Safe Fabrication, Thermal Decomposition Kinetics, and Mechanism of Nanoenergetic Composite NBC/CL-20

Ling Chen, Weidong He,* and Jie Liu*

ABSTRACT: Benefiting from the sol–gel technology and vacuum freeze-drying technology, a novel nanoenergetic composite material nitrated bacterial cellulose (NBC)/CL-20 (hexanitrohexaazaisowurtzitane) has been fabricated. The thermal decomposition kinetic and mechanism have been studied by thermogravimetric analysis–differential scanning calorimetry (TG–DSC) under nonisothermal conditions in a nitrogen atmosphere at multiple heating rates; the process and mechanism of thermal decomposition of NBC/CL-20 have also been probed by TG–DSC–IR. The kinetic and thermodynamic parameters, such as activation energy ($E_a$), per-exponent factor (ln $A_k$), rate constant ($k$), activation heat ($\Delta H^+$), activation free energy ($\Delta G^*$), and activation entropy ($\Delta S^*$) are calculated. The results indicate that NBC/CL-20 presents much lower activation energy than both of raw NBC and raw NC, and NBC/CL-20 exhibits superior thermal performance of heat release and $E_a$. Moreover, there have beenprobe between NBC and CL-20 during the process of thermal decomposition. The structure and composition have been characterized by a series of characterization methods and indicate that CL-20 has been embedded homogeneously in the NBC gel matrix with a prominent porous cross-linked network structure. The impact and friction sensitivities have also been decreased. The whole process effectively avoids high temperatures, and thus ensures operational safety.

1. INTRODUCTION

Currently, the pursuit of high-energy and low-sensitivity propellants to achieve remote suppression, precision strike, and efficient destructive effect are one of the most essential development directions of contemporary weapon systems. Propellants can be typically classified into gun propellants and solid rocket propellants by their work principles and application areas. In order to improve its energy performance to achieve a higher destructive effect, the main approach is through the addition of a high-energy solid explosive. CL-20 (hexanitrohexaazaisowurtzitane) is one of the most attractive high energy density compounds with promising applications in the fields of propellants and explosives. It is expected to improve the specific impulse, detonation pressure, and detonation velocity properties of munitions owing to its unique highly strained molecular cage structure. Nevertheless, the high energy level explosive is often accompanied with poor sensitivities, such as impact, friction, and electrostatic spark, which have greatly hindered the applications of CL-20 in modern military systems. Hence, there is an urgent need of finding novel materials or appropriate methods to not only reduce the sensitivities but also maintain the high energy performance of explosives.

Satisfactorily, the emergence of nanoenergetic materials has attracted remarkable interests of many researchers at home and abroad, attributing to its larger specific surface, shorter transfer distance of heat and mass, and closer contact between solid particles in a mixture. Such as nano-RDX, nano-HMX, nano-CL-20, and nano-NC are prepared and exhibit excellent sensitivities, including mechanical properties, thermal properties, and so on. Up till now, there have been many fabrication methods reported to prepare nanoenergetics, including sol–gel method, mechanical grinding method, freeze evaporation method, electrostatic spraying method, and physical vapor deposition method. Unfortunately, the nanoexplosive particles are easily agglomerated to units, which can not only bring down the energy performance but also encounter the processing technology problems of CL-20 used in propellants and explosives. While, another kind of nanoenergetics, nanoenergetic composite materials (nEMs), has exhibited superior energy density, uniform dispersion, heat release, reactivity, and combustion performance during the
recent years compared with single nanoenergetics. Hence, among the many kinds of fabrication approaches developed so far, the sol–gel technology exhibits outstanding advantages of low-temperature preparation and easy control over the stoichiometry and homogeneity to synthesize nEMs. For example, NC (nitrocellulose)-matrix,23 Fe3O4-matrix,24 SiO2-matrix,25 and RF (resorcinol formaldehyde)-matrix26 nEMs. All those nEMs have presented a prominent thermal property and safety performance with an interpenetrating cross-linked structure. Especially, Wang et al.27 have prepared the nEMs of HMX/NC by sol–gel and proved that the activation energy of HMX/NC (165.03 kJ/mol) is much lower than that of raw HMX (282.50 kJ/mol) and NC (175.51 kJ/mol); Tappan and Brill28 have prepared NC/CL-20, and the thermal decomposition temperature has been increased and the impact sensitivity has also been decreased. Hence, choosing an appropriate binder matrix plays an essential role in preparing nEMs, which are promising to be applied into propellants with a higher energy density, higher detonation, faster rate of reaction, and higher safety performance.

