Electronic Supplementary Material (ESI) for Green Chemistry.

Supporting Information

Scale-up biopolymer-chelated fabrication of cobalt nanoparticles encapsulated in N-enriched graphene shells for biofuel upgrade with formic acid

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Figure S1 Schematic illustration for the scale-up synthesis of Co@NG-6.

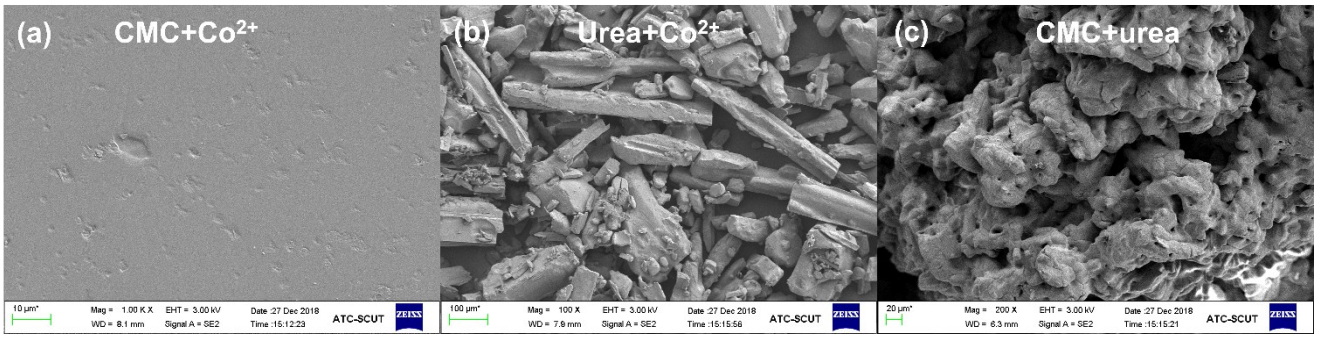

Figure S2 SEM images of unpyrolyzed Co@NG-0 precursor (a), Co/Urea precursor (b), NC-6 precursor (c).

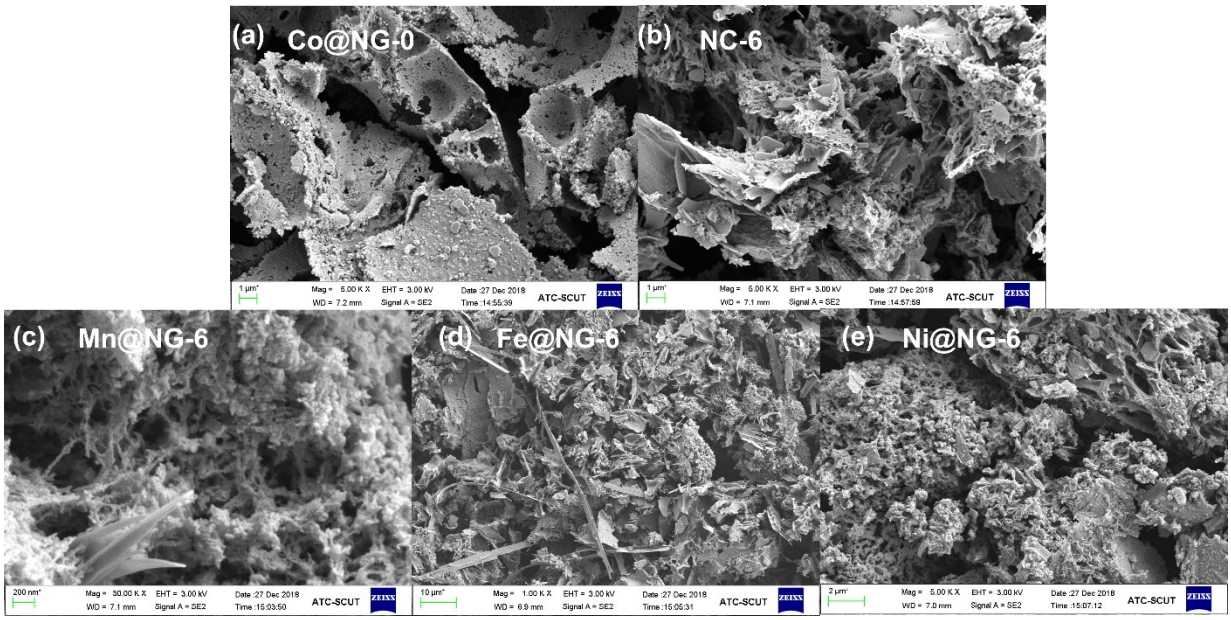

Figure S3 SEM images of NC-6 (a), Co@NG-0 (b), Mn@NG-6 (c), Fe@NG-6 (d) and Ni@NG-6 (e)

