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**Multi-scale directed self-assembly of nanoenergetics utilizing graphene and
characterization by in situ heating and imaging**

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1.0 SUMMARY

The mechanisms and combustion performance of nanothermites assembled via “directed self-assembly” (DSA) are investigated in numerous different material compositions and morphologies. In the DSA process presented here, discrete nanoscale fuel (Al) and oxidizer nanoparticles (NPs) are assembled on 2D scaffold materials including functionalized graphene and MoO₃ sheets. The self-assembly process is initiated in solution through long-range electrostatic forces that attract positively charged fuel and oxidizer to negatively charged 2D material scaffold [1]. The fuel and oxidizer assembled layers assemble further into multi-layered large structures to produce macroscale nanothermite composites. The assembly process discourages phase separation of fuel and oxide particles and promotes enhanced reaction times and more complete reactions. The self-assembly process is used to create high-density macroscale Al/MoO₃ sheet assemblies and is modified to realize very low-density energetic graphene aerogel materials. A diverse set of experiments using variations of the DSA process is detailed in this report.

The 2D material scaffold may provide a structural template or may play an active role in the reaction process of the assembled nanothermite. We demonstrate that chemically-modified graphene may be used to assemble either densely packed macroscale nanothermites or very low density aerogels using variations in processing. In the case of MoO₃ sheets, the 2D material sheets act as the oxidizer. The intimate contact established between Al NPs and conformal 2D materials is also exploited to examine the confined reaction of photothermally heated Al NPs. In the case of Al NPs on MoO₃ sheets, discrete reaction trails are produced along the <001> crystal orientation of the MoO₃ sheet surface. When self-assembled into high density nanothermite composites, these reaction trails are observed as extensions that protrude from reacted Al NPs. We hypothesize that the unique, dynamic morphology change facilitated by the 2D MoO₃ sheets contribute to the observed burn rate of 1,730 m/s -- the faster reported value for this material system.

We also demonstrate that the 2D material scaffold may be chemically functionalized to deliver fluorine directly to Al NPs to assist with the removal of the alumina shells that surround the aluminum fuel. In particular, we use XeF₂ gas to fluorinate graphene oxide. Simultaneous differential scanning calorimetry and thermogravimetric analysis and T-jump mass spectroscopy experiments show that fluorine species leave the graphene oxide host material at low temperatures (200-400°C). The fluorine gas promotes the removal of the alumina shell that surrounds Al NP fuel [2] in pre-ignition reactions, altering the reaction kinetics from a molten Al state without fluorinated GO to a solid-state Al reaction when fluorinated GO is introduced. These initial experiments provide a foundation for chemical species delivery enabled by robust self-assembly of nanoenergetic composite materials.

2.0 INTRODUCTION

2.1 Self-Assembly of Nanoenergetic Materials

Nanoenergetic materials are of great interest due to their high reactivity and packing densities which promote outstanding volumetric energy contents in comparison to conventional materials. Nanoenergetic materials are described as heterogeneous mixtures of metallic fuels (e.g. Al) and inorganic oxidizers (e.g. CuO, Bi₂O₃, MoO₃, Fe₂O₃, KMnO₄ etc.) with nanoscale dimensions. The organization, intimacy, and dimensions of the discrete fuels and oxidizers in the nanoenergetic materials largely influence their combustion kinetics. Increased fuel and oxidizer interfacial contact area enhances reactivity, and consequently there is great recent interest in mechanisms to assemble and organize fuels and oxidizers into densely arranged structures. Significant research efforts have been performed by various research groups for both top-down and bottom-up synthesis methods to achieve this. Phase separation of fuel and oxidizer (poor intermixing) has been a critical issue in the synthesis of nanoenergetic materials. Specifically, ultrasonic mixing of fuel and oxidizer nanoparticles has proven insufficient in forming homogeneous nanoenergetic materials. As a result, their high volumetric energy contents cannot be realized due to incomplete combustion. In addition, the scalability of nanoenergetic synthesis procedures is an issue due to inherent laboratory scale processing limitations because of the extremely high sensitivity of nanoenergetic formulations to ignition stimuli as experienced in the conventional method [3]. Many of the bottom-up methods also have limitations of their own when trying to maintain enhanced combustion properties (e.g. reactivity, combustion wave speed, reduced ignition sensitivity, and scalability). For example, the electrospray assembly process, developed by Zachariah et al., appears to reduce the combustion wave speed because of the use of nitrocellulose, even though internal gas release separates the particles reducing sintering effects [4]. Prakash et al. proposed a core-shell nanoparticle method to increase the shelf life of the nanothermite and to tune the reactivity of nanoenergetic materials by coating a strong oxidizer nanoparticle (potassium permanganate) with a layer of a relatively mild oxidizer (iron oxide) [5]. However, the mild oxidizer inherently reduced the reactivity. A biologically inspired approach to achieve direct assembly was demonstrated with oxidizer loaded Ferritin protein cages onto the surface of aluminum nanoparticles. However, the scalability and convenience issues remain due to performance limitations of the use of Ferritin cages [6]. Our solution to these problems is directed self-assembly (DSA), a process by which discrete components of fuel and oxidizer are driven to organize into well-defined geometries through specific interactions.

2.2 MoO₃ as a 2D Scaffold for Self-Assembly

Layered 2D materials such as graphite, molybdenum disulfide, and molybdenum trioxide have attracted significant attention for numerous applications ranging from composite materials to electronic devices [1–5]. These materials consist of planar sheets

with strong in-plane chemical bonds but weak out-of-plane, van der Waals bonds. Such materials are readily exfoliated to produce single or few-layered atomic sheets for high surface area interaction application [6,7]. These 2D materials have been used as templates to grow nanoparticles of metal or oxides [7,8], and used for enhanced in-plane electron mobility and heat conduction [9,10]. Moreover, the surface properties of these materials can also be controlled by assembly of nanomaterials [11].

Nanoenergetic materials, which are comprised of fuel (Al, Li, Si, etc.) and oxidizer (CuO , Bi_2O_3 , MoO_3 , Fe_2O_3 , etc.) constituents with nanoscale dimensions, benefit greatly from the enhanced surface area of interaction between fuel and oxidizer [11–18]. Reduced particle dimensions improve the homogeneity of the mixture, decreasing the diffusion distance required for reactions [13,15,18,19]. Previously, researchers have employed fuel and oxidizer particles having a rich variety of morphologies such as spherical nanoparticles [20], nanosheets [11,21], nanorods [15,17], and nanowires [15,16] to synthesize nanoenergetic formulations. Most recently, we have reported the self-assembly of Al and Bi_2O_3 nanoparticles directed on to 2D functionalized graphene sheets to synthesize novel nanoenergetic materials with enhanced combustion performance [11,21]. In these works, functionalized graphene oxide (FGO) was used as an energetic additive (only up to 5 wt. %) and our main oxidizer was Bi_2O_3 . Directed assembly of FGO to Al/ Bi_2O_3 increased the combustion performance and ignition sensitivity by promoting high-density particle loading on an FGO scaffold. Long-range electrostatic interactions followed by short-range covalent and van der Waals interactions produce ultradense macrostructure of GO/Al/ Bi_2O_3 that is highly reactive. The significant improvement in combustion performance is a result of employing 2D FGO stimulated our interest to employ 2D metal oxide such as MoO_3 as an exclusive oxidizer and to study the impact on the combustion performance. Though MoO_3 had been used as an oxidizer in energetic formulations in the past, the MoO_3 material used was a regular micron sized particle [22,23].

Aluminum nanoparticles (Al NPs) are attractive as nanoscale fuel due to their ability to generate large heat of combustion when it reacts with oxidizer. However, the thin oxide coating surrounding Al NPs interferes with the combustion of the metallic Al, and the mechanism by which the Al reacts with an oxidizer to initiate combustion is still a matter of debate. In recent years, researchers have proposed the reaction mechanism of nano-sized Al particles mixed with various oxidizers [18,19,24]. Levitas et al. have proposed a melt dispersion mechanism (MDM) during fast heating that generates significant internal pressure within the aluminum core [25]. As the result, a dynamic spallation of the oxide shell ejects the molten aluminum droplets that react with oxidizers. Zachariah et al. proposed a diffusion oxidation mechanism (DOM) based on their experimental evidence whereby both oxygen and aluminum diffuse through the oxide shell [26]. Regardless of the specific combustion mechanism, the intimate proximity of fuel and oxidizer afforded by nanoenergetic composites enhances the observed heat of combustion and flame propagation rate, which is desirable for many applications.

In this work, we report the synthesis of gram scale quantity of 2D MoO_3 nanoflakes per batch by exfoliation of layered bulk MoO_3 utilizing ultrasonication, following the method

reported by Coleman [2]. Though other methods to produce 2D materials including laser thinning, micromechanical cleavage, and vapor phase deposition [27–29] have been reported in literature, scaling up the synthesis is difficult. Al NPs were assembled on the surface of ultrasonically exfoliated 2D MoO₃ sheets to produce nanoenergetic composites with close proximity between fuel and oxidizer. The pressure – time and combustion wave speed measurements were performed and compared to similar composites prepared using bulk MoO₃ powder. Effects of slow and fast heating rate ignition on the combustion mechanisms were evaluated across a range of ignition heating rates. The Al/MoO₃ nanocomposites were characterized using a host of characterization tools such as zeta potential analyzer, scanning electron microscope (SEM), transmission electron microscope (TEM), atomic force microscope (AFM), X-ray diffraction, energy dispersive spectroscopy (EDs) and simultaneous thermal gravimetric analysis (TGA)/differential scanning calorimeter (DSC).

2.3 Energetic Aerogels

Nanoenergetic materials have superior energy density and reaction rates that are unattainable with traditional micron sized materials.[7, 8] 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 [9, 10], including applications on MEMS [11] and microchips [12]. One of the major classes of nanoenergetic materials is a heterogeneous mixture of nanoscale metallic fuel particles (aluminum (Al) [13], boron [14], magnesium [15], silicon [16], etc.) with inorganic or organic oxidizer (metal oxide, such as bismuth trioxide [17], fluorocarbon [15], etc.). Such nanocomposite materials are known as nanothermite and produce self-propagating exothermic reactions with adiabatic flame temperatures in excess of 3000K when ignited.[18] 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.[19, 20]

Physical processing methods, such as ultrasonic mixing and arrested ball milling, produce thermites with a random distribution of oxidizer and fuel particles.[21, 22] 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.[23] Specifically, the threshold ESD ignition energy for neat nanothermites is of the order of microjoules.[24]

Scalable production of nanothermite materials to commercially relevant quantities is hindered by ESD, impact sensitivity, and handling concerns.[23] Traditional methods of creating macroscale structures involves forming nanothermites into pellets under high pressure, which is dangerous and results in reduced reaction kinetics.[25-28] Chemical synthesis routes to form nanoenergetic microstructures or macrostructures of have

required chemical surfactants such as PVP or cause strong phase separation between fuel and oxidizer, which may reduce the energy release severely.

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.[20] By contrast, a graphene aerogel structure offers an ultralight ($\sim 10 \text{ mg / cm}^3$) porous scaffold [29] that absorbs mechanical energy [30], is electrically conductive which may optimize ESD safety [31], facilitates chemical functionalization [32], and may even be 3D printed [33]. 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 [34, 35] or a chemical reduction method. [29, 36] While these methods readily enable graphene-based nanocomposites such as graphene/polymers [37] and graphene/metal oxides,[38, 39] 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 hours of hydrothermal process under 180°C or chemical reduction process for GO using amines under 95°C in water (Figure 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 (Figure 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.

2.4 Fluorinated Graphene as a Nanoenergetic Additive

Beginning with the fluorination of bulk graphite in 1934, [40] exploration of fluorinated carbon-based materials has steadily increased. [41, 42] Fluorine-functionalized polymers in a carbon skeleton have generated commonly-used materials such as polytetrafluoroethylene (PTFE). [43-45] Directly bonding fluorine atoms to sp^2 carbon materials is a controllable and reliable method to prepare fluorographite [46, 47], which is commonly used as a lubricant [48], biomolecular sensing agent, [49] and cathode in lithium cell [50]. More recently, fluorination of carbon nanomaterials such as C_{60} [51], carbon nanotubes [52, 53] and graphene [54, 55] has been demonstrated. Specifically, graphene has been widely recognized to be highly thermally and electrically conductive, mechanically strong and unique in optical properties. [56, 57] However, these properties were dramatically modified after fluorination due to the extreme electronegativity of fluorine. As a result, fluorinated graphene has been applied in high-performance supercapacitors [58], anode material for lithium-ion batteries [59], optical limiting devices [60], and transistors [61]. Various methods have been developed to obtain fluorinated graphene with different F/C ratios. [62] Gas-solid reactions between F_2 with graphene oxide (GO) [63], or XeF_2 with chemical vapor deposition (CVD) graphene [54, 64] generate fluorinated graphene with F/C ratio up to approximately 1. Plasma fluorination of graphene and GO by using different inorganic fluorine compounds as the fluorine source such as SF_6 , CF_4 or Argon/ F_2 , provide a mild F/C ratio up to 0.3. [65-67] Other chemical methods such as hydrothermal [68, 69] and photochemical fluorination [70], or physical exfoliation methods by using fluorographite [71, 72], were also employed to obtain fluorinated graphene. The reaction between graphene or GO and a gaseous fluorination agent such as F_2 or XeF_2 may provide the highest capacity and controllability for fluorine loading. The toxicity of F_2 gas, however, limits its wide application even a high F/C ratio of 1.02 was reached. [63] Investigation of fluorination using XeF_2 has been limited for CVD graphene, and this method has produced fluorinated graphene with no extra functional groups, limiting its further applications. [64] Fluorinating GO using XeF_2 may partially retain oxygen functional groups, enabling the production of chemically functionalized fluorinated graphene oxide (FGO).

Fluorinated graphene has not previously been explored as a reactive additive for nanothermite materials. A typical nanothermite material is a binary mixture composed of solid-state fuel (Al, Mg, Si, B, etc.) and oxidizer (normally metal oxide) nanostructures. Al-based nanothermites are widely investigated because of the abundance and easy production of Al nanoparticles, and its large mass specific energy release.[13] The native alumina shell on the surface of Al nanoparticles, however, severely restricts access to the Al core and reduces the reaction rate of the material. The role of the rigid shell in the reaction mechanism has not been thoroughly understood and is a study in progress, complicating the optimization of Al-based nanothermite composites. [73-75] Fluorine species may exothermally react with and etch the alumina shell, allowing the Al core to diffuse out from the shell and react with oxidizer, even below the Al melting temperature. These pre-ignition reactions between the alumina shell and fluorine species have been observed during the decomposition of fluoropolymers such as PTFE and THV. [12, 76]

Fluorine species may also be delivered to Al nanoparticle from other host material systems. We have previously reported the self-assembly of nanothermite fuel and oxidizer nanoparticles on GO sheets, forming micro- or macro- size nanothermite composites while providing increased energetic performance in terms of energy release and combustion speed.[20, 77]

Here we report a parametric study of GO fluorination using XeF_2 exposure. The produced FGO sample contained both fluorine functional groups and oxygen functional groups, enabling further functionalization and modification of the material. The sample was found to undergo change of functional groups such as acyl fluoride groups in air, and FTIR results showed a change in the material composition time. The release of fluorine from the material with heating was confirmed by mass spectrometry, and detailed decomposition process along with heating was investigated by TGA along with EDS. Additionally, FGO was utilized as an additive in Al nanoparticles and $\text{Al}/\text{Bi}_2\text{O}_3$ nanothermite composite. Confirmed by DSC results, the FGO additive enhanced the energetic performance for Al-based nanothermites by weakening the Al_2O_3 shell of Al nanoparticles.

3.0 METHODS, ASSUMPTIONS, AND PROCEDURES

3.1 Methods and Procedures to Produce Self-Assembly of Nanoenergetic Materials

Our preliminary study of energetic self-assembly exploited the functionalization chemistry of graphene, which interacts through long-range electrostatic and short-range covalent bonding, to produce multifunctional energetic materials through hierarchical and homogeneous self-assembly of nanoscale oxidizers and fuels into highly reactive macrostructures [20]. Specifically, we reported a methodology for directing the self-assembly of Al and Bi_2O_3 nanoparticles on FG sheets leading to the formation of nanocomposite structures within a colloidal suspension that ultimately condense into larger macrostructures that are close to 0.1mm by interconnection of FG-based composites (**Figure 1**). Briefly, Al and Bi_2O_3 nanoparticles were dispersed in 2-propanol and added to dispersed graphene oxide in dimethylformamide (DMF). Over a period of time, ranging from minutes to hours, depending on FG content, Al and Bi_2O_3 self-assembled onto FG sheets and macro particulates of the tertiary system precipitated uniformly from suspension due to charge neutralization and increased mass of the

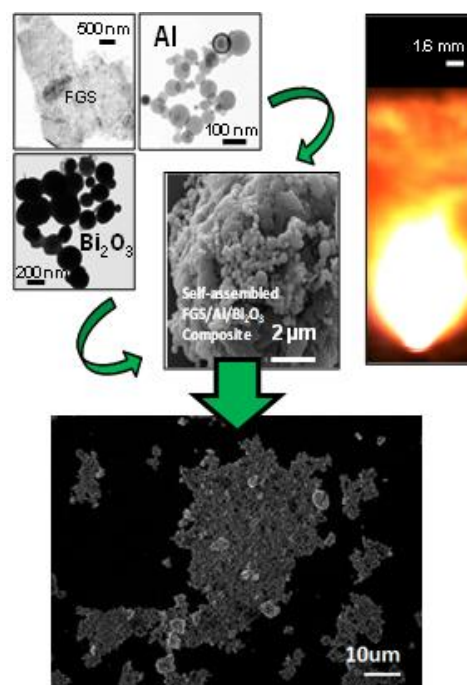


Figure 1. Nanocomposite energetic materials synthesized through self-assembly of Bi_2O_3 oxidizer and Al fuel nanoparticles using FG template to form 10 μm assemblies

assembled materials. The DSA process was designed as follows: upon adding positive surface charged Al nanoparticles to negative surface charged FG in suspension (where surface charge is determined by surface functionalities and the interactions between the nanoparticles and the suspension agent) Al nanoparticles and FG migrate toward each other through long-range electrostatic attraction and in close enough proximity, they covalently bond. The positively charged oxide (Bi_2O_3) component then assembles electrostatically with the FG-Al bonded (together still negatively charged) structures. A remarkable enhancement in energy release from 739 ± 18 to 1421 ± 12 J/g was *experimentally* measured for the FG self-assembled nanocomposites.

The substantial increase in energy release achieved through the incorporation of FG is a direct result of the intimate mixing of Al and Bi_2O_3 without phase separation, reduced sintering of Al nanoparticles, and the introduction of carbon into the nanocomposites to serve as a tertiary reactant. These effects are verified through optical micrograph images of graphene directed versus randomly mixed samples (**Figure 2**) and TEM images of as-prepared material before and after heating the samples to 900°C (**Figure 3**). Although the maximum energy release for FG (5%)/Al/ Bi_2O_3 was substantially higher than Al/ Bi_2O_3 , it was still lower than the theoretical value of 2118 J/g calculated for Al/ Bi_2O_3 which is likely due to the inert Al_2O_3 passivation layer of the Al nanoparticles. Here, we propose to remove this inert Al_2O_3 layer through *in situ* reaction of fluorine (released from fluorinated graphene surface) with Al_2O_3 [2]. The self-assembled nanoenergetic materials demonstrate significant combustion performance improvements in comparison to randomly mixed Al and Bi_2O_3 nanoparticles with enhanced pressure generation from 60 to 200 MPa, reactivity from 3 to 16 MPa/ μs , burn rate from 1.15 to 1.55 km/s, and specific impulse from 41 to 71 sec [78]. For practical applications, our observations revealed that the electrostatic discharge (ESD) ignition sensitivity of the self-assembled Al, Bi_2O_3 , and FG was reduced by four orders of magnitude due to the conductive nature of FG (from a fraction of micro-joule to milli-joule range) without reducing the combustion

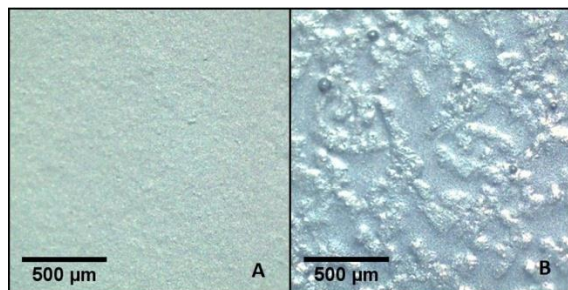


Figure 3. Optical microscopy images of graphene assembled Al/ Bi_2O_3 nanothermite sheets (A) compared to randomly mixed Al/ Bi_2O_3 nanothermite sheets (B) after drying. Phase separation and agglomerations of Al and Bi_2O_3 form during the drying process of randomly mixing.

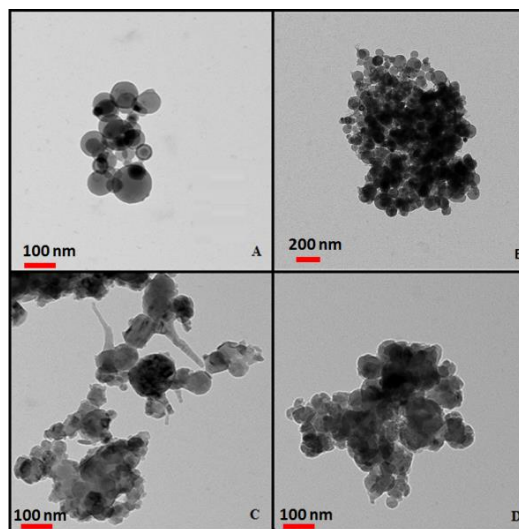


Figure 2. TEM images (A) Al, (B) Al/FG, before and (C) Al (D) Al/FG after heating at 900°C . Sintering of Al nanoparticles is observed when particles are not assembled on FG (C). Strong chemical and electrostatic interaction of Al and FG prevents Al sintering (D).

performance when compared to randomly mixed Al/Bi₂O₃. Our preliminary investigations on unfunctionalized graphene (UFG) sheets which inherently possess negative charge from surface and edge defects show that similar to functionalized graphene, UFG also participates in DSA of positively charged fuel and oxidizer nanoparticles. Therefore, FG/UFG DSA can be used to synthesize nanoenergetic materials with diverse combustion properties and controlled ignition sensitivities which lay the foundation for preparing future generation, multifunctional, and highly reactive energetic materials. The combustion performance benefits are attributed to FG/UFG DSA minimizing heat and mass diffusion lengths which enhance the reaction kinetics, improve the intermixing and intimacy of fuel and oxidizer, accompanied with the beneficial combustive and mechanical properties of graphene. The vast performance benefits reported here are significant in comparison to other works using graphene exclusively as an additive (not as a self-assembly agent), which have shown only minor improvements in combustion performance [79, 80].

3.2 Methods to Produce MoO₃ as a 2D Scaffold for Self-Assembly

Inspired by preliminary results using graphene materials as a scaffold for self-assembly, a 2D MoO₃ oxidizer was substituted for the graphene in the assembly process. The MoO₃ sheets provide the similar self-assembly benefits as graphene, with the added benefit that it plays an active role in the combustion reaction.

Micron size molybdenum trioxide ACS Reagent 99.5% grade powder (Sigma Aldrich) was used as the precursor for liquid exfoliation process to produce nanosheets. It was also used directly to produce micron MoO₃/Al composites. Aluminum nanoparticles (Nova Centrix) with an average particle size (APS) of 80 nm, a 2.2 nm oxide shell thickness, and 79% active content were used as the fuel in the nanoenergetic composites. Isopropyl alcohol (Sigma Aldrich, HPLC grade, 99%) was used in the MoO₃ liquid exfoliation process as well as in the synthesis of nanoenergetic composites.

Molybdenum trioxide powder was oven dried at 100°C prior to exfoliation to ensure moisture was removed. The powder (24 g) was added to 2-propanol, IPA (80 mL) to produce a 300 mg/mL dispersion. IPA provides high stability dispersions of MoO₃ sheets indicated by the zeta potential, as discussed later. 53 mL of the solution was placed in an external ice bath maintaining a temperature around 0°C during the sonication process to avoid any overheating. A Misonix 00 sonic wand with 60 W was utilized, with a duty cycle consisting of 9 seconds on and 2 seconds off for a duration of 10 hours. The sonication processing power and time were optimized to break weak interlayer van der Waals bonds and produce exfoliated 2D sheets from the bulk MoO₃. Many well-established methods have been developed and referenced to compare to our method [2]. To separate exfoliated sheets from the bulk powder, the dispersion was centrifuged for 50 minutes at 3434xg. The residual material was then subjected to further sonication and centrifugation processes. The 2D MoO₃ sheets were then dried at 60°C in a vacuum oven.

