Electronic Supplementary Information

High-thermopower ionic hydrogel for intelligent fire protection

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1. Formula and characterizations

1.1. Formula

Table S1 The formula of HTIG

Sample	AAm (g)	AMPSA (g)	$CaCl_2$ (g)	MBA (g)	APS (g)	TEMED (mL)	H_2O (g)	PDDA (20 wt%) (g)
HTIG0	1.00	1.00	0.50	0.01	0.02	0.02	5.00	0.00
HTIG1	1.00	1.00	0.50	0.01	0.02	0.02	4.00	1.25
HTIG2	1.00	1.00	0.50	0.01	0.02	0.02	3.00	2.50
HTIG3	1.00	1.00	0.50	0.01	0.02	0.02	2.00	3.75
HTIG4	1.00	1.00	0.50	0.01	0.02	0.02	1.00	5.00

1.2. Characterizations

Ionic thermoelectric measurement: The ionic Seebeck coefficients (S_i) of HTIG was measured under ambient conditions in a planar configuration, as shown in Figure 4a. The S_i of HTIG was obtained from the linear relationship between thermopower and temperature difference, measured three times on three duplicate samples with different temperature gradients generated by two Peltiers. The voltage differences (ΔV) between the two electrodes were measured with a multimeter (Keithley instruments DMM6500) and the temperature differences (ΔT) between the two electrodes were evaluated by the K-type thermocouples and measured with thermodetector (Yowexa SSN61, China). The S_i was the negative of the slope of ΔV-ΔT fitting curve.

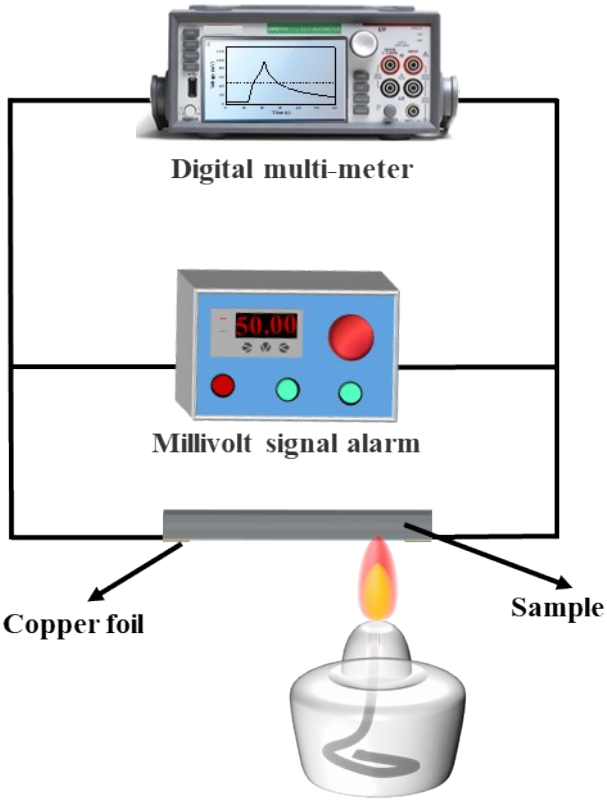
Ionic conductivity measurement: The ionic conductivity (σ_i) was measured by the electrochemical impedance spectroscopy (EIS). Firstly, Nyquist plots of HTIG were

measured by electrochemical workstation (CHI660D, China) with the voltage amplitude of 5 mV and frequency from 10^5 H_Z down to 1 Hz. The sample was cut to a radius of 8 mm with the thickness of about 2 mm and sandwiched between two circular electrodes (r=8 mm). Then σ_i of HTIG was calculated by Equation 1.

$$\sigma_i = \frac{l}{R * S} \tag{1}$$

Where σ_i is the ionic conductivity, l is the thickness of HTIG, S is the effective electrode area and R is the resistance of sample obtained from Nyquist plots.

