Electronic Supplementary Information

Nitrogen Doped Carbon Spheres with Wrinkled Cages for Selective Oxidation of 5-hydroxymethylfurfural to 5-formyl-2-furancarboxylic acid

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EXPERIMENTAL

Catalyst preparation

Synthesis of dendritic fibrous nanosilica (DFNS)

For the synthesis of DFNS-1 and DFNS-4, CTAB (2 g) and urea (2.4 g) were mixed in 100 mL of water at room temperature (RT) and stirred at 1400 rpm for 30 mins. TEOS (5 mL) in cyclohexane (100 mL) was then added dropwise and stirred for 1 hour at RT. The co-surfactant (0.055 mol of 1-hexanol for DFNS-1, 0.055 mol of 1-propanol for DFNS-4) was then added dropwise, and the reaction mixture was further stirred for 30 mins at RT. Subsequently, the reaction mixture was heated to 90 ℃ and kept at this temperature for 12 hours under stirring. When the temperature reached at 90 ℃, the stirring speed reduced to 1000 rpm. After cooling down, the solid products were isolated by centrifugation and washed with water and ethanol, and then dried in an oven at 80 ℃ for 12 h. Finally DFNS-1 and DFNS-4 were obtained by calcination at 550 ℃ for 6 h in air.

For the synthesis of DFNS-2 and DFNS-3, CTAB (10 g, 0.027 mol) and urea (12 g, 0.2 mol) were dissolved in 500 mL water and stirred for 30 min at RT, and then TEOS (150 mL for DFNS-2, 100 mL for DFNS-3) in 500 mL of *p*-xylene was added into the above solution dropwise over 30 mins under stirring. This reaction mixture was further stirred for 30 mins. Subsequently, 1-pentanol (30 mL) was added slowly in the reaction mixture and stirred for 30 min. The reaction mixture was heated to 130 ℃ within 30 mins and refluxed for 6 hours. After cooling down, the solid product was isolated by centrifugation and washed several times with water and ethanol, then dried in an oven at 80 ℃ for 12 h. Finally DFNS-1 and DFNS-2 were obtained by calcination at 550 ℃ for 6 hours in air.

Synthesis of 5,5’-diamino-3,3’-bis(1H-1,2,4-triazole) (DABT)

DABT was prepared according to the procedure in the literature.[1] In brief, hydrochloric acid (100 mL) was added to a stirred mixture of oxalic acid (20.0 g, 159 mmol) and aminoguanidinium bicarbonate (45.4 g, 332 mmol). The reaction was stirred at 70 ℃ for one hour and the precipitate was collected by filtration. The colorless solid was dissolved in water (240 mL) and alkalized with sodium hydroxide to pH = 14. The reaction mixture was heated to reflux for one hour and subsequently acidified with acetic acid to pH = 4. The resulting precipitate was collected by filtration, washed with water and dried in air.

Synthesis of nitrogen doped carbon spheres with wrinkled cages (NCSWCs)

First, 0.9 g DFNS was dispersed in 300 ml of toluene and sonicated for 30 mins, then 0.3 ml (3-Aminopropyl)triethoxysilane (APTES) (for DFNS-4, 0.6 ml APTES was needed.) was added in the above suspension and refluxed at 110 ℃ for 8 hours. After cooling down, the product was filtered and washed with toluene several times, then dried in an oven at 110 ℃ overnight. Subsequently, the amine functionalized DFNS was dispersed in 48 mL of H_2O, 12 mL of ethanol, and 3.6 g of glucose (for DFNS-4, 4.8 g of glucose was added.), then the mixture was heated at 190 ℃ for 40 h in a stainless steel autoclave. After the reaction, the product was filtered and washed with water and ethanol several times, dried in an oven at 110 ℃ overnight. The obtained carbon coated DFNS was mixed with DABT (DABT : the carbon coated DFNS = 3 : 1, mass ratio) in 15 mL methanol, sonicated for 10 mins, and then stirred until methanol was completely evaporated. Subsequently, the product was pyrolyzed in a tubular furnace under Ar atmosphere at 600 ℃ for 3 h with a heating rate of 10 ℃ min^{-1}, and then 800 ℃ (or 950 ℃) for 2 h with a heating rate of 10 ℃ min^{-1}. Finally, the obtained products were immersed in 10 wt.% HF solution for 24 hours to remove the silica cores, then collected by centrifugation, washed with copious DI water and dried at 110 ℃. The monodispersed NCSWCs were designated as NCSWC-N-T (N are

1, 2, 3, or 4, which refers to the hard templates, DFNS-1, 2, 3 or 4, used in the synthesis, respectively; T refers to the pyrolysis temperatures.). For comparison, mesoporous N-doped carbon materials, which was denoted as NMC-800, was prepared based on a previous study.[2]

Catalyst characterization

The contents of C, N, H, and O in various carbon samples were determined using a PerkinElmer 2400 Series-II CHN/O Elemental Analyzer. TEM images were recorded by using a FEI TecnaiG2 F20 S-Twin or Thermo Scientific Talos F2100X. Powder X-ray diffraction (XRD) was performed with a Bruker D8 Advance diffractometer with Cu Kα radiation (λ = 1.5418 Å) at 40 kV and 40 mA. XPS spectra were measured on a Thermo Scientific Escalab 250Xi by using an Al Kα radiation source. The binding energy was calibrated by taking the C 1s peak (BE = 284.8 eV) as a reference. N2 adsorption-desorption isotherms were obtained by using Micromeritics ASAP 2020 instrument at -196 ℃. The samples were degassed under vacuum for 12 h at 150 ℃ before analysis. The Raman spectra were recorded on a Thermo Fisher Scientific Raman Microscope (DXR2) at 532 nm excitation wavelength.

Catalytic activity evaluation

HMF oxidation reactions were carried out in a 25 mL stainless steel microreactor. First, the reaction was conducted at different stirring speeds ranging from 600 to 1000 rpm to study the effect of stirring speed on catalytic performance. It was observed that there was no alteration on HMF conversion and product selectivities when the stirring speed was higher than 800 rpm. Therefore, all of the catalytic experiments were carried out at 800 rpm. In a typical catalytic experiment, 10 mL of 0.05 mol/L HMF aqueous solution, 50 mg catalyst, 70 wt.% TBHP aqueous solution (TBHP : HMF = 4 : 1, molar ratio) were added into the reactor. After 8 h reaction time at 100 ℃ with the stirring speed at 800 rpm, the reaction mixture was made alkaline by dropping a certain amount of NaOH aqueous solution, then the catalyst was removed by filtration, and the liquid products were analyzed by using HPLC equipped with an Aminex HPX-87H column (Bio-Rad Laboratories), diode array detector, and refractive index (RI) detector. The analysis conditions were set as follows: eluent, 5 mM H_2SO_4; flow rate, 1.2 mL/min; column temperature, 50 ℃. The catalytic oxidation reaction was conducted at least twice over each catalyst to confirm the reproducibility of the catalytic results. In addition, for the catalytic cycling experiments, after each run of reaction, the catalyst was reused after centrifugation, washed with a plenty of deionized water and dried at 110 ℃ overnight.

