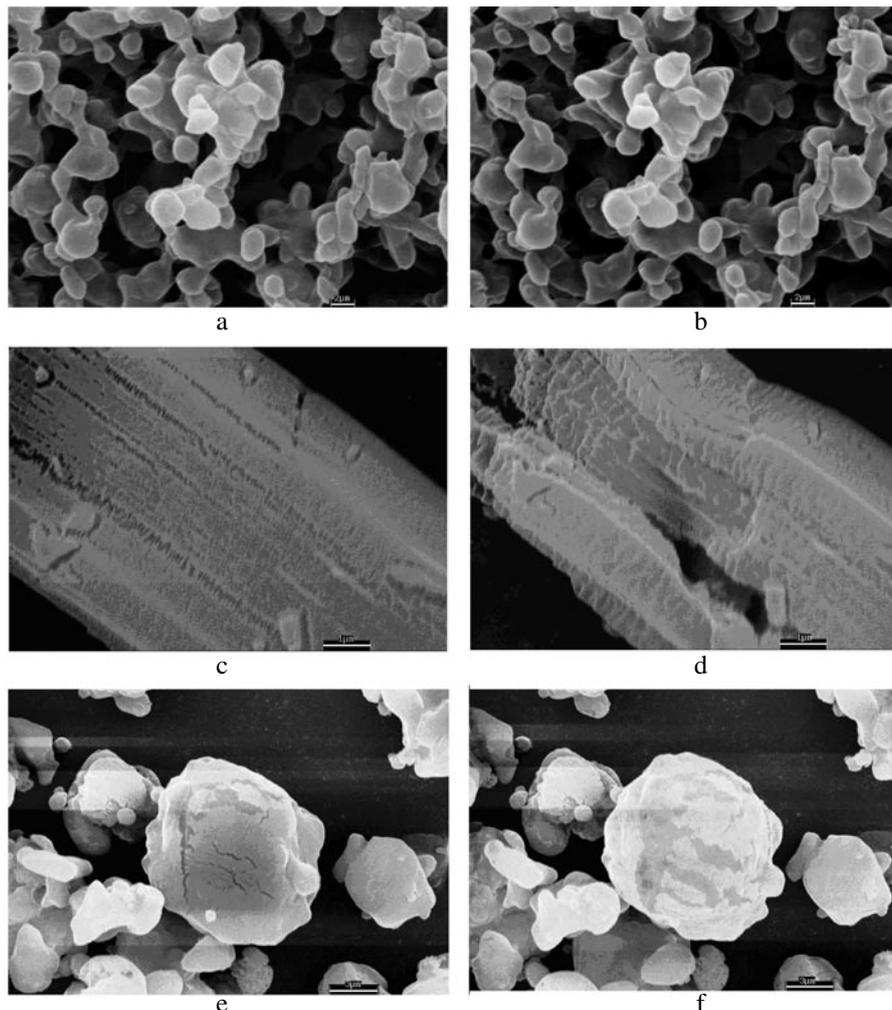

Fig. 1 SEM photographs of ultrafine HMX, NTO & HMX/NTO core/shell composite particles before and after exposure.
(a: ultrafine HMX; b: ultrafine HMX after exposure; c: NTO particle; d: NTO particle after exposure;
e: HMX/NTO core/shell composite particles ; f: HMX/NTO core-shell composite particles after exposure.)

hydrofuran (20 ml) at room temperature, then stirred for 30 min to dissolve the NTO completely. Ultrafine HMX particles (2.1 g) were put into the solution and then subjected to ultrasonic conditions for 2 min. to form a uniform suspension. OP-10 was added as a surfactant. The suspension was injected into a spray dryer with an air flow-rate of 340 l min^{-1} and a liquid flow-rate of 20 ml min^{-1}. A white powder was collected in a cyclone separator. After vacuum drying, the core/shell structure HMX/NTO composite particles (1.4 g) were obtained.

