Electronic Supplementary Material

Flexible and High-Energy-Density Zn-MnO_2 Batteries Enabled by Electrochemically Exfoliated Graphene Nanosheets

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Experimental

1.1 *Sample preparation*

1.1.1 *Synthesis of EG/MnO_2 films*

MnO_2 nanosheets was firstly prepared via a reported method. [1] Typically, $KMnO_4$ and ethyl acetate were employed as starting material. An aqueous solution of $KMnO_4$ (150mL and 20 mM) and 40 mL of ethyl acetate are taken together in 250 mL capacity Three-necked round bottom flask. Thus, a biphasic mixture is formed and kept on a water bath under refluxing condition at 85-90 °C until the color of purple disappear. Washed and centrifuged at 7000rpm for 5 min for 5times, and dispersed in water to form a suspension with a concentration of 8 mg mL^{-1}. Secondly, graphite paper (2 cm×4 cm) is used as the negative electrode, nickel foam is used as the anode, and the electrolyte is KOH (7M, 100mL) to form an electrolytic cell. 10 V for 5min. After that, the mixture was washed to neutral, and ultrasonic in ethanol for 1h, and the EG suspension with a concentration of ~5 mg mL^{-1} was obtained. Finally, 3.6 mL EG nanosheets and 1 mL MnO_2 nanosheets were mixed evenly and filtered to a membrane. After drying process, the flexible MnO_2/EG films were obtained.

1.1.2 *Synthesis of EG/Zn films*

To synthesize EG/Zn films, EG based assembly film, which were fabricated by vacuum filtration of 2.4 mL EG suspension, were employed as the cathode, and Zn foil and 1M $ZnSO_4$ were used as the anode and electrolyte, respectively. The electrodeposition process was conducted with the voltage of 5 V for 25 min.

1.2*Characterization methods*

All samples were characterized by field-emission scanning electron microscopy (SEM, QUANTA 450, 20KV), transmission electron microscopy (TEM, FEI Tecnai G20, 200 KV), X-Ray diffraction (XRD, D/Max 2400 diffractometer, Cu Kα, λ=1.5406 Å), nitrogen adsorption/desorption (Micromeritics ASAP 2020 instrument).

1.3*Electrochemical measurements*

The electrochemical measurements were conducted using CR2016 coin cells at room temperature. EG/MnO_2 and Zn foil were used as cathode and anode, respectively, and the electrolyte was 2.0 M $ZnSO_4$ with 0.1 M $MnSO_4$. The resulting battery was donated as MnO_2/EG//Zn. When EG/MnO_2 cathode was paired with Zn/EG anode, the resulting battery was donated as MnO_2/EG//Zn/EG. The galvanostatic charge/discharge tests were performed on a LAND CT2001A battery tester at different current densities (1 C=302 mA g^{-1}) with a cut-off voltage window of 1-1.8 V. The calculation of the specific capacity is based on the MnO_2 mass of the composite. The cyclic voltammetry (CV) tests were conducted using a CHI660E electrochemistry workstation between 1-1.8 V at a scan rate of 0.1 mV s^{-1}. The electrochemical impedance spectroscopy (EIS) measurements were carried out using a CHI660E workstation by applying AC amplitude of 5 mV over the frequency range of 100 kHz to 0. 1 Hz.

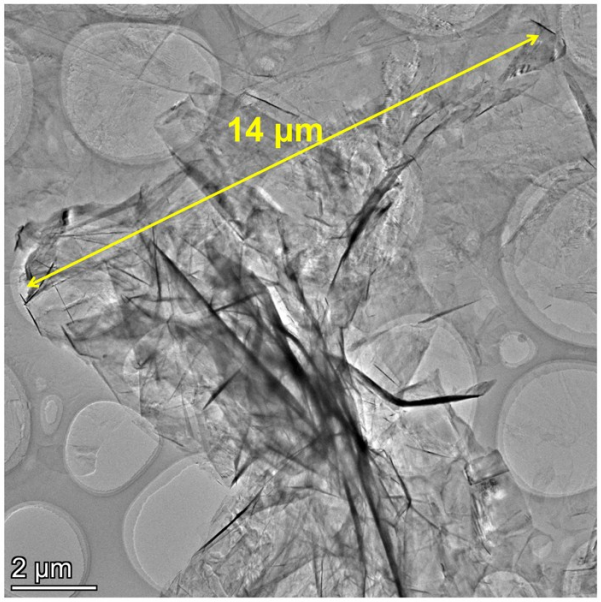

Fig. S1. TEM image of EG nanosheets.

