

Cite this: DOI: 10.1039/c0xx00000x

www.rsc.org/xxxxxx

COMMUNICATION

Sulphur-doped porous carbon from a thiophene-based twin monomer

Falko Böttger-Hiller,^{*a} Alexander Mehner^a, Susann Anders^b, Lothar Kroll^b, Gerhard Cox^c, Frank Simon^d and Stefan Spange^a

Received (in XXX, XXX) Xth XXXXXXXXXX 20XX, Accepted Xth XXXXXXXXXX 20XX

DOI: 10.1039/b000000x

Supporting Information

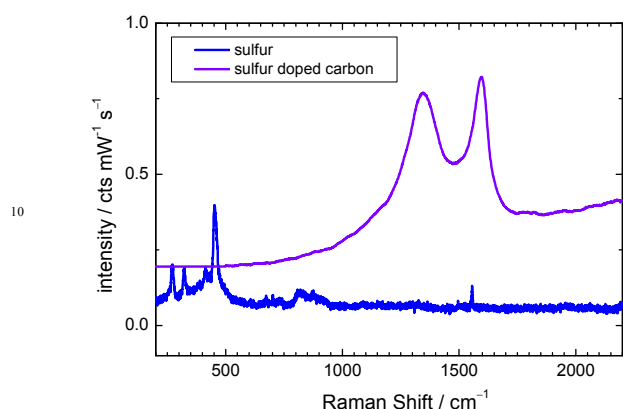


Fig. S1 Raman spectra of pristine sulphur and sulphur-doped carbon from synthesis of Aerosil® OX 50 and 66 m-% **1**. No elementary sulphur was found in the sulphur-doped carbon samples.

Table S1 Elemental composition of polythienyl alcohol/SiO₂ nanocomposite and nanocomposite-coated Aerosil®.

Template	Monomer content [%]	Carbon content [%]	Hydrogen content [%]	Sulphur content [%]
Aerosil®				
–	100	43.5	3.7	25.4
300	89	35.6	2.9	20.8
300	66	29.2	2.7	17.2
300	33	12.9	1.6	9.6
OX 50	66	29.8	2.5	17.2

Table S2 Elemental composition of sulphur-doped carbon.

Template	Monomer content [%]	Carbon content [%]	Hydrogen content [%]	Sulphur content [%]
Aerosil				
–	100	80.3	0.8	15.5
300	89	80.1	0.8	16.5
300	66	73.8	1.5	11.5
300	33	79.6	1.0	16.2
OX 50	66	73.4	1.5	12.4
OX 50*	66	90.4	2.2	2.3

*carbonized at 1100°C

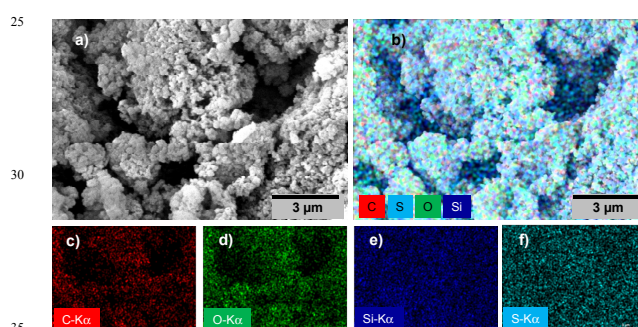


Fig. S2 a) SEM image and b–f) EDX images taken from nanocomposite samples synthesized from 66 m-% **1** on Aerosil® OX 50.

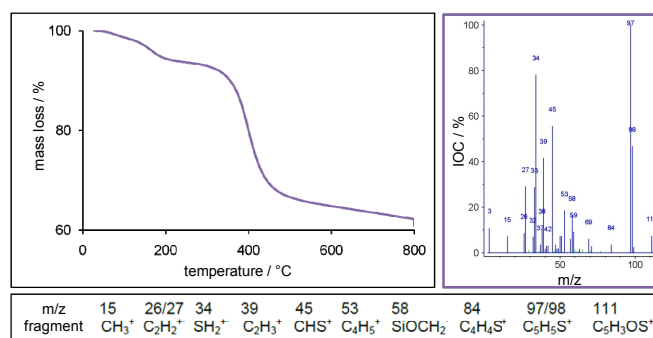


Fig. S3 Thermogravimetric analysis and mass spectrum (fragments released at 380 °C) of the nanocomposite synthesized from 66 m-% **1** and Aerosil® OX 50. No elementary sulphur can be observed during carbonizing the nanocomposites.

