SUPPORTING INFORMATION

MOF-templated syntheses of porous Co₃O₄ hollow-spheres and micro-flowers for enhanced performance in supercapacitors**

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S1. Materials and Methods

1.1. Materials and Instruments.

Reactions were carried out in 35 ml pressure-resistant tubes under autogenous pressure. All the reactants are of reagent-grade quality and used as commercially purchased without further purification.

The power X-ray diffraction patterns (PXRD) were collected by a Bruker D8 Advance using Cu Kα radiation (\(\lambda = 0.154 \text{ nm}\)).

Single gas adsorption measurements were performed in the Accelerated Surface Area and Porosimetry 2020 (ASAP2020, where the bulk Co-BTB-I/II-450 materials were determined in a clean ultra high vacuum system and the N\(_2\) sorption measurement was performed at 77 K.

Thermogravimetric analyses were recorded on a NETZSCH STA 449C unit at a heating rate of 10 °C· min\(^{-1}\) under flowing nitrogen atmosphere.

Field-emission scanning electron microscopy (FE-SEM) images were obtained on a Nova NanoSEM200 scanning electron microscope.

For transmission electron microscopy (TEM), high-resolution transmission electron microscopy (HRTEM), energy dispersive spectroscopy (EDS), high-angle annular dark-field (HAADF), and scanning transmission electron microscopy EDS (STEM-EDS) characterizations, the purified colloid was deposited on copper grids with thin carbon film, which was then dried for 20 min under an infrared lamp. After water was removed completely, the dried sample was observed with a 200 kV JEOL 2100F with an attached EDS and STEM detector.

X-ray photoelectron spectroscopy (XPS) measurements were carried out with a Thermo ESCALAB 250 X-ray photoelectron spectrometer with an excitation source of Al Kα radiation (\(\lambda = 1253.6 \text{ eV}\)). The binding energies were referenced to the C 1s line at 284.6 eV from adventitious carbon.
1.2. Synthesis of hollow spherical Co-BTB-I.

A mixture of Co(NO$_3$)$_3$·6H$_2$O (0.10 mmol, 29.1 mg) and H$_3$BTB (0.025 mmol, 11 mg, H$_3$BTB = 1,3,5-tris(4-carboxyphenyl)benzene) in N-methylformamide (NMF) (5 mL) with the surfactant CTAB (0.08 mmol, 30.0 mg, CATB = hexadecyl trimethyl ammonium bromide) as well as an additional 0.05 ml HNO$_3$ (65 wt %) was placed in a 35 mL pressure-resistant tube, which was inserted into a preheated module holding at 140 °C for 45 min, and then gradually cooled to room-temperature. After being centrifugated and washed by fresh ethanol for 3 times, the light pink products of CATB-assisted hollow Co-BTB-I micro-spheres were obtained in ca. 35% yield based on the organic ligand. The crystalline nature of the sample was confirmed by the powder X-ray diffraction (Figure S2).

1.3. Synthesis of flower-like Co-BTB-II.

Very similarly to the synthesis of Co-BTB-I, a mixture of Co(NO$_3$)$_3$·6H$_2$O (0.17 mmol, 50 mg) and H$_3$BTB (0.025 mmol, 11 mg) in N-dimethylformamide (NMF) (5 mL, without the surfactant CTAB), but still with an additional 0.05 ml HNO$_3$ (65 wt %) was placed in a 35 mL pressure-resistant tube, which was inserted into a preheated module holding at 140 °C for 45 min, and then gradually cooled to room-temperature. After being centrifugated and washed by fresh ethanol, the light pink products of Co-BTB-II micro-flowers were obtained in ca. 42% yield based on the organic ligand. The crystalline nature of the sample was confirmed by the powder X-ray diffraction (Figure S2).


Finally, we learn both MOF-based materials retain their crystalline structure before and after desolvation. And spherical Co$_3$O$_4$-based micro-particles (Co-BTB-I-450) were then synthesized by the direct pyrolysis of Co-BTB-I samples at 450 °C in the air in a conventional CVD furnace. During the calcination process, MOF precursors were gradually decomposed to hollow Co$_3$O$_4$ particles. Same procedure can be found in the synthesis of Co-BTB-II-450, and the compositional phases of
these two kinds of micro-particles have been confirmed by PXRD test (Figure 3, in the main article)

1.4. Electrochemical method.

The electrochemical measurements were carried out in a three-electrode electrochemical cell containing 3.0 M KOH aqueous solution as the electrolyte. Our Co-BTB-I-450 and Co-BTB-II-450 samples are uniformly painted onto the surface of pre-treated Ni foam to constitute the Co-BTB-I/II-450 foam, which were directly used as working electrodes. The area of the working electrodes immersed into the electrolyte was controlled to be ~1 cm². The electrochemical measurements were conducted with a CHI760E electrochemical workstation. A saturated Hg/HgO electrode was used as the reference electrode and a platinum wire as the counter electrode, and all the experiments were done at ambient temperature. EIS measurements were performed by applying an AC voltage with 5 mV amplitude in a frequency range from 0.01 Hz to 100 kHz. The mass loading of the active materials on Ni foam were 2~4 mg cm⁻²
**S2. TGA Data**

*Figure S1.* TGA curves for these two as-prepared spherical **Co-BTB-I** and flower-like **Co-BTB-II** samples.