Nitrated bacterial cellulose (NBC), an original energetic binder has been applied to enhance the mechanical performance and safety property of propellants,29 benefiting from its unique network structure and higher purity compared with a traditional binder nitrocellulose (NC).29 It is first synthesized by Sun et al.30 and Yang et al.31 from the bacterial cellulose which possess a unique network structure. Hence, adopting NBC as an energetic binder matrix to prepare nEMs instead of an inert matrix or partial NC can not only improve the energy and safety performance but also can prevent agglomerate of nanoexplosive particles. Moreover, no relevant literature has been reported on the study of NBC matrix nEMs at present. It is well known that the thermal performance and sensitivity of energetics were influenced greatly by the structure and dimension.32 Therefore, preparing energetic binder NBC-based matrix nanostructured energetic composites and studying its thermal decomposition kinetics can provide base theory.
effectively and are hopeful to be used and improve energy performance, heat release, reactivity, combustion performance, and detonation property of propellants.

This research has fabricated NBC/CL-20 by combining sol–gel technology and freeze-drying technology together, in which the CL-20 particles are embedded uniformly in the porous network gel matrix of NBC. The thermal decomposition kinetics and the decomposition mechanism of NBC/CL-20 are investigated and the sensitivity (impact, friction) has also been tested, which can provide remarkable basic theoretical research for the application of nEMs NBC/CL-20 in gun/rocket propellants.

2. RESULTS AND DISCUSSION

2.1. Morphology Analysis. The morphology of NBC/CL-20 is characterized by scanning electron microscopy (SEM), as shown in Figure 2c–h, in which the CL-20 particles are embedded in the NBC matrix uniformly, and the particle size of CL-20 (100–200 nm) and NBC (200–400 nm) has been decreased to the nanoscale compared with raw CL-20 (40–80 μm) (Figure 2a) and NBC (200–500 μm) (Figure 2b), respectively. Obviously, the morphology of CL-20 has been improved a lot from the irregularity to the spheroid, and NBC exhibits dense porous network cross-link structures. As for the elemental images of NBC/CL-20, mainly consisting of O, N, and C, which correspond to the groups of -N-NO2 and the rings of CL-20 and NBC, while there still remain few S elements from DBTDL, which may not be removed entirely by freeze-drying. It can clearly be seen that there exhibits abundant pores on the surface of the NBC/CL-20 composite in, as shown in Figure 2c–e. In order to prove the existence of a porous cross-linked structure formed by NBC (–OH) and TDI (–NCO), transmission electron microscopy (TEM) images of NBC/CL-20 are shown in Figure 3, in which the CL-20 particles are imbedded in the cross-linked structure uniformly. Moreover, the pore size of NBC gel is about 20–60 nm, which improves the specific surface area of the composite and enhance the interfacial contact of NBC and CL-20 much closer.

2.2. Structure and Composition. To prove whether the crystal form of CL-20 particles has been changed during the fabrication process. The X-ray powder diffraction pattern has been performed, as shown in Figure 4a, it can be obviously seen that the amorphous structure of NBC exhibits no obvious peak. The raw CL-20 presents a distinct crystalline pattern with the main characteristic peaks appearing at 12.56, 25.60, and 30.40°, which correspond to (1, 1, −1), (0, 2, 2), and (2, 0, −3) crystal planes of ε-CL-20, respectively. As for as-sample NBC/CL-20, the typical diffraction peaks of CL-20 are still preserved in the composite; however, the diffraction intensity of some peaks is considerably decreased and has been identified because of the existence of NBC. Another evident phenomenon can be observed that the pattern at 2θ of 16–38° exhibits the amorphous state of NBC. Encouragingly, this research has maintained the stable crystal form of ε-CL-20 with the sol–gel technology and freeze-drying technology. Benefits from the particle size decreased, the X-ray diffraction (XRD) pattern of the composite presented more broadened diffraction peaks compared with raw CL-20.

