Electronic Supplementary Information

High-value utilization of biomass waste: from ocean floating garbage to high-performance rechargeable Zn-MnO_2 batteries with superior safety

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Experimental Section

Preparation of carbonized ocean garbage (COG)

The ocean garbage (OG) of reed straw was collected from the seaside in Bay Area of Berkeley, California and washed with distilled water for several times before carbonization. Then the OG was transferred into a tube furnace (OTF-1200X, Kejing, China) and heated to 240 ^{o}C at a rate of 2 ^{o}C min^{-1} under Ar atmosphere. The samples were retained at this temperature for 1 h, followed by further heating to 800 ^{o}C at the same rate and an isothermal process for another 2 h.

Preparation of COG@MnO_2

The *in situ* growth of MnO_2 on the COG was realized via a typical hydrothermal method. Briefly, the obtained COG was immersed in a $KMnO_4$ aqueous solution, and the solution was kept at 60 ^{o}C for 24 h. The mass loading of MnO_2 could be facilely tuned by adjusting the $KMnO_4$ concentration from 0.5, 1, 2, 5, 10 to 20 mM. The obtained COG@MnO_2 here is the porous 3D electrode. For comparison, the porous electrode material was grinded into powder, and mixed with PVDF in a weight ratio of 9:1 using N-Methyl pyrrolidone as the solvent. The mixtures were then coated on a piece of CNT paper and dried at 60 °C in vacuum to obtain the bulk electrode.

Preparation of COG@Zn

Zn was deposited on COG by an electrodeposition method. In brief, the COG was immersed in a mixed solution of 0.1 M zinc sulphate ($ZnSO_4$) and 0.1 M sodium sulfate (Na_2SO_4). The COG was used as the working electrode and the electrodeposition was conducted at a constant voltage of -1.5 V for 10 min at room temperature.

Assembly of the quasi-solid-state COG@MnO_2//COG@Zn battery

The quasi-solid-state battery was assembled using the COG@MnO_2 as the cathode and the COG@Zn as the anode, with a piece of filter paper as the separator and PVA/LiCl–$ZnCl_2$–$MnSO_4$ gel as the electrolyte. The gel electrolyte was prepared by mixing 1.27 g LiCl, 2.73 g $ZnCl_2$, 0.68 g $MnSO_4$ and 1 g PVA in 10 mL deionized water, followed by vigorous stirring at 85 ^{o}C for 3 h. The electrodes and the separator were soaked in the gel electrolyte for 5 min and then left under ambient conditions to remove the unnecessary water. Finally, the electrodes and the separator were assembled together to form a quasi-solid-state battery.

Material Characterization

The morphologies were observed by SEM (Inspect F50, FEI) at 20 kV and TEM (FEI Tecnai G2 F20) at 120 kV. XRD measurements were carried out on an X-ray diffractometer (X' Pert Pro MPD, Philips) using Cu Kα (1.5406 Å) radiation. XPS spectra were recorded on a Kratos XASAM 800 spectrometer with an Al K α X-ray source (1486.6 eV). Water contact angle (WCA) measurements were carried out and recorded by the contact angle measurement system (DSA 30, Kruss, Germany).

Electrochemical Measurement

Cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) were conducted on a CHI 660E electrochemical workstation (CH Instruments Co., China). EIS tests were performed from 0.01 Hz to 100 kHz with an amplitude of 0.005 V and a potential of 0 V. Energy storage performance was characterized based on galvanostatic testing using a Land 2001A battery testing system (Wuhan, China). The electrochemical characterizations of the obtained electrodes were performed in a two-electrode cell with COG@MnO_2 as the cathode and the COG@Zn as the anode, which were soaked in aqueous solution containing 2 M $ZnSO_4$ and 0.1 M $MnSO_4$.