Fire-warning test: The fire-warning system consisted of a millivolt signal alarm (HB414, Dongguan Daxian Instrument Equipment Co., Ltd., China) and a digital multimeter (DMM6500 6 1/2, Keithley Instrument, US), which were connected as shown in Scheme S1. Before the test, the sample with the length of 50 mm was connected to the system, and the copper foil was used as the electrode, whose length at both ends of the sample were 5 mm. During the test, the flame of the alcohol lamp was about 15 mm away from one end, and the alarm voltage of the millivolt alarm was set to 50 mV and the digital multimeter was opened to record the voltage changes at both ends of the sample.



Scheme S1. The diagram of fire-alarm test.

Mechanical and self-adhesive performances: The mechanical property was investigated by a universal testing machine (Mark-10, USA) with a speed of 50.0 $mm \cdot min^{-1}$ at room temperature. The size of ionogel prepared was 30 mm × 10 mm × 1 mm. The self-adhesive property was tested by lap sheer on the machine (Mark-10, USA). An ionogel (1.5 cm × 1.5 cm) was sandwiched between two substrates (1.5 cm × 4.5 cm) (Figure 2d). The adhered assemblies were loaded to testing machine. All tests were conducted at a speed of 50 $mm \cdot min^{-1}$. Shear strength is determined as the maximum force per unit area.

Flame retardancy: The vertical combustion test involved exposing the sample with a size of 100 mm × 10 mm × 10 mm to an alcohol lamp flame with a length of 20 mm for 120 s. Limit oxygen index (LOI) of sample with a size of 100 mm × 10 mm ×

10 mm was measured by oxygen index tester (JF-3, Nanjing Jiangning Analytical Instrument Co., LTD, China).

Characterization of other properties: The morphology of the hydrogel was characterized by using a scanning electron microscope (Merlin, Carl Zeiss Jena, Germany) coupled with an energy dispersive X-ray spectrometer (X-MaxN 20, Oxford Instruments, Britain) at an acceleration voltage of 15 kV. The samples were prepared by cryo-fracture in liquid nitrogen and freeze-drying at -50 ℃, 260 Pa. FTIR was carried out by using an infrared spectrometer (TENSOR 27, Bruker, Germany). X-ray photoelectron spectroscopy (XPS) was performed on an X-ray photoelectron spectrometer (Axis Ultra DLD, Kratos, Britain). Thermogravimetric analysis was carried out by using a thermogravimetric analyzer (TG209 F1, Netzsch, Germany). The TG-FTIR was performed on a thermogravimeter (SFPA 449C, Netzsch, Germany) connected with an infrared spectrometer (Tensor 27, Bruker, Germany) at a temperature range of 40~800 °C under nitrogen atmosphere with a flow of 40 $mL \cdot min^{-1}$ and heated at a rate of 20 $°C \cdot min^{-1}$. The XRD patterns were measured using an X-ray diffractometer (X pert PRC, PANalytical, Netherlands) with the Cu Kα radiation. The accelerating voltage and current were 40 kV and 40 mA with a scanning speed of 4 $^{o} \cdot min^{-1}$ between 5º and 90º (2θ). The transparency of the sample with thickness of 1 mm was measured by spectrophotometer (UV-Vis/NIR U-3900H, Hitachi, Japan). The DSC test was performed in nitrogen using a TA instrument (DSC204F1, NETZSCH-Gerätebau GmbH, Germany) with a heating rate of 5 $°C \cdot min^{-1}$.

