



# RDX-based nanocomposite microparticles for significantly reduced shock sensitivity

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## ABSTRACT

Cyclotrimethylenetrinitramine (RDX)-based nanocomposite microparticles were produced by a simple, yet novel spray drying method. The microparticles were characterized by scanning electron microscopy (SEM), transmission electron microscopy (TEM), X-ray diffraction (XRD) and high performance liquid chromatography (HPLC), which shows that they consist of small RDX crystals ( $\sim 0.1\text{--}1\ \mu\text{m}$ ) uniformly and discretely dispersed in a binder. The microparticles were subsequently pressed to produce dense energetic materials which exhibited a markedly lower shock sensitivity. The low sensitivity was attributed to small crystal size as well as small void size ( $\sim 250\ \text{nm}$ ). The method developed in this work may be suitable for the preparation of a wide range of insensitive explosive compositions.

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## 1. Introduction

Unintentional detonation of munitions from accidents and asymmetric threats must be prevented to eliminate the loss of innocent lives and infrastructure in modern conflicts. In order to produce safe munitions capable of surviving unwanted mechanical stimuli such as shocks from explosions and impacts by projectiles, the initiation sensitivity of explosives has to be significantly reduced. As most explosives currently in use are heterogeneous and are typically comprised of a solid secondary high explosive (HE) formulated with a polymeric binder, the sensitivity can be reduced by employing HEs that are chemically stable and require very strong mechanical stimuli for initiation. For example, many explosive formulations based on the explosive triaminotrinitrobenzene (TATB) have a remarkably low sensitivity [1]. However, the application of TATB is limited due to high cost and relatively weak power in comparison to more powerful, but sensitive nitramine explosives such as cyclotrimethylenetrinitramine (RDX), which is one of the most widely used HEs. Therefore, there are a lot of research activities targeting to reduce the sensitivity of explosives using powerful and usually also sensitive HEs.

It is generally understood that with heterogeneous explosives, defects such as large voids (i.e., pores) facilitate initiation by promoting energy localization upon mechanical stimuli, giving rise to the formation of hot-spots [2–6]. Hot-spots of critical size and

temperature can ignite the explosive and consequently lead to detonation [7]. Numerous mechanisms have been proposed to explain the formation and role of hot-spots. These include: adiabatic compression of inter- and intra-crystalline voids [2,8–10], shear band formation within the slip planes [11], and dislocation pile-up collapse [6,12]. Elimination of porosity can substantially desensitize an explosive by inhibiting these mechanisms, however, doing so will often be detrimental to performance. Another approach would be to reduce the mean void size, which should also result in a higher threshold for critical hot-spot formation [7].

A straightforward way for reducing the mean void size is by reducing the crystal size of the HE. Prior studies have demonstrated the effectiveness of this approach in lowering the shock initiation sensitivity of crystalline explosives including hexanitrostilbene (HNS) [13] and RDX [14]. Several techniques have been successfully developed for the production of submicron crystals of RDX. Stepanov et al. developed a process based on rapid expansion of supercritical solutions (RESS) [15]. Patel developed a technique based on bead milling [16]. Several drawbacks of these techniques are high cost as well as the requirement for additional processing steps in order to produce realistic explosive formulations. In particular, the need to formulate very small HE crystals into molding powders, which is typically done by slurry coating [17,18], poses added processing complexity and difficulty. Submicron crystals have a higher tendency to form agglomerates, which can lead to poor binder distribution. In addition, handling of unbound small particles poses a health threat, and thus requires additional means of limiting operator exposure [19,20]. Therefore, processing methods that involve the production of submicron HE crystals and

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subsequent formulation of the HE crystals are expected to be cost-prohibitive for most applications.

In this work, we report a novel spray drying-based method to create nanocomposite microparticles that consist of small RDX crystals uniformly and discretely dispersed in a polymeric binder. A key attribute of this method is the co-precipitation of the HE and the binder during spray drying such that the crystallization of the small RDX crystals and formulation are achieved simultaneously in a single step operation. We demonstrate that nanostructured RDX-based compositions can lead to substantial improvements in regard to sensitivity, thus, enabling development of explosives which can meet both safety and performance requirements.

