Preparation of CNTs Coated with Polydopamine–Ni Complexes and Their Catalytic Effects on the Decomposition of CL-20

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ABSTRACT: To improve the condensed-phase reaction rate of ε-CL-20, polydopamine (PDA)–nickel complex-coated multiwalled carbon nanotubes (CNTs) have been prepared and used as combustion catalysts. The PDA–Ni complex has been prepared and in situ coprecipitated with ε-CL-20 by an antisolvent crystallization process in its dimethyl sulfoxide (DMSO) solution. It has been shown that crystalline CL-20 composites included with PDA–Ni complexes are polygon-shaped with a smooth surface and an average diameter of 10–15 μm, whereas it is 140 μm for raw ε-CL-20 crystals. The catalytic reactivity of the complex on thermolysis of CL-20 has been investigated using the differential scanning calorimetry (DSC) and thermogravimetry (TG)-coupled Fourier transform infrared (FT-IR) spectroscopy technique. It has been found that CNT@PDA–Ni complexes have catalytic effects on the decomposition of ε-CL-20 by decreasing/shifting of the exothermic peak from \( T_p = 240.1 \) to 238.7 °C. The FT-IR spectra of CL-20 decomposition products under the effect of the catalyst predominantly show peaks at 1274, 1644 and 1596, 1912, 2265, and 1956 cm\(^{-1}\), indicating the presence of fragments with \( \text{N}_2\text{O}, \text{NO}_2, \text{NO}, \text{HNCO}, \) and \( \text{NO}/\text{CO}, \) respectively. The change in the ε-CL-20 decomposition mechanism should be attributed to the catalytic action of CNT, decreasing the formation of \( \text{NO}_2. \) Also, under the effect of the carbon-based catalyst, the HNCO formation was detected at another temperature in comparison with raw CL-20, with peak absorption at 224.1 vs 232.3 °C and the evolution was completed at 250.8 vs 246.2 °C, respectively.

INTRODUCTION

e-CL-20 (Hexanitrohexaazaisowurtzitane, HNIW) is a poly-cyclic nitramine, which is a relatively new kind of energetic material (EM) with a three-dimensional (3D) cage structure, with quite high energy density, great chemical stability, and detonation performances. Despite its polymorphic transition from \( \varepsilon \) to \( \gamma \), problems in the presence of polar solvents or plasticizers and sensitivity to external factors leading to reduced safety, great energy, and combustion performance have motivated researchers to address these existing disadvantages for future applications.1 CL-20 is usually presented in different polymorphs,2 and among them ε-CL-20 is considered as the best form due to its highest performance and stability.3 It is the most promising candidate replacement of currently used high-energy nitramines such as hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX) or octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine (HMX) compounds.3

The thermal decomposition of CL-20 (micro, nano) has been widely investigated using theoretical techniques such as the molecule dynamic simulation4,5 and various analytical studies including differential scanning calorimetry coupled with thermogravimetry (DSC–TG), dynamic vacuum stability test (DVST), electronization mass spectrometry (EI-MS), Fourier transform infrared spectroscopy (FT-IR), and accelerating rate calorimetry (ARC).7,8 Also, the detailed chemical pathways of the effect of polymer on the decomposition pathways of ε-CL-20 under fast heating (300 K ps\(^{-1}\)) have been modeled by the reactive molecular dynamics simulation (ReaxFF-lg).9 Although much research has been carried out on the thermal decomposition of ε-CL-20 mentioned above, studies based on DSC–TG coupled with FT-IR and mass spectrometry have not been well reported.10,11

