



Flame-retardant liquid metal in cellulose/MXene fire warning sensors[☆]

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ABSTRACT

Developing fast, durable, and multifunctional fire-warning sensors remains challenging, as existing materials struggle to combine rapid response, cyclic stability, and robust mechanical and flame-retardant performance. Here, we fabricated Cellulose/MXene-PDA@LM (CMPL) films via sequential layer-by-layer assembly of MXene/cellulose (CM) gel and PDA@LM layers. This work for the first time introduction of liquid metal (LM) into fire-warning sensors, revealing unexpected flame-retardant functionality. LM significantly reduced the peak heat release rate of CMPL by 65.1% compared to CM film. When integrated into a 12 V circuit with a 30 W warning lamp, the CMPL film responds to thermal stimulus from an alcohol lamp with ultrafast response and recovery times of ~ 4 s and ~ 2 s, respectively. Its resistance responds almost instantaneously to thermal stimulus and changes over 30 orders of magnitude within the fire-warning response period, while maintaining stable cyclic performance for over 1 h. Mechanistic studies reveal that cellulose pyrolysis, PDA carbonization, and LM exothermic oxidation synergistically promote MXene oxidation, forming a dense C-LM_xO_y-doped TiO₂ network that enables sensitive and reversible resistance transitions for rapid fire detection. This work provides a new strategy for designing green, cyclically reusable fire-warning sensors, with strong implications for next-generation fire safety systems.

1. Introduction

Fire remains one of the most unpredictable and catastrophic hazards, posing severe threats to human life, property, and ecosystems worldwide [1,2]. Rapid urbanization and industrialization have increased both the frequency and severity of fire incidents, highlighting the urgent need for efficient and reliable fire-prevention strategies. Traditional fire sensors, such as smoke and gas detectors widely employed in buildings, transportation, and mines, rely on threshold-based concentration detection but suffer from slow response (>100 s), high false-alarm rates, and poor anti-interference capability [3]. To address these limitations, next-generation smart fire alarm sensors have been developed,

combining active fire-detection functionality with intrinsic flame-retardant properties for faster and more precise responses [4–7]. Among them, resistance-transition sensors have attracted particular attention, as they provide rapid and easily quantifiable electrical signals and allow flexible incorporation of flame-retardant components [8,9].

Recently, a variety of materials have been explored for resistance-transition fire sensors. Carbon-based materials such as graphene oxide (GO) [10,11] and carbon nanotubes (CNTs) [12,13] offer high electrical conductivity and large surface area, enabling fast thermal-response signals. However, they generally exhibit poor flame retardancy, structural degradation under flame, and limited stability in complex fire environments. Semiconductor-based sensors (e.g., Fe₃O₄ [14], Ag

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[15,16], SnO₂ [17]) and conductive polymers [18] also show thermoresistive behavior but often require elevated operating temperatures and suffer from slow response, environmental interference, or thermal instability. Therefore, developing fire-warning materials that simultaneously provide ultrafast electrical response, intrinsic flame retardancy, and structural robustness under direct flame exposure remains a critical challenge.

MXene, a new two-dimensional (2D) material composed of transition metal carbides and carbonitrides nanomaterials, has emerged as highly promising candidates for fire warning sensors owing to their metallic-level electrical conductivity, tunable surface chemistry, and intrinsic flame-retardant characteristics [19]. However, pristine MXene films generally suffer from poor mechanical robustness, which limits their practical application in flexible fire-warning sensors. To address this issue, biomass-derived cellulose has been widely integrated with MXene to construct flexible and sustainable composite frameworks, endowing the sensors with improved mechanical strength and structural integrity while maintaining effective fire-response capability [20–22]. Nevertheless, the inherently thermally vulnerable nature of cellulose, particularly its susceptibility to thermal decomposition at elevated temperatures, restricts the overall flame retardancy and thermal stability of cellulose/MXene composites [23]. To further enhance flame resistance, various strategies have been explored, including increasing MXene loading, incorporating inorganic flame retardants, and constructing multilayer or ceramic-containing architectures. For example, He et al. [24] introduced ammonium polyphosphate (APP) into a cellulose/MXene system to suppress the thermo-oxidative degradation of MXene, resulting in an assembled MXene/CNC@APP sensor capable of triggering a rapid fire alarm within 1.79 s under high-temperature exposure (260 °C). Similarly, Zhao et al. [25] incorporated polymethylsilsesquioxane (PMSQ) into cellulose/MXene composites, where the synergistic effect between PMSQ and MXene significantly improved flame retardancy and thermal stability, enabling fire-warning activation within 1.8 s at elevated temperatures. However, enhanced flame retardancy is frequently achieved at the expense of rapid and repeatable fire-warning response, leading to an unresolved trade-off between sensing performance and fire endurance.

To address this trade-off between ultrafast, repeatable fire-warning response and flame-retardant performance in MXene/cellulose composites, we explored a new strategy by introducing gallium-based liquid metals (LMs). Owing to their high electrical and thermal conductivity, along with low toxicity, LMs can reinforce conductive pathways and improve sensing stability without compromising the composites' structural integrity, thereby enabling an optimization of fire warning responsiveness [26–29]. However, the practical use of LMs faces challenges such as leakage, poor interfacial adhesion, and dewetting [30,31]. To address these issues, polydopamine (PDA) was employed to encapsulate LM particles [32,33]. It provides strong adhesion, improved dispersion, and enhanced interfacial interactions with MXene and cellulose [34–36]. Unexpectedly, while the incorporation of PDA@LM was originally intended to improve electrical pathways, the resulting composite film exhibited remarkably enhanced flame-retardant performance under direct flame exposure. This intriguing phenomenon immediately attracted our attention, as such a flame-retardant contribution from liquid metals has not been reported before. This discovery not only reveals an unrecognized function of LMs in improving fire resistance but also provides a new perspective for integrating fast fire-warning response with robust flame-retardant protection.

In this work, we fabricate Cellulose/MXene–PDA@LM (CMPL) films via a layer-by-layer assembly strategy, offering a simple, low-cost, and scalable process with precise spatial control of PDA@LM nanoparticles within the MXene/cellulose matrix. The resulting films exhibit an unusual combination of ultrafast, repeatable fire-warning response and exceptional flame-retardant endurance under direct flame exposure. Through systematic characterization, we elucidate the synergistic mechanisms underlying the simultaneous enhancement of electrical

sensing performance and fire resistance. This work not only expands the functional scope of liquid metals in fire-safety applications but also provides a new design paradigm for multifunctional, sustainable fire-warning materials.

2. Materials and methods

2.1. Materials

MAX (Ti₃C₂Al) was purchased from 11 Technology Co., Ltd. Bacterial cellulose suspension (0.8 wt%) was purchased from Guilin Qihong Technology Co., Ltd. Eutectic gallium indium (EGaIn) alloy (consisting of 75 wt% gallium and 25 wt% indium, with a theoretical melting point of 15.7 °C) and Dopamine hydrochloride (DA-HCl) was supplied by Sigma-Aldrich (Australia). All the chemical reagents were of analytical purity and used as received without further purification.

2.2. Synthesis of (Ti₃C₂T_x) MXene nanosheets

Ti₃C₂T_x MXene nanosheets were synthesized via selective etching of Al from Ti₃AlC₂ using a LiF/HCl system. Typically, 1.0 g of LiF was dissolved in 15 mL of 10 M HCl solution, followed by the slow addition of 1.0 g Ti₃AlC₂ powder under stirring. The mixture was reacted at 35 °C for 24 h to etch away the Al layers. The suspension was repeatedly washed with DI water by centrifugation until the supernatant reached pH ~ 7. After centrifugation at 3500 rpm for 1 h, the supernatant containing few-layer Ti₃C₂T_x MXene nanosheets was collected and stored at 4 °C for further experiments.

2.3. Synthesis of LP (liquid metal@PDA) nanoparticles

Liquid metal @ polydopamine (LM@PDA, LP) nanoparticles were synthesized via an ultrasonic method. Briefly, 30 µL of EGaIn was added to a glass vial containing 15 mL of aqueous DA-HCl solution (2 mg·mL⁻¹) and sonicated in an ice bath using a probe sonicator (Qsonica, 500 W, 20 kHz) for 60 min with a pulse mode of 3 s on and 1 s off. Small-sized LP nanoparticles were obtained by removing large droplets via centrifugation at 1500 rpm for 10 min. Excess DA-HCl in the supernatant was subsequently removed by centrifugation at 9500 rpm for 20 min, and the resulting precipitate was collected and retained for further use.