Self-Powered System Demonstration

The customized wristband and badge with the logo of "Sichuan University" on top were used for demonstration. Before operations, the original batteries were removed from the customized wristband and badge (Figure S11). Three as-prepared quasi-solid-state batteries were connected in series, and wrapped outside with a commercial flexible solar cell (LL200-4.8-37, PowerFilm Inc., USA) to form a self-sustaining power bar (Figure 5a). The system collected and stored energy from light and finally powered the customized wristband or badge for the demonstration.

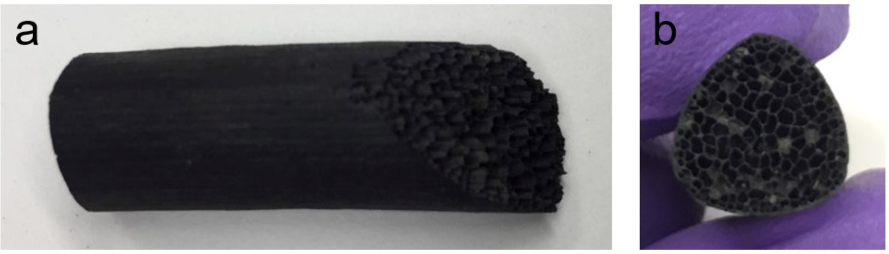

Figure S1. The (a) front and (b) cross-section photographs of the COG.

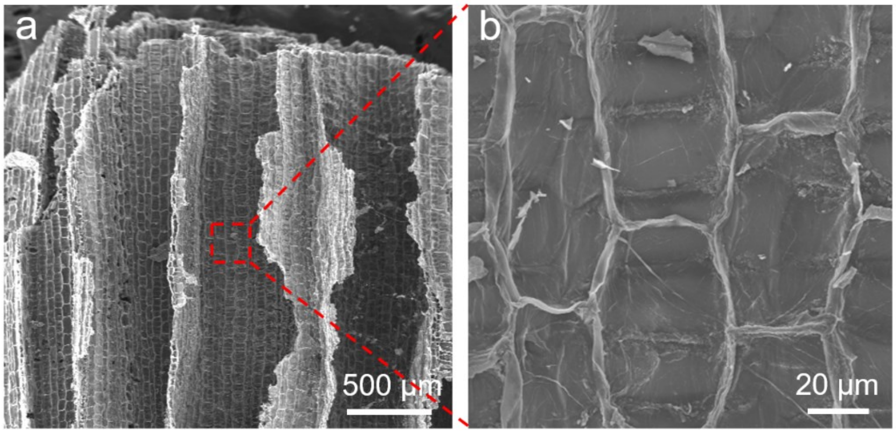

Figure S2. SEM images of COG: cross-section-view images showing the channels under (a) low and (b) high magnification.

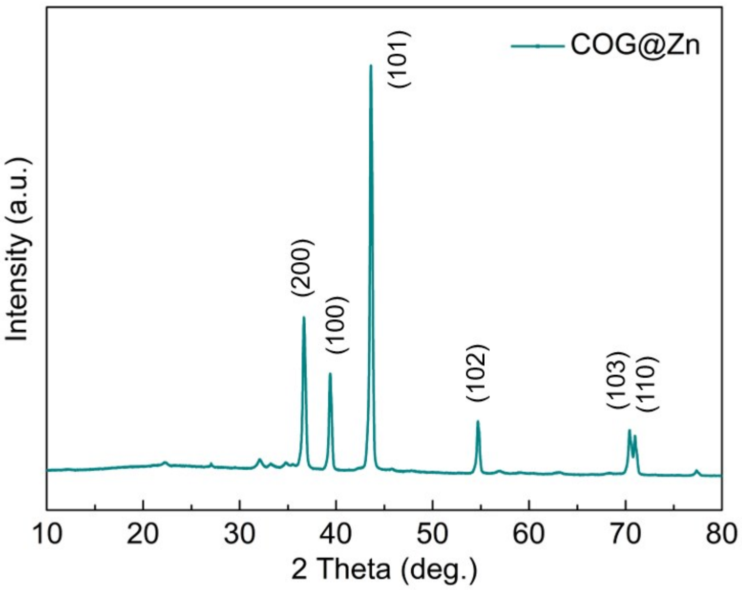

Figure S3. XRD spectra of the COG@Zn electrode.

