Electronic Supplementary Material (ESI) for Sustainable Energy & Fuels.

In Situ-Generated Co embedded in N-doped carbon hybrids for the upgrading of levulinic acid in aqueous phase

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Table S1 Pore structure of the Co@NC catalysts

Samples	Micropore area(m^2/g)	External surface area(m^2/g)	Total surface area(m^2/g)	Pore volume(cm^3/g)	Average pore diameter (nm)
Co@NC-600	---	11.4	7.47	0.01	-
Co@NC-700	133.4	173.6	307.0	0.285	3.82
Co@NC-800	130.6	182.6	313.2	0.293	3.79
Co@NC-900	108.9	222.6	331.5	0.397	3.82
^{10th}Cycle	134.9	178.0	312.9	0.361	3.78

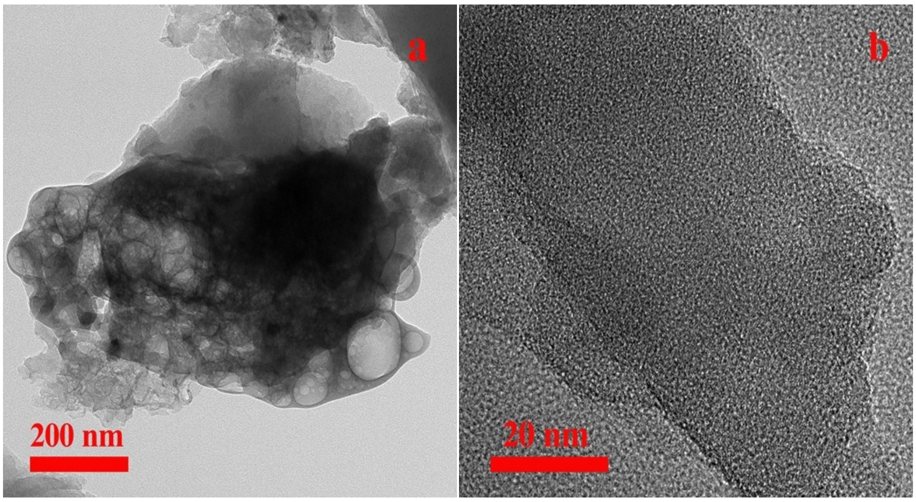

Fig. S1 TEM images of Co@NC-600

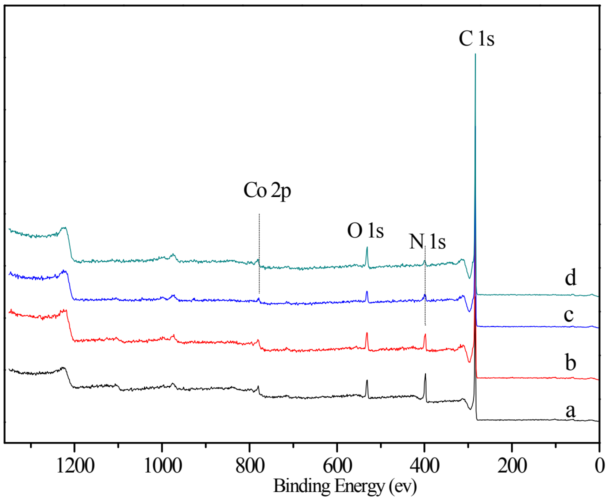

Fig. S2 XPS survey spectrum of (a) Co@NC-600 (b) Co@NC-700, (c) Co@NC-800, (d) Co@NC-900

Table S2 Chemical compositions and structural parameters of Co@NC (wt.%)

Sample	XPS				[a] Element Analyzer		[b] ICP	[c] d_{Co^0} (nm)	I_D/I_G
	N	C	O	Co	N	C	Co		
Co@NC-600	15.7	69.0	8.2	7.1	16.2	62.6	---	---	0.94
Co@NC-700	8.6	79.7	6.8	4.9	6.5	75.5	4.9	19.1	0.95
Co@NC-800	5.1	86.3	5.2	3.5	2.4	81.2	6.5	17.9	1.02
Co@NC-900	2.8	88.7	4.8	3.7	1.23	82.4	11.2	34.5	1.05

[a] The ultimate analysis was analyzed by Vario EL elemental analyzer (Elementar, Germany).

