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Supplementary data

Upcycling of spent functional biocarbon adsorbents to catalysts for conversion of C5/C6 carbohydrates into platform chemicals

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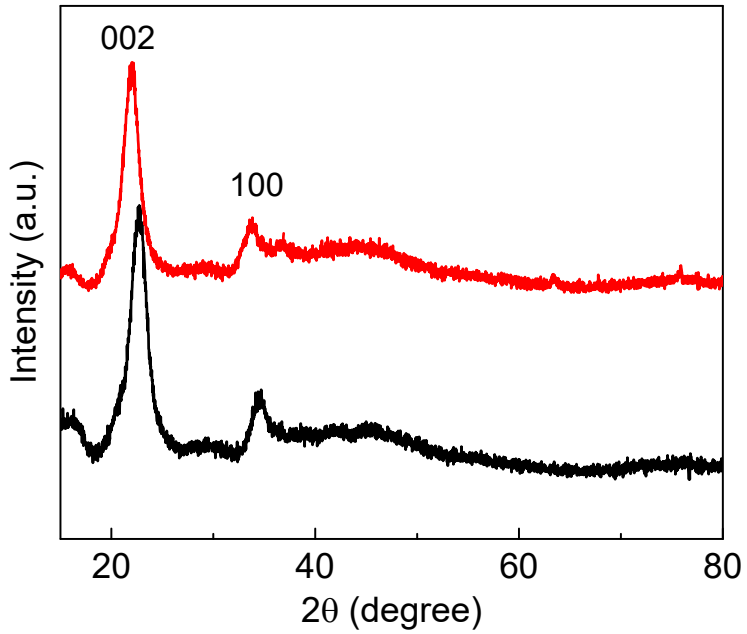

Figure S1. XRD patterns of as-prepared functional biocarbons. Black line: HC; Red line: N-HC.

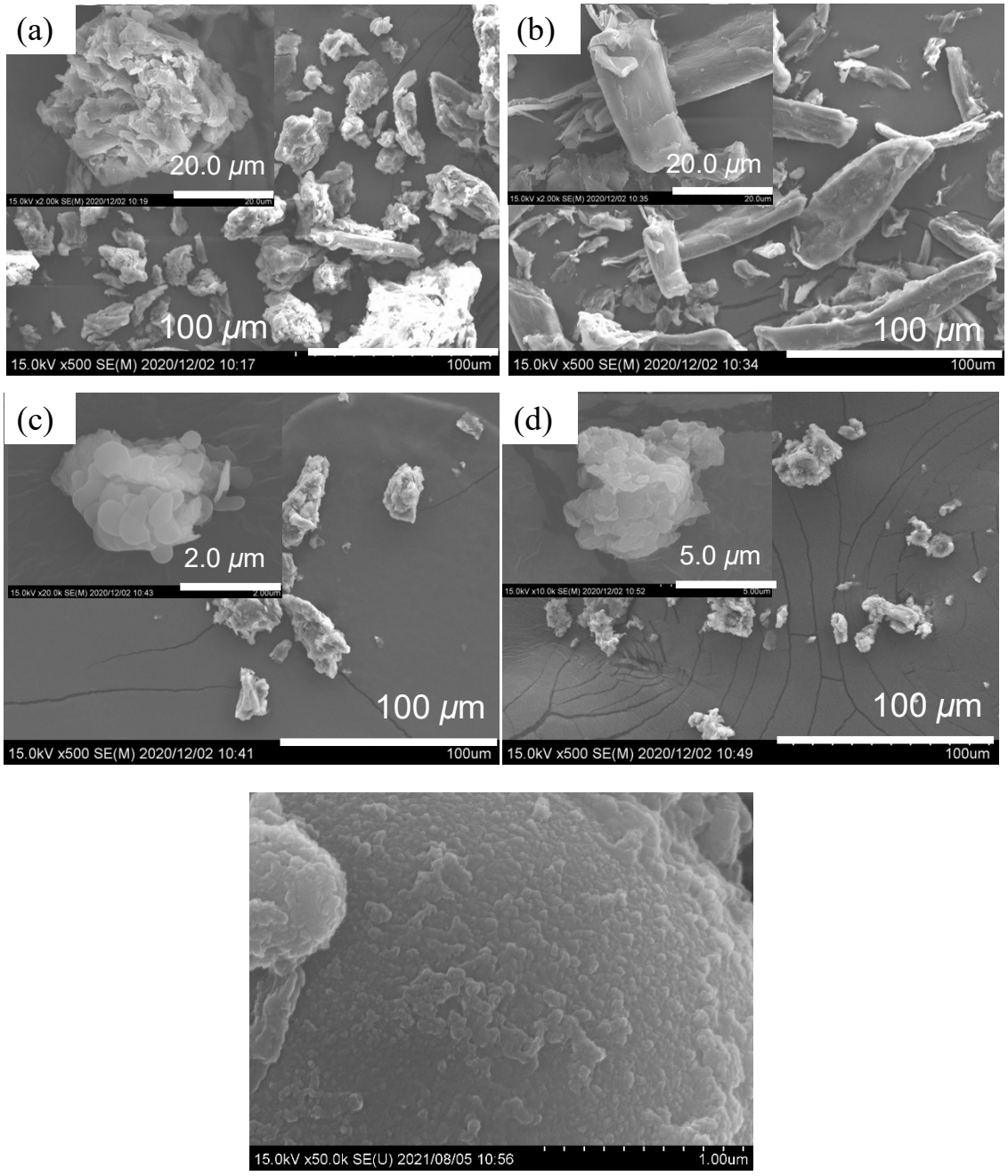

Figure S2. SEM images of as-prepared biocarbon materials (a) HC, (b) N-HC (c) B-HC and (d) BN-HC and (e) Ni-BNS-HC.

