Graphene Oxide: Stable Carbon Framework for Functionalization

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Experimental Section:

Natural flake graphite was obtained from Asbury Carbon. The grade used was 3061. Potassium permanganate, sodium nitrate, sulfuric acid, hydriodic acid and trifluoroacetic acid were obtained from Sigma-Aldrich®. 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 from Elementar Analysensysteme GmbH, Hanau, Germany. Langmuir-Blodgett films were prepared using Langmuir-Blodgett Minitrough from KSV NIMA and films are prepared from MeOH/water mixtures on water as subphase at a pressure of 1.5 mN/m to yield slightly over packed films. These films were used for AFM imaging and scanning Raman spectroscopy. Thermogravimetric analysis (TGA) equipped with a mass spectrometer (MS) was accomplished on a Pyris 1 TGA equipped with Clarus SQ 8 C mass spectrometer with the following programmed time dependent temperature profile: RT-700 °C (TGA-MS) with 10 K/min gradient, and cooling to RT. The initial sample weights were about 1.5 mg and the whole experiment was accomplished under inert gas atmosphere with a N_2 gas flow of 70 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.

Preparation of GO:

The method for preparation is adopted from an earlier publication.[1]

No pre-treatment of graphite was applied. Graphite (1 g, 83 mmol grade 3061, Asbury Carbon) and sodium nitrate (0.5 g, 5.9 mmol) 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, 19 mmol) 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 drop wise 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 5,000g to remove remaining graphite oxide.

Elemental Analysis: C 45.68, H 2.28, N 0.03, S 3.62. Total weight loss according to thermogravimetric analysis (N_2, 25-700 °C): 51.0 %; yield: 750 mg freeze dried.

Preparation of GO-HCl:

Freeze-dried GO (100 mg) was dispersed in water (100 mL) and sonicated using a cup-horn sonicator (30 W, pulsed 1s on, 1s off, 30 s). After sonication the dispersion was centrifuged at (10000g, 20 min) to remove minor amounts of few layered GO. The GO was further washed by water using a centrifuge (20000g, 1 h) for five times. The centrifuged GO was dispersed in hydrochloric acid (0.1 M) and centrifuged (20000g, 1 h). The contact time of acid with GO was kept about 30 min including 20 min centrifugation time. The GO was further washed by water using a centrifuge (20000g, 1 h) for five times. Totally this procedure took about 10 h. Finally, the GO solution was freeze-dried to yield a brownish/greenish fluffy felt that was stored in the fridge at 5 °C.

Elemental Analysis: C 44.86, H 2.72, N 0.03, S 3.45. Total weight loss according to thermogravimetric analysis (N_2, 25-700 °C): 51.0 %.

For reference and probing the stability of GO against HCl the procedure was repeated using HCl (1 M) yielding GO-HCl-2.

Elemental Analysis: C 44.80, H 2.68, N 0.03, S 3.44. Total weight loss according to thermogravimetric analysis (N_2, 25-700 °C): 55.0 %.

Preparation of GO-NaOH:

The method for preparation is adopted from an earlier publication.[2]

Freeze-dried GO (100 mg) was dispersed in water (100 mL) and sonicated using a cup-horn sonicator (30 W, pulsed 1s on, 1s off, 30 s). After sonication the dispersion was centrifuged at (10000g, 20 min) to remove minor amounts of few layered GO. The GO was further washed by water using a centrifuge

(20000g, 1 h) for five times. The centrifuged GO was dispersed in sodium hydroxide solution (0.1 M) and centrifuged (20000g, 1 h). The contact time of base with GO was kept about 30 min including 20 min centrifugation time to avoid decomposition reactions. The GO was further washed by water using a centrifuge (20000g, 1 h) for five times. Totally this procedure took about 10 h. Finally, the GO solution was freeze-dried to yield a brownish fluffy felt that was stored in the fridge at 5 °C. Elemental Analysis: C 43.38, H 2.95, N 0.08, S 1.53. Total weight loss according to thermogravimetric analysis (N_2, 25-700 °C): 48.0 %.

Treated samples at 40 °C:

Procedures for GO-NaOH and GO-HCl were repeated and a dispersion of GO (1 mg/ml) was prepared. Each dispersion was stored at 40 °C for 16 h and purified afterwards, as described above. Results from elemental analysis are summarized in Table S1. The samples are labeled GO-40, GO-HCl-40 and GO-NaOH-40.

GO-40: Elemental Analysis: C 42.11, H 2.86, N 0.12, S 1.16; Total weight loss according to thermogravimetric analysis (N_2, 25-700 °C): 52.0 %.

