Electrospinning Preparation of NC/GAP/Submicron-HNS Energetic Composite Fiber and its Properties

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ABSTRACT: In this work, novel three-dimensional nitrocellulose/glycidyl azide polymer/submicron-2,2′, 4,4′, 6,6′-hexanitrostilbene (NC/GAP/submicron-HNS) composite fibers were prepared by the electrospinning method. As-prepared NC/GAP/submicron-HNS fibers were continuous and possessed a large specific surface area. The structure of fibers was characterized by energy-dispersive X-ray, X-ray photoelectron spectroscopy, X-ray diffraction, and Fourier transform infrared spectroscopy (IR). The results showed that HNS submicron particles were uniformly loaded on the surface of NC/GAP fibers and incorporated with it. Thermal analyses were performed. Such NC/GAP/submicron-HNS fibers showed a low activation energy of 204 kJ⋅mol−1 and large rate constant of 1.74 s−1, indicating high reactivity and fast reaction rate. The result of TG-IR analysis revealed that the main decomposition products of NC/GAP/submicron-HNS were CO2, CO, H2O, N2O, few NO, and fragments such as −CH2O− and −CH−, which were low-signature gases. An evaluation on the energy performance disclosed that the standard specific impulse (Ip) of NC/GAP/submicron-HNS fibers was 2032 N⋅s⋅kg−1, which was higher than 2014 N⋅s⋅kg−1 of NC/GAP. This meant the addition of HNS submicron particles to the NC/GAP fiber was favorable to the improvement of energy performance. Additionally, introduction of submicron-HNS made the energetic fibers becoming very insensitive to impact action. It was expected that as-prepared NC/GAP/submicron-HNS membranes were promising materials applied for solid rocket propellant.

1. INTRODUCTION

2,2′,4,4′,6,6′-Hexanitrostilbene (HNS) is one of the most excellent explosives owing to its superior thermostability, low sensitivity, high density, and high specific impulse.1–3 HNS is usually used in pyrotechnics and plays an important role in the aerospace field.4–6 Especially, the development of aerospace technology puts forward higher requirements on energetic materials.7–9 Submicron-HNS show a more wonderful performance than traditional HNS.10,11 However, HNS submicron particles are prone to aggregation because of the high surface energy of submicron materials.12–14 Thus, it is very much desired that submicron-HNS fibers can load on the surface of a kind of carrier with a high performance, by which the dispersion of submicron-HNS particles are improved remarkably.

Electrospinning is a multipurpose technology applied for fabricating 3D fiber films.15–20 Explosive submicron particles are introduced into fiber matrix through electrospinning technology to prepare composite fibers. It can not only alleviate the agglomeration but also improve the combustion performance. There are few reports on the preparation of energetic composite fibers. Yan prepared nitrocellulose/aluminum–cupric oxide (NC/Al–CuO) fiber via electrospinning, which has a very high burning rate.21 Li realized the incorporation of nanoboron and NC fiber via electrospinning.22 Li found that the activation energy for decomposition of NC/2,4,6,8,10,12-hexanitrostilbene-2,4,6,8,10,12-hexaazaisowurtzitane (NC/CL-20) fibers were significantly reduced compared with raw CL-20.23 All of these researchers have focused on the use of single NC as the substrate for electrospun. However, there will be a major matter with the single NC as the precursor solution, that is, the viscosity is too high. In fact, the harm of high viscosity mainly includes two aspects. First, it makes the electrospun process difficult. Second, it leads to a serious decrease in the load of submicron particles. Thus, in the electrospun process, a polymer, which is of low viscosity and high performance, is desired to incorporate with NC. For this, glycydil azidepolymer (GAP) catches our attention, owing to its high-energy performance, high burning rate, and low viscosity.24–26 Therefore, herein, we employ NC/GAP composites as the matrix to load submicron-HNS via electrospun. NC/GAP/submicron-HNS fibers are expected to have excellent energetic properties.