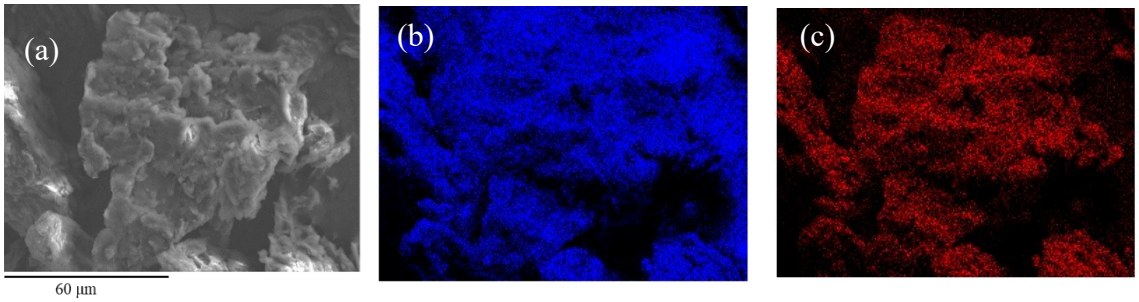

Figure S3. SEM-EDX images of as-prepared HC biocarbon materials: (a) SEM image, and corresponding EDX maps of: (b) carbon, (c) oxygen.

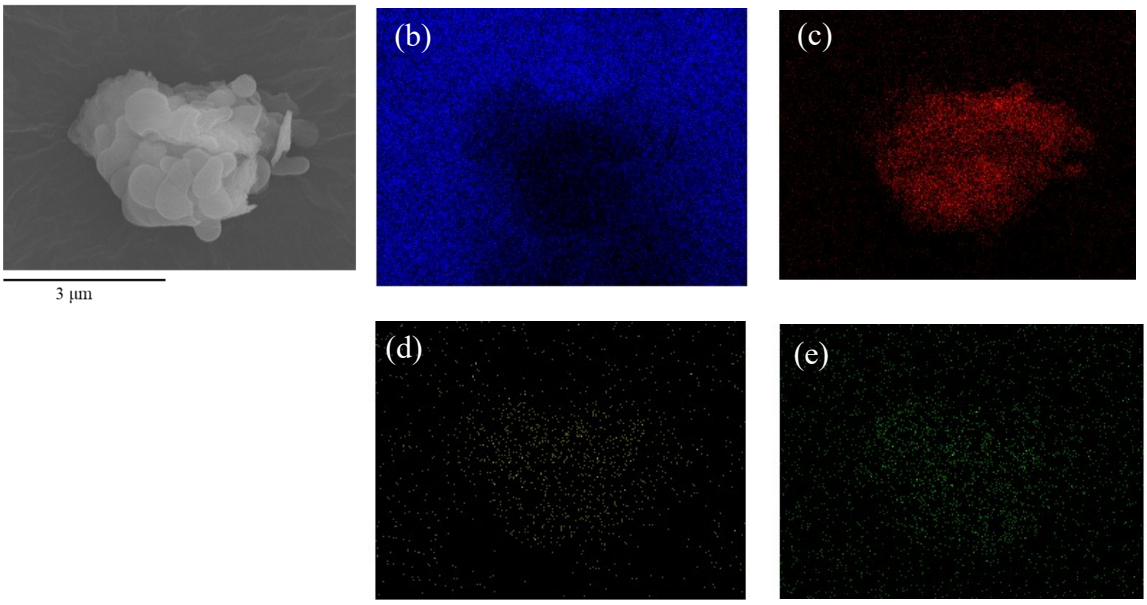

Figure S4. SEM-EDX images of as-prepared B-HC biocarbon materials: (a) SEM image and corresponding EDX maps of (b) carbon, (c) oxygen, (d) nitrogen, (e) sulfur.

