Electronic Supplementary Material (ESI) for Nanoscale

Supporting Information

Controlled Functionalization of Graphene Oxide with Sodium Azide

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Experimental Section

The used graphite was obtained from Asbury Carbon. The grade used was 3061. Potassium permanganate, sodium nitrate, sulfuric acid were obtained from Sigma-Aldrich®. ^{15}N labeled sodium azide was obtained from Cambridge Isotope Laboratories. Freeze-drying was accomplished on an ALPHA 1-4 LDplus from Matrtin Christ, Germany. For centrifugation a Sigma 4K15 centrifuge, Sigma Laborzentrifugen GmbH, Germany, was used. Elemental analysis was performed by combustion and gas chromatographic analysis with a VarioMicro CHNS analyzer Elementar Analysensysteme GmbH, Hanau, Germany. Thermogravimetric analysis (TGA) equipped with a mass spectrometer (MS) was accomplished on a Netzsch STA 409 CD instrument equipped with a Skimmer QMS 422 mass spectrometer (MS/EI) with the following programmed time dependent temperature profile: RT-800 °C (TGA-MS) with 10 K/min gradient, and cooling to RT. The initial sample weights were about 6 to 7 mg and the whole experiment was accomplished under inert gas atmosphere with a He gas flow of 80 ml/min. Bruker Tensor FTIR spectrometer equipped with ZnSe was used for the measurements of GO films. UV/Vis spectroscopy was performed using Lamda 1050 from Perkin Elmer.

SSNMR experiments were conducted at a static magnetic field of 11.7 T using a Bruker Avance III wide-bore NMR spectrometer with a Bruker 3.2-mm triple-resonance E-free MAS probe at a ^{1}H NMR frequency of 500.16 MHz. We first freeze dried the GO-N_3 sample. This sample of 25.3 mg was packed in a MAS rotor for solid state NMR. Basically, no special treatment was performed on the sample analyzed by the NMR analysis. The ^{15}N chemical shifts were referenced to liquid $^{15}NH_3$ at 0 ppm using the indirect referencing of a ^{13}C signal for adamantane.[1, 2] The temperature of cooling air for variable-temperature experiments was set to 280K using a Bruker BCU-X cooling unit at a flow rate of 800 L/h. The MAS spinning speed was set to 22,000 ± 5 Hz. The ^{15}N MAS spectrum was collected with excitation by a $\pi/2$-pulse with a pulse width of 6 μs. As the line widths were relatively broad, a rotor-synchronized echo was used with a pulse interval of one rotation cycle (45.45 μs) between the excitation $\pi/2$-pulse and π-pulses for echo. A total of 8192 scans were accumulated without any ^{1}H RF decoupling as we confirmed that no protons are likely bonded directly to the ^{15}N species observed in the ^{15}N MAS spectrum. The spectrum was apodized with Lorentzian line broadening of 100 Hz.

Ab-initio calculations:

^{15}N Chemical shift calculations were performed using Gaussian 03 (Revision E.01)[3] on a UNIX workstation with two quad-core CPUs (ASA Computers Inc. , Mountain View, CA, USA). A simplified structural model for GO-N_3 in Figure 3A were geometry optimized at the B3LYP/6-31G* level of theory.[4-7] Chemical shielding tensors were calculated using GIAO[8] with BPW91and a 6-311+G* basis set, which was optimized from a previous study on aminopyrimidines and aminobenzenes.[9] The chemical shielding tensors for ^{15}N-N_2-C and N_2-^{15}N-C in GO-N_3were converted to the chemical shift tensor as follows. Ammonia ($^{15}NH_3$) was used as the theoretical reference compound. The isotropic chemical shielding of ^{15}N in an isolated ammonia molecule was calculated at the BPW91/6-311+G* level of theory, after geometry optimization at the same level of theory. The calculated shielding for ammonia gas was converted to the shielding of liquid ammonia by adding the experimentally confirmed difference (−20.7 ppm) between the chemical shift of gas-phase ammonia and that of liquid-phase neat ammonia.[10, 11] This gave the calculated shielding of neat liquid ammonia, which was 236.6 ppm. The calculated shielding tensor values of each nitrogen atom were then subtracted from the calculated isotropic shielding of liquid ammonia at the same level of theory in order to give the calculated ^{15}N chemical shifts. The average of the principal values of the chemical shift tensor yielded the isotropic ^{15}N chemical-shift value.

