Electronic Supplementary Information

Mutually isolated nanodiamond/porous carbon nitride nanosheet hybrid with enriched active sites for promoted catalysis in styrene production

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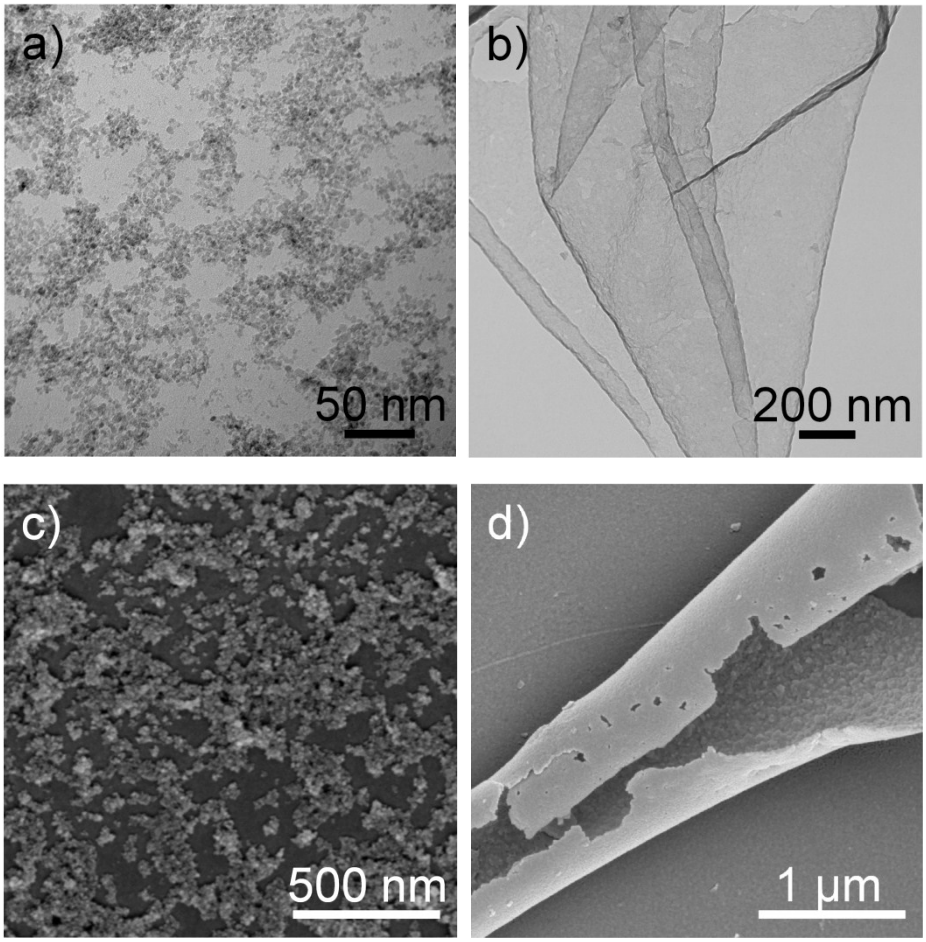

Figure S1. a,b) TEM images and c,d) SEM images of ND-ms (a,c) and CN-ms (b,d).

