Supporting Information

Self-powered and Green Ionic-type Thermoelectric Paper Chips for Early Fire Alarming

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1. Supporting Note S1：Experimental Details

(1) Materials and Characterizations

A4 paper (average thickness~87.5 μm) was purchased from Deli Group Co., Ltd. All ionic liquids were obtained from Lanzhou Greenchem ILS, LIPC, CAS (Lanzhou, China). Gold electrodes were made by magnetron sputtering coater (JCP-200, Beijing Technol Science Co., Ltd.). Electrochemical data was measured by CHI660E electrochemical station (Shanghai CH instrument Co., Ltd, China). The surface temperature changes of paper chips under different heating voltages were recorded by an infrared camera (Fluke Tix 660). Optical images were captured by an Olympus E-PM1 camera. A thermal-gravimetric analysis was operated on a Q50 TGA (Trios AutoPilot Instruments).

(2) The preparation of paper-based ionic thermoelectric chip

All paper-based ionic thermoelectric chips were prepared with the use of A4 paper stripes with 0.5 cm in width and 5.0 cm in length. Gold electrodes with the length of 1.0 cm were sputtered on both sides of paper stripes by magnetron sputtering for 60 seconds. In order to improve the stability of the chip, the gold electrodes were protected by scotch tapes. Two holes were subsequently punched through the gold electrodes for the circuit connections. Ionic liquids were printed on the paper stripes and encapsulated by scotch tapes. The final thermoelectric chip was fabricated by depositing gold electrodes again that were used to connect the inner ionic liquids with external measurement circuits. Following this preparation procedure, paper chips with the use of other ionic liquids or with different size were also prepared. Moreover, single p-type and n-type thermoelectric chips could be alternately connected into thermoelectric arrays to increase the output voltage of the whole system.

(3) The thermoelectric measurement of paper-based ionic thermoelectric chip at different temperature gradients

The commercial Peltier device (TES1-12703) was used to adjust the temperature of one side of thermoelectric chips so that a temperature gradient was generated from one gold electrode to another. In order to quickly cool the hot side, a cooling fan was placed under the Peltier device through the connection of thermal grease. The temperature of thermoelectric chip was synchronously detected by the thermocouple. Here, the thermoelectric performance of the chip was measured at five different temperatures, including 22 K, 32 K, 40 K, 50 K, 60 K. Each cycle of thermoelectric measurements includes two-minute heating process and two-minute cooling process. The voltage between the heating side and cooling side would be different as the change of temperature, and it was collected by the Electrochemical Workstation in open circuit potential-time (OCPT) mode.

(4) Monitoring the temperature gradient of thermoelectric chip when being heated

Based on the measurement setup as stated above, the temperature gradient could be monitored when the thermoelectric chip was heated. Specifically, the voltage of

Peltier devices was adjusted from 4.0 V to 8.0 V at a gradient of 1.0 V. After heating for 2 minutes, the distribution of temperature was monitored by an infrared camera.

2. Supporting Note S2: Theoretical calculations

2.1 Computation details

All density functional theory calculations were performed by VASP software based on Generalized Gradient Approximation (GGA). The generalized gradient approximation for the exchange-correlation has been represented by the Perdew-Burke-Ernzerhof (PBE) functionals with PAW potentials of the core, and the exchange-association functional used RPBE. All the calculated surfaces were Au (111) surfaces. The k point was set to 8×8×8 when calculating the bulk structure, and the k point was set to 2×2×1 when calculating the slab structure. The vacuum space of 17Å was used in the direction normal to the Au (111) slabs to avoid interactions between two layers. The valence electron wave function was expanded using a plane wave basis set. The cutoff energy value was 550 eV. The standard of self-consistent field energy convergence was 1×10^{-5}eV. The atoms have been optimized using quasi Newton algorithm until the forces on the atoms were less than 0.01 eV/Å^3. In some cases, where the forces were relatively higher, we used a conjugate gradient technique followed by quasi Newton approach. The final geometries obtained from these calculations were re-optimized using the DFT-D3(B-J) method of Grimme to include the dispersion correction. Dipole correction has been applied in the direction of the molecular adsorption. During the structure optimization process, the bottom two atomic layers were fixed, and the upper three atomic layers were relaxed. Gibbs free energy was approximately calculated by fixing one ion and moving the other ion.

