Vacuum 169 (2019) 108882

Contents lists available at ScienceDirect

Vacuum

journal homepage: www.elsevier.com/locate/vacuum

Short communication

Enhanced the combustion performances of ammonium perchlorate-based energetic molecular perovskite using functionalized graphene

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ARTICLE INFO

Keywords:
Ammonium perchlorate
Molecular perovskite
Graphene
Combustion performances
Relay-domino-like reactions

ABSTRACT

Ammonium perchlorate-based molecular perovskite (DAP)/graphene energetic composite was prepared and characterized. Molecule perovskite DAP was synthesized by the one-pot reaction of ammonium perchlorate, perchloric acid, and triethylenediamine, and DAP/graphene energetic composite was fabricated by physical mixing. The results suggested functionalized graphene can contribute to the improvement of combustion properties of DAP effectively. The energetic composite have high sustained exothermic capacity as well as good self-propagating combustion performance. Synergistic catalysis combustion mechanism of the composite system was provided based on relay-domino-like reactions, which enhanced heat and mass transfer between each component and promoted energy release. This work maybe offer a new idea for design and fabrication of high performance graphene-based energetic composite.

1. Introduction

Molecular perovskite have attracted much attention recently due to their unique structures and excellent characteristics [1]. In energetic materials, integrated inorganic oxidizer perchlorate with organic fuel triethylenediamine at the molecular level, organic-inorganic perovskite-type hybrid materials were designed and developed by Chen's group [2,3]. As one of the high-energy perchlorate-based molecular perovskite, ammonium perchlorate(AP)-based molecular perovskite ($(H_2dabco)[NH_4(ClO_4)_3]$, DAP) energetic materials which incorporates fuel and oxidizer components into an high-symmetry ternary system via non-covalent interactions not only possessed good detonation properties and thermal stabilities, but low-cost advantages also offered a brilliant prospect [4].

As a potential alternative to AP which is the main component in propellant system, DAP have strong vitality and huge space for further application. Considering the low energy output and release rate, and high ignition threshold of AP [5–7], the combination of oxidizer AP and fuel in DAP crystals seem to avoid these above problems and promote its potential application of a deeper level possibly. It is still a great challenge to improve the continuous combustion performance of DAP by heat and mass transfer enhanced in the energy release process [8–10].

In this work, functionalized graphene, as an important additive, was introduced into composite system and DAP/graphene energetic composite was prepared by physical mixing and the combustion properties were characterized. The energetic composites showed excellent combustion performance and synergistic catalysis combustion mechanism using functionalized graphene was provided based on relay-domino-like reactions. This work maybe offer a new idea to prepare advanced graphene-based energetic composite with high combustion performance.

2. Experimental section

2.1. Materials

The ammonium perchlorate and perchloric acid (70%) were obtained from Shanxi Jiangyang Chem. Eng. Co., Ltd. Triethylenediamine was provided by Shanghai Aladdin Bio-Chem Technology Co., Ltd. Commercial graphene nanosheets (3–10 nm thickness) was provided from Nanjing Xianfeng NANO Materials Technology Co., Ltd.

2.2. Preparation of DAP and DAP/graphene composite

DAP was synthesized by the one-pot reaction. ammonium perchlorate (AP, 0.1 mmol), triethylenediamine (dabco, 0.1 mmol) and perchloric acid ($HClO_4$, 0.2 mmol) were added into 20 ml aqueous

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https://doi.org/10.1016/j.vacuum.2019.108882
Received 1 July 2019; Received in revised form 13 August 2019; Accepted 16 August 2019
Available online 17 August 2019
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solution, respectively. The matrix was dissolved completely with heating and stay at room temperature. After several days, as-prepared samples DAP were obtained by filtration. DAP/graphene composite was prepared by mixing mechanically. 0.9 g DAP and 0.1 g graphene were added into agate mortar. The composite was obtained by artificial mixing for 30 min.

