Supporting information

Transfer hydrogenation of bio-fuel with formic acid over biomass-derived N-doped carbon supported acid-resistant Pd catalyst

Renfeng Nie, Xiaolun Peng, Haifu Zhang, Xiaolong Yu, Xinhuan Lu, Dan Zhou, Qinghua Xia*

Hubei Collaborative Innovation Center for Advanced Organic Chemical Materials, & Ministry-of-Education Key Laboratory for the Synthesis and Application of Organic Functional Molecules, School of Chemistry and Chemical Engineering, Hubei University, Wuhan 430062, P.R. China

* Corresponding author

Qinghua Xia, Hubei University, Wuhan 430062, P.R. China

Tel/Fax: 86-27-88662747

Email: xiaqh518@aliyun.com

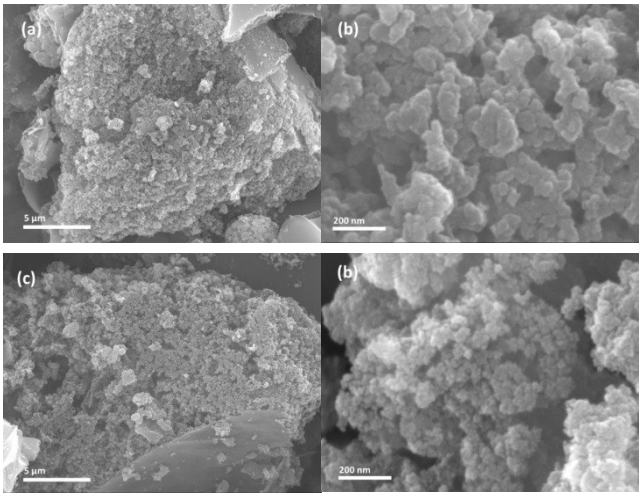

Fig. S1 The SEM images of (a, b) MC and (c, d) NMC.

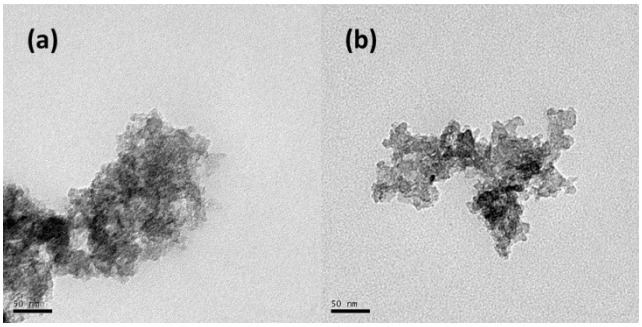

Fig. S2 The TEM images of (a) MC and (b) NMC.

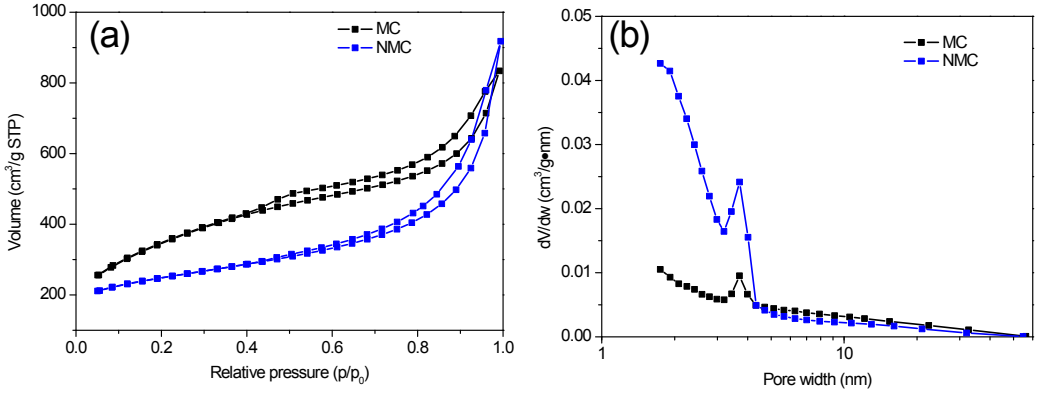

Fig. S3 (a) Nitrogen sorption isotherms and (b) pore size distribution of NMC.

