26 Applications of Graphene in Fuel/Propellant Combustion

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ABSTRACT

Use of nanostructured materials, in particular graphene, in the combustion and ignition of fuels has recently shown promising results in enhancing the fuel burn rate and potential for light-activated volumetrically distributed ignition. For example, the addition of functionalized graphene (FG) sheets to nitromethane, has been demonstrated to act as a catalyst and substantially increase the linear burning rate of the fuel. The functionalization of graphene is considered a great opportunity for tailor-made material with specific properties of interest. For example, it consists of chemical functional groups such as epoxides and hydroxides on the surface, and hydroxides and carboxylates on the edges of the sheet. These oxygen-containing functionalities bring about catalytic properties for fuel decomposition and other intermediate fragments during the fuel oxidation process. The defect structures in the FG sheets have also been shown to act as active sites. Such augmented fuel thermal decomposition and its derivatives have been verified through the use of molecular dynamics (MD) simulations. FG sheets are easily dispersible in many hydrocarbon fuels and propellants with no need for surfactants and may also offer a substantially higher surface area than other nanostructured materials such as metal oxides and carbon nanotubes. Also, because FG is entirely oxidized in high temperature combustion zones with virtually no additional residues other than common combustion products, it can be viewed as a fuel supplement, contributing towards energy density. In this chapter, applications of graphene oxides and FG sheets in the ignition and combustion of fuels are briefly reviewed, highlighting the potential, and future prospects of these materials.

26.1 NANOSTRUCTURED MATERIALS IN FUELS/PROPELLANTS

Nanostructured materials have exhibited unusual and interesting thermal, mechanical, electrical, and optical properties ever since C_{60}, carbon nanotubes (CNTs), graphene, and others have been discovered or inexpensively synthesized. Many of these properties have been used in a wide number of applications, for example as additives in structural materials, as drug carriers in targeted cancer therapies, in high-resolution displays, and many others, for example (see Gogotsi [2006], De Volder et al. [2013], Liu et al. [2012a,b], and Barton et al. [2011]). The use of nanostructured materials in the ignition and combustion of fuels is one rapidly growing and important application of nano-science and technology. The motivation behind such usages are varied and range from enhanced performance and efficiencies to the reduction of harmful pollutants from fossil-fueled combustors for power generation or propulsion systems. A large majority of the work in this area pertains to the use of nanostructured metals and/or oxides or oxyhydroxides, for example (see Mench et al. [1998], Risha et al. [2002, 2004, 2008], and Tyagl et al. [2008]).

Researchers so far reported a host of promising results when metallic nanoparticles (e.g., aluminum) were used as additives in fuels during laboratory experiments such as a significant increase in energy densities and enhanced reaction rates. However, despite these initial exciting results, potential barriers emerged due to passive metal oxide layers on nanoparticles and production of these oxides as additional by-products of the combustion process which must be contained for environmental and health reasons. For detailed coverage and discussion of nano-metallic particles in the ignition and combustion of fuels, readers should consult the references previously mentioned and other citations herein.

Applications of nanostructured carbon and its allotropes in ignition and combustion have recently been demonstrated and are currently the subject of intense research throughout the world. Because CNTs have been available since their discovery by Sumio Lijima (1991), their applications for ignition and combustion naturally came first. Many synthesis approaches have been devised for CNTs which paved the way towards systematic work in the use of CNTs with fuels or propellants

for combustion purposes. As an application example, Moy et al. (2002) were granted a US patent filed in 2002 in which they claimed that about 1% to about 15% by weight CNTs added to fuels can enhance the burning rate and additionally function as an antiknock additive in spark ignited engines.

At the nano scale, Choi et al. (2010) demonstrated that by coupling an exothermic chemical reaction of cyclotrimethylene trinitramine (TNA), a military explosive, with a multiwalled nanotube (MWCNT), or nanowire possessing high axial thermal conductivity, a self-propagating reactive wave can be driven along its length which simultaneously generated an electrical pulse of disproportionately high specific power (thermopower wave). The specific electrical power generated exceeds that of lithium-ion batteries commercialized for automotive and railway applications. This carbon-nanotube-guided combustion might be used for microthrusters which have minute combustion engines used for purposes, for example, such as maintaining relative microsatellite positions within a microsatellite array. The directed pressure wave provides a total impulse (per mass of TNA and MWCNT) that is 4–100 times that of other proposed microthrusters (see Aliev and Baughman [2010]).

