TiO₂ NPs/h-BN: Preparation and catalytic activities of a novel AP catalyst

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The thermal decomposition performance of an oxidizer directly determines the thrust and specific impulse properties of the solid propellant. Hexagonal boron nitride (h-BN) has the characteristics of high catalytic activity and good stability, which can improve the heat release and decomposition temperature of the oxidant, and then improve the energy performance of the propellant. In this study, a novel hybrid material TiO₂ NPs/h-BN was successfully prepared by in situ growth, and it was found that when 5 wt.% TiO₂ NPs/h-BN was added, the initial decomposition temperature of ammonium perchlorate (AP) decreased by 67.6°C. Due to the addition of TiO₂, the gap between the h-BN layers as well as the specific surface increased, which optimized its thermocatalytic performance, and it also proposed a catalytic mechanism for the thermal decomposition process of AP.

KEYWORDS
TiO₂ NPs/h-BN, AP, BN, thermal decomposition, catalytic

Introduction

Solid propellants consisted of oxidants, binders, metal burners, and other additional components. Among them, the oxidant, as the source of oxygen required for propellant combustion, occupied more than 70% of the propellant, and its thermal decomposition performance had a great influence on the combustion of the propellant. Among these oxidants, AP had the advantages of high effective oxygen content and high density and was one of the most commonly used oxidants in solid propellants (Li et al., 2021). However, the properties of AP, such as high thermal decomposition temperature, high reaction activation energy, low heat release, and non-concentrated heat release, were important factors restricting the development of high-energy solid propellants (Huang et al., 2021). Therefore, in order to meet the needs of modern aerospace technology and the world arms race for high-energy solid propellants, it is necessary to improve the thermal decomposition performance of AP (Li et al., 2020a).

Recently, two-dimensional atomic crystals are now attracting increasing attention in various fields and applications, inspired by the “graphene gold rush” (Sun et al., 2018; Li et al., 2020b; Shen et al., 2021a; Shen et al., 2021b; Li et al., 2022). As a typical graphene-like material, h-BN has attracted great research interest because of its good oxidation resistance up to 850°C, excellent acid chemical stability, high thermal conductivity, excellent elastic modulus, and good mechanical flexibility (Sun et al., 2016). More
importantly, h-BN has been identified as a promising dielectric layer or protective encapsulation material (Li et al., 2012; Shen et al., 2020; Wang et al., 2020). Metal oxide semiconductor materials had the advantages of heat resistance, antitoxicity, photosensitivity, heat sensitivity, and impurity sensitivity and were suitable for modulation, so they have attracted much attention in the field of catalysis (Thomas et al., 2016; Zhu et al., 2016; Li et al., 2017; Li et al., 2020c). Therefore, we propose a technical scheme for the preparation of novel composite catalysts using few-layer boron nitride–supported TiO2 (Medvecká et al., 2018).

In this work, we first used a purely physical green peeling method—liquid nitrogen impact method to peel off the multilayer boron nitride (BN)—and then used a one-step synthesis in situ growth method to obtain the target product TiO2 NPs/h-BN, and the thermal catalytic effect of the composite on AP was studied. The results showed that the decomposition temperature of ammonium perchlorate decreased by 67.6 °C when 5% (mass fraction) was added. Also, the catalytic mechanism was studied.

**Experimental**

**Chemicals and apparatus**

Ammonium chloride (99%), aluminithe powder (99.99%), BBr3 (AR), hydrochloric acid (35%), ethanol, glacial acetic acid, butyl titanate, and AP (AR) were obtained from Aladdin (Shanghai, China).

**Preparation of h-BN**

Synthesis experiments were performed in a N2-flow glove box. NH4Cl (0.150 mol), Al (0.100 mol), and BBr3 (0.050 mol) were put into a stainless steel autoclave with a volume of 50 ml. The autoclave was sealed and heated in an oven at a ramp rate of 10°C/min from room temperature to 500°C and held at 500°C for 10 h (Huang et al., 2018). The product was dried under vacuum at 80°C for 10 h.

**Preparation of h-BNNS**

The prepared 5 g of white powder was weighed, placed in a crucible, placed in a muffle furnace, heated to 800°C at a heating rate of 10°C, and kept warm for 30 min. At the end of heat preservation, it was quickly taken out, poured into the prepared liquid nitrogen (L-N2) until the L-N2 gasified completely. The white powder was suddenly cooled, the liquid nitrogen was rapidly evaporated, and the steam-impinging boron nitride powder was boiled. The essence of this strategy lies in the combination of a high temperature–triggered expansion of bulk h-BN and a subsequent L-N2 gasification that exfoliates the h-BN (Li et al., 2019). Repeat the aforementioned steps three times to obtain the target product (h-BNNS). Scheme 1A was gas exfoliation of h-BN triggered by thermal expansion, and Scheme 1B was the photograph of TiO2 NPs/h-BN.

**Preparation of TiO2 NPs/h-BN**

A volume of 5.0 ml ethanol and 2.0 ml of glacial acetic acid were placed in a beaker, then 6.8 ml of butyl titanate was added to it, and at 30°C, under magnetic stirring for 10 min, 0.8 g of h-BNNS was added and labeled as Solution A (Li et al., 2018). Into another beaker was added 4.0 ml of deionized water, 5.0 ml of ethanol, and 7.2 ml of glacial acetic acid and magnetically stirred for 10 min to uniformly mix to obtain Solution B (Xue et al., 2011). After the dropwise addition was completed, stirring was continued for 20 min to obtain a uniform solution. It was allowed to stand at room temperature for 24 h to form a gel and dried in a drying oven at 80°C for 12 h. The ground samples were placed in a muffle furnace, calcined at 400°C for 2 h, and then cooled naturally to obtain TiO2 NPs/h-BN.