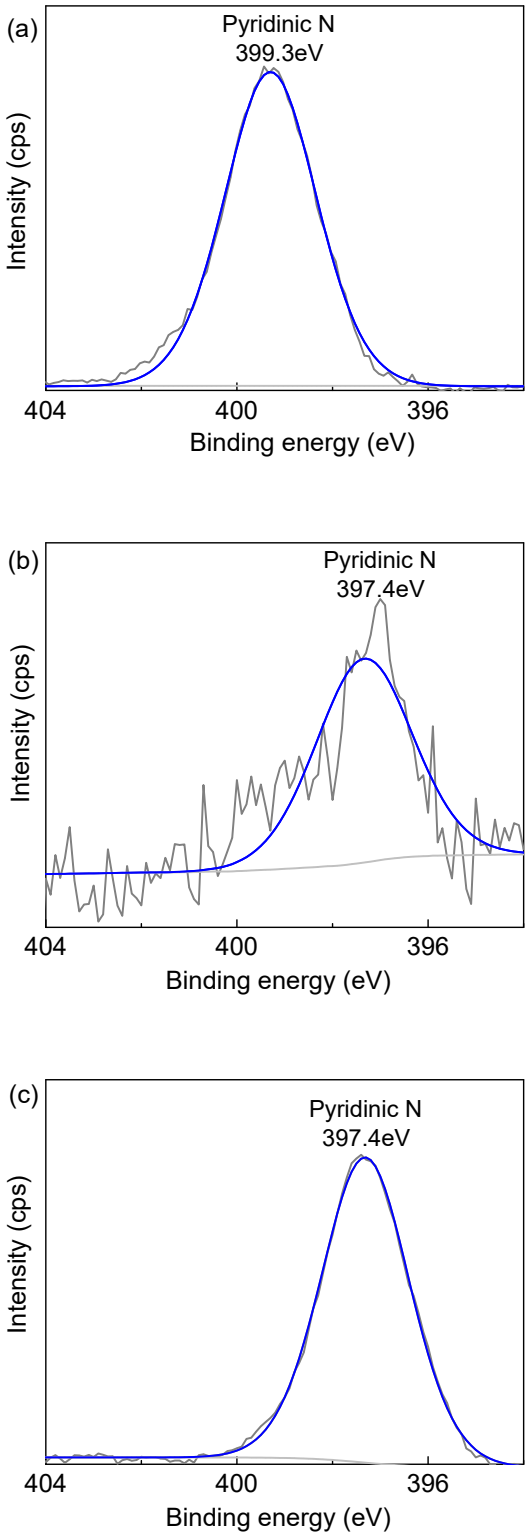

Figure S5. XPS binding energy shifts of N1s for (a) N-HC, (b) B-HC and (c) BN-HC.

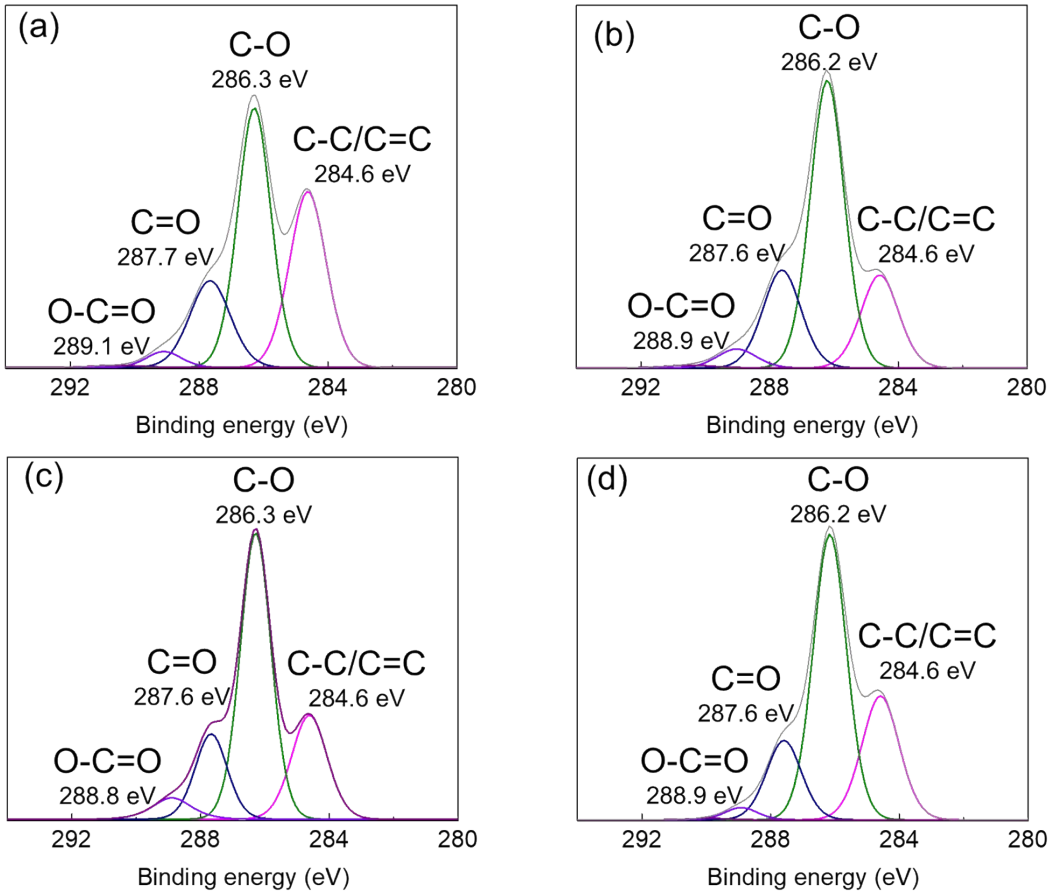

Figure S6. XPS binding energy shifts of C 1s for: (a) HC, (b) N-HTC, (c) B-HC and (d) BN-HC.