Density Functional Theory Calculations

The spin-polarized density functional theory calculations were carried out under the scheme of generalized gradient approximation (GGA), with the use of PBE functional and double numerical polarized (DNP) basis, as embedded in DMol^3 package.[3-6] The orbital cutoff was set with a radius of 4.3 Å, the force on each atom was set as 0.05 eV/Å for the convergence criterion. DNP basis has been extensively tested for geometric optimization, its calculation level is comparable to Gaussian basis 6-311+G** sets, but it can offer higher accuracy.[7] The van der Waals interaction has been considered using the DFT-D3 scheme.[8] Transition state (TS) linking molecular and dissociated water has been searched through complete LST/QST approach, as embedded in DMol^3.[9] As to the reaction energy Er and energy barrier Ea, they were calculated through Er = E(Products) - E(Reactants) and Ea = E(TS) - E(Reactants), respectively, where E(Reactants), E(Products), and E(TS) were the calculated total energies for reactant, product, and transition state, which were obtained under the same computational setting.

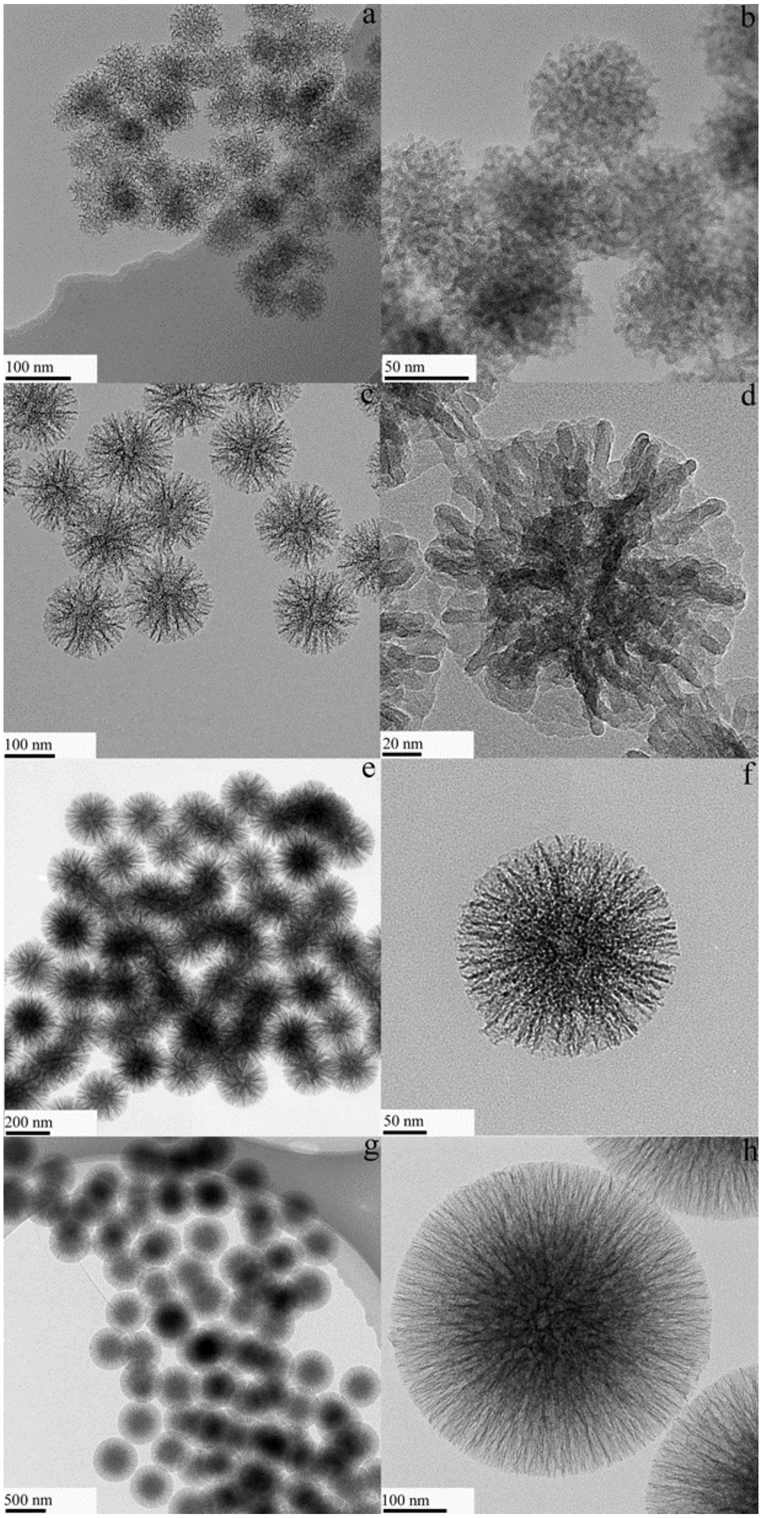

Figure S1 TEM images of DFNS-1 (a, b), DFNS-2 (c, d), DFNS-3 (e, f), and DFNS-4 (g, h).

