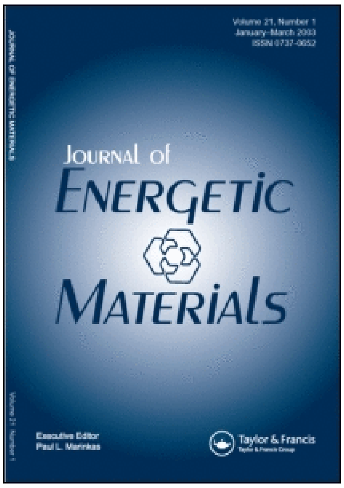

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Synthesis and Characterization of Ultrafine TATB

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An acid recrystallization process for synthesis of ultrafine TATB (UF-TATB) of median particle size $<5\,\mu m$ *is described. The process uses production grade TATB (PG-TATB) of median particle size* $>50\,\mu m$*. PG-TATB is made soluble in DMSO-alkali. Acidification of this basic solution is done with dilute aqueous nitric acid, which causes precipitation of UF-TATB through a reaction crystallization process. The process is simple, economical, and easy to scale up. The effect of various process parameters such as acid concentration and neutralization time on particle size is studied and discussed. UF-TATB is characterized for purity, chloride content, particle size, DSC, STA, SEM, sensitivity, etc., and results have been compared with PG-TATB. Along with particle size, the chloride impurity in UF-TATB is also reduced from 0.7 to* $<0.13\%$*. SEM analysis reveals regular bi-pyramidal shape with sharp edges and corners of UF-TATB crystals*

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compared to porous and rough surfaces of PG-TATB crystals. There is an impact sensitivity gain in UF-TATB. This may be due to the ultrafine nature of the particles.

Keywords: acid recrystallization, DMSO, reaction crystallization, SEM, TATB, ultrafine

Introduction

Interest in 1,3,5-triamino-2,4,6-trinitrobenzene (TATB) as a high explosive has grown in the past decade because of its excellent thermal stability ($>623\,K$) and its insensitivity. TATB was first synthesized in 1887 by Jackson and Wing [1]. Although some alternative routes for TATB synthesis have been recently reported [2,3], they were restricted to laboratory-scale study. The large-scale production of TATB is still an adaptation of the original synthesis technique [4], amination of 1,3,5-trichloro-2,4,6-trinitrobenzene (TCTNB). This laboratory has also adopted this route. The process has been modified and scaled up to pilot plant level (10 kg/batch) [5,6]. The pilot-scale manufacturing technique yields production-grade TATB (PG-TATB) of median particle size higher than 50 μm and is suitable for most of the applications. The insensitivity of PG-TATB is in fact too high to ensure optimum performance reliability of TATB-based explosive initiators and boosters formulations. This may be due to relatively large particle diameter of PG-TATB. One of the methods to enhance the sensitivity of TATB is by decreasing the particle size of the material and correspondingly increasing the surface area per unit mass [7].

Literature [8,9] indicates wide application of fine and ultrafine TATB. Fine TATB (FP-TATB) of particle size (5–10 μm) can be obtained by emulsion amination [7], sonochemical amination [10], or gas jet expansion method [11]. Rigdon et al. [12] patented a process for preparing TATB in submicron particle size (from 0.2 to 0.3 μm) with surface area greater than $3\,m^2/g$ by a precipitation method in a specially fabricated apparatus. TATB was dissolved in DMSO alkali solution and precipitation was achieved by injecting or spraying the TATB solution into vigorously stirred dilute mineral acid solution. But details of process development, feasibility of scale-up, and characterization, especially with respect to sensitivity for submicron TATB particles, were not disclosed. A wider scope of research was found on synthesis, process development, and feasibility of scaling up the process to realize ultrafine TATB (UF-TATB) of particle size 2–5 μm. Synthesized UF-TATB needs to be characterized for particle size, surface morphology by SEM, and sensitivity to find suitable application areas.