Another demonstrated application of nanostructured materials is in diesel engines. For example (see the work by Basha and Anand [2011]). They showed that a CNT-blended water-diesel emulsion fuel (25 and 50 ppm CNT mass fraction) delivered considerable enhancement in the brake thermal efficiency and substantial reduction in harmful pollutants. Recently, Tewari et al. (2013) showed that a blend of MWCNT with biodiesel also delivered a significant enhancement in brake thermal efficiency and considerable reduction in harmful pollutants.

Use of nanostructured carbon have been successfully employed for an innovative light-activated volumetrically distributed ignition of liquid sprays and gaseous fuel/air mixtures by Chehroudi et al. (2009, 2010), Chehroudi (2011), Chehroudi (2012a,b), and Chehroudi (2013). Chehroudi et al. were the first to demonstrate the distributed ignition of dry CNTs (with metal nanoparticle impurities) and their abilities to ignite a host of liquid, gaseous, and solid fuels of interest. Minimum ignition energy (MIE) of such single-walled CNTs (SWCNTs) with an ordinary low-energy camera flash was reported. Experiments were focused on effects of incident pulsed-light exposure duration and wavelength on MIE. Chehroudi (2012b) also showed that lower energy-per-pulse is needed to initiate ignition when shorter flash duration is used. For example, at a flash duration of ~0.2 ms, it required a 30–35 mJ/pulse to initiate the ignition of as-produced fluffy samples in standard air, whereas at 7 ms duration, it needed an 80–90 mJ/pulse to achieve the same result. Average intensities between 10 to 150 W/cm^2 were needed to bring about the ignition of SWCNTs, being a factor of about 80 lower than cases where laser (pulsed or CW) was used in coal particles. An important application of this work, first conceived and proposed by Chehroudi, is in highly efficient, environmentally clean, and homogeneously charged compression-ignition (HCCI) combustion engines in which the heat release

process starts by autoignition of the lean premixed fuel and air mixture (see Chehroudi [2011]). In HCCI engines, good control of the time when the autoignition occurs is critical for successful engine operation. "Controlled" *autoignition* of lean gaseous fuel and air mixture has already been demonstrated in a constant-volume chamber (see Chehroudi [2011], and Berkowitz and Oehlschlaeger [2011]).

26.2 GRAPHENE OXIDE APPLICATIONS IN FUELS/PROPELLANTS

Graphene oxide (GO) is a new member of the nanostructured material family and has certain unique features, one of which is that it carries oxygen with itself (see Figure 26.1). Studies in the use of FG foams for light-activated ignition is discussed in Chehroudi (2011). Interestingly, Cote et al. (2009) were first to demonstrate the photothermal reduction (using a Xenon flash) of GO indicating that it was rapid, clean, and versatile. Figure 26.2 shows the initial results from the ignition and combustion of GO. Here, the GO sample was placed on a paper wetted with ethanol and ignited via a flash of light. The ignition of the graphene material caused the subsequent ignition of the vapor cloud in its neighborhood. After ignition, the deoxygenated graphene sample grows larger due to perhaps exfoliation. The minimum ignition energy required for ignition of dry samples of GO foam was measured in between 1.2 to 1.7 J/pulse at pulse duration of about 1 ms. This was found to be much higher than the 35–85 mJ/pulse measured for SWCNTs (see Chehroudi [2011]). Although the solubility of GO and its oxygen carrying features are attractive, such a relatively large minimum ignition energy is troublesome for ignition applications.

