## **Supplementary Information**

Sustainable natural nanofibrous confinement strategy to ultrafine  $Co_3O_4$  nanocatalysts embedded in N-enriched carbon fibers for efficient biomass-

## derivatives in situ hydrogenation

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Fig. S1 Schematic illustration for the preparation of BC aerogel.



Fig. S2 SEM images of CNF (a), Co<sub>3</sub>O<sub>4</sub>/NCNF (b).



**Fig. S3** SEM images of Co<sub>3</sub>O<sub>4</sub>/C.



Fig. S4 TEM element mapping images (d) of  $Co_3O_4/NCNF$ .



Fig. S5 HRTEM-EDX of Co<sub>3</sub>O<sub>4</sub>/NCNF.



Figure S6 TG and DTG curves of BC and 20% and 40% Co<sub>3</sub>O<sub>4</sub>/NCNF.

		Content (wt.%) <sup>a</sup>	
Catalysts	С	Ν	Н
BC	36.3	1.1	5.0
Co <sub>3</sub> O <sub>4</sub> /C	43.6	0.4	1.1
Co <sub>3</sub> O <sub>4</sub> /CNF	44.9	1.2	2.1
Co <sub>3</sub> O <sub>4</sub> /NCNF	48.4	6.3	2.0

 Table S1 The results of elemental analysis for various catalysts

<sup>a</sup> Determined by elemental analysis.

Entry	Catalysts	CAL COL			
		Conv. (%)	COL Sel. (%) <sup>b</sup>		
1	Blank	0.2	100		
2	Co <sub>3</sub> O <sub>4</sub>	3.1	99		
3	С	0.4	99		
4	CNF	1.4	99		
5	NCNF	4.6	99		
6	Co <sub>3</sub> O <sub>4</sub> /NCNF	36.8	99		
7	Mn <sub>3</sub> O <sub>4</sub> /NCNF	30.25	99		
8	Fe <sub>3</sub> O <sub>4</sub> /NCNF	8.3	99		
9	NiO/NCNF	9.9	99		
10 °	Co <sub>3</sub> O <sub>4</sub> + NCNF	8.2	99		

Table S2 Catalytic results for different catalysts <sup>a</sup>

<sup>a</sup> Reaction conditions: 0.5mmol CAL in 5ml 2-propanol, 50mg catalyst, 160 °C, 3h.

<sup>b</sup> The by product is phenylpropanol. <sup>c</sup>Co<sub>3</sub>O<sub>4</sub> and NCNF were physically mixed.



Fig. S7 Representative MS spectra of the reaction mixture in FAL hydrogenation.



Fig. S8 Raman spectra (a) and FT-IR spectra (b) of  $Co_3O_4/NCNF$  before and after the reaction. N 1s spectrum (c) of recycled  $Co_3O_4/NCNF$ .

Table S3 The results of elemental analysis for various catalysts

Catalysts			Content (wt.%)	
	Co <sup>a</sup>	N <sup>b</sup>	C <sup>b</sup>	O <sup>b</sup>
Co <sub>3</sub> O <sub>4</sub> /NCNF	2.93	4.66	79.85	12.55
Recycled Co <sub>3</sub> O <sub>4</sub> /NCNF	2.67	4.2	76.64	16.48

<sup>a</sup> Determined by ICP-OES.

<sup>b</sup> Determined by elemental analysis.

Entry	Sample	Co <sub>3</sub> O <sub>4</sub> mean size	Application	Ref.
1	Co <sub>3</sub> O <sub>4</sub> /graphene	10-30 nm	Lithium-ion batteries	[1]
2	N-doped PC-Co <sub>3</sub> O <sub>4</sub>	5–10 nm	Lithium-ion batteries	[2]
3	R-Co <sub>3</sub> O <sub>4</sub> /C	3-10 nm	Sodium-Ion Batteries	[3]
4	NC-Co <sub>3</sub> O <sub>4</sub>	10–20 nm	Zinc-Air Batteries	[4]
5	Co <sub>3</sub> O <sub>4</sub> /rGO	30 nm	Li-ion batteries	[5]
6	Co <sub>3</sub> O <sub>4</sub> @NCFs	3–6 nm	lithium/sodium storage	[6]
7	Co <sub>3</sub> O <sub>4</sub> /N-PC	15–30 nm	lithium storage and water splitting	[7]
8	NCA/Co <sub>3</sub> O <sub>4</sub>	5–35 nm	Supercapacitors	[8]
9	Co <sub>3</sub> O <sub>4</sub> /CNFs	3-5 nm	Supercapacitor	[9]
10	Co <sub>3</sub> O <sub>4</sub> @C-MWCNTs	10–25 nm	OER and ORR	[10]
11	Co <sub>3</sub> O <sub>4</sub> -CNFs	20 - 40 nm	Electrodes	[11]
12	HCo <sub>3</sub> O <sub>4</sub> /C	6–12 nm	Peroxymonosulfate activation	[12]
13	Co <sub>3</sub> O <sub>4</sub> @C@PGC	10–20 nm	microwave absorber	[13]
14	Co <sub>3</sub> O <sub>4</sub> -N@C	2–10 nm	Catalysts	[14]
15	CoO <sub>x</sub> @NCNTs	12.9 nm	Catalysts	[15]
16	Co <sub>3</sub> O <sub>4</sub> /MC	3 nm	Catalysts	[16]
17	Co <sub>3</sub> O <sub>4</sub> /carbon	8–25 nm	Catalysts	[17]
18	ZIF-Co <sub>3</sub> O <sub>4</sub> /NCF	5–8 nm	Catalysts	[18]
19	Co <sub>3</sub> O <sub>4</sub> /NCNFs	1.0-2.5 nm	Catalysts	This work

