

Electronic Supplementary Information for: Carbon/Carbon-Nanocomposites Fabricated by Base Catalysed Twin-Polymerization of a Si-Spiro Compound on Graphite Sheets

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Experimental

For the synthesis of the hybrid materials a general procedure was used. 2,2'-spirobi[4*H*-1,3,2-benzodioxasiline] was synthesized as previously described^[S1], the other chemicals were used as purchased without further purification.

In a typical reaction graphite (KS4, BASF SE) was mixed with the base (0.045g DABCO per gram graphite) and the respective amount of 2,2'-spirobi[4*H*-1,3,2-benzodioxasiline], in diisopropylnaphtaline (DIPN) under inert atmosphere. The reaction mixture was vigorously stirred, heated to 160 °C and kept at this temperature for 3 hours. After cooling to room temperature the solid was collected by centrifugation and washed 3 times with toluene. The product was dried under reduced pressure at 110 °C.

For the conversion of the phenolic resin into carbon the hybrid materials was heated to 800 °C with a heating rate of 4.3 K·min⁻¹ and carbonized at that temperature for 3 hours under Argon atmosphere. To remove the SiO₂, 0.2 g of the carbonized composite was boiled 3 h in 60 mL 5 M NaOH. After cooling to room temperature the solid was collected by centrifugation and washed 3 times with hot water and afterwards 3 times with cold water. The carbon/graphite composite was dried for 3 days at 110 °C in vacuum.

Supplemental figures

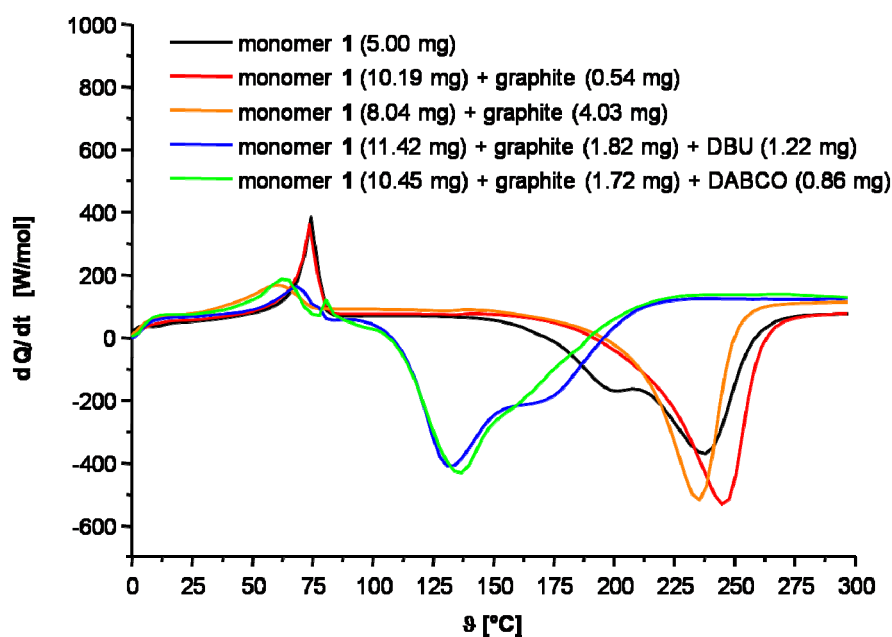


Fig.S1 DSC curve of the polymerization of pure monomer 1 compared with monomer 1 with added carbon and added carbon + base catalyst.