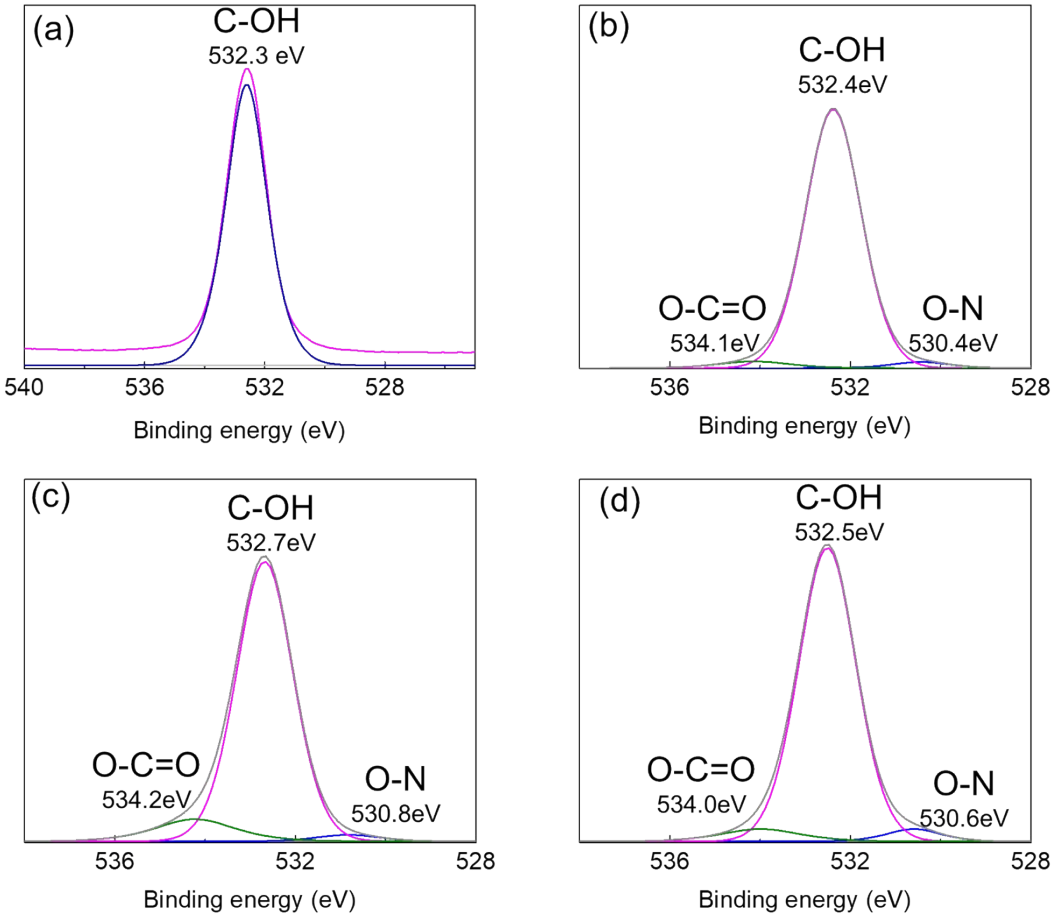

Figure S7. XPS binding energy shifts of O1s for: (a) HC, (b) N-HTC, (c) B-HC and (d) BN-HC.

