

Supplementary Information

Adsorption of pure SO₂ on nanoscaled graphene oxide

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Graphene oxide synthesis

Graphene oxide (GO) was synthesized according to Marcano et al. ¹ and is described in detail in Wang et al. ². Briefly graphite oxide was prepared first by the oxidation of graphite in concentrated sulfuric acid (98%) and potassium permanganate. After 12 hours of reaction, resultant suspension was poured on ice cold water (400ml) with H₂O₂ (3ml). The suspension was stirred for 2 hours and filtered by a qualitative filter paper. The obtained solid material was centrifuged and washed several time with water, 30% HCl, absolute ethanol and ether. Finally, obtained graphite oxide was dried in oven at 100°C for 24 hours to remove moisture present in the sample.

Exfoliation

The as-prepared graphite oxide was suspended in small bottle containing 100 ml water and was ultrasonicated for 2 h. This was followed by soaking in a liquid nitrogen bath for 20 - 30 s. The brownish sample obtained is further sonicated and centrifuged. This process is repeated about 15 times and the exfoliated graphene oxide samples are then dried at 75 °C for 24 hours. Finally the dried sample was grinded mechanically with the help of pestle and mortar and the powder formed was sieved with 100 micron stainless steel strainer.

CO₂ adsorption measurements

Ambient pressure CO₂ adsorption measurements were performed on a modified TG setup (TG209F1 Iris, Netzsch GmbH) according to the method described in Rahimi et al.³. Briefly, about 8 mg of the sample was taken in an Al₂O₃ crucible, evacuated and then heated to 300°C in argon atmosphere. Dedicated mass flow controllers from Bronkhorst (Bronkhorst High-Tech B.V.) were used for delivering pre-determined quantities of gases. The temperature was maintained at 300°C for 2 hours and then cooled down to 35°C under argon. To stabilize the temperature before the adsorption step, the sample was maintained at 35°C under flowing argon for 30 minutes. In the adsorption step, 50 sccm of argon is replaced by 50 sccm of CO₂ for 1 hour. The sample was heated to 300°C before taking out. Prior to the actual measurement with the sample, a correction measurement without the sample was performed to account for the buoyancy corrections.

SO₂ adsorption measurements

SO₂ adsorption measurements were performed in a gravimetric setup in combination with a gas dosing system both from Rubotherm, Bochum (IsoSORP Series SC-HP Static). The incorporated magnetic suspension balance has a resolution of 1 µg. Experimental measurement errors are max. +/- 5% for the loading and pressure reading. The purity of the SO₂ gas used is 99.98% (supplied by Air liquide in the purity N38, H₂O ≤ 50ppmw, H₂SO₄ ≤ 10ppmw as stated by the supplier). Prior to adsorption the sample was degassed at 150°C for 12 h under vacuum better than 5x10⁻² mbar. The maximum SO₂ pressure for adsorption was limited by the temperature of the supply bottle which was stored under ambient conditions in the storage cabinet, yielding a vapor pressure for SO₂ of approximately 2.6 bar. The first adsorption point is taken at 0.9 bar. Buoyancy effects were taken into account by Helium correction measurements of the samples and the blank setup at the studied temperatures with Alphagaz™ 1 Helium supplied by Air liquide (purity 99.999%, N₂ < 5ppmv, O₂ < 2ppmv, H₂O < 2ppmv, HC < 0.2ppmv as stated by the supplier). Prior to each Helium buoyancy correction of the sample, it was degassed as described at 150°C. Prior to blank measurements the setup was degassed at 300°C.

N₂ plasma functionalization

N₂ plasma functionalization was carried out in a radio frequency plasma (rf 13.56 MHz, Femto, Diener electronic GmbH, Germany). The rf generator of the plasma setup has a power rating of 300 W but the maximum power is limited to 200 W. GO placed in a quartz crucible were kept inside the plasma chamber and evacuated to a pressure of < 0.2 mbar followed by the introduction of high purity N₂ (99.999 %) gas. Plasma treatment was carried out for 60 minutes at 20 % power under a chamber pressure of 0.8 mbar.

