Supplementary

Mechanochemical functionalization of Carbon black at room temperature

Desirée Leistenschneider [1], Katharina Zürbes [1], Christina Schneidermann [1], Sven Grätz [1], Steffen Oswald [2], Karl Wegner [1], Benjamin Klemmed [3], Lars Giebeler [2] Alexander Eychmüller [3] and Lars Borchardt [1,*]

[1] Department of Inorganic Chemistry, Technische Universität Dresden, Bergstraße 66, 01062 Dresden, Germany; desiree.leistenschneider@tu-dresden.de (D.L.); katharina.zuerbes@chemie.tu-dresden.de (K.Z.); christina.schneidermann@tu-dresden.de (C.S.); sven.graetz@tu-dresden.de (S.G.); karl.wegner@tu-dresden.de (K.W.)

[2] Institute for Complex Materials, Leibniz Institute for Solid State and Materials Research (IFW) Dresden e.V., Helmholtzstraße 20, 01069 Dresden, Germany; s.oswald@ifw-dresden.de (S.O.); l.giebeler@ifw-dresden.de (L.G.)

[3] Physical Chemistry, Technische Universität Dresden, Bergstraße 66b, 01062 Dresden, Germany; benjamin.klemmed@chemie.tu-dresden.de (B.K.); alexander.eychmueller@chemie.tu-dresden.de (A.E.)

* Correspondence: lars.borchardt@chemie.tu-dresden.de; Tel.: +49-3514-633-4960

1. Raman spectroscopy

Table S1. Ratio of the vibrations of the D and G Band calculated as the ratio of the peak areas fitted as Gaussian.

Sample	I(D) / I(G)
CB	1.09
CB-0.5	1.63
CB-2	0.8
NCB-0.5	1.64
NCB-1	1.47
NCB-2	1.56
NCB-4	1.59

2. XPS analysis

Table S2. Element concentrations from the high resolution spectra.

Sample	C 1s wt.%	N 1s wt.%	O 1s wt.%	Zr 3d wt.%
CB	99.7	n.d.	0.3	n.d.
CB-0.5	88.3	1.5	8.7	1.5
NCB-0.5	84.4	3.9	6.7	5.0

Table S3. The signal-contributing carbon species calculated from the C 1s high resolution spectra.

Sample	Position / eV	Height	Area	%Area
CB	284.5	45788	51265	68
	286.0	4793	13774	18
	288.9	1434	2610	3
	290.7	1570	3253	4
	292.1	1295	5070	7
CB-0.5	284.4	14990	20323	58
	286.0	3148	9047	26
	288.6	911	1658	5

	290.2	764	2029	5
	292.0	492	2010	6
NCB-0.5$_1$	284.4	14751	20079	61
	286.0	2705	7776	24
	288.6	759	1381	4
	290.3	651	1577	5
	292.1	487	1986	6

Species for binding energy positions: C-C ≈ 284.4 eV; C-O ≈ 286.0 eV for phenolic, alcoholic and ether groups, also C=N; O-C-O ≈ 288.6 eV for carbonylic or quinonic groups; O-C=O ≈ 290.2 eV for carboxylic and ester functionalities; π-π* shake-up satellite ≈ 292.0 eV.[1,2]

