

Ultrasonication-aided self-assembly strategy toward PTCDa/RGO film
cathode for organic K-ion full batteries

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Experimental Section

Synthesis

Preparation of PTCDA/RGO

Graphene oxide (GO) solutions were synthesized by modified Hummers' method as previously reported [27, 28]. The PTCDA/RGO film was prepared by ultrasonication-aided method and followed by the thermally reduction treatment. In a typical procedure, 30 mg PTCDA was dissolved in 6 ml GO solution (5 mg ml^{-1}). The mixed solution was then directly placed in an ultrasonic cleaner for 3 h (the frequency was 40 KHz). Next, the as-obtained solution was poured into a culture dish for freeze-drying to obtain the PTCDA/GO film, which were then cut into discs with a diameter of 12 mm. Subsequently, the precursor was heated at $400 \text{ }^\circ\text{C}$ for 4 h in Ar atmosphere. For comparison, the same procedure was adopted to synthesize the films with different mass ratio of PTCDA to GO (1:2, 1:1, 2:1, 4:1, and 0:1), which were denoted as PTCDA/RGO-33%, PTCDA/RGO-50%, PTCDA/RGO-66%, PTCDA/RGO-80% and RGO, respectively. The 33%, 50%, 66% and 80% values refer to the weight percent of PTCDA in the hybrid film.

Preparation of PTCDA

The PTCDA electrode was prepared by mixing 50% PTCDA, 20% PVDF, and 30% ketjen black in N-methylpyrrolidone (NMP) with constant stirring for 12 h to form a homogeneous slurry, which was then coated on an aluminum foil and dried at $70 \text{ }^\circ\text{C}$ in a vacuum oven for 12 h.

Preparation of $\text{K}_4\text{PTC}/\text{EG}$

Typically, PTCDA (200 mg) was first dissolved in concentrated KOH (20 ml) and stirred at $30 \text{ }^\circ\text{C}$ for 6 h. Subsequently, the resultant mixture was poured into ethanol solution, then the obtained yellow precipitations were filtrated and washed with water and ethanol for several times. After dried at $70 \text{ }^\circ\text{C}$, the resulting sample was named as K_4PTC .

1.2 mg EG was placed in ethanol for ultrasonic dispersion for 3 h for pretreatment. Then 0.06 mg K_4PTC aqueous solution was added into the as-prepared EG aqueous dispersion and the mixture was stirred at room temperature for 3 h. The composite was purified by filtration and washing with distilled water. Finally, the product was afforded and named as $\text{K}_4\text{PTC}/\text{EG}$.

Characterization

SEM (Hitachi, S4800), XRD (Bruker D8A A25), TEM (Hitachi, JEL 2100), and XPS (ThermoFischer, ESCALAB Xi+) were used for the characterization of morphology, structure, and chemical composition of the products. The chemical bindings were identified by Fourier transform Infrared spectroscopy (FTIR, Nicolet 6700 instrument, Thermo Fisher, USA). Thermogravimetric analysis (TGA) and differential scanning

calorimetry (DSC) were collected on an STA449 F3 simultaneous thermal analyzer (Netzsch, Germany) coupled under a heating ramping rate of 5 °C min⁻¹ in nitrogen atmosphere.

Electrochemical measurements

The obtained PTCDA/RGO films were directly used as cathode. The anode was prepared by mixing 80 wt% of K₄PTC/EG sample, 10 wt% of Ketjen, and 10 wt% polyvinylidene fluoride (PVDF) with a decent amount of N-methyl-2-pyrrolidone (NMP) as solvent. The uniformly ground slurry was coated with designated thickness onto Cu foil for anode, drying at 80 °C overnight. The 2032-type coin cells were assembled in a glove box (Mikrouna Co., Advanced 2440/750) and contained a metallic K foil as the counter electrode, a glass fiber (GF/D) separator and 0.8 M KPF₆ in ethylene carbonate/dimethyl carbonate (EC/ DMC, 1:1 in volume) as the electrolyte. to test the properties of anode and cathode. Full-cells (PHICs) were assembled using K₄PTC/EG as the anode and PTCDA/RGO as the cathode. Before the assembly of PHICs, K₄PTC/EG anode was prepotassiated in a half-cell at 0.05 A g⁻¹. Galvanostatic charge/discharge (GCD) tests were carried out with CT2001A battery testing system (Wuhan LAND). Cyclic voltammetric (CV) and electrochemical impedance spectroscopy (EIS) tests were performed with CHI 660E workstation.

