Research paper

Nano 1,3,5-triamino-2,4,6-trinitro-benzene particles prepared by "green" recrystallization

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Abstract

A novel, an environmentally friendly process of green recrystallization was employed to prepare TATB nanoparticles. The process was named as solvent/anti-solvent technique using the ionic liquid 1-ethyl-3-methylimidazolium acetate ([Emim] Ac) combined with DMSO as solvent, distilled water as an anti-solvent. The characteristic properties of nano-TATB thus obtained were confirmed by scanning electron microscope (SEM), X-Ray diffraction (XRD), particle size analysis. Moreover, the thermal decomposition properties and impact sensitivity were conducted and analyzed. Results show that the recrystallized TATB particles with a spherical shape range from 30 nm to 100 nm. The XRD pattern of recrystallized TATB is in good agreement with the raw TATB, indicating that this recrystallization process does not change the crystal type of TATB. The recrystallized TATB has a remarkable thermal stability in spite of the low temperature of exothermic peak than the raw TATB at various heating rates. The drop height of recrystallized TATB is higher than 100 cm, revealing that the nano-TATB particles exhibit outstanding insensitive characteristic.

Keywords : TATB, ionic liquid, anti-solvent recrystallization, nanoparticles, thermal decomposition

1. Introduction

Generally, for explosives, high performance has been a prime requirement. But during the past two to three decades, comprehensive property has become desirable[1)-5)]. Synthesization of new energetic materials as well as size reduction and morphology optimization of the known solids serve as measures to improve the properties of explosives. Factually, a crystallization step, usually as the final process, does work not only to modify energetic materials already existed, but also newly developed materials[6)].

As a well known insensitive high explosive, 1,3,5-triamino-2,4,6-trinitro-benzene (TATB) is widely used in modern warheads for its amazing thermal and mechanical stabilities. Recrystallization of TATB can be categorized into two methods: cooling recrystallization and anti-solvent crystallization[7)-9)]. TATB slides contain many strong hydrogen-bonds (H-bond)[10)], which result in extremely insoluble in common solvents such as ethanol, acetone, etc. Actually Dimethyl sulfoxide (DMSO) , sulfolane, concentrated H_2SO_4 and alkali are usually used as solvents for TATB dissolution. Most of the solvents mentioned above show poor solubility such as DMSO of 70 ppm, sulfolane of 13 ppm. But, concentrated sulfuric acid should be stressed, for its distinguished TATB dissolubility of 24 g[11)]. However, recrystallization using sulfuric acid on full scale would result in not only equipment corrosion but also serious environment pollution.

As a result, identifying a suitable solvent of TATB recrystallization becomes especially important. A number of publications describe the attractive dissolubility of TATB in ionic liquids, especially in 1-ethyl-3-methylimidazolium acetate ([Emim]Ac)[11)-16)]. Their results all show that TATB is much more soluble in [Emim] Ac than in other organic solvents. Even with the co-solvent of [Emim] Ac and DMSO, the solubility of TATB is hundreds of times more than that in DMSO. It

opens the way for recrystallization and morphology modification of TATB.

It is well known that nano-energetic materials exhibit amazing performance[17]. For TATB, nano-size means more sensitive to short pulse stimuli [18] as well as better mechanical performance such as preventing the irreversible expansion of PBXs[19]. However, research of nano TATB is very little due to its low solubility in common solvents. Guangcheng Yang et al. prepared nano TATB by solvent / anti-solvent technique using concentrated sulfuric acid as solvent and water as anti-solvent[18]. Nano TATB crystals with size of 60 nm were obtained and characterized using TEM, AFM and XRD. This study was concerning the preparation of the nano-sized TATB using anti-solvent technique with the [Emim] Ac and DMSO as combined solvent. Furthermore, the morphology, crystal type and thermal decomposition properties and impact sensitivity were investigated.