[b] The Co loading content in catalyst quantitative was measured by inductively coupled plasma-atomic emission spectroscopy (ICP-AES, PerkinElmer instruments, Norwalk, 2100 DV, USA).

[c] Calculated from the Scherrer formula according to the (111) diffraction lines.

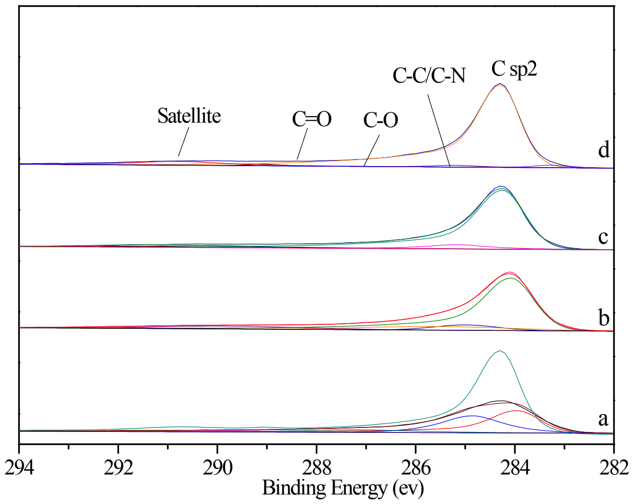

Fig. S3 The C1s spectras of (a) Co@NC-600 (b) Co@NC-700, (c) Co@NC-800, (d) Co@NC-900

Table S3 The different kinds of C species in the Co@NC catalysts

Sample	sp2 (284.4 eV)	C-C (285.3 eV)	C-O (287.4 eV)	C=O (289.2 eV)	Satellite (291.0 eV)
Co@NC-600	46.4	36.1	11.0	4.5	2.1
Co@NC-700	71.5	6.9	11.2	8.9	1.6
Co@NC-800	82.7	6.9	2.6	5.6	2.2
Co@NC-900	88.1	1.7	1.71	1.0	7.5
Spent	51.1	35.4	6.3	5.2	2.0

Table S4 The content of Co species in Co@NC catalysts

Sample	Metallic Co (778.3 ev)	Co (II)-N/O (780.4 ev)	Co (III)-N/O (782.9 ev)
Co@NC-600	9.3	60.1	30.6
Co@NC-700	14.4	56.3	29.3
Co@NC-800	17.0	56.0	27.0
Co@NC-900	18.4	51.5	30.2

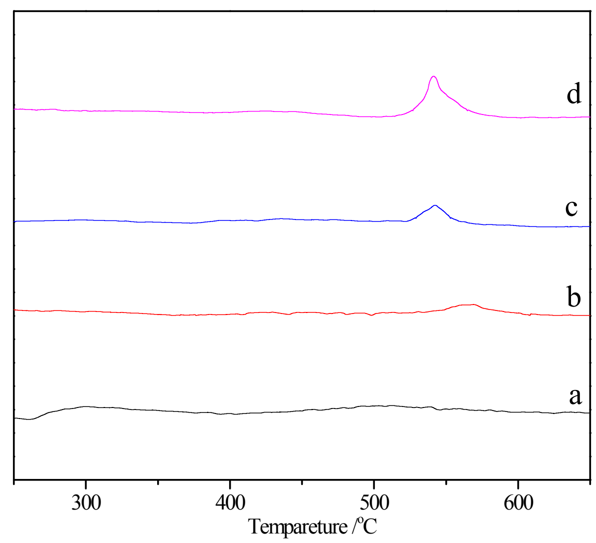

Fig. S4 H_2-TPD of (a) Co@NC-600 (b) Co@NC-700, (c) Co@NC-800, (d) Co@NC-900

Table S5 The Hydrogen adsorption of Co@NC catalysts

Sample	Temp. (℃)	H_2 adsorp. (mmol H_2/g)	Temp. (℃)	H_2 adsorp. (mmol H_2/g)	Total H_2 adsorp. (mmol H_2/g)
Co@NC-600	148	0.058	402	0.026	0.084
Co@NC-700	141	0.067	528	0.017	0.084
Co@NC-800	87	0.039	515	0.016	0.055
Co@NC-900	---	---	525	0.042	0.042

