

Supporting information

Ultra-High Endurance and High-Performance Quasi-Solid-State Fiber-Shaped Zn-Ag₂O

Battery to Harvest Wind Energy

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Materials

Silver Nitrate (AgNO_3), Zinc sulfate heptahydrate ($\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$), Diethanolamine, $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and $\text{C}_4\text{H}_6\text{N}_2$ were supplied by Sinopharm Chemical Reagent, China. Sodium (Na_2SO_4 , 99%), Boric acid (H_3BO_3), PVA ($[\text{CH}_2\text{CH}(\text{OH})]_n$, $n = 1799$), and KOH are purchased from Aladdin. All the chemical reagents are obtained from commercial sources and without any further purification. Components of wind generator were supplied by Ningde new energy technology co. LTD.

Experimental section

Preparation of Zn-MOF/CNTF: The aqueous solution A ($\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, 40 mL, 50 mM) was rapidly mixed with the aqueous solution B ($\text{C}_4\text{H}_6\text{N}_2$, 40 mL, 0.4 M). Then, a piece of oxygen plasma treated CNTF substrate ($\Phi 0.12 \times 5 \text{ cm}^3$), the top side and down side fixed with tapes) was immersed into the mixed solution. Finally, after 4 h, the CNTF was taken out from the solution, washed with deionized water and vacuum dried for 12 h at 60 °C.

Preparation of the MOF derived CNTF-NCA: The prepared Zn-MOF array/CNTF was treated in Ar/H_2 (19:1) for 2 h at 800 °C with a rate of 1 °C min^{-1} , after cooling down to room temperature, the sample was etched in 1M HCl for 90 min and washed with deionized water then vacuum dried for 2 h at 60 °C .

Preparation of the CNTF-NCA- Ag_2O -PEDOT:PSS: 10 ml of AgNO_3 solution (0.1 M) was mixed 10 ml of KOH (0.1 M) in a flask. The AgOH was immediately obtained and slowly deposited at the bottom of the flask. Then, the supernatant was discarded and the precipitation was immersed with 10 ml deionized water, and diethanolamine (DEA) was added by dropwise and

stirred, until the sediment was completely dissolved. About 100 ml of deionized water was added and followed by KOH (0.1 M) until the PH above 11.5. the obtained N-Carbon array-CNTF was then vertically placed in the above solution. After 15 mins the solution slowly turned brown. After reaction for 2h, the CNTF-NCA were coated with black-grey substance. The substrate was electrochemically oxidized at 0.3 V (Vs Ag/AgCl) then washed in deionized water and dried in hot air. Thereafter, the CNTF-NCA-Ag₂O were repeatedly soaked in the commercially available PEDOT:PSS solution (1 mg/mL) and annealed at 120 °C for 2 h at 120 °C for 2 h indicating obtained the advanced cathode (CNTF-NCA-Ag₂O-PEDOT:PSS), the mass of Ag₂O electrode (4.31 mg/cm²) was obtained by electronic scales (METTLER TOLEDO XPU, 0.1 µg).

Preparation of the CNTF-Zn nanoflakes: The Zn nanoflakes were electrodeposited on the CNTF by an electrochemical workstation. Specifically, a piece of oxygen plasma treated CNTF substrate (Φ 0.12 × 5 cm³) was used as a work electrode and a piece of graphite (1 cm × 2 cm × 5 cm) was then used as a counter electrode. Next, 10 g boric acid (H₃BO₃), 62.5 g sodium sulfate (Na₂SO₄), and 62.5 g zinc sulfate (ZnSO₄·7H₂O) were dissolved in 500 mL DI water for use as an electrolyte. The Zn nanoflakes were then electrodeposited on the CNTF at a constant current density of -40 mA/cm² for 25 min at room temperature (9.18 mg/cm²) was obtained by electronic scales (METTLER TOLEDO XPU, 0.1 µg).

Fabrication and assembly of the quasi-solid-state Zn-Ag₂O battery: A quasi-solid electrolyte (PVA/KOH) was prepared: 10 g of PVA was added to 80 mL of deionized water, heated at 95 °C and vigorous stirring until the solution became transparency. Then, 10 mL aqueous solution containing 5.6 g of KOH was added and the mixture was cooled to room temperature. The CNTF

with Ag₂O positive electrodes and Zn nanoflake negative electrodes were immersed in the PVA/KOH electrolyte for 5 min. A separator (Al₂O₃ separator, Nippon Kodoshi Corporation) was used to separate the Ag₂O cathode and Zn anode. When the electrolyte solidified (-18 °C, 12 h), the Ag cathode and Zn anode were twisted together and sealed by a heat-shrinkable tube and Gluegun (ARZ-RJQ) forming a mechanically robust fiber-shaped quasi-solid-state Zn-Ag₂O battery.

Characterizations

Morphologies of the samples are characterized by a scanning electron microscope (SEM) (Hitachi S-4800, 5 kV) and the microstructure and high-resolution transmission electron microscope (TEM) images are obtained via a FEI Tecnai G2 20 high-resolution transmission electron microscope at an acceleration voltage of 200 kV. A Rigaku D/MAX2500 V X-ray diffraction (XRD) with Cu K α radiation ($\lambda = 1.5418 \text{ \AA}$) is applied to gain the X-ray diffraction patterns of samples. X-ray photoelectron spectroscopy (XPS) on an ESCALab MKII X-ray photoelectron spectrometer with non-monochromatized Mg K α X-rays as the excitation source is utilized to analyze the chemical element composition and oxidation states of samples. The surface area of the electrode was determined by the Brunauer-Emmett-Teller (BET) method, based on the amount of N₂ adsorbed at pressures $0.05 < P/P_0 < 0.3$ (ASAP 2020, Micromeritics, USA).

The electrochemical measurements are performed using an electrochemical workstation (CHI 760E, Chenhua). Electrochemical properties of the electrodes are measured by a three-electrode system in 1 M KOH aqueous electrolyte. The materials, the Pt wire and Hg/Hg₂Cl₂ are used as the working, counter and reference electrodes, respectively. The electrochemical impedance

spectroscopy (EIS) measurements are carried out at frequencies from 10^{-2} Hz to 10^5 Hz. The performances of the quasi-solid-state Zn-Ag₂O devices are tested in a two-electrode system.

The capacity of the device is calculated by $C = I \cdot t_{\text{discharge}}/S$, where the I is the discharge current, $t_{\text{discharge}}$ is the discharged time, and S is active materials' mass or electrode area. The energy density

(E) and power density (P) of the full cell were calculated by: $E = \int_0^t IV(t)dt/A$, $P = E/t_{\text{discharge}}$, where I is the discharge current, $V(t)$ is the discharge voltage at t , dt is time differential, and A is the electrode area or the total mass of active materials.

