




Novel electrophoretic assembly design of nano-aluminum@tungsten trioxide (nano-Al@WO₃) energetic coating with controllable exothermic performance

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ABSTRACT

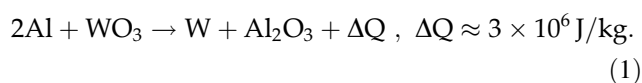
The fabrication of functional nanocomposite films by electrically driven techniques is an emerging method that has attracted increasing research interest because of advantages such as easy operation, low-cost, no secondary pollution. In this study, electrophoretic assembly technique (EAT) was firstly developed to design the promising novel nano-aluminum@tungsten trioxide (nano-Al@WO₃) energetic coating with even distribution of nanoparticles under room temperature and pressure conditions, using the mixed liquor of isopropyl alcohol, PEG-1000, and polyethyleneimine as the optimal dispersion liquid for EAT. High crystallinity and purity of product was demonstrated by X-ray diffractometer. Differential scanning calorimetry (DSC) results that the obtained Al@WO₃ was an outstanding high-energy coating with a high output of heat (~ 2400 J/g) due to the sufficient thermite reaction between nano-Al and WO₃ particles, and the heat-release process of product can be highly controlled by adjusting the solid loading concentration ratio of nano-Al@WO₃ before EAT. Thus, the fabrication method of EAT proposed here has great potentials to high-efficient construction or design of various energetic nanocomposite coatings such as thermite and bimetallic reactive composites with wide applications.

Xiaogang Guo and Taotao Liang have contributed equally to this work.

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1 Introduction

Nano-metastable intermixed composites (MICs) or energetic materials are types of reactive nanocomposites that release energy aggressively under certain external energy stimulus due to typical redox reaction between fuels (Al or Mg) and oxidizing agents (such as CuO, Fe₂O₃, Bi₂O₃, potassium perchlorate) [1–4]. Such energetic materials with superior heat-release performance is widely used in blasting, micro propellant, sensor, welding, etc. [5–7]. Among them, nano-aluminum@tungsten trioxide (nano-Al@WO₃) as a promising MIC has attracted increasing interests because of both extremely fast combustion rate (hundreds of meters per second) and a high theoretical heat (ΔQ) of reaction (as shown in Eq. 1) [8, 9]:



Because of high-energy release, fabricating nano-Al@WO₃ MIC conveniently has become the hot off the press in recent decades. For example, Son et al. [10] designed four kinds of nano-level Al@R_xO_y (R = W, Mo, Cu, Bi) using ultrasonic mixing method and studied the influence law of their reaction ratio on combustion rate and detonation pressure, respectively. In addition, reactive ball milling technique has been applied to design nano-Al@WO₃ MIC, and the influence law of different active carbon-based additives on its deflagration performance was deeply studied by A. Bach group [11]. For practical purpose, design of MIC coating is the key to realize the efficient combination with various substrates or chips. However, how to fabricate nano-Al@WO₃ MIC is still an immense challenge via a convenient and efficient technique.

Due to several advantages of convenient operation, low-cost, high film-forming rate, and outstanding feasibility for complex basal shapes, electrophoretic assembly technique (EAT) has exhibited great potential in constructing coatings or films through movement of charged micro/nanoparticles or micromolecules under a suitable electric field [12–15], which is also successfully proved to be practicable for preparing several MIC coatings (Al@Bi₂O₃, Al@CuO, Al@Ni, etc. [16–18]). Nevertheless, there are no reports on the fabrication of nano-aluminum@tungsten trioxide MIC by EAT.

This is the first study that has designed the nano-Al@WO₃ energetic coating through a EAT process. The optimized dispersion system contains the mixture of isopropyl alcohol, PEG-1000, and polyethyleneimine. The micromorphology and crystal structure of target coating were also studied in detail. The thermodynamic properties of nano-Al@WO₃ energetic coating were analyzed by differential scanning calorimetry (DSC). Simultaneously, the optimization design of heat-release properties were investigated.

2 Experimental section

2.1 Reagents and materials

Polyethyleneimine, polyvinylpyrrolidone (PVP-40,000), ethanol, and nano-Al particles (99.9%) were purchased from Aladdin Inc. Corp. (Shanghai, China). Isopropyl alcohol was used from Kelong Industrial Inc. (Chengdu, China). The other reagents (including PEG-2000) from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China) were of analytical grade purity without further purification. Commercially available nickel sheets are used as electrode materials during EAT process.

