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Synthesis of energetic materials by microfluidics

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ABSTRACT

Energetic materials, characterized by their capacity to store and release substantial energy, hold pivotal significance in some fields, particularly in defense applications. Microfluidics, with its ability to manipulate fluids and facilitate droplet formation at the microscale, enables precise control of chemical reactions. Recent scholarly endeavors have increasingly harnessed microfluidic reactors in the realm of energetic materials, yielding morphologically controllable particles with enhanced uniformity and explosive efficacy. However, crucial insights into microfluidic-based methodologies are dispersed across various publications, necessitating a systematic compilation. Accordingly, this review addresses this gap by concentrating on the synthesis of energetic materials through microfluidics. Specifically, the methods based on micro-mixing and droplets in the previous papers are summarized and the strategies to control the critical parameters within chemical reactions are discussed in detail. Then, the comparison in terms of advantages and disadvantages is attempted. As demonstrated in the last section regarding perspectives, challenges such as clogging, dead zones, and suboptimal production yields are non-ignoble in the promising fields and they might be addressed by integrating sound, optics, or electrical energy to meet heightened requirements. This comprehensive overview aims to consolidate and analyze the diverse array of microfluidic approaches in energetic material synthesis, offering valuable insights for future research directions.

1. Introduction

Energetic materials (EMs) are characterized by their high energy density, capable of swiftly releasing substantial amounts of energy in various forms, including heat, light, electricity, or mechanical work, triggered by specific stimuli [1–3]. As the primary energy source for modern weapons systems, the performance of energetic materials directly affects the reach and destructive capabilities of weapons systems. Beyond the major applications in the field of national defense, energetic materials also play an essential role in the civil fields such as propellants and pyrotechnics [4–7]. In practical scenarios, some critical factors, such as stability, sensitivity, and energy content of the materials should be controlled to satisfy the specific requirement. For example, the explosive hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX), a key component of munitions, is widely used in plastic explosives (such as C-4 and Semtex), boosters, and munitions produced by factories in several countries, including America during World War II [8–10]; Suraj Junghare studied green pyrotechnics, employing a thermite reaction to generate heat and sound by use of mental fuel(aluminum), oxidizer (potassium nitrate), and Sulfur [11]. These examples underscore the diverse applications of energetic materials across both military and civilian spheres, emphasizing the need for precise control over their properties to meet specific functional requirements.

The properties of energetic materials are critical in determining their suitability for specific applications. They include energy density or energy content, sensitivity, stability, burn rate mechanical properties, and others. Actually, some properties of energetic materials present a paradox, such as the challenge in balancing sensitivity and energy content. High energy content, meaning a more powerful explosion or propulsive force, is often desirable, but

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it can also lead to increased sensitivity of the material, making it more dangerous to handle. Some existing methods like spray drying and electrochemical methods may not fully meet the increasingly higher demand [12–15]. For example, the spray drying and melt casting methods may result in the inhomogeneity of crystals, leading to the unreliability and instability of energetic materials [16]. Electrochemical methods may be limited by slower reaction rates and may require complex electrolyte systems and equipment [17]. The mechanical mixing method can be utilized to obtain thermite energetic materials with an appropriate reaction measurement ratio, but it does not allow for film formation and integration with complex micro-devices [18]. The formation process based on different methods faces some challenges, such as the generation of waste and hazardous substances, uncontrollable micro-morphological features, and especially safety impact [19–21]. To address these issues, new requirements are put forward for the development and exploration of novel technologies [22]. Therefore, it is foreseeable that the focus of additional research should be on developing novel methods with high universality, a safe preparation process, environmental friendliness, and better integration with reported mature traditional technologies [23–27].

In the field of microfluidics, researchers focus on manipulating fluids and micro targets at the microscale [28–30]. This technology's precise control over fluid manipulation, including mixing and separation, is particularly well-suited for small-scale and low-batch synthesis [31–34]. Moreover, its capability to produce materials with customizable sizes and shapes is significant and should not be overlooked. The reaction environment occurring in the microfluidic chips can be adjusted easily by controlling the flow rates and designing the structure of microfluidic chips. In recent years, particle preparation based on microfluidics has advanced rapidly and has prominent applications in some fields such as chemical synthesis, materials science, and drug discovery [35–40]. In material synthesis, microfluidic reactors may provide precise control over reaction conditions, facilitating the synthesis of nanomaterials. A particular strength of microfluidics is its ability to modulate particles with unique or optimal morphologies and specialized properties [41,42]. In the studies of Jin et al. [43], 3D polymer porous materials were synthesized by the acoustic-controlled microbubble generation method on the microfluidic platform. Further, maintaining precise control over the crystallization environment on a macroscale presents challenges when using traditional fabrication methods such as mechanical ball milling, the supercritical fluid method, and spray processing [44–46]. Characterized by small volume, microfluidic technology emerges as a novel approach that provides a controlled and safe experimental setting [47,48].

Microfluidic technologies have attracted significant interest among researchers involved in the synthesis of dangerous materials, such as flammable and explosive chemicals [49–51]. For instance, Movsisyan et al. [52] reviewed some studies of the hazardous chemistry synthesized by continuous flow technology and concluded the continuous flow reactor technology enables precise control over the reaction parameters, increasing the overall process efficiency and safety. Additionally, reactions conducted in microfluidic chips benefit from rapid and uniform progress due to the large interfacial area at the micro/nanoscale [53]. Taking ZnO nanoparticles as an example, Popa et al. [49] compared the traditional and microfluidic synthesis methods and concluded that microfluidics provides a precise synthesis of micro-/nanoparticles for various applications due to their several advantages, such as quick reaction time, simple sample preparation, and reduced sample consumption.

Motivated by its superiority, a wealth of published literature appeared in this field. As shown in Fig. 1, the mixing microfluidic devices with different micro-structures are summarized and categorized by their enhancement method—either passive or active. Beyond these, in immiscible fluid situations, microfluidics also allow for the manipulation of particle size and shape by the formation of droplets [54,55]. For instance, with the help of fluorine rubber (F_{2602}.), Jing et al. [56] prepared 2,4,6-Tramino-1,3,5-trinitrobenzene (TATB)-based energetic composite microspheres through coaxial flow droplet generation in a continuous pipe-stream self-assembly device. Han et al. [57] crafted the hexanitrostibene (HNS) microspheres with 1% nitrocotton (NC) as a binder in a flow-focusing microfluidic chip. Droplet generation offers a more refined approach for controlling particle shape and size compared to mixing microfluidics. The morphology of particles obtained can vary from spherical to non-spherical, such as cube-shaped, depending on the ingredients and reaction types within the droplets [58]. Droplets can serve as micro-reactors to produce particles with unique shapes, Suhanya Duraiswamy et al. [59] pumped the gold nanoparticle seeds and growth reagents into the droplets to form anisotropic metal nanocrystals with sharp-edged structure. Similarly, Shi et al. [60] finished the synthesis of CL-20/TNT co-crystal microspheres with the assistance of NC and F_{2602}. In addition to the mixing and droplet microfluidic methods summarized in the following section, there are also film preparation and emulsion methods, which were used by a few researchers [25,61,62].

In this article, the microfluidic devices for the synthesis of energetic materials via the mixing of fluids and the generation of droplets will be included, which is shown in Fig. 1. Effects of passive and active mixing microfluidic chips on the average size and tunable morphology of particles are investigated. The particles including sphericity and non-sphericity prepared by generated droplets in microfluidic chips are researched separately. Meanwhile, the influence of microchannels and microstructures designed on particle characteristics is also summarized. Furthermore, we present the future development perspectives of microfluidics in the synthesis of energetic materials, along with a summary of the challenges involved.

2. Properties of energetic materials

To assess the potential of the energetic materials under various synthesis methods, the value of some key properties, like morphologies, structures, components, and the corresponding explosive should be characterized. While energetic performance is a critical factor in determining a material's suitability for practical application, other considerations such as impact and thermal sensitivity should not be disregarded. Therefore, when assessing the superiority of new methods for preparing energetic materials, the key is to evaluate the balance of all aspects of the performance of the materials prepared.

The interplay between stability and explosive performance, investigated by Zeman et al. [63], often involves a trade-off, where increasing the explosive strength is usually accompanied by an increase in sensitivity, leading to a decrease in stability. Striking a balance between seemingly paradoxical traits, such as heightened stability and denser energy content, necessitates careful consideration of both chemical components and physical structures. On one hand, these elements are always carefully designed and synthesized from chemical perspectives, and on the other hand, the critical properties of EMs, like explosive performance, are highly related to morphology and ingredient distribution [64,65]. For example, Yadav et al. [66] explored the relationship between the components and performance, successfully developing insensitive yet high-performance energetic materials by integrating a five-membered heterocyclic backbone with explosive groups. As for physical structures, Wang et al. [67] used an ultrasonic method to