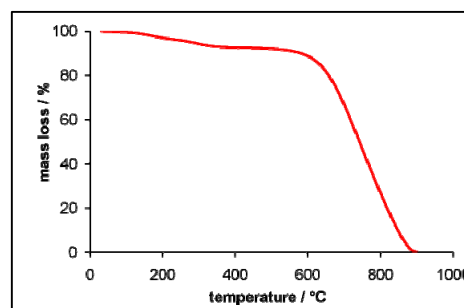


Fig. S4 Representative thermogravimetric analysis of sulphur-doped carbon. The material was fully oxidized and did not contain any residual SiO₂.

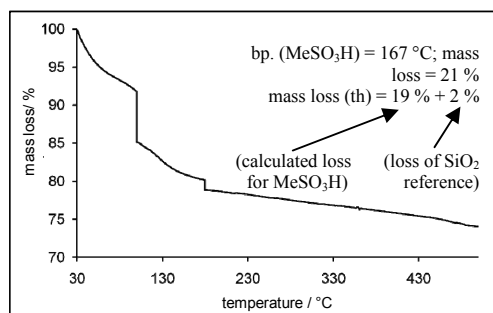


Fig. S5 Representative thermogravimetric analysis and data from elementary analysis of acid-functionalized silica particles. MeSO₃H is fully adsorbed on the SiO₂ surface.

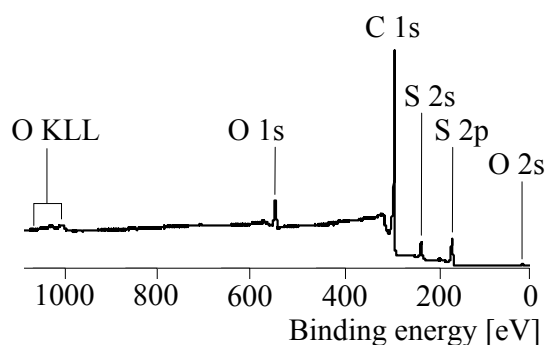


Fig. S6 Wide-scan XPS spectrum recorded from the sample, which was synthesized from **1** and Aerosil® OX 50.

Table S3 Elemental composition of sulphur-doped carbon from synthesis of **1** and Aerosil®OX50 determined by XPS.

Peak	Position [eV]	Atomic concentration [%]	Mass concentration [%]
C 1s	284.5	89.32	80.26
N 1s	399.3	4.89	5.86
O 1s	532.1	5.79	13.88

Table S4 Assignment of the component peaks of the high-resolution C 1s XPS spectrum (shown in Fig. 6). The C 1s spectrum was recorded from the sulphur-doped carbon sample made from **1** and Aerosil®OX50.

Component peak	Position [eV]	Atomic concentration [%]	Assignment
<i>Gr</i>	284.5	65.37	sp ² bonded carbon ^[Si1]
<i>C</i>	286.1	5.52	C–O and C–S ^[Si1]
<i>Shake-up</i>	285.4–290.9	29.10	$\pi \rightarrow \pi^*$ transitions ^[Si2]

Table S5 Assignment of the component peaks of the high-resolution S 2p XPS spectrum (shown in Fig. 6). The S 2p spectrum was recorded from the sulphur-doped carbon sample made from **1** and Aerosil®OX 50.

Component peak	Position [eV]	Mass concentration [%]	Assignment
<i>M</i> and <i>M'</i>	164.1 / 165.3	79.37	C–S ^[Si1,3]
<i>N</i> and <i>N'</i>	165.0 / 166.2	6.36	oxidized sulphur ^[Si1]

Experimental details

40 Monomer **1** was synthesized according to reference [9].

For polymerization in solution 2 g of **1** were added to 10 mL toluene. Then, 240 mg methanesulfonic acid were added. During stirring for 15 h at room temperature the solution slowly turned their colour to black. The reaction product was filtered off and washed with dichloromethane. 1.1 g (yield: 50 %) of a brown solid were obtained.

