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Mechanical Pulverization for the Production of Sensitivity Reduced Nano-RDX*

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[ABSTRACT] Nanoscale particles of hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX) are obtained by means of the bi-directional superfine mill with controlled solid loadings and rotation speeds. 500g of raw RDX is addressed per batch. The size distribution of the nano-RDX is characterized by a laser particle size analyzer. The TEM observation shows that the nano-particles are semispherical having an average size of about 60 nm. The nano-RDX is free of contamination as detected by XPS. The peak thermal decomposition temperature of nano-RDX shows a decrease of 1.6 ℃, compared with that of raw RDX. Significant decrease happens in the friction, impact and shock sensitivities, especially a decrease of 59.9% in the shock sensitivity. It is expecting to promote large-scale manufacture of sensitivity-reduced nano-RDX which would work for insensitive munitions.

[KEY WORDS] nano-RDX, insensitive munitions, mechanical pulverization, process scale-up
[CLASSIFICATION CODE] TQ564 TJ55

1 Introduction

Nitroamine explosives, such as RDX having high detonation velocity, detonation heat and detonation pressure, are very indispensible in the fields of aeronautics and astronautics, Tactical Missile Defense and civil blasting, etc. However, the high mechanical sensitivities of the raw materials restrict their actual applications, so it has become a research focus on reducing their values. Surface coating has been found able to cut down the sensitivities of energetic materials. Synthesized nano CL-20, which was coated with cured nitrocellulose, was testified imperfect in that the thermal decomposition properties and the impact sensitivity were controlled by the coating material[1-2]. The impact and fiction sensitivities of the RDX coated with 2,4,6-trinitrotoluene (TNT) decreased obviously, whereas the explosion heat reduced to a certain extent[3]. As an inspiring fact, the particle size and its distribution affected the sensitivities of explosives significantly[4-5]. The mechanical sensitivities decreased with the decrease of particle size and varied with the change of size distribution and morphology of the particles[6-10]. Thus, much attention had been paid on the preparation of superfine energetic materials.

Nano-RDX was fabricated by Rapid Expansion of Supercritical Solution (RESS) with carbon dioxide as the carrier to achieve an average particle size of 110 ~ 120 nm and a narrow size distribution[11]. A spraying drying method was used to prepare nano-RDX with an average particle size of 40 ~ 60 nm. The superfine energetic materials could be also produced by a sol-gel synthetic approach[12-15]. Using 1,2-epoxypropane as the agent for accelerating the hydrolyzation of Fe(III) ions, nano-RDX particles within the range of 60 ~ 90 nm were obtained by sol-gel method after the complete etching of amorphous Fe_2O_3 by dilute hydrochloric acid[16]. Nano-size HMX with reticular structure was prepared by reprecipitation at room temperature[17]. In addition, solvent/nonsolvent recrystallization was employed to prepare nano-TATB with the size ranging from 27 nm to 41 nm[18].

However, it is very difficult to prepare nano-RDX

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massively and continuously in the aforementioned ways. In this study, 500g nano-RDX per batch can be successfully fabricated by the employment of a bi-directional mill. It is a promising method for the massive and continuous fabrication of insensitive nano explosives.

2 Experimental

2.1 Sample Preparation

The raw RDX, produced by Gansu Yin'guang Chemical Industry Group Co. Ltd, was suspended in a solution. In this suspension, the solid loading was 25% (mass percent) and the solution consisted of 90% (mass percent) deionized water and 10% (mass percent) ethanol. 500g of raw RDX were addressed for each batch.

The above suspension was put into a Bi-directional Superfine Mill designed by Li (Chinese Patent: CN2766956). In this device, the axis and the shell reversely rotated under 50 ℃ for 8 h at their own controlled speeds, respectively. The pulverization system was cooled down by the cycling water.

The optimized technology was determined by some factors, such as solids loadings and rotation speeds. The solid loading need to be controlled in the range of 20% ~ 30% (mass percent), and the appropriate rotation speed is from 90 r/min to 150 r/min. It is impossible to get nano-scaled RDX without selecting proper factors for this technology. The milled RDX was dried in the vacuum environment to obtain the final product.

