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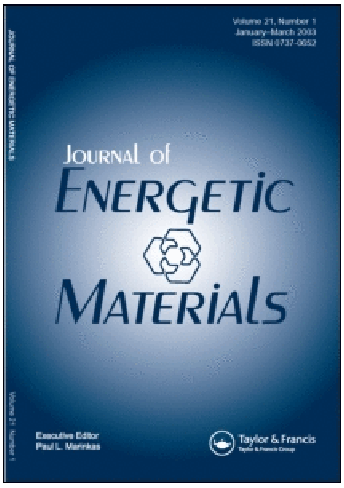

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Preparation and Characterization of Nano-NTO Explosive

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Preparation and Characterization of Nano-NTO Explosive

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Nano-NTO particles (5-nitro-2,4-dihydro-3H-1,2,4-triazole-3-one) were prepared by the spray freezing into liquid (SFL) method. Scanning electron microscopy (SEM), atomic force microscopy (AFM), X-ray diffraction (XRD), thermogravimetric analysis (TG), and differential scanning calorimetry (DSC) analysis methods were used to characterize the particles. The results show that the NTO particles have an elongated shape with a size of 70–90 nm. With NTO particle size reduced to the nanometer range, the XRD diffraction peaks broaden and the peak intensity weakens. Nano-NTO decomposes at a lower temperature and is less sensitive to impact stimuli compared with micro-NTO.

Keywords: energetic materials, nanoparticles, SFL, NTO

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Introduction

In the field of energetic materials, nano-structured components have very important applications. The sensitivity and the performance change significantly when the size of the energetic particles is reduced to nanometer-scale. Preparation of nano-energetic materials is of interest to scientists and engineers. Many researchers [1–5] prepared RDX (cyclotrimethylenetrinitramine), CL-20 (hexanitrohexaazaisowurtzitane), and other explosives and pyrotechnics with nanostructures by the sol-gel method. Frolov et al. [6] obtained nano-sized ammonium nitrate and RDX particles by the sublimation/condensation process. Recently, we [7] have reported the preparation of nano-TATB using the solvent/nonsolvent recrystallization method with concentrated sulfuric acid as solvent and water as non-solvent, resulting in particle size of approximately 80 nm.

5-Nitro-2,4-dihydro-3H-1,2,4-triazole-3-one (NTO) is a compound with high energy and less sensitivity. It possesses high energy release on decomposition and a high velocity of detonation (VOD). In addition, NTO exhibits good thermal stability, low sensitivity to radiation damage, and is relatively less sensitive to impact and spark than RDX. Many applications have been proposed for NTO, such as in melt-castable, general-purpose, and insensitive high-explosive (IHE) formulations and plastic-bonded explosives. This compound is also useful in non-azide inflating propellant compositions for automobile air bags. Owing to the acidic nature of NTO (pKa 3.67), it forms salts with a large number of metals as well as aromatic and aliphatic amines, which are also highly useful. NTO recrystalizes from water as large, jagged, rod-like crystals that tend to agglomerate. This creates problems with explosive formulations where unfavorable crystal shape and size can cause handling difficulties, and formulations may become highly viscous and difficult to pour [8–10]. By using the resolution solvent/non-solvent method Kayser [11] prepared finely divided particles of NTO with surface areas of 5.7 m^2/cm^3. In this article, we report the preparation of nano-NTO by the

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spray freezing into liquid (SFL) method, which is a novel process developed to produce microparticles or nanoparticles. Particles are formed by atomization of an aqueous feed solution containing the objective compound into a cryogenic liquid (e.g., liquid nitrogen or liquid carbon dioxide). Another objective is to develop and demonstrate the use of novel SFL particle engineering technology to minimize the particle size of explosive crystals and to determine the properties of the fine particles so obtained.

Experimental

Materials

Neat NTO with purity of 99% was purchased. Polyoxyethylene (10) alkylphenol ether (OP-10), a surfactant, was obtained from Shanghai Auxiliary Co., Ltd. Ultrapure water was prepared in-house and liquid N_2 was purchased from Sifang Company.