According to a recent report, investigations have reached a unanimity in increasing the thermal conductivity of energetic composites by adding carbon-based nanomaterials (CNMs) with high thermal conductivity.12 It has been shown that various CNMs and their derivatives could be used as an effective additive for the enhancement of desirable characteristics of propellant decomposition and combustion.13 To decrease the sensitivity and improve the stability of ε-CL-20, the most perspective stabilizers used could be the CNMs, such as graphene, carbon nanotubes (CNTs), and fullerenes, which...
have excellent physical properties that benefit the sensitivity of energetic crystals.\textsuperscript{14} Graphene oxide (GO) contains many oxygen-containing functional groups,\textsuperscript{15} and it was considered as a great desensitizing material with a certain level of energy.\textsuperscript{16} It was reported that graphene oxide sheets stabilized the energetic crystals before decomposition\textsuperscript{27} and catalyze the liquid- or gas-phase reactions during the decomposition and combustion process of EMs,\textsuperscript{18} which is very unique and promising for the fabrication of high-performance solid propellants.\textsuperscript{19} It shows that the addition of reduced graphene oxide (rGO)/CNT could improve the thermal conductivity of ε-CL-20 crystals and therefore reduce the probability of hot spot formation under external stimuli.\textsuperscript{20} Similar results were recently confirmed on the synergetic action of carbon mesosphere-decorated hematite nanoparticles (NPs) on the thermal decomposition of nitrocellulose.\textsuperscript{21} Such work can strengthen the new behavior of carbon-based nanomaterials in the field of decomposition of EMs.

It was previously reported that single-walled CNTs demonstrate a lower synergistic enhancing effect in terms of safety and energy release rate than the other carbon nanomaterials such as fullerences or GO nanosheets.\textsuperscript{22} Later on, multiwalled CNTs attracted much attention as catalyst supports on account of their outstanding properties, such as good electrical conductivity, large specific surface area, strong mechanical property, excellent corrosion resistance, and satisfying chemical and thermal stabilities.\textsuperscript{23,24} Nevertheless, owing to the inertness of multiwalled CNTs, there are not enough active sites or functional groups to combine with catalyst supports by well dispersing the active and metal oxide species (Fe\textsuperscript{2+}, Co\textsuperscript{2+}, Cu\textsuperscript{2+}), but without special techniques, it will not be possible to fix the metal ions on the outer walls.\textsuperscript{27} Therefore, the surface pretreatment of multiwalled CNTs via coating with high adhesive polymer appears to be a good solution to depositions of catalyst NPs. Polydopamine (PDA) was presented as a novel coating material in 2007.\textsuperscript{28} The primary advantage of PDA is that it can be easily deposited on virtually all types of inorganic and organic surfaces, including superhydrophobic and wet surfaces. Moreover, the application field of PDA has been rapidly expanded and incorporated into a wide range of fields across the chemical, biological, medical, and materials sciences. Also, dopamine (DA) is useful as an organic ligand for the synthesis of the coordination polymer polydopamine and developing transition-metal–PDA (M@PDA) complexes. PDA-containing carbon and nitrogen atoms, as well as their well-known robust chelating capability with many types of transition-metal ions, became an ideal catalyst ligand for in situ production of N-doped carbon/N-doped metal–carbon hybrid materials without the need of additional chemical pretreatments that are typically required in traditional nonprecious metal catalysts. The beneficial properties of PDA can effectively avoid poor control over the reproducibility and chemical homogeneity, long preparation times, and deterioration of the structure of the target materials. Spectroscopic and electron microscopic studies reveal that the transition-metal ions are chelated with PDA units, forming homogeneous M@PDA complexes.\textsuperscript{29}

Very recently, PDA has been widely utilized for surface modification, where it could be prepared by spontaneous oxidative polymerization of dopamine under weak alkaline conditions, which can be firmly bonded to various substrates.\textsuperscript{31,32} In addition, it is reported that PDA can covalently and noncovalently bind to the surfaces of substrates.\textsuperscript{33} Based on these unique properties of PDA, and the possibility of the synthesis of M@PDA complexes with further functionalization of MWCNTs, it is suggested to be a promising method of the preparation of the novel type of combustion catalysts.