2.4. Fabrication of the interfacial bridged MXene films

A bacterial cellulose dispersion (5 mg·mL⁻¹) was uniformly mixed with a prepared MXene dispersion (28.88 mg·mL⁻¹) under continuous stirring for 2 h to form a homogeneous gel. The resulting MXene–cellulose gel was blade-coated onto a polyvinylidene fluoride (PET) substrate and dried at room temperature. Subsequently, LP nanoparticle dispersion was spray-coated onto the surface of the CM layer and dried. For the fabrication of CMPL films, the blade-coating process involved sequential deposition of 10 CM layers and 9 LP nanoparticle layers, followed by hot-pressing at 70 °C under 5 MPa for 60 min to obtain the final CMPL film. For comparison, Cellulose/MXene (CM), Cellulose/MXene-PDA (CMP), Cellulose-PDA@LM (CPL), and Cellulose/MXene-LM (CML) films were prepared using the same procedures. To systematically investigate the effects of MXene and LM content, a series of films with varying MXene and LM loadings were fabricated, denoted as CM_xPL_y, where x and y represent the weight ratio of cellulose to MXene and the LM content, respectively.

2.5. Characterization

X-ray diffraction (XRD) patterns were recorded on an Empyrean I diffractometer (PANalytical, The Netherlands) using Cu Kα radiation (λ = 1.5406 Å) with a scan range from 5° to 80° with a scan rate of 10° min⁻¹. The surface morphology and elemental composition were

characterized by a field-emission scanning electron microscope (FE-SEM, Auriga, Zeiss, Germany) equipped with an energy-dispersive X-ray spectroscopy (EDS) detector. The detailed microstructures and element distribution of PL particles were further examined by transmission electron microscopy (TEM, JEM-F200, JEOL, Japan). The X-ray photoelectron spectroscopy (XPS) measurements were conducted using an ESCALAB250Xi (Thermo Scientific, USA). Thermogravimetric analysis (TGA) was performed on a NETZSCH STA449F5 under a nitrogen atmosphere with a temperature ramp of $10\text{ }^{\circ}\text{C min}^{-1}$ from 40 to $900\text{ }^{\circ}\text{C}$. Thermal infrared images during combustion were captured using an infrared camera (HIKMICRO M60) with a temperature range of -20 to $650\text{ }^{\circ}\text{C}$. FTIR spectra were recorded using a Bruker ALPHA FTIR spectrometer equipped with a diamond ATR accessory. Spectra were collected in the range of $4000\text{--}400\text{ cm}^{-1}$ with a resolution of 4 cm^{-1} , averaging 32 scans per sample. Microscale combustion calorimetry (MCC) measurements were carried out using a TESTECH micro calorimeter (China) to evaluate the combustion behavior and flame-retardant performance of the films. The heat release rate (HRR), peak heat release rate (PHRR), total heat release (THR), and heat release capacity (HRC) were obtained. The electrical resistance of the samples ($\sim 40 \times 20\text{ mm}^2$) during flame attack was measured using a two-probe method with a Keithley DAQ6500 multifunction source meter. Sample strips for electrical measurements were 2 mm wide and 15 mm long, with copper mesh electrodes attached to opposite ends on the same side. Fire-warning performance of various samples ($40 \times 20\text{ mm}^2$) was evaluated using a homemade fire-warning system consisting of an alarm light connected to a 12 V power supply.

3. Results and discussion

3.1. Fabrication principles of CMPL film

The CMPL composite films were fabricated via a simple layer by layer method followed by hot pressing (Fig. 1a). MXene nanosheets were prepared by selectively etching Al atoms from $\text{Ti}_3\text{C}_2\text{Al}$ powder using LiF/HCl , followed by sonication to achieve exfoliation (Fig. S1a–d). The AFM characterization confirmed that the exfoliated MXene nanosheets exhibited lateral dimensions of several micrometers and a thickness of $\sim 1.46\text{ nm}$ (Fig. S2a, b). Benefiting from abundant hydroxyl groups, cellulose was uniformly coated onto the MXene nanosheets through hydrogen bonding, yielding cellulose–MXene (CM) building blocks (Fig. S2c, d) [34]. These building blocks were further assembled into CM films via blade coating. Eutectic gallium–indium alloy ($\text{Ga}_{75}\text{In}_{25}$, LM), which possesses high deformability and excellent electrical conductivity, was coated with a thin layer of polydopamine (PDA) to obtain PDA@LM (PL) nanoparticles through an ultrasonic polymerization process [37]. The obtained LP nanoparticles exhibited an average diameter of $\sim 100\text{ nm}$ (Fig. S3a), and TEM and mapping images confirmed a uniform PDA coating with a thickness of $\sim 10\text{ nm}$ (Fig. S3bc). The PL nanoparticles were then introduced into the CM films by spray method. During the layer-by-layer assembly of CM gels and PL nanoparticles, the PL nanoparticles were uniformly dispersed between the CM layers. The subsequent hot-pressing step further interconnected the CM layers. SEM imaging and EDS elemental mapping of CMPL film confirmed the uniform distribution of LM within the films (Fig. 1b, c).

The structural evolution and interfacial interactions of CMPL films were systematically investigated by XRD, XPS, and FTIR. The XRD patterns revealed the formation mechanism of the hierarchical structure and confirmed the successful incorporation of PDA@LM into the CM hybrid (Fig. 2a). Compared with the characteristic (002) diffraction peak of the pure MXene film at 6.20° , all composite films exhibited a shift toward lower angles, indicating an enlarged interlayer spacing induced by the intercalation of cellulose and PL [38]. The calculated d-spacing values (Table S1) revealed a clear structural evolution. Compared with the pristine CM film, the incorporation of LM expanded the interlayer spacing ($d_{\text{CMPL}} > d_{\text{CM}}$), indicating the successful

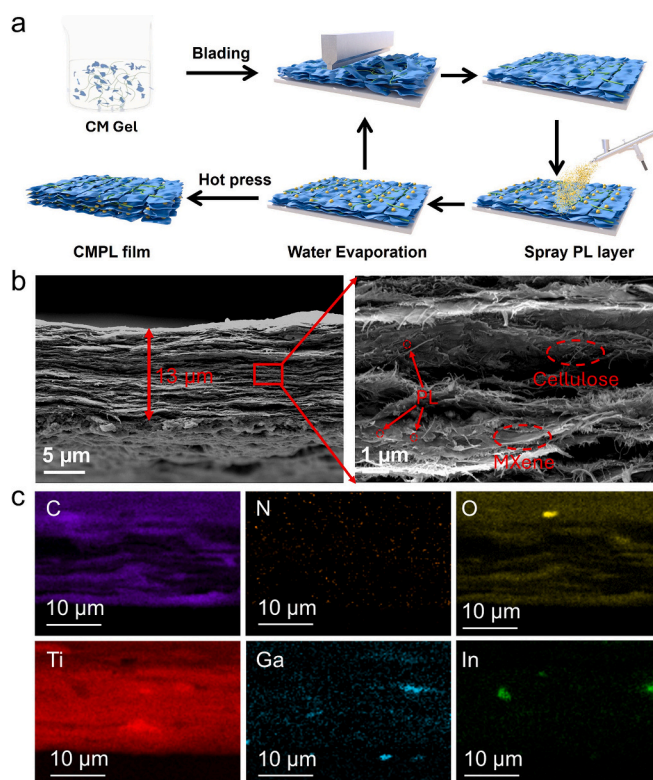


Fig. 1. Schematic fabrication and structural characterization of the CMPL film. (a) Fabrication schematic of the CMPL film prepared via a layer-by-layer assembly strategy involving repeated blade coating and spray cycles followed by hot pressing. (b) Cross-sectional SEM image and (c) corresponding EDS elemental mapping of the CMPL film, confirming its well-defined multilayered architecture and uniform elemental distribution.

intercalation of LM within the MXene layers. However, when LM was encapsulated by PDA to form PDA@LM, the interlayer spacing in the CMPL films decreased from $17.44\text{ \AA}$ to $14.74\text{ \AA}$, suggesting that the presence of PDA enhanced the interfacial interactions and induced a more compact layered structure. Furthermore, the broad diffraction peaks observed at 14.8° and 23° were assigned to the (100) and (200) planes of cellulose, confirming its coexistence within the hybrid films [39]. Notably, no distinct diffraction peaks attributable to the LM phase were observed in the XRD patterns, likely due to its low loading level and nanoscale dispersion within the hybrid matrix.