As illustrated in Figure 4b, the Fourier-transform infrared (FT-IR) spectrum peaks of NBC/CL-201, located at 3246, 3159, 2924, 1558, 1041, and 933 cm\(^{-1}\) are corresponding to the stretching vibrations of C–O and −OH groups, the absorptions peaks of −CH\(_2\)- and εC–H, −NO\(_2\) asymmetry stretching vibrations and −NO\(_2\) symmetry stretching vibrations, and the ring vibrations of raw NBC and CL-20. It can clearly be seen that the stretching vibrations of −OH groups have been decreased in the composite compared with that of raw NBC, indicating that there has been a cross-linked reaction of −OH with −NCO during the preparation process but retains little −OH groups in the NBC skeleton at 3246 cm\(^{-1}\). Moreover, the appearance of H–NCO groups (stretching vibration) indicates that the reaction has happened between −OH and −NCO at 2258 cm\(^{-1}\). Finally, the results have also shown that the crystal form of CL-20 has not changed, which retains the stable structure crystal form of ε-CL-20 corresponding to the XRD analysis perfectly.

Another method to investigate the structure and organic groups of materials is Raman spectra. Figure 4c presents the Raman spectrum of raw NBC, CL-20, and NBC/CL-201, in which the bands located at 780–1000 cm\(^{-1}\) are assigned to the ring vibrations of CL-20, those appearing at 1250–1490 cm\(^{-1}\) are related to the symmetric stretching of −NO\(_2\) and N–N stretching vibrations. While the peaks at 1572–1600 cm\(^{-1}\) are

Figure 3. TEM cross-linked porous structure images of NBC/CL-201:1 (a) and enlarged drawing of 100 nm (b).

https://dx.doi.org/10.1021/acsomega.0c04958
ACS Omega 2020, 5, 31407–31416
attributed to asymmetric $\text{−NO}_2$ stretching vibration and $\text{C−N}$ stretching. As for the bands at about 3000 cm$^{-1}$, they are related to the absorption peaks of $\text{−CH}_3$ and $\text{−C−H}$. Those results indicate that the composite maintains the stable structure; moreover, the molecular vibrations at 2000−2450 cm$^{-1}$ correspond to the stretching vibration of $\text{H−NCO}$ groups, which is in accord with the results of FT-IR spectrum analysis.

2.3. Thermal Analysis. Thermogravimetric analysis—differential scanning calorimetry (TG−DSC) analysis has been performed at multiple heating rates of 5, 10, 15, and 20 °C·min$^{-1}$ to characterize the heat release of samples in the temperature range of 100−350 °C, as shown in Figure 5, and the parameters of thermal decomposition are listed in Table 1. It can be clearly seen the DSC curves of samples (NBC/CL-201:1, NBC/CL-201:2, and NBC/CL-201:3) exhibit only one exothermic peak, indicating that the organic combination is achieved between NBC and CL-20. In addition, the exothermic peak temperature of NBC/CL-201:1 has been advanced visibly compared with raw CL-20. With the content increase of CL-20, the thermal decomposition behavior is mainly controlled by CL-20 instead of NBC. The surface or inside of NBC gel may not provide enough sites to load CL-20 particles for sample 1:2 or 1:3. Consequently, the much closer interfacial contact of the ratio 1:1 composite, the thermal decomposition has been promoted more entirely with a closer transfer distance of heat and mass, resulting in much better heat release. The heat release of NBC/CL-201:1 (>3000 J/g) is much higher than both of the raw materials (<1000 J/g) and other two samples (almost <3000 J/g); this phenomenon illustrates that NBC/CL-201:1 has the best mass ratio between the other two samples, which presents a closer interfacial contact between NBC gel and CL-20 particles. With the content of CL-20 increasing, the surface or inner of NBC gel may not provide enough sites to load CL-20 particles compared with a ratio of 1:1 of NBC and CL-20; furthermore, the much closer interfacial contact and the heat release of the ratio 1:1 is much better than those of the two samples, which has been illustrated in Table 1. A conclusion can be drawn that thermal decomposition has been promoted throughout the whole 1:1 ratio of the composite with a closer transfer distance of heat and mass. Furthermore, with the content of CL-20 increasing, there may be some little agglomeration in the composite which may lead to decrease of the thermal decomposition performance. Consequently, the DSC curve of NBC/CL-201:1 exhibits excellent thermal decomposition performance, including heat release, onset temperature, and the exothermic peak temperature. As for the TG analysis, it is hard to conclude thermogravimetry perfectly. However, the weight loss ratios of composites are lower than that of CL-20 and NBC on the whole, and the onset thermogravimetry temperatures are all higher than both NBC and CL-20. The results can be attributed to the cross-linked structure of NBC and TDI, in which the existence of TDI has increased the mass ratio, resulting in a much lower weight loss ratio. What is more, the temperature of weight loss has also increased than raw CL-20 and increased with the content of CL-20. Therefore, these results are because of not only the particle size of NBC and CL-20 has been reduced to nanometers but also the formation of the cross-linked porous network structure of NBC gel in which CL-20 particles are embedded inside, resulting in a much closer interfacial contact between NBC and CL-20, and the transfer distance of heat and mass has been shortened greatly with excellent thermal decomposition performance.

