Electrospun Nanofiber-Based Thermite Textiles and their Reactive Properties

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Ⓢ Supporting Information

ABSTRACT: In this work, we present a first time fabrication of thermite-based nanofiber mats with a nitrocellulose composite energetic binder to create a new class of energetic 1D nanocomposite. The as prepared thermite based nanofibrous mats were characterized and tested for their burning behavior, and compared with the pure nitrocellulose and nanoaluminum incorporated nanofibers for their combustion performances. Thermite-based nanofibers show enhanced burning rates in combustion tests, which correlate to the mass loading of nanothermite relative to binder in nanofibers. The electrospinning method demonstrates the possibility of avoiding some of the problems associated with melt casting nanometalized propellants.

KEYWORDS: electrospinning, nanoaluminum, nanothermite, energetic materials, nitrocellulose, propellant, nanofiber, combustion
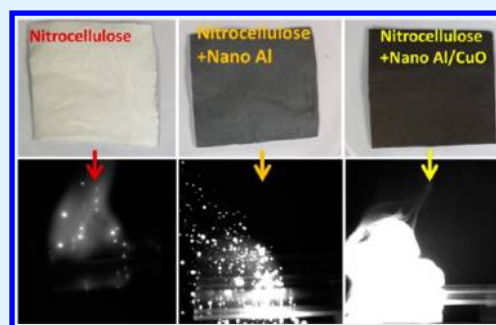
Metal fuels, such as aluminum, have become principle ingredients in many solid rocket propellants for their high energy intensity, high combustion temperature, and abundance. Although additive micrometer-sized aluminum fuel can greatly increase the energy release of the propellant, the burning rate was not found to accelerate much since the oxidation process for micrometer-sized metal particles are very slow.[1] Nanoaluminum has been suggested to be a potential replacement for conventional aluminum powders in propellant systems for its faster oxidization kinetics which can lead to potential significantly enhanced burning rate of the propellant and specific impulse.[2−4] However, the use of nanoaluminum has been hampered by processing challenges such as the increased viscosity of castable propellant mixes at high volume loading of nanoaluminum, and prevention of aggregation.[5,6]

Electrospinning is one of the simplest top down fabrication methods, which allows for easy preparation of nanofibers for many polymer systems.[7−11] Most recently, it has been employed to create nitrocellulose/nanoaluminum fibers for potential application as a propellant.[12]

Ideally one would like to integrate both the fuel and oxidizer in an intimate mixture with high volumetric loading and energy density.[13−16] Nanothermites, a subset of metastable intermolecular composites (MICs), contain metal and metal oxide mixed at nanoscale, which has been demonstrated to yield up to 1000 times increase in the propagation rate compared to its microsize counterparts.[17,18]

In this letter, we present a first time fabrication of thermite based nanofiber mats with a nitrocellulose composite energetic binder to create a new class of energetic 1D nanocomposite. The as prepared fibrous mats were characterized and tested for their burning behavior. Pure nitrocellulose nanofibers and

nanoaluminum incorporated nitrocellulose nanofibers mats were also prepared and characterized for comparison purpose. Combustion tests of the as prepared thermite based fibrous mats show enhanced burning rates, which correlate to the mass loading of nanothermite relative to binder. The electrospinning method offers the possibility of avoiding some of the problems associated with melt casting nanometalized propellants, such as preburning aggregation, postburning agglomeration, as well as the increasing viscosity of the castable propellant mixtures.

Thermite-based nitrocellulose nanofibers were fabricated by a one-step electrospinning process. In a typical experiment, 25 wt % NC/Al-CuO nanofibers, a suspension was prepared by dispersing 100 mg of nanoaluminum (ALEX, <50 nm, Argonide Corp.) and 100 mg of CuO nanoparticles (<50 nm, Sigma-Aldrich) in 1.3 mL of collodion solution (Mallinckrodt Chemical Inc., USP, ~12% nitrocellulose) with an additional 0.9 mL of ether (99.8%) and 0.9 mL of ethanol (99.98%) via vigorous stirring (5 min). The suspension was then ultrasonically mixed for 30 min and magnetically stirred at room temperature for 24h. We added the same mass of nanoaluminum and CuO NPs to form fuel rich thermite formulations accounting for the presence of nitrocellulose (NC). The suspension was electrospun using a homemade electrospinning setup, employing a stainless steel needle with inner diameter of 0.8 mm under a working voltage of 18 kV. The relatively low working voltage <20 kV is chosen to reduce the possibility of spark ignition during the electrospinning. The needle tip-collector substrate distance was kept at 6 cm, and the

solution was fed by a syringe pump at a rate of 4.5 mL/h. A rotating collector covered with aluminum foil was used to collect nonwoven thermite based fibers mats (NC/Al-CuO). Nanofibers mats of pure nitrocellulose (NC) and nano-aluminum incorporated nitrocellulose (NC/Al) were produced by the same procedure. The experimental system was kept and operated in the fume hood and shielded using insulators to reduce the possible dangers posed by spark ignition.

