# **Supporting Information**

#### On-site Evolution of Ultrafine ZnO nanoparticles from Hollow Metal-Organic

#### Frameworks for Advanced Lithium Ion battery Anode

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#### **Experimental section**

**Synthesis of ZIF-8 microcubes.** 1.81 g of zinc nitrate hexahydrate was dissolved in 8 mL of deionized water, and then 1.0 g of 2-methylimidazole was dissolved in 12.09 g of ammonium hydroxide solution; after that zinc nitrate and 2-methylimidazole were mixed together. which was stirred for 10 min at room temperature to complete the crystallization.

**Synthesis of ZIF-8@ZnO microcubes.** Typically, 40 mg ZIF-8 microcubes was spread out on the quartz boat, and moved into the plasma tube reactor which is filled with Ar/H<sub>2</sub> (contain 10 vol % of H<sub>2</sub>) gases, then it was directly treated by plasma (commercial 13.56 MHz RF source) with power of 200 W and pressure of 50 Pa for 3 h. After that, the plasma treated samples were taken out from the plasma tube reactor and exposed to air, which named as ZIF-8@ZnO. Compared with the synthesis of hierarchical ZIF-8@ZnO, 40 mg ZIF-8 microcubes was treated by plasma for three durations of 0, 1, and 4 h. The following procedure is the same asthat for the synthesis of ZIF-8@ZnO microcubes. Similarly, other MOFs, such as ZIF-67, were also treated by the same method to investigate the effect of plasma treatment.

**Synthesis of ZIF-8 cages.** In a typical synthesis, 40 mg of the ZIF-8 microcubes was dissolved into 200 ml of methanol solution containing 1 g of tannic acid. After stirring for 20 min, the product is collected by centrifugation and washed with ethanol.

**Synthesis of hollow ZIF-8@ZnO hybrid structures**. Typically, 40 mg of hollow ZIF-8 cages was spread out on the quartz boat, and moved into the plasma tube reactor which is filled with Ar/H<sub>2</sub> (contain 10 vol % of H<sub>2</sub>) gases, then it was directly treated by plasma (commercial 13.56 MHz RF source) with power of 200 W and pressure of 50 Pa for 3 h. After that, the plasma treated samples were taken out from the plasma tube reactor and exposed to air, which named as h-ZIF-8@ZnO. For comparison, 40 mg hollow ZIF-8 cages were treated by plasma for 4 hours with the same procedure.

**Electrochemical Measurements.** Electrochemical measurements were performed by the use of 2032 coin cell. The cell assembly was carried out in an Ar-filled glovebox with moisture and oxygen concentrations below 1.0 ppm. Li foil served as the counter electrode and reference electrode, and the working electrodes consist of 70 wt.% of active material, 20 wt.% of conductive carbon black (Super-P), and 10 wt.% of polymer binder (polyvinylidene fluoride, PVDF). The electrolyte was a 1.0 M LiPF<sub>6</sub> solution in a mixture of ethylene carbonate/dimethylcarbonate

(EC/DMC) (1:1 in volume), and a polypropylene film(Celgard-2400) was used as a separator. The galvanostatic charge/discharge cycles were carried out on a Land CT2001A battery tester between 0.001 and 3.0 V at various current densities. Electrochemical impedance spectroscopy and cycle voltammetry were conducted on a PGSTAT 302N electrochemical workstation at a scan rate of 0.1 mV s<sup>-1</sup>. At least five parallel cells were tested for each electrochemical measurement, in order to make sure that the results were reliable and represented the typical behavior of the samples.

**The battery disassembly process:** After being tested for 500 cycles, the cycled h-ZIF-8@ZnO electrode was obtained by disassembling the coin cell in an Ar-filled glove box, then subsequently rinsing with dimethyl carbonate (DMC) for several times in the glove box to remove the internal electrolyte and finally dried at 60 °C. The dried electrode materials was scraped from Cu foil and collected for further characterization.