Various Al/MoO₃ composites were prepared by using either the as-purchased MoO₃ powder or exfoliated 2D MoO₃ sheets. To obtain a specific fuel-to-oxidizer mass

ratio, MoO₃ and Al NPs were mixed in equivalence ratios from 1.0, 1.2, 1.4 and 1.6 as shown in Table 1. These equivalence ratios were calculated considering the aluminum oxide shell thickness of 2.2 nm and 79% active Al weight percentage. Based on Table 1, each constituent material was separately weighed and dispersed in 1 mL of IPA for 3 hours using an ultrasonic bath to ensure stable precursor dispersions. Then, MoO₃ and Al NPs suspensions were added and ultrasonically mixed for another 1 hour. Because self-assembly of Al nanoparticles on MoO₃ sheets is imperative, our process demands that the MoO₃ flakes begin in a well-dispersed state. If MoO₃ sheets were allowed to dry into a dry powder after sonication, the material would form MoO₃ aggregates that would discourage high surface area assembly. The current process is also more straightforward, as exfoliation of MoO₃ itself generates a dispersion that may be directly used for assembly. After sonication, the homogeneous mixtures were vacuum-dried at 60 °C for 3 hours to evaporate the IPA.

Table 1. Experimental parameters used in the synthesis of Al/MoO₃ nanocomposites

Equivalence Ratio	Al NP (mg)	Active Al Content (mg)	MoO ₃ (mg)
1.00	32.19	25.43	67.81
1.20	36.29	28.67	63.71
1.40	39.92	31.54	60.08
1.60	43.16	34.10	56.84

The zeta potential, thermal, and surface properties of the constituent materials and mixed composites were characterized using a variety of techniques. Zeta potential and particle size of the material were measured using a Delsa Nano C instrument (Beckman Coulter). Thermal characterization of Al/MoO₃ nanothermite was conducted using a TGA/DSC (TA Instruments Q600-SDT) with dual beam balance. Six milligrams of each sample was evenly dispersed to cover the entire base of the sample container and provide a good thermal contact. The sample was heated from room temperature to 1400°C at a rate of 20°C/min under an argon flow. Surface morphology and elemental analysis of the materials were examined using several characterization techniques. A Bruker Innova atomic force microscope (AFM) was used to observe the topology of 2D MoO₃ sheets after sonication. An FEI Quanta 600 FEG scanning electron microscopy (SEM) and FEI Tecnai F30 twin 300 kV High-Resolution Transmission Electron Microscopy (HRTEM) were used at various stages of processing to inspect the nanoenergetic material composition. Energy dispersive X-ray spectroscopy (EDS) was used in both SEM and TEM to provide elemental analysis of the corresponding material. The HRTEM is equipped with an Oxford ultra-thin window EDX detector, a Gatan ultra-scan, and Fischione high angle annular dark field detectors for STEM imaging. Powder X-ray diffraction (XRD) patterns were recorded on a Rigaku Ultima IV powder X-ray diffractometer operated at 44 kV and 44 mA using a copper X-ray radiation ($\lambda = 1.5438$ Å). Samples were scanned for XRD patterns from 10° to 80° (2 θ) with a step size of 0.02° and scanning speed of 2° /min.

Nanothermite materials were prepared correspondingly to each microscopy measurement. For AFM imaging, 100 μ L of dispersed material in IPA was drop cast on an AMD-cleaned low-doped silicon wafer. The sample was then dried under vacuum for 2 hours. Electron microscopy imaging was performed before and after slow and fast heating. For SEM inspection small amount of each material was deposited onto carbon tape adhered to a SEM stub. Diluted solutions in IPA with 0.001 mg/mL concentration were deposited on a lacey carbon grid for TEM inspection.

Nanoenergetic composite combustion was evaluated using a closed pressure cell configuration. For this experiment, 30 mg of Al/MoO₃ nanocomposite powder was loaded into a 6.2 mm diameter and 2 mm deep cylindrical metal well. A 0.13 mm-diameter Ni-alloy fuse wire was used as an ignitor by applying a DC voltage pulse. Pressure release was recorded using a piezoelectric pressure sensor (PCB Piezotronics Model 119B12), which was clamped to the top of the cylindrical metal well after the fuse wire had been installed.

Linear combustion rate was recorded using an optical sensing method. The experimental setup consisted of a transparent Lexane tube with a dimension of 95 mm length, 9 mm outer diameter, and 3.2 mm inner diameter. Approximately 200 mg of nanocomposite material filled about a half of the tube cross-section at one end of the tube. A spark plug ignited the powder at one end, and a lid confined the other end of the tube. The tube resided within an aluminum block with up to eight fiber optic channels separated by 10.0 mm along the length of the block. Light propagation during combustion was captured via a photodiode array connected to a Tektronix TDS3014B digital oscilloscope. Because the sensors are recessed in high aspect-ratio ports, the acceptance angle for the detection of light is very small. Therefore, detection from the flame occurs only when the flame is underneath the detector. More detailed descriptions of the pressurization rate and linear combustion rate measurement configurations are provided in our previous work [30,31].

3.3 Methods to Produce Isolated MoO₃ sheet and Al Nanoparticles for Reaction

Thin α -MoO₃ flakes were synthesized using the ambient pressure physical vapor deposition (APPVD) method[18]. A 500 nm thick Mo film deposited on a Si wafer by DC sputtering was heated to 540 °C for 10 minutes in air. A freshly cleaved Mica sheet was then placed in contact with the top of the Mo surface. During heating, the Mo oxidized, and thin layers of α -MoO₃ were deposited on the mica surface. The flakes were adhered to the mica by van der Waals forces. A polydimethylsiloxane (PDMS) stamp was pressed to the mica sheet and placed in DI water to separate PDMS from mica sheet to transfer the α -MoO₃ flakes to the desired substrate.

Plasmonic gratings were produced using a polymethylsilsequioxane (PMSSQ) mold of commercially available HD-DVD discs[16]. The PMSSQ mold attained the same grooved profile as the master (height: 60 nm, pitch: 400 nm) and was deposited onto a silicon substrate. A 100 nm layer of Ag was then sputtered onto the free surface of the grating, followed by a 10 nm capping layer of Al₂O₃ deposited by ALD. Before the transfer

of the α -MoO₃ flakes, the grating was first treated with oxygen plasma for 30 seconds at 7W to increase the surface energy. Aluminum nanoparticles with a mean diameter of 120 nm were dispersed in a solution of IPA (0.05 mg/mL) and drop casted onto the grating substrate containing the α -MoO₃ flakes.

After locating Al NPs residing on MoO₃ flakes, the Al NPs were irradiated using a Renshaw inVia Raman System equipped with a linearly polarized 633nm HeNe laser. The laser served as both an optical probe and a heating source to enable Al NP combustion. An Olympus 100X immersion oil objective was used for imaging, creating a beam spot size of <1 μ m, providing highly localized heating. Ignition of the nanoparticles was achieved using a 50% laser intensity, with the incident power measured at sample to be approximately 5.5 mW. The surface topology of the α -MoO₃ flakes was characterized using an atomic force microscope (AFM) (Innova®, Bruker Biosciences Corporation) and AppNano ACTA silicon SPM tips (k: 40 N/m, f: 295 kHz, tip radius: ~6 nm).

TEM imaging and electron beam diffraction were obtained using an FEI Tecnai F30 G2 instrument at 300 KeV. TEM samples were prepared from flakes that were transferred to a PDMS stamp using ethanol and dispersing the flakes on a lacey carbon TEM grid.

Bright field and scattering images were obtained before and after the reaction using an Olympus BX51WI epi-fluorescent microscope coupled to a Sutter Instruments LAMBDA XL light source. To obtain scattering images, the incident light was linearly polarized, and the reflected light passed through an analyzer polarized 90 degrees to the incident light. Using the optical scattering configuration and the plasmonic grating substrate enhanced the electromagnetic field surrounding the Al NPs, facilitating optical imaging with resolution greater than the diffraction limit and allowing the resolution of individual 120 nm Al particles. All imaging occurred using immersion oil to optimize resolution.

3.4 Methods to Fabricate Energetic Aerogels

To initiate the self-assembly process, GO paper, Al nanoparticles and Bi₂O₃ nanoparticles were separately dispersed into propylene carbonate and sonicated for 4 hours. Detailed amounts of samples in different equivalence ratio are listed in Table 2. Equivalence ratio was calculated by the ratio of fuel / oxidizer over stoichiometric value. Afterwards, the dispersions were mixed together in a vial and rested for 16 hours. Then 40 μ L ethylenediamine was injected to the mixture to initiate gelation, and the vial was moved to a 95 °C oven for 8 hours. 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.

Table 2. Typical amount of material used in the samples measured.

GO %	Equivalence Ratio (Φ)	Propylene Carbonate	Al NPs (79%)	Bi ₂ O ₃
30 mg	1.0	3 mL	72.9 mg	497.1 mg
	1.2		85.3 mg	484.7 mg
5 %	1.4		97.1 mg	472.9 mg
	1.6		108.4 mg	461.6 mg

For the control Al/Bi₂O₃ sample made in IPA, we used the standard process reported in prior work. [81] For the control Al/Bi₂O₃ sample made in PC, calculated amount of Al and Bi₂O₃ (200 mg in total, $\Phi = 1.4$) was weighed and dispersed in PC under sonication for 4 hours 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/Bi₂O₃. This control sample was produced from the same material from which the aerogel was produced. After the 16-hour resting step, a portion of the mixture was moved to an aluminum foil bowl and dried under vacuum (bypassing the gelation step).

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 NPs and Bi₂O₃ were both 0.001 mg / mL in PC. Differential scanning calorimetry - thermogravimetric analysis (DSC-TGA) was performed on a TA Instruments SDT Q600 thermal analyzer to measure the heat flow and weight loss. The test was carried out under argon atmosphere (gas flow rate = 200 mL·min⁻¹) at a heating rate of 20 °C·min⁻¹. An environmental scanning electron microscopy (FEI Quanta 600 FEG ESEM) was used to observe the morphology and structure of the sample. The microscopy is equipped with Bruker Quantax 200 Silicon Drift Detector with Xflash 6 for X-ray energy dispersive spectroscopy (EDS) and elemental mapping. X-ray diffraction (XRD) patterns were recorded on a Rigaku Ultima IV powder X-ray diffractometer operated at 44 kV and 44 mA using a copper X-ray radiation ($\lambda = 1.5438$ Å). Samples were scanned from 20° to 80° (2 θ) with a step size of 0.02° and at the scanning speed of 2°/min. FTIR spectrum of the products were measured by using a Thermo Nicolet 4700 FT-IR Spectrometer. The samples were placed on the Germanium stage in the ATR accessory for measurement. The open burning test was conducted inside a polycarbonate box, with high-speed imagery recorded by Phantom fast camera. The frame speed was set at 100,000 fps, so the time difference between frames was 10

μs. ESD sensitivity test was carried out by using a system from Electro-Tech Systems (ETS) Inc (Model 931), which is consisted of a 300 – 20,000 pF capacitor bank charged in a range from 100 V to 26 kV. Samples filled were placed within an electrically grounded stainless-steel well surrounded by a plastic ring.

The stoichiometric fuel/oxidizer ratio is calculated by the normal chemical reaction between Al and Bi₂O₃, and the equivalence ratio (Φ) [82] is defined as

$$\Phi = \frac{[n(\text{fuel})/n(\text{oxidizer})]_{\text{actual}}}{[n(\text{fuel})/n(\text{oxidizer})]_{\text{stoichiometry}}}$$

Since only 5% GO by weight was used during the synthesis, the role of GO is neglected from Φ calculation.[20] If not specially mentioned, the samples consist of 5% GO and 95% Al/Bi₂O₃ nanoparticles with Φ=1.4 (fuel rich).

3.5 Methods to Fabricate Fluorinated Graphene for a Nanoenergetic Additive

GO paper was produced by modified Hummer's method for fluorination with XeF₂. [20] In brief, 1 g graphite (xGnP science, 5 μm) and 1 g NaNO₃ (Aldrich) were dispersed in concentrated 46 mL H₂SO₄ (Fluka) cooled by ice/water bath under magnetic stirring. Next, 6 g of KMnO₄ (Aldrich) was gradually added to the mixture while keeping the dispersion under 20 °C. Subsequently, the mixture was heated to 35 °C for a duration of 1 hour. 80 mL of water was added, and the mixture was heated to 80 °C for 30 minutes. After cooling, 6 mL H₂O₂ (Fluka) was added to the mixture to terminate the reaction. The GO product was then purified by repeatedly washing with water and centrifugation until the resultant supernatant turns neutral. Finally, the dispersion was sonicated in water at a concentration of approximately 3 mg/mL and dried at 70 °C overnight to obtain GO paper.

A custom-built pulsed xenon difluoride (XeF₂) reaction system was used for the fluorination of as produced GO paper. XeF₂ in its vapor phase is pulsed into the reacting chamber until the pressure in the chamber reached 3000mTorr, and the reaction of GO paper with XeF₂ is carried out for 10 minutes before the reaction chamber is pulsed with N₂ to purge XeF₂ to complete one cycle of the pulsed reaction. Two sets of fluorinated GO paper were synthesized, one with 130 pulsed cycles corresponding to 1300 minutes of XeF₂ treatment labeled as FGO-I and the other with 270 cycles corresponding to 2700 minutes of XeF₂ treatment labeled as FGO-II. After reaction, the samples were stored in desiccator at approximately 15% humidity and 25 °C before further characterization.

GO/Al and FGO/Al samples were prepared from the following procedure. FGO samples were used immediately after XeF₂ treatment finished. GO and FGO were first dispersed in isopropanol (IPA, anhydrous, Fluka) at a concentration of 2 mg / mL by sonication for 5 hours. Separately, Al nanoparticles (Novacentrix, 80 nm average diameter with 2.2 nm Al₂O₃ shell, 79% reactive) were dispersed in IPA at a concentration of 20 mg / mL for 4 hours. Calculated amount of Al dispersion was then added to FGO or GO dispersed, and sonication for extra 4 hours. The mixture was finally dried under vacuum.

Al/Bi₂O₃ nanothermite (Al/Bi₂O₃ equivalence ratio = 1.4) was synthesized by 5-hour sonication. Bi₂O₃ nanoparticles (Aldrich, 200 nm) were first sonicated in IPA (400 mg in 1.2 mL) for 1 hour. Thereafter, 82 mg of Al nanoparticles were added directly to the Bi₂O₃/IPA dispersion and sonicated for an additional 4 hours. The dispersion was then dried under vacuum. [20]

The FGO/Al/Bi₂O₃ and GO/Al/Bi₂O₃ nanothermite composite was prepared by a similar 9-hour sonication process. FGO was dispersed in IPA at a concentration of 2 mg / mL by sonication for 5 hours. Simultaneously, Al /Bi₂O₃ was prepared in IPA as well by the 5-hour sonication process described above. Calculated amount of Al/Bi₂O₃ dispersion was then added to FGO dispersions and sonicated for an additional 4 hours. The mixture was finally dried under vacuum to obtain the product. FGO and GO occupied 5% of total mass in the nanothermite composite and the equivalence ratio between Al and Bi₂O₃ was also 1.4, fuel rich. A control Al/Bi₂O₃ sample was also prepared separately compare the energy release with the FGO/Al/Bi₂O₃ and GO/Al/Bi₂O₃ sample.

Thermogravimetry and differential scanning calorimetry (DSC-TGA) was carried out (TA Instruments SDT-Q600) at a heating rate of 20 °C·min⁻¹ under argon flow at 200 mL·min⁻¹. Samples were placed in Pt crucibles during heating.

Fourier-transform infrared spectroscopy (FTIR) spectrum was measured by a Thermo Nicolet Nexus 4700 FT-IR spectrometer. Attenuated total reflectance (ATR) was carried out using the same equipment on a germanium stage.

Mass spectrometry was carried out by a T-jump [83] mass spectrometry hybrid system. The FGO sample was dispersed in IPA and coated on a Pt filament. Then the Pt was heated at a rate of $\sim 3 \times 10^5$ K/s, producing decomposition products which were then ionized at 70 eV and analyzed by a time-of-flight mass spectrometer.

X-ray diffraction (XRD) patterns were recorded on a Rigaku Ultima IV powder X-ray diffractometer operated at 44 kV and 44 mA using a copper X-ray radiation ($\lambda = 1.5438$ Å). Samples were scanned from 5° to 60° (2 θ) with a step size of 0.02° and at a scanning speed of 2°/min.

X-ray Energy Dispersive Spectroscopy (EDS) was analyzed by using Bruker Quantax 200 Silicon Drift Detector with Xflash6 along with FEI Quanta 600 FEG Environmental Scanning Electron Microscope. Measurements were taken at low vacuum mode at 50 Pa to compensate the low conductivity of the material, if necessary.

3. RESULTS AND DISCUSSION

3.1 MoO₃ as a 2D Scaffold for Self-Assembly

The morphology and structure of the MoO₃ powder precursor was first investigated using SEM. As seen in **Figure 4**, the majority of the MoO₃ precursor material is composed of particles from several to tens of micrometers in length and width. The typical cross section was approximately orthorhombic, as opposed to spherical. Average particle thickness was estimated to be several micrometers.

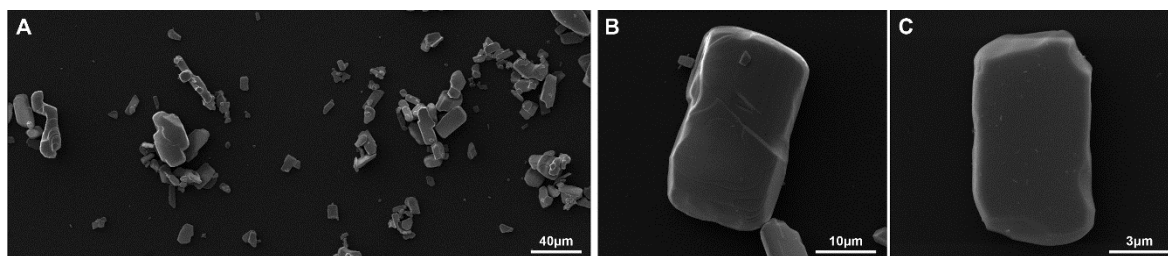


Figure 4. SEM micrographs of as-received MoO₃ powder. A) The MoO₃ powder dimensions ranged from several to tens of micrometers shown. Higher magnification (B and C) reveals the rectangular shape and layered structure of MoO₃.

The morphology of MoO₃ after sonication was examined using AFM to study the exfoliation process. Previously sonicated and dried MoO₃ material was diluted in IPA, treated in an ultrasonic bath for an hour, and dispersed on a silicon substrate. Representative AFM micrographs, shown in Figure 5, indicate the exfoliated MoO₃ nanosheets have a bimodal distribution in regards to their lateral dimension. Numerous islands consist of edge-assembled sheets with an average length of 742 nm and thickness of 2.16 nm. Individual flakes exhibited an average of 133 nm and 1.72 nm in length and thickness, respectively. The individual sheets assembled through edge defect interaction in a manner similar to graphene [32]. When comparing these dimensions to the original MoO₃ powder, it is evident that the sonication did not only break the van der Waals plane-to-plane bonding, but also the in-plane bonding of the initial MoO₃ crystalline structure. Based on thickness measurements, the MoO₃ nanosheets after sonication contain 3-4 layers of the material, where an atomic layer is 0.6 nm thick [33].

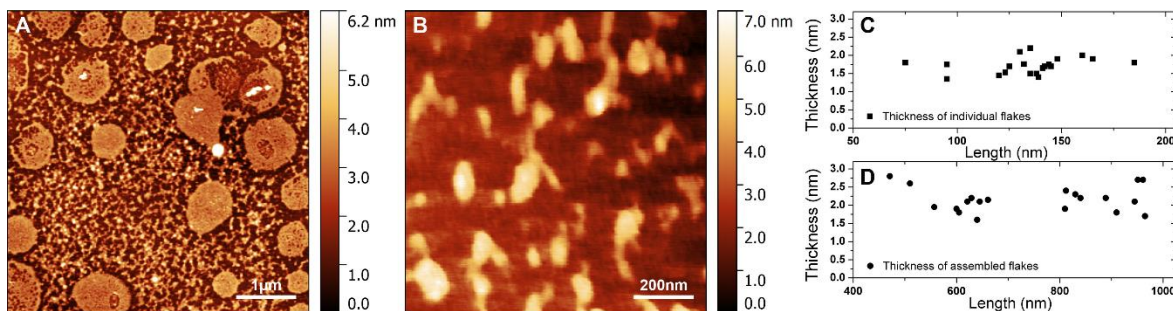


Figure 5. A) AFM micrographs of MoO₃ dispersed on silicon after sonication may be found as large edge-assembled sheets or B) isolated sheets. The distribution of flake thickness as a function of lateral length for C) isolated flakes and D) edge-assembled sheets.

The stability of a suspension is determined by the degree of short-range and long-range forces in colloidal dispersion and can be measured by the zeta potential [34]. Zeta potential measurements were performed on the constituents to study their stability and to understand their electrostatic interaction. Our result indicates that the zeta potential of Al nanoparticle is $+34.28 \pm 1.61$ mV. Similar measurements of MoO₃ after sonication had a zeta potential of -49.43 ± 0.72 mV. These relatively large zeta potential magnitudes indicate that each material is a stable colloidal dispersion. After sonication, repulsive electrostatic forces between nanosheets/nanoparticles prevent particle agglomeration in

suspension. Both Al NPs and MoO₃ nanosheets produced by ultrasonic exfoliation remained dispersed well in the suspension for at least five days if left undisturbed.

It is worth noting that a small portion of the MoO₃ material remains in bulk size due to our inability to filter them out completely during centrifugation process. However, a majority of the MoO₃ is observed to be thin sheets, as observed in **Figure 6**. The opposing zeta potential polarities of the constituents facilitate assembly of Al NPs and MoO₃ nanosheets due to electrostatic attraction. **Figure 6A** illustrates the ordered layer-by-layer assemblies of Al and MoO₃ produced after mixing. The intimate contact between fuel and oxidizer may greatly improve the reaction kinetics. Isolated portions of samples exhibited random mixing of Al and MoO₃ 2D sheets (**Figure 6C**). Increased magnification, shown in **Figure 6B -C**, further illustrates that the exfoliation process created 2D MoO₃ sheets that are thin enough to be electron transparent, as Al particles may be observed underneath the sheets (**Figure 6C**).

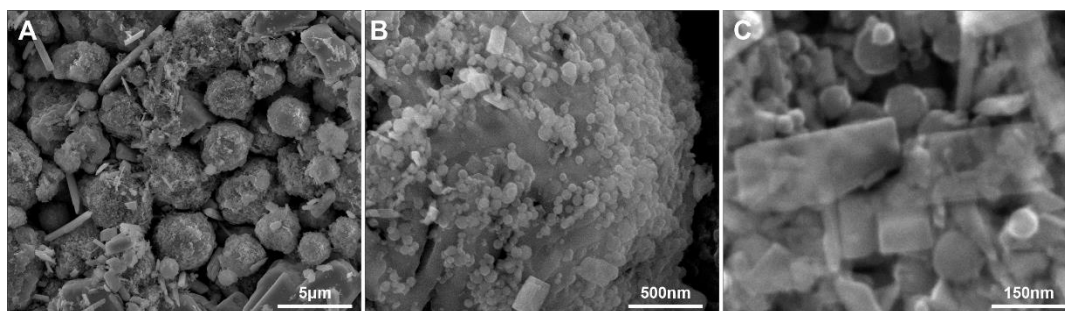


Figure 6. SEM micrographs showing A) self-assembled clusters of tightly-packed Al nanoparticles and MoO₃ sheets with long-range order to many microns. B) Higher magnification of one of the clusters shows the intimacy of Al and MoO₃. C) The 2D morphology of the MoO₃ flakes is readily apparent on the surface of the randomly mixed nanoenergetic composite.

Data from TGA/DSC measurements of 2D MoO₃ sheets alone is presented in **Figure 7A**. Note that the instrument was calibrated using several known materials to facilitate the determination of total heats of reaction. A broad exothermic peak is observed, with a peak occurring at 430°C. Previous TGA/DSC studies of nanoscale MoO₃ particles [35,36] have observed a similar broad peak with a peak near 450°C and has been associated with a crystal reorientation to preferred orthorhombic structures. These results indicate that MoO₃ is mobile even at relatively low temperatures. Two strong endothermic peaks at 785.76°C and 827.33°C, representing the melting and the decomposition temperatures of MoO₃, respectively, were accompanied by a significant weight drop of about 84.95%. The nanoscale confinement of the MoO₃ sheets may be responsible for reducing the bulk melting MoO₃ temperature of 795°C [37].