Instrumentation and Apparatus

The SFL apparatus was made in-house (shown in Fig. 1). Pressurized air (Fig. 1A) at 1.6 MPa was cooled and dried. The stirrer (Fig. 1F) was set at 550–600 r/min. The cryogenic liquid cell (Fig. 1H) was coated with heat insulation. A water purifier by Milli-Q ACAD EMIC was used to prepare purified water. Drying was carried out in a Thermosavant MODULYOD-230 freeze dryer at a temperature of -45°C. Scanning electron microscopy (SEM) studies were conducted with a Stereoscan Leo440s analyzer (Germany) with an accelerating voltage of 25 kv and a scanning rate of 20 frames/s. Atomic force microscope (AFM) images were collected on an SPA300HV analyzer in tapping mode. The sample (0.5 g) was pressed into a tablet ($\phi 10\,\text{mm} \times 5\,\text{mm}$) at 10 KN by a WE-30 machine. X-ray diffraction (XRD) analysis was carried out using a Philips XPERT PRO diffractometer with filtered 0.154-nm monochromatic Cu Kα radiation. The sample was placed in quartz sample holder. Data were collected in the step mode from 3° to 70° with a 0.02° step size. Thermogravimetry and differential

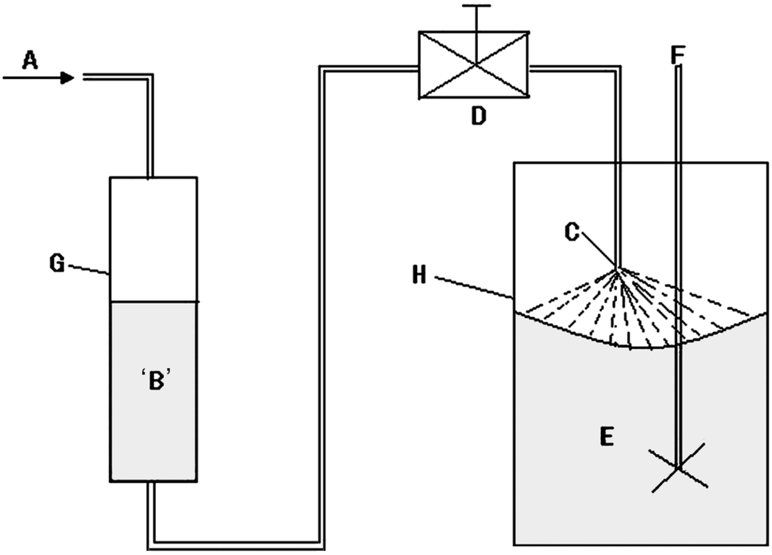

Figure 1. Experimental apparatus for the spray freezing into liquid process. (A) Pressured air, (B) NTO solution, (C) atomization nozzle, (D) valve, (E) liquid nitrogen, (F) stirrer, (G) solution cell, (H) cryogenic liquid cell.

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scanning calorimetric (TG-DSC) studies were conducted using a NTEZSCH STA 449 C instrument at a heating rate of 10°C/min with argon at a flow rate of 2 mL/min and the sample amount was 1.5 mg. The specific surface area was measured using a Brunauer-Emmett-Teller (BET) specific surface area analyzer by Quantachrome, NOVA2000e (America) using nitrogen as adsorbate. The degassing of a sample was conducted at the temperature of 80°C for 6 h. Drop height for 50% initiation (H_{50}) was measured with a WL-1 drop weight impact machine. In this test, a 2.5-kg weight is dropped from a preset height onto a 35-mg powder sample of material.

Spray Freezing into Liquid Nitrogen Process

Neat NTO (2 g) and a small quantity of OP-10 were added to stirred ultra-pure water at room temperature. After complete dissolution, the mixture was filtered to remove the insoluble impurities. The filtrate was added to the SFL apparatus. The SFL process and freeze-drying treatment yielded a white powder product with low bulk density.

Results and Discussion

Preparation of Nano-NTO

SFL is a novel particle engineering process developed for forming microparticles and nanostructured particles by atomizing an aqueous feed solution into a cryogenic liquid. In this study, the cryogenic liquid was liquid N_2 (Fig. 1E). In order to preserve the higher order structure of NTO by avoiding the formation of ice crystals, it is essential for the solution (Fig. 1B) to pass through the vapor over the liquid very rapidly. In the experiments reported by Webb et al. [12], the distance from the nozzle to the surface of the liquid nitrogen was about 8 cm and the individual droplets fell through the vapor phase for about 1 s before reaching the liquid nitrogen surface. During this 1 s, phase separation was induced by freezing, and therefore solute nucleation may occur. To prevent the phase separation induced by the low temperature of the vapor over liquid, pressurized air (1.6 MPa, Fig. 1A) was employed. A high speed of solution droplet was obtained, which minimized the time of the droplet's passing through the vapor and decreased the degree of phase separation in the droplets. Low concentration offers an advantage in controlling the size of production particles, and the much lower concentration of solution for this system may be expected to produce smaller particles. For a given aqueous droplet size, the lower solute concentration will lead to a smaller number of collisions between solute molecules as the water freezes, inhibiting particle growth. Furthermore, as has been seen for polyethylene oxide solutions [13], a lower concentration may also lead to more complete atomization because of the lower viscosity. In this preparation, the atomization of the droplets resulting from the high-pressure drop through the small orifice nozzle produces extremely small droplets. The low temperature of liquid nitrogen (−196°C) and small droplet

