



Reactive nanoenergetic graphene aerogel synthesized by one-step chemical reduction

Anqi Wang^a, Sangho Bok^b, Rajagopalan Thiruvengadathan^b, Keshab Gangopadhyay^b,
Jacob A. McFarland^c, Matthew R. Maschmann^{b,c,*}, Shubhra Gangopadhyay^{b,**}

^a Department of Biological Engineering, University of Missouri, Columbia, MO 65211, United States

^b Department of Electrical and Computer Engineering, University of Missouri, Columbia, MO 65211, United States

^c Department of Mechanical and Aerospace Engineering, University of Missouri, Columbia, MO 65211, United States

ARTICLE INFO

Article history:

Received 6 March 2018

Revised 28 June 2018

Accepted 30 June 2018

Keywords:

Graphene

Aerogel

Nanoenergetics

Nanothermite

Combustion

ABSTRACT

Adoption of nanoenergetic materials into large-scale applications is hindered by problems associated with scalability, particle aggregation, stability, and electrostatic discharge (ESD) sensitivity. We report a macroscale energetic graphene aerogel that simultaneously overcomes each of these problems while increasing the energy production and flame speed with respect to neat nanothermite sample. The aerogel is comprised of reduced graphene oxide (RGO), aluminum (Al) nanoparticles, and bismuth oxide (Bi_2O_3) nanoparticles. Synthesis of the aerogel requires chemical reduction and gelling that preserves the reactivity of embedded fuel and oxide nanoparticles. A new gelation process is adopted in which ethylenediamine was added to a propylene carbonate dispersion to gel and reduce RGO while retaining material reactivity. The energetic aerogel enhances the heat of reaction to 967 J/g, which is 36% higher than that from loose $\text{Al}/\text{Bi}_2\text{O}_3$ powder. A combustion speed of 960 ± 190 m/s under open ambient is measured for RGO/ $\text{Al}/\text{Bi}_2\text{O}_3$ gel, which is the highest value reported for an $\text{Al}/\text{Bi}_2\text{O}_3$ system. Further, the underlying reduced graphene oxide scaffold reduces ESD sensitivity of the aerogel by three orders of magnitude.

© 2018 The Combustion Institute. Published by Elsevier Inc. All rights reserved.

1. Introduction

Nanoenergetic materials have superior energy density and reaction rates that are unattainable with traditional micron sized materials [1,2]. Energetic nanocomposites further enhance the capability to tune one or more physical, chemical, or mechanical attributes of nanoenergetic materials and enables multifunctional combustion systems with enhanced capabilities [3,4], including applications on MEMS [5] and microchips [6]. One of the major classes of nanoenergetic materials is a heterogeneous mixture of nanoscale metallic fuel particles (aluminum (Al) [7], boron [8], magnesium [9], silicon [10], etc.) with inorganic or organic oxidizer (metal oxide, such as bismuth trioxide [11], fluorocarbon [9], etc.). Such nanocomposite materials are known as nanothermite and produce self-propagating exothermic reactions with adiabatic flame temperatures in excess of 3000 K when ignited [12]. Since the exothermic combustion reaction is a solid-state diffusion process, it is essential to realize an

arrangement of oxidizer and fuel that ensures maximized interfacial contact area while discouraging particle sintering [13,14].

Physical processing methods, such as ultrasonic mixing and arrested ball milling, produce thermites with a random distribution of oxidizer and fuel particles [15,16]. The unstructured nature of mixing forms composites with unreliable and irreproducible combustion behavior. The optimum interfacial contact is realizable only if all the components are homogeneously mixed without any phase separation. Further, neat nanothermites are susceptible to unintended ignition due to their high sensitivity to electrostatic discharge (ESD), impact and friction [17]. Specifically, the threshold ESD ignition energy for neat nanothermites is of the order of microjoules [18].

