

## Electronic Supplementary Information

### **A Novel CoNi-Metal-Organic Framework Crystal Derived CoNi@C: Synthesis and Effective Cascade Catalysis**

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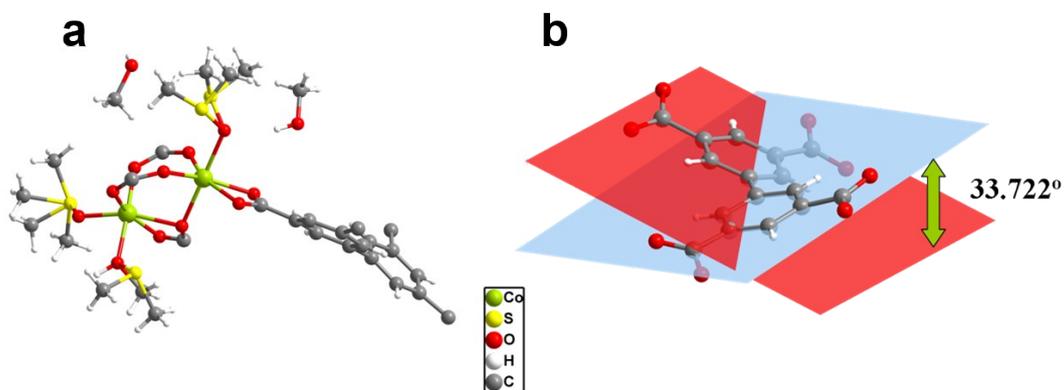
## Characterization

Power X-ray diffraction (PXRD) were carried out on a Rigaku Saturn 70 diffractometer at 113 K with Mo-K $\alpha$  radiation ( $\lambda = 0.71073$  Å). The transmission electron microscopy (TEM) was acquired on JEOL-2010 with an electron acceleration energy of 200 kV. X-ray photoelectron spectroscopy (XPS) measurements were performed by using an ESCALAB 250 high-performance electron spectrometer using monochromatized AlK $\alpha$  ( $h\nu = 1486.7$  eV) as the excitation source. Nitrogen sorption measurement was conducted using a Micromeritics ASAP 2020 system at 77 K. The contents of Co and Ni in samples were analyzed by an Agilent ICP-OES 730 inductively coupled plasma atomic emission spectrometer (ICP-AES). Catalytic reaction products were analyzed and identified by a gas chromatography (GC, Panna A91 Plus) and ultraviolet spectrograph. Thermogravimetric (TG) analysis was carried out on a NETZSCH STA 449F5 integration thermal analyzer from room temperature to 700 °C at a rate of 10 °C min<sup>-1</sup> under N<sub>2</sub> flow.

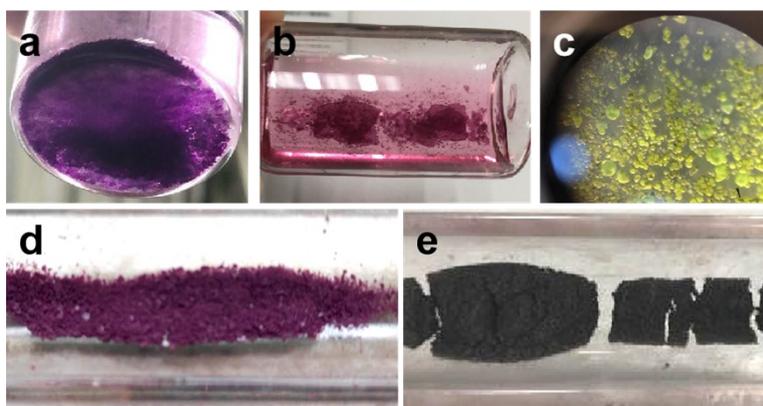
**Table S1** Crystal data and structure refinements for **QDUC-1**.

