Supporting Information

Multimetal-MOFs-derived Transition Metal Alloy NPs Embedded in N-doped Carbon Matrix: Highly Active Catalysts for Hydrogenation Reaction

Jilan Long,[a,b] Kui Shen,[a,*] Liang Chen[c] and Yingwei Li[a,*]

[a] School of Chemistry and Chemical Engineering, South China University of Technology, Guangzhou 510640, china.

[b] Chemical Synthesis and Pollution Control Key Laboratory of Sichuan Province, Collage of Chemistry and Chemical Engineering, China West Normal University, Nanchong 637000, china.

[c] Department of Chemistry and Collaborative Innovation Center of Chemistry for Energy Materials, Fudan University, 220 Handan Road, Shanghai 200433, China.

* To whom correspondence should be addressed. E-mail: cekshen@scut.edu.cn, liyw@scut.edu.cn

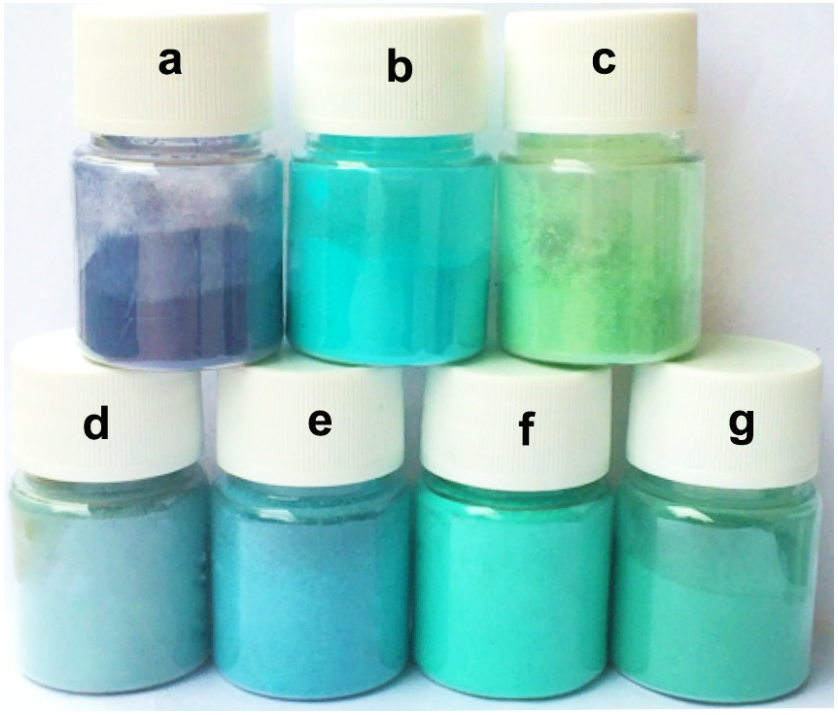

Figure S1. The appearance of various MOFs: (a) Co-MOF, (b) Cu-MOF, (c) Ni-MOF, (d) Co-Ni(3:1)-MOF, (e) Co-Cu(3:1)-MOF, (f) Ni-Cu(1:1)-MOF and (g) Co-Ni-Cu(2:1:1)-MOF.

