Controllable fabrication of binder-free co-crystal microspheres of CL-20 and TNT using 3D coaxial microfluidics

Lianpei Li, Haocheng Li, Zheng Li, Rui Qu, Ruiheng Xie, Ping Ye, Wei Ji*, Changping Guo*

Sichuan Co-Innovation Center for New Energetic Materials, Southwest University of Science and Technology, Mianyang, 621010, China

**Corresponding Author*

E-mail address : guochangping001@163.com

Phone number：+86-15181632394

1. Experimental section

1.1 Formulations of samples

The CL-20 /TNT co-crystal was prepared using the rotary oscillation method.

CL-20 and TNT with a molar mass ratio of 1:1 were dissolved in 2 mL of ethyl acetate, and 10 mL of deionized water containing 2 % SDS was added to form a stable oil-in-water emulsion by the rotary oscillation method. The stable emulsion was uniformly poured into 1000 mL of deionized water containing 1% SDS, and then allowed to wait for the white particles to precipitate from the collection beaker. The sample, after filtration, washing, and drying, was recorded as Osc.

CL-20 / TNT physical mixing

CL-20 and TNT with a molar mass ratio of 1:1 were mixed, and an ethanol solvent was added. The mixture was then ground in a mortar and pestle. The ethanol was then allowed to volatilize to obtain the Mix.

1.2 Statistical calculation and test record of impact sensitivity

Statistical calculation of characteristic drop height

The logarithmic value of the falling height of the characteristic is calculated by formula (1):

$$H_{50} = H_0 + \left(\frac{A}{n} \pm \frac{1}{2}\right)d$$

Where: H_{50}-characteristic drop high, said to two decimals ;

H_0-the falling height when the stimulus sequence number is ' 0' ;

A-calculating factor, calculated according to Equation (2) ;

In the n-effective (up and down) test, the total number of explosions or non-explosions is taken from the small side of the molecule. If the number of explosions is significant, no

The number of explosions, conversely;

' ± ' - When n is calculated by the sum of ni1, take ' - ' ; when n is calculated by the sum of ni0, take ' + ' ;

d-step (logarithmic value).

The calculation factor is calculated according to Equation (2) :

$$A = \sum_i in_i$$

Where: A - Identical (1):

i-stimulus number, i = 0, ± 1, ± 2, ± 3,..., where ' 0 ' is the stimulus serial number that makes Y_0 median or near median. The serial number of stimulus larger than Y_0 is set to 1, 2, 3..., the number of thorns smaller than Y_0, set to-1, -2, -3,... ;

If the sum of n_{i1} is greater than n_{i0}, then n_i is the sum of n_{i0}. If the sum of ni1 is less than n_{i0}, n_i is the sum of n_{i1} ;

The test process data are recorded as follows (Note: Explosion is 1, non-explosion is 0) :

Table S1

The impact sensitivity test process of Mic

Mic	Test No.																								
Drop height (cm)	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25
47					1		1						1												
45		1		0		0		1				0		1		1								1	
43	0		0						1		0				0		1				1		0		0
41										0								1		0		0			
39																			0						

Table S2

The impact sensitivity test process of Osc

Osc	Test No.																								
Drop height (cm)	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25
41																									

39												1		1											
37	1		1								0		0		1		1						1		
35		0		1						0						0		0		1		0		1	
33					1		1		0										0		0				0
31						0		0																	

Table S3

The impact sensitivity test process of Mix

Mix	Test No.																								
Drop height (cm)	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25
22																	1								
20				1		1								1		0		1				1		1	
18	1		0		0		1		1				0		0				1		0		0		0
16		0						0		1		0								0					
14											0														

1.3 Statistical calculation and test record of friction sensitivity

Explosion probability and statistical calculation formula (3) calculation :

$$P = \frac{X}{25}$$

where : P - explosion probability ;

The number of explosions in the X-25 test.

The explosion probability of each test group is calculated using this method.

