

Article

Micron Aluminum Concurrently Encapsulated with Metallic Copper, Cobalt, and Iron Nanoparticles and Its Catalysis on Thermolysis and Combustion of Ammonium Perchlorate and Hexogen

Xiaolan Song ^{1,*} , Hangchen Liu ¹, Wenhui Yan ¹ and Yi Wang ^{2,*} 

¹ School of Environment and Safety Engineering, North University of China, Taiyuan 030051, China; s202514026@st.nuc.edu.cn (H.L.); s202414001@st.nuc.edu.cn (W.Y.)

² School of Materials Science and Engineering, North University of China, Taiyuan 030051, China

* Correspondence: songxiaolan00@126.com (X.S.); wangyi528528@nuc.edu.cn (Y.W.)

Abstract

In the realm of composite solid propellant research, the enhancement of energy performance without altering the underlying formulation holds paramount significance. This investigation employed an in situ displacement technique to establish a highly reactive interface, successfully synthesizing the [nCu+nCo+nFe]/ μ Al composite material, which considerably augmented the energy performance of RDX/AP. The decomposition pathways of ammonium perchlorate (AP) and RDX were optimized, resulting in a reduction in their thermal decomposition temperatures by 1.3 °C and 22.4 °C, respectively. Simultaneously, the highly reactive interface promoted efficient oxygen transport, thereby facilitating more rapid and complete reactions of aluminum. Moreover, the distinct dual-catalyst efficacy of the composite significantly enhanced the combustion efficiency of the composite energy micro-unit. Consequently, the [nCu+nCo+nFe]/ μ Al+RDX/AP composite energetic micro-units exhibited a notable decrease in combustion duration (from 1.58 s to 1.07 s) and elevated combustion flame temperatures (ranging from 1712.8 °C to 2205.6 °C) alongside an expanded combustion area, thus underscoring its potential for advanced propulsion applications.

Keywords: micron-sized aluminum; nanoscale coating; RDX; AP; thermolysis; combustion



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1. Introduction

Composite solid propellants (CSPs) constitute the principal energy source for rocket engines, assuming a critical function within the aerospace industry [1]. Their performance is fundamentally predicated on the redox reactions occurring between high-energy fuel and oxidizer constituents in the formulation, which collectively yield substantial energy outputs for propulsion systems. In the production of composite solid propellants, the process necessitates the sequential incorporation of fuel and binder into the matrix, thereby increasing the distance for heat and mass transfer between the fuel and oxidizer. This extended separation often culminates in diminished combustion efficiency [2]. Currently, conventional composite solid propellants face significant challenges in satisfying the aerospace sector's escalating requirements for enhanced energy output and superior combustion efficiency.

The introduction of composite energetic micro-units resolves this challenge. These micro-units enable uniform blending of oxidizer and fuel, significantly shortening the thermal mass transfer distance between them. This markedly enhances energy and combustion efficiency, offering broad application prospects in propellants. Liu et al. [3] employed component composite technology to design and fabricate an energetic micro-unit: a core-shell powder structure Al@PFPE@AP, wherein the oxidant AP is encapsulated on the surface of fluoride-modified aluminum powder. This methodology effectively lowers the decomposition temperature of the oxidant, while the core-shell micro-unit architecture significantly amplifies the combustion performance of the system, resulting in a notable enhancement in energy levels during the combustion of the propellant's fundamental components. Nonetheless, the intricate oxidation mechanisms of aluminum pose a significant challenge that prevents energetic micro-units from unlocking its full energy potential. As a widely utilized metallic fuel in Composite solid propellants (CSPs), aluminum powder boasts a high energy density coupled with a low bulk density, which considerably boosts the specific impulse and combustion efficiency of propellants. This characteristic confers substantial application significance within the realms of defense and aerospace [4–7]. Nonetheless, aluminum poses an inherent challenge in its practical applications: the development of a robust alumina layer hinders mass transfer between aluminum and oxygen. This phenomenon culminates in heightened ignition temperatures and reduced combustion efficiency, thereby limiting the energy output potential of aluminum [8–11]. The substantially higher melting point of alumina (2072 °C) relative to that of aluminum (660 °C) further exacerbates the increased ignition temperatures encountered during combustion. Consequently, the disruption or modification of the surface oxide layer on micron-sized aluminum powder has emerged as a crucial strategy for augmenting its reactivity. The extant literature delineates that Chengcheng Zeng et al. [12] executed a modification of aluminum nanoparticles by in situ grafting onto an energetic aziridine glycidyl ether polymer (GAP). Similarly, Liangui Guo et al. [13] synthesized carbon-coated aluminum nanoparticles utilizing laser-induced complexation heating within a methane-rich atmosphere. Furthermore, Jie-Yao Lyu et al. [14] developed high-performance graphene oxide-doped poly(vinylidene fluoride) (PVDF)/copper oxide (CuO)/aluminum nanocomposites through the technique of electrospinning. These modification techniques significantly enhance the mass transfer efficiency between aluminum and oxygen; however, they are accompanied by certain drawbacks such as intricate processes, elevated costs, and the persistent challenge of completely eliminating the aluminum oxide layer. To mitigate this issue, researchers have suggested the substitution of aluminum oxide with transition metal particles to effectively eradicate the oxide layer. For instance, Zhipeng Cheng et al. [15] synthesized innovative Co/Al/AP composite fuels through substitution reactions. The cobalt nanoparticles on its surface significantly enhanced the decomposition performance of AP; Yong Kou et al. [16] achieved a uniform coating of iron on the aluminum surface using a one-step reduction method. The thermal decomposition of AP and AN was effectively catalyzed; Zhipeng Cheng et al. [17] developed Cu/Al composites via a displacement reaction. The thermal release of Al catalyzed by Cu was proven. Nevertheless, these investigations primarily concentrated on the modification of aluminum employing a singular transition metal. This study seeks to enhance aluminum concurrently using an amalgamation of three transition metals.

Drawing inspiration from the innovative design principles of magnetic levitation trains, this study advocates for the development of an efficient oxygen transport pathway on aluminum surfaces to significantly enhance oxygen transfer capabilities. Such advancements facilitate an improved interface and reaction kinetics between external oxygen and the aluminum substrate. This enhancement is accomplished through the meticulous etching of the aluminum oxide layer using ammonium fluoride, followed by the strategic

application of EDTA-2Na ($C_{10}H_{14}N_2Na_2O_8$) as an adsorbent to sequester Cu^{2+} , Co^{2+} , and Fe^{3+} ions within the etched voids of the aluminum oxide layer. This meticulous process culminates in the establishment of a highly efficient oxygen transport pathway across the aluminum surface. At elevated temperatures, copper (Cu), cobalt (Co), and iron (Fe) undergo oxidation, resulting in the formation of their respective oxides: CuO_x , CoO_x , and FeO_x . Through self-propagating thermite reactions, oxygen is liberated from these nano-metal oxides and transferred to aluminum, thereby facilitating rapid oxygen delivery. This process not only accelerates the oxidation of aluminum but also releases substantial amounts of energy. The strategic incorporation of Cu, Co, and Fe nanoparticles effectively disrupts the aluminum oxide layer, markedly improving the combustion of aluminum and its energy efficiency, while also reducing agglomeration within the aluminum powder. Importantly, the simultaneous introduction of these three transition metal nanoparticles offers complementary benefits, synergistically enhancing the catalysis of aluminum reactions. In conclusion, the integration of these three transition metals enhances the oxidation pathways of aluminum, resulting in an elevation of both oxidation rates and the efficiency of energy release. Moreover, during the catalysis phase with the oxidant, the trio of transition metals establishes a self-sustaining cyclic system, significantly amplifying the thermal decomposition rates of the oxidant and improving the efficiency of energy liberation.

Ammonium perchlorate (AP) is a widely employed oxidizer in composite solid propellants (CSPs). Upon combustion, it yields exclusively gaseous products and exhibits remarkable attributes, including a high specific impulse, substantial density, and cost-effectiveness. Its oxygen balance of +34% underscores its formidable oxidizing potential within propellant compositions [18]. RDX, known as a high-energy elementary explosive, is distinguished by its rapid detonation velocity and exceptional sensitivity to detonation, cementing its position among the most prevalent explosives in contemporary use [19,20]. The integration of RDX as a high-energy additive in propellant formulations can substantially augment the energetic performance of CSPs. Consequently, it is necessary to investigate the energy performance of aluminum-based composite energetic units ($[nCu+nCo+nFe]/\mu Al+RDX/AP$) formed by copper, cobalt, and iron-coated aluminum combined with AP and RDX, to reflect the application performance of $[nCu+nCo+nFe]/\mu Al$ in propellants. This study prepared composite materials based on RDX and AP ($[nCu+nCo+nFe]/\mu Al+RDX/AP$) by mixing $[nCu+nCo+nFe]/\mu Al$ with RDX and AP. By using ammonium fluoride to disrupt the surface oxide layer of aluminum powder and replacing it with nanoscale transition metals, an efficient oxygen transport pathway was successfully established. This simultaneously catalyzed the decomposition efficiency of the oxidant, enhancing the energy release efficiency of the high-energy additive/oxidant/metal fuel (Al) composite energetic micro-unit. Consequently, its combustion efficiency and energy release efficiency were significantly improved. In summary, this study proposes a novel approach to enhance the energy release efficiency of aluminum-based composite energetic micro-units by optimizing the aluminum powder oxidation pathway. This provides a key concept for the development of innovative high-energy propellants and holds promise for advancing the research and development of next-generation high-energy, high-combustion-efficiency composite solid propellants.

2. Results and Discussion

2.1. Characterization of $[nCu+nCo+nFe]/\mu Al$

Figure 1 presents the scanning electron microscopy (SEM) images of the raw micron-sized aluminum (μAl) and the as-synthesized composites. As shown in Figure 1a–c, the raw μAl particles exhibit a smooth and spherical morphology. The presence of oxygen detected by energy-dispersive spectroscopy (EDS, data integrated in Figure 1) confirms the existence of a native oxide layer (Al_2O_3) on the aluminum surface. This dense Al_2O_3 layer protects

the metallic core and enhances its stability, but it also acts as a barrier that impedes the reaction between atmospheric oxygen and the underlying aluminum. To remove this oxide barrier, fluoride ions (F^-) from ammonium fluoride (NH_4F) were used to etch the Al_2O_3 layer in solution. The F^- ions react with Al_2O_3 , forming a soluble hexafluoroaluminate complex ($[AlF_6]^{3-}$), which creates vacancies on the aluminum surface for subsequent metal deposition. This process facilitates the transformation of aluminum within the oxide layer into highly water-soluble ions, thereby creating vacancies conducive to the adsorption of transition metals. Under the vigorous influence of EDTA-2Na, the transition metal ions liberated into the solution effectively adhere to the outer layer of the exposed aluminum core, resulting in the formation of a distinctive core-shell architecture. The particle clusters surrounding the aluminum depicted in Figure 2d–f provide compelling evidence for this mechanism. Figure 2f distinctly illustrates the homogeneous dispersion of externally loaded transition metals across the aluminum surface. The treatment of $[nCu+nCo+nFe]/\mu Al$ with concentrated hydrochloric acid induces the dissolution of aluminum, thereby leaving behind the shell ($[nCu+nCo+nFe]/\mu Al$ shell), as exhibited in Figure 2g–i. The particle clusters are prominently discernible in these images, signifying the successful encapsulation of transition metals within the outer layer of the aluminum core.

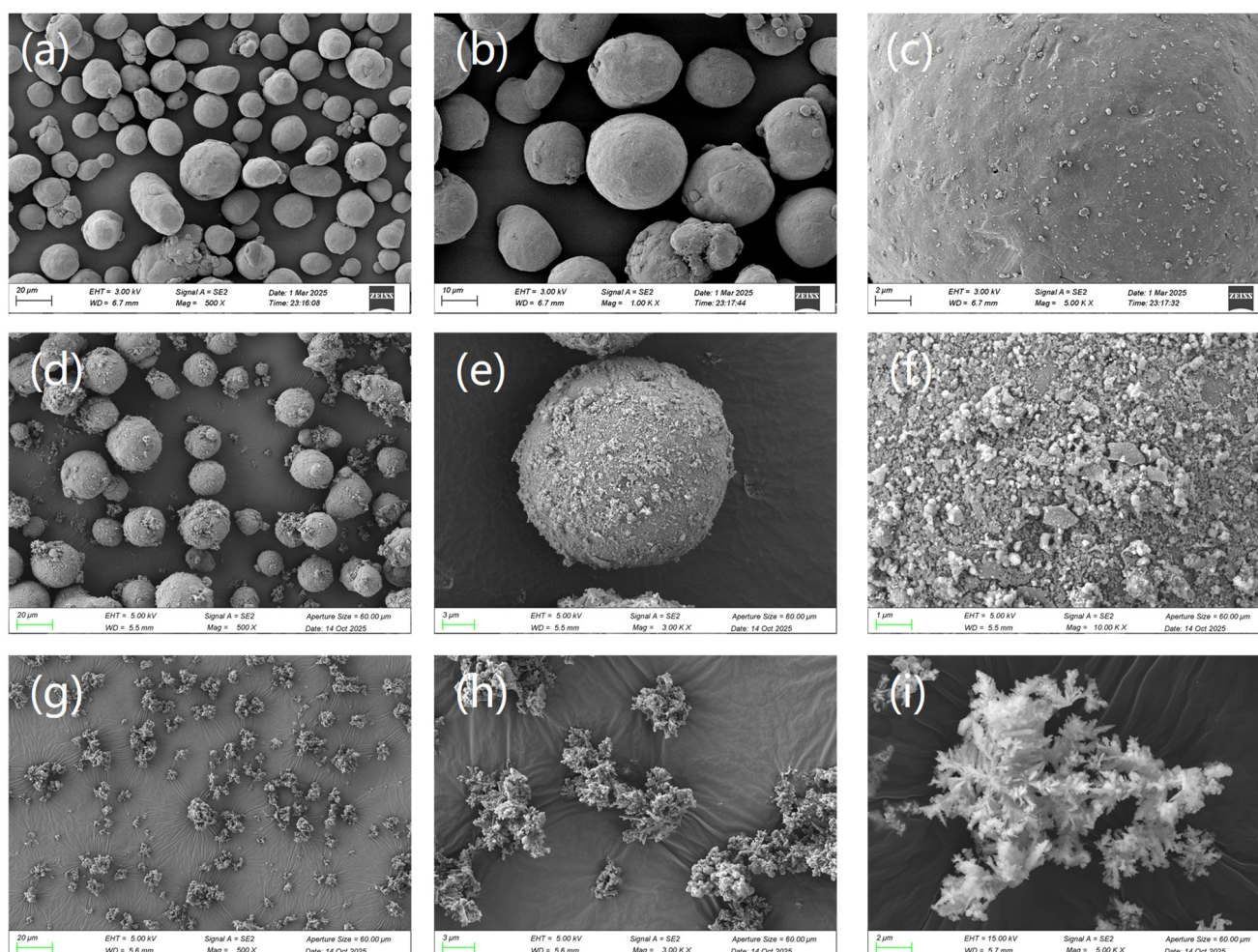


Figure 1. SEM images of samples: SEM images of (a–c) raw μAl ; (d–f) $[nCu+nCo+nFe]/\mu Al$; (g–i) $[nCu+nCo+nFe]/\mu Al$ shell.