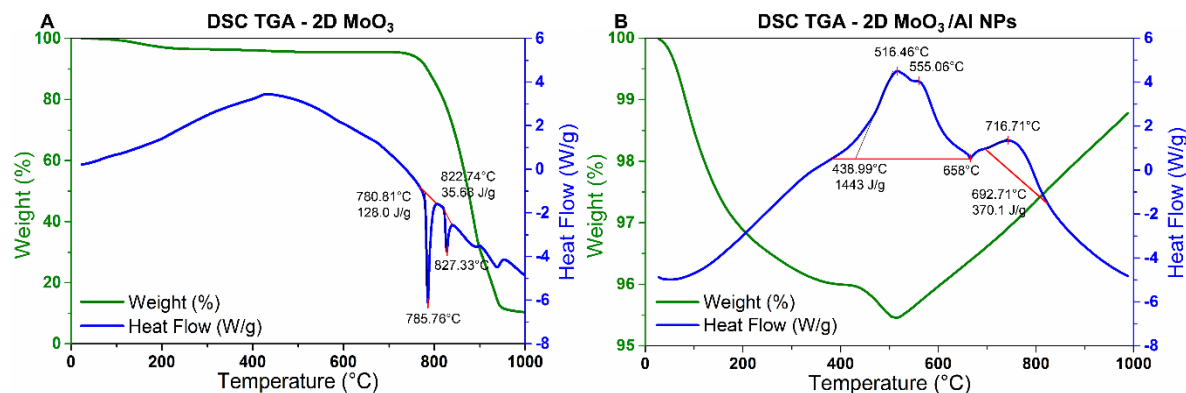


Figure 7. TGA/DSC corrected baseline curves of A) 2D MoO₃ nanosheets and B) Al/MoO₃ nanocomposites with an equivalence ratio of 1.4.

A baseline-corrected TGA/DSC measurement of composite of Al NP and MoO₃ 2D sheets at 1.4 equivalence ratio is presented in **Figure 7B**. An exothermic peak with an onset temperature at 438.99°C and peak temperature at 516.46°C represents the majority of the thermodynamic reaction in the system, releasing 1,443 J/g. This peak terminates with an endothermic peak at 658°C, indicative of Al melting. Within this temperature regime, Al is in the solid state, and the reaction mechanism is limited by transport of Al through the native alumina shell. In addition to the relatively slow process of Al diffusion, a compositional transformation of the shell could possibly occur from amorphous alumina to γ -Al₂O₃ at 590°C resulting in oxide void formation and exposure of the bare Al core [38,39]. The escaped Al reacts with available MoO₃, leading to early exothermic activity even before the melting point of the aluminum core [40,41]. An overlap between exothermic oxidation and the endothermic reaction from aluminum melting is observed between 600 to 658°C [37]. A second exothermic reaction occurred with an onset temperature at 692°C and peak at 716°C and produced 370.1 J/g of heating. This peak represents the initiation of liquid-solid reactions, as it is above the melting point of the Al core yet below the melting temperature of MoO₃. The melting of the confined Al inside of an alumina shell leads to volumetric Al expansion that is restricted by the surrounding oxide shell. As a result, the Al core is compressed, and the oxide shell is in tension, further increasing the diffusion rate of the liquid phase Al and providing a driving force to push Al through potential alumina voids.

Regardless of the escape mechanism, Al that is liberated from the shell is free to react with solid MoO₃ sheets. Recent density functional theory (DFT) studies indicate that Al atoms may spontaneously adsorb into the top-most layer of a MoO₃ crystal with little to no energy barrier [42]. Upon surface or sub-surface adsorption of Al by MoO₃, the oxygen in the lattice binds more tightly to the Al than to the host Mo, leading to reconstruction of the MoO₃ surface layer and an exothermic release of energy. The oxygen is retained in the solid state as the Al is incorporated into the host MoO₃ lattice. In our experiments, a mass decrease of less than 5% during TGA/DSC reaction indicates that much of the available oxygen was retained in the solid state in agreement with the proposed mechanism. The gradual increase in mass above 500°C, observed in **Figure 7B**, is attributed to imperfect background subtraction and is not attributed to reintroduction

of gaseous species. The proposed reaction mechanism is facilitated by a solid and 2D MoO_3 host lattice, restricting the temperature regime of this reaction to below approximately 785°C , the melting temperature of MoO_3 observed in **Figure 7A**. The lack of an endothermic TGA/DSC peak near the MoO_3 melting temperature indicates that the MoO_3 sheets have reacted with Al and are no longer present in the form of MoO_3 .

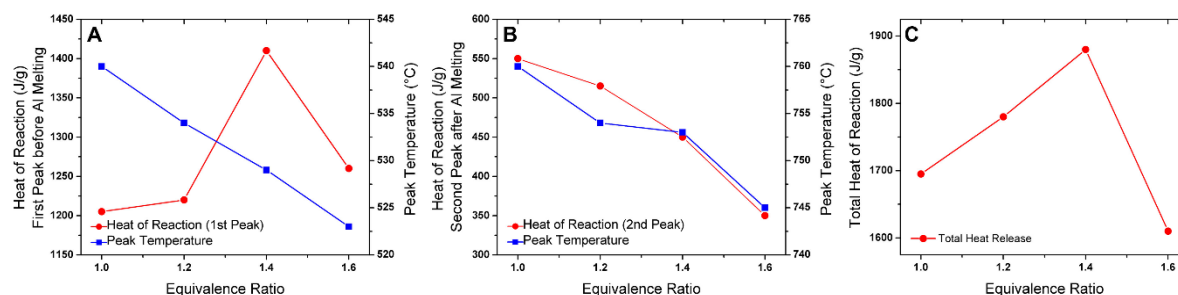


Figure 8. The heat of reaction and peak temperature of the A) first (solid Al) and B) second (liquid Al) exothermic peaks produced from Al NPs with 2D MoO_3 sheets as a function of variable equivalence ratio, measured by TGA/DSC. C) The total heat release from the combined solid and liquid-phase reactions.

TGA/DSC measurements were also performed as a function of Al/ MoO_3 equivalence ratio using exfoliated MoO_3 sheets. The energy release of the first exothermic peak (associated with solid-state reactions) and second exothermic peak (after Al melting) were evaluated, in addition to the temperatures at which the peaks were observed. **Figure 8A-B** shows that as the equivalence ratio increases from 1.0 to 1.6, the temperature of the first and second exothermic peaks decreased monotonically by 17°C and 15°C , respectively. Further, the energy released by solid-state reactions generally increased with equivalence ratio, while the heat of reaction associated with melted Al decreased. An exception to this trend is a decrease in energy solid-state energy release from an equivalence ratio of 1.4 to 1.6. The total heat of reaction, obtained by summing the energy release by solid-state and melted Al reactions, increased linearly with equivalence ratio between 1 – 1.4 from 1,700 – 1,880 J/g, and then diminished to 1,605 J/g at a ratio of 1.6. The homogeneity and proximity of 2D MoO_3 sheets and Al nanoparticles provide a reduced diffusion path for reactive species to proceed in the condensed state, resulting in an elevated heat release from the exothermic reaction [43] that may accelerate reactions between fuel and oxidizer. At equivalence ratios greater than 1.4, we suggest that a relative lack of MoO_3 availability decreases the overall heat of reaction. Note that even the highest temperature reaction of 760°C (**Figure 8B**) occurs before the decomposition temperature of MoO_3 of 786°C from **Figure 7A**.

SEM and TEM analysis of the TGA/DSC product further revealed the morphological evolution and the potential reaction pathways of the nanoenergetic system. Two samples were prepared by limiting the maximum TGA/DSC temperature to 575°C and $1,000^\circ\text{C}$. The SEM and TEM micrographs of Al/ MoO_3 heated to 575°C can be seen in **Figure 9**. Low magnification SEM showed numerous Al and MoO_3 nanostructures and some bulk MoO_3 flakes, as seen in **Figure 9A**. EDS mapping in SEM revealed dispersed Al, Mo, and O throughout the sample. After heating, numerous small nodes appear on the external

surface of spherical Al nanoparticles that were not previously present on the Al nanoparticles prior to heating. TEM micrographs of the same material in **Figure 9B** shows a spherical Al NP with external nodes containing Mo and O, suggesting that the 2D MoO₃ sheets were mobile on the Al NPs surface during heating and assembled, in part, as oblong nodes along the exterior of the Al NPs. The external surface of the oxide shells appear coarse, and traces of Al are observed outside of the spherical particle using EELS, suggesting some diffusion of Al through the alumina shell. These images suggest that Al diffusion and escape occurs at a temperature lower than the bulk melting temperature of 660°C, as supported by TGA/DSC and by findings that suggest that surface tension in nanoscale particles suppress melting temperature [44].

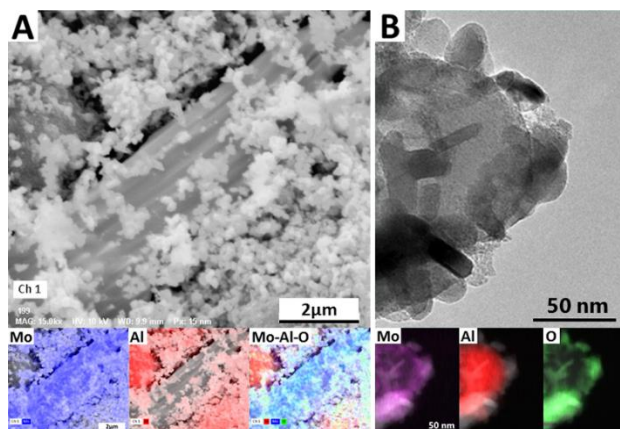


Figure 9. Al/MoO₃ sample heated to 575 °C (TGA/DSC) are examined using A) SEM and EDS mapping and B) TEM bright-field imaging and EELS elemental mapping. Both analyses show well mixed Al and MoO₃, with nanoscale MoO₃ flakes and nodes observed residing on the surface of Al nanoparticles in B).

SEM and TEM analysis of the material heated to 1,000°C by TGA/DSC is shown in **Figure 10**. Note that the exothermic reactions observed by TGA/DSC have completed at this temperature, so the observed products represent fully reacted material. SEM inspection (**Figure 10A**) shows a dramatic change in nanoparticle morphology. Numerous extended sheets are observed protruding from the spherical nanoparticles. This particle morphology is observed uniformly throughout the sample. TEM analysis (**Figure 10B**) indicates that metallic Al has escaped the shell, leaving behind hollow shell with a thickness (20 nm) that is drastically greater than the original shell thickness. This finding indicates that at least some of the Al from the core has oxidized on the external particle surface. The extended sheets observed protruding from the oxide shell in SEM are also observed in TEM. The sheet widths are on the order of 50 nm, and exhibit lengths extending up to 1 μm. The sheets exhibit long-range crystallinity, as observed in **Figure 10C**. EDS elemental mapping of the resulting flakes, shown in **Figure 10D**, indicates that the main constituents of the sheets are alumina, comprised of Al and O. Mo is not found within the flakes, but is rather found in a reduced form as particles dispersed throughout the sample, suggesting that it has been displaced from its original MoO₃ lattice during reaction.

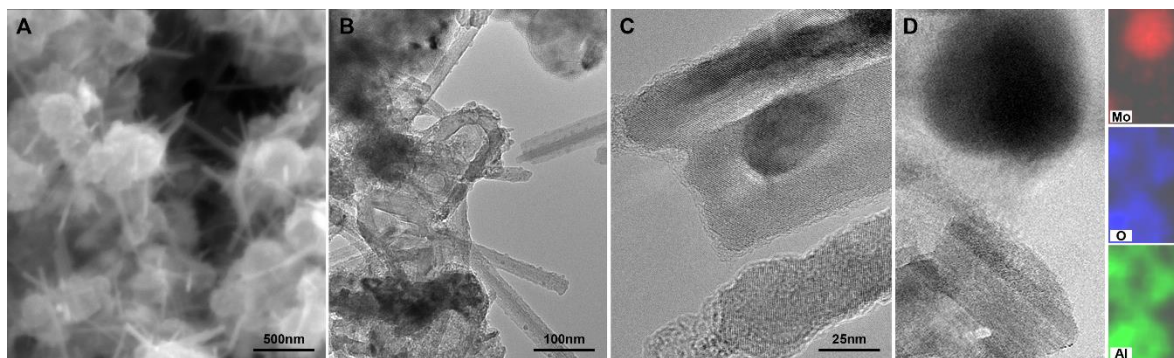


Figure 10. Reaction products from heating Al NPs with 2D MoO₃ to 1,000 °C in TGA/DSC. A) An SEM micrograph shows nanorod-decorated spheres. High magnification TEM micrographs of the extended structures (B and C) show the crystalline nanosheet structure. D) TEM EDS mapping shows that the sheets produced during reaction are comprised of aluminium oxide, while the darker nodes represent particles of reduced Mo.

Based on the DFT simulations performed by others [42], we hypothesize that mobile Al atoms that escape their shell diffuse on the surface of MoO₃ sheets and are adsorbed by a process notionally shown in **Figure 11**. DFT simulations suggest that Al atoms are adsorbed beneath the (010) surface of MoO₃ with no energy barrier, while surface adsorption requires overcoming as little as a 0.2 eV energy barrier. Both processes are highly exothermic and are, therefore, self-sustaining. As Al atoms are adsorbed, regardless of the adsorption site, oxygen in the MoO₃ lattice migrates towards the Al, forming ionic bonds. The host MoO₃ lattice reconfigures and weakens the bonds between Mo and O. The bond energy between Al and O within the lattice exceeds that between Mo and O, and we hypothesize that at sufficient temperature the Mo becomes displaced from the original MoO₃ lattice sites and forms small clusters on the surface of the evolving alumina sheet. The entirety of the MoO₃ sheet is converted to alumina sheet during the process, with the host MoO₃ serving as a solid state template to facilitate ion exchange from Mo to Al. Aluminum diffusion may also interact with neighboring MoO₃ sheets that are not in direct contact with the Al NP, thereby grafting multiple MoO₃ host sheets into a single extended alumina sheet. The 2D morphology of the original MoO₃ sheets is critical in this step, as Al adsorption and lattice reconfiguration is limited to the surface MoO₃ layers. As a surface phenomenon, Al adsorption on bulk MoO₃ powder will influence only a fraction of the MoO₃ volume, while a complete reaction occurs when using 2D MoO₃ sheets. While the alumina extensions and reduced Mo islands are experimentally observed products, the proposed reaction pathway in **Figure 11** is still a hypothesis. In-situ TEM and SEM reactions are planned to further validate the proposed model. Note that the **Figure 11** schematic is not intended to suggest specific crystalline structures or to indicate specific Al adsorption sites, but is rather a phenomenological guide.

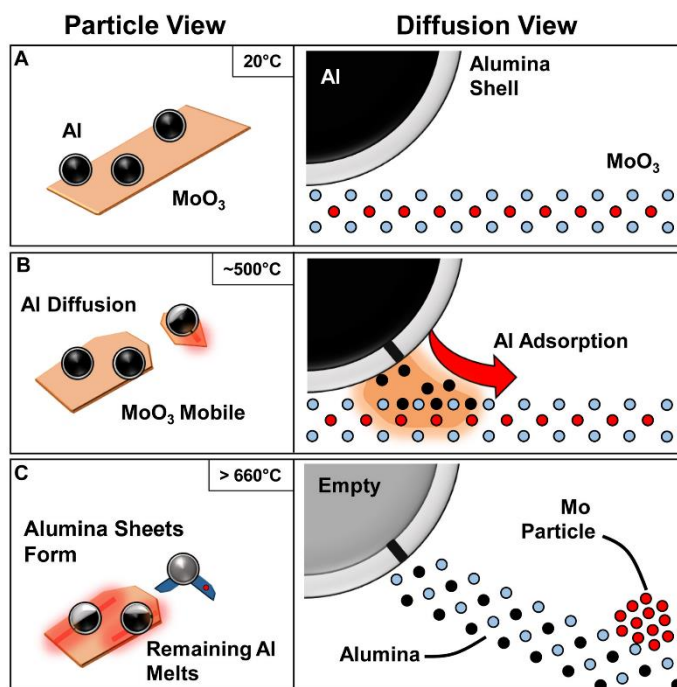


Figure 11. Schematic of the proposed combustion mechanism of a nanoenergetic Al nanoparticles and 2D MoO₃ sheets. Note that in all figures, the position of atoms is not meant to denote a specific crystal structure. A) At ambient conditions, intermixed Al and MoO₃ particles are assembled. B) Heating to elevated temperatures leads to MoO₃ migration to promote intimate contact between solid particles. Al atoms escape some of the nanoparticles and begin an exothermic reaction in which Al adsorbs into the 2D MoO₃ lattice. C) As heating increases past the melting temperature of Al, liquid Al escapes from more of the Al nanoparticles, initiating more Al adsorption and additional energy release. Excess heat displaces Mo from the host MoO₃ sheets, leaving behind alumina sheets and reduced Mo particles.

The electron microscopy analysis corresponds well to the two exothermic peaks observed in TGA/DSC observation. The first exothermic peak represents the diffusion and/or escape of Al through the oxide shell causing a condensed phase and highly exothermic reaction. As the Al remaining in the particle core melts, it is released from the shell to drive further reactions. Furthermore, the extended alumina sheets produced at relatively low temperatures act to separate neighboring Al fuel particles from each other, preventing large-scale agglomeration. Because alumina has a greater melting temperature than Al, these alumina extensions are expected to persist at temperatures far greater than those necessary to initiate and sustain combustion. If these surface extensions could be formed and retained during rapid combustion, the particle morphology could encourage the flow of heated gaseous byproducts between Al particles while preventing Al agglomeration and promoting increased reactive surface area.

The reactivity of several different equivalence ratios for Al/MoO₃ nanothermite were compared using both as-purchased microscale MoO₃ powder and 2D MoO₃ sheets. Pressurization and combustion speed tests were investigated using equipment and techniques described previously, with a heating rate of approximately 10⁸ K/s.

In the Al/MoO₃ energetic system, reactivity is sensitive to the equivalence ratio of the fuel and oxidizer, in addition to the relative size of each precursor material. In our

experiments, we find that an equivalence ratio of 1.4 produces the greatest peak pressure, pressurization rate, and the fastest combustion speed. The optimum equivalence ratio of 1.4 agrees with several previous works [14,19]. The peak pressure and pressurization rate produced by the Al/MoO₃ nanocomposites are at least two times greater than those produced by the Al/MoO₃ using micron-scale oxidizer particles. At 1.4 equivalence ratio, the peak pressure of micron Al/MoO₃ was 19.2 ± 1.43 MPa with rise time of 172 ± 9.54 μ s, leading to pressurization rate of 0.11 ± 0.02 MPa/ μ s. Whereas the peak pressure using 2D MoO₃ sheets was 42.05 ± 1.86 MPa with rise time of 12 ± 0.73 μ s, leading to a rate of 3.49 ± 0.31 MPa/ μ s. The combustion speed of the micron Al/MoO₃ powder was 51.3 ± 7.34 m/s, while nano-scale Al/MoO₃ produces a combustion speed of $1,730 \pm 98.1$ m/s. To the best of our knowledge, this is the highest combustion speed using a MoO₃ oxidizer reported to date, as observed in Table 2.

Table 3. Reported data of Al/MoO₃ combustion wave speed are compared to our measurement result

Author	MoO ₃ Dimension	Al NPs	Combustion Speed (m/s)	Pressurization (MPa/ μ s)	Pressure (MPa)
Pantoya[13]	Micron	10 nm	19		-
J.A. Puszynski [18]	Micron. 1.5 m ² /g specific surface area.	40.6 m ² /g	80*	-	-
J.A. Puszynski [18]	Nanosheets. 76 m ² /g specific surface area.	40.6 m ² /g	362*	-	-
Pantoya [44]	Nanosheets. 42 m ² /g specific surface area.	120 nm	410	-	-
Foley [19]	Nanosheets. ~50nm in length	38 nm	680	0.68	-
S. Son [14]	Nanosheets. 30 x 200 nm in size 64 m ² /g specific surface area	80 nm	950	-	18.6 or 0.165
Levitas [45]	>50 m ² /g specific surface area	50 nm	960	0.045	1.46
S. Son [46]	Nanosheets. 30 x 200 nm in size 64 m ² /g specific surface area	79 nm (81% AC)	1000	-	8
This work	2D sheets	80 nm	1730	3.49	42

Peak pressure and pressurization rate are indeed dependent on mass of energetic material, volume of the combustion chamber, % TMD, morphology (nanorods, nanowire, sheets, spherical nanoparticles that in turn tells the available surface area), self-assembly etc.[17] Therefore, it is not possible to make direct and exact comparison of pressurization data unless all of these measurement parameters are identical. Hence, we have not

attempted to make direct comparison. However, the surface area of the ingredients and the interfacial contacts between oxidizer and the fuel are important parameters for enhancing the kinetics/rate of reaction (burn rate and pressurization rate). Hence, it is reasonable to believe that the significantly enhanced pressurization rate seen in our work is a consequence of employing 2D sheets of MoO_3 .

Previous work has measured the reactivity of micron scale Al/MoO_3 composites, including both pressure and combustion speed measurements. The propagation speed is affected by the thermodynamic state of the products and it is observed that 1.4 equivalence ratio has the optimum proportion between the gas production and fuel interaction. Son et al. analyzed an Al/MoO_3 nanosheet material system with thicker MoO_3 flakes mixed with APS 80 nm Al nanoparticles [14,46]. Their fastest combustion speed was ~ 950 to 1000 m/s and a maximum peak pressure of 8 MPa. Foley et al. conducted Al/MoO_3 reactivity experiments using Al nanoparticle APS 38 nm and MoO_3 particles ranging in size from ~ 50 nm to $1\text{ }\mu\text{m}$ long [19]. This work also confirms an optimum equivalence ratio for Al/MoO_3 of 1.4. The measured combustion speed reached ~ 680 m/s. Pantoya et al. measured Al/MoO_3 reactivity experiments using 50 nm Al NPs and reached 960 m/s for the combustion speed test and 1.46 MPa of peak pressure test [45]. None of the previous works observed the unique post-combustion morphology of particles observed when using a 2D MoO_3 oxidizer. We hypothesize that the unique spike-like morphology, facilitated by 2D MoO_3 sheets, contributes to a more complete reaction and faster combustion speeds by promoting enhanced heat and mass transport through the separated particles.

Post-combustion analysis provides insight into the relative temperature of the reaction and the morphological evolution of the reactants during combustion. The combustion product was inspected in SEM by adhering material directly onto carbon tape. SEM images, shown in **Figure 12**, indicate that the reaction temperature was sufficient to fully melt the reactants. The products appear phase separated, as Mo-rich regions appear isolated in an Al-rich matrix. The combusted product was heterogeneous in nature, with isolated regions exhibiting highly porous regions, as observed in **Figure 12A**. Most of the combusted material appeared re-solidified and relatively smooth, as observed in **Figure 12B**. We propose that the highly porous areas represent regions that were molten during combustion and from which reaction gas escaped, leaving behind a porous structure after re-solidification. Note that the porous regions do not resemble large particle agglomerates that would be anticipated from a high-temperature sintering process. Backscatter electron imaging facilitated differentiation between material compositions via grayscale contrast, whereby elements having a higher atomic number appear brighter. A typical backscatter electron image is shown in **Figure 12B**. Note that relatively bright spheroidal inclusions were surrounded by a relatively dark matrix without an interfacial gap, indicating phase separated regions of Mo surrounded by Al, as confirmed by EDS. The intermixing and geometry of the Mo inclusions further indicate that the reacted material was molten during combustion, suggesting that the reaction temperature exceeded the melting temperature of Mo (2,896 K) and Al_2O_3 (2,345 K). Similar regions were not observed when observing the post-combustion product of micron-scale MoO_3 powder oxidizer.

