RESEARCH ARTICLE

Fabrication of nitrocellulose-based nanoenergetic composites, study on its structure, thermal decomposition kinetics, mechanism, and sensitivity

Ling Chen1,# | Shishuo Liu2,# | Xinfu Cao3 | Jianbing Gao3 | Yingbo Wang1 | Yang Qin2 | Yang Zhang2 | Jianwei Zhang1 | Guorui Jin1 | Moru Wang1 | Jie Liu2 | Weidong He1

1 Key Laboratory of Special Energy Materials, Ministry of Education, Nanjing University of Science and Technology Jiangsu, Nanjing 210094, China
2 National Special Superfine Powder Engineering Research Center of China, Nanjing University of Science and Technology Jiangsu, Nanjing 210094, China
3 Inner Mongolia Synthetic Chemical and Engineering Institute, Huhhot 010010, China

Correspondence
Weidong He, Key Laboratory of Special Energy Materials, Ministry of Education, Nanjing University of Science and Technology, Jiangsu, Nanjing 210094, China. Email: hewedong@njust.edu.cn
Jie Liu, National Special Superfine Powder Engineering Research Center of China, Nanjing University of Science and Technology Jiangsu, Nanjing 210094, China. Email: Jie_Liu_njust@126.com

#Ling Chen and Shishuo Liu are the co-first author.

Funding information
National Natural Science Foundation of China, Grant/Award Number: 51606102

Abstract
In order to investigate the thermal decomposition kinetics and mechanism of nitrocellulose (NC) based nitramine explosives nanocomposite energetic materials, this work prepares NC/RDX (cyclotrimethylenetrinitramine), NC/HMX (cyclotetramethylenetetranitramine), and NC/CL-20 (hexanitrohexaazaisowurtzitane) composites by a combined sol-gel and the freeze-drying technology. The structure is systematically investigated and the results reveal that the explosive particles are dispersed, filled, or embedded homogenously in the gel matrix of NC, thereby restricting the crystal growth of RDX, HMX, CL-20 particles to coarse and achieving submicron/nanometer. The thermal analysis of composites exhibits much lower peak temperature compared with raw explosive crystal, furthermore, the activation energy (E_a) of composites is also lower than that of both NC and explosives. Hence, the unique structure of NC gel matrix embedded explosives inside demonstrated different mechanism of decomposition. Concretely, the rupture of the H-NCO = O bond in the cross-linked structure is detected firstly, subsequently, the macromolecular chains’ scission site of gel firstly occurs at -C-O-C- in the ring, and then the scission of -NO_2 (from NC or explosive crystals) bonds happened. Hence, this study may provide promising fabrication strategy and basic theory for the application of NC-based nanocomposite energetics in high-energy propellants and explosives.

KEYWORDS
mechanism, nanocomposite energetic materials, nitramine explosives, nitrocellulose, thermal decomposition

This is an open access article under the terms of the Creative Commons Attribution License, which permits use, distribution and reproduction in any medium, provided the original work is properly cited.

© 2021 The Authors. Nano Select published by Wiley-VCH GmbH
1 | INTRODUCTION

It is a well-known fact that energetic materials (EMs) can be categorized as propellants, explosives, and pyrotechnics by its specific compositions, performances, and application areas. Nitrocellulose (NC), a typical EMs that has been widely used as a main energy ingredient and an essential role of skeleton support in single-base propellants, double-base propellants, or tri-base propellants, because of its unique features, such as excellent mechanical strength, flammability, rapid drying rate, and compatibility with several stabilizers and plasticizer. In addition, the application fields of NC with different nitrogen content are also variant, for example, NC with nitrogen content of 10.7-12.3% is widely used in printing ink, varnishes, enamels, dyes, and adhesives; prepared by sol-gel technology. The sol-gel method presents promising advantages, including the chemically homogeneous precursor, the preponderance of low temperature preparation, easy control over the stoichiometry and homogeneity that conventional approaches lack.