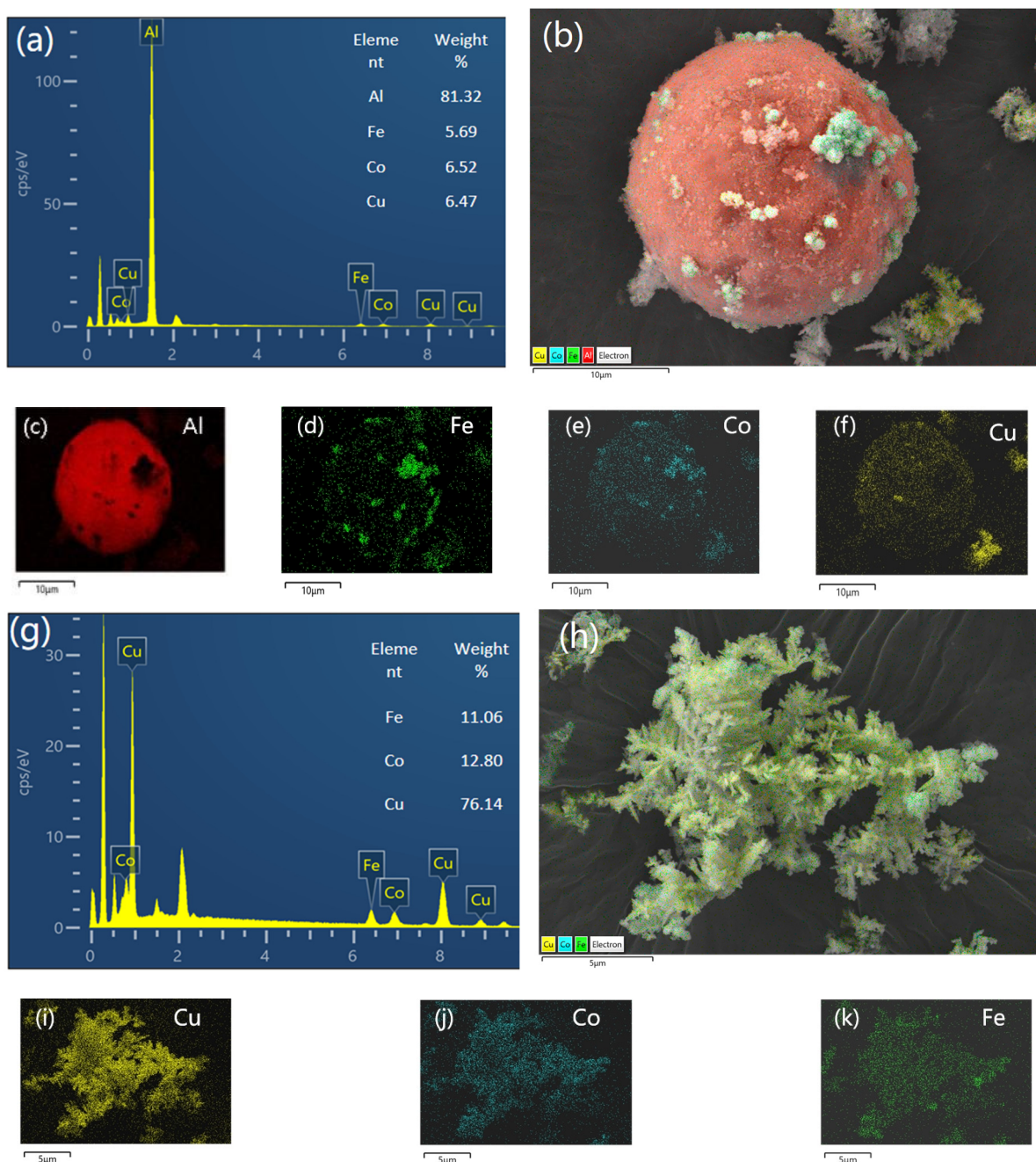


Figure 2. EDS spectra of samples: (a–f) [nCu+nCo+nFe]/μAl; (g–k) [nCu+nCo+nFe]/μAl shell.

The Energy Dispersive Spectroscopy (EDS) patterns of the [nCu+nCo+nFe]/μAl and [nCu+nCo+nFe] configurations are presented in Figure 2. As clearly evidenced by the elemental mapping in Figure 2b–f, the signals for Cu, Co, and Fe are uniformly distributed across the aluminum particle surface, with no observable large-scale aggregation. This homogeneous dispersion confirms the successful formation of a composite shell encapsulating the μAl core. In Figure 2a, initial evidence of cobalt, iron, and copper presence on the surface of the [nCu+nCo+nFe]/μAl composite is apparent. Figure 2b,d–f further elucidate the spatial distribution of these transition metals across the aluminum substrate. The core–shell separation analysis of the [nCu+nCo+nFe]/μAl configuration reveals an outer shell predominantly composed of cobalt, iron, and copper, with particles uniformly dispersed throughout the aluminum matrix. Moreover, Figure 2 convincingly demonstrates the effective encapsulation of cobalt, iron, and copper within the aluminum outer layer.

Furthermore, Figure 2a–f unveil defects within this shell, thereby exposing additional aluminum cores and enhancing their interaction with oxygen. This observation corroborates the successful etching of the aluminum powder using fluorine ions in the prior phase. Collectively, these findings substantiate the successful synthesis of $[\text{nCu+nCo+nFe}]/\mu\text{Al}$ composite microspheres featuring a distinct core–shell architecture.

A more comprehensive analysis of the microstructure and composition of the $[\text{nCu+nCo+nFe}]/\mu\text{Al}$ and $[\text{nCu+nCo+nFe}]/\mu\text{Al}$ shells was performed utilizing X-ray diffraction (XRD) and Raman spectroscopy, with the findings illustrated in Figure 3. The XRD patterns are presented in Figure 3a. The diffraction peaks observed at 38.43° and 78.3° within the $[\text{nCu+nCo+nFe}]/\mu\text{Al}$ composite particles are attributed to aluminum planes (111) and (311) [15,21]. In contrast, the peaks located at 43.32° , 50.5° , and 74.2° correspond to copper's (111), (200), and (220) crystal planes, respectively [22]. A diffraction peak at 44.7° results from the overlap of Co(110), Fe(110), and Al(200) orientations, while the peak at 65.2° is a consequence of the overlapping of Co(200), Fe(200), and Al(220) orientations. Similarly, the peak at 82.5° emanates from the superposition of Co(211) and Fe(211) peaks. The overlapping peaks exhibit a markedly increased full width at half maximum (FWHM), indicative of broadened diffraction features. The diffraction peaks attributed to Cu, Co, and Fe within the $[\text{nCu+nCo+nFe}]/\mu\text{Al}$ shell are distinctly associated with those external to the aluminum peak of the same composite. The diffractive features identified in the X-ray diffraction (XRD) analysis substantiate the successful synthesis of the $[\text{nCu+nCo+nFe}]/\mu\text{Al}$ composite material.

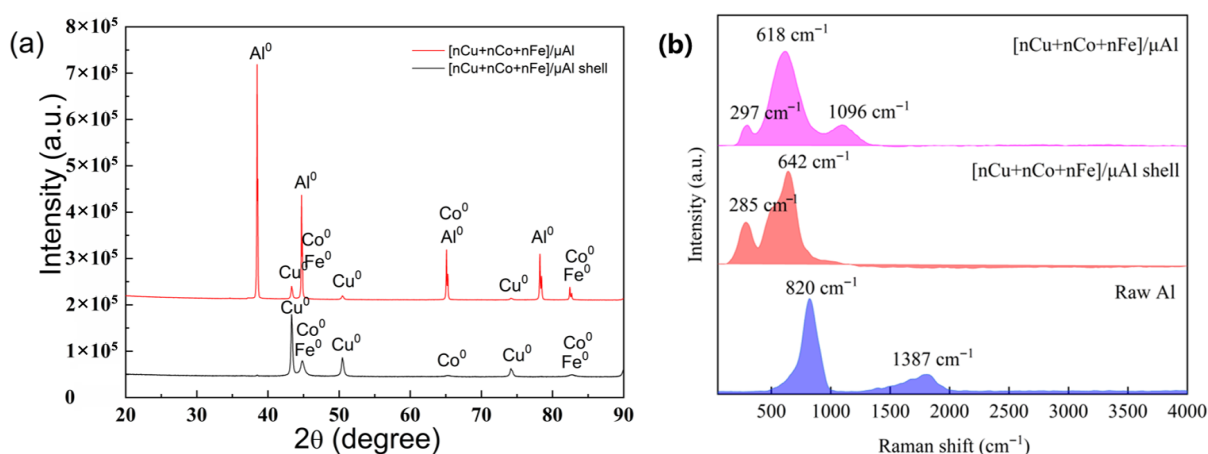


Figure 3. XRD patterns (a) and Raman spectra (b) of samples.

The Raman spectrum of the sample is presented in Figure 3b. Aluminum displays distinct characteristic Raman shifts at 820 cm^{-1} and 1837 cm^{-1} . As aluminum is a pure elemental substance, the presence of Raman peaks is unexpected; this observation may be attributed to the formation of $\gamma\text{-Al}_2\text{O}_3$ during the grinding process [23]. The peak at 820 cm^{-1} corresponds to the stretching vibration of the Al–O bond, while the peak at 1837 cm^{-1} is ascribed to the stretching vibration of the Al–O–C bond [24]. The $[\text{nCu+nCo+nFe}]/\mu\text{Al}$ shell manifests pronounced Raman characteristic peaks at 642 cm^{-1} and 285 cm^{-1} . Notably, the Raman peak at 642 cm^{-1} in this sample exhibits a red shift relative to the peak at 820 cm^{-1} observed in the micrometer-sized aluminum reference sample. This red shift is predominantly attributed to the substitution of copper, cobalt, and iron for a portion of the aluminum oxide, leading to a decrease in Al–O bond energy and the resultant expansion of the core–shell structure [25]. The peak observed at 267 cm^{-1} is ascribed to the stretching vibration of Cu_4O , while the peak at 285 cm^{-1} corresponds to the Cu–O stretching vibration [26]. Furthermore, Co_3O_4 displays Raman spectral bands at 618 cm^{-1} and 687 cm^{-1} ,

which are associated with the F22g and A1g modes, respectively. This implies that the characteristic peak situated to the left of 642 cm^{-1} signifies the superimposed F22g peak of Co_3O_4 [27]. The composite $[\text{nCu+nCo+nFe}]/\mu\text{Al}$ reveals pronounced Raman peaks at 297 cm^{-1} , 618 cm^{-1} , and 1096 cm^{-1} . The spectral peak observed at 618 cm^{-1} is indicative of the stretching vibrations of the Al-O bond; however, its intensity is markedly inferior to that of the Raman peak associated with micron-sized aluminum. This diminution in vibrational energy can be predominantly ascribed to the coordination reactions taking place within the sample. The peak at 297 cm^{-1} is ascribed to Cu-O stretching vibrations, while the one at 618 cm^{-1} is associated with the Al^{3+} vibration mode in Co_3O_4 . Additionally, the peak appearing at 1096 cm^{-1} corresponds to the surface complexes formed between EDTA-2Na and Cu and Fe. This particular peak position bears a striking resemblance to those documented in the literature concerning benzotriazole surface complexes with Cu and Fe, thereby suggesting the presence of Cu and Fe complexes within the sample [28]. In conclusion, the analysis of the emergence, overlap, and shifts in the Raman spectral peaks substantiates the effective encapsulation of Cu, Co, and Ni within micrometer-sized aluminum. This observation is in alignment with the X-ray diffraction (XRD) results, which collectively validate the successful synthesis of the $[\text{nCu+nCo+nFe}]/\mu\text{Al}$ composite material.

Figure 4 showcases the hysteresis loop diagrams generated by Vibrating Sample Magnetometry (VSM) for the $[\text{nCu+nCo+nFe}]/\mu\text{Al}$ composite material and its corresponding $[\text{nCu+nCo+nFe}]/\mu\text{Al}$ shell. Figure 4a,d illustrate that the saturation magnetization of the $[\text{nCu+nCo+nFe}]/\mu\text{Al}$ composite is 6.48 emu/g , in stark contrast to the significantly higher saturation magnetization of 57.7 emu/g observed for the $[\text{nCu+nCo+nFe}]/\mu\text{Al}$ shell. This disparity indicates that the shell exhibits a greater proclivity for separation during robust magnetic extraction processes. Furthermore, Figure 4b,e elucidate the coercive forces, which are measured at 249.2 Oe for the $[\text{nCu+nCo+nFe}]/\mu\text{Al}$ composite and 298.8 Oe for the $[\text{nCu+nCo+nFe}]/\mu\text{Al}$ shell, thereby confirming that the magnetic response to external fields predominantly emanates from the shell layer. Finally, Figure 4c,f present characteristic hysteresis loops for both samples, affirming the presence of the ferromagnetic metals cobalt (Co), iron (Fe), and copper (Cu) within the composite structure [29].