2.2 Sample Tests

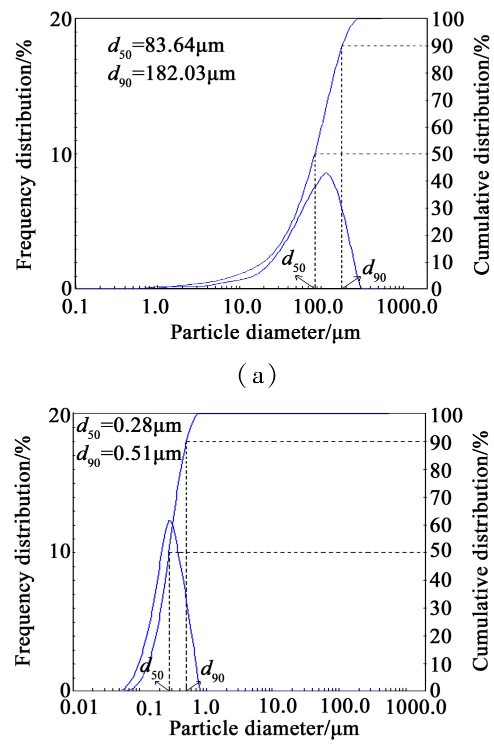
A laser particle sizer, Malvern Mastersizer Micro, was used to trace the particle size distribution of RDX. An optical microscope, Nikon eclipse 55i, was used to characterize the particle size and morphology of the raw RDX. The nano-RDX was characterized by JEOL JEM-200CX Transmission Electron Microscope (TEM). The purity of the milled product was detected by the X-ray Photoelectron Spectroscopy (XPS), PHI 5000 Versaprobe. Thermal properties of the samples were measured by the TA Model Q600 TG/DSC simultaneous thermal analyzer.

Two standards (80°, 2.45 MPa; 90°, 3.92 MPa) were adopted in the friction sensitivity test, and 50 trails were conducted to obtain a mean value of the explosion probability ($\bar{P}$, %) for each standard. The impact sensitivity characterized by the special height ($\bar{H}_{50}$) was calculated from 50 test values. The shock sensitivity was characterized by the Small Scale Gap Test (SSGT), in which the donor columns were made from the RDX refined by acetone with a density of (1.48 ± 0.01) g/cm^3 and the acceptor columns got a density of (1.63 ± 0.01) g/cm^3. The gap thickness (δ) was calculated by 25 effective values.

3 Results and Discussion

3.1 Size and Morphology Characterizations

The mean particle size and its distribution are tested and shown in Figure 1.



(a)

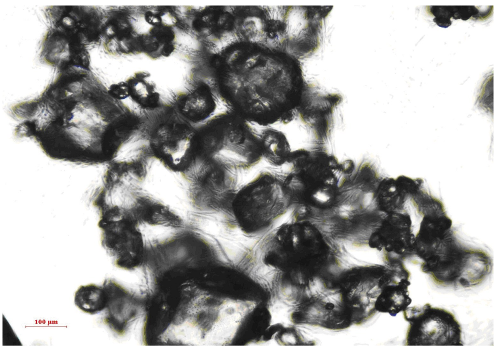
(b)

(a) raw RDX; (b) nano-RDX

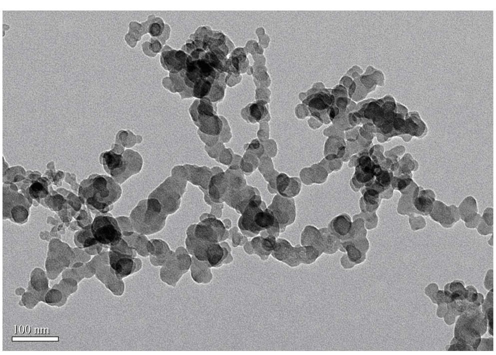
Fig. 1 Particle size distributions of raw RDX and nano-RDX

The whole raw RDX is almost in the micron range, having a mean particle size of 83.64 μm and a wide particle size distribution. The nano-RDX has a mean particle size of 0.28 μm, and most of the particles were under 0.51 μm. The particle size distribution of nano-RDX is much narrower than that of raw RDX.

As shown in Figure 2(a), it is irregular and heterogeneous for raw RDX. Some of the particles are bigger than 100 μm, and some are just several micron. The TEM image of nano-RDX is shown in figure 2(b) that the particles are semispherical and homogeneous having an average size of about 60 nm. The phenomenon, that the characterization result of the particle size analyzer is not in line with that of TEM, can be explained as the following two factors, the resolution and detection limit of the instrument (about 200 nm) and the agglomeration of the nano particles.



