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Boron nanoparticles prepared by milling in the presence of a hypergolic energetic ionic liquid (EIL) are suspendable in the EIL, and the EIL retains hypergolicity, leading to the ignition of the boron. This approach allows for incorporation of a variety of nanoscale additives to improve EIL properties, such as energetic density and heat of combustion, while providing stability and safe handling of the nanomaterials.

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COMMUNICATION

Hypergolic ionic liquids to mill, suspend, and ignite boron nanoparticles†‡

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Boron nanoparticles prepared by milling in the presence of a hypergolic energetic ionic liquid (EIL) are suspendable in the EIL and the EIL retains hypergolicity leading to the ignition of the boron. This approach allows for incorporation of a variety of nanoscale additives to improve EIL properties, such as energetic density and heat of combustion, while providing stability and safe handling of the nanomaterials.

Energetic ionic liquids (EILs, salts which melt below 100 °C with potential as energetic materials)[1] have been reported as hypergolic, indicating they spontaneously ignite on contact with a variety of oxidizers,[2–4] but many challenges still remain to their practical use such as low density[5] and relatively low heats of combustion[6] when compared to the current state of the art hypergols, such as hydrazine.[7] One approach that can be taken to improve EIL performance is to introduce an additive which does not interfere with the desired IL traits such as low or negligible vapor pressure. Ionic liquids are already known as solvent media to synthesize and stabilize nanoscale additives, such as Pt, Ir, and Pd;[8–11] however, we are interested in the ability of an IL to passivate the surface of nanoparticles while providing a stable suspension which could lead to higher energy density EILs.

Boron (B) is widely studied for its use as an energetic additive in both micro[12] and nano[13] sizes as a result of its high heat of combustion; however, because it is normally coated by a passivating oxide layer, it requires temperatures over 1500 °C to ignite.[14] Anderson *et al.* have demonstrated that air-stable and hydrocarbon-dispersible, nanoparticulate B can be prepared by milling micron-sized B with a ligand to create ligand-protected B nanoparticles. For example, oleic acid was utilized as a ligand to create unoxidized B nanoparticles (60 nm in diameter) that are easily dispersible in petroleum based jet fuels.[15,16] Here, we report the use of the IL 1-methyl-4-amino-1,2,4-triazolium dicyanamide ([MAT][DCA]) as milling agent for B. [MAT][DCA] was chosen based both on the hypergolic nature of this IL and the likely amine-B surface interactions, which we hypothesized would form.

Following the protocols developed by Anderson *et al.*, B with an average diameter of 2 μm was ball-milled using a tungsten carbide milling jar and 1/8" diameter spherical balls to create B nanoparticles (<20 nm in diameter).[15,16] Boron (2 g) was added to the ball milling apparatus and dry milled, followed by additional milling with either no ligand, a combination of oleic acid and oleyl amine (1.5 mL, 1 : 1 v/v), or [MAT][DCA] (1.5 mL). Acetonitrile was then added for the final milling as a co-solvent to help reduce the viscosity and easily transfer the nanoparticles.

The resulting acetonitrile suspensions were stable to air and these samples were manipulated on the benchtop. The solvent was removed by rotoevaporation followed by heating and stirring under high vacuum. The samples were taken into a drybox where they were stored in an Ar atmosphere until used.

The suspendability and stability of the milled B particles were investigated by preparing mixtures with the IL 1-butyl-3-methylimidazolium dicyanamide ([BMIM][DCA]). This hypergolic IL was chosen for the initial studies in determining the appropriate loadings and handling conditions due to its easier preparation,[2] characterization,[5,6] and availability. [BMIM][DCA] was freeze thawed to remove any dissolved gases or water by placing the vial in a $N_{2(l)}$ bath while under high vacuum and subsequently allowed to warm, forcing out any trapped gases.

Compositions of 0.2% to 0.7% w/w B from each of the three milled samples were prepared by diluting the weighed B samples with neat [BMIM][DCA] to prepare 1–2 mL samples. Initially a clear IL phase with aggregated B particles resting on the bottom was observed in each case. The vials were then removed from the drybox and vortex mixed and stirred, but without dispersion.

Each of the samples was ultimately dispersed by using a Branson 5510 bath sonicator. The vials were sonicated for consecutive 99 min cycles until no particles were visible, typically at least eight cycles. In each case black colloids formed with very

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weak yellow-orange hues around the edges. These suspensions did settle out over time (see below), however, each sample (all milling conditions and loadings) was easily resuspended upon vortex mixing and sonication (fewer cycles required). All colloids exhibited the same stability whether freshly prepared or redispersed.