2. Experimental parts

2.1 Materials and setup

Analytical grade (AR) DMSO was purchased from Tianjin Kemio Chemical Reagent Co., Ltd. Ionic liquid [Emim] Ac was provided by Shanghai Chengjie Chemical Co., Ltd. Analytical grade ethanol was produced by Tianjin Den Chemical Reagent Co., Ltd. Raw TATB was provided by 204 institute.

2.2 Preparation of nano TATB

With respect of previous work on the experimental conditions of TATB dissolution in DMSO and ionic liquid [Emim] Ac respectively, as well as various mixtures of the two solvents, 10.0 g TATB was dispersed to the mixture of DMSO (950 g) and [Emim] Ac (50 g) in the dissolution tank (1L) which was placed in an ultrasonic generator. The mixed liquid was heated from room temperature to 90°C. As soon as the TATB was dissolved, switch on the magnetic forced stirrer and injecting pump in sequence, carefully controlling the operation parameters at certain values. The precipitates formed in the recrystallizing tank containing 20 L water, in a yellow appearance, were filtered under pressure and washed with water followed by ethanol for several times respectively. Then the process terminated in freeze-drying. Yellow crystals of TATB were obtained finally and characterized by means of special, normative methods one after another.

2.3 Characterizations and properties

2.3.1 Crystal morphology observation

H Scanning electron microscopy (SEM) images were obtained using a Hitachi S-4800 microscope operated at an acceleration voltage of 5.0 kV.

2.3.2 Particle size analysis

The recrystallized TATB solids were dispersed in ultrasonic surged water, which is convenient to the particle size analysis that employs the particle size analysis meter of Brookhaven BI-90Plus.

2.3.3 XRD pattern test

X-ray diffraction data were collected by powder X-ray diffraction using DANDONG HAOYUAN 2700 X-ray diffractometer with Cu-Ka radiation. The X-ray tube operating conditions were set as 40 kV and 30 mA. The samples were scanned from 10° to 55° in 2θ, with an increment of 0.03° and a scan speed of 0.5 s per step.

2.3.4 Thermal decomposition analysis

DSC (differential scanning calorimeter) analysis of TATB was performed employing a GROUPE KAP SETARAM DSC131 instrument. The measurement conditions were sampled quantity of 0.7 ± 0.1 mg, temperature increment of 5, 10, 15K min^{-1}, while the purge gas was nitrogen.

2.3.5 Impact sensitivity

The impact sensitivity was evaluated by using the small -scale gravity drop hammer test according to the normal procedure. This is a standard test used to determine the height required in order to achieve 50% probability of detonation. Before the impact sensitivity test, samples were dried and prepared in a prescriptive way.

3. Result and discussion

3.1 TATB crystal size and morphology

The SEM images of recrystallized and raw TATB are shown in Figure 1.

It can be seen from Figuer 1a and b that the raw TATB exhibits crystals in appearance of rough, fractured, layered structure with the size range of 4.0 ~ 20.0 μm. As shown in Figuer 1c and d, most of the recrystallized TATB particles are spherical in shape and range from 30 nm to 100 nm in diameter, indicating that nano spherical TATB particles are obtained from the solvent-antisolvent process.

During the crystal growing, the water plays an important role in TATB solids spheroidization. Owing to the extensive hydrogen bonds, which are nonsaturable[19], TATB crystals tend to be spherical when much water present. That's the reason why in this research, the volume of anti-solvent is 20 times larger than that of the solvent.

The particle size analysis result is shown in Figuer 2. In the particle size distribution curves, a narrow and unimodal peak is found. The size ranges from 30 nm to 100 nm with the median diameter of 55.9 nm indicating that the particles with size of larger and smaller than median diameter are in equal portions. The results are agreed with the SEM images.