2.2 INCAR file for optimized Au (111) surface

INCAR file for optimized Au (111) surface

system = Au

ISTART=0

ICHARG=2

ENCUT=550

ISMEAR = 0

SIGMA = 0.12

EDIFF=1E-5

GGA=RE

IVDW=12

PREC=Accurate

LREAL=Auto

ALGO=Fast

EDIFFG=-0.01

IBRION=1

POTIM=0.5

NSW=300

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IDIPOL=3

Coordinates of the optimized Au (111) surface

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0.0000000000000000	0.0000000000000000	26.4190998077000003

Au

80

Selective dynamics

Direct

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3. Data section

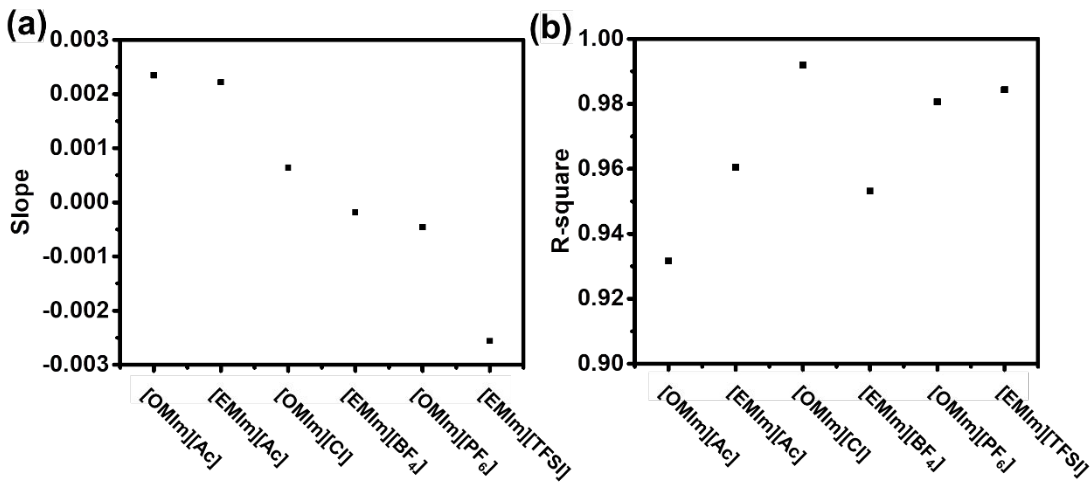

Figure S1. Sensitivity and R-square of temperature-voltage curves of different ionic liquids.

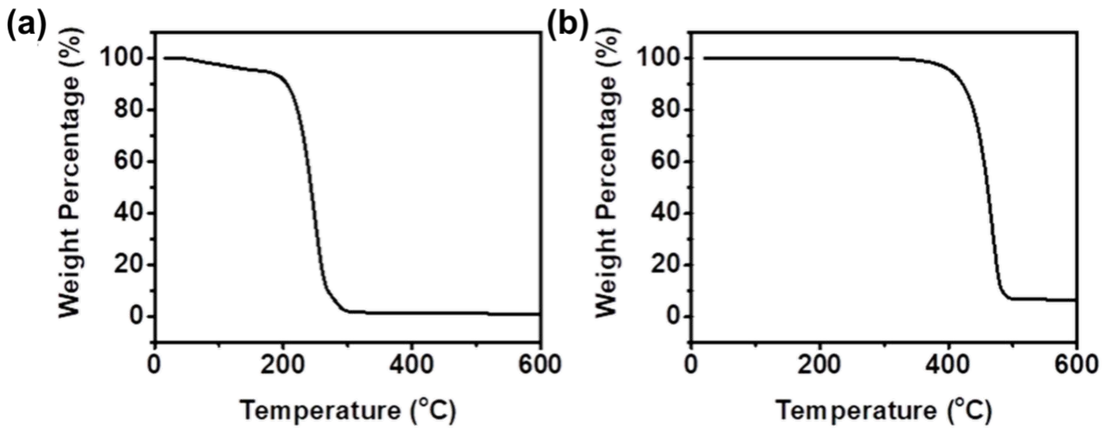

Figure S2. The thermogravimetric analysis of ionic liquids. (A) [EMIm][Ac]; (B) [EMIm][TFSI].

