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ACS Sustainable Chem. Eng., Just Accepted Manuscript • DOI: 10.1021/acssuschemeng.8b00522 • Publication Date (Web): 08 Jun 2018

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Sulfate-based nanothermite: a “green” substitute of primary explosive containing lead

Zhenxin Yi, Qin Ang, Ningrui Li, Congming Shan, Yan Li, Lin Zhang*,
Shuanguan Zhu

School of Chemical Engineering, Nanjing University of Science and Technology,
200 Xiaolingwei Street, Xuanwu, Nanjing 210094, PR China

* E-mail: zhangl@njust.edu.cn (Lin Zhang)

ABSTRACT

Currently, synthesizing a “green” alternative for primary explosives has become a new challenge for researchers, therefore the feasibility of sulfate-based nanothermite n-Al/CuSO₄·5H₂O was investigated in this work. n-Al/CuSO₄·5H₂O was prepared by electrostatic spraying (ES) which formed unified microspheres, CuSO₄·5H₂O particles were coated with n-Al particles. The reactivity was initially evaluated using thermogravimetry (TG) and differential scanning calorimetry (DSC), and the results show that the heat release of n-Al/CuSO₄·5H₂O (ES) is 1.6 kJ/g more than that of n-Al/CuSO₄·5H₂O (PM). A high-speed camera and ignition experiments in a confined bomb were used to assess the combustion performance of the two samples. Results show that n-Al/CuSO₄·5H₂O (ES) exhibited outstanding performance for flame, peak pressure and pressurization rate. The combustion in the confined bomb experiment also demonstrates that a molar ratio up to 8:1 can be the optimum ratio for the reaction between the fuel and the oxidizer. To compare the performance of metallic oxide...
nanothermite, n-Al/CuO was prepared by physical mixing. The n-Al/CuSO₄·5H₂O nanothermite shows more gas release and it is safer than that of n-Al/CuO nanothermite, which was confirmed by the results of combustion in the confined bomb and electrostatic sensitivity experiments. Moreover, in this investigation n-Al/CuSO₄·5H₂O (ES) was used to directly initiate RDX which is a feasible design for replacing lead-based primary explosives.

Keywords: Copper sulfate pentahydrate, Nanothermite, Combustion, Detonation initiation, Electrospray

**INTRODUCTION**

Primary explosives are substances which are used to produce a shock-wave to detonate secondary explosives, these are essential components in both military and civilian explosion fields. The primary explosives that are currently used, lead styphnate and lead azide, have been used for more than 100 years. However, the long-term use of these compounds containing lead ion has been a serious problem, which is harmful to the environment and personal health. Therefore, the research for environmental-friendly primary explosives has been an important task in many countries. New primary explosives have been synthesized and reported such as 4,5-bis(dinitromethyl)furoxanate¹, Potassium 4,4’-Bis(dinitromethyl)-3,3’-azofurazanate² and 3,6-bis(2-(4,6-diazido-1,3,5-triazin-2-yl)-hydrazinyl)-1,2,4,5-tetrazine³. However, the complex synthesis process of the above compounds has some disadvantages such as high cost and low yields. Also, the use of large amounts of organic solvents in the
synthesis process causes new pollution.\textsuperscript{4,5} Recently, G. Yang\textsuperscript{6} and M. Comet\textsuperscript{7} et al. using the compound of MICs (metastable interstitial composites) and explosive as primary explosives have attracted increasing attention.

MICs are composed of a mixture of nanoscale fuel and oxidant, also known as nanothermite.\textsuperscript{8} MICs have become an important field of energetic materials because of their high reactivity and high energy density.\textsuperscript{9,10} MICs can produce a shock wave with a high burning rate during combustion.\textsuperscript{11-13} The applications of MICs have expanded rapidly, these were initially used as pyrotechnic compounds and then used as igniting powders,\textsuperscript{14,15} high-energy additives for explosives,\textsuperscript{6,16,17} MEMS,\textsuperscript{9} electric igniters,\textsuperscript{18} gas generators,\textsuperscript{19} and even the latest application as a biocidal agent.\textsuperscript{20}

