Electronic Supplementary Material (ESI) for New Journal of Chemistry.

Supporting Information

Nitrogen-Doped Hollow Sphere Carbon-Based Catalyst for Efficient Selective Oxidation of C–H bonds under Mild-Conditions

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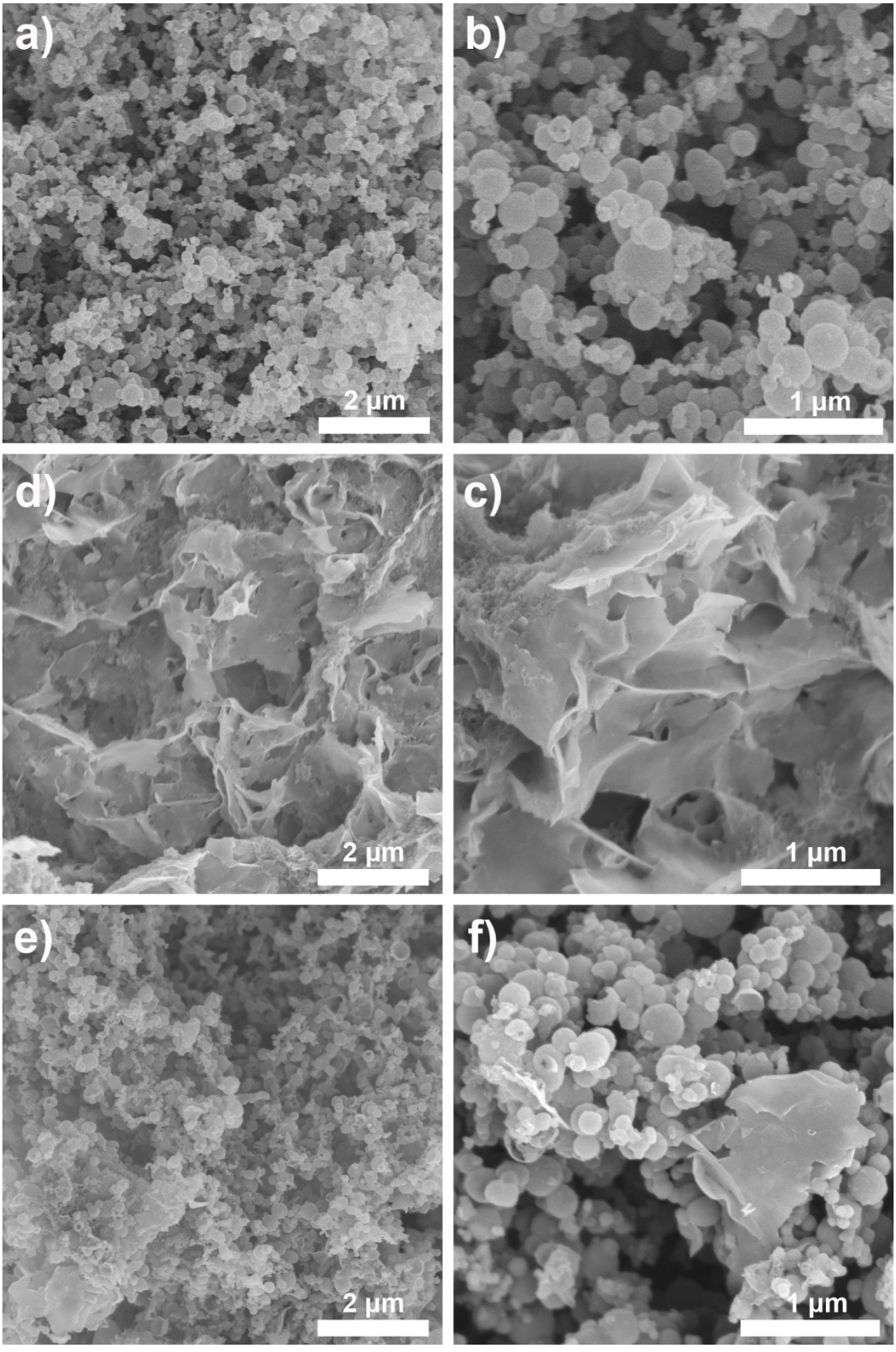


Figure S1. SEM images of (a) and (b) N-HCS-900;(c) and (d) N-HCS-800, (e) and (f) N-HCS-1000, respectively.