This approach could be applied to construct the M@PDA complex in the form of thin coatings on the MWCNT surface, with further carbonization to produce promising combustion catalysts with well-dispersed metal oxide nanoparticles embedded in MWCNTs walls. It is expected that M@PDA@CNTs prepared using this approach show great catalytic properties for the decomposition and combustion of EMs. Therefore, in the present study, these catalysts have been prepared and evaluated in terms of the catalytic effect on the decomposition of a typical high-energy nitramine ε-CL-20. A set of specific experiments of simultaneous DSC–TG coupled with FT-IR have been conducted to study the comprehensive thermal behavior of ε-CL-20 in the presence of these novel catalysts.\textsuperscript{34}

### EXPERIMENTAL SECTION

**Materials.** Hexanitrohexaazaisowurtzitane (CL-20) was provided by Modern Chemistry Research Institute with purity more than 99.5%; multiwalled CNTs (purity = 98%, average diameter > 50–100 nm, length = 10–20 μm) were purchased from Nanotechnology Co., Ltd.; dimethyl sulfoxide (DMSO) and ethyl acetate (C\textsubscript{3}H\textsubscript{6}O\textsubscript{2}) were purchased from Tianjin Fuyu Fine Chemical Co., Ltd.; absolute ethanol (C\textsubscript{2}H\textsubscript{6}O) was purchased from Tianjin Zhiyuan Chemical Reagent Co., Ltd.; tris(hydroxymethyl)aminomethane hydrochloride (Tris-HCl, 99%), dopamine hydrochloride (DA, 98%), and Ni(NO\textsubscript{3})\textsubscript{2}·6H\textsubscript{2}O were purchased from Sigma-Aldrich. All reagents were of analytical grade purity and used as received.

**Preparation of the PDA–Ni Complex.** First, 29 g of Ni(NO\textsubscript{3})\textsubscript{2}·6H\textsubscript{2}O was added to 10 mL of deionized (DI) water in a 50 mL round-bottom flask on a constant temperature heating magnetic stirrer to obtain a high concentration of the metal salt solution. Thereafter, 2 g of DA was added in 150 mL of DI water and mixed with 60 mg of Tris buffer for adjusting the pH to 8.5 using a dropping funnel, which was slowly added dropwise to the metal salt solution until the color became transparent when substantially all of the metal ions were coordinated with the DA. Then, the mixture solution was transferred to an oil bath and heated up to 60 °C. After reaction at 60 °C for 24 h, the resulting mixture was naturally cooled to room temperature. The product was collected by centrifugation and washed several times with DI water to remove residuals. Finally, the obtained product (PDA–Ni) was freeze-dried overnight.

**Preparation of CNTs Coated by the PDA–Ni Complex.** Briefly, CNTs doped by the PDA–Ni complex are prepared using the same procedure as the preparation of the PDA–Ni complex, except that in the polymerization process, 0.2 mg mL\textsuperscript{-1} of multiwalled CNTs (ultrasonically dispersed in ethanol) were suspended in the salt solutions as templates. Then, the polymerization reaction solution was centrifuged and thoroughly cleaned with DI water. Finally, the
obtained product (CNT@PDA−Ni complexes) was freeze-dried overnight.

**Preparation of CL-20/PDA−Ni and CL-20/CNT@PDA−Ni Composites.** To obtain the composites with the best performance, we have attempted the most suitable preparation methods (physical mixture (PM) and antisolvent (Ant) methods). Accurately weighed amounts of catalysts (PDA−Ni or CNT@PDA−Ni) and pure $\epsilon$-CL-20 were mixed by the PM method at a mass ratio of 1:5. A sample of PM was combined with ethyl acetate (0.4 mg mL$^{-1}$) to partially dissolve nitramine during the mixing process in an agate mortar. The prepared substances were filtered through a 0.45 μm membrane and dried at 50 °C for 12 h.

We prepared the CL-20/PDA−Ni composite using the Ant method and chose DMSO and ethyl acetate as solvent and nonsolvent, respectively (components in the mass ratio of 1:5). First, the prepared PDA−Ni was added to 50 mL of ethyl acetate solution and stirred uniformly. Then, 10 mL of the as-prepared solution of CL-20 (saturated solution in DMSO) was uniformly dropped into the ethyl acetate solution mixed with PDA−Ni and evenly stirred with a magnetic stir bar for 20
shown in Figure 2. The average sizes of raw observed with a scanning electron microscope (SEM) as CNT@PDA particles are in the common range of 15 μm. Finally, it was filtered and dried at 50 °C for 12 h, and the mixture of CL-20/PDA–Ni was prepared (Figure 1).