Compound	QDUC-1
Empirical formula	C <sub>22.5</sub> H <sub>27</sub> Co <sub>2</sub> O <sub>12</sub> S <sub>2.5</sub>
Formula weight	687.45
Temperature (K)	134(3)
Crystal system	orthorhombic
Space group	<i>P</i> 2 <sub>1</sub> 2 <sub>1</sub> 2
<i>a</i> (Å)	17.6173(6)
<i>b</i> (Å)	12.7245(6)
<i>c</i> (Å)	12.3363(4)
$\alpha$ (deg)	90.00
$\beta$ (deg)	90.00
$\gamma$ (deg)	90.00
Volume(Å <sup>3</sup> )	2765.45(18)
<i>Z</i>	4
<i>d</i> <sub>calcd.</sub> (g·cm <sup>-3</sup> )	1.651
<i>F</i> (000)	1408
Reflections collected/unique	18236/4955
<i>R</i> <sub>int</sub>	0.0584
Data/restraints/parameters	4955/397/451
GOF on <i>F</i> <sup>2</sup>	1.069
<i>R</i> <sub>1</sub> <sup>a</sup> , <i>wR</i> <sub>2</sub> <sup>b</sup> [ <i>I</i> > 2σ( <i>I</i> )]	0.044, 0.1067
<i>R</i> <sub>1</sub> <sup>a</sup> , <i>wR</i> <sub>2</sub> <sup>b</sup> (all data)	0.0548, 0.1196

<sup>a</sup>  $R_1 = \Sigma ||F_o| - |F_c|| / \Sigma |F_o|$ . <sup>b</sup>  $wR_2 = [\Sigma w(F_o^2 - F_c^2)^2 / \Sigma w(F_o^2)^2]^{1/2}$ .



**Fig. S1** (a) A description of asymmetric unit in QDUC-1. (b) The dihedral angles observed in QDUC-1. (Atom labeling scheme: C, gray; O, red; Co, green; S, yellow.).



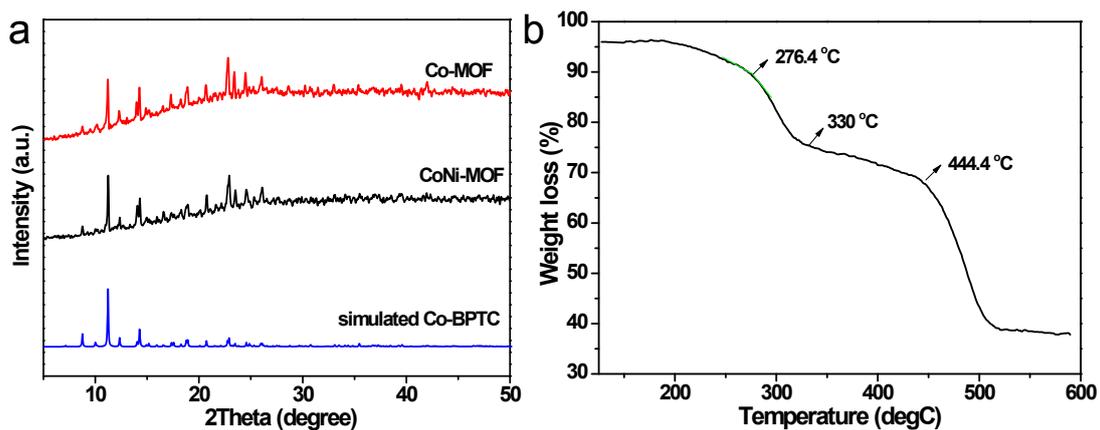
**Fig. S2** The synthetic progress for different MOF crystals can be monitored by the obvious color: (a) Co-MOF: purple, (b) CoNi-MOF: pinkish, (c) the kelly solution: no Ni-MOF production, (d) CoNi-MOF before calcination. (e) The CoNi@C after calcination of CoNi-MOF.