The thermal dynamic parameters are calculated at four different heating rates, as listed in Table 2. The Kissinger equation eq 1

$$\ln\left(\frac{T_p}{\beta}\right) = \frac{A}{E_a} - \frac{B}{T_p}$$

and Arrhenius equation eq 2

$$k = k_0 \exp\left(-\frac{E_a}{R T_p}\right)$$

are chosen to calculate the activation energy ($E_a$), pre-exponential factor ($A_0$), and rate constant ($k$). $T_p$ is the peak temperature in the DSC curves and $\beta$ is the heating rate; $k_0$ and $h$ are the Boltzmann ($k_0 = 1.381 \times 10^{-23}$ J/K) and Planck constants ($h = 6.626 \times 10^{-34}$ J/s), respectively. Figure 6 presents the linear fit of plotted $\ln(\beta/T_p^2)$ against $1/T_p$ of raw materials and composites. Moreover, to investigate the decomposition process of NBC/CL-20, the activation enthalpy ($\Delta H^\ddagger$), activation free energy ($\Delta G^\ddagger$), and activation entropy ($\Delta S^\ddagger$) are calculated by eqs 3−5, respectively. $\Delta H^\ddagger$ is the energy that the molecules absorb to change from the common state to...
the activated state, so the value of $\Delta H^\ddagger$ is close to that of $E_a$ for each sample (288.34, 164.35, 147.21, 149.04, and 163.06 kJ/mol). As for the $\Delta G^\ddagger$ (153.98, 168.71, 168.89, 155.53, and 168.39 kJ/mol) (Table 2), all positive numbers manifest the nonspontaneous progress of samples. Obviously, $E_a$ of raw NBC (299.13 kJ/mol) and CL-20 (168.76 kJ/mol) is higher.

Figure 5. TG–DSC analysis at different heating rates of (a,b) raw NBC, (c,d) CL-20, (e,f) NBC/CL-20_{1:1}, (g,h) NBC/CL-20_{1:2}, and (i,j) NBC/CL-20_{1:3}.
than that of samples (151.49, 153.36, and 167.38 kJ/mol) and is easier to be activated. The calculated activation energies of NBC/CL-20 at different stoichiometric ratios have a similar increasing trend with the increasing content of CL-20. The phenomenon indicates that the particle size of CL-20 and cross-linked porous network structure has great influences on the reactivity of NBC/CL-20 nanocomposites.

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

\[
k = A_K \times \exp \left(-\frac{E_K}{T_p \times R} \right) \\
(2)
\]

\[
A_K \times \left(-\frac{E_K}{T_p \times R} \right) = \frac{k_B T_p}{h} \exp \left(\frac{-\Delta G^\ddagger}{RT_p} \right) \\
(3)
\]

\[
\Delta H^\ddagger = E_K - RT_p \\
(4)
\]

\[
\Delta G^\ddagger = \Delta H^\ddagger - T_p \Delta S^\ddagger \\
(5)
\]

2.4. Sensitivity. The impact and friction sensitivities of composites are tested in Figure 7. It can clearly be seen that the sensitivities of NBC/CL-20 have been reduced significantly. As an energetic binder, NBC exhibits remarkable impact sensitivity of 88.3 cm, while the friction sensitivity (97.6%) is still high compared with raw CL-20 (84.3%), owing to its inherent physical and chemical property. However, the composites present lower impact sensitivity (Figure 7a) at 61.3, 55.6, and 49.5 and friction sensitivity (Figure 7b) is about 68.5, 75.4, and 78.6%, benefiting from its unique nanostructure and closer interfacial contact between NBC and CL-20. The mechanical sensitivities present an increasing trend with the increased content of CL-20, which indicate that the sensitivity is mainly controlled by CL-20. The main reason can be attributed to the existence of the NBC-TDI cross-linked structure, in which CL-20 was embedded in the matrix, and the NBC gel matrix acts as an effective buffer system, which is capable of distributing the energy stimulation, when undergoes some stimulus come from surroundings. Moreover, the particle size of CL-20 has been decreased, which can largely lessen the probability of forming a local explosive hot spot. In addition, the nanometer pores of composites in SEM images can contain less heat and lower temperatures of the hot spot which may lead to explosion. Therefore, nanostructure energetics exhibit lower sensitivities than that of microscale explosives.35