As far as the application of graphene in the combustion of fuels and propellants is concerned, this is currently considered to be in its infancy stage. A pioneering work by Sabourin et al. (2009) is the one to describe here. The idea and excitement in the use of GO is that, many of the problems related to utilization of nano-metallic particles mentioned earlier can be resolved considering that the use of FG sheets which not only catalyzes fuel combustion reactions but also eventually participates energetically and is consumed without producing residual particulates. Graphene sheets show many of the same desirable properties of CNTs, such as high electrical conductivity and good mechanical properties, etc, but do not contain significant quantities of metal particles that are used to catalyze CNT growth. This is because the synthesis of functionalized GO (FGO) does not use metal-containing catalysts. The FG sheets used by Sabourin et al. (2009) contain chemical
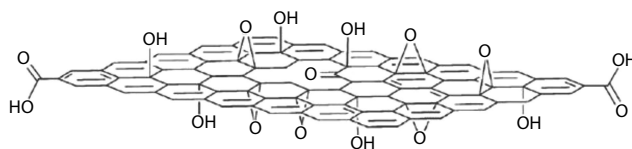

FIGURE 26.1 Molecular structure of a functionalized graphene oxide sheet.
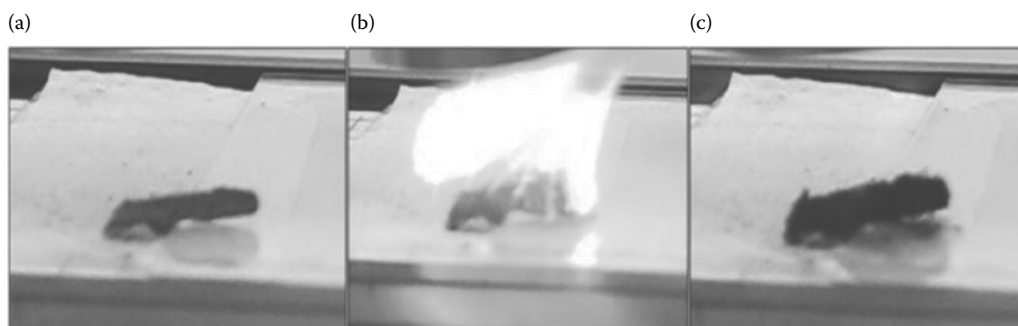
FIGURE 26.2 Ignition of a GO foam sample with an ordinary camera flash, (a) sample on a wetted paper, (b) 7 ms after ignition onset, and (c) about 15 ms after the ignition. Image magnification is the same. (From Chehroudi, B., 2011. *Recent Patents on Space Technology*, 1, 2, 107–122 [16].)

functional groups such as hydroxides and carboxides on the surface, and hydroxides and carboxylates on the edges . The carbon/oxygen mole ratio range from two for GO to higher values depending on the degree of chemical or thermal reduction of the FG sheet. This creates vacancies and topographical defects in the FG sheet.

Additionally, FG sheets have a heat of combustion close to aluminum and are easily dispersible in many hydrocarbon fuels and propellants without the need of surfactants and may have significantly higher surface area than metal oxides. Also, graphene-based additives are most likely burned in an oxygen containing environment at high temperatures and energetically contribute to the combustion process without exhaust particulate matter or plume signatures beyond that produced through the fuel combustion products themselves. Existence of nucleophillic oxygen-containing functionalities on the surfaces and edges of the FG sheets is likely to provide catalytic behavior which can stabilize or encourage reaction intermediates during the combustion process. The ability to adjust the C/O (carbon-to-oxygen) ratio also offers the opportunity to tune solubility in a variety of liquid fuels. For example, the more reduced versions should be more compatible with alkanes and a higher oxygen-containing version is more compatible with more polar and/or ionic hydrocarbons such as alcohols, aldehydes, and ketones.

In an experiment to demonstrate the benefits of FG sheets, Sabourin et al. (2009) used liquid nitromethane (CH_3NO_2) as a fuel and mixed it with FG sheets to examine the burn rate enhancement in a circular cross-section combustion tube. Nitromethane, on account of low oxygen content and reactivity at low pressures, is both considered as a fuel and a monopropellant for rocket applications. Four experiments were conducted on four different mixtures containing pure (neat) NM (nanosized metal), NM and nanosized aluminum oxides, NM and porous nanosized SiO_2, and NM and FG sheet with C/O ratio of 22.