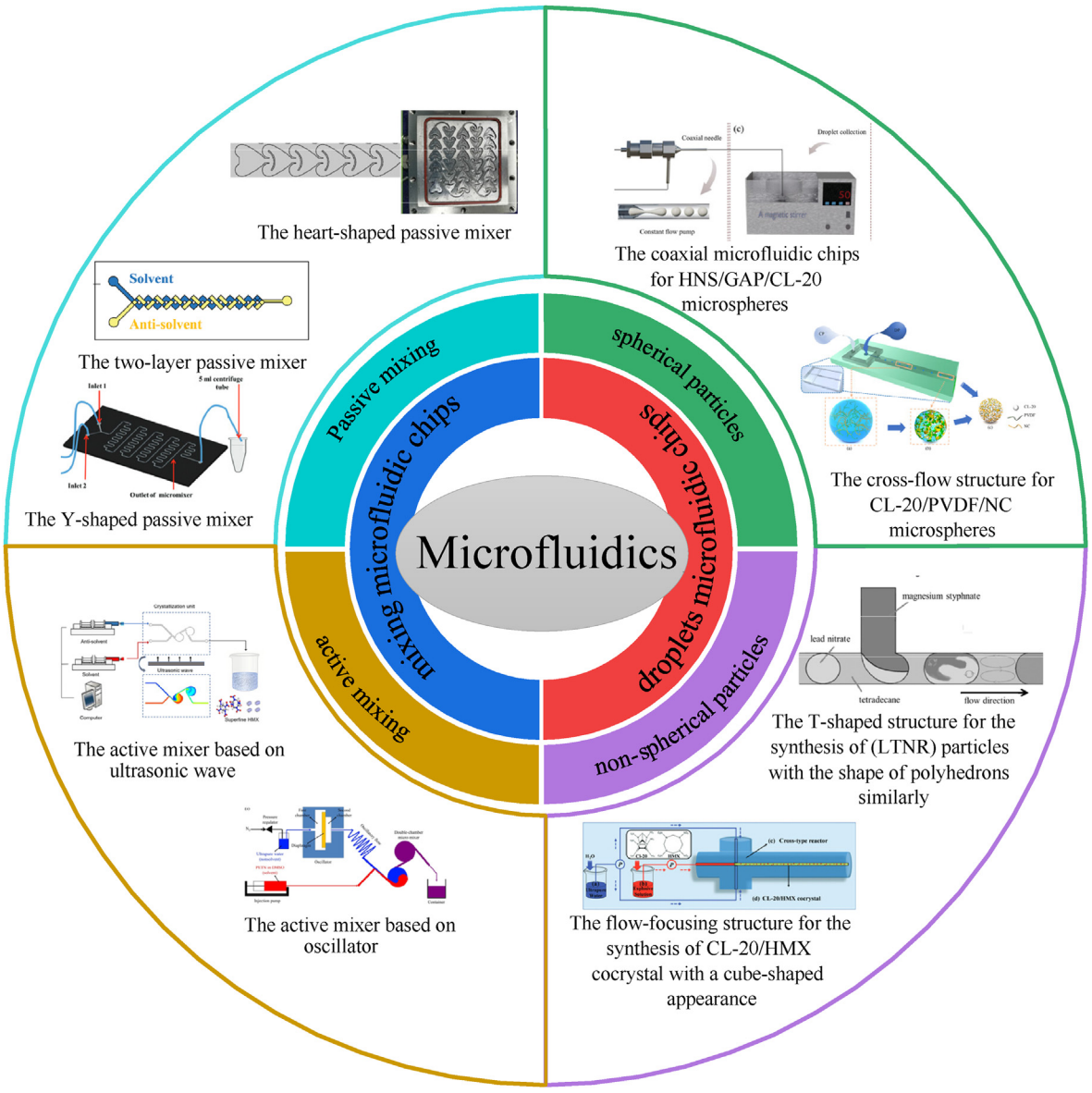

Fig. 1. The microfluidics for the synthesis of energetic materials.

mix and prepare high-energy composite structured explosives. Their approach featured RDX modified by polydopamine as the core and PTFE/Al as the shell, resulting in lower friction and impact sensitivity, as well as higher energy release efficiency and remarkable combustion performance.

The relationship between the properties of energetic materials and particle morphology is intricate and diverse [23,68]. Previous studies have confirmed that the scale effect plays a crucial role, causing energetic materials to display distinct properties due to variations in their microscale morphology [69,70]. For example, Pang et al. [71] noted that the nano-sized energetic materials are characterized by significantly higher burning rates, lower impact sensitivity, and a higher rate of energy released than those of micro-sized energetic materials, owing to unique large specific surface areas (SSA). And Zohari et al. [72] reported that nano-size ingredients of propellants enhance performance, like an increase in the burning rate. Similarly, the sensitivity of propellants to external stimuli can be increased by reducing the particle size of the high-explosive constituents. Additionally, irregularly shaped particles may feature sharp edges or uneven parts on their surface, making them prone to heat concentration and hot spot formation. This feature may trigger local combustion or explosion, resulting in incomplete energy release. An increase in such irregularities may decrease the insensitivity and stability of energetic materials [73,74]. Likewise, research by You et al. [75] suggests that the regular-shaped units, owning a more uniform energy distribution, tend to be more stable and less sensitive to external stimuli. Undoubtedly, the morphology characteristics of energetic materials have a deep influence on their performance [12,71,76,77].

A final requirement for achieving all production properties, including chemical stability, mechanical resistance, and performance, is a tight integration between processing and the acquisition of the resulting functions. For example, Yang et al. [78] prepared Al–Co_3O_4 powders by high-energy ball milling. With the extension of milling time, the powders showed the finer particle size, lower initial oxidation temperature, earlier autoignition, and longer combustion in the water steam at high temperatures than the other samples. In comparison to the original particles, the

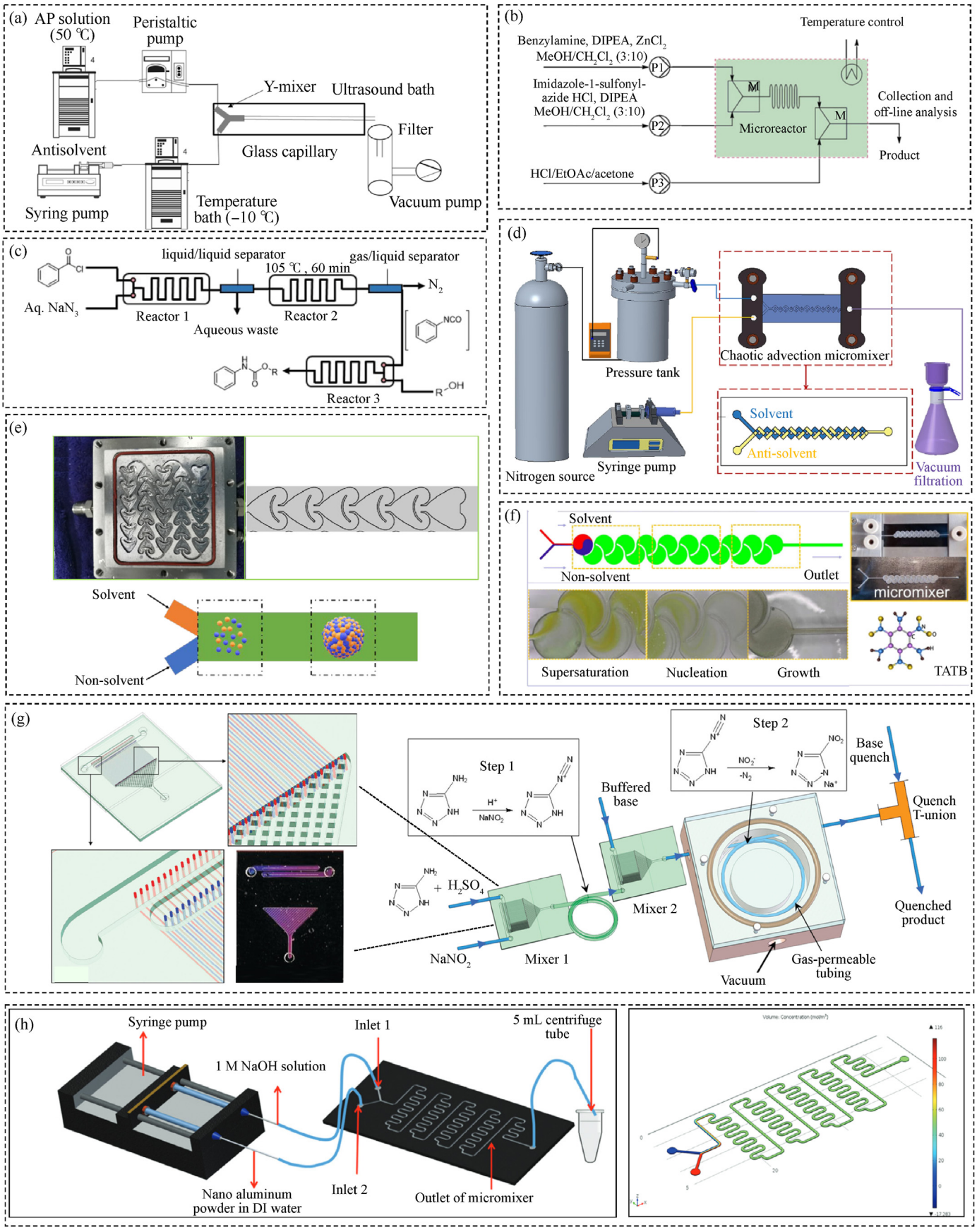

Fig. 2. The structures of the passive microfluidic chips for mixing reactive composites: (a) The system for continuous precipitation of AP based on the Y-type passive microfluidic chip [88]; (b) The system using two Y-shape microchannels for mixing fluids step by step [92]; (c) The micro-total envelope systems (u-TESs) based on the T-shaped microchannel

reactors for the synthesis of acyl azides [87]; (d) The microfluidic crystallization device for preparation of HNS particles, intensified by the chaotic advection with the two-layer structure [93]; (e) The heart-shaped structure of the micromixer, and the structure model for composites of RDX and FOX-7 [95]; (f) Micromixer with continuous circular microchambers, and the nucleation and growth of TATB under optical microscope [91]; (g) Interdigitated silicon micromixer splitting two inlet flows into many sub-channels and constricting the laminated flow to create sub-micrometer diffusion lengths, and the schematic of reaction setup for NaNT synthesis, which can be achieved by the diffusion of fluids in microchannels [97]; (h) The schematic of the experimental setup based on the Y-shaped passive microfluidic chips with longer serpentine microchannels for etching of metal particles, and its simulation of the mixing effect [100].

average particle size of HMX-based composite prepared via the spray drying method ranged from 30 nm to 100 nm, and their thermal sensitivity was much lower than that of pure HMX [79]. Various synthesis methods employ different mixing techniques for reagents to optimize the process, like ultrasonic powder mixing, mechanical mixing, solution mixing, and melt mixing [80–83]. For example, as mentioned by Zhou et al. [84], ultrasonic powder mixing, being the simplest and most traditional method, can adjust stoichiometry readily to maximize energy density. However, taking nano-aluminum as an example, the intrinsic limitations of this ultrasonic mixing at macroscale led to the formation of 4 nm–8 nm thick aluminum oxide shell around Al nanoparticles, reducing energy density and degrading combustion performance.

To address the current paradox and limitations related to the properties of energetic materials (EMs), and to meet the advanced requirements of the next generation of materials, numerous efforts have been made. The researchers leveraged microfluidics techniques, focusing on improved micro mixing and droplet formation, to achieve more precise control over the synthesis process.

3. Synthesis of energetic materials by fluid mixing

3.1. The mixing of reactants by passive ways

Passive microfluidic is a technology that manipulates the fluids by the microscale structures themselves or the driven pressure, without introducing extra interferences. The fluids at the microliter scale range are injected into microfluidic chips by the pumping device, and subsequently, the solutions will react in microchannels or microcavities. Especially, the mixing of solutions in a passive microfluidic device mainly depends on the diffusion effect of the fluids themselves, which may be enhanced by increasing the contact area and time between fluids through designed microchannel configurations and flow rates [85].