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2. RESULTS AND DISCUSSION

2.1. Morphology and Structure. Scanning electron microscope (SEM) images of milled HNS are shown in Figure 1a,b. It is obvious that HNS submicron particles are of spheroid shape. The particle diameter distribution of HNS is calculated by measuring the diameter of ~100 HNS particles. Figure 1c,d shows that the mean size of the milled HNS is \(d_{50} = 0.154 \, \mu \text{m}\). The volume curve is obtained by integrating the frequency curve. Please note that the \(d_{90}\) of the milled HNS is 0.199 \(\mu \text{m}\), which implies that 90 vol % the particles are with the size less than 0.199 \(\mu \text{m}\). Thus, the milled sample is called as "submicron-HNS". The SEM images of NC/GAP and NC/GAP/submicron-HNS fibers are displayed in Figure 2. It is obvious that a 3D network structure forms. The NC/GAP fiber presented in Figure 2a,c appears consecutive and uniform, and its surface is quite smooth. In Figure 3b,d, the submicron-HNS particles are closely fixed on the surface of NC/GAP fiber and incorporate with NC/GAP. Hence, the surface of NC/GAP/submicron-HNS is very rough in comparison with surface of NC/GAP. The introduction of submicron-HNS makes the precursor solution heterogeneous. Thus, the aggregation of HNS submicron particles exists during electrospinning, which is displayed in Figure 2b,d. The Fiber diameter distribution is calculated by measuring the diameter of ~100 fibers, and the results are shown in Figure 2e–h. For NC/GAP, the mean diameter calculated from the frequency curve is 0.469 \(\mu \text{m}\) which is similar to the median diameter (\(d_{50} = 0.478 \, \mu \text{m}\)). The mean diameters of NC/GAP/submicron-HNS are 1.074 and 1.042 \(\mu \text{m}\), respectively. It is clear that the diameter of NC/GAP/submicron-HNS is larger than diameter of NC/GAP. This is because HNS submicron particles are closely coated on the surface of NC/GAP.

The results of EDS analysis are displayed in Figure 3. Figure 3a,b confirms that there are (C, N, and O) three elements existing on the surface of both NC/GAP fibers, demonstrating that the impurity has not been introduced in the process of ball milling and electrospinning, and NC/GAP/submicron-HNS. Figure 3c–h shows the EDS maps of the C, N, and O elements, and the specific element contents are listed in Table 1. It is clear that after coating with submicron-HNS, the N content is significantly reduced, and the contents of O and C increase appreciably. This consists with the element distribution in molecules of HNS, NC, and GAP.

IR analysis is conducted and the spectra are shown in Figure 4a. For NC/GAP/submicron-HNS, the peak at 1083 cm\(^{-1}\) indicates the out-of-plane bending vibration of C–H; the peak at 2101 cm\(^{-1}\) reflects the stretching vibration of −N\(_3\) in present GAP;\(^25\) the peak at 1279 and 1646 cm\(^{-1}\) relate to symmetric and antisymmetric stretching vibrations of −ONO\(_2\), respectively; the peaks at 1339 and 1532 cm\(^{-1}\) correspond to the symmetric and antisymmetric stretching vibrations of −NO\(_2\); and the peak at 3100 cm\(^{-1}\) is ascribed to the stretching vibrations of −C–H in CH\(_2\); the peak located at 1602 cm\(^{-1}\) corresponds to the stretching vibrations of the C≡C skeleton in the benzene ring. These peaks match with the molecular structure of HNS,\(^13\) confirming the existence of submicron-HNS on the surface of the NC/GAP/submicron-HNS fiber. The high-voltage electrostatic force during electrospinning does not bring about the molecular structure change of submicron-HNS and NC/GAP. No chemical reaction occurs among NC, GAP, and HNS, hence, there are no new chemical bonds produced. The X-ray diffraction (XRD) patterns of submicron-HNS, NC/GAP, and NC/GAP/submicron-HNS are shown in Figure 4b. Submicron-HNS is a kind of crystal, and many diffraction peaks appear in its pattern. The NC/GAP fiber is a kind of polymer, and there is no diffraction peak in its pattern. The XRD pattern of the composite fiber shows that some HNS crystal incorporates with the NC/GAP polymer. The crystal phase of HNS does not transform during the process of electrospinning. It has been shown in the literature that for nitramine explosives such as HNIW crystal transformation will occur during recrystallization.
Song prepared nano-HNIW using sol–gel, supercritical desiccation, etching, and the crystal phase of HNIW transformed from ε-HNIW into α-HNIW.27 Herein, HNS is insoluble in acetone. We select acetone to prepare the precursor solution, avoiding recrystal of HNS.

