Construction and Properties of Structure- and Size-controlled Micro/nano-Energetic Materials

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Abstract

This article presents a comprehensive review of recent progress of research dedicated to structure- and size-controlled micro/nano-energetic materials. The development of the construction strategies for achieving zero-dimensional (0D), one-dimensional (1D), two-dimensional (2D), and three-dimensional (3D) micro/nanostructures from energetic molecules is introduced. Also, an overview of the unique properties induced by micro/nanostructures and size effects is provided. Special emphasis is focused on the size-dependent properties that are different from those of the conventional micro-sized energetic materials, such as thermal decomposition, sensitivity, combustion and detonation, and compaction behaviors. A conclusion and our view of the future development of micro/nano-energetic materials and devices are given.

Keywords: Structure; Size; Micro/nano-energetic materials; Construction technologies; Properties

1. Introduction

It is well known that size, structure and shape have significant influence on properties of inorganic/organic materials, such as optics, electrics, optoelectronics, gas-sensor, and magnetic properties \cite{1–9}. Similarly, micro/nano-energetic materials with distinct structures and extremely small feature sizes also exhibit structure- and size-dependent properties, including thermal decomposition, sensitivity and operational performance \cite{10–14}. Therefore, the controllable preparation of micro/nano-energetic materials with different morphologies and sizes is of great importance for achieving desirable properties.

However, it is more difficult for the synthesis of micro/nano-energetic materials than that of inorganic nanostructures because most of energetic compounds feature van der Waals or other weak intermolecular interactions among molecules, and they are dangerous explosives \cite{15–17}. Up to now, relatively few facile and simple approaches have been developed to construct the micro/nanoparticles of energetic materials, mainly including reprecipitation \cite{10,18}, rapid expansion of supercritical solutions \cite{19,20}, and physical vapor deposition (PVD) techniques \cite{21}. Moreover, to the best of our knowledge, there have scarcely been any reports on the detailed researches of micro/nano-energetic materials with various morphologies and dimensions so far. Accordingly, the development of mild and universal methods for the fabrication of micro/nano-energetic materials with novel morphologies is clearly of great urgency but a tremendous challenge.

In this review, the recent progress of the size- and structure-controlled micro/nanomaterials based on energetic compounds is introduced. In Section 2, the advanced
construction strategies developed for the fabrication of energetic micro/nanostructures are reviewed. The preparation methods for energetic micro/nanostructures with diverse dimensions and sizes are discussed in detail. In Section 3, some more recently studied unique properties of micro/nano-energetic materials are introduced, with emphasis on the size-dependent thermal decomposition and tunable sensitivity characteristics. In Section 4, a summary and our view of the future development trend in this area are given.

2. Construction technologies

The development of effective and universal construction technologies is prerequisite to the further investigation of micro/nano-energetic materials. However, most current approaches which have been developed to prepare the inorganic nanomaterials, are not applicable for energetic materials due to the lower melting/sublimation points and huge potential danger. In the field of organic small-molecule nanomaterials, the considerable efforts have been dedicated to the controllable synthesis of various organic nanomaterials with distinct shapes, such as nanoparticles [22–24], nanotubes [25,26], nanowires [27–29], nanorods [30,31], and nanobelts [32,33]. These fruitful attempts should give a useful enlightenment for the design and fabrication of micro/nano-energetic materials with peculiar structures. Therefore, in this section, we just introduce in more detail the recent successful examples of synthesizing micro/nano-energetic materials with the prevalent methods which have been used extensively in other fields.

2.1. Re-precipitation method

2.1.1. Cooling crystallization

Cooling crystallization has achieved a great success in the synthesis of energetic materials with special structures and narrow size distribution [34]. For this technique, the type of co-solvent, cooling rate and solvent composition are the important process parameters to control the morphology and size of the crystals. However, it is difficult to reduce the size of the products when the energetic compounds are used as target sources.

Han and coworkers recently studied the solubility and recrystallization of highly hydrogen-bonded 1,3,5-triamino-2,4,6-trinitrobenzene (TATB) in various ionic liquid solvent systems [35]. They synthesized TATB microparticles grown by the cooling crystallization process in ionic liquid—dimethyl sulfoxide (DMSO) co-solvent systems. It is known that the spherical crystals of energetic materials exhibit improved performance over non-spherical crystals, such as insensitivity to sudden shock, processability and packing density [36,37]. Vijayalakshmi et al. fabricated spherical 3-nitro-1,2,4-triazol-5-one (NTO) particles in NTO : water : N-methyl-2-pyrolidone (NMP) ternary system by using cooling crystallization technique [38]. By adjusting the process parameters, such as cooling rate, agitator configuration and speed, a selective particle size distribution ranging from 10 to 200 μm could be achieved (Fig. 1). Kim and his coworkers used a similar assembly method to prepare spherical NTO particles in the co-solvent of water and NMP [39–43]. The spherical particles with average diameter ranging from 30 to 300 μm were acquired in the ratio of NTO/NMP ranging from 0.2 to 0.6 and in the ratio of water/NMP ranging from 1.0 to 4.8 at the cooling rate of 10 K/min. Besides, Kim’s group used octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine (HMX) as seed to direct the zero-dimensional (0D) core—shell structure growth of HMX/NTO by two-step cooling crystallization [44,45]. The typical scanning electron microscopy (SEM) images of these energetic composites in Fig. 2 reveal that the surface of the core—shell HMX/NTO structures is compact and uniform. They pointed out that the agglomeration kinetic for the coating of NTO on HMX core particles was correlated with the 3rd power of the solution supersaturation and the 2nd power of the number of the suspended particles.

