

FACILE PREPARATION OF HUMINS-LOADED GRAPHITIC
CARBON NITRIDE WITH IMPROVED CATALYTIC
ACTIVITY ON THE THERMAL DECOMPOSITION
OF AMMONIUM PERCHLORATE

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Abstract

Novel g-C₃N₄/humins (denoted as CNH) composite was synthesized through a simple two-step method. The results indicated that humins nanoparticles with sizes ≤ 200 nm were successfully loaded on the surface of g-C₃N₄ (CN). The catalytic effect of the as-prepared composite on the thermal decomposition of ammonium perchlorate (AP) was investigated by means of thermogravimetric and differential thermal analyses (TG-DTA). Compared with pure CN, CNH was proved to catalyze the thermal decomposition of AP more effectively. Specifically, the high temperature decomposition step of AP was decreased by 80.9°C, with an increase of the total heat release to 1320 Jg⁻¹. Besides, the possible catalytic mechanism of AP decomposition was discussed.

Key words: g-C₃N₄, humins, ammonium perchlorate, catalysis

Introduction. As a strong oxidant, AP is the main component (60–80 wt%) of composite solid rocket propellants [1]. Thus, the thermal decomposition characteristics of AP strongly influence the overall combustion performance of the fuel. It is established that the more exothermic heat and lower high-temperature decomposition (HTD) play an important role in the presentation of AP [2]. It has been demonstrated that the decomposition of AP can be accelerated by various

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catalysts. So far, the catalytic effects of nanometer-sized metal powders, transition metal oxides, fullerenes and carbon nanotubes have been reported toward AP thermal decomposition [3]. However, these additives possess high toxicity, high cost, and/or complicated synthetic procedures, which limit their applications.

Li et al. [4] demonstrated for the first time that due to its semiconducting properties, the polymeric graphite-like carbon nitride (CN) could be an effective catalyst for AP decomposition. More specifically, these authors reported that adding 10 wt% CN to AP decreases its HTD by 70 °C and, moreover, the apparent decomposition heat of AP in the presence of CN is much higher than that of the pure AP. Besides, efforts to enhance the catalytic efficiency of CN by coupling with metal oxides have been made [5]. Thus, due to its nontoxicity and ease of preparation, the fabrication of novel CN-based catalysts for AP thermal decomposition is of constant interest.

In this paper we report, to the best of our knowledge, the first realization of a composite material (CNH) comprising CN and humins with enhanced catalytic activity toward AP thermal decomposition. Humins are amorphous carbonaceous by-products derived from the acid-catalyzed dehydration of glucose/pentose obtained from lignocellulosic biomass or via the reaction of concentrated sulphuric acid with sugars [6]. Humins structure consists of a furan-rich polymer network comprising different oxygen-containing functional groups. We demonstrate a simple synthesis route to fabricate CNH via dehydration of sucrose, pre-adsorbed onto CN surface, by concentrated H₂SO₄. The results show that humins act as a co-catalyst and improve the overall performance of CN for AP thermal degradation.

Experimental. All the reagents involved in the experiments were of analytical grade. The starting CN was prepared according to the procedure reported previously in the literature [7]. Briefly, 10 g of urea was calcined at 550 °C for 3 h in a covered corundum crucible placed in an oven. The as-obtained yellow powder was washed with bi-distilled water and dried at room temperature overnight. The construction of CNH was accomplished via two-step synthetic method. At first step, 0.12 g of the previously obtained CN was added to 20 mL 0.2 M sucrose water solution and the suspension was continuously agitated for 24 h at room temperature in order to adsorb sucrose on the surface of CN. After that, the material was filtered and dried in air at room temperature for 12 h. In the second step, the as-obtained material (denoted as CNS) was suspended in 10 mL concentrated sulphuric acid in a beaker and stirred for 20 min. Finally, the as-formed CNH was filtered, washed repeatedly by bi-distilled water and dried at 70 °C for 12 h. The Fourier transform infrared (FTIR) spectra were obtained by using Nicolet 6790 FT-IR (Thermo Scientific) spectrometer in KBr pellets. Transmission electron microscopy (TEM) analyses were performed on a JEOL 2100 scanning microscope. Photoluminescence (PL) spectra at 300 nm excitation were measured using a Perkin-Elmer LS-55 fluorescence spectrometer. For cat-

alytic tests, AP was blended with CN and CNH by slight grinding in the presence of absolute ethanol in an agate mortar for 15 min and dried in an oven at 60 °C overnight. The samples were labelled AP/CN and AP/CNH, respectively. The weight percentage of the catalyst was 10 wt% in both samples. The catalytic effects of CN and CNH on the thermal decomposition of AP were studied by differential thermal analysis (DTA) and thermogravimetry (TG), TA-SDT 600, under pure N₂ atmosphere. The thermal scans were conducted with a heating rate of 10 K min⁻¹.

