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$_4$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$_2$(dhtp) (Ni-MOF-74, CPO-27-Ni) was synthesized following a slight modification to an established procedure. To a solid mixture of H$_4$dhtp (4.79 g, 24.2 mmol) and Ni(NO$_3$)$_2$ · 6H$_2$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$_2$(dhtp) (Co-MOF-74, CPO-27-Co) was also synthesized following a slight modification to an established procedure. To a solid mixture of H$_4$dhtp (2.41 g, 12.2 mmol) and Co(NO$_3$)$_2$ · 6H$_2$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$_2$.

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. N_2 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.
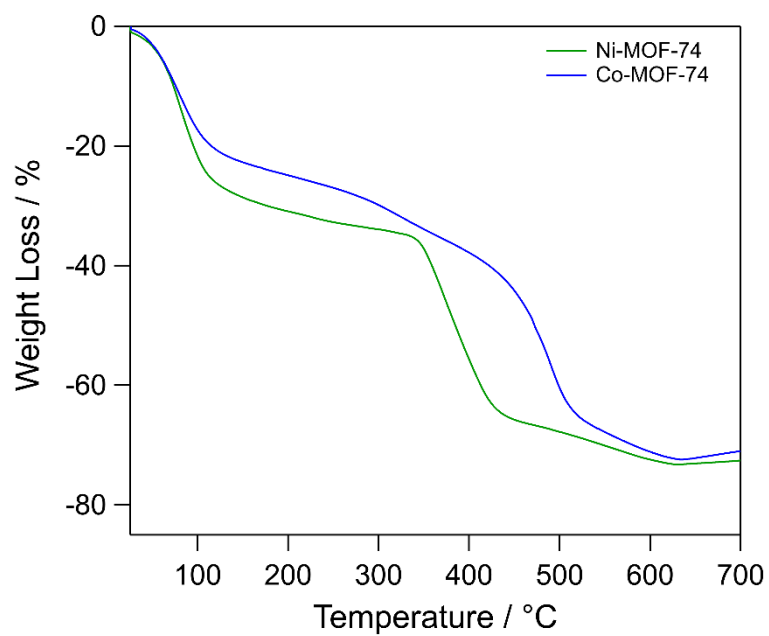
TGA measurements: Ni-MOF-74 and Co-MOF-74

Fig. S1 TGA curves of Ni-MOF-74 (green line) and Co-MOF-74 (blue line).
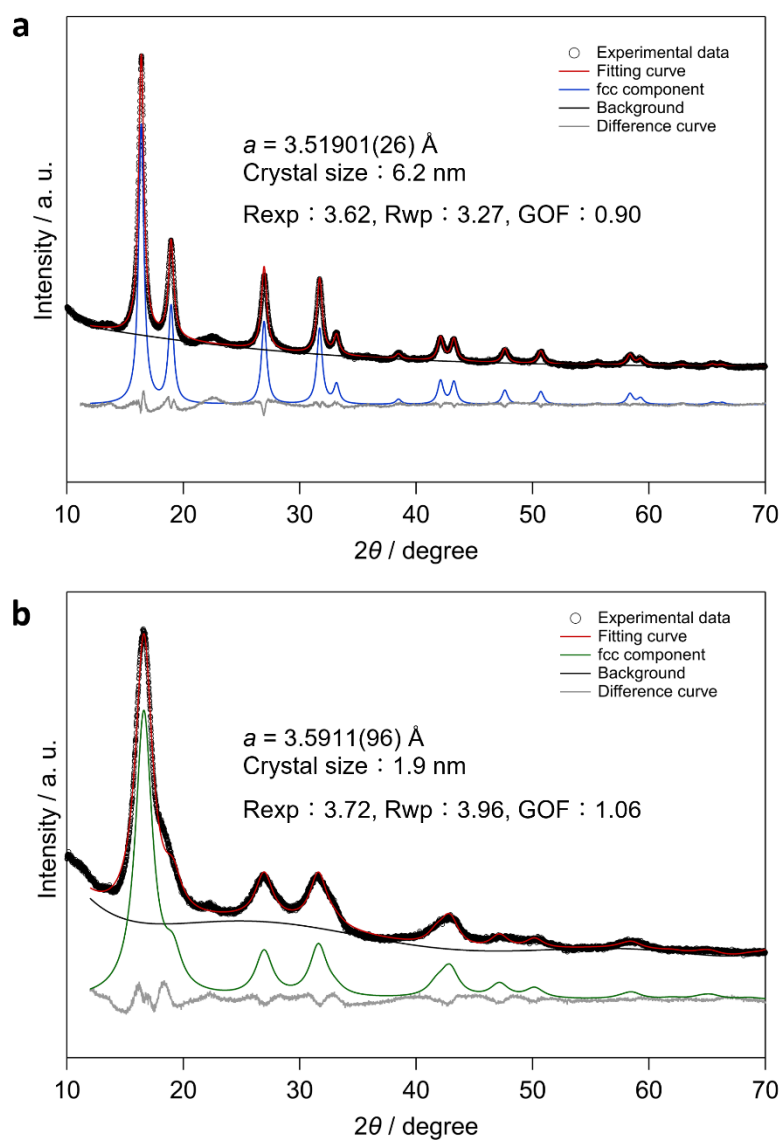
XRD measurements

a

○ Experimental data
— Fitting curve
— fcc component
— Background
— Difference curve

a = 3.51901(26) Å
Crystal size：6.2 nm

Rexp：3.62, Rwp：3.27, GOF：0.90

Intensity / a. u.