2.1.2. Solvent/nonsolvent process

Since the first use of solvent/nonsolvent method in the preparation of organic nanocrystals by Nakanishi in 1993 [46], this technology has been extensively adopted in the field of energetic materials due to its facility and versatility [18,47–50]. The method mainly includes a rapid mixing of concentrated solution of the objective compound in a good solvent with excess of a poor solvent, leading to the nucleation and growth of the molecules to small-sized particles with desired structures. The significant difference between the solubilities of the target molecules in the good and poor
solvents and the good compatibility of the two solvents are essential.

A series of energetic micro/nanoparticles were successfully fabricated by using this method. For example, Liu et al. reported that reticular nano-sized HMX was simply constructed at room temperature [10]. SEM and transmission electron microscopy (TEM) show that the spherical HMX particles with diameter of about 50 nm aggregate into reticularly structured conglomerates, as shown in Fig. 3. Subsequently, Li et al. prepared HMX microcrystals and studied their microscopic morphologies [51,52]. Moore and coworkers also obtained submicron-sized HMX by pouring a solution of HMX in acetone into a cold nonsolvent with strong stirring [53,54]. van der Heijden’s group and Arya’s group prepared hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX) and 2,2,4,4,6,6-hexanitrostilbene (HNS) ultrafine particles, respectively. Our group fabricated 2,6-diamino-3,5-dinitropyrazine-1-oxide (LLM-105) microtubes with a distinctive rectangular cross-section architecture by using ionic liquid 1-butyl-3-methylimidazolium trifluoromethanesulfonate ([Bmim]CF₃SO₃) as good solvent and water as poor solvent [55]. In addition, other various structures and morphologies of ultrafine RDX have also been reported, such as murphy-like, cube-like, and spherical [56]. It is found that the morphologies and sizes of the obtained structures can be controlled by adjusting the experimental parameters.

2.1.3. Nozzle-assisted solvent/nonsolvent process

The above mentioned solvent/nonsolvent method has been used to synthesize the energetic compounds with desired size and special morphology, but it suffers with an issue of process scale-up. Therefore, an instrument with high-pressure jet, which can lead to a rapid nucleation in continuous reaction and crystallization, producing the nanoscale energetic particles with high yield and mass production, was developed in the past few years.

Wang and his coworkers reported the fabrication of submicron HMX and RDX by spraying a solution of the nitr-amine explosive into water at different process parameters [57]. Recently, they also prepared the high-purity HNS nanocrystals with high specific surface area and narrow particle size distribution by using a prefilming twin-fluid nozzle-assisted precipitation method [58,59]. In our laboratory, the large-scale TATB nanoparticles were obtained by atomizing the objective compound to the small droplets through a nozzle at high speed [60,61]. TEM and atomic force microscopy (AFM) images show that the resulting nano-TATB particles have the shape of sphere or ellipsoid with size of about 60 nm (Fig. 4). Bayat and coworkers used a similar method to prepare the submicron particles of HMX and systemically investigated the influence of the experimental parameters, such as antisolvent temperature, compressed air flow rate, and nozzle diameter [62], on the size of HMX particle, while Shokrolahi and coworkers obtained the crystalline nanoparticles of keto-derivative of RDX (K-6) [63].

2.1.4. Ultrasound-assisted solvent/nonsolvent process

Ultrasound-assisted solvent/nonsolvent is an effective and safe technology for preparing the micro/nanoparticles of energetic materials [64,65]. It is generally used to control the nucleation process [66]. Sivabalan et al. combined the ultrasound technology with the solvent/nonsolvent method to control the size and morphology of 2,4,6,8,10,12-hexanitro-2,4,6,8,10,12-hexaazaisowurtzitane (CL-20) [67]. The results reveal that the sonication process offers a uniform morphology without any agglomeration, and the particle size of sonicated CL-20 sample obtained is about 5 μm with a narrow particle size distribution. Bayat and his coworkers introduced the sonication into spaying-assisted precipitative crystallization to prepare the spherical or ellipsoidal CL-20 nanoparticles with an average size of 95 nm [68]. They pointed out that the nanoparticles tend to agglomerate due to their smaller size. Wang and his coworkers also demonstrated that ultrafine CL-20 was synthesized with ethyl acetate as solvent and heptane or n-hexane as non-solvent by using an ultrasound- and spray-assisted precipitation [69].

2.2. Spray drying strategy

2.2.1. Spray drying

Besides the above re-precipitation method, a simple spay drying technology, which has been widely used to prepare the submicrometer- or nanosized inorganic and polymeric nanoparticles [70–72], is utilized to prepare the nanostructures
of energetic materials. For example, Castro-Rosario and his coworkers prepared RDX nanoparticles with an average size of 405 nm by exposing the glass substrate surfaces to an aerosol jet containing RDX [73]. Ultra-fine HNS explosive with spherical morphology was acquired with the aid of spray drying process by Wang’s group, and there was no phase transition in the process of preparation [74]. Recently, Qiu and his coworkers assessed the feasibility of single-step preparation of HMX-based nanocomposite particles with polymeric binder by using spray drying [75]. It was found that the microparticles consist of small crystals uniformly and discretely dispersed in a binder. This facile method may be suitable for the preparation of a wide range of insensitive explosive compositions. Zhigach et al. demonstrated that ultrafine nitramine (RDX, HMX and CL-20) powders with an average crystal size of about 1 μm and aluminized nanocomposites were produced [76]. Our group extended this technology to core—shell binary energetic system. For instance, we prepared and characterized a new type of composite particles with a core—shell structure by injecting a tetrahydrofuran (THF) suspension containing NTO and HMX into a spray dryer. After THF evaporation, NTO crystallized in the shape of small particles on the surface of HMX microparticles, and the core—shell structure of HMX/NTO composite particles was obtained [77]. The surface of the composite particles was “potholed”, while that of HMX particles was smooth. Moreover, the ultrafine TATB/benzotrifuroxan (BTF) core—shell composite particles can also be synthesized by using the spray drying method [78].