Sabourin et al. (2009) showed that by mixing FG sheets with NM, the ignition and combustion rates were substantially enhanced over those achieved by other mixtures. Although the burn rate was also increased by the addition of the nanoparticles, there are advantages in the use of FG sheets. Use of CNT

was not considered in their studies due to concerns about metal contamination in the CNTs which might affect combustion catalysis attributed to nanotubes themselves. However, nowadays SWCNTs with 95% or higher purity are available and worth a comparative study. Nevertheless, compared to the NM-only case, results by Sabourin et al. (2009) showed that the ignition temperature of the NM-and-FGO mixture was lowered and its burn rate significantly enhanced at low pressures (~4 MPa). At higher pressures (>12 MPa), however, burn rates for the neat NM and FG-sheet-doped NM converged and minimal advantage was seen. Despite, addition of FG sheet had made the burn rate less sensitive to pressure changes. This is a positive feature especially in the context of propulsion applications such as rocket motors where pressure instabilities lead to reduced control and performance. It is possible that addition of SWCNTs may bring about even more dramatic results due to the additional nanoparticle catalysts they carry. Some claims have already been made on burn rate enhancement of CNTs in fuels, for example (see Moy et al. [2002]). Everything else being the same, the nanostructured material which provides a faster burn rate is of interest from the practical perspective.

The enhancement mechanism was thought to be increased by heat transfer due to radiation and thermal conductivity. Thermal conductivity is increased due to catalysis and the nitric oxide and FG sheet oxidation reaction, both of which reduce flame thicknesses at lower pressures. The presence of particles within the liquid as well as those entrained within the gas-phase reaction zone provide opportunities for both radiation emitters and absorbers of thermal energy which do not exist in the pure NM combustion process. Thermal conductivity of single sheet graphene is quite high, being near that measured for CNTs. Hence, the heat absorption capacity for the FG-sheet-doped suspension is expected to be much higher than that of the NM-alone mixture. Finally, the catalytic activity at the defect sites were considered as another important mechanism contributing to the enhanced burn rate of the FG-sheet-doped NM. Although, several possible chemical routes were discussed in Sabourin et al. (2009), it appears that formation of aci-anions ($CH_2NO_2^-$), a substance which has been identified as a sensitizing species in the detonation of liquid nitromethane will be the most likely

path (see Engelke et al. [1988a,b] and Engelke et al. [1986]). Note that the reduced FG sheet is known to contain significant landscape defect structures. These defects can act as the sites for free radical formation and stabilization, offering mechanisms not present in the metal oxyhydroxides (which also have oxygen-containing functionalities). Finally, another route possibly contributing to rapid burn rate was cited as the reaction between NO (nitrogen oxide) and carbonaceous materials, in this case the FG sheet. The exothermic reaction between NO and carbon (having similar reaction rates as O_2-C reaction), studied intensively in the context of soot and NO_x reduction in engines, was thought more likely to have an effect on NM burning rates.

In a follow-up study conducted by Liu et al. (2012a,b) at Princeton University, they investigated the observed enhanced thermal decomposition of the NM on FG sheet using ab initio molecular dynamics (AIMD) simulation. Although, suggestions were earlier made by Sabourin et al. (2009) that the catalytic reaction might be in play in the FG sheet and nitromethane reaction, it was impossible to determine the mechanism using the available experimental techniques. Liu et al. (2012a,b), using AIMD, showed that catalytic activity originates from lattice defect complexes within the graphene sheet, notably vacancies functionalized with O_2-containing groups such as hydroxyls, ethers, and carbonyls, and they provided detailed mechanistic insight into the atomic-scale processes leading to complete NM decomposition (see Figure 26.3). In particular, their calculations showed that pristine graphene interacts very weakly with NM, whereas hydroxyl or epoxy groups adsorbed on graphene can form H-bonds with NM and consequently abstract H from NM with much lower barrier than required for the C-N bond scission. Note that, this bond scission takes place in the initial stages of the gaseous NM decomposition without the presence of FG sheets. Interestingly, they showed that while these processes facilitate NM decomposition, they do not lead to "catalytic action" in which the original catalyst is regenerated at the end. This regeneration process is shown in Figure 26.3. In fact, through AIMD calculations, they showed the evolution of the aci-ion population that appeared at the onset of the simulation and subsequently disappeared within ~2 ps after extinction of the NM population, a behavior which interpreted that NM decomposition was initiated by catalytic production of aci-ions. Figure 26.4 shows some of the proposed reactions in the decomposition of NM in presence of the FG sheet.

