Hypergolicity

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Graphene and Graphene Oxide Can "Lubricate" Ionic Liquids based on Specific Surface Interactions Leading to Improved Low-Temperature Hypergolic Performance**

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Graphene, a single layer of hexagonal, planar carbon atoms, has been proposed as a potential energetic additive due to its energetic reactivity and high surface area.[1] Dilute dispersions of nanoscale additives, including reduced graphene oxide (r-GO) sheets, have been previously utilized to catalytically increase burn rates.[2,3] Graphene can also be incorporated into ionic liquids (ILs, salts with melting points below 100 °C) either through direct exfoliation of graphite to create pristine, or surface-pure, graphene[4,5] or through the dispersion of single r-GO sheets by exfoliation of graphite oxide, which contains a degree of surface oxidation.[6] While sheets of pristine graphene and graphene oxide are discussed nearly interchangeably within the literature, the dramatically different surface morphologies and compositions can lead to extensive differences in bulk properties when utilized in dispersions. Here we demonstrate how the use of graphene-based nanomaterials, with differing surface morphology and composition, can improve the low-temperature physical properties of ILs through the manipulation of intermolecular interactions between different IL molecular ions with specific types of graphene.

Energetic ionic liquids (EILs, ILs with potential as energetic materials) have been previously shown to be hypergolic (spontaneous ignition upon contact with an oxidizer)[7] with white fuming nitric acid (WFNA), inhibited red fuming nitric acid (IRFNA), or H_2O_2 by utilizing carefully selected hypergolic anions, such as dicyanamide,[8] nitrocyanamide,[9] and dicyanoborates[10] among others.[11,12] As a result, these hypergolic ILs have been proposed as replacements for hydrazine,[13] which is toxic due to its dangerously high vapor pressure.[14,15] However, hypergolic ILs have only been screened for performance features under ambient conditions, which are not the typical temperatures associated with space or atmospheric flight. For example, ILs based on the dicyanamide ($[N(CN)_2]^-$; DCA) anion have been widely proposed as potential replacements for hydrazine as they have been reported as hypergolic with WFNA while exhibiting low ignition delays[8] and low viscosities under ambient conditions.[16] However, these values both exponentially rise with decreasing temperatures,[17,18] which poses a major problem for the use of these compounds in practical systems. By controlling the low temperature viscosity of hypergolic ILs, these materials could be more effectively employed under realistic conditions.

Graphene sheets have been proposed as lubricating compounds, which in a dispersion act to reduce the system's internal friction[19] and could decrease the viscosity of these compounds. For application with hypergolic ILs, we would need to design the IL/graphene interactions to take place primarily with the cation to ensure that the hypergolic anion is not inhibited;[20] however, the different surfaces and morphologies present in pristine graphene (flat and unoxidized)[5] and r-GO (crumpled and surface-functionalized including a hydrogen bond acceptor)[3,21] provide different options to IL cation design as demonstrated in Figure 1. To test this hypothesis we chose to compare (Table 1) a cation inherently non-coordinating and aromatic (1-butyl-3-methyl-imidazolium, $[BMIM]^+$) with one which is non-coordinating and non-aromatic (*N*-butyl-*N*-methyl-pyrrolidinium, $[Pyrr_{14}]^+$), and

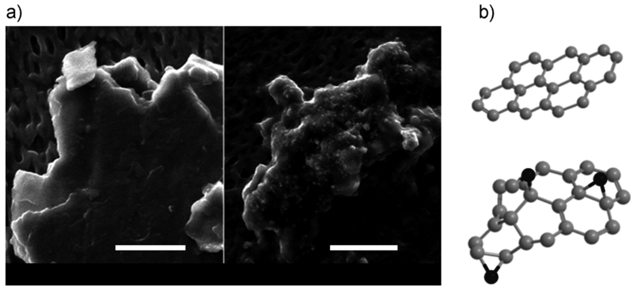

Figure 1. a) SEM micrographs (see Supporting Information) of partially aggregated pristine graphene sheets obtained from [MAT][DCA] demonstrating a flat, sheet-like morphology (left; scale bar 7.5 μm) and dispersed r-GO obtained from [MAT][DCA] demonstrating a roughened surface (right; scale bar 10 μm). b) Surface pristine graphene (top) and the projected disruption of the flat surface morphology observed with traditional graphene oxide chemical exfoliation (bottom; gray C, black O).[26]

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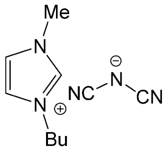
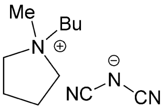
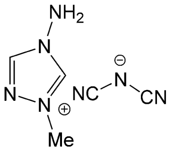
Table 1: Hypergolic ILs utilized and evaluated for low-temperature performance.