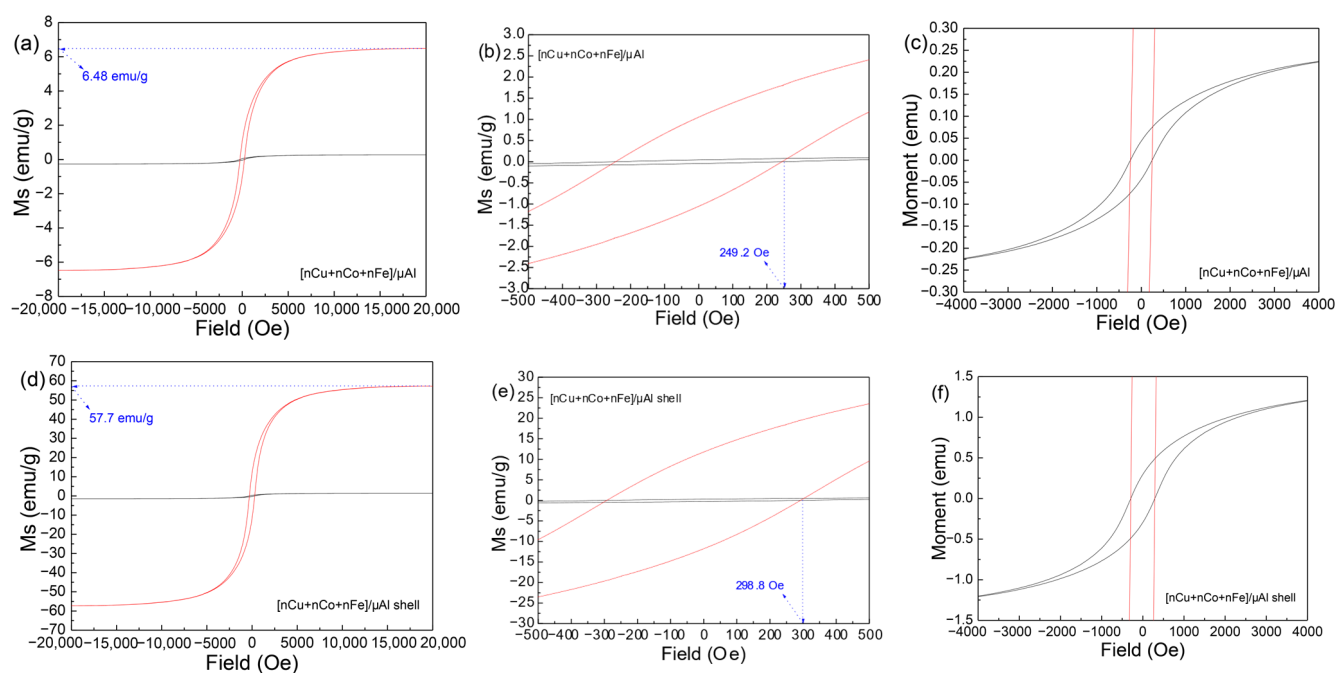


Figure 4. Magnetic hysteresis loop of samples: (a–c) $[\text{nCu+nCo+nFe}]/\mu\text{Al}$; (d–f) $[\text{nCu+nCo+nFe}]/\mu\text{Al}$ shell.

Figure 5 presents the laser-confocal imaging results of the [nCu+nCo+nFe]/ μ Al composite material. Figure 5a–c illustrate a two-dimensional pseudocolor representation of a randomly selected composite microsphere, wherein the external coloration vividly exhibits distinct annular patterns. Figure 5b showcases another two-dimensional pseudocolor map, obtained from a different microsphere measurement; here, the varied hues signify the distances from multiple positions on the microsphere to the reference plane [30]. Notably, these colors predominantly form a circular distribution, indicative of the excellent sphericity of the fabricated composite microspheres. Meanwhile, the contour plots in Figure 5d,e reveal subtle surface protrusions on the microspheres, while the overall surface remains relatively smooth. This observation substantiates that cobalt, iron, and copper are securely encapsulated within the outer aluminum matrix.

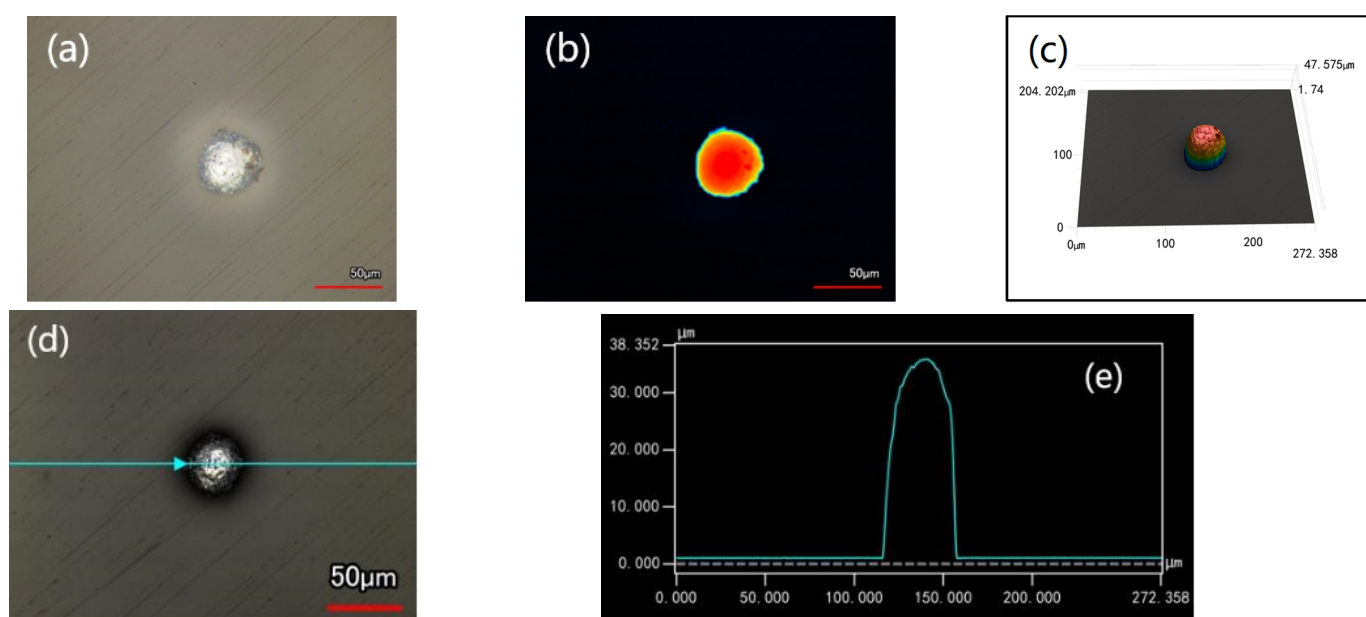


Figure 5. Laser microscope of [nCu+nCo+nFe]/ μ Al.: Color image (a); height image (b); 3D image (c); surface contour image (d,e).

Figure 6 illustrates X-ray Photoelectron Spectroscopy (XPS) spectra, employing advanced quantitative spectroscopic methodologies to ascertain the elemental composition within the surface strata of the sample, specifically within the 1–10 nm range. Figure 6a–f exhibit high-resolution XPS spectra corresponding to the [nCu+nCo+nFe]/ μ Al composite material. These figures unequivocally demonstrate that the [nCu+nCo+nFe]/ μ Al composite is predominantly constituted of cobalt (Co), iron (Fe), copper (Cu), and aluminum (Al). Notable oxide features manifest in the fine structures of Co 2p, Fe 2p, and Cu 2p spectra, particularly highlighted by the presence of a satellite peak corresponding to copper oxide (CuO) within the Cu 2p spectrum. This phenomenon can be attributed to the unavoidable oxidation of highly reactive transition metals induced by extrinsic environmental factors. In contrast, the lack of metal oxides observed in the X-ray Diffraction (XRD) pattern (Figure 3a) suggests a minimal presence of externally oxidized transition metals. Figure 6g–k illustrate the high-resolution X-ray photoelectron spectroscopy (XPS) spectra of the [nCu+nCo+nFe]/ μ Al shell layer. Notably, the spectra reveal an absence of cobalt or iron oxides, a phenomenon likely attributable to the incorporation of concentrated hydrochloric acid during the nucleation process, which presumably facilitated the reduction in any existing oxides. This observation further signifies that cobalt predominantly exists in the +3 oxidation state, thereby exhibiting pronounced oxidizing characteristics. In contrast, the detection of copper oxide can be ascribed to the intricate reaction energy barrier associated

with copper, resulting in an exceedingly sluggish reaction with hydrochloric acid at ambient temperature. Additionally, the XPS spectrum corroborates the presence of cobalt, iron, and copper on the aluminum surface, thereby confirming the successful synthesis of the $[n\text{Cu}+n\text{Co}+n\text{Fe}]/\mu\text{Al}$ composite material.

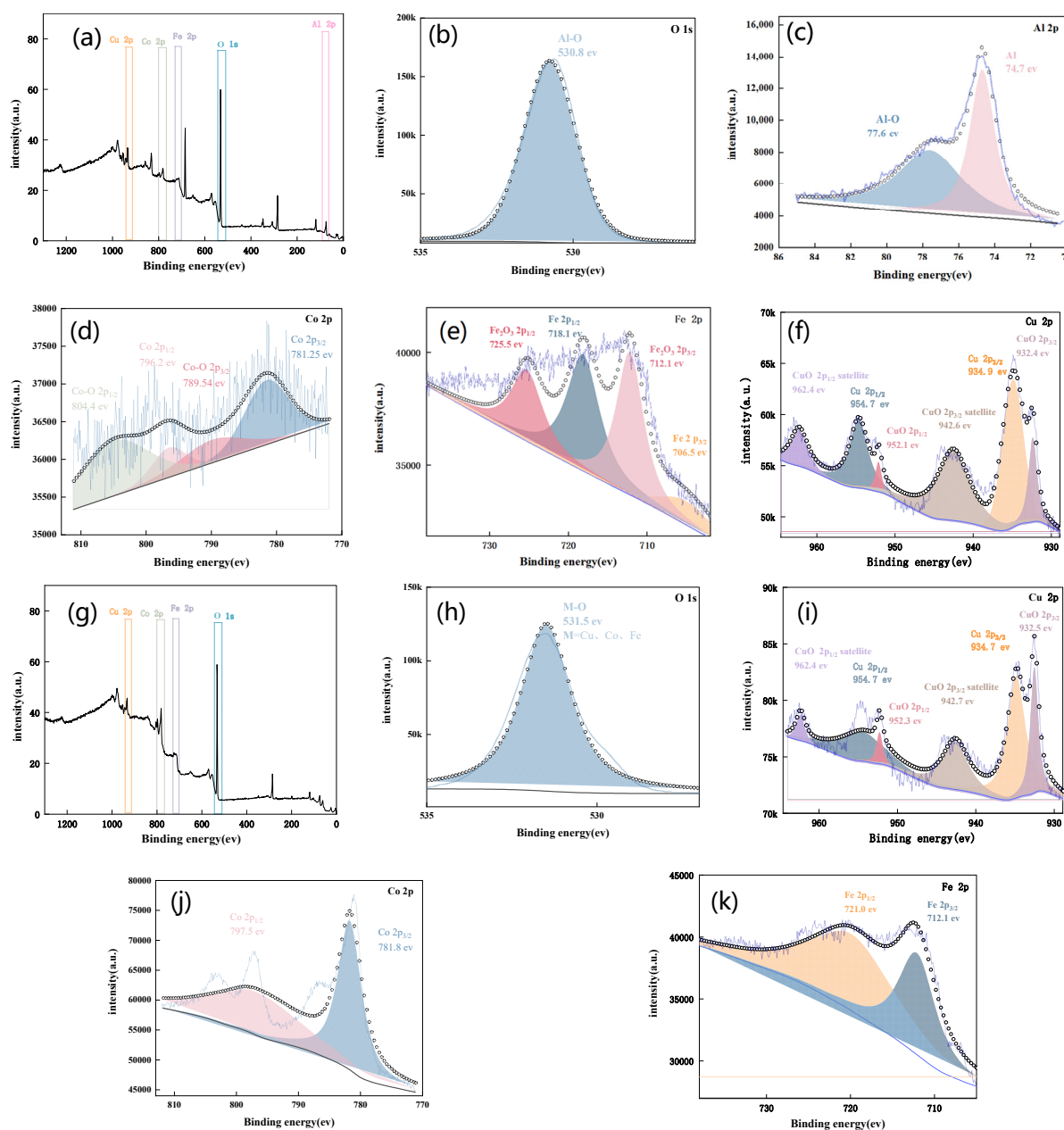


Figure 6. XPS spectra of samples: (a–f) $[n\text{Cu}+n\text{Co}+n\text{Fe}]/\mu\text{Al}$; (g–k) $[n\text{Cu}+n\text{Co}+n\text{Fe}]/\mu\text{Al}$ shell.

2.2. Thermal Analyses

To elucidate the mechanisms underlying thermal oxidation, comparative thermogravimetric-differential scanning calorimetry (TG-DSC) analyses were conducted in an oxygen-rich environment for both the $[n\text{Cu}+n\text{Co}+n\text{Fe}]/\mu\text{Al}$ composite and pure μAl , which served as a control (Figure 7). In the case of pure μAl (Figure 7a), the differential scanning calorimetry (DSC) curve reveals three principal thermal phenomena. A slight exothermic peak emerging at approximately 575 °C is indicative of the transformation of amorphous surface alumina into $\gamma\text{-Al}_2\text{O}_3$. This is succeeded by an acute endothermic peak near 660 °C, signifying the melting of aluminum. Ultimately, a pronounced exothermic peak is observed at 1007 °C, which is linked to the rapid oxidation of molten aluminum following the

disruption of the oxide layer, resulting in the liberation of 137 J/g of thermal energy. In sharp contrast, the [nCu+nCo+nFe]/ μ Al composite demonstrates a significantly intensified and consolidated oxidation process (Figure 7b). The two distinct exothermic events observed in pure aluminum coalesce into a singular robust exothermic peak centered at 913 °C. The heat release associated with this peak attains a remarkable 3853 J/g, approximately 28 times greater than that of pure aluminum. In parallel, the thermogravimetric (TG) curve reveals an almost vertical mass gain step within an exceptionally narrow temperature range of 900–916 °C, indicative of an extraordinarily rapid and complete oxidation reaction. This remarkable enhancement can be attributed to the oxygen transport channels established by the Cu, Co, and Fe nanoparticles. These channels likely facilitate the direct and rapid supply of oxygen to the aluminum core, bypassing the barrier effect of the native alumina layer. Consequently, the oxidation of aluminum is no longer limited by the slow phase transformation and fracture of the oxide film, leading to a highly synchronized and efficient combustion-like reaction.