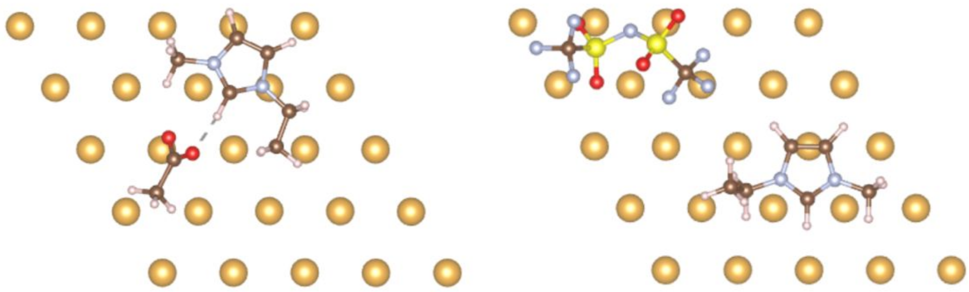

Figure S3. Adsorption structure of ionic liquid on Au(111) surface.

Table S1 Density functional calculation of desorption Gibbs free energy of [EMIm][TFSI] and [EMIm][Ac] at different distances at 0K.

Distance \ ΔG (kJ/mol) \ Ion	$[EMIm]^+$(N)	$[TFSI]^-$(N)	$[EMIm]^+$(P)	$[Ac]^-$(P)
1Å	**66.81619**	**62.79964**	**76.35577**	**61.38211**
2Å	**137.65569**	**140.54447**	**166.25239**	**103.38552**
3Å	**177.93348**	**197.71406**	**248.82714**	**137.25491**
4Å	**229.68306**	**239.06642**	**308.62989**	**164.65335**
5Å	**285.98716**	**270.33004**	**348.40437**	**183.89398**
6Å	**328.99449**	**294.00186**	**376.39085**	**197.34209**
7Å	**361.88476**	**311.98864**	**395.84479**	**207.18693**
8Å	**387.29363**	**325.96376**	**411.25658**	**214.75878**
9Å	**407.71853**	**337.03336**	**423.07295**	**220.90732**

Table S2 Density functional calculation of desorption Gibbs free energy of [EMIm][TFSI] and [EMIm][Ac] at different distances at 298K.

Distance \ ΔG (kJ/mol) \ Ion	$[EMIm]^+$(N)	$[TFSI]^-$(N)	$[EMIm]^+$(P)	$[Ac]^-$(P)
1Å	84.46933	97.24232	94.00892	58.80531
2Å	152.35171	184.5301	180.94841	98.95496
3Å	190.14856	231.55509	261.04222	127.5701
4Å	252.93874	265.50915	331.88557	168.49334
5Å	312.73506	296.07089	375.15228	195.77505
6Å	353.14242	297.81555	400.53878	199.92707
7Å	395.25067	321.28558	429.21069	217.93422
8Å	411.92056	345.64443	435.88351	216.76041
9Å	431.54162	354.32019	447.24028	224.29187

Table S3 Density functional calculation of desorption Gibbs free energy of [EMIm][TFSI] and [EMIm][Ac] at different distances at 333K.

Ion / ΔG (kJ/mol) / Distance	$[EMIm]^{+}$(N)	$[TFSI]^{-}$(N)	$[EMIm]^{+}$(P)	$[Ac]^{-}$(P)
1Å	87.46599	102.81649	83.09752	59.05198
2Å	154.99969	191.50796	174.8109	98.96583
3Å	192.47766	236.99086	259.46906	126.95313
4Å	257.11459	269.73097	306.77774	169.78086
5Å	317.54371	300.1864	364.03735	198.29521
6Å	357.5742	298.72144	399.58899	200.96958
7Å	401.01236	322.82067	414.33982	220.32009
8Å	416.29679	348.69437	441.11611	217.81618
9Å	442.38435	357.08148	442.22324	225.51562

The Caption of Supporting Information Video

In this video, a wireless fire monitoring system was constructed by integrating paper-based thermoelectric module with the single chip microcomputer. The entire fire warning process consists of three stages, namely the beginning, burning and extinguishing moments. The change of voltage during each process was recorded by Electrochemical Workstation and depicted in the illustration in the upper right corner of the video. Once the voltage signal exceeds the threshold voltage that is set for the alarming circuit, the fire alarming system alarms is triggered via lightening the red LED and activating loudspeaker.