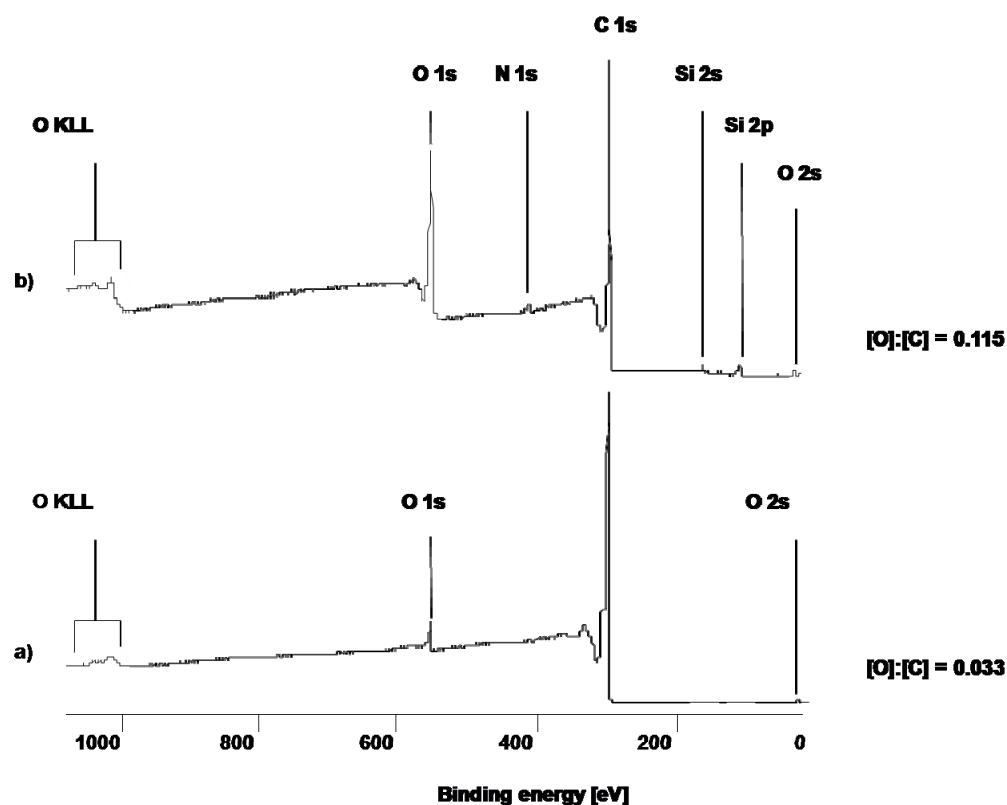


Fig. S2 Wide-scan spectra of pristine graphite (a) and coated graphite (b). The [O]:[C] elemental ratios given in the figure compare the relative contents of the organically bonded oxygen. Additionally, the coated graphite sample (b) shows traces of nitrogen (as N 1s peak) and silicon (as Si 2p and Si 2s peaks). The abbreviation O KLL marks the oxygen Auger peak series.

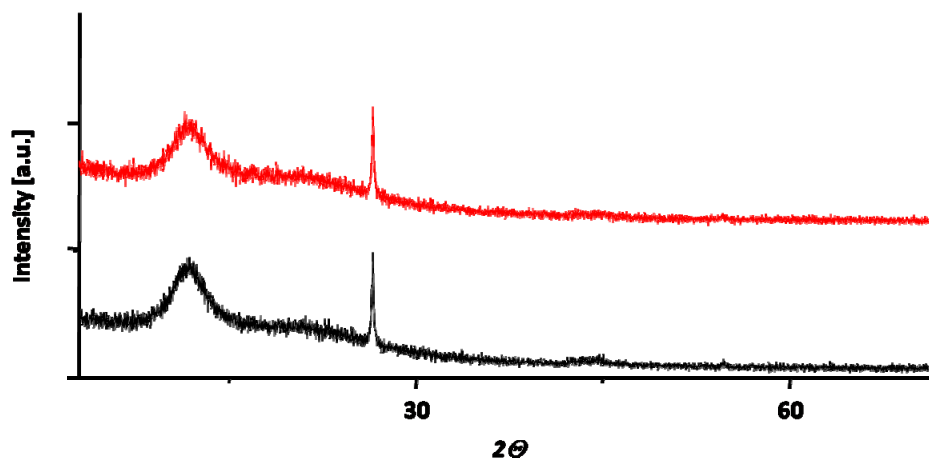


Fig. S3 XRPD spectra of pristine graphite (black) and with twin polymer coated graphite (red).