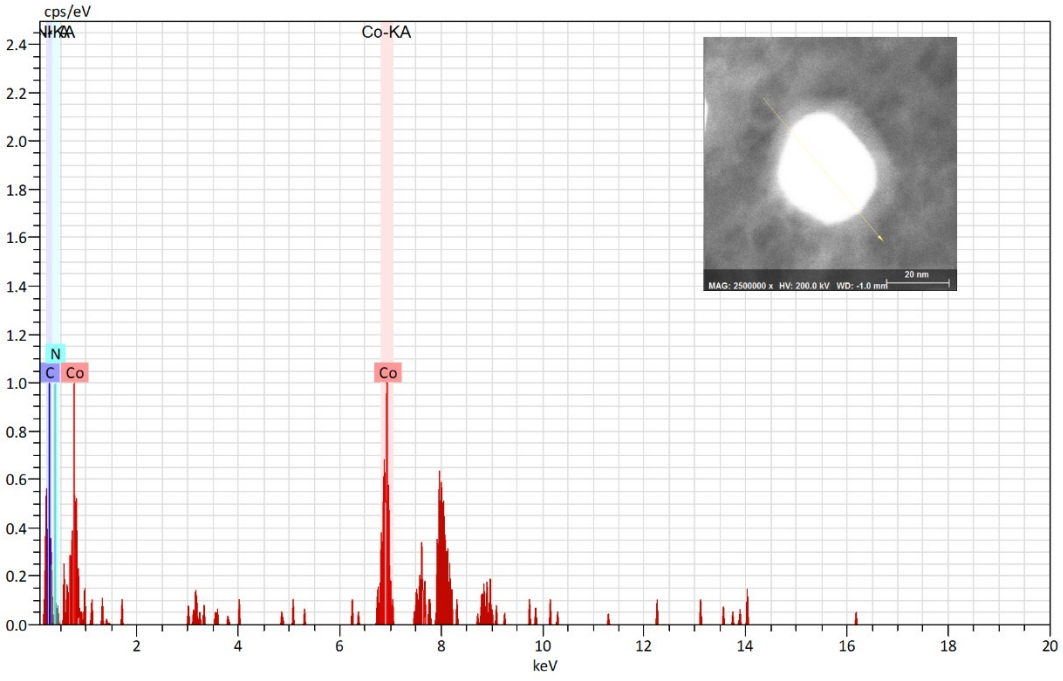

Figure S4 HRTEM-EDX of Co@NG-6.

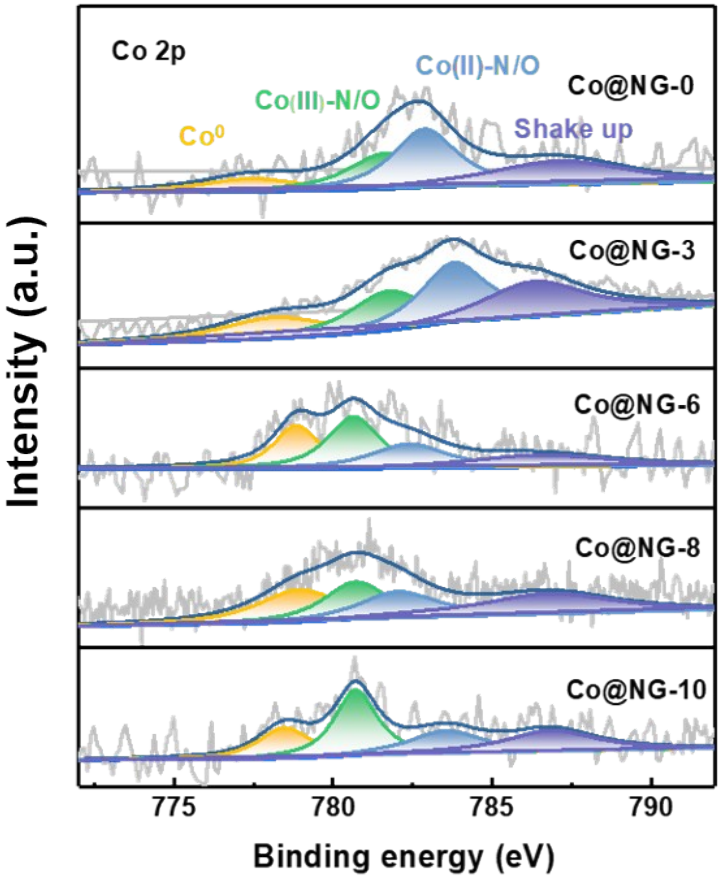

Figure S5 High-resolution Co 2p spectrum of Co@NG-U samples.