3. Results and discussion
3.1 Appearance and surface structure

SEM and AFM were used to observe the appearance of HMX/NTO composite particles. The results of the SEM studies are presented in Fig. 1. Figure 1a shows the appearance of ultrafine HMX particles. After the coating treatment, (Fig. 1e), the surface of HMX particles was changed, however, there were many flaws noted on the particle surface. This phenomenon could be explained by the possibility that in the process of SEM operation, the shell substance was decomposed with the electron beam bombardment. Furthermore, the same area had been exposed to electron beam for a while (2 min. approximately.) and the flaws expanded along the surface, shown in Fig. 1f. Additional electron bombardment experimental was conducted on NTO crystals and ultrafine HMX particles in the same conditions. As shown in Fig. 1d, under the action of an electron beam, NTO crystals were partly decomposed and the shape was changed compared to Fig. 1c which was taken prior to exposure to an electron beam. For ultrafine HMX particles, there was no obvious difference observed between the SEM photographs of before (Fig. 1a) and after (Fig. 1b) exposure. It can be assumed that the decomposed substance on the surfaces of composite particles is NTO and HMX is coated by NTO.

The AFM images of the composite particles and ultrafine HMX particles are shown in Fig. 2. It appears that the surfaces of the composite particles are potholed while the surfaces of HMX particles are smooth. It therefore appears that small NTO particles are deposited on the surfaces of HMX particles and therefore change the appearance of HNX particles. In the process of preparing HMX/NTO core/shell composite particles, the NTO solution was
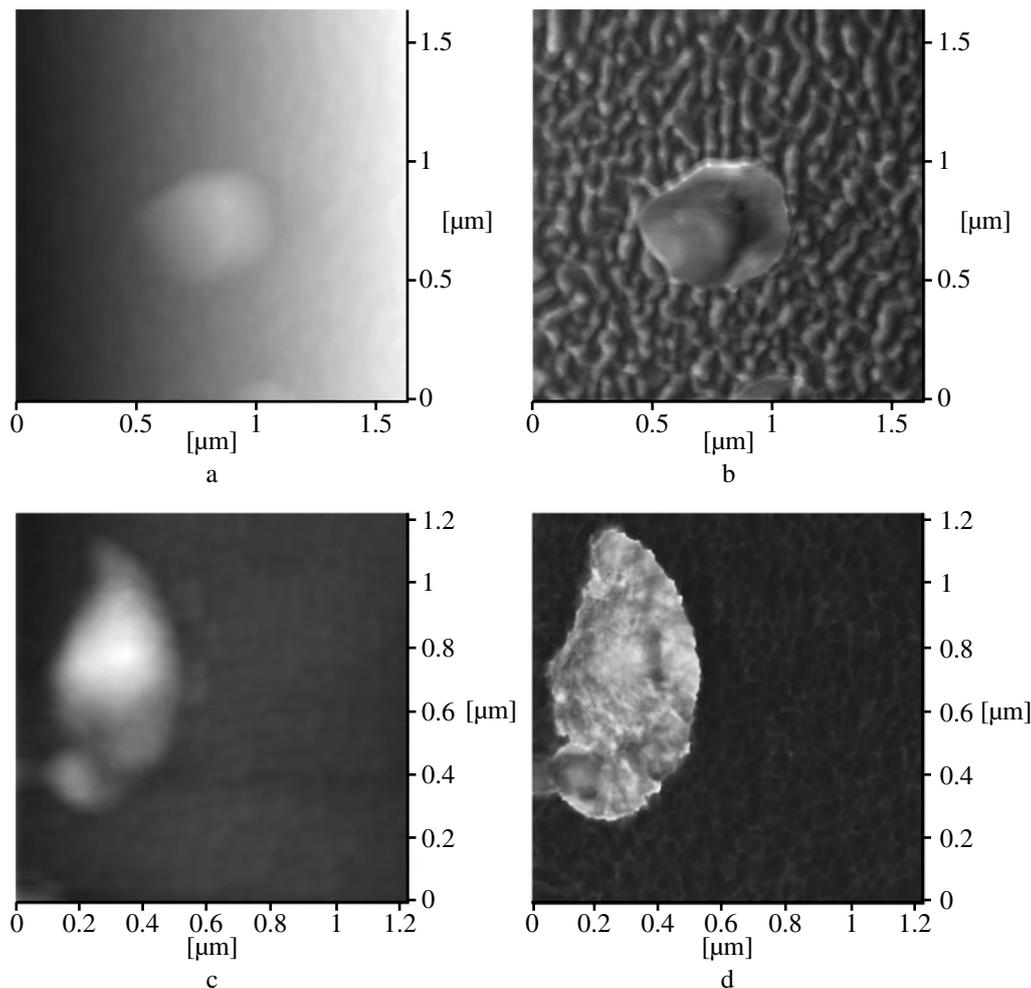