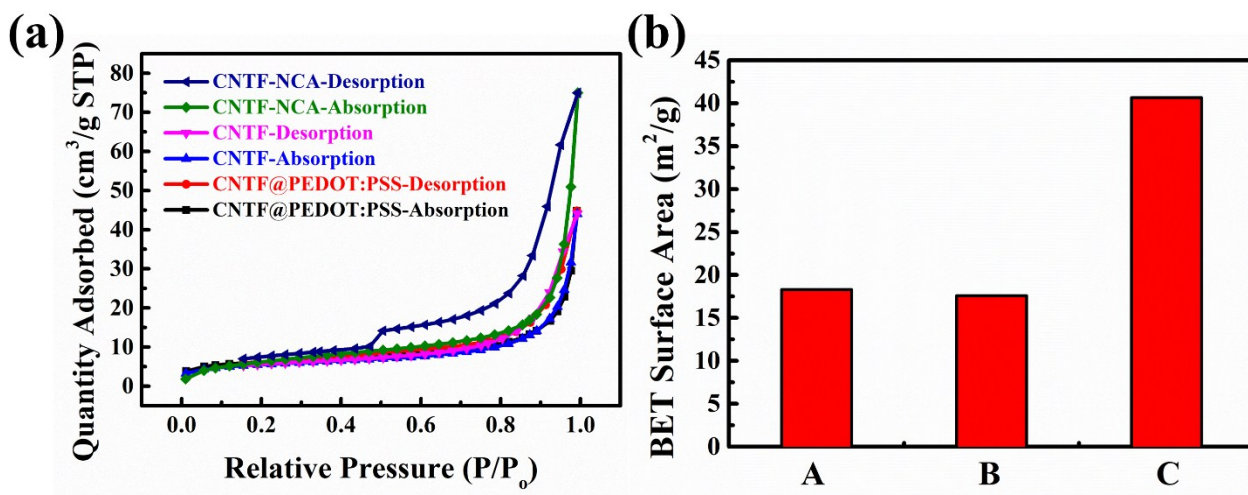


Fig. S1 (a) N_2 adsorption-desorption isotherm of CNTF, CNTF-PEDOT:PSS and CNTF-NCA. (b)

The BET surface area of different simple, A: CNTF, B: CNTF@PEDOT:PSS and C: CNTF-NCA.

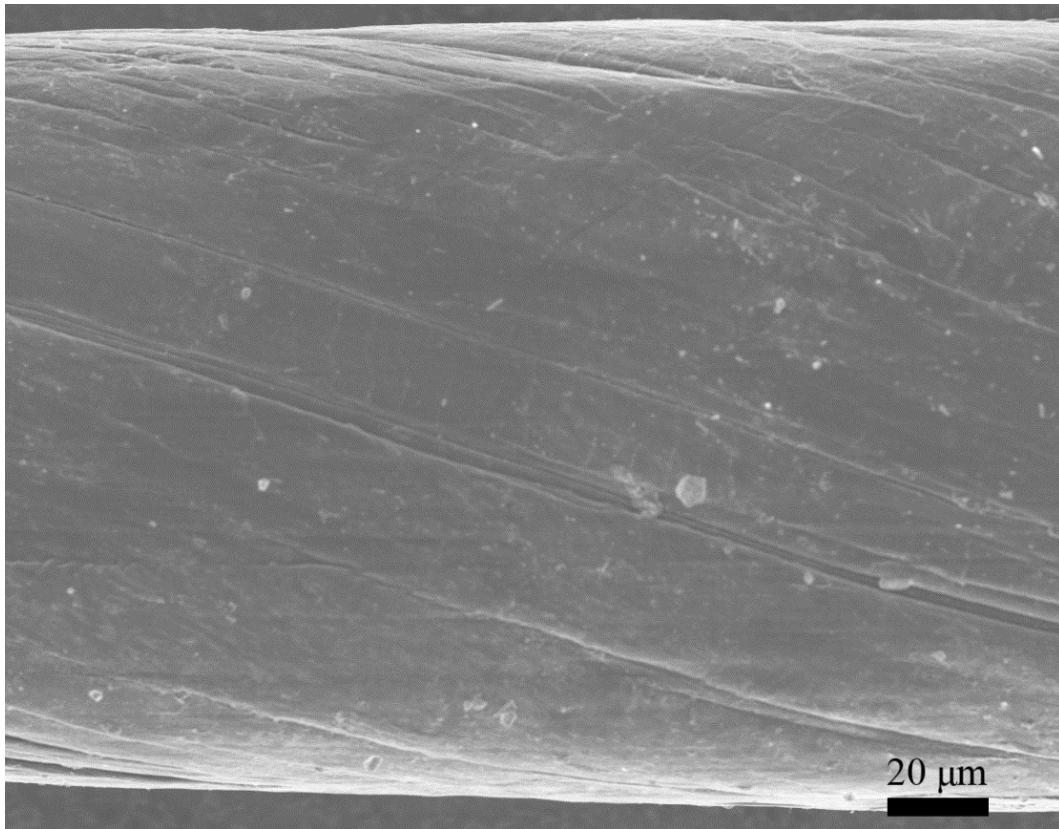


Fig. S2 SEM images of bare CNTF.

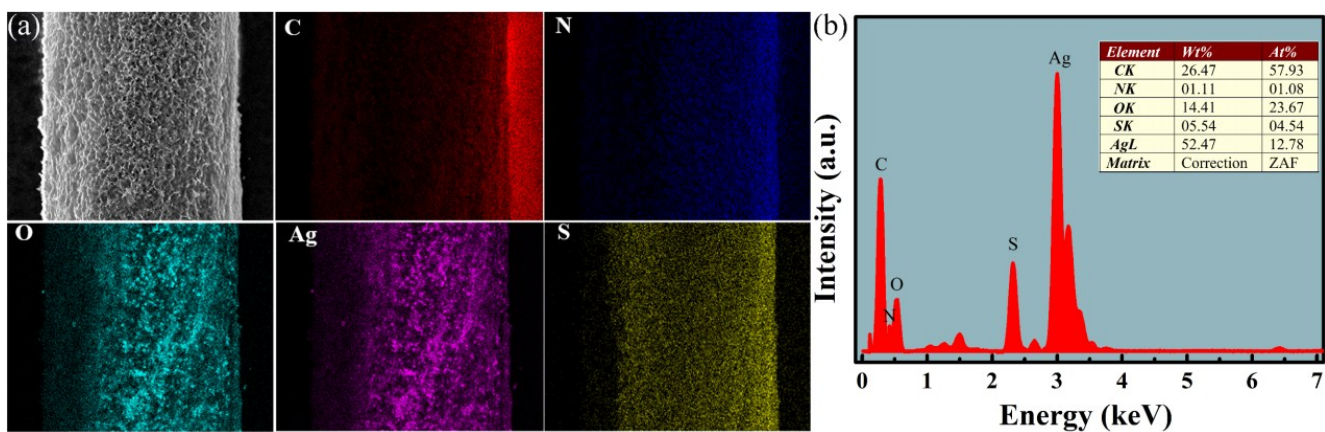


Fig. S3 (a) EDS mapping of the novel CNTF-NCA-Ag₂O@PEDOT:PSS cathode, and (b) quantitative element analysis of the novel CNTF-NCA-Ag₂O@PEDOT:PSS cathode.