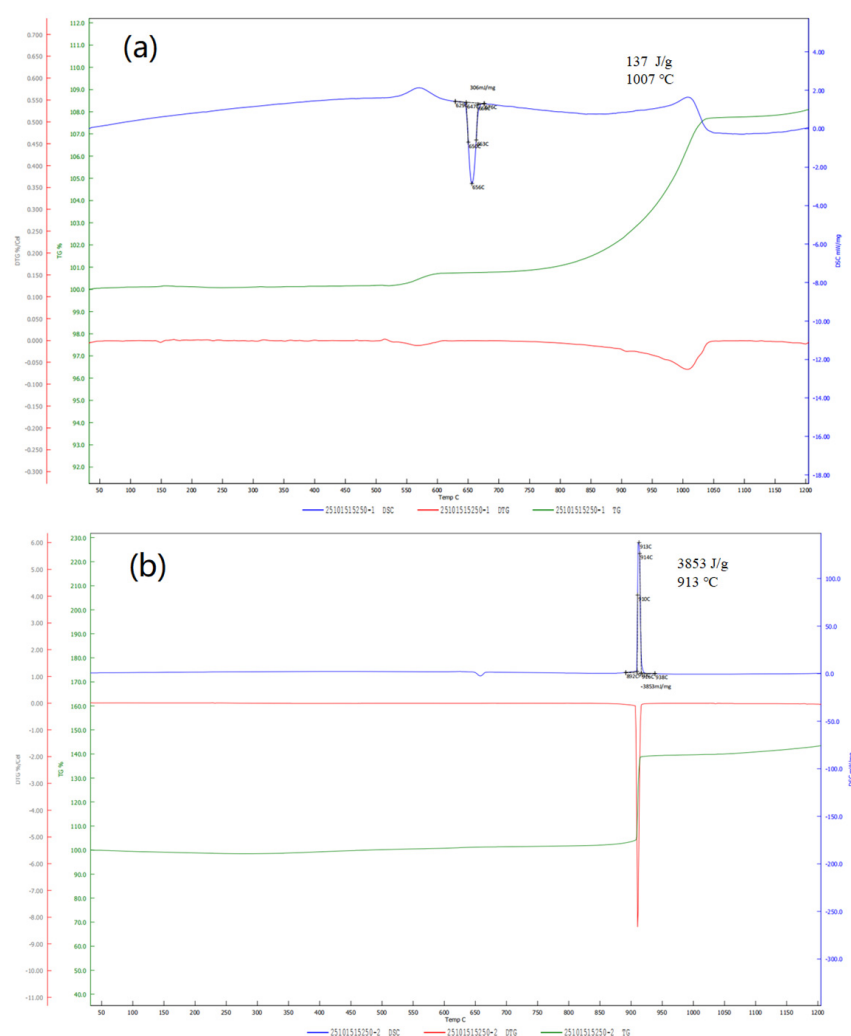


Figure 7. TG-DSC of samples conducted in oxygen atmosphere with heating rate of 10 °C/min: (a) raw μ Al; (b) [nCu+nCo+nFe]/ μ Al.

To examine the impact of copper (Cu), cobalt (Co), and iron (Fe) on the thermal decomposition behavior of aluminum-based energetic microcells, samples were subjected to analysis via differential scanning calorimetry (DSC), with the findings illustrated in Figure 8. The differential scanning calorimetry (DSC) results (Figure 8) indicate that the incorporation of micro-sized aluminum (μ Al) into the original ammonium perchlorate/hexogen

(AP/RDX) mixture modestly decreased the low-temperature decomposition peak temperature (T_p) of ammonium perchlorate from 359.5 °C to 358.2 °C. In stark contrast, the introduction of the [nCu+nCo+nFe]/ μ Al composite elicited a more pronounced effect: the low-temperature decomposition peak of ammonium perchlorate was markedly advanced to 337.1 °C. Moreover, the signature high-temperature decomposition peak observed at approximately 420 °C was entirely obliterated, resulting in the convergence of both thermal events into a singular, intensified exothermic peak. The phenomenon of peak merging observed in this study elucidates that the [nCu+nCo+nFe]/ μ Al composite not only lowers the initial decomposition temperature of ammonium perchlorate (AP) but also alters its decomposition pathway. This composite appears to serve as an efficient catalyst for the subsequent oxidation reactions of intermediate products, such as ammonia (NH₃) and perchloric acid (HClO₄), generated during the low-temperature decomposition of AP. This catalytic activity compels the two exothermic stages of the original kinetic decoupling to become closely coupled and occur in concert. Thus, the optimization of the reaction pathway emerges as a crucial factor in achieving its remarkable catalytic efficacy. In conjunction with the extant literature, the remarkable efficacy of this system can be ascribed to several key factors. Firstly, the presence of nanoscale copper (Cu), cobalt (Co), and iron (Fe) particles endows the material with a high specific surface area and an abundance of active sites, thereby significantly enhancing its intrinsic catalytic activity [31]. Secondly, the porous architecture of the composite shell facilitates superior heat and mass transfer dynamics, thereby promoting the influx of external oxygen to the aluminum core and bolstering the diffusion of reaction heat. Notably, the Cu–Co–Fe composite system exhibits a pronounced ability to catalyze the decomposition of oxidants at reduced temperatures.

Combining existing research, the reasons for its existence are analyzed as follows: Firstly, nano-scale Cu, Co, and Fe particles present an elevated specific surface area, which augments the availability of active sites and consequently manifests a marked enhancement in catalytic activity [31]. Secondly, the shell layer of the [nCu+nCo+nFe]/ μ Al composite material is characterized by a porous architecture, thereby providing significantly improved thermal reaction performance. This phenomenon enhances the ingress of external oxygen into the core, facilitating its reactive interactions with the aluminum substrate and thereby expediting the overall reaction. Notably, the Cu–Co–Fe complex catalyzes the profound decomposition of the oxidant even at low temperatures. Thermodynamic parameters were meticulously derived using Equations (1)–(5) [32] to elucidate its kinetic and thermodynamic characteristics. The results presented in Figure 8j–l exhibit robust linear correlations between $1/T_p$ and $\ln(\beta/T_p^2)$ across all samples, signifying high precision in the derivation of activation energy and pre-exponential factor through differential scanning calorimetry (DSC).

$$\ln \frac{\beta}{T_p^2} = \ln \frac{R \cdot A_K}{E_K} - \frac{E_K}{R} \cdot \frac{1}{T_p} \quad (1)$$

$$k = A_K \cdot \exp\left(-\frac{E_K}{T_p \cdot R}\right) \quad (2)$$

$$A \exp\left(-\frac{E_X}{RT_p}\right) = \frac{K_B T_p}{h} \exp\left(-\frac{\Delta G^\ddagger}{RT_p}\right) \quad (3)$$

$$\Delta H^\ddagger = E_K - RT_p \quad (4)$$

$$\Delta G^\ddagger = \Delta H^\ddagger - T_p \Delta S^\ddagger \quad (5)$$

where T_p is the peak temperature in the DSC trace with a heating rate of 10 °C min^{−1}; K_B and h are the Boltzmann ($K_B = 1.381 \times 10^{-23}$ J/K) and Planck constants ($h = 6.626 \times 10^{-34}$ J/s),

respectively; β is the heating rate; T_{ei} is the extrapolated onset temperature at a specific heating rate; T_{eo} is the extrapolated onset temperature at the heating rate closest to zero; Q is the theoretical decomposition heat per mole of explosive; M is the theoretical mass per mole of explosive; and E_K and A_K are the activation energy and preexponential factor calculated by the Kissinger equation, respectively.

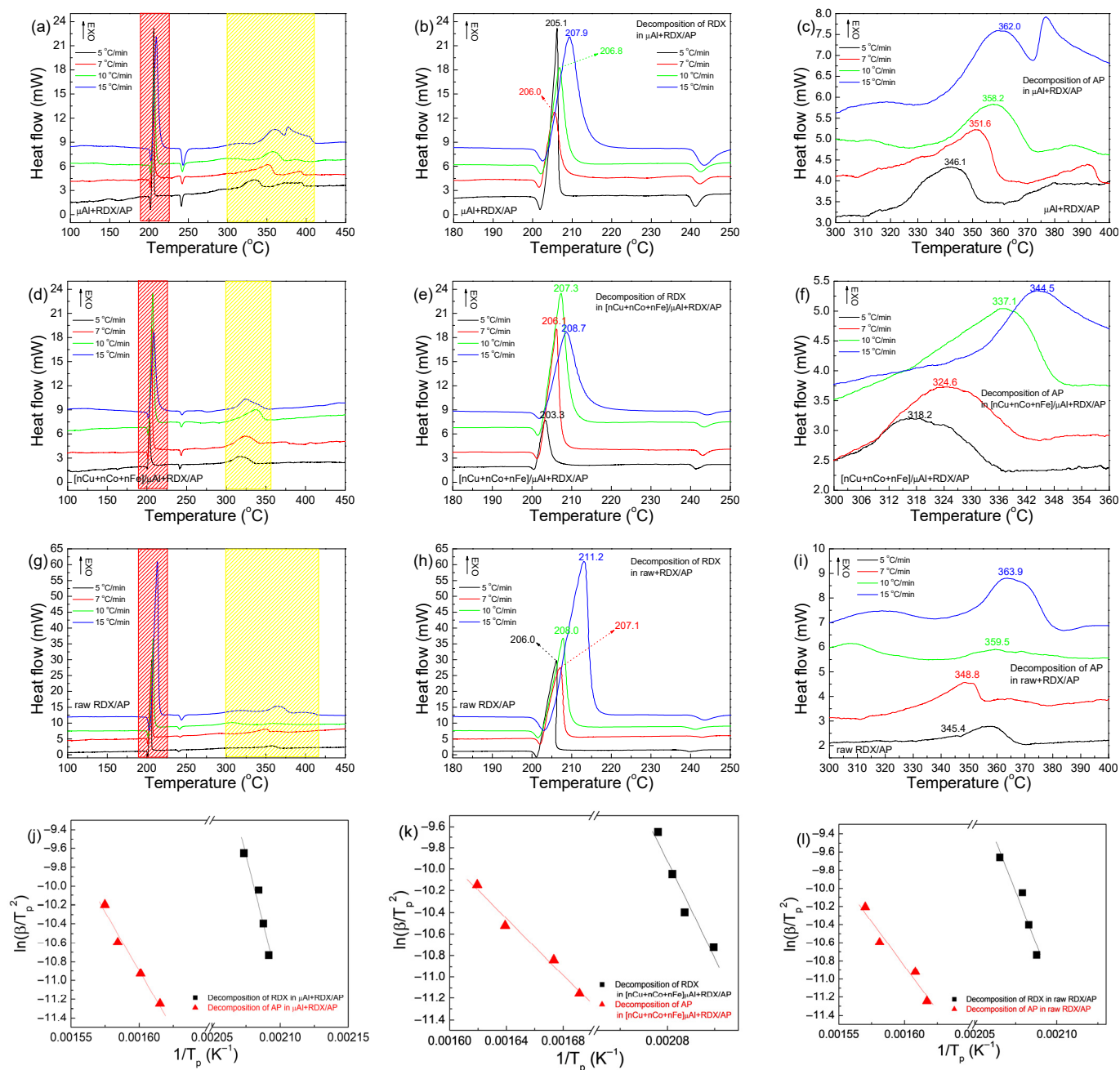


Figure 8. DSC curves of samples: (a–c) $\mu\text{Al}+\text{AP}/\text{RDX}$; (d–f) $[\text{nCu}+\text{nCo}+\text{nFe}]/\mu\text{Al}+\text{AP}/\text{RDX}$; (g–i) AP/RDX ; (j–l) Kissinger Plots.

Table 1 encapsulates the pertinent kinetic and thermodynamic data, derived from the decomposition peak of ammonium perchlorate (AP). The findings reveal that the incorporation of aluminum significantly enhances the activation energy, suggesting that the oxide layer on the aluminum surface obstructs further progression of the reaction and raises the energy barrier for the process. This observation is further substantiated by the elevated value of $\ln A_K$. In contrast, the integration of $[\text{nCu}+\text{nCo}+\text{nFe}]/\mu\text{Al}$ com-

posite materials significantly diminishes the activation energy barrier associated with the reaction. This observation suggests that the composite effectively alleviates the inhibitory influence of the aluminum oxide layer on reactive activity, while the transition metals serve as catalysts for the thermal decomposition of ammonium perchlorate (AP). The parameter $\ln A_K$ denotes the reaction rate of AP thermal decomposition, with the formulation $[\text{nCu+nCo+nFe}]/\mu\text{Al+AP/RDX}$ demonstrating particularly remarkable performance, exhibiting an impressive doubling effect (1.49 times greater than that of AP/RDX alone). Both the activation enthalpy ($\Delta H^\ddagger$) and the activation free energy of $[\text{nCu+nCo+nFe}]/\mu\text{Al+AP/RDX}$ were found to be lower than those of AP/RDX, indicating a reduced requirement for external energy during the decomposition reaction, thereby further corroborating the lowered energy barrier. Collectively, these results compellingly underscore the superior catalytic efficacy of the $[\text{nCu+nCo+nFe}]/\mu\text{Al}$ composite material in facilitating the decomposition of AP/RDX.

Table 1. Data of thermodynamics, kinetics, and 5 s burst points.

Samples	T_P (°C) (10 °C/min)	Thermodynamic			Kinetics		
		$\Delta H^\ddagger$ (kJ/mol)	$\Delta G^\ddagger$ (kJ/mol)	$\Delta S^\ddagger$ (J/mol·K)	E_K (kJ/mol)	$\ln A_K$	k (s ^{−1})
$[\text{nCu+nCo+nFe}]/\mu\text{Al+AP/RDX}$	337.1	158.0	103.1	−0.090	108.2	20.35	0.376
$\mu\text{Al+AP/RDX}$	358.2	161.1	196.3	0.056	201.5	37.92	0.614
AP/RDX	359.5	162.0	157.4	−0.007	162.6	30.32	0.547

Figure 9 illustrates the thermogravimetric (TG), infrared (IR), and mass spectrometry (MS) profiles for the composite $[\text{nCu+nCo+nFe}]/\mu\text{Al+AP/RDX}$ in comparison with its counterparts $\mu\text{Al+AP/RDX}$ and AP/RDX, measured at a heating rate of 10 °C·min^{−1}. In Figure 9a, it is evident that the onset temperature for weight loss in the TG curve of $[\text{nCu+nCo+nFe}]/\mu\text{Al+AP/RDX}$ is significantly shifted to lower temperatures, indicating a reduced duration of weight loss and a steeper TG slope, which collectively suggest a marked increase in reactivity. Figure 9b,c showcase the IR and MS curves associated with $[\text{nCu+nCo+nFe}]/\mu\text{Al+AP/RDX}$. Both profiles demonstrate gas evolution within the temperature ranges of 200–250 °C and 300–400 °C, corresponding to the decomposition of RDX and AP within these intervals. Specifically, the decomposition of RDX occurs between 200 °C and 250 °C, during which $[\text{nCu+nCo+nFe}]/\mu\text{Al+AP/RDX}$ produces substantial quantities of CO₂, N₂O, CH₄, and H₂O. The notable presence of N₂O suggests that the cleavage of C–N bonds predominates during RDX decomposition, indicating that the incorporation of the $[\text{nCu+nCo+nFe}]/\mu\text{Al}$ composite modifies the reaction mechanisms, thereby enhancing the exothermic nature of the decomposition process and facilitating a greater release of heat [33]. At temperatures ranging from 300 to 400 °C, ammonium perchlorate (AP) undergoes decomposition, producing a substantial quantity of carbon dioxide (CO₂), nitrous oxide (N₂O), hydrogen chloride (HCl), and water (H₂O). Notably, the decomposition products of AP are characterized by a significant presence of N₂O in the absence of molecular oxygen (O₂). As illustrated in Figure 8, there is a pronounced shift in the high-temperature decomposition peak towards lower temperatures, culminating in its convergence with the low-temperature peak. This phenomenon is further corroborated in Figure 9d, which lends support to the assertion that the $[\text{nCu+nCo+nFe}]/\mu\text{Al}$ composite modifies the decomposition pathway of AP. Under the influence of this composite, AP transitions to a more rapid and concentrated decomposition route, exhibiting diminished characteristic signals. In conclusion, the $[\text{nCu+nCo+nFe}]/\mu\text{Al}$ composite mate-

rial substantially optimizes the reaction pathway of RDX/AP, thus achieving remarkable catalytic efficacy.