(a)



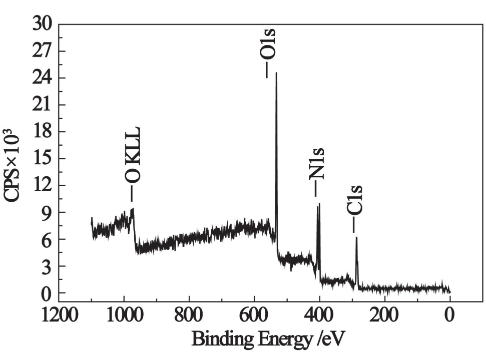
(b)

(a) raw RDX; (b) nano-RDX

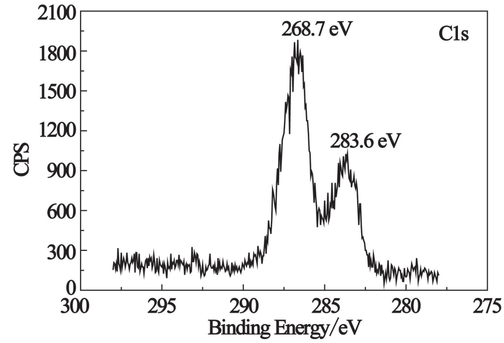
Fig. 2　Micrographs of raw RDX and TEM image of nano-RDX

3.2　Product Purity

The XPS spectrum is shown in Figure 3. Figure 3 (b) to (d) are the separated peaks referred to the electron excitation for C1s, N1s, and O1s of nano-RDX molecular, respectively.



(a)



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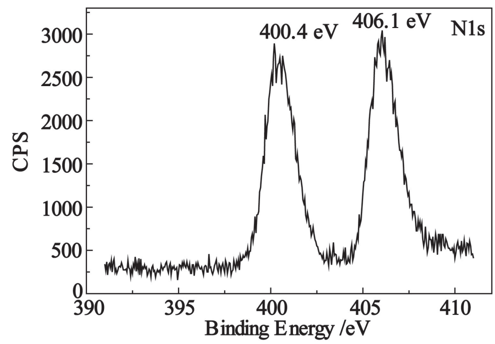
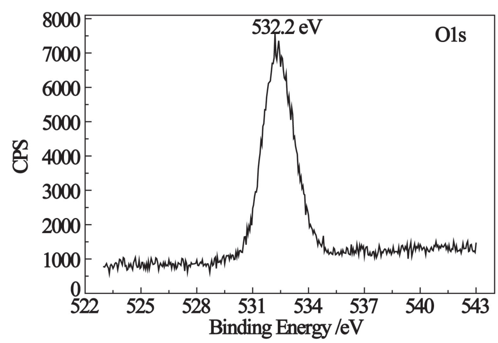


(c)



(d)

(a) the angerelectron of O; (b) the electron of C1s; (c) the electron of N1s; (d) the electron of O1s

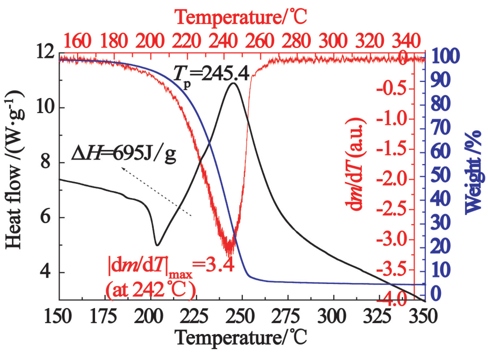
Fig. 3　XPS spectrum of nano-RDX

As shown in Figure 3, the nano-RDX is exhibited 4 kinds of peaks, corresponding to 4 kinds of electrons, the auger electron of O, the electron of C1s, the electron of N1s and the electron of O1s. Furthermore, these aforementioned excited 1-orbital electrons are corresponding to the bonds of N—O, N—N, N—C and C—H. It means that there are only 4 kinds of elements, C, H, O and N, and there are no incoming functional groups. There are no contaminants incoming during the pulverized process.

