

Nanoparticle Triaminotrinitrobenzene Fabricated by Carbon Dioxide Assisted Nebulization with a Bubble Dryer

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Abstract: Carbon dioxide assisted nebulization with a bubble dryer (CAN-BD) was used to reformulate TATB, a notoriously insoluble material, into nanoparticles. The method is reproducible and produces particles consistently in the range of 100–400 nm with a mean of approx.

228 nm. Chemical analyses of the material do not indicate any decomposition or degradation of the TATB resulting from the process, and there does not appear to be any measurable amount of residual solvent or other impurities in the particles.

Keywords: TATB • CAN-BD • Nanoparticles • Explosives

1 Introduction

The molecular crystal explosive 1,3,5-triamino-2,4,6-trinitrobenzene (TATB) is attractive from a safety perspective due to its extreme insensitivity to accidental initiation. There are, however, applications where the insensitivity of TATB is prohibitive. Detonation waves propagating through TATB also exhibit difficulty spreading laterally (corner turning), which results in regions of unreacted material. For a wide variety of explosives, shock sensitivity has been empirically correlated to the size of shock-localizing heterogeneities and indirectly to the particle size of the unconsolidated powders [1,2]. Several research groups have demonstrated that formulations and 'neat' pellets pressed from smaller particle TATB powders exhibit increased sensitivity [3–5] and improved detonation spreading [6]. Of course, sensitivity is inversely linked to the inherent safety of explosive devices, motivating research aimed at optimizing the balance between ease of purposeful initiation and safety. This optimization is application specific, and our approach is to develop a means to tailor the initiation properties of TATB by controllably modifying the particle size and morphology of the powder.

TATB is typically synthesized as a relatively coarse powder with a mean particle size of about 60 μm . Super- and ultra-fine versions with mean particle sizes of 40 and 10 μm , respectively, are available, but despite their designations still have larger particle sizes than many other explosive powders. Decades ago, extremely fine particle TATB (mean diameter approx. 220 nm) was made by crash precipitation at Los Alamos National Laboratory and Lawrence Livermore National Laboratory. Lee [3] reported that crash precipitated TATB was more sensitive to initiation by electrically driven flyer impact, especially for small diameter flyers.

More recently, other groups have produced micro- and nanoparticles of explosives using a variety of novel techniques such as vacuum condensation [7], spray-drying/flash-evaporation [8,9], rapid expansion of supercritical solvent [10,11], plasma-assisted crystallization and electro-spray crystallization [12]. The common approach in all of these techniques is that they involve non-equilibrium processes in which particle size is limited through rapid nucleation and crystallization.

The difficulty in applying rapid recrystallization techniques to TATB comes from its extremely low solubility in most common solvents. Approaches to reduce particle size have therefore either been employed at the last stage of synthesis or through the use of aggressive solvents such as sodium hydroxide dissolved in dimethylsulfoxide [6]. Recently, ionic liquids have been applied as a solvent or cosolvent for better dissolution of TATB [13,14].

Carbon dioxide assisted nebulization with a bubble dryer (CAN-BD) is a versatile method by which materials can be formulated into fairly monodisperse fine particles [15]. Any material that can be dissolved into a solution can be processed by CAN-BD. Briefly, a highly pressurized solution containing a dissolved material is combined with near-supercritical CO_2 in a mixing tee and then forced out a small diameter restrictor tube into a drying chamber where it is rapidly depressurized. The CO_2 acts as antisolvent, crashing the material out of solution as the solvent is evaporated by hot nitrogen. The formed particles of material are then col-

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lected on a filter membrane. The size and dispersity of particles can be tuned by controlling a number of parameters: material concentration, solution and CO₂ pressure, solution flow rate, restrictor length and internal diameter, and drying gas temperature.