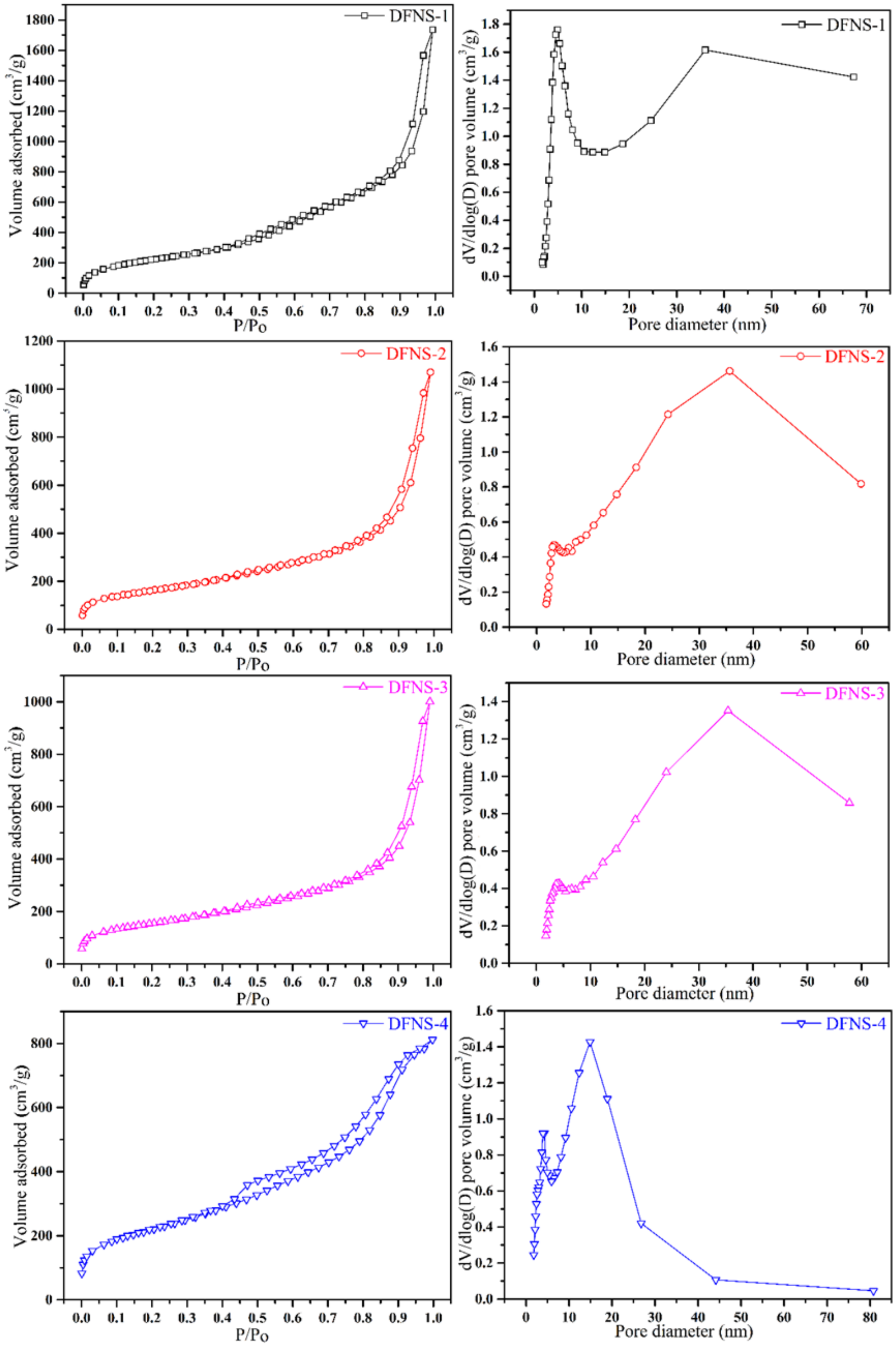

Figure S2 Nitrogen adsorption-desorption isotherms of DFNS-1, DFNS-2, DFNS-3, and DFNS-4 (left) and their corresponding BJH pore size distribution curves (right).

Table S1 Texture properties of DFNS-1, DFNS-2, DFNS-3, and DFNS-4.

Samples	S_{BET} (m^2/g)	$V_{Micro.}$ (m^3/g)	$V_{Meso.}$ (m^3/g)
DFNS-1	822.1	0.007	1.647
DFNS-2	583.7	0.029	1.062
DFNS-3	547.7	0.028	0.915
DFNS-4	783.3	0.080	1.014

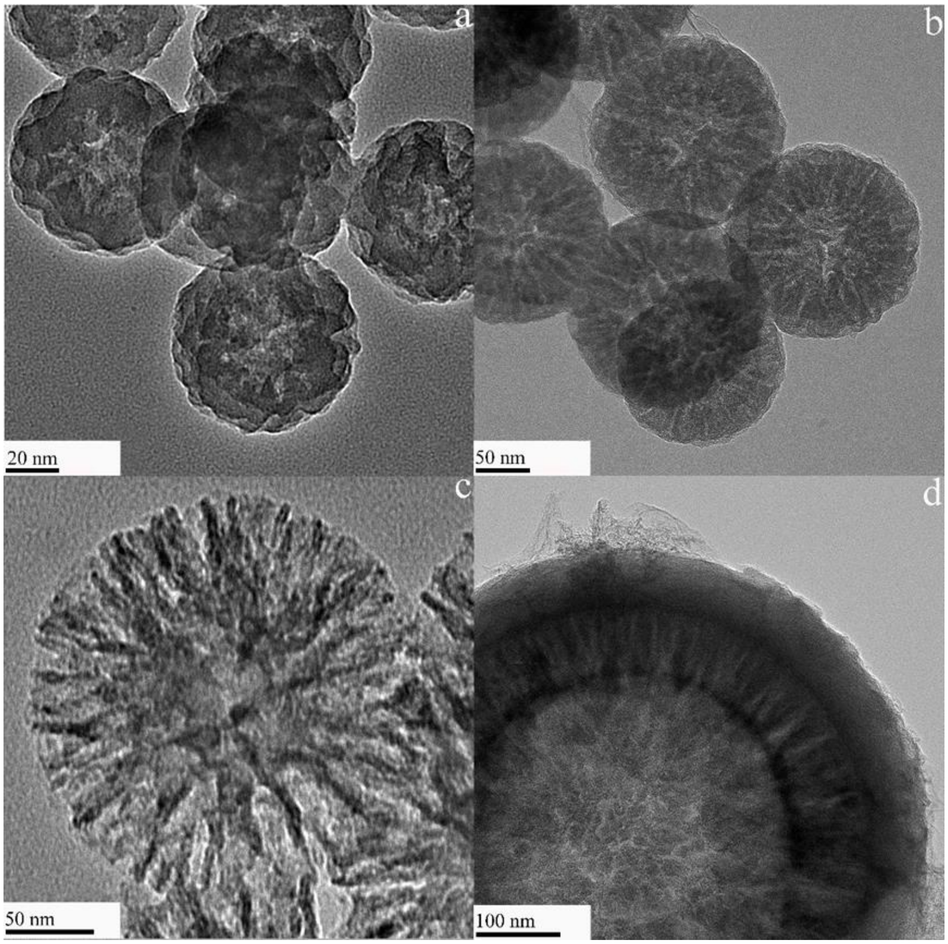

Figure S3 TEM images of NCSWC-1-800 (a), NCSWC-2-800 (b), NCSWC-3-800 (c), and NCSWC-4-800 (d).