**Table S2** The inductively coupled plasma mass spectrometry (ICP-MS) results of CoNi-MOF, CoNi@C, CoNi@C-ZIF and CoNi/AC.

Sample	Element	$m_{\text{metal}}/m_{(\text{Co}+\text{Ni})}$ (wt%)	Content (wt%)
CoNi-MOF	Co	51.3	10.9
	Ni	48.7	10.3
CoNi@C	Co	53.4	23.0
	Ni	46.6	20.1
CoNi@C-ZIF	Co	51.6	22.0
	Ni	48.4	22.5
CoNi/AC	Co	52.9	20.2
	Ni	47.1	21.5

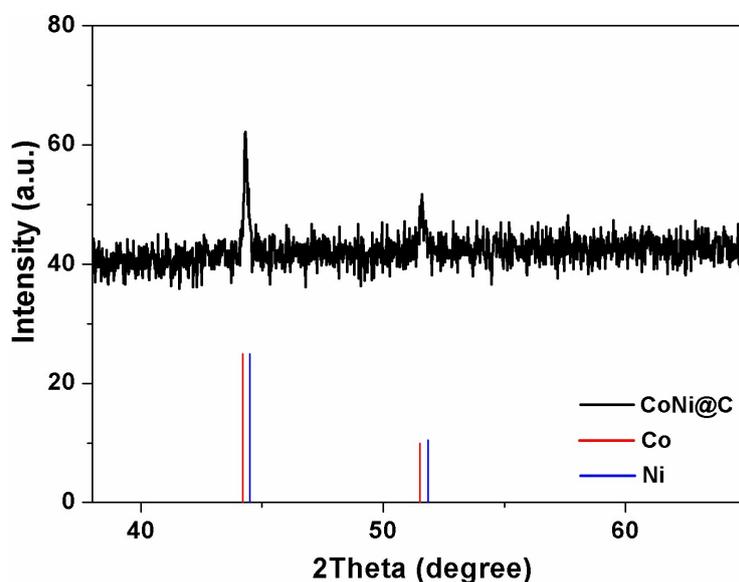
**Table S3.** Comparison of the peak positions of Co element and Ni element in CoNi-MOF and CoNi@C samples with those in literature based on XPS analyses.

Structure	Co-Ox	Ni -Ox	Co (0)	Ni (0)	Refs
BE (eV)	781.4	855.9	778.4	852.8	This work
BE (eV)		856.1		852.4	S1
BE (eV)	780.5		778.5		S2
BE (eV)	782		778		S3
BE (eV)	782.5		778.5		S4
BE (eV)	780.4±0.3	853.8±0.3	778.3±0.3	852.7±0.3	S5 (standard data)

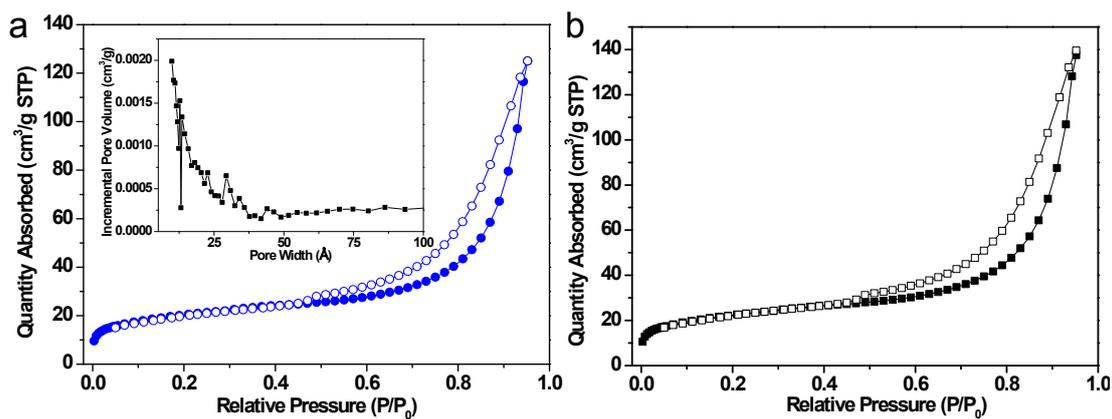


**Fig. S3** (a) PXRD patterns of as-synthesized CoNi-MOF, Co-MOF and simulated Co-MOF crystal. (b) TG curve of CoNi-MOF crystal.