In this communication we report on the production and characterization of nanoparticle TATB made using CAN-BD

2 Results and Discussion

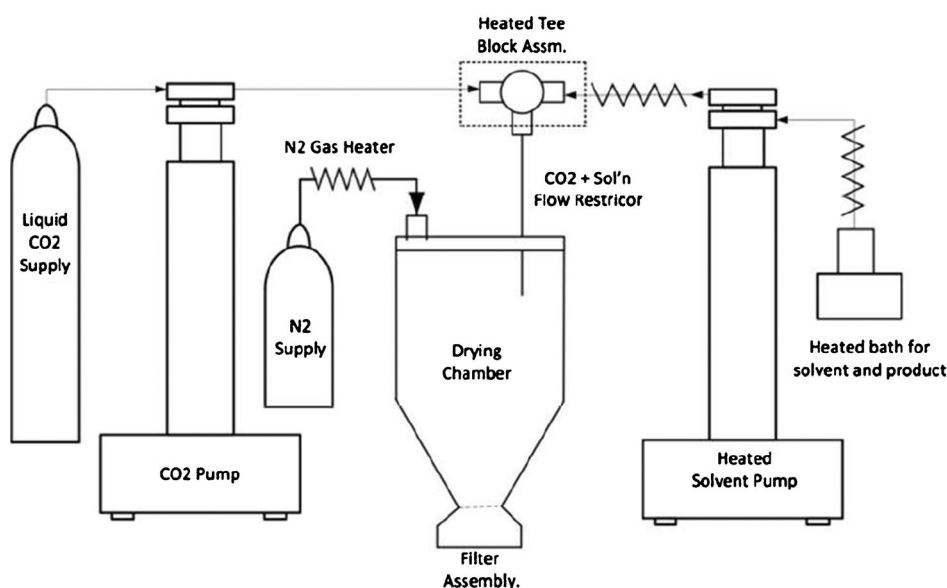
Given the general insolubility of TATB in most common solvents the CAN-BD system had to be modified such that TATB dissolved in hot DMSO could be temperature controlled throughout the process (Scheme 1). A typical ambient temperature CAN-BD system would result in precipitation of TATB particles in the lines resulting in flow problems, pressure build-up and ultimately system failure.

Note the heated lines ensuring proper dissolution of TATB from sample introduction to output from the solution flow restrictor. Due to the extreme processing conditions, PTFE-based membranes were used to collect the generated powder, given their resistance to higher temperatures and DMSO. In addition, the nitrogen drying gas had to be heated to considerable temperature (230 °C) in order to fully dry the particles before collection on the membrane filter. Three separate bubble dryer runs were performed, each with the same operating conditions. Collected yields (amount of material on the filter membrane) were around 35%, though actual yield of CAN-BD TATB is likely higher given losses of material on the collection chamber walls as well as the fact that not all the TATB is processed through the CAN-BD system due to diffusion of material throughout the lines during operation.

Scanning electron microscopy (SEM) was performed to understand the size and morphology of generated particles. As seen in Figure 1, the particles are strikingly different from traditional super- and ultra-fine crash precipitated TATB where surface area is high but particle morphology is varied and inconsistent. The CAN-BD process, as currently configured, produces particles of a much more uniform shape and size.

Particle size measurements were conducted on three runs in order to understand reproducibility and then combined for an average distribution (Figure 1). Mean particle sizes were found to be 217, 248 and 238 nm for Runs 1, 2 and 3, respectively, and similar distributions were found in each run, indicating a well-controlled, reproducible process. To the extent possible, the size of primary particles was measured and not the size of agglomerations, which we believe are indicative of the drying and sampling process (Runs 2 and 3 showed variation in the size of agglomerates compared to Run 1 – see Supporting Information). The combined mean particle size is 228 nm.

Raman spectroscopy and mass spectrometry measurements were taken to ensure that the CAN-BD process did not decompose or otherwise change the molecular structure of the TATB molecules. Raman spectroscopy measurements of each run indicate no undue changes in the material with all peaks matching well with the starting TATB material (Figure 2) [16,17]. The appropriate N–H stretching peaks were also seen at approx. 3230 cm⁻¹ (see Supporting Information). Additionally, the absence of any extraneous peaks from the three runs indicates no major decomposition products or trapped solvent. It should be noted that a small peak can be seen at 487 cm⁻¹ in Run 1 that was not observed in the other runs or the starting material. The peak does not correspond to DMSO nor any common



Scheme 1. Drawing of CAN-BD setup used. Accordion lines indicate transfer lines that can be heated.