Table S4 The comparison of  $Co_3O_4$  nanoparticle size with previously reported catalysts.

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Entry	Catalyst	Substrate	H-donor	Reaction conditions	Conv. (%)	Sel. of alcohol (%)	Ref.
1	1.0Pt-5.3FeO <sub>x</sub> /SiO <sub>2</sub> -GD	CAL	1 MPa H <sub>2</sub>	150 °C, 2 h	41	92	[19]
2	Pt-Re/rGO	CAL	$2 \text{ MPa H}_2$	120 °C, 4 h	94.1	88.7	[20]
3	Au//In <sub>2</sub> O <sub>3</sub>	CAL	$1 \text{ MPa H}_2$	180 °C, 18 h	91	84	[21]
4	CoPt/Fe <sub>3</sub> O <sub>4</sub>	CAL	3 MPa H <sub>2</sub> , 2-propanol	160 °C, 3 h	95	84	[22]
5	Cu-Au/SiO <sub>2</sub>	CAL	$2 \text{ MPa H}_2$	100 °C, 3 h	55.0	53.0	[23]
6	Ni-Co/MWCNT	CAL	$0.5 \text{ MPa H}_2$	150 °C, 8 h	62.6	62.1	[24]
7	Au/Zn <sub>0.7</sub> Fe <sub>0.3</sub> Ox	CAL	2-propanol, 1 MPa H <sub>2</sub>	140 °C, 10 h	75.4	88.5	[25]
8	ZIF-67@SiO <sub>2</sub> -CPTEOS	CAL	2-propanol, 1 MPa N <sub>2</sub>	180 °C, 18 h	99	93.25	[26]
9	2%Pt-1%Re/TiO <sub>2</sub> -ZrO <sub>2</sub>	FAL	$5 \text{ MPa H}_2$	130 °C, 8 h	100	95.7	[27]
10	Co/SBA-15	FAL	$2 \text{ MPa H}_2$	150 °C, 1 h	80	96	[28]
11	Ni-Sn/AlOH	FAL	$3 \text{ Mpa H}_2$	180 °C, 75 min	95	91	[29]
12	Cu:Zn:Cr:Zr(3:2:1:3)	FAL	$2 \text{ MPa H}_2$	170 °C, 3.5 h	100	96	[30]
13	Fe-L4(L5)/C-800	FAL	2-propanol	160 °C, 15 h	91.6	83	[31]
14	LaFeO <sub>3</sub> _N	FAL	2-propanol	180 °C, 3 h	-	-	[32]
15	Pd/Fe <sub>2</sub> O <sub>3</sub>	FAL	2-propanol	180 °C, 7.5 h	100	34	[33]
16	Cu/MgO-Al <sub>2</sub> O <sub>3</sub>	FAL	2-propanol	210 °C, 1 h,	100	89	[34]
17	DyCl <sub>3</sub>	FAL	2-propanol	180 °C, 3 h, (2Mpa N <sub>2</sub> )	98	97	[35]
18	Al <sub>7</sub> Zr <sub>3</sub> @Fe <sub>3</sub> O <sub>4</sub>	FAL	2-propanol	180 °C, 4 h	99.1	90.5	[36]
19	Fe <sub>2</sub> O <sub>3</sub> @HAP	FAL	2-propanol	180 °C, 10 h	96.2	95.3	[37]
20	NiFe <sub>2</sub> O <sub>4</sub>	FAL	2-propanol	180 °C, 6 h	99	95	[38]
21	Cu <sub>2</sub> Al	FAL	methanol	200 °C, 2.5 h, (1Mpa N <sub>2</sub> )	100	94	[39]
22	γ-Al <sub>2</sub> O <sub>3</sub>	FAL	2-propanol	150 °C, 6 h	100	90	[40]
23	e HT_MgFe-3	FAL	2-propanol	170 °C, 6 h	99	90	[41]
24	Co <sub>3</sub> O <sub>4</sub> /NCNF	CAL	2-propanol	160 °C, 5 h	100	95	This work
25	Co <sub>3</sub> O <sub>4</sub> /NCNF	FAL	2-propanol	160 °C, 2 h	91.0	88	This work
26	Co <sub>3</sub> O <sub>4</sub> /NCNF	FAL	2-propanol	160 °C, 3.5 h	99	85	This work

Table S5 The comparison of CTH of CAL and FAL with  $H_2$  or H-donor reaction systems with previously reported catalysts.

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