## 2. Experiments

### 2.1. Materials

RDX crystals used in the work include purified RDX crystals, which contains ~5 wt.% of HMX obtained by recrystallization from acetone of class 5 RDX from BAE Systems and 4- $\mu\text{m}$  fluid energy milled (FEM) RDX crystals from BAE Systems with ~11 wt.% of HMX. The binders used in this work include polyvinyl acetate (PVAc) from Sigma–Aldrich, with a density of 1.19 g/cm<sup>3</sup> and a molecular weight of ~113,000 and a vinyl resin VMCC from Dow, with a density of 1.34 g/cm<sup>3</sup> and a molecular weight of ~19,000. VMCC is a carboxy-functional terpolymer comprised of vinyl chloride, vinyl acetate and maleic acid. Reagent grade acetone from Sigma–Aldrich was used as solvent in preparation of feed solution for spray drying.

### 2.2. Preparation of nanocomposite microparticles

RDX-based nanocomposite microparticles with PVAc or VMCC binders were prepared by spray drying. Both RDX and binder were dissolved into acetone at room temperature with concentrations of 5 wt.% and 1 wt.%, respectively. The solution was spray-dried to produce microparticles using a Buchi 190 spray dryer. The spray dryer was equipped with an ultrasonic nozzle (Model 8700-60, Sono-Tek) operated at 60 kHz and 1.2 W. The flow rate of the feed solution was 3 ml/min. The inlet drying gas (N<sub>2</sub>) temperature was kept at 55 °C.

As a reference, 4- $\mu\text{m}$  FEM RDX crystals were formulated with VMCC by conventional slurry coating. This was accomplished by first suspending RDX crystals in de-ionized water with a solid loading of 10 wt.% and dissolving VMCC in acetone. Then VMCC solution was added into the RDX suspension slowly under vigorous mixing. The dissolved binder precipitated upon addition to the aqueous slurry, coating the dispersed RDX crystals.

### 2.3. Characterization

The nanocomposite microparticles were examined by field-emission scanning electron microscopy (SEM, LEO DSM 982, LEO Electron Microscopy) and transmission electron microscopy (TEM, CM20, Philips). Structural characterization was performed by powder X-ray diffraction (XRD, Rigaku ultima IV XRD system with Cu K $\alpha$  radiation at  $\lambda = 1.5418 \text{ \AA}$ ). Chemical compositions were determined using high performance liquid chromatography (HPLC, Waters Model 2695). Some RDX/PVAc specimens were suspended in a RDX saturated ethanol solution to selectively dissolve the PVAc binder prior to imaging. A focused ion beam (FIB)-SEM (NEON<sup>®</sup> 60, Carl Zeiss) system was employed in preparing and examining the cross-section of a pressed sample.

### 2.4. Shock sensitivity test

The shock sensitivity was evaluated by using the small-scale gap test (SSGT) according to MIL-STD-1751A, Method 1042 [21]. This is a standard test used to determine the shock pressure required in

order to achieve a 50% probability of detonation. Before the shock sensitivity test, samples were pressed into brass cylinders (5.08 mm ID, 25.4 mm OD, 38.1 mm long) at 220 MPa. The samples with VMCC as binder were pressed at room temperature, while those with PVAc as binder were pressed at 55 °C to achieve comparable percentage of theoretical maximum density (TMD), defined as:

$$\frac{\rho_M}{\rho_{HE}C_{HE} + \rho_{Binder}C_{Binder}} \times 100$$

where  $\rho_M$  is the measured density of the pressed samples;  $\rho_{HE}$  and  $\rho_{Binder}$  are the theoretical densities of HE and binder, respectively; and  $C_{HE}$  and  $C_{Binder}$  are the weight fractions of HE and binder, respectively.