Table S1 Pore textural properties of MC and NMC.

Samples	S_{total} (m^2/g)	Pore volume (cm^3/g)			V_{meso}/V_{total}	Pore size
		V_{total}	V_{micro}	V_{meso}	(%)	(nm)
MC	1228	1.28	0.28	1.00	78.4	4.3
NMC	1017	1.41	0.11	1.30	92.1	9.1

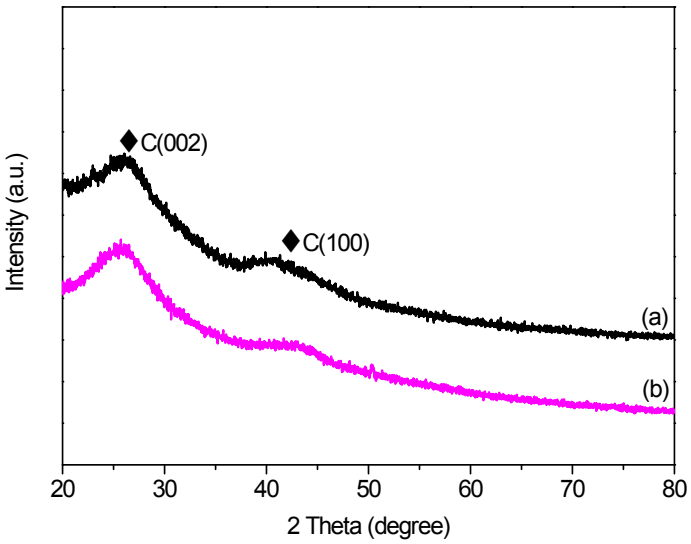

Fig. S4 XRD patterns of (a) MC and (b) NMC.

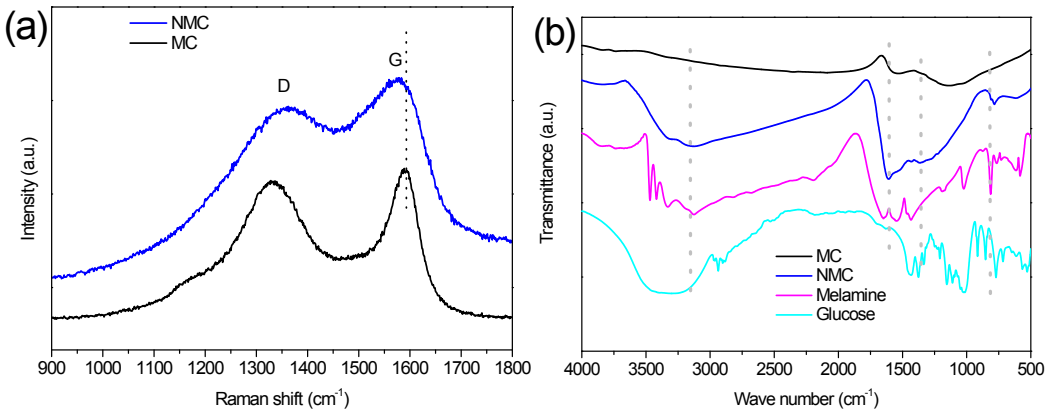

Fig. S5 Raman (a) and FT-IR (b) spectra of carbon materials.

Table S2 Raman and element analysis results of carbons.[a]

Sample	G band position (cm^{-1})	I_D/I_G	Mass concentration (%)				
			C [a]	H [a]	N [a]	N[b]	O (calculated)
MC	1590	0.92	84.72	1.41	0	0	13.87
NMC	1579	0.86	68.33	4.06	15.37	14.85	12.24

[a] Detected by CHNS elemental analysis.