2.5. Possible Mechanism. In order to investigate the process of the thermal decomposition mechanism of the composition, TG−DSC−IR has been recruited to study the gas products for the thermal decomposition of NBC/CL-201:1. According to Figure 9, the main gas products are identified to be NO2, CO2, HCN, and CH2O, and the TG−DSC curve exhibits the peak of thermal decomposition of NBC/CL-201:1 at 225.83 °C. The FT-IR analysis has been conducted to probe the gas products of NBC/CL-201:1, as shown in Figure 9b, which shows strong peaks at 2105−2235 cm−1, corresponding to the existence of large amounts of CO2 gas. The absorption peaks in 2195−2268 and 1760−1830 cm−1 prove the appearance of the N2O and CH2O gas. While the obvious peak at 708 cm−1 shows the existence of HCN resulting from the rupture of the HNCO=O bond in the cross-linked structure. Moreover, lots of CO2 (rather than CO) gas reflects the moderate oxygen balance of NBC/CL-20. On the whole, a small decomposition peak of NBC appeared at relatively low temperatures of about 150−170 °C, and the gas products are very clean. These results may provide a possibility of applying the nanocomposite in low-signature propellants. In addition, the signal of NO2 is detected first by the rupture of NBC (O−NO2) with the lapse of time as well as signals of CH2O and C−O−C have also been detected. These products should result from the pyrolysis of the NBC skeleton because NBC is easier to decompose than CL-20. Subsequently, owing to the gas products of NBC, such as NO2, N2O, and CO2 were not taken entirely by N2 flow, and CL-20 is also decomposed with the temperature increasing and the catalysis of gas products of NBC, the split radical of NO2 (from N2O) then decayed to N2O at an advanced temperature (225.83 °C). On the contrary, the gas products of CL-20 locked in NBC gel matrix are also able to promote the decomposition of NBC, which proceeded nearly to completion with high weight loss about 92.8%. In thermodynamics, producing more CO2 or N2O results in more heat release of the decomposition or combustion; hence, we took into consideration whether more N2O (less CO2) in products would lead to higher heat release and lower thermal decomposition temperature. Fortunately,
Figure 6. Linear fit of plotted $\ln(\beta/T_p^2)$ against $1/T_p$ for the calculation of activation energy ($E_a$), (a) raw NBC, (b) raw CL-20, (c) NBC/CL-201:1, (d) NBC/CL-201:2, (e) NBC/CL-201:3, and (f) $E_a$ comparison of samples.

Figure 7. Impact (a) and friction (b) sensitivities of raw NBC, CL-20, and NBC/CL-20 composites.
the results of FT-IR analysis have proved the mechanism of thermal decomposition of NBC/CL-20, as shown in Figure 8. On the one hand, the particle size of NBC and CL-20 has been decreased to the nanoscale with high thermal reaction activity and the peak temperature has been increased greatly. Moreover, this is owing to the cross-linked porous network structure of NBC gel, in which CL-20 is embedded in the gel with intimate contact, and shortened transfer distance of heat and mass resulting in excellent thermal decomposition performance. The effect of the thermal decomposition of NBC has promoted that of CL-20, and the same process of CL-20 has also promoted that of NBC more completely for their special structure.

3. CONCLUSIONS

In this study, different mass ratios of NBC/CL-20 nano-composites have been fabricated by sol–gel and freeze-drying technology, in which CL-20 particles were embedded uniformly in the porous cross-linked network structure of NBC gel. A conclusion can be drawn that the interfacial contact of nano-CL-20 particles and nano-NBC gel has become closer, resulting in a much shorter transfer distance of heat and more reactivity. The composite NBC/CL-20\textsubscript{1:1} exhibited prominent thermal property and sensitivity performance, especially with lower decomposition peak temperatures, higher heat release, much lower activation energy, and the lowest mechanical sensitivities. Ongoing work focuses on the optimum ratio and systematic investigation of the effect of the metallic oxide catalyst (CuO) as well as metal powder (Al) on the thermal decomposition of the NBC-based nanostructure composite energetic materials.