Table S6 The content of nitrogen species in Co@NC catalysts

Sample	Pyridinic-N (398.3 eV)	Co-Nx (399.1 eV)	Pyrrolic-N (400.1 eV)	Graphitic-N (401.0 eV)	Oxidized-N (403.3 eV)
Co@NC-600	60.1	0	20.1	12.3	7.5
Co@NC-700	48.1	1.5	23.3	14.5	12.6
Co@NC-800	28.9	13.9	10.2	28.3	18.8
Co@NC-900	13.8	23.0	2.2	35.7	25.3

Table S7 The acidity capacity of Co@NC catalysts (mmol NH_3/g)

Sample	Weak acid capacity		Medium acid capacity		Total
	Peak Temp. (℃)	Capacity	Peak Temp. (℃)	Capacity	
Co@NC-600	174	0.142	-	-	0.142
Co@NC-700	178	0.086	520	0.06	0.146
Co@NC-800	-	-	515	0.035	0.035
Co@NC-900	-	-	531	0.034	0.034

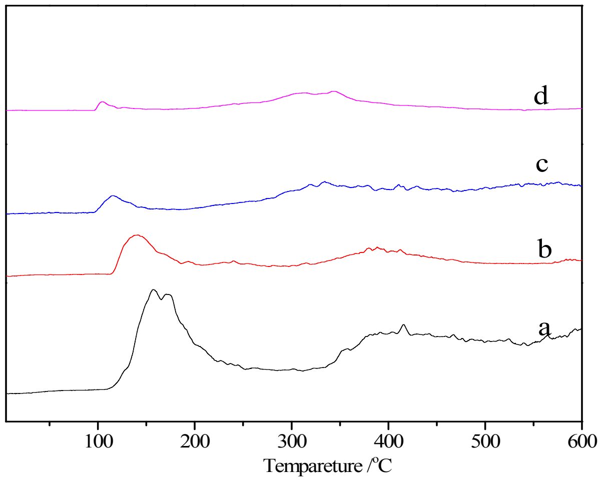