[b] Detected in XPS analysis.

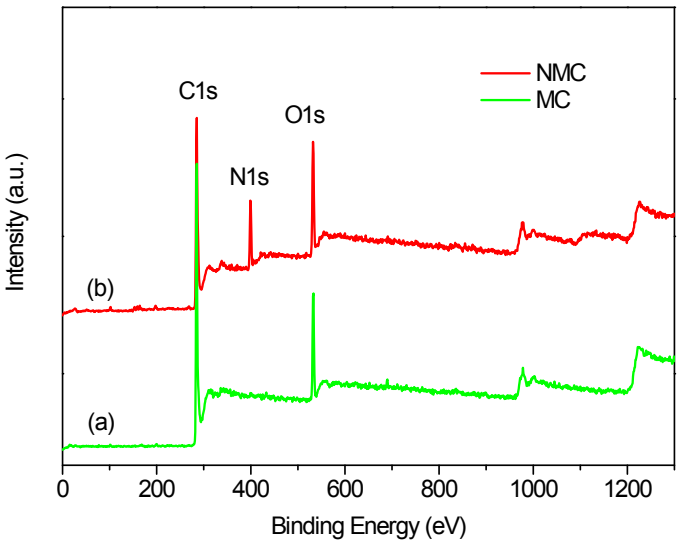

Fig. S6 XPS survey spectra of (a) MC and (b) NMC.

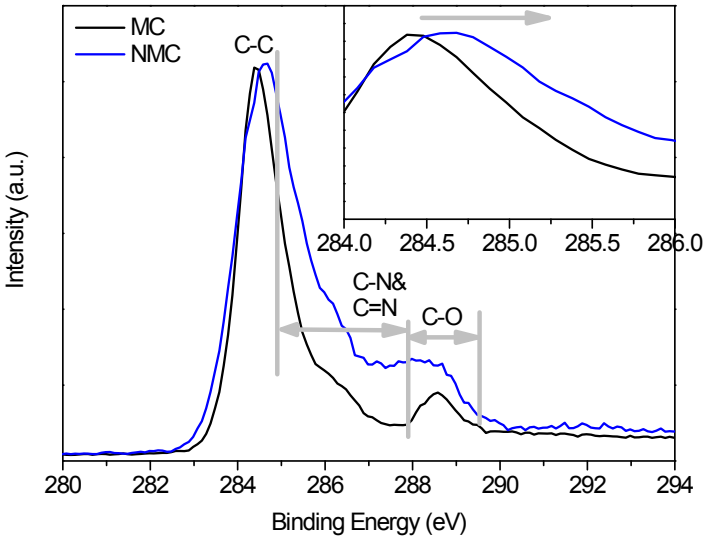

Fig. S7 XPS spectra of C1s of NMC.

