Full Length Article

Highly space-confined ammonium perchlorate in three-dimensional hierarchically ordered porous carbon with improved thermal decomposition properties

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ABSTRACT

The ability to generate more apparent specific heat release at lower temperatures is the future trend of ammonium perchlorate (AP)-based composite solid propellants. To achieve this goal, the development of highly active catalysts for improving the thermal decomposition properties of AP is essential and challenging. Herein, three-dimensional hierarchically ordered porous carbon (3D HOPC) is employed as catalyst to improve AP thermal decomposition though synthesizing a series of AP/HOPC nanocomposites with different AP loading amount. In these nanocomposites, AP nanocrystals (26.2–69.0 nm) are successfully space-confined into the 3D HOPC scaffold and form the compact interfacial contact. Owing to the synergistic effect of the well-connected 3D hierarchically ordered porous structure, the good electrical and thermal conductivity, as well as the size effect of AP nanocrystals, 3D HOPC demonstrates excellent catalytic activity for AP thermal decomposition in decreasing the high-temperature decomposition temperature from 440.9 to 315.4 °C, lowering the activation energy from 176.4 ± 18.8 kJ/mol to 130.8 ± 5.3 kJ/mol, and unprecedentedly increasing the heat release from 371 ± 11 J/g to 3765 ± 10 J/g. It can be foreseen that 3D HOPC is an attractive catalyst for AP thermal decomposition, which may open new potential for high energy application of carbon-based materials as catalysts for AP-based solid propellants.

1. Introduction

Ammonium perchlorate (AP), as an important energetic material and the most commonly used oxidizer in composite solid propellants (CSPs), has continued to attract considerable attention since its thermal decomposition behavior directly influences the combustion performance of the propellants [1,2]. Especially, the enhancement of the burning rate has a close relationship with the high-temperature decomposition (HTD) temperature, the apparent specific heat release and the activation energy of AP thermal decomposition. A lower HTD temperature and more heat release of AP would lead to a higher burning rate of these propellants [3,4]. In this regard, a variety of catalysts have been explored to improve decomposition efficiency of AP in the past decades, including metals [5,6], metal oxides [7,8], complex oxides [9,10], and composite catalysts [11,12]. However, most of the investigations on these catalysts focus on the ability to decrease the HTD temperature, and ignore their influence on the heat release. Taking the most studied nano transition metal oxides as the example,

the recently reported highly active catalysts, such as mesoporous β-MnO_2 [13], nano-Co_3O_4 [14,15] and ZnO micro/nanocrystals [16], could significantly reduce the HTD temperature of AP by 125–161 °C, while the disadvantage of their relatively low heat release is obvious as well. Since the heat release is also one of the most important performance parameters for the propellants, it is therefore urgent and highly desirable to develop high-performance catalysts to improve decomposition efficiency of AP to meet the requirements of higher energy generation at lower decomposition temperature.

In the recent studies, carbon materials with unique structures, for instance carbon nanotubes (CNTs) and graphene, exhibit excellent performance both in decreasing the HTD temperature and increasing the apparent heat release of AP decomposition, due to itself catalytic activity and its combustion exothermic reaction with oxidizing gas products generated from the thermal decomposition process of AP [17–23]. It has been found that the addition of carbon materials into the catalyst systems can effectively increase the apparent heat release of AP decomposition at a lower HTD temperature. Especially, the direct

use of carbon materials as a catalyst can make the apparent heat release as high as to 3236 J/g, while decreasing the HTD temperature by 106 °C [20]. As a result, carbon materials may be an ideal catalyst for AP decomposition, which is expected to solve the problem of low heat release existing in past researches. Despite the progress, the small active surface and the poor contact with AP have limited the catalytic performance of these carbon materials currently used, thus it is still desirable to explore a novel carbon catalyst with higher activity for the thermal decomposition of AP.

In general, the performance of the catalysts is closely related to the contact area between the catalysts and AP. The thermal decomposition kinetics and energy release are drastically enhanced because of the compact interfacial contact between the catalysts and AP at the nanoscale [24]. To achieve a high contact area, considerable efforts have been dedicated and two main strategies have been employed. Direct reduction of the particle size of AP to the sub-micrometer or nanometer scale can significantly enhance contact and then lead to a higher catalytic activity. Unfortunately, this approach suffers from particle aggregation, not mention that superfine AP is dangerous [25]. Another alternative method is to prepare nanocomposites of AP and the catalysts. Compared with those simple physical mixtures, special structured nanocomposites of AP and the catalysts have been demonstrated to have higher contact area and more catalytic active sites, which result in the outstanding catalytic performance [26–28]. Moreover, the structural features of catalysts, such as high surface area and porosity, also can enhance the catalytic activity through accelerating the adsorption and desorption of gas products during the thermal decomposition process of AP [29,30]. Based on the above analysis, it is possible that confining AP into a porous carbon catalyst at the nanoscale may reach the anticipation of desired high-performance catalysts for AP thermal decomposition, which not only exhibit excellent catalytic activity coming from compact interfacial contact, but also have high heat release providing by the combustion of carbon materials.