### RESULTS AND DISCUSSION

#### Analysis of Morphology

The morphologies of PDA–Ni, CNT@PDA–Ni, and their mixtures with ε-CL-20 are observed with a scanning electron microscope (SEM) as shown in Figure 2. The average sizes of raw ε-CL-20 crystal particles are in the common range of 15–20 μm (Figure 2a).35 The magnified SEM image in the inset (Figure 2b–d) highlights the nonhomogeneous morphology of PDA–Ni and CNT@PDA–Ni complexes and CL-20/PDA–Ni particles. Figure 2e shows PDA–Ni complex particles coated by ε-CL-20 obtained by the antisolvent method with anisotropy in their shape having a majority of hexagonal bipyramid-shaped particles. Inset (e) is evidences the sharp corners of ε-CL-20 like the hexagonal geometric morphology having a length of 1–10 μm. Compared with the raw crystal, the particle sizes are slightly reduced. It should be noted that the CL-20/CNT@PDA–Ni–PM sample was not visually destructed by the beam (Figure 2f). Figure 2f shows the morphology of the nonhomogeneous CL-20/CNT@PDA–Ni composite with various sizes in the range of 5–50 μm.

The SEM images in Figure 2f reveal some polygon-shaped CL-20/CNT@PDA–Ni–PM particles with wrapped CNT on the surface. They are distinctly separated from each other along with some particles with a few microns meters. The particle size distributions are uniform and tend to grow into cubic or flake-like crystals when PDA and CNT are combined as a composite dopant. Also, their surfaces are all smooth, free of defects, and they are hybrid crystals with the CNT-based dopants as the crystal seedling centers. However, the composites prepared by the PM method are nonuniformly distributed with many agglomerations. The surface remains smooth without any visible defects and roughness, but small nonreacted PDA particles were formed due to slight polymerization nonuniformity.

#### Mass Loss Properties

To study the effect of PDA–Ni and CNT@PDA–Ni complexes on the thermal decomposition of ε-CL-20, the TGA curves of involved materials under an argon atmosphere are shown in Figure 3. The weight of the catalysts was 20% of the total weight of the samples, and the decomposition characteristics of pristine catalysis are presented in Figure S1. The addition of these complexes would change the decomposition behavior of CL-20 (TG and DTG). The CNT@PDA–Ni–PM complex has the strongest catalytic effect on the decomposition reaction of CL-20, resulting in a high mass loss. The thermal decomposition is better than that obtained by the other catalysts and provides the lowest weight residue. The mass percentages of the residues showed a strong mass loss dependency. It can be seen that the ε-CL-20 in the physical mixtures with CL-20/CNT@PDA–Ni may undergo mass loss with a peak loss rate between 212.8 and 247.9 °C (Figure 3), and overall mass losses for the rate-limiting steps are 75.8 wt %. The effect of other catalysts on the mass loss of the raw sample was lower and does not differ from each other significantly. Although their thermal decomposition almost occurs simultaneously, the catalyst mixture method would strongly affect the stability and performances of ε-CL-20 (Table 1).

It should be noted that the inclusion of CNTs may increase the content of residues, which is logical due to the highly stable and nonvolatile nature of carbon nanomaterials.36–38 It confirms that the residual quantity shows an increasing trend with the increase of the dopant content. The highest mass loss was detected in sample CL-20/PDA–Ni–Ant with 87.9 wt % residual mass.