XPS Measurements

XPS measurements were performed using a K-Alpha XPS spectrometer (Thermo Fisher Scientific, East Grinstead, UK). Data acquisition and processing using the Thermo Advantage software is described elsewhere.⁴ All samples were analyzed using a microfocused, monochromated Al K α X-ray source (30-400 μ m spot size). The K-Alpha charge compensation system was employed during analysis, using electrons of 8 eV energy and low-energy argon ions to prevent any localized charge build-up. The spectra were fitted with one or more Voigt profiles (binding energy uncertainty: + / - 0.2 eV). The analyzer transmission function, Scofield sensitivity factors,⁵ and effective attenuation lengths (EALs) for photoelectrons were applied for quantification. EALs were calculated using the standard TPP-2M formalism.⁶ All spectra were referenced to the C 1s peak of graphite at 284.4 eV binding energy controlled by means of the well-known photoelectron peaks of metallic Cu, Ag, and Au.

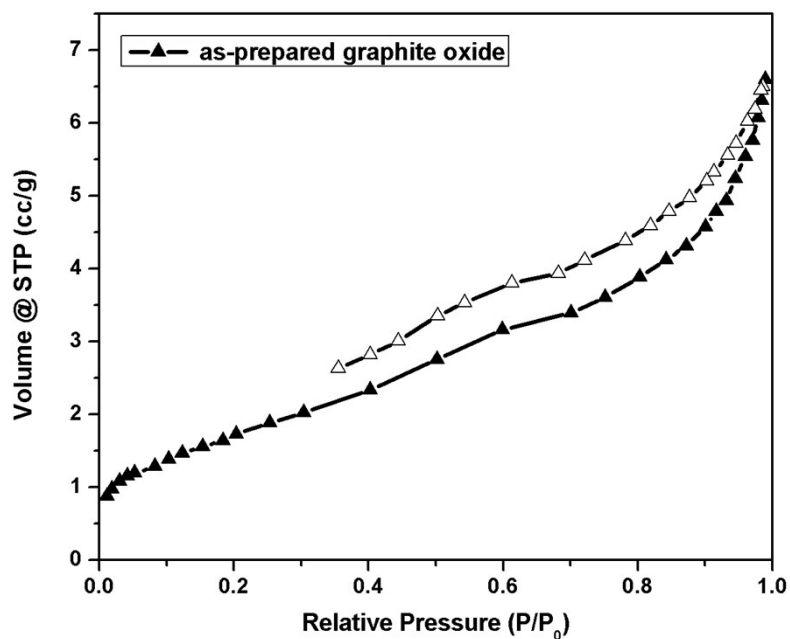


Figure S1: N_2 adsorption isotherm of as-prepared graphite oxide at 77 K. Closed symbols represent adsorption trace and open symbols represent desorption trace