Calculation of the energy density

The energy density (E) of the PTCDA/RGO-50%//K₄PTC/EG full cells were calculated by the following equations [29, 30]:

$$E = C * V \quad (1)$$

where C is the specific capacity of cathode, V is the average discharge voltage of the cell, t is the time for the discharge process.

Computational details

First-principles computations based on density functional theory (DFT) were implemented in the Vienna Ab initio simulation package (VASP). The generalized gradient approximation (GGA) involving Perdew, Burke, and Ernzerhof (PBE) was used for calculating the exchange-correlation energy. The impact of the van der Waals interactions was estimated, implemented in the optimized optB86b vdW functional. A 400 eV cutoff energy was adopted for the plane-wave basis set in conjunction with the projector augmented wave (PAW). The energy and force convergence were set to be 1×10⁻⁴ eV and 3×10⁻² eV respectively. The Brillouin zone was sampled using a 2 × 2 × 1 Monkhorst mesh in structure relaxation, a 4 × 4 × 1 Monkhorst mesh in energy computations. Graphene is used with 7 × 7 × 1 periodic supercell and the thickness of its vacuum layer is 25 Å along the z direction to ensure that no interaction occurred between the adjacent molecules. The binding energy (E_b) of molecular is defined as: E_b = E_{total} - E_{RG} - E_M, where E_{total} denotes the DFT total energy of molecular absorbed on

the Graphene, E_M is the energy of molecular and E_{RG} is the total energy of Graphene.