GO-HCl-40: Elemental Analysis: C 44.11, H 3.04, N 0.21, S 0.41; Total weight loss according to thermogravimetric analysis (N_2, 25-700 °C): 49.0 %.

GO-NaOH-40: Elemental Analysis: C 44.60, H 2.71, N 0.15, S 1.10; Total weight loss according to thermogravimetric analysis (N_2, 25-700 °C): 47.0 %.

Reduction of Langmuir-Blodgett films on Si/SiO_2 wafers:

The wafers were paced in a vial on glass wool and some drops of hydriodic acid (57% in water) were placed on the glass wool. After that some drops of trifluoro acetic acid were dropped on the glass wool also. The vial was closed and after five minutes at room temperature the vial was heated to 80 °C for an additional 10 minutes. After that the wafers were rinsed with water and dried at 80 °C.

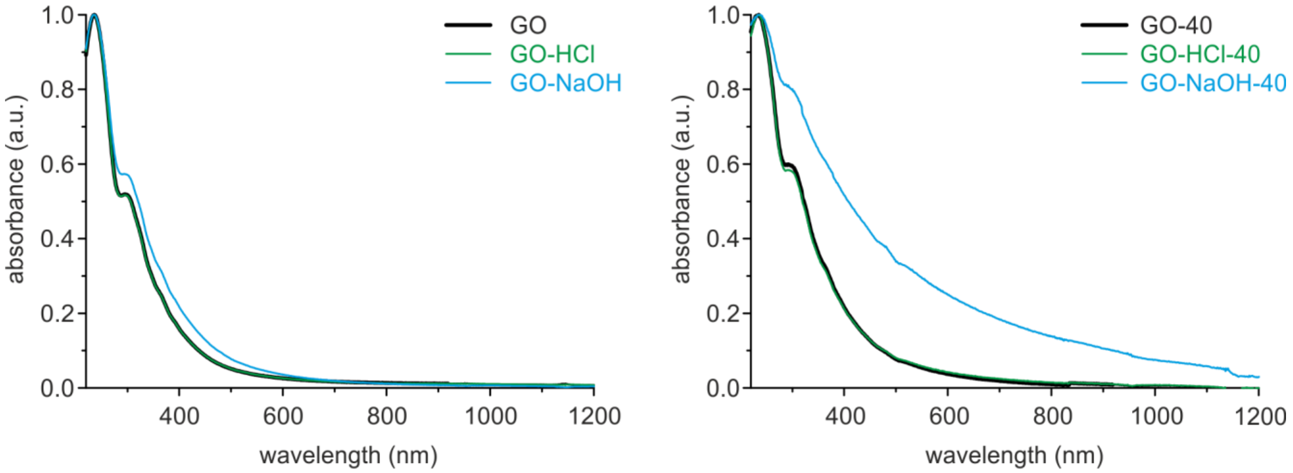

Figure S1. left: UV-Vis spectra of GO, GO-NaOH and GO-HCl (treated with 0.1M HCl; normalized on absorption at 235 nm) and right: UV-Vis spectra of GO-40, GO-NaOH-40 and GO-HCl-40: There are two transitions visible in all spectra. The first at 235 nm is due to π-π* transitions that were assigned C-C and C=C sp^2 hybrid regions. The shoulder at about 300 nm was described as n- π* transition and was assigned to C=O in sp^3 hybrid regions.[3, 4]