The test process data are recorded as follows (Note: Explosion is 1, non-explosion is 0) :

Table S4

The friction sensitivity test process of Mic

Mic	Test No.																								
	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25
Set 1	1	0	1	0	0	1	0	1	0	1	1	1	0	0	1	0	0	1	0	0	1	0	0	0	0
Set 2	0	1	1	0	1	0	0	1	1	1	0	0	0	1	0	0	1	0	1	0	1	1	0	0	1

Table S5

The friction sensitivity test process of Osc

Osc	Test No.																								
	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25
Set 1	0	1	1	0	0	1	0	1	0	1	0	1	0	1	1	0	1	1	0	0	1	0	1	1	0
Set 2	1	1	1	0	1	0	0	1	0	1	0	1	0	1	0	0	1	0	0	0	1	1	1	1	0

Table S6

The friction sensitivity test process of Mix

Mix	Test No.																								
	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25
Set 1	1	0	1	1	1	1	0	1	1	1	0	1	1	1	1	1	1	1	1	1	1	1	1	1	1
Set 2	1	1	0	1	1	0	1	1	1	1	1	1	0	1	0	1	1	1	1	0	1	1	1	1	1

1.4 Calculation of activation energy and kinetic parameters

According to the classical Kissinger equation (4) [6, 7], there is a linear relationship between $\ln(\beta/T_p^2)$ and $1/T_p$, and the kinetic parameters of thermal decomposition can be calculated by obtaining the T_p values at different heating rates and equations (4) and (5). Further, the relevant thermodynamic parameters are calculated by using equations (6 - 8).

$$ln\frac{\beta}{T_p^2} = ln\frac{AR}{E_a} - \frac{E_a}{RT_p} \quad (4)$$

$$k = A \times exp\left(-\frac{E_a}{RT_p}\right) \quad (5)$$

$$A \times exp\left(-\frac{E_a}{RT_p}\right) = \frac{K_B T_p}{h} exp\left(-\frac{\Delta G}{RT_p}\right) \quad (6)$$

$$\Delta H = E_a - RT_p \quad (7)$$

$$\Delta G = \Delta H - T_p \Delta S \quad (8)$$

where β is the heating rate (K/min), T_p is the thermal decomposition peak temperature (K), A is the pre-exponential factor, R is the ideal gas constant (8.314 $J \cdot mol^{-1} \cdot K^{-1}$), E_a is the activation

energy (J/mol), k is the reaction rate constant (s^{-1}), K_B is the Boltzmann constant (1.381×10^{-23} J/K), h is the Planck constant (6.626×10^{-34} J/s). ΔH is the activation enthalpy (J/mol), ΔG is the activation Gibbs free energies (J/mol), and ΔS is the activation entropy (J/mol).

Table S7

Calculation results of activation energy and kinetic parameters

		Thermodynamics			Kinetics		
Samples	T_p (K)	ΔH (kJ/mol)	ΔG (kJ/mol)	ΔS(J/mol·K)	E_a (kJ/mol)	lnA	k
CL-20	520.05	202.3	113.5	170.8	206.6	40.8	24.9
TNT	521.15	45.7	119.7	-142.1	50.0	3.2	6.0
Mix	518.15	193.6	113.2	155.2	198.0	38.8	23.8
Osc	524.85	172.9	115.2	110.0	177.3	33.4	21.3
Mic	524.85	161.2	115.5	87.1	165.5	30.7	19.9

2. Results and discussion

In this study, three key parameters of microfluidic preparation conditions were systematically investigated: the concentration of explosive solution, the ratio of phase flow rate, and the type of surfactant. Specifically, in the explosive concentration experiment, 0.45 g, 0.90 g, and 1.20 g of CL-20 and TNT were dissolved in 10 mL of ethyl acetate, respectively. The molar mass ratio of the two explosives was maintained at 1:1, and the corresponding samples were labeled as Mic-Q1, Mic-Q2, and Mic-Q3, respectively. In the flow rate ratio experiment, the shear/mixing effect was investigated by adjusting the volume flow rate ratio of the continuous phase to the dispersed phase to 1:10, 1:20, and 1:30, while maintaining a constant overall flow rate. The related samples were labeled as Mic-V1, Mic-V2, and Mic-V3. In the aspect of surfactant screening, three commonly used surfactants —Tween-80, sodium dodecyl

sulfate, and Span-80 —were selected, and the corresponding samples were designated as Mic-S1, Mic-S2, and Mic-S3, respectively.