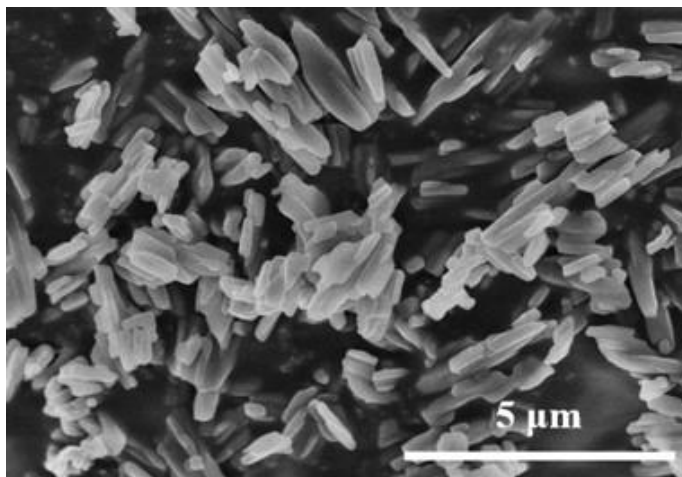


Fig. S1 SEM image of pure PTCDA

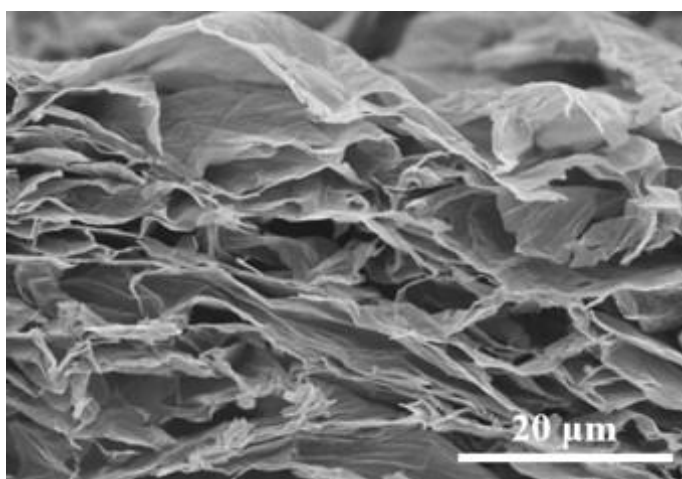


Fig. S2 Cross-sectional SEM images of RGO

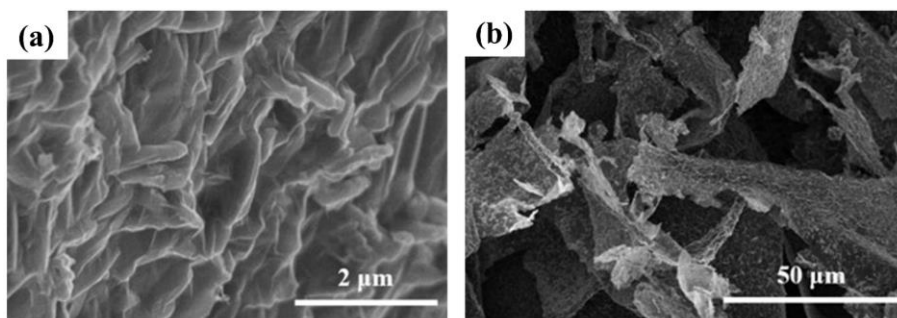


Fig. S3 (a) Top-view and (b) cross-sectional SEM images of PTCDA/RGO-66%

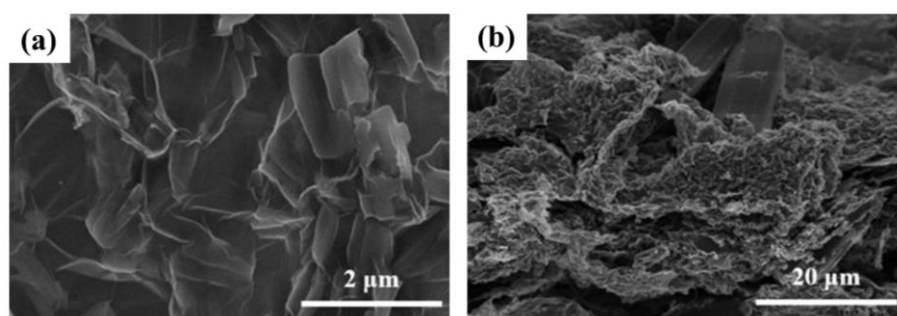


Fig. S4 (a) Top-view and (b) cross-sectional SEM images of PTCDA/RGO-80%

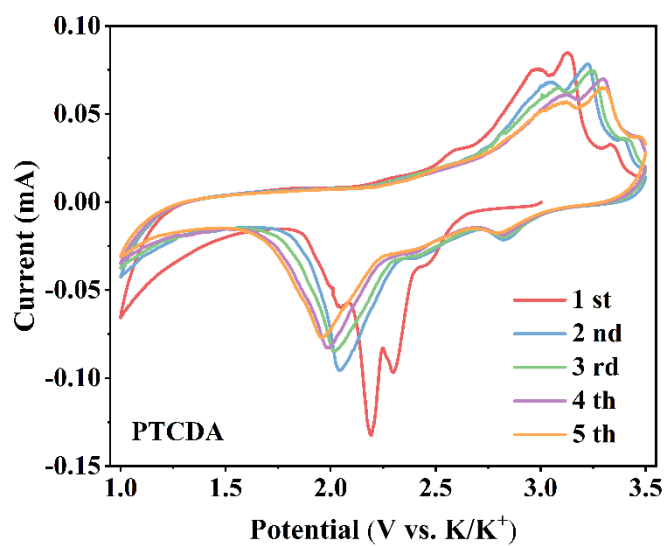


Fig. S5 CV of curves of PTCDA

