Electronic Supplementary Material (ESI) for Green Chemistry.

Supplementary Information

Convergent production of 2,5-furandicarboxylic acid from biomass and CO_2

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Materials and methods

Materials

Lignin (product No. 471003), dicyandiamide, furfural, 2-furoic acid, and 5-hydroxymethylfurfural (HMF) were purchased from Sigma-Aldrich. $Co(NO_3)_2.6H_2O$ and $Zn(OAC)_2.2H_2O$ were purchased from Aladdin. All reagents were of analytical grade and used without further purification.

Assembly of Co/Zn-L complex

Typically, 40 g lignin was dissolved in 4 L deionized water with mechanical stirring to form a homogenous solution. Then, 400 mL metal ions solution containing 0.08 mol $Co(NO_3)_2.6H_2O$ and 0.08 mol $Zn(OAC)_2.2H_2O$ was added into the lignin solution to yield light brown suspension of Co/Zn-L coordination complex. The pH of the mixture solution was adjusted to 6.4 with 10 wt.% aqueous ammonia, and then stirred for 1h. After ~12 h of aging at room temperature, the Co/Zn-L complex was separated by centrifugation at 5000×g for 10 min, followed by rinsing with deionized water for 3 times and dried at 80 ℃ for 12 h. Totally, 70 g of dried Co/Zn-L was obtained after three batches of assembly process. Similarly, the assembly of metal ions and water insoluble lignin can be carried out in aqueous DMF (1:1, v/v) solution.

Catalysts preparation

For the synthesis of Co SAs/N@C, the as-obtained Co/Zn-L complex was mixed with ten-fold weight of dicyandiamide by grinding in a knife mill. The mixed powder was annealed in a tube furnace under argon atmosphere with a flow rate of 70 mL/min. After annealing at 900 ℃ for 4 h, the furnace was cooled to room temperature. The as-prepared catalyst was grinded and named as Co SAs/N@C.

For synthesizing Co NPs/N@C, Co-L complex was prepared by the similar procedures of Co/Zn-L complex. The as-prepared Co-L complex was mixed with ten-fold weight of dicyandiamide and pyrolyzed in the same temperature program.

For synthesizing N@C, Zn-L complex was prepared by the similar procedures of Co/Zn-L complex. The as-prepared Zn-L complex was mixed with ten-fold weight of dicyandiamide and pyrolyzed in the same temperature program.

Characterization

The morphology and elemental mapping of catalysts were investigated by transmission electronic microscopy (TEM) on FEI TF20 with energy-dispersive X-ray (EDX) analysis. Aberration-corrected high-angle annular dark-field (HAADF) images were acquired on JEOL JEM-ARM200F. Surface area and pore structure of catalyst was determined by Brunauer Emmett-Teller (BET) method on Micromeritics ASAP 2460. Metal contents in catalysts were determined by ICP-OES on a Thermo ICAP6300 Radial. Powder x-ray diffraction (XRD) patterns were recorded on a Rigaku Ultima IV diffractometer at 40 mA and 40 kV using Cu Kα radiation. X-ray photoelectron spectroscopy (XPS) was performed on a ThermoFisher Scientific ESCALAB 250 using monochromated Al Kalph source (150 W).

Catalytic evaluation

For aerobic oxidation of furfural to furoate, typically, 1 mmol furfural, 1.5 mmol Cs_2CO_3, Co SAs/N@C ($n_{Co}/n_{furfural} = 0.03$), and 10 mL deionized water were added into a 100 mL round-bottom flask. The flask was evacuated to -0.1 MPa and then flushed with O_2 for five times. The reactant was stirred under 1 bar O_2 at 65 ℃ in a water bath for specific time, followed HPLC analysis.

The activation energy for selective oxidation of furfural over cobalt catalysts was calculated based on the Arrhenius plots. The initial reaction rates of furfural conversion (<20%) were determined in the temperature range of 308-358 K. The TOF values were calculated based on all the Co atoms in catalysts.