## 3. Results and discussion

### 3.1. Structural characterization

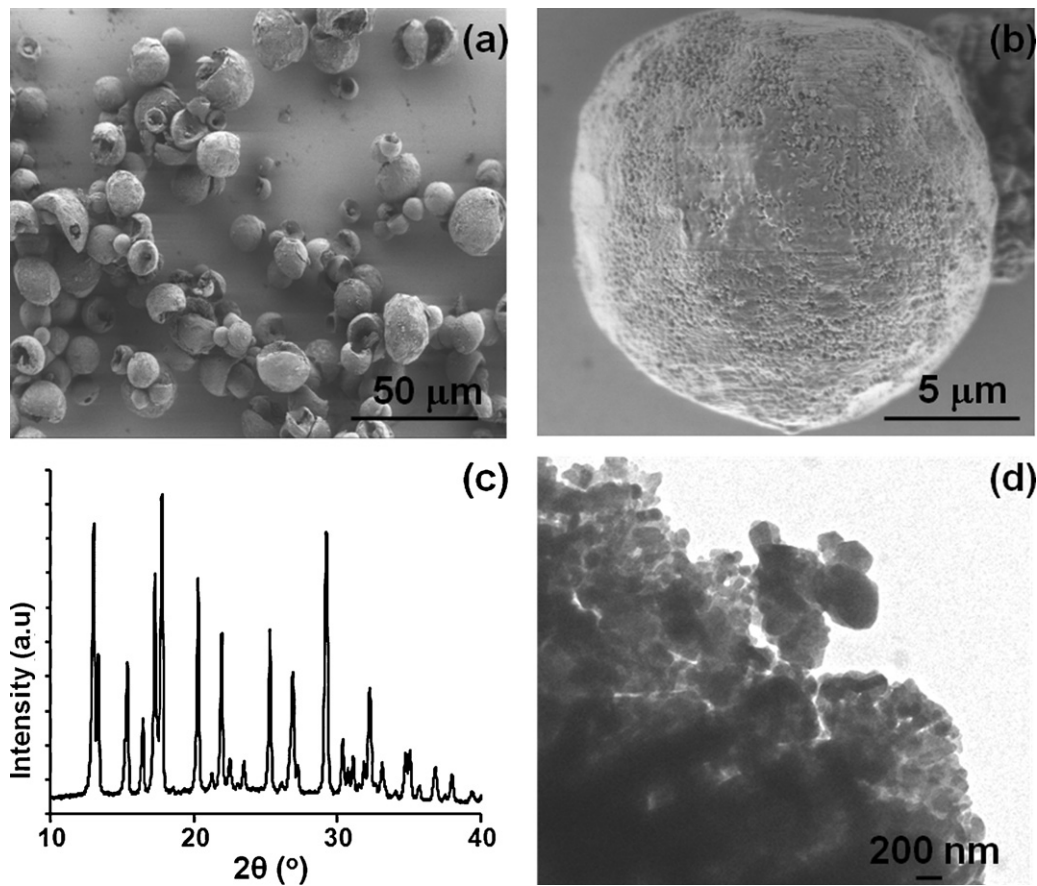
SEM image of nanocomposite microparticles consisting of RDX and PVAc is shown in Fig. 1a. It can be seen that most of the spray-dried RDX/PVAc microparticles formed shells and collapsed during drying. Collapsed shells have been commonly observed during spray drying of other materials upon fast solvent evaporation [20,22,23]. The average microparticle diameter was about 15  $\mu\text{m}$  with most particles in the range of 5–30  $\mu\text{m}$ . The surface morphology of the microparticles is shown in Fig. 1b.

The XRD pattern of the RDX/PVAc microparticles is shown in Fig. 1c. All the diffraction peaks were indexed to RDX, indicating that the RDX phase was crystalline and PVAc was amorphous. The chemical composition of the microparticles was determined to be 83% HE and 17% PVAc by HPLC. The measured composition was identical to the composition of HE and PVAc in the precursor solution, suggesting the composition of the nanocomposite microparticles could be precisely controlled.

The TEM image of the RDX/PVAc microparticles in Fig. 1d shows that the majority of RDX crystals were in the size range of about 100–200 nm at the surface region of the microparticles. This is consistent with the size of the small surface features observed by SEM analysis: (1) on the surface of the as-sprayed microparticles (Fig. 1b) and (2) after PVAc was selectively removed by dissolution in a RDX-saturated ethanol solution (Fig. 2a). An SEM image of a fractured microparticle revealing the crystals in the interior is shown in Fig. 2b. This specimen was also subjected to the selective removal of PVAc prior to SEM characterization. It can be seen that the RDX crystals near the core of the microparticle were considerably larger than those at the surface with some crystals having dimensions of ~1  $\mu\text{m}$ . The SEM, XRD, TEM, and HPLC characterization data suggest that we obtained nanocomposite microparticles in which small RDX crystals, in the range of around one hundred nanometers to one micrometer, were uniformly and discretely dispersed in the PVAc binder.

