Supporting Information

Unlocking the Catalytic Role of Oxygen Functionalities on Carbon-Based Catalysts for Hydrogen Generation from Ammonia Borane

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Table S1: Graphitisation degree (I_D/I_G), oxygen content (O/C) and H_2 productivity of the different carbocatalysts considered.

Sample name	I_D/I_G	O/C	nH_2 at 180'/ mmol*10^{-2}
CNFs	0.86	0.12	5.7
O-CNFs-H_2O_2	0.83	0.14	20.2
O-CNFs-HNO_3	0.87	0.18	45.7
Graphite	0.09	0.02	-
O-Graphite	0.08	0.07	0.9
GNP	0.12	0.03	-
O-GNP	0.13	0.03	-

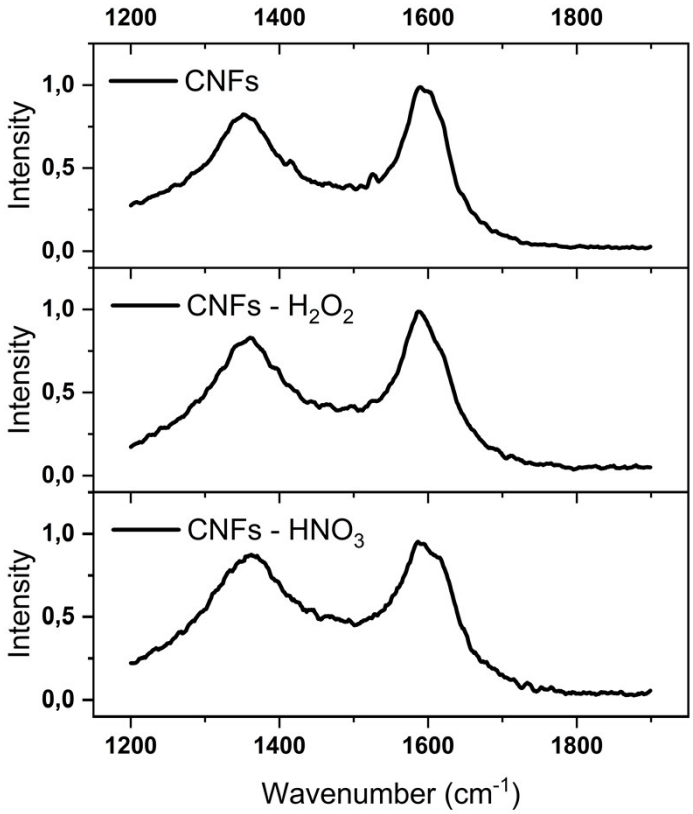

Figure S1: Raman spectra before and after functionalisation procedure.

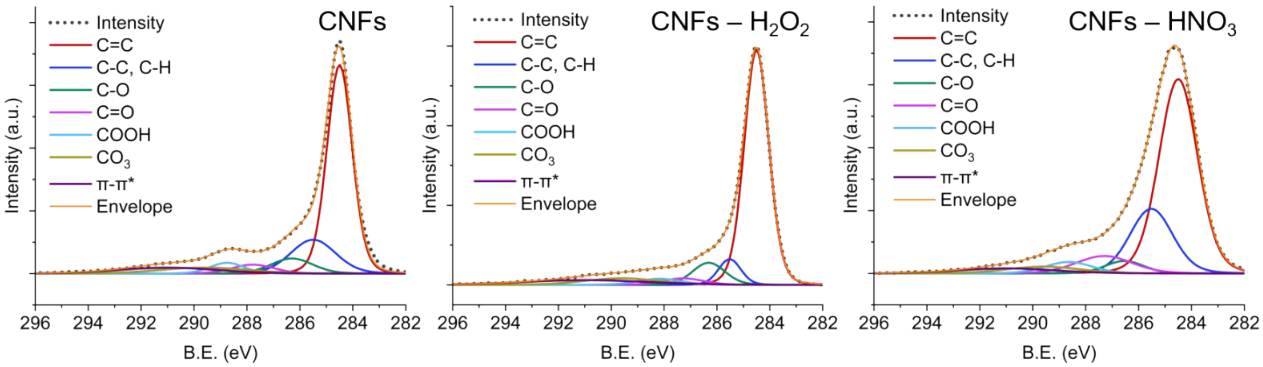

Figure S2: High Resolution analysis of the C1s region of bare and oxidised carbon nanofibers.