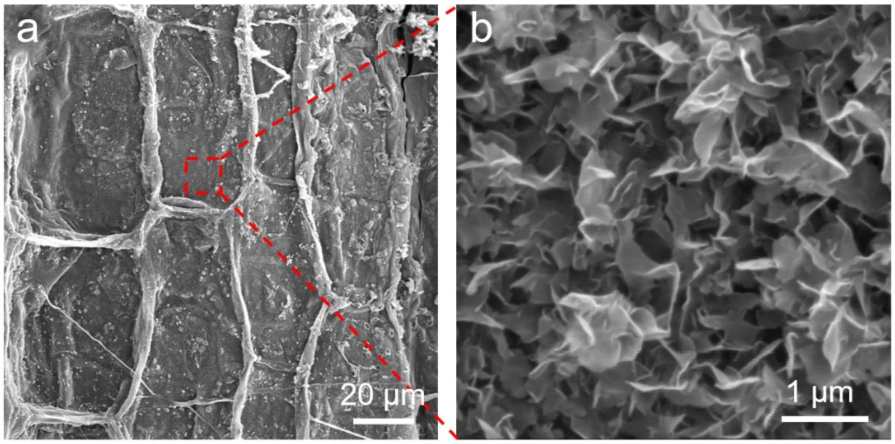

Figure S4. SEM images of (a) the channels in COG@MnO_2 electrode, and (b) the MnO_2 nanosheets *in situ* grown inside the channel.

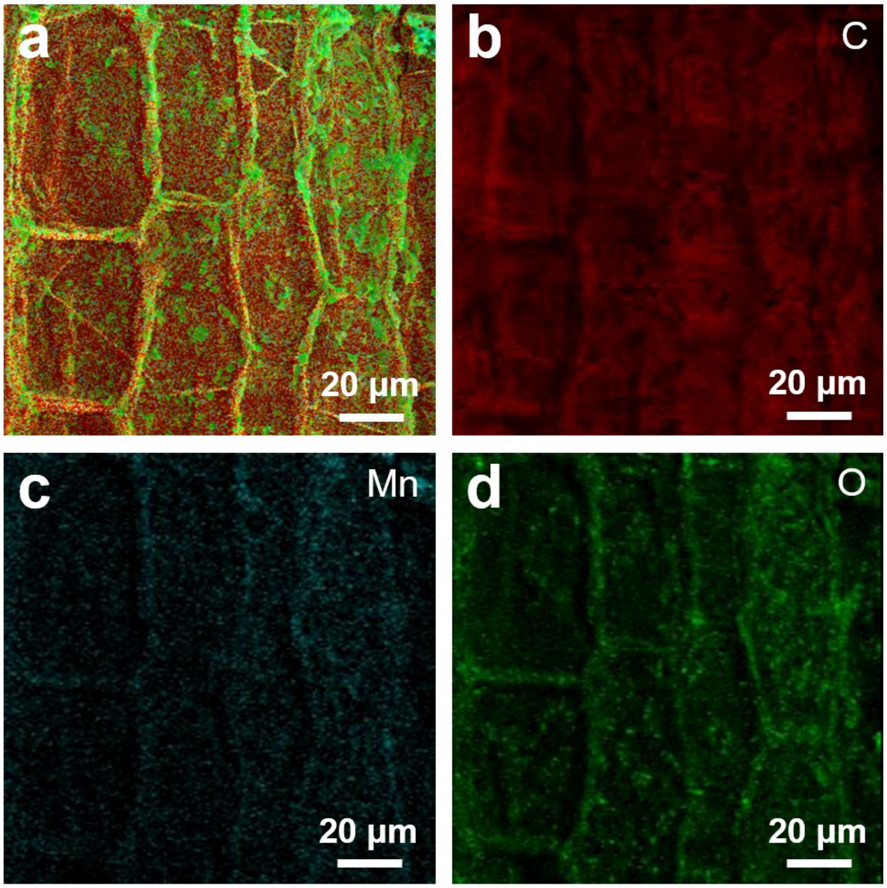

Figure S5. Elemental mapping images of C, Mn and O inside the channel of COG@MnO_2 electrode.

