## **Supporting Information for**

## Metal-organic frameworks templated two dimensional hybrid bimetallic metal oxides with enhanced lithium/sodium storage capability

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## **Figures and Captions**



Increase of Zinc content in samples

**Figure S1** Photograph of Co-MOFs, CoZn(n)-MOFs, and Zn-MOFs nanosheets prepared by designing different Co:Zn molar ratios. The Co:Zn molar ratios of CoZn(n)-MOFs nanosheets are detected by ICP-OES analysis, which are summarized in **Table S1**.

| Sample             | Element  | Content (wt.%)      | Molar ratio (Co:Zn) |
|--------------------|----------|---------------------|---------------------|
| CoZn(2:1)-         | Zn       | 7.21                | 2.308:1.103         |
| MOFs               | Co       | 13.6                |                     |
| CoZn(1:1)-<br>MOFs | Zn<br>Co | $\frac{10.7}{10.1}$ | 1.714:1.637         |
| CoZn(1:2)-         | Zn       | <u>15.0</u>         | 1.179:2.294         |
| MOFs               | Co       | 6.95                |                     |

 Table S1 ICP-OES analysis results of different bimetallic CoZn-MOFs nanosheets.



**Figure S2** (a) PXRD patterns and (b) FT-IR spectrums of Co-MOFs, CoZn(n)-MOFs, and Zn-MOFs nanosheets; TEM images of (b) Co-MOFs, (c) Zn-MOFs, and (d) CoZn(1:1)-MOFs nanosheets.

We can see from **Figure S2b** that all the FT-IR spectrums display the similar shape and show main vibration modes between 400 and 2000 cm<sup>-1</sup>, which also correspond well to our previous study.<sup>1</sup> The results indicate that all our obtained samples possess similar crystalline frameworks. For the typical vibration modes, the peak at 424 cm<sup>-1</sup> is ascribed to Zn-N or Co-N stretching. The peaks around 1142 and 1302 cm<sup>-1</sup> belong to the C-H vibrations, while the peak at 1566 cm<sup>-1</sup> corresponds to C=N vibration.



**Figure S3** SEM images of (a, f) Co-MOFs nanosheets; (b, g) CoZn(2:1)-MOFs nanosheets; (c, h) CoZn(1:1)-MOFs nanosheets; (d, i) CoZn(1:2)-MOFs nanosheets; and (e, j) Zn-MOFs nanosheets.

As shown in **Figure S3**, all the as-obtained MOFs exhibit leaf-like nanosheet morphology with a smooth surface. For Co-MOFs nanosheet, it shows an olive-styled shape (**Figure S3a, f**), while the Zn-MOFs nanosheet exhibits elliptical shape (**Figure S3e, j**). The morphology of CoZn(n)-MOFs (n=2:1, 1:1, 1:2) nanosheets are intermediate to those of Co-MOFs and Zn-MOFs nanosheets, which demonstrate an evolution of morphologies from olive-styled shape to elliptical shape with the Co:Zn molar ratios decrease (the total amount of Co and Zn ions is two molars).



**Figure S4** Elemental mappings of single CoZn(1:1)-MOFs nanosheet. (a) All elements, (b) Co, (c) Zn, (d) C, (e) N, and (f) O; (g) EDX pattern and content analysis of Zn and Co elements.



**Figure S5** Elemental mappings of single Co-MOFs nanosheet. (a) All elements, (b) Co, (c) Zn, (d) C, (e) N, and (f) O; (g) EDX pattern and content analysis of Zn and Co elements.



**Figure S6** Elemental mappings of single Zn-MOFs nanosheet. (a) All elements, (b) Co, (c) Zn, (d) C, (e) N, and (f) O; (g) EDX pattern and content analysis of Zn and Co elements.

| Sample         | Element | Content (wt.%) | Content (at.%) | Molar ratio (Co:Zn) |
|----------------|---------|----------------|----------------|---------------------|
|                | Zn      | 1.3911319      | 1.2554920      | 1.0                 |
| CO-MOFS        | Co      | 98.6088680     | 98.7445079     | $\sim 1.0$          |
| $C_0 Z_n(1,1)$ | Zn      | 53.2570750     | 50.6625378     | 1.1                 |
| MOFs           | Co      | 46.7429249     | 49.3374621     | ~ 1.1               |
| Zn MOEs        | Zn      | 99.4839499     | 99.4277343     | 0.1                 |
|                | Со      | 0.5160500      | 0.5722656      | $\sim 0.1$          |

Table S2 EDX analysis of Co-MOFs, CoZn(1:1)-MOFs, and Zn-MOFs nanosheets.

