Electronic Supplementary Material (ESI) for RSC Advances.

Supplementary Information

Flexible quasi-solid-state zinc ion batteries enabled by highly conductive carrageenan bio-polymer electrolyte

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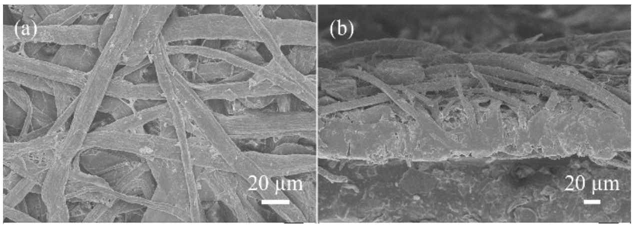

Fig. S1 (a) SEM image of rice paper. (b) The cross-sectional SEM image of rice paper.

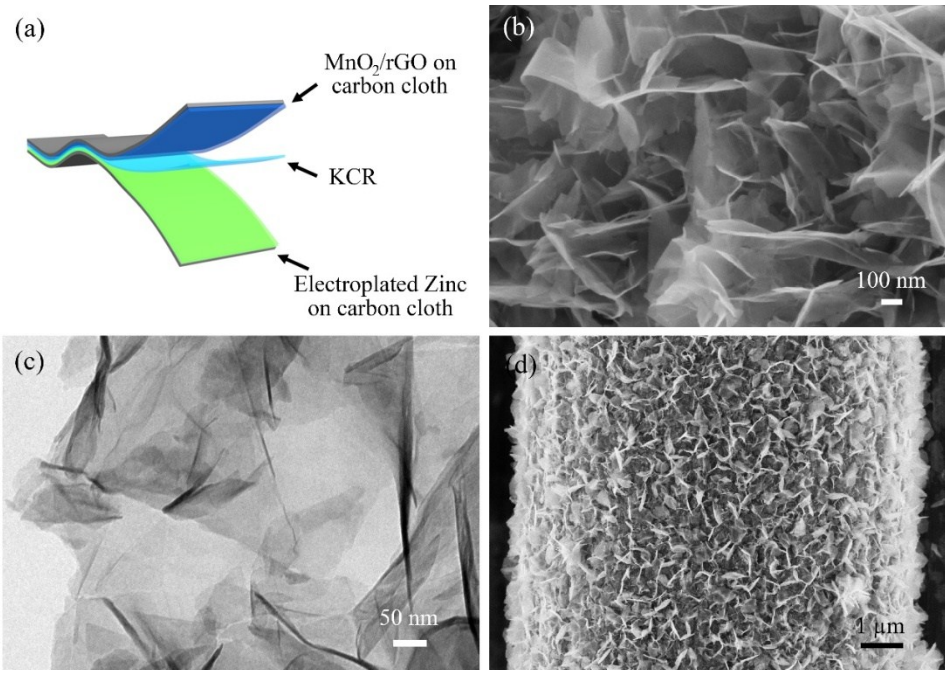

Fig. S2 (a) Schematic illustration for the structure of solid-state Zn-MnO_2 battery. (b) SEM image of the MnO_2 nanosheets. (c) TEM image of the MnO_2 nanosheets. (d)

SEM images of electroplated Zn on carbon cloth.

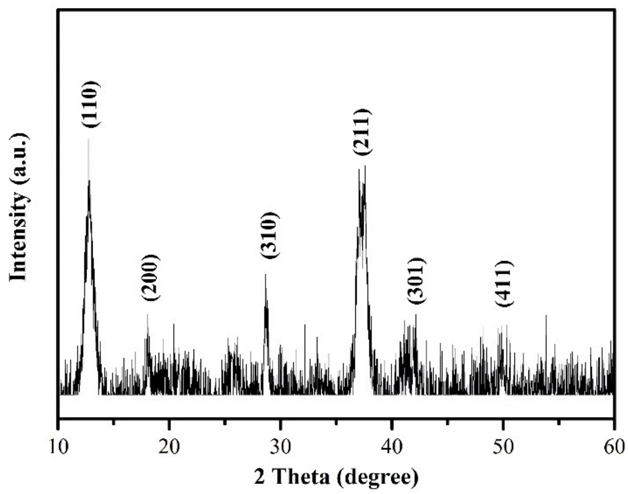

Fig. S3 XRD spectrum of MnO_2.