Results and discussion. Figure 1a presents the FTIR spectra of CN, CNS and CNH. For CN, a broad peak at 3000–3300 cm⁻¹ related to the stretching vi-

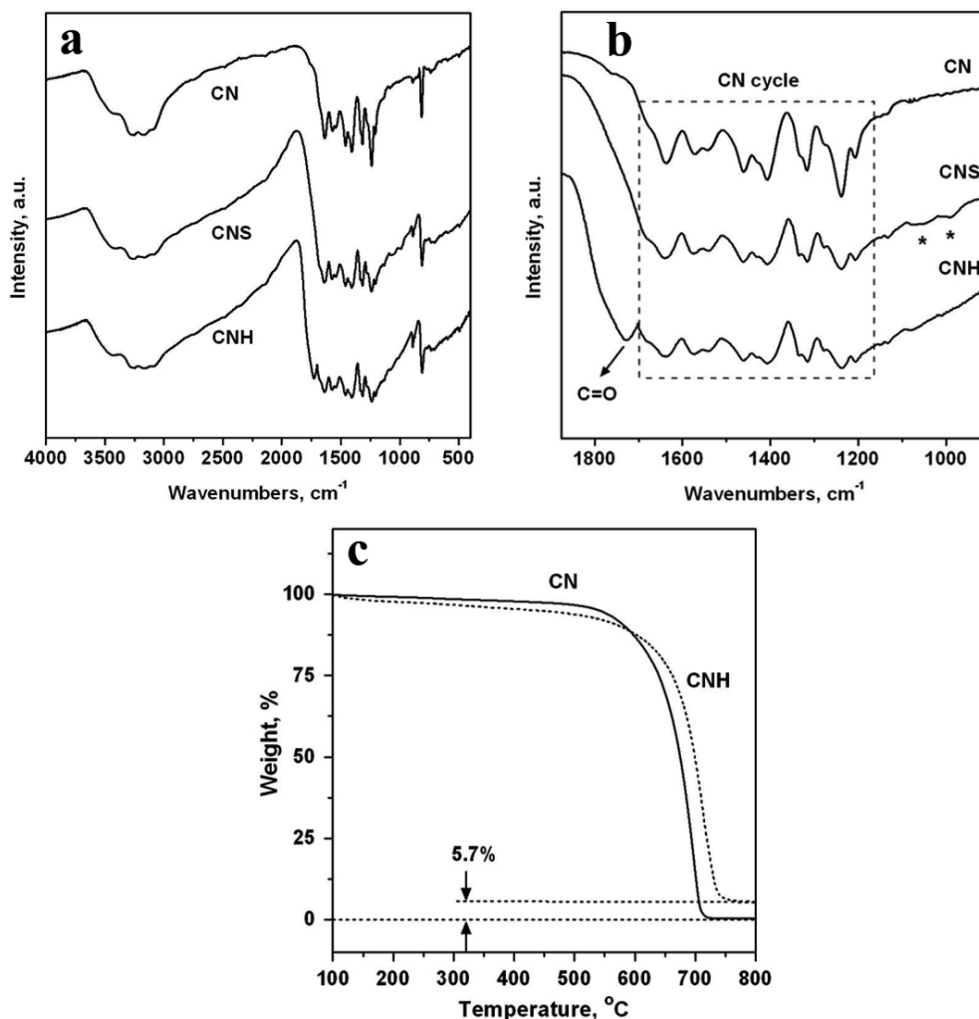


Fig. 1. (a) FTIR spectra of CN, CNS and CNH. (b) An expanded region of the FTIR spectra. The bands of sucrose are marked with asterisks. (c) TG traces of CN and CNH

bration of N–H [7], a strong band ranging from 1200 to 1700 cm^{-1} , ascribed to the stretching vibration of C–N heterocycle [7], and a peak at 798.2 cm^{-1} corresponding to the out of plane breathing mode of triazine units [7] are observed. In the spectrum of CNS small absorption peaks at 994 and 1049 cm^{-1} appear (Fig. 1b). They correspond to glycosidic links and C–O bending/C–OH stretching of sucrose, respectively [8]. This observation confirms the adsorption of sucrose onto CN surface. In the spectrum of CNH the absorption bands of sucrose disappear, but a signal at around 1740 cm^{-1} emerges (Fig. 1b), and according to SUN and LI [9] this is due to the C=O stretching vibration of humins. Thus, the successful loading of CN with humins has been accomplished and, as shown in Fig. 1b, the peaks of C–N heterocycle were fully preserved.