For polymerization on the silica surfaces 1.0 g Aerosil® were suspended in 200 mL dichloromethane. Then, 240 mg methanesulfonic acid were added. After evaporating the solvent the acid-functionalized particles were suspended in 250 mL of toluene and 0.5, 2.0 or 8.0 g of monomer **1** dissolved in 50 mL toluene was given to the reaction mixture. After stirring for 15 h at room temperature the product was filtered off and washed with dichloromethane. Brown solids were obtained in a yield of 80 % in each case.

Samples yielded from the polymerization were subsequently carbonized in an argon atmosphere (heat rate: 6.2 K min⁻¹, 800 °C for 3 h). During the carbonization the masses decreased to 60 %. SiO₂ was removed by samples' treating with aqueous hydrofluoric acid. During this treatment the samples' masses decreased to 20 m-% for the template-free synthesis and 35 m-% for the polymerization on Aerosil®. The values were referred to monomer mass of pristine.

Measurements

70 The solid state ¹³C-¹H}-CP-MAS-NMR-spectra were recorded at 9.4 T on a Bruker Digital Avance 400 spectrometer equipped with 4 mm double tuned probes capable of MAS at 12 kHz.

Elementary analyses were carried out by Vario EL from 75 Elementar Analysensysteme, Hanau.

Raman spectra were measured using monochromatic light in the spectral region from infrared to ultraviolet, which was provided by three lasers: Kr⁺ Innova-300, Ar^{A+} Innova-70, and HeCd 80 Kimmon. The spectral analysis was performed by a Dilor XY 800 triple monochromator equipped with a Peltier cooled Wright CCD detector.

For the analysis of the specific surface area and pore size distribution in general nitrogen physisorption isotherms were measured at -196 °C using a fisons instruments Sorptomatic 1990. Prior to the measurement, the samples were activated in vacuum at 50 °C for 3 hours.

Specific surface areas were calculated using the BET equation 90 (p/p₀ = 0.05–0.2; 0.3). The pore size distribution was estimated according to the QSDFT equilibrium model (QSDFT: Quenched Solid Density Functional Theory, for slit pores) using the Autosorb 1.56 software from Quantachrome.

XPS studies were carried out by means of an Axis Ultra photoelectron spectrometer (Kratos Analytical, Manchester, England). The spectrometer was equipped with a monochromatic Al K α ($h\nu = 1486.6$ eV) X-ray source of 300 W at 20 mA. The kinetic energy of the photoelectrons was determined with a hemispheric analyzer set to a pass energy of 160 eV for the wide-scan spectra and 20 eV for the high-resolution spectra. During all measurements, electrostatic charging of the sample was overcompensated by means of a low-energy electron source working in combination with a magnetic immersion lens. Later, all recorded peaks were shifted by the same amount, which was necessary to set the C 1s peak to 284.5 eV for unsaturated carbon species in a graphite-like lattice. Quantitative elemental compositions were determined from peak areas using experimentally determined sensitivity factors and the spectrometer transmission function. The spectrum background was subtracted according to Shirley. The high-resolution spectra were deconvoluted by means of a computer routine. Free parameters of the component peaks were their binding energy, height, full width at half-maximum, and the Gaussian–Lorentzian ratio.

The TEM analysis was done with a Tecnai F20 Field Emission TEM from FEI company. The different sulphur-doped carbon powders were dispersed with ethanol and put on a holey carbon filmed Cu-grid. The powders were imaged using standard bright TEM imaging.

The thermogravimetric analysis were carried out using a Netzsch thermo-microbalance TG 209 F1 Iris[®] with 85 μ L Al₂O₃-pans, a He-flow of 25 mL min⁻¹ and a heating rate of 10 K min⁻¹. Electron impact (70 eV) mass spectra were collected continuously with a coupling of the thermo-microbalance to a Netzsch mass spectrometer MS 403C Aëolos[®].

[SI 1] S.-A. Wohlgemuth, R. J. White, M.-G. Willinger, M.-M. Titirici, M. Antonietti, *Green Chem.* **2012**, *14*, 1515.

[SI 2] J. F. Moulder, W. F. Stickle, P. Sobol, K. D. Bomben, J. Chastain, *Handbook of X-ray Photoelectron Spectroscopy*, Perkin-Elmer Corp, Eden Prairie, **1992**.

[SI 3] J. P. Paraknowitsch, A. Thomas, J. Schmidt, *Chem. Comm.* **2011**, *47*, 8283.