Optical images of nanofibers mats of nonwoven, thermite based (NC/Al-CuO), pure nitrocellulose (NC) and nano-aluminum incorporated nitrocellulose (NC/Al), fibers mats are shown in Figure 1. As can be seen from Figure 1, macroscopic
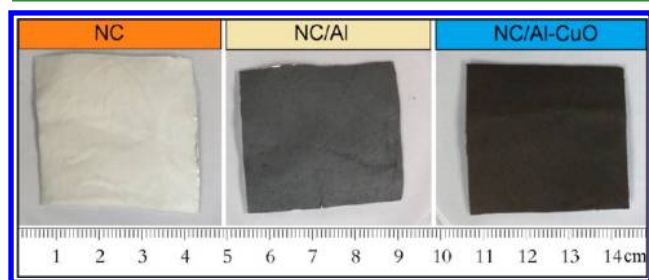
Figure 1. Photographs of the as prepared fibrous mats. The size of all the fibrous mats on the collector is about 10 cm ×12.5 cm. Note: ~50 wt % Al in the NC/Al fiber mat, ~50 wt % thermite in the NC/thermite fibrous mat.

nonwoven mats can be obtained on the centimeter scale and the color changes from white (pure NC) to gray (NC/Al) and black (NC/Al-CuO) result from the loading of the nanoparticles. With appropriate choice of solvent, the nanofibers mats could be generated with nanothermite loading up to as high as 1:1 by weight ratio of nanoparticles to nitrocellulose.

Figure 2a−c show scanning electron microscopy (SEM, Hitachi, SU-70 FEG-SEM) images of the pure NC, NC/Al and NC/Al-CuO nanofibers, respectively. All of the three samples presented in Figure 2 show high uniformity. From Figure 2a, it is clear that uniform and well-defined interconnected fibrous network has been obtained for nitrocellulose fibers. Since the diameter of the fibers could be adjusted by the polymer concentration, we kept the polymer solution concentration the same for all experiments in this study, to reduce the diameter differences caused by the polymer precursor concentrations. As seen in Figure 2a, NC fibers have smooth surfaces with diameters of ~300−400 nm. In comparison, the diameter of the NC/Al and NC/Al-CuO nanofibers are not as uniform and display a relatively wide range from ~300−1000 nm, which we attribute to the fact that addition of nanoparticles makes the precursor polymer solution not as homogeneous as pure

nitrocellulose. Not surprisingly, the NC/Al and NC/Al-CuO nanofibers have rough, irregular surface morphology, compared to the pure NC fibers, probably due to agglomeration of particles during electrospinning and the increased viscosity of the solution. However, for the same mass loading in the nanofibers, NC/Al-CuO nanofibers display a less aggregated surface, whereas NC/Al nanofibers show substantially more aggregation than NC/Al-CuO. Cross sectional SEM and transmission electron microscopy (TEM, JEOL JEM 2100F) images of NC/Al-CuO nanofibers in Figure 3a-b further show that nanoparticles are incorporated inside the fibers and well dispersed. Elemental mapping of the NC/Al-CuO in Figure 3c confirms a homogeneous distribution of the nanoparticles within the nitrocellulose fibers.

These differences between the thermite and nanoaluminum cases have two possible explanations. CuO with a density roughly 2.5 times higher than of Al implies that for the same mass loading the thermite will occupy less total volume fraction than using nanoaluminum. Furthermore, aggregation in solution is greatly influenced by surface charge states which can significantly alter particle stability during the solvent evaporation stage of electrospinning. For example, Zhang et al. found that the Fe_3O_4 nanoparticles with increased surface charge resulted in the formation of the fibers with smoother surfaces presumably because of increased electrostatic repulsion.[19]