The reactive properties of MICs are attributed to the composition, structure and particle size.\textsuperscript{21} Among these properties, composition plays an important role. A ceaselessly increasing body of research presently relates to the use of oxygenated metal salts, such as perchlorates, iodates, periodates, sulfates and persulfates, which are better oxidizers than their corresponding oxides.\textsuperscript{22} Oxide/perchlorate salts with core-shell structure were synthesized using an aerosol-based spray method, and the peak pressure was approximately 30 times higher than that of a single oxide.\textsuperscript{23} Prakash et al. used potassium permanganate as the oxidizer, and the pressurization rate was up to 2 MPa/\textmu s, which is 40 times higher than Al/CuO under the same conditions.\textsuperscript{24} To overcome the limitation of excessively high electrostatic discharge (ESD) sensitivity, M. Comet developed sulfate-based MICs with a high sensitivity threshold for impact, friction and electrostatic discharge, which is safer than oxides-based MICs.\textsuperscript{25}
Numerous studies show that the contact area effect plays a more important role than the particle size effect. Therefore, the structural design of composites has become a research hotspot. L. Qin et al. synthesized core-shell nanothermites (Al@Fe$_2$O$_3$, Al@SnO$_2$ and Al@ZnO) by atomic layer deposition, which decreased the ignition temperature and enhanced reaction rates.$^{26,27}$ Y. Yin et al. improved the specific surface area of porous CuO/Al films to 495.6 m$^2$/g by self-assembly, and the heat release reached to 3.49 kJ/g.$^{28}$ K. Gao et al. analysed the effect of Fe$_2$O$_3$ on the decomposition process of AP. The researchers prepared three systems of Al/AP/Fe$_2$O$_3$ by sol-gel method, and the total heat release of the as-prepared Al/AP/Fe$_2$O$_3$ nanothermite was significantly increased, which becomes an appropriate material for micro thrust.$^{29}$

These methods can increase the contact area between fuel and oxidant, but the problems of complex preparation, long cycle, or the introduction of energy-free impurities into the system could not be ignored. However, electrospray is a simple, quick and feasible method of preparing nano composite materials using charged droplets formed by high voltage of static electricity. Zachariah group prepared Al/CuO, Al/AP/CuO, and Al/I$_2$/CuO composites by an electrostatic spraying system, which greatly improves the reactivity and combustion behaviour.$^{30,31}$

The development of MICs with varied compositions and structures provides new options. Z. Qiao et al. fabricated quasi-core/shell structured materials of RDX@Fe$_2$O$_3$-Al, and the deflagration to detonation transition (DDT) composite process accelerates to a primary explosive level in which the run-to-detonation distance of DDT is below the test-condition limitations.$^6$ To fully use MICs as primary explosives, we attempt to
find a high-reactive MICs system with compositions and a coating structure. Nanothermite n-Al/CuSO₄·5H₂O was reported for its safety, high heat release and quick burning rate.²⁵,³² We were able to know its pressurization rate by experiments, therefore this rate means the greatest possibility of a shock wave generation. For the design of close contact between two compositions, electrostatic spraying is performed because no restriction of blending components exists. Hence, we made use of different size particles to form a coating structure during the spraying process. In this study, n-Al (50 nm) and CuSO₄·5H₂O (1 μm) particles were chosen as the reactants, and a well-distributed composite structure was generated by a spraying method. In this paper the combination of new oxidant and close contact structure form a powerful MICs and n-Al/CuSO₄·5H₂O (ES) that can directly initiate RDX. It is an important result for the research of replacing lead-based primary explosives. Also this result initiates a promising application of MICs. At the same time, using CuSO₄·5H₂O as oxidant made this kind of MICs safer to electrostatic discharge, which is very crucial for the applications of MICs. Hence Al/CuSO₄·5H₂O is a potential substitute of primary explosives because of its initiation power, safety and its lead-free.