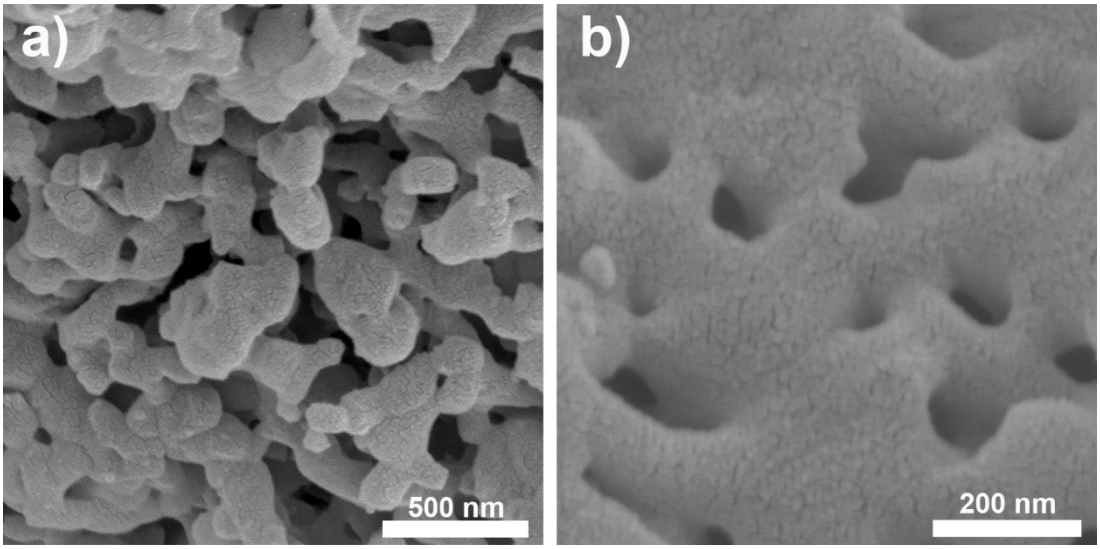


Figure S2. SEM images of (a) and (b) N-HPC.