To further verify the successful incorporation of PDA@LM, XPS analyses were performed. The survey spectrum of CMPL clearly showed the presence of Ga and N signals that were absent in CM, confirming the successful introduction of PDA@LM (Fig. 2b). In the C 1 s spectra, both CM (Fig. S4a) and CMPL (Fig. 2c) exhibited a peak at $\sim 282\text{ eV}$ corresponding to C–Ti bonds [40]. For CMPL film, the peak intensity at 285.6 eV (C–N/C–H) was significantly enhanced, consistent with PDA incorporation [41]. Meanwhile, the cellulose-derived C–O component at 286.3 eV decreased in relative intensity, likely due to dilution by aromatic carbons introduced by PDA. In the O 1 s spectra, CMPL film exhibited a shift toward higher binding energy compared with CM, suggesting a reduction in electron density on oxygen atoms resulting from Ga–O coordination. Moreover, the Ga $2p_{3/2}$ peak at 1118.2 eV , higher than metallic Ga ($\sim 1116\text{--}1117\text{ eV}$) but lower than Ga_2O_3 ($\sim 1119\text{ eV}$), indicated a partially oxidized Ga state, further supporting the presence of Ga–O bonds at the LM–matrix interface [42].

FTIR analysis (Fig. 2f) provided further evidence of changes in functional groups and interfacial interactions. For the CM film, absorption bands were observed at 3363 cm^{-1} (–OH stretching), 2901 cm^{-1} (C–H stretching), 1649 cm^{-1} (–OH bending), and 1064 cm^{-1}

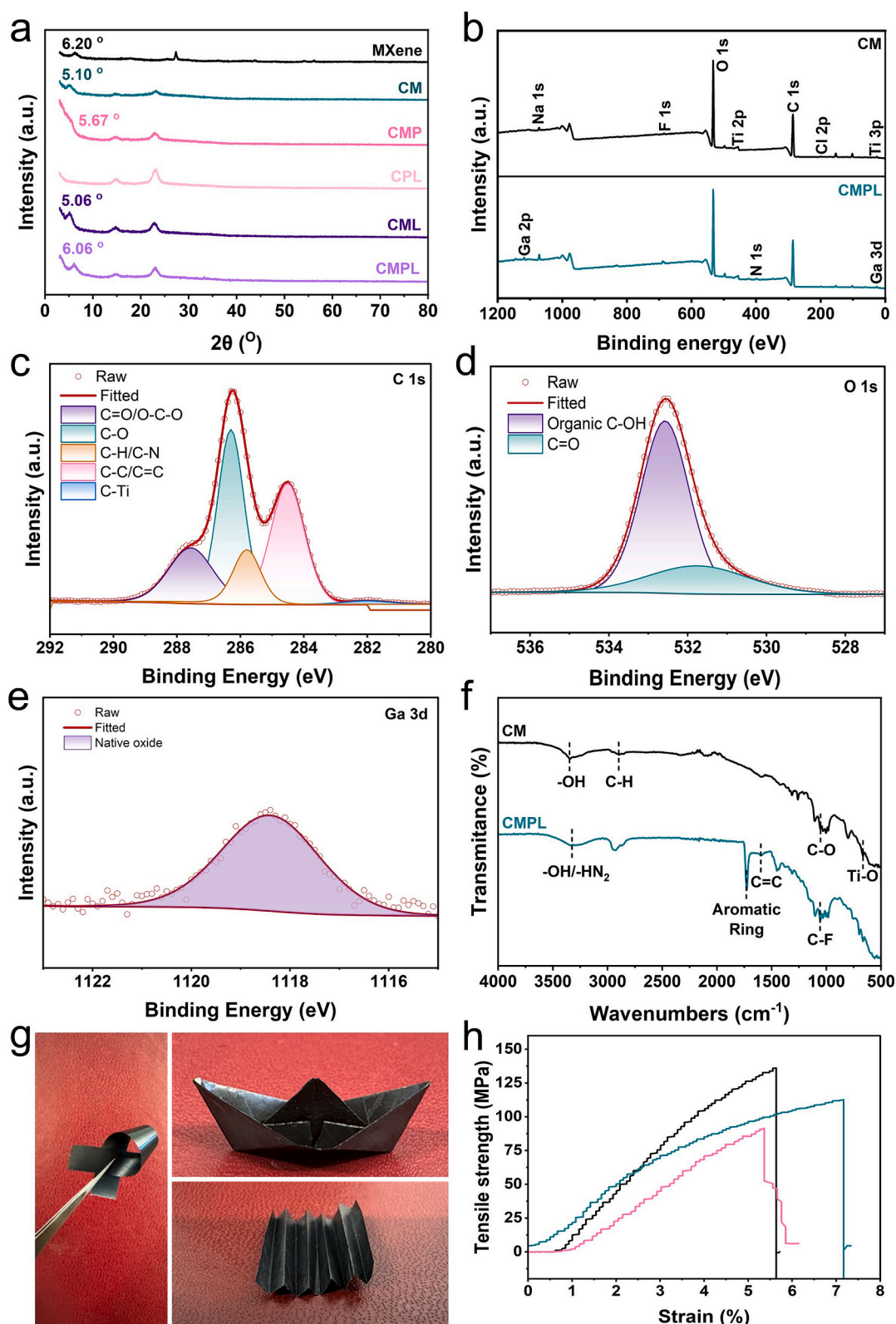


Fig. 2. Structural and chemical characterization of the different composite films. (a) XRD patterns of MXene, CM, CMP, CPL, CML, and CMPL, showing the evolution of interlayer spacing and phase composition. (b) Survey XPS spectra of CM and CMPL films, highlighting their elemental composition. High-resolution XPS spectra of CMPL films: (c) C 1s, (d) O 1s, and (e) Ga 3d, revealing detailed bonding environments. (f) FTIR spectra of CM and CMPL films, evidencing changes in functional groups and interfacial interactions induced by PL incorporation. (g) The digital images of CMPL film can be easily folded, twisted, and shaped into a boat, demonstrating outstanding flexibility. (h) Representative tensile stress-strain curves of CMPL films from three repeated tests, demonstrating outstanding reproducibility, high tensile strength, and good toughness.

(C—O stretching) [43]. In the CMPL film, the broad band in the range of 3000–3700 cm^{-1} became wider and more intense, arising from the overlapping —OH and —NH₂ vibrations introduced by PDA [44]. A new band at 1557 cm^{-1} was assigned to the aromatic ring vibration characteristic of PDA [45]. This assignment was further supported by the FTIR spectra of the comparison samples (CML, CPL, and CMP) (Fig. S4c), which exhibited additional characteristic bands at 1610 cm^{-1} (C=C stretching) and 1502 cm^{-1} (N—H bending) [46]. For the MXene-related signals, bands corresponding to Ti—O (620 cm^{-1}) [31], C—F (1097 cm^{-1}), and O—H (1399 cm^{-1}) were observed, whereas the broad peak at 3437 and the peak at 1636 cm^{-1} were attributed to strongly hydrogen-bonded OH groups [47–49]. The combined FTIR results indicate that PDA not only contributes its own characteristic functional groups but also enhances hydrogen bonding among MXene, cellulose, and PDA, thereby strengthening the interfacial network. To provide semi-quantitative support for these interfacial interactions, interaction energies among MXene and PDA, MXene and cellulose, as well as PDA and cellulose were calculated using the Forcite module in Materials Studio (Fig. S5). The calculated interaction energies (E_{int}) of the MXene–PDA, MXene–cellulose, and PDA–cellulose pairs are summarized in Table S2. The obtained E_{int} values were -3.71 , -14.05 , and -11.11 $\text{kcal}\cdot\text{mol}^{-1}$, respectively. The negative values indicate that all three systems are thermodynamically stable, and a more negative value corresponds to a stronger interfacial interaction. The results reveal that MXene can stably interact with cellulose, while cellulose also forms a strong association with PDA. Furthermore, the stable bonding between PDA and LM has been confirmed in previous studies [50]. Therefore, the overall structure can be regarded as a hierarchically interconnected system, in which MXene, cellulose, PDA, and LM are linked layer by layer through stable interfacial interactions.