Figure 1c compares TG curves of CN and CNH. CN presents a rapid weight loss occurring from about 500 °C to 700 °C, due to the thermal degradation of the sample. The amount of humins (as tar) in the CNH was calculated from the weight residue after heating the sample to 800 °C and was determined to be 5.7 wt%.

The detailed microstructure of the as-prepared CNH was investigated by means of TEM. Figure 2a demonstrates the small sheets with wrinkles of the intact CN, while for CNH (Fig. 2b) irregularly shaped humins structures with sizes ranging from 50 to 200 nm appeared.

The catalytic performance of CN and CNH on the thermal decomposition of AP was investigated by TG-DTA measurements. TG curves of AP, AP/CN and AP/CNH samples are compared in Fig. 3a. Apparently, the weight loss for catalysts-loaded samples takes place at lower temperature range with respect to the intact AP. The DTA curves of the samples are compared in Fig. 3b. For AP, the endothermic peak at 246 °C is due to the orthorhombic to cubic phase transition, while the exothermic peak at 321 °C (low temperature decomposition step, LTD) is due to its incomplete decomposition to gaseous NH_3 and HClO_4 and sublimation of the salt [1]. The exothermic peak at 457 °C (high-temperature decomposition step, HTD) indicates the entire collapse of AP to small molecules [1].

