



# The effect of decorated graphene addition on the burning rate of ammonium perchlorate composite propellants



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## ABSTRACT

Catalysts are often added to solid propellant formulations to tailor burning rates. Nanocatalysts can increase propellant burning rates over standard catalyst sizes due to the increase in surface area per unit weight. However, the increased surface area that the binder must wet can be prohibitive if large amounts of nanocatalysts are used. Additionally, agglomeration of the nanocatalyst can result in micron-scale particles, reducing catalyst effectiveness. In this study a nanoscale iron oxide catalyst has been used to decorate graphene. By decorating graphene with the catalyst, nanoscale features are kept but the catalyst is stabilized to reduce agglomeration. Changes in burning rate between the catalyzed and uncatalyzed propellants are investigated. The effect on burning rate of encapsulating the catalyst inside the fine AP crystals compared to propellants where it is added to the binder is also investigated. We also compare propellants with decorated graphene and propellants with undecorated graphene catalysts. The three comparisons are made for two different graphene preparation methods. It is found that the highest burning rates occur in propellants where the graphene is decorated with catalyst and encapsulated in the fine AP. The next highest burning rates occur in propellants with decorated graphene that is physically mixed into the propellant. The lowest burning rates are found in propellants where the graphene is undecorated, where there is little difference between encapsulated or physically mixed graphene blanks, or compared to a baseline propellant. Burning rates are found to be similar between graphene preparation methods considered.

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## 1. Introduction

Graphene has been a material of interest since its identification in 2004 due to its high surface area, high thermal conductivity, high electrical conductivity, and good optical transmittance [1]. Many of its unique properties come from its two-dimensional structure; it is, in effect, a sheet of carbon that contains no more than ten layers of carbon atoms [2]. The unique chemical properties come from the nanometer dimensions of the sheet as well as a large delocalized electron system [3]. Though it is highly electrically active it is relatively chemically inert [4]. Graphene can be grown on substrates and chemically modified, and remain robust yet flexible [1]. However, due to the large van der Waals forces, graphene tends to easily agglomerate and is also hydrophobic. Functionalized graphene and graphene oxide have a wide variety of uses including electronics components, supercapacitors, hydrogen and lithium storage, field transistors, sensors, bio-imaging, transparent conductive films, clean energy devices, biomedicine, reinforced composites, magnetic resonance imaging applications, drug delivery, cellular imaging, antibacterial materials, heavy metal ion removal, and catalyst supports [1,2,5–9].

Of particular interest to the propellant community is the use of graphene-based materials as a catalyst support for materials that will catalyze ammonium perchlorate (AP). As catalysis is a surface phenomenon, nano-size catalysts have long been considered desirable because of the high surface area per unit mass, resulting in more reaction sites for a given weight than for micron-sized catalysts. However, nano-sized catalysts tend to aggregate, forming clumps that are much larger than the individual catalyst particles that reduce the nanocatalyst efficacy.

Graphene-based materials have been used as a catalyst support in order to prevent such aggregation [10]. Graphene sheets are ideal for use as substrates for supporting secondary components as the graphene sheets are thin, relatively inert, and have a high surface area [7]. By bonding the nano-sized catalysts to the surface and edges of the support, the catalyst particles do not aggregate

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as easily [11–13]. The relationship is symbiotic as well; the high surface area of secondary components promotes good dispersion of the graphene [14]. Additionally, the graphene-based material itself may interact catalytically with the material undergoing catalysis, while being relatively chemically inert [15]. Graphene can be functionalized with a wide variety of materials ranging from transition metals to metal oxides to amino and nucleic acids to polymers [4,14]. The sizes and shapes of the sheets can often be controlled by adjusting solvents and reducing agents [4,14].

Iron oxide [10,16], copper oxide (CuO) [12,17], cobalt oxide (Co<sub>3</sub>O<sub>4</sub>) [18], nitrogen (as nitrated graphene oxide) [19], manganese oxyhydroxide (MnOOH) [13], neodymium oxide (Nd<sub>2</sub>O<sub>3</sub>) [20], nickel [14], and manganese oxide (Mn<sub>3</sub>O<sub>4</sub>) [11] have served as the catalyst in graphene-based material/catalyst hybrids. Graphene oxide has also been used as a catalyst in AP composite propellants [21]. The catalysts deposited on the graphene (G) or graphene oxide (GO) sheet were typically between 5 and 80 nm average diameter, uniformly distributed, and anchored firmly to the sheet. The effect of the catalyst was seen in a more rapid onset of AP high temperature decomposition, and the hybrid catalyst worked better than physical mixtures of the catalyst components. It was postulated in several studies (Ref. [11], for example) that the exceptional electronic characteristics of graphene cause the electron transfer from ClO<sub>4</sub><sup>-</sup> to NH<sub>4</sub><sup>+</sup> and O<sub>2</sub> to O<sub>2</sub><sup>-</sup> to be more rapid than in the material with only the catalyst [11,13].

Though nano-sized catalysts have many advantages, the high surface area of the nanocatalyst can have a deleterious effect on the mechanical properties of a solid rocket propellant. The high surface area of the catalyst requires an increased amount of binder to fully wet all surfaces. Failure to fully wet all surfaces can result in a propellant with poor mechanical properties, while using enough binder in the formulation to fully wet all surfaces can lead to poor mechanical properties and/or a propellant with low specific impulse. The high surface area of a graphene sheet functionalized with a catalyst, though it may do well at catalyzing the material, may cause issues with the propellant packing and preparation.

