NANO MICRO small

# Supporting Information

for *Small*, DOI: 10.1002/smll.201902141

## Langmuir–Blodgett Nanowire Devices for In Situ Probing of Zinc-Ion Batteries

*Qin Liu, Zhimeng Hao, Xiaobin Liao, Xuelei Pan, Shuxuan Li, Lin Xu,* and Liqiang Mai*

# Supporting Information

## Langmuir-Blodgett Nanowire Devices for In-Situ Probing of Zinc-Ion Batteries

*Qin Liu, Zhimeng Hao, Xiaobin Liao, Xuelei Pan, Shuxuan Li, Lin Xu* and Liqiang Mai*

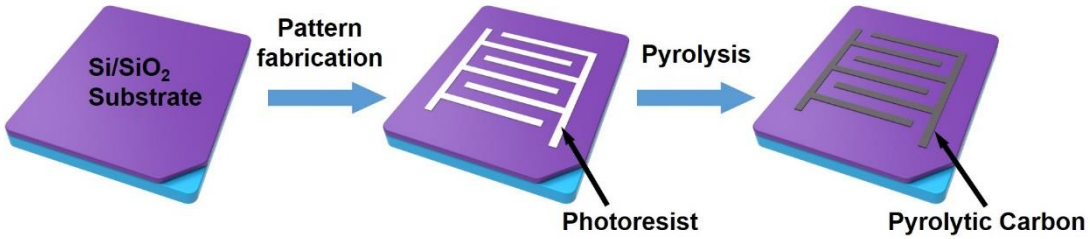


**Figure S1.** Schematic illustration of the fabrication processes of pyrolytic carbon current collectors.

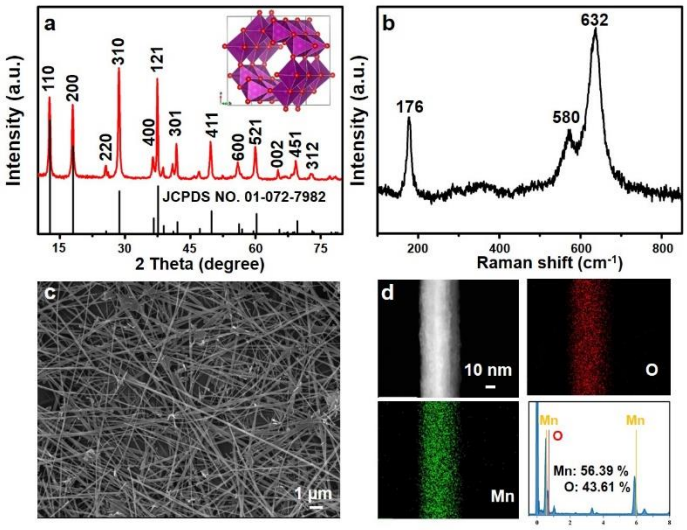