2.2.2. Electrospray crystallization

Electrospray crystallization is one of the effective methods to achieve the nano- and submicron-sized crystals [79]. With the aid of high potential difference, the electrostatic forces could overcome the surface tension, and any flow arriving at the tip of the nozzle is directly emitted as a jet of liquid droplets. As a result, a mist of ultrafine solution droplets is generated, and the subsequent solvent evaporation leads to the formation of submicron-sized crystals [80]. For example, Radacsi’s group developed an electrospray crystallization method (Fig. 5) to prepare the agglomerated RDX hollow spheres with the size of around 4 μm and spherical particles with a size ranging from 200 to 600 nm under the different potential differences [81]. Reus and his coworkers prepared the encapsulated RDX–trinitrotoluene (TNT) core—shell nanoparticles by using the electrospray technique, and the composition of the particles needs further investigation [82].

2.2.3. Ultrasound-assisted spray drying

Ultrasound-assisted spray drying, as one of various atomization techniques, is a favored method because of its excellent energy-efficiency and the inherently low velocity of initial droplets [83]. Accordingly, this outstanding technique has been employed for the preparation of energetic materials with micro/nanostructures.

Spitzer and his coworkers reported the first use of the atomization process for the continuous crystallization of explosive submicrometer- and nano-energetic compounds.
More inspiringly, RDX or 2,2-bis[(nitroxy)methyl]-1,3-propanediol (PETN) nanoparticles can be produced from 1 to 10 g/h by using a reactor containing one ultrasonic piezoelectric transducer, and even can be scaled up using several transducers. Qiu et al. reported that RDX- or CL-20-based nanocomposite consisting of explosive crystals with nanometer-submicron size range can be obtained by ultrasonic spray from an explosive/polyvinyl acetate binder/acetone dilute solution [86–88]. Recently, Koo and his coworkers also utilized this technology to achieve ultrafine RDX with size of 0.8–2.6 μm [89,90]. It could be observed from Fig. 6 that RDX concentration and furnace temperature play an important role in controlling the crystal size and habit. They also concluded that a nucleation inhibitor could be utilized as a habit modifier and the onset time of nucleation is an important factor to improve the crystal shape.

2.3. Spray freeze-drying technique

Spray freeze-drying (SFD) technique, which is considered as one of the advanced ways for the fabrication of nanoparticles, has been widely used for the synthesis of nanostructures of biological medicaments and inorganic materials [91–93]. The particles obtained by this method generally possess the intriguing advantages, such as molecular scale homogeneity because of flash freezing in the cryogen, and minimal agglomeration because of the sublimation of the water ice in the low-temperature vacuum drying condition [94,95]. So far, this system has been used to synthesize the nanostructures of energetic materials.

In the early years, our group reported the fabrication of three-dimensional (3D) nano-network structures of NTO [96]. Since the formed ice limits the aggregation of small particles, the obtained NTO particles have an elongated shape and the size of the particles is in the range of 70–90 nm. With a similar technique, 1,1-diamino-2,2-dinitroethylene (FOX-7) 3D grid nanostructures with different unit sizes were also prepared by the freeze-drying technique mentioned above [97]. The preparation process of FOX-7 3D grid nanostructures is shown in Fig. 7(a). The typical SEM images in Fig. 7(b), (c) indicate that the resulting FOX-7 3D structures are constructed from one-dimensional nanostructures. The size and reticular structures of the as-resulting nano-FOX-7 could be easily controlled by adjusting the concentration of the aqueous solution of raw materials. The further investigation on a possible formation mechanism of this structure reveals that a high degree of supercooling under the liquid nitrogen conditions leads to a high nucleation rate, and the small particles and ice are rapidly formed due to the rapid heat transfer between the aqueous solution and the cryogen. After the sublimation of ice, the small
particles with a relatively high energy start to aggregate by self-assembly, leading to the formation of 3D grid structures. A scheme of this growth process is summarized in Fig. 7(d). More importantly, this facile synthesis strategy may represent a general approach for the preparation of nanostructures of other water-solubility energetic compounds.

2.4. Sol-gel processing

Sol-gel processing is a feasible way to prepare the inorganic/organic nanocomposites under mild conditions [98–102]. The stoichiometry and homogeneity of the nanocomposites can be easily controlled by using this method, and therefore this method could dramatically improve current state-of-the-art technology. Moreover, the sol–gel chemistry has the ability to construct the nanostructured materials with special shapes, such as uniform net-shape geometric solids, fibers, films, and powders with nanoscale size [103,104].

Tillotson’s group used the sol–gel processing to prepare the composite nano-energetic materials [105]. In this process, RDX or PETN was first loaded into the pores of the wet monolithic gel and then was kept there upon supercritical solvent extraction drying, which helps restrain the growth of the explosive particle beyond the nanometer and submicron scale. Brill and his coworkers prepared various unusual energetic composites, in which CL-20 nanoparticles were uniformly coated with energetic polymer gels using sol–gel method [106–108]. Ingale et al. demonstrated that the silica xerogels incorporated with nanocrystalline PETN or PETN/TNT were synthesized, in which the content of energetic materials ranges from 50% to 90% (w/w) [109,110]. Our group used this strategy to prepare laminate-like structured HMX/ammonium perchlorate (AP)/resorcinol-formaldehyde (RF) aerogel with uniform pores [111], as shown in Fig. 8(a), (b). The XRD results show that the mean size of HMX crystals is less than 100 nm and the mixture of HMX and AP is uniform in nano-scale. The specific surface area of HMX/AP/RF is 27 m²/g, which is much less than that of RF aerogel. The mesopores and micropores of HMX/AP/RF composites mainly distribute in the range of 2–20 nm and 0.6–1.6 nm, respectively. Besides HMX/AP/RF, we also prepared RDX/RF gel by means of emulsion process and sol–gel technique [112]. SEM images are given in Fig. 8(c)–(e), which clearly show that the particle size of RDX/RF composites is controlled by adjusting the composition of the surfactant system and the temperature of growth solution. Recently, Luo and his coworkers reported the preparation of an AP/RDX/SiO₂ nanocomposite energetic materials [113]. They found that the distance between the SiO₂ colloidal particles was enlarged due to the presence of RDX and AP, which is contributed to the lower crosslinking structure and the bigger pores.