3.2 XRD pattern of TATB crystals

The XRD pattern of the raw TATB and recrystallized TATB microparticles is shown in Figure 3. Prior X-ray diffraction studies of TATB have indicated that TATB can be indexed as triclinic structure. The pattern of recrystallized TATB measured is in good agreement with the raw TATB, due to almostly the same diffraction angles (28.297°, 28.366°), indicating that the

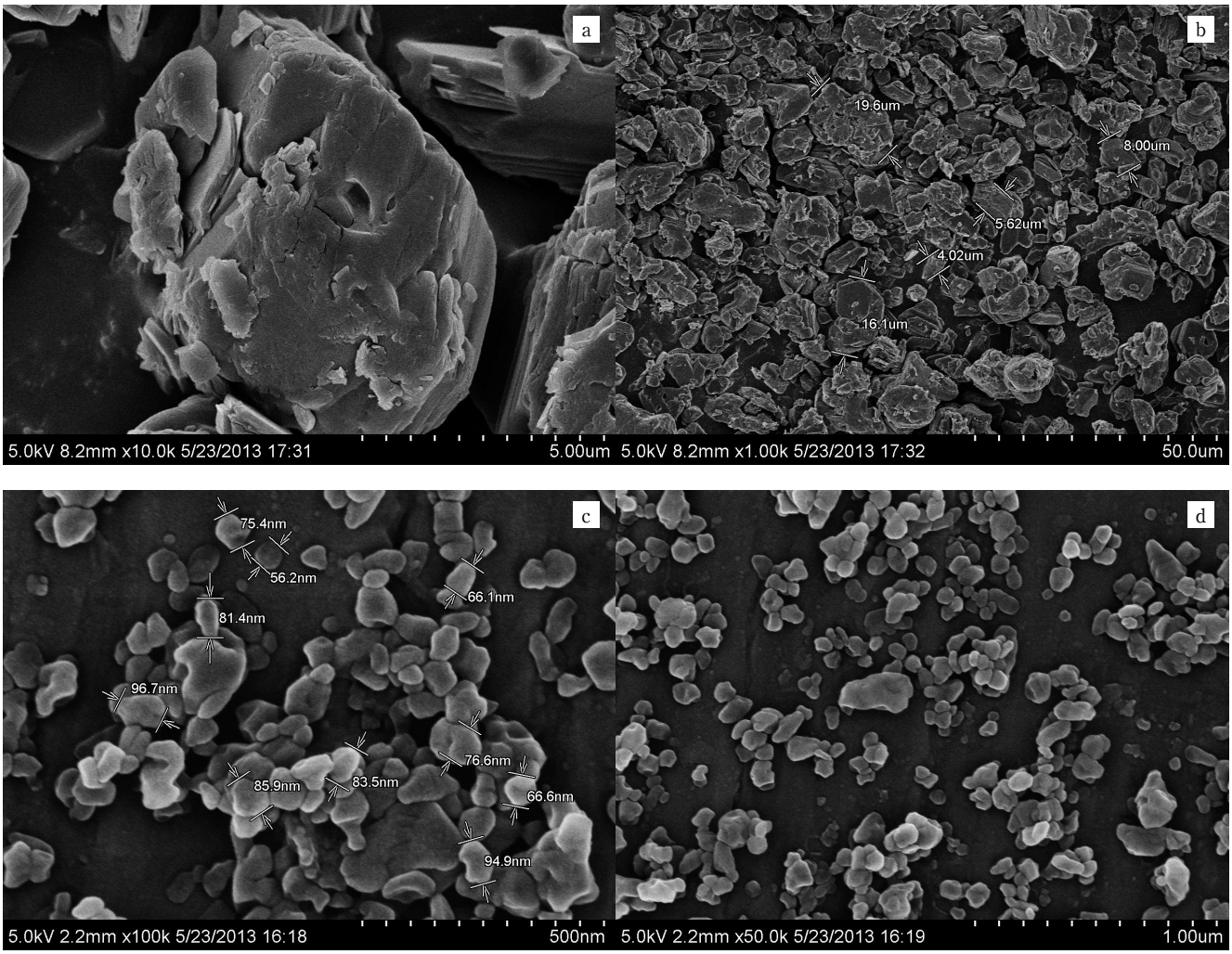

Figure 1 SEM images of TATB crystals. a, b: raw TATB; c, d: the recrystallized TATB.