Fig. 3 shows the SEM images of RDX/VMCC microparticles prepared by spray drying. The size of the RDX/VMCC microparticles is comparable to RDX/PVAc microparticles. The surface is rougher but most of the features are below 1  $\mu\text{m}$ , consistent with the observations of RDX/PVAc microparticles. This implies that other binders can be employed in the production of RDX-based composites by spray drying.

We propose the following mechanism for the formation of the RDX-based nanocomposite microparticles during spray drying. Due to rapid evaporation, the aerosolized solution becomes highly supersaturated with the dissolved species at the droplet liquid–vapor interface [20,24,25]. It appears that precipitation of RDX and binder occurs nearly simultaneously, as evidenced by the uniform distribution of the precipitated RDX and binder phases. As evaporation proceeds, a shell structure forms, which slows down



**Fig. 1.** (a) SEM image showing size and shape variations of spray-dried RDX/PVAc microparticles; (b) SEM images of the surface of a RDX/PVAc composite microparticle; (c) XRD pattern with all peaks indexed to RDX; (d) TEM image of RDX crystals in the surface region of a broken microparticle.

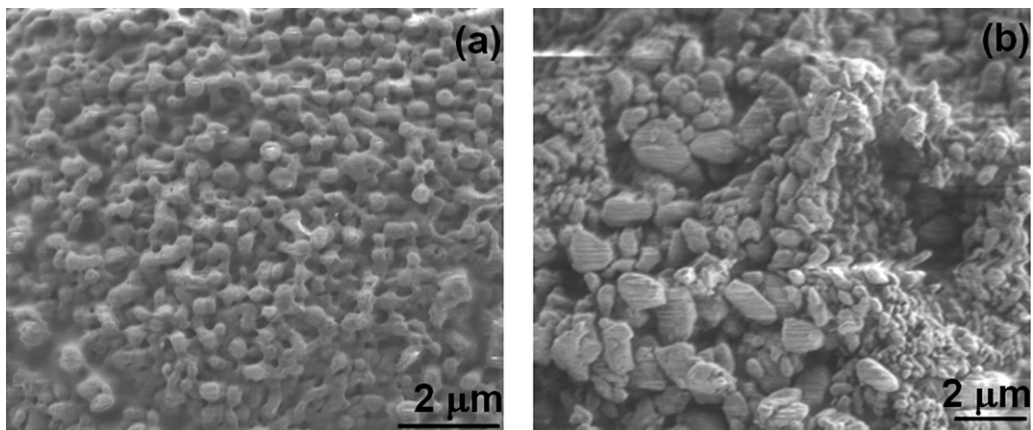
the evaporation rate of acetone. As the evaporation rate decreases so does the supersaturation level during precipitation, resulting in the formation of larger nuclei of RDX with longer crystal growth time. The progressively slower evaporation rate may consequently be responsible for the RDX crystal size gradient observed along the radius of the microparticles as shown in Fig. 2b.

### 3.2. Voids in pressed formulation

The void size in a pressed pellet of RDX/PVAc nanocomposite microparticles was characterized by SEM as shown in Fig. 4. The

pellet was prepared using the same procedure of sample pressing as for the shock sensitivity test and it has a 91.9% of TMD. Large voids, which are beyond a few micrometers and commonly observed in traditional explosives [26], were not observed in both as-fractured cross section of the sample (Fig. 4a) and the cross-section surface prepared by FIB milling (Fig. 4b). Only small voids with an average size of about 250 nm were present (Fig. 4b).

The characterization of the void size clearly demonstrates that despite the high porosity (~8.1%) in the pressed formulation, the mean void size is very small, illustrating the effectiveness of our approach in eliminating large voids in explosive compositions. The



**Fig. 2.** RDX crystals observed on (a) the surface and (b) in the interior section of a microparticle after PVAc was selectively dissolved by RDX saturated ethanol solution.