4. EXPERIMENTAL SECTION

4.1. Materials. NBC (N, 12.6%) was provided by the research group on biological nanocomposites in Southwest University of Science and Technology. CL-20 (purity: 99.9%) were provided by Liaoning Qing yang Chemical Co., Ltd.; acetone, toluene diisocyanate (TDI), ditinbutyl dilaurate (DBTDL), and triethylenediamine (TEDA) were purchased from Shanghai Aladdin Biochemical Technology Co., Ltd. (Nanjing city, Jiangsu P. R. China).

4.2. Synthesis of NBC/CL-20 nEMs. NBC and CL-20 were dissolved in 10 mL of acetone to obtain a homogeneous solution in the mass ratios 1:1, 1:2, of 1:3, with constant magnetic stirring, respectively, and the molecular structures of NBC and CL-20 are illustrated in Figure 1. The mixed solution was stirred for about 3 h and ultrasonicated for 20 min to obtain a homogeneous solution. Then, 0.1 mL of TDI, 0.05 mL of DBTDL, and 0.005 g of TEDA were added into the solution successively. The mixture was vigorously magnetically stirred under an ambient temperature for 15 min until the system became homogenous, called “sol”. After that, the sol was sealed in a weighing bottle and placed in an oven (45 °C) for gelation as well as aging (cross-linking reaction) for 4 days. The “gel” was frozen instantaneously with liquid nitrogen and then dried by vacuum freeze-drying technology. The dry conditions were controlled accurately with an extremely low temperature and vacuum (at −76 °C and 10\textsuperscript{−3} mbar) to ensure experimental safety. The samples were named NBC/CL-20\textsubscript{1:1}, NBC/CL-20\textsubscript{1:2}, and NBC/CL-20\textsubscript{1:3}. The fabrication process of composites is shown in Figure 1.

4.3. Characterization and Tests. The morphological characterizations of samples were observed by field-emission scanning electron microscopy (FESEM, FEI400, Hitachi Co., Ltd. Japan) and TEM (FEI F20, Co., U.S.A). The crystal structure of the samples was investigated with an X-ray diffractometer (XRD, Bruker D8-ADVANCE, Germany). The FT-IR spectroscopic measurement of the organo-functional groups of NBC, CL-20, and NBC/CL-20\textsubscript{1:1} was conducted. To probe the CL-20 crystal structure and disordering degree in the nanocomposites, Raman spectroscopy has been employed (Renishaw inVia microscopic confocal Raman spectrometer).
in the backscattering configuration with 532 nm excitations. The laser beam was focused on the sample surface with 50X objective of a confocal Olympus microscope to a spot of ~2 μm in diameter, exposure time 0.1 s, and laser power 10%. TG–DSC (TA Instruments SDT600) was employed to study the thermal performance, under a pure nitrogen flow (20 mL·min⁻¹) at the heating rates of 5, 10, 15, and 20 °C min⁻¹, and the temperature was ranged from 100 to 350 °C, TG–DSC–FTIR (STA449 F5 Jupiter, Nicolet is 500) has been performed to investigate the gas products of the thermal decomposition process of sample NBC/CL-20, and the temperature ranges from 100 to 350 °C with a pure nitrogen flow of 20 mL·min⁻¹. The impact sensitivity tests were conducted according to GJB772A-97 by an HGZ-3 drop hammer and the testing conditions are as follows: the drop weight of 5.000 ± 0.002 kg, sample mass of 30 ± 1 mg, room temperature of 25 °C, and relative humidity of 25%, and twenty-five drops of the materials were tested. The results were shown in terms of special height (Hₐ) standing for the drop height of 50% explosion probability. The friction sensitivity of the 50 samples was tested with the HGM-3 friction instruments and an explosion probability (P, %) was obtained in each determination.

AUTHOR INFORMATION

Corresponding Authors
Weidong He – Key Laboratory of Special Energy Materials, Ministry of Education, Nanjing University of Science and Technology, Nanjing 210094, Jiangsu, China; orcid.org/0000-0003-3540-1974; Email: hewedong@njust.edu.cn
Jie Liu – National Special Superfine Powder Engineering Research Center of China, Nanjing University of Science and Technology, Nanjing 210094, Jiangsu, China; Email: Jie_Liu_njjust@126.com

Author
Ling Chen – Key Laboratory of Special Energy Materials, Ministry of Education, Nanjing University of Science and Technology, Nanjing 210094, Jiangsu, China

Complete contact information is available at: https://pubs.acs.org/10.1021/acsomega.0c04958

Notes
The authors declare no competing financial interest.

ACKNOWLEDGMENTS

This research was financially supported by the National Natural Science Foundation of China (grant no. 51606102).