UF-TATB (<5 μm) is quite sensitive to very high amplitude shockwaves of very short duration while being as insensitive as PG-TATB to other stimuli such as normal shock loading, thermal stimuli, friction, impact, etc. [13]. UF-TATB is also used as an energetic binder, i.e., adhesive, which provides relatively high pellet densities without any additional binder. It can be used in plastic-bonded explosives (PBXs) along with other powerful high explosives such as HMX, CL-20, etc., without any conventional nonenergetic binder to enhance performance [14].

The insolubility or poor solubility of TATB in most common solvents has made particle size modification (size reduction) by conventional crystallization techniques an uneconomical process [15]. TATB has been made soluble in DMSO in the presence of inorganic base NaOH/KOH. The neutralization (acid recrystallization) of this basic TATB solution with mineral acid produces UF-TATB. This report describes the method of preparing UF-TATB by acid recrystallization technique. UF-TATB is characterized and results have been compared with PG-TATB.

Experimental

Chemicals and Reagents

PG-TATB (Purity: 98.5%; chloride content: 0.75%; particle size [MMD] 67 μm) obtained from the pilot plant of this laboratory was used as starting material. Chemicals such as DMSO, NaOH, KOH, HNO_3, acetone and ethyl alcohol are all laboratory reagent (LR) grade from M/s S. D. Fine Chem. Pvt. Ltd., Mumbai, India.

Preparation of UF-TATB

The method described by Rigdon et al. [12] to dissolve TATB in DMSO was followed in the preparation method. A typical procedure for the synthesis of UF-TATB is as follows: PG-TATB (5.0 g) was dispersed in 200 mL DMSO in a round-bottom flask (500 mL) and 12.5 mL of aqueous NaOH solution (9.3%) was added to it under vigorous agitation with the help of a mechanical stirrer (rpm 600). The mixture was stirred at room temperature (300–305 K) for 1 h. A deep brown-colored solution resulted. This brown solution was acidified with 5 mL of 8 M aqueous solution of nitric acid under vigorous stirring. Ultrafine TATB particles were precipitated out during this neutralization process. These particles were isolated by subsequent filtration of slurry, washing of cake with hot water, acetone/ethyl alcohol, and drying in an oven at 373 K for 3 h.

Characterization

Particle Size

Particle size was determined using Malvern particle size analyzer (Mastersizer-2000, Malvern Instruments Ltd, UK). The instrument uses the principle of Mie scattering theory for measuring the size and distribution of particles suspended in a liquid medium. Two light sources, red light (helium-neon laser) and blue light (solid-state light source), are used in this instrument. After the beam has been scattered by the particles in the measuring cell, it passes through the condenser lens and is focused on 40 unit detectors. The intensity and angle of scattered light are converted into electrical signals, which are then used to calculate size distribution of the particles.

The instrument is capable of measuring particle size ranging from 0.02 to 2000 µm.

A small quantity of TATB powder sample was dispersed in demineralized water (500 mL). TATB-dispersed water was circulated in the measuring cell unit using the instrument's internal pumping system. The sample was added in installments until the laser obscuration level was in the desired range (11–20%) as specified by the instrument manufacturer. Various methods of particle dispersion were examined. The sample was dispersed using the instrument's internal stirring system (rpm = 2050) and with the help of ultrasonic probe (USP).

Thermal Analysis

DSC analysis of TATB was carried out in Perkin Elmer DSC instrument (model DSC-7). Sample quantity, 1–2 mg; heating rate, 10 K/min; purge gas, nitrogen. The thermogravimetric analysis (TGA) and differential thermal analysis (DTA) were carried out in a simultaneous thermal analyzer (STA; model SDT Q 600, TA Instruments, New Castle, DE, USA). Analysis conditions: sample quantity, <1 mg; heating rate, 20 K/min; inert atmosphere, UHP N_2 (flow rate: 0.1 L/min.).

Scanning Electron Microscope (SEM) Analysis

An environmental SEM (model Quanta 200, FEI, Eindhoven, The Netherlands) was used for crystal imaging. Images were taken at room temperature using tungsten filament as electron source of 20–30 kV energy. Large field detector (LFD) was used for secondary electron imaging at pressure range 0.1–1.0 Torr. TATB powder was dispersed in isopropanol with the help of ultrasound. The dispersed mixture was mounted on double-sided adhesive conducting silver tape pasted on Al stub. Solvent was evaporated by drying in an oven. The morphological study of TATB crystals was carried out using voltage below charging limit.