**Figure S2.** Characterization of $MnO_2$ nanowires. a) XRD pattern, b) Raman spectroscopy, c) SEM, d) EDS.

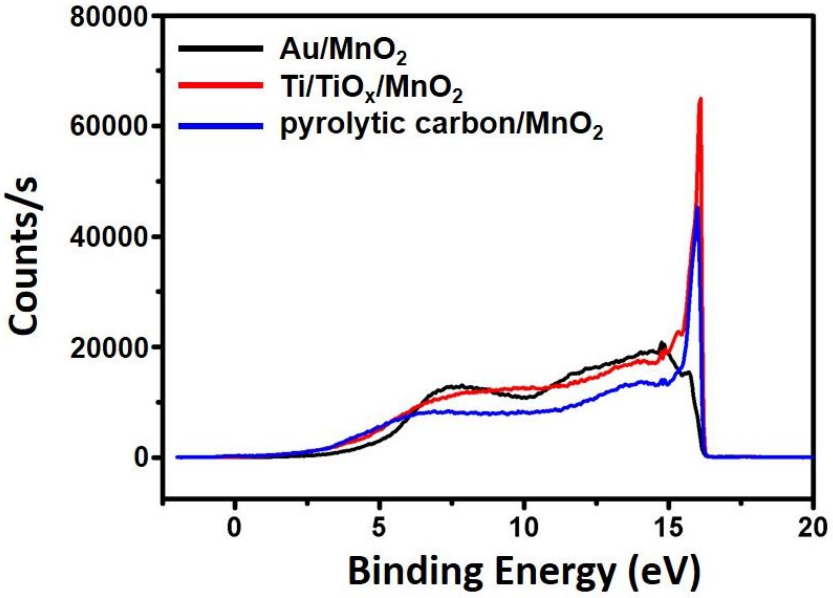


**Figure S3.** The ultra violet photoelectron spectroscopy of different nanowire/current collector interfaces.

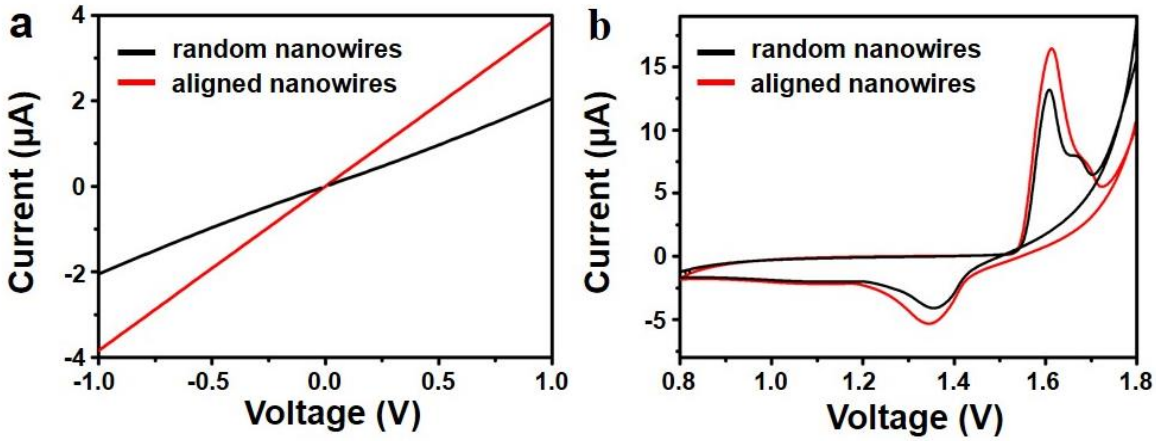


**Figure S4.** Characterization of LBNW film. a) I-V curves of aligned NWs and random NWs with pyrolytic carbon current collector, respectively. b) CV curves of aligned NWs and random NWs with pyrolytic carbon current collectors in $ZnSO_4$ electrolyte with pre-added $Mn^{2+}$.

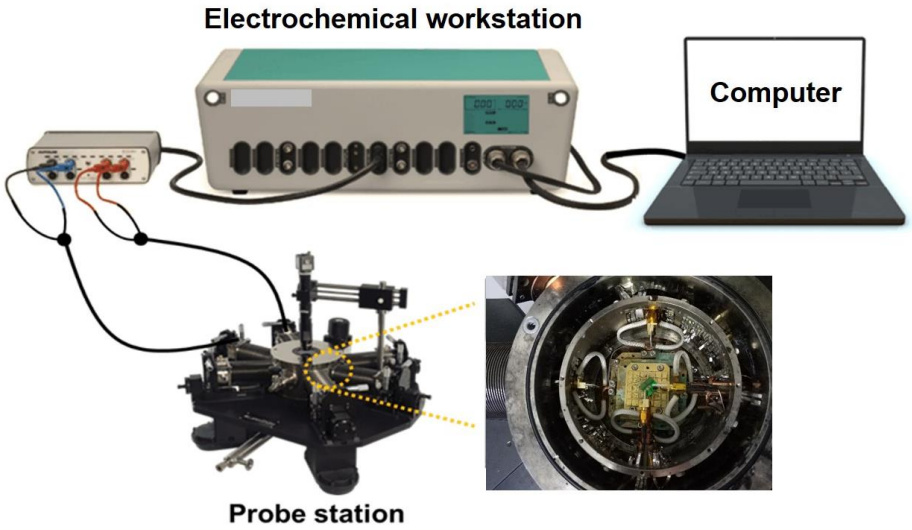


**Figure S5.** Measurement equipment layout with the three-dimensional view: Electrochemical workstation and probe station combined system.