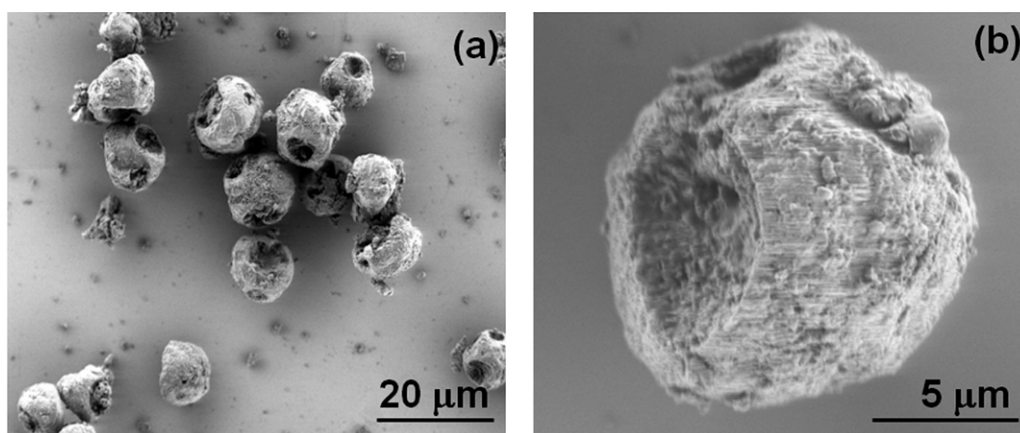


Fig. 3. Low (a) and high (b) magnification SEM images of RDX/VMCC obtained by spray drying.

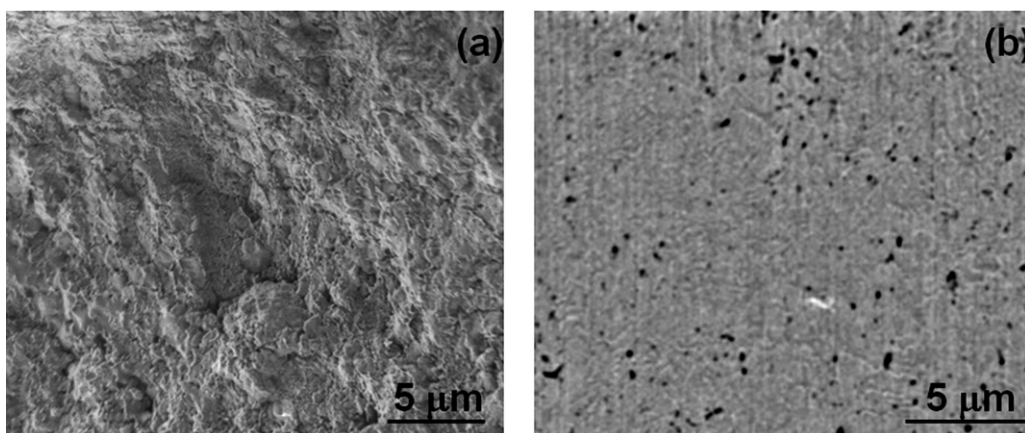


Fig. 4. SEM images of the cross-sections of a pressed sample prepared by (a) fracturing and (b) FIB milling.

**Table 1**  
Shock sensitivity test data.

Composition	Shock sensitivity (GPa)	Density (g/cm <sup>3</sup> )	% TMD	Binder (wt.%)	HMX (wt.%)
RDX/PVAc (spray dried)	4.0	1.58	91.9	17	4
RDX/VMCC (spray dried)	3.3	1.62	92.5	17	9
4- $\mu$ m RDX/VMCC (slurry coated)	2.5	1.64	93.7	17	9

small void size is likely due to the small RDX crystal size and uniform mixing of RDX and PVAc in the spray dried nanocomposite microparticles, and is expected to mitigate hot-spot formation and enhance shock sensitivity.