As a result, this technology was adopted to fabricate abundant of nEMs with low-sensitivity and satisfactory dispersion. For example some inert matrix, SiO₂-matrix, RF (resorcinol-formaldehyde)-matrix, PU (polyurethane)-matrix, cellulose-matrix, and Fe₂O₃-matrix. In addition, previous works also prepared a series of energetic gel matrix, for instance NC-matrix, GAP (glycidyl azide polymer)-matrix, BAMO-THF (3, 3-Bis (azidomethyl) oxetanetetrahydrofuran copolymer)-matrix, and NBC (nitrated bacterial cellulose)-matrix nEMs which can not only reduce the sensitivity, but also maintain the energy performance of composites compared with that of inert matrix nEMs.

Herein, this study adopted NC as the matrix to prepared NC-matrix based nEMs by the sol-gel method and the freeze-drying technology. The composite of NC/RDX, NC/HMX, and NC/CL-20 exerted unique network cross-linked structure of NC gel matrix, in which the energetic crystals were embedded in it homogeneously. In addition, the sensitivity and reduction mechanism of composites were also illustrated and exhibited higher safety performance than that of energetic crystals. Hence, this research may provide basic theory for fabrication of energy binder matrix nEMs and broaden its thermal decomposition theory investigation in application propellants and explosives.

2 | RESULTS AND DISCUSSION

2.1 | Morphology and characterization

Figure 1 gives the photos of raw materials NC, RDX, HMX, and CL-20 with average particle size of about 200–500, 30, 50, and 150 μm, respectively. Compared with raw
materials, the as-prepared samples exhibited different particle size, morphology, and structure. In detail, the structure of composites can be categorized into inner imbedded in NC gel fiber (Figure 2A), filled in porous of NC gel (Figure 2C), and surface inlayed in (Figure 2E) with energetic crystals. It could be clearly seen that the particle size of composite was decreased to submicron/nanometer. It means that these nanometer energetic crystals were embedded or coated tightly on the surface of NC gel matrix, which enhanced the interfacial contact between them and possess potential to improve the thermal decomposition performance of composites. Generally, nanoscale particles always encounter agglomeration because of its large specific surface area and decreased the energy performance of explosive crystals. However, in this study, the uniform dispersion property of energetic crystal with particle size about 400–600 nm was improved visibly in Figure 2E,F. In addition, the morphology of HMX particles imbedded in the NC gel matrix was near spherical. As for the elements mapping images of the composites in Figure 3, the mainly elements were consisted of C, N, and O, which also dispersed homogenously on the surface of NC gel matrix. The main reason was attributed to the sol-gel method assisted with the freeze-drying technology, and ensured the dispersion uniformly of explosive crystals without agglomeration.

2.2 Structure and composition

The crystal structure and component state of raw materials and the composites prepared in this work were carried out with powdered XRD technique and XPS analyses as shown in Figure 4. The diffraction pattern of the NC is not noticeable because of its inherent amorphous structure. In terms of the characteristic diffraction peaks of composites NC/RDX, NC/HMX, and NC/CL-20 in Figure 4A, the typical diffraction peaks of explosives crystals still maintained well, nevertheless, the intensity of portion peaks reduced to some extent or the position shifted slightly. The main reason could be attributed to the existence of amorphous polymer NC, which may cover up or decrease partial peaks of energetic crystals. From another hand, the decreased particle size of explosive crystals to nanoscale may also decrease the intensity of peaks and broaden the width of diffraction peaks. Last but not the least, it is a well-known fact that the polymorphic crystal phase can transfer from one to another under certain conditions, especially for HMX and CL-20, which possess many kinds of crystal form (e.g., CL-20: α, β, γ, δ, ε; HMX: α, β, γ, σ). Fortunately, this study preserved the stable crystal structure of β-HMX and ε-CL-20 during the process of fabrication triumphantly. In detail, during the process of “sol” transforming to “gel,” the cross-link structure can prevent the flow of solutions, and the solvent
was hindered to evaporate due to the sealing of the aging procedure. Finally, the explosive particles are formed by crystallization along with the evaporation of acetone under the low temperature of vacuum freeze-drying technology instead of transformation of crystal structure. As a result, the crystal structure of energetic crystals was preserved.