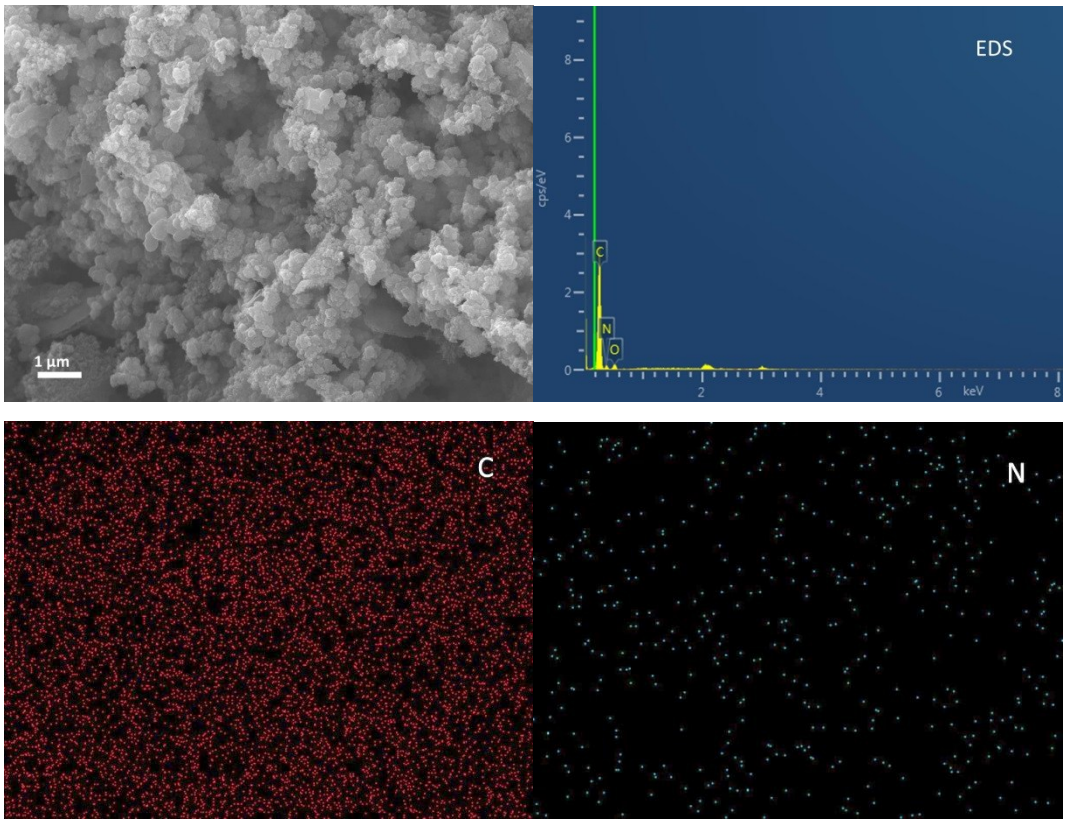

Fig. S8 Surface EDS analysis of NMC.

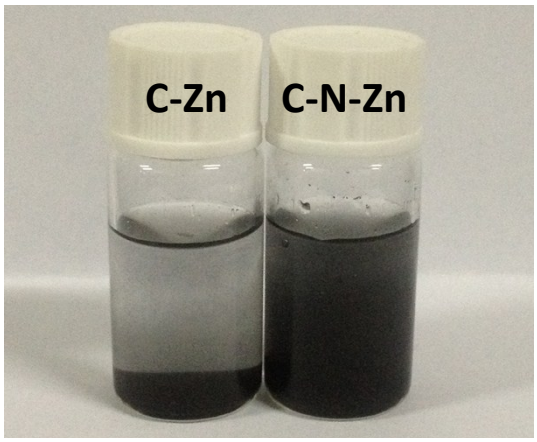

Fig. S9 Photographs of the dispersions of MC and NMC in water, after sonication for 5 min and storage for 10 min under ambient conditions.

As shown in Fig. S9, when MC and NMC are suspended in water, followed by sonicated for 5 min, N-doped carbon is well dispersed in water after storage for 10 min under ambient conditions, while pure carbon sample is easily to precipitate.

Table S3 Pore textural properties of NMC from different ratio of glucose to melamine.

Samples[a]	S_{total} (m^2/g)	N content (wt. %)	Pore volume (cm^3/g)			V_{meso}/V_{total} (%)
			V_{tota}	V_{micro}	V_{meso}	
MC(8:0)	1228	0	1.28	0.28	1.00	78.4
NMC(6:2)	1149	9.11	1.21	0.17	1.04	85.7
NMC(1:1)	1017	15.37	1.41	0.11	1.30	92.1
NMC (2:6)	723	17.24	1.14	0.23	0.91	79.8
NMC (1:7)	540	21.43	0.67	0.19	0.48	71.6
NMC (0:8)	-[b]	-	-	-	-	-

[a] The parenthesis is the weight ratio of glucose to melamine.

[b] No product is obtained.