The mechanical properties of the CMPL films were evaluated to assess their flexibility and structural integrity. As shown in Fig. 2g, the films could be folded into small boat-like shapes and repeatedly bent without cracking or delamination, demonstrating outstanding macroscopic flexibility. Owing to their thin configuration (~ 13 μm) and robust internal network, the CMPL films maintained their structural integrity even after multiple deformation cycles. Stress–strain curves (Fig. 2h) revealed that the CMPL films exhibited an ultimate tensile strength of ~ 118 MPa, a strain at break of $\sim 6\%$, and a Young's modulus of ~ 2.1 GPa, confirming a desirable combination of strength and elasticity. These values are comparable to or higher than those reported for many MXene/cellulose-based films [51,52]. Such a balance between high strength and moderate deformability places the CMPL films among mechanically robust MXene-based materials suitable for flexible fire-warning applications. The enhanced mechanical stability mainly originates from the reinforcing effect of cellulose within the MXene–polymer framework. Such superior flexibility and mechanical resilience ensure that the CMPL films can maintain reliable performance under repeated deformation, supporting their suitability for foldable and reusable fire-warning sensors.

3.2. Flame-retardant performances and mechanism analysis

Combustion tests were carried out on both CM and CMPL films to evaluate their flame retardant properties. As shown in Fig. S6 and Movie S1, the CM film rapidly burned out within 30 s under an alcohol flame, leaving a discontinuous and crack-rich char layer. This defective char morphology provided insufficient physical shielding and accelerated combustion, which can be attributed to the weak structural reinforcement of the MXene–cellulose network under flame exposure [22]. In contrast, the introduction of PL nanoparticles significantly improved the flame retardancy of CMPL films (Fig. 3a and Movie S2). Although the CMPL films could be ignited, they self-extinguished within 1 s and retained their structural integrity even after 120 s of continuous flame exposure. The formation of a dense, compact char layer confirms that PL nanoparticles effectively promote condensed-phase flame retardancy.

As shown in Fig. 3b, Thermographic analysis further confirmed these observations. Upon direct flame contact, the CMPL film exhibited an ultrafast temperature rise to ~ 364 $^{\circ}\text{C}$ within 1 s, followed by stabilization below 400 $^{\circ}\text{C}$ for the duration of flame exposure. This rapid heat response demonstrates that LM, owing to its high thermal conductivity, efficiently absorbs and dissipates flame heat across the film, enabling fire alarm activation within 2 s, as discussed later. The effective heat dissipation also prevents thermal accumulation, enhancing the thermal stability of CMPL films, which remained structurally intact even after 120 s of continuous burning [53,54]. By contrast, CM films required ~ 5 s to reach 400 $^{\circ}\text{C}$, and their temperature continued to rise under flame attack, leading to complete decomposition within 30 s.

Thermogravimetric analysis (TGA) was conducted to investigate the thermal degradation behavior of the composite films (Fig. 3c, d), and the corresponding characteristic parameters are summarized in Table S3. Among all samples, CMPL₃₀ exhibited the lowest $T_{5\%}$ (240.54 $^{\circ}\text{C}$), which can be attributed to the combined effects of PDA, MXene, and EGaIn. The —OH and —NH₂ groups in PDA decompose at relatively low temperatures (100–240 $^{\circ}\text{C}$), while MXene simultaneously loses its surface terminations (—OH, —F, —O), releasing small molecular species [55,56]. In addition, the presence of EGaIn, with its intrinsic oxidation and high thermal conductivity, facilitates rapid heat redistribution throughout the matrix, thereby accelerating the apparent onset of weight loss [57]. Interestingly, as the EGaIn content increased (e.g., CMPL₉₀), the $T_{5\%}$ shifted toward a higher temperature. This reversal trend is likely governed by multiple synergistic factors rather than heat transfer alone. At higher loadings, EGaIn droplets can form a more continuous and well-dispersed phase, which not only enhances global heat dissipation but also acts as a physical barrier that restricts the diffusion of volatile degradation products and oxygen during early-stage decomposition. Moreover, the PDA coating on EGaIn promotes stronger interfacial interactions with both MXene and cellulose, which may further constrain polymer chain mobility and delay the initiation of thermal degradation [58]. These findings suggest a dual role of EGaIn: at low concentrations, enhanced thermal conductivity dominates and accelerates apparent mass loss, whereas at higher concentrations, barrier effects and interfacial stabilization become increasingly significant, collectively improving early-stage thermal stability. Regarding the T_{max} , the CM film exhibited a single degradation peak at ~ 326 $^{\circ}\text{C}$, whereas all other samples displayed two degradation stages. Similar two-stage thermal degradation behavior has been reported in MXene-organic hybrid and cellulose/MXene systems [59,60]. The first stage (326–338 $^{\circ}\text{C}$) is primarily associated with the decomposition of cellulose and PDA, while the second stage (383–462 $^{\circ}\text{C}$) corresponds to the incorporation of PDA and EGaIn, involving chain scission, structural rearrangements, and the gradual oxidation of MXene into TiO₂, thereby revealing a modified degradation pathway. Notably, the PL-containing systems exhibit a markedly higher T_{max} in this latter stage, confirming their improved high-temperature stability compared to other samples.

The char yield at 900 $^{\circ}\text{C}$ further highlights the cooperative effect among the MXene, PDA, and EGaIn. As cellulose constitutes the predominant mass fraction of the films, it serves as the primary carbon source during thermal decomposition, while MXene, PDA, and EGaIn function as key regulators of the carbonization process. The removal of any single component—CMP, CPL, or CMPL—resulted in a marked reduction in residual char, confirming their indispensable contributions to carbonization. MXene facilitates char formation through in situ generation of TiO₂, which catalyzes the stabilization of carbonaceous frameworks [61]. Although PDA contributes only a minor amount of carbon compared to cellulose, its aromatic structure promotes dehydration, aromatization, and crosslinking reactions of cellulose-derived intermediates, thereby enhancing char continuity and stability. Meanwhile, EGaIn does not act as a carbon source but significantly influences the carbonization pathway of cellulose by enhancing heat transfer and generating protective Ga/In oxide layers at elevated temperatures [62]. Increasing the EGaIn content significantly improved the final char yield,