Preparation of GO:

No pre-treatment of graphite was applied. Graphite (1 g, grade 3061, Asbury Carbon) and sodium nitrate (0.5 g) were dispersed in concentrated sulphuric acid (24 mL). The dispersion was cooled to about 0 °C. After that, over a period of three hours potassium permanganate (3.0 g) was added. The temperature of the reaction mixture was kept below 10 °C and stirred for an additional 16 h. The reaction mixture was still cooled and during cooling diluted sulphuric acid (20 mL, 10 %) was continuously added to the reaction mixture over 2 h. After that water was added (60 mL, 6 h) and the temperature of the reaction mixture was kept below 10 °C. The reaction mixture was then poured on ice (500 mL) and hydrogen peroxide (20 mL, 3 %) was added dropwise until gas evolution was completed, and the temperature was kept below 10 °C. The obtained graphite oxide was purified by repeated centrifugation and dispersion in cooled water (below 10 °C) until the pH of the supernatant was neutral. Finally, GO was yielded by mild sonication using a bath sonicator. Even without sonication graphite oxide exfoliated to GO in some extent. The suspension was finally centrifuged three times at 5000 g to remove remaining graphite oxide.

Elemental Analysis of GO:

C 45.68, H 2.28, N 0.03, S 3.62. Total weight loss according to thermo-gravimetric analysis (He, rt-800 °C): 50.0 %; yield: 510 mg freeze dried.

Preparation of GO-N_3 and GO-$^{15}N^{14}N_2$:

Sodium azide (80 mg, 1.23 mmol) was added as a solid to a dispersion of GO (100 ml, 1 mg/ml). The mixture was stirred for 1 h at 10 °C. After that the reaction mixture was freeze dried. The freeze dried reaction mixture was dispersed in cooled water (10 °C, 100 ml). Next, the raw product was purified by repeated, five times, centrifugation and dispersion in cold water. In addition a temperature of 10 °C was used during centrifugation. Finally, the product was isolated by freeze drying.

Elemental Analysis of GO-N_3:

C 46.25, H 1.93, N 4.13, S 1.67. Total weight loss according to thermogravimetric analysis (He, rt-800 °C): 50.0 %; yield: 80 mg freeze dried.

Analysis of supernatant after purification of GO-N_3:

During purification of GO-N_3 the supernatants were collected and freeze dried. After that the residue was taken up in hydrochloric acid (10 ml, 1 M). A solution of $BaCl_2$ (0.1 M) was added in excess and the precipitate was formed rapidly and complete within 1 h. The precipitate was filtered and washed with water until there was no AgCl formed after adding $AgNO_3$ (three drops, 0.1 M) to the washing solution. The precipitate was dried at 160 °C and finally analyzed by FTIR spectroscopy making KBr pellets. For reference fresh $BaSO_4$ was prepared by a similar procedure using sodium sulfate and $BaCl_2$.

Preparation films of GO-N_3 on ZnSe for FTIR analysis:

A dispersion of GO-N_3 (1 mg /ml) in water was prepared using freeze-dried GO-N_3. About 5-10 drops were placed on ZnSe and dried at ambient conditions. The thickness of the film was qualitatively evaluated by using the z-indicator of a Zeiss microscope. *In solids:* GO-N_3 films on ZnSe were iteratively characterized by FTIR heating the ZnSe window in a drying furnace. *In dispersion:* GO-N_3 films on ZnSe were iteratively prepared after heating a dispersion (1 mg/ml) of GO-N_3 in a closed vial equipped with a temperature sensor and magnetic stir bar, at RT, 40 °C, 60 °C, 80 °C and 100 °C for 30 min and at RT, 40 °C, 60 °C and 80 °C for 16 hours.