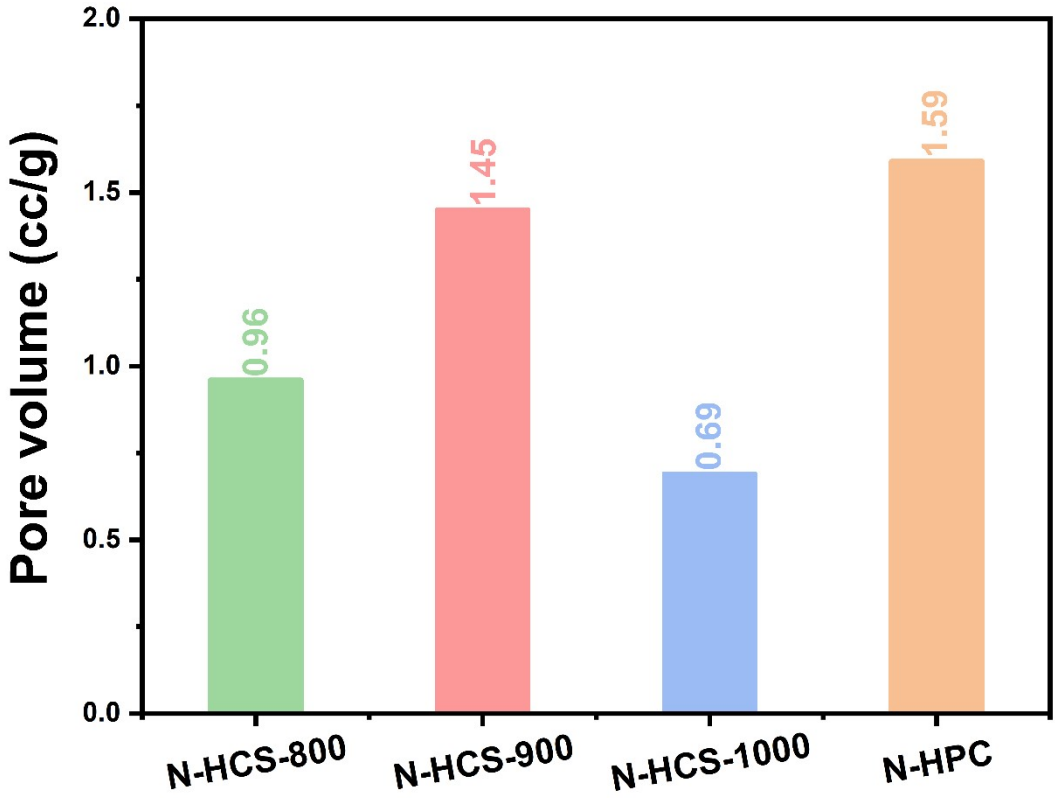


Figure S3. The total pore volume of N-HCS-800, N-HCS-900, N-HCS-1000, and N-HPC, respectively.

