Supporting Information

High Performance, Environmentally Benign and Integratable Zn//MnO₂ Microbatteries

Wenhui Lai a, Yang Wang a, Zhanwu Lei a, Ronghe Wang a, Ziyin Lin b, Ching-Ping Wong b, Feiyu Kang a,c, Cheng Yang a*

a Division of Energy and Environment, Graduate School at Shenzhen, Tsinghua University, Shenzhen 518055, PR China.
b School of Materials Science and Engineering, Georgia Institute of Technology, Atlanta, 30332, GA, USA.
c School of Materials Science and Engineering, Tsinghua University, Beijing 100084, P. R. China.

*Corresponding author e-mail: yang.cheng@sz.tsinghua.edu.cn
Experimental Section

Calculations. The mass specific capacitance \( C_m \), volumetric specific capacitance \( C_v \), volumetric energy density \( E_v \) and power density \( P_v \) were calculated from the GCD curves according to the equations below.

\[
C_m = \frac{\int I \cdot \Delta t}{m} \quad (1)
\]

\[
C_v = \frac{\int I \cdot \Delta t}{V} \quad (2)
\]

\[
E_v = \int I \frac{U dt}{V} \quad (3)
\]

\[
P_v = \frac{E}{\Delta t} \quad (4)
\]

where \( I \) is the applied current, \( \Delta t \) is the discharge time, \( m \) is the mass of the active material, \( V \) is the total volume of the active material, and \( U \) is the discharge voltage.
Supporting Figures

**Fig. S1.** (a-c) Cross-view SEM images of NCAs scaffold. NCAs displayed a high aspect ratio, with an average height of 1 μm, which could support more electroactive materials loading. Besides, there were enough gaps among Ni matrix for the placement of the reaction intermediates so that to accommodate the enormous volume changes and alleviate the concomitant huge stresses.
**Fig. S2.** TEM characterization of electrode materials. (a) TEM image of MnO$_2$ deposited onto NCAs. (b) HRTEM image of MnO$_2$. Inset is the selected area electron diffraction (SAED) pattern of MnO$_2$, which indicates the low crystallinity of MnO$_2$. (c) TEM of Zn anode deposited on NCAs. (d) HRTEM of Zn anode deposited on NCAs. Inset is the SAED pattern of Zn, which confirms the highly crystalline nature of the close-packed hexagonal structure of Zn nanosheets, which can be further confirmed by XRD analysis.
Fig. S3. Photographic images of the rechargeable Zn//MnO$_2$ MB arrays before and after electrodeposition. (a-c) Optical photographs of Zn//MnO$_2$ interdigital microelectrodes after laser etching. The top layer of microelectrodes is NCAs substrate, the white area is PET layer, insert is the picture of real product after laser etching. (d-e) Optical photographs of Zn//MnO$_2$ interdigital microelectrodes after electrodeposited electrode materials. The light blue is Zn anode, the brown black is MnO$_2$ cathode, insert is the picture of real product after electrodeposition. It is obvious that MnO$_2$ and Zn can uniformly coat on the NCAs by electrodeposition technology.
Fig. S4. The XRD patterns of the as-obtained samples. The three diffraction peaks of NCAs are corresponded to the three crystal faces of Ni (JCPDS NO.: 04-0850): (111), (200), (220), respectively. MnO$_2$ prepared by electrodeposition method showing a low crystallinity is consistent with previous reports. The XRD analysis of Zn anode displays four diffraction peaks, which is in good agreement with the crystal faces of Zn (JCPDS NO.: 87-0713): (002), (101), (102), (201), respectively, and indicates the hexagonal close-packed phase of Zn.
**Fig. S5.** The XPS spectra of MnO$_2$ and Zn deposited onto the NCAs. (a) The XPS full spectrum, (b) Mn 2p and (c) O 1s core level XPS spectrum of MnO$_2$, indicating the presence of MnO$_2$. (d) The XPS full spectrum of Zn. Inset is the Zn 2p core level XPS spectrum. A typical peak at 1021.6 eV is attributed to the Zn 2p, confirming the as-prepared sample is Zn.
Fig. S6. (a) CV curves of MNC positive electrode in different electrolyte at 0.1 mV s$^{-1}$ (red: 2 M ZnSO$_4$ and 0.2 M MnSO$_4$ based electrolyte; black: 2 M NaSO$_4$ electrolyte). It’s obvious that MNC electrode displays larger area under 2 M ZnSO$_4$ and 0.2 M MnSO$_4$ based electrolyte comparing to 2 M NaSO$_4$ electrolyte, which indicates that ZnSO$_4$ based electrolyte has a contribution to the total capacity. (b) CV curves of the MNC and MCI electrode at the scan rate of 0.1 mV s$^{-1}$, and (c) CV curves of the MNC, MCI, MNP, MNF electrode at the scan rate of 1 mV s$^{-1}$. Under the same preparation and test condition, NCAs with a high aspect ratio can support more mass loading to improve the capacity comparing with other conductive substrates. (d) Nyquist plots of MNC, MCI, MNP, MNF electrode. The improved electrochemical impedance spectroscopy (EIS) performance of MNC electrode is due to the uniform Ni matrix, which maintains a direct electrical connection with the electrode materials resulting in a shortened diffusion distance of ions and a rapid rate of electron collection and transport.
Fig. S7. The equivalent circuit model of MNC positive electrode used for fitting impedance spectra.
Fig. S8. (a) CV curves of the aqueous Zn//MnO$_2$ MB at different scan rates ranging from 0.2 mV s$^{-1}$ to 1.0 mV s$^{-1}$. When the scan rate goes faster, there are no significant differences in the shape of the curves, showing excellent rate ability. (b) Discharge curves of the full cells under different C rates. When the C rate increases from 1, 4, 6, 9 to 15 C, the discharge capacity of the full MB decreases from 53.5, 31.3, 19.6, 16.9 to 10.2 μAh cm$^{-2}$ μm$^{-1}$, respectively, indicating superior capacitance performance and rate property. (c) Nyquist plots of the Zn//MnO$_2$ MB based on NCAs scaffold or not, inset is a magnification of the high-frequency region. NCAs as a metal conductive support reveals good EIS performance.
Fig. S9. Photographic images of the rechargeable Zn//MnO$_2$ MB arrays. (a) The planar display image of the Zn//MnO$_2$ MB arrays (2 × 6) packaged by a thin PET film. Insert: demonstration of the flexible Zn//MnO$_2$ MB arrays, which can be rolled onto a pen. (b) Photograph demonstrate of the thickness of the Zn//MnO$_2$ MB device. The total thickness of the encapsulated Zn//MnO$_2$ MB cell is just 74 μm, which as an ultrathin and lightweight component reveals great prospects in flexible, wearable electronic devices.
Fig. S10. Demonstration of three LEDs driven by a single rechargeable Zn//MnO$_2$ MB.