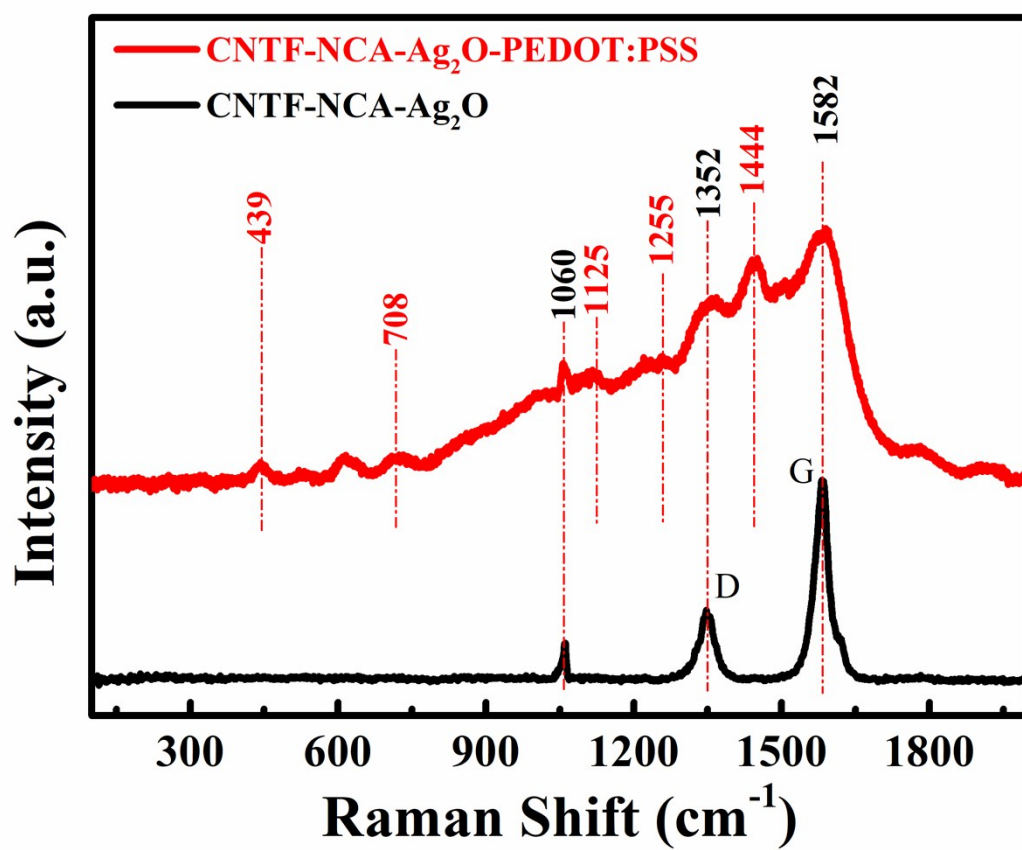


Fig. S4 Raman spectrum of the CNTF-NCA-Ag₂O and CNTF-NCA-Ag₂O@PEDOT:PSS samples.

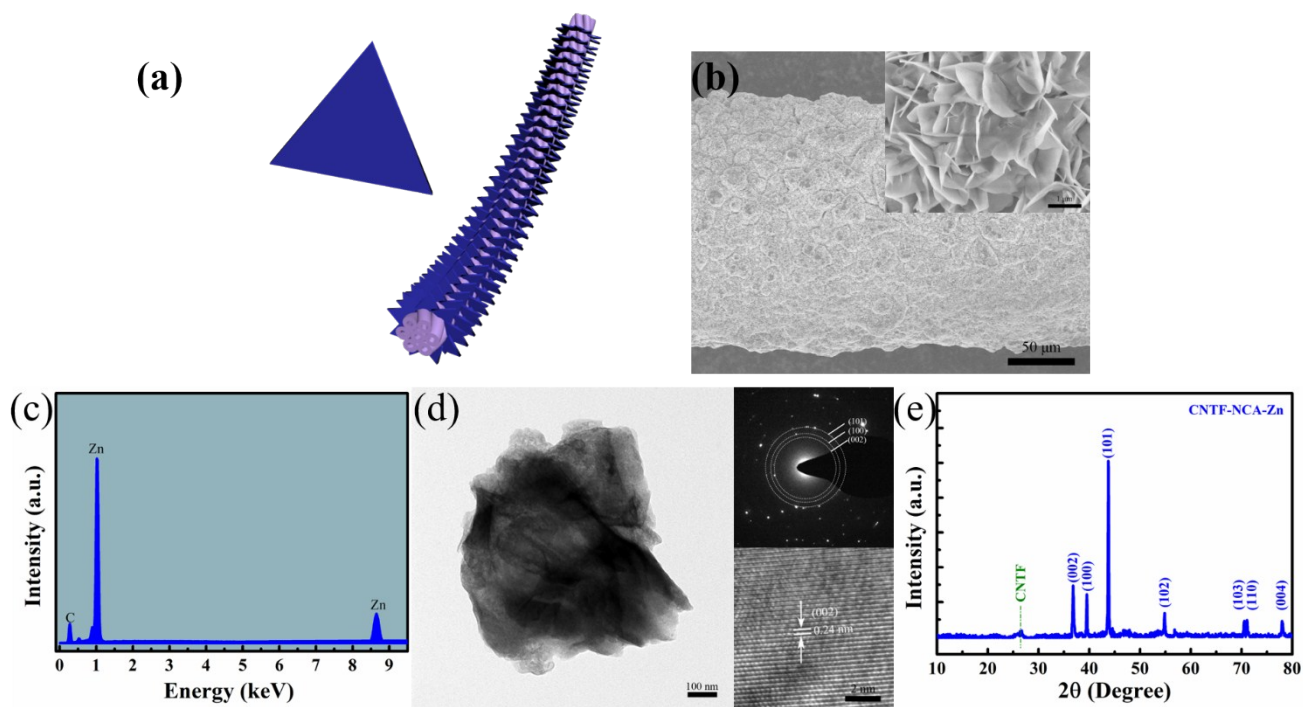


Fig. S5 (a) Schematic diagram, (b) SEM images, (c) Quantitative elements analysis, (d) TEM, HRTEM and SAED pattern, and (e) XRD profile of CNTF-Zn nanosheets.