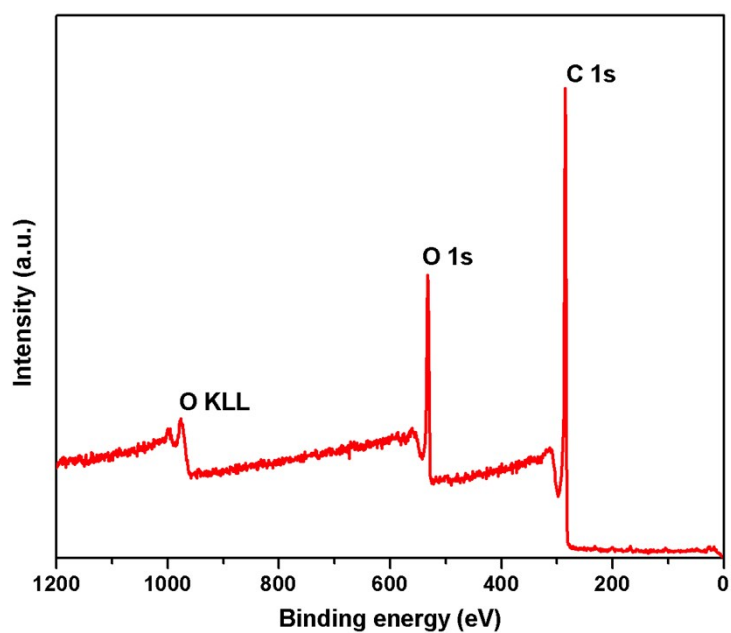


Figure S2: XPS survey spectrum of graphene oxide

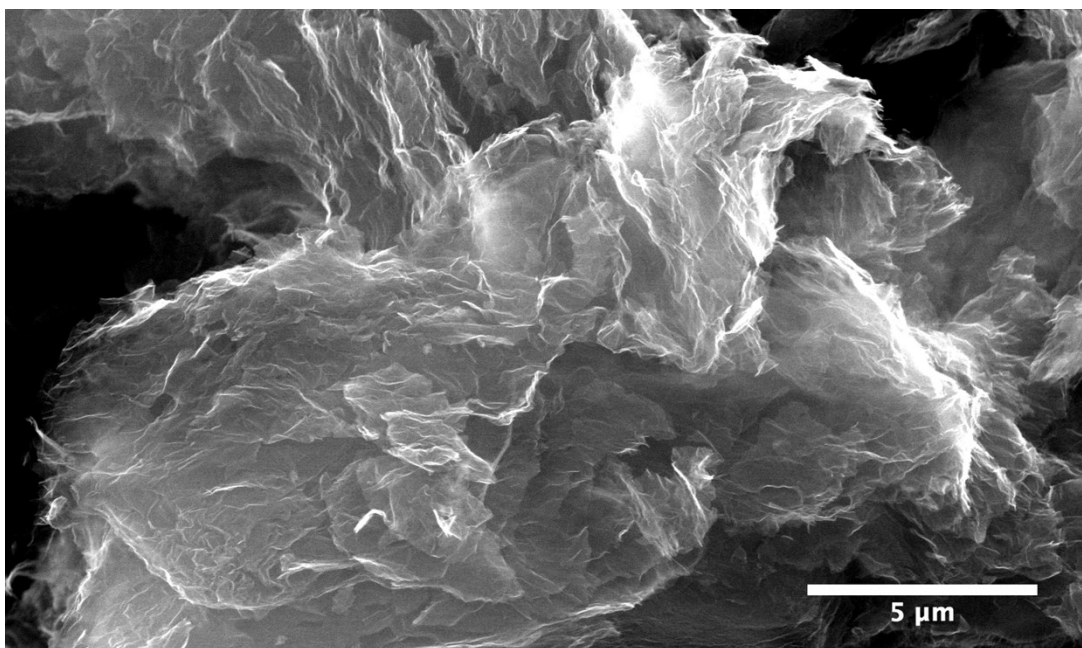


Figure S3: SEM image of N₂ plasma treated graphene oxide

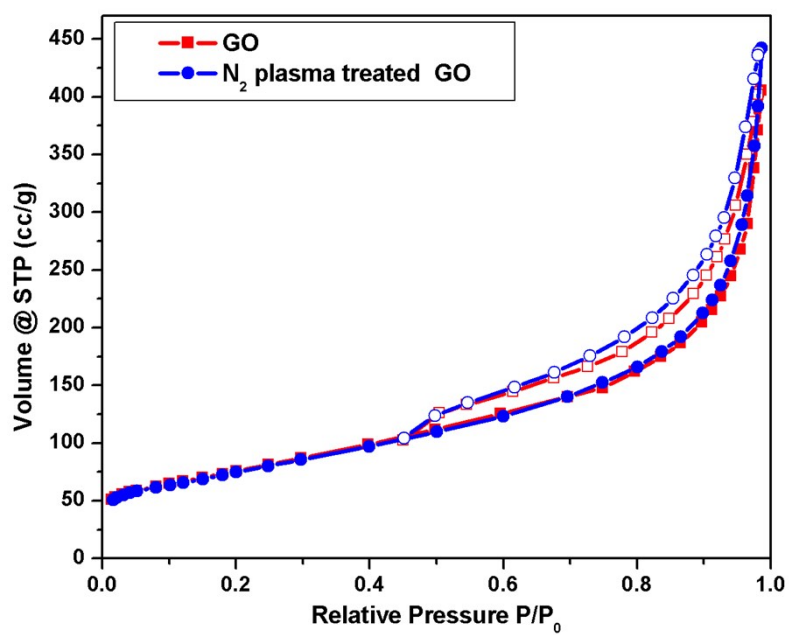


Figure S4: Comparison of N₂ adsorption isotherm of GO and N₂ plasma treated GO. Closed symbols represent adsorption trace and open symbols represent desorption trace