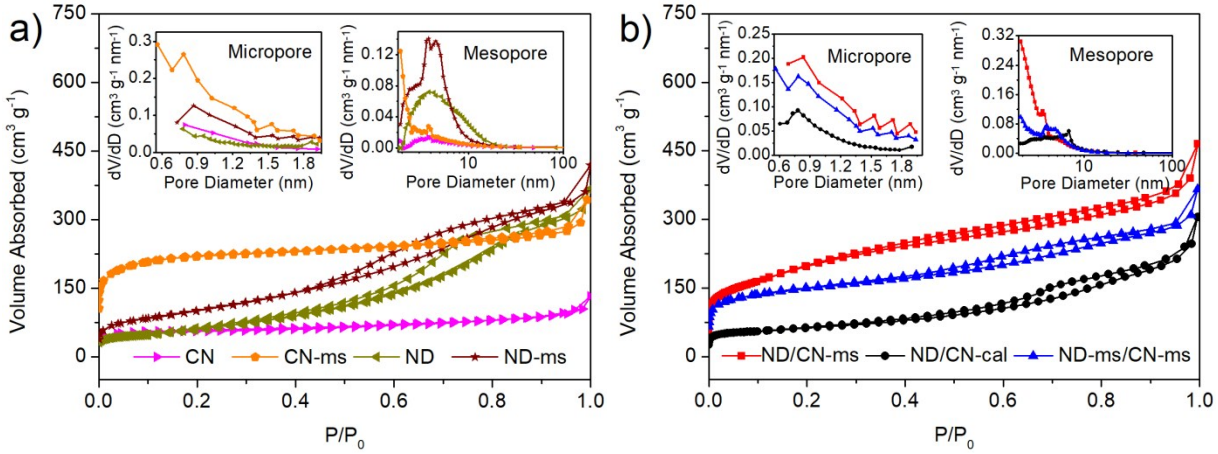

Figure S2. N2 adsorption isotherms of the single carbon materials including CN, CN-ms, ND, ND-ms (a) and the as-prepared ND/CN-ms, ND/CN-cal, ND-ms/CN-ms hybrids (b). Insets: the mesopore size distribution by Barrett-Joyner-Halenda (BJH) method from the desorption branches, and micropore size distribution calculated by Horvath-Kawazoe (H-K) method.

Table S1. Textural properties of the prepared materials.

Samples	S_{total}[a] ($m^2\ g^{-1}$)	S_{micro}[b] ($m^2\ g^{-1}$)	S_{meso}[c] ($m^2\ g^{-1}$)	V_{total}[d] ($cm^3\ g^{-1}$)	V_{micro}[e] ($cm^3\ g^{-1}$)	V_{meso}[f] ($cm^3\ g^{-1}$)
ND	230	0	230	0.57	0.08	0.49
CN	185	120	65	0.21	0.09	0.12
ND/CN-cal	214	0	241	0.47	0.09	0.38
ND-ms	376	0	376	0.65	0.14	0.51
CN-ms	702	616	86	0.53	0.33	0.20
ND-ms/CN-ms	494	216	278	0.57	0.22	0.35
ND/CN-ms	702	486	216	0.72	0.27	0.45
ND/CN-ms-o	704	453	251	0.71	0.23	0.48

[a] Total surface area, obtained from multipoint Brunauer–Emmett–Teller (BET) method. [b] Microporous surface area, determined by T-plot method. [c] Mesoporous surface area, calculated by S_{Total} minus S_{micro}. [d]Total pore volume. [e] Micropore volume, determined by H-K method. [f] Mesoporous pore volume, calculated by V_{Total} minus V_{micro}.