2.5. Supercritical fluid precipitation processes

Supercritical fluids have been used as solvents for a wide variety of applications in the field of organic and inorganic materials [114–116]. On the basis of above fluids, various supercritical fluid-based precipitation methods have been developed and have attracted extraordinary attention due to unique micronization processes compared with conventional
crystallization techniques, such as milling, crushing, spray drying, and crystallization from liquid solution [117,118]. The supersaturation and nucleation rates, and the size and morphology of micro/nanoparticles can be easily controlled by varying the process parameters. To date, the supercritical fluid processes, mainly including rapid expansion supercritical solutions (RESS) process and supercritical anti-solvent (SAS) process [19,119], have been used for explosives.

2.5.1. Rapid expansion of supercritical solutions (RESS)

RESS, which is to saturate a supercritical fluid with the objective compound and then depressurize this solution into a low pressure chamber through a heated nozzle, is a simple process for explosive that enables the growth of micro/nanoparticles without the need for a drying process [19]. Morris measured the solubility of RDX in carbon dioxide (CO₂) at 303–353 K and 6.9–48.3 MPa, and confirmed a maximum

![Diagram of crystallization process](image_url)

Fig. 7. (a) Flow chart of FOX-7 quasi-three-dimensional grids fabricated via SFD technique; (b) low magnification; (c) high magnification of SEM images of FOX-7 nanostructures prepared with \( C_{FOX-7} = 0.1 \) g/L; (d) a probable formation process of FOX-7 network structures under the same supercooling rate [97].

![SEM images](image_url)

Fig. 8. (a), (b) SEM micrographs of HMX/AP/RF aerogel [111]. SEM images of the as-obtained RDX/RF composite at different temperatures and proportions of the surfactant, respectively; (c) 70 °C, 5%; (d) 90 °C, 5%; (e) 70 °C, 2% [112].
solubility of about 0.25 mg of RDX/g of CO₂ [120]. Subsequently, Kröber et al. reported that TNT and NTO can be micronized by the RESS process [121]. RDX was precipitated to the ultrafine particles with spherical morphology by using compressed liquid dimethyl ether (DME) as a solvent [122]. Krasnoperov’s group produced RDX nanocrystals by RESS [123]. The experiments were performed by expanding the supercritical solution of RDX in carbon dioxide through sapphire nozzles, as shown in Fig. 9(a). SEM images indicate that the tunable particle size of resulted RDX nanocrystal is in the range of 110–220 nm with a narrow size distribution (Fig. 9(b)–(d)). Moreover, they also further investigated the optimized conditions and initiation sensitivity [20,124–126]. The significant change of properties of nano-RDX compared with that of the bulk material will be discussed in Section 3.

2.5.2. Supercritical anti-solvent process (SAS)

In the SAS process, a compressed gas or supercritical fluid is used as an anti-solvent that causes the precipitation of solid raw material dissolved initially in a liquid solvent. This process offers several advantages, such as control of particle size, size distribution, crystal structure and crystal phase [127]. Therefore, the SAS process is also adopted in micronization of explosives as a promising crystallization method.

In recent years, Lee’s group prepared micronized RDX by using a SAS process and systemically investigated the influence of different solvents on morphology, size, and size distribution [128]. Fig. 10 shows the SEM images of the recrystallized RDX particles obtained in different solvents. It can be seen from Fig. 10 that the morphology and size of recrystallized RDX are dependent on the used solvent. In addition, they proved that the SAS technique is an effective method for the preparation of size- and morphology-controllable HMX particles [129,130]. Similar results were also found by Lee and his coworkers when they tried to prepare the microparticles of nitroamine explosives (RDX and HMX) [131–133]. With the aid of the SAS process, Pourmortazavi et al. successfully synthesized HMX nanoparticles by employing Taguchi robust design as a statistical optimization method to optimize the experimental variables [134].

2.6. Template technique

The template technique is a straightforward approach to fabricate micro/nanostructures by inducing the target materials to grow according to the patterns of the templates. This strategy provides a simple way for the synthesis of micro/nanomaterials with desired shape and size, and has been widely applied in the construction of different dimensional micro/nanostructures. The templates adopted in this method can be generally divided into two sorts: rigid and soft ones.

2.6.1. Rigid template

The rigid template method for the preparation of micro/nanostructures has been developed independently in various fields of nanotechnology. It has become one of the most common methods in the fabrication of inorganic, organic and...
polymeric micro/nanomaterials [135–138]. Now the commonly used templates include ordered porous membranes [139], silica [140], nanochannel glass [141], monodisperse colloids [142], and iontrack-etched polymers [143].