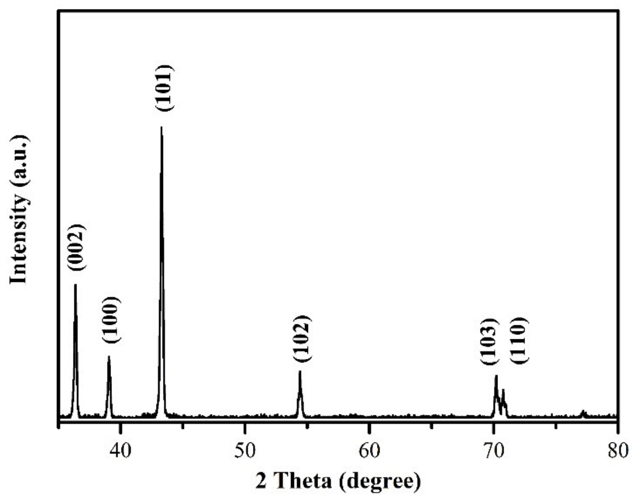

Fig. S4 XRD spectrum of electroplated Zn on carbon cloth.

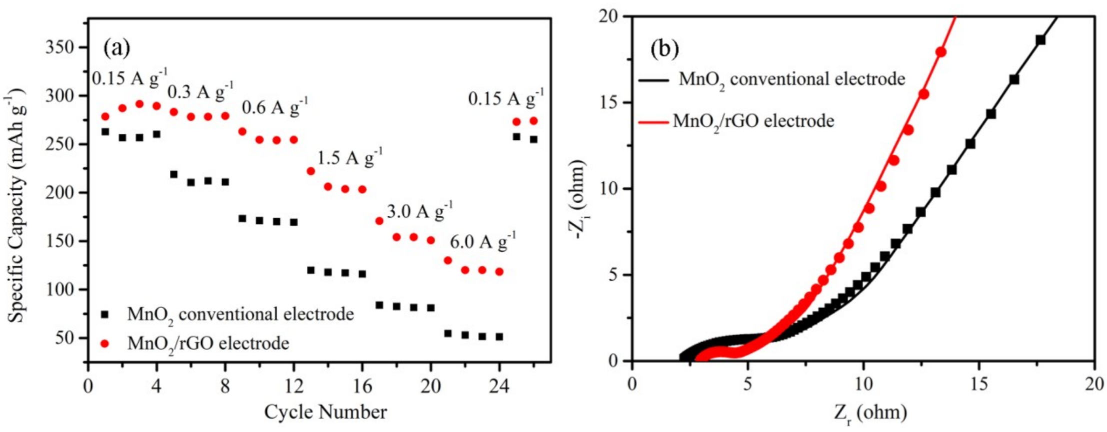

Fig. S5 (a) Specific capacities of solid-state ZIBs with MnO_2 conventional electrode and MnO_2/rGO electrode at various current density. (d) Nyquist plots of the samples after charging to ~1.9 V vs. Zn2+/Zn.

As shown in Fig. S5a, solid-state ZIBs with MnO_2/rGO electrode can deliver discharging capacity of ~291.5 mAh g^{-1} at 0.15 A g^{-1}. When the rate is increased to 6.0 A g^{-1}, the cell achieves a discharge capability of 120.0 mA h g^{-1}. As a comparison, solid-state ZIBs with conventional MnO_2 electrode exhibit much lower discharge capacity, that is, ~262.9 mA h g^{-1} at 0.15 A g^{-1}, and further drops to ~54.7 mA h g^{-1} at 6.0 A g^{-1}. The electrochemical impedance spectroscopy (EIS) measurements were also carried out on the cell with MnO_2/rGO electrode and conventional MnO2 electrode. The corresponding Nyquist plots (dot) and fitting results (line) are shown in Fig. S5b. The charge-transfer resistance of MnO_2/rGO sample is 1.3 Ω, which is lower than that of conventional MnO_2 sample (3.7 Ω). On the basis of the results above, the incorporation of rGO in MnO_2-based electrodes improves rate performance of the cells. This enhancement ascribed to the formation of conductive pathways for electron transport during the charging/discharging process, as evidenced in decreased charge transfer resistance.