In Figure 4, the high-resolution XPS spectra of C 1s N 1s and O 1s spectra for NC/CL-20 composite was shown. Typically, the high-resolution C 1s spectrum (Figure 4B) can be resolved into four overlapped peaks located at 284.6, 285.4, 287.3, and 288.7 eV, which correspond to the groups of C-C and C-H, C-N, C-O, and C = O, respectively. While the O 1s spectrum showed typical components with binding energy located at 533.9 (C = O), 534 (C-O-C, C-OH), and 534.8 (-NO2) eV. In consideration of the high-resolution N 1s, which could be divided into two peaks at 401.5 (-NO2) and 407.2 (-C-N) eV. Hence, the results demonstrated the existence of CL-20 particles which are embedded on the surface of NC gel matrix.

The FT-IR and Raman spectroscopy were illustrated in Figure 5 to characterize the vibration peaks of the functional groups in the composites. As displayed in Figure 5A, the peaks located at 3098 cm⁻¹ was corresponding to the absorptions peak of -CH₂- and ν C-H. While the FT-IR spectra peaks at 1667 and 1263 cm⁻¹ were related to the -NO₂ asymmetry stretching vibrations and -NO₂ symmetry stretching vibrations from NC and explosive crystals.

Table 1 and Table 2. It could be clearly seen that both the raw materials and composites presented only one exothermic peak, which indicated that the components of explosive crystals and NC gel were combined well and just as described in SEM characterization. The peak temperature

2.3 | Thermal analysis

The DSC-TG analysis was carried out to study the thermal decomposition of raw materials and as-prepared composites at different heating rates of 5, 10, and 15 °C·min⁻¹ in the temperature range of 100–400°C, as shown in Figure 6 and Figure 7, and the parameters are enumerated in Table 1 and Table 2. It could be clearly seen that both the raw materials and composites presented only one exothermic peak, which indicated that the components of explosive crystals and NC gel were combined well and just as described in SEM characterization. The peak temperature
FIGURE 4  The X-ray powder diffraction spectra of raw materials and composites (A) and the high-resolution XPS spectra of C 1s (B), N 1s (C), and O 1s (D) regions for NC/CL-20

FIGURE 5  FT-IR (A) and Raman (B) spectrum of raw materials and the as-prepared samples
FIGURE 6  DSC-TG curves of raw NC (A), RDX (B), HMX (C), and CL-20 (D) at different heating rate 5, 10, and 15 °C-min⁻¹.
of composites was also decreased visibly compared with raw energetic crystals, which manifested that the process of thermal decomposition was mainly controlled by NC gel matrix. As for the decomposition temperature of TG curves, it was almost in accord with peak temperature of DSC analysis, that is, both of them were increasing with the heating rate increasing. Besides, the melting endothermic peak appeared in the DSC curves of raw RDX, HMX, and CL-20, it was disappeared in the composites. The reason could be attributed to the earlier decomposition of NC gel matrix, and the heat-release of NC was not enough to provide the energy or heat to melt the energetic crystal. In addition, the weight loss of composites is slightly lower than that of raw materials, this was on account of the...
FIGURE 8  Linear fit of plotted $\ln(\beta/T_p^2)$ against $1/T_p$ for the calculation of activation energy ($E_a$), (A) raw NC, RDX, HMX, CL-20 and (B) NC/RDX, (C) NC/HMX, and (D) NC/CL-20

existence of TDI, which was cross-linked with -OH from NC gel, or there may be still little of curing agent has not been got out rid of entirely. Notably, the DSC curves of NC/CL-20 presented abundant of heat-release, however, that of the NC/RDX and NC/HMX was not evident, this was because the unique structure of gel matrix in which some of explosives were trapped inside and would not decomposition entirely. Therefore, the further investigation on the mechanism of decomposition is urgent to be done and illustrated about this phenomenon, which was discussed in the section of TG-IR analysis.