Supporting Data

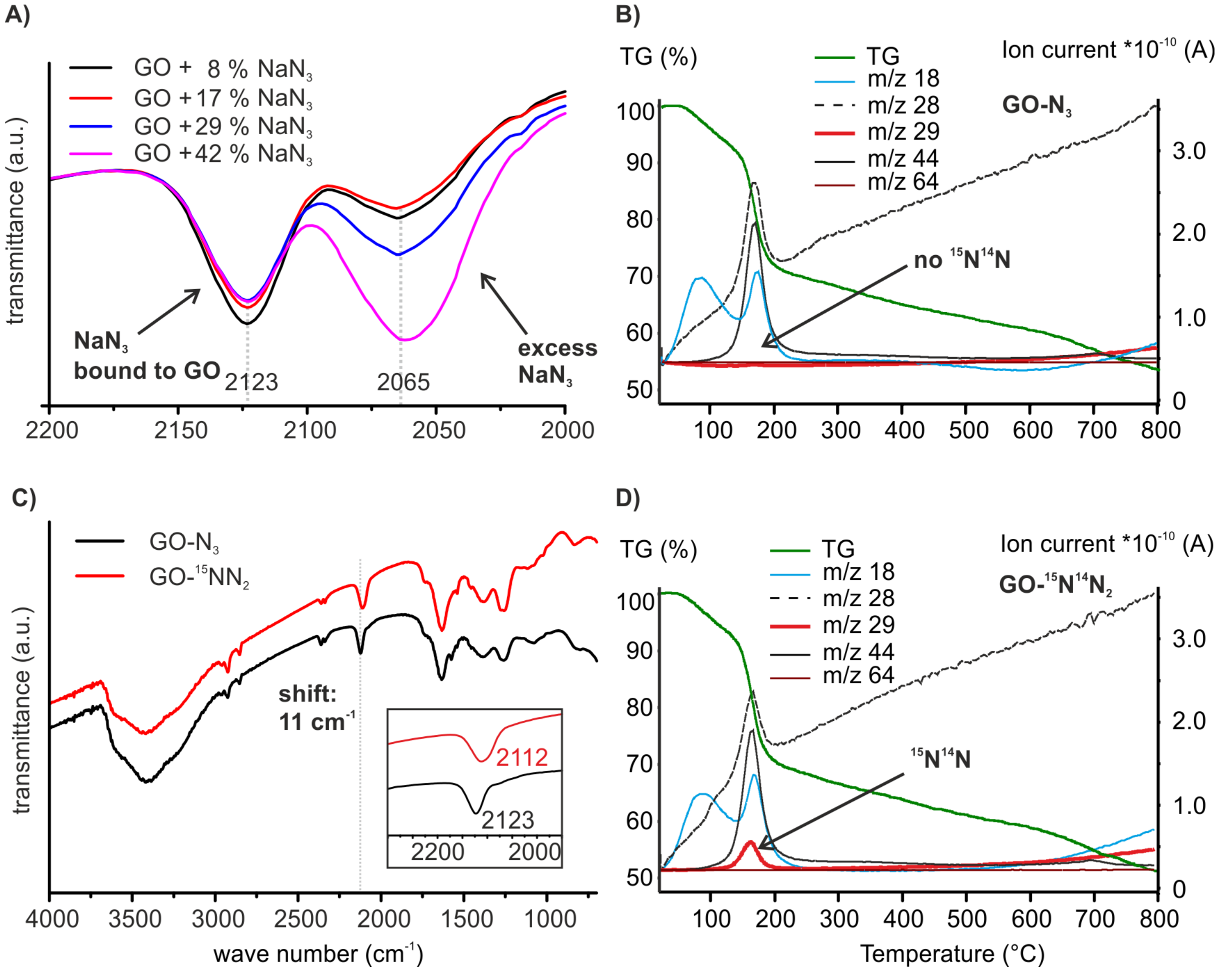

Figure S1: A) FTIR spectra of GO films on ZnSe treated with different amounts of NaN_3 ranging between 8% and 42%; B) TG-MS analysis of GO-N_3, showing decomposition products with m/z 18 (water), 28 (nitrogen/carbon monoxide, 29 (labeled nitrogen), 44 (carbon monoxide), 64 (sulfur dioxide); C) FTIR of GO-N_3 and GO-$^{15}N^{14}N_2$; D) TG-MS analysis of GO-$^{15}N^{14}N_2$ showing decomposition products with m/z 18 (water), 28 (nitrogen/carbon monoxide, 29 (labeled nitrogen), 44 (carbon monoxide), 64 (sulfur dioxide).