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sizes produced by high-pressure atomization allowed very rapid freezing rates to be achieved. It has been reported that the maximum cooling rates achievable with liquid nitrogen are in the order of $10^3\,\mathrm{Ks}^{-1}$ when the droplet size is less than $10\,\mu\mathrm{m}$ [14, 15]. Under typical industrial freeze-drying conditions, solutions are cooled relatively slowly, perhaps on the order of $1\text{–}10\,\mathrm{Ks}^{-1}$ [16]. Furthermore, the rapid freezing rates utilized in the SFL process generate significant supersaturation and thus rapid nucleation rates of dissolved substances [16]. The rapid nucleation and restricted growth that occur after the fine droplets are formed and frozen leads to extremely small primary particles following sublimation at low temperature and low pressure.

Appearance

The appearance of nano-NTO was observed using SEM and AFM. The results are shown in Figs. 2 and 3, respectively. In the SEM photograph, the nano-NTO particles have an elongated shape, and the width of the particles is in the range 70–90 nm. For nanoscale materials, a large proportion of atoms are on the surface or interface. The particles were provided with high surface energy and tended to aggregate. In the AFM photograph, the shapes of the particles were changed by the pressing process, but the particle sizes were observed to be in the range of 50–100 nm. Various factors contributed to the limited particle growth during SFL processing. The atomized droplets were immediately frozen upon the rapid freezing rate, and the rapid freezing rates shortened the time for particle growth. Also, the surfactant in the unfrozen domains in the sprayed droplets inhibits particle coalescence and crystal growth. Various other factors may broaden the particle size distribution. As the atomized droplets pass through the vapor gap above the liquid nitrogen, they may collide and coalesce. The solutes may precipitate and grow in the unfrozen liquid droplets as they cool or coalesce. The particle morphology is not stable until the droplets are fully solidified on contact with the liquid nitrogen phase below the vapor. Therefore, we obtained the

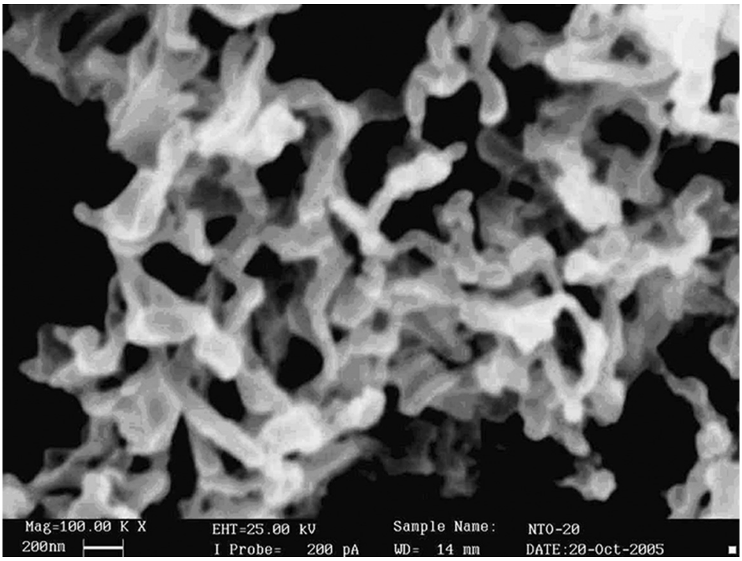

Figure 2. Scanning electron microscopy of nano-NTO.

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nanostruactured particles with width of 70–90 nm and length of 200–300 nm. The specific surface area (BET) was determined by the BET method and the result is 18.1 m^2/g.