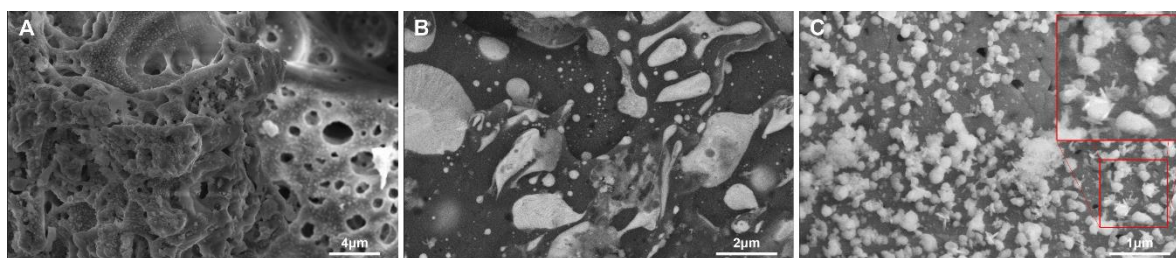


Figure 12. SEM micrographs of rapidly combusted nanoparticle Al / MoO₃ nanocomposite show varying morphology. A) Porous regions indicate solidified regions from which reaction gasses escaped during combustion. B) Resolidified and phase separated regions of Mo (bright) within an Al (dark) matrix indicate that the material was molten during combustion. C) Adjacent to resolidified material, discrete Al nanoparticles with radially oriented extended surfaces are observed, indicating that Al sintering was mitigated at reaction temperatures.

Solid spherical particles were often found near or on solidified reaction products, as indicated in **Figure 12C**. Because of the proximity of these particles to the molten region during reaction, it may be assumed that these particles were heated to an elevated temperature during reaction. The particles are in close proximity and are directly decorated with extended alumina protrusions, similar to the particles observed after slow TGA/DSC heating to 1,000°C. These results indicate that the extended 2D alumina sheets form and extend from reacting Al NPs rapidly, providing a physical barrier to separate fuel particles that are reacting from those that remain unreacted and preventing sintering. The free space between separated particles allows a pathway for high-temperature reaction gas to preheat particles in the vicinity of the reaction zone, increasing the rate at which heat can propagate within the composite. The elevated melting temperature of alumina ensures that the protrusions sustain their morphology even at temperatures at which the Al nanoparticle fuel initiates combustion. These responsive material attributes have not been previously observed, and they represent mechanisms that promote a more rapid and more efficient combustion.

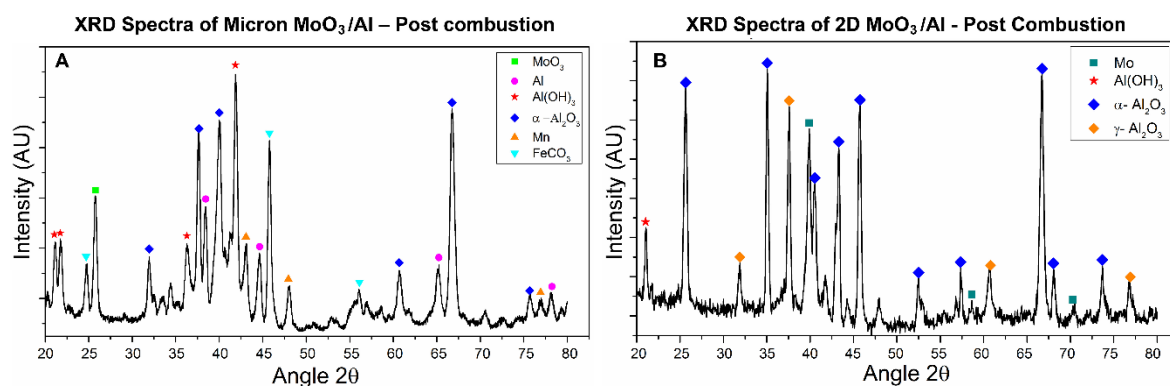


Figure 13. XRD result comparison between the combustion products of A) micron MoO₃/Al and B) 2D MoO₃/Al.

Finally, separate XRD spectra were obtained from combusted material utilizing exfoliated 2D MoO_3 and microscale MoO_3 powder oxidizers at an equivalence ratio of 1.4. As seen in **Figure 13A**, the combustion product when using micron-size MoO_3 powder oxidizer shows γ – Al_2O_3 , unreacted Al, and unreacted MoO_3 peaks. By contrast, the combustion products produced from 2D MoO_3 exhibits strong peaks α – and γ – Al_2O_3 without unreacted Al or MoO_3 , as shown in Fig 11B. Further, Mo peaks are observed when using 2D MoO_3 oxidizer, indicating that MoO_3 was fully reduced in the reaction, consistent with the proposed combustion mechanism. Contaminants such as FeCO_3 and Mn in the XRD spectra are thought to originate from the synthesis of MoO_3 powder and are largely removed during the exfoliation and centrifuge processing to form 2D sheets.

3.2 Combustion of Isolated Al NPs on α - MoO_3 Sheets

The as-prepared α - MoO_3 sheets were examined using TEM to confirm the crystal structure and crystal orientation. As seen in **Figure 14a**, the sheets typically form high aspect ratio orthorhombic structures that are thin enough to bend about the lacey carbon support of the TEM grid. The electron beam diffraction pattern can be indexed to be along the MoO_3 [110] zone axis. The diffraction pattern reveals that the long axis of the crystal corresponds with the $\langle 001 \rangle$ direction. Such orientation is typical for CVD-grown MoO_3 crystals, with a length in the $\langle 001 \rangle$ that is up to 15 times greater than that of the $\langle 100 \rangle$ direction[20–22]. Accordingly, the long axis of the MoO_3 sheets in the current study will be assigned the $\langle 001 \rangle$ direction, consistent with these measurements and previous reports.

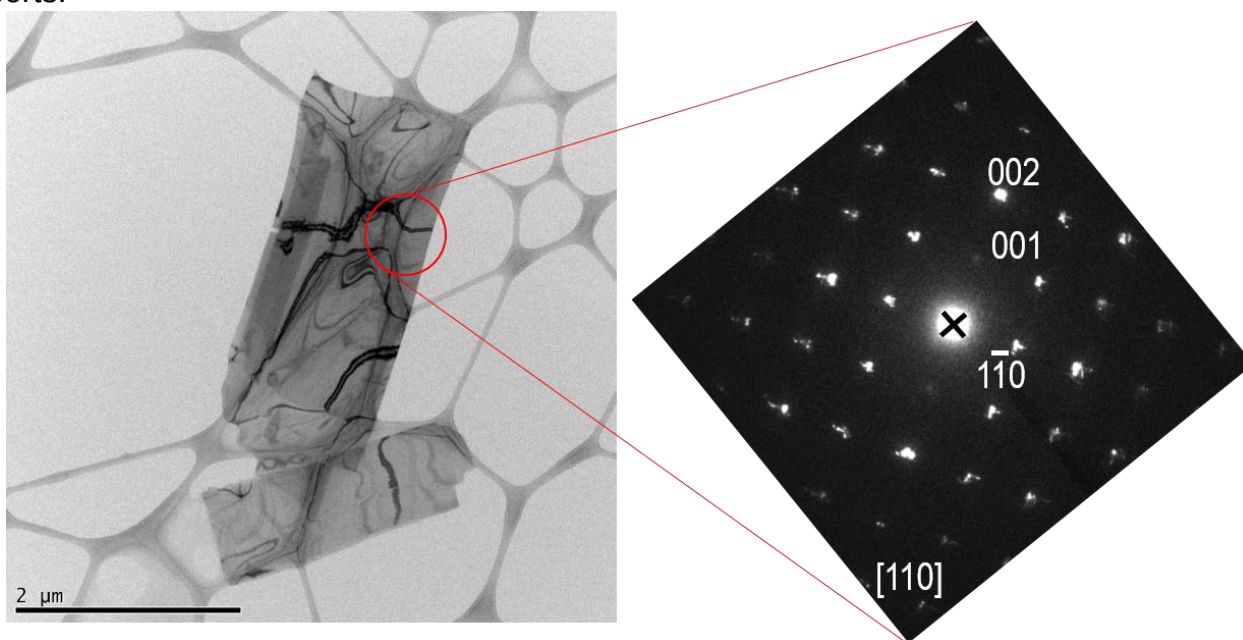


Figure 14. TEM analysis of as-synthesized α - MoO_3 flakes. High aspect ratio, orthorhombic flakes are observed with well-defined crystal facets. The electron beam diffraction pattern along the [110] zone axis shows a highly crystalline structure, with the long axis of the α - MoO_3 flakes corresponding to the $\langle 001 \rangle$ direction.

Photothermal heating experiments began by locating Al NPs residing on α -MoO₃ flakes. Optical images of a typical α -MoO₃ flake decorated with Al NPs obtained at 100x magnification in scattering and bright-field modes are shown in **Figure 15**. Note that the plasmonic grating itself is visible in the background of the optical images as a series of parallel grooves. Individual Al NPs are readily observed in scattering mode as bright particles due to the large scattering cross section of the Al NPs[6]. All Al NPs observed in **Figure 15** occur as particle aggregates rather than as isolated particles. The aggregate residing near the northern side of the MoO₃ flake (denoted as ‘region 1’ in **Figure 15**.) is composed of 2 Al NPs, while we estimate approximately 30 Al NPs comprise the aggregate toward the bottom of the flake (denoted as ‘region 2’ in **Figure 15**).

The cluster denoted as region 1 was illuminated by 10% laser intensity (1.1 mW), while the cluster denoted as region 2 was illuminated using 50% intensity (5.5mW). Power was varied to scale with cluster size. During irradiation, the Raman spectra was disrupted by a large-intensity spike in signal, indicating emission of photons. The typical irradiation time to observe this phenomenon was on the order of 5 seconds. If a reaction temperature between Al NPs and MoO₃ sheets is assumed to be on the order of 439 °C based on previous DSC-TGA results[7], then a heating rate on the order of 100 °C/s can be estimated for first reaction. Evidence of a reaction can be seen clearly in the optical scattering image obtained after irradiation, shown in **Figure 15c-d**. Reacted Al NPs appear dark in optical scattering mode, as the reacted oxide material does not scatter light as strongly as metallic Al. After photothermal heating, the entirety of the Al NP particle aggregate reacted in region 1, while only the left-most half of region 2 cluster reacted. Unreacted metallic Al NPs appear as bright spheres in this cluster, although individual NPs appear sintered when compared to **Figure 15a-b**.

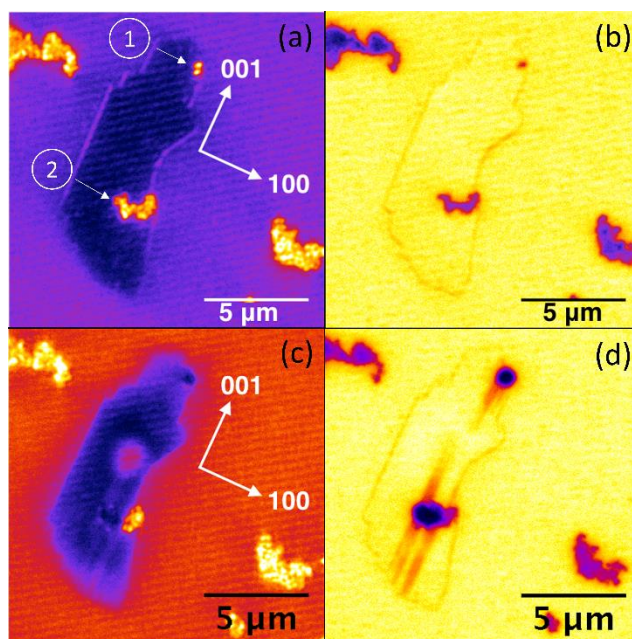


Figure 15. Optical micrographs of Al nanoparticles decorating a MoO₃ flake via (a) scattering and (b) bright-field mode before laser illumination. Al nanoparticle clusters of interest are denoted as

regions 1 and 2. The same regions were examined after reaction in (c) scattering and (c) bright field modes. Images are false colored and were obtained at 100x magnification

While faintly visible in optical scattering mode (**Figure 15c**), extended linear regions of high contrast along the α -MoO₃ flake are readily apparent in the bright-field image (**Figure 15d**). The streaks extend for several microns from the reacted Al NPs and propagate along the <001> direction of the α -MoO₃ flake. The streaks do not extend past the projection of the Al NPs in the <100> direction, indicating that the reaction mechanism in the <100> direction is not energetically favorable. Also visible in the scattering image (**Figure 15c**) is a high-contrast oval region located between region 1 and region 2. As will be observed via SEM and AFM, this region of the MoO₃ flake was morphologically altered by wrinkles during the reaction. We note that the extended reaction zones were not observed when irradiation occurred on α -MoO₃ flakes in the absence of Al NPs (see Supporting Information).

Raman spectra show a clear compositional change has occurred within the linear reaction region, as displayed in **Figure 16a**. Numerous Raman peaks corresponding to MoO₃ were observed before and after reaction, occurring between 99 - 379 cm⁻¹. Other MoO₃ peaks existed at 667, 820, 996, 1003, and 1031 cm⁻¹ [19,23] (**Figure 16b**). A peak at 290.92 cm⁻¹ observed in the baseline scan, corresponding to γ -Al₂O₃, is likely a result of the ALD Al₂O₃ layer applied to the plasmonic grating surface during fabrication. After laser irradiation, new Raman peaks at 414 and 445 cm⁻¹ emerge in the linear reaction regions, corresponding to the formation of α -Al₂O₃[24]. Simultaneously, the intensity of MoO₃ peaks diminish in these areas. The intensity of the α -Al₂O₃ phase peak is greatest at the reaction regions indicated as spot 1, spot 4 and spot 3 in **Figure 16**, while it is lower at spot 2 and spot 5. We note that spots 2 and 5 correspond to sites originally occupied by Al NPs and are not part of the linear reaction regions. Nevertheless, the Raman spectra indicate that the α -Al₂O₃ reaction zones are crystalline throughout the length of the observed streaks. Solid-state solutions of α -Al₂O₃ and α -MoO₃ have previously been observed when Al₂O₃ and MoO₃ were calcined at temperatures of 850 °C[25,26]. Additional α -Al₂O₃ Raman modes at 378, 418, 430, 451, 578, 645, and 750 cm⁻¹ [27] are observed after reaction. Based on the ratio of the intensities of the peaks at 418 and 750 cm⁻¹, we suggest that we are probing the lattice plane of Al₂O₃ perpendicular to the c-axis[24,27].

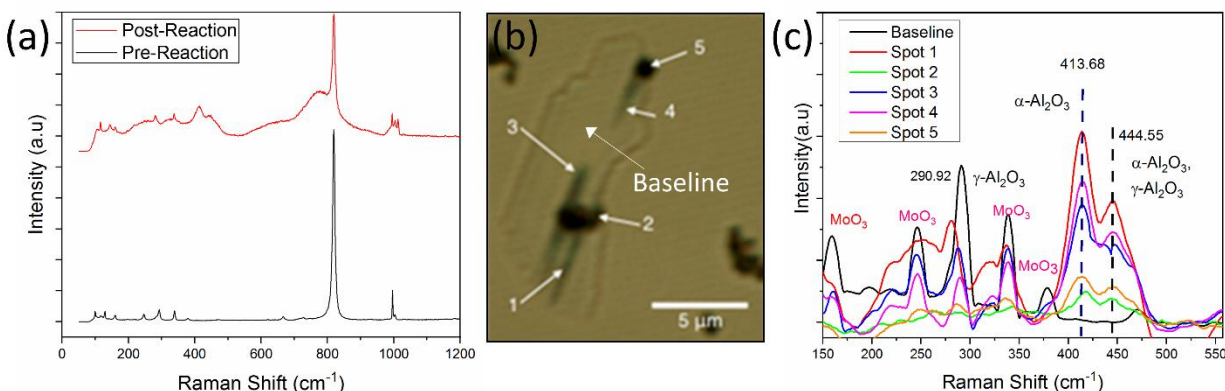


Figure 16. Raman spectra (a) before and after Al nanoparticle reaction. Spectra are offset for clarity. (b) An optical image obtained by the Raman microscope after Al nanoparticle reaction is overlaid with numbers indicating the location of (c) Raman spectra used to probe the material composition.

Further evidence of the compositional change of the α -MoO₃ flakes was sought using X-ray diffraction (XRD). **Figure 17** shows the XRD scan of the multiple samples, including a bare plasmonic grating, an Al NP-decorated α -MoO₃ flake placed on the grating before reaction, and an Al NP-decorated α -MoO₃ flake on the grating after reaction. Diffraction patterns of the grating alone show only peaks for silver – one of the constituents of the grating itself. To reveal peaks from thin MoO₃ flakes and Al NPs, in-plane scans were obtained. In-plane XRD scans show peaks from MoO₃ and Al peaks prior to irradiation, indicative of the starting materials. After reaction, α -Al₂O₃ peaks emerge at 46.46 and 70.24, confirming that the reaction between MoO₃ and Al NPs generated α -Al₂O₃, consistent with Raman spectroscopy analysis. We also note that a room-temperature sputtering of a 1 nm Al layer onto similar α -MoO₃ flakes in a separate experiment exhibited no traces of Al₂O₃, suggesting that thermal energy is required to initiate reaction.

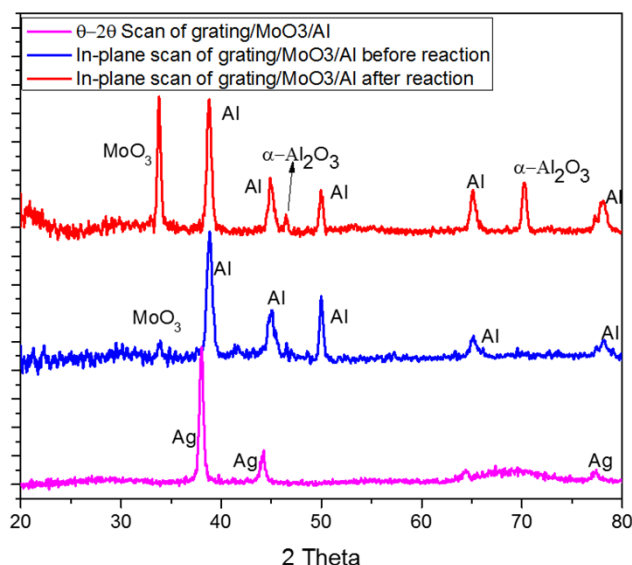


Figure 17. XRD spectra from a bare plasmonic grating and a grating with Al nanoparticle-decorated α -MoO₃ flakes before and after laser irradiation

Previous density functional theory (DFT) studies by others have investigated the interaction of atomic Al with the α -MoO₃ lattice. Wu *et al.* examined the adsorption energy of individual Al adatoms at various sites along the (010) crystalline plane of α -MoO₃[28]. This study showed that sub-surface adsorption of an Al atom is more stable than surface adsorption, and that Al sub-surface adsorption occurs preferentially between terminal oxygen pairs in the $\langle 001 \rangle$ direction. The subsurface adsorption occurred only in the surface layer of MoO₃, leaving sub-surface layers unaffected. This adsorption process had an energy barrier of 0.20 eV per atom; however, an exothermal energy release of 1.03 eV per atom occurs upon adsorption, providing additional energy to the surrounding

to sustain further diffusion and reaction. If a net exothermal energy release of 0.83 eV per adsorbed Al atom is assumed, the surface absorption mechanism releases 2.968 kJ per gram of Al. Moreover, Kim *et al.* showed that lithium adsorption in the (010) plane of α - MoO_3 preferentially occurred at the same site and that neighboring intralayer sites along the $\langle 001 \rangle$ direction, creating a one-dimensional tunnel for transport[29]. Based on our observations, we believe that Al adatoms were released from the heated Al NPs and were transported by surface diffusion away from the Al NPs. The Al then adsorbed just below the surface along the energetically favorable $\langle 001 \rangle$ direction. This type of reaction mechanism would likely be relatively slow, as Al would require time to diffuse from the Al NP and along the surface of the MoO_3 before finding a suitable unoccupied host site for adsorption within the MoO_3 . Note that the host MoO_3 is not consumed by the proposed interactions; rather, Al atoms are introduced to interstitial sites along the top-most MoO_3 layer.

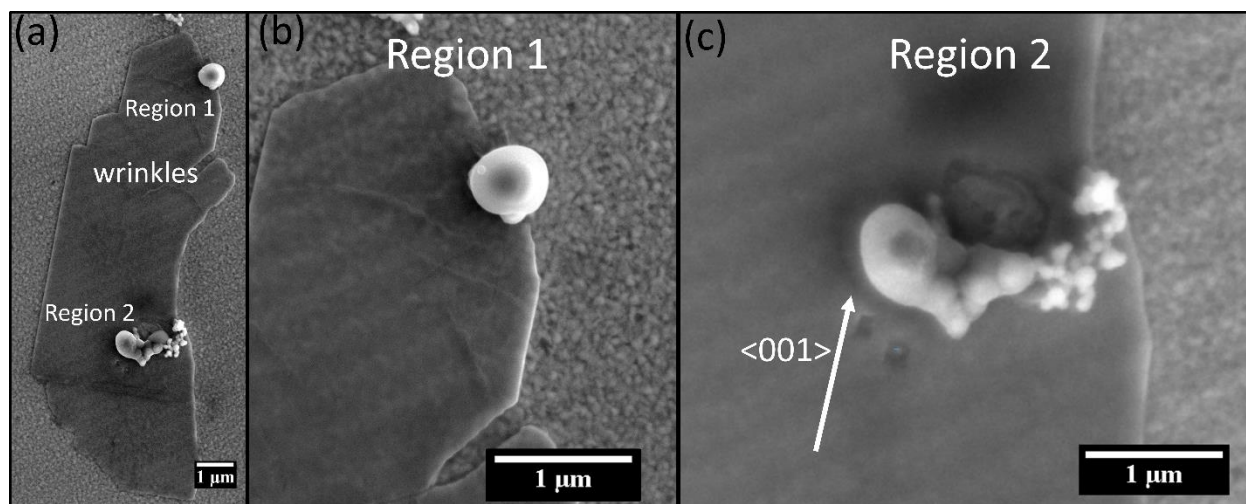


Figure 18. SEM micrograph of the α - MoO_3 flake shown in Figure 15 after laser irradiation. (a) Low magnification shows the entire flake and the two distinct Al nanoparticle reaction zones. (b) High-magnification of region 1 shows that all Al nanoparticles sintered to form one large particle after reaction. (c) Region 2 shows a mixture of sintered and unreacted Al nanoparticles, an irregular region north of the reacted particles, and sub-surface particles with impressions extending in the $\langle 001 \rangle$ orientation. Note that the extended surface reaction zones observed by optical microscopy are not readily visible by SEM analysis.

SEM analysis was performed after irradiation using a low acceleration voltage of 2 kV to examine only the top-most layers of the α - MoO_3 flake. Analysis confirmed that Al NPs reacted and sintered in response to photothermal heating (**Figure 18**). The group of Al NPs in region 1 of (**Figure 18b**) appear to have sintered into a single large spherical cluster. No obvious transformation of the surrounding MoO_3 is observed, including the extended reaction zones previously observed using optical microscopy. Between reacted regions 1 and 2, the surface of the MoO_3 flake appears wrinkled, as denoted in **Figure 18a**. This region corresponds with the emergence of a darkened area in the optical scattering image shown in **Figure 15a**. The large Al NP cluster denoted as region 2 **Figure 18c** showed clear evidence of reaction, sintering, and melting. As suggested by

the optical scattering images, only the left half of the large Al NP cluster appears to have reacted, while the right-most Al NPs appear unaffected. The large irregular region located just north of the reacted particles in **Figure 18** indicates that a large amount of material collected in this area. AFM scans shown later will reveal that this area is raised relative to the MoO₃ surface, indicating that an abundance of melted Al was likely present to sustain a combustion reaction. Note that the melting temperature of bulk MoO₃ is 795 °C, suggesting that melted MoO₃ may have also contributed to this raised area. This region showed only faint signatures of α -Al₂O₃ via Raman spectroscopy (**Figure 16b**), indicating that the composition of this region was quite different from that of the extended linear reaction regions.

Approximately 200 nm below the reacted Al NP cluster in region 2, two small sub-surface rectangular features appear to penetrate below the MoO₃ surface (**Figure 18c**). The right-most feature appears to contain a small NP fragment at its center. We hypothesize that the fragment is likely from heated Al ejected during the Al heating. The sub-surface reaction is quite different than the surface reaction, as the MoO₃ appears to be consumed in the reaction, suggesting highly localized combustion in these regions. Furthermore, when the $\langle 001 \rangle$ direction is overlaid near the reaction area (**Figure 18c**), it is clear that the elongated edges of these sub-surface regions are oriented along the $\langle 001 \rangle$ direction, likely signifying that Al surface diffusion and adsorption also occurred in this region. These two sub-surface pits are located within one of the α -Al₂O₃ bands observed after Al NP combustion and may have provided, in part, an Al source to facilitate surface reactions. We note that EDS mapping and EDS line scans were performed on the sample at 2kV and 5kV acceleration voltages. The EDS data did not conclusively demonstrate increased Al within the reaction regions, as the penetration depth of the electron beam was sufficient to sample the Al the 10 nm alumina layer deposited on the grating substrate. Later efforts to lift the MoO₃ flake for TEM analysis using focused ion beam micromanipulator liftoff proved unsuccessful and destructive, as reacted flakes did not readily release from the host grating substrate.