For mixing process, the diminutive scale of the channels, on one hand, can increase the surface-to-volume ratio and enlarge the contact area; on the other hand, it would limit the fluid's development to a turbulent state [86]. In addition to setting higher driven pressure and flow rates, many passive mixers with different structures are designed to improve submicron fluid diffusion and enhance mixing by extending contact time. Out of common types, such as T-shaped [87] and Y-shaped [88] channels, some special structures, like two-layer microchannels [89], heart-shaped microchambers [90], and circular microchambers [91] were designed to improve the efficiencies of mixing and were used to optimize the preparation of various energetic materials. Various passive methods, applied in the preparation of energetic materials, are summarized in the followings.

The mixers with simple structures like Y-shaped and T-shaped channels have been easily tried and widely used in many synthesis systems for the hazardous products. As is shown in Fig. 2(a), the most basic Y-shaped channel was adopted by Pal et al. [88] to continuously synthesize ammonium perchlorate (AP) particles through mixing the solvent and antisolvent. The resulting particle size ranges from 8.98 μm to 16.98 μm. To extend the mixing length, a long channel was added after the Y-shaped part by Delville et al. [92], as is shown in Fig. 2(b). And the synthesis efficiency is further improved, leading to the production of approximately 1 g of benzyl azides per hour in a microreactor. Furthermore, the T-shaped channel would induce a more intense mixing due to the liquid convection. With this structure, the efficiency and safety of producing dangerous chemicals like acyl azides, have been improved by Singh et al. [87] through their system (shown in Fig. 2(c)).

For hexanitrostibene (HNS), known as its good thermal stability and high short-duration shock pulse sensitivity, its size and crystal shape can be controlled by adjusting the mixing efficiency of solvents and the compositions. A kind of two-layer crossing channel was designed by Zhao et al. [93] to promote the mixing significantly at low Reynolds numbers, as shown in Fig. 2(d). The mixing efficiency of solvents in this platform can be adjusted by changing parameters such as the length of the mixing zone, the total flow rate, and the flow rate ratio. And they achieve morphology control of ultrafine HNS with the help of controllable mixing process. In the optimal mixing, the particle size of the HNS prepared ranges from 91 nm to 255 nm, smaller than the size ranging from 106 nm to 615 nm from the beaker, the traditional reactors. In addition to size, the crystal shape of the HNS can also be controlled to be at the nanoscale, two-dimensional nanosheets, or short rod crystals by adding materials with different concentrations, such as low, moderate, and sufficient CL-20 respectively. Furthermore, based on this highly efficient platform, the most appropriate poly-coated explosive composite system can be screened out quickly, and the resulting HNS composite with glycidyl azide polymer as the binder exhibited better performance than others in terms of thermal stability, and mechanical properties [76]. In addition to the crystallization, other synthesis reactions can also be enhanced in this low-risk platform, which enables the better morphology than that of products from beakers. For example, the silver azides (SA) prepared from this platform correspond to the more uniform particle size and own spherical or spherical-like shape, which is significantly different from the traditional pyramidal morphology with sharp points [94]. These improvements are beneficial to its flowability and stability.

To enhance mixing efficiency, numerous specialized microchannel structures have been designed to break the laminar state and accelerate the diffusion between miscible solutions. As shown in Fig. 2(e), the detachable passive mixer with an array of heart-shaped structures, designed by Zhang et al. [95], can increase the contact area and elongate the contact time than the general mixer like T-shaped with the same channel length. The mixing efficiency was improved by the chaotic fluids in the heart-shaped structures, and can optimize the preparation of various explosives, such as elemental materials, composites with another energetic material, and composites with non-energetic materials. For example, the distribution of TATB in HMX solution is more homogeneous with the help of the mixers, and the TATB/HMX composite with high energy can be prepared continuously and stably for 80 min [90]. For the RDX/FOX-7 composites synthesized by Yu et al. [96], the uniform dispersion of the binder FOX-7 in RDX due to the mixing of vortex reduces the sensitivity and particle size distribution, and the structure model of composites is shown in Fig. 2(e). Similarly, benefiting from the continuous circular chambers, the vortices can be more easily facilitated (shown in Fig. 2(f)). This allows for better mixing and helps Guo et al. [91] obtain the nano-TATB, with an average particle size of 93.12 nm and a particle size distribution of 43 nm–151.4 nm proving better uniformity than that from Y-type mixers.

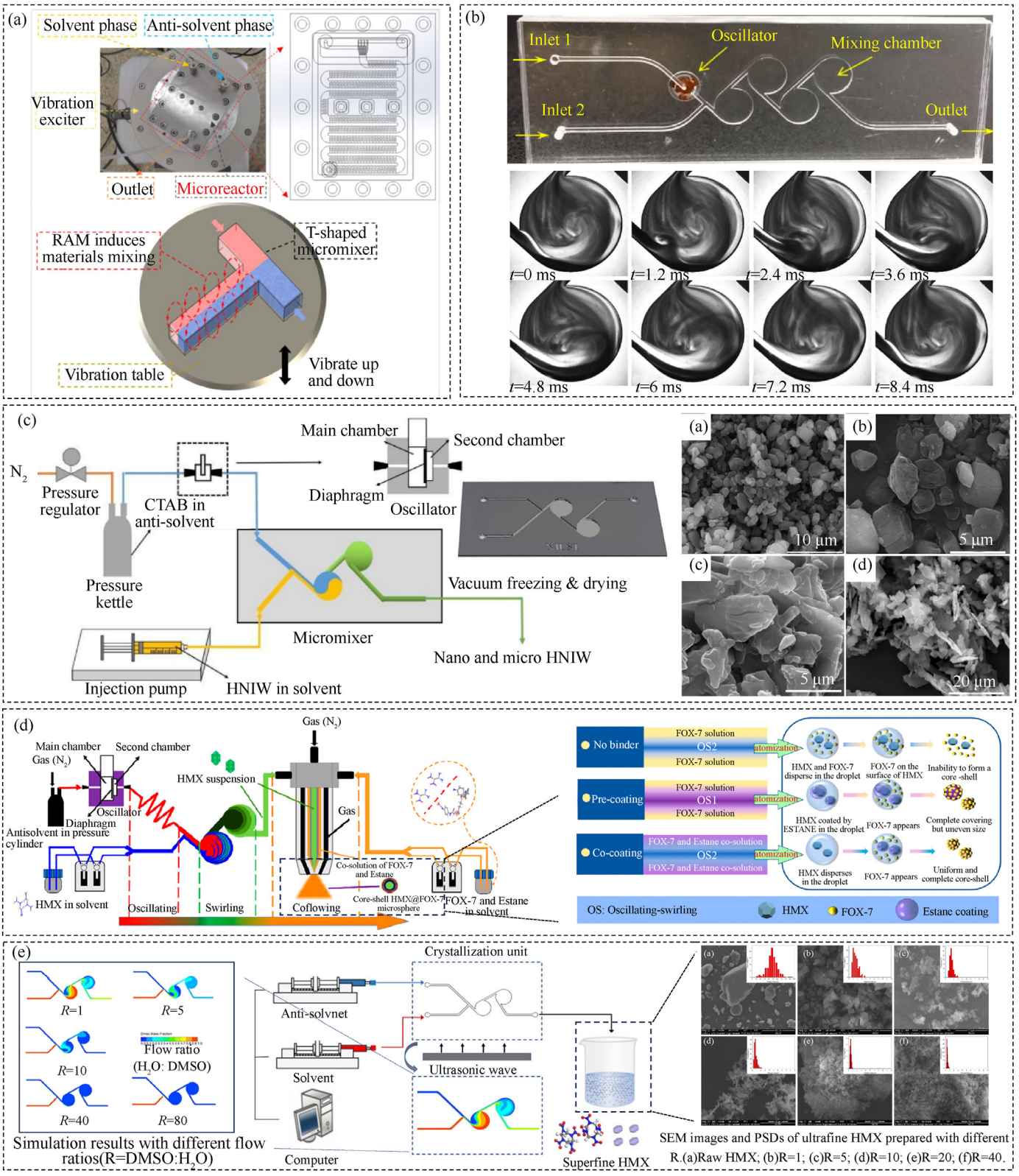

Fig. 3. The schematics of energetic materials synthesis based on various active mixing microfluidic chips: (a) The microreactor with T-shaped micromixer and its internal structure by a column with a diameter of 0.5 mm [105]; (b) The micromixer consisting of one oscillator and four circular chambers, and the mixing mechanism in the circular chambers [106]; (c) The schematic diagram of the microfluidic platform consisting of a detachable oscillator and the double-chambers micromixer, and SEM images of HNIW obtained with different solvents like DMSO, DMF, acetone, and ethanol [107]; (d) The continuous microfluidic platform for the preparation of core-shell HMX/FOX-7 microspheres, and its formation process under different composite forms [110]; (e) The active microfluidic platform with ultrasonic wave, the simulation results (the left chart), and the SEM images (the right one) with different flow ratios [111].

As is shown in Fig. 2(g), in the flowchart for preparing NaNT, the main channels split into a large number of sub-channels, constricting the diffusion length of the laminated flow to the submicrometer, greatly increasing the contact area and decreasing the diffusion time required. In addition, the mixer allows for high flow rate pumping to maximize production due to the minimal pressure drop resulting from an interdigitated laminar mixer design with flow focusing. And Zaborenko et al. [97] achieved the direct synthesis of NaNT at a rate of 4.4 g/h from a highly energetic intermediate, outperforming the commercial methods for materials synthesis. Meanwhile, by being confined to submicron subchannels, the reaction became safer.

In some other situations, metal particles are mixed in energetic materials for a higher energy output [98,99]. After a good mixture, the metal particles can react with oxygen during combustion, creating higher temperatures and pressures and resulting the better explosive performance. For example, aluminum in nano form is widely used as a catalyst in biomass burning, detonators, microelectronics, and liquid propellants to enhance energy density. To improve combustion rate and stability, Kant et al. [100] employed a serpentine channel layout, as shown in Fig. 2(h), to achieve precise control over the etching rate of the aluminum nanoparticle size during the mixing before output, and the size of the resulting particles became more uniform and decreased from 100 nm to 9.2 nm (±3 nm).

Generally, passive mixing intensifications in microfluidics have been widely used in the preparation of energetic materials. By fabricating special channel structures to extend diffusion time and enlarge contact area, a more efficient, precise, and controllable chemical reaction process can be achieved. Compared to others, passive methods offer several advantages, including higher reliability and stability, easier to use and assemble, wide range of applications. However, limited by the low Reynold number the mass transfer efficiency can be only improved by a larger throughout and locally complex flow path to break the laminar state. This method potentially increases operation risks like clogging and lack of capacity to control the synthesis process. For this reason, in some situations where higher precise fluid control is required, some other techniques in a more active way, like disturbing the fluids with the energy field from outside, have come up.

