Supplementary Information

Ni@onion-like carbon and Co@amorphous carbon: Control of carbon structures by metal ion species in MOFs

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Experimental section
Reagents. 2,5-Dihydroxyterephthalic acid (H<sub>4</sub>dhtp) was purchased from Tokyo Chemical Industry Co., Ltd. All other chemicals were purchased from Wako Pure Chemical Industries. Products were used as received.

Synthesis of Ni-MOF-74. Ni<sub>2</sub>(dhtp) (Ni-MOF-74, CPO-27-Ni) was synthesized following a slight modification to an established procedure. To a solid mixture of H<sub>4</sub>dhtp (4.79 g, 24.2 mmol) and Ni(NO<sub>3</sub>)<sub>2</sub>・6H<sub>2</sub>O (23.8 g, 81.8 mmol) was added a 1:1:1 (v/v/v) mixture of N,N-dimethylformamide (DMF)–ethanol–water (2 L) in a 3 L eggplant flask. The suspension was mixed until homogeneous and then heated to 100 °C. After 5 days, the sample was cooled to RT. A yellow material was isolated and washed with methanol (1 L). The washing was repeated four times over 2 days. The material was then washed twice with deionized water (1 L). The solvent was removed under vacuum at RT over 1 day.

Synthesis of Co-MOF-74. Co<sub>2</sub>(dhtp) (Co-MOF-74, CPO-27-Co) was also synthesized following a slight modification to an established procedure. To a solid mixture of H<sub>4</sub>dhtp (2.41 g, 12.2 mmol) and Co(NO<sub>3</sub>)<sub>2</sub>・6H<sub>2</sub>O (11.9 g, 40.9 mmol) was added a 1:1:1 (v/v/v) mixture of DMF–ethanol–water (2 L) in a 3 L eggplant flask. The suspension was mixed until homogeneous and then heated to 100 °C. After 24 h, the sample was cooled to RT. An orange material was isolated and washed with methanol (500 mL). The washing was repeated four times over 15 h. The material was then washed twice with deionized water (1 L). The solvent was removed under vacuum at RT over 1 day.

Heat treatment of MOF-74. Ni@onion-like carbon and Co@amorphous carbon were synthesized using thermal decomposition. Synthesized each Ni-MOF-74 and Co-MOF-74 was heated under vacuum. BEL-prep was used for heat treatment.

Thermogravimetric analysis (TGA). TGA of Ni-MOF-74 and Co-MOF-74 was performed using a NETZSCH Japan TG-DTA 2,000SA instrument applying a heating rate of 5 K per minute under a constant flow of N<sub>2</sub>.

Powder X-ray diffraction (PXRD) measurements. PXRD patterns were measured using beamline BL02B2 of SPring-8 (λ = 0.998, 1.000, 0.580 Å).

TEM/STEM observation. Transmission electron microscopy (TEM) images were obtained using a HITACHI HT7700, at an accelerating voltage of 100 kV. High-resolution scanning transmission electron microscope (HR-STEM) images were obtained using a JEOL JEM-ARM200F at an accelerating voltage of 120 kV.

Raman spectra. Raman spectra were collected using a JASCO NRS-1000, with a microscope, at RT. A Showa Optronics JUNO 532-100S Nd:YAG laser provided the excitation line (532 nm).
**Electrical resistivity measurements.** The electrical resistivity of Ni 400-12h and Co 430-24h was measured using a four-probe method. Samples comprised compressed pellets. Four gold wires (diameter 50 μm) were attached to the pellets, using gold paste.

**Nitrogen sorption.** N₂ adsorption/desorption isotherms were measured using a BELSORP-max at 77 K, up to 1 bar pressure. Prior to commencing the adsorption measurements, each sample was activated by heating under vacuum at 120 °C for 12 h.
TGA measurements: Ni-MOF-74 and Co-MOF-74

Fig. S1 TGA curves of Ni-MOF-74 (green line) and Co-MOF-74 (blue line).
Fig. S2 Results of Le Bail fitting of (a) Ni 400-12h and (b) Co 430-24h. (Radiation wavelength 0.580 Å.)
The STEM tilt-series images

**Fig. S3** HR-STEM images of Ni 400-12h taken at different tilt angles.
TEM images

Fig. S4 TEM images of (a) Ni-MOF-74, (b)(c) Ni 400-12h, (d) Co-MOF-74 and (e)(f) Co 430-24h.

Table S1. Mean diameter of nanoparticles.

<table>
<thead>
<tr>
<th></th>
<th>Mean diameter [nm]</th>
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<tbody>
<tr>
<td>Ni 400-12h</td>
<td>4.5 ± 1.2</td>
</tr>
<tr>
<td>Co 430-24h</td>
<td>3.7 ± 0.7</td>
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</table>
Raman spectra

Fig. S5 Raman spectra with fitting results for (a) Ni 400-12h and (b) Co 430-24h.

Table S2 Properties of the deconvoluted Raman peaks.

<table>
<thead>
<tr>
<th></th>
<th>Pos. D [cm$^{-1}$]</th>
<th>Pos. G [cm$^{-1}$]</th>
<th>$I_D/I_G$</th>
<th>D FWHM [cm$^{-1}$]</th>
<th>G FWHM [cm$^{-1}$]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni 400-12h</td>
<td>1345.2</td>
<td>1587.3</td>
<td>1.94</td>
<td>140.2</td>
<td>91.3</td>
</tr>
<tr>
<td>Co 430-24h</td>
<td>1349.5</td>
<td>1592.5</td>
<td>4.43</td>
<td>344.7</td>
<td>90.6</td>
</tr>
</tbody>
</table>
Nitrogen sorption

**Fig. S6** Nitrogen adsorption isotherms for (a) Ni-MOF-74 and Ni **400-12h** and (b) Co-MOF-74 and Co **430-24h** at 77 K, up to 1 bar. The solid and open symbols represent adsorption and desorption, respectively.

<table>
<thead>
<tr>
<th>Sample</th>
<th>( S_{\text{BET}} ) [m(^2)/g]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni-MOF-74</td>
<td>1262.7</td>
</tr>
<tr>
<td>Co-MOF-74</td>
<td>1190.9</td>
</tr>
<tr>
<td>Ni 400-12h</td>
<td>163.5</td>
</tr>
<tr>
<td>Co 430-24h</td>
<td>263.3</td>
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</tbody>
</table>

**Table S3.** BET specific surface area of samples.