Gram scale synthesis of FA was carried out in a 1 L three-neck flask with bubbled O_2. The reaction system contains 30 mmol furfural, 45 mmol Cs_2CO_3, 2.4 g Co SAs/N@C, and 300 mL deionized water. The mixture was stirred at 65 ℃ for 12 h with 20 mL/min of O_2 flow. After the completion of reaction, the catalyst was separated by filtration with 0.22 μm membrane and washed with excessive water, then dried at 500 ℃ for 1 h under the argon atmosphere for next batch usage. The furoate and Cs_2CO_3 in the filtrate was obtained by concentration and lyophilization. The mixture was ground and directly used for FDCA synthesis.

Synthesis of FDCA

The appropriate amount of as-prepared mixture (contain 1 mmol FA) was weighed out into a quartz boat and placed in a tube furnace. The reactant mixture was heated to 150 ℃ for 1 h to completely remove of water under argon flow. Then, the reaction was proceeded at 260 ℃ under CO_2 flowing at 50 mL/min for 18 h, 24 h, and 36 h. After cooling to room temperature, the samples' concentration was analyzed by HPLC.

FDCA was also prepared by oxidizing HMF over Co SAs/N@C in aerobic atmosphere. 0.5 mmol HMF, 0.5 mmol Na_2CO_3, Co SAs/N@C catalyst ($n_{Co}/n_{HMF} = 0.06$), and 10 mL deionized water were added into a 100 mL round-bottom flask. The flask was evacuated to -0.1 MPa and then flushed with O_2 for five times. The reactant was stirred under 1 bar O_2 at 85 ℃ in an oil bath for12 h, followed HPLC analysis.