Table S2: Summary of the HR analysis of the C1s region of bare and oxidised carbon nanofibers.

Sample Name	C=C / BE (At. %)	C-C, C-H / BE (At. %)	C-O / BE (At. %)	C=O / BE (At. %)	O=C-O / BE (At. %)	π-π* / BE (At. %)	CO_3 / BE (At. %)

CNFs	284.5 (56.7)	285.5 (16.3)	286.3 (6.7)	287.8 (4.1)	288.8 (4.0)	291.0 (6.5)	289.6 (5.8)
O-CNFs-H_2O_2	284.5 (66.1)	285.5 (6.6)	286.3 (8.3)	287.3 (3.1)	288.2 (3.1)	291.0 (7.1)	289.6 (5.8)
O-CNFs-HNO_3	284.5 (55.8)	285.5 (21.0)	286.5 (3.6)	287.3 (7.4)	288.6 (4.1)	291.0 (3.8)	289.6 (3.8)
O-Graphite	284.5 (69.0)	285.5 (11.9)	286.1 (4.0)	287.0 (4.0)	288.4 (2.3)	291.0 (8.0)	289.6 (0.7)
O-GNP	284.5 (57.4)	285.5 (14.3)	286.5 (6.3)	287.1 (4.5)	288.6 (3.4)	291.0 (10.0)	289.5 (1.5)

Table S3: Summary of the HR analysis of the O1s region of bare and oxidised carbon nanofibers.

Sample Name	C-O-C / BE (At. %)	C-OH / BE (At. %)	C=O / BE (At. %)	COOH / BE (At. %)	H_2O / BE (At. %)
CNFs	532.9 (19.5)	533.4 (14.3)	531.4 (26.7)	532.3 (32.3)	535.0 (7.3)
O-CNFs-H_2O_2	533.2 (23.1)	533.1 (18.2)	531.1 (24.5)	532.1 (29.3)	535.1 (7.9)
O-CNFs-HNO_3	533.1 (7.4)	534.0 (4.4)	531.3 (37.7)	532.8 (44.4)	535.0 (6.2)
O-Graphite	533.4 (21.6)	534.1 (9.1)	531.4 (25.2)	532.4 (40.3)	535.5 (3.9)
O-GNP	533.4 (23.3)	534.0 (11.5)	531.5 (28.1)	532.4 (32.3)	535.5 (4.7)

As reported in the Results section, three possible activation pathways are reported:

$$NH_3BH_3 + * \rightarrow {NH_3}^* + {BH_3}^* \qquad \text{pathway a}$$

$$NH_3BH_3 + * \rightarrow {NH_3}^* + {BH_2}^* + H^* \qquad \text{pathway b}$$

$$NH_3BH_3 + * \rightarrow {NH_4}^+{}_{(aq)} + [BH_2]^{-*} \qquad \text{pathway c}$$

Table S4: Entropic and zero-point energy contributions for each functional group.