During the past several years, this technique has also been used to prepare the energetic nanocomposites. Smeug et al. investigated the confinement of energetic molecules inside carbon nanostructures by molecular structure and total energy calculations [144]. The calculation results predict that each energetic molecule, including FOX-7, RDX, HMX, 3,6-di-(hydrazino)-1,2,4,5-tetrazine (DHT), 3,6-diazido-1,2,4,5-tetrazine (DiAT), 3,3′-azo-bis(6-amino-1,2,4,5-tetrazine) (DAAT), and N-oxides of DAAT (DAATO
\n\text{n}, n = 1–5) could be stabilized by 32–53 kcal/mol if a carbon nanotube (CNT) with appropriate size is selected. Recently, Hu and his coworkers achieved the fabrication of KNO₃@CNTs nano-energetic materials by combining the wet chemical-assistant electrophoretic deposition (EPD) with rigid template method (Fig. 11(a)) [145]. The TEM images of KNO₃@CNTs nanocomposites are shown in Fig. 11(b)–(d). It can be seen that the hollow cavities of CNTs are homogeneously filled with crystalline KNO₃ without any impurities attached on the outer surface.

Several host-guest nanocomposites, such as 2,4,6-trinitrophenol (PA)/mesoporous carbon FDU-15, FOX-7/FDU-15 and CL-20/mesoporous silica SBA-15, were prepared based on self-assembly of energetic molecules in nanometer-scale channels of an ordered mesoporous material [146–148]. The design and synthesis of these kinds of materials are beneficial to understand the reaction characteristics of energetic ordered arrays and further fabricate the micro/nano-devices with high performance and efficiency. Similarly, FOX-7 immobilized in the pores of silica MFI-type zeolite nanocrystals was fabricated by Mintova and his coworkers [149]. Choosing a porous chromium (III) oxide (Cr₂O₃) matrix produced by the combustion of ammonium dichromate as a template, the RDX/Cr₂O₃ nanocomposites were obtained via a facile solvent evaporation process by Spitzer and his co-workers [150,151]. The method may be suitable for the preparation of a wide range of sensitive explosive compositions embedded in the porous materials.

2.6.2. Wet chemical-assisted soft template

So-called soft templates can be dissolved in the liquid phase, mainly including surfactant micelles and copolymers [152–154]. It is well-known that the surfactant micelles and inverse micelles with different shapes (spherical, rod-like, and so on) are formed in the solutions when their concentrations reach the critical micelle concentration (CMC) [155]. Thus, these micelles can then be used as the soft templates for the fabrication of organic and inorganic micro/nanostructures.

It is well-known that TATB is not soluble in the most common solvents due to significant intra- and inter-molecular hydrogen bonds [156,157], and thus most of methods commonly used in the synthesis of organic nanomaterials, such as solvent volatilization, rigid template, and vapor deposition, are not suitable for the fabrication of TATB nanostructures. In our recent work, a ternary microemulsion system of water/dioctyl sulfosuccinate sodium salt (AOT)/toluene was developed to directly synthesize one-dimensional (1D) twinned TATB nanobelts [158]. A series of experiments confirm that the urea as an aminating reagent plays a key role in the formation of highly crystalline nanobelts with perfect mirror symmetry, because the aminating reaction could be easily controlled by adjusting the hydrolysis rate of urea. By using this route, besides twinned nanobelts, various TATB micro/nanostructures, such as particles, leaves, banana leaves, and wedge-shaped ribbons with different sizes, could be directly prepared by changing the experimental parameters.

Subsequently, we developed a facile surfactant-assisted self-assembly technique for constructing 3D dendritic 2,6-diamino-3,5-dinitropyrazine (ANPZ) microstructures in nontoxic ethanol solvent using urea as the aminating reagent (Fig. 12(a)–(d)) [159]. With the assistance of surfactant Pluronic P123 block copolymer, the size and morphology of ANPZ micro/nanostructures can be easily tailored by varying the operating conditions. Moreover, the growth mechanism of ANPZ dendrites was also proposed on the basis of a detailed time-dependent morphology evolution study, as illustrated in Fig. 12(e). Recently, Mandal and his coworkers synthesized the spherical particles of FOX-7 by using the concept of a micelle-based nanoreactor [160]. The diameters of these spherical particles are in the range of nanometer to
submicrometer. Significantly, the size and shape of FOX-7 particles can be adjusted by varying the water–surfactant molar ratio in the microemulsion system.

2.7. Physical vapor deposition (PVD)

PVD is a simple and outstanding method for preparing nanomaterials, and has achieved great success in the synthesis of inorganic nanostructures and polymeric thin films [161–163]. The morphology, size, and dispersity of the products are easily controlled by tuning the experimental conditions, such as saturation level, temperature, and time.

Frolov et al. reported the first synthesis of nano-RDX, nano-HMX, nano-NH₄NO₃, or their composites by employing vacuum sublimation and condensation process [21,164–166]. The obtained energetic particles have an average diameter of about 50 nm. Although this technique has a low yield, it provides useful information for the design and fabrication of energetic molecule micro/nanostructures. Zhang synthesized PETN films with desired surface morphology in a controllable and reproducible way by thermal evaporation on different substrates [167,168]. Recently, 2D one-molecule-thick single-crystalline nanosheets of LLM-105 supported on highly oriented pyrolytic graphites (HOPG) were prepared by vapor self-assembling method at 220 °C and atmospheric pressure (Fig. 13) [169]. The nanosheet with rectangular shape and lateral dimension, which is very sensitive to electricity and force stimuli, provides an opportunity to write optional patterns and fabricate high-sensitive force sensor.