In order to further investigate thermal properties of the composites, the thermal decomposition of kinetics was calculated by Kissinger formula (1): in which the $E_a$ is the apparent activation energy, $A_K$ is the frequency factor, $T$ is the absolute temperature, $\beta$ is the heating rate, $R$ is the gas constant, $T_p$ is the peak temperature. As shown in Figure 8, it can be clearly seen that the $E_a$ of raw materials (NC: 219.6 J·g⁻¹; RDX: 275.5; HMX: 265.9; CL-20; 219.8 J·g⁻¹) was much larger than that of the composites (<208 J·g⁻¹). The main reason could be explained from two aspects, on one hand, the reduced particle size of NC and energetic crystals with larger specific surface, which may be easier to be activated than micron scale of raw materials. On the other hand, the network cross-linked structure of NC gel matrix in which the energetic crystals were embedded tightly in the gel matrix, which mean that the transfer distance of heat and mass between NC gel matrix and explosives was shortened, and result in enhanced of interfacial contact. Finally, the $E_a$ of the composites was reduced with lower $A_K$. Hence, this study exerted the superior thermal decomposition performance of composites by sol-gel and freeze-drying technology.

\[
\ln \frac{\beta}{T_p^2} = \ln \frac{R \times A_K}{E_K} - \frac{E_K}{R} \times \frac{1}{T_p}
\]  

(1)

For the sake of disclosing the thermal decomposition mechanism of the composites, TG-IR analysis was performed to study the gas products of decomposition.
In Figure 9. In theory, the decomposition mechanism of those composites should almost the same with each other benefit from its similar compositions with NC and energetic crystals. The decomposition temperature of TG curves for three composites were keeping in with that of DSC curves in Figure 7. By means of analyzing the IR spectra in Figure 9B-D, the main gas products were identified to be HCN, N₂O, NO₂, CH₂O, CH₄, CO₂, and H₂O. To be specific, the strong peaks located at 2260–2386 cm⁻¹ was related to the existence of a large amount of CO₂ gas, while the obvious absorption peaks in 2165–2250 cm⁻¹ was corresponding to the appearance of the N₂O and NO₂ gas. The peaks in 1680–1820 cm⁻¹ was accounted for the fragment of CH₂O. Notably, the visibly peak at 668 cm⁻¹ reflects the existence of HCN from the rupture of the H-NCO = O bond in the cross-linked structure, which also proved the happened of cross-linked reaction between -OH and -NCO. In addition, abundant of CO₂ rather than CO indicated the moderate oxygen balance of composites. On the whole, it could be found that, with the lapse of time, signal of HCN was detected firstly; meanwhile, signals of CH₂O and C-O-C were also detected. These products should result from pyrolysis of NC skeleton and cross-linked structure because of which is easier to decompose than nitramine explosive crystals. Subsequently, RDX, HMX and CL-20 also decomposed, respectively, thereby the N₂O or NO₂ were probed from the split radical of -NO₂ (from N-NO₂ or O-NO₂) decayed to at elevated temperature. Therefore, this result demonstrated that the unique porous network of NC gel matrix in which the energetic crystals imbedded in granted the composites outstanding thermal decomposition performance, and benefited from the shorter transfer distance of heat and mass and enhanced interfacial contact.

2.4 Sensitivity test

So as to probe safety property of the composites, the impact and frication sensitivities were tested as described in
Figure 10. It could be clearly seen that the sensitivity of the composites was reduced greatly compared with the raw energetic crystals. Generally, the explosion of EMs is mainly caused by the formation of hot spots, which are always experienced some extrinsic stimulations and go through three processes generation, growth, and spreading. In addition, the happen of explosion is also influenced by the temperature of hot spot. Consequently, to reduce the occurrence possibility of hot spot or decrease the critical temperature of hot spots to happen may be the effective way to prevent the explosion caused by hot spots. In this study, the composites were prepared by sol-gel and freeze-drying technology, wherein the recrystallization process of energetic crystals under the condition of freeze-drying, which would not only reduce the impurities and cracks to ensure the safety process of fabrication, but also could improve the crystal morphology, decrease the particle size of explosives and improve the dispersion uniformly significantly. Furthermore, the unique 3D porous network of gel matrix (Figure 2B) could promote the diffusion of critical temperature and finally reduce the probability formation of the hot spots. In other words, the 3D porous cross-linked network structure of NC gel matrix trapping the explosives inside, when suffers some stimulations form surroundings, it could act as a buffer system to release the energy and would be firstly attacked to dissipate the external stimulation into external environment or reduce the temperature of part formed hot spots. Hence, the sensitivities of impact and friction were reduced benefiting from the smaller size, the larger surface areas and regular morphology of energetic crystals, and the special structure of the composites.