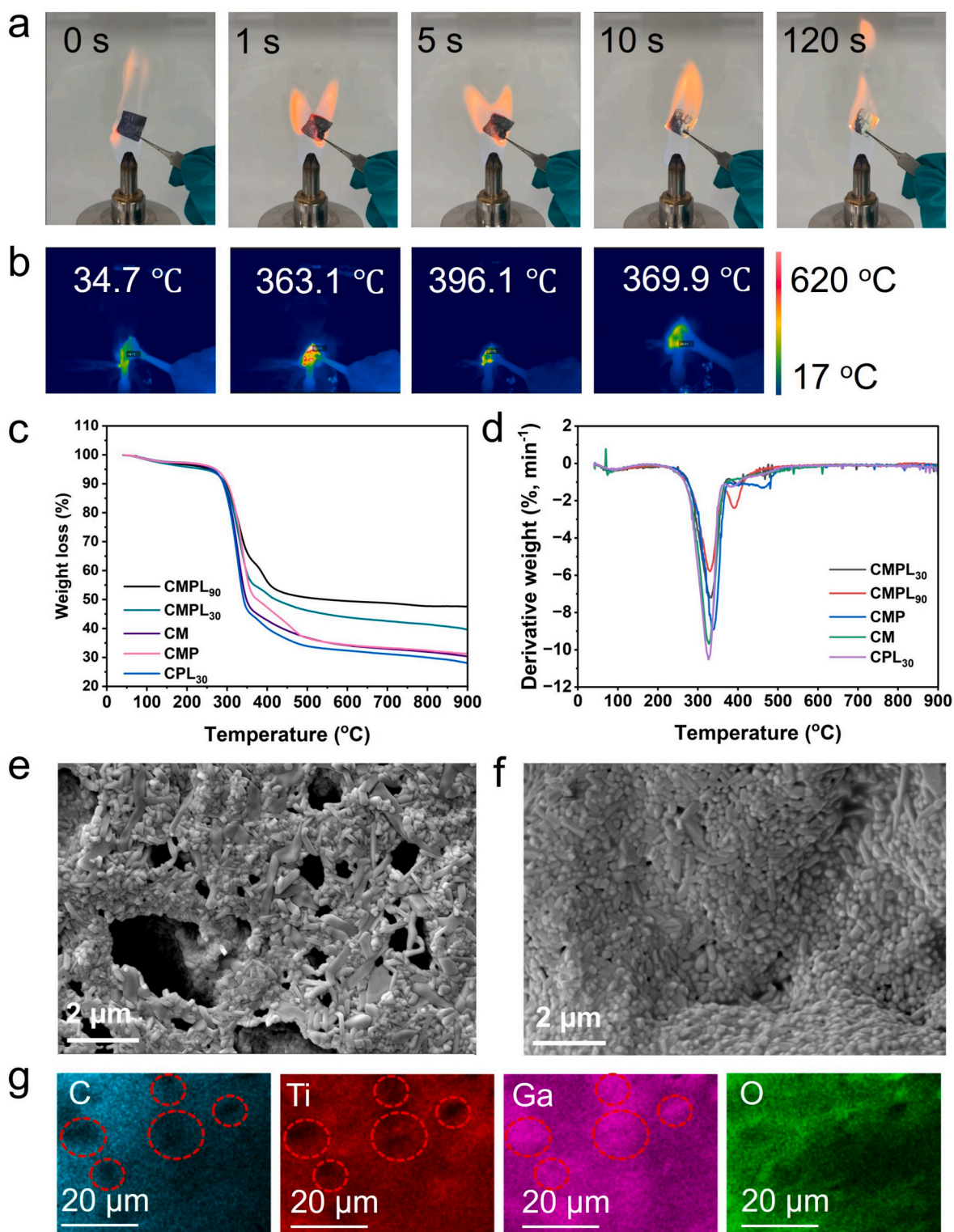


Fig. 3. Combustion behavior and thermal stability of the composite films. (a) Photographs showing combustion process and (b) the corresponding thermographic images of MCPL films, indicating that the films maintained their structural integrity even after 120 s of flame exposure. (c) TGA and (d) DTG curves of all composite films. (e) SEM image of the CM film after 30 s of burning, showing a loose and porous char structure, and (f) SEM image of the CMPL film after 90 s of burning, exhibiting a dense and compact char layer. (g) EDS elemental mapping of the CMPL film after 90 s of combustion, revealing a complementary elemental distribution of C, Ti, and Ga.

which is attributed to the synergistic catalytic effect of Ga/In oxides and their interaction with PDA-derived carbon. Collectively, these results demonstrate that the integration of MXene, PDA, and EGaIn modifies the early-stage decomposition and high-temperature carbonization

behavior of cellulose, leading to enhanced char stabilization and thermal resistance of the CMPL films. SEM images of the char residues of flame exposure further corroborated these findings. The CM film (Fig. 3e) formed a loose, porous char structure consistent with rapid

combustion, whereas CMPL (Fig. 3f) developed a dense and compact char layer that effectively inhibited oxygen and heat penetration. Furthermore, EDS elemental mapping of the CMPL residue after 90 s (Fig. 3g) showed a complementary distribution of Ti, O, and Ga elements. This pattern indicates that Ti- and Ga/In-based oxides are mainly distributed in separate but cooperative regions. Such a heterogeneous elemental arrangement contributes to the formation of a dense and continuous char layer, where TiO_2 enhances the structural framework while Ga/In oxides promote surface sealing. The synergistic action of these oxides effectively reinforces the integrity and thermal stability of the protective barrier [63]. These morphological and compositional observations provide compelling evidence for the cooperative roles of MXene, PDA, and EGaIn. Together, they promote the generation of a robust, oxygen-impermeable char layer and endow the CMPL films with superior flame retardancy and thermal endurance.

In actual fire incidents, smoke and toxic gases are the leading causes of casualties [64]. Therefore, analysing the gas-phase pyrolysis products is crucial for evaluating their smoke and toxicity suppression performances. The 3D FT-IR spectra of volatile species evolved during thermal degradation of CM and CMPL films, obtained from TG-IR analysis, are shown in Fig. 4a and b. Both samples exhibited characteristic absorption bands corresponding to H_2O ($\sim 3400\text{ cm}^{-1}$), CO_2 ($\sim 2350\text{ cm}^{-1}$), carbonyl compounds ($\text{C}=\text{O}$, $\sim 1740\text{ cm}^{-1}$), and C–O–C stretching vibrations ($\sim 1200\text{--}1000\text{ cm}^{-1}$), which are typically associated with the pyrolysis of cellulose and PDA components [65]. However, compared with CM, the overall absorbance intensity of CMPL was significantly weaker, and the onset of gas release occurred at a higher temperature. These differences indicate that the incorporation of PL effectively suppresses the release of volatile degradation products and delays the thermal decomposition process [66,67]. The reduced signal intensities

further suggest enhanced carbonization and a more complete char formation in CMPL, consistent with its improved thermal stability observed in the TGA results.

Microscale combustion calorimetry (MCC) was conducted to quantitatively evaluate the flame-retardant properties of the composite films [68], and the detailed results are listed in Table S4. As shown in Fig. 4c and d, the CMPL films exhibit significantly lower peak heat release rate (PHRR), total heat release (THR), and heat release capacity (HRC) compared with the reference samples (CM, CML, and CMP). These results demonstrate a clear synergistic flame-retardant effect arising from the integration of MXene, PDA, and LM components. Furthermore, the flame-retardant performance of CMPL films improves progressively with increasing LM content. Specifically, the CMPL₉₀ film shows much lower PHRR (50.122 and $60.771\text{ W}\cdot\text{g}^{-1}$), THR ($13.539\text{ kJ}\cdot\text{g}^{-1}$), and HRC (50.419 and $61.685\text{ J}\cdot\text{g}^{-1}\cdot\text{K}^{-1}$) values than the CMPL₃₀ film, corresponding to reductions of approximately 26.1 and 38.7%, 1.9%, and 25.3 and 36.6%, respectively. The gradual decline in HRC with higher LM loading indicates that LM incorporation effectively suppresses heat release and reduces the material's tendency to sustain combustion [69]. Notably, even at a relatively low LM loading, the CMPL₃₀ film already shows a pronounced improvement in flame retardancy compared with the pristine CM film. Specifically, the PHRR of CMPL₃₀ decreases from 139.108 to $84.277\text{ W}\cdot\text{g}^{-1}$ (65.1% reduction), while the THR slightly increases from 13.055 to $13.797\text{ kJ}\cdot\text{g}^{-1}$ (−5.4% reduction). This indicates that the maximum combustion intensity is mitigated, but the overall energy released during combustion is not proportionally reduced. At this low loading level, the barrier and char-forming effects from LM-related components are likely limited, which may explain why THR is not significantly suppressed despite the reduction in PHRR. In addition, the HRC is reduced from 132.863 to $84.277\text{ J}\cdot\text{g}^{-1}\cdot\text{K}^{-1}$,