EXPERIMENTAL SECTION

Materials and Preparation. Nano aluminium powder was purchased from Jiaozuo Nanomaterial Co., Ltd. (Henan Province, China), with particle size of 50-100 nm and an activity of 75%. CuSO₄·5H₂O (Sinopharm Chemical Reagent Co., Ltd) was refined by spray drying (B290, BUCHI) with an average particle size of 1 μm.
In this study, physical mixing (PM) and electrostatic spraying (ES) were used to prepare MICs particles with CuSO$_4$·5H$_2$O as oxidant. To fabricate MIC composites of n-Al/CuSO$_4$·5H$_2$O (ES) containing about 5 wt. % nitrocellulose, the solution used in the tube was prepared by uniformly dispersing CuSO$_4$·5H$_2$O and n-Al into a collodion solution (4 wt. % nitrocellulose) with additional isopropyl alcohol (99.8%) followed by magnetic stirring (2 h). The solution was electrosprayed using homemade electrospray installation at room temperature with a working voltage of 19 kV and a flow rate of 4.5 mL/h. The sample n-Al/CuSO$_4$·5H$_2$O (ES) was collected on an aluminized paper, which kept a distance of 10 cm from the needle tip. Nanothermite n-Al/CuSO$_4$·5H$_2$O (PM) was prepared by dispersing CuSO$_4$·5H$_2$O and n-Al into an isopropyl alcohol (99.8%) uniformly via ultrasonic mixing (2 h) and then dried for 1 h at 40°C. We also fabricated n-Al/CuO nanothermite with ultrasonic mixing to compare the performance.

**Measurement and Characterization.** The morphologies and surface appearance of the samples were characterized using field emission scanning electron microscopy (FESEM, S-4800, Hitachi). The Powder X-ray diffraction (PXRD, D8, Bruker Gemany) results were taken to compare the diffraction intensity of CuSO$_4$·5H$_2$O and n-Al in different samples. PXRD used a Kα Cu radiation with a wavelength of 0.15406 nm. The data was collected over the angles ranging from 10° to 80°. The reaction process was recorded by TG-DSC (STA 449 C, NETZSCH) with a typical weight of 1.5-2.0 mg. The sample was placed in an alumina crucible in a dynamic atmosphere of argon. The temperature increased from 40°C to 1000°C at a rate of 10°C/min.
Combustion properties. A thin nickel chrome wire (length 1 cm, diameter 200 μm, resistance about 1 Ω) was used to ignite Nanothermite n-Al/CuSO₄·5H₂O to evaluate its performance, and then, the burning process was recorded by a high-speed camera (FASTCAM, Photron) at a speed of 20000 frames per second. The flame characteristics and ignition delay time were considered.33

Measurement in a confined bomb. To obtain the peak pressure and pressurization rate in a confined bomb, we used a pressure sensor (Fst800-ZQ-BZ, Fistrate) and a digital oscilloscope (MDO 3034, Tektronix) to measure the pressure generated by the samples over time. The sensor was supplied with a voltage of 24 V, and it transformed the pressure signal into an electric signal with a linear relationship. The 2 mL closed bomb test system was adopted in the experiment. There was 20 mg of dispersed powder in the closed bomb, and it was heated by a nickel chrome wire. When the powder was ignited, a digital oscilloscope was used to record the pressure changing over the time in a curvilinear manner. Different molar ratios of n-Al/CuSO₄·5H₂O (ES) and n-Al/CuSO₄·5H₂O (PM), n-Al/CuO were used.

Electrostatic safety. For comparison, some commonly used MICs composites and primary explosives were tested. By taking references of the military specifications of China GJB 891.27-2006, electrostatic spark sensitivity tester (JGY-50III) was used to measure the 50%-firing voltage and the minimum firing energy was obtained by using Neyer D-Optimal method.34,35 Approximately 20 mg powder was loaded on the steel plate. There was 0.12 mm between the electrodes and a charging capacitor of 500 pF was employed. Twenty-five samples of each MIC and primary explosive were tested.
Detonation initiation of RDX. The power of n-Al/CuSO₄·5H₂O (ES) was explored by initiating RDX without a primary explosive. For this purpose, 300 mg RDX was pressed in the bottom of the steel tube with a height of 25 mm and a diameter of 6 mm. Then, n-Al/CuSO₄·5H₂O (ES) (10 MPa) was placed on the pressed RDX. It is worth mentioning that there was 100 mg of dispersed RDX between pressed RDX and n-Al/CuSO₄·5H₂O (ES) for the purpose of improving RDX sensitivity. As Comparison, Al/CuSO₄·5H₂O (PM), LA and LS were explored by initiating RDX under the same conditions.