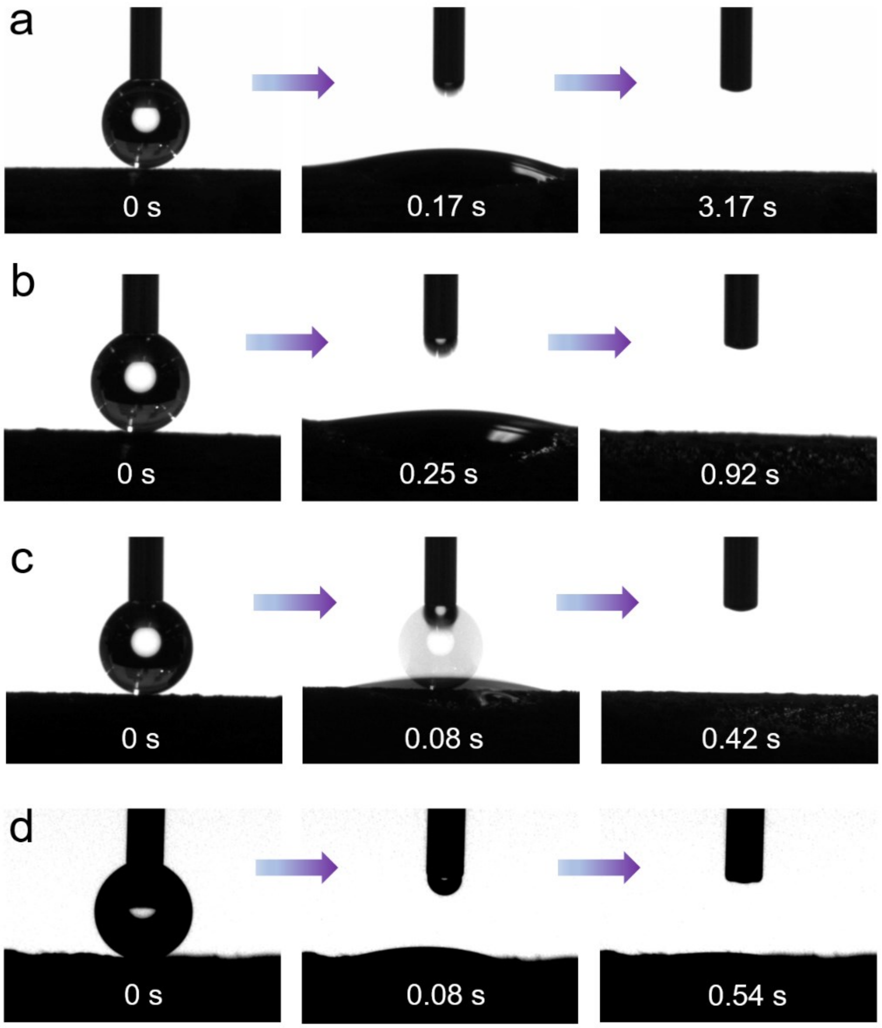

Figure S6. Photographs showing the measurements of hydrophilicity of (a) COG, (b) COG@Zn, (c) porous COG@MnO_2 and (d) bulk COG@MnO_2.