The three LEDs can be lighted more than 90 s after the Zn//MnO$_2$ MB charging for a moment.
Fig. S11. Photography demonstration of RFID tags fabricated by laser processing strategy. (a) Demonstration of RFID tags identified by the ultra-high frequency (UHF) RFID reader. The antenna of RFID tag and Zn//MnO$_2$ MB were fabricated in a one-step laser process on the same substrate, picture of real products is in the lower right corner. From the enlarged view of computer, it is obvious that the RFID tag prepared by this strategy can be identified, whose tag number is consistent with the same style of commercial tag (No: e2006008131501550630d3ff). (b) Photography view of the commercial RFID tag. (c) Wireless charging demonstration of Zn//MnO$_2$ MB.
### Table S1. The electrochemical properties comparison of different MBs and MSCs

<table>
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<tr>
<th>MBs/MSCs</th>
<th>Maximized discharge capacity (μAh cm$^{-2}$ μm$^{-1}$)</th>
<th>Maximized energy density (μWh cm$^{-2}$ μm$^{-1}$)</th>
<th>Maximized power density (μW cm$^{-2}$ μm$^{-1}$)</th>
<th>Cycling performance</th>
<th>Reference</th>
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<tr>
<td>All-MXene MSCs</td>
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<tr>
<td>PPyNW MSCs</td>
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<td>1.53</td>
<td>1784</td>
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<td>LMO//NiSn MBs</td>
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<tr>
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<td>49500</td>
<td>-</td>
<td>[10]</td>
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<tr>
<td>Zn//MnO$_2$ MBs</td>
<td>53.5</td>
<td>71.3</td>
<td>1621.4</td>
<td>60.2% after 100 cycles</td>
<td>This work</td>
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Note. MXene, transition metal carbides and nitrides (Ti$_3$C$_2$T$_x$); PPyNW, PPy nanowires; MPG, methane (CH$_4$)-plasma reduced graphene; LMO, lithiated manganese oxide.
Reference