Liu et al. (2012a,b) also demonstrated that the reaction rate decreases when NM density is reduced, roughly proportional to the density. Although, they did not investigate the effect of lower NM initial temperature, they indicated that it should reduce the burning rate dramatically. However, they commented that at lower temperatures, the FG sheet should play an even more important role in initiating the combustion as the heterogeneous reaction promoted by the FG sheet has a significantly lower activation barrier than the alternative homogeneous reactions. The key conclusions were that graphene with carbon vacancies is an effective catalyst for NM combustion and that FG sheet initiates the NM decomposition
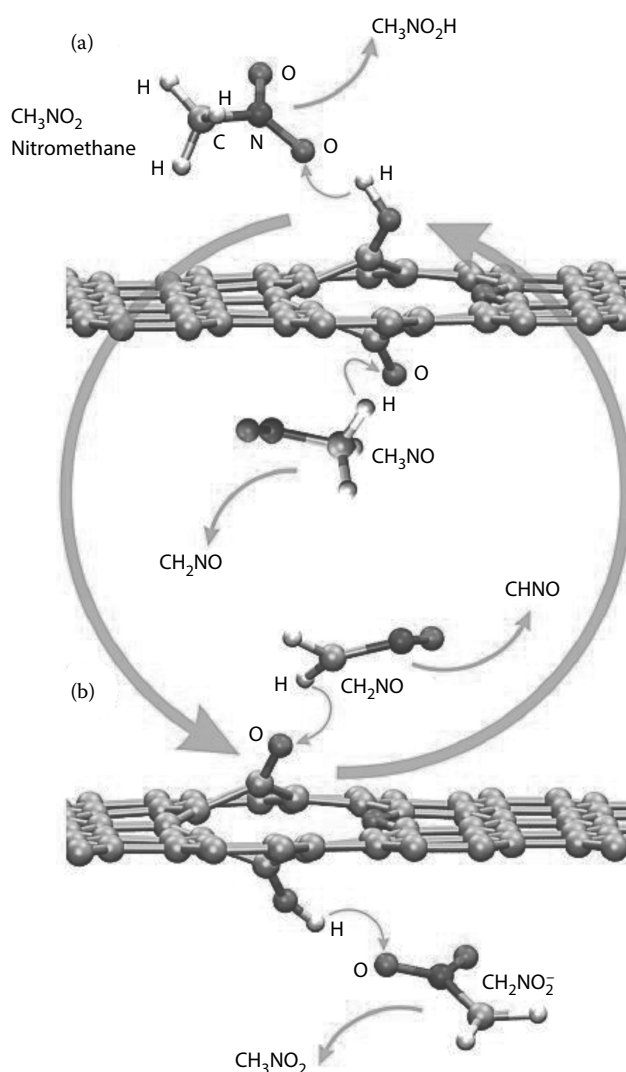

FIGURE 26.3 Shows the catalytic role that FG sheet plays in the decomposition of nitromethane. (a) An example of a proton transfer from a hydroxyl group on an FG sheet to a nitromethane molecule forming a reactive intermediate is indicated. (b) The subsequent regeneration of the hydroxyl group caused by a proton transfer from a nitromethane derivative to a carbonyl on the FG sheet is shown. Other examples of proton transfer mechanisms are depicted below the sheet, representing a small set of potential reactions that take place between FG sheet and nitromethane and FG sheet and NM derivatives. White and gray balls are hydrogen and carbon and light black and dark black are oxygen and carbon, respectively as shown. (From Liu, L.-M. et al., 2012b. *Journal of American Chemical Society (JACS)*, 134, 19011–19016.)