![Figure 3. TG curves from thermal decomposition of different samples: raw ε-CL-20, CL-20/PDA–Ni–PM, CL-20/PDA–Ni–Ant, and CL-20/CNT@PDA–Ni–PM at 5 K min⁻¹ heating rate under argon flow.](https://doi.org/10.1021/acsomega.1c03392)

### Table 1. TG/DTG Parameters of the Investigated Samples under a Heating Rate of 5 K min⁻¹

| sample                  | TG curves | DTG peaks |
|-------------------------|-----------|-----------|
|                         | T onset   | T offset  | Res | T onset | T offset | L max |
| raw CL-20               | 226.8     | 246.6     | 22.4 | 219.2   | 250.2   | 37.7  |
| CL-20/PDA–Ni–PM        | 225.2     | 245.3     | 49.1 | 220.7   | 246.5   | 29.1  |
| CL-20/PDA–Ni–Ant       | 222.3     | 244.1     | 46.6 | 216.1   | 246.1   | 24.4  |
| CL-20/CNT@PDA–Ni–PM    | 222.7     | 245.7     | 24.2 | 217.8   | 248.1   | 33.7  |

*a*T onset, the onset temperature for thermal decomposition, in °C; Res, the residual, in %; L max, the maximum mass loss rate, in % min⁻¹; and T offset, the end of decomposition temperature, in °C.

ACS Omega 2021, 6, 22866–22875
It is evident from the thermograms that the overall trends of mass loss of the composites are consistent with that of raw ε-CL-20, of which only one-step decomposition (unimolecular decomposition) was observed. It is noted that the temperature of thermal decomposition under the effects of these energetic complexes varies from 230.6 to 223.1 °C (5 K min⁻¹). The values of temperature were slightly decreased after the inclusion of CNTs, which implies that CNT doping would modify the thermal behavior of CL-20.

**Heat Flow Properties.** The catalytic action of PDA–Ni and CNT@PDA–Ni on thermal decomposition of CL-20 by different mixing methods in a ratio of 1:5 was also evaluated by DSC curves obtained at a heating rate of 5 K min⁻¹ (Figure 4).

![Figure 4. DSC curves from thermal decomposition of different samples: PDA–Ni, CL-20/PDA–Ni-PM, CL-20/PDA–Ni-Ant, and CL-20/CNT@PDA–Ni-PM at a heating rate of 5 K min⁻¹ under an argon flow.](image)

The peak maximum temperature (T_p) of decomposition for raw CL-20 is 241.5 °C. The T_p of exothermic decomposition for CL-20/PDA–Ni-PM, CL-20/PDA–Ni-Ant, and CL-20/CNT@PDA–Ni-PM are 240.1, 238.2, and 238.7 °C, which decreases by 1.4, 3.3, and 2.8 °C, respectively.

In the presence of the PDA–Ni complex (prepared by physical mixture), T_p was decreased slightly from 241.5 to 240.1 °C. It indicates that the PDA–Ni coordination complex has a thermal stabilization effect for CL-20. The addition of CNT may have a catalytic effect in the case of PDA–Ni, resulting in a lower T_p. The inclusion of CNT also decreases the T_p of CL-20 from 240.1 to 238.7 °C in comparison with PDA–Ni samples (Figure 4).

A certain decrease of heat release after the introduction by modified carbon-based materials of CNT is noted. As shown in Table 2, the heat release of raw CL-20 is 2312 J g⁻¹, but those of CL-20/PDA–Ni-PM, CL-20/PDA–Ni-Ant, and CL-20/CNT@PDA–Ni-PM are 2247.5, 2826.3, and 2050.0 J g⁻¹, respectively. Compared with the others, CL-20/PDA–Ni-Ant has the highest heat release (2826.3 J g⁻¹), and the corresponding exothermic peaks are located at 229.3 and 246.9 °C.

The comparison of the DSC–TG data for raw CL-20 and CL-20 in the presence of PDA–Ni and CNT@PDA–Ni clearly shows that the introduction of additives has a catalyst effect. The T_onset were decreased to around 1.4–6 °C. The addition of PDA–Ni and CNT@PDA–Ni complexes significantly affected the energy release. We may conclude that the CNT has a stabilization effect due to their thermal conductivity and heat transfer. The agglomeration problem of nanosized catalysts is excluded in the presence of CNT as the supported dispersion media, resulting in better contact with the CL-20 crystals. The catalytic performance of CNT@PDA–Ni for the thermal decomposition of CL-20 is superior to that of PDA–Ni, which may be caused by the synergetic effect of CNT to exhibit the best result.