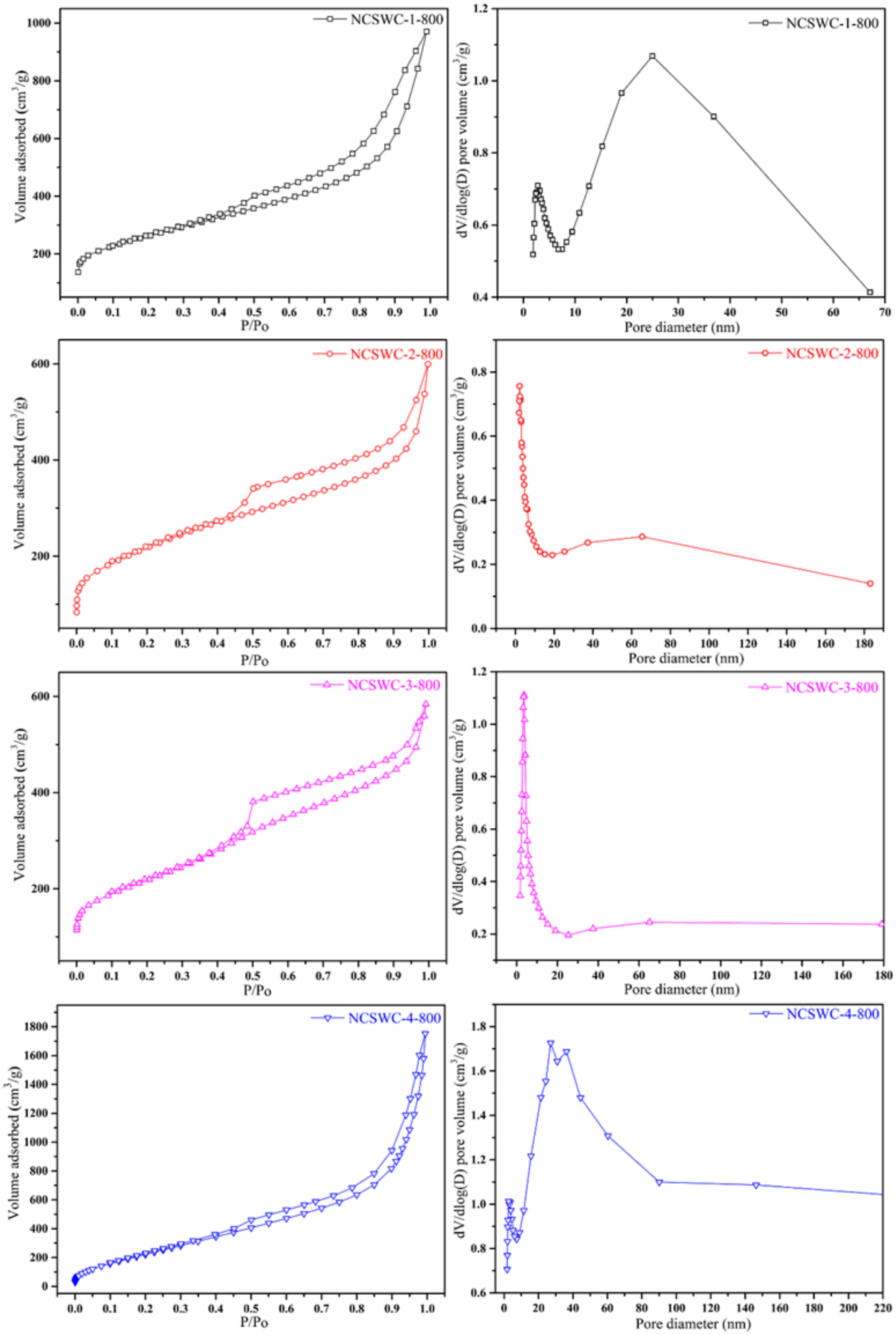

Figure S4 Nitrogen adsorption-desorption isotherms of NCSWC-1-800, NCSWC-2-800, NCSWC-3-800, and NCSWC-4-800 (left) and their corresponding BJH pore size distribution curves (right).

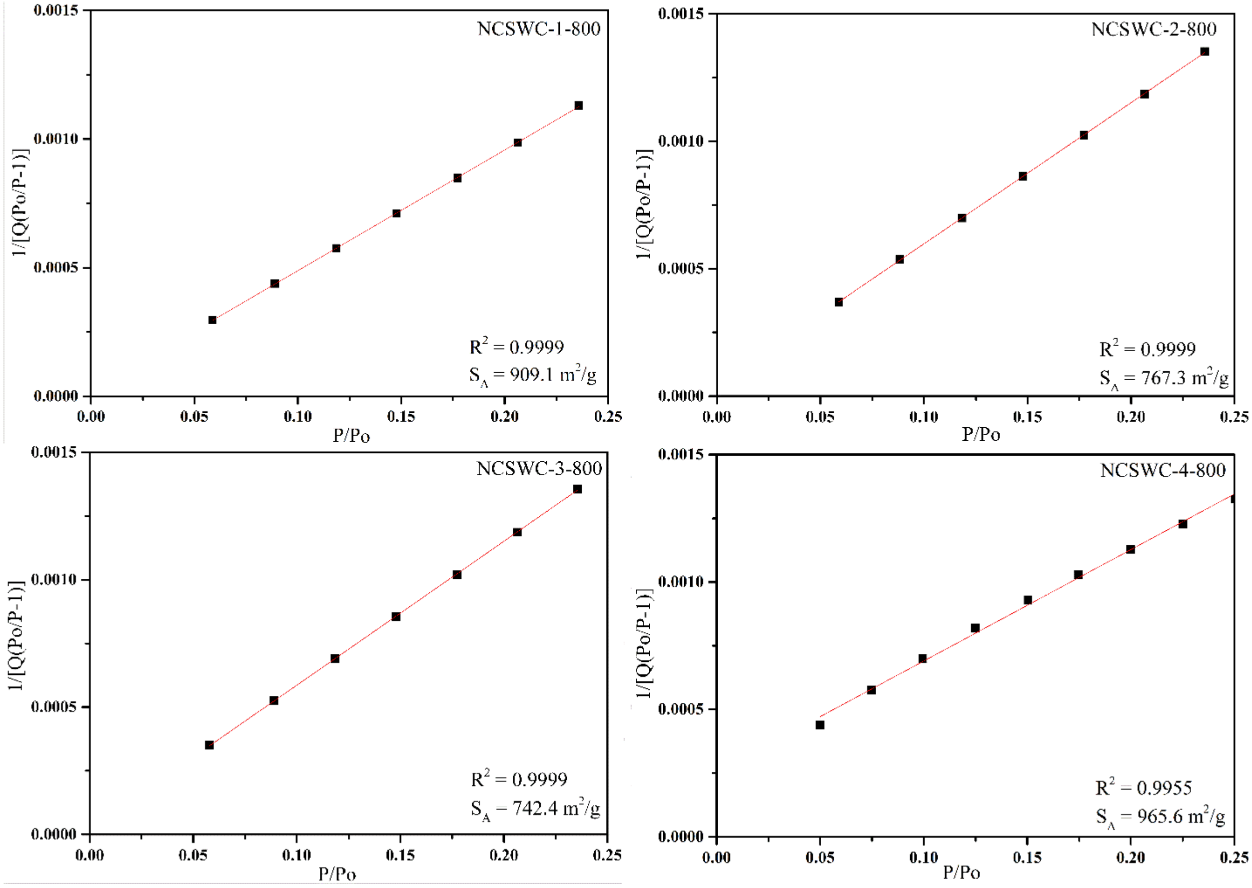

Figure S5 BET plot for NCSWC-1-800, NCSWC-2-800, NCSWC-4-800, and NCSWC-4-800 calculated from nitrogen adsorption-desorption isotherms.