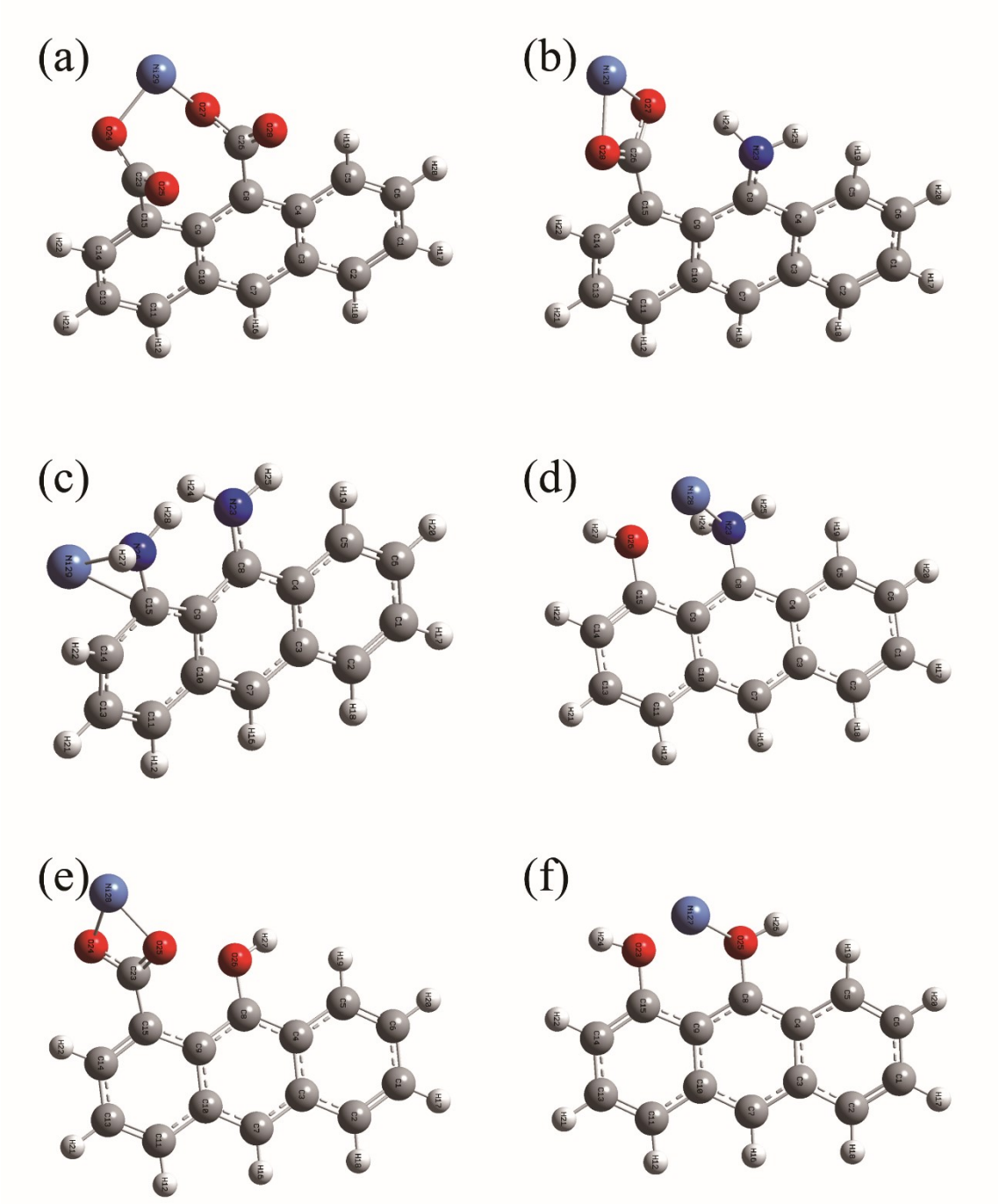

Figure S8. Calculated structures of Ni-carbon complexes by DFT calculations. (a) COO^- group. (b) NH_2, COO^- group. (c) NH_2 groups. (d) OH and NH_2 groups. (e) COO^- and OH groups. (f) OH groups. Atom colors are H (white), C (gray), O (red), N (dark blue), and Ni (light blue).

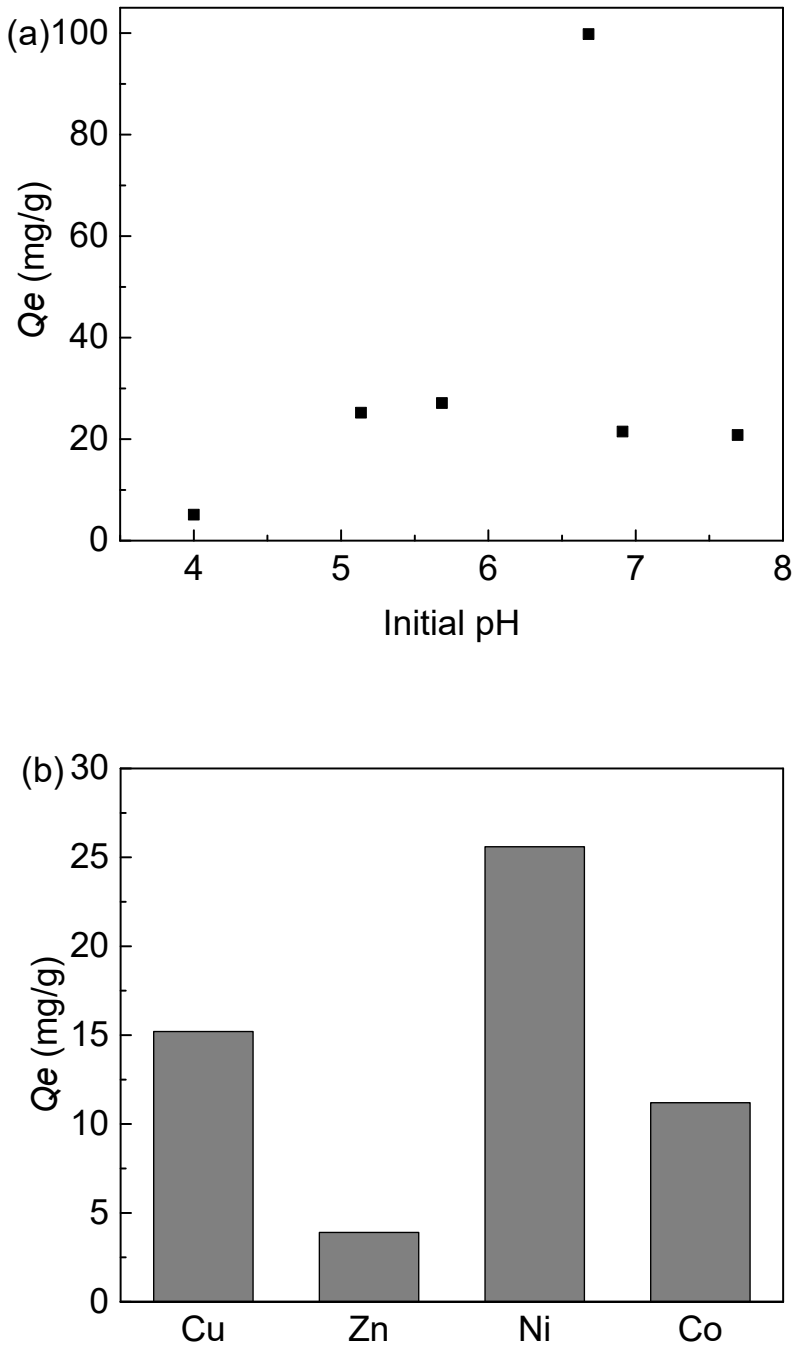

Figure S9. (a) Adsorption of Ni^{2+} onto BN-HC biocarbon as a function pH (20 mL of 50 mM of Ni^{2+}, 0.05 g of adsorbent, 20 ^{o}C, after 30h); (b) Adsorption of Cu^{2+}, Zn^{2+}, Ni^{2+} and Co^{2+} onto HC biocarbon (Conditions: 20 mL of 10 mM of metal solution, 0.02 g of adsorbent, after 1 h, 20 ^{o}C).