and strongly enhances the rate of successive relations. This property in conjunction with high dispersive and thermal characteristics makes FG sheet a high-performing additive for future propulsion systems. The basic mechanisms in play was associated with the highly defective regions which form in FG sheet during the thermal reduction of GO. Finally, the concentration of these defects increases with an increase in the C/O ratio provided that thermal annealing is prevented through process temperature control methods.
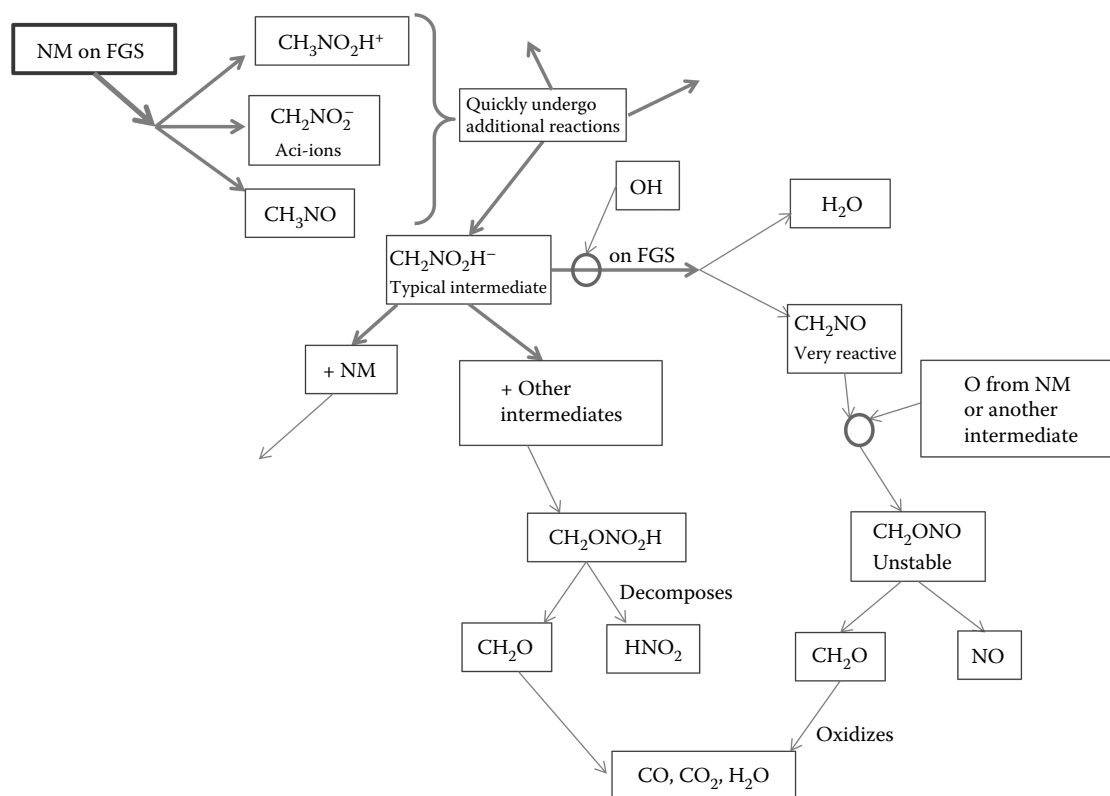
FIGURE 26.4 Complex flow of reactions for the nitromethane in presence of FG sheet is summarized.

Although, this is not considered as a use of graphene in fuels/propellants for burn-rate enhancement, chemically modified graphene as GO has been recognized as a promising flame retarding nanoadditive in polymers, for example (see Higginbotham et al. [2009]). However, according to early reports, it can be easily decomposed with ignition upon application of heat. Reduction of GO has been recognized as highly exothermic, about 10 times the energy of the heat input. The reduction reaction can be triggered at one end of the GO film by hot soldering iron (~400°C) where the reaction rapidly propagates through the whole film as shown by Shi and Li (2011). The obtained reduced-GO was reported very stable and no carbon combustion occurred after exposing clean reduced-GO to a flame which is in good agreement with the flame retardancy of GO. However, it is important to note that the thermal stability of the reduced-GO significantly decreases in the presence of alkali impurities such as potassium salts. For example, self-propagating carbon combustion is observed when reduced-GO is exposed to a flame in the presence of even a small amount of KOH salts, perhaps due to the canalization effect from the alkali metal. In addition, GO solids containing potassium ions becomes highly flammable in clear contrast to the expected good thermal stability of pristine GO. Kim et al. (2010) also showed that GO strips after extensive purification are flame retardant. Unfortunately, the typical chemical exfoliation process for production of GO sheets involves using oxidants such as $KMnO_4$ or $NaNO_3$. Hence extensive removal of residual salts after chemical exfoliation is essentially important if GO or reduced-GO materials are to be used as flame retardants. Past research efforts are summarized and discussed in Table 26.1.