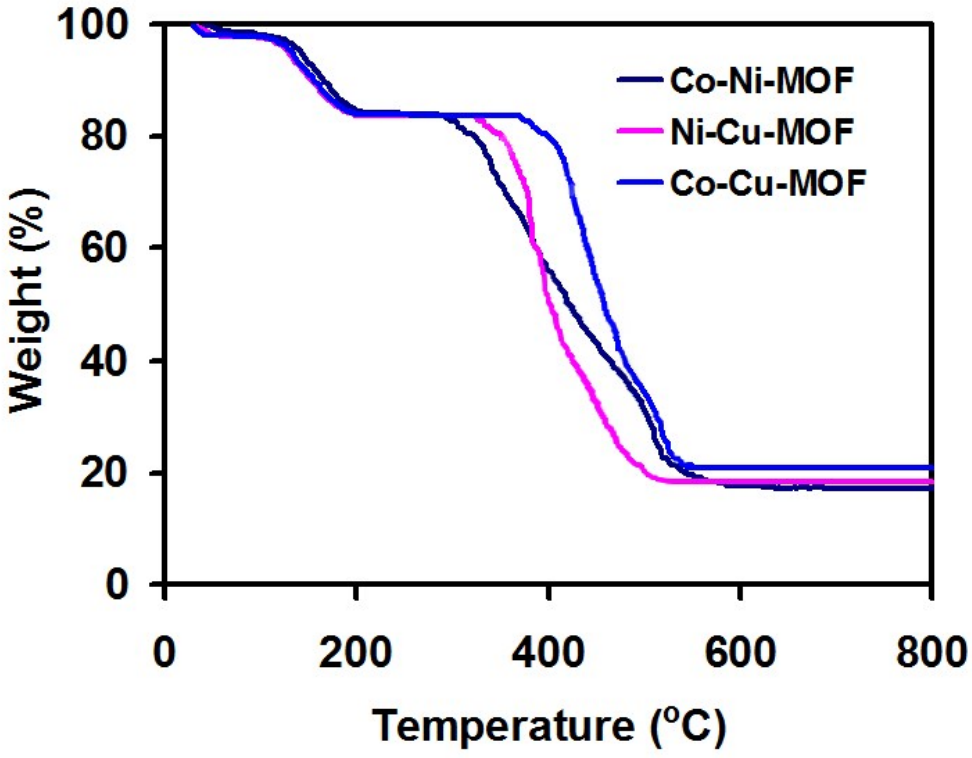

Figure S2. TGA curves of the Co-Ni-MOF, Ni-Cu-MOF and Co-Cu-MOF.

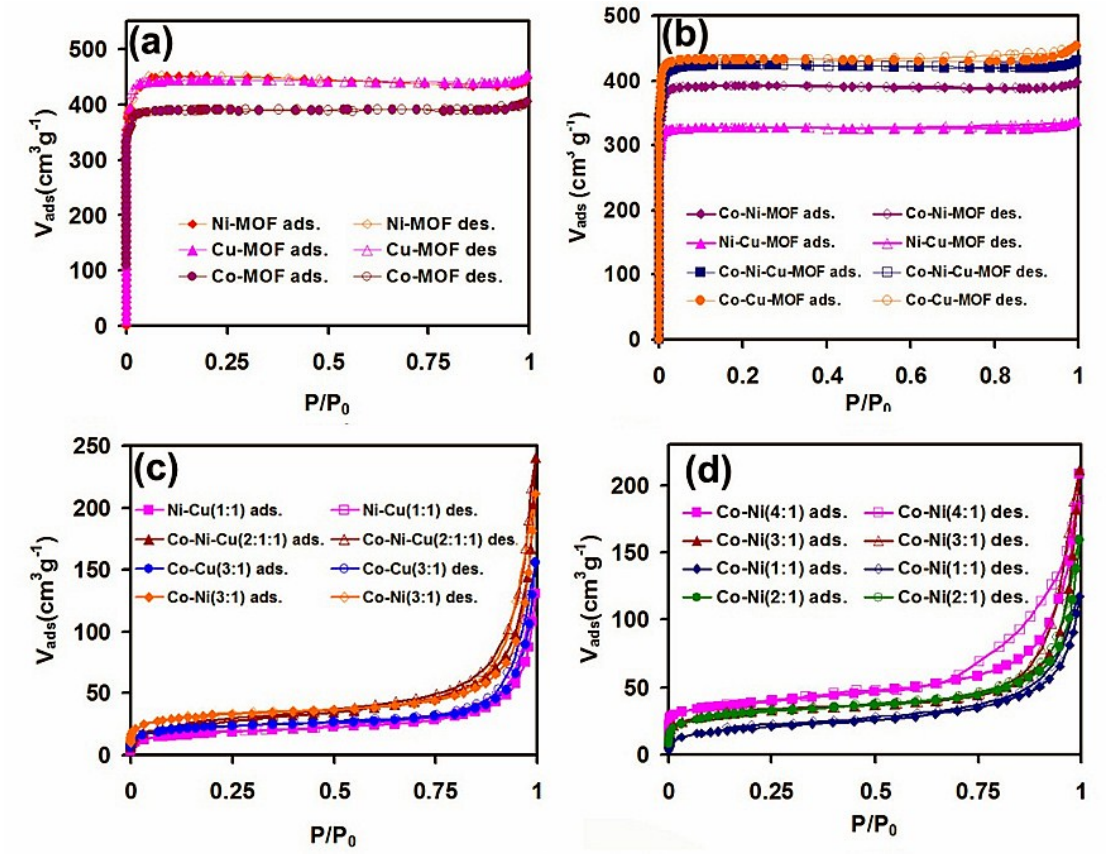

Figure S3. The nitrogen adsorption/desorption isotherms at 77 K: (a) mono-metallic MOFs, (b) hetero-dinucler MOFs, (c) various kinds of M-M'@C-N catalysts, (d) Co-Ni@C-N catalysts with different Co-Ni molar ratio.