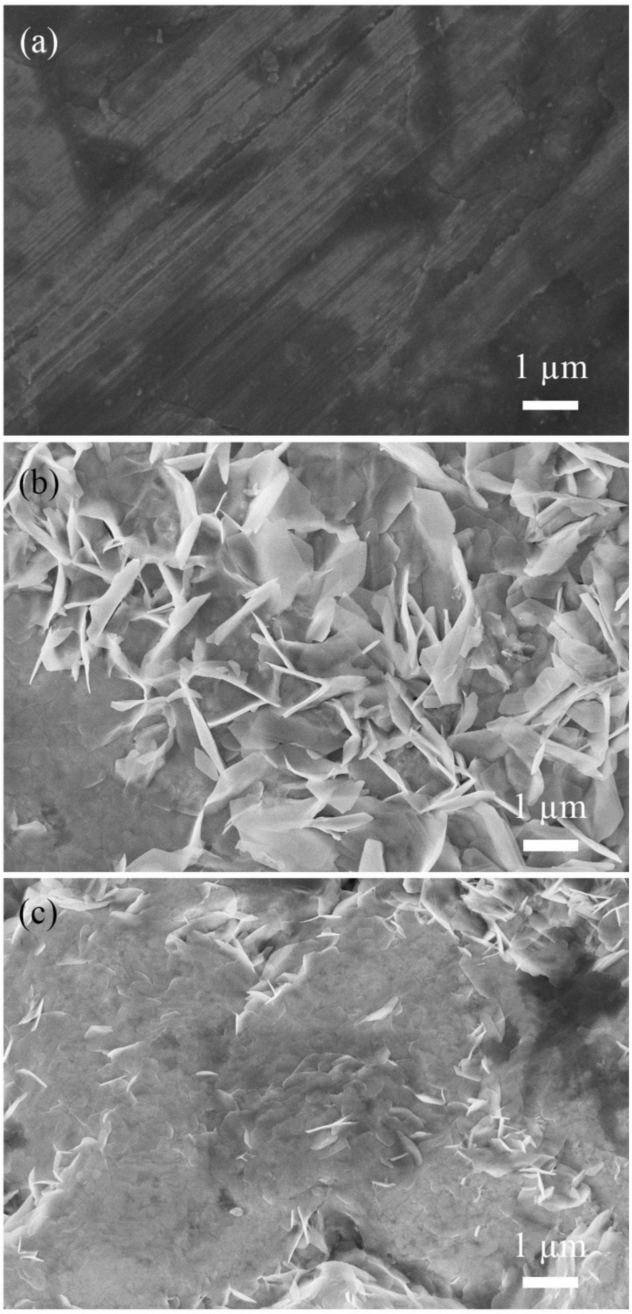

Fig. S6 SEM images of (a) fresh zinc foil, zinc foil after 100 cycles (at 6 A g^{-1}) in (b) aqueous electrolyte and (c) KCR electrolyte.

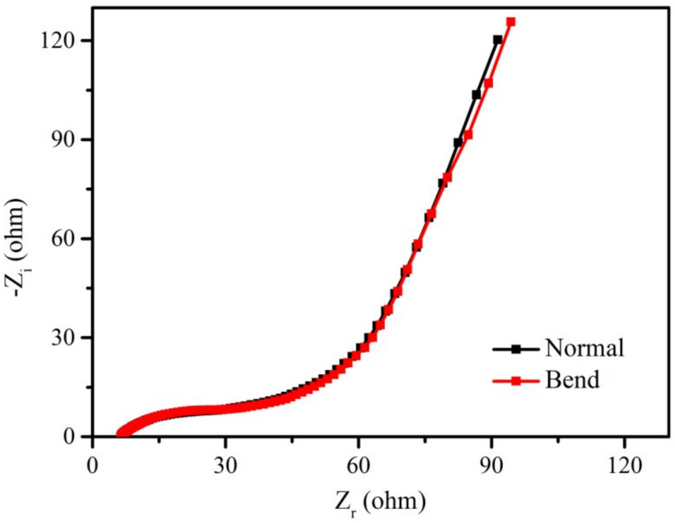

Fig. S7 AC impedance spectra of the solid-state ZIBs with KCR electrolyte under normal and bending conditions.

Table S1. Comparison of KCR electrolyte with some zinc-salt-polymer-electrolytes in terms of ionic conductivity in the literatures.