### 3.3. Shock sensitivity analysis and broader impact

Shock sensitivity data obtained from the SSGT test along with the corresponding density and composition is summarized in Table 1. With binder PVAc content of 17 wt.% and HMX impurity at  $\sim$ 4 wt.%, RDX/PVAc nanocomposite has a measured shock sensitivity of 4.0 GPa. High binder content and low HMX impurity may contribute to this low shock sensitivity. However, this extreme low shock sensitivity was regarded as being mainly enabled by the unique nanostructure of the spray dried microparticle, including small RDX crystal size and uniform mixing of RDX crystals with binder. This is illustrated by directly comparing spray dried RDX/VMCC microparticles to the slurry coated RDX/VMCC, which had similar pressed density and same binder and HMX content. The spray dried RDX/VMCC microparticles have a significantly reduced shock sensitivity of 3.3 GPa, comparing to a shock sensitivity of

2.5 GPa from slurry coated 4- $\mu$ m FEM RDX crystals using VMCC as binder. The comparison confirms the effectiveness of the spray drying method and is consistent with prior observations that lowering HE crystal size, and therefore lowering the void size, can desensitize explosive materials to mechanical stimuli by mitigating the formation of critical hot-spots [7,13].

The manufacturing potential of this spray drying approach appears to be tremendous since spraying drying is a well-established, cost-effective method for producing large quantities of ceramic, drug, and food microparticles [22,27–30]. Furthermore, the simplicity of our “all-liquid” precursor makes the spray drying process easy and straightforward without concerns associated with handling of small crystals. More fundamentally, the results from this investigation provide an important insight as to how a new class of explosive materials could be designed and produced for insensitive munitions applications.

## 4. Conclusions

We have produced RDX-based nanocomposite microparticles using a novel, one-step spray drying-based approach. Characteriza-

tion revealed that the microparticles consist of small RDX crystals uniformly and discretely dispersed in the polymeric binder. We attribute this desired structure of the microparticles to the near-simultaneous and rapid precipitation of RDX and binder during spray drying. The novel RDX-based composite exhibited considerably low shock sensitivity, mostly enabled by the small RDX crystal size as well as small void size. The novel method developed in this work may be suitable for the preparation of a wide range of insensitive explosive compositions, helping bridge the gap between low sensitivity and high performance.