AFM imaging reveals a highly resolved topology of the MoO₃ flake. An edge scan of the flake, shown in **Figure 19b-c**, reveals a total flake thickness of approximately 48 nm, or approximately 34 MoO₃ layers. An AFM scan of the extended Al₂O₃ reaction regions indicates no discernable topological features, either raised or lowered. We note that some waviness of the MoO₃ flake is induced by the periodic ridges of the underlying plasmonic grating substrate. While step edges are common along the $\langle 001 \rangle$ direction of α -MoO₃[20], these were not observed near the reaction zones. Based on the proposed sub-surface Al adsorption mechanism, Al atoms adsorb into the interstitial sites between adjacent terminal oxygen sites on the face of MoO₃, minimally altering the bond length within the MoO₃ host[28]. Such a mechanism would produce an unperceivable change in surface topology, consistent with our observations. The sub-surface pits formed at the southern side of the large reacted particle cluster was also measured. The measured depth of the pit was approximately 30 nm; however, the particle at the center of the pit (observed in SEM) is also observed in the AFM scan, obscuring the true depth of the pitted region. It is possible that a molten Al fragment was ejected from a heated Al cluster

with sufficient energy to produce a secondary combustion reaction that consumed the MoO_3 oxidizer through the entire depth of the MoO_3 sheet. A distinct wrinkled morphology is observed between the two combusted regions in an area corresponding with the darkened oval observed in optical scattering microscopy. These wrinkles may have formed as a result of mechanical strain induced by incorporating Al into the MoO_3 lattice the linear reaction regions. Whereas some of the linear reaction regions terminate at the edge of a MoO_3 flake, the wrinkled region represents an area where linear reaction regions terminate from both sets of reacted Al NP clusters.

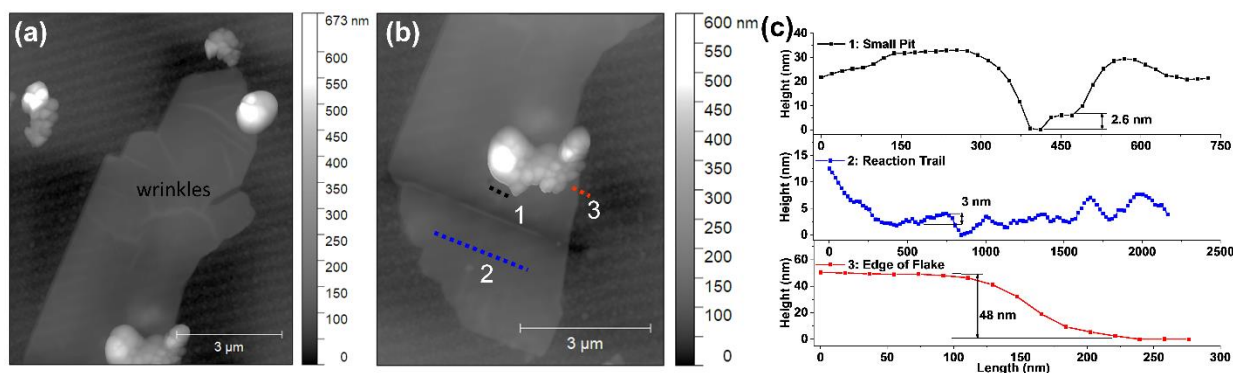


Figure 19. Atomic force images of the reacted Al / MoO_3 sheet. (a) The top-most section of the flake shows the reacted Al nanoparticle regions with surface wrinkles between reacted Al NP zones. (b) A scan of the bottom section of the flake with dashed lines indicating the locations of linear height scans to measure surface topology in (c). (c) Line scan profiles of (1) the sub-surface features, (2) the reaction trail extending from the bottom-most reacted Al nanoparticles, and (3) the edge of the host flake.

Based on these observations, we speculate that two distinct reaction mechanisms occurred between Al and MoO_3 during photothermal heating. The extended $\alpha\text{-Al}_2\text{O}_3$ streaks in the $\langle 001 \rangle$ direction are believed to occur by a process consisting of surface diffusion and subsequent sub-surface adsorption of Al into the $\alpha\text{-MoO}_3$ lattice. These reaction regions extend for several microns away from the heated Al NPs, suggesting that the process was self-sustaining away from the original heat source. The mechanism by which ordered $\alpha\text{-Al}_2\text{O}_3$ forms the adsorbed Al within the host MoO_3 is not yet clear; however, the excess energy released by sub-surface Al adsorption may facilitate the transformation. Previous DFT studies have not investigated many-atom adsorption, and more research is needed to fully understand the formation of crystalline $\alpha\text{-Al}_2\text{O}_3$. Attempts to more fully analyze the reaction zones by TEM failed, as micromanipulator liftoff of reacted flakes was destructive and not successful.

The presence of small ejected Al particles away from the Al NP clusters indicates that a violent reaction may have occurred, and may indicate the presence of a mechanical dispersion. The melt dispersion mechanism (MDM) suggests that rapid heating in excess of 10^6 K/s melts and expands the Al core before the outer oxide layer cracks, resulting in an elevated pressure that bursts the oxide layer and ejects the molten aluminum outwards at high velocities[30]. Because the photothermal heating rate of particles was on the order of 100 K/s, if MDM occurred on our sample, the rapid heating would be caused by

Al/MoO₃ reactions rather than direct photothermal heating. Other mechanisms outside of MDM may be responsible for ejected particles may also be possible. Nevertheless, our results indicate that subsurface adsorption of Al on the (010) MoO₃ surface to form monolayer α -Al₂O₃ sheets may proceed in parallel with conventional combustion reactions.

3.3 Synthesis and Combustion of Energetic Aerogels

Our gelation method in PC allows for precise control of GO content, sample shape and size (**Figure 20A-B**). The synthesis was similar to a molding process in which the gel took the shape of the host container. The finished gel was homogeneous in color, indicating well dispersed Al and Bi₂O₃ NPs throughout the structure, indicative of a well-dispersed precursor mixture formed before the onset of gelation process. The mass density of the gel varied from 20 to 250 mg / cm³, depending on the percentage of GO in the reactant. Importantly, phase separation between Al and Bi₂O₃ NPs was minimized, overcoming a significant shortcoming of Al/Bi₂O₃ nanothermite produced by conventional sonication and drying.[73] Uniform dispersion of particles and their stability were confirmed by dynamic light scattering (DLS) and zeta potential tests, respectively. GO, Al and Bi₂O₃ dispersions all measured high negative surface charge with particle sizes indicative of single or few-particle clusters. Achieving a surface charge of similar polarity for all particles is critical, as agglomeration and settling of the mixed products was avoided.

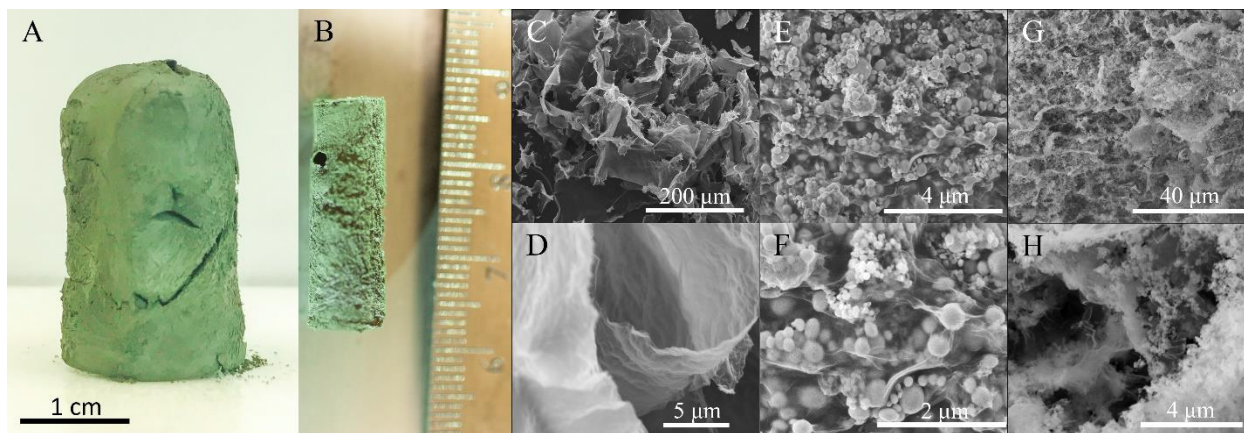


Figure 20. Optical picture of RGO/Al/Bi₂O₃ gel formed in vial (A) and glass tube (B, ruler in cm), SEM images of freeze-dried pure RGO gel (C, D), RGO/Al/Bi₂O₃ gel before (E, F) and after (G, H) slow heating to 1200 °C

SEM images displaying the microstructure of the aerogel before and after slow heating to 1200 °C in argon (within DSC-TGA) are shown in **Figure 20C-H**. The RGO prepared without particle loading showed porosity on the order of tens of microns (**Figure 20C-D**), similar to RGO gels prepared with water.[29] The gelation processes occurred due to the crosslinking and π - π stacking between the reduced GO sheets, producing thin-walled

RGO porous scaffolds.[35, 36, 84] RGO structures loaded with nanoscale fuel and oxidizer particles are shown in **Figure 20E-F**. Smaller Al NPs (~80 nm) and larger Bi₂O₃ NPs (~200 nm) could be clearly distinguished individually, wrapped by RGO sheets. Particle agglomeration and phase separation of the NPs was not observed. The homogeneous mixing was also confirmed by EDS mapping. Discrete fuel and oxidizer particles are no longer observed after being heated to 1200 °C. Rather, a porous Al₂O₃ framework intermixed with graphene sheets was produced during the reaction (**Figure 20G-H**). Note that some Bi content evaporated during DSC-TGA heating due to its high vapor pressure when the temperature is above 1000 °C. [85] EDS confirms that the atomic percentage of bismuth dropped from 17.72% to 0.08% after slow heating while the relative content of carbon and aluminum were only slightly altered. The occurrence of a high-temperature thermite reaction was confirmed by XRD results, which showed the emergence of α -Al₂O₃ produced during the Al-Bi₂O₃ reaction. [22] The specific surface area of the freeze-dried RGO gel without Al and Bi₂O₃ NPs, measured by BET, was 32.49 m²/g, which is lower than some values reported [86] due to the thick RGO sheets form from stacking, as shown in **Figure 20D**. While the RGO/Al/Bi₂O₃ aerogel was 34.31 m²/g despite only 5 % GO content. The increased surface area suggests that large-scale particle agglomeration was avoided during the gelation process, as confirmed by SEM.

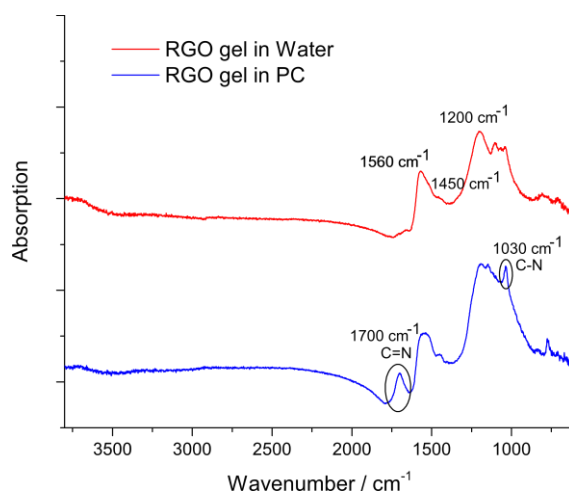


Figure 21. FTIR spectra of RGO gels formed in water and PC

FTIR spectra, shown in **Figure 21**, confirmed that nitrogen functional groups supplied by EDA were responsible for promoting gelation. A peak at 1700 cm⁻¹ was present in the gel formed in PC as a result of the carbon-nitrogen double bond. This peak was not present in the gel formed in water. This peak indicated that the C=N bond formed more often in PC than in water, due to the reaction between EDA and the carboxyl group in the basal plane of GO. Therefore, EDA acted as both a reducer and a linking agent during the reaction. Raman spectrum confirmed the reduction of GO to RGO since the I_D/I_G increased from 1.095 for GO to 1.239 for RGO gel. The gelation process started upon

introduction of EDA into the system at room temperature, unlike gelation processes in water that requires heating. For the synthesis in PC, conducting the reaction at 95 °C accelerated the reaction significantly while retaining the chemical reactivity of Al and Bi₂O₃. Considering the negative surface charge for all the well-dispersed GO, Al, and Bi₂O₃ precursors, a homogeneous mixture was formed before the gelation process, as confirmed by images obtained 16 hours of dispersion. When EDA was injected into the PC dispersion, the reaction occurred, and the gel formed. The mechanism is shown schematically in **Figure 22**.

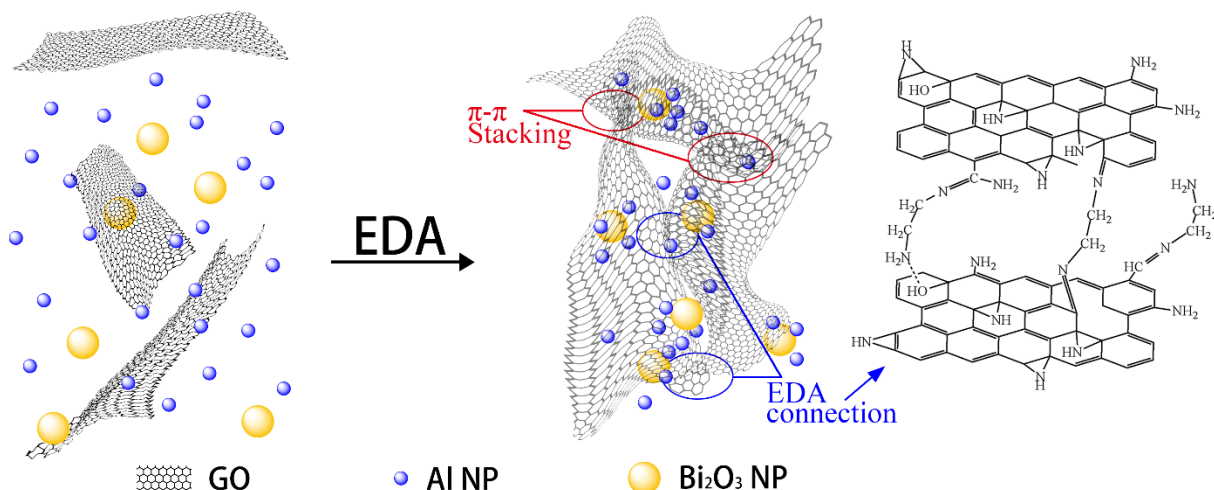


Figure 22. Formation mechanism of RGO/Al/Bi₂O₃ gel

Simultaneous differential scanning calorimetry and thermogravimetric analysis (DSC-TGA) were conducted to examine the energetic properties of the RGO/Al/Bi₂O₃ gel. Two separate control Al/Bi₂O₃ samples ($\Phi=1.4$, without RGO) were prepared using PC in one case and IPA in another. An additional sample was synthesized by drying a dispersion of GO/Al/Bi₂O₃ prior to gelation. Energy release of the samples was quite different and directly related to the composite morphology produced during assembly. **Figure 23a** shows that the Al/Bi₂O₃ control sample made in IPA produced an energy release of 709 ± 11 J/g. The control sample made in PC showed visible phase separation upon drying, with yellow Bi₂O₃ precipitating to the bottom of the sample. This phase-separated sample produced an energy release of only 352 ± 8 J/g, with about half of the energy released after the melting of Bi₂O₃ at 817°C. Introducing GO produced a homogeneous material without phase separation. Considering the negative surface charge of GO, Al and Bi₂O₃, the phase separation between Al and Bi₂O₃ in PC after drying was prevented. The dried GO/Al/Bi₂O₃ mixture that did not undergo gelation produced an energy release of 755 ± 30 J/g. This energy release was slightly higher than the Al/Bi₂O₃ control sample made in IPA due to the minimized phase separation. The RGO/Al/Bi₂O₃ aerogel produced the highest energy release of 967 ± 17 J/g, indicating that it possessed the best intermixing between Al and Bi₂O₃ particles among all the samples. As seen from the SEM images, Al

and Bi_2O_3 NPs assembled between RGO sheets during the gelation process, enhancing the interfacial contact between fuel and oxidizer particles.

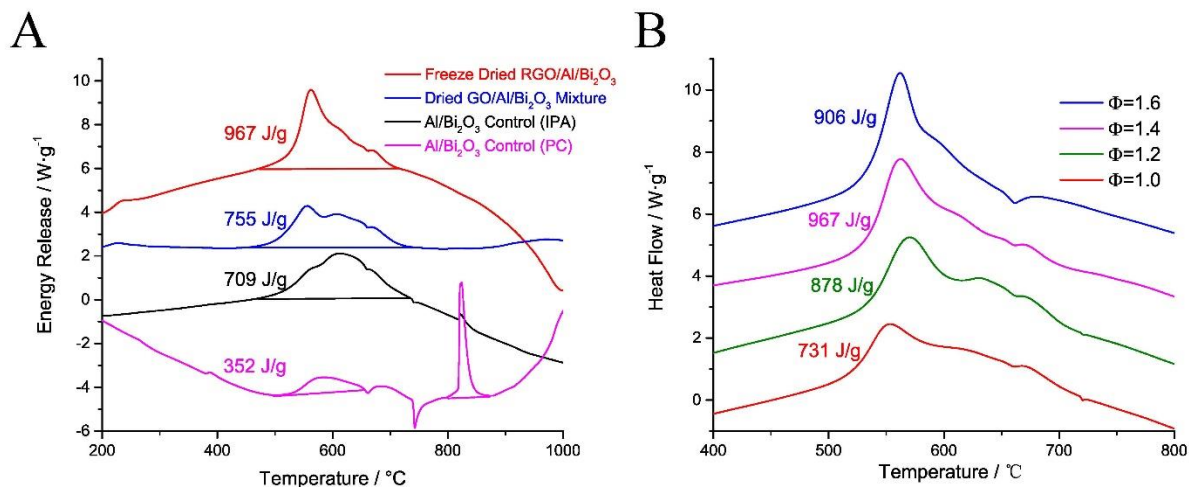


Figure 23. DSC curves of $\text{Al}/\text{Bi}_2\text{O}_3$ control samples made in PC and IPA, dried $\text{GO}/\text{Al}/\text{Bi}_2\text{O}_3$ dispersion before gelation and freeze-dried $\text{RGO}/\text{Al}/\text{Bi}_2\text{O}_3$ (A). DSC curves of freeze-dried $\text{RGO}/\text{Al}/\text{Bi}_2\text{O}_3$ with different equivalence ratios (B). Note that the curves are offset such that the energy release and heat flow axes are relative.

Condensed phase reactions between Al and Bi_2O_3 particles produced the greatest energy release for all samples, excluding the phase-separated control sample formed in PC. These reactions occurred prior to Al melting at 665 °C, indicated by an endothermic peak in each curve. Note that liquid-phase Al – Bi_2O_3 reaction [87, 88] accounted for less than 10% of the energy released within the aerogel but was responsible for a greater percentage of the energy released for other compositions. Enhancement of the condensed phase reaction between Al and Bi_2O_3 particles was facilitated by increased interfacial contact and homogeneous mixing. These conditions promoted decreased diffusion lengths between mobile Al atoms that diffuse through the Al_2O_3 shell. [89] Furthermore, the temperature associated with the peak energy release decreased from 600 °C for the IPA control sample without graphene to approximately 560 °C for the samples self-assembled on RGO. Within the self-assembled RGO composites, Al and Bi_2O_3 NPs are embedded between RGO sheets, reducing the effects of Al NP sintering [73] and enhancing energy release at lower temperatures. $\text{RGO}/\text{Al}/\text{Bi}_2\text{O}_3$ aerogels produced with different equivalence ratios were also analyzed by DSC-TGA and are displayed in **Figure 23B**. The sample with an equivalence ratio of 1.4 (fuel rich) showed the highest energy release, which is consistent with self-assembled $\text{GO}/\text{Al}/\text{Bi}_2\text{O}_3$ or Al/MoO_3 nanothermite.[20, 88] Note that the strongest endothermic peak at 665 °C associated with melting of unreacted Al occurred at $\Phi = 1.6$, indicating that the fuel mixture ratio for optimum reaction was exceeded. Energy release increased with equivalence ratios prior to $\Phi = 1.6$.

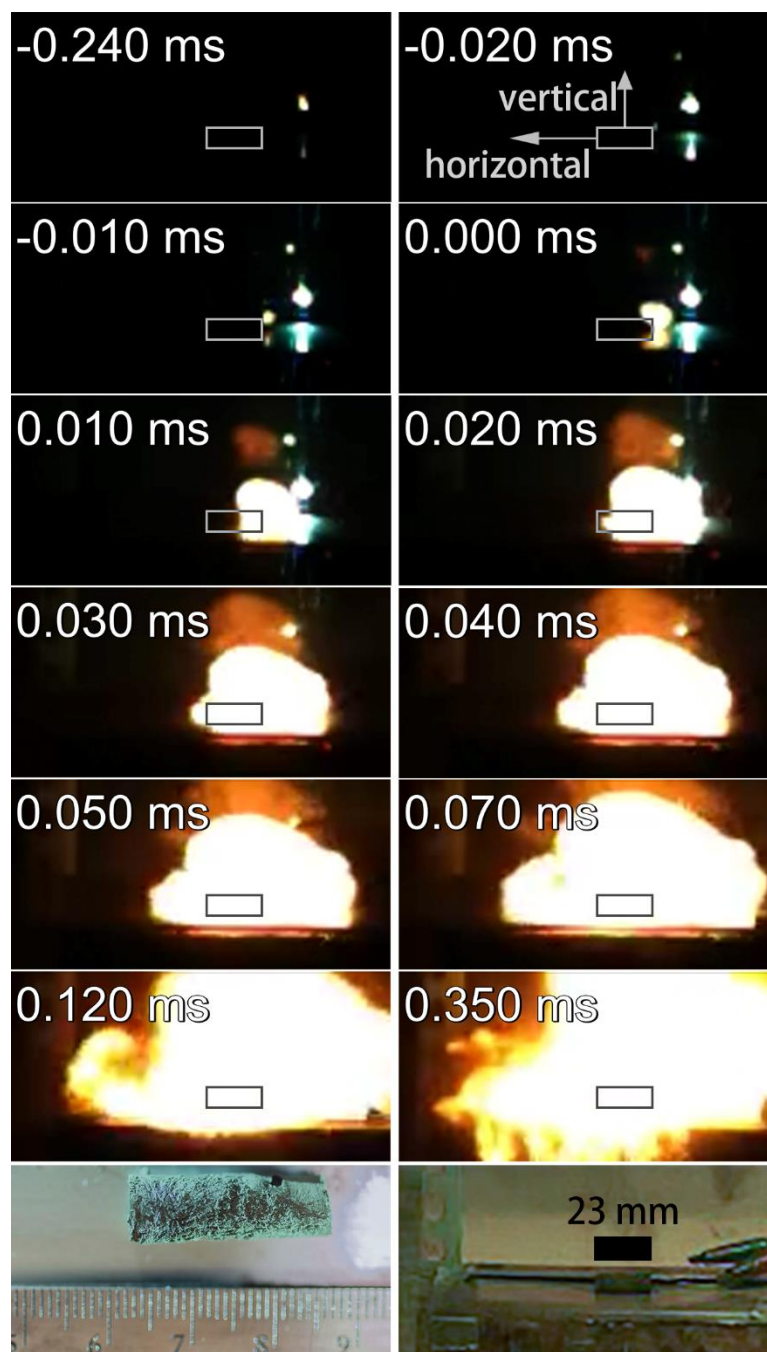


Figure 24. High-speed camera frames of the open burn of RGO/Al/Bi₂O₃ nanothermite aerogel, the rectangles in each frame indicates the position of the aerogel

The burn rate of the energetic graphene aerogel (5% GO in mass, $\Phi = 1.4$) was examined using a high speed camera in an open burn chamber.[90] **Figure 24** shows key frames obtained by a high speed camera imaging at 100,000 fps. The frame at the time of ignition was set to $t = 0$. The combustion front propagated across the entire 23-mm nanothermite aerogel between the frames obtained at 0.020 – 0.030 ms, translating to a flame propagation speed of 960 ± 190 m/s. The accuracy of the flame speed was limited

by the frame acquisition rate of fast camera. This value was much higher than the open burning speed for Al/Bi₂O₃ nanothermite powder as measured by Sanders *et al.*, which gave a maximum 425 m/s open burning rate at $\Phi = 1.3$ among $\Phi = 0.8, 1.0, 1.3, 1.6$ and 1.8. [91] We performed an open burn control experiment using a similar sized and weighed sample of Al/Bi₂O₃ ($\Phi = 1.4$) nanothermite powder made in IPA. The powder exhibited a flame propagation speed around 460 m/s, which is quite close to the value found by Sanders, but still much lower than the propagation speed of the gel.