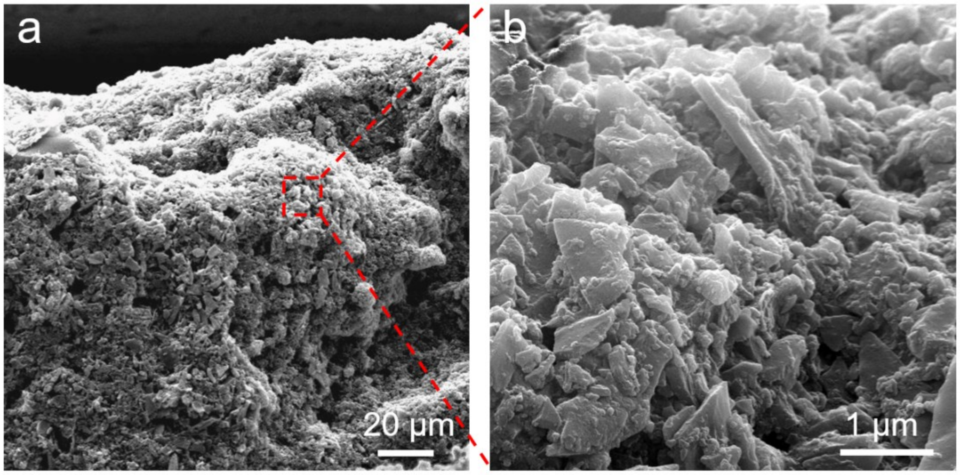

Figure S7. SEM images of the bulk COG@MnO_2 electrode with (a) low and (b) high magnification.

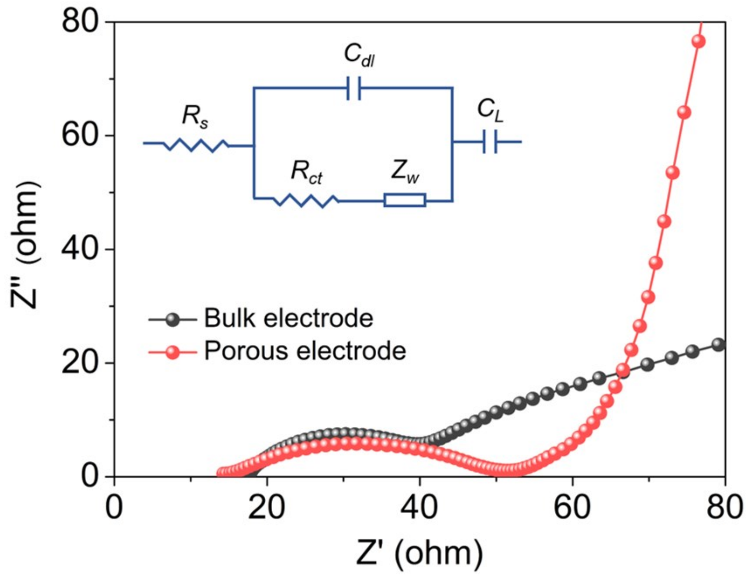

Figure S8. Nyquist plots for the porous and bulk COG@MnO_2 electrodes, the inset is the equivalent circuit.

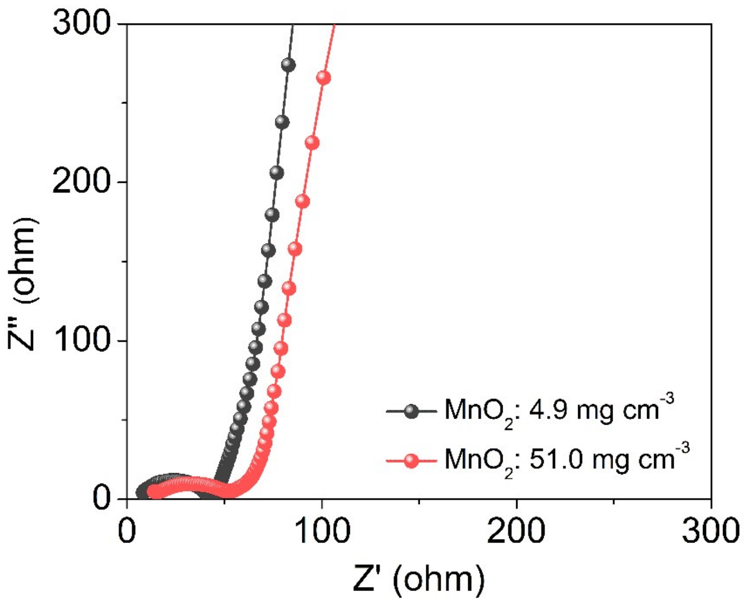

Figure S9. Nyquist plots for the COG@MnO$_2$ electrodes with different MnO$_2$ loadings.