3 | CONCLUSION

In summary, this research prepared a series of NC-based nanocomposite energetic materials by combining sol-gel and the freeze-drying technology, wherein the explosive crystals were dispersed homogeneously trapped, coated, or embedded in the unique network structure of NC gel matrix. The dispersion property and crystal structure of nanoscale energetic crystals were improved and maintained well. In addition, the thermal decomposition properties were also probed and presented a low peak temperature, kinetics with low $E_a$ and mechanism of decomposition. Besides, the sensitivity of the composites was enhanced distinctly owning to the reduced particle size and the existence of NC gel matrix. Accordingly, this fabrication strategy, property and mechanism of the composites in this study, may provide basic theory for promising application of NC-based nanocomposite energetic materials in propellants and explosives.

4 | EXPERIMENTAL

4.1 | Materials

NC, (12.6 % nitrogen) were supplied by Luzhou North Chemical Industry Co., Ltd. The RDX (purity,99%), HMX (purity,98%), and CL-20 (purity,99%) crystals with an average particle size of 30, 50, and 100 µm were obtained from Liaoning Qing yang Chemical Co., Ltd. and used as received. Acetone, $\gamma$-butyrolactone, toluene diisocyanate (TDI), Ditinbutyl dilaurate (DBTDL), and
triethylenediamine (TEDA) were purchased from Shanghai Aladdin Biochemical Technology Co., Ltd.

### 4.2 Sample preparation

Figure 11 illustrated the preparation process of cross-linked structure of NC-based gel matrix energetic composites by sol-gel and the freeze-drying technology. The typical synthesize strategy of composites are followed in previous work:[36] firstly, a half gram of NC was dissolved in 10 mL acetone to obtain homogeneously solutions. Then the one times quality of explosives (RDX, HMX, CL-20) than NC was dissolved into the NC solutions, respectively. After that, the volume ratio of 2:1 (TDI: DBTDL), and 0.005 g of TEDA were tardily added into above mentioned solutions with magnetic stirring for 15 min until the system became homogenous, we called “sol.” Then the sols were sealed and placed in an oven (45 °C) for gelation and aging to form “gel.” Finally, the gel was dried by vacuum freeze-drying technology. The dry condition is controlled precisely with an extremely low temperature and vacuum (at -76 °C and 10⁻³ mbar) to ensure the operation safety. The samples were named as NC/RDX, NC/HMX, and NC/CL-20.

### 4.3 Characterization

The morphology of cross-linked structure was observed through a field-emission scanning electron microscope (FESEM, FEI400, Hitachi Co., Ltd. Japan). X-ray diffraction (XRD, Bruker D8-Advanced, Germany), Fourier-transform infrared (FT-IR), and Raman (Renishaw inVia microscopic confocal) were performed to characterize the structure of composites. Differential scanning calorimeter-thermogravimetric analysis (DSC-TG, TA Instruments SDT 600) was carried out to analysis the thermal properties of composites. In addition, the TG-FTIR (STA449 F5 Jupiter, Nicolet is 50) was employed to investigate the gas products of the decomposition process with temperature ranges from 100 to 400°C. The impact sensitivity was tested by GJB772A-97 with an HGZ-3 drop hammer and the testing conditions were as follows: the drop weight of 5.000 ± 0.002 kg, sample mass of 35 ± 1 mg, room temperature of 24 °C, and relative humidity of 30% and 25 samples were tested. The results were shown in terms of special height)\(H_{50}\) (standing for the drop height of 50 % explosion probability. Friction sensitivity of the samples was tested with the HGM-3 friction instruments, wherein 50 samples were tested and an explosion probability \((P, \%)\) was obtained in each determination.