**Results and discussion**

**Sample characterization**

The FT-IR result is shown in Figure 1A. The two absorption peaks at 1388.6 cm⁻¹ and 813.4 cm⁻¹ are the in-plane stretching vibration of B-N and the out-of-plane bending B-N-B vibration, respectively. The absorption peak at 3433.8 cm⁻¹ is the in-plane stretching vibration of N-H (Thomas et al., 2008). The Raman spectrum showed that the G-band frequency of h-BNNS was shifted up relative to that of bulk h-BN (1366.8 cm⁻¹ vs. 1365.8 cm⁻¹; Figure 1B). The G-band shift could be attributed...
to the reduction of h-BN layers, which led to higher in-plane strain and weaker interlayer interactions.

As shown in Figure 2, the scanning electron microscope images of the parent h-BN and h-BNNS are shown in Figures 2A,B. Compared with the bulky h-BN precursors, h-BNNS was much smaller in size and possessed nanosheet-like morphology (Lei et al., 2018).

The SEM results also proved that we successfully prepared TiO$_2$ NPs/h-BN, as shown in Figure 3. TiO$_2$ NPs were uniformly dispersed on the surface of the h-BN (Hosseini et al., 2018). In addition, EDS showed that TiO$_2$ was uniformly distributed on boron nitride nanoparticles.

Figure 4 shows the TEM of TiO$_2$ NPs/h-BN. We found that TiO$_2$ had microspherical morphology, and the outer layer was covered by h-BN. It was consistent with the SEM characterization results.

**Figure 5A** shows the XPS of TiO$_2$ NPs/h-BN. The characteristic peaks at 458.9 and 464.7 eV correspond to the binding energies of Ti 2p1/2 and Ti 2p3/2, respectively, indicating that Ti was at positive 4 valence, Ti$^{4+}$. Nitrogen adsorption/desorption isotherms were conducted at 77 K to study the textural properties of TiO$_2$ NPs/h-BN (Figure 5B). Because of its spherical structure, its specific surface area was large. Based on the nitrogen adsorption and desorption curves, the BET surface areas of TiO$_2$ NPs/h-BN was 112.5 m$^2$ g$^{-1}$.

**Catalytic activities of TiO$_2$ NPs/h-BN in the thermal decomposition of AP**

In order to fully demonstrate the effectiveness of TiO$_2$ NPs/h-BN in catalyzing the thermal decomposition of AP, we carried
out research work by means of thermal analysis. As shown in Figure 6A, compared with the DTA curve of pure AP, the decomposition peak temperature of AP was advanced to 395.7°C by the catalysis of TiO2. After the addition of TiO2 NPs/h-BN, the HTD temperature was further advanced to 380.8°C, confirming the intrinsic catalytic effect of TiO2 NPs/h-BN on AP. This conclusion is also confirmed by the TGA-DTG results, as shown in Figure 5B; in the TGA curve of AP, the two characteristic weight loss steps correspond to the LTD and HTD phases where the weight loss rate reaches 25% and 74%, respectively (Jacobs and Russell-Jones, 1968; Morales-Verdejo et al., 2018; Yuan et al., 2018).

As shown in Figure 7, we collected samples before and after thermal catalysis and performed by XRD. Diffraction peaks existed in all samples: 2θ = 25.5°, 37.8°, 48.2°, 53.7°, 55.2°, 62.6°, 68.9°, 70.4°, and 75.3°, which corresponding to this diffraction peak was (0002), (004), (112), (200), (0004), (204), (116), (220), and (215); these diffraction peaks were compared with h-NB and TiO2. We collected the catalytic effect and recovery rate of the TiO2 NPs/h-BN after two cycles of thermocatalysis in Table 1.

### Catalytic mechanisms

The addition of h-BNNS inhibited the agglomeration of TiO2 particles during the preparation process and synergistically enhanced the catalytic activity by forming a hybrid structure (Al-Ani and Hogarth, 1985; Al-Kuhaili et al., 2002; Cui et al., 2012; Xu et al., 2013; Zhao et al., 2016). The catalytic effect of h-BN was attributed to the negatively charged h-BN surface (Shen et al., 2006; Tu et al., 2014), which facilitated the transfer of induced holes to the TiO2 surface due to the electrostatic attraction between them to form OH− or -OH radicals, which
initiated subsequent surface degradation reaction (Li et al., 2008; Sharma et al., 2014; Eslami et al., 2017). The catalytic process is shown in Figure 8. The adsorption of HClO4 and NH3 obtained from the first decomposition prevented the decomposition of AP. (Reid et al., 2007; Li et al., 2015a; Li et al., 2015b; Abazari and Mahjoub, 2017). As the temperature increased, conduction band electrons and valence band holes were generated on the surface of h-BN, and the generated electrons reacted with HClO4, resulting in the reduction of HClO4 to a superoxide radical anion. O2− further reacted with NH3 to generate H2O, NO2, and N2O (Zhang et al., 2014; Jain et al., 2019).

**Conclusion**

A novel TiO2 NPs/h-BN hybrid material with strong interfacial interactions has been successfully constructed by in situ solvothermal growth. Experiments showed that the TiO2 NPs/h-BN exhibited a good catalytic effect on the decomposition of AP, which reduced the high thermal decomposition temperature of AP by 67.6°C. At the same time, we deeply
analyzed TiO₂ NPs/h-BN as a novel catalyst to provide a mechanism for thermal decomposition of AP.

Data availability statement

The original contributions presented in the study are included in the article/Supplementary Material; further inquiries can be directed to the corresponding author.

Author contributions

JZ was responsible for the design of the test scheme, and DN was responsible for the writing of the manuscript.

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