Fig. S5 H_2-TPR of (a) Co@NC-600 (b) Co@NC-700, (c) Co@NC-800, (d) Co@NC-900

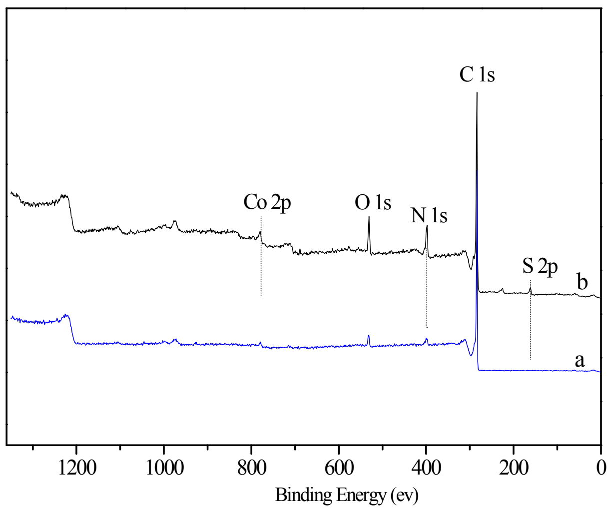

Fig. S6 XPS survey of (a) Co@NC-800 (b) Co@NC-800 after adsorbing SCN^-

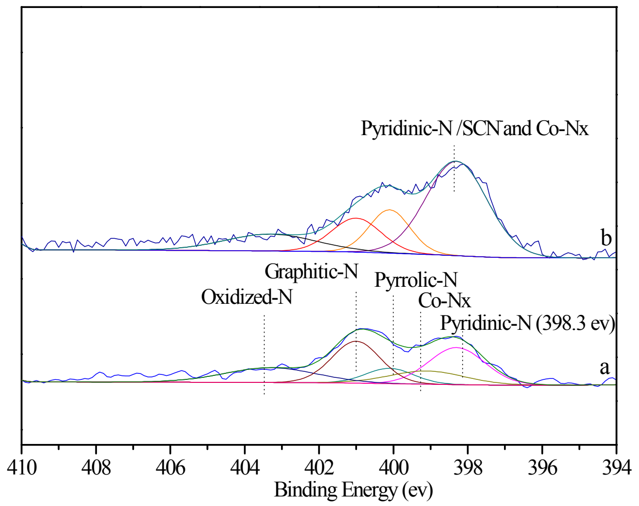

Fig. S7 The N 1s spectra of (a) Co@NC-800, (b) Co@NC-800 after adsorbing SCN^-

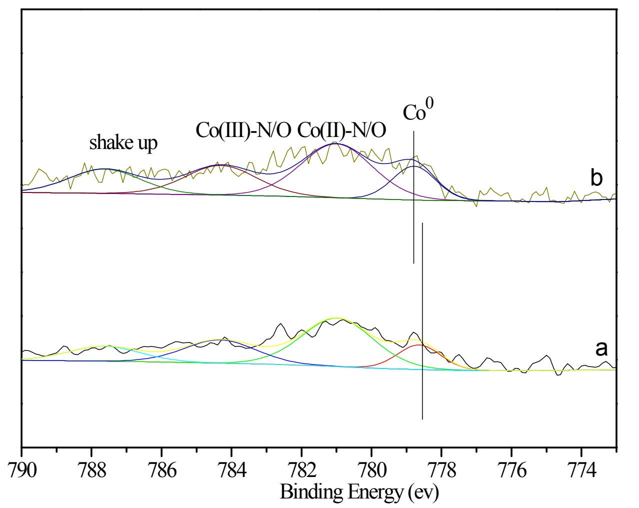

Fig. S8 The Co 2p spectra of (a) Co@NC-800, (b) Co@NC-800 after adsorbing SCN^-

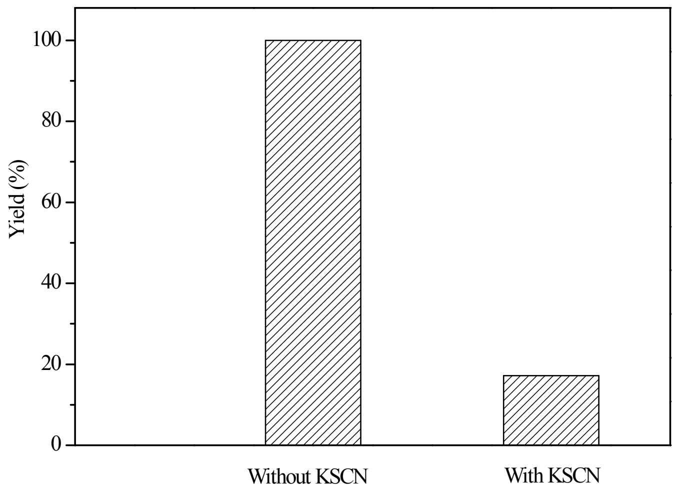

Fig. S9 Poisoning test of the Co@NC-800 catalyst with KSCN
Reaction condition: 10 ml H_2O, 1g of LA, 0.1g catalyst, 2MPa, 220℃, 5h. Co@NC-800 with 3 equiv. of KSCN.