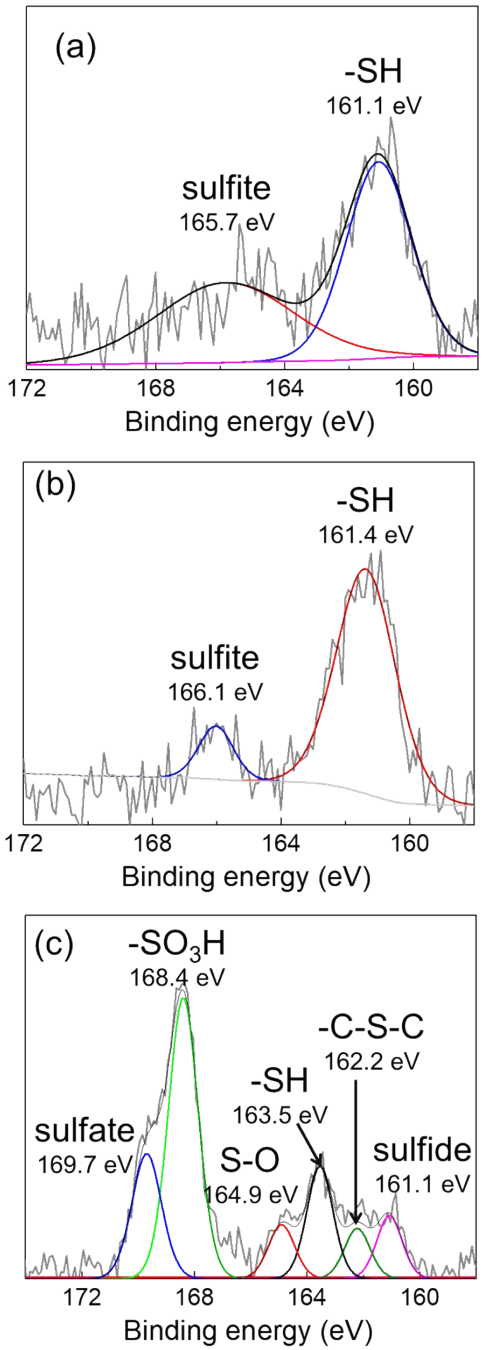

Figure S10. XPS binding energy shifts of S 2p for (a) B-HC and (b) BN-HC and (c) Ni-BNS-HC.

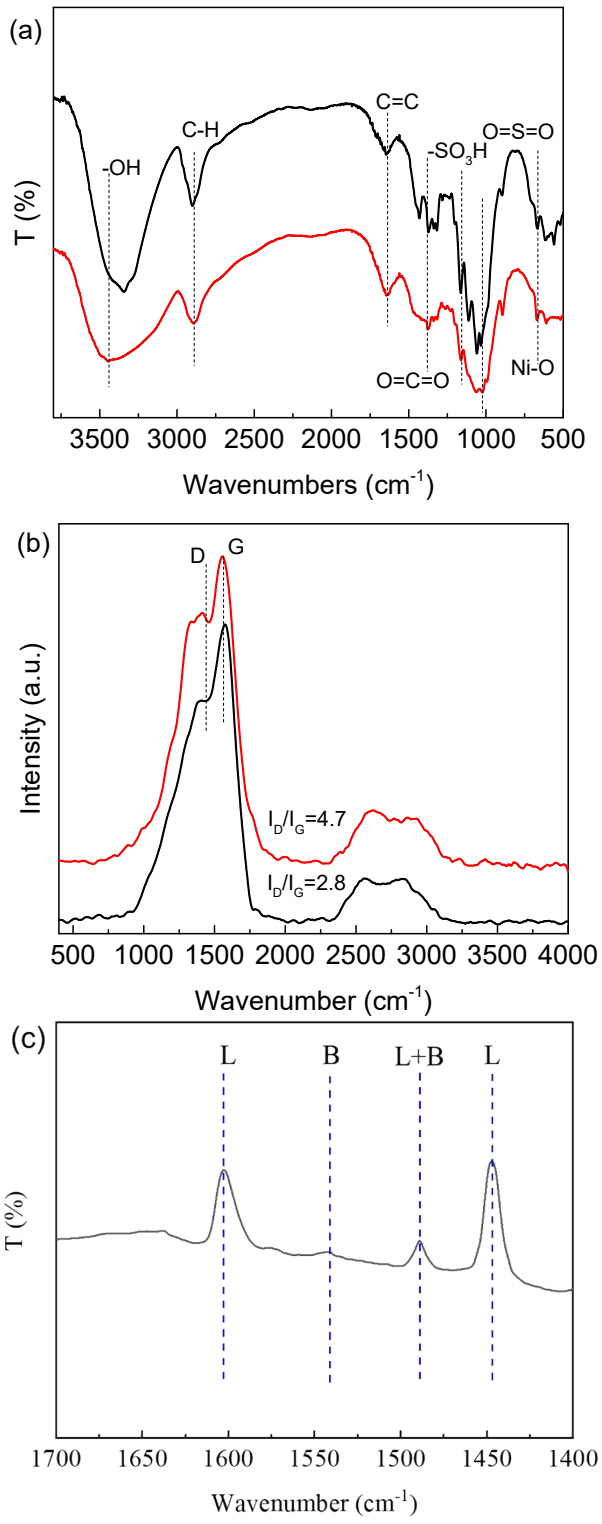

Figure S11. (a) FT-IR spectra of Ni-BN-HC (red line) and Ni-BNS-HC (black line); (b) Raman spectra of BNS-HC (black line) and Ni-BNS-HC (red line) and (c) Py-FTIR spectra (150 °C) of Ni-BNS-HC (Lewis acidity (L), Brønsted acidity (B)).