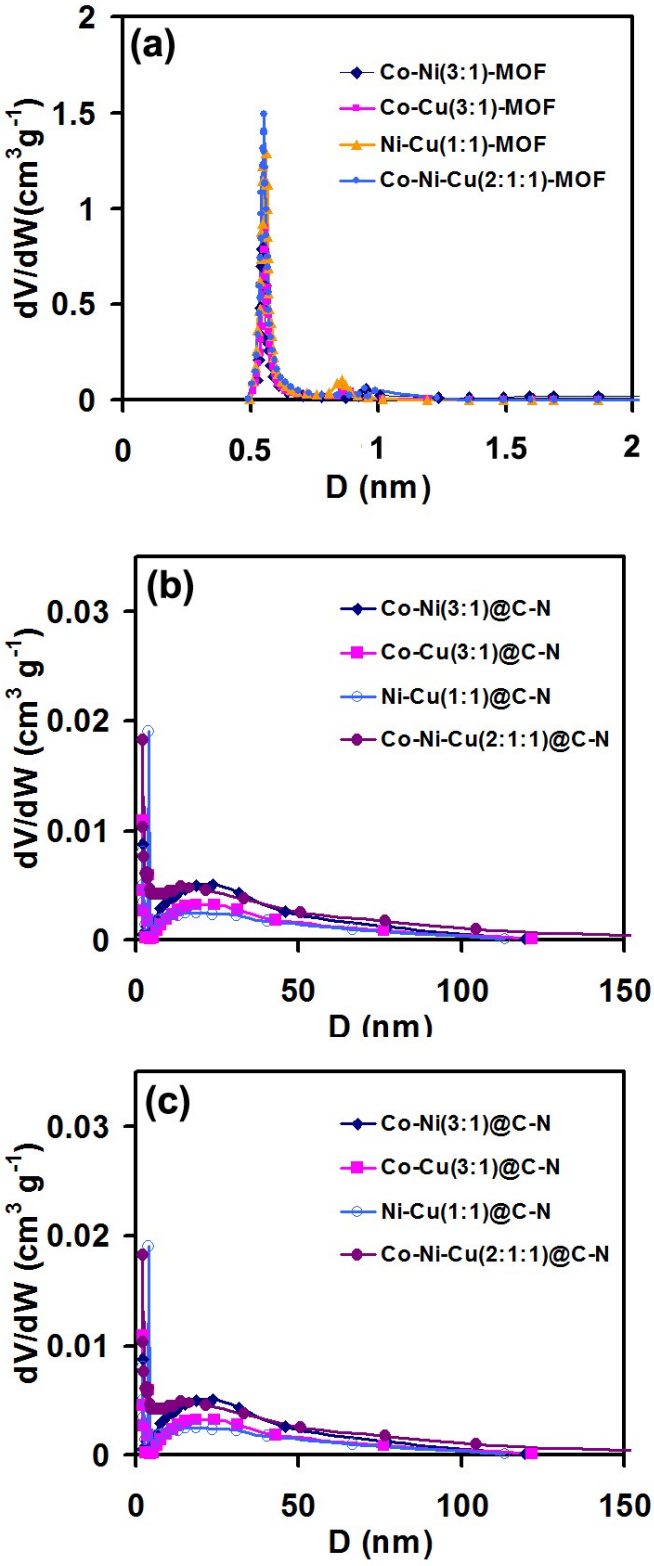

Figure S4. (a) The Horvath−Kawazoe pore-size distribution curves of a series of hetero-dinucler MOFs, (b) the BJH pore-size distribution curves of various M-M'@C-N catalysts, and (c) the BJH pore-size distribution curves of a series of Co-Ni@C-N catalysts with different molar ratios.