One of our objectives was to maximize the mass loading of the nanothermite. We found that for the solvent mix used in this study loadings beyond 50% became increasing difficult to electrospin, and that at ~65% the instability in the Taylor cone resulted in severe particle agglomeration as shown in Figure 4.
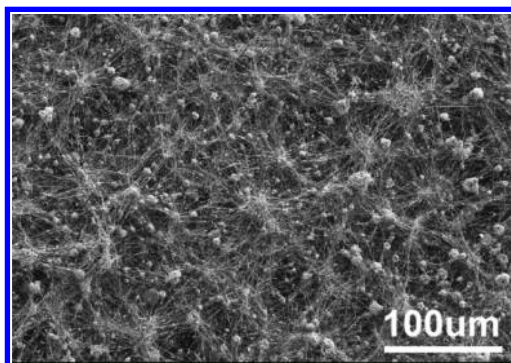
Combustion propagation velocity of the thermite based nanofibers was characterized using a high speed camera (Phantom v12.0) with a frame rate of 10000 frames per second. Combustion propagation velocities of all nanofiber mats (3 cm length, 1 cm width) were measured in open air conditions on a ceramic substrate, igniting at one end by a windproof igniter and using the camera to monitor the reaction front. Figure 5 gives sequential snapshots of all nanofibers mats burning in the air captured by a high speed video camera. Clearly, NC/Al-CuO nanofibers show much more luminous burning as compared with that of NC and NC/Al, and have the fastest combustion propagation front. As determined from the high speed camera analysis, the average burning velocity for the three samples were 12.4 (NC), 4.8 (NC/Al), and 106 cm/s (NC/Al-CuO), respectively. Though adding nanoaluminum decreases the combustion propagation velocity of the NC nanofiber, presumably because of mass transfer limits in the
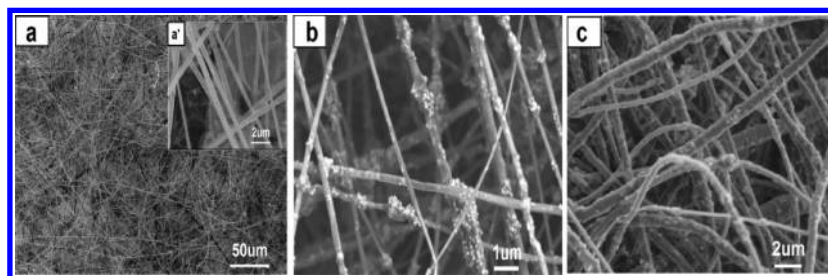
Figure 2. SEM images of (a) pure NC, (b) NC/Al (50 wt %), and (c) NC/Al-CuO (50 wt %). All samples are coated with graphite before SEM characterization to prevent melting of NC caused by electron beam irradiation.
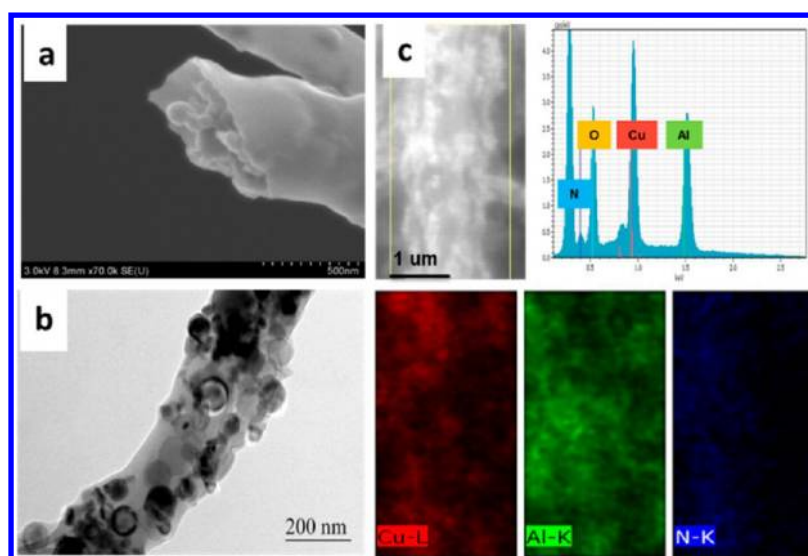
Figure 3. Cross-sectional (a) SEM image, (b) TEM image, and (c) energy-dispersive X-ray spectroscopy analysis and elemental mapping of the NC/Al-CuO with 50 wt % thermite nanofibers. Note: The first peak in 3c X-ray spectroscopy analysis is attributed to carbon.

Figure 4. SEM image of NC/Al-CuO nanofibers with 65 wt % Al-CuO.

oxidizer, incorporating nanothermite significantly increases the combustion propagation velocity.