EDX analysis results are summarized in **Table S2**. The molar ratios of Zn<sup>2+</sup>/Co<sup>2+</sup> for Co-MOFs, CoZn(1:1)-MOFs, and Zn-MOFs nanosheets are about 1:0, 1:1, and 0:1, respectively, which is consistent with ICP-OES result. The elemental mapping and EDX analysis demonstrate the absence of Zn element for Co-MOFs nanosheet (**Figure S5**) and Co element for Zn-MOFs nanosheet (**Figure S6**), corresponding to the initial experimental design. The copper element detected in **Figure S4g**, **S5g and S6g** is derived from the lacey support film.



**Figure S7** TG curves of as-synthesized Co-MOFs, CoZn(2:1)-MOFs, CoZn(1:1)-MOFs, CoZn(1:2)-MOFs and Zn-MOFs nanosheets recorded under flowing air with a heating rate of 10 °C/min.



**Figure S8** PXRD patterns of CoZn-O2 obtained at 400 °C and 700 °C kept for 2 minutes with a heating rate of 10 °C/min.

To determine the thermal decomposition temperature of the as-synthesized MOFs nanosheets, the thermogravimetry (TG) measurements were conducted (Figure S7). Taking CoZn(1:1)-MOFs nanosheets as an example, the mass loss of 2.25% before 213 °C was due to the removal of absorbed water molecules. In the second step of TG curves between 213 °C and 335 °C, the mass loss of 16.25% may be ascribed to the removal of the unreacted and the weakly linked ligand (2-methylimidazole) and the CoZn(1:1)-MOFs became to decompose.<sup>2</sup> After then, it became to oxidize to  $Co_3O_4/ZnO$  and a further significant weight loss of 50.39% at 585 °C indicated that CoZn(1:1)-MOFs was totally transferred into Co<sub>3</sub>O<sub>4</sub>/ZnO. To further confirm this process, the PXRD patterns of CoZn-O2 obtained at 400 °C and 700 °C kept for 2 minutes with a heating rate of 10 °C/min were conducted (Figure **S8**). We can see that the two patterns can be well indexed to cubic  $Co_3O_4$  phase [JCPDS Card No. 74-2120] and hexagonal ZnO phase [JCPDS Card No. 89-1397], demonstrating Co<sub>3</sub>O<sub>4</sub>/ZnO appeared in the beginning of the third step of TG curves. However, in this work, the heating rate was 0.5 °C/min and kept at 400 °C for 30 min. There was enough time to decompose the ligands in MOFs nanosheets, which could be confirmed by the XPS spectra of Co<sub>3</sub>O<sub>4</sub>, CoZn-O1, CoZn-O2, CoZn-O3 and ZnO nanosheets obtained at 400 °C with a heating rate of 0.5 °C/min (Figure 3c). These spectra showed absent BE peak of nitrogen element (~400 eV), which is an imperative composed element of 2methylimidazole.



Figure S9 Rietveld refined XRD patterns of (a) CoZn-O1, (b) CoZn-O2, and (c) CoZn-O3.