**FT-IR Tests.** FT-IR-coupled DSC–TG technology was applied to analyze the gaseous products during thermolysis by the temperature/time-resolved method. In the diagrams, the intensity corresponding to the vibration modes of the different bonds or functional groups is represented by the wavenumber or temperature. The calibration factors were employed to estimate the gas composition. The thermolysis behavior of ε-CL-20 is depicted in the DSC–TG curve. The thermal decomposition process of ε-CL-20 was monitored by FT-IR spectroscopy at a heating rate of 5 K min⁻¹. Figure 5 shows the gaseous products with the decomposition of ε-CL-20, when the intensity of the FT-IR series has a maximum value. The temperature is about 240 °C. There are certainly N₂O (1274 cm⁻¹), NO₂ (1644 and 1596 cm⁻¹), HNO₂ (737 cm⁻¹), CO₂ (670 cm⁻¹), NO (1912 cm⁻¹), HNCO (2265 cm⁻¹), and NO/CO (1956–1800 cm⁻¹). FT-IR spectra show that the main gaseous products for thermal decomposition of ε-CL-20 are N₂O, NO₂, and HCN, which are also comparable with the literature.

It should be noted that the nitrogen gas cannot be registered by FT-IR–IR spectrometry, but its formation is unambiguous as it was detected by mass spectrometry during the decomposition of other experiments. The analysis of the temporal behavior (initial temperature) of the evolved gases detected by

| Table 2. Thermal Decomposition Peak Data and Physical Performance of Modified CL-20 Crystals with Different Dopants at a Heating Rate of 5 K min⁻¹.¹ |
| --- |
| **sample** | C_d | T_p | T_onset | T_offset | ΔH |
| raw CL-20 | 0.20 | 241.5 | 230.6 | 246.8 | 2312.0 |
| CL-20/PDA–Ni-PM | 0.20 | 240.1 | 230.0 | 247.3 | 2247.5 |
| CL-20/PDA–Ni-Ant | 0.20 | 238.2 | 229.3 | 246.9 | 2826.3 |
| CL-20/CNT@PDA–Ni-PM | 0.20 | 238.6 | 228.8 | 246.0 | 2050.0 |

¹C_d ratio of the catalyst; T_onset, the onset temperature for thermal decomposition, in °C; T_p, the peak of maximum temperature, in °C; T_offset, the end of decomposition temperature, in °C; ΔH, the heat release, in J g⁻¹.
shows an initial increase in NO₂ and HNCO closely followed by a synthetic release of all other species (NO, N₂O, etc.). As the reaction rate increased, NO₂ became the predominant species, as indicated by the increasing absorbance value of NO₂. The thermolysis of the CL-20/CNT@PDA–Ni-PM composite product distribution showed another picture: first, in the gas phase, HNCO appears and only after that, the other products followed by NO are released. The comparison of the gas composition for both compounds shows that the amounts of HNCO, N₂O, NO, NO₂, and others not listed (CO₂, CO, HCN) in Figure 6, decreased.

The CO₂ absorption peak at 670 cm⁻¹ of the raw CL-20 sample (Figure 6) can be clearly seen. As the temperature increased, the absorption peak gradually increased. It can be seen that CO₂ has continuously been released throughout the experiment. The NO₂ and HNCO absorption peaks at 1631 and 2239 cm⁻¹, respectively, in the middle portion appear at around 233 °C. The absorption peak at 715 cm⁻¹ for the HCN structure and other minor gases began to appear at 235 °C. The CO₂ signal was continuously released throughout all ranges of the experiment and had a maximum intensity peak located at 243 °C.