2.3. Testing methods

The morphology of nano CNTs and DAP was observed by scanning electron microscopy (SEM, TESCAN Mira3, Brno, Czechia). X-ray diffraction (XRD) patterns were recorded on a Philips X'Pert Pro X-ray diffractometer (PANalytical, Holland). Fourier transform infrared (FT-IR) spectra were collected on a Nicolet 5700 Fourier spectrometer. Raman spectra were collected on a Raman spectrophotometer (Renishaw, England). Differential scanning calorimeter (DSC) was carried out on a STA449F3 calorimeter (Netzsch, Germany) at a heating rate of 10 °C/min. Ignition process was recorded on by the high speed photography device. The Hartmann tube (1.2 L) was used as combustion cell where a capacitor discharge ignition (Operating voltage: 10 KV) and the nitrogen air flow of powder injection (Sample mass: 0.4 g) were built below one atmospheric pressure.

3. Results and discussion

Molecule perovskite DAP samples fabricated by the facile one-pot reaction of components AP, $HClO_4$, and dabco at the mole ratio of 1:2:1 had a high yield of 73.6%. The morphologies of samples were characterized by SEM in Fig. 1a. Micron-sized cube large particles (side length: 200–500 μm) can be observed. Macro defects caused incomplete morphologies. And the XRD patterns of as-obtained DAP samples and DAP simulation were shown in Fig. 2. Compared from diffraction peaks of AP, Main diffraction peaks which located at 21.1°, 24.4°, 27.4°, 36.6° and 38.2° of XRD pattern of DAP reflected from crystal planes (222), (400), (420), (531), and (600), respectively, which are in good agreement with XRD stimulation (CCDC: 1528108). According to the literature [2], the structure of DAP crystals is the perovskite type ABX_3. As shown in Fig. 1b, protonated H_2dabco^{2+} was regarded as A cation, NH_4^+ as B cation, and ClO_4^- as X bridges in molecular perovskite cell.

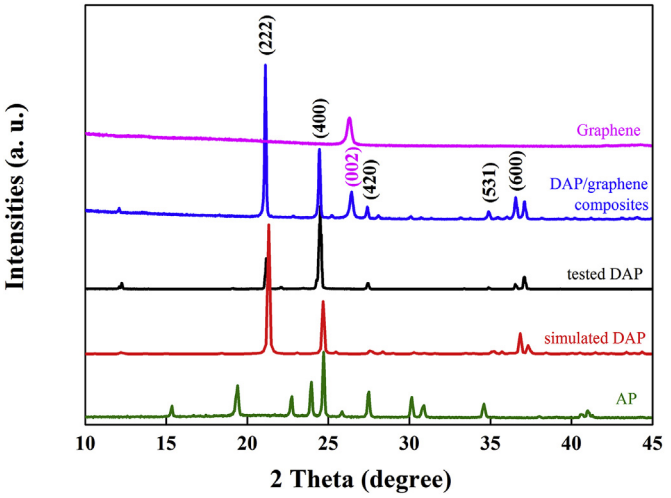

Fig. 2. The XRD patterns of graphene, DAP/graphene composite, DAP samples and simulated data, raw AP materials.