| Table 53 XRD refinement parameters of CoZn-O1, CoZn-O2, and CoZn-O3. |                                |                                                                                                    |                         |                |         |
|----------------------------------------------------------------------|--------------------------------|----------------------------------------------------------------------------------------------------|-------------------------|----------------|---------|
| Sample                                                               | Phase                          | Lattice parameters                                                                                 | Unit-cell volume        | Content (wt.%) | R       |
| CoZn-O1                                                              | Co <sub>3</sub> O <sub>4</sub> | a=b=c=8.09547 Å,<br>$\alpha=\beta=\gamma=90^{\circ}$                                               | 530.5 (Å <sup>3</sup> ) | 79.8           | 0.46%   |
|                                                                      | ZnO                            | a=b=3.25213 Å, $c=5.19913$ Å,<br>$\alpha=\beta=90^{\circ}, \gamma=120^{\circ}$                     | 47.6 (Å <sup>3</sup> )  | 20.2           | 9.40%   |
| CoZn-O2                                                              | Co <sub>3</sub> O <sub>4</sub> | a=b=c=8.08784 Å,<br>$\alpha=\beta=\gamma=90^{\circ}$                                               | 529.1 (Å <sup>3</sup> ) | 60.6           | 11 02%  |
|                                                                      | ZnO                            | <i>a</i> = <i>b</i> = 3.25080 Å, <i>c</i> = 5.19995 Å,<br><i>α</i> = <i>β</i> =90°, <i>γ</i> =120° | 47.6 (Å <sup>3</sup> )  | 39.4           | 11.0270 |
| CoZn-O3                                                              | Co <sub>3</sub> O <sub>4</sub> | a=b=c=8.10905 Å,<br>$\alpha=\beta=\gamma=90^{\circ}$                                               | 533.2 (Å <sup>3</sup> ) | 39.2           | 10 210/ |
|                                                                      | ZnO                            | a=b=3.25173 Å, $c=5.20315$ Å,<br>$\alpha=\beta=90^{\circ}, \gamma=120^{\circ}$                     | 47.6 (Å <sup>3</sup> )  | 60.8           | 10.2170 |



Figure S10 SEM images of (a, d)  $Co_3O_4$  nanosheets; (b, e) ZnO nanosheets; (c, f)  $Co_3O_4$ /ZnO hybrid (CoZn-O2) nanosheets.



**Figure S11** (a, d) Low-magnification TEM images, (b, e) high-magnification TEM images, and (c, f) HRTEM images of (a-c) Co<sub>3</sub>O<sub>4</sub> and (d-f) ZnO nanosheets.



**Figure S12** EDX pattern of CoZn-O2 nanosheet. The detected carbon and copper elements are derived from the lacey support film.

Table S4 Surface areas, Pore volume analysis of Co<sub>3</sub>O<sub>4</sub>, Co<sub>3</sub>O<sub>4</sub>/ZnO and ZnO nanosheets

| Samples                             | $S_{BET}$ (m <sup>2</sup> /g) | S <sub>Langmuir</sub> (m <sup>2</sup> /g) | V <sub>pore</sub> (cm <sup>3</sup> /g) | R <sub>pore</sub> (nm) |
|-------------------------------------|-------------------------------|-------------------------------------------|----------------------------------------|------------------------|
| C0 <sub>3</sub> O <sub>4</sub>      | 7.2                           | 8.5                                       | 0.097                                  | 26.9                   |
| Co <sub>3</sub> O <sub>4</sub> /ZnO | 38.6                          | 41.1                                      | 0.417                                  | 21.6                   |
| ZnO                                 | 73.5                          | 80.6                                      | 0.607                                  | 16.5                   |

| Samples                        | Co (yes/no) | Zn (yes/no) | Value of O2/O1 | Value of Co <sup>2+</sup> /Co <sup>3+</sup> |
|--------------------------------|-------------|-------------|----------------|---------------------------------------------|
| Co <sub>3</sub> O <sub>4</sub> | yes         | no          | 0.35           | 0.60                                        |
| CoZn-O1                        | yes         | yes         | 1.06           | 1.06                                        |
| CoZn-O2                        | yes         | yes         | 3.61           | 1.55                                        |
| CoZn-O3                        | yes         | yes         | 2.19           | 1.14                                        |
| ZnO                            | no          | yes         | 0.27           | /                                           |

Table S5 Element content analysis of Co<sub>3</sub>O<sub>4</sub>, ZnO, and their hybrids.



**Figure S13** Photoluminescence (PL) spectra for Co<sub>3</sub>O<sub>4</sub>, CoZn-O1, CoZn-O2, CoZn-O3, and ZnO samples.

As shown in **Figure S13**, the PL emission peak at ~400 nm corresponds to the recombination of holes with two-electron-trapped O-vacancy, and the more intensive the peak is, the more oxygen vacancies the sample possesses.<sup>3</sup> The CoZn-O2 nanosheets showed the highest luminescence intensity, indicating more oxygen vacancies in the CoZn-O2 nanosheets.