FTIR Analysis

A Shimadzu infrared spectrometer (FTIR-8400) was used for this characterization. KBr was mixed with the sample. The powder was placed in the cup of diffuse reflectance assembly and spectra were recorded.

Chemical Analysis and Sensitivity Tests

Analytical method described elsewhere was followed for purity estimation and chloride content analysis. TATB purity was determined by amino groups estimation method in a modified Kjeldhal apparatus [16]. The chloride content in TATB was estimated by potentiometric titration using Ag/AgCl electrode (DG141) in a Mettler-Toledo Autotitrater (model DL55, Mettler-Toledo GmbH, Switzerland) [17]. Friction sensitivity of TATB was determined in Julius Peter apparatus and impact sensitivity by Fall Hammer method (Bruceton staircase method) as per standard procedure [18].

Results and Discussion

Insolubility of TATB is undoubtedly related to the strong intra and intermolecular hydrogen bonds. Infinite planes of hydrogen-bonded TATB result in a layered structure similar to that observed for hexagonal graphite and boron nitride [19,20]. The introduction of base ($^{-}$OH) in DMSO breaks the hydrogen bonds present in PG-TATB crystals and thus it gets dissolved.

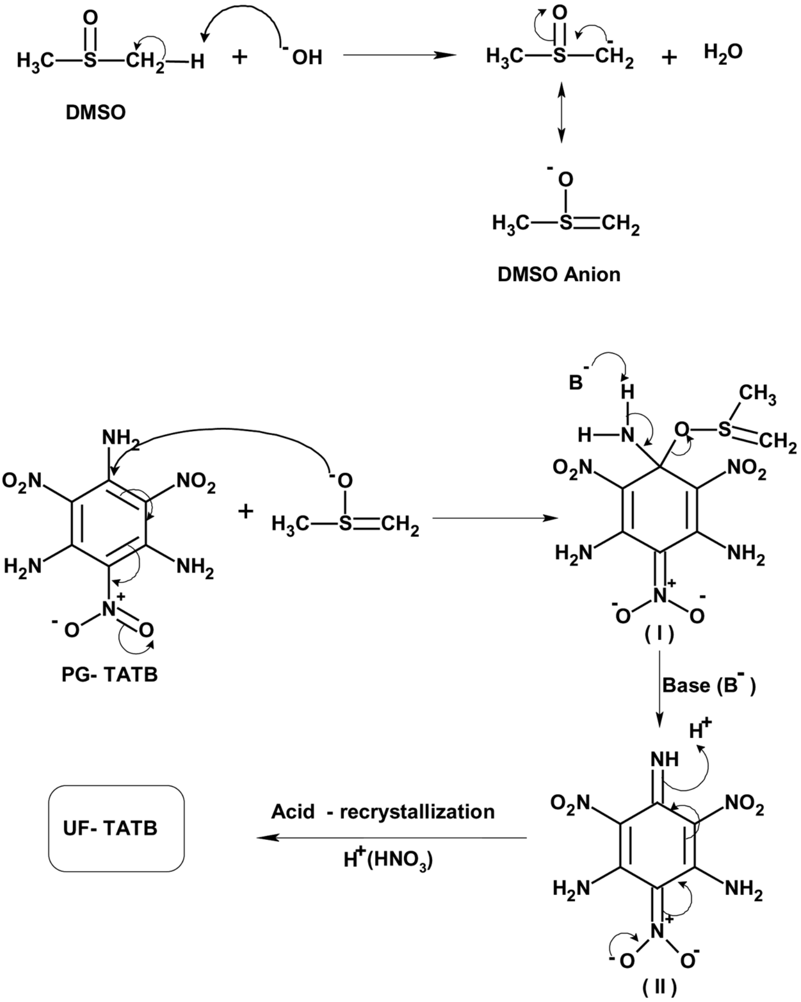
DMSO is a highly polar water-miscible aprotic solvent. Miscibility with water is essential as it gives single liquid phase during acid recrystallization. An attempt was made to understand the role of DMSO in the reaction Scheme. TATB does not get dissolved in other highly polar water-miscible aprotic solvent like N,N-dimethylformamide (DMF) in the presence of NaOH. TATB is also not soluble in aqueous NaOH solution (6 M) at room temperature. This implies that $^{-}$OH is not the attacking species and DMSO has a certain role to play in breaking the hydrogen bonds.