RESULTS AND DISCUSSION

n-Al/CuSO₄·5H₂O (molar ratio of 8:1) with different preparation methods was used to discuss the effects of contact area on the combustion process. The morphology of raw materials is shown in Figure 1(a). After treating with CuSO₄·5H₂O, the particles in Figure 1 (a) are spheroidal in shape with stratiform-deposited structure, and the particle size is approximately 1 μm. As shown in Figure 1(b), n-Al/CuSO₄·5H₂O (PM) exhibits a cracked and inhomogeneous configuration, which is likely caused by ultrasonic vibration. However, after electrostatic spraying, most of the CuSO₄·5H₂O particle surface was covered with n-Al (Figure 1 (c)). From Figure 1 (d), the elements Al (green), S (purple) and Cu (yellow) were evenly distributed. It was implied that n-Al and CuSO₄·5H₂O were in close contact. The method of electrostatic spraying increases the contact area between n-Al and CuSO₄·5H₂O and reduces the agglomeration of n-Al powders.
Figure 1. SEM images of (a) CuSO₄·5H₂O, (b) n-Al/CuSO₄·5H₂O (PM), (c) n-Al/CuSO₄·5H₂O (ES) and (d) element mapping image of n-Al/CuSO₄·5H₂O (ES).
The compositions of n-Al/CuSO₄·5H₂O (PM) and n-Al/CuSO₄·5H₂O (ES) (molar ratio of 8:1) were examined by PXRD measurements, as shown in Figure 2. The apparent and sharp reflection peaks correspond to the Powder Diffraction Standards of CuSO₄·5H₂O and Al. The PXRD pattern reveals that CuSO₄·5H₂O intensities become weak, and Al intensities become strong in n-Al/CuSO₄·5H₂O (ES) compared with n-Al/CuSO₄·5H₂O (PM). The surface of CuSO₄·5H₂O and n-Al are both hydrophilic, and thus, they tend to adhere to each other. Moreover, the particle size of CuSO₄·5H₂O is 20 times larger than n-Al particles. Thus, when CuSO₄·5H₂O and n-Al powders are sprayed together, they contact closely, and the large particles are surrounded by the small ones, which may result in the uniform distribution of n-Al powders on the surface of CuSO₄·5H₂O. This coating structure is confirmed by the XRD where there is an increase in the intensity of Al and decrease in the intensity of CuSO₄·5H₂O in Figure 2.

![Figure 2. PXRD analyses for n-Al/CuSO₄·5H₂O prepared by ES and PM](image-url)
TGA and DSC of Al/CuSO$_4$·5H$_2$O (molar ratio of 8:1) was conducted to assess the reaction process and decomposition temperature as shown in Figure 3 in which the first weight loss (40°C - 240°C) is attributed to dehydration of CuSO$_4$·5H$_2$O. The heat flow increased gradually up to 532°C, and it follows a weight gain which is caused by the reaction between n-Al and water vapour. Moreover, the weight gain rate of n-Al/CuSO$_4$·5H$_2$O (ES) is 2.5% more than that of n-Al/CuSO$_4$·5H$_2$O (PM), which means a more intense reaction process. Then, the results show a clear weight loss (605°C) due to the decomposition of CuSO$_4$. Similarly, the weight loss rate of n-Al/CuSO$_4$·5H$_2$O (ES) is 3.03% higher than n-Al/ CuSO$_4$·5H$_2$O (PM), indicating a faster release of abundant gaseous products and resulting in higher reactivity than that of n-Al/CuO. The decomposition products CuO, SO$_2$ and O$_2$ react with n-Al following a strong exothermic reaction. It is also noted that the decomposition temperature of CuSO$_4$ (650°C) is lower in composite material, which accelerates the ignition of the entire reaction. Comparing n-Al/CuSO$_4$·5H$_2$O (PM) with n-Al/CuSO$_4$·5H$_2$O (ES) from the DSC curves, it is obvious that the heat release of n-Al/CuSO$_4$·5H$_2$O (ES) (1.6 kJ/g) is much higher than n-Al/CuSO$_4$·5H$_2$O (PM) (0.7 kJ/g). However, the heat release of n-Al/CuSO$_4$·5H$_2$O (ES) and n-Al/CuSO$_4$·5H$_2$O (PM) are both greater than n-Al/CuO (0.3 kJ/g). In addition, the decomposition temperature of ES sample is about 300 °C, which is earlier than PM sample (510 °C). The good performance of ES sample might be due to the lower decomposition temperature and the greater heat released. A possible reaction process can be proposed from the TGA and DSC with the following four steps:

i) The dehydration of CuSO$_4$·5H$_2$O,
ii) The reaction between n-Al and steam,

iii) The decomposition of CuSO₄, and

iv) The reaction between n-Al and the products of CuSO₄.