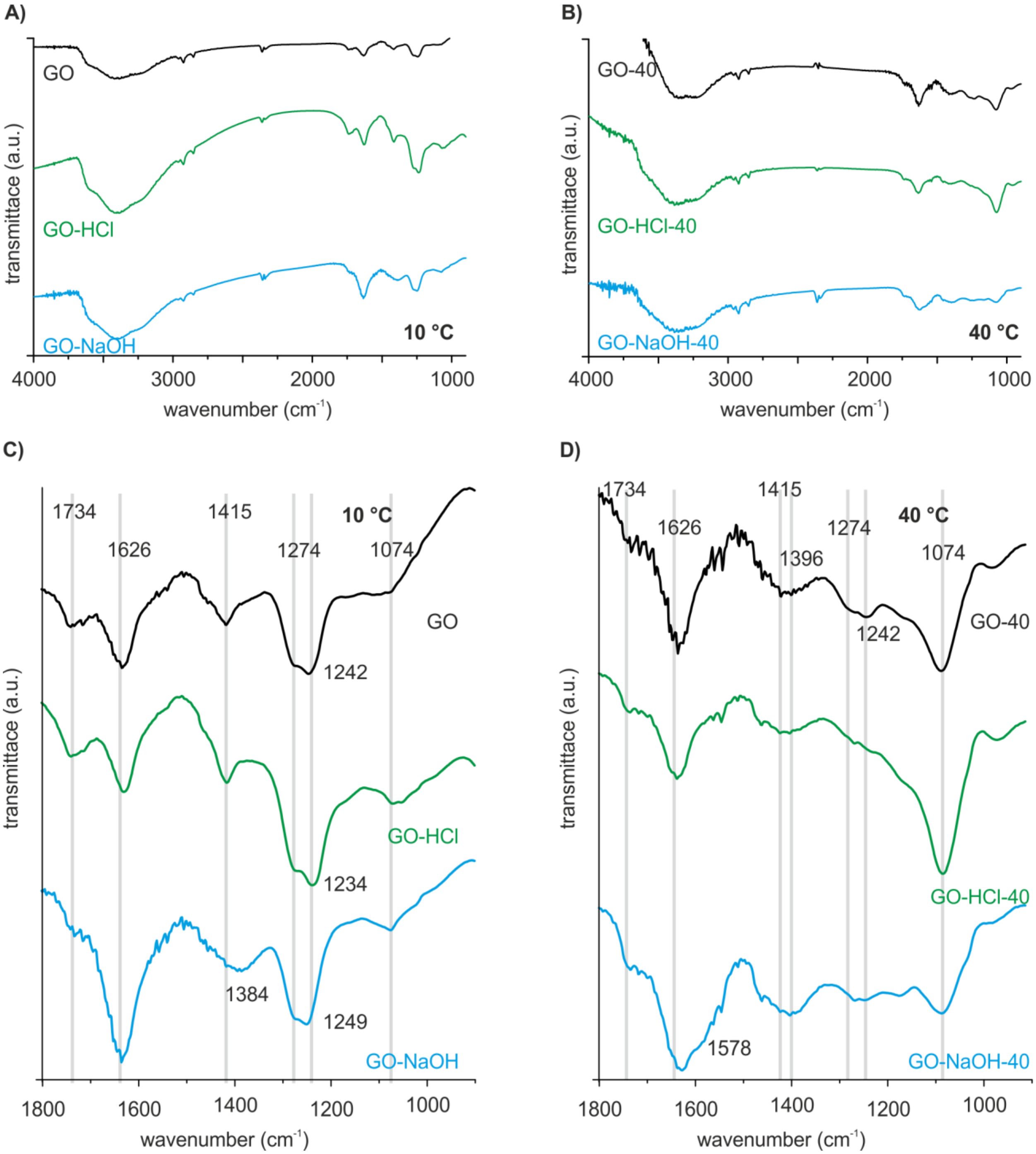

Figure S2. FTIR spectra of GO, GO-HCl and GO-NaOH and GO-40, GO-HCl-40 and GO-NaOH-40; A) and B) overview of GO samples treated at 10 °C or 40 °C and C and D) enlargement of the fingerprint region (1800-900 cm^{-1}) of GO samples treated at 10 °C or 40 °C.

