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Facile formation of nitrocellulose-coated Al/Bi_2O_3 nanothermites with excellent energy output and improved electrostatic discharge safety

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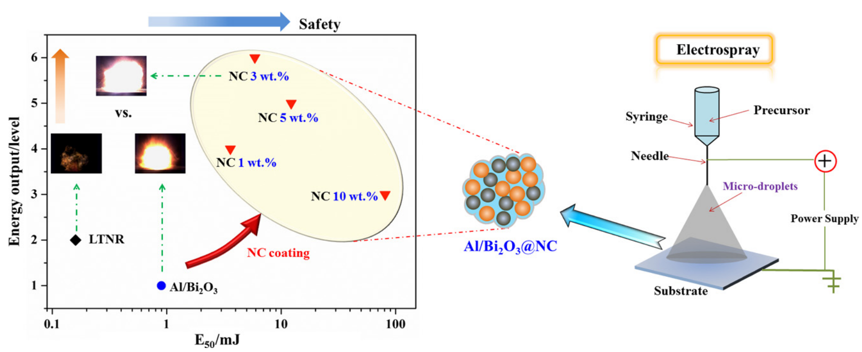
HIGHLIGHTS

- Nitrocellulose (NC) coated Al/Bi2O3 nanothermites were prepared by facile electrospray method.
- The NC coating improves the safety of Al/Bi2O3 nanothermites to electrostatic discharge (ESD).
- Optimal addition of NC coating remarkably enhances the energy output.
- Compared with lead styphnate (LTNR), Al/Bi2O3@NC demonstrates higher energy output and improved safety.

GRAPHICAL ABSTRACT



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ABSTRACT

Nanothermites are attracting much attention for energetic applications. However, they suffer from high electrostatic discharge (ESD) sensitivity which makes their handling hazardous. Developing safe yet powerful nanothermites is still a challenge. In this work, nitrocellulose (NC) was adhered to the surface of Al and Bi_2O_3 nanoparticles by a facile electrospray method aiming to improve the ESD safety and energy output of Al/Bi_2O_3. The morphological and compositional characterization of Al/Bi_2O_3@NC confirms the NC-coated structure. Benefiting from the structure, the ESD safety of coated Al/Bi_2O_3 is improved, for instance, the Al/Bi_2O_3@NC containing 10 wt% of NC has a ESD ignition threshold to be 81 mJ instead of 1 mJ for the Al/Bi_2O_3 without NC. On the other hand, tunable energy output is obtained by the addition of NC coating. Specifically, Al/Bi_2O_3@NC (3 wt%) exhibits remarkably enhancements in pressurization, combustion reaction and heat release, which even outperforms the most widely used primary explosive lead styphnate (LTNR). The enhancements are attributed to the fact that NC serves as a gas-generating agent to prevent the nanoparticles from sintering to larger particles and enables sufficient combustion. These results suggest that the electrospray formation of NC-coated nanothermites is a facile strategy for obtaining novel nanothermites.

1. Introduction

Nanothermites consisting of metal fuel and oxidizer at nanoscale are new class of energetic materials, which can rapidly release chemical energy by combustion or explosion. When compared with the traditional thermites composed of microparticles, nanothermites offer enhancement in combustion rate by a factor of 100 or more, owing to enhanced interfacial contact and decreased diffusion length scale between the fuel and the oxidizer [1–4]. The volumetric energy density of nanothermites is higher than that of conventional explosives such as 2,4,6-trinitrotoluene (TNT) and hexahydro-1,3,5-trinitro-1,3,5-triazizine (RDX) [5,6]. In

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Table 1
Formulations of the nanothermites with varied NC content.

#	Al (mg)	Bi_2O_3 (mg)	NC (mg)	NC (wt%)	Ether/Ethanol (mL)
1	101.6	498.4	0	0	1/3.5
2	100.5	493.5	6	1	1/3.5
3	98.5	483.4	18	3	1/3.5
4	96.4	473.5	30	5	1/3.5
5	91.4	448.6	60	10	1/3.5

addition, nanothermites are not as toxic as lead-based primers in terms of raw materials and combustion products during preparation and handling [7,8]. Therefore, much attention has been drawn on the development of nanothermites for potential civilian and military applications, including gas generator [9–11], bonding [12], propulsion [13–15], micro-actuator [16,17], fast ignition and initiation [18–21].