**Materials Characterization.** The morphology and microstructure of all samples were investigated by scanning electron microscope (SEM, Hitachi, S-4800) and transmission electron microscope (TEM, FEI, F20 S-TWIX). The X-ray diffraction (XRD) measurements used a Rigaku D/MAX 2500 diffractometer with Cu Kα radiation. The thermogravimetric analysis (TGA) was carried out by a STA449C instrument with a heating rate of 5 °C min<sup>-1</sup> from the room temperature to 1000 °C in air. The nitrogen adsorption-desorption isotherms were measured at liquid nitrogen temperature (77 K) using a volumetric adsorption analyzer (Micromertics ASAP 2020HD88). The chemical characteristics of the samples were analyzed by Fourier transform infrared spectrometer (FTIR, WQF-410), the spectra were recorded in FTIR spectrometer with the samples prepared as KBr discs. The X-ray photoelectron spectroscopic (XPS) measurements were carried out with an ESCALAB 250Xi using a monochromic Al X-ray source (200 W, 20 eV). The Electron paramagnetic resonance (EPR) measurements were carried out at a Bruker model A300 spectrometer. The synchrotron X-ray spectroscopy measurements at Zn K-edge were performed at BL20A at the National Synchrotron Radiation Research Center (NSRRC), Taiwan.

# **Supplementary Figures captions**



Figure S1. The SEM images of ZIF-8 treated by plasma etching with different time (a)

0 h; (b) 1 h; (c) 3 h; (d) 4 h.



Figure S2. The SEM images of (a) ZIF-67 and (b) ZIF-67 after Ar/H $_2$  plasma etching.



Figure S3. (a-c) The FESEM, TEM, HRTEM images of ZIF-8 cage (denoted as h-ZIF-8)



**Figure S4.** The SEM images of (a) ZIF-8 cages and (b) hollow ZIF-8@ZnO hybrid structures which after the plasma etching.



Figure S5. The SEM images of (a) a broken ZIF-8 cage and (b) after the Ar/H $_{\rm 2}$  plasma

etching (h-ZIF-8@ZnO).



Figure S6. The SEM images of the hollow ZIF-8@ZnO hybrids after the  $Ar/H_2$  plasma etching for 4 h.



Figure S7. The XRD patterns of ZIF-8 with Ar/H $_2$  plasma for different time (0 h, 1 h, 3

h, and 4 h).



Figure S8. (a) The  $N_2$  adsorption-desorption isotherms and (b) pore size distribution of

ZIF-8@ZnO and ZIF-8;



Figure S9. High-resolution XPS spectrum of N 1s of h-ZIF-8@ZnO hybrids.



**Figure S10**. (a) XPS survey spectrum and high-resolution XPS spectrum of (b) C 1s, (c) O 1s, (d) N 1s, (e) Zn 2p, and (f) Zn LMM of ZIF-8 and ZIF-8@ZnO. We can clearly see that the peaks of O=C-N, C-O, and metal oxides (Zn-O) are strongly enhanced after plasma etching, which suggests the slight oxidation of carbon species and the existence of Zn-O bonding on the surface of the ZIF-8@ZnO after plasma treatment. In addition, the reduction of the N 1s spectrum for ZIF-8@ZnO also indicated that

some ligands were destroyed after plasma. Interestingly, after Ar/H<sub>2</sub> plasma treatment, the Zn 2p and Zn LMM peaks of ZIF-8@ZnO showed a slight broadening and shifting to lower binding energy, which may be attributed to the broken of Zn-N coordination bonds and the coordinatively unsaturated Zn species were easily oxidized to form Zn-O bonds when exposed to air.



**Figure 11**. The EPR results of the ZIF-8@ZnO and ZIF-8.



Figure S12. The CV curves of (a) ZIF-8@ZnO, (b) ZIF-8 cage, and (c) solid ZIF-8 anodes

at a scan rate of 0.1 mV s<sup>-1</sup> in the voltage range of 3.0-0.001 V.



Figure S13. Discharge-charge profiles of hollow ZIF-8 at a current density of 0.2 A g<sup>-1</sup>

in the voltage range of 3.0-0.001 V.



**Figure S14.** Cycling performance of the h-ZIF-8@ZnO anodes synthesized with different plasma treatment time (0h, 1h, 3h, and 4h) at the current density of 0.2 A g<sup>-1</sup>. The h-ZIF-8@ZnO electrode (treated by plasma for 3h) exhibited an initial discharge and charge capacity of 1368.2 and 960.9 mAh g<sup>-1</sup>, respectively, with the capacity retention about 70.2%. After 100 cycles, the h-ZIF-8@ZnO (plasma-3h) electrode achieves a reversible capacity of 759.9 mAh g<sup>-1</sup>, displaying that the good cycling stability. While the initial discharge/charge capacity of h-ZIF-8@ZnO (plasma-4h), h-ZIF-8@ZnO (plasma-1h), and h-ZIF-8 samples are 1490.2/ 796.8, 942.6/ 649.8, and 651.2/ 356.4 mAh g<sup>-1</sup>, with the capacity retention about 53.4%, 68.9%, and 54.7%, after 100 cycles, the capacity remains at 676.5, 554.1, and 404.7 mAh g<sup>-1</sup>, respectively. Given these results, we can deduce that the h-ZIF-8@ZnO electrode which treated by plasma for 3 h could be the optimized anode materials.