2.2 EAT design of nano-Al@WO₃ energetic coatings

For fabricating the nano-Al@WO₃ energetic coating, the EAT technique was exploited, and the mechanism diagram is illustrated in Fig. 1. Firstly, WO₃ nanoparticles with the diameter of ~ 50 nm were synthesized by a typical solution using PVP-40,000, PEG-2000, and ammonium metatungstate as precursor reagents in our previous study [19].

Then, the nano-Al and WO₃ particles with different molar ratios were added into the dispersing agent of isopropyl alcohol, PEG-1000, and polyethyleneimine (volume ratio = 100:2:1), and the corresponding stable suspension was obtained after ultrasonic process of 200 W for 0.5 h at room temperature. Before EAT, nickel substrates with 1 × 2 × 4 cm³ as working electrode and counter electrode were polished using sandpapers with different mesh numbers (100[#]–1000[#]), followed by alkaline washing using a mixture of sodium hydroxide and sodium carbonate, ultrasonic cleaning by ethanol and deionized water,

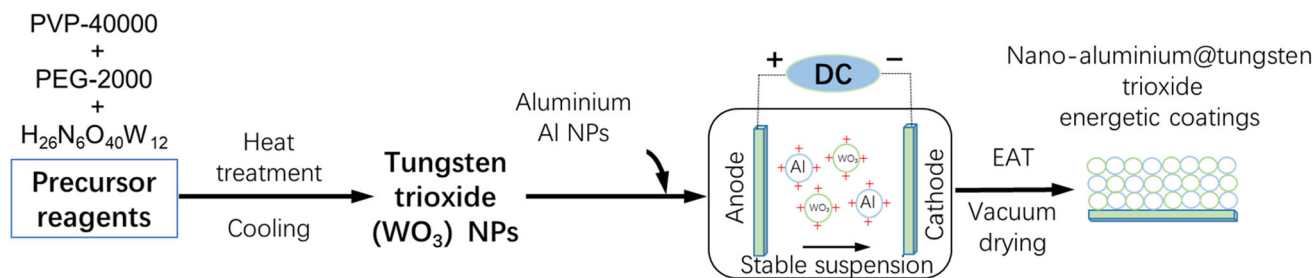


Fig. 1 Schematic diagram of the facile fabrication of the nano-Al@WO₃ energetic coatings

and vacuum drying at 353.15 K, respectively. Two treated electrodes were perpendicularly inserted into stable suspension with a distance of 1.0 cm during EAT process which was conducted under a comparatively low field strength of 20 V/mm. After EAT process for 0.2 h at room temperature, the nano-Al@WO₃ energetic films deposited on working electrode was removed to a vacuum drying oven at 378.15 K for 1.0 h. In final, the target energetic coating was obtained after cooling to ~ 398.15 K naturally. Each experiment was repeated three times for high accuracy.

2.3 Material characterization

The macro/micromorphologies, element distribution, and phase composition of the nano-Al@WO₃ energetic coatings were analyzed by a field emission scanning electron microscope (FESEM; Auriga, Zeiss, Germany) equipped with energy-dispersive X-ray spectroscopy (EDX) and X-ray diffractometer (XRD-6000, Shimadzu, Japan) with a scanning rate of 5°/min, respectively. Atomic absorption spectroscopy (AAS, 180-80, Exeter Analytical) was used to calculate the mole ratio of reactants in the obtained energetic coating. The heat release of product was measured by differential scanning calorimetry (DSC) (NETZSCH, STA449F3, Germany) carried out at a low heating rate of 15 K/min under Ar flow (99.999%).

3 Results and discussion

The XRD technique was used to analyze the crystal structures of the nano-Al@WO₃ energetic coatings, which are shown in Fig. 2. Almost all sharp diffraction peaks were marked, indicating a high crystallinity. Clearly, the XRD pattern of EAT energetic coating was completely indexed as Al (JCPDS card