Experiments performed by Plantier *et al.* [82] suggested that open burns produce flame propagation rates that are approximately one third those produced for confined burn experiments using identical chemical compositions. Open burn experiments allowed the combustion energy and shock wave to propagate out in a 3D space, resulting in a decaying wave similar to a Taylor-Sedov blast wave.[92, 93] Compared to a neat Al/Bi₂O₃ control sample, the greatly enhanced burn rate of the RGO/Al/Bi₂O₃ aerogel was likely a result of both enhanced overall energy release and the porosity afforded by the internal aerogel structure. Internal pores allowed the hot combustion products to become entrained behind shock waves propagating through the multiphase material. The propagating gases preheated the material ahead of the initial reaction while shock wave focusing may lead to “hot spot” formation within the RGO scaffold.[94] The porous RGO aerogel itself might lead to a “self-confining reaction” within the RGO scaffold, leading to a mixture of both non-confined and confined burning characteristics. This was evident by the rapid flame propagation down the horizontal axis of the sample (right to left in Figure 23) compared to slower vertical, open air flame propagation, forming a “rectangular” flame shape. However, in the combustion of neat Al/Bi₂O₃ powder, the flame expanded from the ignition point more spherically in all directions, showing no apparent preferential direction. Therefore, the self-confinement of the RGO/Al/Bi₂O₃ led to a more restricted energy release in and along its dimensions and limited the blast ejection of energetic material which likely occurred for the nanothermite powder control case.

The ESD energy threshold for the RGO/Al/Bi₂O₃ gel was 0.89 mJ, measured by electrostatic discharging system including a capacitor charged to a high voltage, a discharging tip and a steel sample holder with samples in a plastic ring, as shown in Figure S14. This value is more than 3 orders higher than the value of Al/Bi₂O₃ nanothermite (0.125 μ J) as reported by Puszynski *et al.*[24] It was also found that the EDA chemical reduction of GO to RGO is incomplete,[29] as the C/O ratio was only increased from 1.95 in GO [20] to 2.74 in the pure RGO gel, limiting the electrical conductivity of the composite. Further reduction may result in still greater ESD thresholds.

Table 4. Mass and Atomic percentage of RGO gel.

Element	Mass Percentage	Atom Percentage
Carbon	62.39%	68.25%
Nitrogen	7.29%	6.84%
Oxygen	30.33%	24.91%

3.4 Synthesis of Properties of Fluorinated Graphene

GO paper underwent a color change as a result of the XeF_2 fluorination process, as shown in **Figure 25**. The initial GO paper was dark brown (**Figure 25A**). After 1300 minutes of XeF_2 treatment, the FGO paper was a light, translucent yellow (**Figure 25B**), similar to fluorination of GO by F_2 . [63] After three days in a desiccator, the FGO paper turned brown although lighter than the original GO, indicating further composition change (Figure 1C). FGO-II sample (2700 min exposure) showed a similar change.

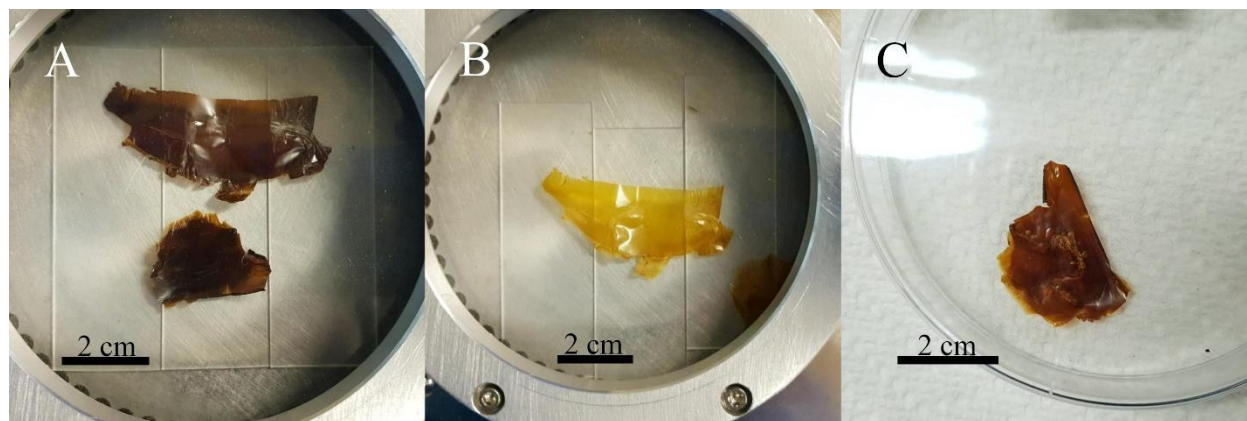


Figure 25. Optical pictures of GO (A) FGO-I right after XeF_2 treatment (B) and after 3 days in desiccator (15% humidity) (C).

FT-IR measurements to investigate the change in chemical structure of GO after reaction with XeF_2 , is shown in Figure 27. The strong peak present in GO located at $3000 - 3700 \text{ cm}^{-1}$, corresponds to the O-H stretching in C-OH groups and -COOH groups, was significantly reduced in FGO-I after reaction with XeF_2 for 1300 minutes, and almost disappeared in FGO-II after 2700 minutes, indicating the replacement of hydroxyl groups by fluoride groups. Previous reports showed that the bonded hydrogen atoms in macromolecules, such as polymers, could be readily substituted by fluorine, [95] and the potential HF product might further catalyze the fluorination reaction. [96] The absorption band at 1730 cm^{-1} , attributed to the C=O stretching in the GO structure, remained similar after XeF_2 treatment, indicating no significant reaction between the carbonyl groups in GO and XeF_2 . The asymmetric and symmetric stretching of -COO- in the carboxyl acid groups in GO, shown by the absorption bands at 1620 cm^{-1} and 1420 cm^{-1} respectively,

were reduced significantly after reaction. Correspondingly, an extra absorption band showed up at 1840 cm^{-1} , representing the C=O stretching in acyl fluoride (F-C=O), produced by the substitution of -OH groups in carboxyl acid by fluorine atoms. The absorption bands for stretching of the C-O bond in C-O-C and C-OH groups at 1220 cm^{-1} and 1050 - 1060 cm^{-1} were also diminished. The sharp peak at 1235 cm^{-1} reflects the formation of C-F covalent bonding, the chemical bond between fluorine and sp^3 hybridized carbon. The peak around 1140 cm^{-1} in FGO-I revealed the formation of the semi-ionic C-F bond between fluorine and sp^2 hybridized carbon, which was also found in the carbon nanotube fluoride produced below 100 $^{\circ}\text{C}$. [62, 97] In FGO-II, the peak shifted to around 1100 cm^{-1} , indicating the formation of CF_x ($x > 1$) in the structure. The presence of these unique peaks indicated the successful fluorination of GO after fluorination reaction by using XeF_2 gas for 1300 or 2700 minutes. The scheme of the reaction is concluded in **Figure 28**.

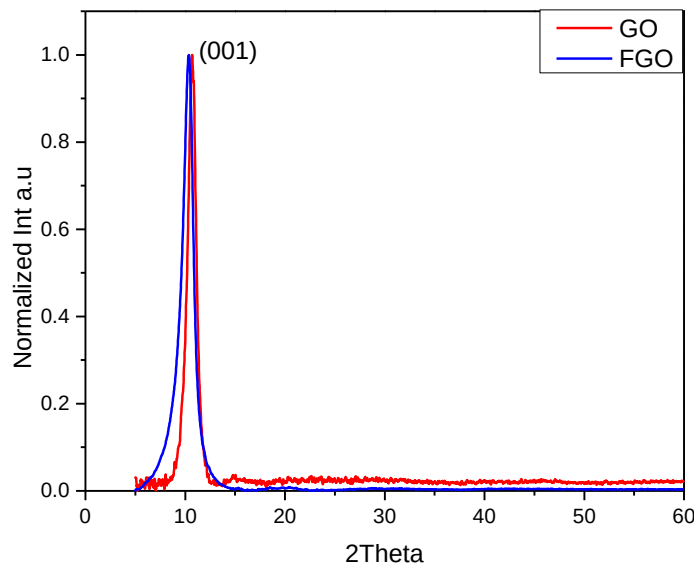


Figure 26. XRD patterns of GO and FGO-I

The XRD results of GO and FGO-I are shown in **Figure 26**. The XRD spectra of GO and FGO-I was measured in the range of 5° to 60° and both the samples shows a peak (001) at $2\theta \sim 10.5^{\circ}$. Due to fluorination of GO, there is small change in the peak (001) value, it is postulated that oxygen-containing groups in the stacking were replaced by fluorine atoms thereby changing the interlayer distance. It is also noted that the FWHM of FGO increased, an indication of a lower degree of crystallinity as compared to GO. Due to a small change in the interlayer distance (d), the majority of oxygen functional groups remained in the structure suggesting only minor incorporation of fluorine atoms during the XeF_2 treatment of GO.

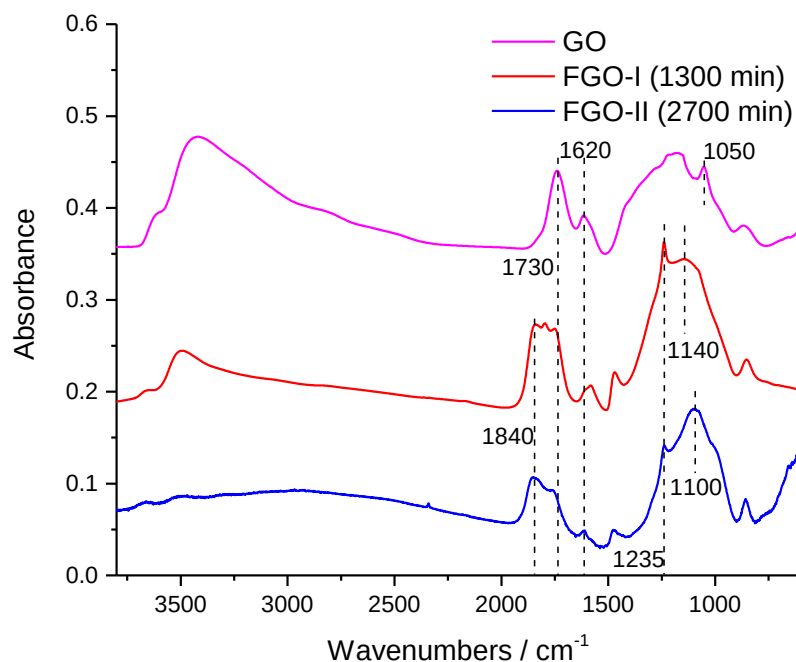


Figure 27. FT-IR curves of GO, FGO-I (1300 min) and FGO-II (2700 min)

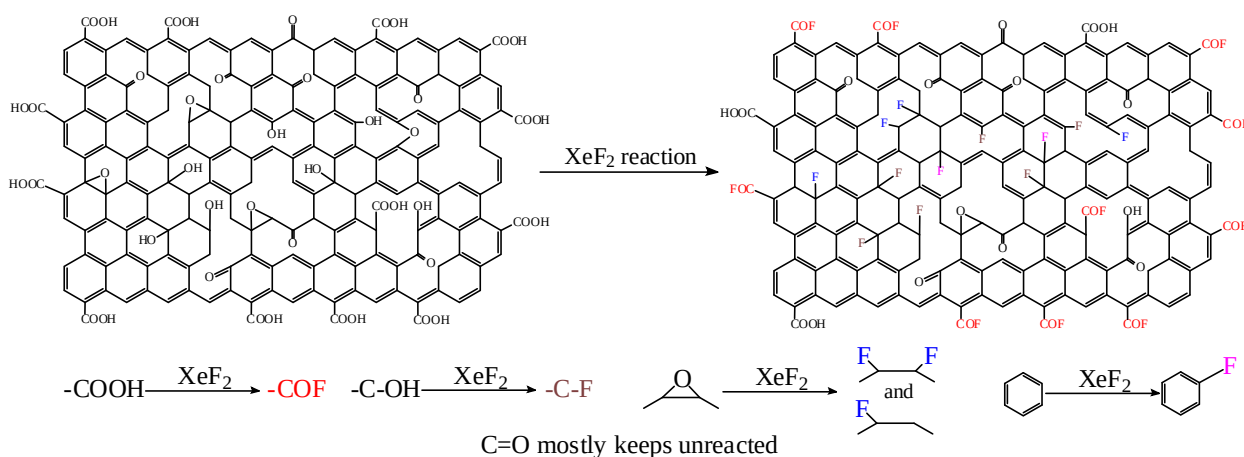


Figure 28. Scheme of reactions during the XeF₂ treatment

FT-IR was also employed to investigate the stability in the FGO structure when stored in a desiccator environment (~15% humidity), as shown in **Figure 27**. After only few days stored in desiccator, the absorption band of C=O stretching in acyl fluoride (1840 cm⁻¹) was significantly reduced, remaining only as a small shoulder due to the hydrolysis reaction of acyl fluoride groups with free water in atmosphere ($\text{-COF} + \text{H}_2\text{O} \rightarrow \text{-COOH} +$

HF). The -OH absorption band from 3200 – 3700 cm^{-1} slightly increased due to the same process. Additionally, the sharp C-F covalent peak at 1235 cm^{-1} was reduced, and the C-F semi-ionic peak around 1140 cm^{-1} also shifted to around 1170 cm^{-1} , indicating the decomposition of some C-F bonds in the structure. This result corresponds with the results reported by Stine et al that fluorine bonded with carbon on basal plane decomposed with time of storage. [64] A small shoulder also appeared at 1060 cm^{-1} , indicating the formation of more C-OH groups during storage. Therefore, after GO was fluorinated by XeF_2 , its structure changed during storage due to the reaction with water vapor in the atmosphere, leading to the loss of part of the fluorine functional groups and a return back to a structure similar to GO.

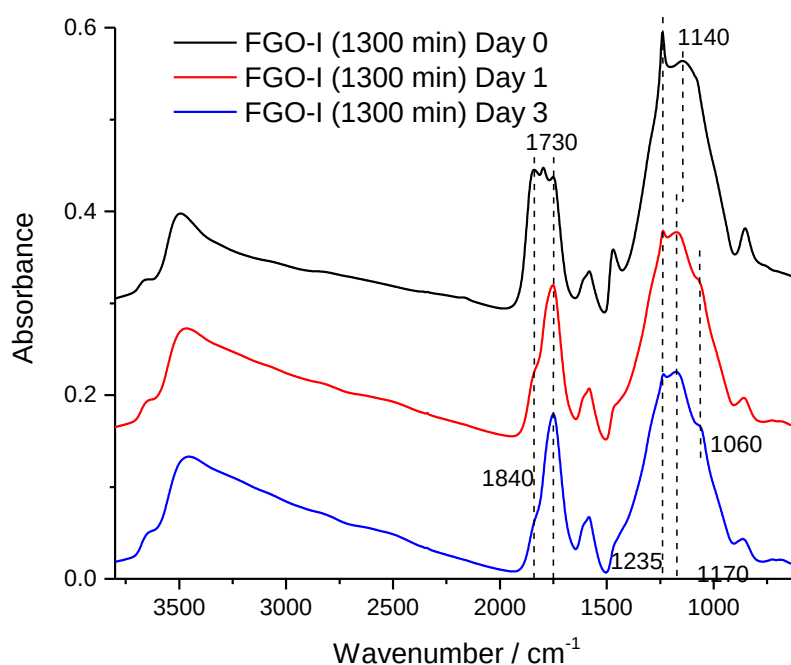


Figure 29. FTIR curves of GO and FGO-I (Reacted with XeF_2 for 1300 min) after storage in a desiccator

DSC-TGA was carried out to measure the changing thermal stability of FGO samples as time. Results are shown in **Figure 29**. Neat GO paper was examined as a baseline. The GO paper decomposed exothermically from 150 $^{\circ}\text{C}$ to 300 $^{\circ}\text{C}$, with a peak energy release at 178 $^{\circ}\text{C}$. Newly prepared FGO-I samples began losing mass at 245 $^{\circ}\text{C}$, while samples stored in a desiccator for 2 weeks began losing mass at 219 $^{\circ}\text{C}$, as shown in **Figure 30B**. The weight loss of GO and exothermal reactions were attributed to the decomposition process of oxygen containing functional groups, including hydroxyl, epoxide, carbonyl and carboxyl groups. **Figure 30B** shows that the weight loss can be divided into two different stages. Stage I is from 150 $^{\circ}\text{C}$ to around 210 $^{\circ}\text{C}$, which showed a clear peak in the differential thermos gravimetry (DTG) curve in **Figure 30B**, indicating

the evaporation of trapped water and removal of labile oxygen functional groups such as epoxy or hydroxyl groups in the basal plane of graphene. [98, 99] After that, Stage II occurred from 210 °C to about 300 °C and reflected a slower weight loss. The removal of more stable oxygen functional groups, such as carboxyl and carbonyl groups, occurred in this stage. In the DTG curve of the FGO-I sample shortly after fluorination in **Figure 30B**, the initiation of weight loss occurred at 210 °C, indicating that most labile epoxy and hydroxyl groups had been removed from the structure during XeF₂ treatment. After storage of the FGO paper in a desiccator, the decomposition temperature of FGO-I reduced to 219 °C after 16 days, indicating that some of the fluorinated groups decomposed during storage. Meanwhile, the temperature associated with peak energy release also decreased in FGO-I sample with storage time based on DSC results, shown in **Figure 30C**. The total energy release also decreased with storage, revealing that some fluorine functional groups were unstable at room temperature, the material reacted spontaneously and reached a state with lower energy. More detailed change in functional groups will be discussed below with FTIR results.

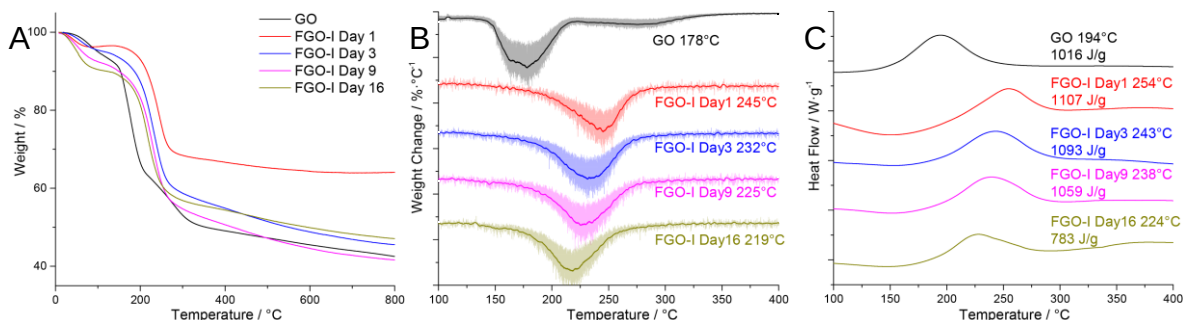


Figure 30. TGA (A), DTG (B) and DSC (C) curves of FGO-I in 2 weeks after synthesis. In figure B, half transparent background is the differential of TGA, while the solid curve represents the smoothed data. The temperature indicates the peak temperature of smoothed line of each sample. Figure C shows DSC curves from GO and FGO samples after various storage times. The temperature shown above the DSC curves represents the peak of DSC curves, and the energy release is obtained from the integration of heat flow peak. Upward is exothermic.

FGO-II showed similar DSC-TGA trends, as observed in **Figure 31**. The FGO-II sample contained a greater quantity of fluorine and produced a greater decomposition temperature compared to FGO-I at comparable storage times. The integrated energy release during decomposition, the peak temperature of weight loss and the peak temperature of heat release reduced significantly after 2 weeks of storage. It also confirmed that XeF₂ treated GO might return to a structure similar to GO during storage due to the reaction and decomposition of some fluorine functional groups. However, the DSC-TGA data after Day 1 and Day 7 of storage were very similar. This result is in contrast to those of FGO-I which showed a significant difference even after 3 days of storage. Therefore, increased fluorine content seems to have increased the stability of FGO to moisture.

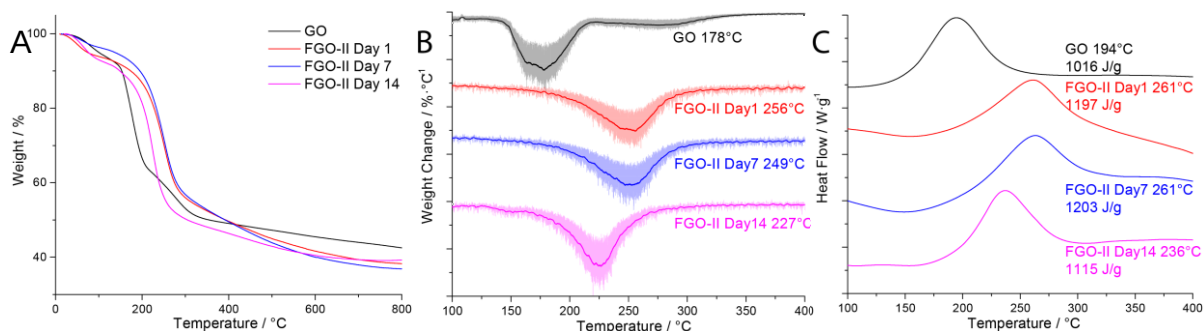


Figure 31. TGA (A), DTG (B) and DSC(C) curves of FGO-II in 2 weeks after synthesis. In figure B, the transparent background represents the unsmoothed differential TGA data, while the solid curves represent smoothed data. The temperature indicates the peak temperature of smoothed line of each sample. Figure C shows DSC curves from GO and FGO samples after various storage times. The temperature shown above the DSC curves represents the peak of DSC curves, and the energy release is obtained from the integration of heat flow peak. Upward is exothermic.

To further investigate FGO decomposition during heating, the elemental composition of FGO-I was measured by SEM-EDS after heating to 150 °C, 300 °C, 450 °C, and 600 °C and held isothermally for 5 minutes, with results listed in Table 1. After 1300 minutes of XeF₂ treatment, the fluorine content was approximately 11 at. %. Upon heating to 150 °C, and before the main decomposition starts (as identified by DSC-TGA), the fluorine content decreased to approximately 7%, implying that some fluorine species are extremely unstable and may be associated as intercalated fluorine molecules, such as HF, stabilized between GO sheets due to the intermolecular forces. Note that while the F/O ratio decreased, the C/O ratio remained stable when heated to 150 °C, indicating the reduction of GO did not commence as yet. At higher temperatures, the C/O ratio increased as the oxygen functional groups in FGO reduced. At the same time, fluorine content decreased at a faster rate than oxygen, as confirmed by the decreasing F/O ratio with temperature.

Table 5. Composition of FGO-I after heating to different temperatures by SEM-EDS

Temperature	Element content (Atomic)			Element Ratio	
	Carbon	Oxygen	Fluorine	C/O	F/O
No heating	51.46%	35.86%	10.97%	1.43	0.306
150 °C	53.80%	37.64%	6.78%	1.43	0.180
300 °C	68.52%	27.62%	2.36%	2.48	0.085
450 °C	77.24%	20.64%	0.56%	3.74	0.027
600 °C	83.40%	14.74%	0.42%	5.66	0.028

FTIR-ATR on heated samples to determine the change in functional groups are shown in **Figure 32**. The sample was stored for overnight after synthesis when the measurement was taken. The change of different functional groups can be clearly seen. Acyl fluoride (F-C=O, shoulder at 1840 cm⁻¹) reduced after heating to 150 °C, and disappeared at 300 °C. The C-F covalent bond (1235 cm⁻¹, as denoted by the short orange line to the left of

C-O-C peak in **Figure 32**) showed a small peak in unheated samples and those heated to 150 °C but disappeared at higher temperatures. The C-F covalent peak might overlap with C-O-C peak, but the absence of the small peak indicated its significant reduction. Similarly, C-F semi-ionic bond (1140 cm^{-1}) also significantly reduced after heating to 300 °C. After being heated to 600 °C, all other peaks disappeared except a small peak corresponding to semi-ionic C-F bond. Therefore, fluorine semi-ionically and covalently bonded to carbon atoms in graphene plane was more stable against heating, while other forms of fluorine functional groups decomposed at low temperature.