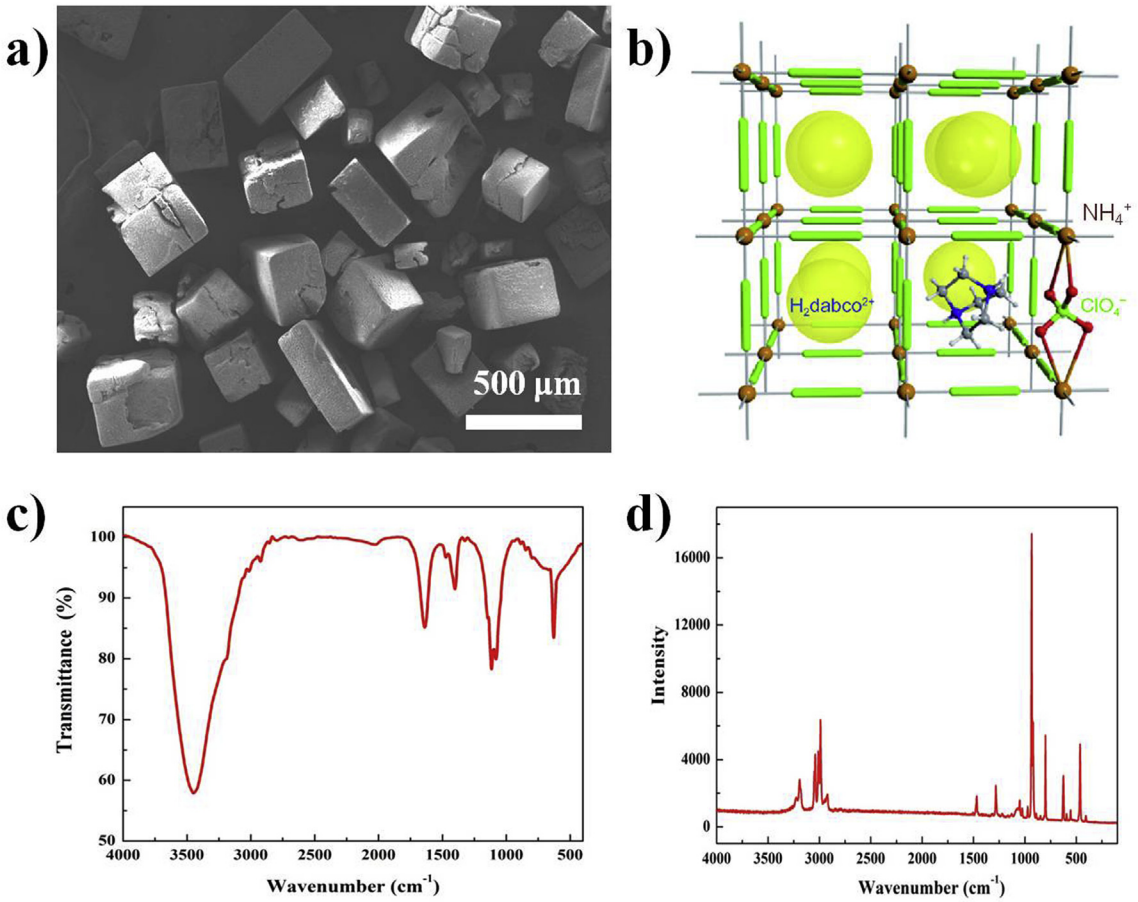

Fig. 1. The (a) SEM images, (b) the schematic of perovskite structure [2], (c) FT-IR and (d) Raman spectrum of DAP.

NH_4^+ cations are located on the corners, face and body centers of the cubic cell, which interacted with twelve O atoms from six ClO_4^- anions by the Coulomb interactions and hydrogen bonds. ClO_4^- anion can be seem as bridges with ambient two NH_4^+ ions, resulted in forming a three-dimensional anionic framework consisting of cages, where protonated H_2dabco^{2+} is embedded to balance the over all charged to zero. Namely, the AP-based molecular perovskite DAP with stable perovskite structure was constructed by molecular assembly strategy.

The FT-IR spectra of DAP was shown in Fig. 1c. The ClO_4^- peaks located at 1118 cm^{-1} and 627 cm^{-1}, NH_4^+ at 3451, and 1402 cm^{-1}, and protonated H_2dabco^{2+} at 1637, 1078 cm^{-1}, indicated the formation of inorganic-organic hybrid perovskite materials. The Raman spectrum was also shown in Fig. 1d. The characteristic vibrational Raman peaks at 935, 627, and 437 cm^{-1} was scattered from ClO_4^-, and the peaks from 3100 to 3300 cm^{-1} corresponds to NH_4^+. For protonated H_2dabco^{2+}, the peaks located at 1469, 1284, and 798 cm^{-1} are corresponding with the E_{1g} band of C-N deformation, E_{1g} band of CH_2 twist/C-N rock, and A_g band of the CH_2 rock, respectively [11,12]. The peaks at 2850-3000 cm^{-1} corresponds to C-H/N-H stretching vibration of H_2dabco^{2+}. Which suggested the FT-IR and Raman results can testify each other.

DAP/graphene composite was obtained by mechanical mixing simply and characterized with XRD in Fig. 2. For XRD pattern of DAP/graphene composite, the main diffraction peak at 21.04°, 24.38°, 27.30°, 36.45°, and 39.57° corresponded to crystal planes (222), (400), (420), (531), and (600) of energetic components molecular perovskite DAP, respectively. Obvious diffraction peaks of graphene can be observed at 26.3°, which reflected from (002) of graphene. The XRD results suggested energetic composite was obtained by simple physical mixing between DAP microparticles and graphene nanosheets.