Figure 6 shows the average combustion propagation velocities of all composite nanofibers samples as a function of the mass loading of particles in the nanofibers. As shown in Figure 6a, pure NC nanofibers (0 wt % point in the plot) have an average velocity of ~12.4 cm/s. The combustion propagation velocity of NC/Al nanofibers decreases with the increasing of the mass loading of Al nanoparticles. This suggests that even though a higher energy density can be achieved with the loading of Al nanoparticles in the nitrocellulose nanofibers, this approach results in a lower combustion propagation velocity of the nanofibers. In contrast, the combustion propagation velocities of NC/Al-CuO nanofibers (Figure 6b) do not show much change as the mass loading increased to 25 wt %, but jump sharply (~9 time increasing) for high mass loading ~50 wt % NC/Al-CuO nanofibers. A decrease in combustion propagation velocity shows up when the mass loading of Al-CuO is reduced to ~14%. This is probably due to the larger distances between Al and CuO nanoparticles at low mass loading, and thus less intimate contact between Al and CuO nanoparticles. The direct result of less intimate mixture of Al and CuO in NC matrix is that NC/Al-CuO performs similar to Al/NC fibers. However, at higher mass loading (>25 wt %), the intimate contact between nano-Al and CuO could
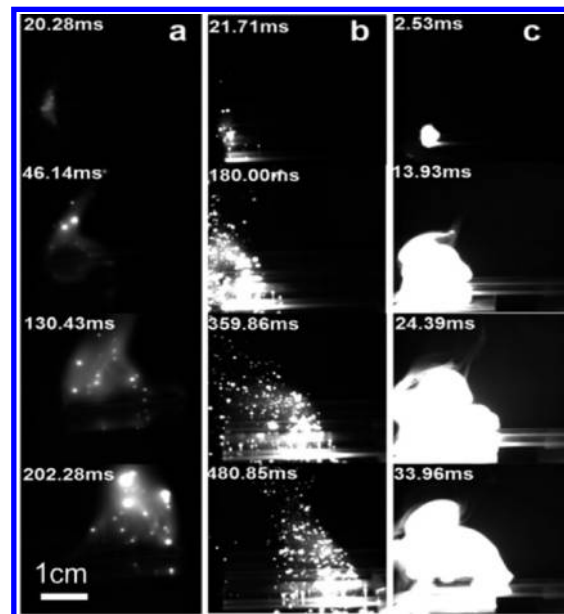

Figure 5. Sequential snapshots of (a) pure NC nanofibers mat, (b) Al/NC nanofibers mat with 50 wt % of Al and (c) NC/Al-CuO nanofibers mat with 50 wt % of thermite burning, as captured by high speed video camera.

dramatically increase the reaction kinetics and lead to much higher flame propagation rates.[13−16,20]

In summary, we have reported a novel way to prepare thermite based nitrocellulose nanofibers via an electrospinning approach. With the nanothermite being electrospun in the nitrocellulose polymer matrix, the total energy release as well as combustion propagation velocity could be dramatically increased, suggesting its potential application in the solid rocket propellant systems. The same electrospinning approaches could also be used to prepare nanothermite-based HTPB nanofibers, which will be our next focus.
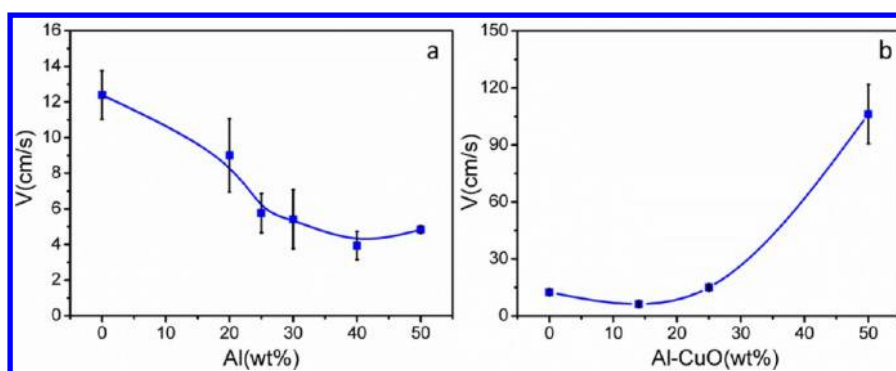
Figure 6. Combustion propagation velocities of (a) NC/Al and (b) NC/Al-CuO nanofibers as a function of particles mass loading. Note: Error bars for first three points are too small to be seen in Figure 6b.

ASSOCIATED CONTENT

Ⓢ Supporting Information

Schematic diagram of electrospinning apparatus. TEM images of the purchased Al-NPs and CuO NPs. SEM image and X-ray elemental analysis of a single NC/Al-CuO nanofiber with 50 wt % thermite. Schematic drawing of flame propagation velocities measurement system. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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