2.1 Morphology of CL-20/TNT co-crystals prepared under different microfluidic conditions

Systematic comparison based on optical microscopy and SEM. Under the concentration condition: Q1 (low concentration), the number of particles is small, the particle size span is large, and the irregular/dendritic sample and the massive particles coexist under the microscope; sEM showed that the surface was rough, the anisotropy was apparent, and there were local agglomerations. Q2 (medium concentration): the field of view is dominated by regular spheres, and the particle size distribution is significantly narrowed; sEM showed dense, continuous surface, high roundness, and little adhesion. Q3 (high concentration) : small particles and aggregates increased, ' satellite ' particles, series or wrinkled surfaces appeared ; cladding / multi-core clusters can be seen in SEM. The medium solute level achieves a balance between ' nucleation-growth ', which is conducive to the formation of mononuclear, uniform growth of dense spheres; if too low, it is easy to grow and produce dendrites. If too high, the secondary nucleation is frequent, and the dripping and agglomeration are intensified. The ionic interface stability and higher HLB value of SDS are more conducive to reducing interfacial tension and providing electrostatic repulsion, thereby inhibiting coalescence and flocculation. In contrast, the stability of non-ionic additives in this system is relatively insufficient, making it easy to produce bridging or flocs.

In summary, the optimum preparation conditions were as follows: 0.9 g of CL-20 and TNT were dissolved in 10 mL of ethyl acetate, with a flow rate ratio of 1:20, and sodium dodecyl sulfate was used.