In most formulations of nanothermites, aluminum is widely utilized as fuel due to its low cost, availability and high enthalpy. Varieties of oxidizers have been used including, but not limited to, Fe_2O_3, CuO, WO_3, MoO_3 and Bi_2O_3 [22–25]. For developing high performance nanothermites, interest in understanding the effect of different oxidizers on the reaction performance of nanothermites has recently increased. Martirosyan and co-workers have found the combustion front velocities of Al/Bi_2O_3 reached 2500 $m \cdot s^{-1}$ which had the same order of magnitude as the detonation rate of explosives [11,26]. The fastest burning speed in unconfined channel and the highest pressurization rate were also measured for Al/Bi_2O_3 in comparison to Al/CuO, Al/MoO_3 and Al/PTFE by Glavier et al. [27]. Regrettably, the obstacle strongly limiting the practical application of Al/Bi_2O_3 is the excessively high sensitivity (or low ignition thresholds). For instance, the electrostatic discharge (ESD) ignition thresholds of Al/Bi_2O_3 are generally below 1 mJ, making them hazardous in the process of preparation, storage and usage [28]. The challenge presented is to desensitize the nanothermites without suppressing their reaction rate and energy output in a large extent. Recently, several attempts have been made to reduce the sensitivity of nanothermites for safely handling these materials. One previous research have shown that separating the oxidizer and fuel by enclosing one component into carbon nanofibers can greatly lower the sensitivity of nanothermites [29]. However, the reactivity is hindered to some extent as a result of separation of fuel and oxidizer. Pichot et al. have succeeded in desensitizing Al/Bi_2O_3 nanothermites to friction and ESD by adding nanodiamond [30]. Nevertheless, increasing the content of nanodiamond from 0% to 2.65 wt% leads to the reduction of combustion rate from 500 $m \cdot s^{-1}$ to 100 $m \cdot s^{-1}$.

Nitrocellulose (NC), obtained by the nitration of cellulose, is an important industrial polymer with the applications including coatings, binder and membranes [31–33]. When using as a coating, NC can be easily dissolved in organic solvent to form collodion solution and has excellent interaction with the raw particles at the solid/liquid interface, likely obtaining the modified particles with coated structure after evaporation of the solvent. Benefiting from this advantage, the low-cost NC has been recently selected to modify some energetic materials for specific application. Kim et al. have employed NC as a hydrophobic coating additive for Al/CuO based nanocomposites and the composites demonstrate successful underwater ignition and fast self-sustained combustion [34]. According to the work of Ye et al., NC can be introduced to coat the RDX and the NC-modified energetic materials exhibit decreased hazard to the impact and improved thermal stability [35]. In addition, NC itself is an energetic material offering chemical reactivity and gas production, which is commonly used in propellant or explosive [36]. These properties inspire us to utilize NC to coat the Al/Bi_2O_3 nanothermites with tunable ignition sensitivity and energy output.

To introduce the NC to the surface of Al/Bi_2O_3 nanothermites, we employ electrospray (ES) to rapid formation of Al/Bi_2O_3@NC composites. ES has been developed to fabricate energetic materials and demonstrate several advantages such as low cost, easy to operate, the ability to

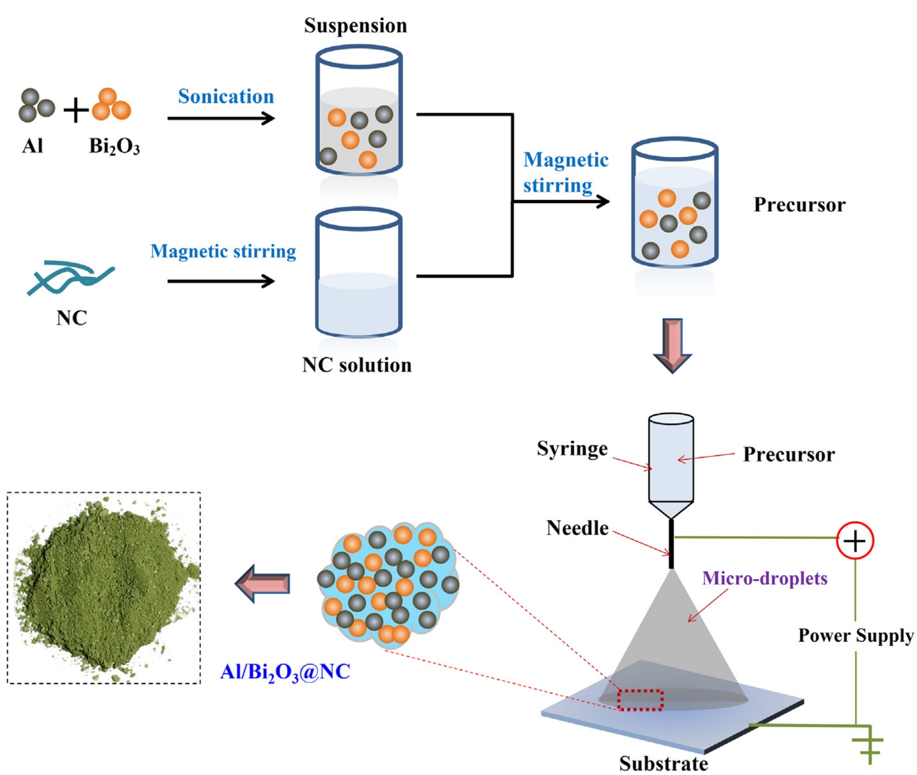

Fig. 1. Schematic of electrospray formation of Al/Bi_2O_3@NC.