No. 04-0787) with the special space group of Fm-3 m (225) with constants of $a = b = c = 4.049\text{Å}$ and axial angle of $\alpha = \beta = \gamma = 90^\circ$, and WO₃ (JCPDS No. 20-1323; P-1(2)) with the corresponding crystal (cell) size of $a = 7.3\text{Å}$, $b = 7.52\text{Å}$, $c = 7.69\text{Å}$, and axial angle of $\alpha = 88.83^\circ$, $\beta = 90.91^\circ$, and $\gamma = 90.93^\circ$. In addition, there were scarcely any other obvious diffraction peaks (e.g., Al₂O₃, W), which demonstrated that product possessed high pureness, and no redox reaction occurred during the EAT process. These results not only indicated the presence of both nano-Al and WO₃ in the deposit, but also the successful EAT of nano-Al@WO₃ energetic coatings. Furthermore, the isopropyl alcohol, PEG-1000, and polyethyleneimine mixture also turns out to be a suitable dispersion medium for the design of EAT of nano-Al@WO₃ energetic system.

The electrophoretic nano-Al@WO₃ energetic sample coatings prepared in optimized suspension are shown in Fig. 3a. It can be seen that a gray energetic

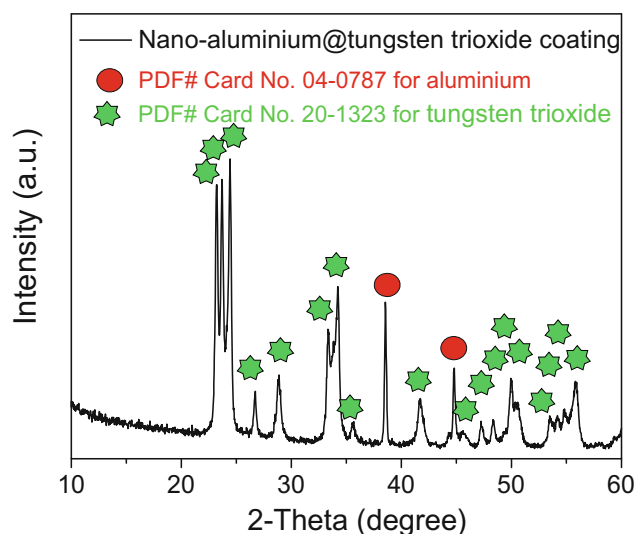


Fig. 2 Typical XRD pattern of the nano-Al@WO₃ energetic coatings

coating with smooth and uniform micromorphology was successfully prepared by EAT based on metallic substrate, and there are almost no lumpy areas or local cracks and delamination, demonstrating the structural superiority of product. This result also indicated that the obtained nano-Al@WO₃ energetic deposits have sufficient quality in terms of adhesion to the substrate and structural integrity. Further, Fig. 3b and c displays the FESEM microstructure image with different magnifications of product. Clearly, the surface of target energetic coating was fairly evenly distributed with few reunion areas in lower-resolution FESEM image of product in Fig. 3b. Moreover, the particle size of nano-Al or WO₃ in deposited coating was nanoscale with a diameter of ~ 50nm in the higher-resolution FESEM image (Fig. 3c), which can largely enhance the contact area of fuel (nano-Al) and oxidizer (WO₃) to improve the sufficiency of the exothermic reaction of obtained energetic coating [16]. It is worth mentioning that there are lots of tiny gaps among nanoparticles (Fig. 3c) as indispensable heat flow channels during

heat-release process and thereby increases the heat output capacity of product.

In addition, the elemental compositions in the nano-Al@WO₃ energetic coatings were investigated by the EDX analysis (seen in Fig. 4). The typical elemental mapping of product based on the top view FESEM image (yellow virtual box area in Fig. 3b) is displayed in Fig. 4. The elemental mapping showed that Al, W, and O were distributed evenly, indicating the homogeneous mixing of nano-Al and WO₃ in product, which is consistent with the XRD analysis. Notably, there are few slight or obvious agglomeration of nanoparticles. Moreover, all expected EDX spectrum peaks of Al, W, and O were obviously observed in Fig. 4, which also demonstrated that the desirable compositional homogeneity in an electrophoretic nano-Al@WO₃ energetic coating could be achieved.