Figure 3. Results of TG-DSC analyses for (a) n-Al/CuSO₄·5H₂O (ES) and (b) n-Al/CuSO₄·5H₂O (PM)

At the same time, the heat release effect of 4 wt. % nitrocellulose addition was evaluated and shown in Figure 4. There was exothermic for PM sample with NC at 260 °C, however, the heat release was negligible compared with the total amount of heat release between 400 °C and 600 °C.

Figure 4. DSC results of n-Al/CuSO₄·5H₂O by ES, PM and PM contain NC
The combustion of n-Al/CuSO₄·5H₂O (molar ratio of 8:1) on a nickel chromium wire under fast heating was shown in Figure 5. It is obvious from the images that n-Al/CuSO₄·5H₂O (ES) (Figure 5(a)) shows a much more violent reaction than that of n-Al/CuSO₄·5H₂O (PM) (Figure 5(b)). The ignition delay time and total burning time for n-Al/CuSO₄·5H₂O (ES) was 1.25 ± 0.31 ms and 18.03 ± 4.55 ms, respectively, while those for n-Al/CuSO₄·5H₂O (PM) were 2.17 ± 0.58 ms and 21.12 ± 7.12 ms, respectively. These results suggest much faster energy release and pressurization rate for n-Al/CuSO₄·5H₂O (ES).

**Figure 5** High-speed video images: (a) n-Al/CuSO₄·5H₂O (ES) and (b) n-Al/CuSO₄·5H₂O (PM)

**Combustion in a confined bomb.** It is reported that convection is the dominant heat transmission method when violent reaction occurs in MICs, so the gaseous products relate to whether the reaction could be self-sustaining or not. This finding is mainly because the greater the pressure of gaseous products generated, the faster the convection process accelerates, which is more beneficial to ignition. The upward peak in the figures is the response of the piezoelectric sensor to the pressure change in the closed bomb.
Figure 6 (a) shows the peak pressure ($P_{\text{max}}$) under different molar ratios of n-Al/CuSO$_4$·5H$_2$O, and the optimum ratio of n-Al / CuSO$_4$·5H$_2$O (8:1) was determined, and it will be used in the subsequent experiment. When the molar ratio is greater or less than 8, fuel or oxidant appears as surplus, so the reaction is not complete. $P_{\text{max}}$ decreases especially with the increase of n-Al powder content. Figure 6 (b) shows the pressure traces of n-Al/CuSO$_4$·5H$_2$O (PM), n-Al/CuSO$_4$·5H$_2$O (ES) and n-Al/CuO when they were ignited in the closed bomb. Table 1 shows conditions and calculation results of Figure 6 (b), the $P_{\text{max}}$ of n-Al/CuSO$_4$·5H$_2$O (ES) was approximately 1.5 times greater than that of n-Al/CuSO$_4$·5H$_2$O (PM) and 10 times greater than n-Al/CuO. Both the pressurization times of n-Al/CuSO$_4$·5H$_2$O (PM) and n-Al/CuSO$_4$·5H$_2$O (ES) are evidently shorter than n-Al/CuO; the average pressurization rate of n-Al/CuSO$_4$·5H$_2$O (ES) is nearly 2 times greater than that of n-Al/CuSO$_4$·5H$_2$O (PM) and 20 times greater than n-Al/CuO. The main reasons for high pressure and pressurization rate are greater release of O$_2$ and SO$_2$ when CuSO$_4$ is decomposed and higher exothermicity.