Fig. 2 AFM images. a: topography of ultrafine HMX, b: phase imaging of ultrafine HMX, c: topography of composite particle, d: phase imaging of composite particle.
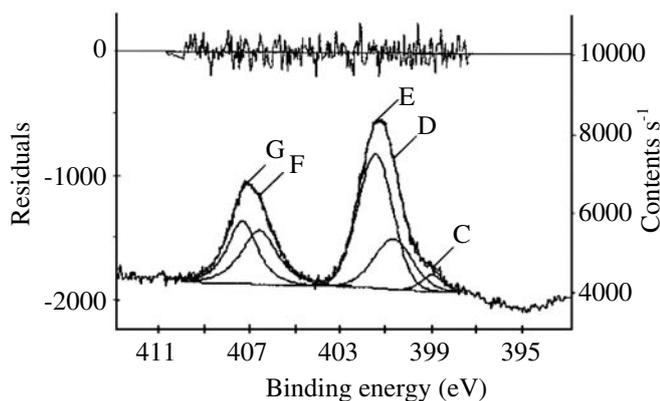
Fig. 3 N1S XPS spectrum for HMX/NTO core/shell composite particles.

atomized and crystallized from tetrahydrofuran and many small particles were formed, then deposited on the surface of HMX particles. However, due to polymer agglutination and volume limitations, it was difficult for NTO crystalline growth to occur.

Elemental composition of the composite particle surface was determined by XPS. Both HMX and NTO contain the element C, H, O and N. However, there was some difference between their N1s spectrum. The N1s spectrum of composite particles (shown in Fig. 3) was resolved into five peaks with two main peaks (G and E) at 407.34 eV and 401.49 eV respectively, corresponding to nitro-nitrogen bond and the other nitrogen bonds peculiar to NTO. The peaks (F and D) at 406.59 eV and 400.69 V respectively, contributed to the nitro-nitrogen bond and amine-nitrogen bond of HMX. The integrated areas of peak G and peak D were 2724.76 (cps·eV) and 2925.38 (cps·eV)

respectively and the area ratio was approximately 1:1. Therefore, the molecule ratio of NTO:HMX on the surface of composite particles was approximately 4:1 and the mass ratio was approximately 1.76 : 1. Additionally, the XPS spectrum revealed that some of the HMX particles were not coated or coated incompletely.

3.2 Thermal properties

A TG-DSC of the composite particles was conducted in order to determine the effect of the core/shell structure on thermal stability. As shown in Fig. 4, The DSC curve showed one endothermic peak and two exothermic peaks. The strong exothermic peak at 277 °C was the characteristic peak for the thermal decomposition of HMX and the endothermic peak at 189.7 °C corresponded to the phase transition of HMX. The exothermic peak with onsets at 246.8 °C and peak at 248.5 °C were due to NTO thermal decomposition. There was a shift of 5.4 °C toward the lower temperature region compared with the DSC results on a mixture of NTO and HMX particles at the same ratio. This could be explained by the possibility that a decrease in average particle size caused NTO decompose at lower temperature. As shown in the TG results, two evident mass losses occurred in the ranges of 230 °C - 254 °C and 254 °C - 347 °C . The mass loss at the lower temperature region apparently resulted from the rapid decomposition of NTO corresponding to the exothermic peak at 248.5 °C in the DSC curve. It is reported that NTO would lose approximately 67 wt% in the region between 205 °C and 262 °C, followed by a gradual loss of the remaining mass until approximately 330 °C [10]~[12]. Our experiment obtained similar results.