2.8. Inkjet printing

It is noteworthy that inkjet printing technique has been recently extended as a low-cost processing method in the field of energetic materials due to its advantages of excellent accuracy and surface finishes. For example, this technology was explored as a new way to directly deposit and pattern energetic materials for trace explosive detection application [170,171]. Lee reported the inkjet-print RDX crystals, which were dispersed in a cellulose acetate butyrate (CAB) matrix by direct-phase transformation from organic solvent-based all-liquid inks. They found that a variety of crystal morphologies could be obtained by changing the ink deposition parameters [172,173]. They also reported that this effective strategy is used to control the droplet coalescence during inkjet printing, and consequently to tailor the nanoscale morphology of organic composites [174]. They found that the decrease in coalescence increased the evaporation rate of solvent, the supersaturation of the solutes, and the nucleation density of the organic crystals. Utilizing this method, the average size of PETN crystals dispersed in an adhesive binder [poly(vinyl acetate) or a chlorinated wax] matrix from 0.2 to 100 μm was easily tailored (Fig. 14). In addition, the inkjet technique was also used to prepare other energetic samples (HMX, TNT and...
NH₄NO₃) with controlled size and distribution by Hernandez-Rivera and coworkers [175].

3. Properties

Besides the exploration of the construction strategies, much effort has also been focused on investigating the significant change of properties of micro/nano-energetic materials obtained by above technologies. In this section, we give an overview of present studies on the unique properties of micro/nano-energetic materials. First, the size-dependent thermal properties are discussed, then more attention is paid to various sensitive characteristics, and finally the combustion/detonation performance and compaction behavior are also introduced briefly.

3.1. Size-dependent thermal properties

It is well addressed that small particles in the nanometer size regime exhibit unique physical and chemical properties that differ markedly from those of the bulk material. The size-dependent properties of nanomaterials were established initially from inorganic materials [176,177]. Subsequently, the size-dependent properties can also be observed in micro/nano-energetic compounds, such as HMX [10,52,179], HNS [18], TATB [60,178], RDX [63,123], CL-20 [69], and nitrocellulose (NC) [180]. In our previous work, FOX-7 nanoparticles with average diameters ranging from 100 to 800 nm were obtained by SFD technique [97]. We systematically investigated the thermal properties of prepared FOX-7 nanostructures. As shown in Fig. 15(a), the differential scanning calorimetry (DSC) patterns of both the FOX-7 nanostructures and the
micro-sized raw material display two exothermal peaks with the maximum in the range of $240^\circ C$ to $256^\circ C$ and $280^\circ C$ to $298^\circ C$, respectively. It can be clearly seen that the first exothermal peak shifts to higher temperature with the decrease in FOX-7 particle size. This phenomenon can be explained by the theory of topochemical reactions that the small-sized FOX-7 particle generally requires a higher decomposition temperature due to its less lattice defects and smaller internal stress [181]. For the second exothermal peak, it shifts to lower temperature with the decrease in the particle size, and there is a shift of approximate $13^\circ C$ to lower temperature compared to FOX-7 raw material. This regular shift is considered to result from the increased

Fig. 13. (a) Topographical image of a LLM-105 nanosheet in contact mode. (b) High-magnification current image of LLM-105 nanosheet with size of $20 \text{ nm} \times 20 \text{ nm}$ under the conductive AFM mode with load of $0.2 \text{ nN}$, bias of $0.2 \text{ V}$, and scanning rate of $0.5 \text{ Hz}$. (c) The logo pattern of our institute, ICM, wrote on an explosive nanosheet of LLM-105. (d) Dynamic force microscope (DFM) topographical of LLM-105 nanosheet on HOPG, the dark squares in nanosheet in regions of $50 \text{ nm} \times 50 \text{ nm}$ and $200 \text{ nm} \times 200 \text{ nm}$ were scanned at bias value of $5 \text{ V}$ with conductive AFM [169].

Fig. 14. (a) Surface morphology of a single layer deposition printed under maximum coalescence-like conditions using a $d_{1,2}$ of $5 \mu\text{m}$; (b) surface morphology of a multilayer deposition printed under minimum coalescence-like conditions using a $d_{1,2}$ of $100 \mu\text{m}$ (c) and (d) higher magnification images of characteristic morphology in areas labeled “c” and “d”, respectively, in (b) [174].
ratio of surface atoms to interior atoms when the particle size decreases. Thermogravimetry (TG) curves in Fig. 15(b) exhibit a distinct weight loss and no evident inflexion for nanoparticles. It is suggested that nano-sized FOX-7 has a much higher decomposition rate, which is in accordance with the results of DSC.

In addition, our group also reported the thermal properties of other micro/nano-energetic materials [159]. We prepared ANPZ micro/nanoparticles with different morphologies via a facile surfactant-assisted solvothermal process. It is interesting to note that the morphology evolution from 2D nanosheets to 3D hierarchically self-assembled dendrites was accompanied by a regular change in decomposition temperature, which exhibited a unique morphology-dependent thermal effect. That may be due to the fact that the size changes from nanometer to micrometer as the morphology evolves from nanosheets to dendrites. Therefore, the ratio of surface atoms to interior atoms significantly decreases as the particle size increases. The ANPZ dendritic microstructures have a lower surface energy and are more difficult to be stimulated under thermal initiation than small-sized nanostructures. On the basis of above analysis, the ANPZ micro-/nanostructures exhibited a seeming morphology-dependent thermal effect that is actually size-dependent.

Very recently, Mohammadi and coworkers studied the thermal decomposition of RDX nanoparticles with various sizes produced by a wet ball milling technique in hexane solvent [182]. The results show that the thermal decomposition temperature of RDX and its decomposition activation energy are significantly enhanced as the particle size of RDX is increased. The activation energy for micro-RDX is 1.5 times higher than that for nano-RDX, which was ascribed to the decrease in reactivity and localized hotspots. Furthermore, based on calculated kinetic data, the gradual increase in the critical ignition temperature of RDX samples was also found in the order: 180 nm RDX < 250 nm RDX < 300 nm RDX < 50 μm RDX, which is in good accordance with the DSC results.