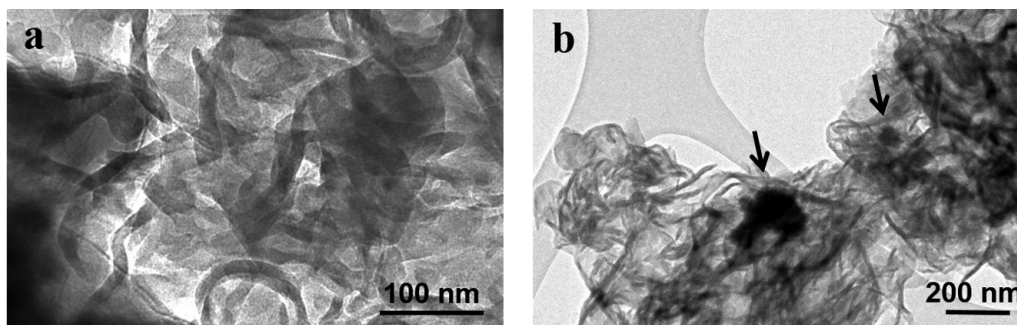


Fig. 2. TEM images of (a) CN and (b) CNH. The arrows indicate humins structures

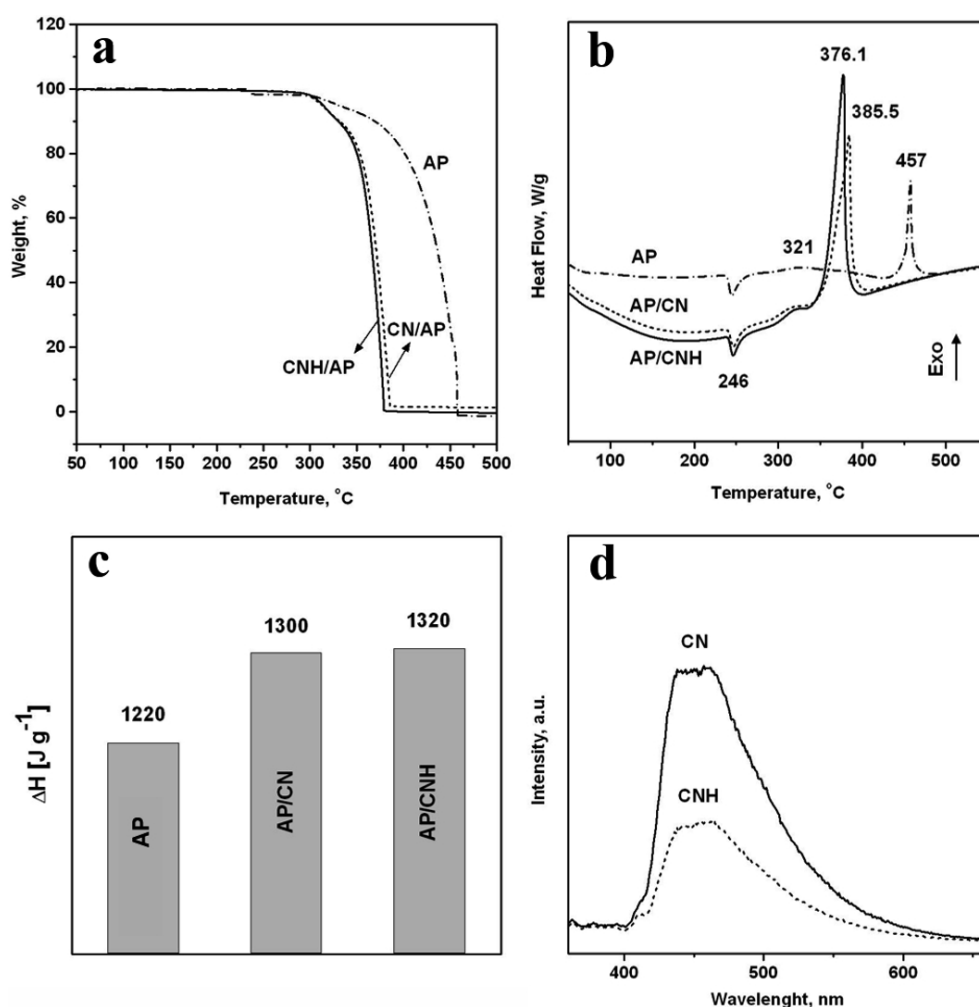


Fig. 3. (a) TG and (b) DTA scans of AP, AP/CN and AP/CNH. (c) The total heat release associated with the exothermic processes in the samples. (d) PL spectra of CN and CNH

As shown, CN and CNH do not affect the temperature of the endothermic and the LTD peaks of AP, whereas the temperature of the HTD is significantly decreased. For AP/CN, the HTD step occurs at 385.5 °C, which agrees well with the value reported by Li et al. [4]. Remarkably, the addition of CNH decreases the decomposition temperature of AP to 376.1 °C. It was also found that the total heat (ΔH) released due to AP decomposition (1220 Jg⁻¹) increases to 1300 Jg⁻¹ for AP/CN, while for AP/CNH an increase to 1320 Jg⁻¹ is obtained (see Fig. 3c). These experimental findings indicate that the as-synthesized CNH composite possesses better catalytic performance than that of CN.

It is noteworthy that the HTD temperature decrease of AP in the presence of CNH is larger than the previously reported values for other carbon-based addi-

tives like graphene (412.5 °C) [10] and, furthermore, is comparable with the result obtained for fullerenes (375.8 °C) [11]. Thus, the newly prepared CNH composite appears to be very attractive catalyst for AP decomposition due to its simple and cost-effective fabrication process.

In order to understand the mechanism of thermal degradation of AP over CNH, it is important to recall that CN is a polymeric semiconductor with a band gap of 2.7 eV that easily meets the requirements of heat excitation. According to Li et al. [4] conduction band electrons (e^-) and valence band holes (h^+) could be generated on the surface of CN during heating. The generated electrons react with $HClO_4$ to form a superoxide radical anion $\bullet O^{2-}$. The as-formed $\bullet O^{2-}$ and h^+ participate in the reduction of $HClO_4$ and oxidation of NH_3 to small molecules, respectively. In view of the synergistic effect of humins, the generated electrons on CN transfer to the humins, and, therefore, the probability of recombination between electrons and holes would decrease. Figure 3d displays the PL spectra of CN and CNH at 300 nm excitation. As seen, the intact CN has a main emission peak at about 460 nm, which decreases after coupling with humins. This result indicates the efficient inhibition of the electron-hole pair recombination in the CNH, when excited by heat and/or light. Clearly, humins can be regarded as a co-catalyst, which serves as an electron sink to increase the lifetime of the active charge carriers, thus reducing the temperature of HTD step of AP degradation.

Conclusions. In summary, the catalytic effect of g- C_3N_4 /humins composite on AP thermal decomposition is reported for the first time. The composite achieves a substantial lowering of the high temperature decomposition step of AP by 80.9 °C and increases the total heat release by 8.2%. This work demonstrates a simple way to enhance the catalytic activity of g- C_3N_4 under the synergetic effect of humins. Further optimizations of the composite composition and its preparation conditions may improve the catalytic proficiency of the material.

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