

Supporting Information

Engineering the morphology and particle size of high energetic compounds using Drop-by-Drop and Drop-to-Drop solvent antisolvent interaction methods

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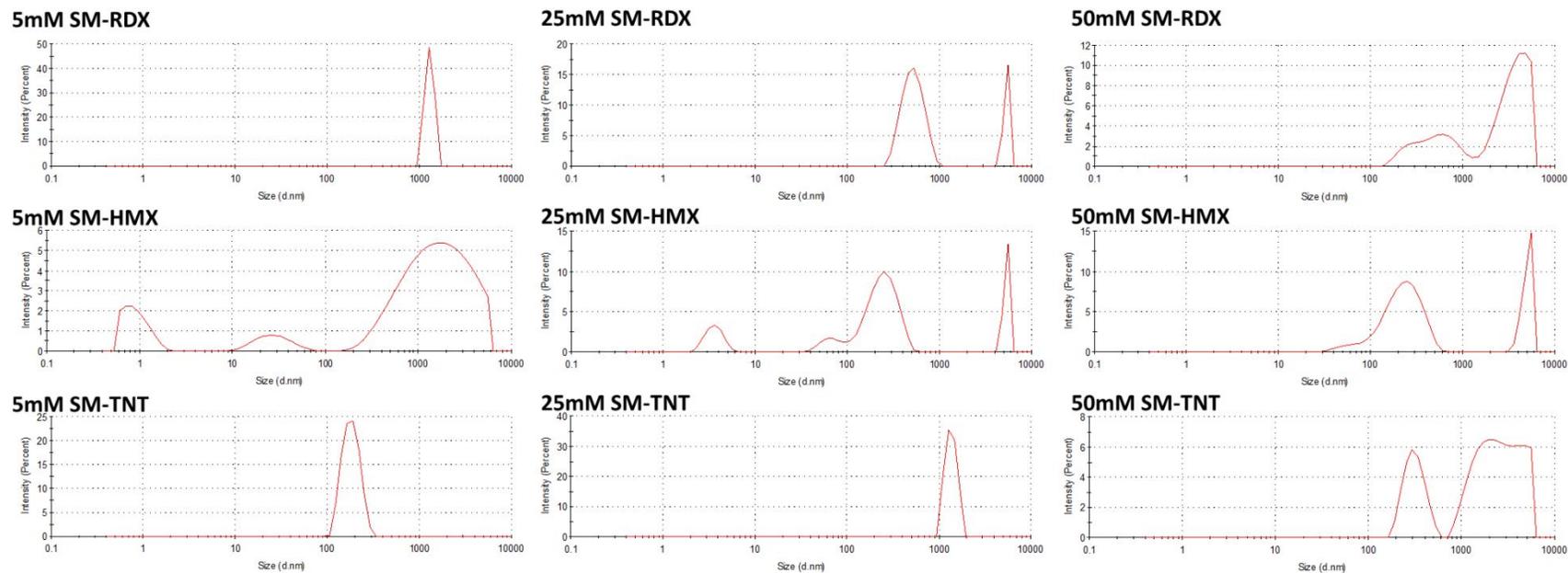


Figure S1 Particle size distribution of the high energetic compound submicron (SM) particles that were prepared using drop-by-drop addition of solution to the antisolvent (water) from acetone solutions of various concentrations.