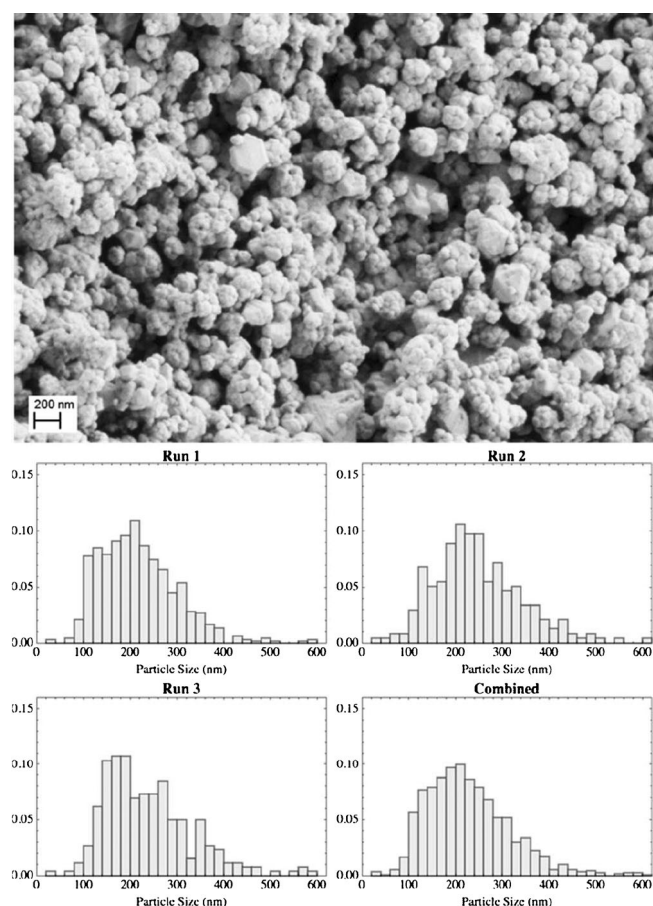


Figure 1. Representative SEM (top) and particle size distribution histograms (bottom) of CAN-BD TATB. SEM image is from Run 1. Y-axis on graphs denotes relative amount of a given particle size.

DMSO decomposition products and given that all runs were using the same starting material does not appear to be an impurity carried through the run. Additionally, the other analyses (SEM, MS) did not indicate any differences except for the aforementioned difference in agglomeration. Given the nature of the experiments and other data collected we consider the peak to an anomaly.

Mass spectra were also collected on the starting material and different runs. Desorption off of a glass probe was necessary due to the low solubility of TATB in common solvents. Due to the operating parameters used, especially the atmospheric pressure ionization, fragmentation was minimal, resulting in a large molecular ion $[M-H]^-$ peak at 257.02 that corresponds to TATB. Fragmentation that did occur generally consisted of losses of NH_2 groups, conversion of NO_2 to NO via ionization loss of an oxygen atom, loss of H_2O to form furazan, or combinations thereof [18,19]. The spectra collected for each run and the starting material are all very similar in constitution and fragmentation (see Supporting Information). No erroneous or extra peaks were seen in any spectra from the CAN-BD runs vs. the starting material.

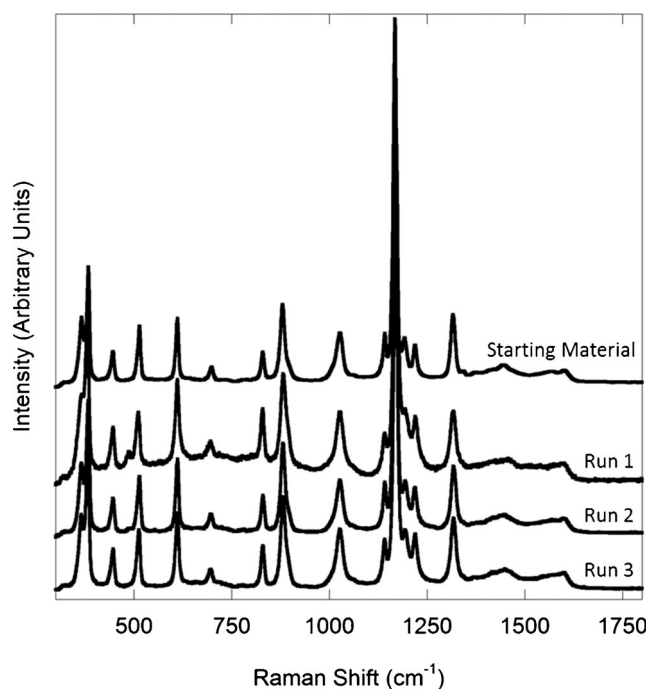


Figure 2. Raman spectra of TATB starting material (line at the top) and the three CAN-BD runs (Run 1 – second line, Run 2 – third line, Run 3 – line at the bottom).