Figure S14 The *ex-situ* XRD patterns of CoZn-O2 electrode at different discharge/charge states.



**Figure S15** The initial, second and fifth discharge/charge profiles at 100 mA  $g^{-1}$  of (a) Co<sub>3</sub>O<sub>4</sub>, (b) CoZn-O1, (c) CoZn-O2, (d) CoZn-O3, and (e) ZnO; Cycling performaces at (f) 200 mA  $g^{-1}$  and (g) 1000 mA  $g^{-1}$  of Co<sub>3</sub>O<sub>4</sub>, CoZn-O1, CoZn-O2 and CoZn-O3.



**Figure S16** Nyquist plots of (a)  $Co_3O_4$ , CoZn-O1, CoZn-O2, CoZn-O3 and ZnO electrodes. Inset: corresponding equivalent electrical circuit; (b) CoZn-O2 electrodes after 1<sup>st</sup> cycle, 5<sup>th</sup> cycle, and 10<sup>th</sup> cycle at 200 mA g<sup>-1</sup>.

| Samples                        | $R_{s}(\Omega)$ | $\boldsymbol{R}_{ct}\left(\Omega ight)$ |
|--------------------------------|-----------------|-----------------------------------------|
| C0 <sub>3</sub> O <sub>4</sub> | 1.45            | 201.22                                  |
| CoZn-O1                        | 1.77            | 151.06                                  |
| CoZn-O2                        | 1.83            | 138.90                                  |
| CoZn-O3                        | 1.74            | 161.38                                  |
| ZnO                            | 1.87            | 466.05                                  |
| CoZn-O2 1 <sup>st</sup> cycle  | 1.35            | 105.36                                  |
| CoZn-O2 5 <sup>th</sup> cycle  | 1.02            | 89.59                                   |
| CoZn-O2 10 <sup>th</sup> cycle | 1.09            | 92.14                                   |

 Table S6 The corresponding EIS simulation parameters.

The electrochemical impedance spectra (EIS) were measured to further confirm the advantage of the CoZn-O2 electrode. **Figure S16a** shows the Nyquist plots which consist of a semicircle in high frequency region and a sloping line in low frequency region. The inset of **Figure S16a** is the corresponding equivalent electrical circuit.  $R_s$  stands for the combination of electrolyte resistance and ohmic resistances of cell components.  $R_{ct}$  is mainly due to charge-transfer resistance. The  $R_{ct}$  of CoZn-O2 was simulated to be 138.90  $\Omega$ , which is much small than other counterparts, as listed in **Table S6**. Furthermore, the  $R_{ct}$  of CoZn-O2 decreases after cycling, as shown in **Figure S16b** (105.36  $\Omega$  after 1<sup>st</sup> cycle, 89.59  $\Omega$  after 5<sup>th</sup> cycle, and 92.14  $\Omega$  after 10<sup>th</sup> cycle). The decrease of charge-transfer resistance has been proven to be an important factor for good rate performance and long-term cyclic stability.<sup>4, 5</sup> The results demonstrated the enhanced kinetics of electronic transportation for CoZn-O2 electrode, which resulted in the excellent electrochemical performance for LIBs.



**Figure S17** The cycled SEM images of CoZn-O2 electrodes after (a) 1<sup>st</sup> cycle, (b) 5<sup>th</sup> cycle, and (c) 10<sup>th</sup> cycle at 200 mA g<sup>-1</sup>.