Little change in oxygen functional groups was found between the unheated samples and those heated to 150 °C. Hydroxyl groups (-OH, 3000 – 3700 cm^{-1} , C-OH, 1050 – 1060 cm^{-1}) were significantly reduced between 150 – 300 °C and almost disappeared when heated to 450 °C. A similar trend occurred for the peak of carboxylic acid (-COOH, 1620 cm^{-1}). It overlapped with alkane bond (C=C, 1580 cm^{-1}) peak when the sample was heated to 300 °C, giving a peak between 1580 and 1620 cm^{-1} . When the sample was heated to higher temperature (450 and 600 °C), the peak of carbonyl groups (-C=O, 1730 cm^{-1}) and ether groups (C-O-C, 1220 cm^{-1}) decreased significantly, indicating their decomposition at elevated temperature.

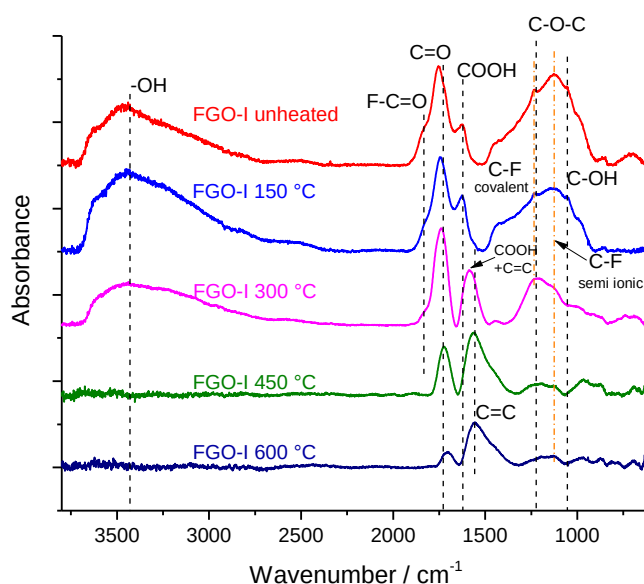


Figure 32. FTIR-ATR of FGO-I (by XeF_2 for 1300 min) after being heated to different temperatures

T-Jump TOFMS was employed to confirm the release of fluorine during the decomposition process found in DSC-TGA. FGO-I was dispersed in IPA under sonication right after XeF_2 fluorination to avoid any further contact with environmental moisture. The HF^+ fluorine peak appeared in the integrated mass spectrum in **Figure 33**, confirming the existence of fluorine in the XeF_2 treated sample. Note that H_2O^+ , N_2^+ and NO^+ peaks represent unavoidable background signals. C^+ , O^+ , CO^+ and CO_2^+ arise from the decomposition GO and the oxygen functional groups. Additionally, the time-resolved

intensity curve in **Figure 33B** clearly showed that the fluorine content was released simultaneously with CO_2^+ . We may conclude that release of fluorine species occurs simultaneously with decomposition of GO, with an onset temperature of about 265 ± 50 °C, consistent with the decomposition at $245 / 254$ °C found in the DTG and DSC results. It is interesting that the loss of fluorine content started below 150 °C as found in DSC-TGA, while the presence of the fluorine ion in mass spectrometry appeared above 250 °C. It is reasonable to consider that some fluorine loss occurred during the sample preparation for mass spectrometry, especially those that escaped from the structure below 150 °C as found in DSC-TGA.

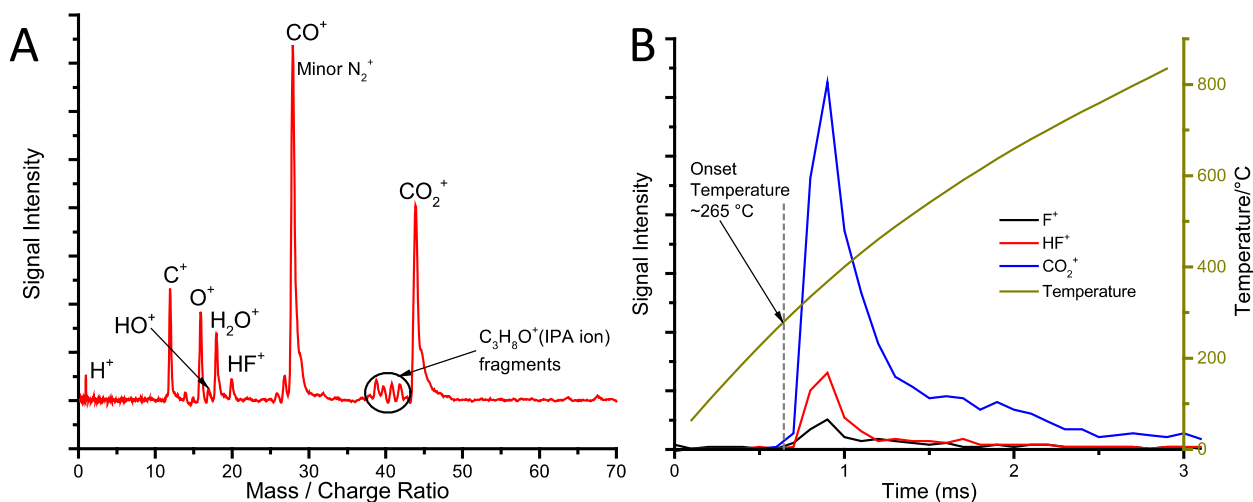


Figure 33. Integrated (A) and time-resolving (B) mass spectrometry results of FGO-I dispersed in IPA

Due to the high fraction of oxygen functional groups retained after fluorination, the FGO samples can be dispersed in a variety of solvents under sonication. The dispersing behavior of FGO was similar like that of GO [100], which enhances its potential application by dispersing in different kinds of solvents. FTIR and SEM-EDS analysis of the vacuum dried dispersions prepared in IPA, THF, propylene carbonate (PC), THF, and cyclohexane was then obtained to determine the change in composition. It is clear that extra C-H peaks showed up in all dried FGO dispersions as evidenced from $2800 - 3000$ cm^{-1} in FTIR curves, which was absent in the FTIR curve of FGO-I, indicating that some solvent might be trapped or bonded in the dried sample. Moreover, the peak of acyl fluoride at 1840 cm^{-1} of FGO-I in **Figure 29** almost disappeared, confirming the decomposition of acyl fluoride during sonication. Therefore, the fluorine species that loosely intercalated or bonded between graphene sheets escaped from the structure during the exfoliation of graphene under sonication. As a result the fluorine content dropped from more than 10% in FGO-I to only 1 – 3.5% in these dried dispersions. The F/O ratio also dropped from 0.3 to only about 0.1. The remained fluorine content mostly existed in C-F covalent and semi-ionic bonds, which are thermally more stable.

These results indicate that XeF₂ can be employed as a means for the fluorination of GO to FGO while retaining a majority of oxygen functional groups. However, the fluorine content in the material degraded with time in the presence of even a relatively small quantity of water vapor. Part of the fluorine content formed acyl fluoride and can be easily hydrolyzed with the moisture in atmosphere or can react with solvent during dispersing process for further utilization. Almost 40% of fluorine escaped from the material when heated to 150 °C. Despite the loss of acyl fluoride during heating, some fluorine structures such as H-F molecules which are not strongly chemically bonded to graphene plane might exist in the structure. This fluorine content can be easily removed from the structure under heating to low temperature, during the exfoliation of graphene sheets under sonication, or even slowly escape from the structure during storage. Therefore, fluorine showed significantly reduced stability when compared to oxygen in the FGO synthesized by GO with XeF₂.

One of the potential application of FGO is as a component in nanoenergetic formulations. Al nanoparticle is a common fuel and possesses a naturally formed inert Al₂O₃ shell on its surface, which protects the Al core from further oxidation under ambient conditions, but also acts as a reaction limiting barrier between fuel Al and oxidizer. Fluorine may however be a source to remove or weaken the Al₂O₃ shell and accelerate the reaction (Al₂O₃ + “F” → AlF₃ + O, where “F” indicates a highly reactive fluorine species). [76] To investigate the role of FGO additive in nanoenergetic materials, DSC-TGA measurements were carried out on samples composed of GO, FGO, Al and Bi₂O₃, as summarized in Table 2.

Table 6. Energetic samples measured by DSC-TGA with different compositions

Sample Name and mass ratio	Mass (Total mass = 100 mg)			Remark
	GO/FGO	Al (80% active)	Bi ₂ O ₃	
GO/Al – I (70/30)	70 mg	30 mg	0	
FGO-I/Al – I (70/30)	70 mg	30 mg	0	
GO/Al – II (30/97)	23.5mg	76.5 mg	0	GO(FGO)/Al ratio same as in GO(FGO)/Al/Bi ₂ O ₃ .
FGO-I/Al – II (30/97)	23.5 mg	76.5 mg	0	
GO/Al/Bi ₂ O ₃ (30/97/473)	5 mg	16.2 mg	78.8 mg	5% GO(FGO) by mass. Equivalence ratio (ER) of Al/Bi ₂ O ₃ = 1.4. ER of Al/Bi ₂ O ₃ = 1.4.
FGO-I/Al/Bi ₂ O ₃ (30/97/473)	5 mg	16.2 mg	78.8 mg	
Al/Bi ₂ O ₃ (97/473)	0	17 mg	83 mg	

A representative DSC curve of GO/Al – I (**Figure 34**) shows no significant reaction before melting of Al. The small exotherms between 500 – 620 °C result from reaction

between the Al core and generated OH species such as H₂O from GO, mainly from the decomposition of hydroxyl groups bonded in GO structure. These species were adsorbed on the amorphous alumina shell and reacted with Al when the core started to diffuse as the temperature was elevated above 500 °C giving the small exotherms observed. A sharp endotherm of Al melting is seen at 660 °C, followed by the main exothermic reaction between Al and GO, indicating that Al primarily reacts in the liquid phase after it may readily flow out of the shell. When GO was replaced by FGO-I, the DSC indicated that the largest exothermic reaction occurred before the melting of Al. The main reaction peak is between 610 to 660 °C indicated that Al₂O₃ shell was weakened by the fluorine species generated from FGO-I decomposition, allowing Al to escape the shell before melting. The disappearance of the small exotherms between 500 – 620 °C in FGO-I/Al – I compared to GO/Al – I was due to the removal of hydroxyl groups during fluorination. Al was not fully reacted before its melting, indicating that the fluorine and oxygen content in FGO-I was not sufficient to weaken all alumina shells prior to Al melting. Some Al melted and then reacted with graphene. The total reaction energy between the two samples was similar (118 J/g for GO/Al – I and 104 J/g for FGO-I/Al – I), but the fraction of energy released before and after Al melting was significantly different between the two materials.

As an additive in nanothermite composite, graphene or functionalized graphene is usually no more than 5% mass with Al and metal oxide [20], or no more than 30% mass with Al only [101] to obtain optimized energetic performance. Therefore, we analyzed the DSC of GO/Al – II and FGO-I/Al – II samples with a lower FGO (GO) percentage of 23.5%. The GO/Al – II showed a very similar exotherm between 520 – 600 °C, as a result of the decomposed OH species penetrating the shell and reacting with the Al. While in FGO/Al – II, unlike in the sample described above with 70% of FGO, the fluorine content in the composite was not enough to react extensively with diffusing Al after being adsorbed and reacted with the alumina shell. Therefore, there was not a dominating exothermic reaction in DSC like in **Figure 34A** (FGO/Al – I) before Al melting. However, some small exotherm still showed up around 610 °C, which is close to the large exothermic peak in **Figure 34A** (FGO/Al – I). It indicated that the Al core was able to diffuse out from the shell easier and react with the FGO surrounding it before reaching its melting point, even with only about 1/3 mass of FGO compared to Al and 3% fluorine content after preparing the sample.

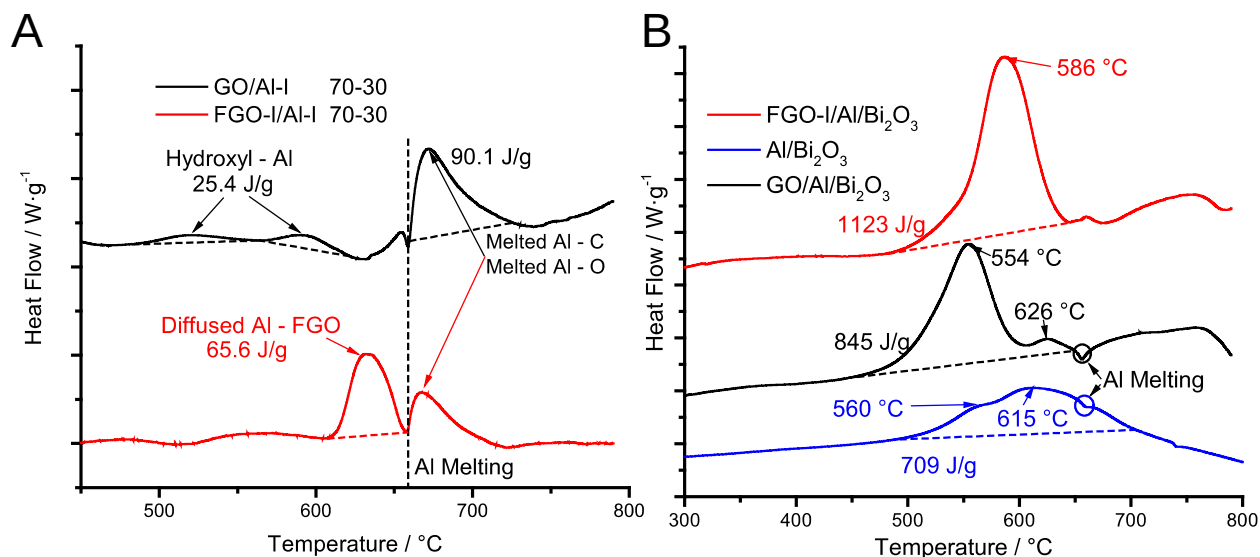


Figure 34. DSC results of GO/Al – I and FGO-I/Al – I (A) and FGO-I/Al/Bi₂O₃, GO/Al/Bi₂O₃ and Al/Bi₂O₃ (B). Upward is exothermic.

Metal oxide such as Bi₂O₃ is commonly used in Al-based nanoenergetic composites due to its remarkable energetic behavior such as propagation and pressurization rate. [20, 77, 102] **Figure 34B** shows the reaction heat of Al/Bi₂O₃ nanothermite involving GO and FGO-I. In Al/Bi₂O₃ loose powder, the reaction initiated at 500 °C due to the start of Al core diffusion out of the shell, peaked at around 615 °C and was completed at about 700 °C after the melting of Al. Neat Al/Bi₂O₃ mixtures are known to be inhomogeneous as a result of phase separation. [20, 77] The low-temperature reaction likely occurred between surface contacted Al and Bi₂O₃ nanoparticles, while part of reaction had to occur after the melting and free flow of Al nanoparticles. [77] When GO was added to the Al/Bi₂O₃ nanocomposite mixture, GO/Al/Bi₂O₃ showed the lowest onset exothermic temperature around 460 °C, likely resulting from a mechanism similar to that observed previously when testing GO/Al (70 – 30). OH species generated from GO reacted with diffused Al in the Al₂O₃ shell when the sample was heated to about 480 °C. It caused locally overheat in the sample, accelerating the diffusion and reaction of Al core. The energy release of GO/Al/Bi₂O₃ was slightly enhanced by approximately 20% compared to neat Al/Bi₂O₃ due to the reduced phase separation as a result of GO addition. [20] The improved Al and Bi₂O₃ intermixing in the presence of GO reduced diffusion length scales for mass transport and the peak reaction temperature for the GO/Al/Bi₂O₃ compared to Al/Bi₂O₃. [20] After the first reaction, GO/Al/Bi₂O₃ showed a second reaction peaking at 626 °C as Al flew easier and reacted with farther away Bi₂O₃ at higher temperature. It is notable that the melting peak of Al was observed in both Al/Bi₂O₃ loose powder and GO/Al/Bi₂O₃, indicating that part of the Al core remained unreacted prior the melting point of Al at 660 °C. However, with the addition of FGO-I, the melting peak of Al was not observed, and the reaction was nearly completed before the melting temperature of Al. Because of fluorine etching of the alumina shells, it was easier for the Al core to escape from the Al₂O₃ shell and react with Bi₂O₃ nanoparticles before Al melted. Due to the absence of

OH groups after XeF_2 fluorination, FGO-I/Al/ Bi_2O_3 didn't give onset temperature as low as GO/Al/ Bi_2O_3 . However, its weakened Al_2O_3 shell still allowed Al core to diffuse out and react with Bi_2O_3 nanoparticles easier at a temperature around 480 °C, lower than the onset temperature in Al/ Bi_2O_3 . Moreover, FGO/Al/ Bi_2O_3 showed an energy release of over 1100 J/g, which was 60% higher than Al/ Bi_2O_3 loose powder and 33% higher than GO/Al/ Bi_2O_3 . The main reaction gave a single peak at 586 °C, which might be overlapping of two reaction peaks around 560 and 600 °C. The addition of FGO in Al/ Bi_2O_3 converted to energetic reaction into a complete "solid-state" reaction in DSC-TGA.

4.0 CONCLUSIONS

The foregoing work demonstrated the benefit of the self-assembly process towards the generation of large-scale and highly-reactive nanothermites with diverse morphology and combustion behaviors. To facilitate assembly, 2D materials provide a robust scaffolding because of their large surface area and tunable chemistry. As an example of the diversity of materials produced via self-assembly processing, we demonstrate the use of graphene oxide to fabricate ultra-low density reactive aerogel materials and as a vehicle to deliver fluorine to Al NPs. Thin MoO_3 sheets were used both to assemble micrometer and millimeter scale assemblies and to study the isolated combustion reaction between few Al NPs and oxidizer. In the case of MoO_3 sheets, the 2D material served as both a structural agent and as the primary oxidizer to drive combustion. Thin α - MoO_3 sheets were also utilized as an isolated reaction system to study the detailed reaction between photothermally heated Al NPs and MoO_3 . The combined effort detailed in this report demonstrates the amenability of 2D energetic nanoparticles to form densely-packed macroscale assemblies with diverse properties to deliver a desired combustion performance.

4.1 Nanoenergetic Assemblies Utilizing MoO_3 Sheets

Exfoliated 2D MoO_3 sheets were assembled with Al NPs to form a highly reactive nanoenergetic composite material. The exfoliated MoO_3 sheets provided a large surface area of interaction and reducing the mass diffusion length between the fuel and oxidizers, greatly enhancing the nanoenergetic energy release of the system. The observed combustion speed of 1,730 m/s is the faster reported value for this material system. Analysis of the combustion products indicates that MoO_3 sheets produced a greater reaction temperature, sufficient to melt the Mo and Al_2O_3 , and approaching the adiabatic reaction temperature of 3,253 K. We hypothesize that the enhanced reactivity of the material is enabled by a morphological response of reacting Al and MoO_3 . Extended alumina protrusions extend radially from the external surface of Al fuel particles after reaction in both slow and rapid heating environments. This particle morphology is unique and is potentially advantageous for complete and rapid combustion. We propose that the 2D MoO_3 sheets were converted to extended alumina sheets by surface and sub-surface Al adsorption. These assumptions were further validated when we reacted isolated Al

nanoparticles on the exposed surface. α - MoO_3 sheets. Heat from the adsorption displaces the host Mo from the solid lattice, where it collects on reaction products to form small Mo particles. Because the reaction is limited to the surface layers of MoO_3 , only 2D sheets are fully reacted via the proposed mechanism, whereas complete combustion of MoO_3 micron size powder cannot proceed along a similar path. These results stress the importance of nanoscale material geometry to increase reactive surface area and reduced diffusion lengths within nanoenergetic materials and the importance of material self-assembly to ensure homogeneous distribution of reactants.

4.2 Reactive Nanoenergetic Graphene Aerogels

Another self-assembly process was utilized to attract Al NPs to GO sheets in solution. By using processing steps that are compatible with nanoenergetic fuel and oxide nanoparticles, a reactive graphene aerogel material was produced. The loading of energetic NPs within an RGO aerogel scaffolding produced a material with superior energy release, flame speed, and ESD sensitivity relative to the neat NP mixture. Integration of the energetic NPs was facilitated by a novel gelation process in which EDA was added to a PC dispersion to induce gelation and mild chemical reduction. Particle dispersion was encouraged in PC, while EDA served as a mild gelation and reduction agent that retained the reactivity of the energetic NPs. The RGO/Al/ Bi_2O_3 nanoenergetic aerogel obtained by this process exhibited structural homogeneity with well-dispersed particle loading. The aerogel scaffold was of critical importance from applications' perspectives as it confined fuel and oxide NPs in intimate contact, linked to the NPs to discourage sintering, provided an electrically conductive pathway to reduce ESD sensitivity, and provided a mechanism that tends to partially confine flame propagation for enhanced burn rates. Although the process was demonstrated using embedded Al and Bi_2O_3 NPs, the procedure itself can be extended to produce aerogels with numerous other types of embedded reactive NP to obtain different nanothermite responses. This process was also amenable for the gelation of materials that are sensitive to high temperature or water.

4.3 Functionalized Graphene Oxide as a Chemical Delivery Agent

Direct fluorination of graphene oxide (GO) using low-pressure XeF_2 gas was carried out and the oxygen functional groups in GO were successfully retained. The successful preservation of oxygen functional groups enabled the easy dispersing of FGO in different solvents, wider application and further functionalization. The stability of the synthesized FGO was studied, including the change of functional groups and elemental composition under regular storage and different processing strategies. The fluorine content was not as stable as oxygen in FGO due to some intercalated fluorine components and highly reactive acyl fluoride in the structure. Moisture, mild heating, or dispersing in solvents will cause the loss of part of fluorine content. The FGO can be utilized in some fields such as nanoenergetic materials. The fluorine content was highly reactive and could help to weaken or even remove the shell of Al nanoparticles, leading to an all "solid-state"

reaction between Al and Bi₂O₃ at lower temperature and 60% higher energy release than Al/Bi₂O₃ loose powder.

5.0 BIBLIOGRAPHY

- [1] M. Kosmulski, P. Prochniak, J.B. Rosenholm, Control of the Zeta Potential in Semiconcentrated Dispersions of Titania in Polar Organic Solvents, *The Journal of Physical Chemistry C* 113(29) (2009) 12806-12810.
- [2] M.L. Pantoya, S.W. Dean, The influence of alumina passivation on nano-Al/Teflon reactions, *Thermochimica Acta* 493(1-2) (2009) 109-110.
- [3] D. Stamatis, X. Zhu, M. Schoenitz, E.L. Dreizin, P. Redner, Consolidation and mechanical properties of reactive nanocomposite powders, *Powder Technol.* 208(3) (2011) 637-642.
- [4] C. Huang, G. Jian, J.B. De Lisio, H. Wang, M.R. Zachariah, Electrospray deposition of energetic polymer nanocomposites with high mass particle loadings: A prelude to 3D printing of rocket motors, *Adv. Eng. Mater.* 17(1) (2014) 95-101.
- [5] A. Prakash, A.V. McCormick, M.R. Zachariah, Tuning the reactivity of energetic nanoparticles by creation of a core-shell nanostructure, *Nano Lett.* 5(7) (2005) 1357-1360.
- [6] J.M. Slocik, C.A. Crouse, J.E. Spowart, R.R. Naik, Biologically tunable reactivity of energetic nanomaterials using protein cages, *Nano Lett.* 13(6) (2013) 2535-2540.
- [7] X. Zhou, M. Torabi, J. Lu, R.Q. Shen, K.L. Zhang, Nanostructured Energetic Composites: Synthesis, Ignition/Combustion Modeling, and Applications, *Acs Applied Materials & Interfaces* 6(5) (2014) 3058-3074.
- [8] M.R. Weismiller, J.Y. Malchi, J.G. Lee, R.A. Yetter, T.J. Foley, Effects of fuel and oxidizer particle dimensions on the propagation of aluminum containing thermites, *Proceedings of the Combustion Institute* 33 (2011) 1989-1996.
- [9] D.M. Badgujar, M.B. Talawar, S.N. Asthana, P.P. Mahulikar, Advances in science and technology of modern energetic materials: an overview, *Journal of hazardous materials* 151(2-3) (2008) 289-305.
- [10] D.D. Dlott, Thinking big (and small) about energetic materials, *Materials Science and Technology* 22(4) (2006) 463-473.
- [11] C. Rossi, K. Zhang, D. Esteve, P. Alphonse, P. Tailhades, C. Vahlas, Nanoenergetic materials for MEMS: A review, *J. Microelectromech. Syst.* 16(4) (2007) 919-931.
- [12] B. Chen, H. Zheng, M. Riehn, S. Bok, K. Gangopadhyay, M.R. Maschmann, S. Gangopadhyay, In Situ Characterization of Photothermal Nanoenergetic Combustion on a Plasmonic Microchip, *ACS Applied Materials & Interfaces* 10(1) (2018) 427-436.
- [13] S. Apperson, R.V. Shende, S. Subramanian, D. Tappmeyer, S. Gangopadhyay, Z. Chen, K. Gangopadhyay, P. Redner, S. Nicholich, D. Kapoor, Generation of fast propagating combustion and shock waves with copper oxide/aluminum nanothermite composites, *Applied Physics Letters* 91(24) (2007) 243109.
- [14] B.J. Bellott, W. Noh, R.G. Nuzzo, G.S. Girolami, Nanoenergetic materials: boron nanoparticles from the pyrolysis of decaborane and their functionalisation, *Chemical Communications* (22) (2009) 3214-3215.