Three-dimensional hierarchically ordered porous carbon (3D HOPC) with well-connected ordered porous structure, high surface area as well as good electrical and thermal conductivity has recently become an attractive material for catalytic application. Compared with the limited active surface of CNTs and graphene, 3D HOPC possesses plentiful exposed catalytic active sites and shortened diffusion paths for gas products transfer and adsorption during thermal catalytic process due to its hierarchically porous structure and good pore connectivity [31,32]. Meanwhile, its remarkable electrical and thermal conductivity can facilitate the electron transfer and heat conduction during the thermal decomposition process of AP [33,34]. Most noteworthy, our previous work demonstrated that 3D HOPC could impregnate and confine energetic materials into its porous channels at the nanoscale to realize observably improved thermal performance [35,36]. However, to our knowledge, the catalytic behavior of 3D HOPC for the thermal decomposition of AP has never been reported. Herein, AP/HOPC nanocomposites with different percentages of AP were prepared to investigate the thermal catalytic performance of 3D HOPC for AP decomposition. A significant enhancement of the thermal decomposition properties of AP was achieved for the synergistic effect of the well-connected 3D hierarchically ordered porous structure, the excellent electrical and thermal conductivity, and the size effect of AP nanocrystals. In the presence of AP/HOPC nanocomposites with 80 wt% of AP, 3D HOPC has the most excellent catalytic effect in decreasing the HTD temperature from 440.9 to 315.4 °C, lowering the activation energy from 176.4 ± 18.8 kJ/mol to 130.8 ± 5.3 kJ/mol, and unprecedentedly enhancing the heat release from 371 ± 11 J/g to 3765 ± 10 J/g. This work clearly suggests that 3D HOPC will be a superior catalyst for AP thermal decomposition, and may provide new insight to design high-performance catalysts for AP-based composite solid propellants.

2. Experimental section

2.1. Materials

All chemicals used were analytical grade without further purification. Triblock copolymer Pluronic F127 ($EO_{106}PO_{70}EO_{106}$, $M_w = 12600$) was purchased from Sigma-Aldrich. Phenol, formaldehyde (37 wt%), aqueous ammonia (28 wt%), sodium hydroxide, tetraethyl orthosilicate (TEOS), hydrofluoric acid, ethanol, and acetone were purchased from Sinopharm Chemical Reagent Co. Ltd. AP was provided by Institute of Chemical Materials (ICM). Deionized water was used in all experiments.

2.2. Preparation of 3D HOPC

3D hierarchically ordered macro-/mesoporous carbon materials were fabricated through a dual-templating method [37]. Silica colloidal crystals, serving as the template, were obtained by sedimentation of monodisperse silica microspheres with a uniform diameter of (280 ± 5) nm, which were prepared via using the Stöber's method [38]. The 20 wt% resol solution in ethanol, serving as the carbon source, was prepared by a basic polymerization method. Typically, a homogeneous ethanol solution of resol and the structure-directing agents F127 (mass ratio resol/F127/ethanol = 2/1/10) immersed the silica colloidal crystals monolith for 24 h at 25 °C. After the evaporation of ethanol, the composite monolith was heated at 70 °C for 4 h to further polymerize resol, and subsequently calcined at 600 °C for 3 h with a heating rate of 3 °C/min under N_2 flow to decompose F127 for forming the mesoporosity. Finally, the carbon/silica composite was immersed in HF aqueous solution (10 wt%) to remove the silica, resulting in the macroporosity. After washing with water and drying at 60 °C in vacuum, the 3D HOPC scaffold with well-interconnected porous structures was obtained.

2.3. Preparation of AP/HOPC nanocomposites

The AP/HOPC nanocomposites were prepared via a solvent evaporation induced dispersion process [39]. In brief, the saturated acetone solution of AP was added dropwise into the 3D HOPC monolith scaffold and then the mixture was left undisturbed at room temperature to evaporate the solvent completely. This process was repeated until the loading amount of AP in the composites reached the desired target. The final product was still black monolith and dried at 60 °C in vacuum. Composites with different AP loading amount of approximately from 30 wt% to 90 wt%, which determined by TG analysis, were fabricated and denoted as C-X, wherein X represented the weight percentage of AP in nanocomposites.

2.4. Characterization and analysis

The microstructure of the as-prepared 3D HOPC scaffold and nanocomposites was determined using field-emission scanning electron microscopy (FESEM, ZEISS SIGMA HD) and transmission electron microscopy (TEM, JEOL 2011). The X-ray powder diffraction (XRD) analysis was examined by Bruker D8 Advance diffractometer with Cu K_α radiation. Elemental composition analysis was performed with energy dispersive X-ray spectroscopy (EDS). The porous properties of the samples were measured by Nitrogen sorption isotherms at 77 K with a Quantachrome NovaWin analyzer after the samples were degassed overnight at 100 °C under vacuum. The Brunauer−Emmett−Teller (BET) method and the Barrett−Joyner−Halenda (BJH) model were used to calculate the specific surface area (S_{BET}), the pore size distributions and pore volumes, respectively. The total pore volumes (V_t) were determined from the adsorbed amount at P/P_0 of 0.95. The thermal decomposition properties of AP/HOPC nanocomposites were investigated using differential scanning calorimetry-thermogravimetry