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## References

- [1] D.M. Badgular, M.B. Talawar, S.N. Asthana, P.P. Mahulikar, Advances in science and technology of modern energetic materials: an overview, *J. Hazard. Mater.* 151 (2008) 289–305.
- [2] F.P. Bowden, A.D. Yoffe, *Initiation and Growth of Explosion in Liquids and Solids*, Cambridge University Press, 1952.
- [3] S.M. Walley, J.E. Field, M.W. Greenaway, Crystal sensitivities of energetic materials, *Mater. Sci. Technol.* 22 (2006) 402–413.
- [4] G.M. Swallowe, J.E. Field, Ignition of a thin layer of explosive by impact—the effect of polymer particles, *Proc. R. Soc. Lond. Ser. A* 379 (1982) 389–408.
- [5] R.B. Frey, Cavity collapse in energetic materials, in: Eighth Symposium (International) on Detonation, U.S. Naval Surface Weapons Center, Washington, DC, 1985, pp. 68–80.
- [6] J.E. Field, Hot spot ignition mechanisms for explosives, *Acc. Chem. Res.* 25 (1992) 489–496.
- [7] C.M. Tarver, S.K. Chidester, A.L. Nichols III, Critical conditions for impact- and shock-induced hot spots in solid explosives, *J. Phys. Chem.* 100 (1996) 5794–5799.
- [8] I.B. Mishra, L.J.V. Kieft, Novel approach to insensitive explosives, in: 19th International Annual Conference at ICT, Karlsruhe, Germany, 1988.
- [9] L. Borne, Influence of intragranular cavities of RDX particle batches on the sensitivity of cast wax bonded explosives, in: 10th International Symposium on Detonation, Boston, MA, 1993.
- [10] J.E. Balzer, J.E. Field, M.J. Gifford, W.G. Proud, S.M. Walley, High-speed photographic study of the drop-weight impact response of ultrafine and conventional PETN and RDX, *Combust. Flame* 130 (2002) 298–306.
- [11] C.S. Coffey, Initiation due to plastic deformation from shock or impact, in: P.A. Politzer, J.S. Murray (Eds.), *Energetic Materials*, Volume 13, Part 2, Detonation, Combustion (Theoretical and Computational Chemistry), Elsevier Science, Amsterdam, Netherland, 2003, p. 101.
- [12] R.W. Armstrong, C.S. Coffey, V.F. Devost, W.L. Elban, Crystal size dependence for impact initiation of cyclotrimethylenetrinitramine explosive, *J. Appl. Phys.* 68 (1990) 979–984.
- [13] R.E. Setchell, Grain-size effects on the shock sensitivity of hexanitrostilbene (HNS) explosive, *Combust. Flame* 56 (1984) 343–345.
- [14] V. Stepanov, Production of Nanocrystalline RDX by RESS: Process Development and Material Characterization, Ph.D. thesis, New Jersey Institute of Technology, US, 2008.
- [15] V. Stepanov, L.N. Krasnoperov, I.B. Elkina, X. Zhang, Production of nanocrystalline RDX by rapid expansion of supercritical solutions, *Propell. Explos. Pyrotech.* 30 (2005) 178–183.
- [16] R. Patel, Slurry coating process for nano-RDX produced by a bead mill, in: *Insensitive Munitions and Energetic Materials Technology Symposium*, Miami, Florida, 2007.
- [17] K.V. Biert, D.A. Geiss, Insensitive Explosives for High Speed Loading Applications, US Patent 678,361,5B1 (2004).
- [18] L. Borne, J. Mory, F. Schlessler, Reduced sensitivity RDX (RS-RDX) in pressed formulations: respective effects of intra-granular pores, extra-granular pores and pore sizes, *Propell. Explos. Pyrotech.* 33 (2008) 37–43.
- [19] J. Kim, O. Wilhelm, S.E. Pratsinis, Nanoparticle packaging, *Adv. Eng. Mater.* 4 (2002) 494.
- [20] N. Tsapis, D. Bennett, B. Jackson, D.A. Weitz, D.A. Edwards, Trojan particles: large porous carriers of nanoparticles for drug delivery, *Proc. Natl. Acad. Sci. U.S.A.* 99 (2002) 12001–12005.
- [21] MIL-STD-1751A, US Department of Defense Test Method Standard, Safety and Performance Tests for the Qualification of Explosives (High Explosives, Propellants, and Pyrotechnics), 2001.
- [22] G.L. Messing, S.-C. Zhang, G.V. Jayanthi, Ceramic powder synthesis by spray pyrolysis, *J. Am. Ceram. Soc.* 76 (1993) 2707–2726.
- [23] R. Vehring, Pharmaceutical particle engineering via spray drying, *Pharm. Res.* 25 (2008) 999–1022.
- [24] K.H. Leong, Morphological control of particles generated from the evaporation of solution droplets: theoretical considerations, *J. Aerosol Sci.* 18 (1987) 511–524.
- [25] R. Vehring, W.R. Foss, D. Lechuga-Ballesteros, Particle formation in spray drying, *J. Aerosol Sci.* 38 (2007) 728–746.
- [26] H. Czerski, M.W. Greenaway, W.G. Proud, J.E. Field, Links between the morphology of RDX crystals and their shock sensitivity, *AIP Conf. Proc.* 845II (2006) 1053–1056.
- [27] J. Raula, H. Eerikainen, E.I. Kauppinen, Influence of the solvent composition on the aerosol synthesis of pharmaceutical polymer nanoparticles, *Int. J. Pharm.* 284 (2004) 13–21.
- [28] P. Giunchedi, U. Conte, Spray-drying as a preparation method of microparticulate drug delivery systems: an overview, *S. T. P. Pharma Pratiques* 5 (1995) 276–290.
- [29] B.F. Gibbs, S. Kermasha, I. Alli, C.N. Mulligan, Encapsulation in the food industry: a review, *Int. J. Food Sci. Nutr.* 50 (1999) 213–224.
- [30] A. Gharsallaoui, G. Roudaut, O. Chambin, A. Voilley, R. Saurel, Applications of spray-drying in microencapsulation of food ingredients: an overview, *Food Res. Int.* 40 (2007) 1107–1121.