2. Figures

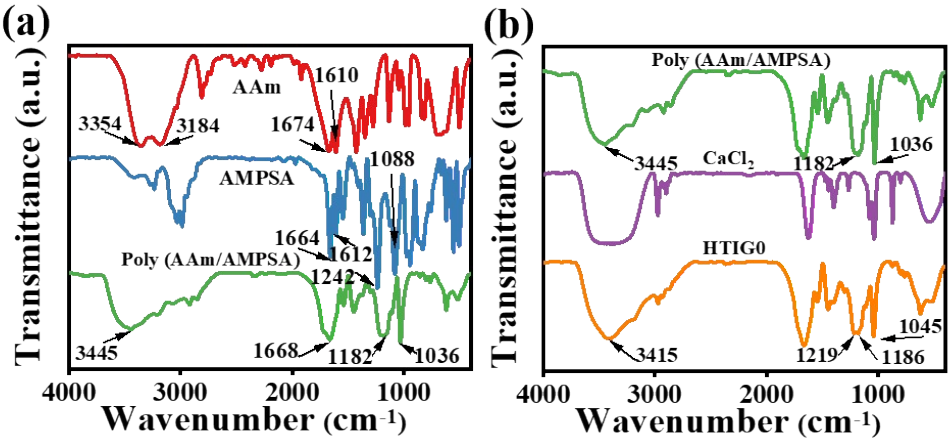


Fig. S1. FTIR spectra of AAm, AMPSA, Poly (AAm/AMPSA), $CaCl_2$ and HTIG0. The results showed successful polymerization of AAm and AMPSA, and interaction between Ca^{2+} and -NH_2, -SO_3^-groups.

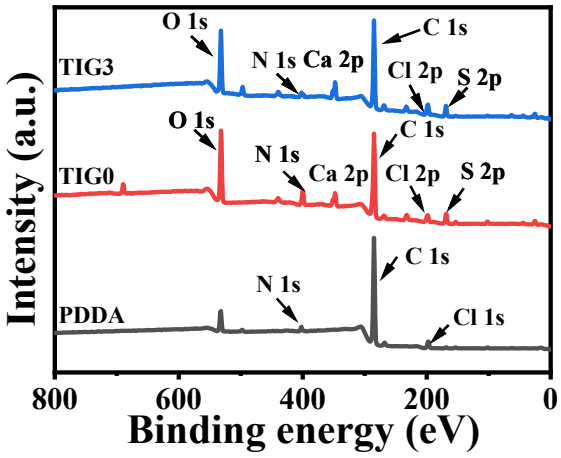


Fig. S2. XPS spectra of (a) PDDA, (b) freeze-drying HTIG0 and (c) freeze-drying HTIG3.

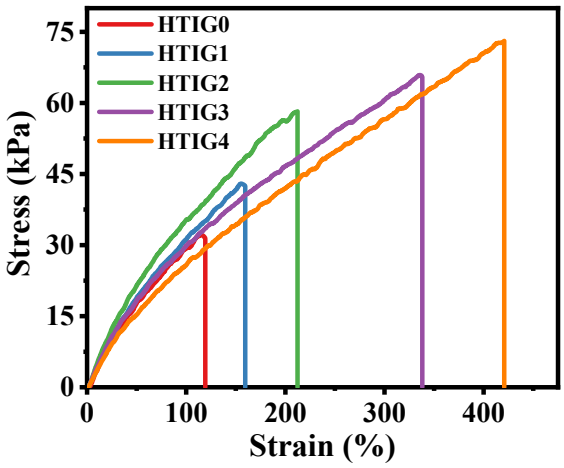


Fig. S3. Tensile stress-strain curve of HTIG.