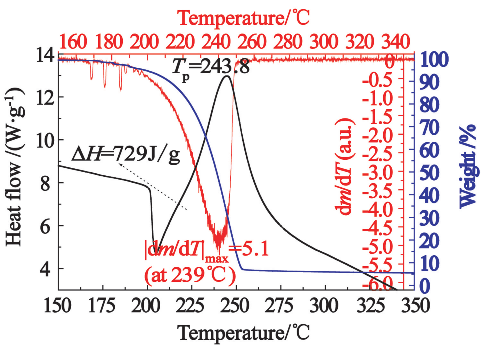
3.3　Thermal Characterizations

The TG/DSC traces and DTG curves are shown in Figure 4.

The initial and the ending weight loss temperatures of nano-RDX are both a bit lower than those of raw RDX. The maximum weight loss temperature for nano-RDX is 3 ℃ lower than that of raw RDX, and the peak thermal decomposition temperature of nano-RDX is 1.6 ℃ lower than that of raw RDX. It is also shown that the maximum weight loss rate of nano-RDX is 1.7



(a)



(b)

(a) raw RDX; (b) nano-RDX

Fig. 4 TG/DSC traces and DTG curves of raw RDX and nano-RDX

higher than that of the raw material and the calculated decomposition heat (ΔH) for nano-RDX is 34 J/g higher than that of the raw one. These are attributed to the greater specific surface area and the higher surface energy of nano-RDX, compared with the raw one.

3.4 Sensitivity Analysis

The friction sensitivity is tested and the results are listed in Table 1.

Tab. 1 Friction sensitivity of raw RDX and nano-RDX

Samples	$\bar{P}$ /%	
	80°, 2.45MPa	90°, 3.92MPa
raw RDX	74	98
nano-RDX	58	94

The average explosion possibility of nano-RDX is lower than that of raw RDX for 16% at 80°, 2.45 MPa and 4% at 90°, 3.92 MPa, respectively. This can be explained that the increase of stimulus would lead to the decrease of test resolution.

As listed in Table 2, the special height of nano-RDX is higher than that of raw RDX by 32.60 cm under the 2 kg drop-hammer and 6.92 cm under 5 kg drop-hammer, respectively. The impact sensitivity is reduced 71.6% under the 2 kg drop-hammer and 45.4% under the 5 kg drop-hammer, when the raw materials are pulverized to be in the nano-scale.

Tab. 2 Impact sensitivity of raw RDX and nano-RDX

Samples	2 kg hammer		5 kg hammer	
	$\bar{H}_{50}$/cm	$S_{dev.}$	$\bar{H}_{50}$/cm	$S_{dev.}$
raw RDX	45.53	1.30	15.25	1.17
nano-RDX	78.13	1.10	22.17	1.12

As listed in Table 3, the gap thickness for nano-RDX is 9.21 cm lower and the standard deviation ($S_{dev.}$) is smaller than those of the stuff. The shock sensitivity is reduced 59.9% and the detonation stability is better, when raw materials is milled for nano particles.

Tab. 3 Shock sensitivity of raw RDX and nano-RDX

Samples	gap thickness (δ)	
	δ/mm	$S_{dev.}$
raw RDX	15.38	0.41
nano-RDX	6.17	0.32

4 Conclusions

Five hundred gram nano-RDX per batch is obtained by means of the bi-directional superfine mill. The nano particles are semispherical and pure having an average size of about 60 nm. The maximum weight loss rate and the decomposition heat of nano-RDX are higher than those of the raw materials.

The mechanical sensitivities are decreased apparently, especially the shock sensitivity, decreased by 59.9%. The reduction of sensitivities may mainly be attributed to the decrease of occlusions and dislocations after the raw RDX milled.

Reference

[1] Tappan B C, Brill T B. Thermal decomposition of energetic materials 85: cryogels of nanoscale hydrazinium diperchlorate in resorcinol-formaldehyde [J]. Propellants, Explosives, Pyrotechnics, 2003, 28(2): 72-76.

