Supplementary Information

Robust MOF-derived carbon-supported bimetallic Ni-Co catalysts for aqueous phase hydrodeoxygenation of vanillin

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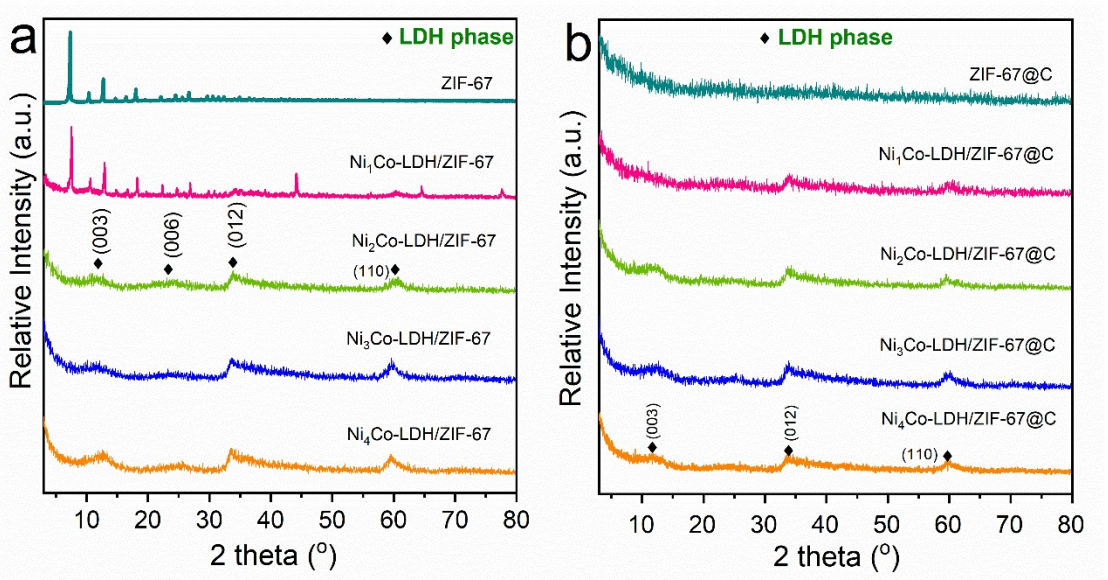

Fig.S1. Wide angle powder XRD patterns of Ni_xCo-LDH/ZIF-67 precursors (a) and Ni_xCo-LDH/ZIF-67@C composites (b).

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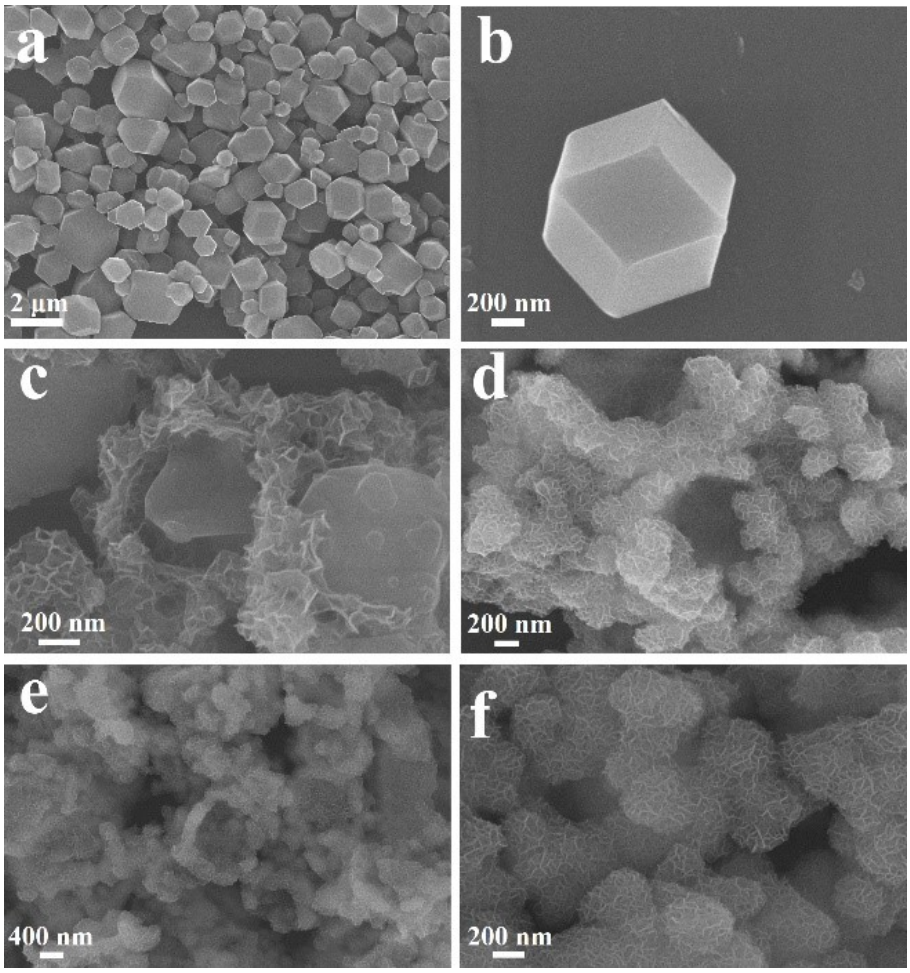