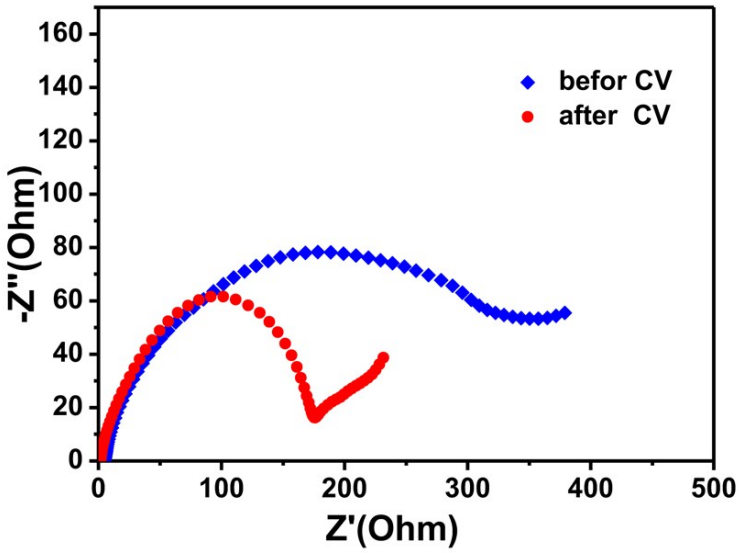

Fig. S2. Electrochemical impedance spectra of MnO_2/EG//Zn coin cell before and after CV tests.

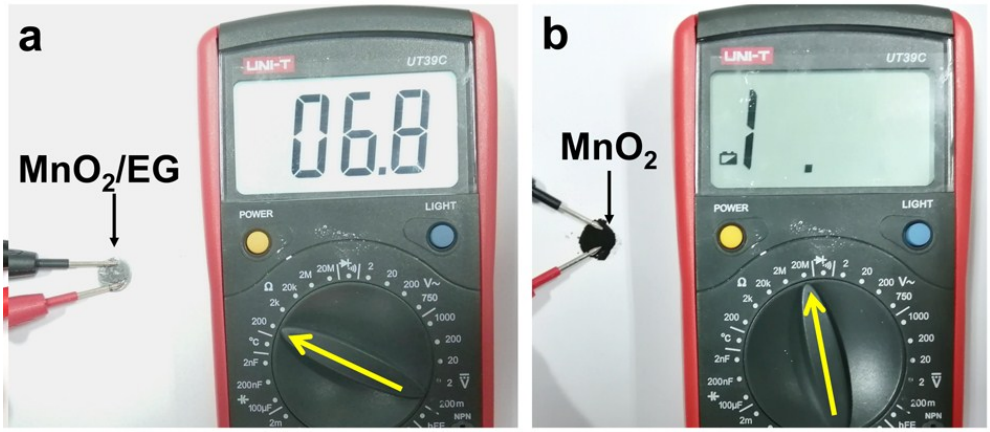

Fig. S3. The conductivity testing of (a) a MnO_2/EG film and (b) a pressed MnO_2 based circle slice.

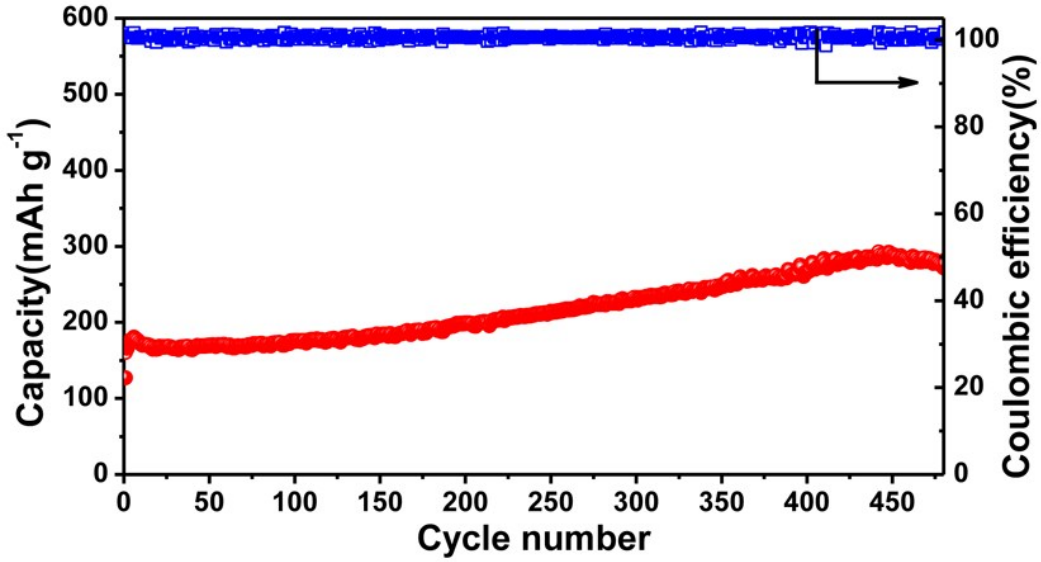

Fig. S4. Cycling stability and coulombic efficiency of MnO_2/EG//Zn battery at the current density of 0.5 C.