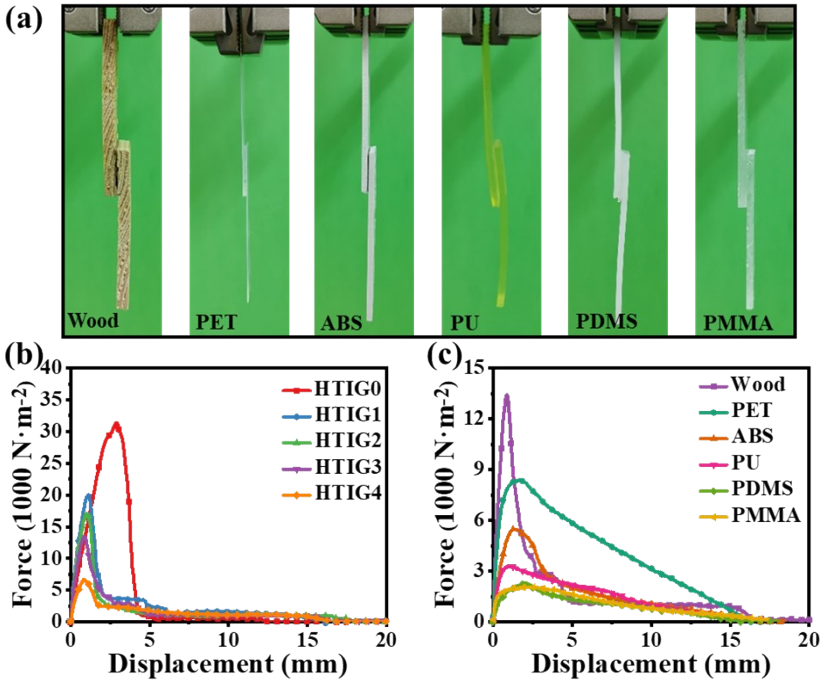


Fig. S4. (a) Photos of hydrogels coated on wood, PET, ABS, PU, PDMS, PMMA. Lap sheer curves of (b) HTIG coated to wood and (c) HTIG3 with various adherends. The results showed that HTIG3 exhibited good adhesion properties to various flammable substrates.

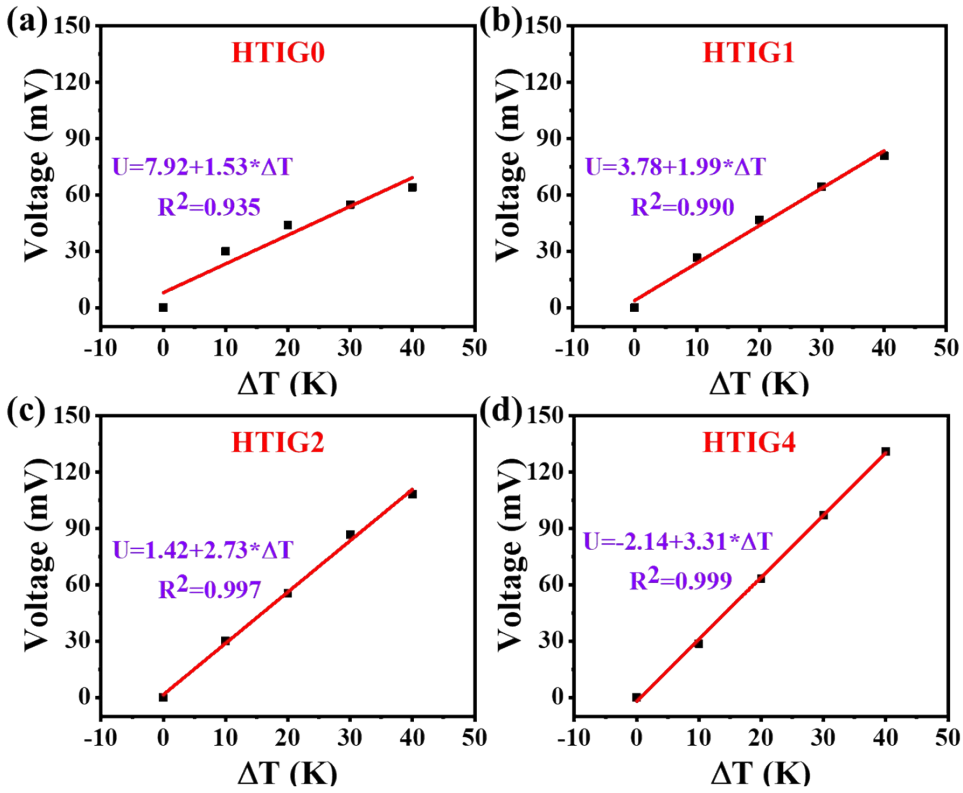


Fig. S5. The output voltage *vs* temperature difference of HTIG. The results showed that the thermoelectric voltage of HTIG exhibited an excellent linear relationship with temperature difference.