Fig.S2. SEM images of ZIF-67 (a,b), Ni_1Co-LDH/ZIF-67 (c), Ni_2Co-LDH/ZIF-67 (d), Ni_3Co-LDH/ZIF-67 (e), and Ni_4Co-LDH/ZIF-67 (f) samples.

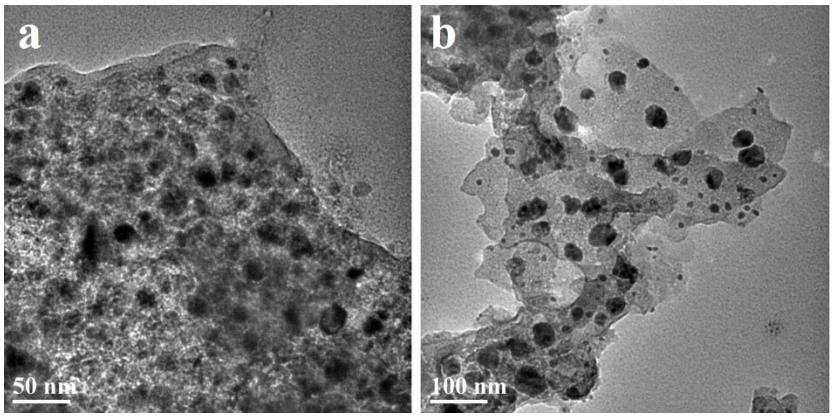

Fig.S3. TEM images of Co@NC (a) and Co@NC@C (b) samples.

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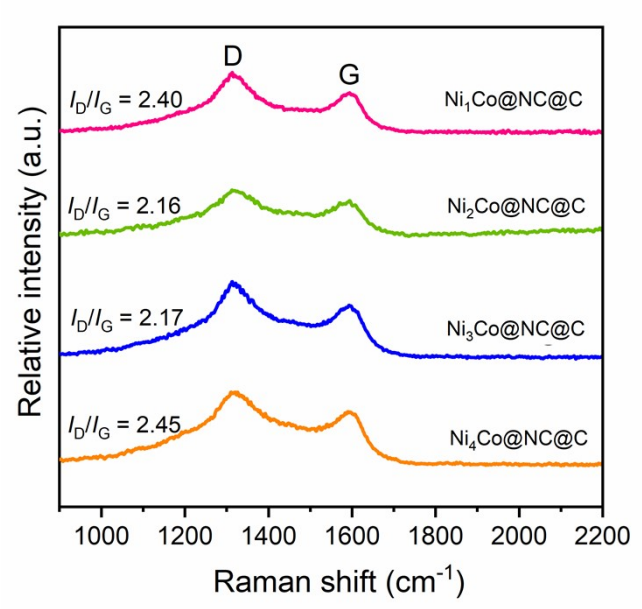

Fig.S4. Raman spectra of different $Ni_xCo@NC@C$ samples.

