Covalent Bulk Functionalization of Graphene

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S1 Procedure for the synthesis of the diazonium salts

S1.1 Experimental details: Synthesis of 4-tert-butylphenyldiazonium tetrafluoroborate (BPD)

2 mL of tert-butylaniline (1.87 g; 12.6 mmol) were mixed with 30 mL of bidest. water in a round bottom flask at room temperature. 7 mL 50% HBF₄ (56.1 mmol) were slowly added and the reaction mixture was diluted with bidest. H₂O until all precipitate dissolved. After cooling this mixture to 0°C, a saturated aqueous solution of 1.82 g NaNO₂ (26.4 mmol) was added slowly, keeping the temperature well below 5°C. Subsequent stirring at 0°C for 15 minutes, filtration, washing with icewater and drying in high vacuum afforded the product as pale orange powder stable at room temperature.

Yield: 1.18 g (40 %)

¹H-NMR (400 MHz, D₂O) [ppm]: δ 8.44 (d, J = 8.99 Hz, 2H), 7.98 (d, J = 8.98 Hz, 2H), 1.36 (s, 9H)
S1.2 Experimental details: Synthesis of 4-sulphonylphenyldiazonium chloride (SPD)

To an ice-cooled solution of 6.50 g (37.6 mmol) sulphanilic acid in 500 mL hydrochlorid acid (1M) a solution of 2.85 g (41.3 mmol) NaNO₂ in 42 mL water was added dropwise maintaining the temperature well below 5°C. After stirring the reaction mixture for 45 minutes the reaction product was obtained by filtration, washing with small amounts of icewater and drying in high vacuum as crystalline gray powder stable at room temperature.

Yield: 2.80 g (34 %)

S1.3 Experimental details: Sulphur marked graphene

In order to obtain sulphur marked covalently functionalized graphene we used the reaction conditions applied for highly BPD functionalized graphene described in the methods section and quenched the reduced graphene solution with 4-sulphonylphenyldiazonium chloride. The sulphonate is used as marker in EDX and XPS experiments and was isolated in the form of its potassium salt which is reasonable considering the strongly basic reaction conditions applied.
S2: Thermogravimetric data (TGA/MS)

TGA profile (weight loss) of BPD functionalized graphene (black curve) and unfunctionalized graphite (dotted black curve) using a heating rate of 10K/min. The peak mass loss takes place at 206°C (adsorption) and 477°C (covalent attachment). For the covalent mass loss of -12% a bulk functionalization degree of 1.2% can be estimated, conservatively. Two relevant molecule fragments - \( m/z = 15 \) [-CH₃] and \( m/z = 58 \) [-C(CH₃)₃] - are detached from the material and detected during periods of high mass change.

S3.1 Microscopic image of the starting material
S3.2 Microscopic images of the defunctionalized sample

S3.3 Photograph of the BPD functionalized material after thermal annealing compared to the unfunctionalized graphite reference of the same weight
S4.1 Raman study of thermal annealing process

A series of Raman spectra from the starting material (green, top), highly BPD functionalized material (black, middle) and annealed material obtained from highly functionalized graphene. Significant changes in the peak width are observed after thermal defunctionalization. The reversibility of the functionalization is accompanied with restacking into graphitic structures. The shape and intensity of the 2D-band is in agreement with this observation.

S4.2 Peak deconvolution of the 2D-band of the starting and annealed material
S5 Additional microscopic data

S5.1 Bright- and dark-field images of an intercalated graphene flake (Fig. 2b)

S5.2 Bright- and dark-field images of an exfoliated graphene monolayer

S5.3 Bright- and dark-field images of a medium BPD functionalized monolayer
S6 Micromechanically exfoliated reference

S6.1 Raman spectrum recorded at 532 nm laser wavelength

![Raman spectrum](image1)

S6.2 Exemplary AFM image of a micromechanically exfoliated graphene flake

![AFM image](image2)
S7: Additional AFM images of highly BPD functionalized graphene
S8 Raman Peak fitting and signal deconvolution

S8.1 Peak fitting on the intercalated flake (exemplary)

S8.2 Peak fitting on the electrostatically exfoliated monolayer (exemplary)

S8.3 Peak fitting on a medium BPD functionalized monolayer (exemplary)
S9 Raman mappings

S9.1 Intercalated flake Raman spatial intensities (lateral scale is given in micrometers)
S9.2 Exfoliated monolayer spatial Raman intensities (lateral scale is given in micrometers)

- **G-band**
- **D-band**
- **2D-band**
S9.3 Highly BPD functionalized graphene monolayer spatial Raman intensities

G-line

D-line

$I_D/I_G$-ratio

$I_{2D}/I_G$-ratio

Raman shift [cm$^{-1}$]
S9.4 Spatial Raman mapping of BPD functionalized monolayers

Spatial Raman intensity mappings for the characteristic bands of graphene and ratios calculated from those values are presented together with the optical image acquired prior to the measurement on the Raman microscope. From this data G-band threshold maps were generated with different minimum G-band intensities. White areas in those maps correlate to pixels that fulfill the required criterion. With increasing thresholds rim areas and small graphene deposits can be filtered from the matrix data.
S9.5 Additional statistical data on G-Band threshold maps
S10.1: EDX data from HRTEM micrographs

EDX on BPD functionalized graphene

EDX on sulphur marked functionalized graphene

S10.2 Diffraction patterns obtained from SPD functionalized graphene
S10.3 Additional HRTEM micrographs for BPD functionalized graphene

S10.4 Additional HRTEM micrographs for sulphur marked graphene
S10.5 Large version of BPD functionalized graphene micrographs
S10.6 Large version of SPD functionalized graphene micrographs
X-ray photoelectron spectra (Al Kα) obtained from SPD functionalized graphene (top), BPD functionalized graphene (middle) and graphite reference material. For SPD functionalized graphene signals for the S2s (232 eV) and S2p core levels (168.3 eV for S2p 3/2) are clearly visible. In addition minor Si contaminations are present, which are in line with SiOₓ (glass) species. Increased O1s intensity is also observed (partly from SiOₓ), in contrast to BPD and graphite samples, where the low oxygen content is attributed mainly to residual water. No salt contaminations have been found in any sample.
S11.2 S2p XPS core level spectrum for sulphur marked graphene

![S 2p XPS core level spectrum](image)

X-ray photoelectron spectrum (Al Kα) in the S2p region for SPD functionalized graphene. The S2p\textsubscript{3/2} binding energy of 168.3 eV is in agreement with SO\textsubscript{x} species such as sulphonic acid and sulphonates, whereas thiol groups would be characterized by much lower S2p\textsubscript{3/2} binding energies around 162-163 eV.

S12 Absorption spectroscopy on re-dispersed functionalized material in chloroform

![Absorption spectroscopy](image)

UV/vis spectra obtained from redispersed and centrifuged BPD functionalized graphene in CHCl\textsubscript{3}. For medium BPD functionalization 1.2 µg/mL can be calculated while high BPD functionalization yields amounts as high as 27 µg/mL based on the published extinction coefficients.