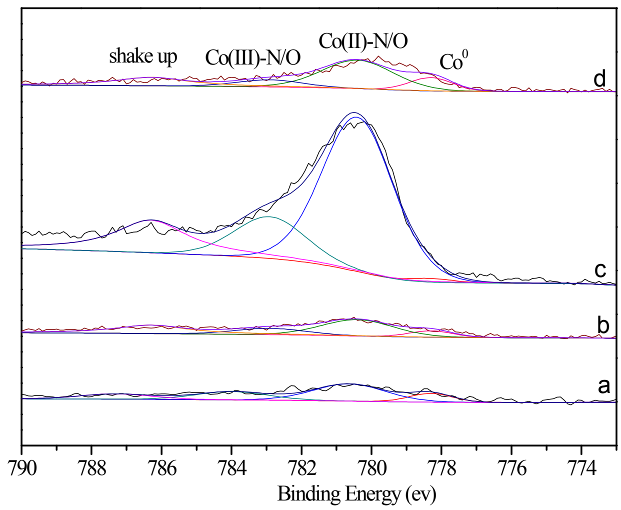

Fig. S10 The Co 2p spectra of (a) Co@NC-800 (b) Co@C-800, (c) Co@N-800, (d) Co/NC-800

Table S8 The content of Co species in Co@NC catalysts

Sample	Metallic Co (778.3 ev)	Co(II)-N/O (780.4 ev)	Co(III)-N/O (782.9 ev)	ICP Co wt%
Co@NC-800	17.0	56.0	27.0	6.5
Co@C-800	7.5	61.8	23.7	9.3
Co@N-800	1.1	77.8	21.1	71
Co/NC-800	18.6	66.2	15.2	7

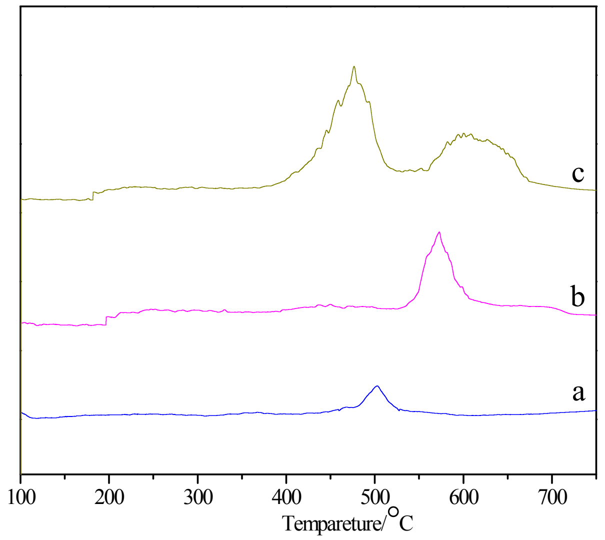

Fig. S11 NH_3-TPD of (a) Co@NC-800 (b) Co@C-800, (c) Co@N-800

Table S9 The acidity capacity of Co@NC catalysts (mmol NH_3/g)

sample	Acidity (weak)		Acidity (medium)		Acidity		Total acidity
	Temp. （℃）	Acidity	Temp. （℃）	Acidity	Temp. （℃）	Acidity	
Co@NC-800	89	0.008	515	0.035	---	---	0.043
Co@C-800	155	0.037	549	0.117	---	---	0.154
Co@N-800	135	0.028	444	0.215	598	0.122	0.365