Depending on the comparatively low intensity of NO₂ and HNCO, it becomes difficult to evaluate their appearance temperature. However, the signals remained in their respective places. The T_onset, T_peak, and T_offset for the main ion numbers and the possible assignments are summarized in Table 3. The CL-20/PDA–Ni-PM formation temperature of the gas products shifted to the right side. The intensity of all absorption peaks was lower than the pure CL-20. The HNCO absorption peak appeared at about 240 °C, and the absorption peaks of NO₂ and CO₂ appeared at 242 °C. The absorption peak of minor gases located around 715, 1307, and 1912 cm⁻¹ appeared at 244 °C. Compared with the raw CL-20 and CL-20/CNT@PDA–Ni-PM, the NO₂ absorption peak at 1631 cm⁻¹ significantly decreased but appeared at the same temperature. The HNCO absorption peak was also lower than the first two samples and located at a more narrow range of temperature.

The temperatures of the maximal gas release were determined between 235 and 245 °C. The NO₂ absorption peaks at 1631–1590 cm⁻¹ of all of the above samples (Figure 7) can be clearly seen. As the temperature increases up to 229 °C, the absorption peak immediately increased. It can be seen that NO₂ was rapidly released without reaching the end of the experiment and reaches a maximum value between 235 and 245 °C. The end temperatures of raw CL-20 decomposition (244–260 °C) show only NO₂, indicating the leftover carbon being oxidized by traces of oxygen in the system (Figure 8). As seen from the three-dimensional FT-IR spectrum, the intense release of NO₂ is restricted to the relatively narrow range of temperature (about 231–245 °C). The formation of HNCO is similarly restricted to the relatively narrow range of temperature (about 229–247 °C), but it continues until the end of the experiment in small amounts. Also, shown is a temporal evolution of HNCO appearing during the thermal decomposition of different samples at a heating rate of 5 K min⁻¹ under a nitrogen atmosphere is shown. It can be seen that the intensity of HNCO has a large value, appearing in a wide range of temperatures, and does not depend on the presence of PDA–Ni or CNT@PDA–Ni.

In contrast, the main decomposition products of the CL-20/PDA–Ni-PM composite included the same gas products mapping (NO₂, NO, HCN, N₂O, etc.), as shown in Figure 8.
The intensity of the FT-IR spectrum of the composite decomposition products was very different from that of the decomposition products of raw CL-20.

**Figure 7.** Temporal evolution of NO2 and HNCO species appearing from different samples: CL-20, CL-20/PDA–Ni–PM, CL-20/PDA–Ni–Ant, and CL-20/CNT@PDA–Ni–PM during the thermal decomposition at a heating rate of 5 K min−1.

Table 3. FT-IR Spectral Analysis of Gaseous Products of Various Samples, Thermal Decomposition Corresponding to Temperatures (T onset−T peak−T offset), and Wavenumber

| possible assignment | n | T onset−T peak−T offset | T peak | wavenumber, cm−1 |
|---------------------|---|-------------------------|--------|-------------------|
| Raw CL-20           |   | 229.4−246.6             | 241.1  |                   |
| CO2                 | 670 | 229.4−246.6             | 241.1  |                   |
| HCN                 | 715 | 240.7−248.1             | 240.6  |                   |
| N2O                 | 1307 | 236.5−247.2             | 240.6  |                   |
| NO2                 | 1631 | 233.7−248.1             | 240.1  |                   |
| NO                  | 1912 | 235.8−248.9             | 240.6  |                   |
| HNCO                | 2239 | 232.3−246.2             | 241.1  |                   |
| CL-20/PDA–Ni–PM    |   | 242.4−255.6             | 248.4  |                   |
| CO2                 | 670 | 228.8−246.8             | 238.1  |                   |
| HCN                 | 715 | 232.5−249.1             | 241.1  |                   |
| N2O                 | 1307 | 232.3−244.9             | 241.2  |                   |
| NO2                 | 1631 | 230.1−245.3             | 238.5  |                   |
| NO                  | 1912 | 232.8−244.8             | 241.1  |                   |
| HNCO                | 2239 | 230.3−252.2             | 241.2  |                   |
| CL-20/PDA–Ni–Ant   |   | 231.2−243.7             | 236.5  |                   |
| CO2                 | 670 | 230.1−243.7             | 236.5  |                   |
| HCN                 | 715 | 229.1−249.2             | 238.1  |                   |
| N2O                 | 1307 | 233.5−248.2             | 238.2  |                   |
| NO2                 | 1631 | 235.7−246.1             | 240.1  |                   |
| NO                  | 1912 | 233.8−248.9             | 238.1  |                   |
| HNCO                | 2239 | 224.1−250.8             | 238.5  |                   |