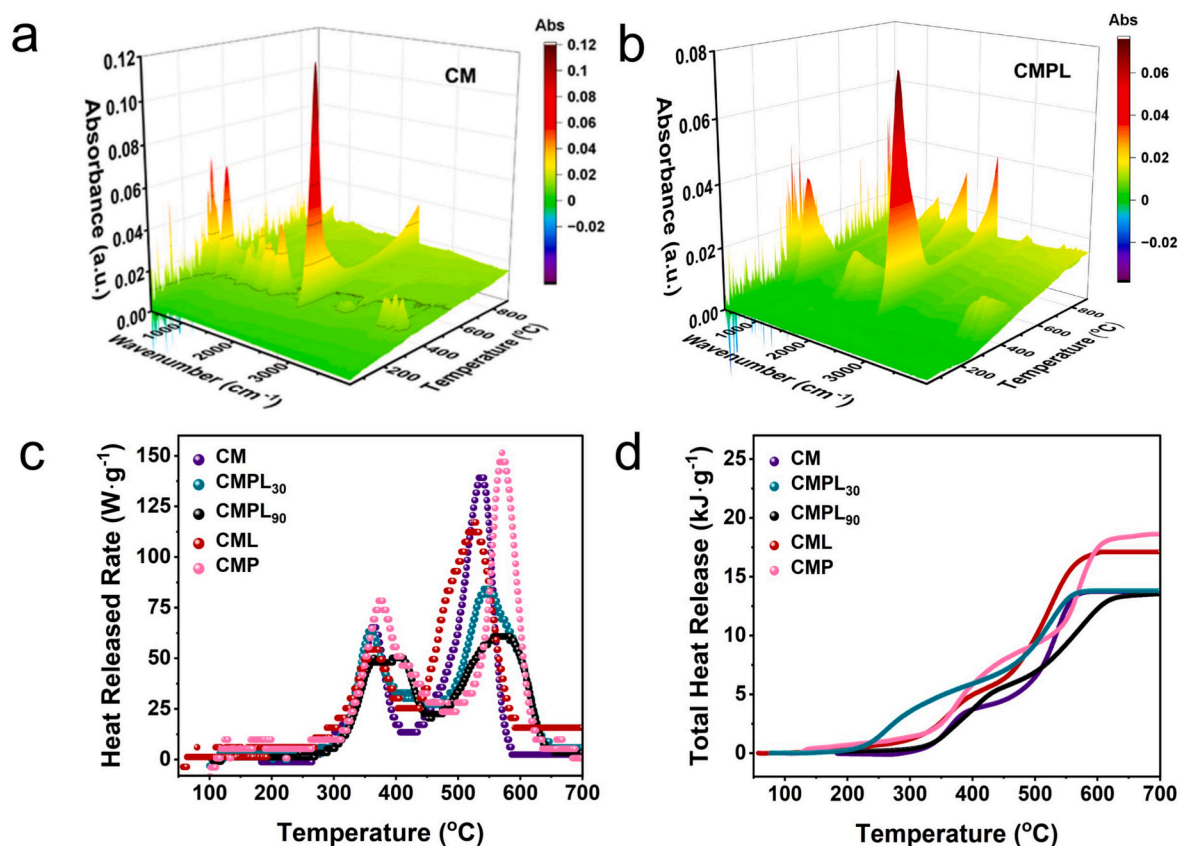


Fig. 4. (a) 3D TGA-FTIR spectra of gaseous products released from CM and (b) CMPL films, illustrating that the incorporation of PL suppresses volatile product release and delays thermal decomposition. MCC analysis of the composite films. (c) Heat release rate (HRR) and (d) total heat release (THR) as a function of temperature for CM, CMP, CML and CMPL films. The CMPL films exhibit the lowest PHRR and THR, indicating superior flame-retardant performance.

corresponding to a decrease of approximately 57.7%. These results indicate that the introduction of LM is already effective in suppressing heat release and moderating combustion intensity at low loadings. Moreover, the temperature corresponding to the PHRR (T_{PHRR}) shifts from 537.2 °C for CM to 571.6 °C for CMPL₉₀, indicating that LM addition delays the combustion process and enhances the thermal stability of the hybrid films [70]. The improved flame retardancy can be attributed to the synergistic barrier and catalytic effects of the hybrid layer composed of LM-derived oxides (LM_xO_y), TiO_2 nanoparticles, and carbonaceous char. This hybrid protective layer functions as an efficient thermal and oxygen barrier while catalyzing in situ char formation during combustion. Consequently, the PHRR peaks of the CMPL films become broader and less intense, reflecting a moderated and extended degradation process [71]. In summary, the MCC results confirm that the integration of MXene, PDA, and LM yields a composite film with significantly reduced combustion enthalpy, enhanced char formation, and superior overall flame-retardant performance, demonstrating their threefold synergistic contribution to fire resistance.

3.3. Fire warning performance and mechanism analysis

The fire-warning sensor performance of the composite films was conducted by connecting them to a low-voltage power source (12 V) and a 30 W electric bulb via several conductive wires. The response time and alarm duration of the CMPL film were recorded in Movie S3 and shown in Fig. 5a. Upon flame exposure, the CMPL film triggered a warning signal within approximately 4 s, which persisted continuously during the exposure. Once the flame was removed, the alarm light extinguished within 2 s, and this process was fully reversible. Notably, the measured current gradually decreased over repeated heating cycles, which can be attributed to progressive oxidation of the LM phase. This oxidation increased the electrical resistance of the CMPL composite, consistent with the XRD analysis presented below.

To further quantify the fire-warning behavior, the electrical resistance changes of the films were monitored under flame exposure (Fig. 5b, c). Compared with CM film, the CMPL film exhibited a higher initial resistance, reflecting the intrinsic properties of the composite. Upon flame contact, the resistance of CMPL decreased rapidly by approximately two orders of magnitude, owing to the excellent thermal conductivity of the LM. This observation was complied with thermal imaging results discussed before in Fig. 3b, which showed a sharp temperature rise in the CMPL film immediately upon flame contact. During the subsequent ~5 s, both CM and CMPL films displayed gradual resistance decreases, primarily driven by cellulose combustion. Within the following second, the CMPL film exhibited another abrupt resistance drop, likely resulting from the exothermic oxidation of LM phase. Consequently, the CMPL film reached its minimum resistance significantly faster than that of CM film (5 s v. 13 s). After 15 s of flame exposure, the CM film was burned through and lost electrical continuity, leading to circuit interruption, whereas CMPL film showed a reversible resistance recovery once the flame was removed and attached. It should be noted that some variations in the measured resistance values are normal, as they depend on factors such as the electrical contact quality and the flame-sample contact height. Since the entire process was manually controlled, a certain degree of measurement error is inevitable.

To further assess the robustness and repeatability of these fire-warning responses, the long-term cycling behavior of all CMPL samples was evaluated. A series of CMPL films with different cellulose/MXene mass ratios (CM_{0.2}PL₃₀, CM₁PL₃₀, CM₃PL₃₀, CM₅PL₃₀, CM₇PL₃₀, and CM₁₅PL₃₀) were prepared to systematically investigate the influence of composition on fire-warning performance. Taking CM₇PL₃₀ as a representative example, the film maintained stable resistance switching over 1 h of repeated flame exposure (Fig. 5d). The locally magnified resistance traces (Fig. 5e) reveal that all films responded ultrafast and reproducibly upon flame contact. Specifically, the measured resistance

decreased sharply from beyond the instrument's upper detection limit (denoted as "OL", approximated as $10^{38} \Omega$ for plotting) to $\sim 10^7 \Omega$ within 0.5 s, and further dropped to the minimum resistance over the next ~3 s. Upon flame removal, the resistance recovered to its initial insulating state ($\sim 10^{38} \Omega$) within ~1 s. The cycling stability of all CM_xPL₃₀ films was further evaluated over the 2300 s testing period, during which all samples remained fully reusable and structurally intact (Fig. S8). Tests were concluded at 2300 s due to time limitations; however, the films retained both functional and structural integrity beyond this period. The primary distinction among the samples was the minimum resistance achieved upon flame exposure, which varied significantly with the cellulose/MXene ratio (Fig. 5f). Specifically, the minimum resistances for CM_{0.2}PL₃₀, CM₁PL₃₀, CM₃PL₃₀, CM₅PL₃₀, CM₇PL₃₀, and CM₁₅PL₃₀ were approximately 50, 1.0×10^3 , 4.5×10^3 , 8.0×10^3 , 1.2×10^4 , and $3.0 \times 10^5 \Omega$, respectively. These rapid, reversible resistance transitions clearly demonstrate the exceptional responsiveness and durability of CMPL films, highlighting their potential for advanced fire-sensing applications.