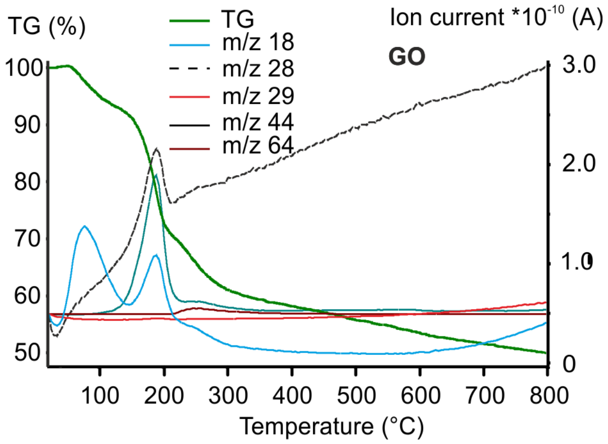

Figure S2: TG-MS analysis of GO showing decomposition products with m/z 18 (water), 28 (nitrogen/carbon monoxide, 29 (labeled nitrogen), 44 (carbon monoxide), 64 (sulfur dioxide). The weight-loss of GO treated up to 300 °C is about 40%. Up to about 100 °C the loss of water is mainly detected (8-10%). Up to 200 °C about 20% of weight is lost as water, CO and CO_2 as a consequence of the decomposition of epoxy groups and hydroxyl groups. An additional weight-loss of 10% is detected up to 300 °C which we recently assigned to the decomposition of organosulfate (relates to about 3% sulfur content).[12]

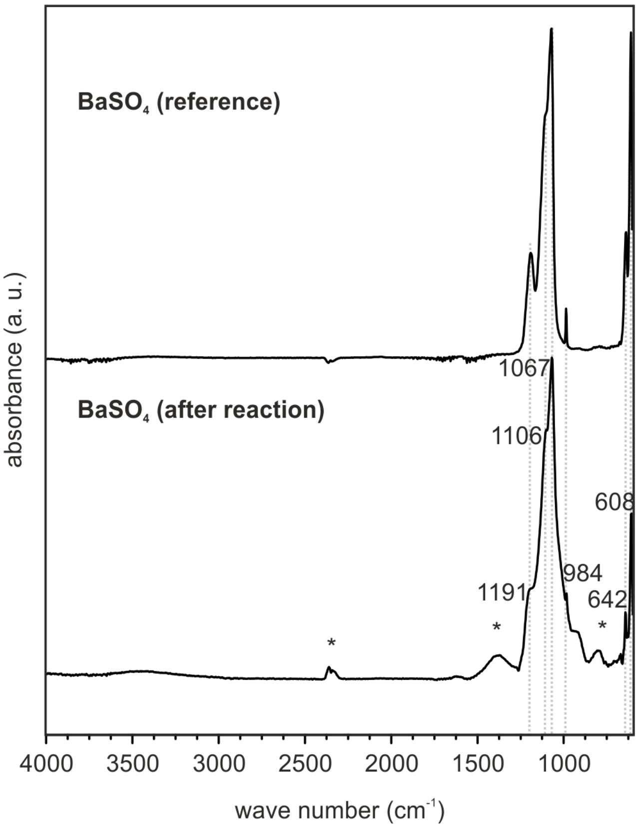

Figure S3: FTIR spectra of $BaSO_4$ as isolated from the reaction of GO with sodium azide and pure $BaSO_4$ freshly prepared from $BaCl_2$ and Na_2SO_4.

