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Combustion of aluminum nanoparticles and exfoliated 2D molybdenum trioxide composites

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ABSTRACT

Exfoliated two-dimensional (2D) molybdenum trioxide (MoO_3) of approximately 3-4 monolayers in thickness was produced from sonicating bulk MoO_3 powder, and then mixed with 80 nm diameter Al nanoparticles to prepare nanoenergetic composites with high interfacial contacts between the fuel and oxidizer. Combustion measurements demonstrated peak pressures as high as 42.05 ± 1.86 MPa, pressurization rates up to 3.49 ± 0.31 MPa/μs, and linear combustion rates up to 1,730 ± 98.1 m/s, the highest values reported to date for Al/MoO_3 composites. TGA/DSC measurements indicate energetic reactions between the Al and 2D MoO_3 sheets occur prior to the melting temperature of Al. SEM and TEM analysis of the composites prior to combustion suggests high interfacial contact area between the Al and MoO_3. After reaction, we observe that the 2D MoO_3 sheets are converted to extended alumina flakes during reaction in a process attributed to Al adsorption and diffusion processes. These alumina features act as a physical barrier against Al NP sintering while also provide separation for reaction gases to flow and preheat unreacted materials.

1. Introduction

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

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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. Rai 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 Hanlon et al. [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 MoO_3 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 MoO_3 powder. Effects of slow and fast heating rate ignition on the combustion mechanisms were evaluated across a range of ignition heating rates. The Al/MoO_3 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. Experimental section

2.1. Materials

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 MoO_3/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 MoO_3 liquid exfoliation process as well as in the synthesis of nanoenergetic composites.

2.2. Sonication process

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 MoO_3 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 s on and 2 s off for a duration of 10 h. The sonication processing power and time were optimized to break weak interlayer van der Waals bonds and produce exfoliated 2D sheets from the bulk MoO_3. 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 min at 3434 × g. The residual material was then subjected to further sonication and centrifugation processes. The 2D MoO_3 sheets were then dried at 60 °C in a vacuum oven.

Table 1
Experimental parameters used in the synthesis of Al/MoO_3 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

2.3. Assembly procedure

Various Al/MoO_3 composites were prepared by using either the as-purchased MoO_3 powder or exfoliated 2D MoO_3 sheets. To obtain a specific fuel-to-oxidizer mass ratio, MoO_3 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 h using an ultrasonic bath to ensure stable precursor dispersions. Then, MoO_3 and Al NPs suspensions were added and ultrasonically mixed for another 1 h. Because self-assembly of Al nanoparticles on MoO_3 sheets is imperative, our process demands that the MoO_3 flakes begin in a well-dispersed state. If MoO_3 sheets were allowed to dry into a dry powder after sonication, the material would form MoO_3 aggregates that would discourage high surface area assembly. The current process is also more straightforward, as exfoliation of MoO_3 itself generates a dispersion that may be directly used for assembly. After sonication, the homogeneous mixtures were vacuum-dried at 60°C for 3 h to evaporate the IPA.

2.4. Material characterization

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/MoO_3 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 MoO_3 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