Through thermogravimetric analysis, the inherent thermal decomposition properties were thoroughly examined, with the findings illustrated in Figure 10. The activation energy (E) was determined utilizing the methodology outlined in reference [34]. The T_{5s} values for all three samples were observed to reside within the range of 490 K to 545 K, with a reduction in the explosion delay period concomitant with the increase in temperature. Notably, the incorporation of aluminum yielded a nearly invariant T_{5s} value. The raw data curve exhibited a striking resemblance to that of AP/RDX. The addition of $[n\text{Cu}+n\text{Co}+n\text{Fe}]/\mu\text{Al}$ significantly reduced T_{5s} (by 14.38 K) and the activation energy (E) by 2.17 kJ/mol, indicating its excellent thermal properties. This phenomenon is due to the efficient heat conduction network formed by transition metal composite particles. This effect is attributed to the effective thermal conduction network established by the composite particles of transition metals. When subjected to external thermal stimuli, the heat diffusion into the RDX/AP matrix accelerates, engendering rapid localized temperature spikes that facilitate decomposition. This observation underscores the capacity of the $[n\text{Cu}+n\text{Co}+n\text{Fe}]/\mu\text{Al}+\text{AP}/\text{RDX}$ system to initiate swift combustion reactions with diminished external energy requirements. Moreover, it suggests that the $[n\text{Cu}+n\text{Co}+n\text{Fe}]/\mu\text{Al}$ composite acts as a catalyst for the decomposition of RDX/AP.

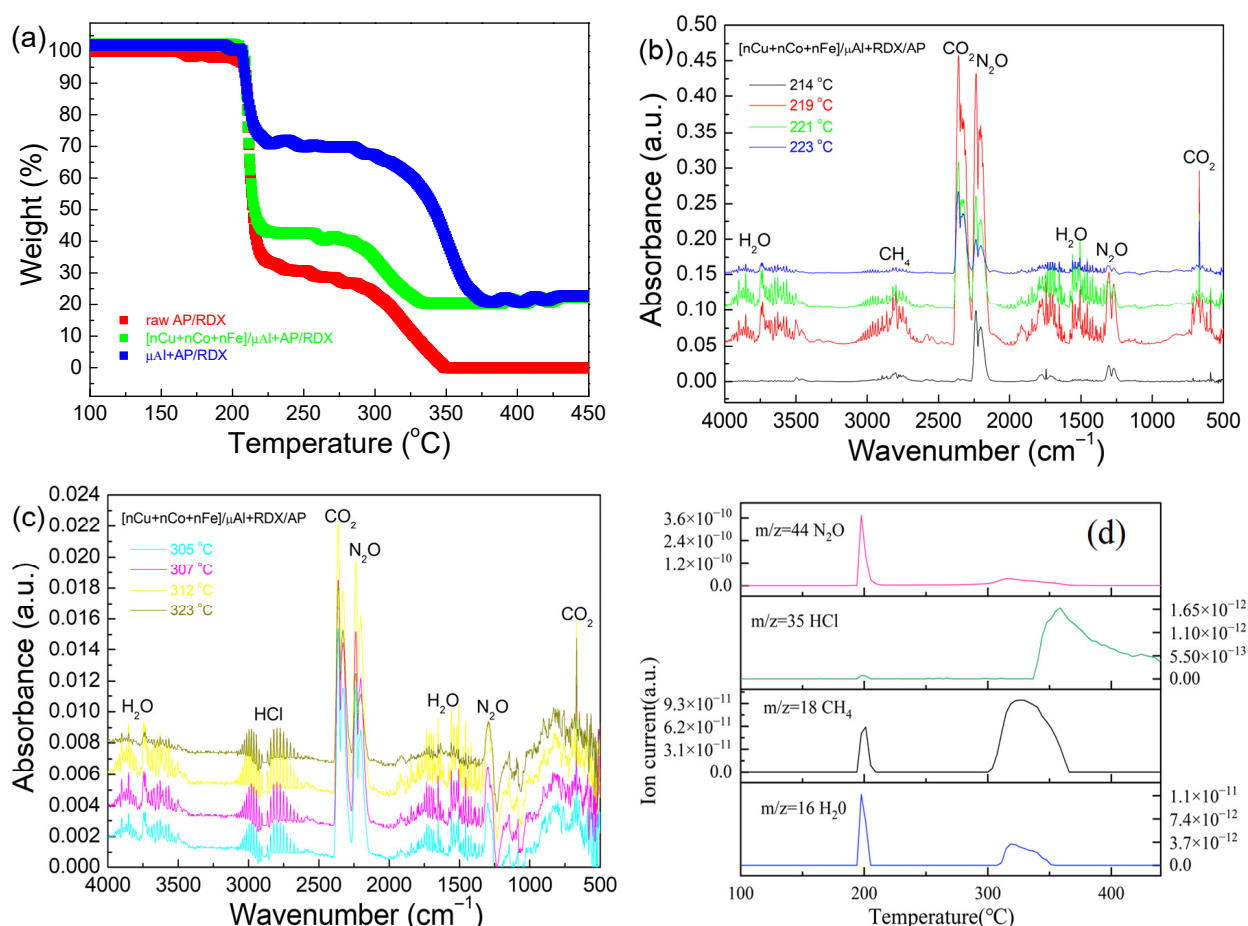


Figure 9. TG-IR-MS united analyses of samples: (a) TG curves; (b,c) IR spectra of decomposition products of $[n\text{Cu}+n\text{Co}+n\text{Fe}]/\mu\text{Al}+\text{AP}/\text{RDX}$; (d) MS spectra of decomposition products of $[n\text{Cu}+n\text{Co}+n\text{Fe}]/\mu\text{Al}+\text{AP}/\text{RDX}$.

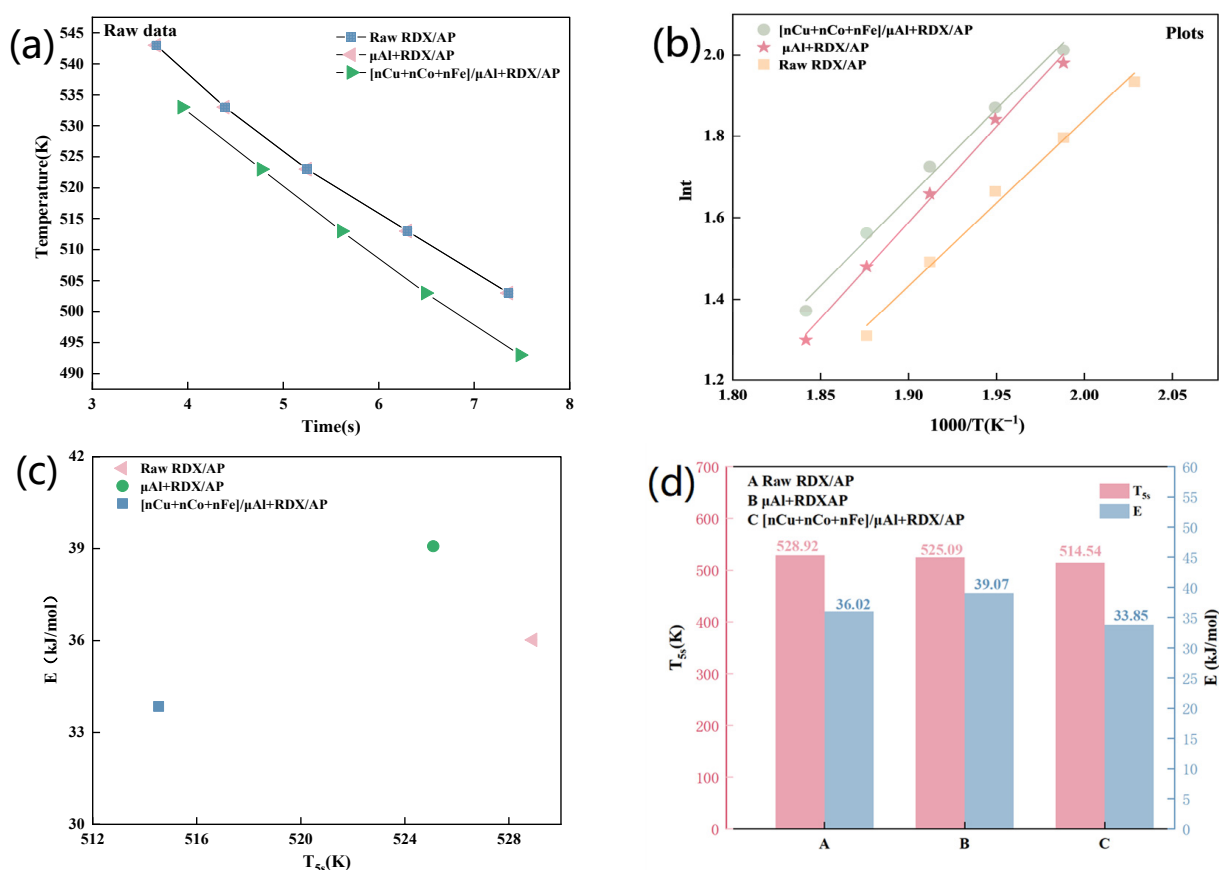


Figure 10. Thermal sensitivity of the samples: (a) the raw data; (b) the plots; (c) relationship of T_{5s} to E ; (d) the comparison of E and T_{5s} .

2.3. Combustion Performance

2.3.1. Combustion in a Closed Bomb

To investigate the combustion characteristics of the samples, a closed bomb, a pressure sensor, and a high-speed camera were employed to meticulously observe the initiation, growth, and decline of combustion while concurrently capturing pressure fluctuations in real time. The findings are illustrated in Figure 11. The AP/RDX composite exhibited the lowest flame intensity, characterized by an elliptical morphology at peak intensity. Upon the introduction of aluminum powder, there was a marked enhancement in flame intensity, accompanied by the spattering of metallic particles and a substantial increase in luminosity. The incorporation of $[\text{nCu}+\text{nCo}+\text{nFe}]/\mu\text{Al}$ further amplified both the brightness and intensity of the combustion process. Notably, during the phase of flame growth, the expulsion of metallic particles, as evidenced at 300 ms in Figure 11b, was absent, signifying a more complete combustion process. Upon attaining peak intensity, the ejection of metallic particles was indeed observed, albeit at a notably earlier juncture, thereby considerably reducing the overall duration of combustion. This finding illustrates that the composite $[\text{nCu}+\text{nCo}+\text{nFe}]/\mu\text{Al}$ significantly enhances the combustion performance of RDX/AP formulations. As depicted in Figure 11d, the pressure profiles recorded during combustion of the samples reveal a two-stage pressure characteristic for both AP/RDX and $\mu\text{Al}+\text{AP}/\text{RDX}$. Furthermore, Figure 11e indicates that the combustion pressure of the sample supplemented with aluminum experienced an increase, doubling (and indeed, escalating threefold), while the heightened rate of pressure rise suggests a markedly more vigorous reaction. Most notably, the $[\text{nCu}+\text{nCo}+\text{nFe}]/\mu\text{Al}$ composite elicited a remarkable enhancement in pressure. The peak pressure generated by the $[\text{nCu}+\text{nCo}+\text{nFe}]/\mu\text{Al}+\text{AP}/\text{RDX}$ composite was approximately 17 times greater than that of the baseline AP/RDX formulation and nearly

five times surpassing that of the $\mu\text{Al}+\text{AP}/\text{RDX}$ combination (Figure 11d). Moreover, the pressure profile reveals a single-stage ascent, with the time required to attain this maximum pressure (t_{max}) being significantly shorter compared to the other two formulations (Figure 11d,e). These quantitative findings—amplified P_{max} and abbreviated t_{max} —clearly demonstrate that the $[\text{nCu}+\text{nCo}+\text{nFe}]/\mu\text{Al}$ composite confers both an elevated combustion pressure and an accelerated burning rate to the AP/RDX matrix. This synergistic effect serves as a definitive indicator of markedly improved energy release kinetics, a crucial performance parameter for advanced solid propellants.