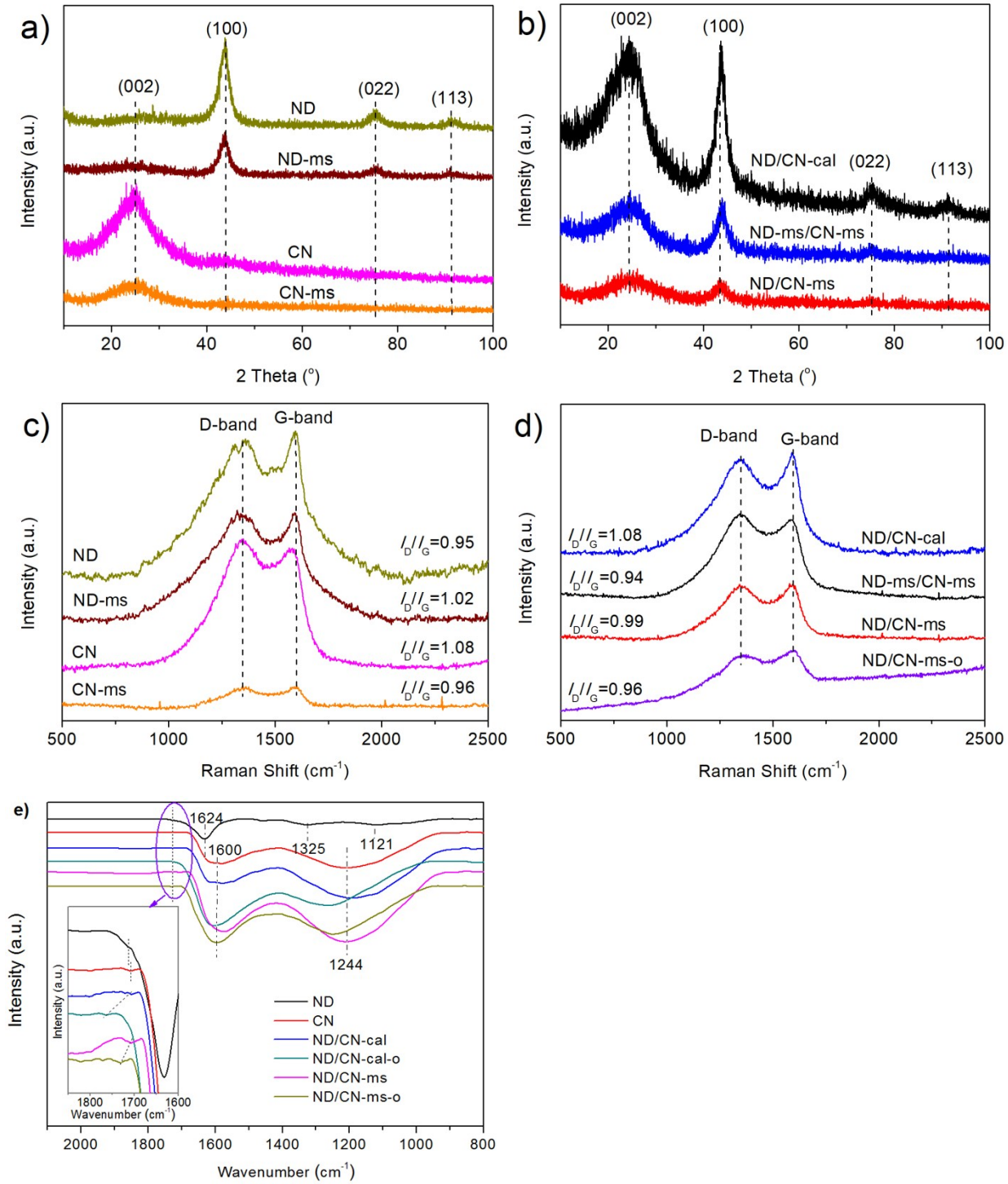

Figure S3. a,b) XRD patterns of the CN, CN-ms, ND, ND-ms single nanocarbon materials (a) and the as-prepared ND/CN-ms, ND/CN-cal, ND-ms/CN-ms hybrids (b). c,d) Raman spectra of the CN, CN-ms, ND, ND-ms single nanocarbon materials (c) and the as-prepared ND/CN-cal, ND-ms/CN-ms, ND/CN-ms, and ND/CN-ms-o hybrids (d). e) FT-IR spectra of ND, CN, ND/CN-cal, ND/CN-cal-o, ND/CN-ms and ND/CN-ms-o (Inset: magnified zone).

Table S2. The results for elemental analysis of the as-prepared ND/CN-cal and ND/CN-ms hybrid materials.

Samples	C [wt%]	N [wt%]	C/N atomic ratio
ND/CN-cal	77.56	8.083	11.19
ND/CN-ms	77.88	5.576	16.29