X-ray photoelectron spectroscopy (XPS) analysis is conducted to further characterize the surface elements of NC/GAP/submicron-HNS, and the result is displayed in Figure 5. In Figure 5a, the peaks at 285.2, 407, and 534 eV are assigned to the binding energy of C 1s, N 1s, and O 1s, respectively. Figure 5b displays the C 1s spectrum. Three peaks at 284.5, 286.5, and 288.1 eV relates to C−C, C−N, and C−O, respectively. Figure 5c illustrates the N 1s spectrum, in which four types of nitrogen atoms with different chemical states were detected.28 The peak at 400.2 eV is assigned to the −N3 group in GAP molecules. The peaks at 400.6 and 404.2 eV correspond to the −NO2 and C−N in HNS molecules. The peak at 407.8 eV attributes to the presence of −ONO2 in NC molecules. Figure 5d shows the O 1s spectrum. The O 1s spectrum comprises four peaks located at 531.8, 532.6, 533.6, and 534.4 eV, which is ascribed to C−O, −NO2, −O−NO2, and −O−NO2 groups, respectively.29 Upon these, we deduce that HNS exists at the surface of the composite fiber.

Figure 2. SEM images and diameter distribution of fibers: (a,c) for NC/GAP; (b,d) for NC/GAP/submicron-HNS; (e−h) diameter distribution.
Figure 6 shows the N2 adsorption—desorption isotherms of NC/GAP and NC/GAP/submicron-HNS fibers. The specific surface area, pore volume, and pore size of samples are exhibited in Table 2. The curve is typical IV adsorption isotherms with H3-type hysteresis loop. It possesses the feature of the mesoporous material. Single-molecule adsorption exists in the low specific pressure zone, but there is no obvious boundary between single-molecule adsorption and subsequent multilayer adsorption. Capillary condensation occurs when the adsorbed layer on the pore walls reaches a sufficient thickness during the adsorption process, and when desorption is carried out at the same p/p0 as adsorption, only the molecules on the surface of the capillary are desorbed. Hence, it does not desorb the molecules adsorbed under p/p0. To desorb it, a smaller p/p0 is required, so the hysteresis of desorption arises. The specific surface area of NC/GAP/submicron-HNS was somewhat larger than that of NC/GAP, probably attributed to the rough surface of NC/GAP/submicron-HNS. Electrospun fibers have larger specific surface area than energetic composite fabricated by other methods. The specific surface area of NC/GAP/CL-20 prepared by sol—gel is lower than that NC/GAP/submicron-HNS fibers.

2.2. Thermal Analysis. Differential scanning calorimeter (DSC) traces of samples collected at different heating rates are shown in Figure 7a—c. The kinetic and thermodynamic parameters for thermal decomposition of samples are calculated with their DSC data, and the results are listed in Table 3. For all samples, the peak temperature increases as the heating rate increases. For submicron-HNS, there is a slight endothermic peak just before decomposition, corresponding to melting of submicron-HNS. For NC/GAP/submicron-HNS, there is only one exothermic peak, indicating that the NC and GAP decompose simultaneously. Furthermore, the exothermic peak temperature of NC/GAP/submicron-HNS is lower than those of NC/GAP and submicron-HNS. Please note that for NC/GAP/submicron-HNS, there is also only one exothermic peak.
peak existing in the DSC trace. This means that NC, GAP, and submicron-HNS decompose simultaneously. Meanwhile, the peak temperature for NC/GAP/submicron-HNS is somewhat lower than that of NC/GAP and is substantially lower than that of submicron-HNS. Thus, we propose that decompositions of NC, GAP, and submicron-HNS induce each other. NC and GAP have a strong induction and catalysis for the thermal decomposition of HNS, which causes HNS to decompose in advance. Meanwhile, the heat released by HNS benefits to the thermal decomposition of NC and GAP. Overall, the thermolysis of NC, HNS submicron particles, and GAP cooperates with each other. What counts is that the specific surface area of the fibers obtained by electrospinning is relatively large and the submicron-HNS is closely dispersed in the NC/GAP fibers. Hence, the thermal conductivity is high, the heat-mass transfer process is easier, and the thermal decomposition temperature is lower. The apparent activation energy ($E_a$), pre-exponential factor ($A$), and rate constant ($k$) are calculated by Kissinger equation (eq 1) and Arrhenius equation (eq 2). The $E_a$ for NC/GAP/submicron-HNS is 204 kJ·mol$^{-1}$, which is higher than $E_a$ for NC/GAP and is lower than $E_a$ for submicron-HNS. The $k$ value for NC/GAP/submicron-HNS is higher than the other two. These mean that NC/GAP/submicron-HNS is of a high decomposition rate.