The probable reaction mechanism is proposed based on literature [21] and is shown in Scheme 1. The mechanism suggests that DMSO is converted to DMSO anion in presence of base. This anion is a low-energy stabilized intermediate. DMSO anion attacks the ring carbon and intermediate (I) is produced. Further base attack on $-NH_2$ proton of intermediate (I) gives brown-colored intermediate (II). Acidification of (II) produces TATB in the form of ultrafine crystals.

The maximum solubility of PG-TATB in alkaline-DMSO was found as 25 g/L of DMSO at room temperature (303 K). The molar ratio of TATB:NaOH was 1:15. The dissolution of TATB in DMSO-NaOH solution at room temperature yields a deep brown-colored solution. The color is due to the absorption of visible light by the intermediate (II). Heating is avoided as it converts TATB to a highly water-soluble compound, trinitrophloroglucinol (1,3,5-trihydroxy-2,4,6-trinitrobenzene) with evolution of ammonia gas [16,17]. This basic solution is neutralized with aqueous nitric acid (HNO_3). Other mineral acids such as HCl and H_2SO_4 are avoided as it incorporates Cl^- and SO_4^{2-} in the product, which are difficult to remove by washing. Ultrafine TATB particles are precipitated instantaneously in the neutralization process. The slurry was filtered and cake was washed several times with cold and hot water to remove all possible water-soluble/miscible impurities such as trinitrophloroglucinol, nitrophenols, DMSO, etc.

Acidification is a reaction crystallization process. Acidification of anion (structure II of Scheme 1) produces TATB, which is insoluble in the reaction medium (DMSO-water). The rapid chemical reaction quickly develops a very high supersaturation level. This induces rapid crystallization with a very high nucleation rate, which results in precipitation of ultrafine TATB crystals.

Acidification was carried out at room temperature with addition of acid to DMSO-TATB-NaOH solution. Agitation was applied during acid addition to ensure development of uniform supersaturation level in the crystallization process. The reverse addition (solution to the acid) was not found suitable due to agglomerate formation. Experimental results



Scheme 1. Reaction mechanism of acid recrystallization process.

on synthesis of UF-TATB are shown in Table 1. The yield was found to be more than 90% in most of the experimental batches. Loss of $<10\%$ yield is more due to the process loss during filtration, material transfer, etc., than incomplete

Table 1
Experiments on optimization of process parameter on acid recrystallization to synthesize UF-TATB

Expt. no.	Acid conc. (M)	Molar ratio $HNO_3/NaOH$	Acid addition time (min)	Yield (%)	Median particle size (µm)
1	0.4	0.85	15.0	90.8	5.03
2	0.8	0.86	10.0	95.2	3.08
3	4.0	1.04	3.0	94.0	2.80
4	4.0	1.04	6.0	75.7	5.74
5	5.0	0.98	4.0	96.4	2.13
6	6.0	0.98	1.5	90.0	1.71
7	6.0	0.98	3.0	95.8	2.68
8	7.0	1.02	2.0	93.8	2.48
9	8.0	1.3	3.0	89.7	2.58
10	8.0	1.04	1.0	83.4	2.78
11	10.0	0.98	2.0	92.0	3.53
12	4.0	1.33	10	96.0	2.76
13	5.0	1.33	7.0	94.0	2.69
14	6.0	1.40	7.0	97.0	2.69
15	7.0	1.40	5.0	96.4	2.99

Experiments 4, 5, 7–10, at 10 g (PG-TATB); for others, 5 g scale; for experiments 12–15, KOH was used.

acidification. UF-TATB of particle size 2–3 µm was realized in most of the cases with acid concentration 5–8 (M) and neutralization time 5–10 min. Ethyl alcohol wash was necessary to prevent agglomeration during filtration. Filtration was found difficult and slow with normal (G4) sintered-glass crucible filter medium. This is due to the clogging of the pores of the filter medium. Other filter mediums (filter paper, cloth) were not found suitable.