Recently, however, a novel method of decreasing the required binder wetting area while maintaining the high surface area of the nanocatalyst has been introduced. Nano-sized iron oxide was encapsulated in the fine AP particles. The composite particles then took the place of the fine AP in the propellant composition [22–26]. Encapsulating the catalyst results in propellant burning rates higher than those of a propellant with a nanocatalyst mixed into the binder as is customary [26]. Not only did the fine AP/binder matrix burn faster by itself due to the intimate contact between the fine AP and catalyst, but the diffusion flames formed between the fine AP/binder matrix and the large AP particles formed close to the propellant surface at higher pressures than for the baseline propellant. The increased heat feedback from the hot diffusion flames helped increase the burning rate. The combination of these two effects resulted in an increased global propellant burning rate. Encapsulating the graphene-catalyst hybrid particles in the AP in a similar manner could result in increased burning rates with fewer issues with poor mechanical properties.

### 1.1. Objectives

The objectives of this study are:

- 1 Investigate the effect of graphene/iron oxide hybrids on propellant burning rate.
- 2 Compare burning rates of propellants with blank graphene catalysts to propellants with decorated graphene catalysts.
- 3 Compare burning rates of propellants with encapsulated hybrids to propellants with physically mixed hybrids.
- 4 Investigate the effect on GO reduction process on burning rate.

## 2. Methods

### 2.1. Description of hybrids

Graphene surface functionalization was performed as described in Ref. [27]. Briefly, graphene oxide was prepared following a modified Hummers' method. The mildly reduced graphene oxide was collected and washed several times. The mildly reduced graphene oxide was redispersed in deionized (DI) water. If the material being prepared was SO<sub>3</sub>H-graphene, sulfanilic acid, concentrated sulfuric acid, and sodium nitrite were added in a molar ratio of 1:1:1, and the mixture was then kept at 60 °C for four hours. The obtained SO<sub>3</sub>H-mildly reduced graphene was washed with DI water and ethanol, then redispersed in DI water and refluxed with hydrazine at 100 °C overnight with constant stirring, yielding SO<sub>3</sub>H-graphene. The NH<sub>2</sub>-graphene was similarly prepared, but *p*-phenylenediamine and concentrated nitric acid were used instead of sulfanilic acid and sulfuric acid, respectively.

Iron oxide (Fe<sub>3</sub>O<sub>4</sub>) nanoparticles were synthesized by reduction of ferric chloride using ethylene glycol via a solvothermal process [28,29]. First, FeCl<sub>3</sub> (1.35 g, 5 mmol) was fully dissolved in 40 ml ethylene glycol solution, followed by the addition of sodium acetate (3.6 g) and polyethylene glycol (1.0 g). The well-dissolved mixture was then transferred to a Teflon-lined stainless-steel autoclave (45 mL capacity) that was heated to 200 °C at 5 °C/min. After 8 h the products thus obtained were washed several times using copious ethanol and water and dried overnight in the vacuum oven at 60 °C. The iron oxide was subsequently re-dispersed in dry toluene, to which 0.5 ml of aminopropyltrimethoxysilane (APS) was added and refluxed for 24 h to yield APS-modified iron oxide as described in Ref. [30]. Graphene/Fe<sub>3</sub>O<sub>4</sub> hybrid catalysts were made by mixing APS-modified iron oxide with SO<sub>3</sub>H-graphene or NH<sub>2</sub>-graphene in aqueous solution under mild magnetic stirring for two days. The products were then collected by centrifuge and washed with DI water.

The iron oxide loading determined by thermogravimetric analysis (TGA) was 77%; that is, for every 1 mg of functionalized graphene there is 0.77 mg of iron oxide. Two different types of supports were used, SO<sub>3</sub>H-prepared graphene and NH<sub>2</sub>-prepared graphene. The different types of supports were under investigation as well as the burning rate. The SO<sub>3</sub>H and NH<sub>2</sub> are used to keep the graphene from aggregating and keeping it soluble in water [31,32]. The SO<sub>3</sub>H preparation produces negatively charged graphene hybrids and the NH<sub>2</sub> preparation produces positively charged graphene hybrids. Four different samples were created: SO<sub>3</sub>H-graphene supporting (or decorated with) Fe<sub>3</sub>O<sub>4</sub>, SO<sub>3</sub>H-graphene blanks, NH<sub>2</sub>-graphene supporting (or decorated with) Fe<sub>3</sub>O<sub>4</sub>, and NH<sub>2</sub>-graphene blanks. The term "blanks" here refer to undecorated graphene supports.

### 2.2. Naming convention

Eight propellant formulations and a baseline propellant were studied. For simplicity, the naming convention of the graphene-containing propellants is as follows. The name for each propellant formulation has three sets of letters. The first set describes the synthesis method. The letters NH<sub>2</sub> or SO<sub>3</sub>H indicate the graphene is functionalized with NH<sub>2</sub> or SO<sub>3</sub>H, respectively.

The second set of letters is either EN or PM, where EN stands for encapsulated and PM stands for physical mixture. Encapsulation, described further below, indicates that the catalyst is located inside the fine AP, while if the catalyst is in a physical mixture it has been mixed into the binder as is customary.

The third set of letters is either BL or DFG. If a graphene substrate has been decorated with catalyst particles it has the code DFG (decorated functionalized graphene), while blanks, or

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