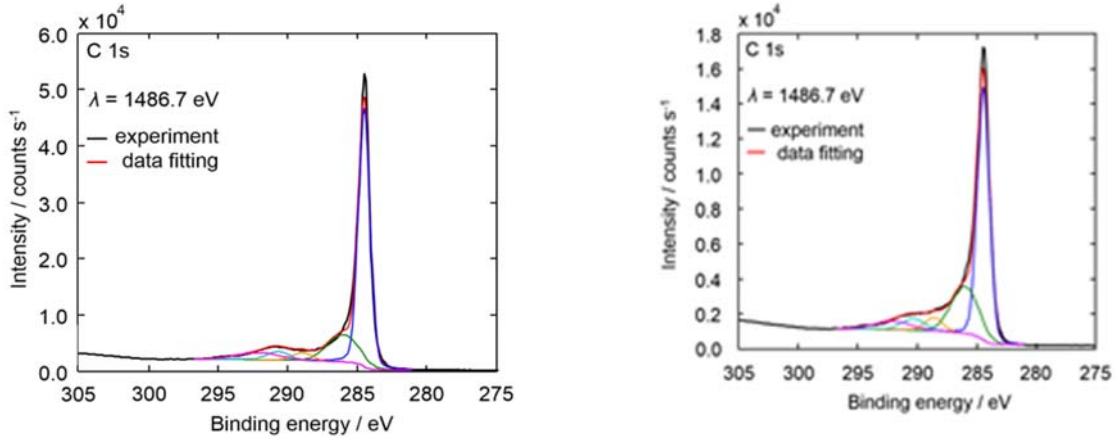


Figure S1. (**a**) Fitted C 1s spectrum of CB and (**b**) fitted C 1s spectrum of CB-0.5. Blue = C-C; green = C-O; dark yellow = O-C-O; turquois = O-C=O; magenta = π-π*

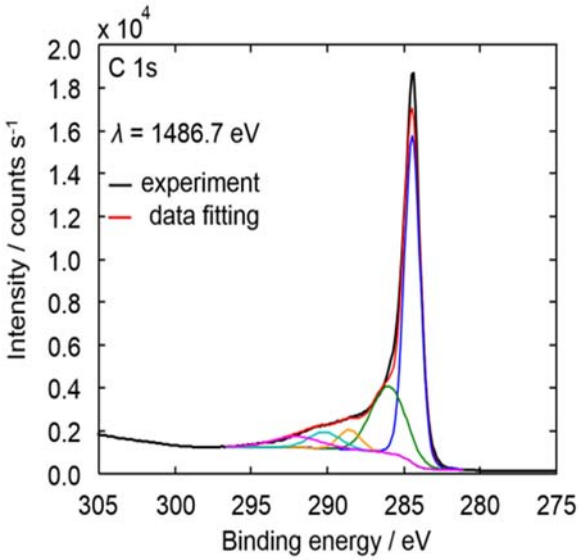
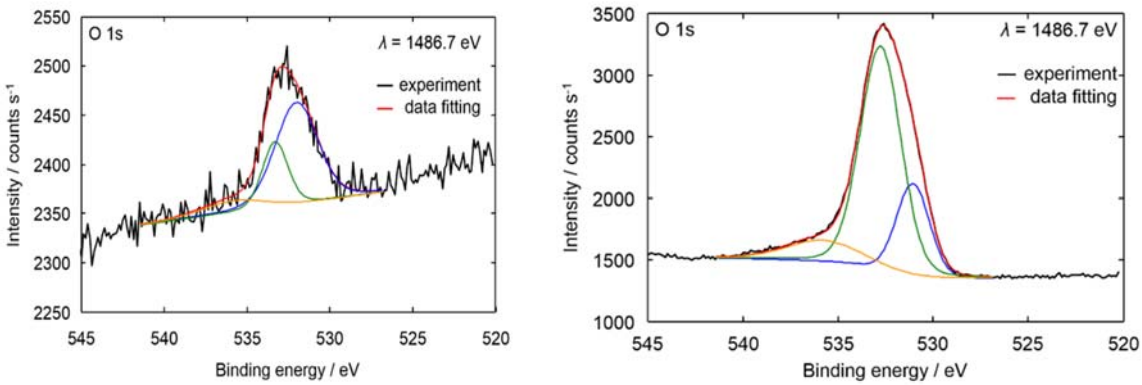


Figure S2. Fitted C 1s spectrum of NCB-0.5$_1$. Blue = C-C; green = C-O; dark yellow = O-C-O; turquois = O-C=O; magenta = π-π*.

Table S4. The signal-contributing oxygen species calculated from the O 1s high resolution spectra.

Sample	Position / eV	Height	Area	%Area
CB	532.0	103	365	64
	533.3	66	139	25
	535.8	12	62	11
CB-0.5	531.0	739	1619	21
	532.8	1805	5135	67
	535.8	170	881	12
CB-NH_3	531.3	1121	2614	50
	532.9	805	2221	43
	535.8	72	352	7

Species for binding energy positions: C=O ≈ 531-532 eV; C-OH/C-O-C groups ≈ 533 eV; shake-up satellite = 535.8 eV.[3,4]



(a) (b)

Figure S3. (**a**) O 1s signal of CB and (**b**) O 1s signal of CB-0.5. Blue = C=O; green = C-OH/C-O-C; dark yellow = shake-up satellite.