In order to explore the change of morphology after cycling, which plays an important role for cyclic stability, we have conducted the SEM images of CoZn-O2 electrode after different cycles of 1<sup>st</sup> cycle, 5<sup>th</sup> cycle, and 10<sup>th</sup> cycle at 200 mA g<sup>-1</sup>, as shown in **Fig. S17**. Although there were some fragments, the nanosheets structure was well-maintained after cycling, which to a large extent contributes to the long-term cyclic stability of CoZn-O2 electrode. The surfaces of nanosheets are rough, which is mainly due to the binder, conductive carbon black and the formation of solid electrolyte interphase (SEI).

| Electrode<br>materials                                                              | High rate capability<br>/mA h g <sup>-1</sup>                                                      | Capacity retention based on the second cycle (cycle number)                                       | Ref.        |
|-------------------------------------------------------------------------------------|----------------------------------------------------------------------------------------------------|---------------------------------------------------------------------------------------------------|-------------|
| CoZn-O2                                                                             | 716 (1000 mA g <sup>-1</sup> )<br>625 (2000 mA g <sup>-1</sup> )<br>404 (4000 mA g <sup>-1</sup> ) | No fading at 200 mA g <sup>-1</sup> (50 cycles)<br>95.6% at 3000 mA g <sup>-1</sup> (1000 cycles) | Our<br>work |
| Co <sub>3</sub> O <sub>4</sub> @MnO <sub>2</sub>                                    | 675 (480 mA g <sup>-1</sup> )<br>388 (960 mA g <sup>-1</sup> )                                     | 73.2% at 120 mA g <sup>-1</sup> (100 cycles)                                                      | 6           |
| CuO@NiO<br>hollow spheres                                                           |                                                                                                    | No fading at 100 mA g <sup>-1</sup> (200 cycles)                                                  | 7           |
| ZnO/ZnCo <sub>2</sub> O <sub>4</sub><br>submicron rod                               | 700 (445 mA g <sup>-1</sup> )                                                                      | ~84% at 45 mA g <sup>-1</sup> (30 cycles)                                                         | 8           |
| NiO-ZnO hybrid                                                                      | 707 (3200 mA g <sup>-1</sup> )                                                                     | 91.47% at 200 mA g <sup>-1</sup> (120 cycles)                                                     | 9           |
| SnO <sub>2</sub> @Fe <sub>2</sub> O <sub>3</sub>                                    | Inferior rate capability                                                                           | Poor cycling performance                                                                          | 10          |
| ZnO/ZnCo <sub>2</sub> O <sub>4</sub><br>nanosheets                                  | 630 (10000 mA g <sup>-1</sup> )                                                                    | 87% at 2000 mA g <sup>-1</sup> (250 cycles)                                                       | 11          |
| ZnO-NiO-Co <sub>3</sub> O <sub>4</sub><br>hybrid                                    | 667 (2000 mA g <sup>-1</sup> )                                                                     | No fading at 500 mA g <sup>-1</sup> (300 cycles)                                                  | 12          |
| 3CoO/CoFe <sub>2</sub> O <sub>4</sub><br>nanocomposites                             | ~400 (6400 mA g <sup>-1</sup> )                                                                    | 54.8% at 1000 mA g <sup>-1</sup> (100 cycles)                                                     | 13          |
| Co <sub>3</sub> O <sub>4</sub> /TiO <sub>2</sub><br>composite                       | ~400 (1000 mA g <sup>-1</sup> )                                                                    | ~83% at 100 mA g <sup>-1</sup> (120 cycles)                                                       | 14          |
| ZnO/ZnCo <sub>2</sub> O <sub>4</sub> /C<br>hybrids                                  | 715 (1600 mA g <sup>-1</sup> )                                                                     | 68.7% at 500 mA g <sup>-1</sup> (250 cycles)                                                      | 15          |
| Fe <sub>2</sub> O <sub>3</sub> /Co <sub>3</sub> O <sub>4</sub><br>hollow microcubes | 272 (800 mA g <sup>-1</sup> )                                                                      | ~40% at 100 mA g <sup>-1</sup> (50 cycles)                                                        | 16          |
| ZnO-NiO hybrid<br>microspheres                                                      | 432 (1000 mA g <sup>-1</sup> )                                                                     | No fading at 100 mA g <sup>-1</sup> (200 cycles)                                                  | 17          |
| Co <sub>3</sub> O <sub>4</sub> /CuO<br>composite                                    | 500 (2500 mA g <sup>-1</sup> )                                                                     | 97% at 100 mA g <sup>-1</sup> (150 cycles)<br>~70% at 1000 mA g <sup>-1</sup> (400 cycles)        | 18          |

 Table S7 The comparison of electrochemical performances of bimetallic hybrids for LIBs anode.

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