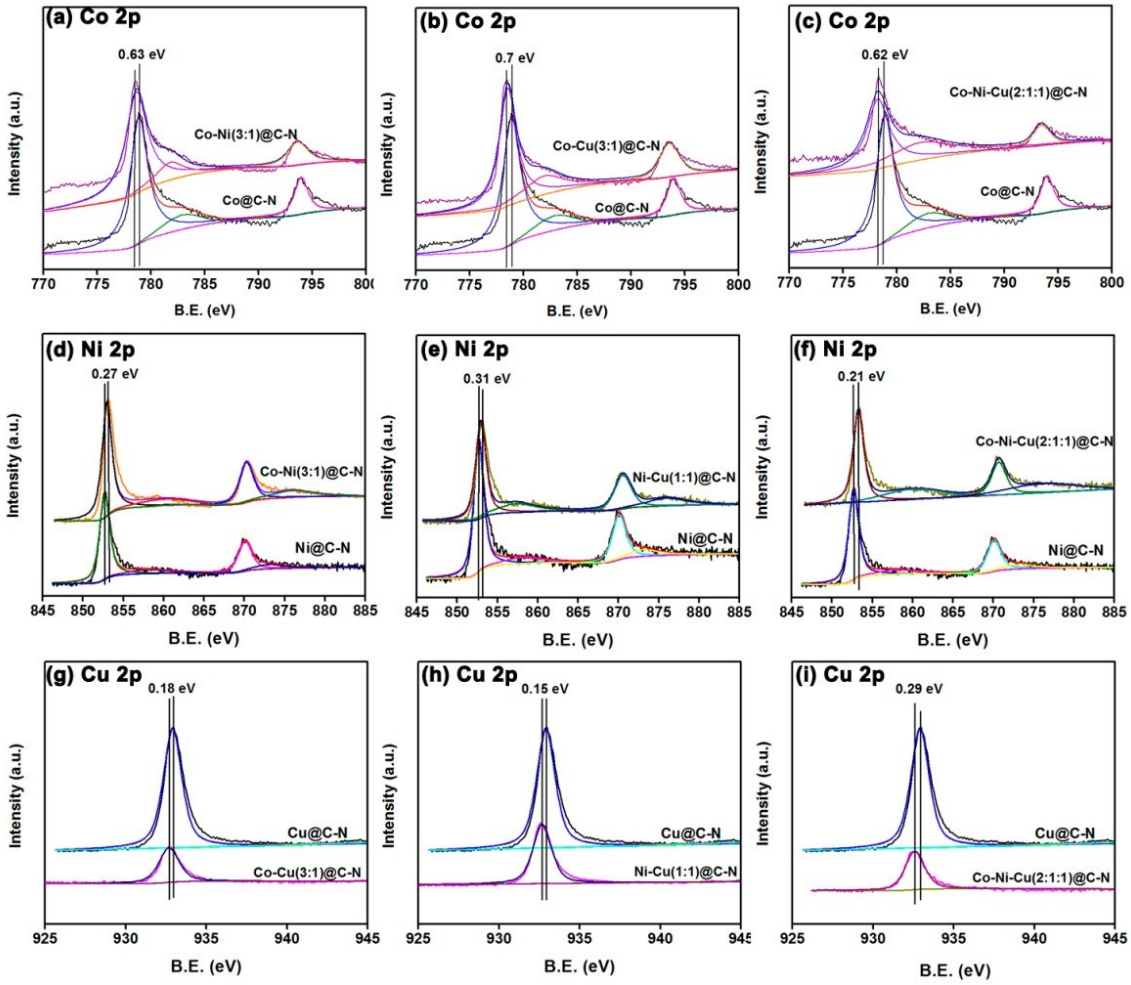

Figure S5. The XPS comparison spectra between zero-valent single metal nanoparticles and alloy nanoparticles. Co 2p of (a) Co@C-N *vs* Co-Ni(3:1)@C-N, (b) Co@C-N *vs* Co-Cu(3:1)@C-N, (c) Co@C-N *vs* Co-Ni-Cu(2:1:1)@C-N, and Ni 2p of (d) Ni@C-N *vs* Co-Ni(3:1)@C-N, (e) Ni @C-N *vs* Ni-Cu(1:1)@C-N, (f) Ni@C-N *vs* Co-Ni-Cu(2:1:1)@C-N, as well as Cu 2p of (g) Cu@C-N *vs* Co-Cu(3:1)@C-N, (h) Cu@C-N *vs* Ni-Cu(1:1)@C-N, (i) Cu@C-N *vs* Co-Ni-Cu(2:1:1)@C-N.