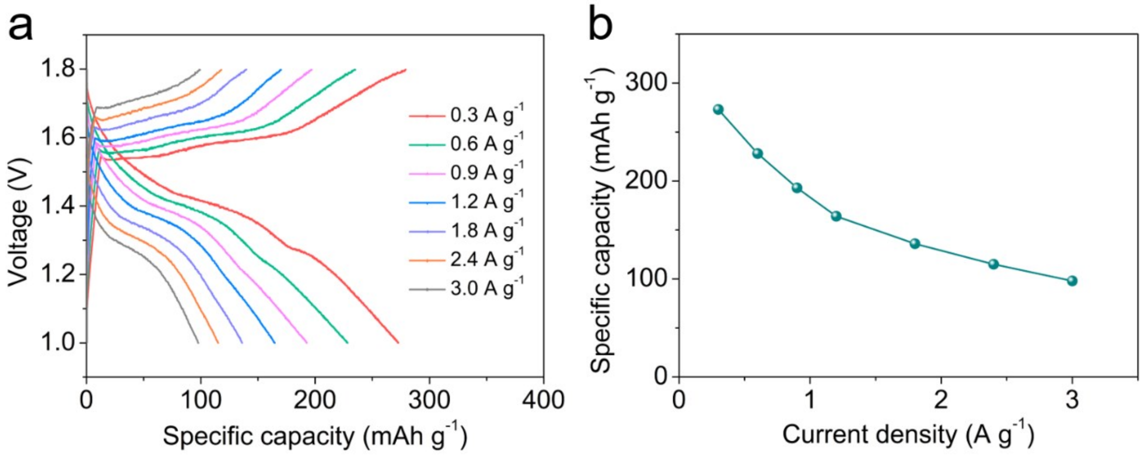

Figure S10. (a) Galvanostatic charge/discharge curves and (b) specific capacities of the bulk COG@MnO_2 electrode at different current densities.

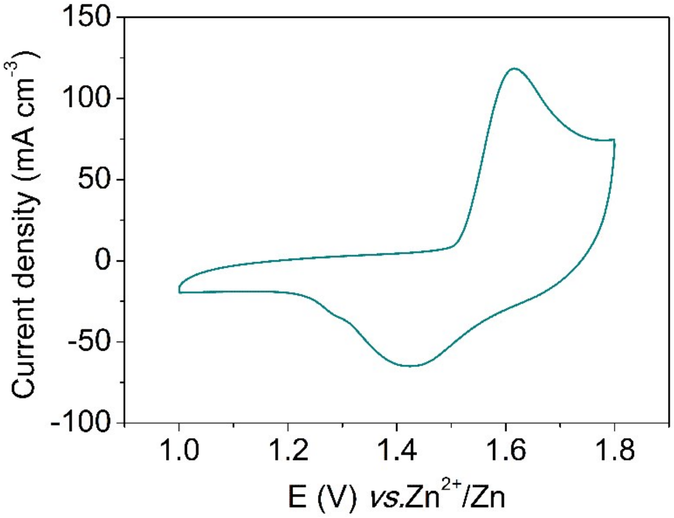

Figure S11. CV curve of the quasi-solid-state COG@MnO$_2$//COG@Zn battery at 1 mV s^{-1}.