Table S2 Textual properties and chemical compositions of various NCSWCs.

Samples	S_{BET} (m^2/g)	$V_{Micro.}$[a] (m^3/g)	$V_{Meso.}$[b] (m^3/g)	$V_{Macro.}$[b] (m^3/g)	Chemical Composition					
					C[c]	N[c]	O[c]	C[d]	N[d]	O[d]
NCSWC-1-800	909.1	0.066	1.089	0.221	78.09	13.69	7.09	72.77	19.29	7.94
NCSWC-2-800	767.3	0.029	0.509	0.233	75.96	16.34	6.62	68.85	23.69	7.46
NCSWC-3-800	742.4	0.052	0.625	0.151	76.96	14.92	7.34	72.56	19.42	8.02
NCSWC-4-800	965.6	0.096	1.689	0.919	77.41	15.21	6.72	71.93	20.53	7.54
NCSWC-4-600	867.0	0.093	1.381	0.484	66.30	26.18	6.67	56.89	35.78	7.33
NCSWC-4-950	1140.3	0.172	1.151	0.514	88.01	6.77	4.73	83.91	10.98	5.11
NCSWC-4-600-M	/	/	/	/	71.93	17.09	10.57	63.17	23.32	13.51
NCSWC-4-800-M	949.0	0.065	1.616	0.914	83.89	7.12	8.46	77.87	11.26	10.87
NMC-800	821.3	0.133	1.683	0.077	80.63	11.34	7.34	75.53	16.19	8.28

a: Micropore volume was obtained by *t*-plot method;

b: The mesopore and macropore volumes were obtained from BJH Adsorption Pore Distribution Report;

c: The contents of C, N, and O were determined using an elemental analyzer (wt.%);

d: The contents of C, N, and O were measured by XPS (at.%).

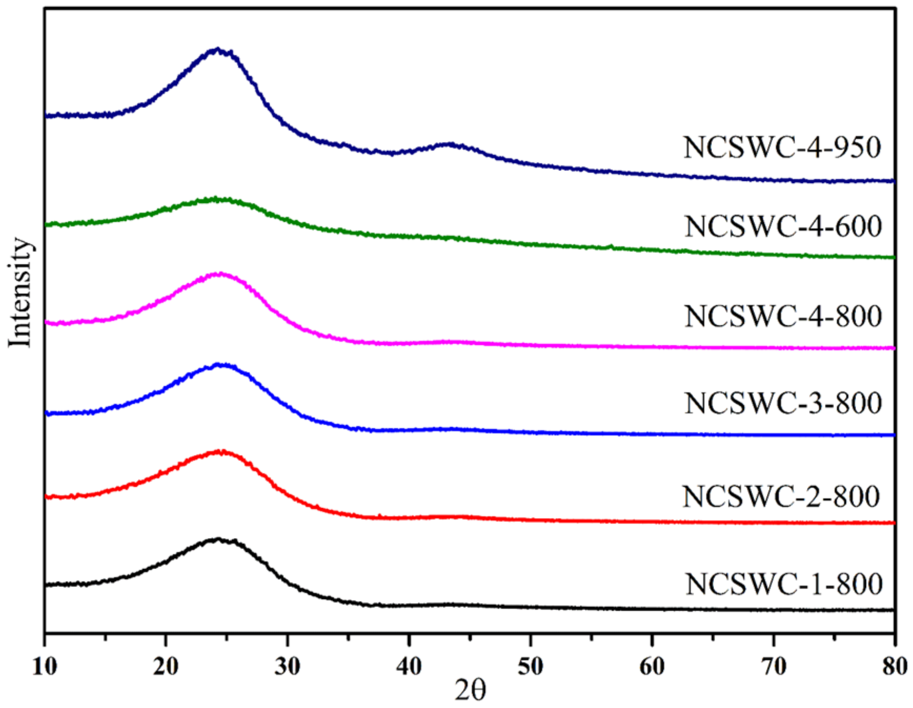

Figure S6 XRD patterns of NCSWCs.

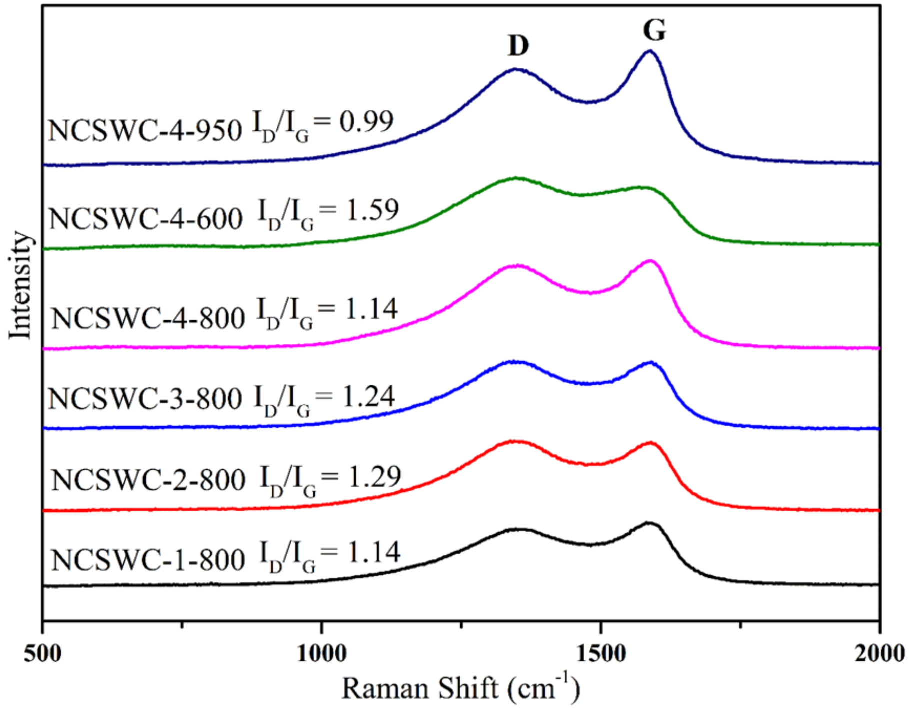

Figure S7 Raman spectra of NCSWCs.