Interesting differences in the stabilities of the particles milled under different conditions were noted. Boron milled with no surfactant gave the least stable colloids with aggregation in less than 24 h. Boron particles milled with the surfactant mixture were slightly more stable, lasting 24 h, however, the compositions with B milled in [MAT][DCA] had the greatest stability with colloids lasting 48 h. In all cases, higher B loadings (0.5–0.7%) were more prone to aggregation, but little difference in stability was noted for either the 0.2% or the 0.33% loadings. Boron nanoparticles from the three milling conditions were next loaded to 0.33 wt% in [MAT][DCA] utilizing the methods described above (Fig. 1).

Thermal gravimetric analyses were performed on the colloidal nanofluids in [BMIM][DCA] and [MAT][DCA]. The addition of B nanoparticles from any preparation did not have an effect on the decomposition temperature or the characteristic decomposition profile of either IL (see ESI‡). When these tests were conducted with an air purge, mass gain was noted corresponding to the oxidation of the B above 400 °C.

Combustion microcalorimetry was used to determine the heats of combustion of neat [BMIM][DCA] and the colloids using a Parr (series 1425) semimicro oxygen bomb calorimeter (see ESI‡). The samples with B exhibited lower heats of combustion compared to the neat IL and to the values expected when calculated using the B contributions indicating that the energies and temperatures were insufficient to combust B.

Hypergolic drop tests were then conducted to determine the effects, if any, the B nanoparticles might have on ignition delay and other ignition characteristics. The hypergolic apparatus and tests described by Schneider *et al.*[2] were employed. A droplet (10 μL) of the IL was added to a vial, *via* a Hamiltonian syringe, containing the oxidizer in large excess (500 μL of 98% white fuming nitric acid (WFNA)) at 23 °C to ensure complete ignition of the fuel. The ignition delay and flame duration times were determined using a Redlake MotionPro HS-4 high speed camera at 1000 frames per second. Each experiment was repeated for three ignitions and the values for ignition delay and ignition duration were averaged. The results are presented in Table 1.

The incorporation of 0.33 wt% B from any of the three preparations did not have any effect on the observed ignition delay of either IL tested (Table 1) within the accuracy of determination. However, as discussed below, differences in the number, intensity, and duration of the resulting flames were clearly different depending on which capping agent was utilized in the B milling step.

Neat [BMIM][DCA] exhibited a single medium intensity flame (See ESI‡) as also reported in the literature.[2,17] Incorporation of the B milled with no ligand significantly reduced hypergolic performance leading to smaller flames with observable residual mass deposited on the sides of the vial after ignition. Utilizing B particles milled in the oleic acid/olelyl amine surfactant mixture led to a complex flame behavior reproducibly exhibiting two flames which lengthened the overall time of combustion. The samples loaded with B milled in [MAT][DCA] gave the most complicated behavior with three flames (Fig. 2).

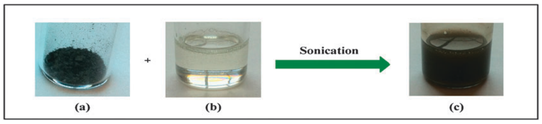
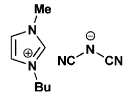
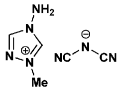


Fig. 1 (a) [MAT][DCA]-milled B, (b) [MAT][DCA], and (c) 0.33% B.

Table 1 Hypergolic and stability properties of nanoparticle dispersions

Compound	Colloidal stability (h)	Ignition delay[a] (ms)	Ignition duration (ms)	Notes
[BMIM][DCA]				
	N/A	44(2)[b,c]	106(6)	One Flame – Medium
0.33% B no ligand	<24	44(3)	108(41)	One Flame – Very weak
0.33% B surfactant	24	43(3)	110(50)	Two Flames – Medium
0.33% B [MAT][DCA]	48	44(3)	130(31)	Three Flames – Medium and High
[MAT][DCA]				
	N/A	37(6)	77(18)	One Flame – Medium
0.33% B no ligand	<24	43(9)	52(12)	One/Two Flames – Very weak
0.33% B surfactant	24	45(11)	56(7)	One Flame - Medium
0.33% B [MAT][DCA]	48	45(14)	43(4)	One Flame – Very Strong

[a] As measured from the time the drop hits the oxidizer until the first sign of a flame. [b] 47 ms has been reported in the literature for this IL.[2] [c] Numbers in paranthesis denote calculated standard deviations.