26.3 COMMERCIALIZATION POTENTIAL

Although at this time, no serious ignition and combustion related commercialization of the observations discussed here is in process, the great potential of CNTs and graphene for ignition and combustion enhancements should be perceivable/possible. One reason that it is not yet so is that more research and development activities are needed. Another reason is the high price of the graphene at this stage of knowledge development and manufacturing technology, despite the small amounts used in these studies. The other issue is related to potential health and environmental impacts of such nanostructured materials, if beyond a yet-to-be-determined limit amount escapes the combustion process and ends up in the atmosphere. Although most studies indicated that the carbon nanostructures burn during the combustion process, their concentrations in the exhaust of the combustion systems in which they are used are to be investigated.

26.4 CONCLUSIONS

Use of functionalized GO in fuels and propellants is considered at its early stages of growth. However, initial results showed great potential for future applications, particularly in the ignition process and for burn-rate enhancement of their subsequent combustion. Preliminary results from the light-activated fuel

TABLE 26.1

Applications of CNTs and Graphene in Ignition and Combustion

Researchers	Material Used	Application
Moy et al. (2002)	CNTs	1%–15% by weight added to fuels enhanced burning rate and acted as ani-knock in SI engines
Choi et al. (2010)	MWCNTs	TNA (an explosive) and MWCNTs creates a self-propagating reactive wave which generates high specific power electricity
Aliev and Baughman (2010)	CNTs	CNT-guided combustion was proposed as providing thrust for microthrusters
Basha and Anand (2011)	CNTs	CNT-blended water-diesel emulsion fuel was demonstrated to deliver enhanced engine thermal efficiency and reduction of pollutants
Tewari et al. (2013)	MWCNTs	MWCNTs blended with biodiesel showed enanced engine thermal efficiency and reduction in emission of pollutants
Chehroudi et al. (2009, 2010), Chehroudi (2011, 2012a,b, 2013)	SWCNTs	Demonstrated light-activated volumetrically distributed ignition of liquid sprays and gaseous fuel/air mixtures with applications for rockets and HCCI engines
Cote et al. (2009)	GO	First to demonsterate photothermal reduction (with Xenon flash). It was rapid, clean, and versatile
Chehroudi (2011)	GO	Light-activated ignition of fuels
Sabourin et al. (2009)	FG sheets	Used nitromethane mixed with FGO and demonstrated the ignition and combustion rates were substantially enhanced over other nanostructured material/fuel mixtures and at low pressures (~4 MPa)
Liu et al (2012a,b)	FG sheets	Using AIMD simulation, showed that catalytic activity originates from lattice defect complexes within graphene sheet
Higginbotham et al. (2009)	Chemically modified graphene	Potential as flame retardant in polymers
Shi and Li (2011)	Reduced-GO	No carbon combustion seen after exposing clean reduced-GO to a flame indicating flame retardancy of GO. However, even small addition of alkali impurity such as potassium salt reverses the flame retardancy

ignition with GO showed potential in volumetrically distributed ignition strategy, although comparatively higher ignition energies, with respect to the as-produced CNTs, is an area that needs improvement. Mixing FG sheets with nitromethane showed substantial burn-rate enhancement at low pressures, a result that is likely to be carried when other fuels/propellants are tested in future. AIMD of the decomposition of nitromethane on FG sheets suggested catalytic reaction pathways aided by structural defects in the graphene sheets where they were functionalized on the surface, as hydroxides and carboxides.

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