Table S3 The composition of nitrogen species in NCSWCs and NMC-800.

Samples	XPS Analysis						
	Total N Content (at.%)	Relative peak area (%)				$N_{graphitic}$ Content (at.%)	$N_{pyridinic}$ Content (at.%)
		$N_{graphitic}$	$N_{pyrrolic}$	$N_{pyridinic}$	$N_{oxidized\ N}$		
NCSWC-4-800	20.53	42.32	29.54	28.14	/	8.69	5.78
NCSWC-4-600	35.78	9.84	33.73	56.43	/	3.52	20.19
NCSWC-4-950	10.98	51.98	25.24	22.78	/	5.71	2.50
NCSWC-4-600-M	23.32	14.94	44.57	40.49	/	3.48	9.44
NCSWC-4-800-M	11.26	20.64	33.94	45.42	/	2.32	5.11
NMC-800	16.19	36.79	26.61	36.60	/	5.96	5.93

Table S4 The results of three repeated catalytic experiments over various catalysts NCSWC-1-800, NCSWC-2-800, NCSWC-3-800, and NCSWC-4-800 in HMF oxidation.

Samples	HMF Conv. (%)		Selectivity (%)							
			DFF		HMFCA		FFCA		FDCA	
	Exp. 1	Exp. 2	Exp. 1	Exp. 2	Exp. 1	Exp. 2	Exp. 1	Exp. 2	Exp. 1	Exp. 2
NCSWC-1-800	79.1	77.3	8.3	8.8	1.1	1.0	89.2	88.9	1.1	1.0
NCSWC-2-800	86.7	85.4	7.2	6.5	1.2	1.3	90.1	90.7	1.2	1.2
NCSWC-3-800	85.4	84.2	7.9	7.2	1.6	1.8	88.6	89.0	1.5	1.7
NCSWC-4-800	92.3	91.1	5.8	6.1	1.4	1.3	90.5	90.5	1.9	1.7

Reaction condition: 10 mL HMF aqueous solution (0.05 mol/L), 50 mg catalyst, 70 wt.% TBHP aqueous solution (TBHP/HMF = 4, molar ratio), reaction temperature=100 ℃, reaction time=8 h.

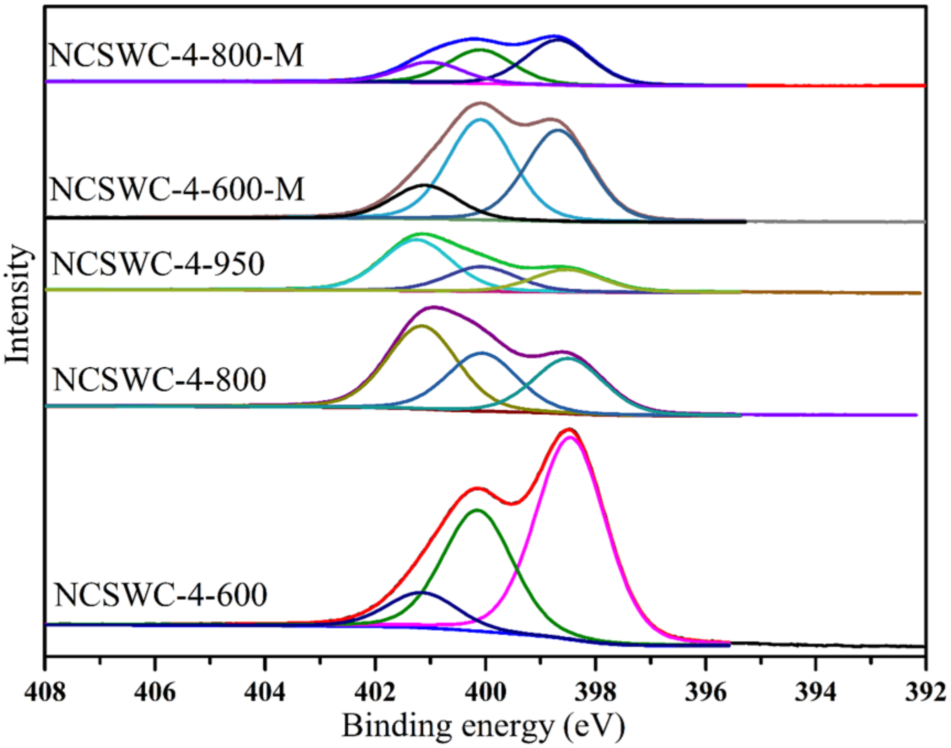

Figure S8 XPS N 1s spectra of NCSWC-4-600, NCSWC-4-800, NCSWC-4-950, NCSWC-4-600-M, and NCSWC-4-800-M.