3.2. The mixing of reactants by active ways

In addition to flow driving, like pumping, active mixing intensifications utilize external force including physical fields (such as acoustic, electrical, or mechanical forces) to enhance mixing and control material formation. By integrating with a specially designed flow path structure, the external energy field introduced can achieve a better effect. For example, acoustic forces can induce cavitation and vortexes to greatly disturb the surrounding fluids in microchannels with structures such as sharp edges and holes, and mechanical forces can break up agglomerates. In such cases, the reaction process can be effectively controlled and manipulated to achieve efficient and uniform mixing. Actually, for some microfluidic chips based on active method, they retained the passive mixing intensification by special channels and leveraged the external forces to further improve their performance. Others, while, required a customized microchannel structure to fit the introduced physical fields. Generally, the efficiency of fluids mixing in active microfluidic chips would be higher than the passive ones under the same flow-driving additions. Especially, the recrystallization process, under external intervention, can be actively tuned on microscale, so it is suitable for preparing explosives with small particles and narrow size distribution.

However, considering the high sensitivity of some kinds of energetic materials, some physical fields, like electric forces, are not suitable. In recent studies, acoustic vibration is often combined with microfluidics, making it a powerful tool in some explosive synthesis. Resonant acoustic mixing (RAM) technologies working on low frequency have been applied to the formation of energetic materials, biology, and medicine due to the shorter mixing time, and slight stimulus to samples [101–104]. Zhang et al. [105] combined continuous flow microfluidic with RAM working on low frequency (40 Hz–80 Hz) for the preparation of nano-energetic particles, like nano-TATB. As shown in Fig. 3(a), excited by the vibrating table, multiple vortices appeared inside the T-shaped channel, where the mass transport was significantly accelerated. Additionally, a micropillar array was designed to further enhance the mixing process passively. With this reactor, the synthesis of nano-TATB, using the ionic liquid (1-ethyl-3-methylimidazolium acetate) and Dimethyl sulfoxide (DMSO) as a solvent and the deionized water as a non-solvent, was completed. Under the frequency of 60 Hz, the average particle size and particle size distribution of TATB products reached the smallest, being better than previously reported results.

In some other studies, the oscillators are introduced to vibrate the flow and create a chaotic state in the microcavities. A micromixer consisting of a microfluidic oscillator and divergent circular chambers was designed by Wu et al. [106] for the preparation of nano-RDX particles. Being in an oscillating state and entering in the tangential direction, the fluids easily formed the vortex in circular chambers as shown in Fig. 3(b). During one cycle of the oscillator, the flow rate of fluid 1 (inlet 1) gradually increases, and after around 7.2 ms, its flow rate decreases. The periodic variation of the flow rate has caused strong stirring effects, making the flow become chaotic and leading to more efficient mixing. Under the optimal mixing conditions, the nano-RDX particles ranged in size from 150 nm to 900 nm, with an average size of 290 nm.

With a similar method, to decrease the complexity and reduce the dead zone, the number of chambers and the placement of the oscillator in the mixers were optimized by Shi et al. [107], and the microfluidic platform preparing HNIW particles and its SEM images with different solvents are shown in Fig. 3(c). Based on this platform, the correlations of crystal morphology to the synthesis conditions were explored. The results show that the mean particle size of HNIW obtained through rapid mixing with the swirling and oscillatory flow was 1.4 μm, and the particle size ranged from 1 μm to 20 μm. Meanwhile, the synthesis of PETN, nanoscale HNS particles was also conducted based on the identical system and it produced smaller particles than previous conditions and enabled good reproducibility [108,109]. In addition to the single energetic materials mentioned above, this platform allows for the fabrication of highly homogeneous HNS and HMX composite materials, resulting in better compositional distribution, enhanced reproducibility, and higher combustion heat.

Furthermore, by combining oscillating fluids for mixing and coflowing structure for droplet formation (discussed in the later section), a more complex synthesis platform was proposed by Shi et al. [110] to produce core-shell and spherical HMX/FOX-7 microspheres with different composites, as shown in Fig. 3(d). By mixing the solvent and antisolvent via swirling and oscillatory flow, the HMX suspension containing particles with narrow particle size distribution can be collected. And passing through the coflowing structure, the double-layered droplets with HMX suspension as the core and FOX-7/Etane as the shell can be generated. After these treatments, the HNS microspheres prepared from this platform were proven to have very smooth surfaces, ensuring superior safety and output performance.

Besides exciting the oscillating state at low frequency, the ultrasonic wave was also introduced to enhance the mixing and

relieve the blockages of channels by Jiang et al. [111]. As shown in Fig. 3(e), the platform exhibits minimal reagent consumption, quick response, and excellent mixing performance. Their results show that those critical parameters, like the crystal type (β-HMX or γ-HMX), morphology (polygonal-block, sphere-like shapes or flaky shapes), and size (ranging from 368 nm to 1.33 μm) of ultrafine HMX can be accurately controlled.

Active microfluidic methods provide higher degrees of freedom and accuracy in operations but often require more complex equipment and control systems, resulting in higher costs. More importantly, in some situations, the synthesis safety should be evaluated. For example, ultrasonic mixing with high mixing performance may lead to local high pressure and high temperature caused by acoustic cavitation, increasing the experimental risk in the field of EMs [112]. In conclusion, while passive microfluidic methods are advantageous for their simplicity and cost-effectiveness, active microfluidic methods can realize a higher efficient and controllable synthesis. The choice between passive and active methods depends on the specific requirements of materials, cost considerations, and complexity of the desired operations. However, for some energetic materials where sphericity and granularity are very important, another preparation method is to constrain the reactions within the droplets based on the microfluidic chips.

4. Synthesis of energetic materials by micro-droplets

4.1. Spherical particles prepared by micro-droplets

Sphericalness was a kind of desired morphology for most energetic materials because of larger specific surface area, more homogeneous particle size distribution, and better liquidity compared with other morphological features. For the preparation of energetic microspheres, micro-droplets generated by the shear force of continuous phase fluid provide an appropriate and uniform reaction chamber. The glass-substrate chips with the flow-focusing channels are the usual and effective platform.

As shown in Fig. 4(a), the flow-focusing microfluidic chip was fabricated by the group of Han [113] to generate droplets consisting of energetic materials and binders, and the droplets with

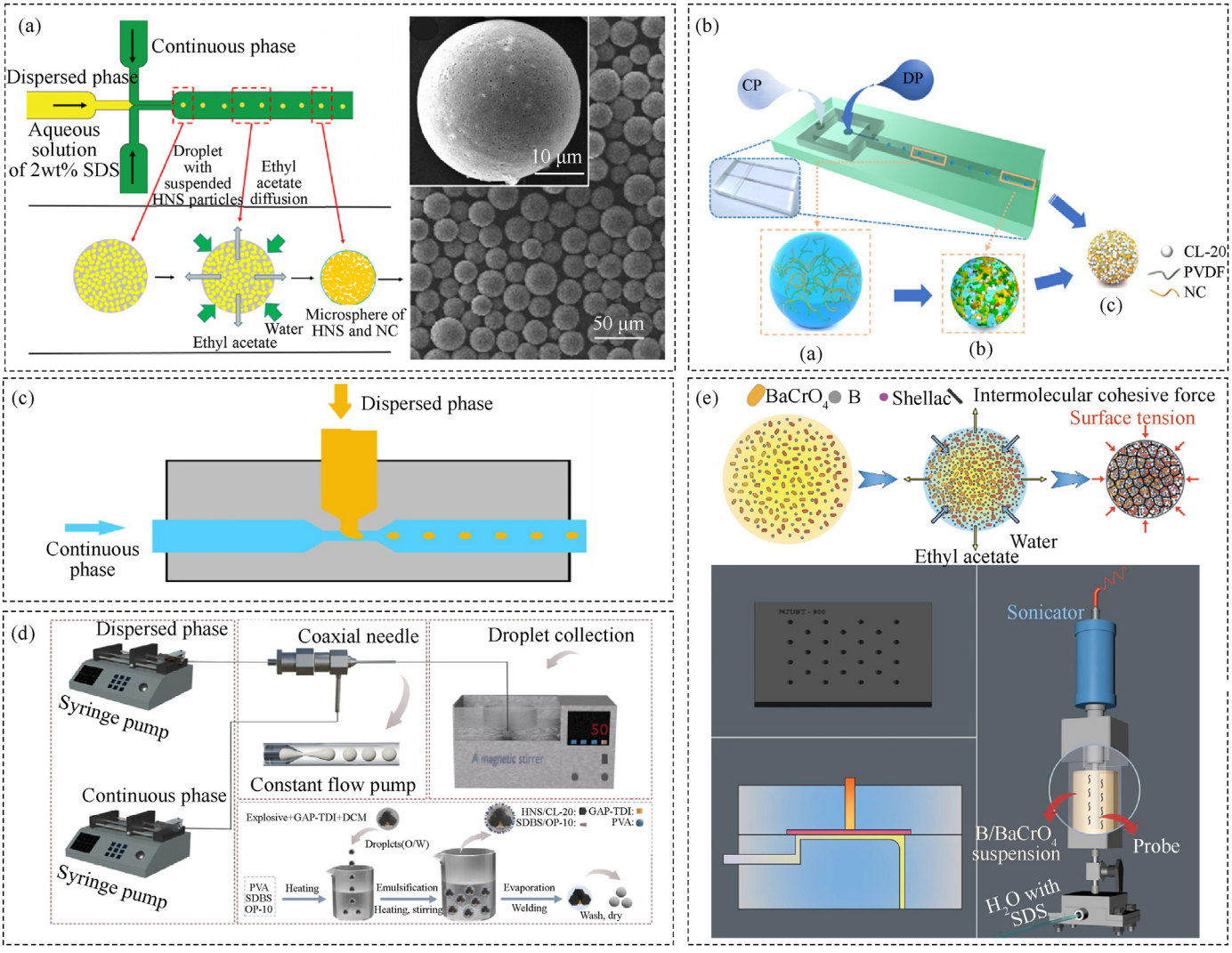

Fig. 4. The structure of droplets microfluidic chips for the synthesis of spherical particles: (a) The flow-focusing microfluidic chip to form the microsphere of HNS and NC [113]; (b) The preparation model of CL-20/PVDF/NC composite propellants with micro/nano hierarchical structure [116]; (c) The flow-focusing microfluidic chip for the formation of HMX/(Cu/n-Al) microspheres [120]; (d) The coaxial droplet microfluidic chips for the synthesis of HNS/GAP/CL-20 microspheres [122]; (e) The microfluidic system based on the microdroplets-confined coupling polymer theory for the synthesis of B/BaCrO4 nano-composite particles [123].

nitrocellulose (NC) as blinders were solidified into micro-spherical hexanitrostilbene (HNS) particles in the dispersed phase. When flow rates of the dispersed phase (2 wt% aqueous SDS solution) and continuous phase (20 wt% HNS and 1 wt% NC in ethyl acetate (EA) solution) were set to 50 μL/min and 2000 μL/min respectively, monodisperse droplets of EA suspended with HNS particles are formed by shearing multiphase fluids. As the EA in the suspended HNS microdroplets continually diffused into the water phase, the droplets would gradually solidify in the environment of deionized water. Complete solidification would be achieved after being collected into a breaker (full of Deionized water). The solvent exchange between the droplets and the water environment enables the microspheres to have better sphericity and uniformity [113]. The particle size of HNS microspheres formed in this technique ranged from 10 μm to 40 μm, and the median particle size was 23 μm. Recently, Han et al. [57] got HNS-IV(the main component of the exploding foil initiators) microspheres using microfluidic chips with the same structure as in Fig. 4(a), which have high sphericity, with an average particle size of 20.52 μm (coefficient of variation less than 0.2), and a specific surface area of 21.62 m^2/g.