Table 2. BET Surface Area and Pore Structure Parameters of Fibers

| samples                  | BET surface area (m$^2$·g$^{-1}$) | pore volume (cm$^3$·g$^{-1}$) | pore size (nm) |
|-------------------------|-----------------------------------|-------------------------------|----------------|
| NC/GAP                  | 4.3573                            | 0.004422                      | 4.05911        |
| NC/GAP/submicron-HNS    | 4.6885                            | 0.004466                      | 3.81053        |

Figure 5. XPS spectra of NC/GAP/submicron-HNS: (a) typical XPS survey spectra; (b) C 1s XPS spectra; (c) N 1s XPS spectra; (d) O 1s XPS spectra.

Figure 6. BET data: (a) NC/GAP; (b) NC/GAP/submicron-HNS fibers.
activation reaction, whose values are positive numbers, implying that all activation processes are nonspontaneous. \( \Delta H \neq \) represents the energy required for molecular activation. Compared with submicron-HNS, the activation process of NC/GAP/submicron-HNS need less energy. Figure 7e shows kinetic compensation effect among decomposition of the three samples. It indicates that the three points do not locate in a straight line. This means that in kinetics, the decomposition mechanisms of the three samples are different.

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

(1)

To further investigate the decomposition mechanism of the samples, TG-IR analysis is employed to reveal the gas products.

Table 3. Thermodynamic and Kinetic Parameters Deduced from DSC Traces

| samples                      | \( T_p \) (K) | \( \Delta H^\circ \) (kJ·mol\(^{-1}\)) | \( \Delta G^\circ \) (kJ·mol\(^{-1}\)) | \( \Delta S^\circ \) (J·mol\(^{-1}\)·K\(^{-1}\)) | \( E_K \) (kJ·mol\(^{-1}\)) | \( \ln A_k \) | \( k \) (s\(^{-1}\)) |
|-----------------------------|---------------|----------------------------------------|----------------------------------------|-----------------------------------------------|-----------------------------|-------------|-----------------|
| submicron-HNS               | 616           | 219                                    | 156                                    | 104                                           | 224                         | 44          | 0.98            |
| NC/GAP                      | 469           | 176                                    | 115                                    | 130                                           | 180                         | 47          | 1.43            |
| NC/GAP/submicron-HNS        | 455           | 200                                    | 111                                    | 196                                           | 204                         | 54          | 1.74            |