3.3 Impact and friction sensitivity

Impact and friction sensitivity results of the core/shell composite explosive and the physical mixture are summarized in Table 1. Two samples were tested having the
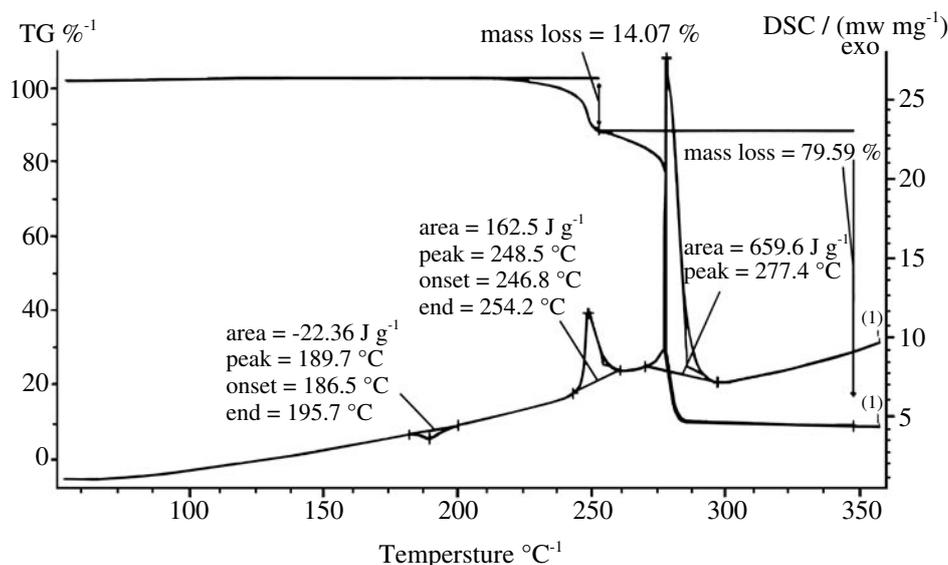

Fig. 4 TG-DSC curves for HMX/NTO composite particles. (Heat rate: 10 °C min⁻¹. Atmosphere : argon at flow rate of 2 ml min⁻¹. The sample amount: 1.4 mg)

Table 1　Summary of impact and friction sensitivity results.

Sample	Impact sensitivity	Friction sensitivity
Core/shell composite particles	8 %	12 %
Physical mixture	84 %	92 %
7 μm HMX	100 %	100 %
NTO	8 %	4 %

same mass ratio of NTO: HMX, however, the sensitivity of the core/shell composite material and a simple mixture to impact and friction were much different. The sensitivity to impact and friction of core/shell composite particles were much lower than that of the physical mixture. The composite particles were apparently desensitized by the process of coating. Both impact sensitivity and friction sensitivity of composite particles were close to those of neat NTO explosive.

4.　Conclusion

In this study, a spray drying method was used to prepare HMX/NTO core/shell energetic composite particles. The composite explosive obtained was studied by SEM, AFM, XPS, FTIR, TG-DSC and sensitivity tests to verify the structure and the influence of this process on the sensitivity properties of the composite explosive. According to experimental results, the major conclusions are summarized as following:

1) The spraying drying process coated small NTO particles onto the surface of the HMX particles and formed shell layer. This layer cracked when exposed to voltages of 20 kv from an SEM. From examination of SEM images, the flaws on the surface of composite particles increased with increased exposure to electron beam.

2) The AFM results showed that the surface of HMX particles were smooth, while the surface of the composite particles was potholed. In the process of coating, small NTO particles were absorbed onto HMX and resulted in a change the appearance of the HMX.

3) N1s of XPS data indicates that the mass ratio of NTO: HMX on the surface of the composite particles was 1.76 : 1, while the mass ratio was approximately 1 : 4 on average. More NTO was accumulated on surfaces of composite particles and the HMX particles were coated effectively.

4) The exothermic peak of NTO decomposition occurred at a temperature of 248.5 °C, a shift of 5.4 °C toward the lower temperature region compared with that of a simple HMX/NTO physical mixture with the same ratio of NTO:HMX. Apparently, the finer the particle, the lower the decomposition temperature.

5) The composite explosive was more insensitive to impact and friction stimuli and close to that of neat NTO explosive.

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