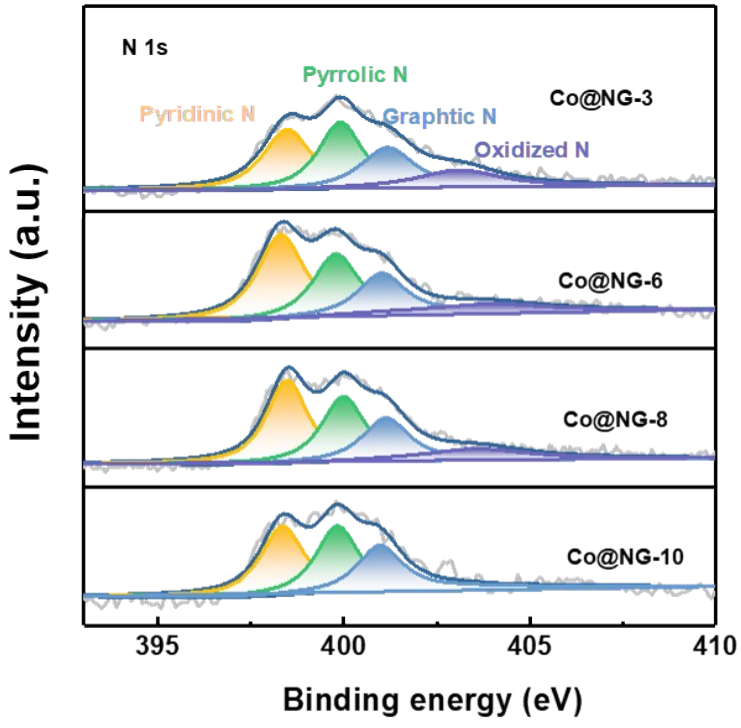

Figure S6 High-resolution N 1s spectrum of Co@NG-U samples.

Table S1. The physical properties, compositions and elemental analysis results of various catalysts.

Catalysts	S_{BET} ($m^2 \cdot g^{-1}$) [a]	Pore volume (cm^3/g) [b]	Average pore diameter (nm) [c]	Atomic content (%) [d]				Co loading (%) [e]
				Co	N	C	O	
Co@NG-0	177.16	0.32	7.66	0.18	0.2	96.1	3.52	1.22
Co@NG-3	427.95	0.33	3.69	0.73	3.44	89.6	6.23	0.88
Co@NG-5	465.01	0.33	3.61	1.12	6.33	86.67	5.88	0.90
Co@NG-6	626.66	0.37	1.93	0.54	6.72	86.94	5.80	1.01
Co@NG-8	440.05	0.33	3.84	0.36	7.04	86.00	6.60	1.34
Co@NG-10	305.81	0.26	2.97	0.64	4.32	89.82	5.21	0.87

[a] BET surface area was obtained from N_2 adsorption isotherm.
[b] Volume of pores was estimated from BJH Adsorption cumulative volume of pores.
[c] Average pore diameter was estimated from the adsorption average pore diameter.
[d] Determined by XPS analysis.
[e] Determined by ICP-OES.

Table S2. Ratio analysis of the peaks in XPS Spectra in Co@NG-U samples.

Catalysts	relative atomic percentage of N (%)				relative atomic percentage of Co (%)		
	pyridinic N	pyrrolic N	graphitic N	pyridine oxide-N	Co^0	Co(III)−N/O	Co(II)−N/O
Co@NG-0	31.7	31.5	22.7	14.1	17.3	34.4	48.4
Co@NG-3	31.1	32.6	33.0	3.2	30.9	33.7	35.4
Co@NG-6	37.6	30.4	21.2	10.7	35.0	38.8	26.3
Co@NG-8	33.2	41.4	25.4	0.0	27.9	39.5	32.6
Co@NG-10	31.7	31.5	22.7	14.1	27.6	46.5	26.0

Figure S7 Digital photo of the Co@NG-6 suspension (120 mg was dispersed in 10 mL water).