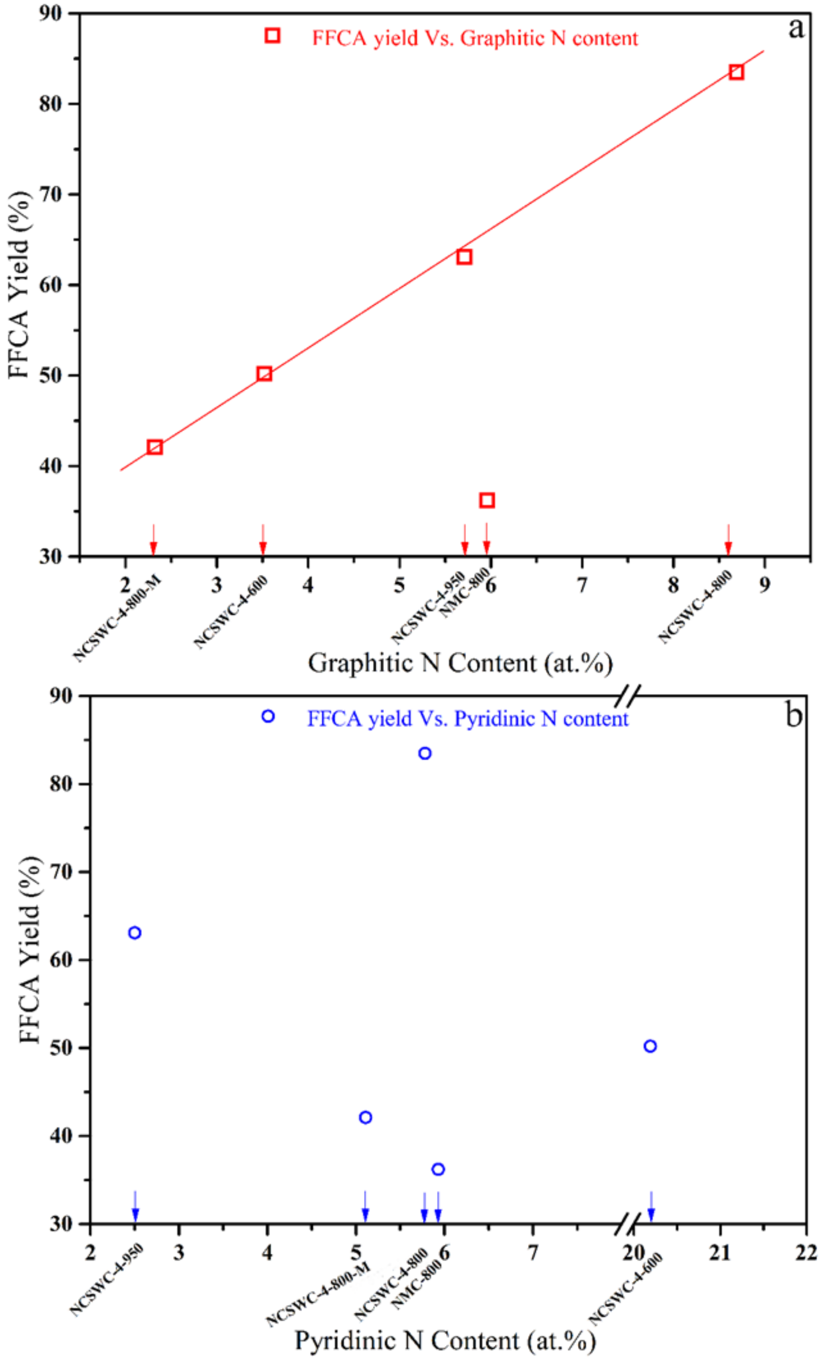

Figure S9 The relationships between the yield of FFCA and graphitic N (a) and pyridinic N (b) contents on various NCSWCs and NMC-800. Reaction condition: 10 mL HMF aqueous solution (0.05 mol/L), 50 mg catalyst, 70 wt% TBHP aqueous solution (TBHP/HMF = 4, molar ratio), reaction temperature = 100 ℃, reaction time = 8 h.

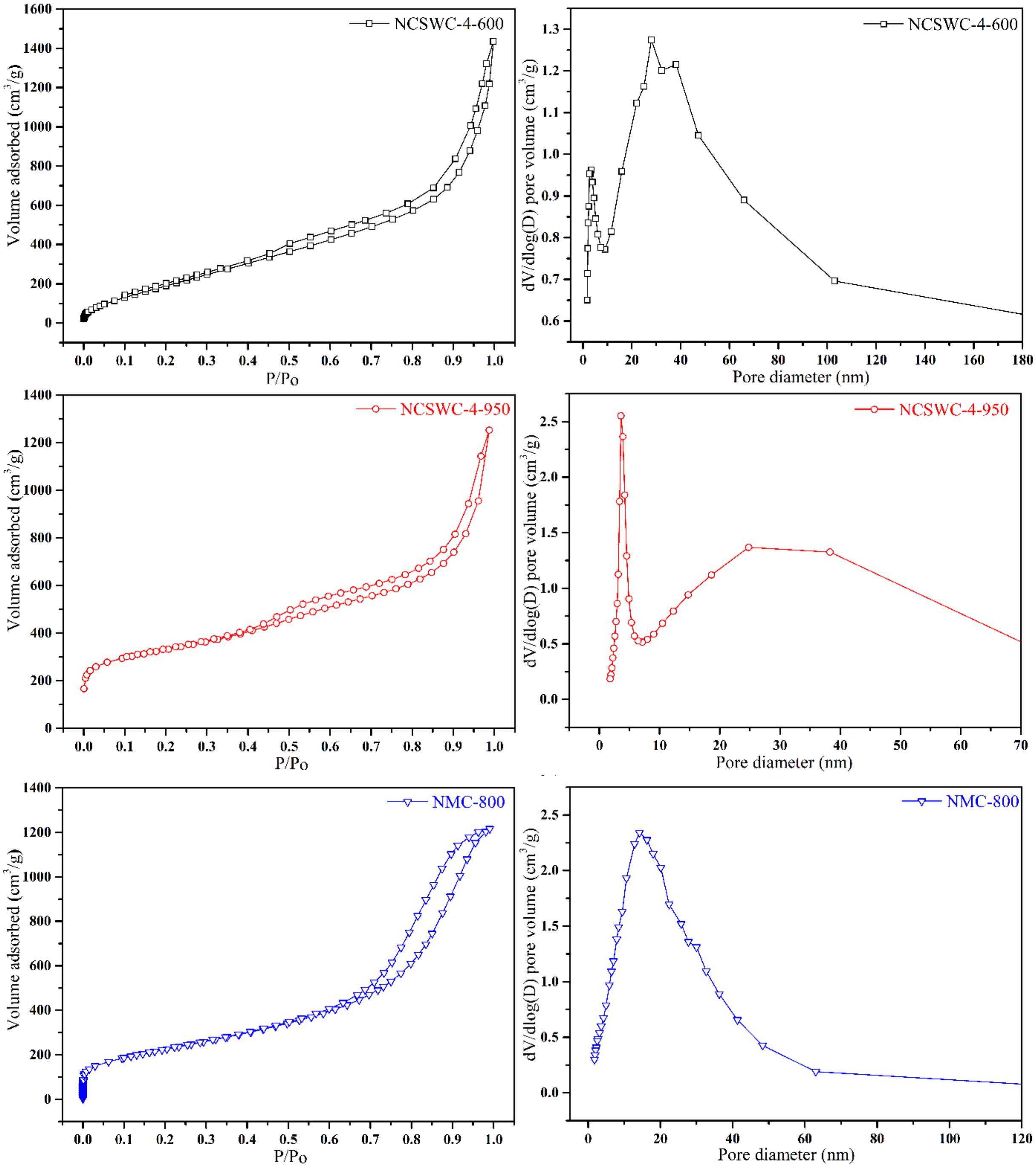

Figure S10 Nitrogen adsorption-desorption isotherms of NCSWC-4-600, NCSWC-4-950, and NMC-800 (left) and their corresponding BJH