The component proportion of target coating is essential to the heat-release performance. Thus, EDX and AAS techniques were used to analyze the mole ratio of all elements, and the corresponding results are shown in Fig. 5. Clearly, for EDX analysis based

Fig. 3 a Optical and (b low resolution; c high resolution) typical FESEM images of the nano-Al@WO₃ energetic coatings fabricated by EAT

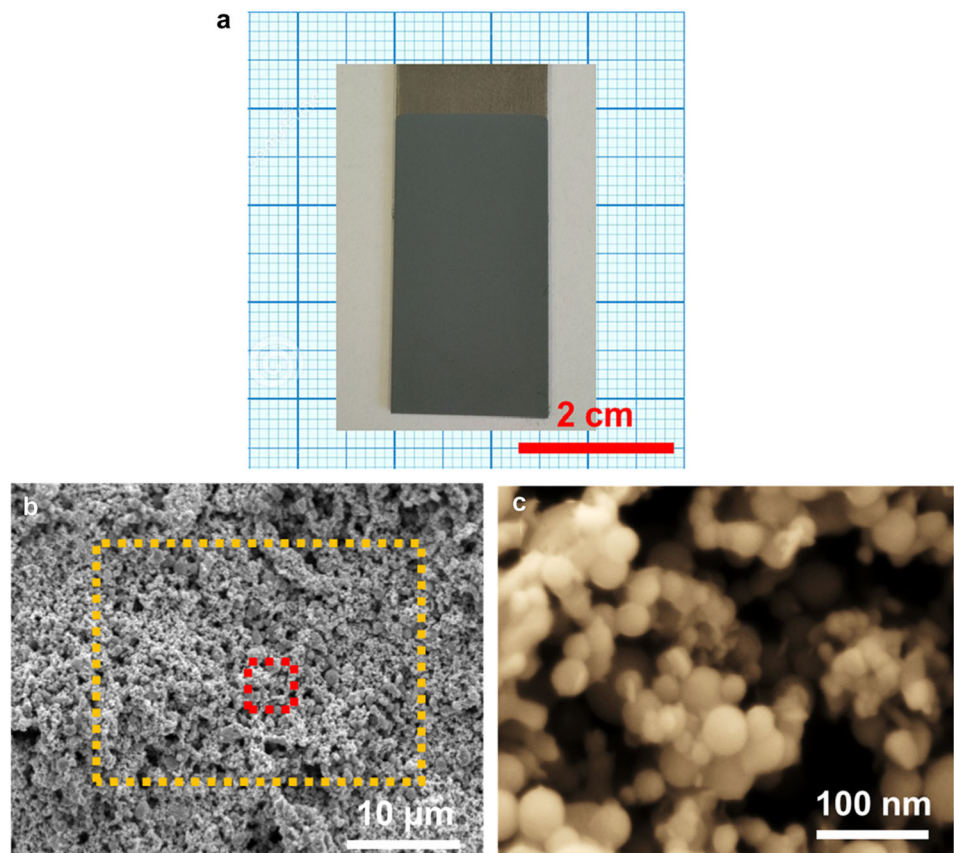
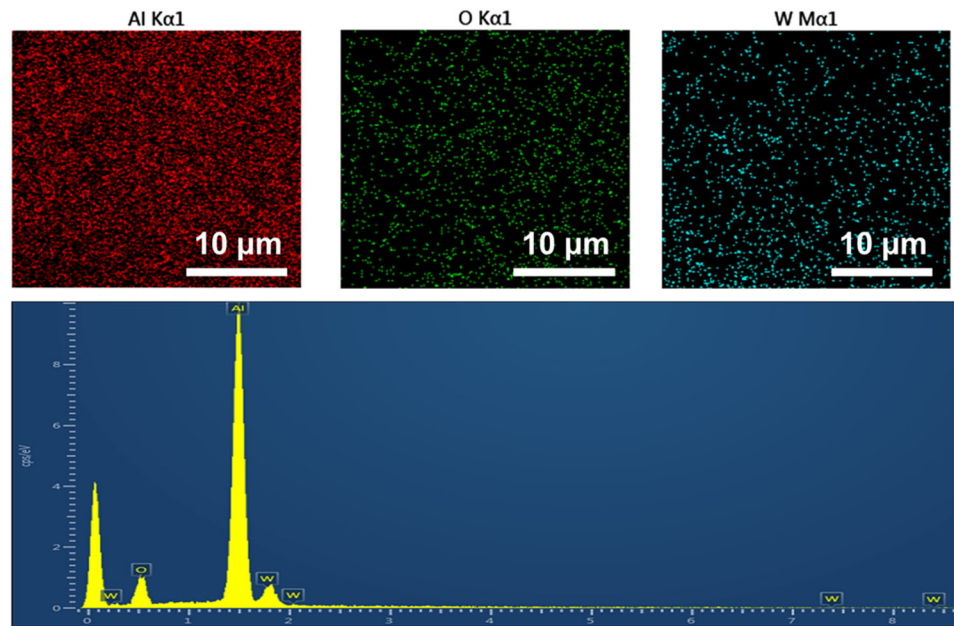