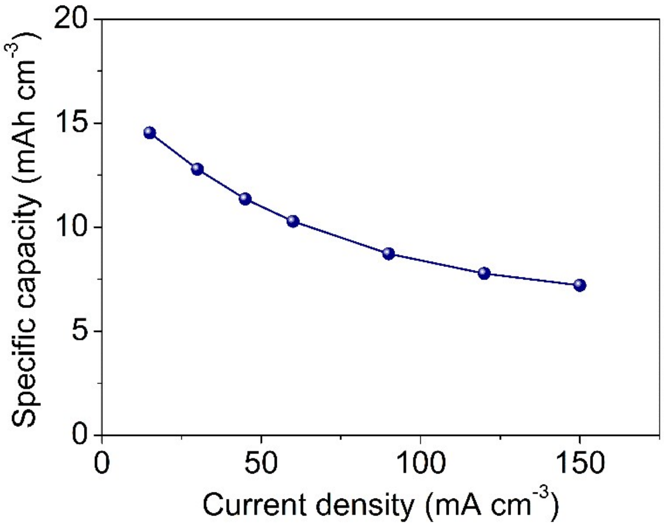

Figure S12. Specific capacities of the quasi-solid-state COG@MnO_2//COG@Zn battery at various current densities.

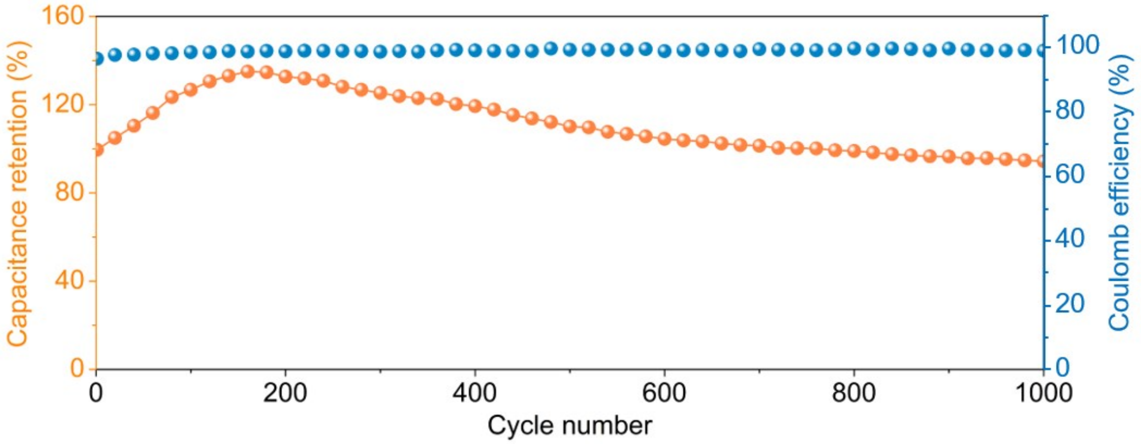

Figure S13. Long-term cycling performance and the corresponding Coulombic efficiency of the quasi-solid-state battery collected at 90 mA cm^{-3}.

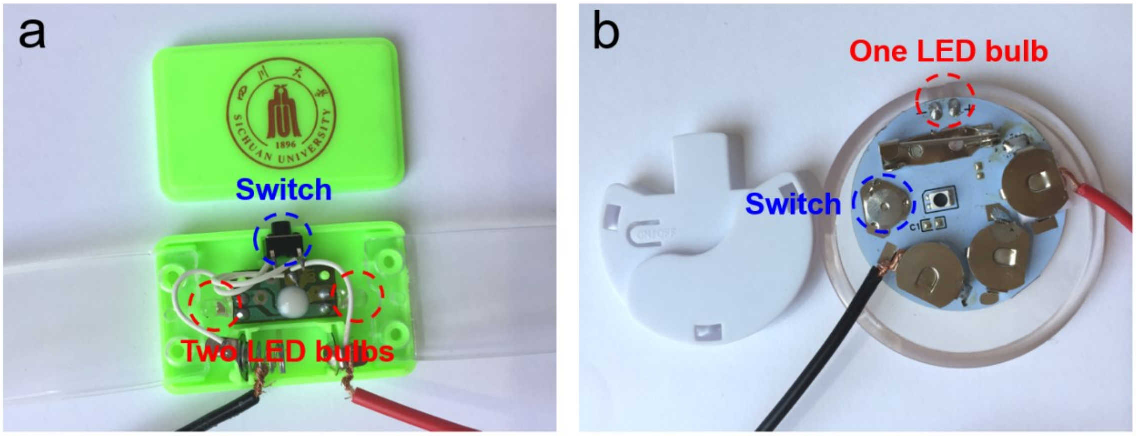

Figure S14. Photographs showing the interior of (a) the watch and (b) the badge.