Building on the previous analysis of CMPL films with varying cellulose/MXene ratios, we further investigated the role of LM in the conductive network. CMPL films with different LM contents (CM₇PL₃₀ and CM₇PL₉₀) were prepared and compared to elucidate their impact on electrical behavior under flame exposure (Fig. 5g). Before flame exposure, the film with a higher LM content (CM₇PL₉₀) exhibited a larger initial resistance ($2.2 \times 10^7 \Omega$) than CM₇PL₃₀ ($6.9 \times 10^6 \Omega$). This difference arises from microscopic phase separation of Ga and In during ultrasonication, wherein Ga preferentially segregates to the surface while In enriches the core, as confirmed by TEM-EDS mapping (Fig. S3c) [72]. Given that the electrical resistivity of In ($8.0 \times 10^{-8} \Omega\cdot\text{m}$) is substantially higher than that of EGaIn ($0.294 \times 10^{-8} \Omega\cdot\text{m}$) [73,74], films with higher LM content correspondingly exhibit higher initial resistance. Upon flame exposure, films with higher LM content displayed faster resistance decreases and recoveries during the first and second cycles, reflecting the superior thermal conductivity of LM that facilitates rapid heat transfer across the composite matrix. With prolonged flame exposure, the overall resistance of the film increased markedly due to full oxidation of the LM phase. This increase is attributed to the formation of poorly conductive Ga_2O_3 and In_2O_3 , which impede electron transport. At this stage, oxidized LM no longer directly contributes to the conductive pathways, instead existing as dispersed nanoscale oxide particles within the matrix. Consequently, the optimal electrical response of the film is governed by the conductivity balance between the metallic LM core and its oxidized shell. To further verify the temperature-dependent effects of LM redistribution and oxidation, supplementary experiments were conducted at 200 °C in the absence of direct flame exposure. The results confirmed that PL incorporation increases the film's resistance under elevated temperatures (Fig. S10), consistent with the proposed mechanism of LM phase segregation and oxidation observed during flame testing.

To display this work from the perspective of current state-of-the-art early fire alarms, a table between this fire alarm and reported fire alarms based on several key parameters has been provided in Table 1. Because the measured response time in resistance-change-based fire-warning systems is highly dependent on the circuit configuration, including the internal resistance of the sensing material, the applied voltage, and the power rating of the external indicator lamp. As a result, minor differences of a few seconds in response time are not strictly comparable across different studies. In contrast, alarm duration and repeatability offer more meaningful metrics for evaluating the practical fire endurance and long-term operational stability of fire-warning systems. The parameter comparison focuses primarily on response time, alarm duration, repeatability, and the type of warning signal conversion. Most reported MXene-based fire-warning systems trigger within 5 s, demonstrating ultrafast response behavior. However, as summarized in Table 1, these systems typically exhibit short alarm durations—ranging from several seconds to only a few minutes—and many suffer from irreversible failure or poor repeatability after a single alarm event,

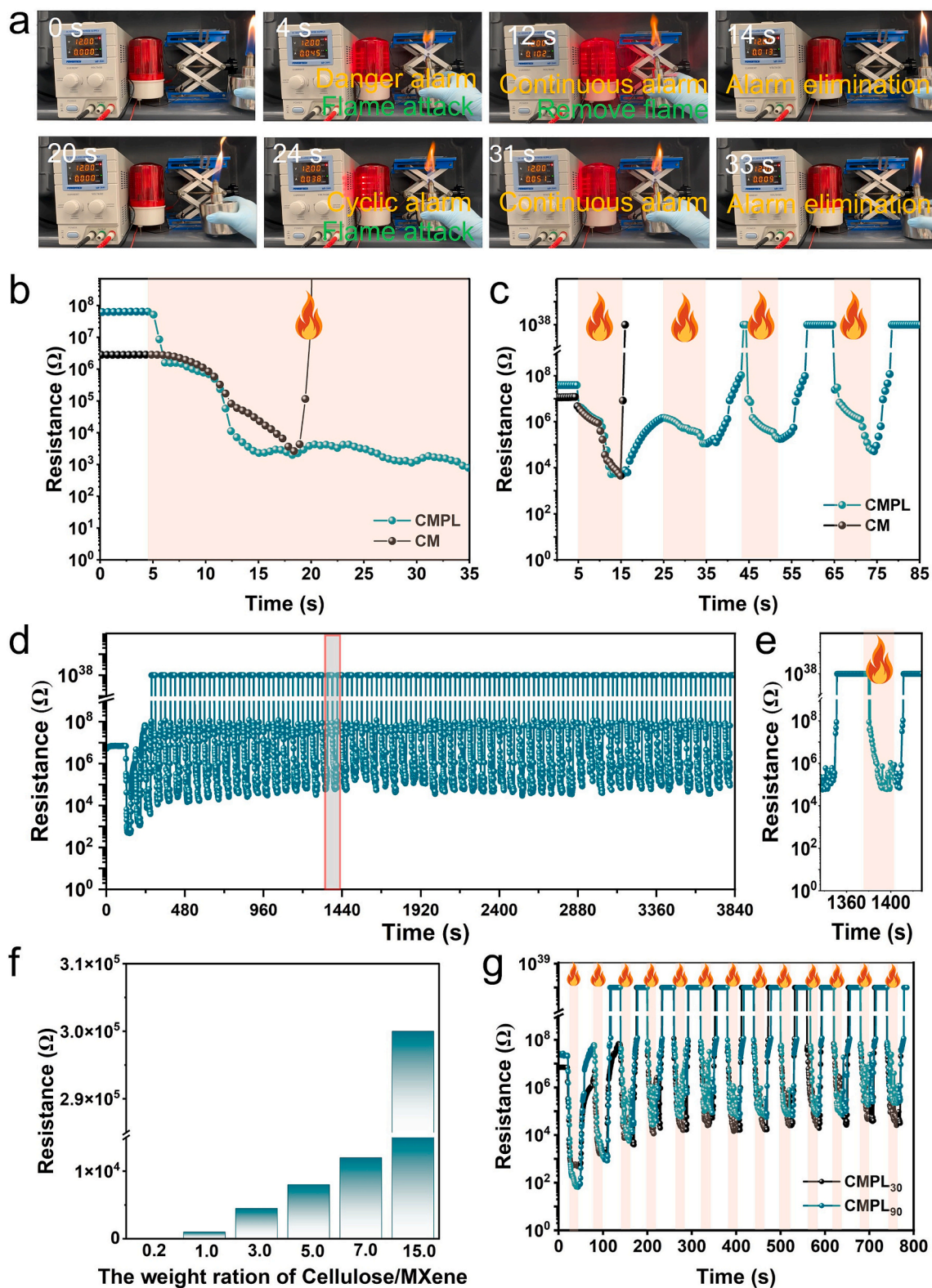


Fig. 5. Fire-warning performance of CMPL films. (a) The digital images of cyclic fire detecting sensor device based on CMPL film, demonstrating rapid alarm triggering and recovery (~4 s/1 s). (b) Representative resistance changes of CM and CMPL films during the first flame exposure, showing CM failure within 15 s, whereas CMPL maintains repeatable fire warning performance. (c) Resistance-time curves of CM and CMPL films over three flame cycles with 10 s exposure per cycle. (d) Cyclic resistance response of CMPL films under repeated flame exposure (~30 s per cycle) over 1 h, demonstrating excellent durability. (e) Partial enlarged detail of cyclic resistance response curves, highlighting ultrafast and reversible transitions. (f) The minimum resistance of CM_{xPL30} with different weight ratio of Cellulose and MXene, illustrating the effect of composition on response behavior. (g) Resistance changes curves of the different LM content (CM_{PL30} and CM_{PL90}) over 12 flame attack cycles (flame attacking time of 30 s in each cycle), showing that higher LM content leads to faster response and recovery time.

Table 1

Comparison of early fire alarms performance among our CMPL film and other fire-warning systems in literatures.

Sample systems	Response time	Duration time	Repeatability	Signal conversion method	Ref.
UPC/MXene-MMT	3.1 s	60 s	NM	Flame	[20]
Cellulose/MXene	<1 s	4 h	NM	Flame	[23]
Cellulose/MXene-APP	1.79 s	442 s	NM	Flame	[24]
PMSQ/MXene/cellulose aerogel	1.8 s	10	NM	Flame	[25]
Cellulose/MXene-GO/PA	2 s	NT	NM	250 °C	[75]
CMPL	4 s	>1 h	Yes	Flame	This work

Note: UPC: 2-ureido-4[1H]-pyrimidinone-containing cellulose; MMT: montmorillonite; APP: ammonium polyphosphate; PMSQ: polymethylsilsesquioxane; GO: graphene oxide; PA: phytic acid. NM: not mentioned.

indicating insufficient fire durability and long-term reliability. By comparison, the CMPL film developed in this work simultaneously

achieves stable fire-warning behavior and prolonged alarm duration. Although its response time (~ 4 s) is slightly longer than the fastest reported values, the CMPL system can continuously sustain an alarm signal for over 1 h and, more importantly, exhibits excellent repeatability under repeated flame exposure. This level of performance surpasses most previously reported MXene/cellulose-based fire-warning systems, which typically lose functionality after a single alarm cycle. Collectively, these comparative results demonstrate that CMPL effectively overcomes the long-standing trade-off between ultrafast response and durable, repeatable fire-warning capability, highlighting its strong potential for practical fire safety applications.