Scalable production of nanothermite materials to commercially relevant quantities is hindered by ESD, impact sensitivity, and handling concerns [17]. Traditional methods of creating macroscale structures involves forming nanothermites into pellets under high pressure, which is dangerous and results in reduced reaction kinetics [19–22]. Chemical synthesis routes to form nanoenergetic microstructures or macrostructures of have required chemical surfactants such as PVP [23] or cause strong phase separation between fuel and oxidizer [24], which may reduce the energy release severely.

* Corresponding author at: Department of Mechanical and Aerospace Engineering, University of Missouri, Columbia, MO 65211, United States.

** Corresponding author.

E-mail address: maschmannm@missouri.edu (M.R. Maschmann).

One particularly attractive means to enhance scalability of nanothermite that has yet to be explored is the integration of fuel and oxidizer nanoparticles into the structure of graphene aerogels. We have recently found that chemically functionalized graphene can be engineered to facilitate directed self-assembly of dense nanoenergetic composite pellets with enhanced energy release [14]. By contrast, a graphene aerogel structure offers an ultralight ($\sim 10 \text{ mg/cm}^3$) porous scaffold [25] that absorbs mechanical energy [26], is thermally conductive [27], is electrically conductive which may optimize ESD safety [28,29], facilitates chemical functionalization [30], and may even be 3D printed [31]. Conventional graphene aerogel synthesis methods, however, are not chemically compatible with nanoenergetic material integration. For integration of nanoenergetic NPs into the aerogel, the gelation process must not oxidize the fuel or reduce the oxide particles, and the nanoparticles must not interfere with the gelation process itself. Furthermore, the fuel and oxide NPs must be adequately integrated into the aerogel matrix to facilitate homogeneous integration.

Existing graphene aerogel synthesis processes involve a hydrothermal/solvothermal process [32,33] or a chemical reduction method [25,34]. While these methods readily enable graphene-based nanocomposites such as graphene/polymers [35] and graphene/metal oxides [36,37], they are incompatible with nanothermite integration since it is necessary to keep both fuel (Al) and metal oxide unreacted during the synthesis. Our experiments confirmed that the transformation of Al NP fuel to Al_2O_3 after 8 h of hydrothermal process under 180°C or chemical reduction process for GO using amines under 95°C in water (Fig. S1A). Solvothermal processing in organic solvents can retain the activity of Al, but we found that oxide NPs are reduced to pure metals, again deactivating the reactivity of the composite (Fig. S1B). Therefore, new methods are required to synthesize a macroscale nanothermite aerogel that retains the reactivity of embedded fuel (Al) and oxidizer nanoparticles.

Here we report a novel one-step chemical reduction process to obtain a highly reactive RGO/Al/ Bi_2O_3 ternary nanoenergetic aerogel. The aerogel exhibits even greater reactivity than the neat Al/ Bi_2O_3 mixture, an outstanding non-confined burn rate, and reduced ESD sensitivity. The synthesis process utilizes ethylenediamine (EDA) as the reduction and gelling agent to form a 3D porous RGO structure in propylene carbonate (PC). Fuel (Al) and oxidizer (Bi_2O_3) nanoparticles (NPs) are embedded homogeneously within the RGO sheets comprising the aerogel walls, providing an energy release of 967 J/g and an unconfined burn rate of $960 \pm 190 \text{ m/s}$. Further, the ESD sensitivity of these RGO/Al/ Bi_2O_3 was reduced by more than three orders, potentially enabling safe handling and secured operation. The methodology is extensible to the formation of a rich variety of nanoenergetic aerogels mixtures having other metal oxides and fuel NPs through minimal tailoring of the process parameters.