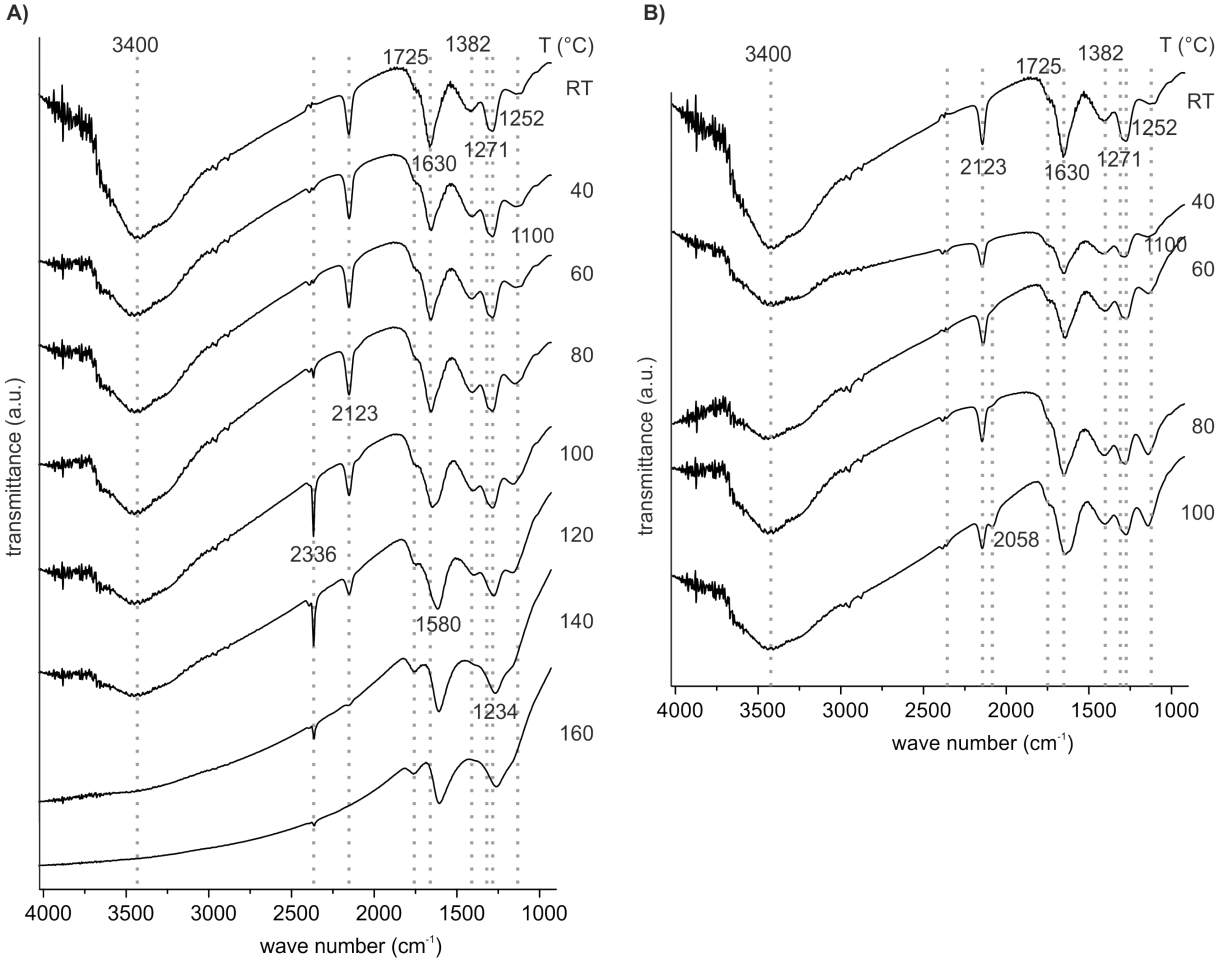

Figure S4. FTIR spectra of thermally treated GO-N_3; A) in solids: GO-N_3 treated at RT, 40 °C, 60 °C, 80 °C, 100 °C, 120 °C, 140 °C and 160 °C on ZnSe; B) in dispersion: GO-N_3 treated aqueous dispersions 1 mg/ml at RT, 40 °C, 60 °C, 80 °C and 100 °C for 30 min followed by FTIR analysis on ZnSe. A) GO-N_3 decomposition in solids starts at about 80 °C. The signal at 2336 cm^{-1} is due to evolution of CO_2 that stems from oxygenated functional groups of GO-N_3. The CO_2 intercalates the GO-N_3 layers, accumulates in blisters that start bursting at temperatures higher that 120 °C. We studied the CO_2 intercalation behavior of GO before.[12] B) GO-N_3 decomposition in aqueous dispersion starts at 80 °C, indicated by the shoulder at 2058 cm^{-1}. After heating GO-N_3 dispersion to 100 °C the shoulder develops to a signal at 2058 cm^{-1} what relates to cleaved azide (compare **Figure S1A**).