2θ / degree

b

○ Experimental data
— Fitting curve
— fcc component
— Background
— Difference curve

a = 3.5911(96) Å
Crystal size：1.9 nm

Rexp：3.72, Rwp：3.96, GOF：1.06

Intensity / a. u.

2θ / degree

Fig. S2 Results of Le Bail fitting of (a) **Ni 400-12h** and (b) **Co 430-24h**. (Radiation wavelength 0.580 Å.)
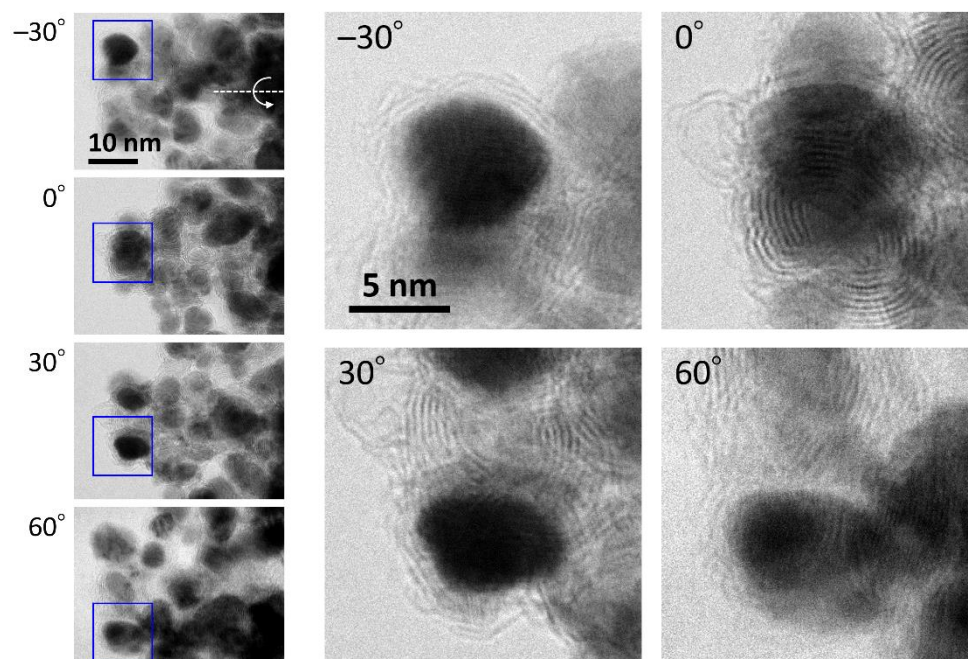
The STEM tilt-series images

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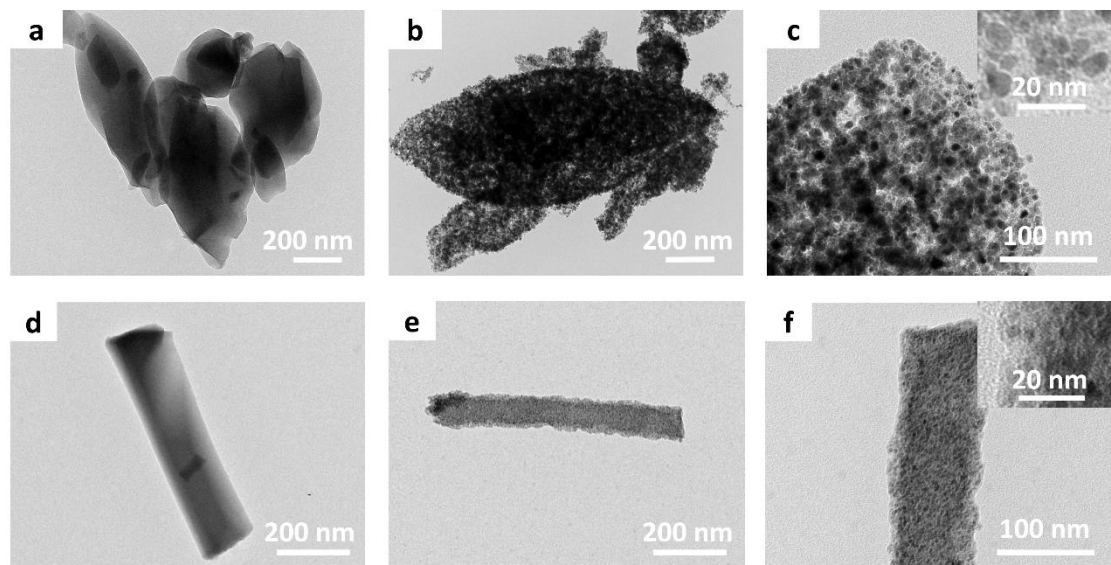
TEM images

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.