Based on the above analysis, the working mechanism of the cyclic fire warning responses of CMPL film is primarily governed by the resistance transition of the TiO_2 -based conductive network (Fig. 6a). In the first flame attack, the LM, owing to its high thermal conductivity, can rapidly absorb and transfer the heat from flame. Simultaneously, the LM oxidation releases additional heat, while the thermal decomposition of cellulose and PDA polymer chains generates gaseous products (CO , CO_2 , NO_x , etc.) and oxygen-containing radicals. These species react with adjacent MXene layers, accelerating their oxidation to form TiO_2 nanoparticles. This mechanism is supported by the significant reduction in the C/O atomic ratio from ~ 3.1 to ~ 0.4 before and after burning (Figs. 2b and 6b) and corroborated by XRD analysis (Fig. 6c), where MXene peaks disappear and TiO_2 peaks emerge within 1 s of flame exposure. The simultaneous pyrolysis of organics, the oxidation of MXene and LM produce strong exothermic effects, accounting for the

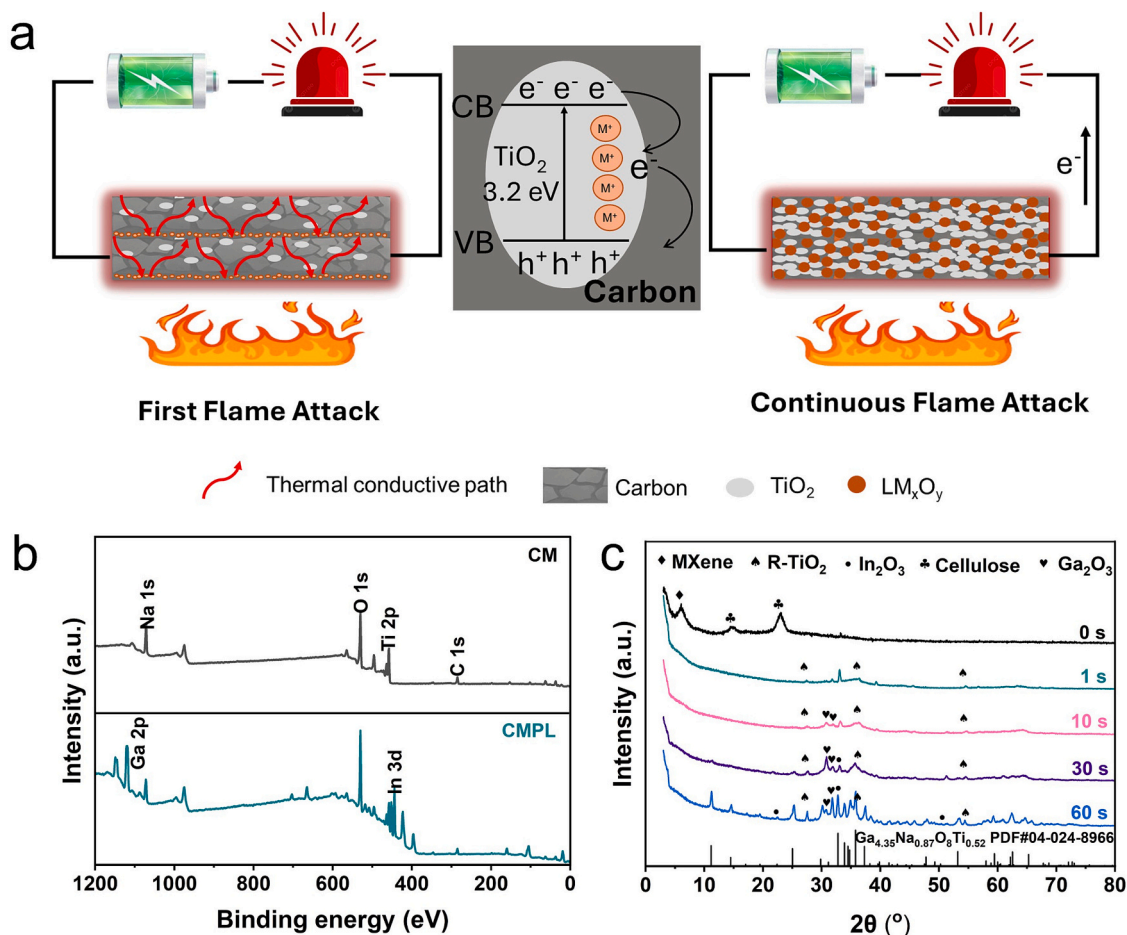


Fig. 6. (a) Schematic illustration for resistance transition mechanism of the C-LM_xO_y-TiO₂ network during the cyclic flame detecting process. (b) XPS summary spectra results indicate the residual C element can be still observed in the final samples, indicating the possible C-LM_xO_y-TiO₂ network during the burning process. (c) XRD patterns of CMPL after different flame attack time of 0 s, 1 s, 10 s, 30 s and 60 s, respectively. These results demonstrate the formation of the C-LM_xO_y-TiO₂ interconnected network after burning.

higher surface temperature observed for CMPL compared to CM during flame exposure (Figs. 3b and S6). Microstructural (Figs. S7, 8) and XRD analyses (Figs. 6c and S12) further reveal that the residual carbon from polymer pyrolysis bonds with TiO_2 and LM_xO_y nanoparticles, forming a conductive C-doped TiO_2 - LM_xO_y hybrid network. Under continuous flame exposure, thermally excited electrons and holes are generated within the C- LM_xO_y doped- TiO_2 network due to its oxygen-vacancy-dependent band structure, which exhibits a relatively low band gap (~ 3.2 eV) [76]. This facilitates electron excitation from the valence band (VB) to the conduction band (CB) [77,78], leading to a pronounced transition from the insulating to the conductive state. Furthermore, incorporation of C- LM_xO_y into TiO_2 further narrows the effective band gap, reducing the excitation energy and enhancing carrier transport to the surface. These processes underpin the ultrafast, reversible charge transfer and fire-warning response of CMPL films, highlighting the synergistic role of LM, MXene, and polymer-derived carbon in establishing a durable, responsive conductive network [79,80].

4. Conclusion

In summary, we developed previously unexplored strategy for constructing fast, durable, and intrinsically flame-retardant fire-warning sensors by integrating PDA-coated liquid metal into cellulose/MXene networks. The resulting CMPL films exhibit a unique combination of ultrafast alarm activation (~ 4 s), rapid resistance recovery (~ 2 s), and exceptional cyclic stability, while achieving a substantial reduction in heat release and markedly enhanced char formation. The synergistic interplay among cellulose pyrolysis, PDA carbonization, MXene oxidation, and LM exothermic oxidation leads to the in-situ formation of a dense C- LM_xO_y - TiO_2 conductive-insulating network, which simultaneously strengthens condensed-phase flame retardancy and enables reversible thermoresistive switching. Such integration of structural protection and rapid electrical response effectively overcomes the long-standing trade-off between flame endurance and sensing speed in fire-warning materials. Overall, this study establishes a versatile and scalable design paradigm for creating multifunctional, reusable fire-warning systems and highlights the untapped potential of liquid metal chemistry in next-generation fire-safety materials.

CRedit authorship contribution statement

Yu Lei: Writing – review & editing, Writing – original draft, Conceptualization, Methodology. **Lulu Xu:** Visualization, Investigation. **Yuan Xien Lee:** Visualization, Investigation. **Yan Zhang:** Validation, Resources. **Yao Yuan:** Supervision, Resources, Funding acquisition. **Anthony C.Y. Yuen:** Formal analysis, Data curation. **Vipul Agarwal:** Supervision, Resources. **Kate T.Q. Nguyen:** Investigation, Formal analysis. **Guan Heng Yeoh:** Supervision, Funding acquisition. **Cheng Wang:** Methodology, Investigation. **Qing Nian Chan:** Writing – review & editing, Software. **Wei Wang:** Writing – review & editing, Supervision, Funding acquisition.

Declaration of competing 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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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.cej.2026.174679>.

Data availability

Data will be made available on request.

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