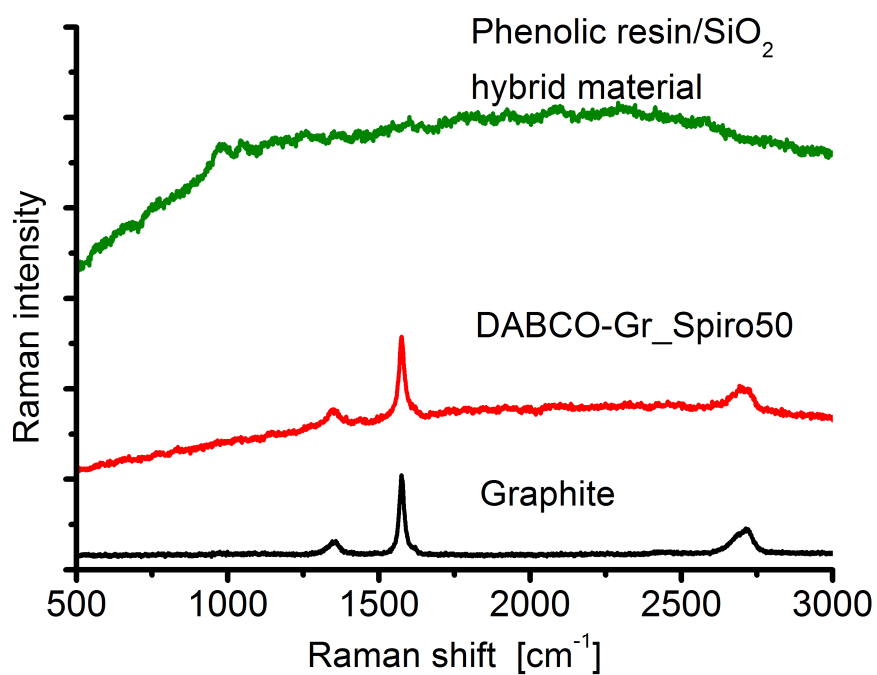


Fig. S4 Raman spectra of pristine graphite, hybrid material coated graphite and pure phenolic resin/SiO₂ hybrid material measured with a 514.5 nm laser.

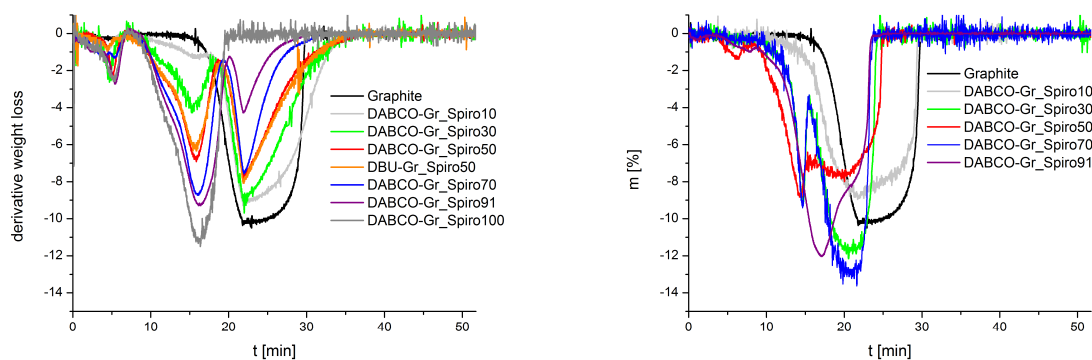


Fig. S5 Derivative TGA curves of the annealing of the twin polymer/graphite hybrid material (a) and the carbon coated graphite (b) under air atmosphere. The samples were heated to 900 °C with 40 K·min⁻¹ with an air flow of 20.0 mL·min⁻¹ and maintained at this temperature for 30 minutes.

Table S1 Position of D and G Raman signals and I_D/I_G -ratio of the carbon-graphite composites displayed in Fig. 5.

Compound name	Position of D peak [cm^{-1}]	Position of G peak [cm^{-1}]	I_D/I_G -ratio
Graphite	1357	1576	0.21
DABCO-Gr_Spiro10	1346	1576	0.31
DABCO-Gr_Spiro30	1351	1580	0.77
DABCO-Gr_Spiro50	1336	1598	0.86
DABCO-Gr_Spiro70	1340	1598	0.88
DABCO-Gr_Spiro91	1341	1599	0.89

The composition of the final carbon/graphite composites depend on the amount of graphite in the composite. With increasing graphite ratio the carbon content is increased (see table S2). Further increase can be achieved by higher carbonization time or temperature but were not subject of this investigation.

Table S2 Elemental analysis of the carbon coated carbons.

Compound name	Carbon content [wt%]	Hydrogen content [wt%]	Oxygen content [wt%] ^a
Graphite	99.5	0.2	0.3
DABCO-Gr_Spiro10	98.9	0.4	0.7
DABCO-Gr_Spiro30	96.8	0.6	2.6
DABCO-Gr_Spiro50	94.4	0.6	5.0
DABCO-Gr_Spiro70	89.7	1.1	9.2
DABCO-Gr_Spiro91	86.2	1.5	12.3

^a Oxygen content is determined by difference.

Supplemental Reference

- [S1] S. Spange, P. Kempe, A. Seifert, A. A. Auer, P. Ecorchard, H. Lang, M. Falke, M. Hietschold, A. Pohlers, W. Hoyer, G. Cox, E. Kockrick, and S. Kaskel, *Angew. Chem. Int. Ed.*, 2009, **48**, 8254.