FTIR spectra of both PG- and UF-TATB are shown in Fig. 1. The spectra match each other, indicating that chemical

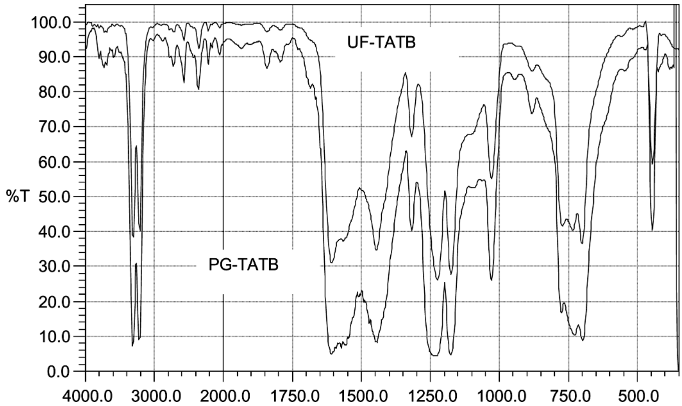


Figure 1. FTIR spectra of PG- and UF-TATB.

structure of TATB remains intact during precipitation and there is no impurity in UF-TATB.

Particle size analysis data are shown in Table 2. The typical particle size distribution curve for UF-TATB is compared with the same for PG-TATB (Fig. 2). Both of them show monomodal size distribution. A comparatively narrow distribution pattern was observed for UF-TATB. The effect of ultrasound (25 kHz) as an additional particle dispersion aid during size analysis is shown in Table 3. Ultrasound breaks the agglomerates and makes a marginal decline on average particle size value.

Thermal analysis of few UF-TATB samples was carried out with STA and DSC. STA data are shown in Table 4. The STA profile of both PG- and UF-TATB is shown in Fig. 3. UF-TATB shows DTA exotherm peak at 653 ± 4 K with 80–90% decomposition weight loss. The initial temperature of decomposition is at 528 ± 10 K. PG-TATB shows decomposition at slightly lower temperature (644 K) with 97% decomposition. UF-TATB shows DSC exotherm peak at 658 K and DSC profile is very much similar to PG-TATB (exotherm peak temp. 652 ± 10 K).

SEM picture of PG-TATB (Figs. 4a and 4b) reveals large crystals ($>50\,\mu$m) of layered structure with porous and rough surfaces. NH_4Cl is coprecipitated with TATB in the amination

Table 2
Average particle size data of UF- and PG-TATB

	Average particle size (μm)*			
Sample code	D [4,3]	D [3,2]	D [0,5]	Span
UF-TATB-1	3.08	1.78	2.67	1.80
UF-TATB-2	2.89	1.73	2.47	1.73
UF-TATB-3	3.38	1.84	2.78	2.07
PG-TATB	89.8	47.2	66.6	2.43

*D [4,3], volume-weighted mean dia; D [3,2], surface-weighted mean dia; D [0,5], mass median dia.

process. NH_4Cl impurity in coprecipitated crude PG-TATB is removed by hot water (363 K) digestion. NH_4Cl goes into water leaving porous structure to the crystal's surface. The rough surface might be due to the unequal crystal growth of organic compound TATB and inorganic compound NH_4Cl.

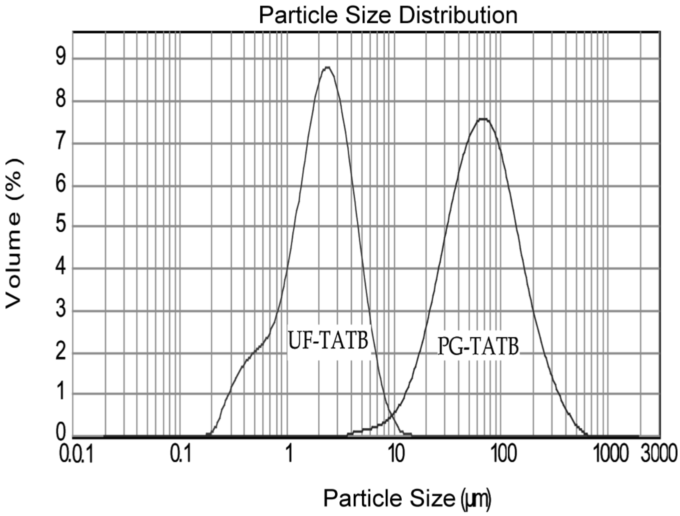


Figure 2. Typical particle size distribution curves for UF- and PG-TATB.