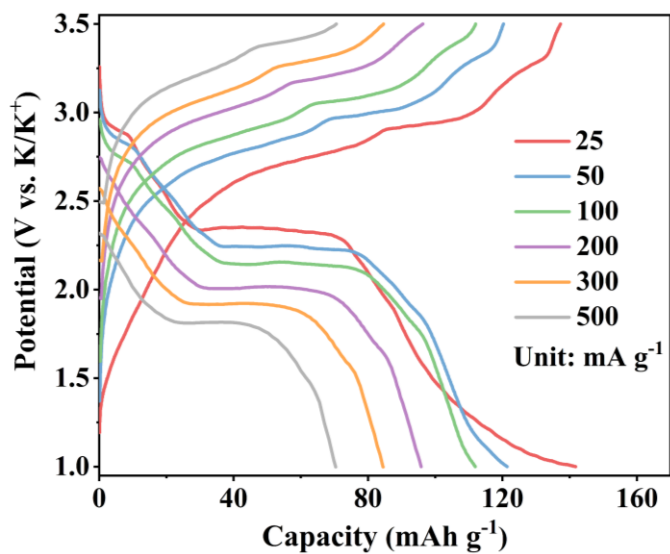


Fig. S6 Charge–discharge curves at different current densities of the PTCDA/RGO-50% cathode

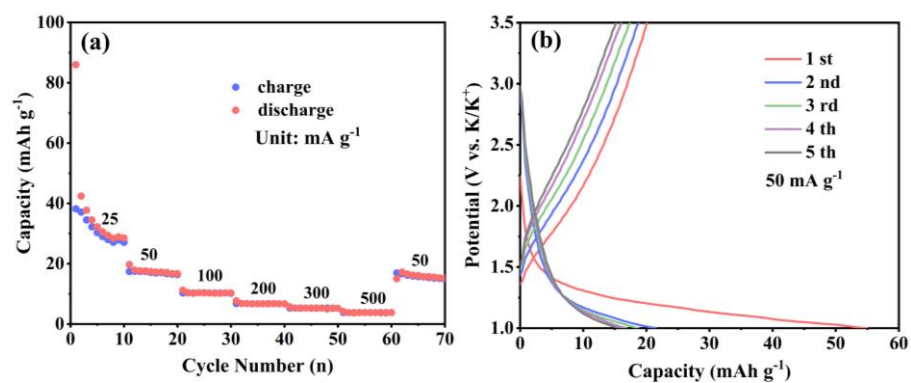


Fig. S7 Electrochemical performance of RGO cathode for KIBs. (a) rate capability, (b) Discharge and charge profiles at 0.05 A g^{-1}

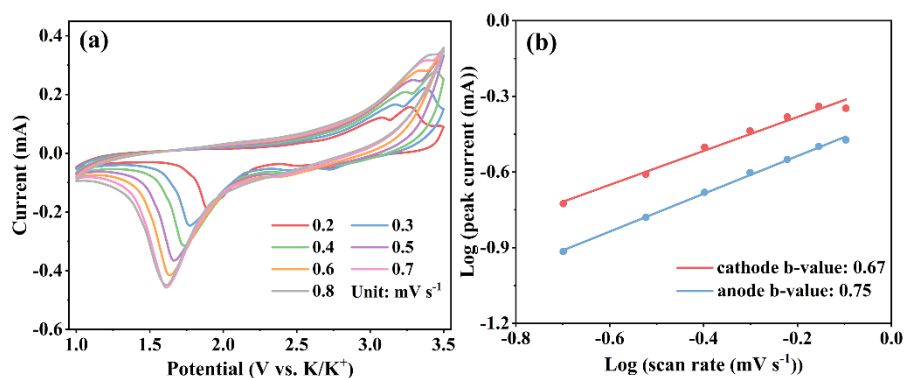


Fig. S8 CV curves at different scan rates, (b) the logarithm relationship between the scan rates and the peak current densities of PTCDA/RGO-50% cathode