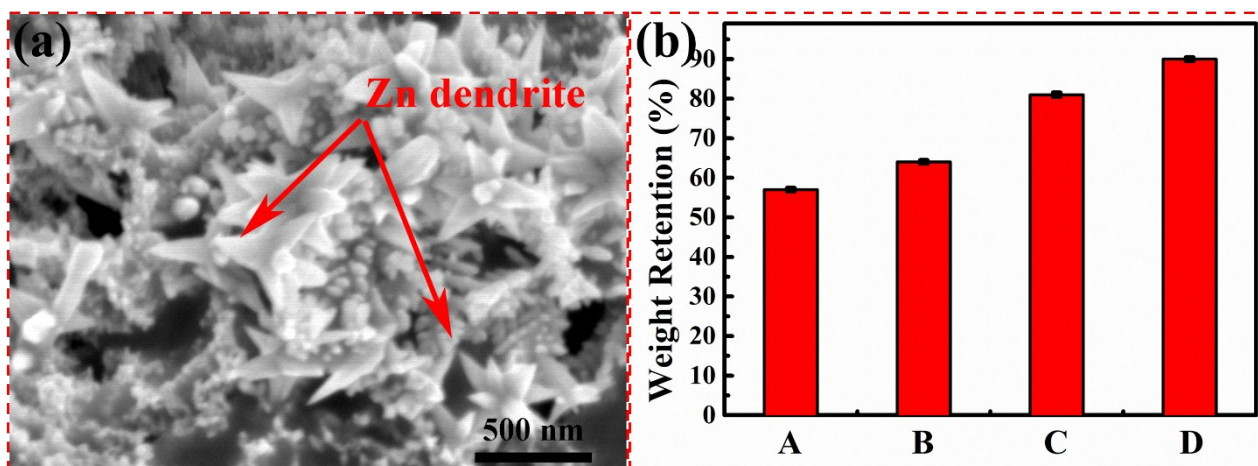


Fig. S6. (a) SEM of anode and (b) active substance retention after circulations for 200 times (A: Ag_2O battery; B: NCA- Ag_2O battery; C: $\text{Ag}_2\text{O}@$ PEDOT:PSS and D: NCA- $\text{Ag}_2\text{O}@$ PEDOT:PSS battery).

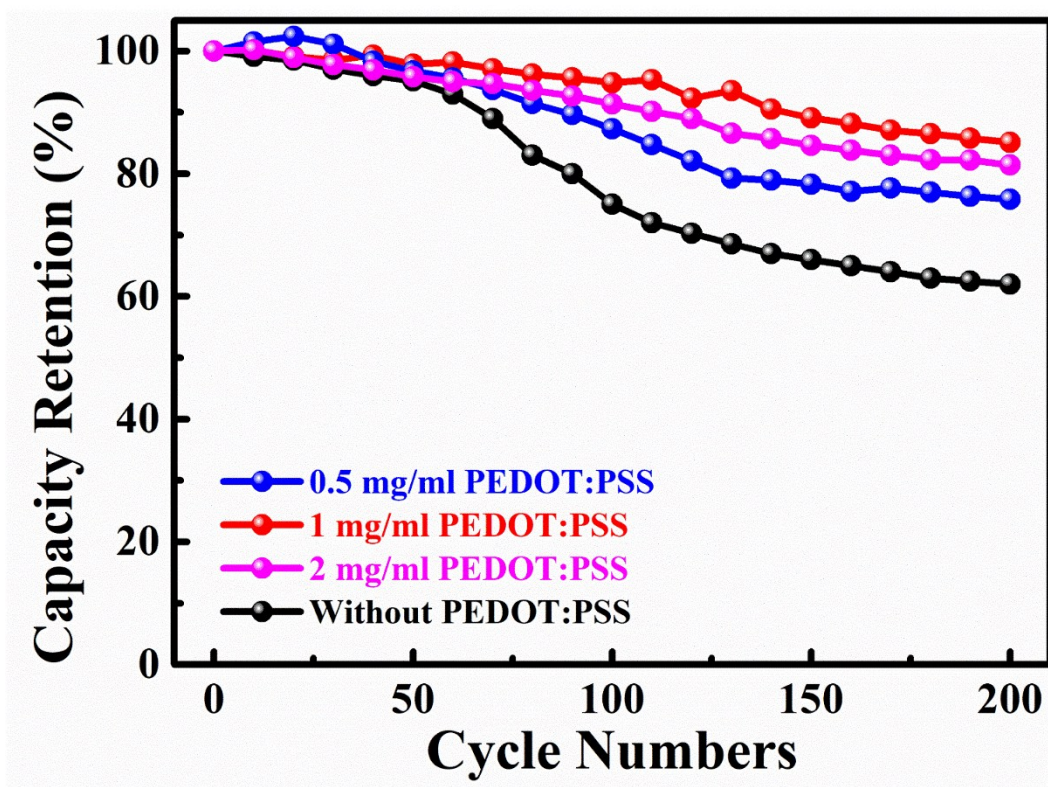


Fig. S7 The relationship between the durability of the NCA-Zn-Ag₂O battery and the concentration of PEDOT:PSS.

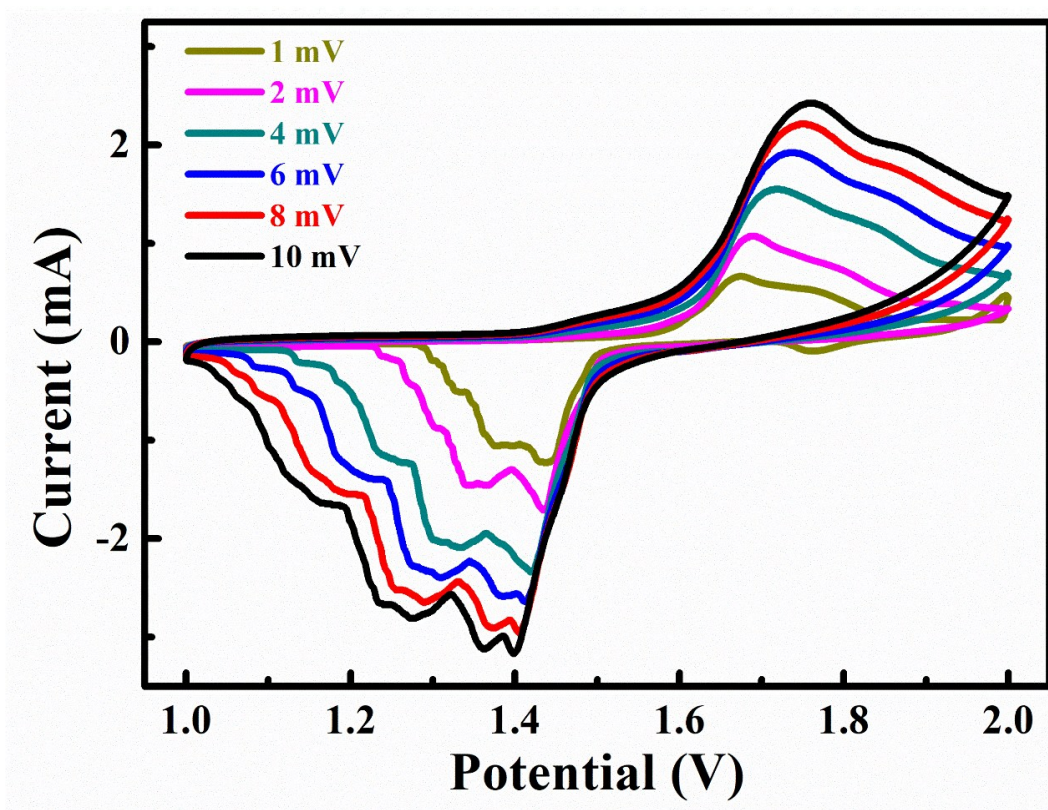


Fig. S8 The CV profiles of the aqueous Zn-Ag₂O battery.