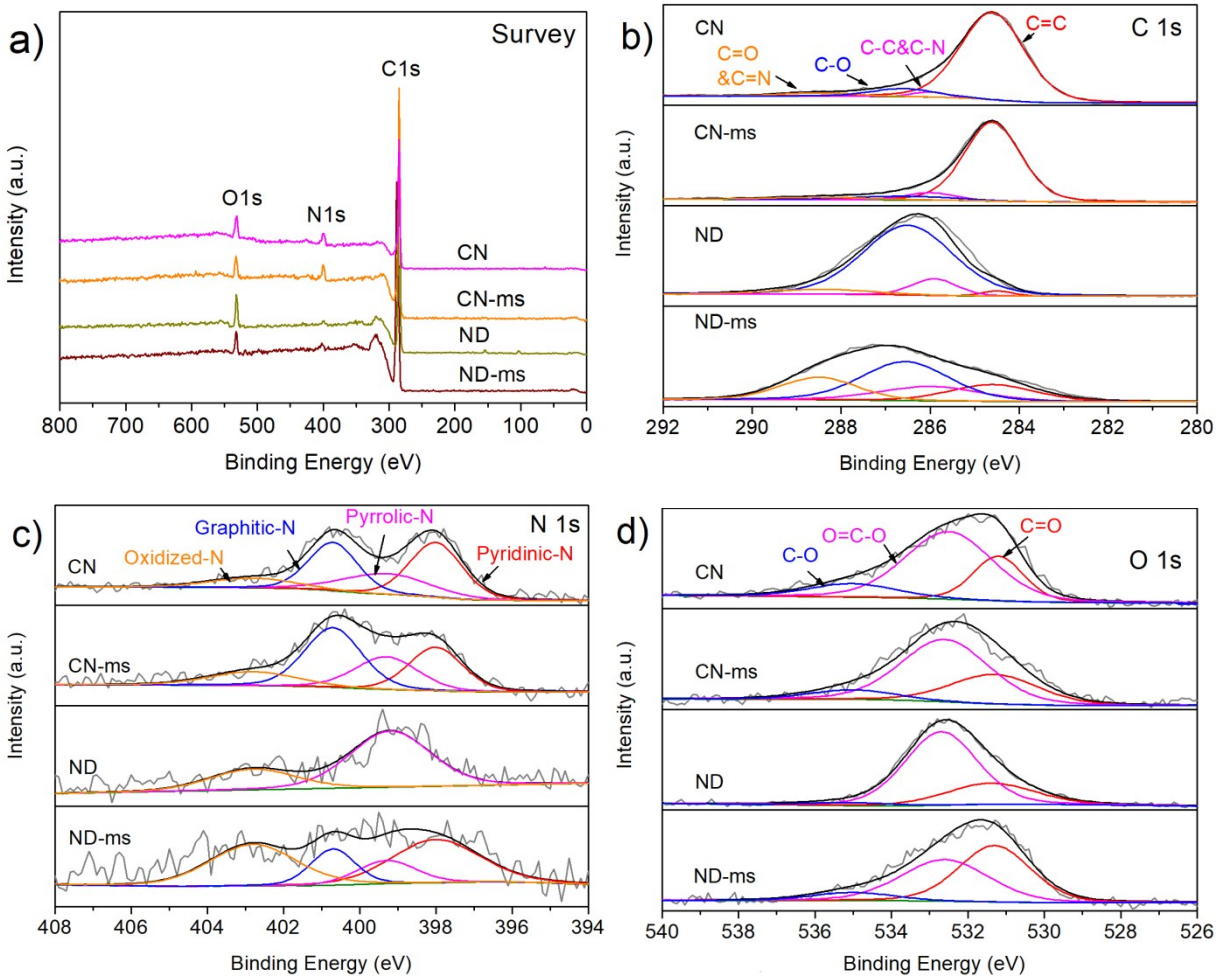

Figure S4. a) Survey, b) C 1s, c) N 1s, and d) O 1s XPS spectra of the CN, CN-ms, ND and ND-ms materials.