Functional group	Specie	TS / eV	E_{ZPE} / eV	ΔE / eV	ΔG / eV
C-OH	NH_3* BH_3*	1.14	2.58	0.79	0.99
	NH_4^+ BH_2*	0.43	1.05	-0.11	-0.20
C-O-C	NH_4^+ BH_2*	0.17	0.67	-0.01	-0.22
C=O	NH_3* BH_3*	1.04	2.06	0.02	-0.21
	NH_3* BH_2* H*	1.14	2.52	0.77	0.90
	NH_4^+ BH_2*	0.32	0.74	-1.54	-1.84
COOH	NH_3* BH_3*	1.01	2.30	0.49	0.54
	NH_3* BH_2* H*	1.51	2.87	0.66	0.78
	NH_4^+ BH_2*	0.18	0.55	-0.93	-1.27
	NH_4^+	0.36	0.88	-	-
	NH_3BH_3	0.61	1.85	-	-
	NH_4BO_2	0.76	1.53	-	-

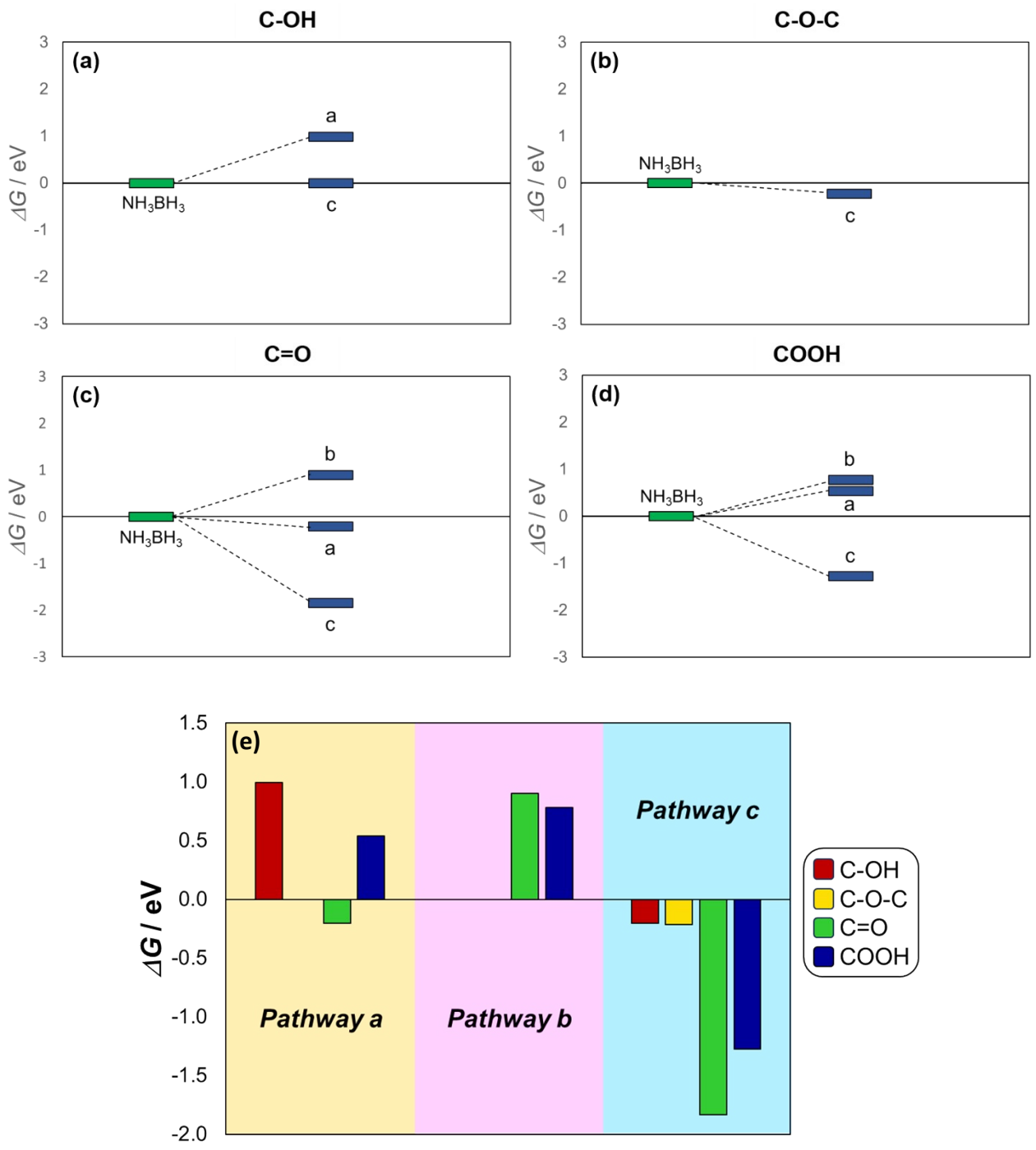

Figure S3: free energy diagrams for C-OH (a), C-O-C (b), C=O (c) and COOH (d) systems. (e) Comparison of the free energy of the different functional groups for the pathways considered in the study. In particular, the adsorption step of NH_3BH_3 is reported; the considered pathways are explained above and in the main text in the results section.