X-Ray Analysis

To study the effect of SFL on the crystal structure and to estimate the crystal size, X-ray characterization was used and the result is shown in Fig. 4. The X-ray curves of nano-NTO (Fig. 4B) and micro-NTO (Fig. 4A) were compared. It is found that the peaks of nano-NTO have pretty much the same diffraction angles as those of micro-NTO, implying that this nano-NTO is α-NTO, the same phase as micro-NTO. Furthermore, in Fig. 3, the peak broadening and strength weakening of nano-NTO are observed. When the grain size of a material is reduced to the nanometer range, its X-ray yield strength decreases with decreasing grain size. The estimation of grain size is usually achieved by analyzing the peak broadening of one or more

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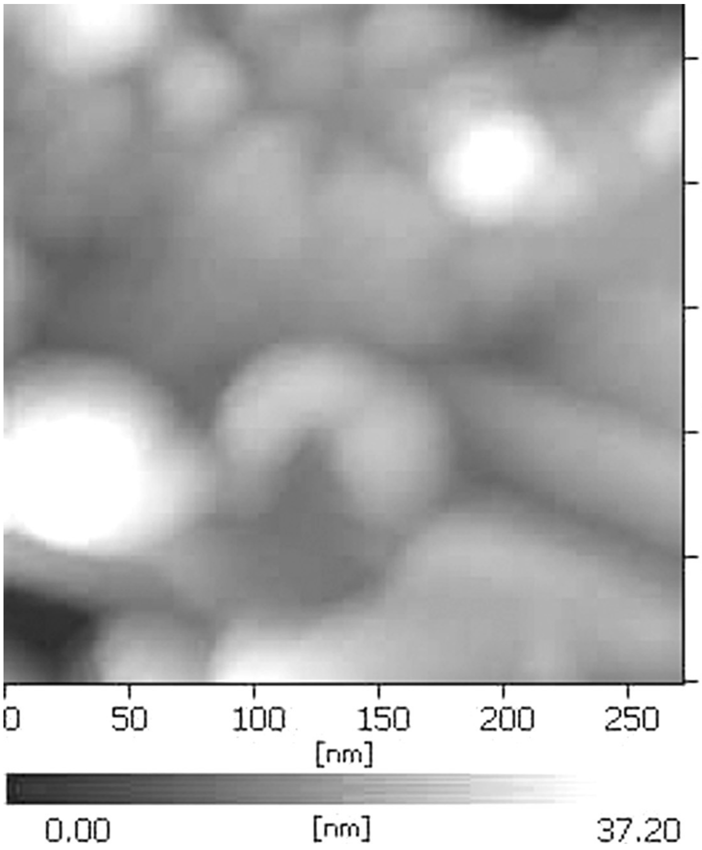

Figure 3. Atomic force micrograph of nano-NTO.

diffraction peaks. According to the Scherrer formula, the grain size L can be expressed as a function of the full-width at half-maximum (FWHM) of the diffraction peak

$$L = 0.89\lambda/\beta\cos\theta \tag{1}$$

where λ is the wavelength of the X-ray source (0.154 nm), β is the width at half height after correcting for the instrument broadening, and θ is the Bragg angle of the peak used for the calculation. β was determined by $\beta = B - b$, where B is the actual peak width and b is determined by the fraction peak

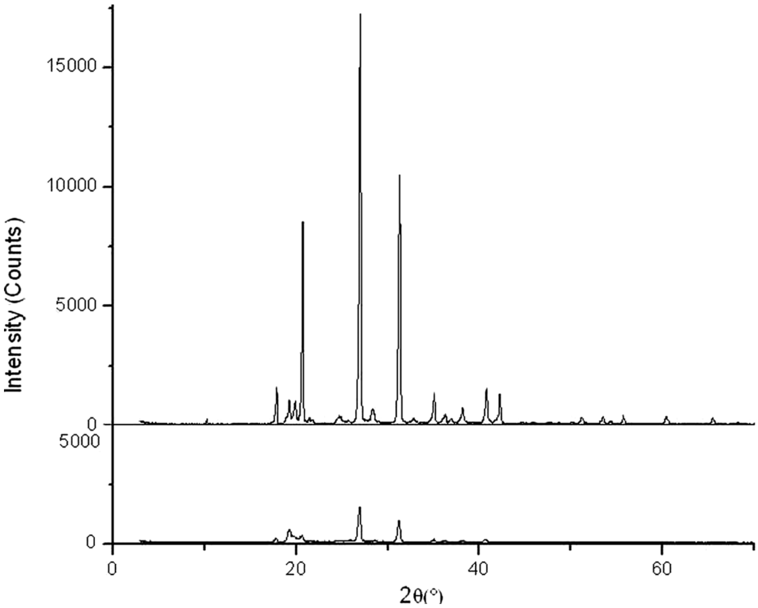

Figure 4. XRD curves of micro-NTO (a) and nano-NTO (b).