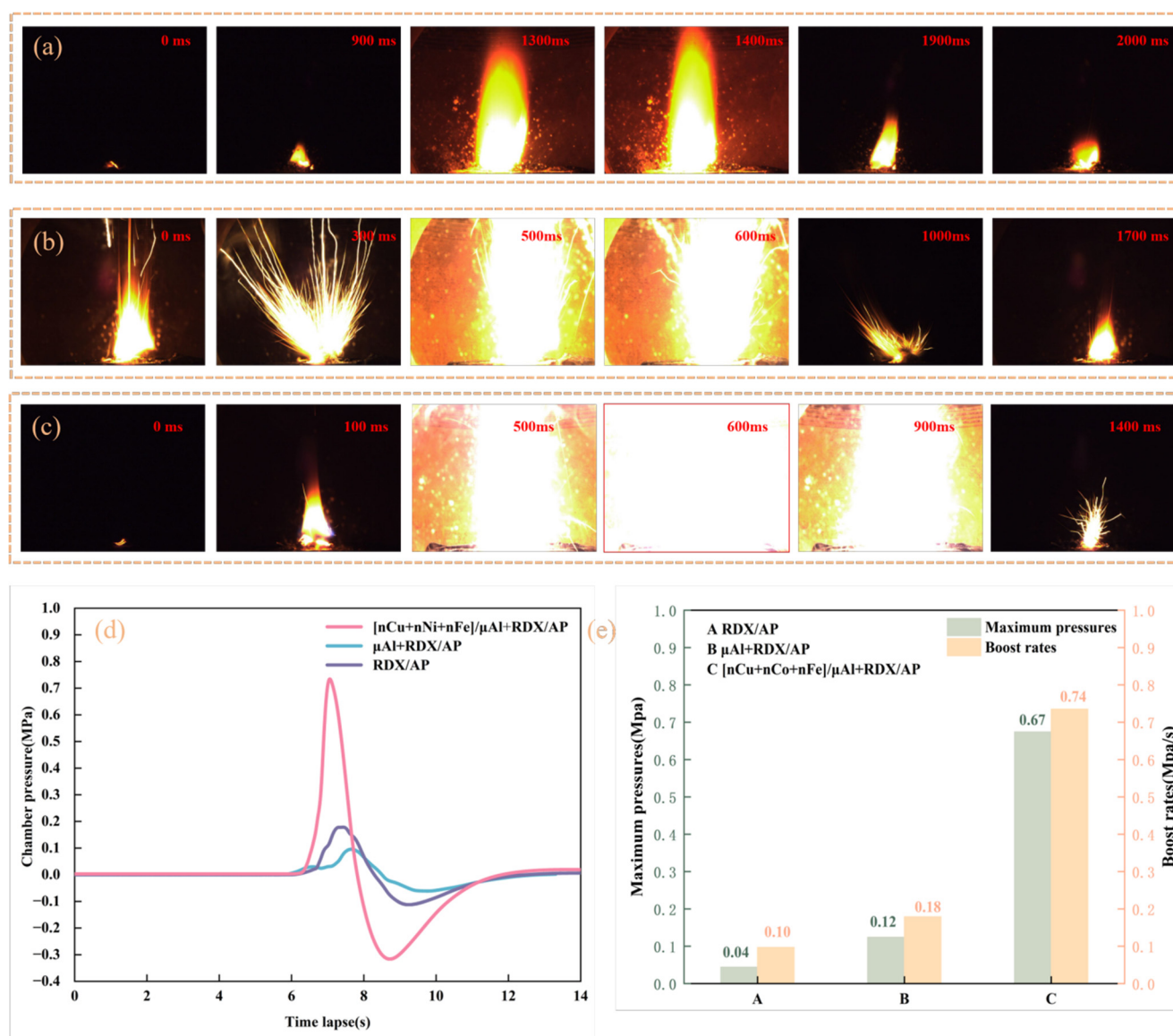


Figure 11. Results of constant volume combustion: (a) flame images of raw AP/RDX; (b) flame images of $\mu\text{Al}+\text{AP}/\text{RDX}$; (c) flame images of $[\text{nCu}+\text{nCo}+\text{nFe}]/\mu\text{Al}+\text{AP}/\text{RDX}$; (d) pressure curve images; (e) max pressures and boost rates.

2.3.2. Combustion in the Air

Utilizing an infrared thermal imager, we meticulously documented the combustion characteristics of the samples subjected to atmospheric pressure, including both the duration of combustion and the resultant flame temperature. The findings are illustrated in Figure 12. Notably, the flame temperature of AP/RDX measured a modest $1712.8\text{ }^{\circ}\text{C}$, whereas that of $\mu\text{Al}+\text{AP}/\text{RDX}$ attained an impressive $1900.2\text{ }^{\circ}\text{C}$. The flame temperature

of $[\text{nCu}+\text{nCo}+\text{nFe}]/\mu\text{Al}+\text{AP}/\text{RDX}$ achieved the highest value of $2205.6\text{ }^{\circ}\text{C}$, demonstrating a marked increase in combustion intensity. The integration of $[\text{nCu}+\text{nCo}+\text{nFe}]/\mu\text{Al}$ significantly elevated the height of the flame, a phenomenon accompanied by the partial spattering of metals upon attaining peak temperature, as illustrated in Figure 11. It is noteworthy that, due to the elevated ignition temperature of aluminum-attributable to its protective oxide layer-the combustion duration of $\mu\text{Al}+\text{AP}/\text{RDX}$ surpassed that of AP/RDX alone. Conversely, the inclusion of $[\text{nCu}+\text{nCo}+\text{nFe}]/\mu\text{Al}$ resulted in a marked reduction in combustion time, shortening it by approximately 0.5 s in comparison to AP/RDX . In examining the decomposition dynamics of RDX/AP , the augmented flame intensity is attributable to the ratio of $[\text{nCu}+\text{nCo}+\text{nFe}]/\mu\text{Al}$, which not only facilitates the reactivity of aluminum but also acts as a catalyst in the decomposition of RDX/AP , resulting in a significant enhancement in combustion performance. The effective transport pathways established by copper, cobalt, and iron substantially optimize the oxidation processes of aluminum, thereby amplifying its reactivity and markedly improving the combustion efficacy of high-energy additive/oxidizer components. This development paves the way for the extensive utilization of $[\text{nCu}+\text{nCo}+\text{nFe}]/\mu\text{Al}$ composites in the formulation of composite solid propellants.

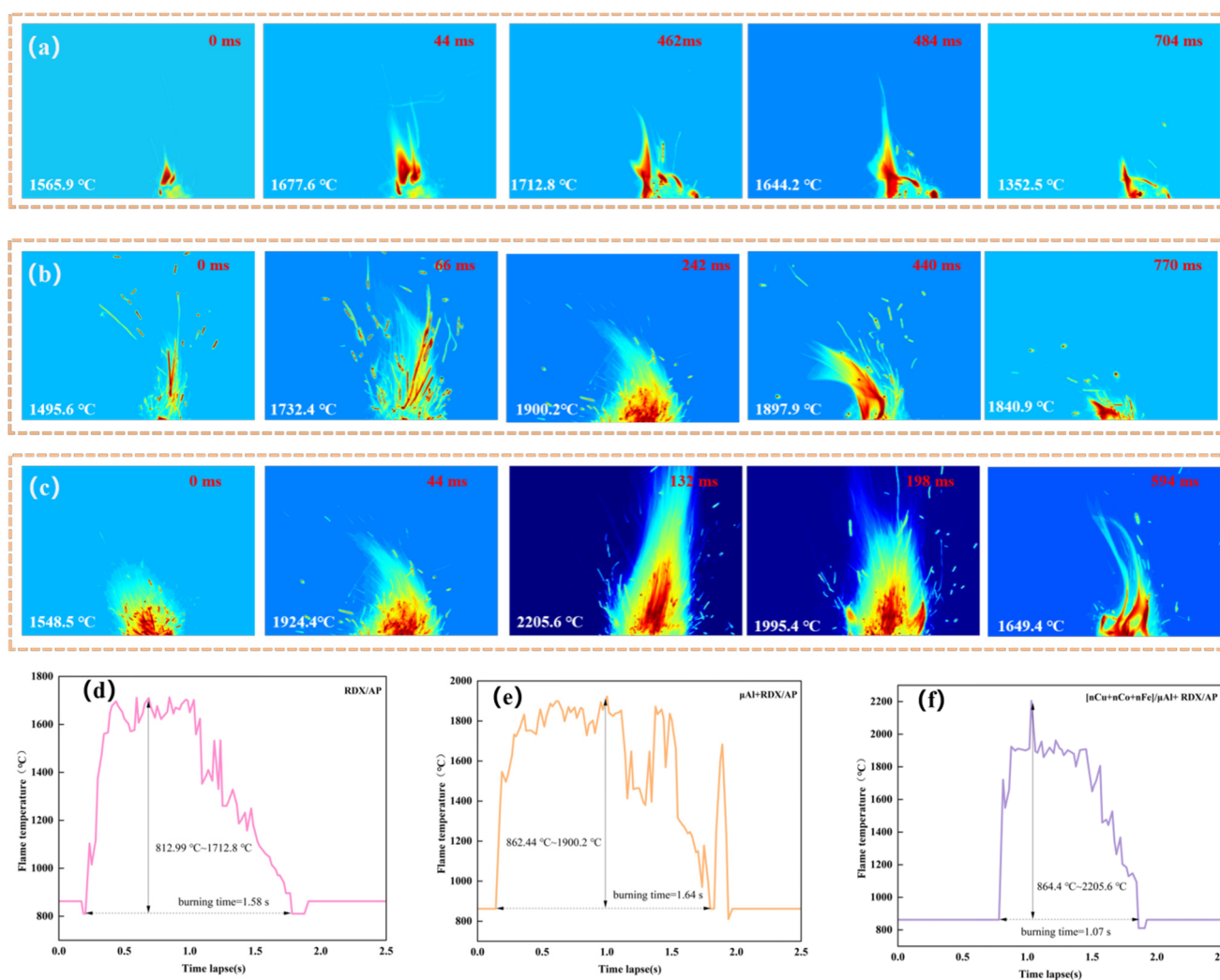


Figure 12. Thermal infrared images of (a) RDX/AP , (b) $\mu\text{Al}+\text{ADN}/\text{AP}$, and (c) $[\text{nCu}+\text{nCo}+\text{nFe}]/\mu\text{Al}+\text{ADN}/\text{AP}$; (d) for RDX/AP ; (e) for $\mu\text{Al}+\text{RDX}/\text{AP}$; (f) for $[\text{nCu}+\text{nCo}+\text{nFe}]/\mu\text{Al}+\text{RDX}/\text{AP}$.

The results of the flame spectral analysis conducted using the OPT2000 apparatus (Beijing Normal University Optoelectronic Technology Co., Ltd., Beijing, China) are illustrated in Figure 13 and delineated in Table 2. The color coordinates for the RDX/AP mixture are situated within the orange-red spectrum ($x = 0.4298, y = 0.3498$). Its spectrum displays an interference peak associated with Na^+ at 589 nm, alongside a prominent peak at 620 nm, which can be attributed to carbon-containing intermediate products generated during the incomplete combustion of RDX. Conversely, the color coordinates for the $\mu\text{Al} + \text{RDX}/\text{AP}$ mixture fall within the yellow-green spectrum ($x = 0.4298, y = 0.3498$), a phenomenon linked to the presence of Al-O. The color coordinates for the $[\text{nCu} + \text{nCo} + \text{nFe}]/\mu\text{Al} + \text{RDX}/\text{AP}$ mixture occupy the region of white light, a result of the exceedingly high combustion intensity which causes a vigorous mixing of light, ultimately resulting in a white appearance. Notably, the positions of the spectral peaks in both analyses show broad similarities. Furthermore, the luminous intensity of the $[\text{nCu} + \text{nCo} + \text{nFe}]/\mu\text{Al} + \text{RDX}/\text{AP}$ mixture markedly exceeds that of both the $\mu\text{Al} + \text{RDX}/\text{AP}$ and the RDX/AP mixtures.

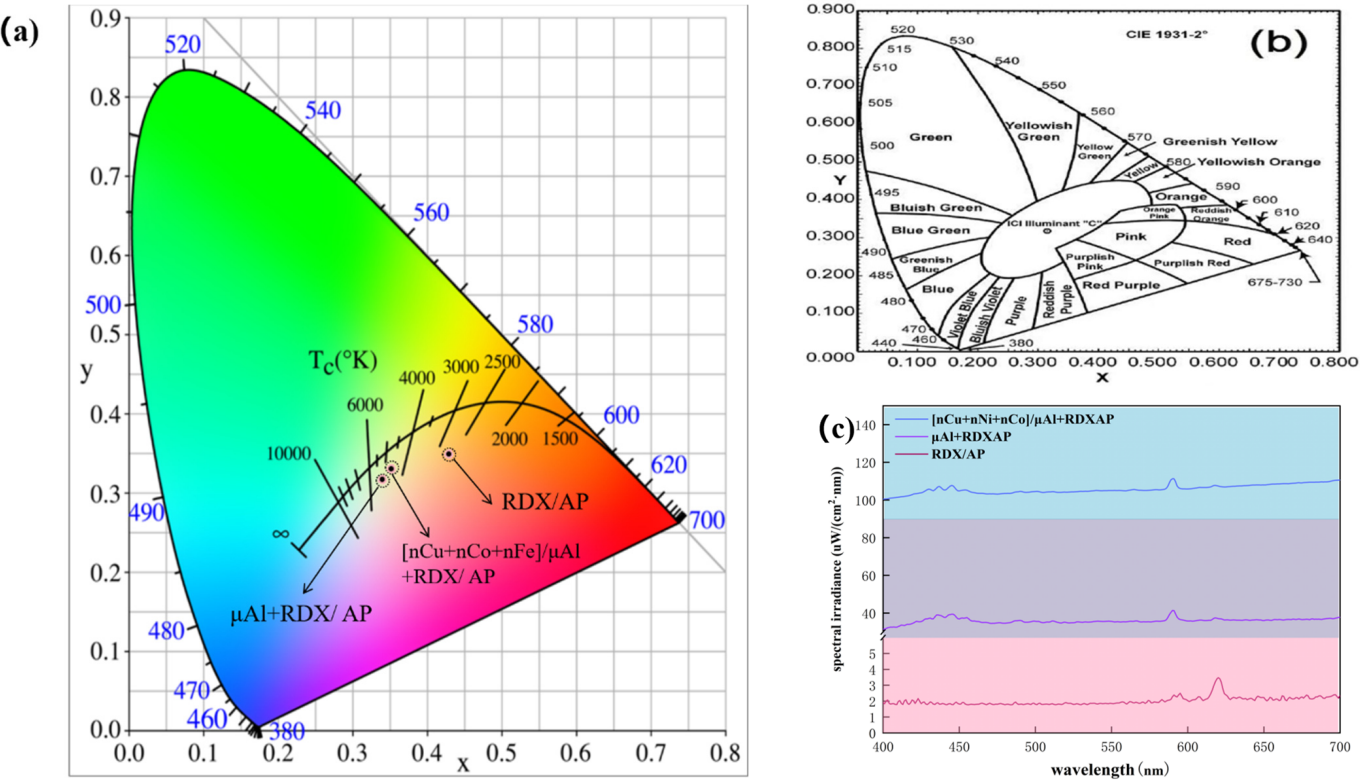


Figure 13. (a) color coordinates; (b) CIE1931 chromaticity diagram; (c) spectra.

Table 2. Testing results of color pyrotechnics.