2. Experiment

2.1. Chemicals

Graphite nanoplatelets (xGnP H-5) with a $5 \mu\text{m}$ average particle size was purchased from XG Science, Lansing, MI and served as a precursor for synthesizing graphene oxide (GO). Sulfuric acid (H_2SO_4), potassium permanganate (KMnO_4), and hydrogen peroxide (H_2O_2) were purchased from Fisher Scientific. Sodium nitrate (NaNO_3) was purchased from Sigma-Aldrich. All of these chemicals above were ACS reagent grade and used for synthesis of GO. Aluminum particles, which have an average diameter of 80 nm , alumina (Al_2O_3) shell thickness of 2.2 nm and 79% active Al content as specified by the manufacturer, were purchased from Novacentrix, Austin, TX. Bi_2O_3 nanoparticle and Ethylenediamine were

purchased from Sigma-Aldrich. Propylene carbonate (PC, 99.7%) in HPLC grade was purchased from Sigma-Aldrich. Tertiary butanol used as free-drying agent was purchased from Fisher Scientific.

2.2. Synthesis process

2.2.1. Synthesis of graphene oxide (GO)

Graphene oxide was synthesized by oxidation reaction of graphite using the modified Hummer's method [14]. Briefly, 46 mL H_2SO_4 was added slowly into a beaker with mixture of 1 g graphite nanoplatelets and 1 g NaNO_3 inside under cooling by ice bath and magnetic stirring. After 10 min , 6 g of KMnO_4 was added into the beaker and the solution was stirred for 1 h under 35°C . Subsequently, 80 mL of deionized water was added into the beaker dropwise and the water bath was heated to 90°C and maintained for half an hour. Then, 200 mL deionized water was added slowly into the reacting agent. After cooling down to ambient temperature, 6 mL H_2O_2 was dropped into the suspension, and the mixture color changed to pale brown. A washing procedure was then employed to remove impurities and purify GO product. The centrifuging and dispersing washing step were carried out until the pH of surfactant reached 6, when all the impurities were removed. The GO was then dispersed into deionized water at a concentration around 5 mg mL^{-1} and sonicated for 45 min to exfoliate the material into flakes. The material was then centrifuged for another 30 min at 4000 rpm to remove the unoxidized graphite. The supernatant was then transferred into a glass petri dish and heated in oven at 80°C until the water evaporated. The resulting GO paper was then removed.

2.2.2. Synthesis of RGO/Al/ Bi_2O_3 aerogel

To initiate the self-assembly process, GO paper, Al nanoparticles and Bi_2O_3 nanoparticles were separately dispersed into propylene carbonate and sonicated for 4 h . Detailed amounts of samples in different equivalence ratio are listed in Table S1. Equivalence ratio was calculated by the ratio of fuel/oxidizer over stoichiometric value. Afterwards, the dispersions were mixed together by vortexing for 10 min in a vial and rested for 16 h . Then $40 \mu\text{L}$ ethylenediamine was injected to the mixture to initiate gelation, and the vial was moved to a 95°C oven for 8 h . After the gelling process, the product was cooled in ambient air to room temperature. The organogel was then placed in a beaker filled with tert-butanol to undergo solvent exchange. Lastly, the material was freeze-dried to remove solvent. Optical pictures and material amounts are given in Figs. S2, S3 and Table S1.

2.2.3. Synthesis of control sample

For the control Al/ Bi_2O_3 sample made in IPA, we used the standard process reported in prior work [38]. For the control Al/ Bi_2O_3 sample made in PC, calculated amount of Al and Bi_2O_3 (200 mg in total, $\phi = 1.4$) was weighed and dispersed in PC under sonication for 4 h , respectively. Then the dispersions were mixed and sonicated for one more hour. The mixture was then moved to an aluminum foil bowl and dried under vacuum.

An additional control sample was sought that incorporated GO with the Al/ Bi_2O_3 . This control sample was produced from the same material from which the aerogel was produced. After the 16-h resting step, a portion of the mixture was moved to an aluminum foil bowl and dried under vacuum (bypassing the gelation and solvent change step).

2.3. Characterization

Both Zeta potential analysis and dynamic light scattering (DLS) size distribution analysis were obtained using a Delsa Nano Potential and Submicron Particle Size Analyzer. The concentrations of Al

Download English Version:

<https://daneshyari.com/en/article/6593385>

Download Persian Version:

<https://daneshyari.com/article/6593385>

[Daneshyari.com](https://daneshyari.com)