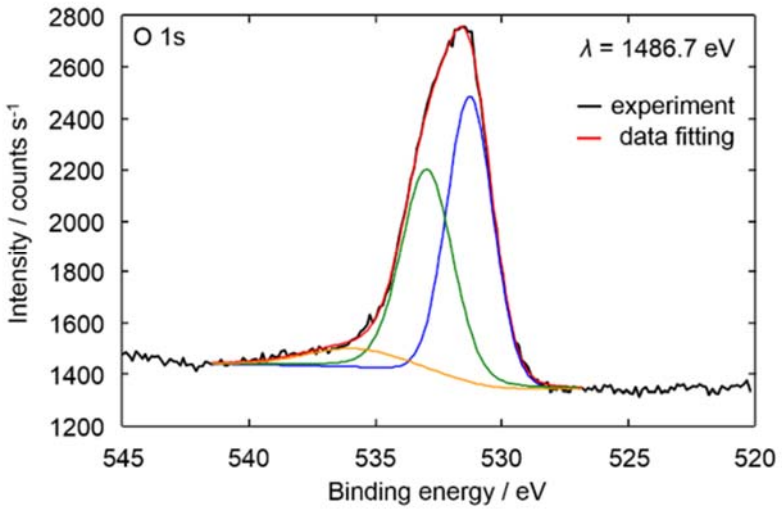


Figure S4. O 1s signal of NCB-0.5. Blue = C=O; green = C-OH/C-O-C; dark yellow = shake-up satellite.

Table S5. The signal-contributing nitrogen species calculated from the N 1s high resolution spectra.

Sample	Position / eV	Height	Area	%Area
CB-0.5	398.8	115	214	22
	400.3	236	583	61
	403.9	32	165	17
NCB-0.5	398.9	454	1071	44
	400.2	330	812	33
	403.9	80	573	23

Species for binding energy positions: pyridinic groups ≈ 398.8 eV; imine/amide/amine groups ≈ 400.3 eV; pyridin-N-oxide = 403.9 eV.[5,6]

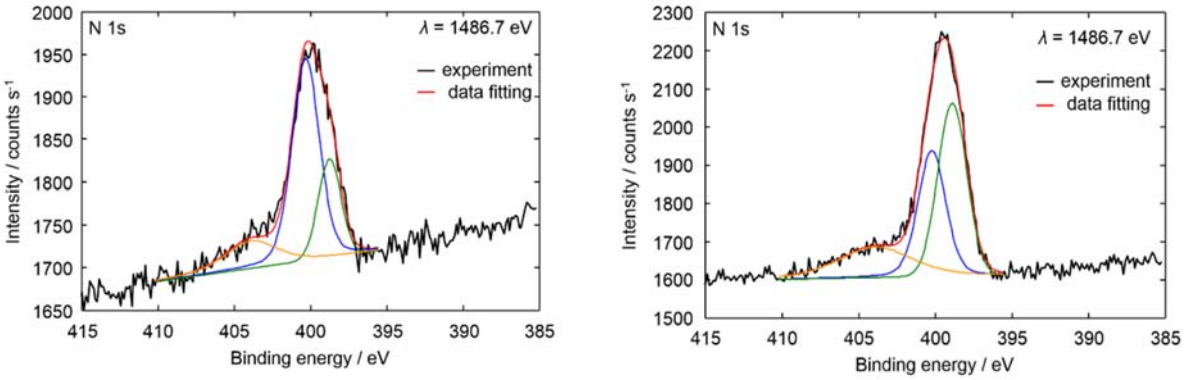


Figure S5. (a) N 1s signal of CB-0.5 and (b) N 1s signal of NCB-0.5. Green = pyridinic groups; blue = imine/amide/amine groups; dark yellow = pyridin-N-oxide.

3. Elemental analysis

Table S6. Elemental composition determined by elemental analysis.