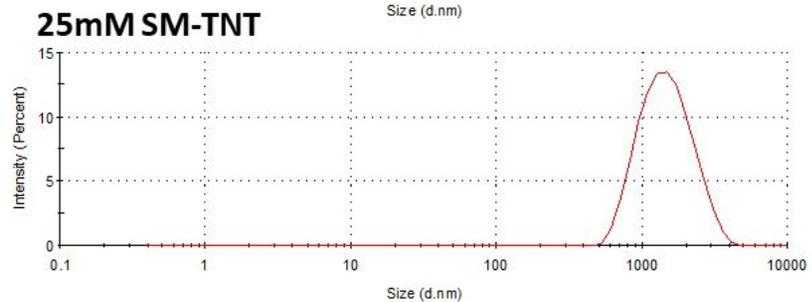
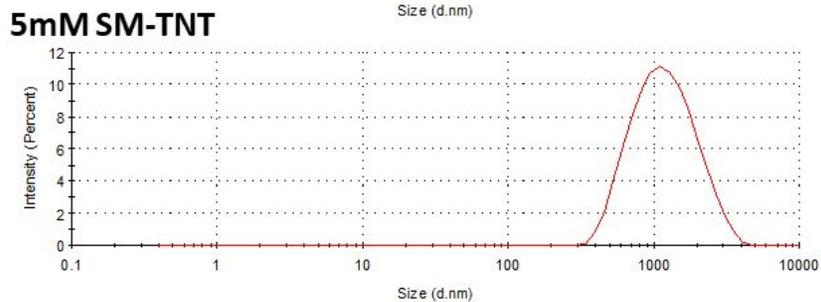
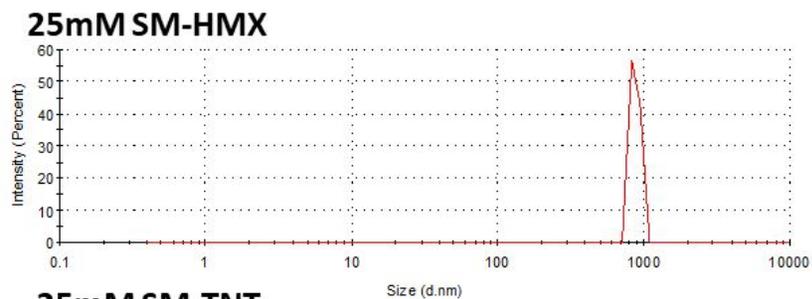
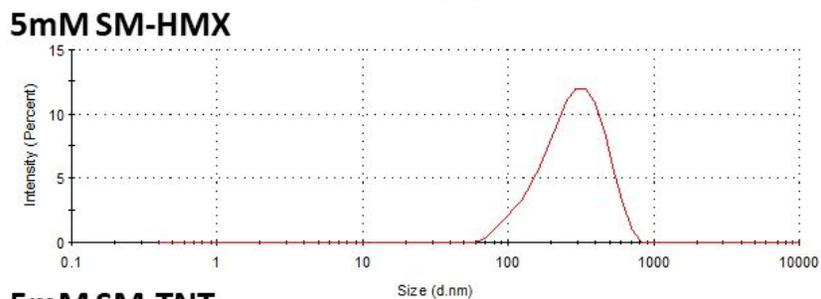
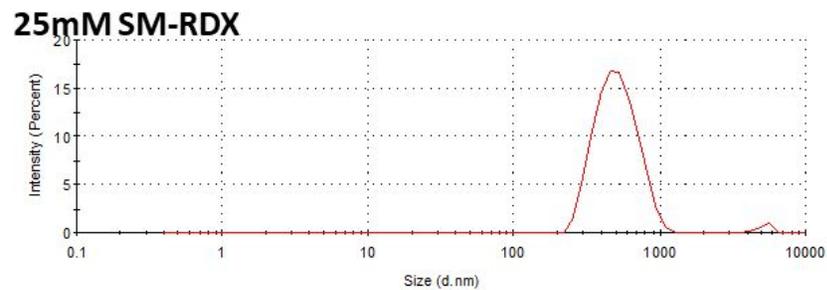
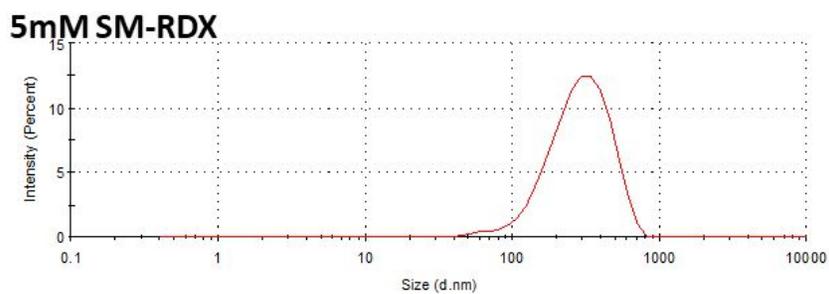


Figure S2 Particle size distribution of the high energetic compound submicron (SM) particles that were prepared using drop-to-drop addition of solution to the antisolvent (water) from acetone solutions of various concentrations.