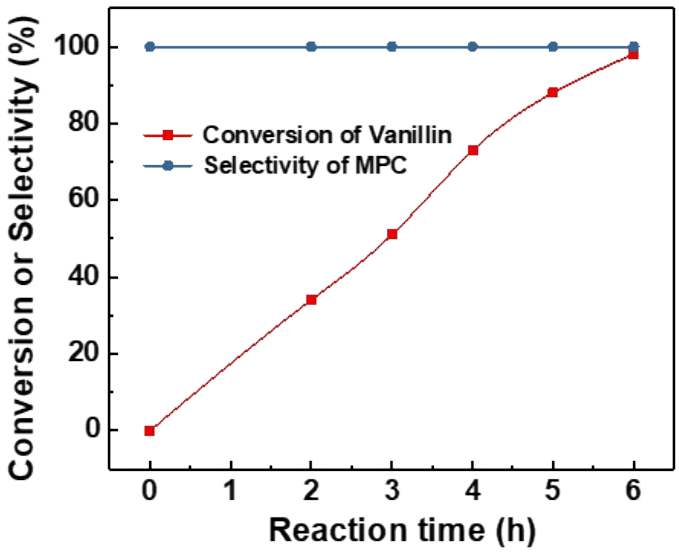

Figure S8 Effect of reaction time on THD of vanillin. Reaction conditions: 0.5mmol vanillin in 10 mL water, 250 mg FA, 160 °C, Co@NG-6 catalyst (2.3 mol% metal).

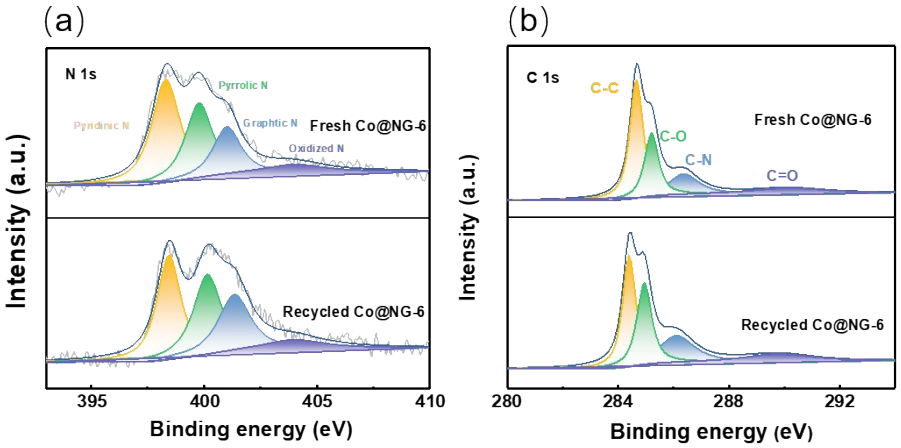

Figure S9 XPS N 1s spectrum (e) and C 1s spectrum of Co@NG-6 before and after reaction.

Table S3. Ratio analysis of Co speciation and Raman results of fresh and recycled Co@NG-6.

Catalysts	Atomic content (%) [a]			Total Co [a] (at %)	I_D/I_G [b]	I_{2D}/I_G [b]
	Co^0	Co(III)−N/O	Co(II)−N/O			
Fresh Co@NG-6	29.9	41.8	28.3	0.54	1.02	0.77
Recycled Co@NG-6	35.3	39.4	25.3	0.39	1.02	0.68

[a] Determined by XPS analysis.

[b] Determined by Raman test.

Table S4. The comparison of catalytic performance between the Co@NG-6 and previous reported catalysts.

Catalyst	Active components	Hydrogen source	Reaction pressure	T (℃)	t (h)	Vanillin Conv. (%)	MPC Selec. (%)	Reference
Ru_1/mpg-C_3N_4	Noble metal	H_2	4 MPa	160	2	100	100	1
Pd@$CN_{0.132}$	Noble metal	H_2	1 MPa	150	6	100	100	2
Au/CNT	Noble metal	H_2	1 Mpa	150	8	98	100	3
Cu_3Pd_1@BBA-1	Noble metal	H_2	1 MPa	140	8	99	94	4
Ru/CNTs	Noble metal	H_2	1 MPa	150	6	100	96	5
Co/N-C-600	Non-noble metal	H_2	1 MPa	150	8	99	99	6
Pd/TiO_2@N-C	Noble metal	HCOOH	0.5 Mpa N_2	150	4	99	100	7
Au–Pt/CeO2	Noble metal	HCOOH	1.5 Mpa N_2	150	4.5	99	100	8
Co@NC-700 (7.9 mol% Co)	Non-noble metal	HCOOH	0.5 Mpa N_2	180	4	96	100	9
15 wt%-Cu/AC-600	Non-noble metal	2-propanol	-	180	5	99	99.1	10
Cu/$Zn_{15}Al_4Sn_1$-LDH	Non-noble metal	2-propanol	-	180	4	98.5	99	11
Co@NG-6 (4.6 mol% Co)	Non-noble metal	HCOOH	-	160	6	99	100	This work

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