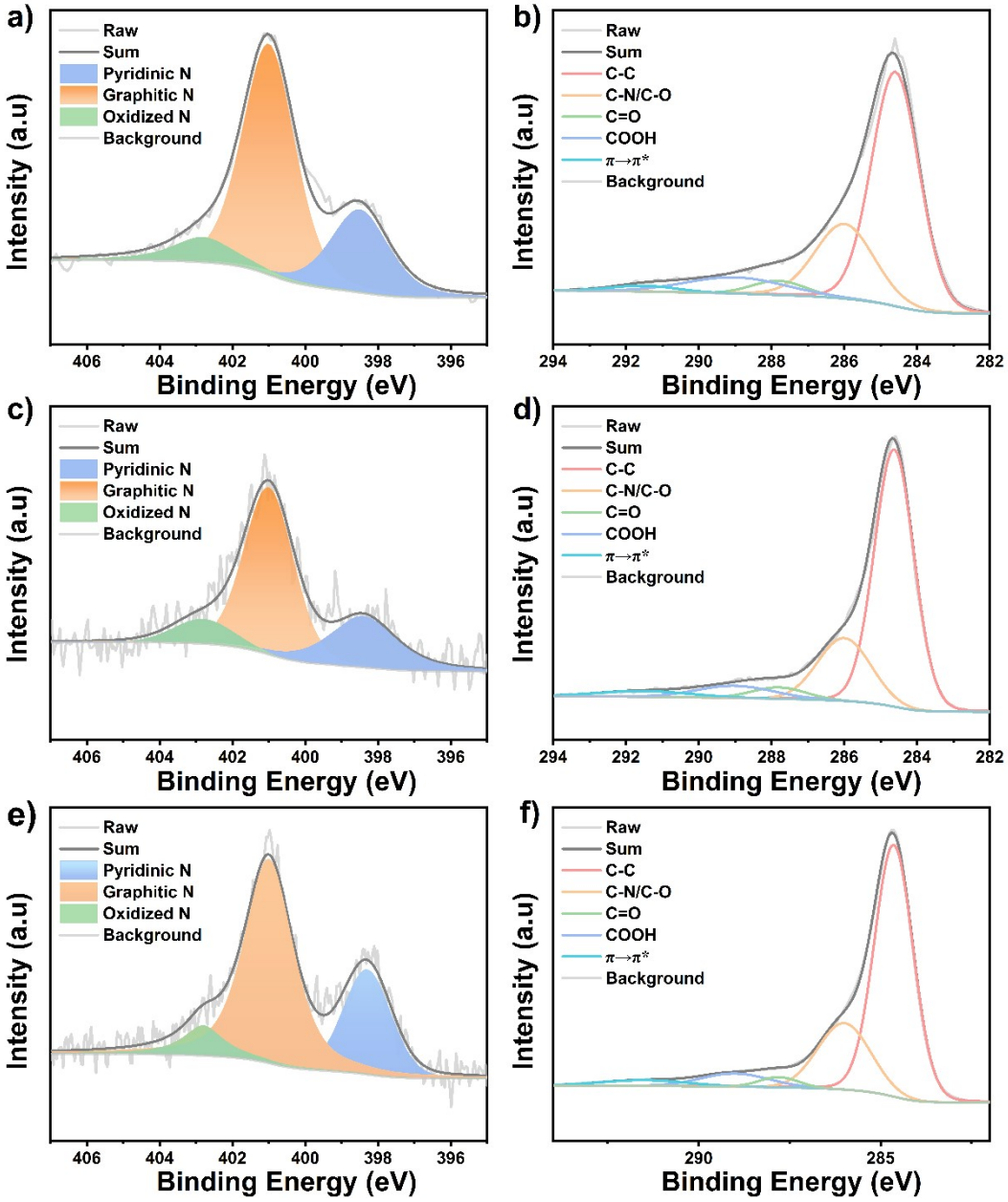


Figure S4. X-ray photoelectron spectroscopy N 1s spectra of (a) N-HCS-800, (c) N-HCS-1000 and (e) N-HPC, respectively. X-ray photoelectron spectroscopy C 1s spectra of (b) N-HCS-800, (d) N-HCS-1000 and (f) N-HPC, respectively.

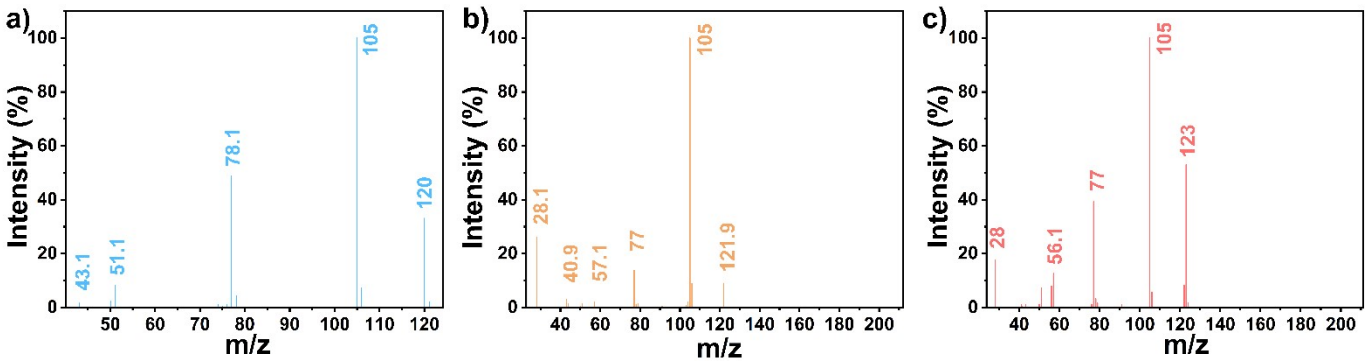


Figure S5. GC-MS spectrum of one product after the reaction catalyzed by N-HCS-900 with retention time in 6.836-6.911 min (a). This is matched with GC-MS spectrum of acetophenone.

GC-MS spectrum of one product after the reaction catalyzed by N-HCS-900 with retention time in 8.685-8.718 min (b). This is matched with GC-MS spectrum of phenyl benzoate.

GC-MS spectrum of one product after the reaction catalyzed by N-HCS-900 with retention time in 8.844-8.891 min (c). This is matched with GC-MS spectrum of 2-methylpropyl benzoate.