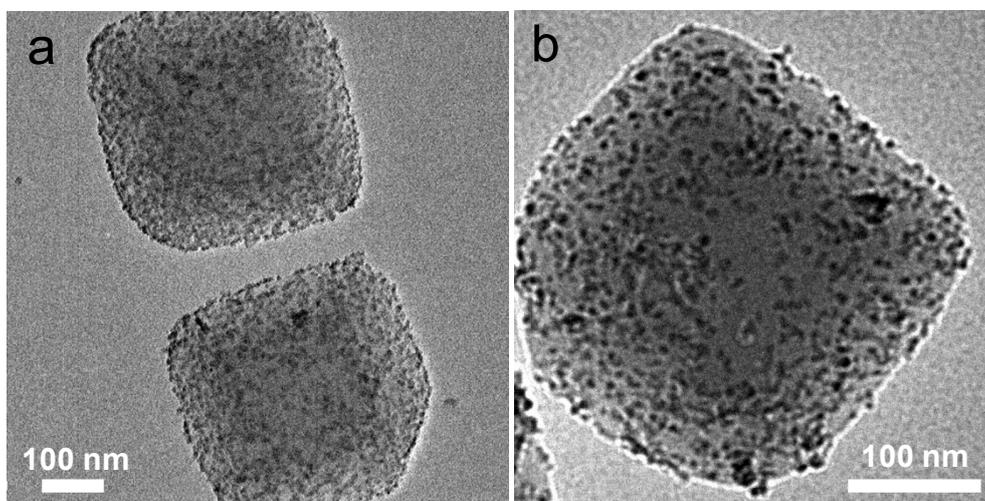
TG curve of CoNi-MOF shows a weight loss of ~12% in the range of 20-280 °C, which could be attributed to the loss of solvent molecules, such as methanol and DMF within the MOF pores. Following that, the de-solvated framework starts to collapse from 300 °C and then rapidly loses weight from 444 °C.



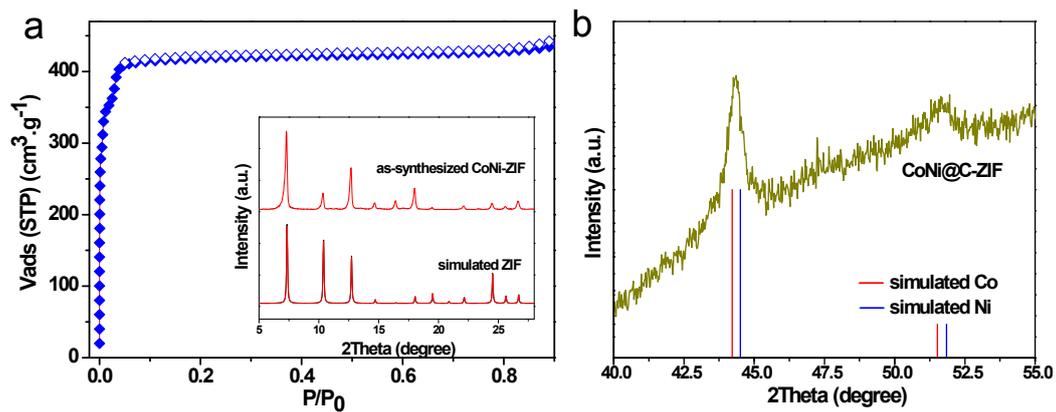
**Fig. S4** PXRD patterns of as-synthesized CoNi@C, and simulated metallic Co and Ni.