In addition to the HNS, other energetic materials with controllable particle sizes were prepared in the form of droplets. When Zhou et al. [114] increases the flow rate ratio of continuous phase to dispersed phase from 10 to 25, the average size of HMX/F_{2602} microspheres with good morphology and thermal stability decreases from 106 μm to 32 μm. Further, the droplet microfluidics can also help to fabricate the complex compounds. The HMX/TATB mixture microspheres with the NC/CAP (1:4) as binders, correspond to higher explosive power and lower sensitivity than those of single component due to the interaction and mutual inhibition of HMX and TATB [115].

In some studies of droplet-based synthesis, the polymer binder is specially designed as a critical component to facilitate the transition from droplets into microspheres to achieve better performance. As shown in Fig. 4(b), the porous and 3D structure of the PVDF and NC composite framework, solidified from the droplet, can provide a model architecture to load high-energy fuels and achieve high-performance combustion by compensating the heat and pressure loss. Yang et al. [116] tried to prepare 90% loading CL-20 spherical particles with tens to hundreds of microns, using 5% NC and 5% PVDF as the binders. The CL-20/PVDF/NC composites show uniform particle sizes and highly efficient combustion performance (long burning time from 540 ms to 560 ms and bright flame), by virtue of high CL-20 loading.

The synthesis based on droplet formation with the cross-flow structure is suitable not only for energetic materials dissolved in organic solvents but also for energetic metal and metalloid nanopowders as high-energy fuel or energetic additive of propellants, such as aluminum and boron. However, the easy agglomeration of nano aluminum (nAl) powder and its high ignition temperature greatly hinder the reaction in the process of explosion. To solve this problem, Zhou et al. [117] utilized the droplet as a model to form the three-dimensional spherical skeletons by adsorbing the HMX particles and Al particles using the binder. And the ultrasonic liquid injector was chosen to keep the dispersion state of nanoparticles before entering the channel. The obtained high-quality and homogeneous spherical HMX/nAl microspheres demonstrate much better dispersion and combustion performance and that the particle size ranges from 39 μm to 90 μm. Further, copper (Cu) was also introduced into aluminized explosives for inhibiting the agglomeration and increasing the combustion rate of the microspheres by Zhang et al. [118]. In other studies, the boron nanoparticles (nBs), with homogeneously dispersed organometallic catalyst (M = Mo, Fe and Co), are uniformly encapsulated in droplets with chitosan (CS) as the binder by Xue et al. [119] to fabricate the energetic-microcapsules (nB@M − CS). And the microcapsules' structure shortened the mass transfer distance and promoted the contact area between nBs and mental catalyst.

In addition to the cross-flow channels, being simpler structures, T-shaped channels are also frequently utilized for droplet generation and synthesis. Cheng et al. [120] developed this kind of microfluidic chip to simplify the preparation of Al/CL-20-based energetic materials. As shown in Fig. 4(c), with nAl, PVDF, and CL-20 dissolved in ethyl acetate as the dispersion phase, and with deionized water as the continuous phase, ethyl acetate microdroplets were generated near the T-shaped structure. After subsequent washing, filtration, and drying steps, the nAl/PVDF/CL-20 solid composite microspheres were obtained. The products exhibited excellent sphericity, dispersibility, and uniform particle size distribution, with particle sizes ranging from 10 μm to 20 μm and a median particle size of 14.18 μm. The composite microspheres exhibited superior uniformity in particle size distribution compared to the particles prepared from Liu et al. [121], with sizes ranging from 200 μm to 400 μm.

In some studies, the coaxial flow method can also be employed for preparing energetic material in droplet form. Compared with the cross-flow or T-shaped structure, the coaxial flow method has better stability as droplets formed along the central axis barely touch the wall. As shown in Fig. 4(d), in the study by Liu et al. [122], HNS/CL-20 composite droplets were generated within the coaxial flow and solidified into microspheres with poly-glycidyl azide polymer (GAP) as the binder. The HNS/CL-20 microspheres by this platform showed high sphericity (sphericity of 0.927 with a span of 0.040) and particle size uniformity(the average size of 54.43 μm with a span of 0.41 and the coefficient of variation of 12.69%).

Instead of shear stress between immiscible fluids, high throughput formation of energetic material droplets can be achieved by squeezing the dispersion phase fluid through pores of the membrane. Recently, Zhou et al. [123] proposed a microdroplet-confined coupling polymer self-assembly theory to improve the delay precision of B/BaCrO4 such composite particulates. The high-frequency vibration of the sonicator on the solid particles in the dispersed phase can solve the settling problem of particles, leading to the homogeneously dispersed suspension. The stainless steel-based microporous array chip was used as the microdroplet template to obtain the B/BaCrO4 particulates (an average particle size of 265 nm and a span of 0.52) by squeezing the droplets out from the porous, as shown in Fig. 4(e). By this method, the combustion reaction heat of the composite energetic particulates can reach 3943 J/g and the relative range Rr (criteria of delay precision) is as low as 3.438%.

4.2. Non-spherical particles prepared by micro-droplets

The morphological characteristics of EMs particles, though, can be regulated by the droplets before solidification, the shape of the final products, in many situations, was not well spherical due to the inhomogeneous reaction, and molecular structure of the material. Even with the assistance of binders, the size of the spherical particles prepared in the previous section was slightly smaller than that of the original droplets due to the dissolution of solvents in the curing process of droplets. In many relevant studies, non-spherical particles may be obtained.

Mono-disperse lead trinitroresorcinate (LTNR) clusters have been widely used as a primary explosive in SCBs (semi-conductor bridges), initiators, and propellants for micro-electro mechanical systems (MEMS) solid-propellant thrusters array chips because of its considerable flame sensitivity and low brisance. For producing LTNR, Zhou et al. [124] designed a segmented synthesis system containing a T-junction microchannel reaction module as shown in

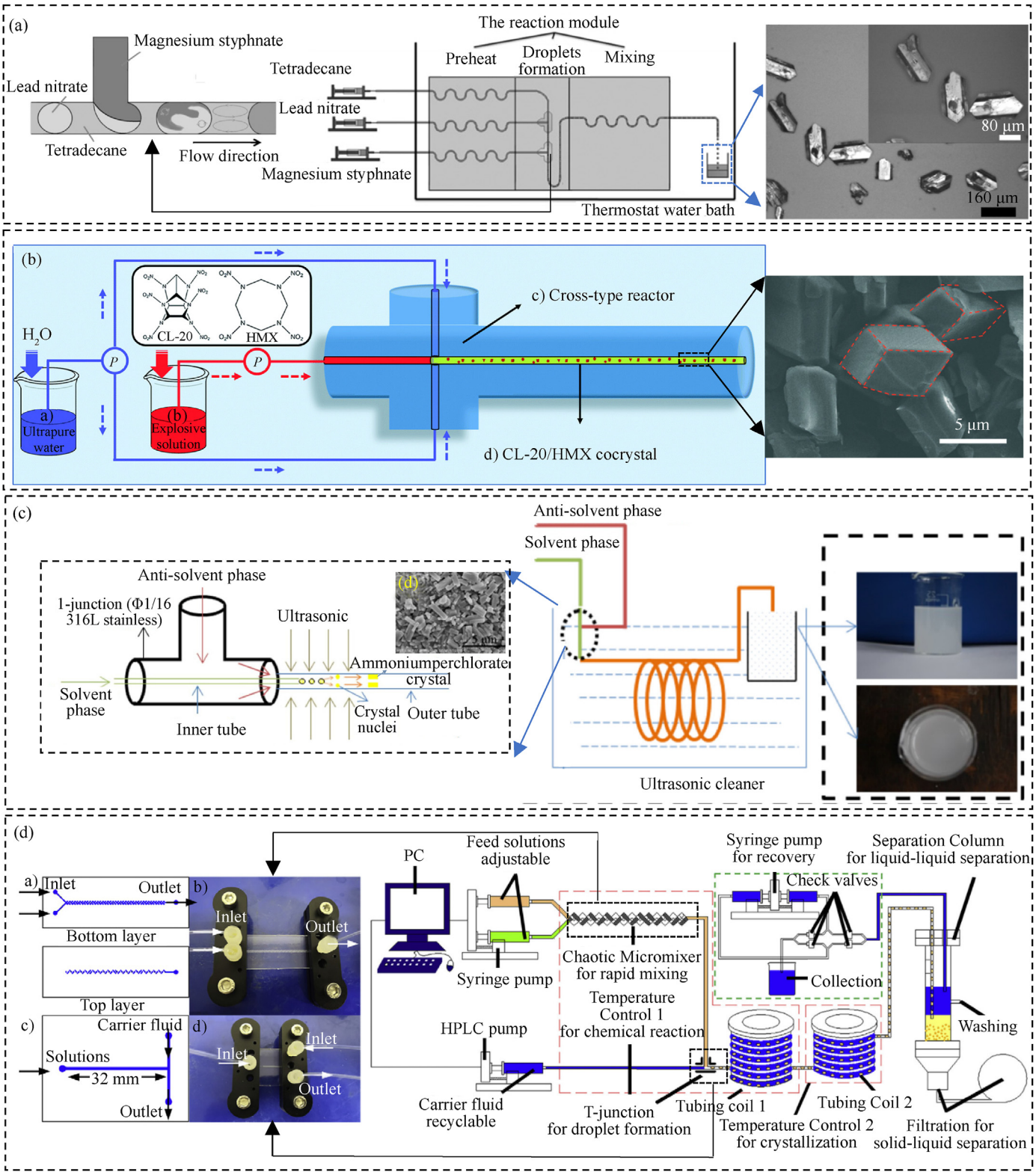

Fig. 5. The structure of droplets microfluidic chips for the synthesis of non-spherical particles: (a) The microfluidic system based on the design of T-shaped microchannels, and the reaction inside the droplets for the synthesis of (LTNR) particles with the shape of polyhedrons similarly [124]; (b) The flow-focusing microfluidic chips for the synthesis of CL-20/HMX cocrystal with a cube-shaped appearance [125]; (c) The ultrasonic-assisted microfluidic system for the ultra-fine AP crystals with the cubic morphology [126]; (d) The micro-reaction system based on the microfluidic mixing and the droplet microfluidics for the synthesis of the porous and spherical BaTNR [127].