Ionic liquids	Dispersion loading (w/w) %	Stability	Lowest hypergolic temperature
 [BMIM][DCA]	neat	N/A	0 °C
	0.03 % graphene	48 h	−10 °C
	0.03 % r-GO	∞[a]	0 °C
 [Pyrr$_{14}$][DCA]	neat	N/A	N/A[b]
	0.03 % graphene	< 4 h	N/A[b]
	0.03 % r-GO	< 4 h	N/A[b]
 [MAT][DCA]	neat	N/A	−20 °C
	0.03 % graphene	48 h	−40 °C
	0.03 % r-GO	3 weeks	−40 °C

[a] On the timescale of publication (ca. 8 months). [b] Hypergolicity not tested due to poor colloidal stability.

one capable of hydrogen bond donation (1-methyl-4-amino-1,2,4-triazolium, [MAT]$^+$).

Even though the [MAT]$^+$ contains a hydrazine-like linkage and this contributes to its use as an energetic material, such "trigger" groups are not the only requirements for the compound to be a hypergol. There are numerous [MAT]$^+$ based ILs that are not hypergolic, including [MAT][N$_3$], which demonstrates a very strong interaction with WFNA, but does not result in hypergolic ignition as the oxidizer reacts with the cation and anion to form a variety of intermediates instead of undergoing a rapid decomposition and ignition.[22] However, the reaction of WFNA and [DCA]$^-$ is fast enough and releases enough energy to undergo a rapid decomposition and ignition before any subsequent competition with the [MAT]$^+$.[8,23]

Pristine graphene layers were exfoliated directly from graphite powder utilizing procedures developed by our group.[4] Graphite powder was added directly to the neat hypergolic ILs to obtain a concentration of 0.03 % (w/w), which initially deposited as a sediment at the bottom of the vial. The mixture was capped and placed in a Branson 5510 bath sonicator for three consecutive 99 min cycles to obtain a black colloid with a deep green hue. Reduced graphene oxide flakes were synthesized through the chemical reduction of exfoliated graphite oxide with hydrazine hydrate and obtained from Prof. Rodney Ruoff's group.[24] r-GO dispersions were then prepared by the addition of r-GO flakes to the ILs to yield a concentration of 0.03 % (w/w) to directly compare to the pristine graphene dispersions. The resulting mixtures were dispersed after being capped and placed in a bath sonicator for three consecutive 99 min sonication cycles, which resulted in a black colloid with no visible aggregated solid along the bottom of the vial.

Graphene and r-GO dispersions in [Pyrr$_{14}$][DCA] were not stable and sedimentation was complete after less than 4 h. The lack of stability for this non-aromatic system supports earlier theoretical evidence that the [Pyrr$_{14}$]$^+$ cation would adopt an unfavorable conformation leading to a higher energy barrier when physically separating two graphene layers.[25] Conversely, colloids of pristine graphene sheets were equally stable utilizing either [BMIM][DCA] and [MAT][DCA] without any noticeable sedimentation up to 48 h. Any of the particles which did sediment after 48 h were easily resuspended by repeating the original sonication cycle. Interestingly, r-GO dispersions in [BMIM][DCA] (no observable sedimentation) and [MAT][DCA] (three week stability) are extremely stable with no observed sedimentation after extended periods of a few weeks. This might be expected as the oxidized surfaces could interfere with the reformation of the graphite intersheet structures.

A study of the effects on viscosity of the dispersion of the graphene and r-GO (Figure 2) reveal some interesting trends. The addition of graphene or r-GO to [BMIM][DCA] results in a slight reduction of the viscosity of the dispersion at 20 °C; however, at lower temperatures, graphene's ability to disrupt the interionic interactions becomes evident by large decreases in viscosity. There is not a major difference between the viscosities nor trends in lowering viscosities for pristine graphene versus r-GO dispersions in [BMIM][DCA] where only aromatic–aromatic interactions are expected with either type of graphene.

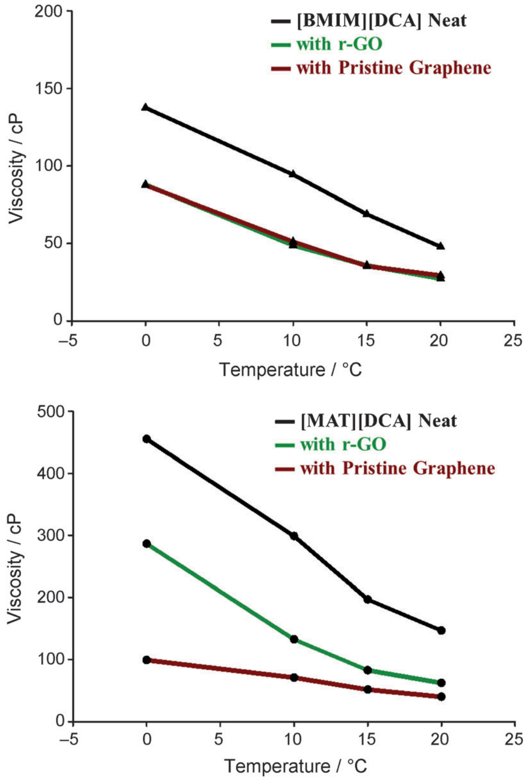


Figure 2. Viscosity versus temperature for neat ILs and dispersions of pristine graphene versus r-GO.