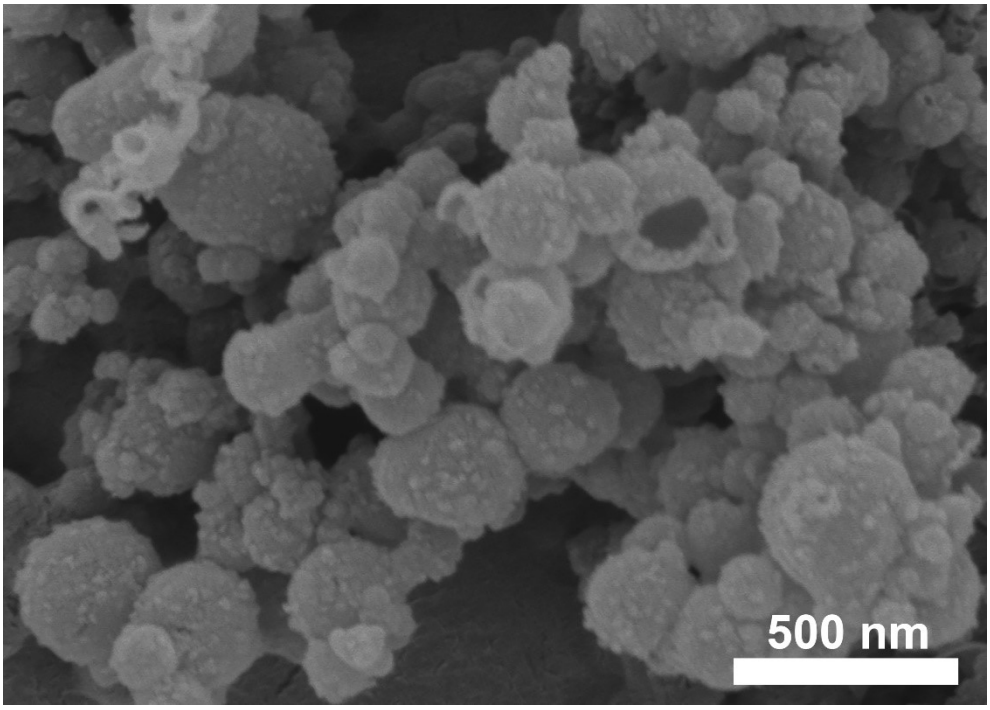


Figure S6. SEM image of the HCS.

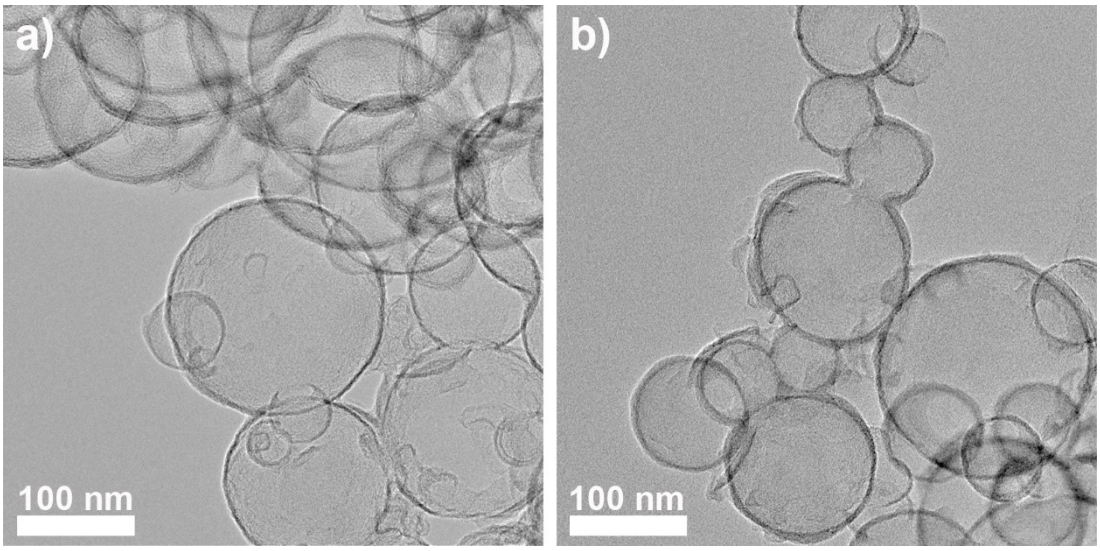


Figure S7. TEM images of the N-HCS-900 after 5 cycles reaction.