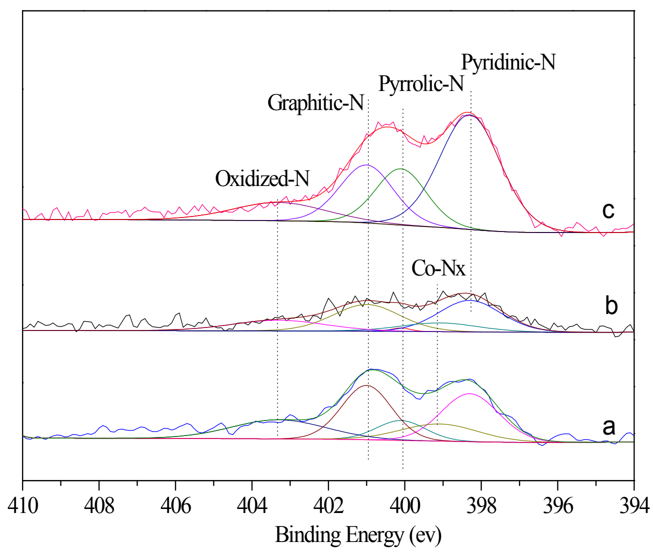

Fig. S12 The N 1s spectra of (a) Co@NC-800 (b) Co@N-800, (c) Co/NC-800

Table S10 The content of nitrogen species in Co@NC catalysts

Sample	pyridinic-N (398.3 eV)	Co-Nx (399.1 eV)	Pyrrolic-N (400.1 eV)	Graphitic-N (401.0 eV)	Oxidized-N (403.3 eV)
Co@NC-800	28.9	13.9	10.2	28.3	18.8
Co@N-800	35.7	12.4	1.2	32.45	18.2
Co/NC-800	47.5	0	19.5	21.3	11.7

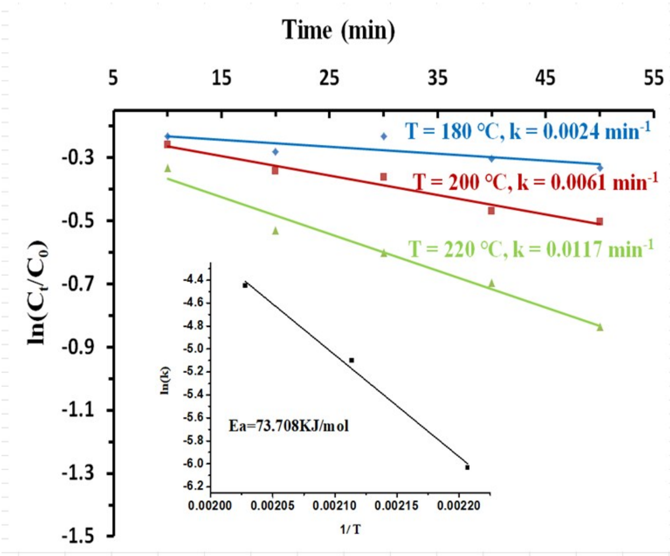

Fig. S13 Plot of $\ln(C_t/C_0)$ versus time for the hydrogenation of LA over the Co@NC-800 catalyst at different temperatures. The inset shows the corresponding Arrhenius plot. Reaction conditions: LA (1g), Co@NC-800 catalyst (0.1g), H_2O (10 mL), H_2 pressure (2 MPa).

