Supporting Information

Defect engineering via the F-doping of $\beta$-MnO$_2$ cathode to design hierarchical spheres of interlaced nanosheets for superior high-rate aqueous zinc ion batteries

Seoyeong Kim$^{a,1}$, Bon-Ryul Koo$^{b,c,1}$, Yong-Ryun Jo$^d$, Ha-Rim An$^e$, Young-Geun Lee$^a$, Chun Huang$^{b,c,*}$, Geon-Hyoung An$^{a,f,**}$

$^a$Department of Energy Engineering, Gyeongsang National University, Jinju, Republic of Korea

$^b$Department of Engineering, King’s College London, London WC2R 2LS, UK

$^c$Department of Materials, University of Oxford, Oxford, OX1 3PH, UK

$^d$Advanced Photonics Research Institute (APRI)

$^e$Center for Research Equipment, Korea Basic Science Institute, Daejeon 34133, Republic of Korea

$^f$Future Convergence Technology Research Institute, Gyeongsang National University, Jinju, Republic of Korea

*Corresponding author.

E-mail address: ann.huang@kcl.ac.uk (C. Huang)

** Corresponding author.

E-mail address: ghan@gnu.ac.kr (G.-H. An)

$^1$These authors contributed equally to this work.
Table S1. Comparison of specific surface area and pore volume among all samples.

<table>
<thead>
<tr>
<th>Samples</th>
<th>S_{BET} (m^2 g^{-1})</th>
<th>Total pore volume (cm^3 g^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bare MnO_2</td>
<td>14.86</td>
<td>0.08</td>
</tr>
<tr>
<td>4F-MnO_2</td>
<td>26.88</td>
<td>0.09</td>
</tr>
<tr>
<td>5F-MnO_2</td>
<td>79.37</td>
<td>0.15</td>
</tr>
<tr>
<td>6F-MnO_2</td>
<td>53.84</td>
<td>0.11</td>
</tr>
</tbody>
</table>

Fig. S1. (a) DSC curve of bare MnO_2, NH_4F, and 5F-MnO_2 measured in range from room temperature to 200 °C of air atmosphere.
Fig. S2. High-magnification SEM images of 5F-MnO$_2$ obtained at different calcination temperature of (a) 100 °C and (b) 150 °C.
Fig. S3. Enlarged XRD patterns of all samples.
Fig. S4. (a) UPS spectra, (b) VBM spectra, and (c and d) curve of $(\alpha h\nu)^2$ versus photon energy of bare MnO$_2$ and 5F-MnO$_2$. 
Fig. S5. Comparison of the rate performances between bare MnO$_2$ and heat-treated MnO$_2$ without the F-doping process.