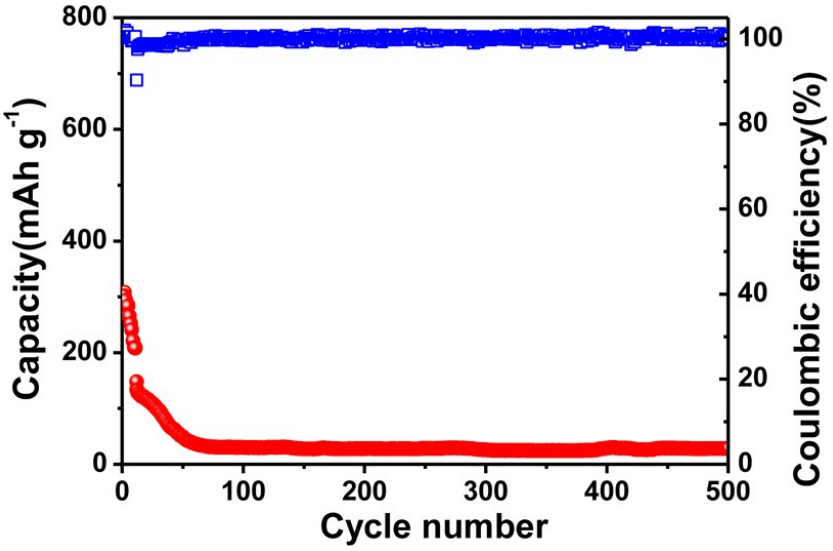

Fig. S5. Cycling stability and coulombic efficiency of MnO_2/EG//Zn battery in electrolyte of 2 M $ZnSO_4$ with 0.5 M $MnSO_4$ additive.

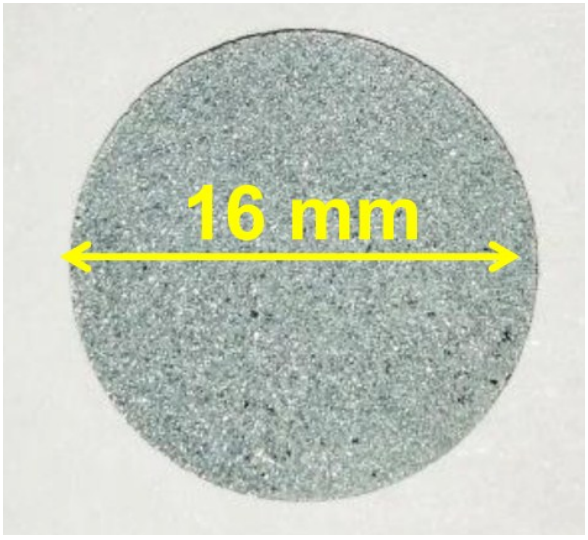

Fig. S6. A photo of circled Zn/EG film with a diameter of 16 mm.

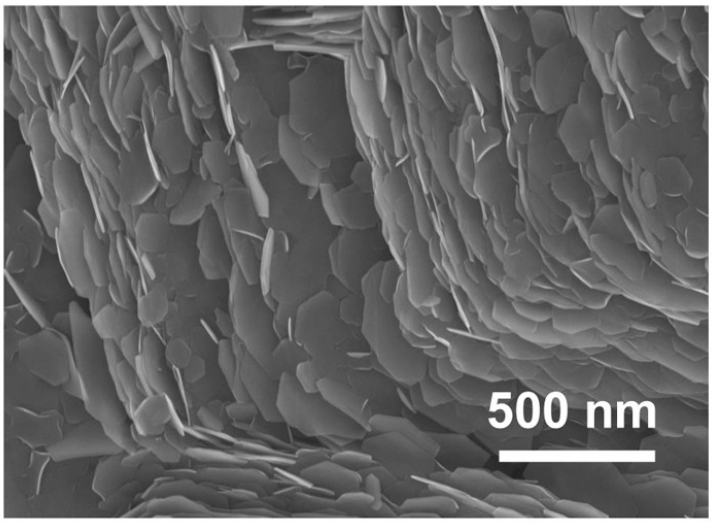

Fig. S7. SEM image of electrodeposited Zn nanosheets.