Polymer matrices	Ionic conductivity (mS cm^{-1})	Zinc salts	Reference
Kappa-Carrageenan	33.2	$ZnSO_4$	This work
xanthan gum	14.6	$ZnSO_4$	J. Mater. Chem. A**,** 2018**,** 6**,** 12237
A gelatin and PAM based hierarchical polymer	17.6	$ZnSO_4$	Energy Environ. Sci.**,** 2018, 11, 941
Gelatin	5.68	$ZnSO_4$	
poly(vinilydenefluoride-co-hexafluoropropylene)	1.73	$Zn(CF_3SO_3)_2$	J. Membrane Sci., 2014, 469, 499
PEO	0.5~0.8	$ZnCl_2$	Solid State Ion., 2005, 176, 1797
PEO	2~4	$ZnCl_2$	J. Electrochem.Soc., 2007, 154, A554

Poly-ε-caprolactone Express	0.88	$Zn(CF_3SO_3)_2$	Polym. Lett., 2013,7,495
Poly(4-vinylpyridine)	2×10^{-5}	$Zn(ClO_4)_2$	Macromolecules, 2004, 37, 192
PAN	0.22	$ZnSO_4$	J. New Mat. Electr. Sys., 2001, 4, 135
PAN	0.78	$ZnCl_2$	J. New Mat. Electr. Sys., 2001, 4, 135
poly(vinylidene fluoride -co-hexafluoropropylene)	3.82	$ZnTf_2$	Electrochim. Acta, 2015,176, 1447
poly(vinylidenefluoride)	3.94	zinc triflate	Solid State Ion., 2003,160,289

Table S2. Comparison of the rate performance of ZIBs ($Zn\text{-}MnO_2$) with KCR electrolyte and other solid-state electrolyte in the literature.

Solid-state Electrolyte	Rate	Ref
Kappa-Carrageenan/rice paper electrolyte $+ZnSO_4/MnSO_4$	120 mAh g^{-1} at 6.0 A g^{-1} 206 mAh g^{-1} at 1.5 A g^{-1}	This work
EG based waterborne anionic polyurethane acrylates/polyacrylamide $+ZnSO_4/MnSO_4$	162 mAh g^{-1} at 1.6 A g^{-1}	*Energy Environ. Sci.* **2019**, *12*, 706
polyacrylamide+gelatin+ $ZnSO_4/MnSO_4$	150 mAh g^{-1} at 1.848 A g^{-1}	*Energy Environ. Sci.* **2018**, *11*, 941
xanthan gum+ $ZnSO_4/MnSO_4$	120-150 mAh g^{-1} at 3.08 A g^{-1}	*J. Mater. Chem. A* **2018**, *6*, 12237
poly(vinyl alcohol)/LiCl+$ZnCl_2/MnSO_4$	201 mAh g^{-1} at 6.0 A g^{-1}	*J. Mater. Chem. A* **2017**, *5*, 14838

poly(vinyl alcohol)/LiCl+$ZnCl_2$/$MnSO_4$	76 mAh g^{-1} at 5.58 A g^{-1}	*Adv. Mater.* **2017**, *29*, 1700274
1-Buthyl-3-methylimidazolium trifluoromethanesulfonate+$ZnTf_2$	78 mAh g^{-1} at 2 A g^{-1}	*Electrochem. Commun.* **2015**, *60*,190
poly(vinylidenefluoride)+zinc triflate	37 mAh g^{-1} at 200 μA cm^{-2} (66 mA g^{-1})	*Solid State Ion.* **2003**, *160*, 289
poly(vinyl alcohol)+ZnTFS	45 mAh g^{-1} at 2 A g^{-1}	*ACS Appl. Mater. Interfaces* **2018**, *10*, 24573
1-Ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl) imide+ $ZnTf_2$	125 mAh g^{-1} at 1 mA cm^{-2}	*Electrochim. Acta* **2015**, *176*, 1447

Table S3. Comparison of the rate performance of ZIBs (Zn-MnO_2) with KCR electrolyte and other solid-state electrolyte in the literature.

Electrochemical energy storage devices	Energy density and Power density	Ref
Kappa-Carrageenan/rice paper electrolyte +$ZnSO_4$/$MnSO_4$	400 W h kg^{-1} / 0.2 kW kg^{-1} 171 W h kg^{-1} / 7.9 kW kg^{-1}	This work
solid state ZIB ($ZnSO_4$/$MnSO_4$-xanthan gum)	364 Wh kg^{-1} at 1C 2.5 KW kg^{-1} at 10C	*J. Mater. Chem. A* **2018**, *6*, 12237
solid state ZIB (LiCl-$ZnCl_2$/$MnSO_4$-PVA)	504.9 W h kg^{-1} / 0.67 kW kg^{-1} 117 W h kg^{-1} / 8.6 kW kg^{-1}	*Adv. Mater.* **2017**, *29*, 1700274
solid state ZIB (LiCl-$ZnCl_2$-PVA)	360 W h kg^{-1} / 0.1 kW kg^{-1}	*ACS Appl. Mater. Interfaces* **2018**, *10*, 24573