**Figure 6.** $P$-$t$ curves in a confined bomb: (a) $P_{\text{max}}$ of different molar ratio of n-Al/CuSO$_4$·5H$_2$O by ES and (b) n-Al/CuSO$_4$·5H$_2$O (ES), n-Al/CuSO$_4$·5H$_2$O (PM) and n-Al/CuO
Table 1. Measurement of peak pressure and pressurization time for nanothermite

<table>
<thead>
<tr>
<th>Samples</th>
<th>Molar ratio (n-Al:CuSO$_4$·5H$_2$O)</th>
<th>Peak pressure (MPa)</th>
<th>Pressurization time (ms)</th>
<th>Average Pressurization rate (GPa/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>n-Al/ CuSO$_4$·5H$_2$O</td>
<td>8:1</td>
<td>43.87</td>
<td>2.14</td>
<td>21.43</td>
</tr>
<tr>
<td>(ES)</td>
<td></td>
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<td></td>
<td></td>
</tr>
<tr>
<td>n-Al/ CuSO$_4$·5H$_2$O</td>
<td>8:1</td>
<td>27.65</td>
<td>2.24</td>
<td>12.34</td>
</tr>
<tr>
<td>(PM)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>n-Al/CuO</td>
<td>2:3</td>
<td>4.28</td>
<td>2.59</td>
<td>1.65</td>
</tr>
</tbody>
</table>

**Electrostatic safety.** The application of MICs is strictly limited by their excessively low sensitivity thresholds to electrostatic discharge (ESD), which are often below 0.14 mJ. As showing in Table 2, all of the sulfate-based nanothermite did not fired at the maximum output energy (225 mJ) of instrument. Compare to common primary explosives LA (lead azide), DDNP (diazodinitrophenol), LS (lead styphnate) and MICs n-Al/CuO (Φ=1), n-Al/Fe$_2$O$_3$ (Φ=1), n-Al/ CuSO$_4$·5H$_2$O is more insensitive to ESD. The existence of "solid water" in CuSO$_4$·5H$_2$O increases the conductivity of n-Al/CuSO$_4$·5H$_2$O in electrostatic discharge, and it absorbed part of the heat of electrostatic discharge.$^{27}$ Therefore, the electrostatic sensitivity threshold of n-Al/CuSO$_4$·5H$_2$O composite particles is obviously higher than that of n-Al/CuO. In
contrast, sulfate-based nanothermites makes their wide-use promising because of their outstanding insensitivity to ESD.

**Table 2.** ESD sensitivity for different energetic compounds

<table>
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<tr>
<th></th>
<th>ESD energy / mJ</th>
<th>Standard Deviation</th>
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<tbody>
<tr>
<td>n-Al/CuSO₄·5H₂O</td>
<td>&gt; 225</td>
<td>-</td>
</tr>
<tr>
<td>DDNP</td>
<td>12</td>
<td>0.20</td>
</tr>
<tr>
<td>n-Al/Fe₂O₃</td>
<td>11.4</td>
<td>0.67</td>
</tr>
<tr>
<td>LA</td>
<td>7</td>
<td>0.11</td>
</tr>
<tr>
<td>LS</td>
<td>0.9</td>
<td>0.89</td>
</tr>
<tr>
<td>n-Al/CuO</td>
<td>0.3</td>
<td>1.12</td>
</tr>
<tr>
<td>n-Al/Bi₂O₃</td>
<td>0.2</td>
<td>1.04</td>
</tr>
</tbody>
</table>

**Detonation initiation of RDX.** The perforation of lead plates is a simple qualitative method to evaluate the performance of primary explosives. As Figure 7(a) shows, the plate was placed in touch with the bottom of a steel tube. The diameter of the hole was an indicator of detonation ability. The MICs are considered as a promising substitute for primary explosive because of their higher heat release and large amount of hot gases. However, there are no reports that MICs could directly detonate secondary explosives. In this experiment, Figure 7(b) and Figure 7(c) show that the lead plate was perforated by RDX with n-Al/CuSO₄·5H₂O (ES) but not n-Al/CuSO₄·5H₂O (PM). The main reason is that there is a higher temperature and pressure zone formed with more heat and gases in n-Al/CuSO₄·5H₂O (ES), and these heat and gases entered into RDX through the convection heat transfer mechanism, which is more conducive to the
formation of “hot spots” in explosives and is helpful to the detonation of RDX. The lead plate was perforated by LA (Figure 7 (d)) but not by LS (Figure 7 (e)) mainly because of the energy density of LA is higher than LS. To be sure, the detonating capacity of n-Al/CuSO$\textsubscript{4}$$\cdot$$5H$_2$O (ES) is commensurate with LA and better than LS. In addition, high reactivity can be reasonably attributed to the gaseous products release from the oxidizer. Meanwhile the contribution of the well-distributed MICs structure could not be ignored.