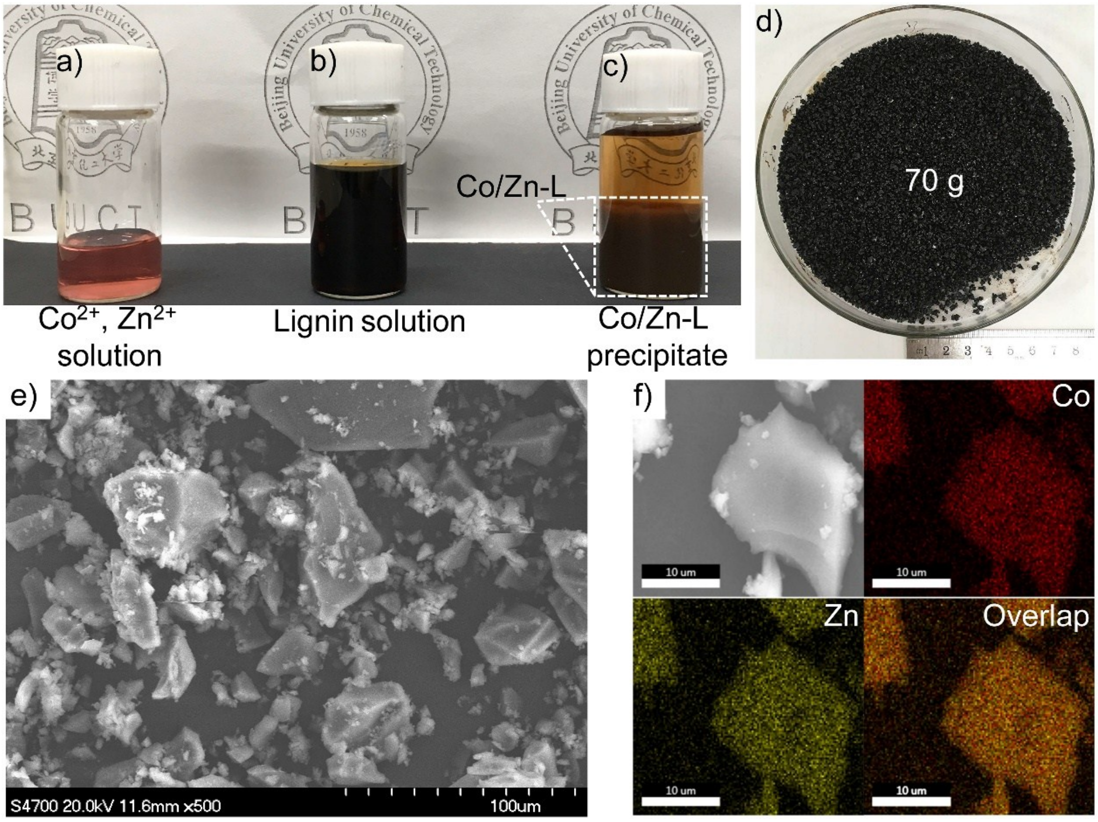

Fig. S1. Assembly of Co/Zn-L complex. (a-c) Photographic illustration of the assembly process of metal-lignin coordination complex, (d) dried Co/Zn-L, (e) SEM image of granular Co/Zn-L, and (f) EDS of Co/Zn-L.

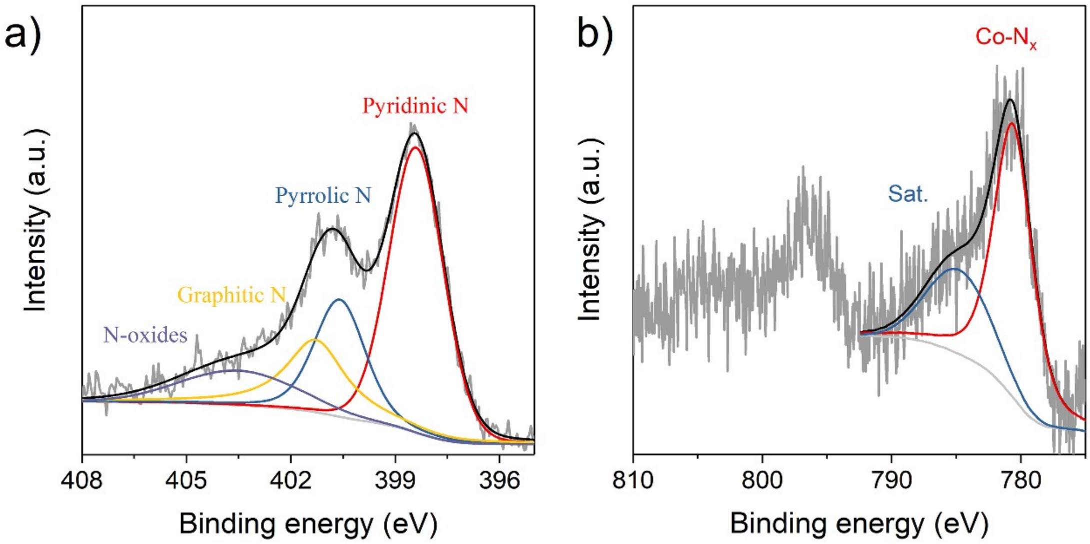

Fig. S2. a) N1s and b) Co2p XPS spectra of Co SAs/N@C.

The nitrogen species and chemical state of Co in Co SAs/N@C were investigated by x-ray photoelectron spectroscopy (XPS). As shown in Fig. S5a, the N1s spectrum demonstrate the presence of pyridinic N (398.4 eV), pyrrolic N (400.6 eV), graphitic N (401.3 eV), and N-oxides (403.5 eV) in carbon matrix.[1] The enrichment of pyridinic N and pyrrolic N in Co SAs/N@C helps to the stabilization of isolated Co atoms.[1, 2] For the Co2p XPS of Co SAs/N@C in Fig. S5b, the binding energy of Co (780.6 eV) at Co2p$_{3/2}$ is higher than that of Co^{II} (779.2 eV), but lower than that of Co^{III} (781 eV), indicating the oxidation state of Co due to the formation of Co–N$_x$ species.[2]