Fig. 5(a). Two reagents were encapsulated into the droplets and subsequently induced chemical reactions within these micro-chambers. The LTNR particles with an average size of 100 μm will be obtained following preheating, droplet formation, and solidification in a thermostat water bath. The resulting morphology of the LTNR particles exhibited prisms with six sides, smooth surfaces,

and better size uniformity than those through the traditional method, the batch reaction. In addition, the heat release of LTNR in their studies increased by 353.52 J/g in comparison to that formed through traditional experiments, accompanied by a 13% increase in synthesis yield.

The droplet microreactor has also been used to control the co-crystallization reaction, which is one of the most usual approaches to make new chemical compounds through the assembly of multiple molecules in the solid state. A microchannel-confined crystallization strategy has been proposed by Li et al. [125] to prepare CL-20/HMX cocrystal. As shown in Fig. 5(b), with a flow-focusing microchannel and a mixing length of 9 cm, the CL-20/HMX cocrystal with a cube-shaped appearance and a particle diameter of 21.8 μm can be obtained in the microchannel, free from other operations such as solidification, rinsing, and so on. The results show that the mechanical sensitivity of the cocrystal outperforms the two pure components and is also superior to most previous cocrystals with a morphology of a flower cluster together with a platelet. Due to the controllable crystallization environment and one-step fabrication procedure, the microchannel confined crystallization strategy might also be easily applicable to other cocrystal systems and scale-up production.

The co-crystallization reaction can be further controlled with the assistance of the non-contact force during the preparation. As shown in Fig. 5(c), the ultrasonic-assisted crystallization was developed by Ma et al. [126]to synthesize the ultra-fine ammonium perchlorate crystals in the flow-focus microfluidic chips. The morphology of the crystals was cuboid and polyhedron respectively when methanol and DMF were used as solvents and the size of the AP particles was less than 1 μm.

The group of Zhou et al. [127] combined droplet microfluidics and mixing intensification to ensure the homogeneity of particle nucleation and growth, as shown in Fig. 5(d). This system, consisting of a two-layer cross-channel micromixer and a liquid segment flow, has shown clear advantages over the traditional method with respect to crystal morphology, particle size distribution, and thermal stability for the synthesis of some harmful ionic primary explosives. Taking lead-2,4,6-trinitroresorcinate styphnate (LTNR) and barium-2,4,6-trinitroresorcinate (BaTNR) for example, the results show that the particle size of LTNR ranged from 30 μm to 90 μm, while the heat release was 230.1 J/g greater than that of LTNR prepared by the micro-segmented type chips. Likewise, the heat release of obtained BaTNR was 168.7 J/g greater than before.

5. Conclusions

Microfluidics serves as a powerful tool for preparing the energetic materials particles, allowing to tune particle size and morphology. Furthermore, these physical features can deeply influence the explosive performance of energetic materials. Two main strategies were discussed to prepare energetic nanoparticles in microfluidic chips, including the direct mixing of fluids and the formation of droplets as dispersed reaction chambers. In particular, two strategies can be selected and optimized according to the target performance of EMs, like ensuring the high sensitivity of the detonator and the high energy density of explosives.

Energetic materials have traditionally been prepared by mixing reagents in experiments. However, microreactors offer a more precise method of mixing reagents at the micro-scale by designing parameters such as microchannel geometry and fluid flow rate. The small size of microfluidic chips enables the minimization of reactant consumption while maintaining rapid mixing and highly efficient reactions. Especially for energetic materials, the synthesis safety will also be greatly improved due to the reduction in reagent usage. To achieve shorter mixing time and depress the blockage of the microchannels in the passive microfluidic chip, some external physical fields, like acoustic field and electrical field, are introduced to break the limits [101,102]. However, the safety of active microfluidic chips should be evaluated due to external energy dissipation within the reactions, such as thermal effects from high-frequency vibration fields. So how to balance the higher control capacity and safety is a challenge for future studies.

Additionally, if the special size and shape of particles are required for better liquidity and higher load density, the EMs preparation based on the microscale droplets can be selected. The usual usage of the droplet is to refine and modify the energetic materials with the assistance of special reagents during the recrystallization. The sizes of energetic material particles, whether spherical or non-spherical, are mainly determined by the diameter of droplets generated by the shear forces of fluids. The formation of spherical particles can be regarded as one or more kinds of energetic materials micro-crystallites crystallized in the solvent, bonded into energetic material microspheres under the action of binder crystallite. However, different materials exhibit different crystallization habits inside the droplets. For instance, HNS [128] typically forms long, elongated crystals, while HMX [129] tends to form blocky or granular crystals. Without suitable binders and surfactants, the crystallites may not form homogeneous spherical shapes after seed growth.

A foreseeable trend in this field is to combine the advantages of microfluidic mixing chips and droplet microfluidic chips. It involves the rapid mixing of reactants through fluid mixing, followed by refinement and modification of the materials using microdroplet chips, ultimately resulting in desired particles of energetic materials. During this process, various parameters can be adjusted to modulate the characteristics of energetic materials, such as the control of the fluids, flow channel design, and the optimization of reaction conditions of the fluids. In short, to prepare energetic material particles with satisfaction, we need to select a suitable reaction system and make full use of the precise control capabilities of microfluidic technology.

In summary, by virtue of highly efficient mixing, uniform droplet formations, and more external physical interferences, more microfluidics have been used to prepare various energetic materials with excellent performance. Through precise reaction control at the microscale, particle manipulation, and assembly, the preparation of high-performance and high-stability energetic materials can be realized, and innovation and development in the field of energetic materials have been truly promoted. In the future, the integration of microfluidic technology with physical fields, like magnetic [130] and acoustic field [131,132], will hold great potential not only in the field of high-energy material preparation, but also in areas such as chemical synthesis, particle fabrication, and nanomaterial research.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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References