**Figure S15**. (a) FESEM image and (b) TEM image of the h-ZIF-8@ZnO electrode after 500 cycles at 1.0 A g<sup>-1</sup>. As indicated by the FESEM and TEM images, the hollow structure of h-ZIF-8@ZnO electrode is reasonably preserved after cycling test.

## **Supplementary Chart and Table**

**Chart S1**. Atomic ratio of ZIF-8 and ZIF-8@ZnO from XPS. It could be found that the atom ratio of Zn to N for ZIF-8@ZnO increased, indicating Zn-N coordination bonds were partially destroyed by plasma, and the high contents of O (25.48 %) in comparison to that of pure ZIF-8, further indicating the increased oxygen of ZIF-8@ZnO after plasma etching.



| Sample    | C 1s    | N 1s    | O 1s    | Zn 2p3 |
|-----------|---------|---------|---------|--------|
| ZIF-8     | 61.52 % | 27.38 % | 2.63 %  | 8.47 % |
| ZIF-8@ZnO | 56.10 % | 12.38 % | 25.48 % | 6.04 % |

Table S1. Elemental composition determined by XPS.

**Table S2**. Impedance parameters derived using equivalent circuit model for ZIF-8, ZIF-8@ZnO, hollow-ZIF-8 and hollow-ZIF-8@ZnO as the anode materials for LIBs beforecycling, respectively.

| Samples     | Rs, Ω | Rct, Ω |
|-------------|-------|--------|
| ZIF-8       | 4.58  | 245    |
| ZIF-8@ZnO   | 3.13  | 209    |
| h-ZIF-8     | 3.68  | 108    |
| h-ZIF-8@ZnO | 2.81  | 91.2   |

 Table S3.
 Summary of electrochemical performances of different ZnO-based

| Sample              | Current<br>density<br>(A g <sup>-1</sup> ) | Initial<br>discharge/charge<br>capacity (mAh g- | Reversible<br>capacity (mAh g <sup>-</sup><br><sup>1</sup> )/Cycles/Current | References |
|---------------------|--|---|---|------------|
|                     |  | 1)  | density (A g <sup>-1</sup> )  |            |
| Hollow ZIF-8@ZnO    | 0.2  | 1368.2/960.9                                    | 637.9/ 500/ 1.0   | This work  |
| hybrids             |  |   |   |            |
| AgC@ZnO-C@Ag-C      | 0.1  | 2396/ 1569                                      | 1250/ 150/ 1.0  | 1          |
| ZnO@ZnO QDs/C core- | 0.5  | 785/ 712  | 699/ 100/ 0.5   | 2          |
| shell NRAs          |  |   |   |            |

electrodes as anodes in Lithium Ion Batteries.

| ZnO-ZnCo <sub>2</sub> O <sub>4</sub>    | 1.0   | 1299/ 987   | 1016/ 250/ 2.0 | 3 |
|---|-------|-------------|----------------|---|
| nanosheet                               |       |             |                |   |
| ZnO/ZnO@C                               | 0.1   | 1442/ 878   | 307/ 500/ 5.0  | 4 |
| ZnO/ZnCo <sub>2</sub> O                 | 0.045 | 1599/ 1071  | 900/ 30/ 0.045 | 5 |
| $ZnO@\alpha$ -Co(OH) <sub>2</sub> Core- | 0.2   | 1425/ 1070  | 1127/ 150/ 0.2 | 6 |
| Shell Hierarchical                      |       |             |                |   |
| Microspheres                            |       |             |                |   |
| ZnO-Cu-C porous                         | 0.2   | 1472/ 876   | 769/ 500/ 0.2  | 7 |
| Porous ZnO nanosheets                   | 0.05  | 1120/ 750   | 400/ 100/ 0.5  | 8 |
| ZnO/ZnCo <sub>2</sub> O <sub>4</sub> /C | 0.5   | 1278.8/ 974 | 669/ 250/ 0.5  | 9 |
| Hybrids                                 |       |             |                |   |

## Supplementary References

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