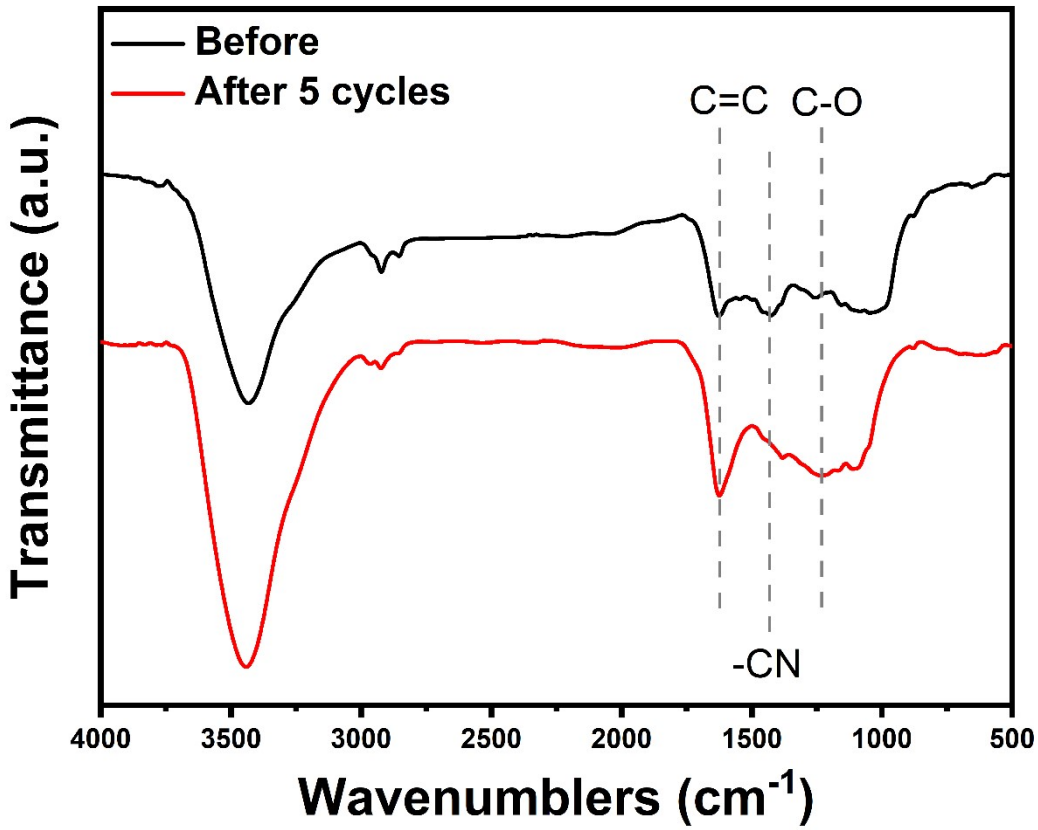


Figure S8. FTIR spectra of N-HCS-900 before and after 5 cycles reaction, respectively.

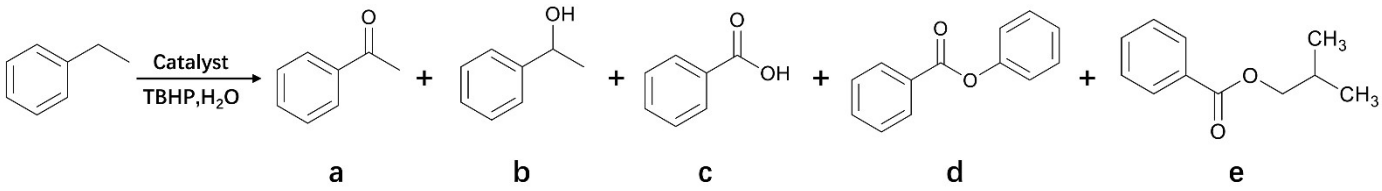
Table S1. Quantitative XPS measurements of chemically doped carbon materials.

Sample	C at. %	O at. %	N at. %		
			Pyridinic N	Graphitic N	Oxidized N
N-HCS-800	87.3	5.3	2.0	4.7	0.7
N-HCS-900	88.2	5.6	1.0	4.0	1.2
N-HCS-1000	91	3.4	1.6	3.4	0.6
N-HPC	88	5.3	1.8	4.2	0.7

Table S2. The atomic percentages of surface functional groups from deconvoluted C 1s XPS spectral fitting.