[1] Bhattacharya A, Guo Y, Bernstein ER. Nonadiabatic reaction of energetic molecules. Acc Chem Res 2010;43:1476–85.
[2] Field JE. Hot spot ignition mechanisms for explosives. Acc Chem Res 1992;25:489–96.
[3] Yang GL, Zhu SG, Shen RQ. Study on ignition property of energetic material by semiconductor bridge. Chin J Energetic Mater 2012;20(4):391–6.
[4] Blair LH, Colakel A, Vrcelj RM, et al. Metal–organic fireworks: MOFs as integrated structural scaffolds for pyrotechnic materials. Chem Commun 2015;51:12185–8.
[5] Mathieu J, Stucki H. Military high explosives. CHIMIA 2004;58:383. 383.
[6] Meda L, Marra G, Galfetti L, et al. Nano-aluminum as energetic material for rocket propellants. Mater Sci Eng C 2007;27:1393–6.
[7] Sikder AK, Sikder N. A review of advanced high performance, insensitive and thermally stable energetic materials emerging for military and space applications. J Hazard Mater 2004;112:1–15.
[8] Cary TJ, Rylott EL, Zhang L, et al. Field trial demonstrating phytoremediation of the military explosive RDX by XplA/XplB-expressing switchgrass. Nat Biotechnol 2021;39:1216–9.
[9] Millar DI, Oswald ID, Francis DJ, et al. The crystal structure of β-RDX—an elusive form of an explosive revealed. Chem Commun 2009;0:562–4.
[10] Howa JD, Lott MJ, Chesson LA, et al. Carbon and nitrogen isotope ratios of factory-produced RDX and HMX. Forensic Sci Int 2014;240:80–7.
[11] Junghare S, Kumari S, Chaudhary A, et al. Thermite reaction driven pyrotechnic formulation with promising functional performance and reduced emissions. J Hazard Mater 2022;424:127345.
[12] Jia XL, Hou CH, Tan YX, et al. Fabrication and characterization of PMMA/HMX-based microcapsules via in situ polymerization. Cent Eur J Energ Mater 2017;14:559–72.
[13] Huang B, Qiao Z, Nie F, et al. Fabrication of FOX-7 quasi-three-dimensional grids of one-dimensional nanostructures via a spray freeze-drying technique and size-dependence of thermal properties. J Hazard Mater 2010;184:561–6.
[14] Risse B, Schnell F, Spitzer D. Synthesis and desensitization of nano-β-HMX. Propellants, Explos Pyrotech 2014;39:397–401.
[15] Bayat Y, Pourmortazavi SM, Ahadi H, et al. Taguchi robust design to optimize supercritical carbon dioxide anti-solvent process for preparation of 2,4,6,8,10,12-hexanitro-2,4,6,8,10,12-hexaazaisowurtzitane nanoparticles. Chem Eng J 2013;230:432–8.
[16] Jeong SY, Cho JS. Dataset on the effect of carbon sources on the morphology and crystallite size of Fe/C composite microspheres prepared by the spray drying process. Data Brief 2020;28:1050–2.
[17] Yount J, Piercey DG. Electrochemical synthesis of high-nitrogen materials and energetic materials. Chem Rev 2022;122:8809–40.
[18] Sanders VE, Asay BW, Foley TJ, et al. Reaction propagation of four nanoscale energetic composites (Al/MoO3, Al/WO3, Al/CuO, and B12O3). J Propul Power 2007;23:707–14.
[19] Chatterjee S, Deb U, Datta S, et al. Common explosives (TNT, RDX, HMX) and their fate in the environment: emphasizing bioremediation. Chemosphere 2017;184:438–51.
[20] Groom CA, Halasz A, Paquet L, et al. Accumulation of HMX (Octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine) in indigenous and agricultural plants grown in HMX-contaminated anti-tank firing-range soil. Environ Sci Technol 2002;36:112–8.
[21] Burtoloso ACB, Momo PB, Novais GL. Traditional and new methods for the preparation of diazocarbonyl compounds. An Acad Bras Cienc 2018;90:859–93.
[22] Kuchurov IV, Zharkov MN, Fershtat LL, et al. Prospective symbiosis of green chemistry and energetic materials. ChemSusChem 2017;10:3914–46.
[23] Chen L, Ru C, Zhang H, et al. Progress in electrohydrodynamic atomization preparation of energetic materials with controlled microstructures. Molecules 2022;27:2374.
[24] Vorozhtsov A, Lerner M, Rodkevich N, et al. Preparation and characterization of Al/HTPB composite for high energetic materials. Nanomaterials 2020;10:2222.
[25] Zhu HY, Liu YH, Sun HY, et al. New technology for preparing energetic materials by nanofiltration membrane (NF): rapid and efficient preparation of high-purity ammonium dinitramide (ADN). RSC Adv 2023;13:16536–48.
[26] Zhang J, Zhang Q, Vo TT, et al. Energetic salts with π-stacking and hydrogen-bonding interactions lead the way to future energetic materials. J Am Chem Soc 2015;137:1697–704.
[27] Fu X, Zhu Y, Li J, et al. Preparation, characterization and application of nano-graphene-based energetic materials. Nanomaterials 2021;11:2374.
[28] Liu Z, Fontana F, Python A, et al. Microfluidics for production of particles: mechanism, methodology, and applications. Small 2020;16:1904673.
[29] Illath K, Kar S, Gupta P, et al. Microfluidic nanomaterials: from synthesis to biomedical applications. Biomaterials 2022;280:121247.
[30] Jaradat E, Weaver E, Meziane A, et al. Microfluidics technology for the design and formulation of nanomedicines. Nanomaterials 2021;11:3440.
[31] Nan L, Jiang Z, Wei X. Emerging microfluidic devices for cell lysis: a review. Lab Chip 2014;14:1060–73.
[32] Bian F, Sun L, Cai L, et al. Colloidal crystals from microfluidics. Small 2020;16:1903931.
[33] Xie X, Wang Y, Siu SY, et al. Microfluidic synthesis as a new route to produce novel functional materials. Biomicrofluidics 2022;16:041301.
[34] Xia L, Li G. Recent progress of microfluidic sample preparation techniques. J Separ Sci 2023;46:2300327.
[35] Fattahi Z, Hasanzadeh M. Nanotechnology-assisted microfluidic systems for chemical sensing, biosensing, and bioanalysis. TrAC, Trends Anal Chem 2022;152:116637.
[36] Rodrigues T, Schneider P, Schneider G. Accessing new chemical entities through microfluidic systems. Angew Chem (International ed. in English) 2014;53:5750–8.
[37] DeMello AJ. Control and detection of chemical reactions in microfluidic systems. Nature 2006;442(7101):394–402.
[38] Feng J, Neuzil J, Manz A, et al. Microfluidic trends in drug screening and drug delivery. TrAC, Trends Anal Chem 2023;158:116821.
[39] Sun XT, Guo R, Wang DN, et al. Microfluidic preparation of polymer-lipid Janus microparticles with staged drug release property. J Colloid Interface Sci 2019;553:631–8.
[40] Zhao Z, Wang Z, Li G, et al. Injectable microfluidic hydrogel microspheres for cell and drug delivery. Adv Funct Mater 2021;31:2103339.
[41] Chen CH, Shah RK, Abate AR, et al. Janus particles templated from double emulsion droplets generated using microfluidics. Langmuir 2009;25:4320–3.
[42] Ziegler J, Merkulov A, Grabolle M, et al. High-quality ZnS shells for CdSe nanoparticles: rapid microwave synthesis. Langmuir 2007;23:7751–9.
[43] Jin S, Wei X, Yu Z, et al. Acoustic-controlled bubble generation and fabrication of 3D polymer porous materials. ACS Appl Mater Interfaces 2020;12:22318–26.
[44] Hu Y, Yuan S, Li X, et al. Preparation and characterization of nano-CL-20/TNT cocrystal explosives by mechanical ball-milling method. ACS Omega 2020;5:17761–6.
[45] Sivabalan R, Gore GM, Nair UR, et al. Study on ultrasound assisted precipitation of CL-20 and its effect on morphology and sensitivity. J Hazard Mater 2007;139:199–203.
[46] Ren XT, Sun ZX, Cao YL. Preparation and passivation of fine ε-CL-20. Huozhayao Xuebao/Chinese Journal of Explosives and Propellants 2011;34:21–5.
[47] Lignos I, Maceiczyk R, deMello AJ. Microfluidic technology: uncovering the mechanisms of nanocrystal nucleation and growth. Acc Chem Res 2017;50:1248–57.
[48] Niculescu AG, Chircov C, Bîrcă AC, et al. Nanomaterials synthesis through microfluidic methods: an updated overview. Nanomaterials 2021;11:864.
[49] Popa ML, Preda MD, Neacșu IA, et al. Microfluidic synthesis of ZnO nanoparticles. Int J Mol Sci 2023;24:1875. https://doi.org/10.3390/ijms24031875.
[50] Wang J, Song Y. Microfluidic synthesis of nanohybrids. Small 2017;13:1604084.
[51] Li Y, Cai S, Shen H, et al. Recent advances in acoustic microfluidics and its exemplary applications. Biomicrofluidics 2022;16:031502.
[52] Movsisyan M, Delbeke EI, Berton JK, et al. Taming hazardous chemistry by continuous flow technology. Chem Soc Rev 2016;45:4892–928.
[53] Ward T, Faivre M, Stone HA. Drop production and tip-streaming phenomenon in a microfluidic flow-focusing device via an interfacial chemical reaction. Langmuir 2010;26:9233–9.
[54] Nette J, Montanarella F, Zhu C, et al. Microfluidic synthesis of monodisperse and size-tunable CsPbBr3 supraparticles. Chem Commun 2023;59:3554–7.
[55] Han JY, La Fiandra JN, DeVoe DL. Microfluidic vortex focusing for high throughput synthesis of size-tunable liposomes. Nat Commun 2022;13:6997.
[56] Jing J, Gao F, Liu H, et al. Preparation and characterization of TATB-based energetic composite microspheres by continuous pipe-stream self-assembly technology. Chem Eng J 2023;471:144710.
[57] Han RS, Lu FP, Zhang F, et al. Thermal and ignition properties of hexanitrostilbene (HNS) microspheres prepared by droplet microfluidics. Defence Technology 2023;25:166–73.
[58] Giudice FD, D'Avino G, Maffettone PL. Microfluidic formation of crystal-like structures. Lab Chip 2021;21:2069–94.
[59] Duraiswamy S, Khan SA. Droplet-based microfluidic synthesis of anisotropic metal nanocrystals. Small 2009;5:2828–34.
[60] Shi J, Wu B, Zhou J, et al. One-step rapid preparation of CL-20/TNT co-crystal assembly and spheroidized coating based on droplet microfluidic technology. Defence Technology 2023;27:251–62.
[61] Huo H, Ye B, Shi Y, et al. Preparation of HNS microspheres by rapid membrane emulsification. Particuology 2023;79:35–44.
[62] Hou C, Li C, Jia X, et al. Facile preparation and properties study of CL-20/TATB/VitonA composite microspheres by a spray-drying process. J Nanomater 2020;2020:e8324398.
[63] Zeman S, Jungová M. Sensitivity and performance of energetic materials. Propellants, Explos Pyrotech 2016;41:426–51.
[64] Zhang J, Mitchell LA, Parrish DA, et al. Enforced layer-by-layer stacking of energetic salts towards high-performance insensitive energetic materials. J Am Chem Soc 2015;137:10532–5.
[65] Tang Y, Mitchell LA, Imler GH, et al. Ammonia oxide as a building block for high-performance and insensitive energetic materials. Angew Chem Int Ed 2017;56:5894–8.
[66] Yadav AK, Ghule VD, Dharavath S. Promising thermally stable energetic materials with the combination of pyrazole–1,3,4-oxadiazole and pyrazole–1,2,4-triazole backbones: facile synthesis and energetic performance. ACS Appl Mater Interfaces 2022;14:49898–908.