### ACKNOWLEDGMENTS

Ling Chen, Shishuo Liu are co-first authors of this paper. This research did not receive any specific grant from funding agencies in the commercial or not-for-profit sectors. This research was financially supported by the National Natural Science Foundation of China (Grant No. 51606102).

### CONFLICTS OF INTEREST

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

### DATA AVAILABILITY STATEMENT

Research data are not shared.

### ORCID

Weidong He https://orcid.org/0000-0003-3540-1974
REFERENCES

1. X. Zhou, M. Torabi, J. Lu, R. Shen, K. Zhang, ACS Appl. Mater. Interfaces. 2014, 6, 3058.
2. B.F.d.S. Defanti, L.G.d. Mendonça-Filho, J. Nicolele, Combust. Flame. 2020, 221, 212.
3. G. Li, B. Jin, Z. Chai, L. Liao, S. Chu, R. Peng, Polym. Test. 2020, 86, 106493.
4. X. Meng, C. Pu, P. Cui, Z. Xiao, Propellants, Explos., Pyrotech. 2020, 45, 1194.
5. X. Zhang, K.S. Ziemen, K. Zhang, D. Ramirez, L. Li, S. Wang, L.J. Hope-Weeks, B.L. Weeks, ACS Appl. Mater. Interfaces. 2014, 6, 3058.
6. B.F.d.S. Defanti, L.G.d. Mendonça-Filho, J. Nichele, Combust. Flame. 2020, 221, 212.
7. G. Li, B. Jin, Z. Chai, L. Liao, S. Chu, R. Peng, Polym. Test. 2020, 86, 106493.
8. X. Meng, C. Pu, P. Cui, Z. Xiao, Propellants, Explos., Pyrotech. 2020, 45, 1194.
9. X. Zhang, K.S. Ziemen, K. Zhang, D. Ramirez, L. Li, S. Wang, L.J. Hope-Weeks, B.L. Weeks, ACS Appl. Mater. Interfaces. 2014, 6, 3058.
10. B.F.d.S. Defanti, L.G.d. Mendonça-Filho, J. Nichele, Combust. Flame. 2020, 221, 212.
11. G. Li, B. Jin, Z. Chai, L. Liao, S. Chu, R. Peng, Polym. Test. 2020, 86, 106493.
12. X. Meng, C. Pu, P. Cui, Z. Xiao, Propellants, Explos., Pyrotech. 2020, 45, 1194.
13. X. Zhang, K.S. Ziemen, K. Zhang, D. Ramirez, L. Li, S. Wang, L.J. Hope-Weeks, B.L. Weeks, ACS Appl. Mater. Interfaces. 2014, 6, 3058.
14. B.F.d.S. Defanti, L.G.d. Mendonça-Filho, J. Nichele, Combust. Flame. 2020, 221, 212.
15. G. Li, B. Jin, Z. Chai, L. Liao, S. Chu, R. Peng, Polym. Test. 2020, 86, 106493.
16. X. Meng, C. Pu, P. Cui, Z. Xiao, Propellants, Explos., Pyrotech. 2020, 45, 1194.
17. X. Zhang, K.S. Ziemen, K. Zhang, D. Ramirez, L. Li, S. Wang, L.J. Hope-Weeks, B.L. Weeks, ACS Appl. Mater. Interfaces. 2014, 6, 3058.
18. B.F.d.S. Defanti, L.G.d. Mendonça-Filho, J. Nichele, Combust. Flame. 2020, 221, 212.
19. G. Li, B. Jin, Z. Chai, L. Liao, S. Chu, R. Peng, Polym. Test. 2020, 86, 106493.
20. X. Zhang, B.L. Weeks, J. Therm. Anal. Calorim. 2015, 122, 1061.
21. X. Zhang, B.L. Weeks, J. Am. Chem. Soc. 2014, 136, 1253.