Table 3
Effect of ultrasound of average particle size value of UF-TATB

Dispersion conditions	Average particle size (μm) D [4,3]	D [3,2]	D [0,5]	Span
Without USP*	2.51	1.40	2.13	1.97
1 min USP at energy level 2.5	2.28	1.30	1.92	1.96
2 min USP at energy level 2.5	2.20	1.27	1.86	1.95
5 min USP at energy level 10.0	1.54	1.09	1.39	1.54

*USP: Application of ultrasonication probe.

An SEM picture of UF-TATB (Figs. 5a and 5b) reveals the smaller crystal size (< 5 μm). Crystals have regular bi-pyramidal shape with sharp edges and corners. Crystal surfaces are smooth and do not have porosity. This gives an advantage to UF-TATB over PG-TATB.

A sensitivity test indicates that there is no difference in friction sensitivity. Both PG- and UF-TATB show friction insensitivity up to 36 kg (upper limit of the testing facility). PG-TATB assumes a graphite-like layered structured. Unaltered

Table 4
Characterization of UF-TATB by STA (DTA + TGA)

Sample code	DTA-exotherm peak (K)	Initial temp. of decomposition (K)	Wt. loss on decomposition (%)
1	656	525	89.67
2	651	537	80.97
3	657	523	90.02
PG-TATB	643	524	97.64

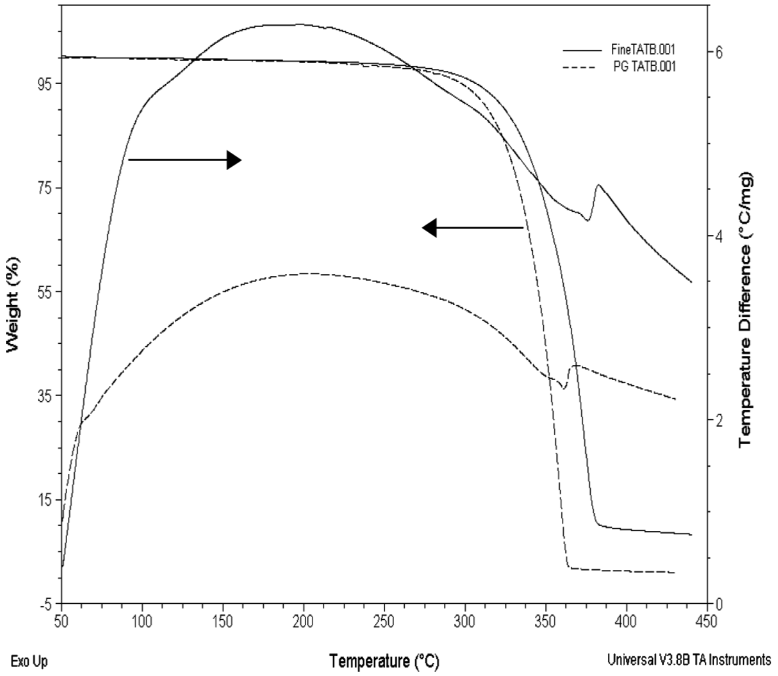


Figure 3. Typical STA (DTA + TGA) curve of UF- and PG-TATB.

friction sensitivity data indicate that the layered structure remains unchanged in UF-TATB.

There is an impact sensitivity gain in UF-TATB. Height for 50% explosion (H_{50}) of impact sensitivity is reduced from a range of 150–170 to 89–138 (Table 5). This may be due to the ultrafine nature of the material. Regular bi-pyramidal shape with sharp edges and corners of UF-TATB crystals are also perhaps responsible for the sensitivity gain.