Table T1 Comparison of different methods for crystallization of RDX

Entry	Method	Particle size	Key results of the study	Comments
1	Rapid Expansion of Supercritical Solutions ¹	110-220 nm	Aggregated particles are with round and oval shaped, smaller size distribution and crystalline. No change in melting point after crystallization.	Process is difficult and expensive to install and maintain.
2	EASAI method ²⁻⁴	< 100 nm	Spherical nanoparticles of RDX and HMX could be prepared. Found acetone as a suitable solvent for preparing nanoparticles of high energetic compounds with size below 100 nm	Simple process for the production of high energetic compounds with size below 100 nm. However, it is a batch process having low solid loading and hence difficult to upscale.
3	RESS ⁵	73 nm	Prepared RDX nanoparticles. A new experimental approach for the in-situ monitoring of nanoparticles formed during the rapid expansion of supercritical solutions was developed.	Process is difficult and expensive to install and maintain.
4	RESS-AS ⁶	100 nm	RDX nanoparticles having polymer coating could be prepared.	The process need dedicated experimental setup and trained expert.
5	Ultrasonic spray ⁷	800 nm	Particles of RDX range from 800 nm to 2.6 μ m, with number of random shape crystals due to coalescence. PVP acts as nucleation inhibitor and Brij97 and oleyamine promoted nucleation.	Not suitable for the preparation of pure nanoparticles of RDX. Difficult to control size and shape.
6	Pneumatically Assisted Nebulization ⁸	80-500 nm	Studied the preparation of RDX on different surfaces such as glass, silicon and stainless steel. Prepared particles are having different shapes, broad size distribution and aggregated.	Difficult to control the particle size and shape.
7	Spray drying ⁹	100-500 nm	Prepared spherical particle with good crystallinity	Difficult to prepare monodispersed and large scale
9	Present study	<500 nm	Developed continuous nanoparticle preparation process with high solid loading.	Suitable for continuous preparation of other organic compounds and industrial application.
10	Drowning out crystallization ¹⁰	< 5 μ m	Prepared nanoparticles of RDX were rod and oval shaped at different conditions.	The particle are micron sized with controlled morphology

References

- (1) Stepanov, V.; Elkina, I. B.; Matsunaga, T.; Chernyshev, A. V.; Chesnokov, E. N.; Zhang, X.; Lavrik, N. L.; Krasnoperov, L. N. Production of Nanocrystalline RDX by Rapid Expansion of Supercritical Solutions. *Int. J. Energ. Mater. Chem. Propuls.* **2007**, *6* (1), 75–87.
- (2) Kumar, R.; Siril, P. F.; Soni, P. Tuning the Particle Size and Morphology of High Energetic Material Nanocrystals. *Def. Technol.* **2015**, *11* (4), 382–389.
- (3) Kumar, R.; Siril, P. F.; Soni, P. Optimized Synthesis of HMX Nanoparticles Using Antisolvent Precipitation Method. *J. Energ. Mater.* **2015**, *33* (4), 277–287.
- (4) Kumar, R.; Siril, P. F.; Soni, P. Preparation of Nano-RDX by Evaporation Assisted Solvent-Antisolvent Interaction. *Propellants, Explos. Pyrotech.* **2014**, *39* (3), 383–389.
- (5) Matsunaga, T.; Chernyshev, A. V.; Chesnokov, E. N.; Krasnoperov, L. N. In Situ Optical Monitoring of RDX Nanoparticles Formation during Rapid Expansion of Supercritical CO₂ Solutions. *Phys. Chem. Chem. Phys.* **2007**, *9* (38), 5249.
- (6) Essel, J. T.; Cortopassi, A. C.; Kuo, K. K.; Leh, C. G.; Adair, J. H. Formation and Characterization of Nano-Sized RDX Particles Produced Using the RESS-AS Process. *Propellants, Explos. Pyrotech.* **2012**, *37* (6), 699–706.
- (7) Kim, J.-W.; Shin, M.-S.; Kim, J.-K.; Kim, H.-S.; Koo, K.-K. Evaporation Crystallization of RDX by Ultrasonic Spray. *Ind. Eng. Chem. Res.* **2011**, *50* (21), 12186–12193.
- (8) Barreto-Cabán, M. A.; Pacheco-Londoño, L.; Ramírez, M. L.; Hernández-Rivera, S. P. Novel Method for the Preparation of Explosives Nanoparticles. In *proceedings of SPIE*; Carapezza, E. M., Ed.; International Society for Optics and Photonics, 2006; Vol. 6201, p 620129.
- (9) Qiu, H.; Stepanov, V.; Di Stasio, A. R.; Surapaneni, A.; Lee, W. Y. Investigation of the Crystallization of RDX during Spray Drying. *Powder Technol.* **2015**, *274*, 333–337.
- (10) Institute of Industrial Organic Chemistry (Poland), A.; Nandi, A. K.; Newale, S. P.; Gajbhiye, V. P.; Prasanth, H.; Pandey, R. K. *Central European Journal of Energetic Materials : CEJEM.*; Institute of Industrial Organic Chemistry, 2004.