Furthermore, the catalytic behavior of inorganic nano-materials on the thermal decomposition of high-energy explosives attracted some attention in the past years because of improved thermal efficiency. As a consequence, the considerable efforts have been devoted to the controllable construction of inorganic nanoparticles, such as metals [183,184] and metal oxides [185–189], in order to obtain higher catalytic activity, in which micro-sized explosives are selected as catalytic targets. However, there has been scarcely any report so far on the catalytic thermal decomposition of ultrafine explosives. Zhigach and coworkers developed a convenient approach for preparing the alumined nanocomposites by spray drying of a suspension of Al nanoparticles in a solution of nitramine (RDX, HMX and CL-20) [76]. SEM images reveal that the nitramine powders with an average crystal size of about 1 μm were obtained and nano-sized Al particles were uniformly distributed in the energetic matrix of composite materials. Unfortunately, there is no report on the catalytic thermal decomposition of alumined nanocomposites.

### 3.2. Tunable sensitivity characteristics

#### 3.2.1. Impact sensitivity

The impact sensitivity of energetic materials to unintended initiation is an important safety factor during their uses. In general, the reduction in particle size leads to the decrease in impact sensitivity. For instance, NTO nanoparticles with a size of 70–90 nm were prepared by spray freezing drying technology [96], and the mechanical sensitivity measurement show that the determined H50 for micro-NTO and nano-NTO are 26.2 and 35.5 cm, respectively. This result shows that the as-synthesized ultrafine powder has lower impact sensitivity than that of the NTO raw material. It was proposed that the average pore diameter of ultrafine particles was too small to become a hot spot under the impact stimulus, thus leading to the decrease in impact sensitivity. Wang and his coworkers also investigated the effect of particle size on the impact sensitivity of energetic materials. As mentioned above, a
nozzle-assisted solvent/non solvent method was developed for the preparation of nanoparticles from HNS and CL-20 [58,69]. The impact test indicates that both nano-HNS and nano-CL-20 are less sensitive than that of their raw material. In particular, the impact sensitivity of composite energetic materials was also studied by Brill’s group and Luo’s group [107,113]. The tunable impact sensitivity characteristics of these nanocomposites were confirmed.

3.2.2. Friction sensitivity

As expected, the particle size of energetic materials has an important effect on friction sensitivity, but the reported results are controversial. Recently, Roßmann et al. reported that the ultrafine HMX particles were synthesized by using a bead milling technology [190]. It was revealed that the friction sensitivity of HMX decreased greatly as the crystal size was reduced from 4.5 μm to 171 nm. Radacsi and his coworkers also performed the friction sensitivity tests at the highest possible load (360 N) and found that the friction sensitivity of the submicron-sized RDX particles is much lower than that of the conventional RDX crystals [81]. The author assumed that the decrease in the friction sensitivity was mainly attributed to the defect and internal quality of the energetic crystals. Li and his coworkers fabricated three kinds of HMX samples with spherical, needle-like and polyhedral microstructures by wet milling, solvent/non solvent and riddling methods, respectively [52]. It is interesting to note that the friction sensitivity increases gradually as particle size decreases for spherical β-HMX particles, but the friction sensitivity of needle-like γ-HMX linearly increases with the increase in particle size from 2.98 to 16.1 μm. However, for polyhedral β-HMX sample, its friction sensitivity did not display some rule as a function of particle size. The above results show that the safety of HMX is dependent strongly on the size and structure of HMX particles. This phenomenon can be explained by the “hot spot” growth mechanism [191].

3.2.3. Electrostatic spark sensitivity

It was mentioned in Section 2 that our group presented a facile strategy for the construction of 3D FOX-7 nanostructures and investigated the response of nanoparticles to ignition stimulus under the electrostatic discharge conditions [97]. The results of electrostatic spark sensitivity of nano-FOX-7 indicate that its 50% critical ignition voltage (V_{50}) and 50% critical ignition energy (E_{50}) are 13.19 kV and 2.65 J, respectively, which are lower than those of FOX-7 raw material, 16.42 kV and 4.11 J. The decrease in ignition energy may be explained by the fact that the FOX-7 nanostructures with higher surface energy are easy to be stimulated.

3.2.4. Shock sensitivity

In order to produce the safe munitions which are capable of withstanding the unwanted mechanical stimuli, such as shocks from explosions, it is necessary to substantially reduce the initiation sensitivity of energetic materials. A great number of experimental data prove that energetic materials with decreased particle size have great changes in safety under the condition of shock initiation stimuli. The prior studies have demonstrated that the shock initiation sensitivity of some explosives, such as HNS, HMX, RDX and TATB, has been effectively lowered [192–195]. In the case of RDX, the nanoparticles generated by the RESS process show different shock behaviors compared to the bulk material [125], as illustrated in Fig. 16. The RDX with the size of 4.8 μm shows that the small scale gap test result is 19.6 kbar, while the bulk material exhibits higher sensitivity. However, the shock sensitivity results of Types A nano-RDX and Types B nano-RDX are 20.6 and 26.1 kbar, respectively. The above data clearly show that the shock sensitivity decreases as the crystal size is reduced down to the nano-scale, meaning that long-pulse shock sensitivity can be tuned by changing the particle size. Similarly, Stepanov and Qiu also found that the RDX-based nanocomposites exhibited lower shock sensitivity, which is attributed to small crystal size as well as small void size. [87,88] Additionally, Wang and his coworkers developed a novel technique to prepare the ellipsoidal HNS nanocrystals with high specific surface and narrow particle size distribution [58]. The obtained HNS samples were subjected to small scale gap test, and the results indicate that crystalline HNS nanoparticles are less sensitive to shock stimuli than micro-sized HNS (50 μm).