αT onset, the onset temperature for thermal decomposition, in °C; T peak, the peak of maximum temperature, in °C; T offset, the end of decomposition temperature, in °C; n, wavenumber, in cm−1.

Figure 8 shows the three-dimensional FT-IR mapping of gaseous products of thermal decomposition of CL-20. From the point of view of CL-20 decomposition, the evolution of NO2 gas is very interesting. As mentioned before, the main release event of NO2 is within the temperature range from 231 to 245 °C, where the intensity reached the largest value in comparison to other gases. This intensity range is much lower than that observed in the case of decomposition of the other samples. The change in the CL-20 decomposition mechanism should be attributed to the catalytic action of CNT, decreasing the formation of NO2.

First, the infrared absorption of HNCO became extremely low (less than 200 units). In addition, the absorption bands of N2O, CO, and HCN disappeared and the absorption bands of NO and NO2 weakened. Compared to the intensity of the previous sample, which is 900−1350 absorbance units (e.g., for NO2 gas), the amount of gas is lower but evident.

**CONCLUSIONS**

In summary, PDA–Ni and CNT@PDA–Ni complexes were successfully prepared by the DA polymerization method. The effect of these catalysts on ε-CL-20 thermal decomposition was investigated by DSC–TG coupled with FT-IR techniques. The main conclusions are as follows.

The CNT-stabilized Ni complexes of polydopamine had great impact on the decomposition of ε-CL-20 due to the excellent electron conductivity and catalytic properties. First, transition-metal complexes of polydopamine, which is very reactive, decreases the decomposition onset temperature of CL-20. Second, carried by CNTs, the PDA–Ni complex shows improved thermal stability in comparison to the complexes without CNTs. Such characterization results in a kind of EM with excellent thermal stability and high catalytic activity. The results of the thermal analysis showed that the modification can also effectively improve the phase stability of CL-20. The exothermic peak temperature for thermal decomposition was improved by 6 °C with the increased heat release of 514.3 J g−1. The heat release of CL-20/PDA–Ni–Ant is 2826.3 J g−1, higher than that of the raw ε-CL-20 (2312 J g−1). The combination of PDA–Ni and CNTs makes it achieve the best synergistic catalytic effect on the thermal decomposition of CL-20. In particular, the CNTs, due to a larger specific surface area, can be effectively dispersed in matter. It formed numerous heat flows and also could combine with PDA–Ni to exhibit a better thermal decomposition efficiency of CL-20.

From the above analyses, it is assumed that in the presence of the novel catalysts the homolytic cleavage of the N-NO2 and HNCO bonds is the basic act that a thermal decomposition of CL-20/PDA–Ni–PM, CL-20/PDA–Ni–Ant, and CL-20/CNT@PDA–Ni–PM during the thermal decomposition at a heating rate of 5 K min−1.
mechanism of the temporal evolution of gaseous species. However, the product still needs to be tested for combustion performance. Hence, the future experimental direction is still to reduce the sensitivity of CL-20 and conduct a more indepth study of modified samples.

**ASSOCIATED CONTENT**

- **Supporting Information**
  The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.1c03392.
  Preparation methodology, SEM images, DSC–TG results, and other experimental data (PDF)

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**Notes**
The authors declare no competing financial interest.

**ACKNOWLEDGMENTS**
This paper was funded by the NSAF Project (Grant No. U2030202) and the funding of the National Natural Science Foundation of China (51776176).

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