Figure 7. Thermal analysis of samples. (a–c) for DSC traces of samples; (d) for Kissinger plots of \( \ln(\beta/T_p^2) \) to 1000/\( T_p \); (e) for the kinetic compensation effect.
for thermolysis of NC/GAP and NC/GAP/submicron-HNS. The TG and DTG curves are shown in Figure 8a,b, and the IR spectra extracted at different temperatures are presented in Figure 8c,d. Figure 8a indicates that the decomposition of NC/GAP initiates at 177 °C and its decomposition rate reaches the highest value at 197 °C; the decomposition ends at 199 °C. For NC/GAP/submicron-HNS, the onset temperature increases to 188 °C; the highest value is at 194 °C; the decomposition ends at 200 °C. This means that the decomposition process of NC/GAP/submicron-HNS is more concentrated. In IR spectra, the peaks located at 2308−2360 cm⁻¹ relate to the existence of CO₂. The weak peak at 2240 cm⁻¹ indicates the existence of few N₂O gas. The existence of NO accounts for the peak located at 1908−1920 cm⁻¹. The peaks located at 3264−3345 and 1667−1780 cm⁻¹ correspond to the existence of −CH and CH₂O fragments, respectively. The peak in 2096−2177 cm⁻¹ represents the existence of CO. The −N₃ group, which is an energetic group of GAP, should decompose to N₂. However, N₂ is a kind of nonpolar molecule and cannot be detected by IR spectrometer. The decomposition products of NC/GAP/submicron-HNS are almost same as that of NC/GAP. The only difference lies in the existence of −C=O−C=− fragments in the case of NC/GAP, that is, there are no −C=O−C=− fragments existing in decomposition products of NC/GAP/submicron-NHS. Additionally, for NC/GAP/submicron-HNS, the peak intensity of −CH₂O fragments is obviously lower than that for NC/GAP. These imply that more −C=O−C=− and CH₂O fragments are oxidized to CO₂, CO, and H₂O in the case of NC/GAP/submicron-HNS because the introduction of submicron-HNS improves the oxygen balance of the fiber. The signal of CO₂ is stronger than others for both samples. CO₂ is a ideal product gas.¹⁷ This is because more CO₂ in decomposition products benefits to heat liberation of the decomposition, owing to the lowest formation enthalpy of CO₂ compared with other gas products such as CO, N₂O, and NO.

2.3. Energetic Properties. It is important to test the sensitivity and evaluate the energy performance of NC/GAP/submicron-HNS because these two aspects exhibit their energetic properties. The standard specific impulse (Iₛ𝐩), characteristic velocity (C*), combustion chamber temperature (Tₛ), and average molecular weight of combustion products (Mₛ) are calculated and the results are listed in Table 4.

![Figure 8. TG-IR analysis of samples. (a,b) TG and DTG curves; (c,d) IR spectra of decomposition products at different temperatures.](image-url)

| samples                      | impact sensitivity | energy performance |
|------------------------------|--------------------|--------------------|
|                              | Hₛ (cm)            | Iₛ (N·s·kg⁻¹)     | C* (m·s⁻¹) | Tₛ (K) | Mₛ (g·mol⁻¹) |
| NC (50%)/GAP (50%)          | 59                 | 2014               | 1240      | 1556   | 22          |
| HNS (100%)                  | 94                 | 2130               | 1359      | 2396   | 26          |
| NC (37.5%)/GAP (37.5%)/HNS (25%) | 79                | 2032               | 1260      | 1705   | 23          |

*¹²Iₛ is standard specific impulse; C* is characteristic speed; Tₛ is combustion chamber temperature; Mₛ is average molecular weight of combustion products. All the parameters were calculated by means of software ProPep 3.0 at conditions of Pₛ/Pₑ = 70/1 (Pₑ = 0.1 MPa) and T₀ = 298 K.

Meanwhile, the impact sensitivity of submicron-HNS, NC/GAP, and NC/GAP/submicron-HNS are tested and the results are also tabulated in Table 4. Moreover, the combustion products and their molar ratio are calculated and the results are shown in Figure 10. In the sensitivity test, the special height (Hₛₒ) of NC/GAP/submicron-HNS is obviously higher than Hₛₒ of NC/GAP and is slightly lower than Hₛₒ of submicron-HNS. This means that the impact sensitivity of NC/GAP/
submicron-HNS is clearly lower than that of NC/GAP and is somewhat higher than that of submicron-HNS, that is, introduction of submicron-HNS benefits to the decrease of impact sensitivity. For energy performance, it is distinct that $I_{sp}$ of NC/GAP/HNS is higher than $I_{sp}$ of NC/GAP. However, this does not mean that HNS is a kind of high-energy explosive, and the real reason should be ascribed to the higher formation enthalpy ($\Delta H_f$) and higher C/H mass ratio of HNS compared with those of NC/GAP.\footnote{\textsuperscript{31,34}} Especially, the $\Delta H_f$ of HNS is up to +128.03 kJ·kg$^{-1}$, but the $\Delta H_f$ of NC (50%)/GAP

![Figure 9](image-url)

Figure 9. Energy performances of NC/GAP/HNS fibers as a function of weight percentage of HNS: (a) for $I_{sp}$; (b) for $C^*$; (c) for $T_c$; (d) for $M_c$.