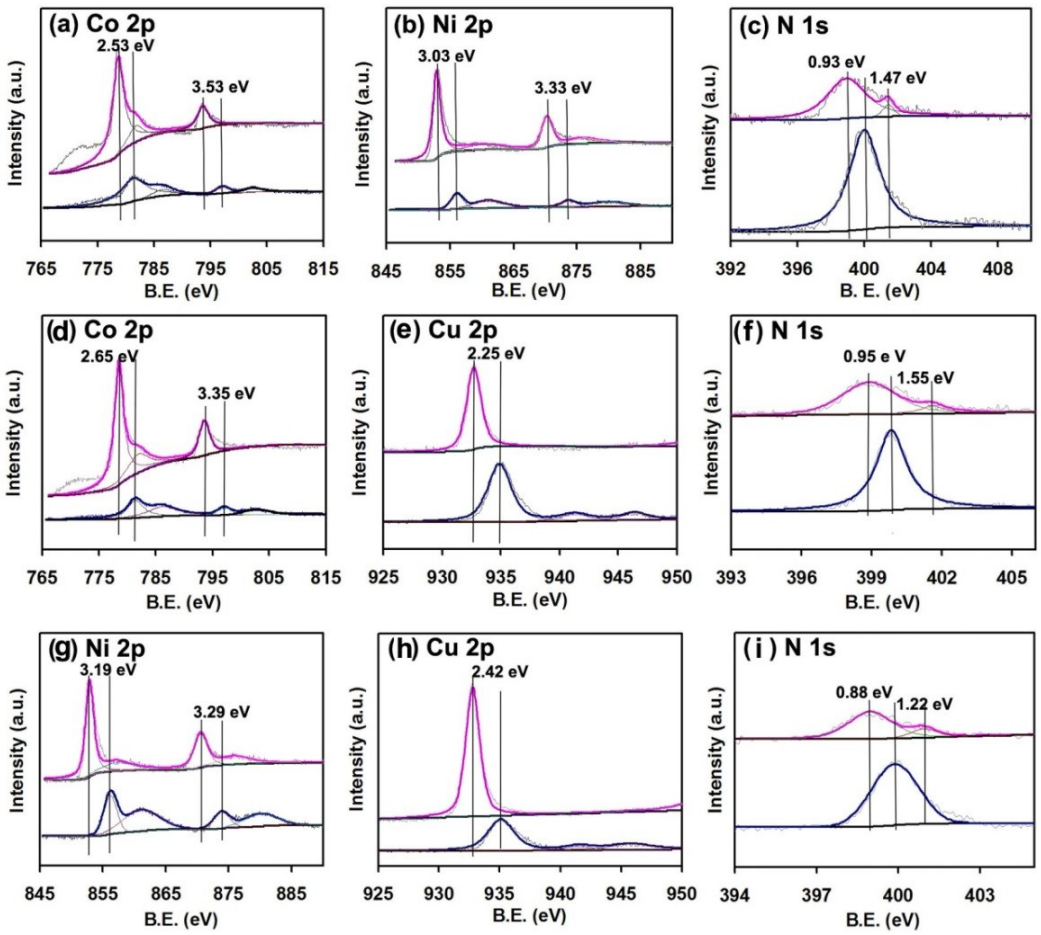

Figure S6. The XPS spectra of Co-Ni-MOF vs. Co-Ni@C-N(a-c), Co-Cu-MOF vs. Co-Cu@C-N (d-f) and Ni-Cu-MOF vs. Ni-Cu@C-N (g-i). The red line represents the catalyst, and the blue line represents the corresponding parental MOFs.

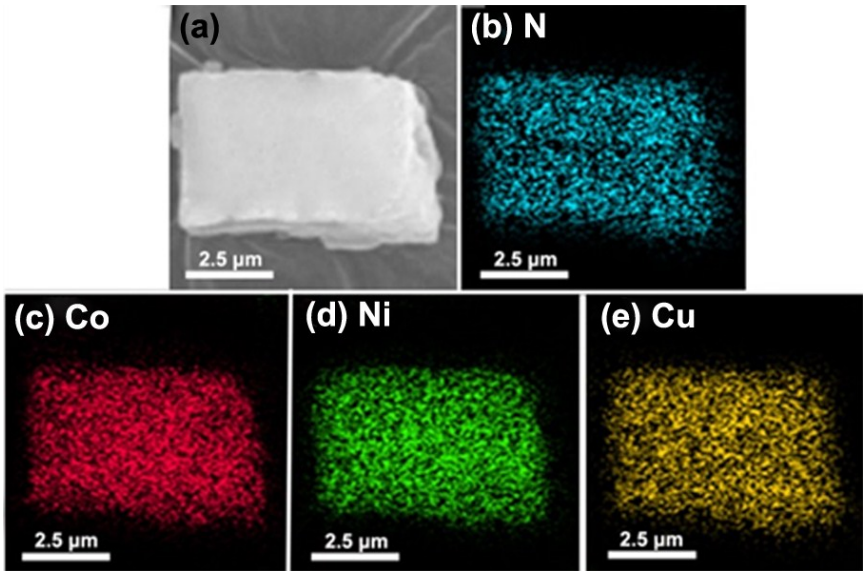

Figure S7. The SEM image of Co-Ni-Cu(2:1:1)-MOF and the corresponding elemental mappings.