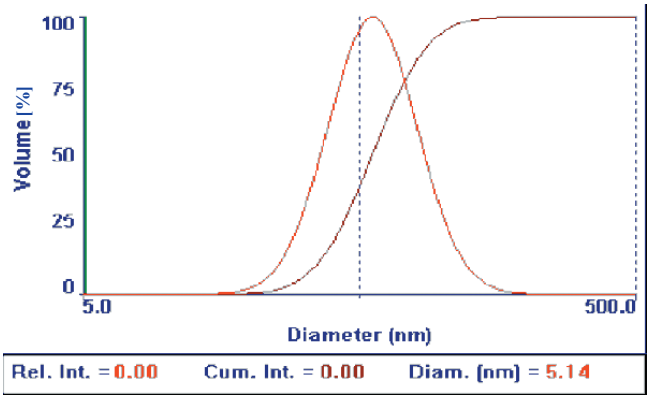

Figure 2 Particle size distribution of recrystallized TATB.

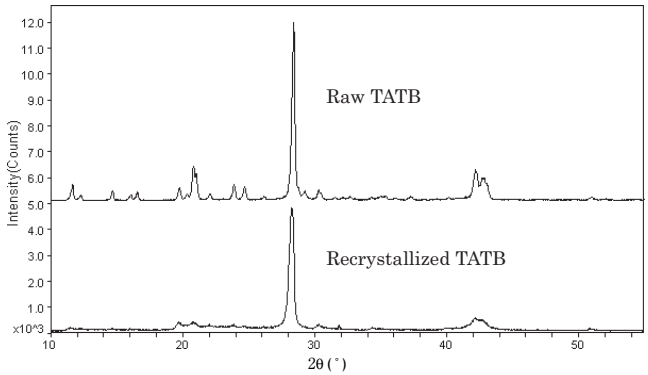

Figure 3 XRD patterns of TATB.

recrystallization process doesn't change the crystal type of TATB. The diffraction peak of raw TATB has an intensity of 6950, FWHM of 0.347° while the recrystallized TATB of 4830 and 0.174° rspectively, revealing the smaller size of recystallized TATB. Because the size of raw TATB is smaller than 5 μm, the intensity decrease of the nano-TATB is not as obvious as the broadening is. The intensity decrease as well as the broadening is attributed to the properties of fine particles. One is that fine particles have more surface defects than big grains, steming from high surface free energy. Another is that big grains have strong preferred orientation, resulting crystal texture while fine particles, especially with near-spherical apperance, allivate the preferred orientation, exhibting outstanding mechanical properties[19].

3.3 Thermal decomposition

The results of thermal analysis of raw TATB and recrystallized TATB are shown in Figure 4 and the DSC profile of raw TATB and recrystallized TATB are tabulated in Table 1.

When the heating rate is 5°C min^{-1}, the recrystallized TATB shows exotherm peak at 361.11°C, due to thermal decomposition, with the onset temperature of 354.38°C and