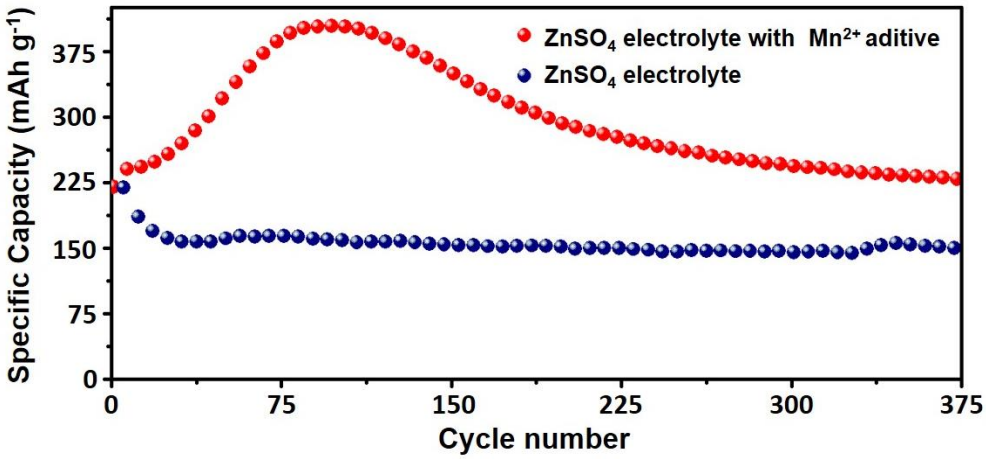


**Figure S6.** Cycling performance of $MnO_2$ LBNWs in $ZnSO_4$ electrolyte and $ZnSO_4$ electrolyte with pre-added $Mn^{2+}$, respectively.