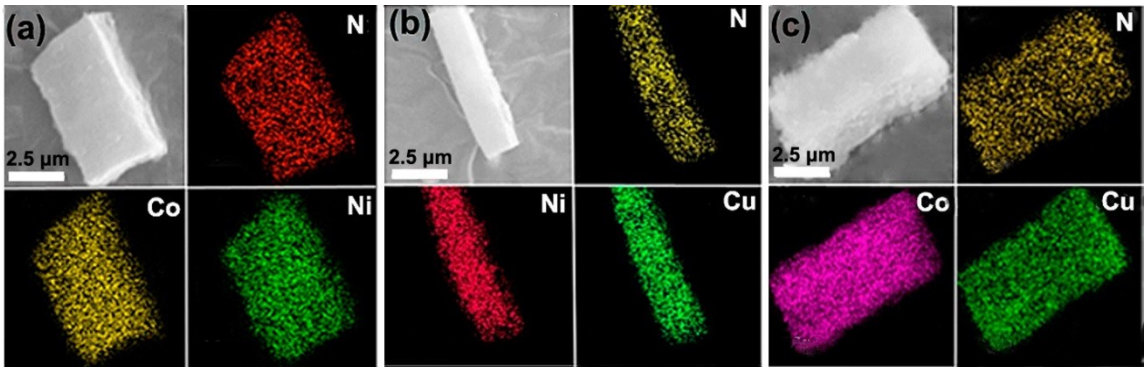

Figure S8. The SEM images of (a)Co-Ni(3:1)-MOF, (b) Ni-Cu(1:1)-MOF and (c) Co-Cu(3:1)-MOF, as well as the corresponding elemental mappings.

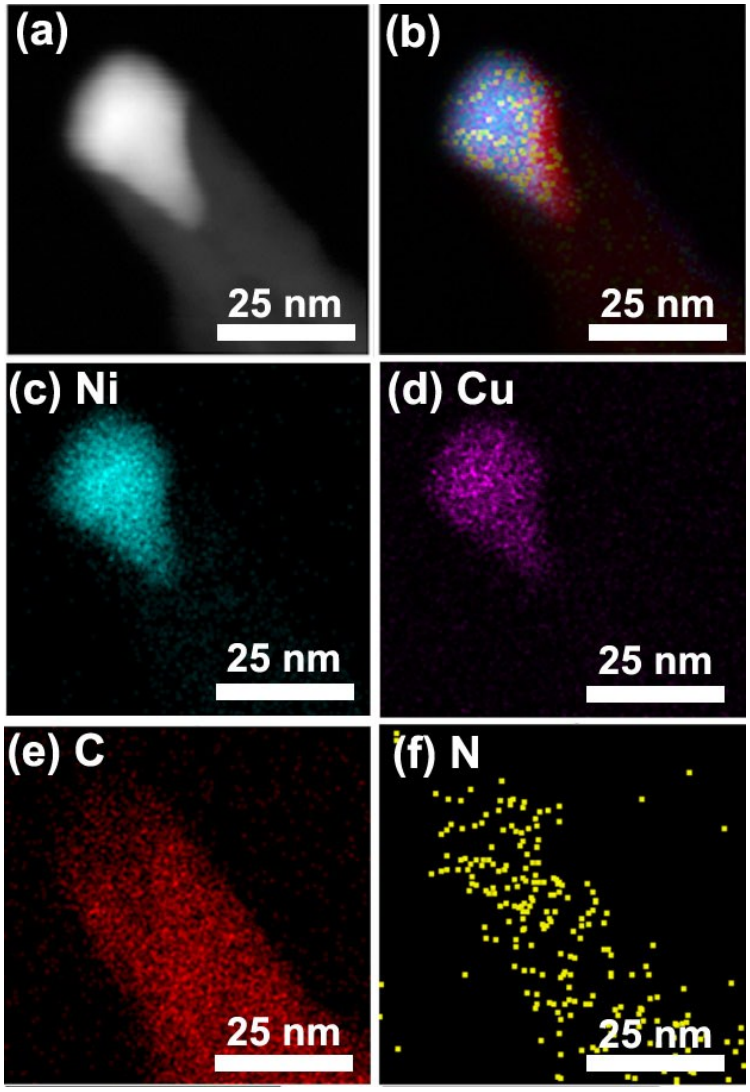

Figure S9. HAADF-STEM image for an individual alloy nanoparticle of Ni-Cu(1:1)@C-N (a) and the superimposed EDX images (b), as well as the corresponding elemental mappings for (c) Ni, (d) Cu, (e) C and (f) N.