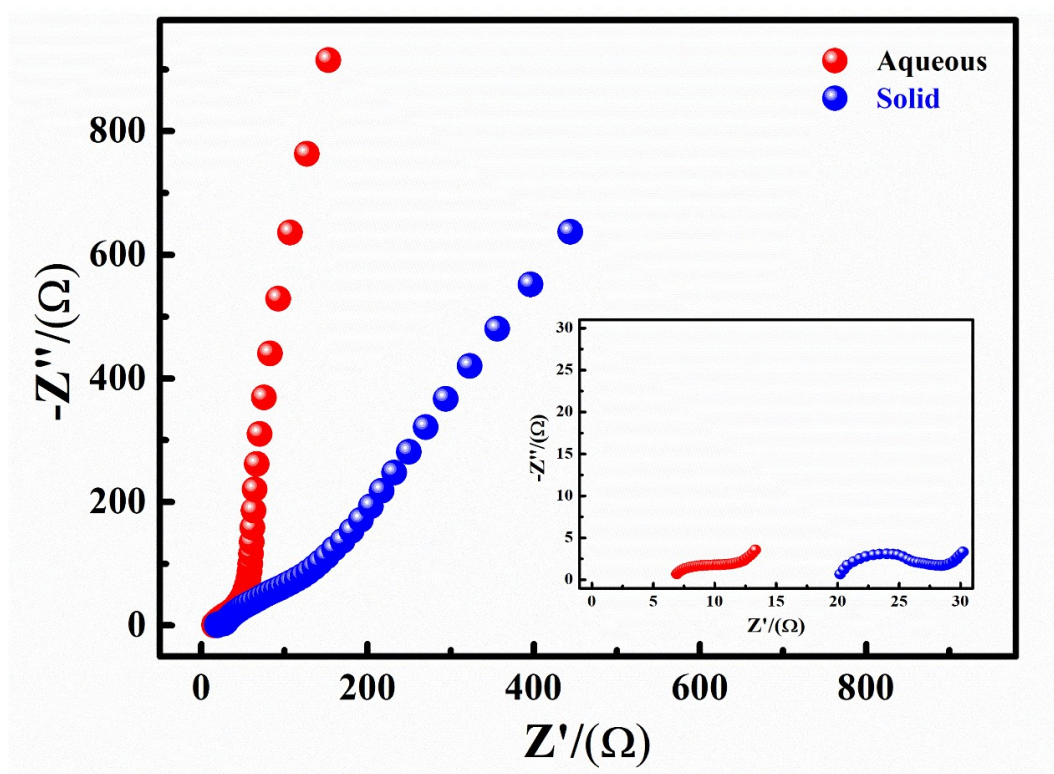


Fig. S9 The Nyquist of the aqueous and quasi-solid-state Zn-Ag₂O@PEDOT:PSS battery.

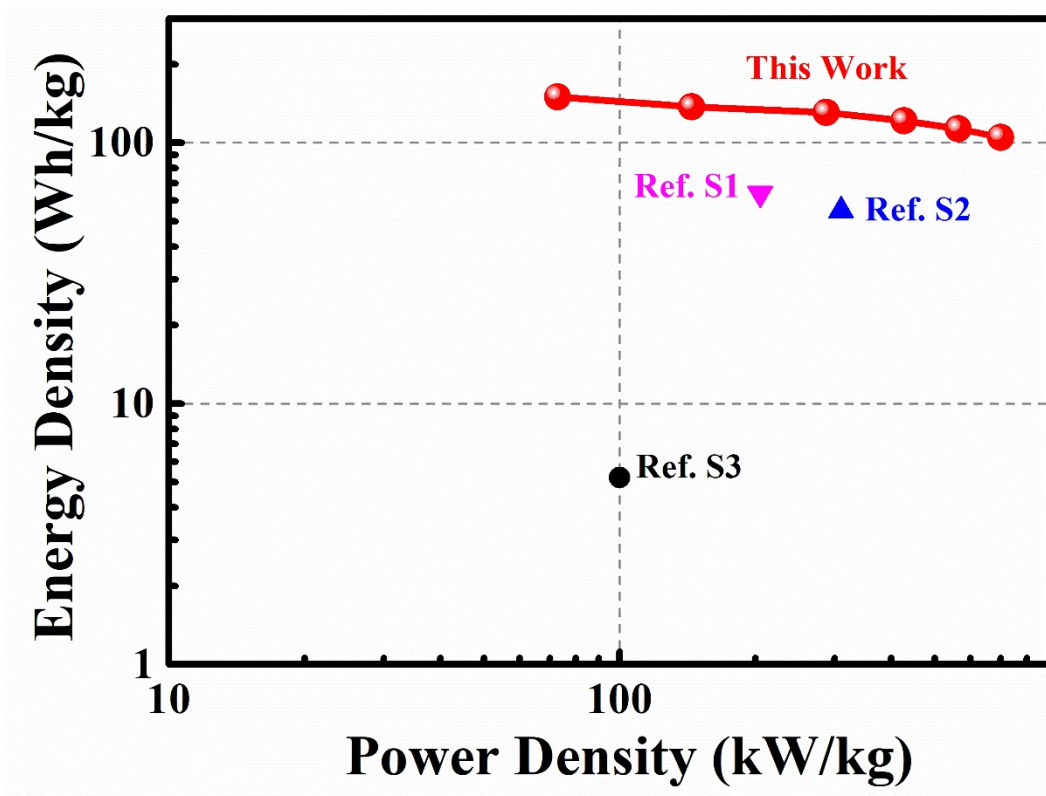


Fig. S10 The gravimetric power (P) and energy density (E) of the advanced flexible quasi-solid-state Zn-Ag₂O@PEDOT:PSS battery.