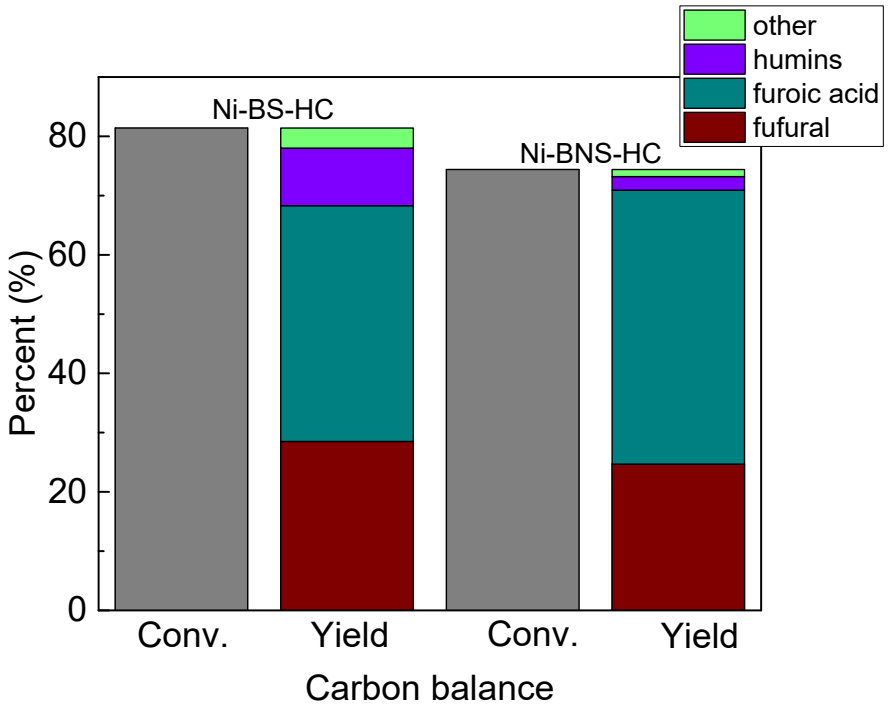

Figure S12. Carbon balance calculation for the conversion of xylose with Ni-BS-HC or Ni-BNS-HC at 150 °C after 4 h reaction time.