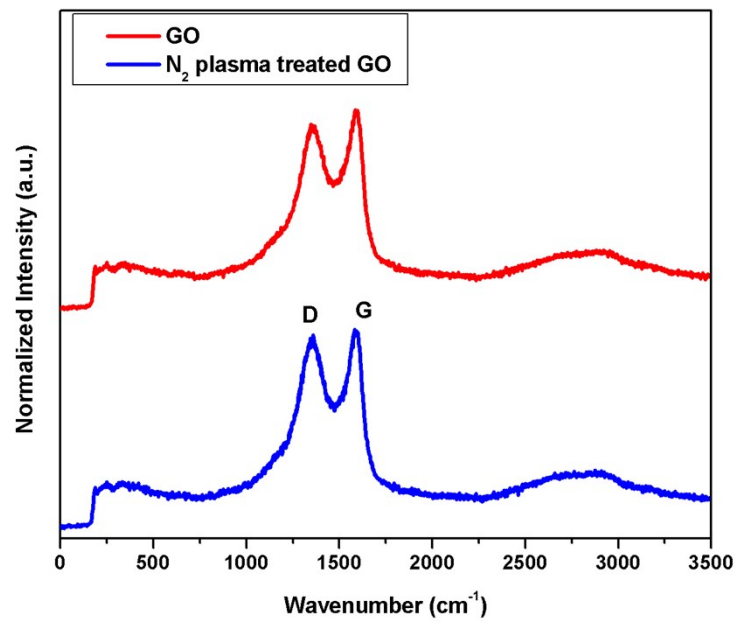


Figure S5: Raman spectra of GO before and after N₂ plasma treatment

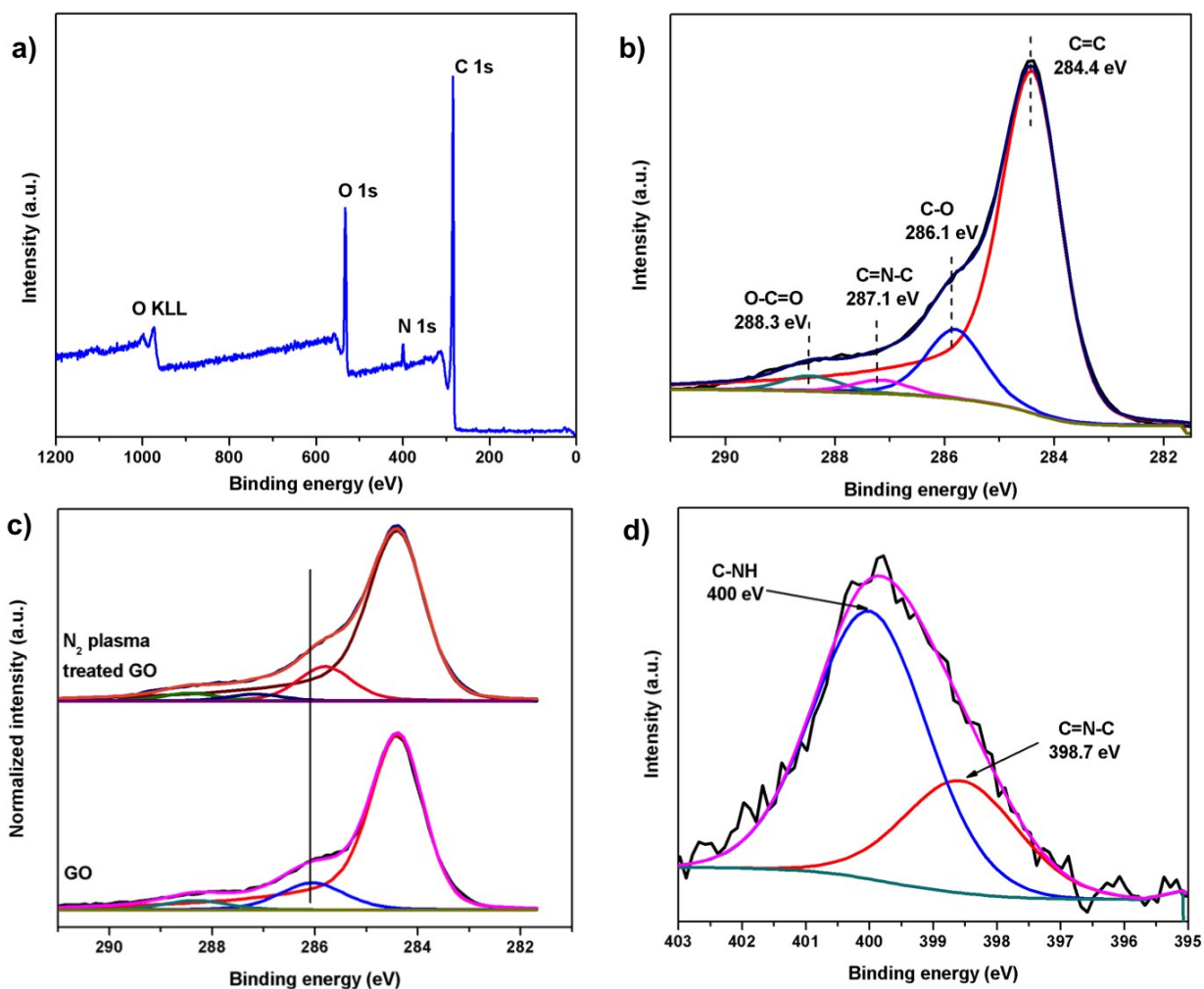


Figure S6: a) Survey spectrum of N₂ plasma treated GO b) High resolution C 1s spectrum of N₂ plasma treated GO c) Comparison of C 1s spectra of GO and N₂ plasma treated GO d) high resolution N 1s spectrum of N₂ plasma treated GO

	C at. %	N at. %	O at. %
GO	80.7	0	19.3
N ₂ plasma treated GO	77.5	3.5	19

Table 1: XPS analysis result of GO and Nitrogen plasma treated GO

Isosteric Heat of adsorption

Isosteric heat of adsorption is calculated according to the method of Czepirski et al. ⁷ using a virial type equation given by

$$\ln(P) = \frac{1}{T} \sum_{i=0}^{l1} a_i n^i + \sum_{i=0}^{l2} b_i n^i + \ln(n)$$