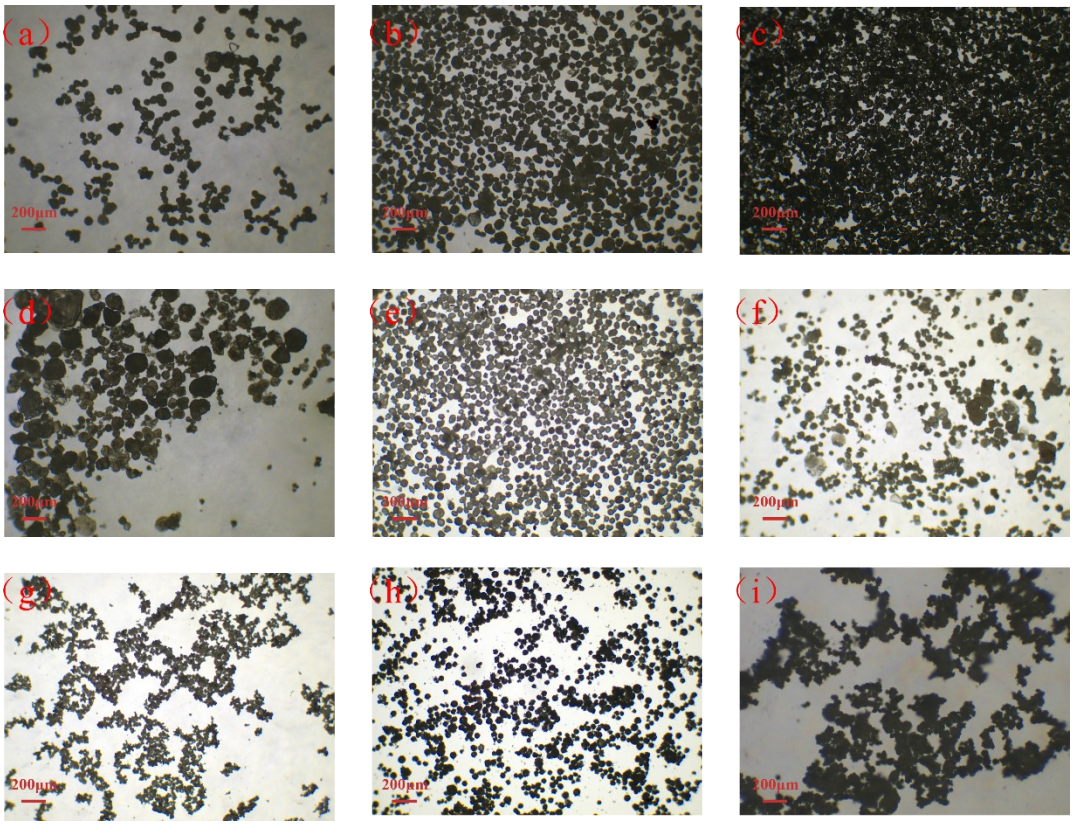

Fig. S1. Microscopic morphology under different preparation conditions : (a) Mic-Q1 ; (b) Mic-Q2 ; (c) Mic-Q3 ; (d) Mic-V1 ; (e) Mic-V2 ; (f) Mic-V3 ; (g) Mic-S1 ; (h) Mic-S2 ; (i) Mic-S3

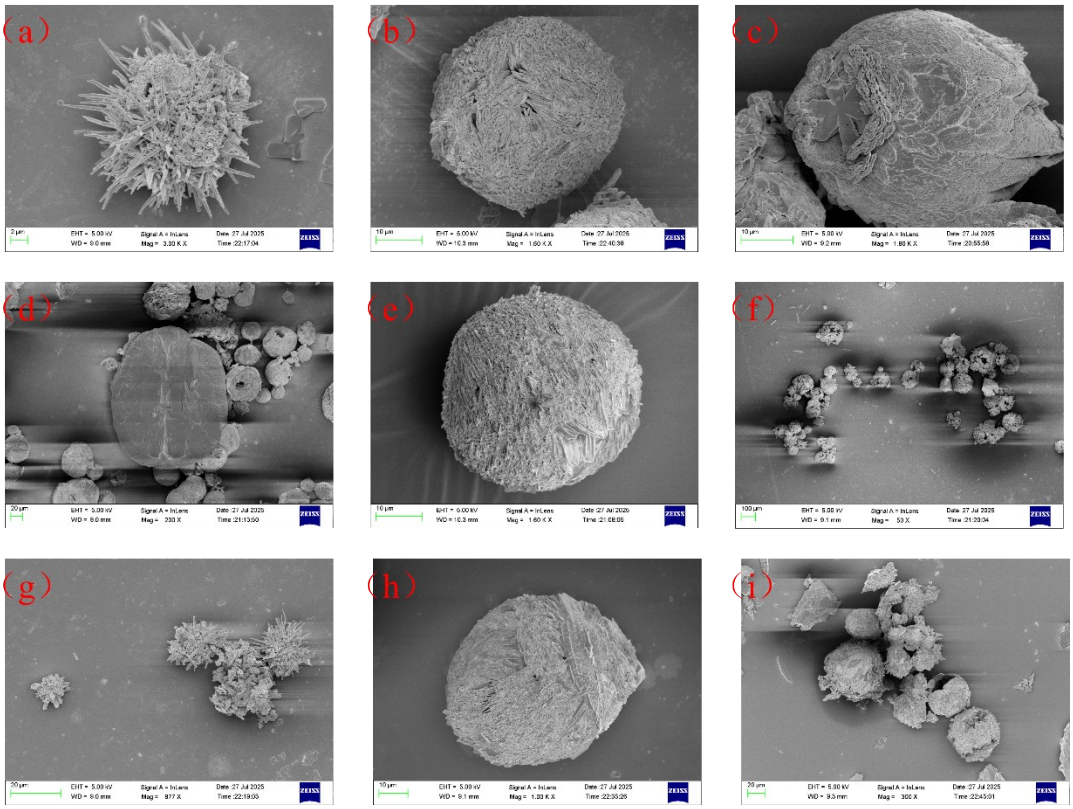

Fig. S2. SEM morphology under different preparation conditions : (a) Mic-Q1 ; (b) Mic-Q2 ; (c) Mic-Q3 ; (d) Mic-V1 ; (e) Mic-V2 ; (f) Mic-V3 ; (g) Mic-S1 ; (h) Mic-S2 ; (i) Mic-S3