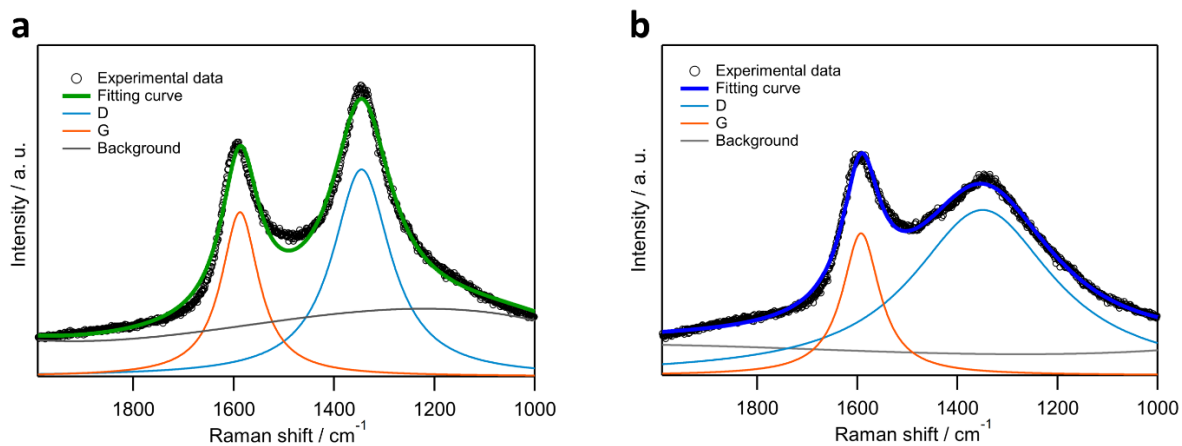|	Mean diameter [nm]
Ni 400-12h	4.5 ± 1.2
Co 430-24h	3.7 ± 0.7

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.

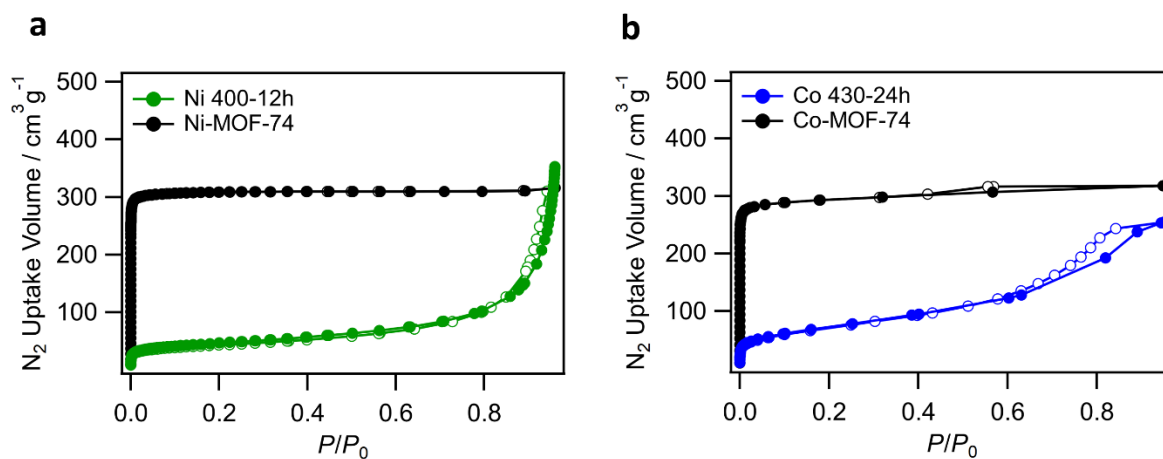|	Pos. D [cm⁻¹]	Pos. G [cm⁻¹]	I_D/I_G	D FWHM [cm⁻¹]	G FWHM [cm⁻¹]
Ni 400-12h	1345.2	1587.3	1.94	140.2	91.3
Co 43024h	1349.5	1592.5	4.43	344.7	90.6

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 S3. BET specific surface area of samples.

	S_{BET} [m^2/g]
Ni-MOF-74	1262.7
Co-MOF-74	1190.9
Ni 400-12h	163.5
Co 430-24h	263.3