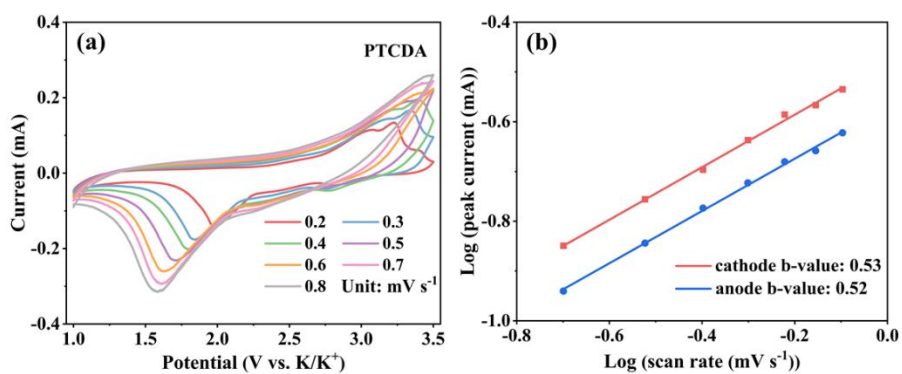


Fig. S9 CV curves at different scan rates, (b) the logarithm relationship between the scan rates and the peak current densities of PTCDA cathode

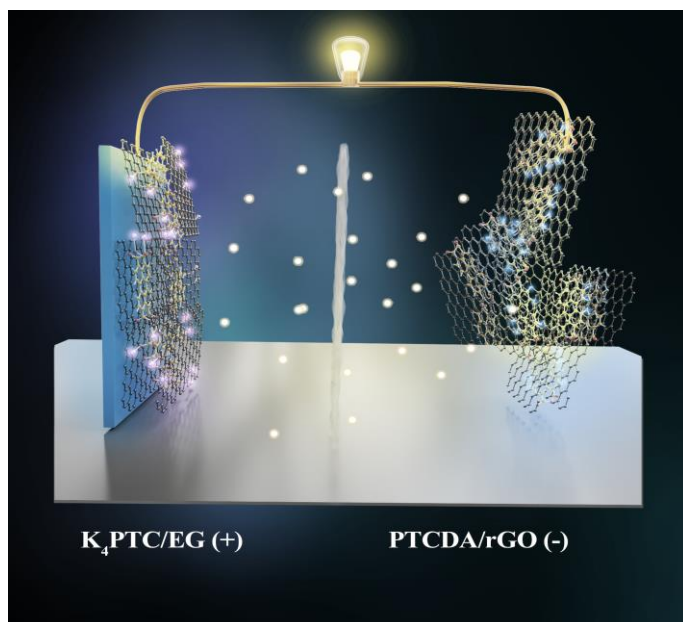


Fig. S10 Schematic illustration of PTCDA/RGO-1//K₄PTC/EG full cell.