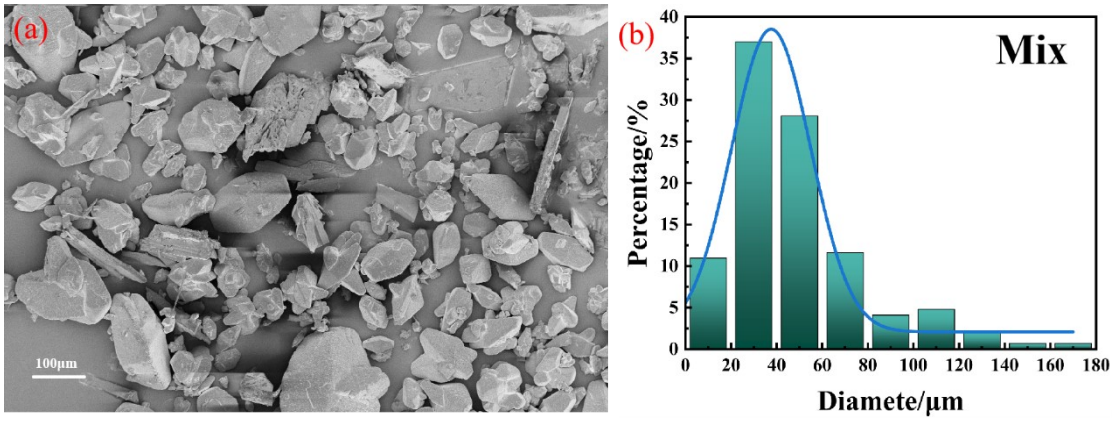

Fig. S3. Physically mixed electron microscopy and particle size distribution

2.2 The structure of CL-20/TNT co-crystals prepared under different microfluidic conditions

The diffraction peak positions of the nine samples are essentially the same, and their spectral types are consistent with each other. No new diffraction peaks or prominent missing peaks are observed, indicating that the different preparation conditions do not introduce new crystal phases or

phase transitions, and the crystal structure of the system remains unchanged. Nitro-related absorption bands appeared in the 1600 ~ 1500 cm^{-1} and 1350 ~ 1250 cm^{-1} regions of each sample, and the positions of characteristic peaks, such as aromatic/heterocyclic skeleton vibration, were consistent. No new functional group absorption or significant displacement was observed, indicating that no chemical reaction or change in molecular skeleton occurred. The chemical composition and molecular structure of the samples obtained by different processes were in good agreement.

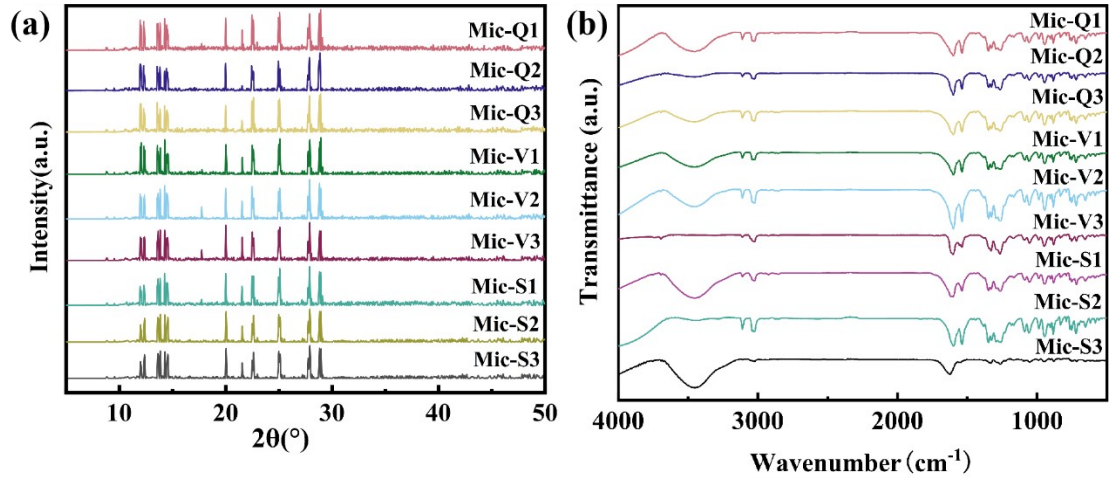

Fig. S4. Structural characterization under different preparation conditions : (a) XRD ; (b) FT-IR