**Figure 7.** Pictures of 5-mm-thick lead plates: (a) schematic diagram of initiating device and (b) perforation induced by RDX initiated by n-Al/CuSO$\textsubscript{4}$$\cdot$$5H$_2$O (ES); (c) deformation induced by RDX initiated by n-Al/CuSO$\textsubscript{4}$$\cdot$$5H$_2$O (PM); (d) perforation induced by RDX initiated by LA; (e) deformation induced by RDX initiated by LS

**CONCLUSION**

In summary, sulfate-based nanothermite was prepared by electrostatic spraying and could directly detonate secondary explosive RDX. Compared with metallic oxide nanothermite, n-Al/CuSO$\textsubscript{4}$$\cdot$$5H$_2$O is superior for heat release and amounts of gaseous
products. Through the p–t curves in a closed bomb, the peak pressure of n-Al/CuSO₄·5H₂O was 10 times higher than that of n-Al/CuO, and the average pressurization rate was 20 times faster than that of n-Al/CuO. More importantly, the outstanding safety to ESD was compared with metal oxide-based MICs, which make MICs applications more practical. The performances of n-Al/CuSO₄·5H₂O were also promoted by electrostatic spraying. It is clear that the components were uniformly assembled, and the CuSO₄·5H₂O surface was coated by n-Al particles, which increased the contact area between the fuel and the oxidant. The heat release of n-Al/CuSO₄·5H₂O (ES) is 1.6 kJ/g greater than that of n-Al/CuSO₄·5H₂O (PM). The results demonstrate that the electrostatic spraying method improved the initiation power of n-Al/CuSO₄·5H₂O and it has been a new substitute of lead-containing primary explosive.

**Acknowledgments**

This work was supported by the Project Funded by the Priority Academic Program Development of Jiangsu Higher Education Institutions. We thank Dr. Yanchun Li for her guidance and advice about thermal analysis during this work.

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(35) MIL-STD-23659D. Deral specification initiators, electric, general de-sign specification For[S]. **2003**
Figure 1. SEM images of (a) CuSO₄·5H₂O, (b) n-Al/CuSO₄·5H₂O (PM), (c) n-Al/CuSO₄·5H₂O (ES) and (d) element mapping image of n-Al/CuSO₄·5H₂O (ES)

262x367mm (150 x 150 DPI)
Figure 2. PXRD analyses for n-Al/CuSO4·5H2O prepared by ES and PM

400x199mm (300 x 300 DPI)
Figure 3. Results of TG-DSC analyses for (a) n-Al/CuSO4·5H2O (ES) and (b) n-Al/CuSO4·5H2O (PM)
Figure 3. Results of TG-DSC analyses for (a) n-Al/CuSO4·5H2O (ES) and (b) n-Al/CuSO4·5H2O (PM)
Figure 4. DSC of n-Al/CuSO4·5H2O by ES, PM and PM contain NC

272x208mm (300 x 300 DPI)
Figure 5. High-speed video images: (a) n-Al/CuSO4·5H2O (ES) and (b) n-Al/CuSO4·5H2O (PM)
Figure 6a. P-t curves in a confined bomb: (a) Pmax of different molar ratio of n-Al/CuSO₄·5H₂O by ES and (b) n-Al/CuSO₄·5H₂O (ES), n-Al/CuSO₄·5H₂O (PM) and n-Al/CuO

289x202mm (300 x 300 DPI)
Figure 6b. P-t curves in a confined bomb: (a) Pmax of different molar ratio of n-Al/CuSO₄·5H₂O by ES and (b) n-Al/CuSO₄·5H₂O (ES), n-Al/CuSO₄·5H₂O (PM) and n-Al/CuO

272x208mm (300 x 300 DPI)
Figure 7. Pictures of 5-mm-thick lead plates: (a) schematic diagram of initiating device and (b) perforation induced by RDX initiated by n-Al/CuSO₄·5H₂O (ES); (c) deformation induced by RDX initiated by n-Al/CuSO₄·5H₂O (PM); (d) perforation induced by RDX initiated by LA; (e) deformation induced by RDX initiated by LS
Sulfate-based nanothermite has substitution leaded primary explosives based on its ESD safety and high detonating capacity.