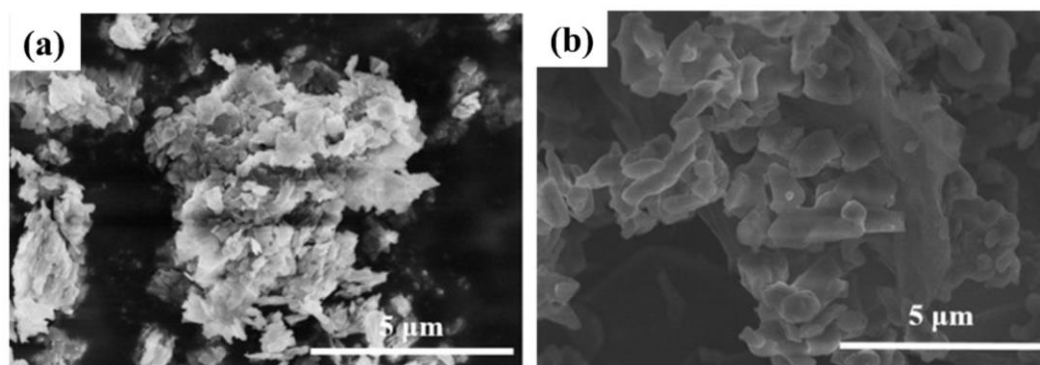


Fig. S11 SEM of (a) K₄PTC and (b) K₄PTC/EG

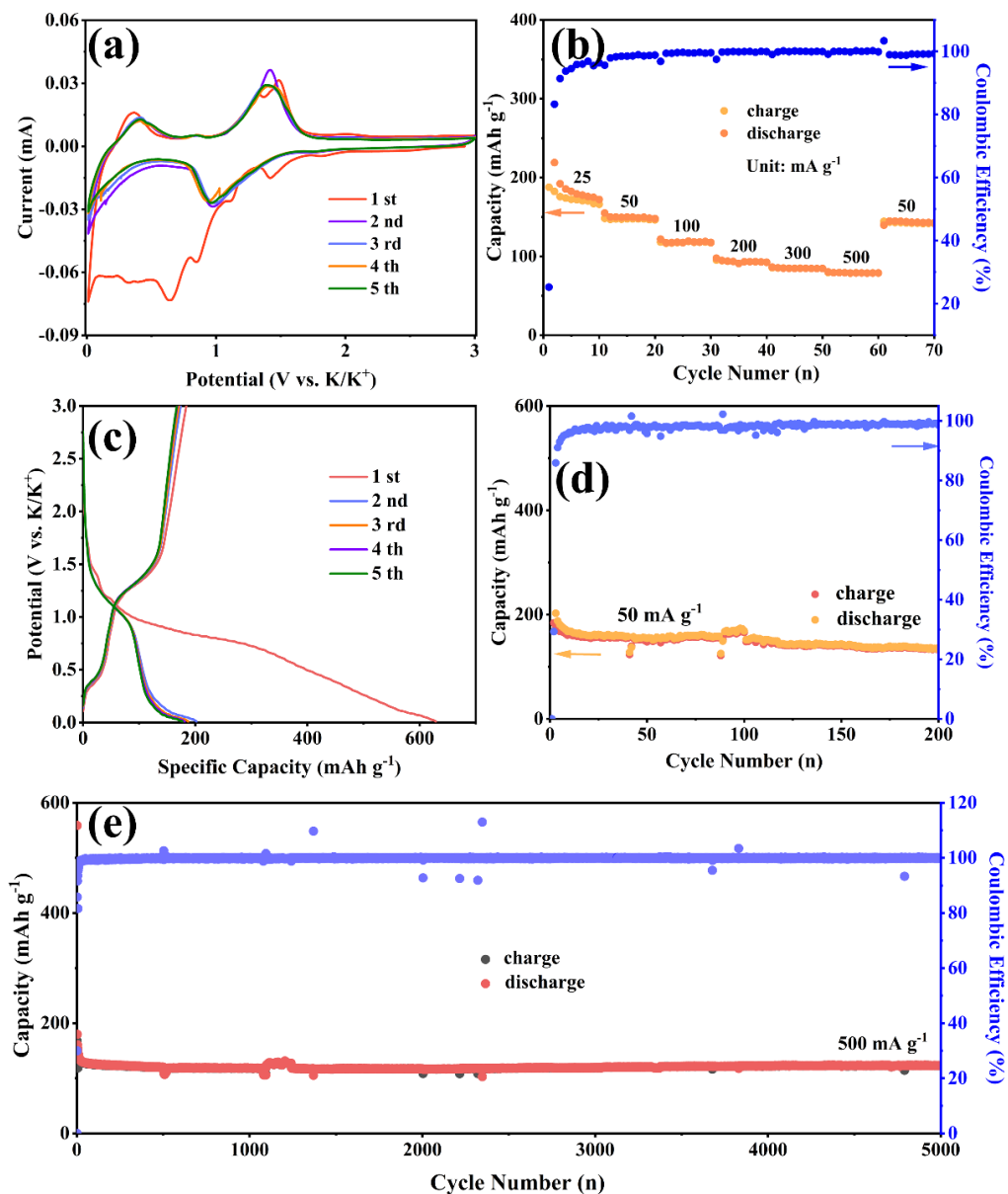


Fig. S12 Electrochemical performance of K₄PTC/EG anode for KIBs. (a) CV curves, (b) rate capability, (c) discharge and charge profiles of the initial five cycles, (d, e) long-term cycling capability at 0.05 A g⁻¹ and 0.5 A g⁻¹.