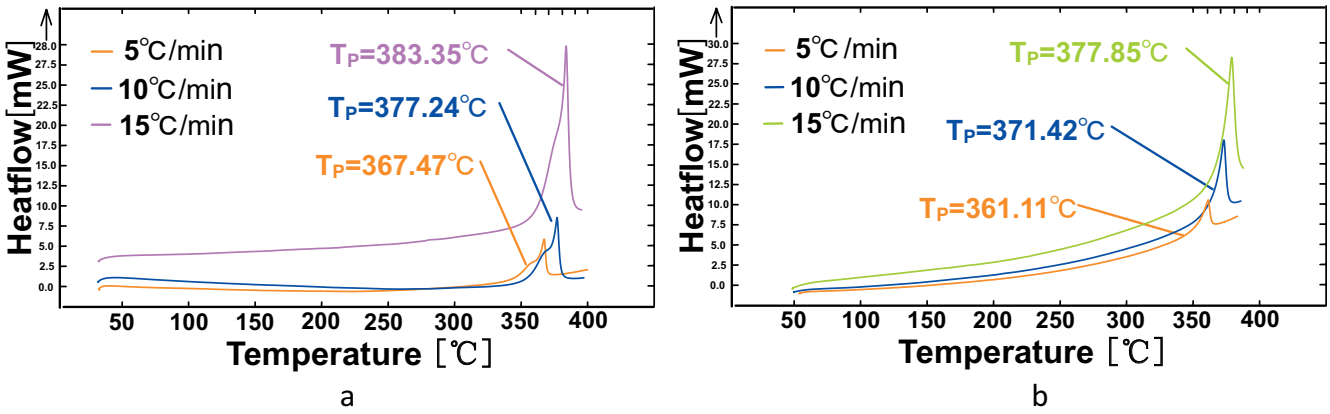

Figure 4 DSC curves of TATB. a : raw TATB, b : recrystallized TATB.

Table 1 DSC analysis result of TATB

Increment rate/β [℃ min^{-1}]	Raw TATB				Recrystallized TATB			
	Onset Point [℃]	Enthalpy [J g^{-1}]	Exothermic peak T [℃]	Energy barrier of decomposition [kJ mol^{-1}]	Onset Point [℃]	Enthalpy [J g^{-1}]	Exothermic peak T [℃]	Energy barrier of decomposition [kJ mol^{-1}]
5	360.85	−777.6506	367.47	231.39	354.38	−280.1818	361.11	214.83
10	370.97	−795.8386	377.24		364.73	−546.3074	371.42	
15	377.20	−1428.663	383.35		370.27	−425.486	377.85	

enthalpy of -280.1818 J g^{-1}, while the raw TATB is 367.47℃, 360.85℃, -777.6506 J g^{-1}respectively. For exothermic peak and onset temperature, there is a shift of approximately 7℃ toward lower temperature compared with raw TATB indicating that recrystallized TATB is more easy to decompose due to smaller TATB solid has more surface area. At the other two routes, 10℃ min^{-1} and 15℃ min^{-1}, the results are analogous. At the same time, the enthalpy value of recrystallized TATB is smaller than that of raw TATB revealing that the recrystallized TATB is more safe. Although, it can be concluded that the recrystallized TATB remains available to use as a heat-resistibility explosive.

The same conclusion of that recrystallized TATB is more easy to decompose can be arrived at from another aspect. The activation energy of decomposition can be calculated according to the Arrhenius formula[20] as following.

$$ln\left(\frac{\beta}{T^2}\right) = D - \frac{E_a}{R}\cdot\frac{1}{T}$$

where β is the heating rate, K ;
T is the exotherm peak, K ;
E_a is the activation energy, kJ mol^{-1} ;
R is the gas constant with the value of 8.314 J K^{-1} mol^{-1} ;
D is the intercept of the fitting line.

As a result, the activation energy values of raw TATB and recrystallized TATB are calculated as 231.4 kJ mol^{-1} and 214.8 kJ mol^{-1}, respectively.

3.4 Impact sensitivity of TATB

It is generally understood that optimization of crystal including eliminating porosity and smoothing the solids in a regular shape can substantially desensitize an explosive[21), 22)]. A straightforward way for solving the problem above is to reduce the crystal size of the HE. The drop height of the nano TATB is higher than 100 cm (10 kg hammer), which is much higher than that of the nano-HMX (26.4 cm at 5 kg hammer) [23)], nano-RDX (45.3 cm at 5 kg hammer) [17)] and other nano explosives, revealing that TATB is a respectably insensitive explosive.

4. Conclusions

In this study, nano TATB particles are prepared by a green solvent/anti-solvent technique, in which the co-solvent of ionic liquid [Emim] Ac and DMSO is used to dissolve TATB. Due to its high boiling point, the ionic liquid can be reclaimed by a well designed process. Thus, the process deserves the virtue of environmental friendship. The nano TATB particles obtained are spherical in shape and range from 30 nm to 100 nm in size. The recrystallization process does not change the crystal type of TATB. Excitingly, nano TATB shows remarkable property in thermal decomposition as well as impact insensitivity.

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