[2] Tappan B C, Brill T B. Thermal decomposition of energetic materials 86: cryogel synthesis of nanocrystalline CL-20 coated with cured nitrocellulose [J]. Propellants, Ex-

plosives, Pyrotechnics, 2003, 28(5): 223-230.
[3] An C W, Li F S, Song X L, et al. Surface coating of RDX with a composite of TNT and an energetic-polymer and its safety investigation [J]. Propellants, Explosives, Pyrotechnics, 2009, 34(5): 400-405.
[4] Song Xiaolan, Li Fengsheng, Zhang Jinglin, et al. Influence of particle size, morphology and size distribution on the safety and thermal decomposition properties of RDX [J]. Journal of Solid Rocket Technology, 2008, 31(2): 168-172.
[5] Siviour C R, Gifford M J, Walley S M, et al. Particle size effects on the mechanical properties of a polymer bonded explosive [J]. Journal of Materials Science, 2004, 39 (4): 1255-1258.
[6] Yang Binlin, Chen Rongyi, Cao Xiaohong . Influence of particle size of RDX on the detonation properties [J]. Initiators and Pyrotechnics, 2004 (3): 50-52, 56.
[7] Song Xiaolan, Li Fengsheng. Dependence of particle size and size distribution on mechanical sensitivity and thermal stability of hexahydro-1, 3, 5-trinitro-1, 3, 5-triazine [J]. Defence Science Journal, 2009, 59(1): 37-42.
[8] Liu Yucun , Wang Jianhua , An Chongwei , et al. Effect of particle size of RDX on mechanical sensitivity [J]. Chinese Journal of Explosives and Propellants, 2004, 27 (2): 7-9.
[9] Song Xiaolan, Wang Yi, An Chongwei, et al. Dependence of particle morphology and size on the mechanical sensitivity and thermal stability of octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine [J]. Journal of Hazardous Materials, 2008, 159(2-3): 222-229.
[10] Song Xiaolan, Guo Xiaode, Zhang Jinglin, et al. Dependence of size and size distribution on safety performance of nitramine explosives and the multi-component explosives [J]. Initiators and Pyrotechnics, 2007(4): 17-21.
[11] Stepanov V, Krasnoperov L N, Elkina I B, et al. Production of nanocrystalline RDX by rapid expansion of supercritical solutions [J]. Propellants, Explosives, Pyrotechnics, 2005, 30(3): 178-183.
[12] Tillotson T M, Hrubesh L W, Simpson R L, et al. Sol-gel processing of energetic materials [J]. Journal of Non-Crystalline Solids, 1998, 225(1): 358-363.
[13] Cudzilo S, Kiciński W. Preparation and characterization of energetic nanocomposites of organic gel-inorganic oxidizers [J]. Propellants Explosives Pyrotechnics, 2009, 34(2): 155-160.
[14] Tillotson T M, Gash A E, Simpson R L, et al. Nanostructured energetic materials using sol-gel methodologies [J]. Journal of Non-Crystalline Solids, 2001, 285 (1-3): 338-345.
[15] Li J, Brill T B. Nanostructured energetic composites of Cl-20 and binders synthesized by Sol gel methods [J]. Propellants, Explosives, Pyrotechnics, 2006, 31(1): 61-69.
[16] Song Xiaolan, Li Fengsheng, Zhang Jinglin, et al. Preparation, mechanical sensitivity and thermal decomposition characteristics of RDX nanoparticles [J]. Chinese Journal of Explosives and Propellants, 2008, 31 (6): 1-4.
[17] Zhang Yongxu, Liu Dabin, Lü Chunxu. Preparation and characterization of reticular nano-HMX[J]. Propellants, Explosives, Pyrotechnics, 2005, 30(6): 438-441.
[18] Yang Guangcheng, Nie Fude, Huang Hui, et al. Preparation and characterization of nano-TATB explosive [J]. Propellants, Explosives, Pyrotechnics, 2006, 31(5): 390-394.

机械粉碎法制备不敏感纳米 RDX

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［摘　要］ 使用双向旋转球磨机,通过控制固含量和转速,成功制备了纳米 RDX。实验过程中,RDX 单次处理量为 500 g。采用激光粒度仪表征纳米 RDX 的粒度分布,并通过透射电子显微镜(TEM)观察纳米 RDX 颗粒的大小和形貌,发现其平均粒径在 60 nm 左右,呈类球形。通过 X 光电子能谱(XPS)分析表明,纳米 RDX 中不含有污染物。与原料 RDX 相比,纳米 RDX 的热分解峰温提前了 1.6 ℃;其机械感度降低明显,尤其是冲击波感度,降幅为 59.9%。结果表明:有望实现纳米 RDX 的大规模生产并为不敏感弹药服务。

［关键词］ 纳米 RDX　不敏感弹药　机械粉碎　大规模