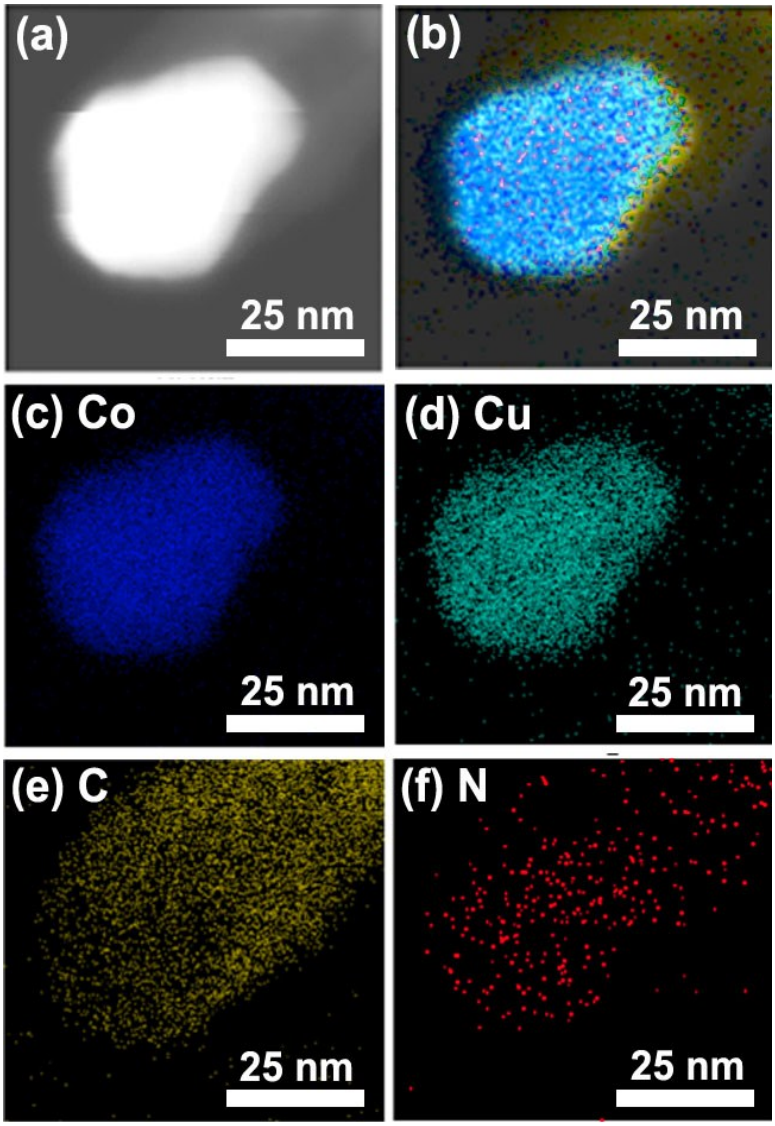

Figure S10. HAADF-STEM image for an individual alloy nanoparticle of Co-Cu(3:1)@C-N (a) and the superimposed EDX images (b), as well as the corresponding elemental mappings for (c) Co, (d) Cu, (e) C and (f) N.

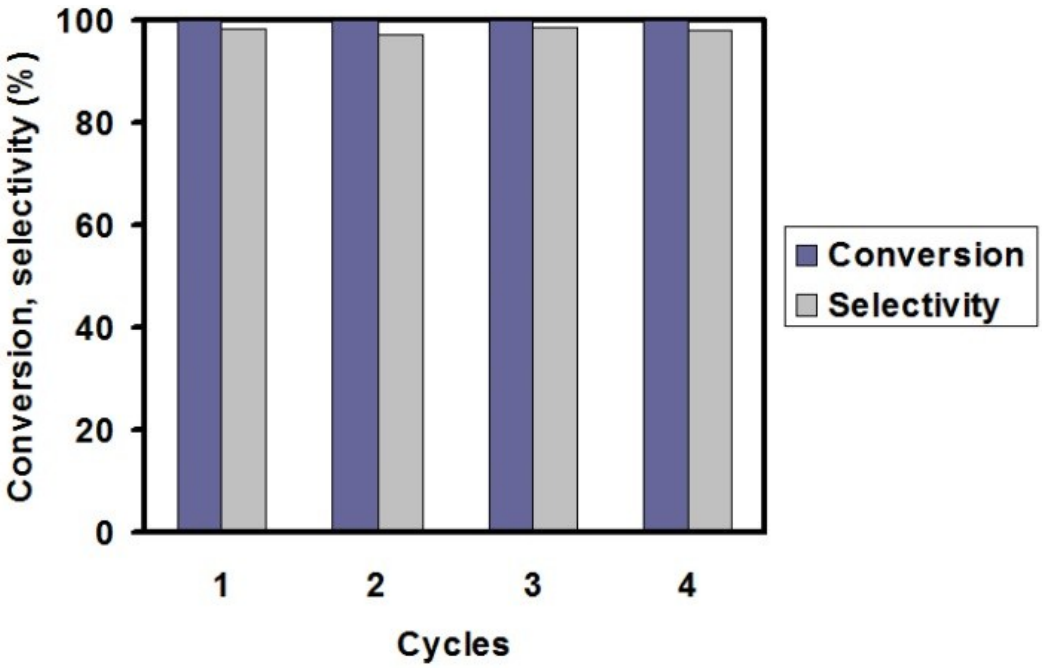

Figure S11. Reuses of the Co-Ni(3:1)@C-N catalyst in the transfer hydrogenation nitrile.