Sample	C / wt.%	H / wt.%	N / wt.%	S / wt.%	Residual / wt.%
CB	100.35	0.54	n. d.	n. d.	-
CB-0.5	90.37	n. d.	n. d.	n. d.	8.66
NCB-0.5$_1$	80.86	0.73	2.02	n. d.	16.289
NCB-1	85.43	0.42	2.94	n. d.	11.21
NCB-2	86.35	0.54	2.32	n. d.	10.79
NCB-4	62.41	1.13	2.20	n. d.	34.24
NCB-0.5$_2$	84.66	0.67	2.74	n. d.	11.93
NCB-0.5$_3$	86.09	0.39	2.31	n. d.	11.21

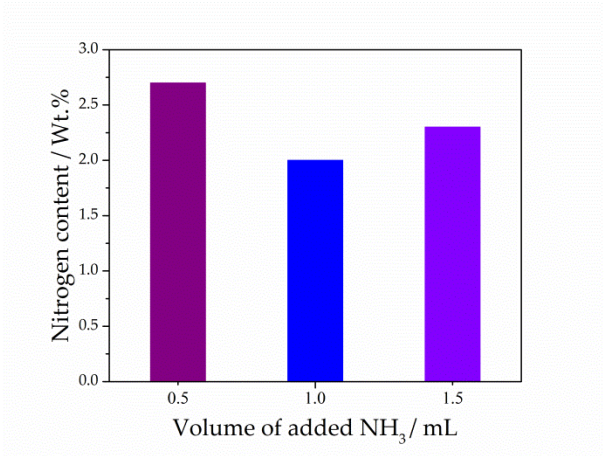


Figure S6. Content of incorporated nitrogen correlated with the volume of added NH_3.

4. SEM images

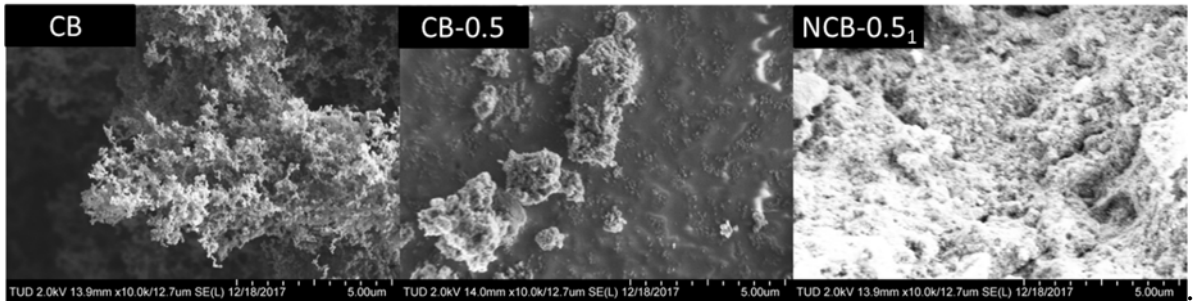


Figure S7. SEM images of the sample CB, CB-0.5 and NCB-0.5_1.

References

1. Moulder, J.F.; Stickle, W.F.; Sobol, P.E., Bomben, K.D. In: *Handbook of X-ray Photoelectron Spectroscopy: A Reference Book of Standard Spectra for Identification and Interpretation of XPS Data*; Chastain, J., Ed.; Perkin-Elmer Corporation, Physical Electronics Division, Minnesota, 1995, ISBN 9780964812413.
2. Reis, M.J.; Botelho do Rego, A.M.; Lopes da Silva, J.D.; Soares, M.N. An XPS study of the fibre-matrix interface using sized carbon fibres as a model. *J. Mater. Sci*. **1995**, *30*, 118-126, doi: 10.1007/BF00352140.
3. Darmstadt, H.; Roy, C.; Kallaguine, S. ESCA characterization of commercial carbon blacks from vacuum pyrolysis of used tires. *Carbon* **1994**, *32*, 1399-1406, doi: 10.1016/0008-6223(94)90132-5.
4. Seredych, M.; Hulicova-Jurcakova, D.; Lu, G.Q.; Bandosz, T.J. Surface functional groups of carbons and the effects of their chemical character, density and accessibility to ions on electrochemical performance. *Carbon* **2008**, *46*, 1475-1488, doi: 10.1016/j.carbon.2008.06.027.
5. Jansen, R.J.J.; van Bekkum, H. XPS of nitrogen-containing functional groups on activated carbon. *Carbon* **1995**, *33*, 1021-1027, doi: 10.1016/0008-6223(95)00030-H.
6. Pels, J.R.; Kapteijn, F.; Moulijn, J.A.; Zhu, Q.; Thomas, K.M. Evolution of nitrogen functionalities in carbonaceous materials during pyrolysis. *Carbon* **1995**, *33*, 1641-1653, doi: 10.1016/0008-6223(95)00154-6.