Fig. 4 EDX spectrum and element mapping images of the target energetic coating based on FESEM top view image of product (yellow virtual box area in Fig. 3b)



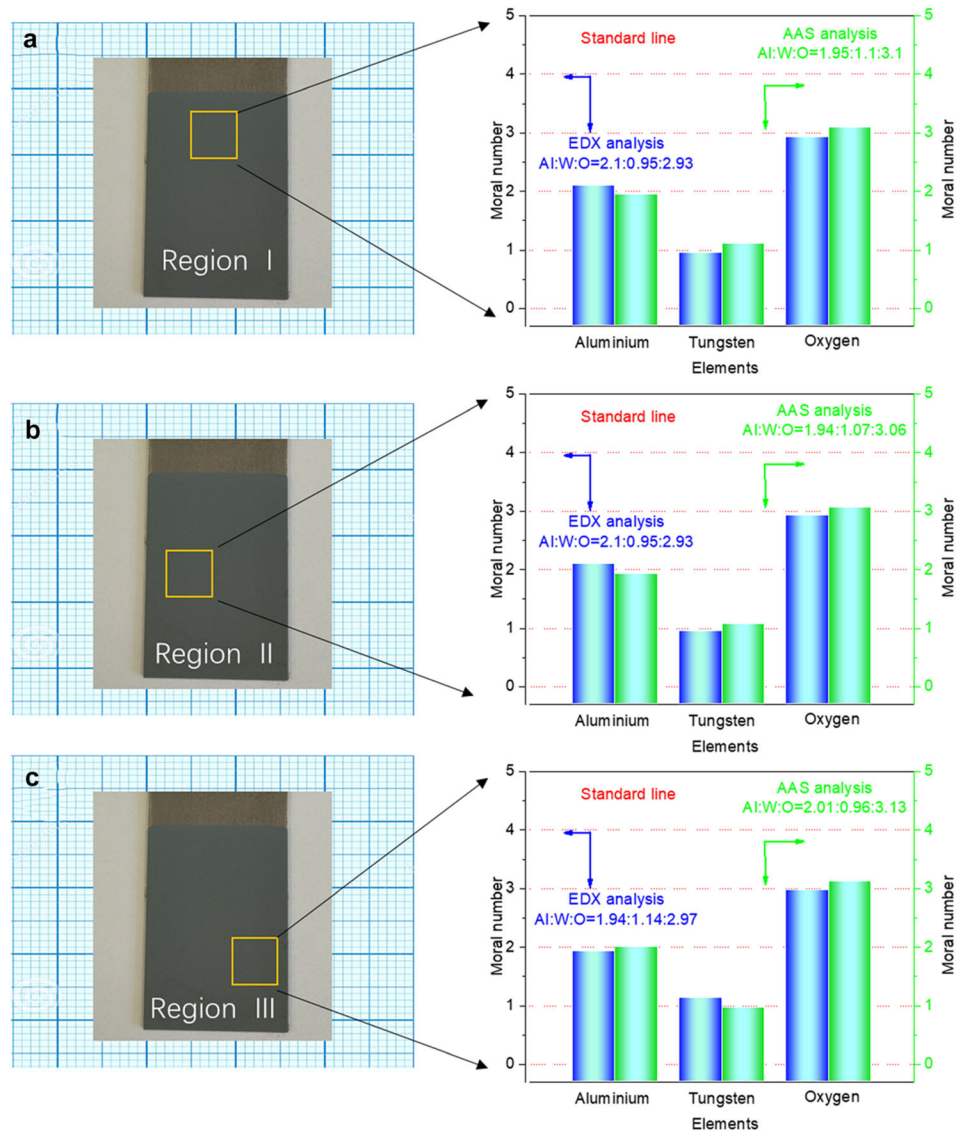
on Fig. 4, the mole ratio of Al, W, and O in the EDX mapping region in Fig. 4 is 2.1:0.95:2.93 (blue bar chart in Fig. 5a), which was close to the theoretical reaction ratio of product ($2.0:1.0:3.0$, $2\text{Al} + \text{WO}_3 \rightarrow \text{Al}_2\text{O}_3 + \text{W} + Q_{\text{Heat-release}}$). Moreover, it is worth noting that the results of elemental molar ratio of sample by AAS analysis were similar to that by EDX technique and theoretical value (green bar chart in Fig. 5a), which provided the solid component foundation of product to release violent energy. Further, two other random regions were used to verify the reliability of uniform distribution of components in nano-Al@WO₃ energetic coatings (Fig. 5b and c). It can be seen that the differences between test results were minimal among the elemental molar ratio of Al, W, and O in three random regions analyzed by EDX and AAS technique, respectively, indicating the structural superiority of product by EAT.