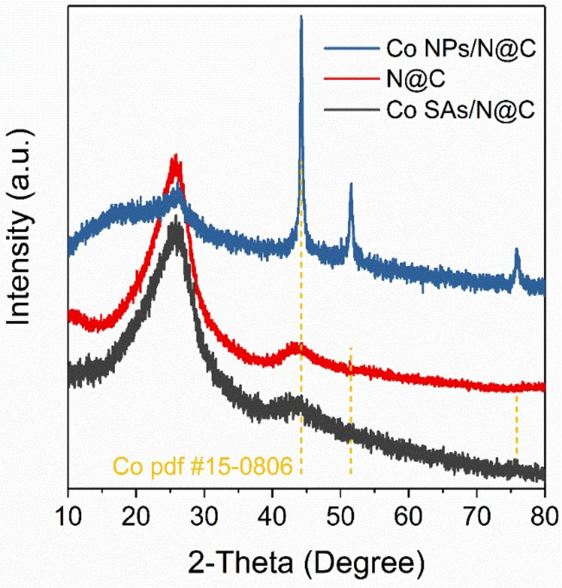

Fig. S3. XRD patterns of Co SAs/N@C, Co NPs/N@C, and N@C.

The atomically dispersion of Co atoms in Co SAs/N@C lead to the absence of diffraction peaks of metallic Co in the XRD pattern of Co SAs/N@C (Fig. S3). The content of Co in the Co SAs/N@C sample is 3.7 wt.%, determined by inductively coupled plasma optical emission spectrometry (ICP-OES).

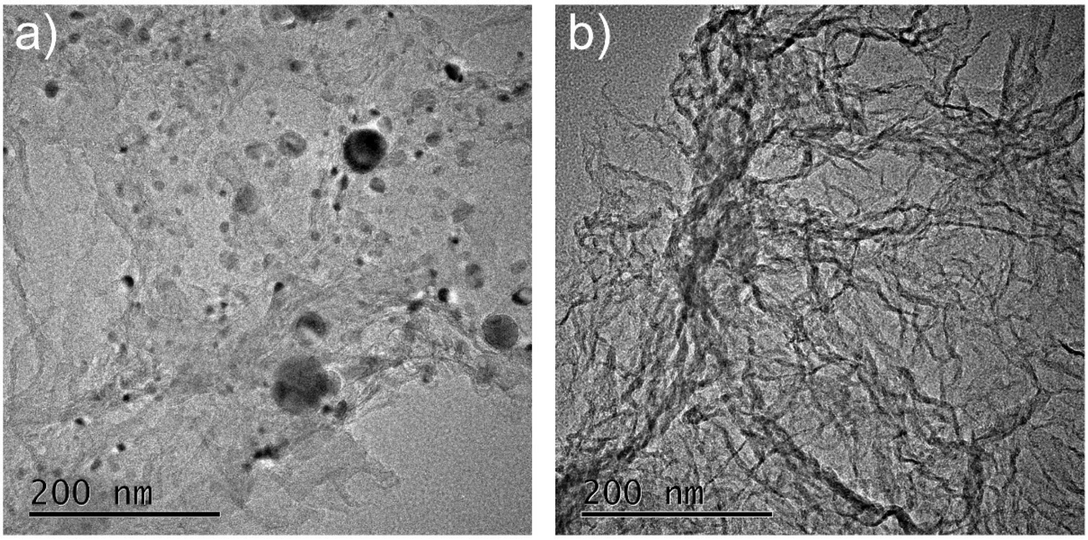

Fig. S4. TEM images of Co NPs/N@C (a) and N@C (b).