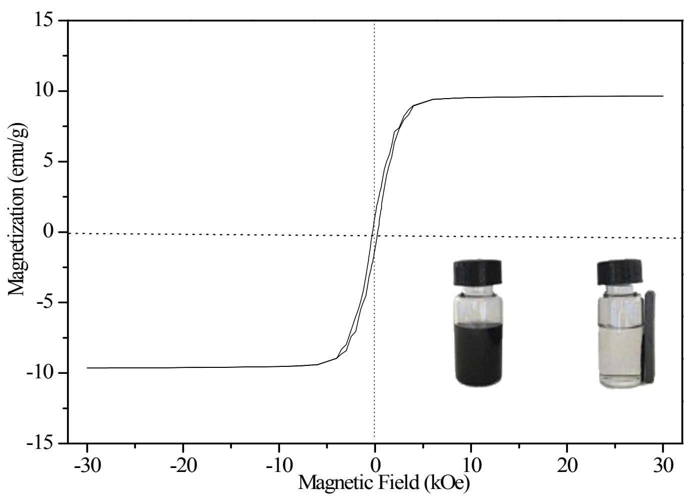

Fig. S14 Magnetic hysteresis loops of Co@NCNT-800

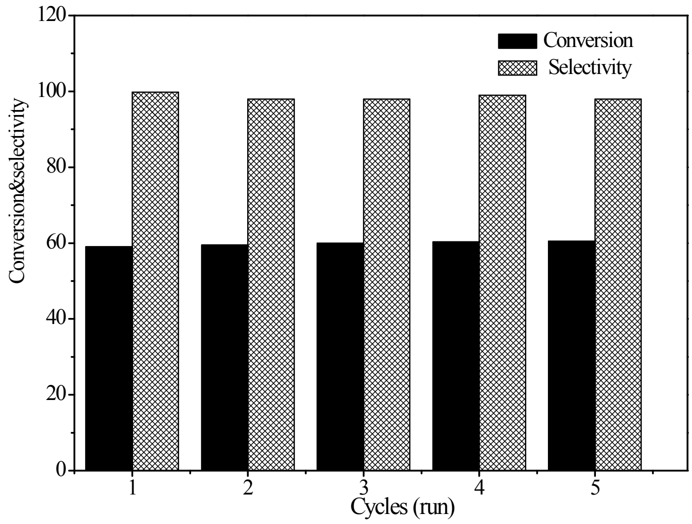

Fig. S15 The reusability results of Co@NC-800 at low conversion. Reaction conditions: LA (1g), catalyst (0.1g), H_2O (10mL), 220 ℃, 0.5 MPa H_2 and 5 h.

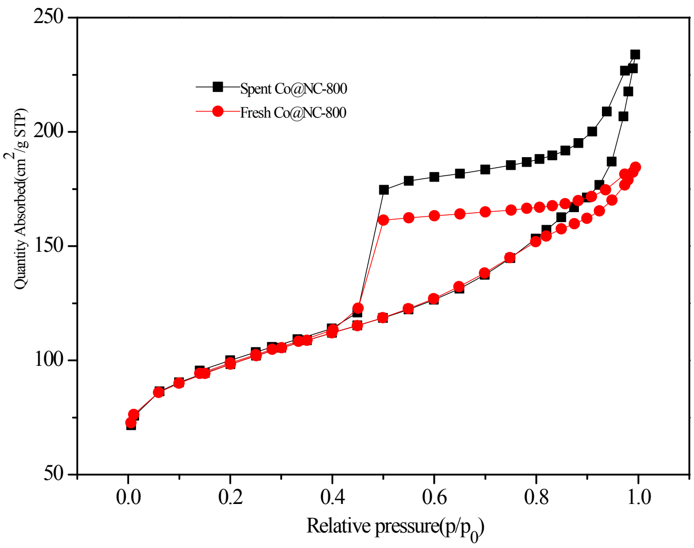

Fig. S16 N_2 sorption isotherms of the fresh and 10^{th} recycled catalysts

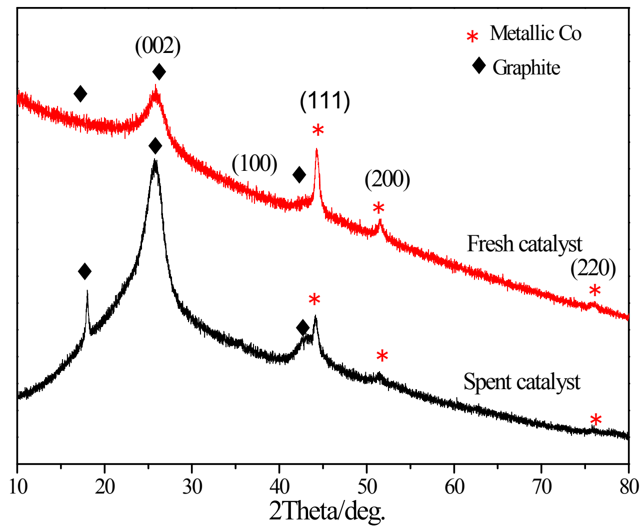

Fig. S17 XRD patterns of the fresh Co@NC-800 and spent Co@NC-800