The thermal decomposition performances were investigated as shown in Fig. 3. For the component AP, the thermal decomposition process involved two stages (low-temperature decomposition and high-temperature decomposition) and the relative exothermic peaks appeared at 309.7 °C and 427.9 °C in the inserted DSC curve. For molecular perovskite DAP, the unique and important exothermic peak at 385.0 °C can be observed and heat release from thermal decomposition process of DAP can reach up to 3421 J/g more than AP (578 J/g), revealed the novel molecular perovskite DAP combined oxidizer and fuel possessed higher thermal stability and heat release. With adding graphene nanosheets, heat release of DAP/graphene composite become less than pure materials slightly. But the decomposition peak have been reduced down to 372.3 °C, which demonstrated novel energetic composite showed the lower decomposition activation energy, because

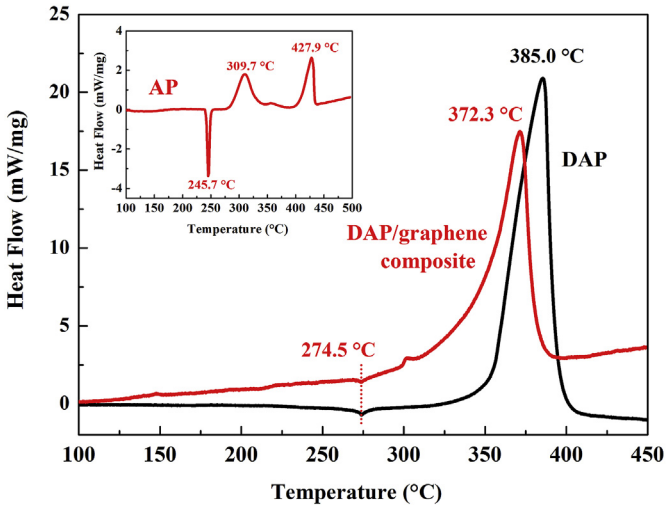

Fig. 3. DSC curves of DAP and DAP/graphene composite, and the DSC curve of the component AP as insert.

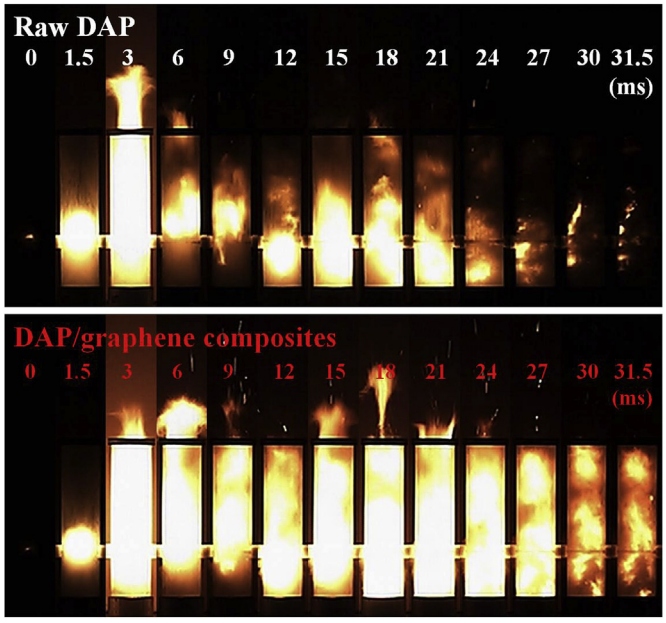

Fig. 4. The ignition and combustion processes of DAP and DAP/graphene composite.

functionalized graphene nanosheets can promote hydrogen transfer from protonated H_2dabco^{2+} to ClO_4^- and catalyze the thermal decomposition of DAP further.