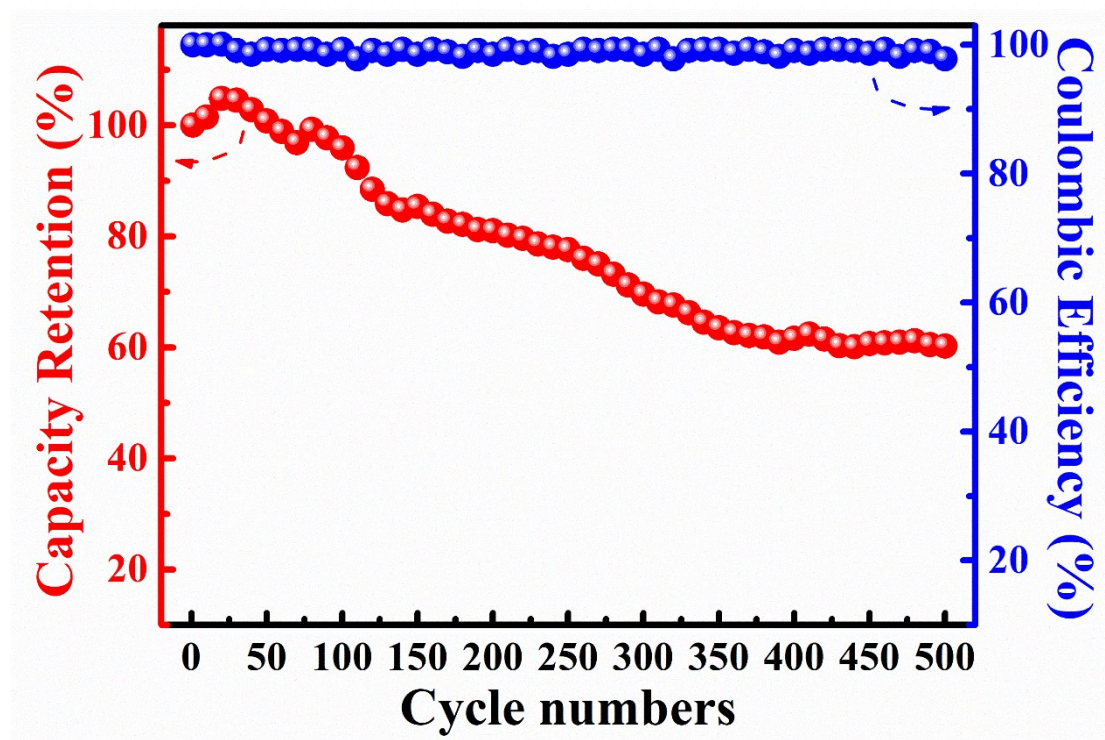


Fig. S11 The cycle performance of the quasi-solid-state Zn-Ag₂O@PEDOT:PSS battery collected at 0.5 mA/cm² over 500 cycles.

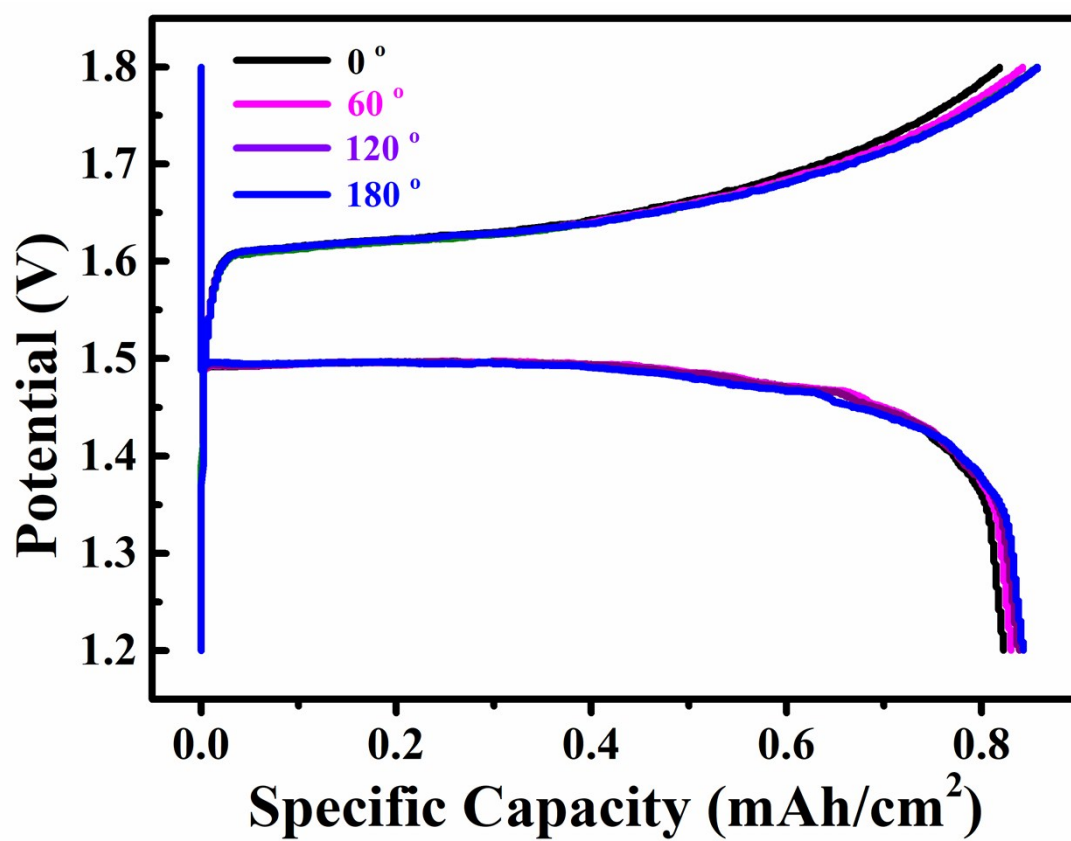


Fig. S12 The GCD curves of quasi-solid-state Zn-Ag₂O@PEDOT:PSS battery bent at different angles (3 mA/cm²).

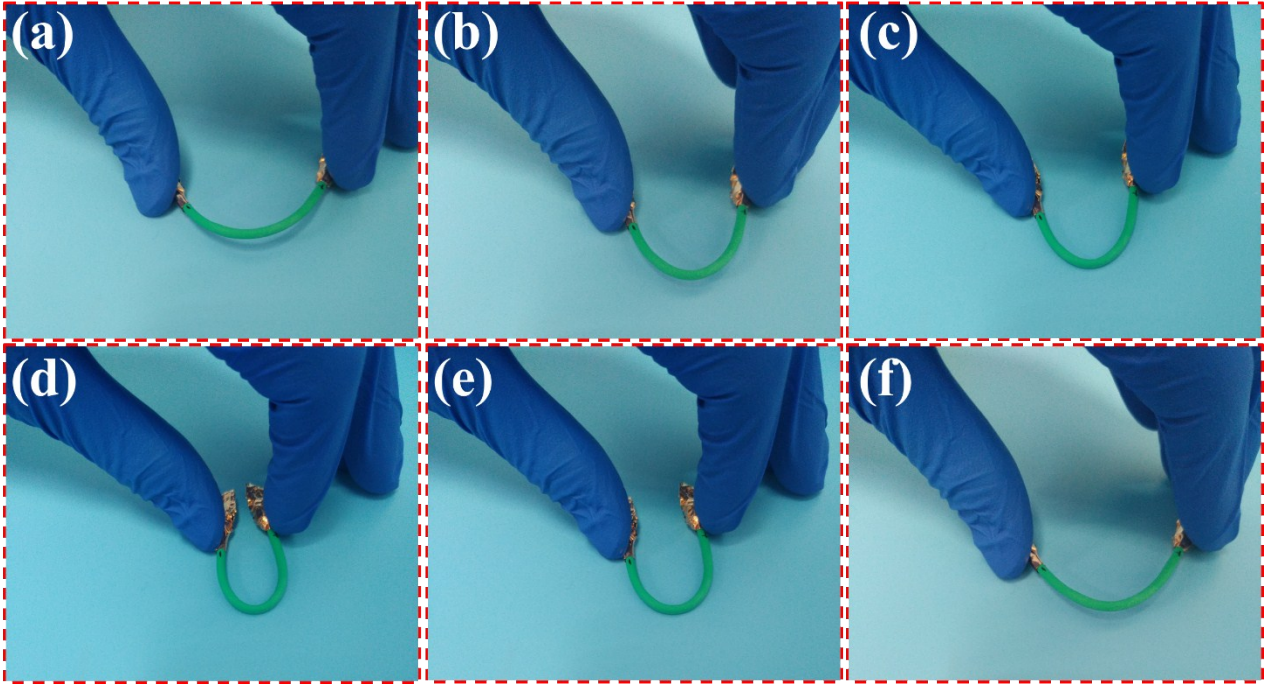


Fig. S 13 The photo image of flexible quasi-solid-state as-made battery at different bent angle.

