

Tuning the particle size and morphology of high energetic material nanocrystals

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Abstract

Morphology controlled synthesis of nanoparticles of powerful high energetic compounds (HECs) such as 1,3,5-trinitro-1,3,5-triazinane (RDX) and 1,3,5,7-tetranitro-1,3,5,7-tetrazocane (HMX) were achieved by a simple solvent–antisolvent interaction (SAI) method at 70 °C. The effects of different solvents on particle size and morphology of the prepared nano-HECs were studied systematically. Particle size and morphology of the nano-HECs was characterized using field emission scanning electron microscopy (FE-SEM) imaging. X-ray diffraction (XRD) and Fourier transform infrared (FTIR) spectroscopy studies revealed that RDX and HMX were precipitated in their most stable polymorphic forms, i.e. α and β , respectively. Thermogravimetric analysis coupled with differential scanning calorimetry (TGA-DSC) studies showed that the thermal response of the nanoparticles was similar to the respective raw-HECs. HEC nanoparticles with spherical and rod shaped morphology were observed under different solvent conditions. The mean particle size also varied considerably with the use of different solvents. Copyright © 2015, China Ordnance Society. Production and hosting by Elsevier B.V. All rights reserved.

Keywords: Nano-RDX; Nano-HMX; High energetic materials; Spherical nanoparticles; Nanorods; Morphology control

1. Introduction

High energetic materials (HEMs) are rich sources of energy stored in the form of chemical bonds [1]. They are thermodynamically unstable, but the kinetics of energy

Abbreviations: RDX, 1,3,5-trinitro-1,3,5-triazinane; HMX, 1,3,5,7-tetranitro-1,3,5,7-tetrazocane; CL, 2,4,6,8,10,12-hexanitro-2,4,6,8,10,12-hexazaisowurtzitane; TATB, 1,3,5-triamino-2,4,6-trinitrobenzene; ICDD, The International Centre for Diffraction Data; HMX_n, Bulk-HMX; HMX_n, nano-HMX; T_{m,p}, melting point; T_{exo}, exothermic peak temperature; T_{endo}, endothermic peak temperature; ΔH , enthalpy change; T_{id}, initial decomposition temperature; T_{fd}, final decomposition temperature; Δ mass, mass loss; TBRL, Terminal Ballistics Research Laboratory; AC, acetone; EA, ethyl acetate; EN, ethanol; MN, methanol; DMSO, dimethyl sulfoxide; DMF, dimethylformamide; NMP, N-methylpyrrolidone.

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release can be controlled. They have found extensive use in explosives, rocket propellants and gas generators for automobile air bags [1,2]. Focus of research on HEMs has recently been to synthesize novel molecules with high energy density combined with insensitivity to hazardous stimuli [1,2]. Unfortunately, the research and development of new HECs has been very slow. RDX and HMX, which were developed many decades ago, are still being used as the main explosives due to their technological-economical characteristics such as their ready availability in large scale [2]. Powerful explosives such as CL-20 and octanitrocubane have much higher energetic performance than RDX and HMX [2,3]. But, their sensitivity to accidental stimuli is a matter of concern. Sensitivity of explosives is related to their chemical as well as physical characteristics [4]. The physical properties such as crystal size, shape, morphology, purity, inclusions and crystal defects can be altered to improve the performance of existing explosives [5,6]. Previous studies reported that the

novel behaviour in deflagration to detonation transition was observed with submicron particles [7]. A few studies have indicated that the particle size of explosives influences the impact sensitivity and maximum energy output from a detonation [8]. Thus, the preparation of micrometer or sub-micrometer sized solid particles is of great interest in explosives.