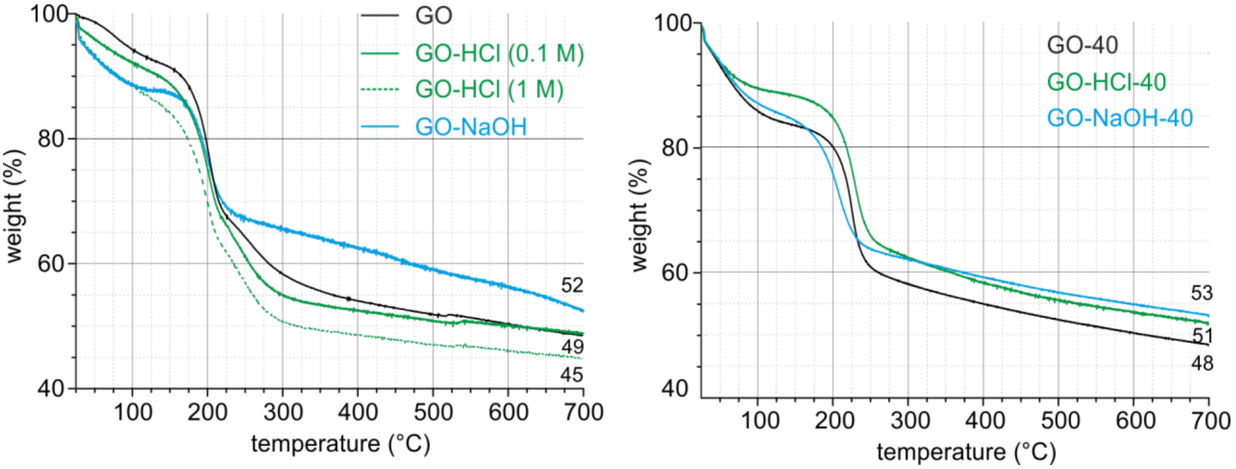

Figure S3. TG-MS analysis of left: GO (black), GO-HCl (treated GO with 0.1M HCl, green) and GO-HCl (treated GO with 1M HCl, green dashed line) and GO-NaOH (blue); right: GO-40 (black), GO-HCl-40 (green) and GO-NaOH-40 (blue); numbers correlate to the remaining weight; the main weight-loss is due to the decomposition of hydroxy groups and epoxy groups up to about 200 °C; the weight-loss step between 200 and 300 °C originates from the decomposition of organosulfate as described earlier.[2, 5]

Table S1. Elemental analyses of GO, GO-HCl, GO-HCl-2 GO-NaOH, GO-40, GO-HCl-40 and GO-NaOH-40

Sample	C (%)	H (%)	N (%)	S (%)
GO	45.68	2.28	0.03	3.62
GO-HCl	44.86	2.72	0.03	3.45
GO-HCl-2	44.80	2.68	0.03	3.44
GO-NaOH	43.38	2.95	0.08	1.53
GO-40	42.11	2.86	0.12	1.16
GO-HCl-40	44.11	3.04	0.21	0.41
GO-NaOH-40	44.60	2.71	0.15	1.10

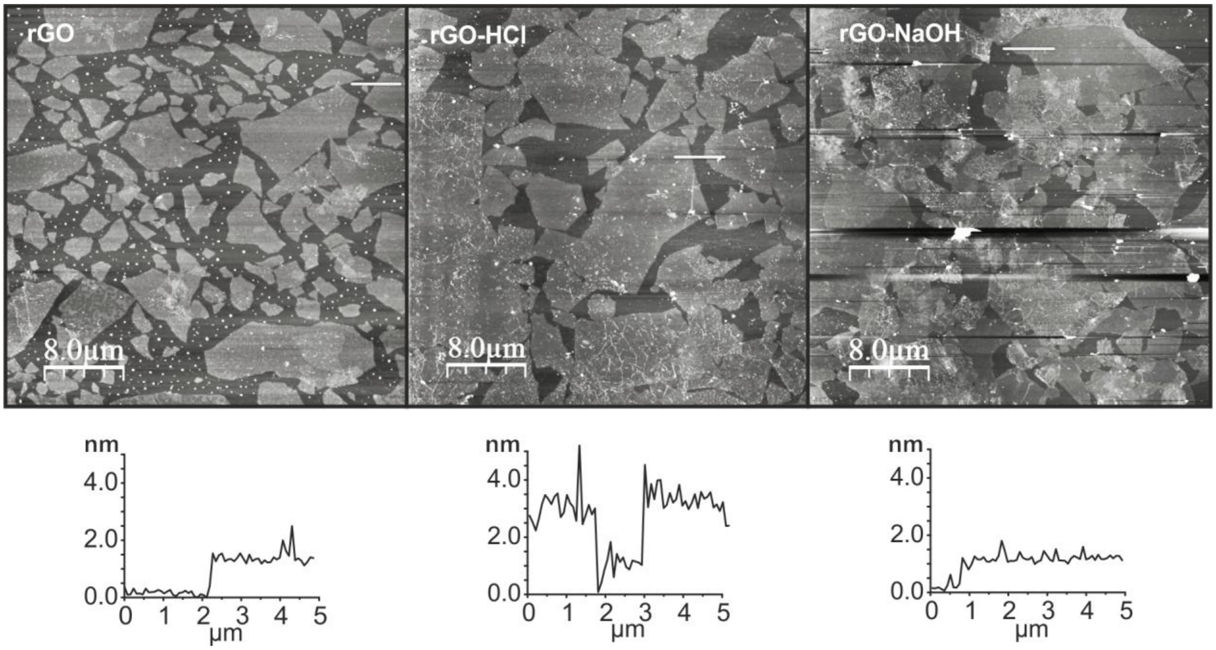

Figure S4. AFM images of reduced GO (rGO), rGO-HCl and rGO-NaOH on Si/SiO_2 substrates with height-profiles below.