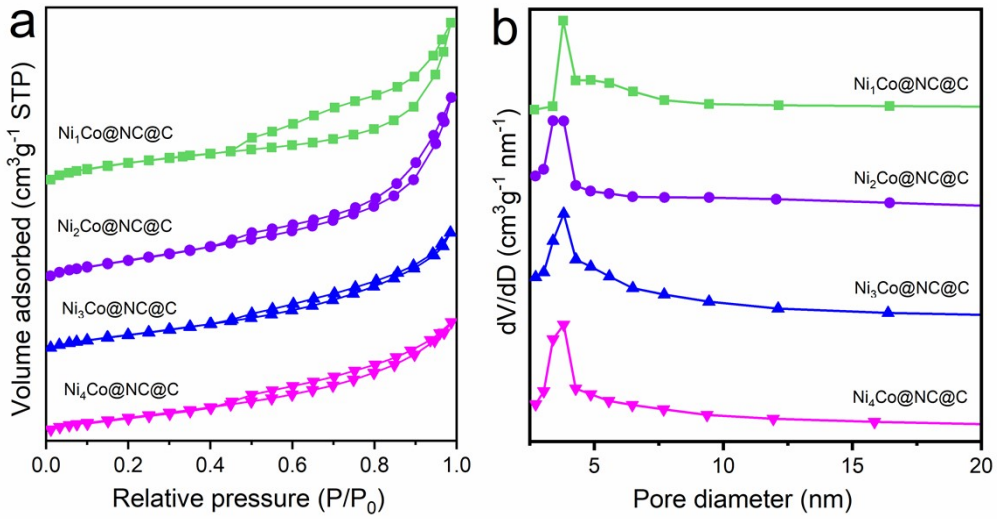

Fig.S5. Low-temperature N_2 adsorption-desorption isotherms of $Ni_xCo@NC@C$ samples (a) and corresponding pore size distributions (b).

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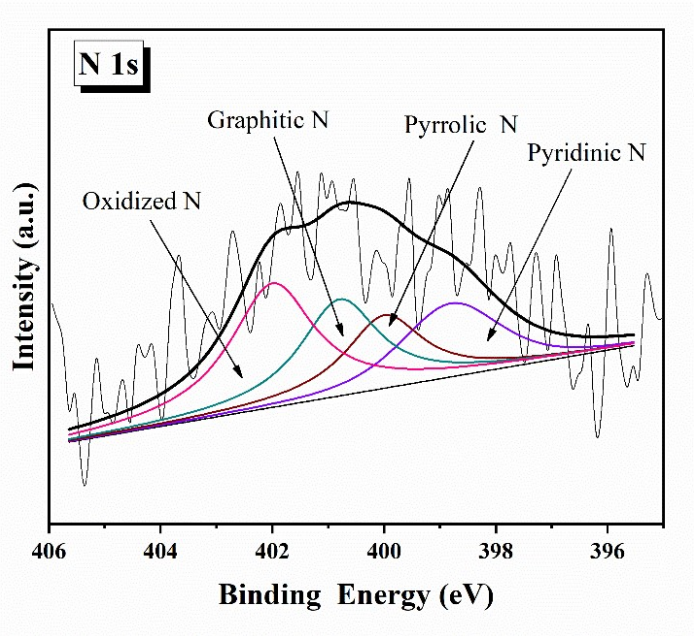

Fig.S6 XPS of N 1s region for the representative Ni_3Co@NC@C sample.

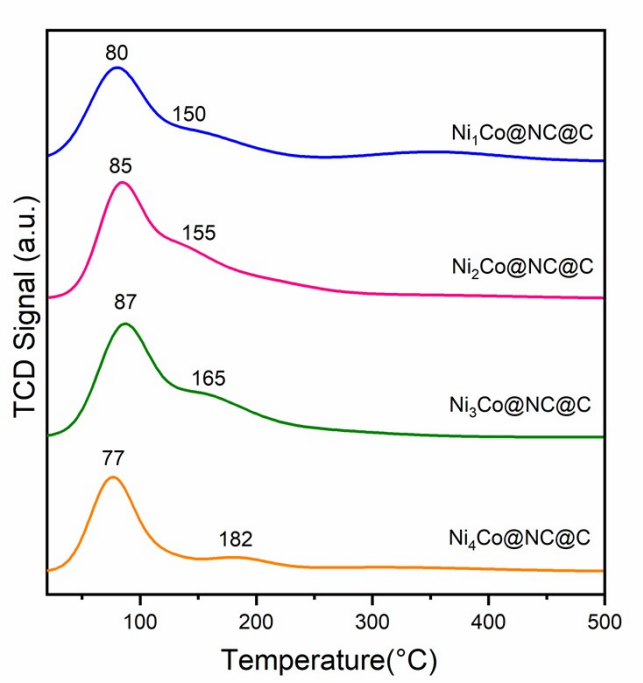

Fig.S7 H_2-TPD profiles of different samples.