It is clear from comparing the runs with neat [BMIM][DCA] with those loaded with B nanoparticles (*e.g.*, Fig. 2c–g) that addition of the B nanoparticles did not enhance the reaction. There is also no evidence that the B ignited in these experiments. Additionally, such complicated behavior and multiple flames would provide extremely poor performance.

The hypergolic behavior of [BMIM][DCA] can be contrasted to that of [MAT][DCA] where significant differences suggest a more robust hypergolic system. Incorporation of B nanoparticles milled with no ligand to [MAT][DCA] shortened the duration of the burn and led to very weak flames. Adding the B milled with the oleic acid/oleyl amine surfactant mixture also led to a shorter burn, but flame intensity observed was only slightly reduced.

Adding B milled in [MAT][DCA] led to significant enhancements in performance (Fig. 3). When the 0.33% B loaded [MAT][DCA] was dropped into WFNA, an extremely powerful and intense single flame appeared with a very short burn indicating a very quick and powerful ignition. *These drop tests led to the largest and most intense flames of any of the tested materials*. The extremely bright, white flames qualitatively indicated B ignition.[13,14]

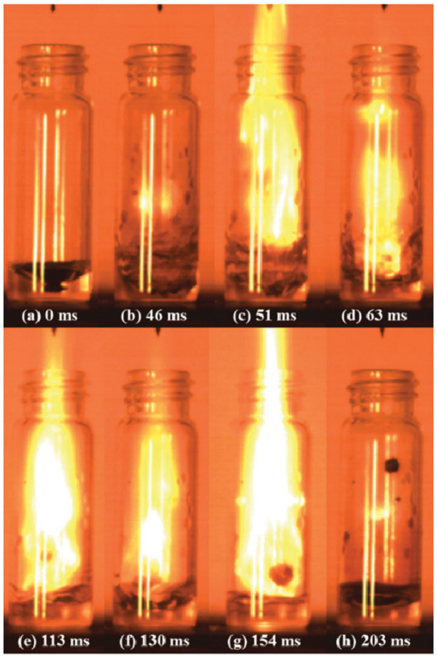


Fig. 2 [BMIM][DCA] and 98% WFNA with 0.33% B milled in [MAT][DCA]: (a) drop hitting, (b) first sign of ignition, (c) flame from first ignition, (d) end of first flame, (e) second flame, (f) second flame diminishes, (g) third flame starts, (h) last indication of burn.

FT-IR data (see ESI‡) suggests at least one partial explanation for the differences in the hypergolicity after adding B to the two ILs. The data indicate that the hypergolic anion is interacting with the B surface in [BMIM][DCA], but not in [MAT][DCA] with its coordinating cation. Studies to confirm the exact nature of the IL/B surface interactions are currently in progress.

Production of B nanoparticles by milling B in the presence of the hypergolic IL [MAT][DCA] leads to more stable dispersions of these nanoparticles in [BMIM][DCA] and [MAT][DCA]. The presence of these nanoparticles does not change the hypergolic ignition delay for these ILs, however, when added to [BMIM][DCA] there is little enhancement of the hypergolic burn and instead a complicated burn pattern emerges. By contrast, when B nanoparticles are milled in [MAT][DCA] and then dispersed in this IL, a single, shorter, much more intense burn is observed suggesting ignition of the B. These differences could be the result of the differing coordinative abilities of the two ILs to B, where, for example [BMIM][DCA] can coordinate B *via* the anion, while [MAT][DCA] can coordinate B with the cation, the anion or both.

Taken as a whole, the results reported here suggest EILs can be designed to provide unique stabilizing environments for reactive nanoparticles and that the nanoparticles can provide unique enhancements of the EIL properties such as increased density or hypergolic performance. Future work from our Groups will focus on understanding the surface interactions of the ILs and nanoparticles in an effort to find suitable IL/nanoparticle combinations that will provide infinitely suspendable nanofluids with appropriate properties needed for new energetic materials.

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Fig. 3 [MAT][DCA] neat (a and b) and loaded with 0.33 % B milled in [MAT][DCA] (c and d) with 98 % WFNA: (a and c) first sign of ignition and (b and d) burn ongoing. The resolution was lowered to fit the larger flames: vial sizes in all runs are identical.

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