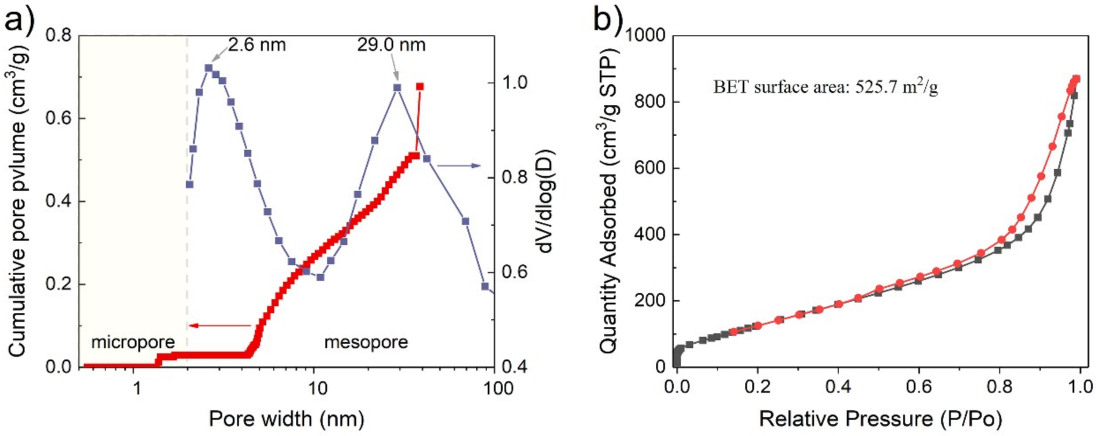

Fig. S5. Pore structure and surface area analysis. (a) Pore size distribution and (b) N_2 adsorption-desorption isotherms of Co SAs/N@C catalyst.

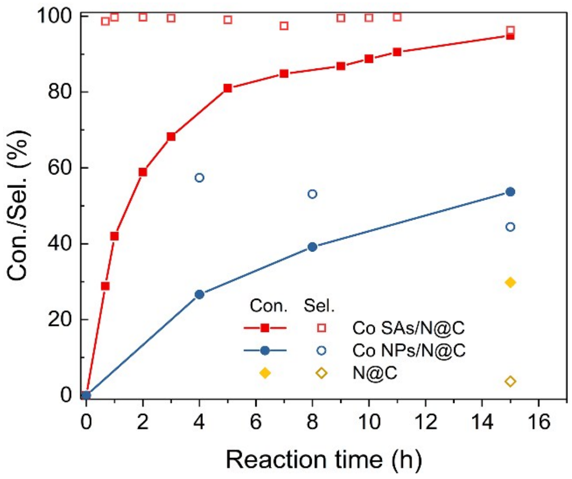

Fig. S6. Dynamic reactions. Comparison of the catalytic performance of Co SAs/N@C, Co NPs/N@C, and N@C as a function of reaction time. Reaction conditions: 1 mmol furfural, 1.5 equiv. Cs_2CO_3, catalyst ($n_{Co}/n_{furfural} = 0.03$), 10 mL H_2O, 65 ℃, 1 bar O_2.

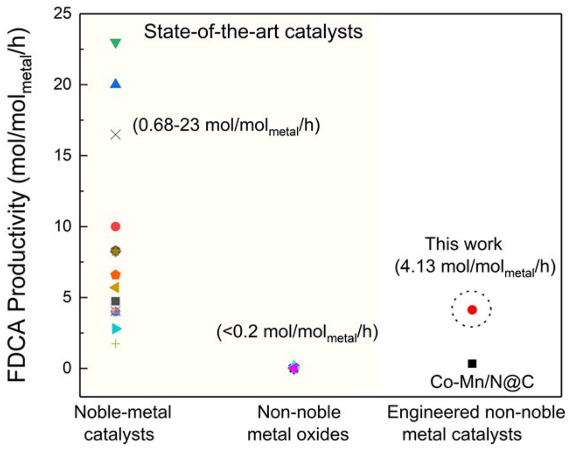

Fig. S7. The FDCA productivity of Co SAs/@C catalyst and that of literatures in C6 route. The detailed data were summarized in Table S2.

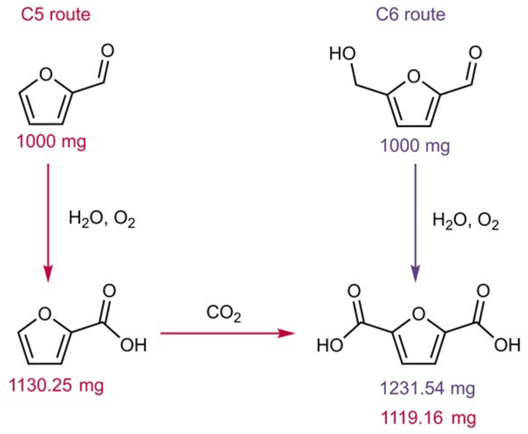

Fig. S8. The mass flow for the synthesis of FDCA via C5 and C6 route.