Table S1. Characterization of FTIR spectra from GO-N_3 films shown in **Figure S4A and S4B** (1-3 µm, ZnSe):

3600 - 3200 cm^{-1}	O-H stretching vibration of free water, associated hydroxyl groups in GO and adsorbed water molecules.
2924 and 2852 cm^{-1}	C-H vibrations
2336 cm^{-1}	stretching vibration of intercalated/trapped CO_2 within layers of GO-N_3 films
2123 cm^{-1}	stretching vibration of azide bound to GO
2058 cm^{-1}	stretching vibration of azide cleaved from GO
1720-1730 cm^{-1}	carbonyl signals
1630 cm^{-1}	adsorbed water
1580 cm^{-1}	C-C double bonds
1382 cm^{-1}	O-H deformation vibrations
1270, 1252, ~1100 cm^{-1}	mainly due to C-O vibrations of epoxy and hydroxyl groups; overlaps with C-N vibrations are possible as well
1000-1100 cm^{-1}	may originate from skeletal C-C vibrational modes

Table S1: FTIR vibration correlated to functional groups. [13,14,15]

Thermal stability of GO-N_3 in aqueous dispersion treated for 16 hours:

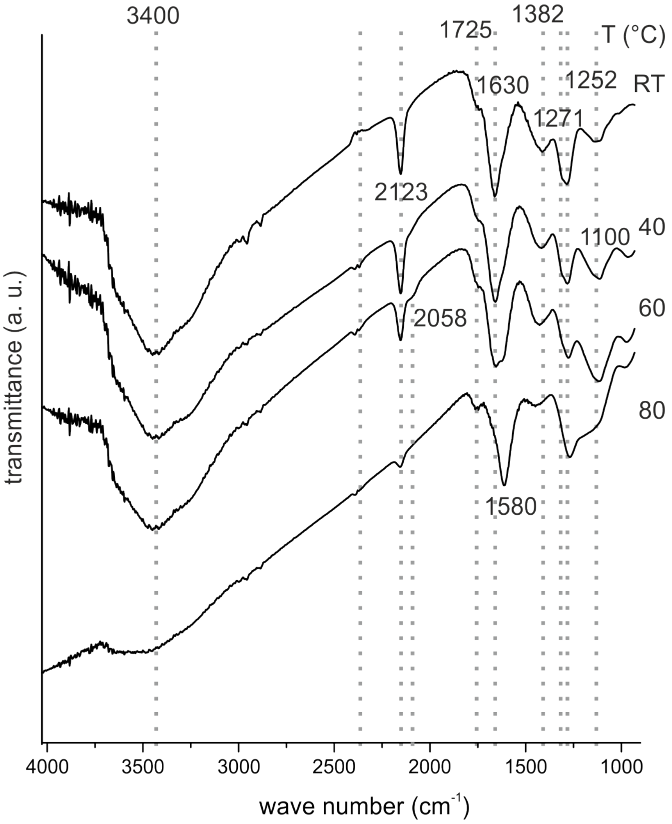

Figure S5. FTIR spectra of GO-N_3 on ZnSe after treatment of an aqueous dispersion for 16 hours at RT, 40 °C, 60 °C and 80 °C. The stretching vibration of azide at 2123 cm^{-1} is visible as a strong signal for dispersions treated at RT, 40 °C and 60 °C. However, a small shoulder develops for the 60 °C sample sample at 2058 cm^{-1}. At 80 °C decomposition is observed and the relative intensity of the azide stretching vibration declines. However, the signal at 2058 cm^{-1}, related to inorganic azide is not visible, as it is for the 100 °C sample in Figure S4B. This indicates that azide reacted further and was not only cleaved.

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