![Figure 10](image-url)

Figure 10. Combustion products and their molar ratios for NC/GAP/HNS fibers. (a) For NC (50%)/GAP (50%); (b) for HNS (100%); (c) for NC (37.5%)/GAP (37.5%)/HNS (25%). The results in the figure were calculated by means of software ProPep 3.0 at conditions of $P_c/P_e = 70/1$ ($P_e = 0.1$ MPa) and $T_0 = 298$ K.
(50%) is low to $-1188.8 \text{ kJ kg}^{-1}$. Hence, the introduction of HNS to NC/GAP is quite beneficial to the improvement of the energy performance in thermodynamics. In addition, the C/H mass ratio of HNS is 28.03, but that of NC (50%)/GAP (50%) is mere 8.36. Please note that the value of oxygen balance ($\text{OB}_{\text{CO}_2}$) is also important for evaluating the energy performance. For different samples, their values of the C/H mass ratio are of comparability only under the condition that the samples are of closed $\text{OB}_{\text{CO}_2}$ values. $\text{OB}_{\text{CO}_2}$ of HNS is $-67.5\%$ which is close to the $\text{OB}_{\text{CO}_2}$ of NC (50%)/GAP (50%) ($-78.1\%$). Upon this, we conclude that obviously the higher C/H mass ratio results in a remarkable increase in combustion temperature ($T_c$), which accounts for the result listed in Table 4. The value of $T_c$ is determined by the heat release from the combustion of propellants, which represents the chemical energy storage of an energetic formulation. Figure 9c reveals that the value of $T_c$ increases linearly with increasing of weight percent of HNS. This indicates that chemical energy storage of HNS is higher than that of NC/GAP. Of course, for energy performance, the discrepancy cannot be fully explained only on the aspect of chemical energy storage. The work done by the gas products is also very important. Heat released from the combustion of propellant must be converted to work as much as possible. This is called “energy conversion efficiency”. The hydrogen content in the molecules of energetic materials is responsible for this. The decrease of hydrogen content leads to an increase of average molecular weight ($M_n$), which is adverse to energy conversion efficiency of the combustion. Higher hydrogen content in energetic molecules will result in higher $H_2$ percent in the combustion products. Figure 10a,b indicates that the $H_2$ percent for combustion of NC (50%)/GAP (50%) reaches 28% and the $H_2$ percent for combustion of HNS is only 14%. This accounts for the high $M_n$ value of HNS compared with low $M_n$ value of NC/GAP. Thus, Figure 9d shows that $M_n$ increases with increasing of weight percent of HNS. Lower $M_n$ value means that the same heat, released from combustion of propellants, does less work. However, herein, despite the lower $M_n$ value, NC/GAP also possesses an obviously lower $I_{sp}$ than HNS. This is because for NC/GAP, its rich hydrogen content cannot compensate its poor C/H mass ratio, that is, the storage of chemical energy dominates the energy performance. Of course, besides the C/H mass ratio, high formation enthalpy of HNS also contributes its high energy storage of an energetic formulation. Figure 9c reveals that the NC/GAP fiber leads to increases of $T_c$ and $I_{sp}$ which means addition of HNS is propitious to the enhancement of energy performance. The impact sensitivity of NC/GAP/submicron-HNS is obviously lower than that of NC/GAP, illustrating that as-spun NC/GAP/submicron-HNS possesses observable safety. Therefore, the composite fiber shows a potential application in solid propellants. It is believed that this operable technology is universal and could be used to fabricate other energetic composite fibers.

4. EXPERIMENTAL SECTION

4.1. Materials. Raw 2,2′,4,4′,6,6′-hexanitrostilbene (HNS) was obtained from Gansu Yinguang Chemical Co., Ltd (Baoyin city, Gansu province, P. R. China). NC (12.6% N, industrial grade) was purchased from Foshan Junyuan Chemical Co., Ltd (Foshan city, Guangdong province, P. R. China). GAP (M<sub>n</sub> = 4000, hydroxyl value of 0.49 mmol·g⁻¹) was purchased from the 42nd Institute of the Fourth Academy of China Aerospace Science and Technology Corporation. Ethanol (EtOH) and acetone were purchased from Tianjin Guangfu Chemical Co., Ltd (Tianjin city, China).