However, the limited production strategies are only available for making organic nanoparticles in general compared to the large array of methods that are available for the preparation of inorganic nanoparticles. Some of the methods for the preparation of sub-micron sized HEMs includes rapid crystallisation from solvent by the addition of antisolvent [9,10], sol–gel method [11,12], rapid expansion of supercritical solution (RESS) [13,14], mechanical milling [15–17] and aero-sol method [18]. An excellent review on the various methods for the preparation of nanoenergetic materials was published recently [19]. Unfortunately, many of these techniques proved to be less attractive in large scale production of organic nano-sized materials. Among various techniques for the reduction of particle size, the antisolvent precipitation process is a simple and effective technique to produce the nanosized particles by introducing the organic solution containing an active substance to the antisolvent (e.g. water) that is solvent-miscible under rapid mixing, which generates high supersaturation leading to fast nucleation rates [20–25]. Instantaneous precipitation occurs by a rapid desolvation of the hydrophobic active ingredient in the antisolvent medium [26–29]. The antisolvent may contain hydrophilic stabilizers such as polymers or surfactants. The hydrophilic stabilizer in the antisolvent gets adsorbed on the particle surface to inhibit particle growth [20–25]. We have recently prepared nano-HECs by a simple evaporation assisted solvent-antisolvent interaction (EASAI) method using acetone as solvent at 70 °C [26,27]. The same method was also used to prepare nanodrugs [28,29]. It has been shown that the particle size can be controlled by varying a number of experimental parameters such as the concentration, ratio of solvent to antisolvent, temperature of the antisolvent during injection, stirring speed etc. Infact, a lot more experimental parameters such as ultrasonication, nozzle geometry, mixing rate, nature of solvent and nature of antisolvent also are known to affect the particle properties [30]. Although there has been some studies on the effect of many of these experimental parameters, only very few reports are there in the literature about the effects of different solvents on particle size and morphology of HECs. Here we demonstrate that particle size and even morphology of nano-HECs can be tuned by changing the solvent using the SAI method.

2. Materials and methods

2.1. Materials

RDX (98.2%) and HMX (99.1%) were prepared in an in-house facility using Bachmann process [31]. Solvents,

dimethylsulfoxide (DMSO), dimethyl formamide (DMF), ethyl acetate (EA), N-methyl-2-pyrrolidone (NMP), methanol (MN) and ethanol (EN) were purchased from Sigma Aldrich and used as received. Ultra-pure water (18.2 MΩ-cm) from double stage water purifier (ELGA PURELAB Option-R7) was used throughout the process of preparation. HPLC micro syringe was purchased from Hamilton, USA. Syringe filter with pore size of 0.22 μm was purchased from Millipore, USA. Whatman Anodisc® 25 filter with pore size of 0.02 μm was purchased from Sigma Aldrich, India.

2.2. Preparation of RDX and HMX nanoparticles

Solution of HECs (5 mM) in different solvents was prepared by adding accurately weighted amount of HECs. The solution (100 μl, 5 mM) was quickly injected into water (25 ml) as antisolvent at 70 °C under magnetic stirring using an HPLC micro-syringe to precipitate nanoparticles. The solution of HECs was always filtered using a syringe filter with pore size of 0.22 μm before injection to ensure that no particle was present in it. The nanoparticles were collected by filtration using Whatman Anodisc® 25 filter membrane (diameter = 25 mm and pore size = 20 nm). The membrane was dried in an oven at 40 °C for 24 h to collect the sample for further characterization.

2.3. Particle size and morphology

Accurate particle size and morphology of the prepared nanoparticles were observed using an FESEM (Zeiss FEI Quanta FEG 450 and Supra 55 VP model). The suspension of RDX and HMX nanoparticles in water was drop-coated on an 1 cm² glass slide and dried. The dried sample containing the glass slide was kept on a clean aluminum stub that was covered with carbon tape. The sample was subsequently sputter-coated with gold at 20 mA for 180 s before the FESEM observation. Particle size of more than 300 nanoparticles from different FESEM images that were taken from different regions of the sample was calculated in each experimental condition using Image J software.

2.4. FTIR spectroscopy

FTIR spectroscopy was performed using the Perkin Elmer FTIR emission spectrometer (Spectrum Two). The FTIR spectra of raw and nanoparticles of RDX and HMX were recorded in the frequency range from 4000 to 600 cm⁻¹ with a resolution of 4 cm⁻¹. The samples were properly grounded with KBr powder and then pressed to obtain a suitably sized pellet for FTIR spectrum measurement. Pure KBr pellet was used for background correction.

2.5. Powder X-ray diffraction (XRD)

XRD patterns were recorded on a smart lab X-ray diffractometer (Rigaku, Japan) using Cu Kα radiation as X-ray source ($\lambda = 0.15418$ nm) at room temperature. The voltage

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