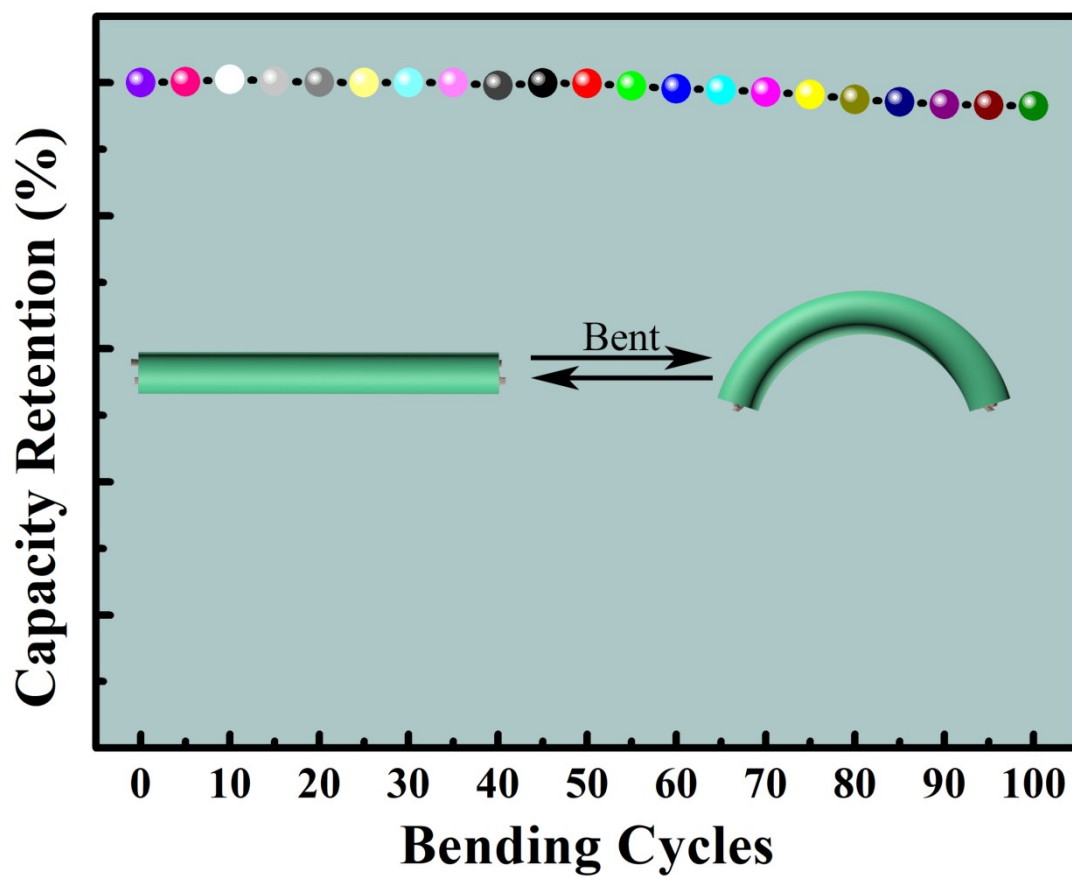


Fig. S14 The capacity retention of quasi-solid-state Zn-Ag₂O@PEDOT:PSS at different cycles at 3 mA/cm².

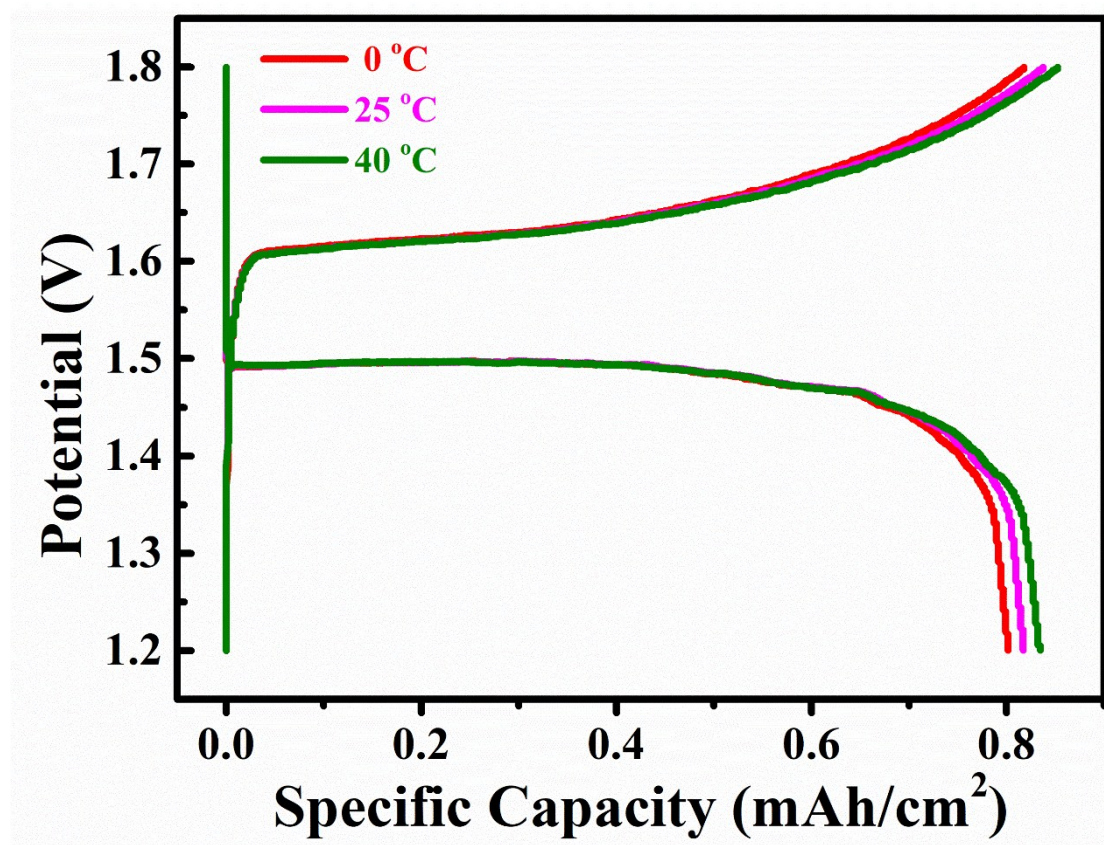


Fig. S15 The GCD profiles of quasi-solid-state Zn-Ag₂O@PEDOT:PSS under different environmental temperatures at 3 mA/cm².