![Fig. 16. Shock sensitivity of uncoated samples of Class 1, 4.8 micron, Type A nano-RDX (a specific surface area around 15–20 m²/g), and Type B nano-RDX (a specific surface area around 5–6 m²/g) [125].](image)

Fig. 16. Shock sensitivity of uncoated samples of Class 1, 4.8 micron, Type A nano-RDX (a specific surface area around 15–20 m²/g), and Type B nano-RDX (a specific surface area around 5–6 m²/g) [125].
It is worth noting that a completely opposite result can be obtained if the test of shock sensitivity is carried out under the slapper initiation stimuli. Gifford and coworkers studied the behavior of short duration shock of PETN with different sizes and found that there were no changes when PETN microparticles were initiated using laser-driven flyer though some limited reaction. In contrast the ultrafine PETN particle was readily initiated at flyer velocities of around 5 mm µs⁻¹ [196]. Wang et al. also reported that the ultrafine HNS is more sensitive to short duration shock wave than its conventional counterpart [74]. These studies show that the initiation form plays an important role in determining test results of small-sized explosives. For the small scale gap test, its shock wave is low pressure-long pulse, and the relative shock sensitivity is controlled by ignition process [197], but oppositely, the shock wave is high pressure-burst pulse and the sensitivity is controlled by detonation buildup for the slapper initiation test [198].

3.3. Improved combustion and detonation performance

Nano-scaled energetic materials have attracted wide interest by virtue of their unusual combustion and detonation performance. Therefore, there have been a number of experimental and theoretical studies on these properties of nano-energetic materials and nanocomposite propellants [199,200]. Pivkina’s work shows that there was a significant difference in burning rate of pure RDX nanopowders in comparison to micron-sized component [166]. As shown in Fig. 17, a monopropellant of RDX nanoparticles with the size of about 50 nm, prepared by a vacuum condensation technique, exhibits burning rate twice greater than conventional powder at an elevated pressure of 10 MPa, indicating that the size has considerably important influence on the mechanism of RDX combustion. Muravyev and coworkers also investigated the combustion parameters of HMX as a monopropellant [201]. It was shown that although combustion velocity is almost same for micro-HMX and ultrafine HMX, the combustion of the ultrafine HMX is more complete than that of micro-HMX. To fulfill the control of the combustion performance of high explosives, the solidification of energetic phases in a porous matrix (Cr₂O₃) is used to fabricate and stabilize the nano-scale explosive particles (RDX) [151]. The studies show that the combustion rate is remarkably increased by decreasing the size of the reactants, and the highest rates can be obtained with the mixtures in which each reactant is structured at nano-scale.

Additionally, Wang et al. tested the detonation performance of each formulation by probe method and found that the detonation velocity of superfine explosives (HMX and RDX) is obviously higher than that of the coarse particles [57]. This is probably because the superfine particles with high specific surface area can burn faster than the conventional counterpart and hence more energy is transferred to the detonation reaction zone. Gogulya’s group achieved the similar result when they used a pulverization drying method to synthesize the ultrafine HMX particles [202].

3.4. Unique compaction behavior

In addition to the properties mentioned above, the compaction behavior of small-sized energetic materials has also been reported in the past few years. For example, Lowe et al. investigated the relationship between particle size and compaction behavior of granular bed [203,204]. They designed a modeling and experimental method to study the compaction behaviors of two types of granular HMX: coarse HMX (mean diameter of 40 µm) and microfine HMX (mean diameter of less than 5 µm). The results show that the granular bed of the microfine HMX with the particulate structure is more strength than the coarse bed. Agarwal and coworkers prepared fine TATB particles (2–5 µm) with the assistance of reprecipitation and found that its mechanical strength/compared strength was significantly improved in comparison to coarse TATB (55 µm) alone in plastic bonded explosive (PBX) formulations [47].

4. Conclusions and future perspective

In this paper, a review of recent research on controllable preparation of micro/nano-energetic materials with special structures and sizes was presented. We introduced various advanced strategies for the construction of structure- and size-controlled micro/nano-energetic materials. Besides the preparation of 0D energetic nanoparticles, we focused on the construction of 1D twinned nanobelts, 2D nanosheets and banana-like nanoleaves, 3D nanogrids, dendritic micro/nanostructures and hierarchical microspheres. The structures and sizes of energetic materials are easily controlled by means of molecular design and synthetic strategies. More emphasis is placed on the unique properties of structure- and size-controlled micro/nano-energetic materials. The size-dependent thermal properties of several kinds of high-energy explosives are first introduced, and then the sensitive properties, such as impact sensitivity, friction sensitivity, shock sensitivity, and electrostatic spark sensitivity, are reviewed, and finally the combustion, detonation, and compaction behaviors are also briefly presented.

Currently, the research on micro/nanomaterials based on energetic compounds is still in its infancy, and there is a lot of work to do in this area. In our opinion, several research directions should be paid more attention in the future. Firstly, it is still necessary to develop the methods for the design and controllable construction of micro/nano-energetic materials with large scale, special dimensions, desired structures and sizes [190,205–207], although some progress has been made to date. At the same time, the development of better characterization methods is equally important to further understand the nature of the nano-energetic materials at the molecular level. Secondly, we think that the systematic study, especially for relationship between detailed structures/shapes and various fundamental properties, should be carried out [169]. Thirdly, it is necessary to explore and improve the stability, safety and reliability of micro/nano-energetic materials [208,209]. In addition, as to the great potential application of micro/nano-
energetic materials, the micro-electromechanical systems (MEMS) has proved to be a promising direction for micro/nano-scale energetic materials with specific structures [210], and the fabrication of thin films and patterns composing of the nanostructured building blocks on solid substrates, such as glass, ceramic, and crystalline silicon, is essential for the realization of practical devices [211–214].

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