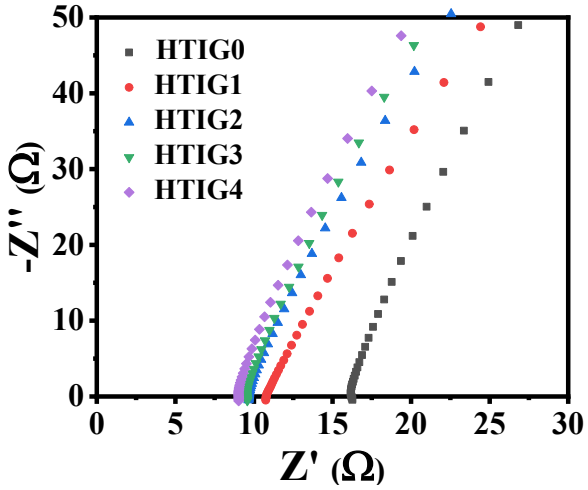


Fig. S6. The Nyquist plots of HTIG.

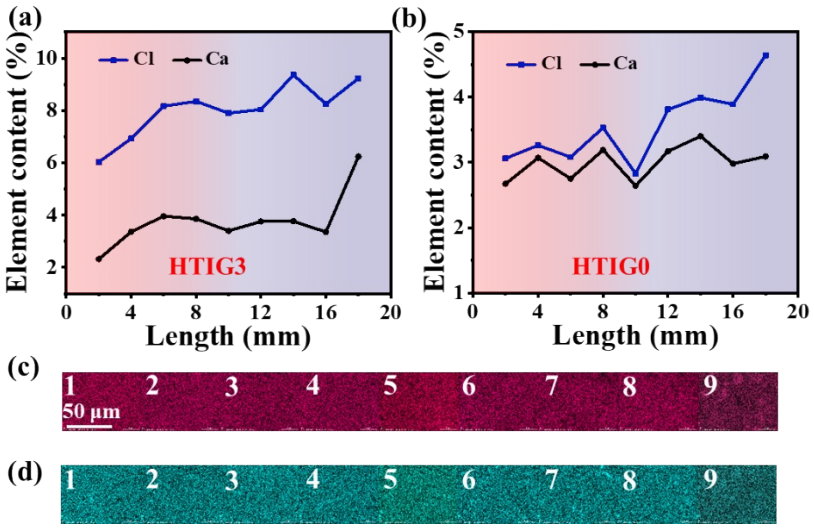


Fig. S7. The contents of chlorine and calcium in different positions after (a) HTIG3 and (b) HTIG0 placed at ΔT of 10 K for 1h. EDS maps of (b) Cl and (c) Ca at different position after HTIG0 placed at ΔT of 10 K for 1h. The results showed that in the case of temperature difference, the content of Ca^{2+} and Cl^{-} at the cold end of HTIG was higher than that at the hot end, indicating that ions migrate from the hot end to the cold end.