3 Experimental Section

Dimethylsulfoxide (ACS grade, >99.9%) was purchased from Sigma–Aldrich and used as received. TATB was sourced internally at Sandia and used as received. PTFE-based filter membranes (0.5 μm pore size) were purchased from Cole Palmer.

A typical CAN-BD run was as follows: TATB (40 mg) was dissolved in DMSO (40 mL) at 100 °C. This solution was siphoned into a heated syringe pump (85 °C) through heated stainless steel lines (85 °C). The material was then pressurized to 10,000 kPa as was the CO_2 in the CO_2 pump. The pressure from the pumps to the mixing tee and restrictor was kept constant throughout the experiment. The solvent loop (20 mL) was loaded with TATB/DMSO sample and then opened toward the mixing tee and the experiment started. A total of 27 mL (to help offset for dead volume from sample loop to mixing tee and diffusion of sample throughout experiment) was run at 0.3 mL min⁻¹. The mixing tee was kept at 160 °C. The restrictor was 10 cm long and made of fused silica (internal diameter 75 μm). Nitrogen (approx. 80 °C exit temperature) was blown through the drying chamber (30 L min⁻¹) to facilitate sample drying before collection on the filter membrane. The pressure inside the chamber was monitored to ensure adequate flow through the membrane throughout the experiment (pressure was stable between 14 and 21 kPa throughout the CAN-BD experiment).

SEM analysis was conducted with a Zeiss Supra 35 VP SEM operating at 1.1 kV. Samples were coated with iridium (approx. 5 nm) before analysis. Images were taken at different magnifications and at different locations within samples to assure a proper representation of material.

Particle sizes were measured by drawing a line across a particle and taking the length to be the particle's diameter. In order to minimize sampling bias, particles were selected from each image by generating 6 lines with random orientation and position and choosing to measure those particles touched by a line. Several hundred particles were measured from each of the 3 runs (1164 particles total). See Supporting Information for more information on the particle size measurements.

Raman spectroscopy was completed using a Thermo Nicolet Almega system equipped with a 785 nm laser (used at 50% power) and a 10 \times objective with a 100 μ m aperture, producing an approx. 3 μ m interrogation spot size. Data were collected with a 5–10 second integration time and 16 co-added scans. Data were collected from 300 to 1800 cm^{-1} and from 2900 to 3500 cm^{-1} .

Mass spectrometry was performed with a Waters Xevo G2 quadrupole-time of flight (QTOF) mass spectrometer in negative mode ionization with a m/z range of 30–800 Daltons. The instrument was mass calibrated in resolution mode using a negative mode electrospray source and sodium formate for the lock mass(es) and was performed per the manufacturer's instructions. A typical sample was prepared by adsorbing a small amount of TATB (approx. 1 mg) onto a glass atmospheric solids analysis probe (ASAP) and introducing the sample via thermal desorption (ramp from 50 $^{\circ}\text{C}$ to 400 $^{\circ}\text{C}$) at atmospheric pressure. The sample was ionized with corona discharge (operated in current mode – corona current of 2.2 μA , sampling cone voltage at 4 kV and extraction cone voltage at 4.3 kV – no gas flow at cone). The inlet temperature was kept at 120 $^{\circ}\text{C}$ and the desolvation gas (N_2) flow rate held constant at 500 Lh^{-1} . Spectral data were collected over a period of 1 min with 0.1 min collection intervals and an acquisition rate of 25 kHz.

Supporting Information (see footnote on the first page of this article): Additional SEM images of the different CAN-BD runs, an in-depth explanation of the particle size measurements, Raman spectra of the N–H stretching region, and additional mass spectrometry data.

4 Conclusion

These results mark the first time TATB has been formulated via CAN-BD or any other spray dry process. Well-controlled particles with diameters of approx. 100–400 nm were created. The CAN-BD process did not decompose or otherwise alter the TATB molecular structure resulting in a process that can be further tuned and developed for better size/morphology control and higher yield of material.

Future work will focus on utilizing ionic liquids to enhance TATB solubility such that TATB can be formulated with CAN-BD on the gram scale, allowing enough material to study aging effects and to press pellets for experiments to elucidate microstructure and detonation aspects of the material.

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