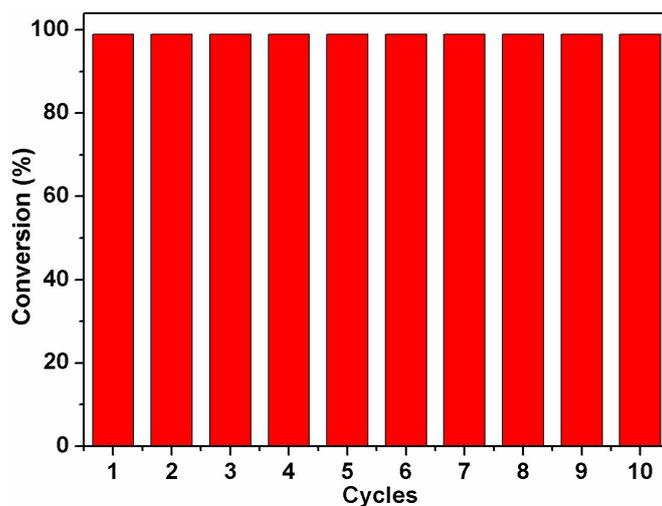
**Fig. S5** N<sub>2</sub> sorption isotherms at 77 K of (a) as-synthesized CoNi@C-600 and (b) CoNi@C-600 after 30 cycles with CoNi content of ~43 wt%. Pore size distribution for CoNi@C hybrid carbon materials based on the density functional theory (DFT) method (inset in a).



**Fig. S6** Enlarged TEM images of CoNi@C, (a) before reaction and (b) after catalytic runs.



**Fig. S7** (a) N<sub>2</sub> sorption isotherms at 77 K and Powder XRD patterns (inset) for as-synthesized CoNi-ZIF. (b) Powder XRD patterns for as-synthesized CoNi@C-ZIF and simulated metallic Co and Ni.



**Fig. S8** Recyclability test for the hydrogenation of nitrobenzene through ten consecutive runs over Co@C catalyst (every reaction time is 1 hour).

**Table S4** Cascade reactions of  $\text{NH}_3\text{BH}_3$  dehydrogenation and nitroarene hydrogenation over  $\text{Co}@C$ .

Entry	Substrate	Product	Yield <sup>b</sup>	Time
1			>99 %	1 h
2			>99 %	1 h
3			>99 %	1 h
4			>99 %	1 h
5			>99 %	1.5 h
6			>99 %	1.5 h
7			>99 %	1.5 h
8			>99 %	1.5 h
9 <sup>c</sup>		-	-	1 h

<sup>a</sup>Reaction conditions: 0.1 mmol nitroarenes, 15 mg  $\text{NH}_3\text{BH}_3$ , 20 mg  $\text{Co}@C$ , 10 mL MeOH, 10 mL  $\text{H}_2\text{O}$ , 25 °C. <sup>b</sup>Catalytic yield was identified by gas chromatography. <sup>c</sup>Without any catalysts.

**Table S5** Cascade reactions of  $\text{NH}_3\text{BH}_3$  dehydrogenation and hydrogenation of unsaturated double bond by  $\text{CoNi@C}$  catalyst at 50 °C.

Entry	Substrate	Product	Yield <sup>b</sup>	Time
1			>99 %	5 min
2			>98 %	10 min
3			>98 %	10 min
4			>98 %	10 min
5			>98 %	10 min
6			>98 %	10 min
7 <sup>c</sup>		-	-	5 min

<sup>a</sup>Reaction conditions: 0.1 mmol olefin, 15 mg  $\text{NH}_3\text{BH}_3$ , 20 mg  $\text{CoNi@C}$ , 20 mL  $\text{H}_2\text{O}$ , 50 °C.

<sup>b</sup>Catalytic yield was identified by gas chromatography. <sup>c</sup>Without any catalysts.

## References

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