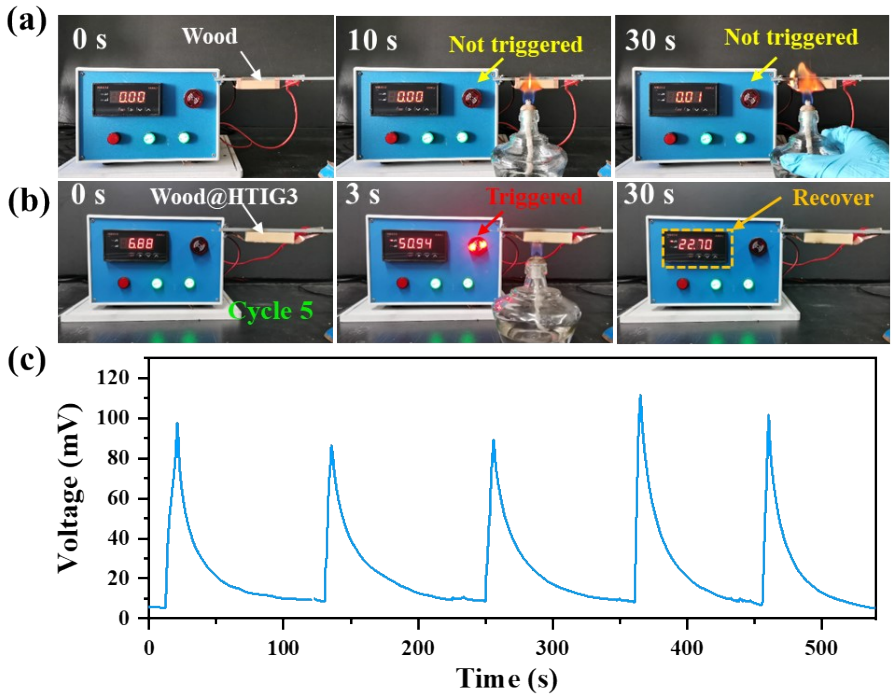


Fig. S8. (a) The video screenshots of Wood during the first fire warning test. (b) The video screenshots of Wood@HTIG3 during the fifth fire warning test. (c) The voltage curve of the Wood@HTIG3 during the cyclic fire-warning test. The results showed that HTIG endowed wood with repeated fire-warning ability.

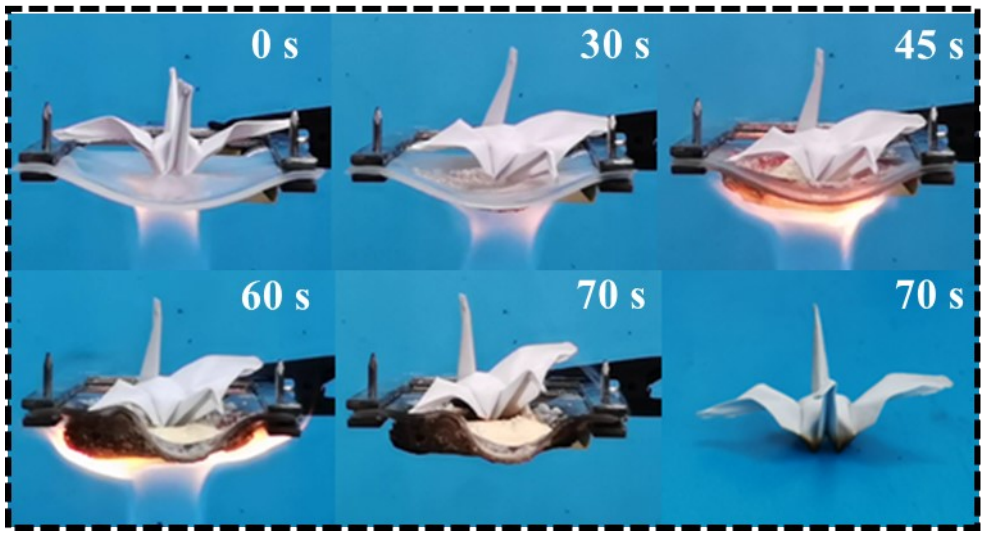


Fig. S9. The screenshots from a video of a paper crane protected by HTIG3 . This results showed the excellent fire protection performance of HTIG3.