Sample	C–C	C–N/C–O	C=O	COOH	π→π*
	284.6 eV	286.0 eV	287.8 eV	289.0 eV	291.5 eV
N-HCS-800	53.23%	21.40%	3.47%	7.44%	1.76%
N-HCS-900	54.06%	19.40%	4.49%	6.21%	4.04%
N-HCS-1000	60.04%	19.05%	3.47%	5.35%	3.09%
N-HPC	54.00%	20.85%	5.21%	5.02%	2.92%

Table S3. Catalytic activity of N-HCS/N-HPC catalysts for the selective oxidation reaction of ethylbenzene in water[a].



Entry	Catalyst	Temperature (°C)	Conversion (%)	Selectivity (%)				
				a	b	c	e	f
1	AC	50	17.65	62.39	10.88	1.64	24.76	trace
2	HCS	50	6.05	62.39	4.28	26.80	6.53	trace
3	N-HCS -800	50	86.01	93.63	0.10	0.66	5.41	0.20
4	N-HCS -900	30	46.19	93.00	0.51	trace	6.49	trace
5	N-HCS -900	40	78.32	96.41	trace	trace	3.59	trace
6	N-HCS -900	50	98.38	99.33	trace	trace	0.54	0.13
7	N-HCS -900	80	99.45	99.25	trace	trace	0.33	0.42
8	N-HCS -1000	50	87.75	97.98	0.20	0.17	1.65	trace
9	N-HPC	50	94.72	98.09	trace	trace	1.32	0.59

[a]Reaction conditions: 10.0 mg of catalyst, 0.5mmol of substrate, 500 µL of TBHP as a 70 wt% aqueous solution diluted with 6.5 mL of water for 12h. The conversion and selectivity were determined by GC analysis system equipped with HP-5 capillary and an FID.

Table S4. Comparison table of the catalytic performance of N-HCS-900 catalysts with those reported in literatures.

Entry	Catalyst	Reaction conditions	Conv. (%)	Sel. (%)	TOF[a] mole$_{substrate}$ g$^{-1}_{cat}$ h^{-1}	Ref.
1	N-HCS-900	50°C, H_2O solvent, 500 µL TBHP, 0.5 mmol substrate, 10 mg catalysts,12h	98	99	4.10×10^{-3}	This work
2	N-HCS-900	80°C, H_2O solvent, 500 µL TBHP, 0.5 mmol substrate, 10 mg catalysts, 12h	99	99	4.14×10^{-3}	This work
3	LC-N-8.9 (N-doped layer carbon with 8.9% nitrogen)	80°C, H_2O solvent, 3 mmol TBHP, 0.5 mmol substrate, 10 mg catalysts, 24h	98	91	4.08×10^{-3}	Ref. [1]
4	NGG-4-900 (N-doped graphene gel)	80°C, H_2O solvent, 500 µL TBHP, 0.5 mmol substrate, 10 mg catalysts, 12h	99	99	4.13×10^{-3}	Ref. [2]
5	NMC (N-doped mesoporous carbon)	80°C, H_2O solvent, 3 mmol TBHP, 1 mmol substrate, 10 mg catalysts, 24h	88	60	3.67×10^{-3}	Ref. [3]
6	NOMC-800 (N-doped mesoporous carbon)	80°C, H_2O solvent, 3 mmol TBHP, 1 mmol substrate, 50 mg catalysts, 12h	63	84	1.06×10^{-3}	Ref. [4]

7	3/3-DIRA-900 (3D N-doped meso/micro porous carbon beads)	100°C, TBHP in 3 mL substrate, 100 mg catalysts, 12h	83	93	1.71×10^{-2}	Ref. [5]
8	PDNSC-800 (Polymer-derived N,S co-doped carbon catalysts)	80°C, H_2O solvent, 500 µL TBHP, 1.0 mmol substrate, 20 mg catalysts, 10h	99	99	4.95×10^{-3}	Ref. [6]
9	NPS-HCS (N,P,S co-doped hollow carbon shells)	80°C, H_2O solvent, 500 µL TBHP, 1.0 mmol substrate, 10 mg catalysts, 12h	99	99	8.25×10^{-3}	Ref. [7]

[a] Turnover frequency (TOF): $\text{TOF} = \frac{\text{amount of the converted substrate (mol)}}{\text{mass of catalyst (g)} \times \text{reaction time (h)}}$

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