UF-TATB was fully characterized and results were compared with PG-TATB (Table 6). Chloride (Cl^-) content in UF-TATB is reduced to $\sim$0.1%, which is conducive to the storage life of the explosive chloride is corrosive to metal casing and reduces the shelf life of the explosive. Cl^- in PG-TATB is mainly due to occluded NH_4Cl formed in the TCTNB

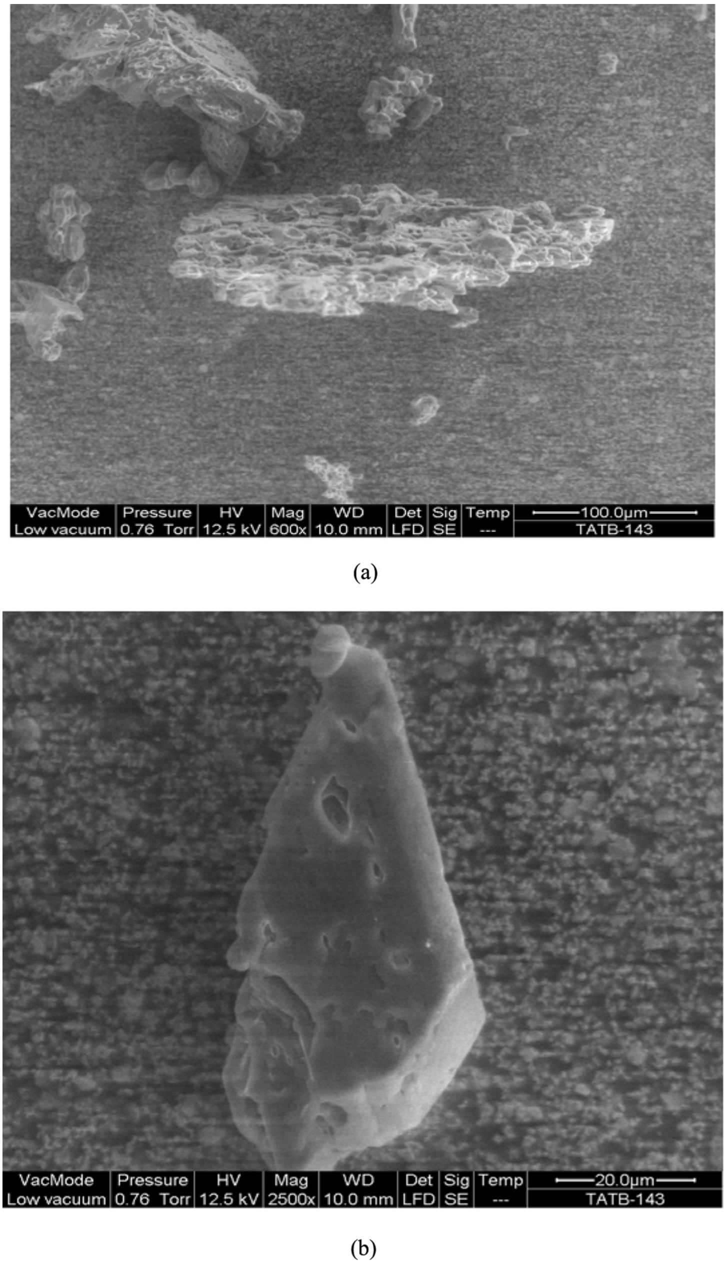
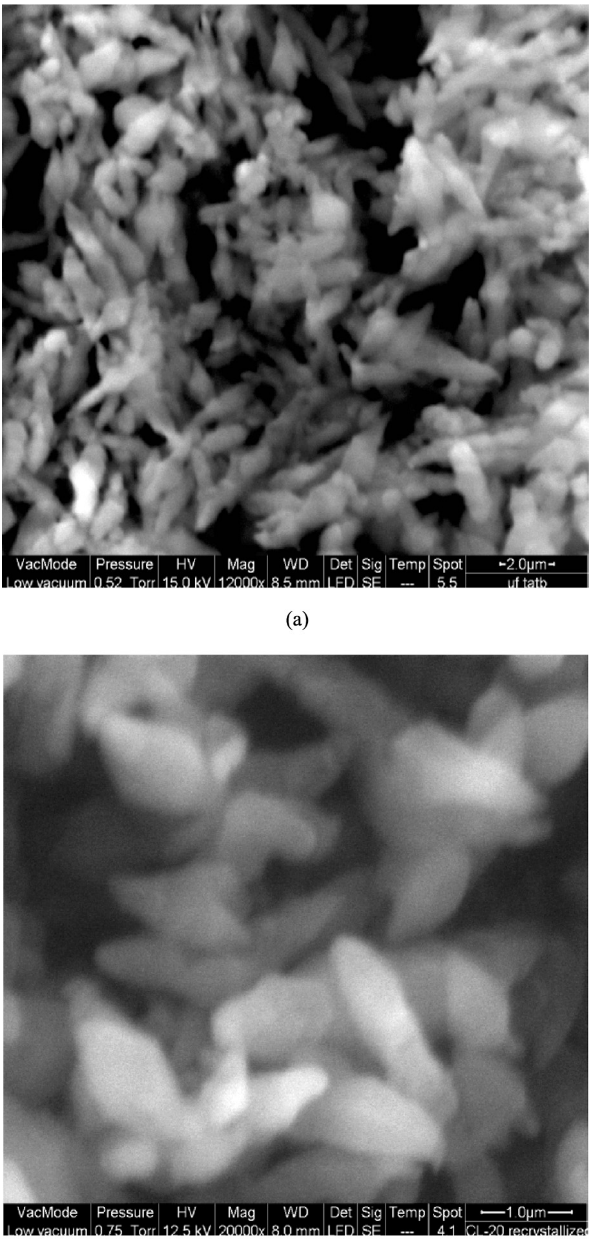