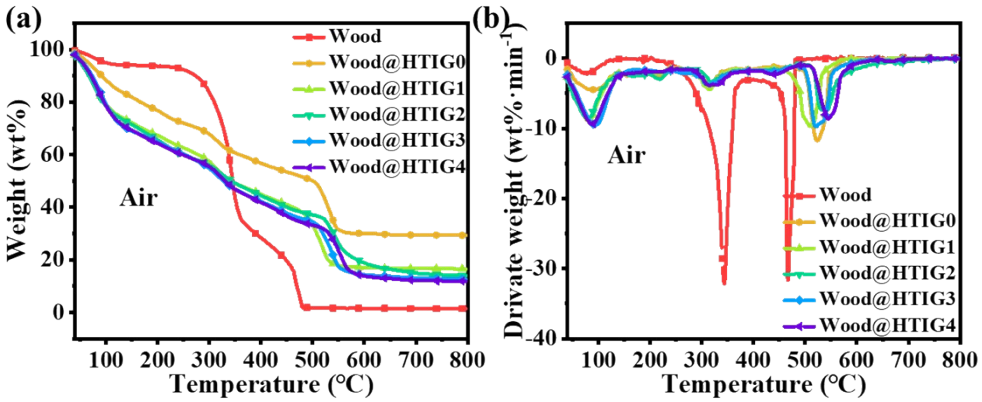


Fig. S10. (a) TG curves and (b) DTG curves of Wood and Wood@HTIG in air atmosphere. This results showed that HTIG significantly improved the thermal stability of Wood.

Table S2. Characteristic parameters of TG and DTG for the Wood and Wood@HTIG under air atmosphere

Sample	T_{max-1} (°C)	T_{max-2} (°C)	T_{max-3} (°C)	R_{max-1} (wt%·min^{-1})	R_{max-2} (wt%·min^{-1})	R_{max-3} (wt%·min^{-1})	Residue at 800 °C (wt%)
Wood	78.5	343.5	466.5	2.2	32.2	31.7	1.4
Wood@HTIG0	90.4	317.4	523.4	4.5	3.8	11.8	29.3
Wood@HTIG1	81.4	315.4	509.4	9.0	4.5	9.7	16.5
Wood@HTIG2	78.2	315.2	541.2	8.6	3.6	7.4	14.0
Wood@HTIG3	93.3	309.3	521.3	9.6	3.7	9.8	12.7
Wood@HTIG4	87.1	313.1	544.1	9.4	3.8	8.6	11.9

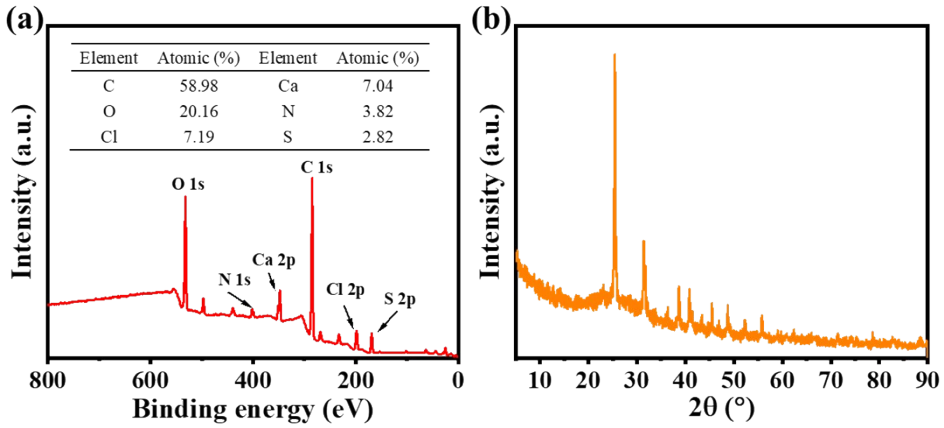


Fig. S11. (a) XPS and (b) XRD spectrum of the carbon layer formed after Wood@HTIG3 combustion. The results showed the formation of high thermal stability inorganic salt $CaSO_4$ after combustion of HTIG.