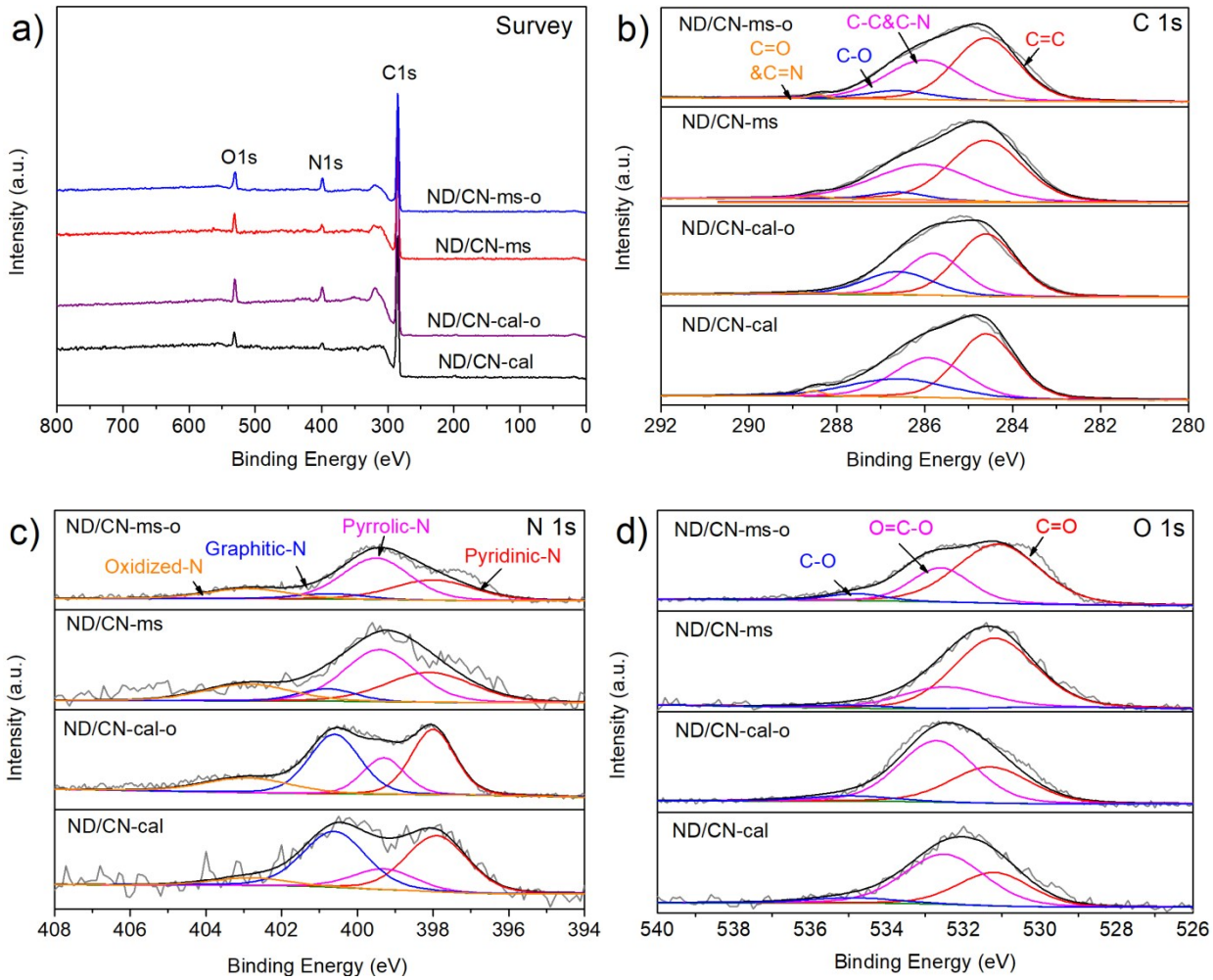

Figure S5. a) Survey, b) C 1s, c) N 1s, and d) O 1s XPS spectra of ND/CN-ms-o, ND/CN-ms, ND/CN-cal-o and ND/CN-cal materials.

Table S3. Relative integrated intensity of deconvoluted N 1s XPS spectra of the prepared materials.

Samples	N[a] (%)	pyridinic N (%)	pyrrolic N (%)	graphitic N (%)	oxidized N (%)
ND	1.2		71.7		28.3
CN	6.4	39.3	14.3	38.9	7.5
ND-ms	2.3	36.5	13.1	15.5	34.9
CN-ms	5.7	30.8	23.7	34.0	11.5
ND/CN-cal	5.7	39.2	14.5	40.0	6.3
ND/CN-cal-o	4.7	32.8	17.6	34.8	14.8
ND/CN-ms	4.6	30.5	43.9	8.3	17.3
ND/CN-ms-o	4.3	30.1	49.9	7.3	12.7

[a] Nitrogen atomic percentage in the samples.

Table S4. Relative integrated intensity of deconvoluted O 1s XPS spectra of the prepared materials.

Samples	O[a] (%)	Surface C=O (%)	Molar percentage (%)		
			C=O	O=C-O	C-O
ND	6.9	1.7	25.0	71.4	3.6
CN	7.9	1.9	24.2	63.2	12.6
ND-ms	3.0	1.5	48.5	43.6	7.9
CN-ms	4.9	1.4	29.0	61.8	9.2
ND/CN-cal	4.0	1.4	35.0	58.3	6.7
ND/CN-cal-o	4.4	1.6	35.9	57.4	6.7
ND/CN-ms	4.4	3.0	67.8	28.8	3.5
ND/CN-ms-o	5.7	3.8	67.4	27.1	5.4

[a] Oxygen atomic percentage in the samples.