The third IL, [MAT][DCA], exhibits a much higher viscosity at room temperature than [BMIM][DCA], presumably due to the additional hydrogen bond donating and accepting sites in the amine substituent. While both graphene and r-GO do act to reduce the viscosity in [MAT][DCA], pristine graphene led to viscosity reductions of up to 350 cP at 0 °C compared to reductions of only 150 cP for r-GO dispersions. Interestingly, unlike the observations for [BMIM][DCA], the dispersions of [MAT][DCA] varied greatly based on the chosen surface morphology of the graphene-based nanosheet, which might suggest a unique surface–IL interaction that causes the increase in viscosity seen in r-GO dispersions compared to those dispersions containing pristine graphene.

In contrast to pristine graphene, r-GO has surface functional groups, such as epoxides, alkoxides, and carbonyl derivatives,[26] that can be involved in more than aromatic–aromatic interactions with the $[MAT]^+$ cation; specifically hydrogen bond donation from the amine to the oxide on the surface. Non-covalent interactions between graphene oxide sheets and ILs have been previously shown to improve exfoliation of graphite oxide to graphene oxide,[27] however, these interactions produced increased viscosities compared with dispersions containing pristine graphene layers. Thus, dramatically different physical properties can be obtained through proper modification of the surface of the graphene-based nanomaterial.

To determine if the reduced viscosity did indeed lead to lower temperature hypergolic behavior, hypergolic drop tests were conducted on both the neat ILs, as well as the samples loaded with pristine graphene and r-GO at 23, 0, −10, −20, and −40 °C. The test apparatus we have used previously[20] was slightly modified (see Supporting Information). A droplet (10 μL) of the IL, with or without added graphene, was dropped into a vial containing 500 μL of 99.5 % WFNA, which was precooled for 5 min in a dry ice/solvent mixture to achieve the desired temperature. The oxidizer was used in large excess to ensure the complete ignition of the entirety of the fuel, as well as proper control of the temperature of the reaction. Values for the ignition delay, defined as the time between contact with the surface and the first sign of ignition, were monitored using a Redlake MotionPro HS-4 high-speed CCD camera at 1000 frames/s.

Neat [BMIM][DCA] was ignitable upon contact with the oxidizer only until 0 °C (Table 1), where intermittent ignitions were observed with an ignition delay of around 300 ms. [MAT][DCA] remained hypergolic to −20 °C where an ignition delay of 153 ms was observed. The incorporation of pristine graphene or r-GO did result in reactions of the IL dispersions at lower temperatures (Table 1). r-GO in [BMIM][DCA] did not lead to ignition at lower temperatures, however, significantly more smoke and visual evidence for a violent reaction was observed at −10 °C. Incorporating pristine graphene layers in [BMIM][DCA], however, were consistently ignitable at −10 °C. Interestingly, the ignition temperature for [MAT][DCA] dispersions were decreased to −40 °C by addition of r-GO or pristine graphene.

As graphene-based nanomaterials have been previously reported as catalytic burn rate enhancers for nitromethane,[3] initially a catalytic process was suggested. However, by comparing the ignition delays for the neat samples with the dispersions, it was evident that the ignition delays actually increased in the dispersions, more so for r-GO than pristine graphene (Figure 3). The greater increase in ignition delay for r-GO versus graphene was also observed when dispersed in [BMIM][DCA].

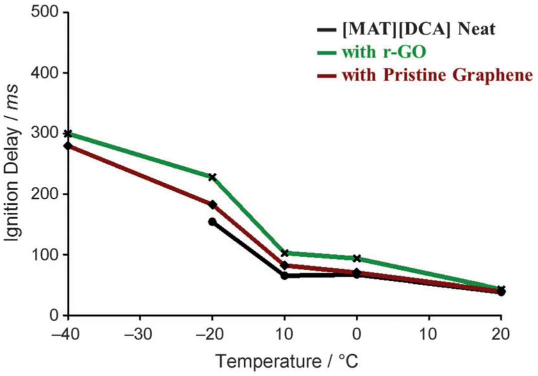


Figure 3. Ignition delay of graphene or r-GO dispersions in [MAT][DCA] versus temperature.

Incorporation of graphene or graphene oxide into hypergolic ILs can depress viscosities leading to lower temperature hypergolic ignition, however, the type of graphene surface and the potential IL/graphene interactions can lead to dramatically different behavior. Dispersions of r-GO sheets led to lower viscosities than neat ILs at low temperatures, but its functionalized surface can form hydrogen bonds with the IL ions that can inhibit its viscosity reducing effect when paired with an IL capable of such hydrogen bonding. IL dispersions containing pristine graphene layers demonstrated improved low-temperature ignition performance by sufficiently controlling the typical viscosity increases associated with lower temperatures. These dispersions in [MAT][DCA] exhibited large viscosity decreases (ca. 350 cP) at 0 °C compared with the neat sample. Thus, proper consideration of the surface of the nanomaterial additive and matching these surfaces with desired IL ion interactions can be a powerful tool towards control of bulk physical and ignition properties of hypergolic ILs.

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