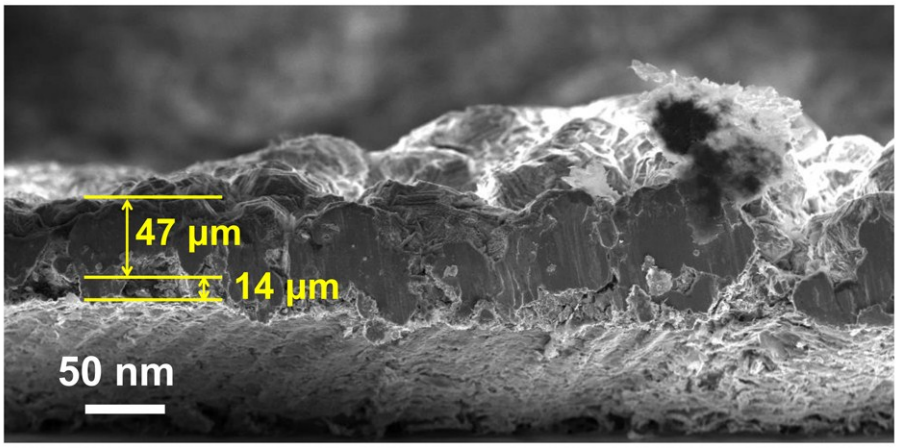

Fig. S8. Cross-section SEM image of Zn/EG hybrid film, in which the thickness of electrodeposited Zn layer and EG layer could be measured to be 47 μm and 14 μm.

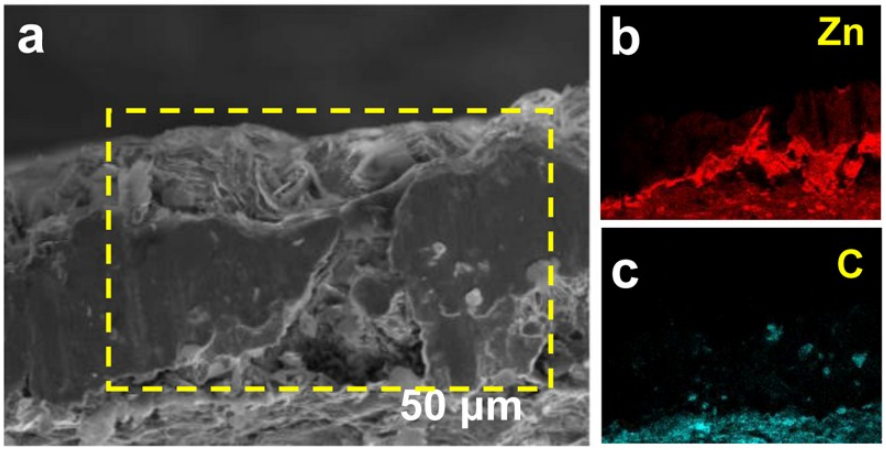

Fig. S9. (a) Cross-section SEM image of Zn/EG film. Elemental mapping analysis of (b) element Zn and (c) C in the marked zone in (a).

Table S1 The Zn storage performance of MnO_2/EG film cathode compared with other reported Mn based electrodes

Active materials	Electrochemical performance	Reference
MnO_2/EG film	**374 mAh g^{-1} at 0.2 C 315 mAh g^{-1} at 0.5 C 264 mAh g^{-1} at 1 C (308 mA g^{-1}) 182 mAh g^{-1} at 2 C 147 mAh g^{-1} at 3 C 128 mAh g^{-1} at 4 C**	**This work**
a-MnO_2	210 mAh g^{-1} at 0.5 C	Ref [2]
a-MnO_2 nanofibres	285 mAh g^{-1} at 1/3 C, 260 mAh g^{-1} at 1C	Ref [3]
β-MnO_2	258 mAh g^{-1} at 0.65 C	Ref [4]
Mn_3O_4 nanoparticles	232 mAh g^{-1} at 0.2 A g^{-1}, 195 mAh g^{-1} at 0.5 A g^{-1}, 106 mAh g^{-1} at 0.5 A g^{-1} after 300 cycles	Ref [5]
polyaniline-intercalated MnO_2	260 mAh g^{-1} at 0.16 C	Ref [6]
MnO_2-birnessite cathode	266 mAh g^{-1} at 0.33 C, 242 mAh g^{-1} at 0.67 C	Ref [7]
flower-like Mn_3O_4	296 mAh g^{-1} at 0.1 A g^{-1}	Ref [8]
oxygen-defect $K_{0.8}Mn_8O_{16}$	216 mAh g^{-1} at 0.1A g^{-1} for the 1st cycle, 278 mAh g^{-1} at 0.1A g^{-1} after 50 cycles	Ref [9]
$MgMn_2O_4$-400	269 mAh g^{-1} at 100 mA g^{-1}	Ref [10]
ramsdellite MnO_2	150 mAh g^{-1} at 100 mA g^{-1}, 135 mAh g^{-1} at 300 mA g^{-1}	Ref [11]
MnO_2 nanorods	252.9 mAh g^{-1} at 1 C	Ref [12]
Akhtenskite MnO_2	225 mAh g^{-1} at 100 mA g^{-1}, 182 mAh g^{-1} at 200 mA g^{-1}	Ref [13]

Reference

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