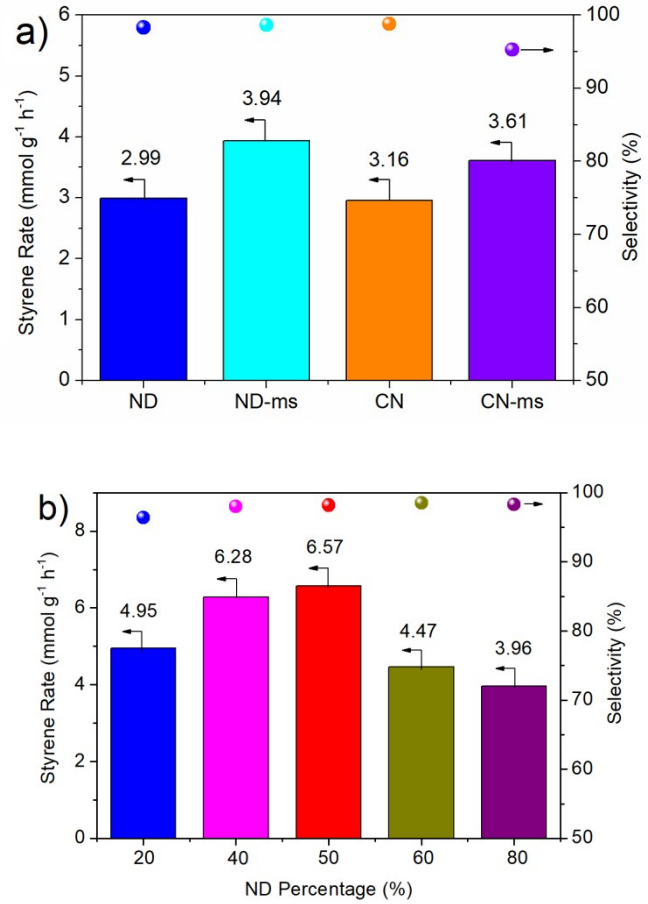

Figure S6. a,b) Steady-state styrene rate and selectivity (20 h of time on stream) for the direct dehydrogenation of ethylbenzene to styrene over the CN, CN-ms, ND and ND-ms catalysts (a) and the as-prepared ND/CN-ms hybrid catalysts with different ND percentages (b).

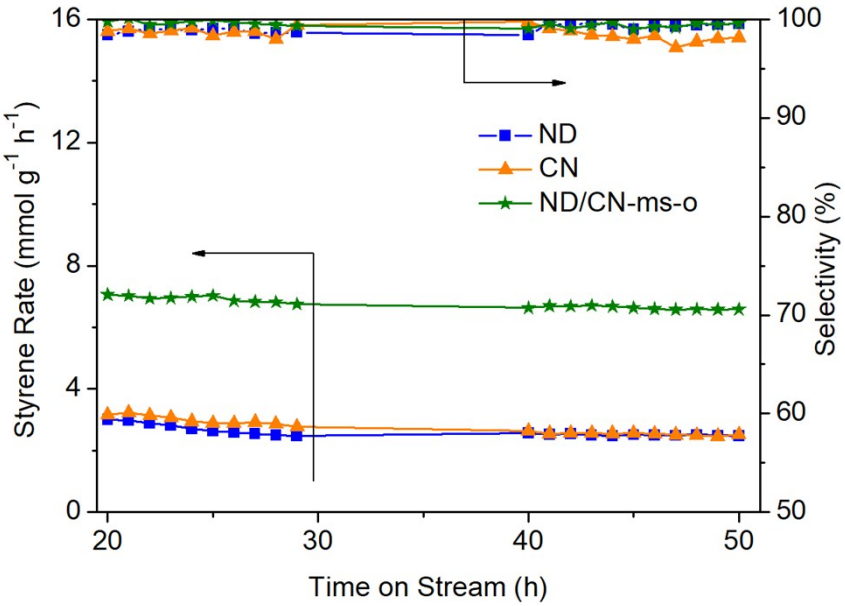

Figure S7. The catalytic stability of the developed ND/CN-ms catalyst for direct dehydrogenation of ethylbenzene to styrene under steam and oxidant-free conditions. Reaction conditions: Catalyst (25 mg), 550 °C, 2.8% ethylbenzene in Ar, 10 ml min^{-1} GHSV.