The ignition and combustion experiments of as-obtained sample were conducted in an open environment. For AP, no combustion occurred, resulted from its ultrahigh electric ignition threshold, although high ignition energy (10 KV) is used in this process. By molecular assembly strategy, the DAP and their composite show good deflagration behavior. Two-stage combustion phenomenon are shown in Fig. 4. By electric ignition triggering, a drastic deflagration process from 1 ms to 3 ms with fast flame propagation can be observed at the first stage. And the intermittent slow combustion process occurred in the second stage from 6 ms to 27 ms subsequently, because of the poor self-propagating properties intrinsically. DAP/graphene composite also showed a similar combustion process from the first stage to another stage. A self-sustained deflagration reaction existed during the whole process. The sustained deflagration process with violent flames can be observed from 3 ms to 27 ms, which indicated that graphene could enhance the combustion performances of DAP in composite system.

Combined the experimental process and results, synergistic catalysis combustion mechanism of the energetic composite was provided based on relay-domino-like reactions [10] in Fig. 5. Compared with AP, the electric ignition threshold of DAP had been reduced by molecular assembly strategy of AP. And the combustion of DAP occurred, but non-sustained combustion process existed. The lower heat release energy can't trigger the continuous decomposition/combustion of surrounding DAP particles. As shown in Fig. 5a, the domino reaction can't continue effectively. With graphene adding [13], graphene nanosheets can be dispersed well in the composite system by physical mixing. More reaction heat can be released by the reaction of oxidizer DAP and graphene from the deflagration process. And based on the excellent capability of heat transfer and mass transfer, graphene at neighboring sites of reaction zone can diffuse heat energy around. More DAP particles can be activated and sequential combustion have been achieved in Fig. 5b.

4. Conclusion

In summary, DAP/graphene energetic composite was prepared and the combustion characteristics were characterized. Molecular

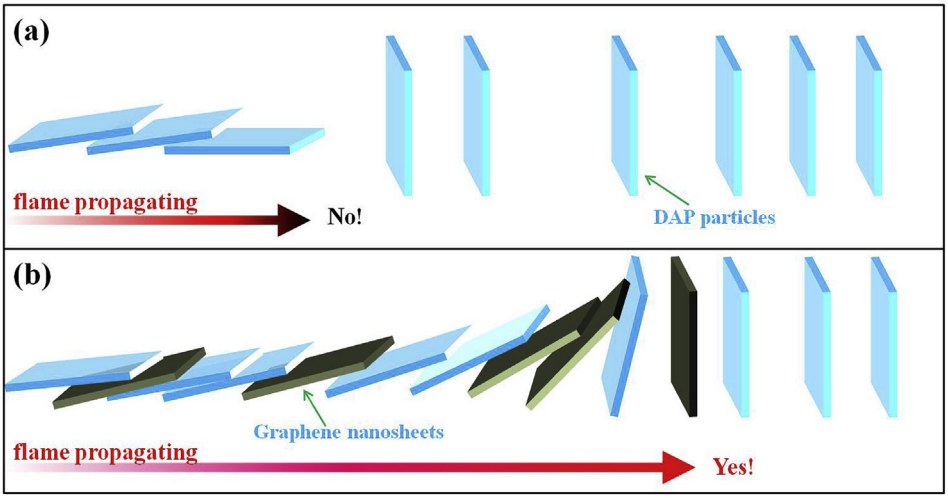

Fig. 5. Schematic illustration of relay-domino-like reactions. (a) the poor propagating of raw DAP particles, and (b) enhanced the combustion propagating of DAP particles using functionalized graphene.

perovskite-type materials DAP were synthesized successfully by the one-pot reaction of AP, $HClO_4$, and dabco, and DAP/graphene energetic composite was obtained by physical mixing. The combustion results demonstrated DAP/graphene composite have high sustained exothermic capacity and good self-propagating combustion performance. Furthermore, the synergistic catalysis combustion mechanism combustion mechanism of the composite system was provided based on relay-domino-like reactions. Functionalized graphene can promote heat release and enhance heat and mass transfer of the system. This work maybe offer a new idea for design and fabrication of high performance graphene-based energetic composite.

Acknowledgments

This work was supported by Natural Science Foundation of China (No: 50972016). And authors thank Prof. Weixiong Zhang and Ph. D. Shaoli Chen (School of Chemistry, Sun Yat-Sen University) for supports and help.

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