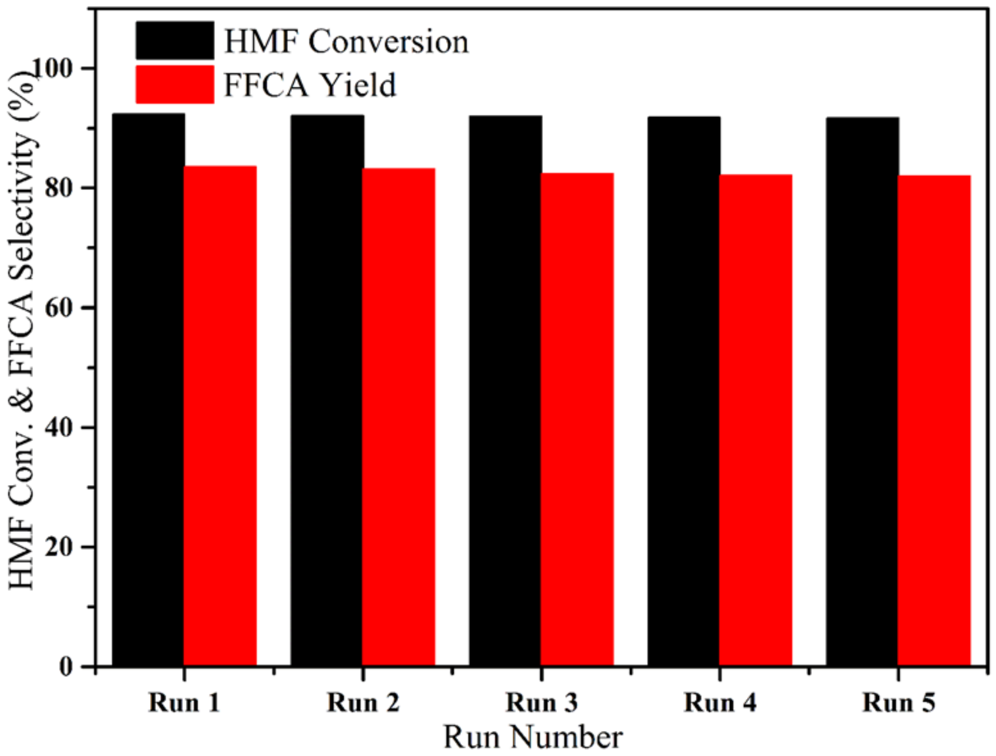

Figure S11 The catalytic cycling results of NCSWC-4-800 in HMF oxidation to FFCA under base-free conditions at 100 ℃ with 8 h reaction time.

Table S5 Literature survey for HMF oxidation to FFCA over metal-based catalysts under base and base-free conditions.

Entry	Catalysts	HMF Conv. (%)	Temp. (ºC)	O_2 pressure (MPa)	T (h)	FFCA Yield (%)	Refs
1	$CuO\cdot CeO_2$	99	110	0.9	3	90	10
2	$MgO\cdot CeO_2$	99	130	0.9	9	90	11
3	AuNPs-sPSB[a]	>99	80	1.5	16	81	12
4	Mn_3Fe_7 mixed oxide[b]	83.0	140	3.0	1.5	37.7	13
5	CdS nanorod	91.1	80	c	48	91.1	14
6	NCSWC-4-800	92.3	100	c	8	83.5	This study

a: in the presence of Cs_2CO_3; b: in the presence of Na_2CO_3; c: TBHP as the oxidant

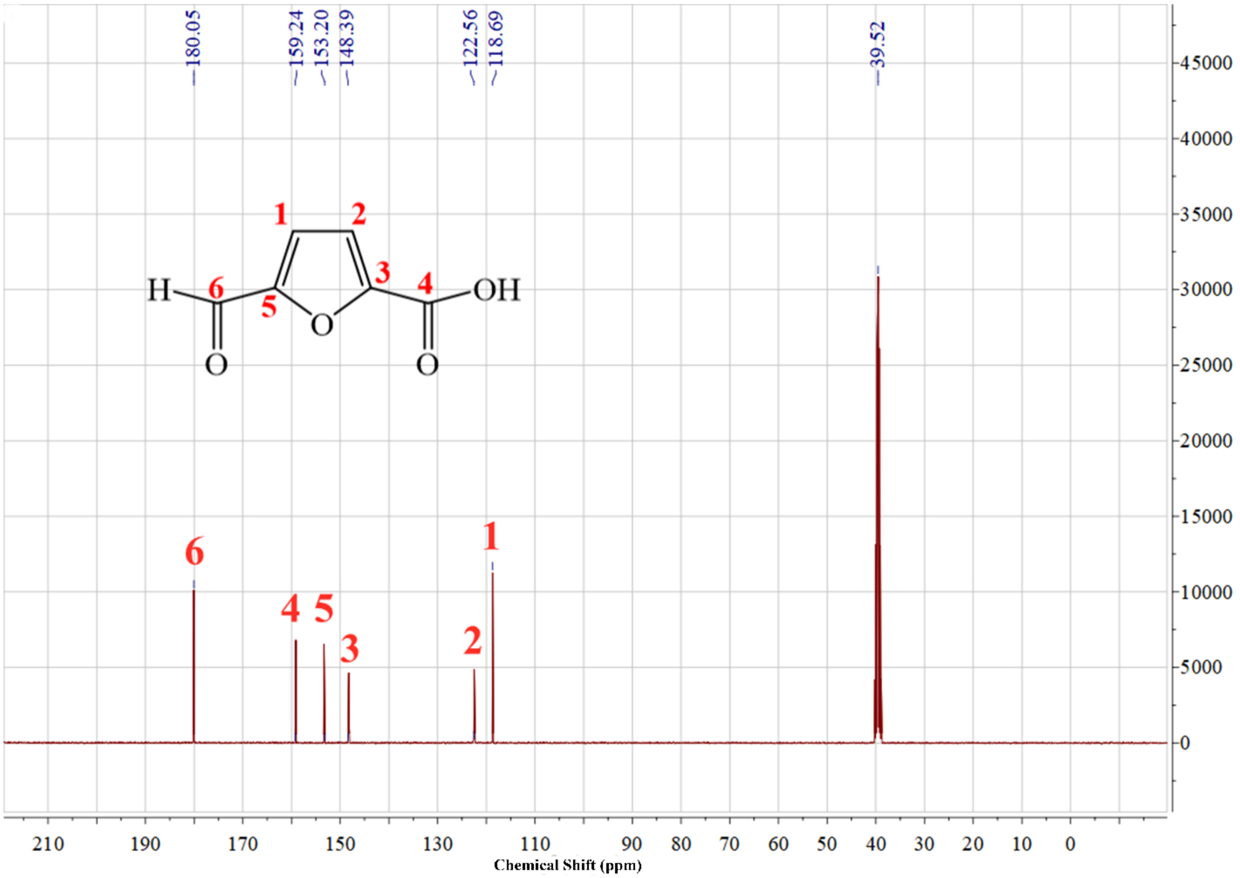

Figure S12 ^{13}C NMR spectrum of FFCA.

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