4.2. Preparation of NC/GAP/Submicron-HNS Composite Fiber. First, submicron-HNS was obtained by the mechanical milling method. The ingredients, including 200 g balls, 6 g HNS, 60 mL deionized water, and 60 mL EtOH, were added into a mill jar. Four jars were sealed and fixed on the ball mill. The mill rotated at 350 rpm for 6 h. The HNS submicron particles were separated from the suspension and dried by freeze drying. The 0.3 g submicron-HNS was added into 4.4 g acetone to obtain suspension solution (a) (0.45 g NC and 0.45 g GAP were dissolved into 4.4 g acetone to obtain suspension solution (b). Suspension solution (a) was slowly introduced into suspension (b) to form the precursor solution (12 wt %), in which the mass ratio of NC, GAP, and submicron-HNS was set to 3:3:2. For comparison, NC/GAP precursor solution (12 wt %) was also prepared by dissolving 0.6 g NC and 0.6 g GAP into 8.8 g acetone, in which the mass ratio of NC and GAP was set to 1:1. In both electrospinning processes, the inner diameter of the needle is 0.8 mm; the flow rate was set as 3–5 mL·h⁻¹, and the applied voltage was fixed at 12–18 kV; the collection distance was kept at 12 cm; the humidity was controlled at 40–50%. The obtained electrospun fibers were collected on an aluminum foil. The preparation scheme is described in Figure 11.

4.3. Characterization. The morphology of fiber is observed by a SEM (Hitachi SU8010). energy-dispersive X-ray, XRD, XPS, and IR analyses were conducted to characterize the structure of fibers. The diameter of particles and fibers are measured by the software Nano Measurer 1.2.5. The XRD analysis is performed on a DX-2700 X-ray diffractometer (Haoyuanyuan) with Cu Kα radiation. The IR spectrum is obtained on an infrared spectrometer (American Thermo Fisher Scientific Nicolet 6700). XPS is conducted with XPS and a PHI5000 Versa-Probe (ULVAC-PHI). The Brunauer–Emmett–Teller (BET) measurements are performed utilizing the nitrogen adsorption with the Micrometrics ASAP 2010 instrument. Thermal analysis is conducted on a DSC (TA Model Q600) at heating rates of 5, 10, 15, and 20 °C/min. TG-IR analysis is performed on a thermal analyzer system (TG/DSC, Mettler Toledo) coupled with a Fourier transform infrared spectrometer in the nitrogen atmosphere. The impact

3. CONCLUSIONS

The NC/GAP/submicron-HNS fiber membrane is successfully prepared by the electrospinning method, in which HNS submicron particles incorporate with NC/GAP fibers. With the submicron-HNS being assembled in the NC/GAP matrix, the decomposition temperature as well as activation energy could be significantly decreased, and decomposition rate should be remarkably improved. This suggests that the NC/GAP/submicron-HNS fibers decompose comparatively easily and rapidly. Thermal decomposition of NC/GAP/submicron-HNS occurs at relatively low-temperature range of 174–185 °C. The decomposition products of NC/GAP/submicron-HNS are similar to that of NC/GAP. The quite clean products enable NC/GAP/submicron-HNS to be a prospective candidate material in low-signature propellants.

Both energy performance and safety are pivotal properties of energetic materials. The introduction of submicron-HNS to NC/GAP fiber leads to increases of $T_c$ and $I_{sp}$ which means addition of HNS is propitious to the enhancement of energy performance. The impact sensitivity of NC/GAP/submicron-HNS is obviously lower than that of NC/GAP, illustrating that as-spun NC/GAP/submicron-HNS possesses observable safety. Therefore, the composite fiber shows a potential application in solid propellants. It is believed that this operable technology is universal and could be used to fabricate other energetic composite fibers.
sensitivity of samples is tested by using an HGZ-1 impact equipment.

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**Notes**

The authors declare no competing financial interest.

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