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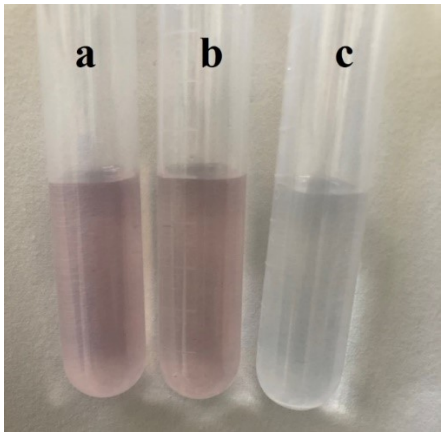

Fig.S8 Picture of reaction solutions over Co@NC@C (a), Co@NC (b), Ni_3Co@NC@C (c) after reaction.

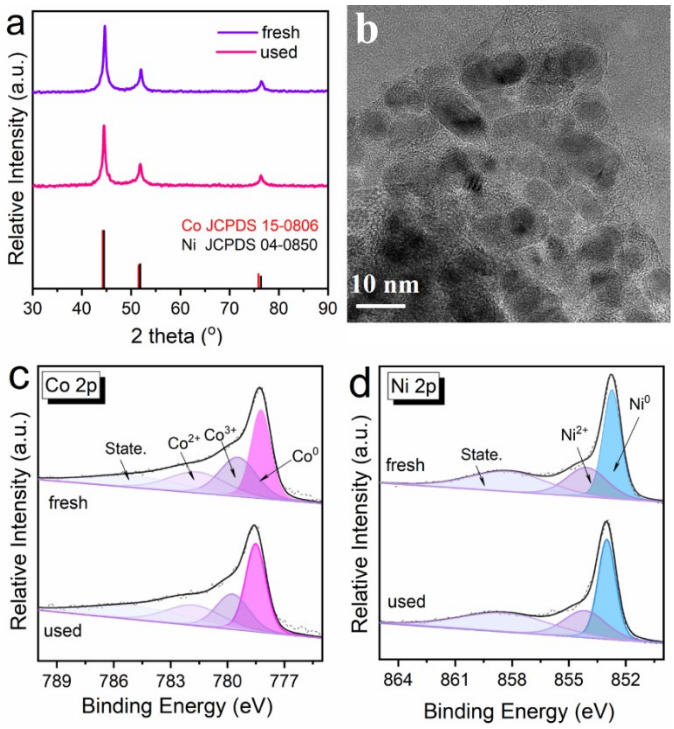

Fig.S9 XRD patterns (a), HRTEM image (b), and XPS of Co $2p_{3/2}$ (c) and Ni $2p_{3/2}$ (d) regions for spent Ni_3Co@NC@C catalyst after five succestive runs.

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Table S1 Comparative results of catalytic HDO of vanillin over other metal-based catalysts.

Catalysts	Solvent	Temp. (°C)	Time (h)	H_2 (MPa)	Conv. (%)	Selectivity (%)		TOF (h^{-1})	Refs.
						VAL	MMP		
Pd/Ru@GO	methanol	25	12	2.5	100	0	96	222.5	[16]
Pd@UiO-66(Hf)	water	90	2	0.3	99	0	99	--	[45]
CoNi/Al_2O_3-2	water	150	1	1	100	0.1	98.9	1872	[13]
15 wt%-Cu/AC-600	water	120	5	2.0	99.9	7	93	--	[46]
Cu/ZnAlSn	isopropanol	180	4	N_2	100	2	98	--	[47]
Cu-Ga/HNZY	methanol	180	2	1.0	100	0	99	--	[48]
Cu_3Pd_1@BBA-1	isopropanol	140	8	1.0	94.3	0	97	--	[49]
Cu-Ni/ZrO_2	water	160	24	2.5	98	0	94	--	[50]
Ni/NCB-900	water	150	2	0.5	74.4	35	65	--	[51]
Ni_3Co@NC@C	water	170	0.5	1.0	100	0	100	6990 [b]	This work

[a] performed in a fixed-bed reactor. [b] obtained at 140 °C.

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