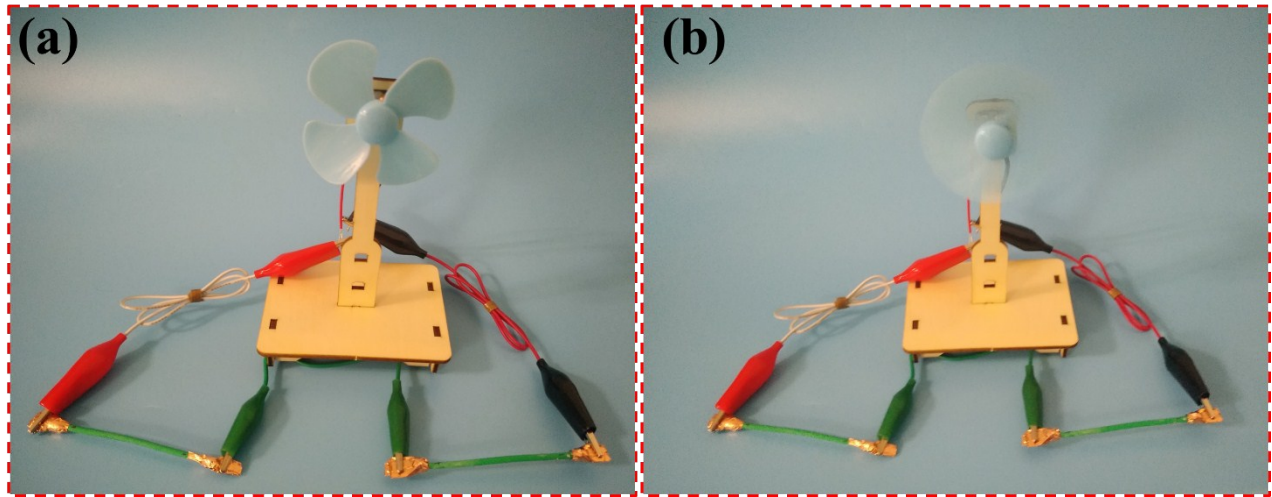


Fig. S16 The photo image of our prepared battery integrated with wind power generator, (a) Without wind and (b) Windy conditions.

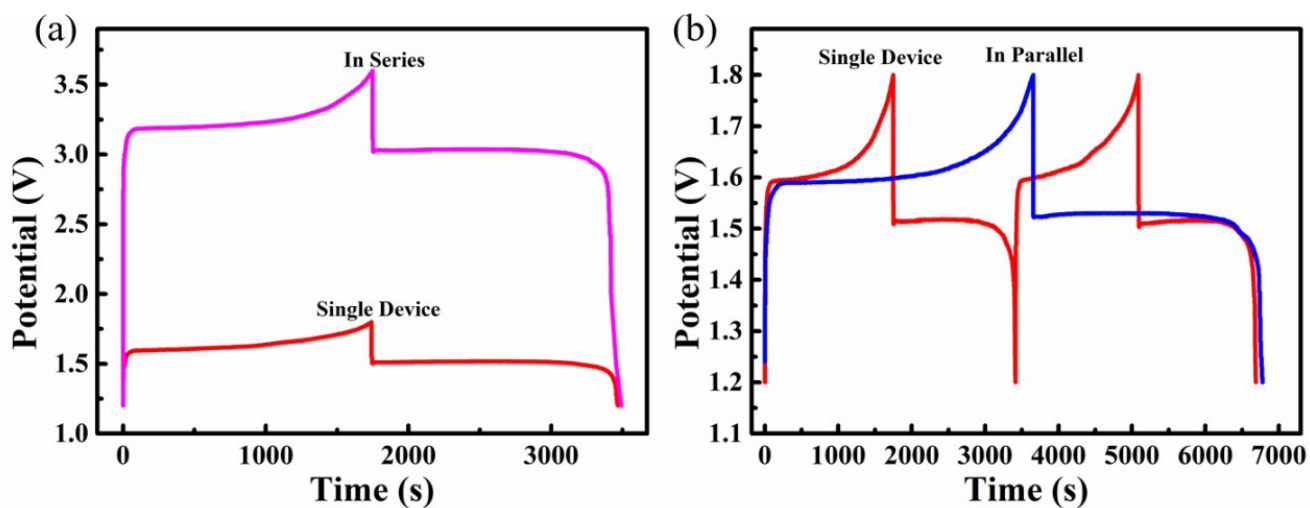


Fig. S17 (a) GCD curves of a single quasi-solid-state Zn-Ag₂O@PEDOT:PSS devices and two devices in series, and (b) GCD curves of a single quasi-solid-state Zn-Ag₂O@PEDOT:PSS device and two devices in parallel at 5 mA/cm².

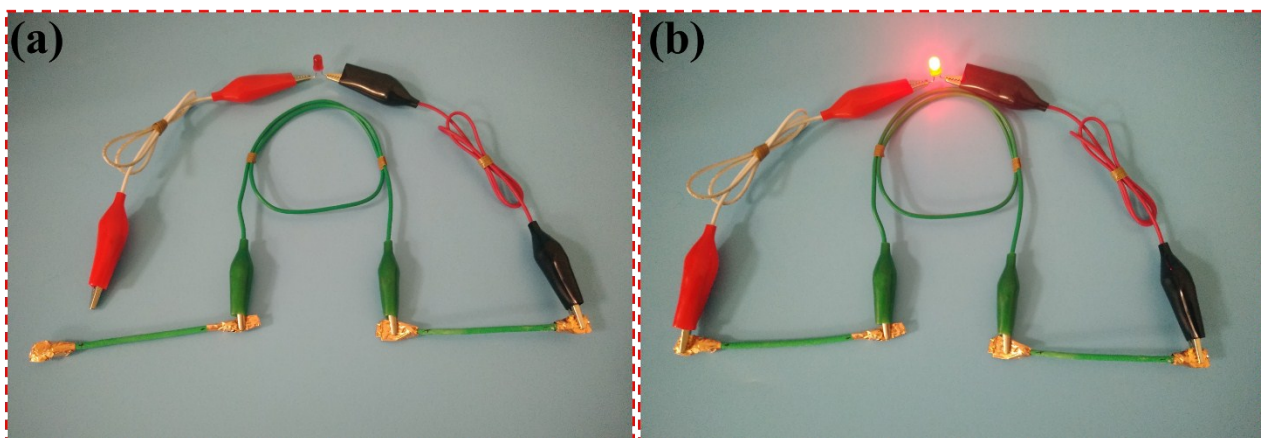


Fig. S 18 The photo images of two quasi-solid-state as-made batteries in series powered a red LED (a) without connection and (b) connection.

References

- S1. B.J. Hertzberg, A. Huang, A. Hsieh, M. Chamoun, G. Davies, J.K. Seo, Z. Zhong, M. Croft, C. Erdonmez, Y.S. Meng, D., *Chem. Mater.*, 2016, **28**, 4536.
- S2. W. Tang, L.L. Liu, Y.S. Zhu, H. Sun, Y.P. Wu, K. Zhu, *Energy. Enviro Sci.*, 2012, **5**, 6909.
- S3. M. Pasta, C.D. Wessells, R.A. Huggins, Y. Cui, *Nat. Commun.*, 2012, **3**, 1149.