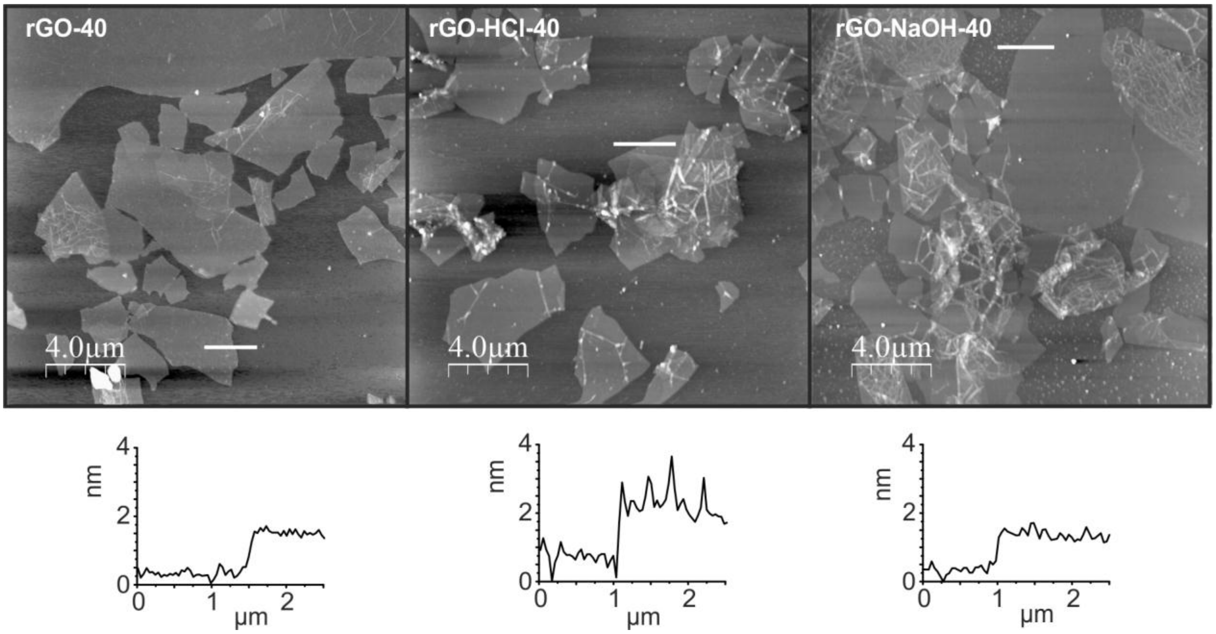

Figure S5. AFM images of rGO-40, rGO-HCl-40 and rGO-NaOH-40 on Si/SiO_2 substrates with height-profiles below.

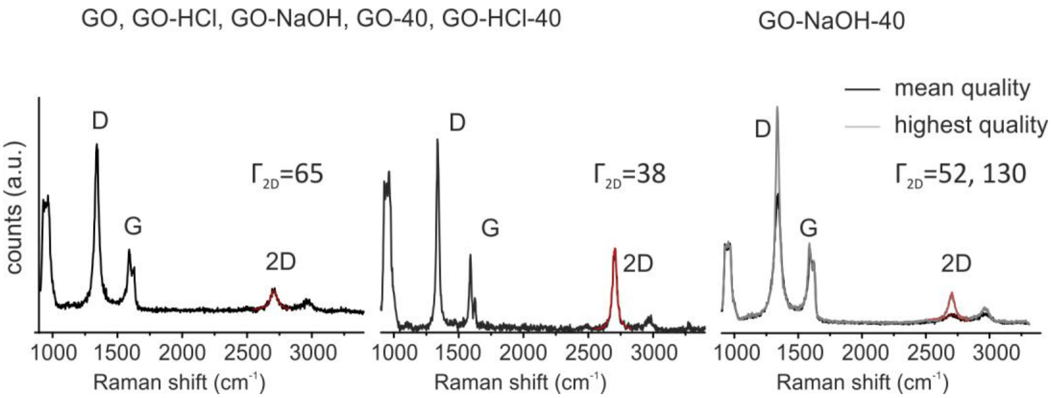

Figure S6. Typical Raman spectra of rGO; left: mean quality of spectra (rGO, rGO-HCl, rGO-NaOH, rGO-40, rGO-HCl-40 and middle: Raman spectrum of high-quality flakes; right: Raman spectra of rGO-NaOH-40; mean quality with Γ_{2D}=130 cm^{-1} and highest quality with Γ_{2D}=52 cm^{-1}.

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