Figure 4. (a) SEM picture of PG-TATB crystals; (b) SEM picture (closer view) of another PG-TATB crystal.



(a)

(b)

Figure 5. (a) SEM picture of UF-TATB crystals; (b) SEM picture (closer view) of UF-TATB crystals.

Table 5
Impact and friction sensitivity of UF-TATB

Sample code	Impact test #		Insensitive to friction (kg)
	H_{50} (cm)	Figure of insensitivity (FOI)	
1*	138	169	36
2*	100	122	36
3	103	126	36
4	122	150	36
5	89	109	36
PG-TATB	150–170	204–224	36
CE(Std.)	57	—	—

H_{50}, height of 50% explosion with 2 kg drop wt.; FOI (figure of insensitivity) w.r.t. standard CE(tetryl) *KOH was used during synthesis; # relative humidity = 45%, temp. 306 K.

Table 6
Comparison of characterization data of PG- and UF-TATB

Parameters	PG-TATB	UF-TATB
Melting point (K)	Did not melt up to 593	Did not melt up to 593
Purity (%)	98.0 (min)	99.0
Chloride content (%)	0.5–0.8	<0.125
DSC exotherm peak (K)	652 ± 10	658
Particle size (μm, median)	60–90	1.5–5.0
Friction sensitivity (kg)	36	36
Impact sensitivity (cm)	$H_{50} = 150–170$; FOI = 204–224	$H_{50} = 89–138$; FOI = 109–169
Ignition temperature (K)	Not ignited up to 623	Not ignited up to 623

amination process [16,17]. The dissolution of TATB crystals on alkali treatment makes NH_4Cl free, which goes into the aqueous medium and thus Cl^- in precipitated UF-TATB is reduced substantially.

Conclusion

Ultrafine TATB of median particle size 2–3 µm can be realized by an acid recrystallization method. The method is simple, economical, and easy to scale up. However, the process involves handling of hazardous solvent DMSO. Ethyl alcohol wash to the filter cake is very effective in preventing agglomeration. The chloride content in UF-TATB is reduced substantially, which is conducive to the storage life of the explosive. There is an improvement of sensitivity in UF-TATB due to the ultrafine nature of the crystals. Other properties of UF-TATB are similar to PG-TATB. However, a sufficient quantity of the material needs to be synthesized for actual application trials. The credibility of this material can be understood after testing various high-explosive formulations using UF-TATB. This laboratory is presently scaling up the process to bench-scale level (1 kg).

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