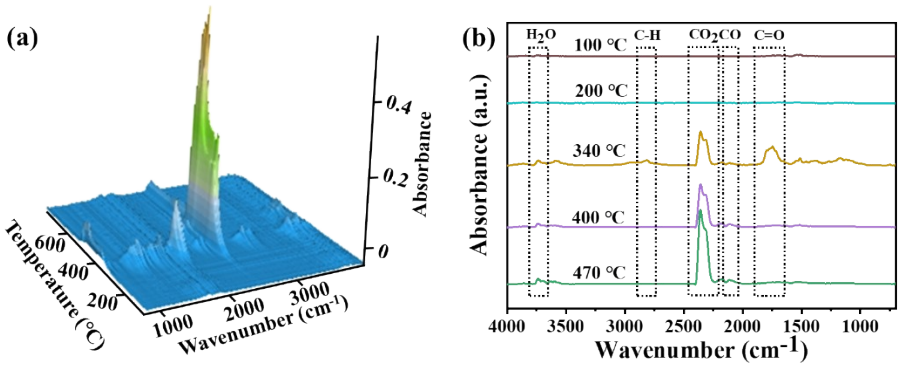


Fig. S12. (a) 3D TG-FTIR spectra and (b) the corresponding FTIR spectra at different temperature of Wood@HTIG3. This results showed that the thermal degradation products of wood were mainly alkanes, carbon monoxide and carbon dioxide, etc.

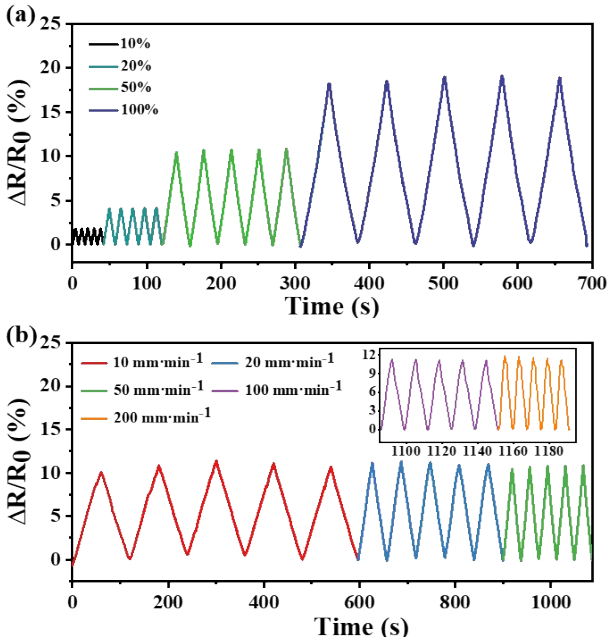


Fig. S13. The resistance variation response curves under (a) different elongation at 50 mm·min^{-1} elongation rate and (b) different elongation rate at 50% elongation. The results showed that HTIG3 exhibited good resistance response to different tensile rates and lengths.

3. Videos

Video S1: Fire warning test of Wood@HTIG3. When being burned, Wood@HTIG3 triggered the fire alarm in 4 s, indicating that Wood@HTIG3 was endowed with ultrasensitive fire-warning capability.

Video S2: Vertical burning test of HTIG3. Being exposed to a 20 mm vertical flame for 120 s, HTIG was hard to be ignited and it self-extinguished immediately after removing of the flame. The results indicated that HTIG3 possessed outstanding flame retardancy.

Video S3: Vertical burning test of Wood and Wood@HTIG3. Being exposed to a 20 mm vertical flame for 120 s, the Wood burned violently and charred. While being exposed to a 20 mm vertical flame for 120 s, Wood@HTIG was hard to be ignited and it self-extinguished immediately after removing of the flame. The results indicated that HTIG3 shown a good fire protective effect on Wood.

Video S4: Limit oxygen index test of Wood and Wood@HTIG3. Wood burned intensely in a space containing 28% oxygen, which exceeding 5 cm was burned in 70 s. Wood@HTIG3 burned slowly in a space containing 80% oxygen, and less than 3 cm was burned in 180 s. The results also indicated that HTIG3 shown a good fire protective effect on Wood.