Samples	Chromatic Coordinates		BT/s	DW/nm	SP/%	LI/cd	LE /cd·s·g ^{−1}	Color Category
	x	y						
[nCu+nCo+nFe]/μAl+AP/RDX	0.3517	0.3303	1.07	675	4.6	1069.086	3813.07	white
μAl+AP/RDX	0.3405	0.3171	1.64	525	3.3	816.917	4465.81	yellow-green
AP/RDX	0.4298	0.3498	1.58	598	33.9	58.755	451.643	orange-red

BT is the burning time; DW is the dominant wavelength; SP is the spectral purity; LI is the light intensity; LE is the luminous efficiency.

Thermodynamic simulations of combustion conducted using REAL 2.0 software (as summarized in Table 3) reveal that the combustion enthalpy ($\Delta H_{C,cal}$) for the RDX/AP system is $-5316.8 \text{ kJ}\cdot\text{kg}^{-1}$. The incorporation of μAl results in an increase in this enthalpy value to $-6785.3 \text{ kJ}\cdot\text{kg}^{-1}$, attributable to the exothermic reaction associated with aluminum oxidation. Conversely, the composite system, presenting an enthalpy of $-6356.5 \text{ kJ}\cdot\text{kg}^{-1}$, demonstrates an endothermic oxidation process involving the transition metal component. The experimentally determined maximum temperature, denoted as $T_{TOP,exp}$, was recorded under open atmospheric conditions at standard pressure. The predicted maximum combustion temperature, $T_{ad,cal}$ derived from the REAL 2.0 simulation, demonstrates a remarkable concordance with the empirical data, thereby affirming the integrity of the experimental findings. The systematic discrepancy observed between adiabatic flame temperatures and experimental results can be attributed to the influence of hydrogen content in the oxidant, which affects the enthalpy of compound formation [35]. An excess of hydrogen diminishes the enthalpy of the products and the heat released during combustion, ultimately resulting in incomplete metal combustion. Figure 14 illustrates the anticipated combustion products along with their respective molar fractions for the three samples analyzed. In this context, N_2 and H_2O emerge as the predominant sources of thrust. Notably, the combustion of RDX/AP yields only 52% N_2 and H_2O , while the composite system generates 57.8% N_2 and H_2O , thereby providing a significant enhancement in specific impulse.

Table 3. Thermodynamic data of the combustion of samples at atmospheric pressure.

Samples	$T_{TOP,exp}$ ($^{\circ}\text{C}$)	$T_{ad,cal}$ ($^{\circ}\text{C}$)	$H_{R,cal}$ (kJ/kg)	$H_{P,cal}$ (kJ/kg)	$\Delta H_{C,cal}$ (kJ/kg)
[nCu+nCo+nFe]/ μAl +AP/RDX	2205.6	3096.6	−1166.7	−7523.2	−6356.5
μAl +AP/RDX	1900.2	2716.7	−1325.8	−8111.1	−6785.3
AP/RDX	1712.8	2648.7	−1395.6	−6712.4	−5316.8

Note: In Table 3, $T_{TOP,exp}$ represents the highest flame temperatures measured from the combustion of the sample at $P_C = 1 \text{ atm}$; $T_{ad,cal}$ represents the adiabatic flame temperature calculated using REAL2.0 at $P_C = 1 \text{ atm}$ and $\Delta H = 0 \text{ kJ/kg}$; $H_{R,cal}$ represents the total enthalpy of the sample before combustion calculated using REAL2.0 at $P_C = 1 \text{ atm}$ and $T_0 = 298 \text{ K}$; $H_{P,cal}$ represents the total enthalpy of the combustion products of the sample calculated using REAL2.0 at $P_C = 1 \text{ atm}$ and $T_0 = 298 \text{ K}$; and $\Delta H_{C,cal}$ represents the enthalpy change (total heat release) of the sample during combustion calculated using REAL2.0 at $P_C = 1 \text{ atm}$ and $T_0 = 298 \text{ K}$.

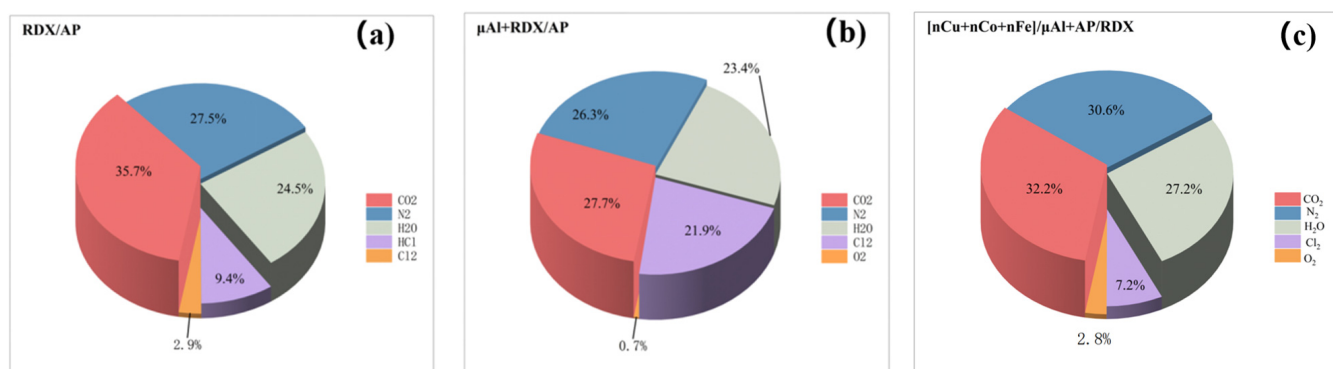


Figure 14. Mole ratio of sample combustion: (a) [nCu+nCo+nFe]/ μAl +AP/RDX; (b) μAl +AP/RDX; (c) AP/RDX.

To investigate the calorific values of the three samples, measurements were conducted using an automatic calorimeter under 3 MPa pure oxygen conditions (as shown in Figure 15). The combustion heat of [nCu + nCo + nFe]/ μAl + RDX/AP was $26,476.0 \text{ kJ/kg}$, significantly exceeding that of μAl + RDX/AP ($9441.3 \text{ kJ}\cdot\text{kg}^{-1}$) and RDX/AP ($7429.1 \text{ kJ}\cdot\text{kg}^{-1}$). This represents a remarkable enhancement, demonstrating the exceptional energy performance of [nCu+nCo+nFe]/ μAl +RDX/AP.

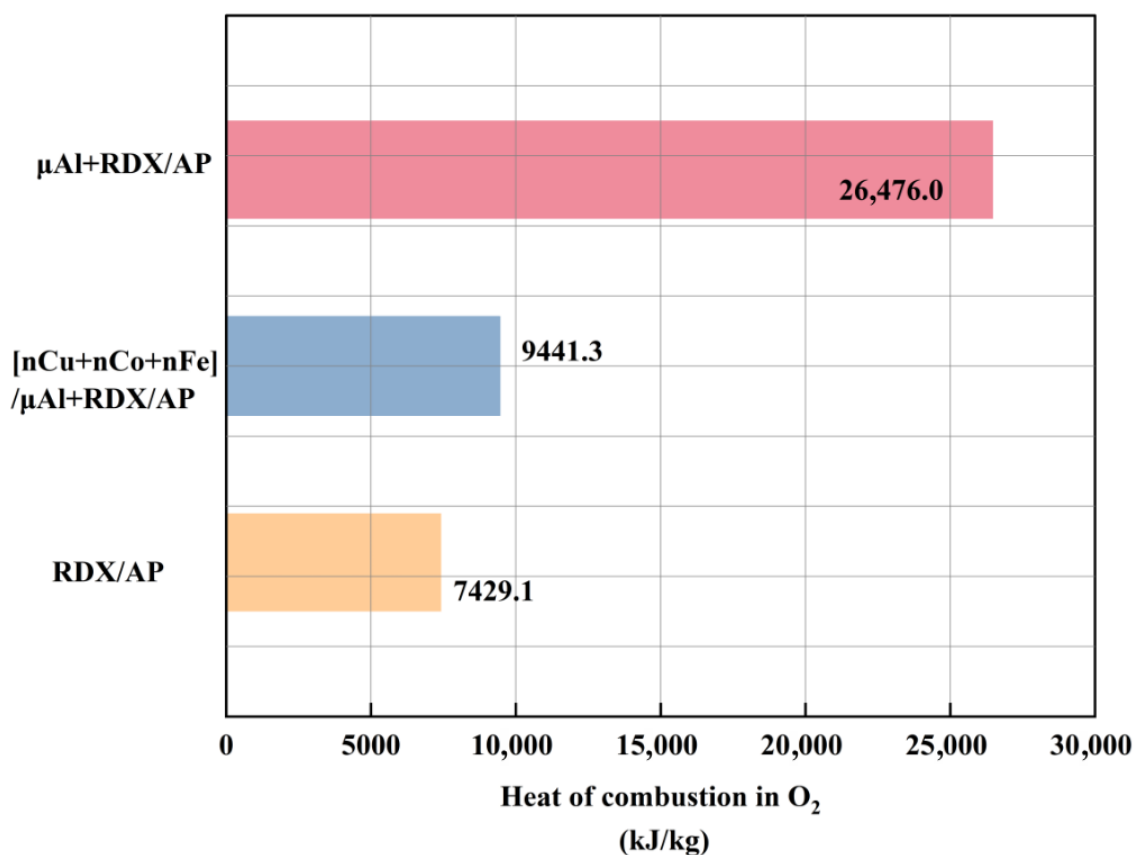


Figure 15. Combustion heat release diagram.

Drawing upon an analysis of the previously referenced experimental findings, we propose a plausible reaction mechanism for the composite system $[\text{nCu}+\text{nNi}+\text{nCo}]/\mu\text{Al}+\text{ADN}/\text{AP}$ under thermal stimulation, as illustrated in Figure 16. In the case of the $[\text{nCu}+\text{nNi}+\text{nFe}]/\mu\text{Al}+\text{RDX}/\text{AP}$ composite material, the metallic nanoclusters of Co, Cu, and Fe exhibit commendable dispersion across the metallic surface. This advantageous phenomenon consequently enhances the uniformity within the aluminum-core composite, effectively diminishing particle agglomeration. A pivotal aspect of the decomposition process of AP/RDX is the transfer of electrons to O_2 , leading to the formation of superoxide anions, O_2^- . It is noteworthy that Co, Cu, and Fe share analogous properties [36], each demonstrating the capability to facilitate electron transfer and the generation of superoxide radicals. The autocyclic aluminothermic reaction involving aluminum and the oxides of cobalt, copper, and iron significantly enhances electron transfer processes, facilitating the movement of electrons from perchlorate ions (ClO_4^-) to ammonium ions (NH_4^+) and from molecular oxygen (O_2) to the superoxide anion (O_2^-). This phenomenon promotes the subsequent decomposition of ammonia (NH_3) and the pyrolysis products of perchloric acid (HClO_4), thereby enabling expedited and more comprehensive redox reactions in the RDX/AP system that yield elevated thermal energy [37]. Importantly, the acidic byproducts generated during the decomposition of ammonium perchlorate (AP) catalyze the cleavage of the nitrogen-nitrogen (N-N) bonds in RDX, while transition metals further facilitate the breakdown of nitrogen-nitro (N- NO_2) bonds. Simultaneously, the oxidation of aluminum liberates a considerable amount of heat, which accelerates the decomposition kinetics of both RDX and ammonium perchlorate [38].

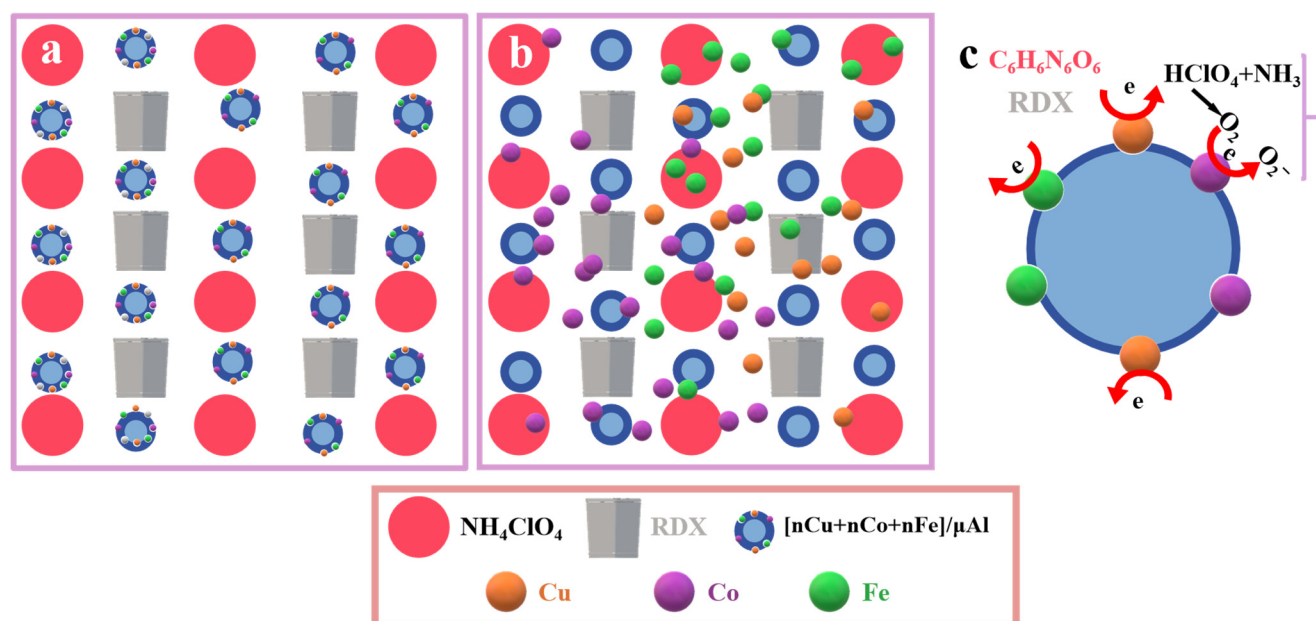


Figure 16. Diagram of the combustion process and catalytic mechanism of the sample: (a) unburned $[\text{nCu}+\text{nCo}+\text{nFe}]/\mu\text{Al}+\text{RDX}/\text{AP}$; (b) burning $[\text{nCu}+\text{nCo}+\text{nFe}]/\mu\text{Al}+\text{RDX}/\text{AP}$; (c) the speculated promotion mechanism of nCu and nCo and nFe on themolysis of RDX/AP.