- [15] X. Zhou, D. Xu, G. Yang, Q. Zhang, J. Shen, J. Lu, K. Zhang, Highly Exothermic and Superhydrophobic Mg/Fluorocarbon Core/Shell Nanoenergetic Arrays, *ACS Applied Materials & Interfaces* 6(13) (2014) 10497-10505.
- [16] C.R. Becker, S. Apperson, C.J. Morris, S. Gangopadhyay, L.J. Currano, W.A. Churaman, C.R. Stoldt, Galvanic Porous Silicon Composites for High-Velocity Nanoenergetics, *Nano Letters* 11(2) (2011) 803-807.
- [17] R. Thiruvengadathan, A. Bezmelnitsyn, S. Apperson, C. Staley, P. Redner, W. Balas, S. Nicolich, D. Kapoor, K. Gangopadhyay, S. Gangopadhyay, Combustion characteristics of novel hybrid nanoenergetic formulations, *Combustion and Flame* 158(5) (2011) 964-978.
- [18] K.J. Blobaum, M.E. Reiss, J.M. Plitzko, T.P. Weihs, Deposition and characterization of a self-propagating CuOx/Al thermite reaction in a multilayer foil geometry, *J. Appl. Phys.* 94(5) (2003) 2915-2922.
- [19] R.J. Jacob, G.Q. Jian, P.M. Guerieri, M.R. Zachariah, Energy release pathways in nanothermites follow through the condensed state, *Combustion and Flame* 162(1) (2015) 258-264.
- [20] R. Thiruvengadathan, S.W. Chung, S. Basuray, B. Balasubramanian, C.S. Staley, K. Gangopadhyay, S. Gangopadhyay, A Versatile Self-Assembly Approach toward High Performance Nanoenergetic Composite Using Functionalized Graphene, *Langmuir* 30(22) (2014) 6556-6564.
- [21] S.M. Umbrajkar, S. Seshadri, M. Schoenitz, V.K. Hoffmann, E.L. Dreizin, Aluminum-rich Al-MoO₃ nanocomposite powders prepared by arrested reactive milling, *Journal of Propulsion and Power* 24(2) (2008) 192-198.
- [22] J.A. Puszynski, Processing and characterization of aluminum-based nanothermites, *Journal of Thermal Analysis and Calorimetry* 96(3) (2009) 677-685.
- [23] M. Comet, B. Siegert, F. Schnell, V. Pichot, F. Cizek, D. Spitzer, Phosphorus-Based Nanothermites: A New Generation of Pyrotechnics Illustrated by the Example of n-CuO/Red P Mixtures, *Propellants, Explosives, Pyrotechnics* 35(3) (2010) 220-225.
- [24] J.A. Puszynski, C.J. Bulian, J.J. Swiatkiewicz, Processing and Ignition Characteristics of Aluminum-Bismuth Trioxide Nanothermite System, *Journal of Propulsion and Power* 23(4) (2007) 698-706.
- [25] C.S. Staley, K.E. Raymond, R. Thiruvengadathan, J.J. Herbst, S.M. Swaszek, R.J. Taylor, K. Gangopadhyay, S. Gangopadhyay, Effect of Nitrocellulose Gasifying Binder on Thrust Performance and High-g Launch Tolerance of Miniaturized Nanothermite Thrusters, *Propellants, Explosives, Pyrotechnics* 39(3) (2014) 374-382.
- [26] C.S. Staley, K.E. Raymond, R. Thiruvengadathan, S.J. Apperson, K. Gangopadhyay, S.M. Swaszek, R.J. Taylor, S. Gangopadhyay, Fast-Impulse Nanothermite Solid-Propellant Miniaturized Thrusters, *Journal of Propulsion and Power* 29(6) (2013) 1400-1409.
- [27] S.J. Apperson, A.V. Bezmelnitsyn, R. Thiruvengadathan, K. Gangopadhyay, S. Gangopadhyay, W.A. Balas, P.E. Anderson, S.M. Nicolich, Characterization of Nanothermite Material for Solid-Fuel Microthruster Applications, *Journal of Propulsion and Power* 25(5) (2009) 1086-1091.
- [28] P.M. L., G.J. J., Combustion Behavior of Highly Energetic Thermites: Nano versus Micron Composites, *Propellants, Explosives, Pyrotechnics* 30(1) (2005) 53-62.

- [29] H. Hu, Z. Zhao, W. Wan, Y. Gogotsi, J. Qiu, Ultralight and Highly Compressible Graphene Aerogels, *Advanced Materials* 25(15) (2013) 2219-2223.
- [30] Y. Wu, N. Yi, L. Huang, T. Zhang, S. Fang, H. Chang, N. Li, J. Oh, J.A. Lee, M. Kozlov, A.C. Chipara, H. Terrones, P. Xiao, G. Long, Y. Huang, F. Zhang, L. Zhang, X. Lepró, C. Haines, M.D. Lima, N.P. Lopez, L.P. Rajukumar, A.L. Elias, S. Feng, S.J. Kim, N.T. Narayanan, P.M. Ajayan, M. Terrones, A. Aliev, P. Chu, Z. Zhang, R.H. Baughman, Y. Chen, Three-dimensionally bonded spongy graphene material with super compressive elasticity and near-zero Poisson's ratio, *Nature Communications* 6 (2015) 6141.
- [31] M.A. Worsley, P.J. Pauzauskie, T.Y. Olson, J. Biener, J.H. Satcher, T.F. Baumann, Synthesis of Graphene Aerogel with High Electrical Conductivity, *Journal of the American Chemical Society* 132(40) (2010) 14067-14069.
- [32] Z. Yu, M. McInnis, J. Calderon, S. Seal, L. Zhai, J. Thomas, Functionalized graphene aerogel composites for high-performance asymmetric supercapacitors, *Nano Energy* 11(Supplement C) (2015) 611-620.
- [33] Q. Zhang, F. Zhang, S.P. Medarametla, H. Li, C. Zhou, D. Lin, 3D printing of graphene aerogels, *Small* 12(13) (2016) 1702-1708.
- [34] Y.Q. Sun, Q. Wu, G.Q. Shi, Supercapacitors based on self-assembled graphene organogel, *Phys. Chem. Chem. Phys.* 13(38) (2011) 17249-17254.
- [35] Y.X. Xu, K.X. Sheng, C. Li, G.Q. Shi, Self-Assembled Graphene Hydrogel via a One-Step Hydrothermal Process, *Acs Nano* 4(7) (2010) 4324-4330.
- [36] P. Chen, J.-J. Yang, S.-S. Li, Z. Wang, T.-Y. Xiao, Y.-H. Qian, S.-H. Yu, Hydrothermal synthesis of macroscopic nitrogen-doped graphene hydrogels for ultrafast supercapacitor, *Nano Energy* 2(2) (2013) 249-256.
- [37] R. Li, C.B. Chen, J. Li, L.M. Xu, G.Y. Xiao, D.Y. Yan, A facile approach to superhydrophobic and superoleophilic graphene/polymer aerogels, *J. Mater. Chem. A* 2(9) (2014) 3057-3064.
- [38] V. Velmurugan, U. Srinivasarao, R. Ramachandran, M. Saranya, A.N. Grace, Synthesis of tin oxide/graphene (SnO₂/G) nanocomposite and its electrochemical properties for supercapacitor applications, *Materials Research Bulletin* 84 (2016) 145-151.
- [39] K.F. Zhou, Y.H. Zhu, X.L. Yang, C.Z. Li, One-pot preparation of graphene/Fe₃O₄ composites by a solvothermal reaction, *New J. Chem.* 34(12) (2010) 2950-2955.
- [40] O. Ruff, O. Bretschneider, Die Reaktionsprodukte der verschiedenen Kohlenstoffformen mit Fluor II (Kohlenstoff-monofluorid), *Zeitschrift für anorganische und allgemeine Chemie* 217(1) (1934) 1-18.
- [41] A.M. Panich, Nuclear magnetic resonance study of fluorine-graphite intercalation compounds and graphite fluorides, *Synthetic Metals* 100(2) (1999) 169-185.
- [42] W. Tiedemann, Electrochemical Behavior of the Fluorographite Electrode in Nonaqueous Media, *J. Electrochem. Soc.* 121(10) (1974) 1308-1311.
- [43] S. Ebnesajjad, *Expanded PTFE Applications Handbook: Technology, Manufacturing and Applications*, Elsevier 2016.
- [44] A.L. Logothetis, Chemistry of fluorocarbon elastomers, *Progress in Polymer Science* 14(2) (1989) 251-296.
- [45] C.D. James, G.W. Franklin, *Fluorocarbon vinyl ether polymers*, United States, 1967.

- [46] R.J. Lagow, R.B. Badachhape, J.L. Wood, J.L. Margrave, Some new synthetic approaches to graphite–fluorine chemistry, *Journal of the Chemical Society, Dalton Transactions* (12) (1974) 1268-1273.
- [47] W. Rüdorff, Graphite Intercalation Compounds, in: H.J. Emeléus, A.G. Sharpe (Eds.), *Advances in Inorganic Chemistry and Radiochemistry*, Academic Press 1959, pp. 223-266.
- [48] H.E. Sliney, Graphite Fluoride (CF_x)_n - A New Solid Lubricant AU - Fusaro, Robert L, *A S L E Transactions* 13(1) (1970) 56-65.
- [49] X. Chia, A. Ambrosi, M. Otyepka, R. Zbořil, M. Pumera, Fluorographites (CF_x)_n Exhibit Improved Heterogeneous Electron-Transfer Rates with Increasing Level of Fluorination: Towards the Sensing of Biomolecules, *Chemistry – A European Journal* 20(22) (2014) 6665-6671.
- [50] C. Delabarre, M. Dubois, J. Giraudet, K. Guérin, A. Hamwi, Electrochemical performance of low temperature fluorinated graphites used as cathode in primary lithium batteries, *Carbon* 44(12) (2006) 2543-2548.
- [51] R. Taylor, J.H. Holloway, E.G. Hope, A.G. Avent, G.J. Langley, T.J. Dennis, J.P. Hare, H.W. Kroto, D.R.M. Walton, Nucleophilic substitution of fluorinated C₆₀, *Journal of the Chemical Society, Chemical Communications* (9) (1992) 665-667.
- [52] A. Hamwi, H. Alvergnat, S. Bonnamy, F. Béguin, Fluorination of carbon nanotubes, *Carbon* 35(6) (1997) 723-728.
- [53] E.T. Mickelson, C.B. Huffman, A.G. Rinzler, R.E. Smalley, R.H. Hauge, J.L. Margrave, Fluorination of single-wall carbon nanotubes, *Chemical Physics Letters* 296(1) (1998) 188-194.
- [54] J.T. Robinson, J.S. Burgess, C.E. Junkermeier, S.C. Badescu, T.L. Reinecke, F.K. Perkins, M.K. Zalalutdniov, J.W. Baldwin, J.C. Culbertson, P.E. Sheehan, E.S. Snow, Properties of Fluorinated Graphene Films, *Nano Letters* 10(8) (2010) 3001-3005.
- [55] X. Yang, X. Jia, X. Ji, Acid induced fluorinated graphene oxide, *RSC Advances* 5(13) (2015) 9337-9340.
- [56] A.K. Geim, K.S. Novoselov, The rise of graphene, *Nat. Mater.* 6(3) (2007) 183-191.
- [57] K.P. Loh, Q. Bao, P.K. Ang, J. Yang, The chemistry of graphene, *Journal of Materials Chemistry* 20(12) (2010) 2277-2289.
- [58] H. An, Y. Li, P. Long, Y. Gao, C. Qin, C. Cao, Y. Feng, W. Feng, Hydrothermal preparation of fluorinated graphene hydrogel for high-performance supercapacitors, *Journal of Power Sources* 312(Supplement C) (2016) 146-155.
- [59] S. Huang, Y. Li, Y. Feng, H. An, P. Long, C. Qin, W. Feng, Nitrogen and fluorine co-doped graphene as a high-performance anode material for lithium-ion batteries, *J. Mater. Chem. A* 3(46) (2015) 23095-23105.
- [60] N. Liaros, A.B. Bourlinos, R. Zboril, S. Couris, Fluoro-graphene: nonlinear optical properties, *Opt. Express* 21(18) (2013) 21027-21038.
- [61] F. Withers, M. Dubois, A.K. Savchenko, Electron properties of fluorinated single-layer graphene transistors, *Phys. Rev. B* 82(7) (2010) 073403.
- [62] W. Feng, P. Long, Y. Feng, Y. Li, Two-Dimensional Fluorinated Graphene: Synthesis, Structures, Properties and Applications, *Advanced Science* 3(7) (2016) 1500413.
- [63] X. Wang, Y. Dai, J. Gao, J. Huang, B. Li, C. Fan, J. Yang, X. Liu, High-Yield Production of Highly Fluorinated Graphene by Direct Heating Fluorination of Graphene-oxide, *ACS Applied Materials & Interfaces* 5(17) (2013) 8294-8299.

- [64] R. Stine, W.-K. Lee, K.E. Whitener, J.T. Robinson, P.E. Sheehan, Chemical Stability of Graphene Fluoride Produced by Exposure to XeF₂, *Nano Letters* 13(9) (2013) 4311-4316.
- [65] Y.-Y. Yu, B.H. Kang, Y.D. Lee, S.B. Lee, B.-K. Ju, Effect of fluorine plasma treatment with chemically reduced graphene oxide thin films as hole transport layer in organic solar cells, *Applied Surface Science* 287 (2013) 91-96.
- [66] S.B. Bon, L. Valentini, R. Verdejo, J.L. Garcia Fierro, L. Peponi, M.A. Lopez-Manchado, J.M. Kenny, Plasma Fluorination of Chemically Derived Graphene Sheets and Subsequent Modification With Butylamine, *Chemistry of Materials* 21(14) (2009) 3433-3438.
- [67] K. Tahara, T. Iwasaki, A. Matsutani, M. Hatano, Effect of radical fluorination on mono- and bi-layer graphene in Ar/F₂ plasma, *Applied Physics Letters* 101(16) (2012) 163105.
- [68] Z. Wang, J. Wang, Z. Li, P. Gong, X. Liu, L. Zhang, J. Ren, H. Wang, S. Yang, Synthesis of fluorinated graphene with tunable degree of fluorination, *Carbon* 50(15) (2012) 5403-5410.
- [69] K. Samanta, S. Some, Y. Kim, Y. Yoon, M. Min, S.M. Lee, Y. Park, H. Lee, Highly hydrophilic and insulating fluorinated reduced graphene oxide, *Chemical Communications* 49(79) (2013) 8991-8993.
- [70] P. Gong, Z. Wang, Z. Li, Y. Mi, J. Sun, L. Niu, H. Wang, J. Wang, S. Yang, Photochemical synthesis of fluorinated graphene via a simultaneous fluorination and reduction route, *RSC Advances* 3(18) (2013) 6327-6330.
- [71] M. Dubois, K. Guérin, Y. Ahmad, N. Batisse, M. Mar, L. Frezet, W. Hourani, J.-L. Bubendorff, J. Parmentier, S. Hajjar-Garreau, L. Simon, Thermal exfoliation of fluorinated graphite, *Carbon* 77 (2014) 688-704.
- [72] C. Sun, Y. Feng, Y. Li, C. Qin, Q. Zhang, W. Feng, Solvothermally exfoliated fluorographene for high-performance lithium primary batteries, *Nanoscale* 6(5) (2014) 2634-2641.
- [73] K.T. Sullivan, N.W. Piekiele, C. Wu, S. Chowdhury, S.T. Kelly, T.C. Hufnagel, K. Fezzaa, M.R. Zachariah, Reactive sintering: An important component in the combustion of nanocomposite thermites, *Combustion and Flame* 159(1) (2012) 2-15.
- [74] G.C. Egan, K.T. Sullivan, T. LaGrange, B.W. Reed, M.R. Zachariah, In situ imaging of ultra-fast loss of nanostructure in nanoparticle aggregates, *J. Appl. Phys.* 115(8) (2014) 6.
- [75] V.I. Levitas, Burn time of aluminum nanoparticles: Strong effect of the heating rate and melt-dispersion mechanism, *Combustion and Flame* 156(2) (2009) 543-546.
- [76] M.L. Pantoya, S.W. Dean, The influence of alumina passivation on nano-Al/Teflon reactions, *Thermochimica Acta* 493(1) (2009) 109-110.
- [77] A. Wang, S. Bok, R. Thiruvengadathan, K. Gangopadhyay, J.A. McFarland, M.R. Maschmann, S. Gangopadhyay, Reactive nanoenergetic graphene aerogel synthesized by one-step chemical reduction, *Combustion and Flame* 196 (2018) 400-406.
- [78] R. Thiruvengadathan, C.S. Staley, J. Geeson, S. Chung, K. Raymond, K. Gangopadhyay, S. Gangopadhyay, Enhanced combustion characteristics of bismuth trioxide-aluminum nanoenergetic materials prepared through graphene oxide directed self-assembly, *Propellants Explos Pyrotech* (Submitted for Review).

- [79] K. Kappagantula, M.L. Pantoya, Experimentally measured thermal transport properties of aluminum-polytetrafluoroethylene nanocomposites with graphene and carbon nanotube additives, *Int. J. Heat Mass Transf.* 55(4) (2012) 817-824.
- [80] J.L. Sabourin, D.M. Dabbs, R.A. Yetter, F.L. Dryer, I.A. Aksay, Functionalized graphene sheet colloids for enhanced fuel/propellant combustion, *ACS Nano* 3(12) (2009) 3945-3954.
- [81] C.S. Staley, C.J. Morris, R. Thiruvengadathan, S.J. Apperson, K. Gangopadhyay, S. Gangopadhyay, Silicon-based bridge wire micro-chip initiators for bismuth oxide–aluminum nanothermite, *Journal of Micromechanics and Microengineering* 21(11) (2011) 115015.
- [82] K.B. Plantier, M.L. Pantoya, A.E. Gash, Combustion wave speeds of nanocomposite Al/Fe₂O₃: the effects of Fe₂O₃ particle synthesis technique, *Combustion and Flame* 140(4) (2005) 299-309.
- [83] G.C. Egan, T. LaGrange, M.R. Zachariah, Time-Resolved Nanosecond Imaging of Nanoscale Condensed Phase Reaction, *Journal of Physical Chemistry C* 119(5) (2015) 2792-2797.
- [84] J. Che, L. Shen, Y. Xiao, A new approach to fabricate graphene nanosheets in organic medium: combination of reduction and dispersion, *Journal of Materials Chemistry* 20(9) (2010) 1722-1727.
- [85] W. Gerhartz, F. Ullmann, Y.S. Yamamoto, F.T. Campbell, R. Pfefferkorn, Ullmann's encyclopedia of industrial chemistry, 5th edition, Weinheim, Federal Republic of Germany ; Deerfield Beach, FL, USA : VCH Publishers 1985 to Present.
- [86] M.A. Worsley, S.O. Kucheyev, H.E. Mason, M.D. Merrill, B.P. Mayer, J. Lewicki, C.A. Valdez, M.E. Suss, M. Stadermann, P.J. Pauzauskie, J.H. Satcher, J. Biener, T.F. Baumann, Mechanically robust 3D graphene macroassembly with high surface area, *Chemical Communications* 48(67) (2012) 8428-8430.
- [87] G.Q. Jian, S. Chowdhury, K. Sullivan, M.R. Zachariah, Nanothermite reactions: Is gas phase oxygen generation from the oxygen carrier an essential prerequisite to ignition?, *Combustion and Flame* 160(2) (2013) 432-437.
- [88] N. Zakiyyan, A. Wang, R. Thiruvengadathan, C. Staley, J. Mathai, K. Gangopadhyay, M.R. Maschmann, S. Gangopadhyay, Combustion of Aluminum Nanoparticles and Exfoliated 2D Molybdenum Trioxide Composites, *Combustion and Flame* 187 (2018) 1-10.
- [89] A. Rai, L. Zhou, M. R. Zachariah, Understanding the mechanism of aluminium nanoparticle oxidation, *Combustion Theory and Modelling* 10(5) (2006) 843-859.
- [90] M.L. Pantoya, V.I. Levitas, J.J. Granier, J.B. Henderson, Effect of Bulk Density on Reaction Propagation in Nanothermites and Micron Thermites, *Journal of Propulsion and Power* 25(2) (2009) 465-470.
- [91] V.E. Sanders, B.W. Asay, T.J. Foley, B.C. Tappan, A.N. Pacheco, S.F. Son, Reaction Propagation of Four Nanoscale Energetic Composites (Al/MoO₃, Al/WO₃, Al/CuO, and Bi₂O₃), *Journal of Propulsion and Power* 23(4) (2007) 707-714.
- [92] G.I. Taylor, The formation of a blast wave by a very intense explosion I. Theoretical discussion, *Proceedings of the Royal Society of London. Series A. Mathematical and Physical Sciences* 201(1065) (1950) 159-174.
- [93] L.I. Sedov, Propagation of strong shock waves, *Journal of Applied Mathematics and Mechanics* 10 (1946) 241-250.

- [94] M.R. Baer, J.W. Nunziato, A two-phase mixture theory for the deflagration-to-detonation transition (ddt) in reactive granular materials, *International Journal of Multiphase Flow* 12(6) (1986) 861-889.
- [95] A.P. Kharitonov, Practical applications of the direct fluorination of polymers, *Journal of Fluorine Chemistry* 103(2) (2000) 123-127.
- [96] W. Zhang, P. Bonnet, M. Dubois, C.P. Ewels, K. Guérin, E. Petit, J.-Y. Mevellec, L. Vidal, D.A. Ivanov, A. Hamwi, Comparative Study of SWCNT Fluorination by Atomic and Molecular Fluorine, *Chemistry of Materials* 24(10) (2012) 1744-1751.
- [97] M. Adamska, U. Narkiewicz, Fluorination of Carbon Nanotubes – A Review, *Journal of Fluorine Chemistry* 200 (2017) 179-189.
- [98] S. Park, J. An, J.R. Potts, A. Velamakanni, S. Murali, R.S. Ruoff, Hydrazine-reduction of graphite- and graphene oxide, *Carbon* 49(9) (2011) 3019-3023.
- [99] M.P. Araújo, O.S.G.P. Soares, A.J.S. Fernandes, M.F.R. Pereira, C. Freire, Tuning the surface chemistry of graphene flakes: new strategies for selective oxidation, *RSC Advances* 7(23) (2017) 14290-14301.
- [100] J.I. Paredes, S. Villar-Rodil, A. Martinez-Alonso, J.M.D. Tascon, Graphene oxide dispersions in organic solvents, *Langmuir* 24(19) (2008) 10560-10564.
- [101] Y. Jiang, S. Deng, S. Hong, J. Zhao, S. Huang, C.-C. Wu, J.L. Gottfried, K.-i. Nomura, Y. Li, S. Tiwari, R.K. Kalia, P. Vashishta, A. Nakano, X. Zheng, Energetic Performance of Optically Activated Aluminum/Graphene Oxide Composites, *ACS Nano* 12(11) (2018) 11366-11375.
- [102] R. Thiruvengadathan, C. Staley, J.M. Geeson, S. Chung, K.E. Raymond, K. Gangopadhyay, S. Gangopadhyay, Enhanced Combustion Characteristics of Bismuth Trioxide-Aluminum Nanocomposites Prepared through Graphene Oxide Directed Self-Assembly, *Propellants Explosives Pyrotechnics* 40(5) (2015) 729-734.

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