The thermogravimetric analysis (TGA) curve of the as-obtained **Co-BTB-I** as well as **Co-BTB-II** samples are conducted in the temperature range of 30-800 °C under a flow of nitrogen with the heating rate of 10 °C min⁻¹, and they exhibit the first weight loss of 7.5 and 15.1 wt % at the temperature of 100 °C and show another weight loss of ~13.1 and ~3.2 wt% between 100 °C and 200 °C, corresponding to the loss of H₂O molecules and guest N-methylformamide molecule. After 450 °C, we also learn that the main structure starts to collapse gradually, in which both Co-BTB frameworks begin the breakdown of Co-COO bonds and decomposition of BTB linkers, thus leading to the formation of our targeted Co₃O₄.
S3. PXRD Patterns

Figure S2. PXRD patterns of spherical Co-BTB-I and flower-like Co-BTB-II, where two strong peaks centered at 6.0 and 10.4 can be observed which indicate highly ordered and crystalline structures with several other weak peaks.

In order to find the matched structure from the powder X-ray diffraction (PXRD) measurement, we learnt that hollow-Co-BTB (Co-BTB-I) and flower-like-Co-BTB (Co-BTB-II) micro-particles are crystalline materials (Figure S2a). On the other hand, a similar XRD pattern derived from a Co-BTB MOF structure (from any of the numerous MOF libraries in CCDC database, which is constructed from Co(II) and H₃BTB, CCDC No.: 890977) could be observed as above, while the VESTA structures of the Co-BTB-I as well as Co-BTB-II microparticles viewed from a, b, c-axes are presented in the right column.
Figure S3. (a) The experimental N\textsubscript{2} adsorption/desorption isotherms at 77 K for the desolvated spherical Co-BTB-I and flower-like Co-BTB-II samples, both exhibiting the type-I isotherms (typical characteristics of microporous materials); (b) The pore size distribution of these two materials.
Summary (Co-BTB-I)

BET Surface Area: $765.5022 \pm 1.3102 \text{ m}^2/\text{g}$

Slope: $0.127442 \pm 0.000218 \text{ g/mmol}$

Y-Intercept: $0.000021 \pm 0.000003 \text{ g/mmol}$

C: $6127.834066$

Qm: $7.84543 \text{ mmol/g}$

Correlation Coefficient: $0.9999429$

Molecular Cross-Sectional Area: $0.1620 \text{ nm}^2$
Summary (Co-BTB-I)

Langmuir Surface Area: 869.8358 ± 1.5418 m²/g
Slope: 0.11217 ± 0.00020 g/mmol
Y-Intercept: 0.050 ± 0.011 kPa·g/mmol
b: 2.22490 1/kPa
Qm: 8.91471 mmol/g
Correlation Coefficient: 0.999912
Molecular Cross-Sectional Area: 0.1620 nm²
Summary (Co-BTB-II)

BET Surface Area: \(457.2234 \pm 0.7975 \text{ m}^2/\text{g}\)

Slope: \(0.213397 \pm 0.000372 \text{ g/mmol}\)

Y-Intercept: \(0.000006 \pm 0.000003 \text{ g/mmol}\)

C: \(33806.297386\)

Qm: \(4.68596 \text{ mmol/g}\)

Correlation Coefficient: \(0.9999817\)

Molecular Cross-Sectional Area: \(0.1620 \text{ nm}^2\)
Summary (Co-BTB-II)

Langmuir Surface Area: $515.6475 \pm 0.6350 \text{ m}^2/\text{g}$

Slope: $0.18922 \pm 0.00023 \text{ g/mmol}$

Y-Intercept: $0.079 \pm 0.012 \text{ kPa} \cdot \text{g/mmol}$

$b$: $2.39804 \text{ 1/kPa}$

$Q_m$: $5.28473 \text{ mmol/g}$

Correlation Coefficient: $0.999955$

Molecular Cross-Sectional Area: $0.1620 \text{ nm}^2$
Figure S4. (a) The experimental N$_2$ adsorption/desorption isotherms at 77 K for the desolvated Co-BTB-I-450 micro-spheres and Co-BTB-II-450 micro-flowers, where Co-BTB-I-450 exhibits the type-IV isotherm with hysteresis loop (typical characteristics of mesoporous materials), while Co-BTB-II-450 shows the type-III isotherm implying only surface-based adsorption in relatively high pressure zone; (b) Pore size distribution of the desolvated Co-BTB-I-450 micro-spheres.
Summary (Co-BTB-I-450)