Table S5: Gibbs free energy values for each functional group with and without considering the role of the solvent.

Functional group	Pathway	ΔG / eV	ΔG_{SOLV} / eV
C-OH	a	0.99	1.28
	c	-0.20	-0.40
C-O-C	b	-0.22	-0.41
C=O	a	-0.21	0.13
	b	0.90	1.23
	c	-1.84	-1.86
COOH	a	0.54	0.96
	b	0.78	1.06
	c	-1.27	-1.01

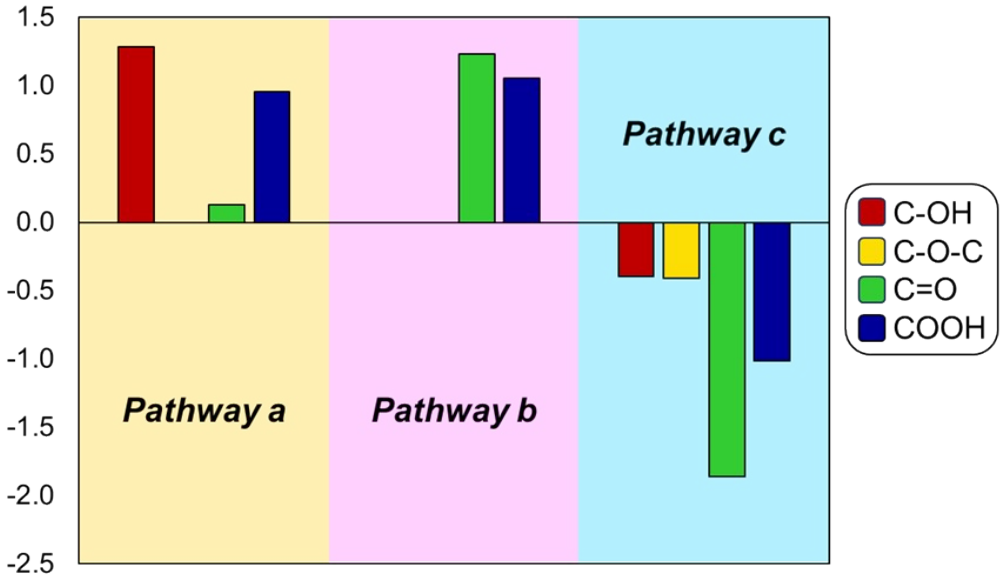

Figure S4: free energy diagrams for C-OH (a), C-O-C (b), C=O (c) and COOH (d) systems considering implicit solvation model. In particular, the adsorption step of NH_3BH_3 is reported; the considered pathways are explained above and in the main text in the results section.

Table S6: evolution of C-O bond distances in the considered functional groups according to the chosen pathway

Functional group	Pathway	*d(C-O)* / Å
C-OH	-	1.35
	a	1.41
	c	1.34
C-O-C	-	1.49
	c	1.40 - 2.35
C=O	-	1.23
	a	1.40
	b	1.30
	c	1.36
COOH	-	1.22
	a	1.33
	b	1.30
	c	1.31