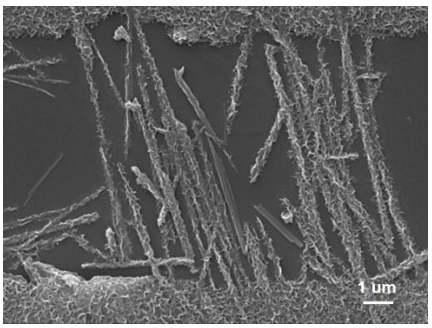


**Figure S7.** SEM image of $MnO_2$ nanowires after 100 cycles.

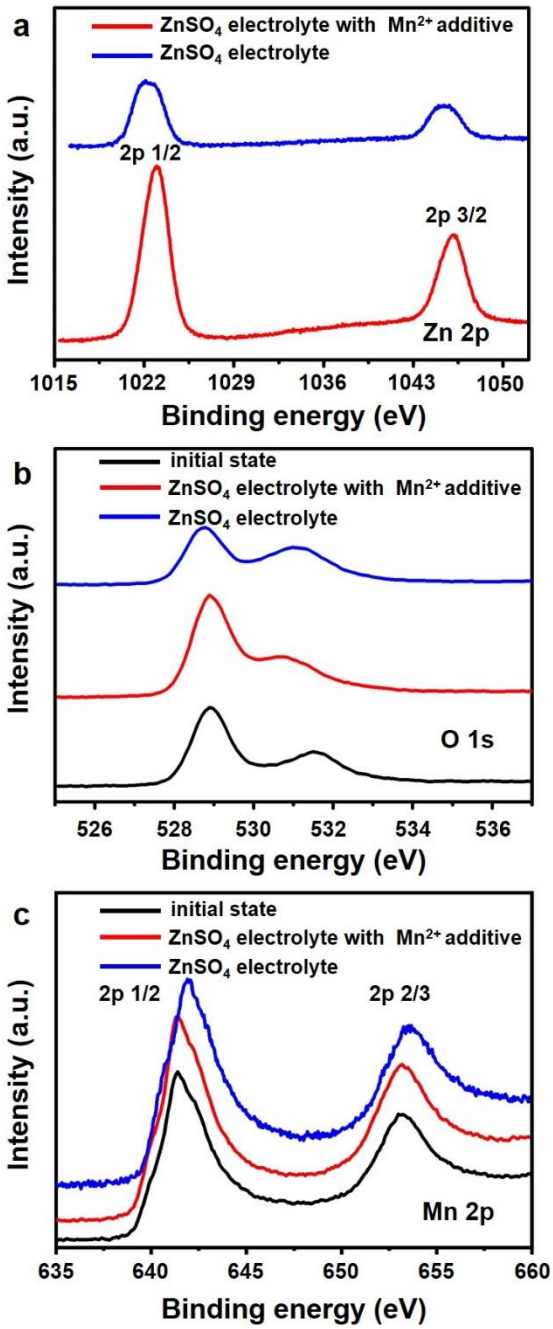


**Figure S8.** High-resolution XPS characterization of LBNWs at different states. a) Zn 2p, b) O 1s, c) Mn 2p XPS spectroscopy for $MnO_2$ electrode materials at different states: black, initial state; red, after 100 galvanostatic charging at 1 μA $cm^{-2}$ in $ZnSO_4$ electrolyte; blue, after 100 galvanostatic charging at 1 μA $cm^{-2}$ in $ZnSO_4$ electrolyte with $MnSO_4$ additive.

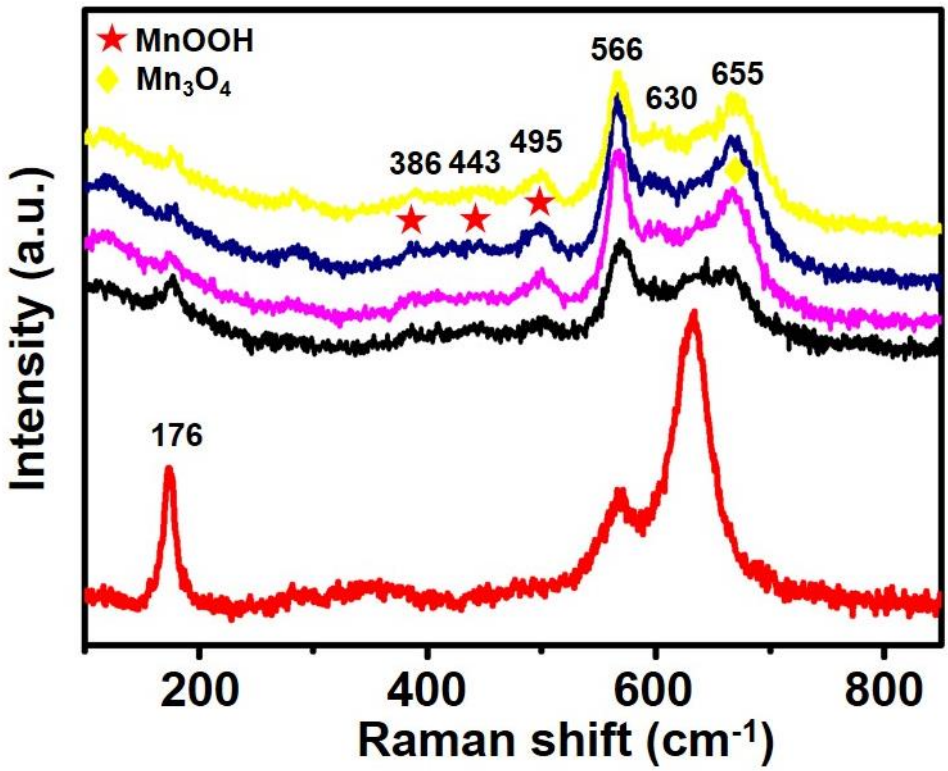


**Figure S9.** Raman spectroscopy evolution of $MnO_2$ LNNWs at different charge/discharge states. Red, initial state; dark, after 10th galvanostatic charging; pink, after 20th galvanostatic charging; navy, after 50th galvanostatic charging; yellow, after 375th galvanostatic charging.

**Table 1.** Zn, Mn, O element ratio after 100 cycles.

| Element | Ratio |
|---|---|
| **Oxygen** | **33.5** |
| **Manganese** | **43.6** |
| **Zinc** | **23.3** |