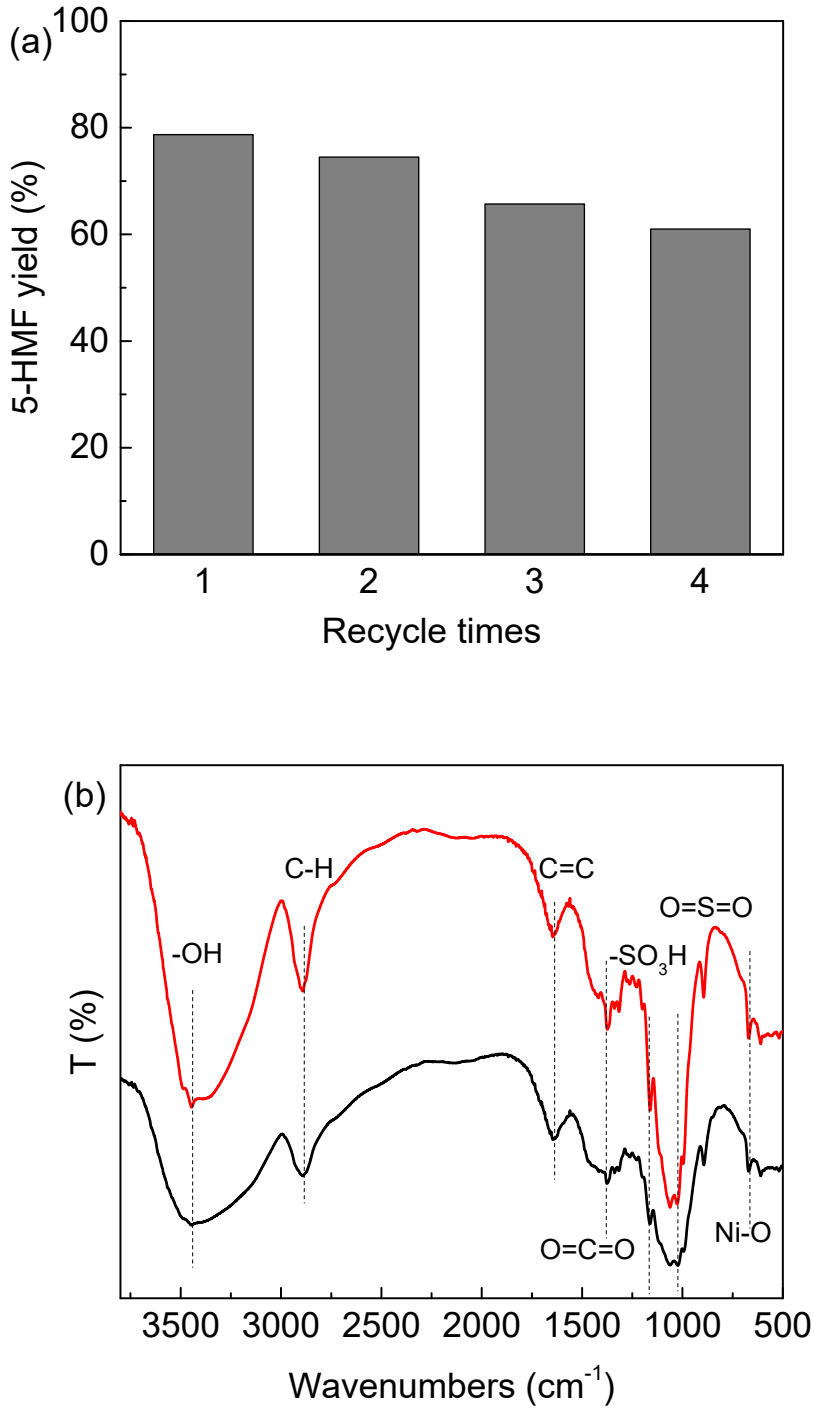

Figure S13. Recycle of Ni-BNS-HC as catalyst for conversion of fructose to 5-HMF: (a) Change in 5-HMF yield with recycle times, (b) FT-IR spectra of fresh Ni-BNS-HC (black line) and Ni-BNS-HC after four recycles (red line). Reaction conditions: 0.1 g of fructose, 2 g of [BMIM]Cl ionic liquid, 0.05 g of catalyst at 120 ºC and 1.5 h reaction time.

Table S1. Properties of hydrothermal biocarbons (HC) according to ball-milling with L-cysteine (B-HC), synthesis with ammonia solution (N-HC) and combination (BN-HC) treatment.

Catalyst	S_{BET}	Dp	Functional groups (mmol/g)			Elemental content XPS (%)			
	(m^2/g)	(nm)	-OH[a]	-COOH[b]	Amino[c]	C	O	N	S
HC	1.1	25.0	1.03	1.39	-	63.4	36.6	-	-
B-HC	1.4	18.6	1.81	1.11	-	57.8	41.7	0.3	0.2
N-HC	1.8	17.8	1.49	2.37	2.37	59.3	38.8	1.9	-
BN-HC	2.2	18.4	0.53	1.59	5.4	60.1	36.5	3.2	0.2
Ni-BNS-HC	<5	-	-	-	-	30.7	59.7	2.4	1.8

[a]Obtained by subtracting titration results using Na_2CO_3 from calculated values of NaOH

[b]Obtained by subtracting concentration of sulfonic groups from titration results with $NaHCO_3$

[c]Obtained by XPS analysis.

Table S2. Langmuir and Freundlich parameters for isothermal adsorption of Ni^{2+} onto functional hydrothermal biocarbon (HC) and amino-functional hydrothermal biocarbon (N-HC).

Entry	Adsorbent	Langmuir			Freundlich			F-test (Langmuir/Freundlich)
		K_L (L/mg)	Q_m (mg/g)	R^2	K_F	n	R^2	F
1	HC	9.6×10^{-5}	285.7	0.96	0.07	1.17	0.99	0.47
2	N-HC	1.0×10^{-4}	312.5	0.87	0.04	1.07	0.98	0.96
3	B-HC	1.0×10^{-4}	130.0	0.93	0.02	1.09	0.99	0.004
4	BN-HC	1.2×10^{-4}	313.5	0.93	0.05	1.07	0.99	0.005

Table S3. Analysis of the residuals from Langmuir and Freundlich models with F-test.

Cs(mM)	Q_{date} (mg/g)	Q_{model} (mg/g)		Residual		F-test[a]
		Langmuir	Freundlich	Langmuir	Freundlich	
HC						0.47
0	0	0	0	0	0	
19.5	28.6	28.3354	28.4862	0.0700	0.0130	
29	39.7	40.1977	39.9663	0.2477	0.0709	
38.7	51.2	51.2321	51.1224	0.0010	0.0060	
44.1	58	56.9558	57.1493	1.0905	0.7236	
N-HC						0.96
0	0	0	0	0	0	
19.5	29.8	32.6509	30.8054	8.1276	1.0108	
28.7	46.4	45.7978	44.2469	0.3626	4.6357	
38.4	59.8	58.3847	58.1237	2.0032	2.8098	
46	66	67.4460	68.8385	2.0909	8.0571	
B-HC						0.004
0	0	0	0	0	0	
18.6	33.7	37.5932	34.7832	15.1570	1.1732	
28.7	53.4	54.4603	52.1539	1.1242	1.5528	
37.2	66	67.1354	66.4509	1.2891	0.2033	
46.6	80.4	79.7822	82.0118	0.3817	2.5979	
BN-HC						0.005
0	0	0	0	0	0	
19.7	12.8	12.7295	12.6148	0.0050	0.0343	
29.7	18	18.2816	18.3631	0.0793	0.1318	
39.8	23.5	23.3794	24.0002	0.0145	0.2502	
50	30.7	28.0758	29.5692	6.8865	1.2787	

[a] F-test on data fits comparing Langmuir and Freundlich models.