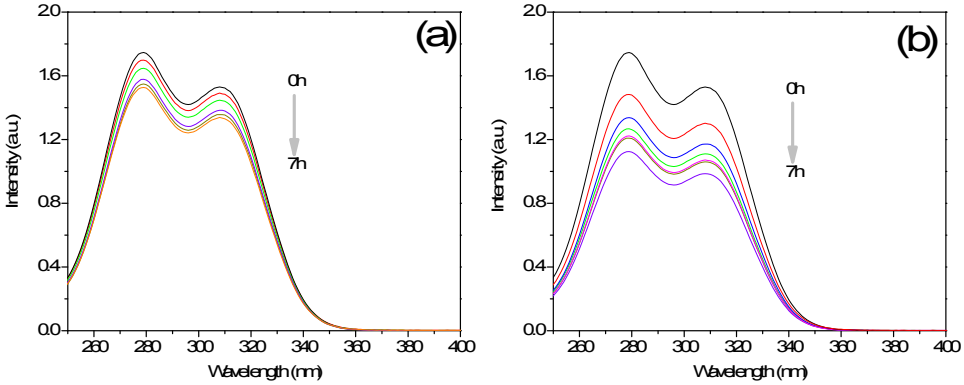

Fig. S10 The UV-vis spectra of vanillin adsorption on (a) MC and (b) NMC.

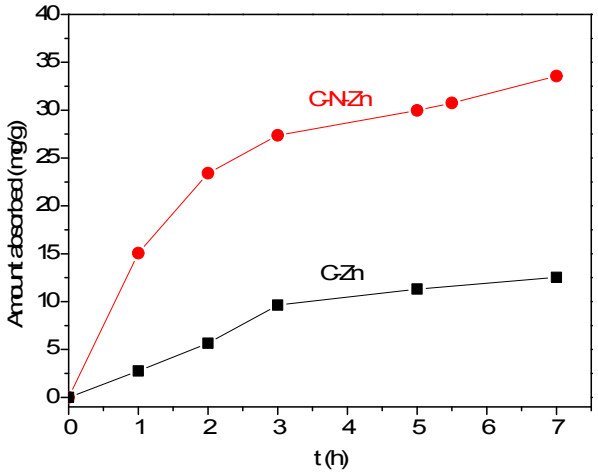

Fig. S11 The amount of vanillin absorbed on MC and NMC.

Table S4 Hydrogenation of vanillin with molecule H_2 over Pd/NMC catalyst.

Entry	T (°C)	t (h)	Vanillin conversion (%)	MMP selectivity (%)
1	80	0.5	100	100
2	80	1	100	100
3	150	1	100	100

Reaction conditions: vanillin (0.5 mmol), catalyst (20 mg), H_2O (10 mL), 0.5 MPa H_2.

Table S5 Decomposition of FA over Pd/NMC catalyst.

Entry	T (°C)	t (h)	Conversion of FA (%)
1	80	1	8.1
2	80	2	10.7
3	150	2	96.2

Reaction conditions: FA (3 mmol), catalyst (20 mg), H_2O (10 mL).

From **Table S4**, it can be found that vanillin is smoothly transformed into MMP with 100 % conversion and 100 % selectivity at 150 °C for 1 h. Further decreasing temperature (80 °C) or time (0.5 h) can still afford 100 % yield of MMP. As shown in **Table S5,** FA is hard to decompose over Pd/NMC at 80 °C, while increasing temperature to 150 °C, FA conversion could achieve as high as 96.2 %. These results indicate that vanillin hydrogenation is easier than that of FA decomposition over Pd/NMC. That is to say, FA decomposition is the rate-determined step in the transfer hydrogenation of vanillin with FA over Pd/NMC catalyst.

Table S6 The ICP analysis of fresh and reused Pd/NMC by 5 times.

Catalysts	Pd loading (wt. %)		Leaching (%)
	Fresh	Reused	
Pd/MC	2.14	1.98	7.3
Pd/NMC	2.21	2.19	0.6