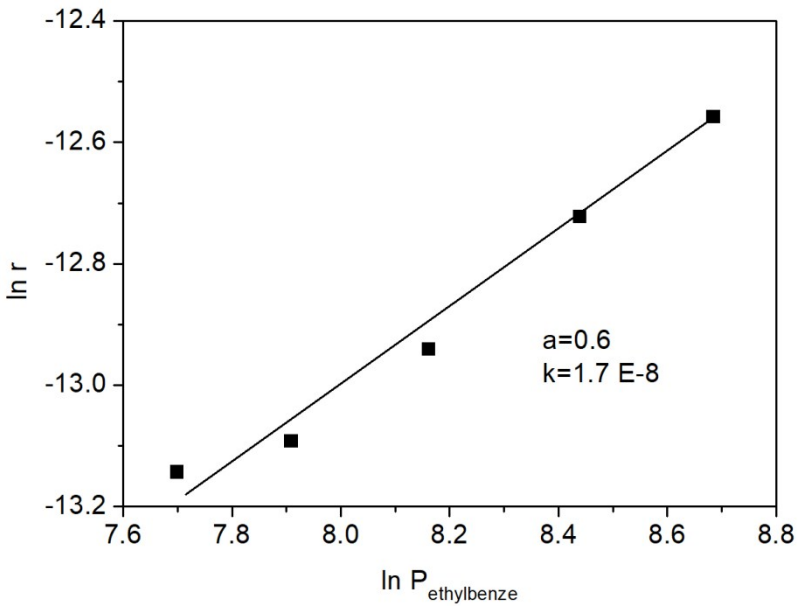

Figure S8. The reaction orders of DDH over the ND/CN-ms-o.

Table S5. Comparison of the catalytic performance of the ND/CN-ms with the reported carbon materials.

Catalyst	Mass (mg)	T (^{o}C)	Select. (%)	ST rate (mmol g^{-1} h^{-1})	Ref.
ND/CN-ms	25	550	99.2	6.57	This work
ND-CN	25	550	99.3	5.61	2
N-RGO/ND	25	550	97.0	4.86	3
DUT-1	25	550	93.6	3.44	4
NMCS	100	550	85.0	1.75	5
ND@NMC	150	550	99.6	5.80	6
ND/CNF-FLG	300	550	96.4	2.03	7
ND-FLG	300	550	99.0	1.95	8

References

1 S. N. Talapaneni, J. H. Lee, S. H. Je, O. Buyukcakir, T.-W. Kwon, K. Polychronopoulou, J. W. Choi, A. Coskun, *Adv. Funct. Mater.,* 2017, **27**,1604658.
2 G. Ge, Z. Zhao, *Appl. Catal. A, Gen.,* 2019, **571**, 82-88.
3 Z. Zhao, Y. Dai, G. Ge, Q. Mao, Z. Rong, G. Wang, *ChemCatChem,* 2015, **7**, 1070-1077.
4 Z. Zhao, Y. Dai, J. Lin, G. Wang, *Chem. Mater.,* 2014, **26**, 3151-3161.
5 J. Wang, H. Liu, J. Diao, X. Gu, H. Wang, J. Rong, B. Zong, D. Su, *J. Mater. Chem. A*, 2015, **3**, 2305-2313.
6 Y. Liu, H. Ba, J. Luo, K. Wu, J.-M. Nhut, D. Su, C. Pham-Huu, *Catal. Today*., 2018, **301**, 38-47.
7 H. Ba, L. Truong-Phuoc, Y. Liu, C. Duong-Viet, J.-M. Nhut, L. Nguyen-Dinh, P. Granger, C. Pham-Huu, *Carbon*, 2016, **96**, 1060-1069.
8 H. Ba, S. Podila, Y. Liu, X. Mu, J.-M. Nhut, V. Papaefthimiou, S. Zafeiratos, P. Granger, C. Pham-Huu, *Catal. Today*., 2015, **249**, 167-175.