Table S1. Comparison of the capacity of our Zn-MnO_2 battery with different aqueous batteries reported before.

Battery	Capacity (mAh g^{-1})	Reference
Zn-MnO_2	210	1
Zn-MnO_2	225	2
Zn-MnO_2	285	3
Zn-MnO_2	302.1	4
Zn-MnO_2	307	5
Zn-$ZnMn_2O_4$	150	6
Zn-PTO	336	7
Zn-$NiCo_2O_4$	183.1	8
Zn-MoS_2	202.6	9
Ni-Zn	265	10
Zn-V_2O_5@PEDOT	360	11
Zn-MnO_2	**369.7** (MnO_2 loading of 4.9 mg cm^{-3})	**This study**
Zn-MnO_2	**306.7** (MnO_2 loading of 51 mg cm^{-3})	**This study**

Note: the capacities of batteries were calculated based on the mass of active materials.

Table S2. Comparison of the volumetric energy density of our Zn-MnO_2 battery with other recently reported energy storage devices.

Energy storage devices	Powder density (W cm^{-3})	Energy density (mWh cm^{-3})	Reference
All metal nitrides supercapacitors	52.9	0.61	12
Fe-MnO_2 ASC	0.36	0.89	13
alkali-ion batteries	4.7	1.3	14
WON-MnO_2 ASC	0.62	1.27	15
MoN-MnO_2 ASC	0.1	2.29	16
Zn-Ni battery	148.54	4.05	17
Zn-NiCo battery	0.03	8	18
Na-ion battery	0.016	11.2	19
Zn-MnO_2 battery	0.15	17.4	20
Zn-MnO_2 battery	**21.1**	**20.5**	**This study**

Table S3. Comparison of the energy density of our Zn-MnO_2 battery with other biomass-derived energy storage devices.

Biomass-based Energy storage devices	Powder density (W kg^{-1})	Energy density (Wh kg^{-1})	Reference
Bacterial cellulose-based supercapacitor	220	5.8	21
Bamboo-based supercapacitor	100.2	6.68	22
Lignin-based supercapacitor	15	5.7	23
Wood-based MnO_2 supercapacitor	4.6	16	24
Biomass-based MnSi supercapacitor	604.8	24.6	25
Flowers-based supercapacitor	273	64	26
Kapok fiber-based Li-ion battery	83	100	27
Cellulose-based Zn-ion battery	160	117.5	28
Zn-MnO_2 battery	**135.3**	**131.5**	**This study**

Note: the energy density and power density were calculated based on the total mass of the energy storage devices.

Supporting Movies:

Movie S1. Demonstration of the quasi-solid-state battery powering an electronic thermometer and hygrometer under normal conditions.

Movie S2. Demonstration of the quasi-solid-state battery that can safely power an electronic thermometer and hygrometer under puncturing.

Movie S3. Demonstration of the quasi-solid-state battery that can safely power an electronic thermometer and hygrometer under bending.

Movie S4. Demonstration of the quasi-solid-state battery that can safely power an electronic thermometer and hygrometer under hammering.

Movie S5. Demonstration of the quasi-solid-state battery that can safely power an electronic thermometer and hygrometer under cutting.

Movie S6. Demonstration of the quasi-solid-state battery that can safely power an electronic thermometer and hygrometer under cropping.

Movie S7. Demonstration of the self-sustaining power bar powering the customized watch.

Movie S8. Demonstration of the self-sustaining power bar powering the customized badge.

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