Table S1. Screening of reaction conditions for selective oxidation of furfural over Co SAs/N@C.[a]

Entry	T (℃)	t (h)	Conversion (%)	Selectivity (%)
1[b]	65	15	27.9	2.9
2[c]	65	15	7.0	44.4
3	65	11	90.5	99.8
4	25	48	77.5	97.4
5	25	56	82.5	95.5
6	75	7	94.8	94.2
7	85	6	93.9	87.8
8[d]	65	11	34.7	28.3

[a]: Reaction conditions: 1 mmol furfural, 1.5 equiv. Cs_2CO_3, catalyst ($n_{\mathrm{Co}}/n_{\mathrm{furfural}}$ = 0.03), 10 mL H_2O, 1 bar O_2. [b]: Same as ‘a’ without catalyst, [c]: Same as ‘a’ without base, [d]: Same as ‘a’ and the O_2 was replaced by N_2.

Table S2. Comparison of results in HMF oxidation to FDCA over reported heterogenous noble and non-noble catalysts.

Catalyst	Additive (equiv.)	O_2 (bar)	T (℃)	t (h)	HMF (%)	FDCA (%)	FDCA Productivity (mol/mol_{metal}/h)	Ref.
Au/CeO_2	0.2/ Na_2CO_3	5	140	15	99.9	91	4.73	[3]
Au/HSAG-N	2/$NaHCO_3$	10	90	12	99	75	10	[4]
AuCe25Zr	0.02/NaOH	10	70	4	100	80	20	[5]
Au-Ce	4/NaOH	10	70	4	100	92	23	[6]
Au/HT-AC	-	5	100	12	100	99	8.25	[7]
Pd Nanocrystals	4/$NaHCO_3$	1	90	4	100	91.3	5.7	[8]
Pd-HT-5	-	1	100	7	99.9	98	2.8	[9]
Pd/HPGS	1/NaOH	1	50	6	100	83.1	8.31	[10]
Au-Pd/MgO	-	5	100	12	100	99	8.25	[11]
Pd-Au/HT	-	1	60	6	100	90	-	[12]
γ-Fe_2O_3@HAP-Pd	0.5/K_2CO_3	1	100	6	97	92.9	6.59	[13]
Pd/C@Fe_3O_4	0.5/K_2CO_3	1	80	6	98.4	86.7	3.99	[14]
Pt/C	-	40	110	16	100	93	1.74	[15]
Pt-ACS-800	-	10	110	5	100	75	16.49	[16]
Pt/C-O-Mg	-	10	110	12	99	97	4.04	[17]
Ru/C	$CaCO_3$	2	120	5	100	95	3.8	[18]
Ru-Fe_3O_4@SiO_2	-	10	110	48	92	80.6	0.68	[19]
Ru/$MnCo_2O_4$	-	24	120	10	100	99.1	3.3	[20]
Ru/$Mn_6Ce_1O_Y$	-	10	120	18	100	95	2.6	[21]
Ru/$ZrO_{2\ \text{H-aero}}$	-	10	120	16	100	97	1.89	[22]
MnO_2	2/$NaHCO_3$	10	100	24	99	91	0.013	[23]
MnO_2	3/$NaHCO_3$	10	100	24	99	91	0.007	[24]
MnO_2	-	9	130	12	99	74.7	0.15	[25]

$MnCo_2O_4$	-	24	120	10	57.8	10.9	0.004	[20]
Mn0.75/Fe0.25	4/NaOH	8	90	24	93	29.76	-	[26]
MnO_x-CeO_2	2/$KHCO_3$	20	110	12	98.5	88.7	-	[27]
$CuO\cdot MnO_2\cdot CeO_2$	-	2	130	3	99	97.7	0.08	[28]
Co-Mn-0.25	2/$NaHCO_3$	10	120	5	99	95.2	-	[29]
$Fe_{0.6}Zr_{0.4}O_2$	-	20	160	24	99.7	60.6	0.026	[30]
Co-Mn/N@C	1/ Na_2CO_3	1	85	12	99.7	96.1	0.33	[31]
Co SAs/N@C	1/ Na_2CO_3	1	85	3	99.4	74.4	4.13	This work
				8	100	99.5	2.07	

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