where n is the amount adsorbed at pressure P and temperature T . a_i and b_i are empirical parameters. The equation was fitted using least square fit method and the best fit was obtained for $l1 = 2$ and $l2 = 0$. The respective parameters are listed in table 1. The best fit obtained is shown in figure S8.

Isosteric heat of adsorption is calculated using

$$q_{st} = -R \sum_{i=0}^{l1} a_i n^i$$

where R is the universal gas constant

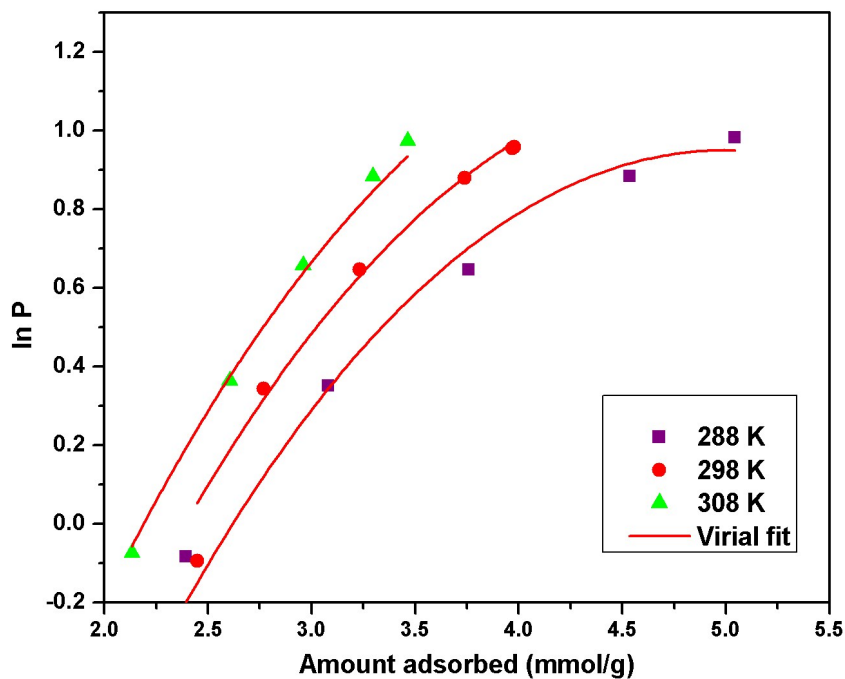


Figure S7: Virial fit of SO₂ adsorption on GO at 288, 298 and 308 K

Parameter	Value
a_0	-2329.88 ± 203.15
a_1	339.9 ± 46.70
a_2	-39.798 ± 6.649
b_0	4.9843 ± 0.655
reduced χ^2	0.0037
adjusted R^2	0.97638

Table 2: Virial equation fit parameters

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