3. Experimental Sections

3.1. Materials

Micron aluminum powder (μAl , $d_{50} \approx 20 \mu\text{m}$, $>98\%$), ferric chloride ($\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$, C.P.), copper chloride ($\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$, C.P.), Cobalt chloride ($\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$), tartaric acid ($\text{C}_4\text{H}_6\text{O}_6$, C.P.), EDTA-2Na ($\text{C}_{10}\text{H}_{14}\text{N}_2\text{Na}_2\text{O}_8$, C.P.), and ammonium fluoride (NH_4F , C.P.) were obtained from Sino Pharm of China (Beijing China). Ammonium perchlorate (NH_4ClO_4 , AP) and hexogen ($\text{C}_3\text{H}_6\text{N}_6\text{O}_6$, RDX) were purchased from Gansu Yinguang Chemical Factory (Lanzhou, China).

3.2. Preparation of $[\text{nCu}+\text{nCo}+\text{nFe}]/\mu\text{Al}$

The composite material $[\text{nCu}+\text{nCo}+\text{nFe}]/\mu\text{Al}$ represents a core–shell nanostructure, with nCu, nCo, nFe, and μAl signifying nano-scale copper, cobalt, iron, and micro-scale aluminum, respectively. Synthesis was performed at room temperature and atmospheric pressure, and the general preparation scheme is depicted in Figure 17a. A key challenge is the native oxide film that invariably forms on μAl particles. If this alumina layer is not removed, it prevents the underlying aluminum metal from undergoing displacement reactions with transition metal ions in solution. Therefore, the successful fabrication of the nanocomposite first requires the stripping of this passivating layer. While strong acids or bases can rapidly dissolve alumina in aqueous media, they also cause substantial etching of the metallic aluminum core. Through systematic experimentation, ammonium fluoride was identified as an optimal agent for this purpose. By carefully controlling its concentration, ammonium fluoride selectively dissolves the oxide layer while minimizing attack on the elemental aluminum. The mechanism involves fluoride ions reacting with alumina to generate soluble hexafluoroaluminate ($[\text{AlF}_6]^{3-}$) complexes. This selective dissolution not only eliminates the oxide barrier but also promotes the subsequent displacement reaction between aluminum and transition metal ions under mild alkaline conditions. The corresponding reaction mechanism is schematically presented in Figure 17b.

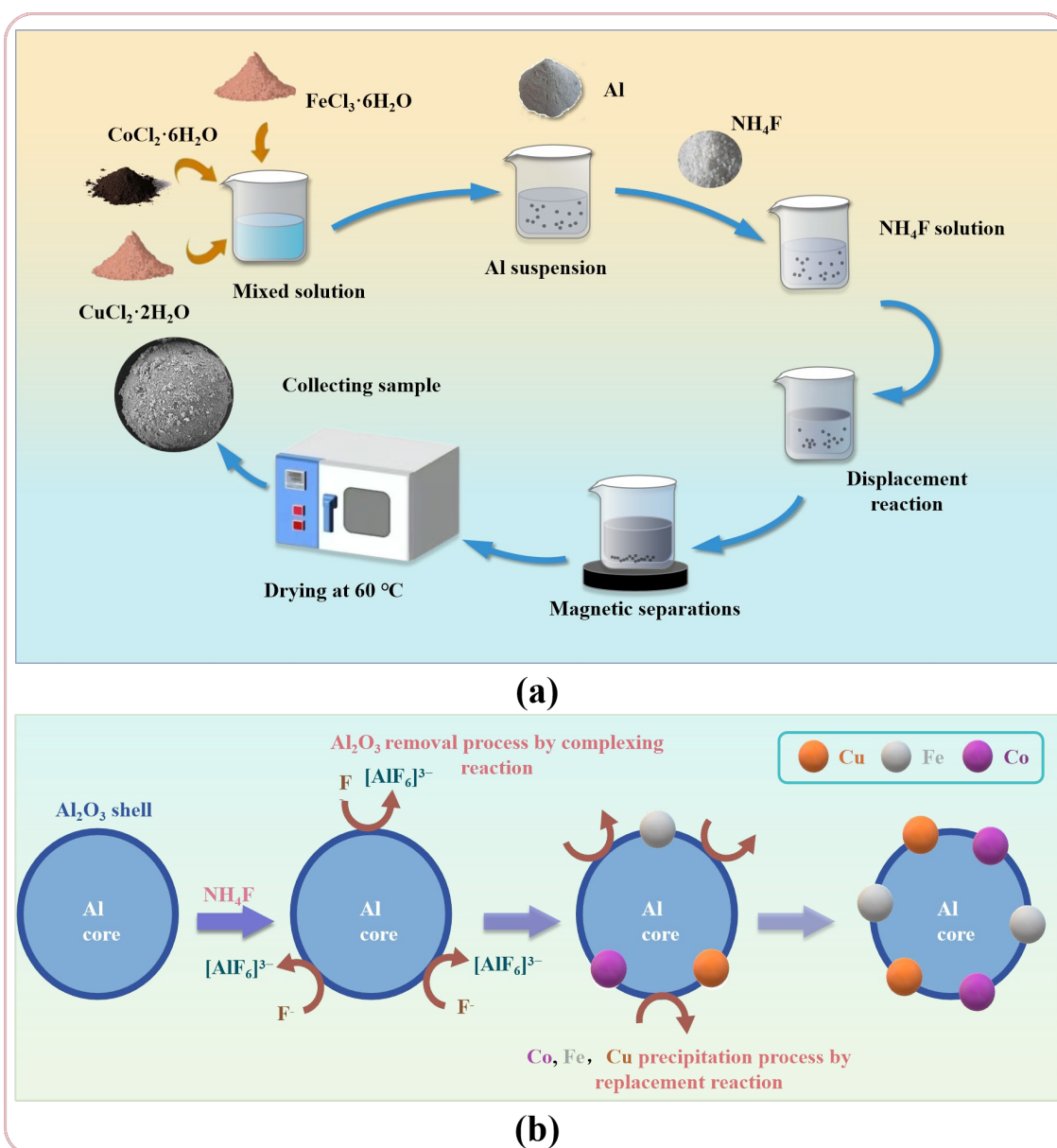


Figure 17. Preparation of the nanocomposites: (a) preparation flowchart; (b) schematic of the principle.

The $[\text{nCu}+\text{nCo}+\text{nFe}]/\mu\text{Al}$ nanocomposite was synthesized via the following procedure. Initially, 20 g of cupric chloride dihydrate ($\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$), 20 g of cobalt chloride hexahydrate ($\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$), 20 g of ferric chloride hexahydrate ($\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$), 10 g of tartaric acid, and 8 g of disodium ethylenediaminetetraacetate (EDTA-2Na) were dissolved in 1600 mL of deionized water under stirring. After complete dissolution, 8 ice cubes were introduced into the mixture. Subsequently, 150 g of micro-sized aluminum powder (μAl , median particle size $d_{50} \approx 20 \mu\text{m}$) was weighed, lightly ground, and added to the solution under continuous agitation, followed by the addition of 16 ice cubes. Finally, 53 g of ammonium fluoride (NH_4F) was dissolved separately in 100 mL of deionized water and then gradually introduced into the reaction system. The entire reaction was allowed to proceed for 5 min. The resulting product was collected by magnetic separation using a strong magnet placed at the bottom of the beaker, yielding the final nanocomposite particles, which are designated in this study as $[\text{nCu}+\text{nCo}+\text{nFe}]/\mu\text{Al}$.

3.3. Fabrication of Nanocomposite+AP/RDX

To elucidate the impact of $[\text{nCu}+\text{nCo}+\text{nFe}]/\mu\text{Al}$ on the reactivity of AP/RDX, a homogeneous mixture was prepared. This mixture comprises 18 wt.% μAl (or 18 wt.% $[\text{nCu}+\text{nCo}+\text{nFe}]/\mu\text{Al}$), 50 wt.% Ammonium perchlorate (AP), and 32 wt.% RDX. All components were then carefully blended and homogenized using a mortar and pestle to produce the final energetic composite formulation, designated as $[\text{nCu}+\text{nCo}+\text{nFe}]/\mu\text{Al}+\text{AP}/\text{RDX}$.

3.4. Characterization and Tests

The morphological characteristics of the samples were examined using a TESCAN MIRA3 (Beijing Tianyao Technology Company, Ltd., Beijing, China) scanning electron microscope (SEM). To ensure sufficient conductivity for imaging, the specimens were sputter-coated with a thin layer of gold prior to analysis. Elemental composition was determined via energy-dispersive spectroscopy (EDS) coupled to the SEM system. Crystalline phase identification was performed with an X-ray diffractometer (XRD) (Netherlands Panaco Company, Almelo, Holland) while chemical state analysis was conducted by X-ray photoelectron spectroscopy (XPS) (ULVAC JAPAN LTD, Mazaki, Japan). Magnetic properties were measured using a vibrating sample magnetometer (VSM, Nanomagnetism, Oxford, UK). Surface topography parameters, including roughness and sphericity, were evaluated with an OLS5000 laser scanning microscope (Olympus Corporation, Tokyo, Japan). The thermal behavior and exothermic properties were investigated through simultaneous thermogravimetry and differential scanning calorimetry (TG-DSC) (PerkinElmer, Inc.; Waltham, MA, USA). For the study of AP/RDX thermal decomposition, differential scanning calorimetry (DSC-100) (Shanghai Jiezhun Co., Ltd.; Shanghai, China) was employed at heating rates of 5, 7, 10, and 15 °C/min with a sample mass of 5 mg. Sensitivity to thermal stimulus was assessed according to the GJB772A-97 [39] standard, method 606.1 (5 s burst point test), wherein a quantified sample was immersed in a heated Wood's metal bath and the reaction delay time was recorded.

3.5. Combustion Performance Test

The combustion test was conducted by loading a 50 mg sample into a sealed explosion vessel at atmospheric pressure (Figure 18). The pressure evolution during combustion was monitored using a pressure transducer (Y1001E-2Mpa) (Shenzhen Youtai Technology Development Co., Ltd., Shenzhen, China), and the signal was recorded with a dynamic signal analyzer (XY-U9004) (Shenzhen Xunye Precision Technology Co., Ltd., Shenzhen, China). From these pressure-time profiles, the duration required for each sample to attain peak pressure was determined. Simultaneously, the ignition and combustion behaviors were visually captured using an industrial area-scan camera (USB3.0) to characterize the combustion progression and flame morphology. To obtain a non-invasive and efficient measurement of flame temperature, a 250 mg sample was placed on a dedicated loading stage. Based on sensor imaging principles, the temperature of the combustion flame was measured and recorded with a thermal imaging camera (HT30-300010001) (HIKMICRO, Hangzhou, China). The heat of combustion was quantified using an automatic calorimeter (ZDHW-4) (Hebi Hongyang Instrument Co., Ltd., Hebi, China). For this measurement, a 0.15 g specimen was placed in the crucible under an oxygen pressure of 2.8–3.0 MPa. The ambient temperature was maintained between 0 and 40 °C, and ignition was triggered by a 24 V voltage. The test procedure involved a 6 min initial period to equilibrate the water temperature before ignition. The main measurement period commenced 8 min post-ignition, with the total experiment duration set at 15 min. The resulting calorific value was documented by a micro-thermal printer.

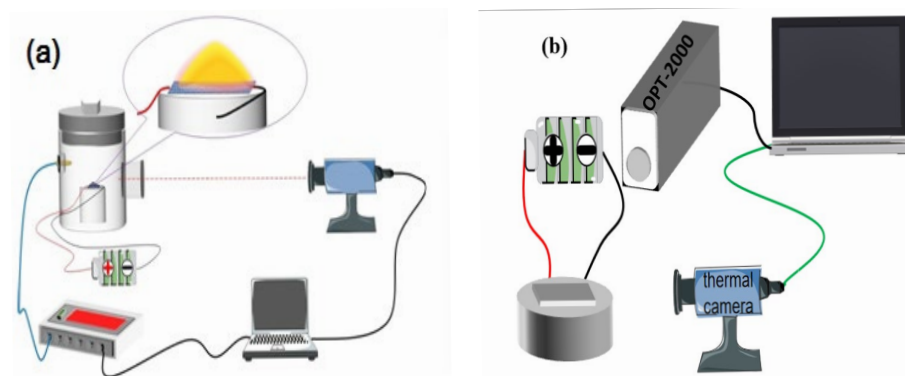


Figure 18. Diagram of the combustion performance testing device: (a) combustion in a closed bomb; (b) combustion in air.

4. Conclusions

In conclusion, this study adeptly fabricated an innovative $[\text{nCu}+\text{nCo}+\text{nFe}]/\mu\text{Al}$ composite energetic material through an in situ displacement reaction, with the objective of augmenting the energy release efficiency of aluminum-based propellant formulations. Rigorous characterizations—including scanning electron microscopy (SEM), energy-dispersive X-ray spectroscopy (EDS), X-ray diffraction (XRD), Raman spectroscopy, X-ray photoelectron spectroscopy (XPS), and vibrating sample magnetometry (VSM)—substantiated the emergence of a distinctive core-shell architecture. Within this structure, uniformly distributed nanoparticles of copper, cobalt, and iron successfully supplanted the native alumina layer on the aluminum surface, thereby establishing efficient pathways for oxygen transport. The synthesized composite demonstrated remarkable dual-functional catalytic activity. It markedly reduced the thermal decomposition temperatures of RDX and AP by $22.4\text{ }^{\circ}\text{C}$ and $1.3\text{ }^{\circ}\text{C}$, respectively, while also effectively coalescing the high- and low-temperature decomposition peaks of AP. This observation suggests a facilitated and concentrated pathway for decomposition. When integrated into energetic micro-units based on AP/RDX, the composite elicited a notable synergistic augmentation in combustion efficiency. The heat release during the oxidation of aluminum surged dramatically, exhibiting an increase of approximately 28-fold compared to pure aluminum. Through constant-volume combustion experiments, the formulation $[\text{nCu}+\text{nCo}+\text{nFe}]/\mu\text{Al}+\text{AP}/\text{RDX}$ manifested a peak pressure nearly 17 times superior to that of the baseline AP/RDX, alongside a significantly reduced burn duration. Furthermore, the combustion flame temperature under atmospheric conditions soared to an impressive $2205.6\text{ }^{\circ}\text{C}$. These remarkable findings can be ascribed to a constructive feedback mechanism: the catalytic decomposition of AP/RDX generates intense localized heat, which in turn facilitates the rapid oxidation of aluminum through pre-existing oxygen pathways; conversely, the heat liberated from aluminum oxidation further accelerates the decomposition of the oxidizer and the explosive material. Consequently, the $[\text{nCu}+\text{nCo}+\text{nFe}]/\mu\text{Al}$ composite, by synergistically combining enhanced oxygen transfer and dual catalytic mechanisms, presents an exceptionally effective approach for the advancement of composite solid propellants characterized by high energy density and superior combustion efficiency.

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