BET Surface Area: $78.6139 \pm 0.3196 \text{ m}^2/\text{g}$

Slope: $0.054937 \pm 0.000223 \text{ g/cm}^3 \text{ STP}$

Y-Intercept: $0.000438 \pm 0.000033 \text{ g/cm}^3 \text{ STP}$

C: $126.456554$

Qm: $18.0589 \text{ cm}^3/\text{g STP}$

Correlation Coefficient: 0.9999342

Molecular Cross-Sectional Area: $0.1620 \text{ nm}^2$
Summary (Co-BTB-II-450)

BET Surface Area: 8.3141 ± 0.0886 m²/g

Slope: 0.507433 ± 0.005493 g/cm³ STP

Y-Intercept: 0.016159 ± 0.000961 g/cm³ STP

C: 32.402046

Qm: 1.9099 cm³/g STP

Correlation Coefficient: 0.9995315

Molecular Cross-Sectional Area: 0.1620 nm²
S5. Additional images for Co-BTB-I/Co-BTB-II Microparticles

Figure S5. SEM and TEM images of the as-prepared Co-BTB-I microspheres.
Figure S6. SEM and TEM images of the as-prepared Co-BTB-II microflowers.
Figure S7. (a) EDX curve of Co-BTB-I; (b) Height profiles of single Co-BTB-I particle for C N O Co elements; (c) HAADF-STEM images and mapping of Co-BTB-I precursors.
Figure S8. (a) EDX curve of Co-BTB-II; (b) Height profiles of single Co-BTB-II particle for C N O Co elements; (c) HAADF-STEM images and mapping of Co-BTB-II precursors.
S6. Electrochemical Measurements

Two main redox reactions involved in our system could be listed as below:

\[
\begin{align*}
\text{Co}_3\text{O}_4 + \text{OH}^- + \text{H}_2\text{O} &\rightarrow 3\text{CoOOH} + e^- \\
\text{CoOOH} + \text{OH}^- &\rightarrow \text{Co}_2 + \text{H}_2\text{O} + e^-
\end{align*}
\]

Figure S9. The 3-electrode system we used in our lab.
Figure S10. Cyclic voltammograms of Co-BTB-II-450 at different scan rates of 2-100 mV/s;

For Figure S9 above and for Figure 4a in the manuscript, we simultaneously learn that the cathodic potential becomes more negative and the anodic one tends to be more positive in CV curves.
Table 1. The specific capacitance of other reported $\text{Co}_3\text{O}_4$ electrode materials:

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Substrate</th>
<th>Electrolyte</th>
<th>Current density</th>
<th>Special capacitance</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZnO@Co$_3$O$_4$</td>
<td>Ni foam</td>
<td>2 M KOH</td>
<td>1 A g$^{-1}$</td>
<td>857.7 F g$^{-1}$</td>
<td>1</td>
</tr>
<tr>
<td>atomic layer Co$_3$O$_4$ nanofilm</td>
<td>Ni foam</td>
<td>2 M KOH</td>
<td>1 A g$^{-1}$</td>
<td>1400 F g$^{-1}$</td>
<td>2</td>
</tr>
<tr>
<td>Co$_3$O$_4$/VAGN/CF</td>
<td>carbon fabric</td>
<td>2 M KOH</td>
<td>1 A g$^{-1}$</td>
<td>3480 F g$^{-1}$</td>
<td>3</td>
</tr>
<tr>
<td>NPC Co$_3$O$_4$</td>
<td>GCE</td>
<td>0.1 M KOH</td>
<td>2.5 A g$^{-1}$</td>
<td>885 F g$^{-1}$</td>
<td>4</td>
</tr>
<tr>
<td>Co$_3$O$_4$/GF film</td>
<td>Ni foam</td>
<td>2 M KOH</td>
<td>2 A g$^{-1}$</td>
<td>652 F g$^{-1}$</td>
<td>5</td>
</tr>
<tr>
<td>Co$_3$O$_4$/C NAs</td>
<td>Ni foam</td>
<td>3 M KOH</td>
<td>1 mA cm$^{-2}$</td>
<td>776.5 F g$^{-1}$</td>
<td>6</td>
</tr>
<tr>
<td>CWs-Co$_3$O$_4$</td>
<td>stainless-steel wire mesh</td>
<td>6 M KOH</td>
<td>0.5 A g$^{-1}$</td>
<td>978.9 F g$^{-1}$</td>
<td>7</td>
</tr>
<tr>
<td>Co$_3$O$_4$/CNN</td>
<td>GCE</td>
<td>0.1 M KOH</td>
<td>20 mV s$^{-1}$</td>
<td>90.8 F g$^{-1}$</td>
<td>8</td>
</tr>
<tr>
<td>Co$_3$O$_4$/rGO/NF</td>
<td>Ni foam</td>
<td>1 M KOH</td>
<td>1 A g$^{-1}$</td>
<td>1016.4 F g$^{-1}$</td>
<td>9</td>
</tr>
</tbody>
</table>