REFERENCES

(1) Pichtel, J. Distribution and Fate of Military Explosives and Propellants in Soil: A Review. Appl. Environ. Soil Sci. 2012, 2012, 617236.
(2) Wu, Z.; Liu, N.; Zheng, W.; Chen, J.; Song, X.; Wang, J.; Cui, C.; Zhang, D.; Zhao, F. Application and Properties of CL-20/HMX Cocrystal in Composite Modified Double Base Propellants. Propellants, Explos., Pyrotech. 2020, 45, 92–100.
(3) Liu, N.; Duan, B.; Lu, X.; Mo, H.; Xu, M.; Zhang, Q.; Wang, B. Preparation of CL-20/DNDAP cocrystals by a rapid and continuous spray drying method: an alternative to cocrysal formation. CrystEngComm 2018, 20, 2060–2067.
(4) Yang, Z.; Ding, L.; Wu, P.; Liu, Y.; Nie, F.; Huang, F. Fabrication of RDX, HMX and CL-20 based microcapsules via in situ polymerization of melamine–formaldehyde resins with reduced sensitivity. Chem. Eng. J. 2015, 268, 60–66.
(5) Mao, X.; Li, Y.; Li, Y.; Jiang, L.; Wang, X. Thermal properties of decomposition and explosion for CL-20 and CL-20/n-Al. Chin. J. Energy Mater. 2019, 38, 98–110.
(6) Yan, M.; Liu, Y.; Xu, J.; Yang, L.; Zhang, L.; Nie, F.; Huang, S. Porous RDX with Reduced Sensitivity Prepared by a Solution/ Desolvation Method. Cryst. Growth Des. 2020, 20, 5387–5394.
(7) Song, C.-K.; An, C.-w.; Li, H.-q.; Wang, J.-y. Preparation and Performance of Micro/nano CL-20/HMX Energetic Cocrystal Materials. Initiators Pyrotech. 2018, 9.
(8) Zheng, X.; Yu, S.; Wen, W.; Wen, Y.; Wang, P.; Lan, L.; Dai, X.; Han, Y.; Li, J.; Li, Y. Inside Cover: Sensitivity and Phase Transition of Heated -CL-20 in Drop-Weight Impact Test. Propellants, Explos., Pyrotech. 2018, 43, 1080.
(9) Zarko, V. E. Nanoenergetic Materials: A New Era in Combustion and Propulsion. Nanoenergetic Materials; Springer, 2016; Chapter 1.
(10) He, B.; Stepanov, V.; Qin, H.; Krasnoperov, L. N. Production and Characterization of Composite Nano-RDX by RESS Co-Precipitation. Propellants, Explos., Pyrotech. 2015, 40, 659–664.
(11) Ji, W.-s.; Cao, H.-a.; Xie, Q.-m.; Gu, Z.-g. Analysis of Safety and Characterization on Nano RDX Produced by Wet Grinding. JIP Conf. Ser.: Mater. Sci. Eng. 2018, 392, 062045.
(12) Singh, H.; Jahagirdar, N.; Banerjee, S. Sonochemically assisted synthesis of nano HMX. Def. Technol. 2019, 15, 837–843.
(13) Jia, X.; Wang, J.; Hou, C.; Tan, Y. Green Preparation, Spheroideal, and Superior Property of Nano-1, 5, 3, 5, 7-Tetranitro-1, 3, 5, 7-Tetrazocane. J. Nanomater. 2018, 2018, 583937.
(14) Bayat, Y.; Zeynali, V. Preparation and Characterization of Nano-CL-20 Explosive. J. Energ. Mater. 2011, 29, 281–291.
(15) Guo, X.; Ouyang, G.; Liu, J.; Li, Q.; Wang, L.; Gu, Z.; Li, F. Massive Preparation of Reduced-Sensitivity Nano CL-20 and Its Characterization. J. Energ. Mater. 2015, 33, 24–33.
(16) Sovizi, M. R.; Hajimirsadeghi, S. S.; Naderizadeh, B. Effect of particle size on thermal decomposition of nitrocyclotolene. J. Hazard. Mater. 2009, 168, 1134–1139.
(17) Wang, Y. T.; Xu, J. B.; Shen, Y.; Wang, C. G.; Yang, T. L.; Li, F. W.; Zhang, Z. H.; Chen, J.; Ye, Y. H.; Shen, R. Q. Fabrication and Characterization of Al-CuO nanocomposites prepared by Sol-Gel method. J. Phys.: Conf. Ser. 2020, 1507, 022024.
(18) Acosta, J. A.; Petry, A. L.; Gould, S. A.; Jones, C. K.; Stark, C. R.; Fahrenholz, A.; Patience, J. F. Effects of grinding method and particle size of wheat grain on energy and nutrient digestibility in growing and finishing pigs. Transl. Anim. Sci. 2020, 4, 682.
(19) Li, X.; Huang, B.; Li, R.; Zhang, H. p.; Qin, W.; Qiao, Z.; Liu, Y.; Yang, G. Laser-Ignited Relay-Domino-Like Reactions in Graphene Oxide/CL-20 Films for High-Temperature Pulse Preparation of Bi-Layered Photothermal Membranes. Small 2019, 15, 1900338.
(20) Yi, Z.; Ang, Q.; Li, N.; Shan, C.; Li, Y.; Zhang, L.; Zhu, S. Sulfate-Based Nanothermite: A Green Substitute of Primary Explosive Containing Lead. ACS Sustainable Chem. Eng. 2018, 6, 8584–8590.
(21) Shivarvan, K.; Forrest, E. C. Modeling physical vapor deposition of energetic materials. J. Vac. Sci. Technol., A 2018, 36, 03E103.
(22) Luo, T.; Wang, Y.; Huang, H.; Shang, F.; Song, X. An Electrosprun Preparation of the NC/GAP/Nano-LLM-105 Nanofiber and Its Properties. Nanomaterials 2019, 9, 854.
(23) Li, J.; Brill, T. B. Nanostructured Energetic Composites of CL-20 and Binders Synthesized by Sol Gel Methods. Propellants, Explos., Pyrotech. 2006, 31, 61–69.
(24) Tillotson, T. M.; Gash, A. E.; Simpson, R. L.; Hrubesh, L. W.; Satcher, J. H.; Poco, J. F. Effects of grinding method and particle size of wheat grain on energy and nutrient digestibility in growing and finishing pigs. Transl. Anim. Sci. 2020, 4, 682.
(27) Wang, Y.; Song, X.; Song, D.; Liang, L.; An, C.; Wang, J. Synthesis, thermolysis, and sensitivities of HMX/NC energetic nanocomposites. J. Hazard. Mater. 2016, 312, 73–83.