Exploration of exothermic performance is necessary to high-energy materials, including nano-Al@WO₃ energetic system [20–22]. The DSC is a common technique used to analyze heat-release process of product, and the corresponding DSC curve measured in Ar atmosphere is clearly displayed in

Fig. 6. It can be seen that with the temperature increase, the heat release (mW/mg) basically increased at first and reached to the peak value at ~ 800 °C, and then decreased sharply as the temperature continued to increase. It is worth mentioning that there was a small endothermic peak marked by green rectangle (Fig. 6) at ~ 660 °C because of the melt process of Al [23]. The main obvious exothermic peak was due to the drastic heat release or thermite reaction between Al and WO₃ in nano-Al@WO₃ coatings [9, 24, 25]. After a fitting calculation, the output of heat of the target energetic system fabricated by EAT technique can reach up to ~ 2400 J/g that was approximately 80% of theoretical value, demonstrating the well sufficient heat exposure process and exhibiting wide potential application in fields of microelectronics, military, etc.

Superiority of EAT in designing nano-Al@WO₃ energetic coating is also verified by adjusting the EAT process parameters (e.g., EAT time, the distance of electrodes, EAT temperature) to analyze the heat process stability of product. Figure 7a displays the relationship of heat release of product and the distance (D) between working electrode and counter electrode. It can be seen that the heat release

Fig. 5 Molar proportion analysis of all elements (Al, W and O) in product based on different random regions (a region I, b region II and c region III) by EDX and AAS technique, respectively

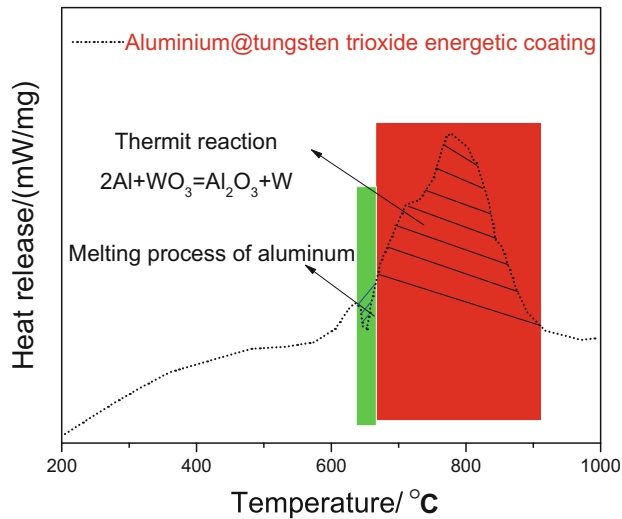


increased slowly with the “D” increase from 4 to ~ 10 mm and then kept almost stable, which indicated that the exothermic performance is hardly influenced by the value of “D”. The effect of the EAT time and temperature on the output of heat of sample is shown in Fig. 7b and c. Clearly, as the EAT increased, there was a small fluctuation in the value of heat release, whose variation range was < 5%, which also indicated the good stability of particle concentration in optimized suspension and the highly controllable EAT process used, combined with

wide potential applications for designing other kinds of promising micro/nano-energetic systems.

4 Conclusion

In summary, the novel nano-Al@WO₃ energetic coating with even distribution has been successfully fabricated using one-step electrophoretic assembly technique under mild conditions. The optimized suspension was the mixture of isopropyl alcohol, PEG-1000, and polyethyleneimine. The product



possessed a high crystallinity and purity which was demonstrated by XRD pattern analysis. FESEM and EDX results showed that WO_3 nanoparticles relatively evenly distributed among fuel (nano-Al particles) with few agglomerations, and the molar ratio of reagents was determined by EDX and AAS techniques. In addition, the violent exothermic process of product was investigated by DSC curve and the total output of heat was as high as ~ 2400 J/g with the promising stability, showing wide applications in fields of military, trigger, etc.