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width of the micro-NTO with approximately 100 µm. The calculated grain sizes of the sample are listed in Table 1.

As shown in Table 1, the corrected average particle size is approximately 170 nm. The particle has an elongated shape with width of approximately 70–90 nm and length

Table 1
Grain size of nano-NTO determined by scherrer analysis of XRD data

Position (2θ)	B (°)	B (°)	$\beta = B - b$ (rad)	Corrected average particle size (nm)
20.2	0.31	0.15	0.000883	174
26.9	0.34	0.18	0.000917	154
31.2	0.35	0.20	0.000794	179

approximately 250 nm. Therefore, the calculated corrected average particle size is close to that observed.

Thermal Properties

Owing to their extremely small size, nanometer structured materials are characterized by a large proportion of surface or interface atoms. The vibrational and positional enthalpy and entropy of surface or interface atoms of nanometer materials evidently differs from that of atoms within the crystals, which may significantly alter a variety of physical properties, including thermal properties. Nano-NTO and micro-NTO were examined by TG and DSC analyses. The results are shown in Fig. 5. It is indicated that the exothermic peak of nano-NTO, due to thermal decomposition, occurs in the range of 240°C–270°C. There is a shift of approximately 16°C toward the lower

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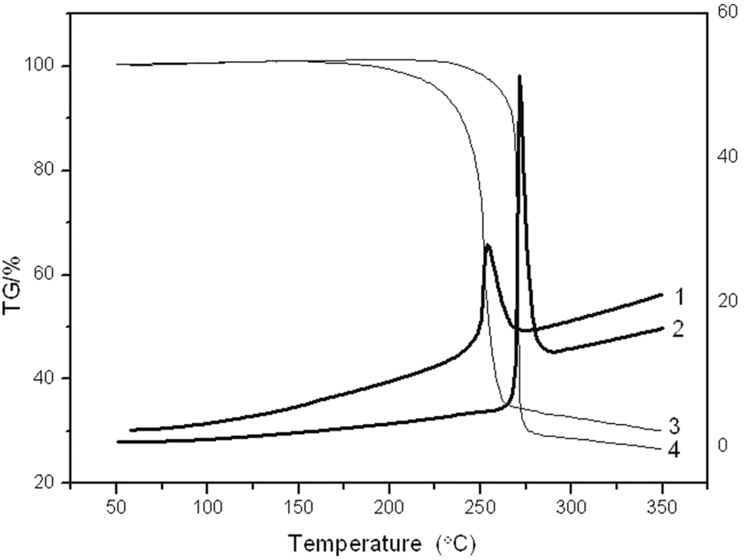

Figure 5. Thermal analysis results of micro-NTO and nano-NTO. (1, DSC curve of nano-NTO; 2, DSC curve of micro-NTO; 3, TG curve of nano-NTO; 4, TG curve of micro-NTO).

temperature region compared with the DSC result of the micro-NTO. Furthermore, TG curves show that nano-NTO begins losing weight at about 170°C, moving up approximately 40°C compared with that of the micro-NTO. This can be explained by the fact that a decrease in average particle size causes NTO decompose at lower temperature.

Impact Sensitivity

The impact sensitivity of an energetic material to unintended initiation is an important safety factor in their use. The determined H_{50} for micro-NTO and nano-NTO were 26.2 and 35.5 cm, respectively. This shows that, through the SFL process, the collected fine powder has lower impact sensitivity than the NTO starting material. This decrease can be explained by the possibility that the average pore diameter in ultra-fine particles is too small to become a hot spot under the impact stimulus.

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Summary

SFL is a novel method for the production of microparticles and nanoparticles. The fine atomization and ultra-rapid freezing with no capillary forces in the sublimation process enabled the formation of particles with a small size and a higher content. By spraying the NTO aqueous solution through a nozzle directly into liquid nitrogen, nano-NTO particles with elongated shape and size of 70–90 nm were prepared. The XRD peaks of nano-NTO are obviously different from those of micro-NTO; peak broadening and strength weakening of nano-NTO are observed. Experimental results shows that nano-NTO decomposes at a lower temperature and is less sensitive to impact stimuli compared with micro-NTO.

Acknowledgment

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