[67] Wang R, Yang L, Zhang Z, et al. Preparation of quasi-core/shell structured composite energetic materials to improve combustion performance. RSC Adv 2023;13:17834–41.
[68] Zhang W, Yang Y, Shi S, et al. Regulation of stability and density of energetic materials via isomerism. Phys Chem Chem Phys 2023;25:20168–72.
[69] Lai Q, Pei L, Fei T, et al. Size-matched hydrogen bonded hydroxylammonium frameworks for regulation of energetic materials. Nat Commun 2022;13:6937.
[70] Wu F, Dong Y, Su YF, et al. Benchmarking the effect of particle size on silicon anode materials for lithium-ion batteries. Small 2023;19:2301301.
[71] Pang W, Deng C, Li H, et al. Effect of nano-sized energetic materials (nEMs) on the performance of solid propellants: a review. Nanomaterials 2022;12:133.
[72] Zohari N, Keshavarz MH, Seyedsadjadi SA. The advantages and shortcomings of using nano-sized energetic materials. Cent Eur J Energ Mater 2013;10.
[73] Kosareva EK, Gainutdinov RV, Michalchuk AAL, et al. Mechanical stimulation of energetic materials at the nanoscale. Phys Chem Chem Phys 2022;24:8890–900.
[74] Chen MW, You S, Suslick KS, et al. Hot spots in energetic materials generated by infrared and ultrasound, detected by thermal imaging microscopy. Rev Sci Instrum 2014;85:023705.
[75] You S, Chen MW, Dlott DD, et al. Ultrasonic hammer produces hot spots in solids. Nat Commun 2015;6:6581.
[76] Yan F, Zhu P, Zhao S, et al. Microfluidic strategy for coating and modification of polymer-bonded nano-HNS explosives. Chem Eng J 2022;428:131096.
[77] Tariq R, Zhan C, Zhao X, et al. Numerical study of a regenerative counter flow evaporative cooler using alumina nanoparticles in wet channel. Energy Build 2018;169:430–43.
[78] Xiao F, Li J, Zhou X, et al. Preparation of mechanically activated aluminum-rich Al-Co3O4 powders and their thermal properties and reactivity with water steam at high temperature. Combust Sci Technol 2018;190:1935–49.
[79] Pang W, Fan X, Wang K, et al. Al-based nano-sized composite energetic materials (Nano-CEMs): preparation, characterization, and performance. Nanomaterials 2020;10:1039.
[80] Li C, Li H, Xu K. High-substitute nitrochitosan used as energetic materials: preparation and detonation properties. Carbohydr Polym 2020;237:116176.
[81] Song L, Zhang S. A simple mechanical mixing method for preparation of visible-light-sensitive NiO–CaO composite photocatalysts with high photocatalytic activity. J Hazard Mater 2010;174:563–6.
[82] Sharip NS, Ariffin H, Yasim-Anuar TAT, et al. Melt- vs. Non-melt blending of complexly processable ultra-high molecular weight polyethylene/cellulose nanofiber bionanocomposite. Polymers 2021;13:404.
[83] Ozeki T, Akiyama Y, Takahashi N, et al. Development of a novel and customizable two-solution mixing type spray nozzle for one-step preparation of nanoparticle-containing microparticles. Biol Pharm Bull 2012;35:1926–31.
[84] Zhou X, Torabi M, Lu J, et al. Nanostructured energetic composites: synthesis, ignition/combustion modeling, and applications. ACS Appl Mater Interfaces 2014;6:3058–74.
[85] Lee CY, Chang CL, Wang YN, et al. Microfluidic mixing: a review. Int J Mol Sci 2011;12:3263–87.
[86] Lee CY, Wang WT, Liu CC, et al. Passive mixers in microfluidic systems: a review. Chem Eng J 2016;288:146–60.
[87] Singh R, Lee HJ, Singh AK, et al. Recent advances for serial processes of hazardous chemicals in fully integrated microfluidic systems. Kor J Chem Eng 2016;33:2253–67.
[88] Pal S, Madane K, Kulkarni AA. Antisolvent based precipitation: batch, capillary flow reactor and impinging jet reactor. Chem Eng J 2019;369:1161–71.
[89] Bayat Y, Zarandi M, Zarei MA, et al. A novel approach for preparation of CL-20 nanoparticles by microemulsion method. J Mol Liq 2014;193:83–6.
[90] Zhang S, Zhan L, Zhu G, et al. Continuous, safe and large-scale preparation of insensitive high-energy TATB/HMX composite particles by microfluidic self-assembly technology. Chem Eng Sci 2022;264:118160.
[91] Guo Y, Zhou J, Liu S, et al. A novel micromixer for efficient mixing and nano-TATB preparation. Propellants, Explos Pyrotech 2023;48:e202300048.
[92] Delville MME, Nieuwland PJ, Janssen P, et al. Continuous flow azide formation: optimization and scale-up. Chem Eng J 2011;167:556–9.
[93] Zhao S, Chen C, Zhu P, et al. Passive micromixer platform for size- and shape-controllable preparation of ultrafine HNS. Ind Eng Chem Res 2019;58:16709–18.
[94] Chen C, Zhao S, Zhu P, et al. Improvement of silver azide crystal morphology and detonation behavior by fast mixing using a microreaction system with an integrated static micromixer. React Chem Eng 2019;5:154–62.
[95] Zhang S, Zhan L, Zhu G, et al. Rapid preparation of size-tunable nano-TATB by microfluidics. Defence Technology 2022;18:1139–47.
[96] Yu J, Jiang H, Xu S, et al. Preparation and properties of RDX@FOX-7 composites by microfluidic technology. Crystals 2023;13:167.
[97] Zaborenko N, Murphy ER, Kralj JG, et al. Synthesis and kinetics of highly energetic intermediates by micromixers: direct multistep synthesis of sodium nitrotetrazolate. Ind Eng Chem Res 2010;49:4132–9.
[98] Fedorov SG, Guseinov SL, Storozhenko PA. Nanodispersed metal powders in high-energy condensed systems. Nanotechnologies in Russia 2010;5:565–82.
[99] Armstrong RW, Baschung B, Booth DW, et al. Enhanced propellant combustion with nanoparticles. Nano Lett 2003;3:253–5.
[100] Kant R, Singh H, Bhattacharya S. Nanoscale etching of particles in continuous flow reactor. J Nanosci Nanotechnol 2017;17:5241–51.
[101] Smith PC, Huf JP, Williams CA. Rocket propellant comparison: conventional planetary mixing and resonant acoustic mixing. Propellants, Explos Pyrotech 2022;47:e202100028.
[102] Beckel E, Oyler K, Mehta N, et al. Primary explosive processing in the resonant acoustic mixer. Propellants, Explos Pyrotech 2021;46:697–704.
[103] Yalcin D, Rajesh S, White J, et al. Resonant acoustic mixing method to produce lipid-based liquid-crystal nanoparticles. J Phys Chem C 2021;125:10653–64.
[104] Tanaka R, Takahashi N, Nakamura Y, et al. Verification of the mixing processes of the active pharmaceutical ingredient, excipient and lubricant in a pharmaceutical formulation using a resonant acoustic mixing technology. RSC Adv 2016;6:87049–57.
[105] Zhang S, Zhan L, Zhang Y, et al. Continuous flow resonance acoustic mixing technology: a novel and efficient strategy for preparation of nano energetic materials. FirePhysChem 2023;3:29–36.
[106] Wu JW, Xia HM, Zhang YY, et al. An efficient micromixer combining oscillatory flow and divergent circular chambers. Microsyst Technol 2019;25:2741–50.
[107] Shi J, Zhu P, Zhao S, et al. Microfluidic strategy for rapid and high-quality control of crystal morphology of explosives. React Chem Eng 2020;5:1093–103.
[108] Yang Z, Zhu P, Zhang Q, et al. Microcrystalline PETN prepared using microfluidic recrystallization platform and its performance characterization. Propellants, Explos Pyrotech 2021;46:1097–106.
[109] Zhao S, Wu J, Zhu P, et al. Microfluidic platform for preparation and screening of narrow size-distributed nanoscale explosives and supermixed composite explosives. Ind Eng Chem Res 2018;57:13191–204.
[110] Shi J, Zhu P, Zhao S, et al. Continuous spheroidization strategy for explosives with micro/nano hierarchical structure by coupling microfluidics and spray drying. Chem Eng J 2021;412:128613.
[111] Jiang H, Wang X, Yu J, et al. Size, morphology and crystallinity control strategy of ultrafine HMX by microfluidic platform. Nanomaterials 2023;13:464.
[112] Yang M, Gao Y, Liu Y, et al. Integration of microfluidic systems with external fields for multiphase process intensification. Chem Eng Sci 2021;234:116450.
[113] Han R, Chen J, Zhang F, et al. Fabrication of microspherical Hexanitrostilbene (HNS) with droplet microfluidic technology. Powder Technol 2021;379:184–90.
[114] Zhou J, Wu B, Wang M, et al. Accurate and efficient droplet microfluidic strategy for controlling the morphology of energetic microspheres. J Energetic Mater 2023;41:411–28.
[115] Wu B, Zhou J, Guo Y, et al. Preparation of HMX/TATB spherical composite explosive by droplet microfluidic technology. Defence Technology 2023;21:62–72.
[116] Yang L, Shi X, Li C, et al. Microfluidic assisted 90% loading CL-20 spherical particles: enhancing self-sustaining combustion performance. Defence Technology 2023;22:176–84.
[117] Zhou J, Wu B, Zhu R, et al. High-quality and homogeneous HMX-based aluminized explosives using droplet microfluidic technology. Energetic Materials Frontiers 2022;3:219–25.
[118] Zhang D, Shi J, Wu B, et al. Using microfluidic technology to prepare octogen high-energy microspheres containing copper–aluminum composite particles with enhanced combustion performance. Mater Des 2023;229:111874.
[119] Xue K, Li H, Pan L, et al. Preparation and performance characterization of functionalized boron-based energetic-microcapsules with uniform size. Chem Eng J 2023;469:143917.
[120] Cheng YZ, Wan Q, Ren H, et al. Preparation and characterization of nAl@PVDF@CL-20 composite energetic particles assembled via microfluidic method. Chin J Energetic Mater 2022;30(4):341–8.
[121] Liu HM, Li ZQ, Wang YJ, et al. Preparation and characterization of spherical propellant by microfluidic technology. Chin J Energetic Mater 2017;25(9):717–21.
[122] Liu Y, Guo Y, Zhu R, et al. Crystal phase control and ignition properties of HNS/CL-20 composite microspheres prepared by microfluidics combined with emulsification techniques. Particuology 2024;85:241–51.
[123] Zhou X, Zhu P, Shi J, et al. Self-assembly assisted by microdroplet templates confinement for the preparation of ultramixed composite energetic particulates. Chem Eng J 2023;454:140204.
[124] Zhou N, Zhu P, Rong Y, et al. Microfluidic synthesis of size-controlled and morphologically homogeneous lead trinitroresorcinate produced by segmented flow. Propellants, Explos Pyrotech 2016;41:899–905.
[125] Li L, Ling H, Tao J, et al. Microchannel-confined crystallization: shape-controlled continuous preparation of a high-quality CL-20/HMX cocrystal. CrystEngComm 2022;24:1523–8.
[126] Ma Z, Pang A, Li W, et al. Preparation and characterization of ultra-fine ammonium perchlorate crystals using a microfluidic system combined with ultrasonication. Chem Eng J 2021;405:126516.
[127] Zhou X, Chen C, Zhu P, et al. Microreaction system combining chaotic micromixing with fast mixing and particle growth in liquid-segmented flow for the synthesis of hazardous ionic materials. Energetic Materials Frontiers 2020;1:186–94.
[128] Wang JY, Huang H, Dong J, et al. Study on morphology control of submicron HNS explosive. Chin J Energetic Mater 2009;17:190–3.

[129] Duan X, Wei C, Liu Y, et al. A molecular dynamics simulation of solvent effects on the crystal morphology of HMX. J Hazard Mater 2010;174:175–80.
[130] Yang Z, Jin S, Zhang C, et al. Microfluidics-assisted synthesis of hydrogel microparticles with acoustic-magnetic control. Chem Eng Sci 2023;281:119082.
[131] Qin X, Wei X, Li L, et al. Acoustic valves in microfluidic channels for droplet manipulation. Lab Chip 2021;21:3165–73.
[132] Jin S, Ye G, Cao N, et al. Acoustics-controlled microdroplet and microbubble fusion and its application in the synthesis of hydrogel microspheres. Langmuir 2022;38:12602–9.