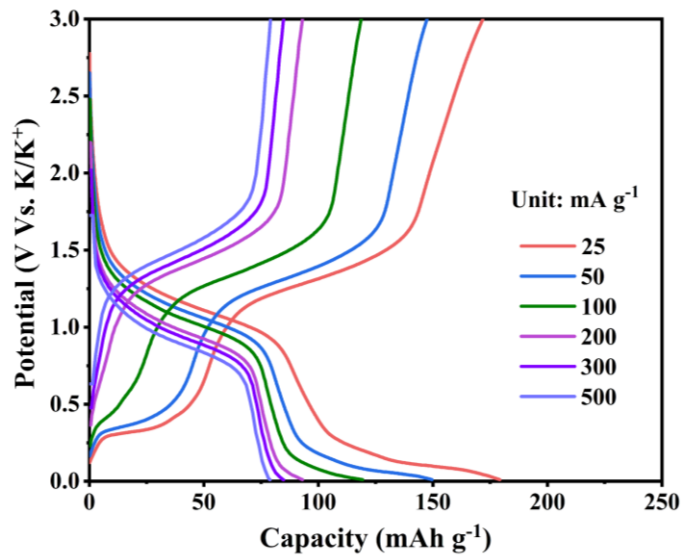


Fig. S13 Charge–discharge curves at different current densities of the PTCDA/RGO-50%/K₄PTC/EG PIFCs

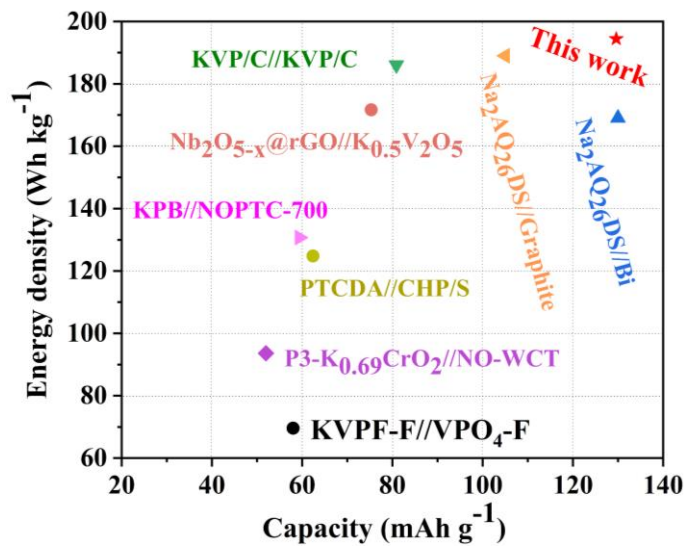


Fig.S14 Electrochemical performances comparison with the other reported works.

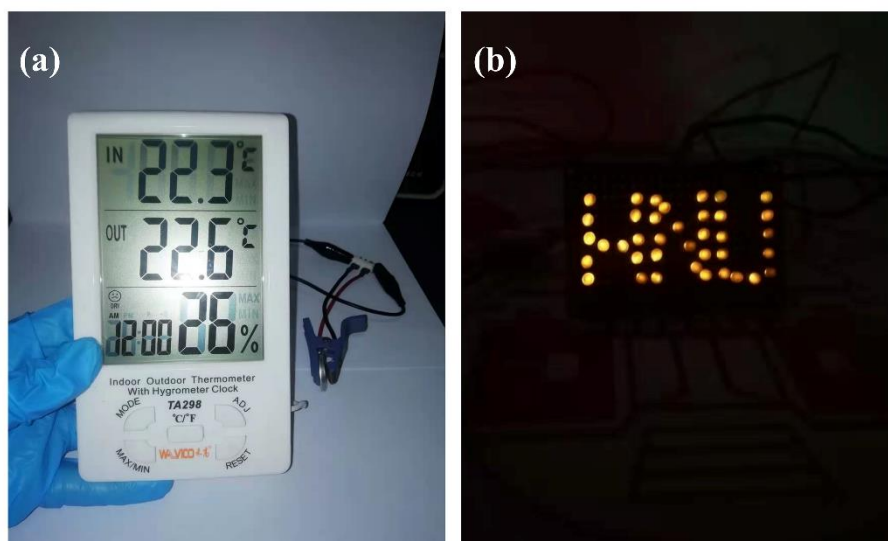


Fig. S15. Photographs of the operating thermometer and LED light powered by PTCDA/RGO-50%//K₄PTC/EG PIFCs.