(28) Tappan, B. C.; Brill, T. B. Thermal Decomposition of Energetic Materials 86. Cryogel Synthesis of Nanocrystalline CL-20 Coated with Cured Nitrocellulose. Propellants, Explos., Pyrotech. 2003, 28, 223–230.

(29) Huang, X.; Luo, Q.; Zhu, J.; Li, Z.; Li, C.; Pei, C. The Preparation and Rheological Properties of Novel Energetic Composites TEGDN/NBC. Propellants, Explos., Pyrotech. 2020, 45, 101.

(30) Sun, D.-P.; Ma, B.; Zhu, C.-L.; Liu, C.-S.; Yang, J.-Z. Novel Nitrocellulose Made from Bacterial Cellulose. J. Energ. Mater. 2010, 28, 85–97.

(31) Yang, Q.; Peng, B. H.; Liang, G.; Luo, Q. P.; Pei, C. H. Preparation and Characterization of Nitrated Bacterial Cellulose. Chin. J. Explos. Propellants 2012, 35, 88.

(32) Jin, M.; Wang, G.; Deng, J.; Li, G.; Huang, M.; Luo, Y. Preparation and properties of NC/RDX/AP nano-composite energetic materials by the sol–gel method. J. Sol-Gel Sci. Technol. 2015, 76, 58–65.

(33) Kissinger, H. E. Reaction Kinetics in Differential Thermal Analysis. Anal. Chem. 1957, 29, 1702–1706.

(34) Pourmortazavi, S. M.; Hosseini, S. G.; Rahimi-Nasrabadi, M.; Hajimiradeghi, S. S.; Momenian, H. Effect of nitrate content on thermal decomposition of nitrocellulose. J. Hazard. Mater. 2009, 162, 1141–1144.

(35) Wang, Y.; Jiang, W.; Song, X.; Deng, G.; Li, F. Insensitive HMX (Octahydro-1, 3, 5, 7-tetranitro-1,3,5,7-tetrazocine) Nanocrystals Fabricated by High-Yield, Low-Cost Mechanical Milling. Cent. Eur. J. Energ. Mater. 2013, 10, 277–287.