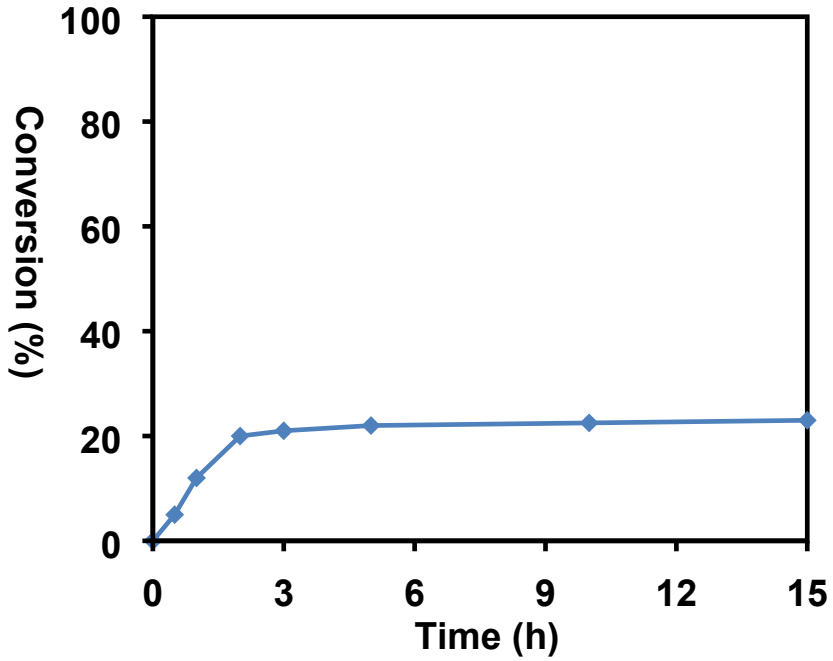

Figure S12. The conversion of benzonitrile after removing the Co-Ni(3:1)@C-N catalyst from the solution at 2 h.

Table S1. Surface areas and pore distribution of the materials.

Entry	Catalyst	S_{BET} (m^2 g^{-1})	Pore volume (cm^3 g^{-1})	Pore size (nm)
1	Co-MOF	1501	0.70	0.56
2	Ni-MOF	1767	0.79	0.57
3	Cu-MOF	1687	0.75	0.57
4	Co-Cu-MOF	1666	0.73	0.56
5	Co-Ni-MOF	1412	0.68	0.56
6	Ni-Cu-MOF	1323	0.61	0.56
7	Co-Ni-Cu-MOF	1599	0.72	0.56
8[a]	Co-Ni(4:1)@C-N	125	0.22	7.07
9[a]	Co-Ni(2:1)@C-N	103	0.16	6.09
10[a]	Co-Ni(1:1)@C-N	68	0.13	7.37
11[a]	Co-Ni(3:1)@C-N	103	0.19	7.35
12[a]	Co-Cu(3:1)@C-N	69	0.12	7.06
13[a]	Ni-Cu(1:1)@C-N	60	0.12	7.65
14[a]	Co-Ni-Cu(2:1:1)@C-N	91	0.14	6.77

[a] the catalysts prepared by calcining their parental MOFs at 500 ^{o}C for 8 hours.

Table S2. The main element contents of various MOFs and catalysts

Materials	C content (wt%)[a]	N content[a] (wt%)	H content (wt%)[a]	Metal content (wt%)[b]
Co-MOF	46.9	9.5	5.6	20.5
Ni-MOF	47.2	9.7	5.3	20.3
Cu-MOF	46.3	9.9	5.8	20.7
Co-Ni(3:1)-MOF	45.9	9.2	5.4	(Co)16.3, (Ni)5.7
Co-Cu(3:1)-MOF	46.2	9.4	5.5	(Co)16.1, (Cu)5.3
Ni-Cu(1:1)-MOF	46.9	9.4	5.7	(Ni)10.1, (Cu)10.5
Co-Ni-Cu(2:1:1)-MOF	47.0	9.5	5.4	(Co)10.2, (Ni)5.1, (Cu)5.4
Co-Ni(3:1)@C-N	56.2	1.5	1.0	(Co)31.1, (Ni)10.0
Co-Cu(3:1)@C-N	55.4	1.3	1.1	(Co)31.8, (Cu)10.4
Ni-Cu(1:1)@C-N	56.4	0.9	1.2	(Ni)20.2, (Cu)21.1,
Co-Ni-Cu(2:1:1)@C-N	54.4	1.1	0.9	(Co)21.3, (Ni)10.1, (Cu)12.1

[a] Measured by elemental analysis.

[b] Measured by AAS.