Fig. 6 DSC curve of the obtained nano-Al@ WO_3 energetic coatings

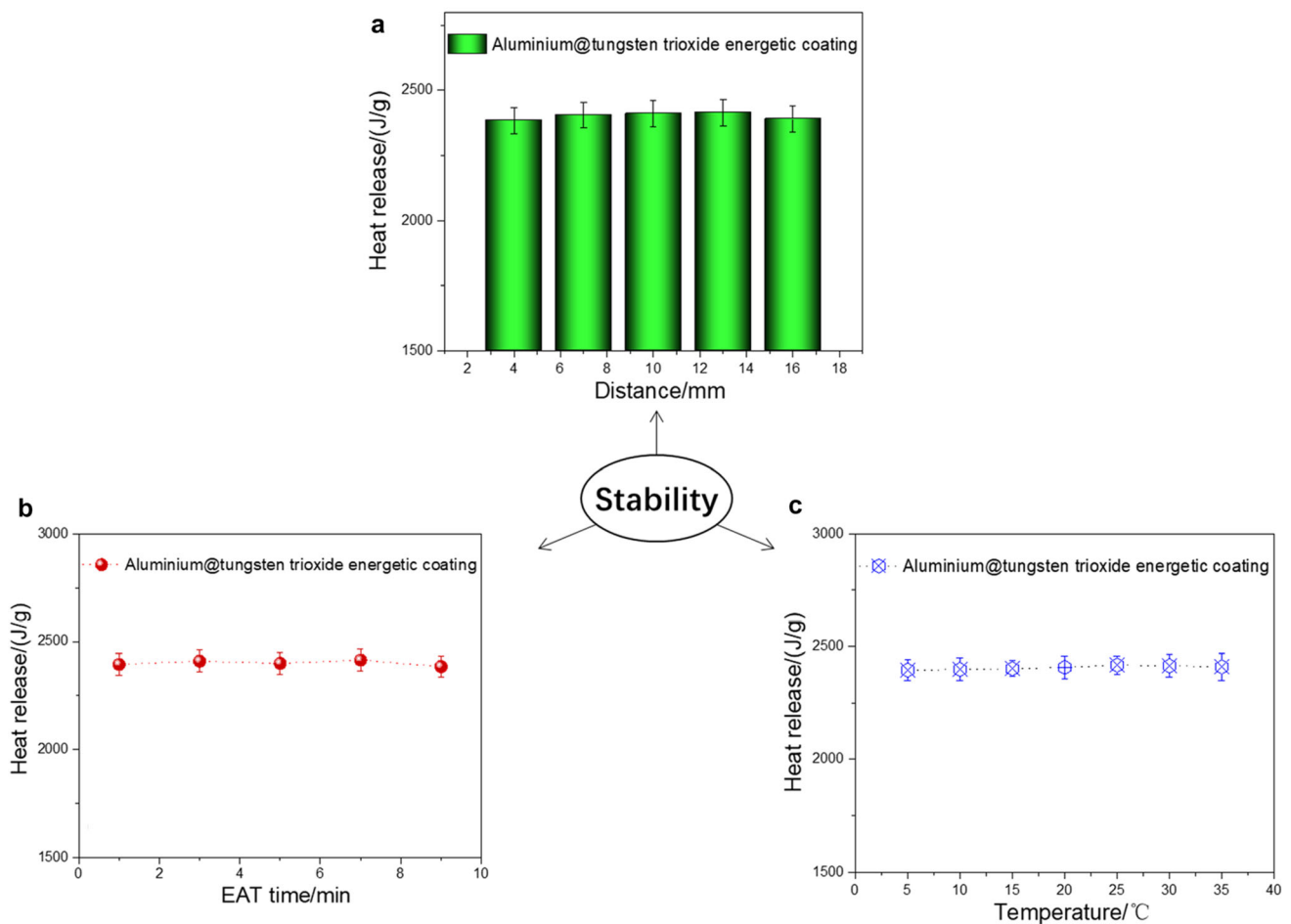


Fig. 7 The thermostability of product: heat release of product as functions of **a** distance of electrodes, **b** EAT time and **c** temperature

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Declarations

Conflict of interest The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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