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Electronic Supplementary Information

High quality reduced graphene oxide flakes by fast kinetically controlled and clean indirect UV-induced radical reduction

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Experimental Section:

All chemicals were of analytical grade, bought from commercial vendors and used as received.

Two different GO samples have been investigated in this work: a) single-layered GO purchased from Cheaptubes.com (USA; further called CT-GO), and b) home-made oxo-functionalized graphene (oxo-G_1) synthesized according to Eigler *et al.*[1].

Solutions were always freshly prepared in Millipore water (R > 18.2 MΩ) shortly before irradiation. For more details see [2, 3].

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The photoreduction of aqueous GO dispersions were conducted in a closed quartz cell (3 ml, irradiated surface 3 cm^2). Commercial UV lamps (Radium for 222 nm and PL-S 9W/TUV Philips for 254 nm) generating the light with λ = 222 (6.4 mW/cm^2) or 254 nm (16 mW/cm^2), corresponding to photon fluxes of 1.2 x 10^{-8} or 3.4 x 10^{-8} Einstein/cm^2 x s, respectively were employed.

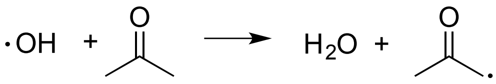
Changes of the optical spectra of the GO solutions were followed using a TIDAS-II UV-VIS spectrometer (Spectralytics GmbH, Essingen, Germany).

Raman spectra were recorded from 1050 to 3410 cm^{-1} with a LabRAM ARAMIS (HORIBA Jobin Yvon) confocal microscope at 532 nm (2.33 eV) excitation wavelength from dip coated silicon-oxide (300 nm) wafer.

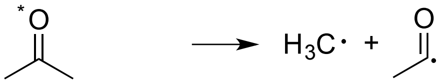
XPS spectra were recorded on Axis Ultra (Kratos, Manchester, UK) using monochromatized Al Kα radiation. Conductivity/sheet resistance measurements were done on a four-point probe from Materials Development Corporation (Chatsworth, CA), employing a probe head with a pin-distance of about 1 mm.

All experiments were conducted at room temperature.

Reaction Schemes



(S1)



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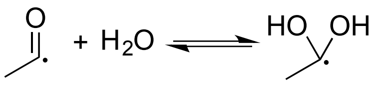

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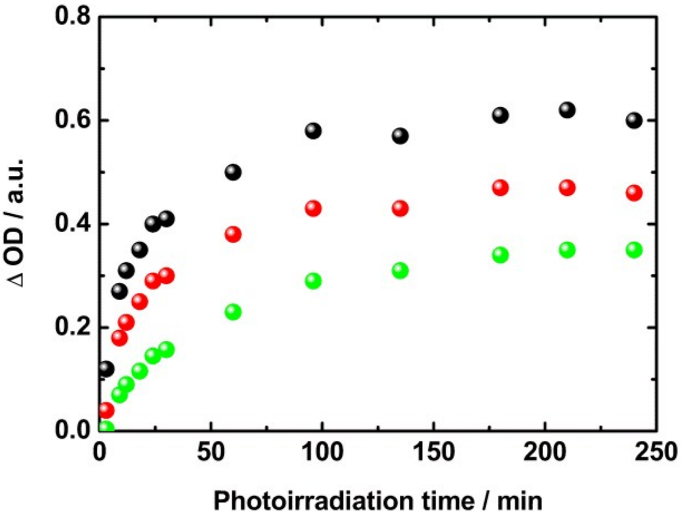

Figure S1. The optical changes monitored at 280 nm (black), 500 nm (red) and 700 nm (green) during direct photolysis at 254 nm of 0.04 g l^{-1} CT-GO nitrogen-saturated aqueous dispersions at pH 5.

Raman characterization of reduced CT-GO

Recently, spectra of such defective rGO were critically and systematically evaluated.[4] Using this approach, we treated the obtained Raman spectra with Lorentz functions. They possess broadened D and G bands (deconvoluted into D, D** and G bands, see Fig. S2a). In analogy, the so-called 2D region of Raman spectra was fitted with three peaks located at around 2700, 2950 and 3200 cm^{-1} (Fig. S2a), and are assigned to 2D (or G´), D + D´(or D + G or S3) and 2 D´ (or G + D´) Raman modes, respectively. All bands from the 2D region are significantly broadened causing a bump like appearance of the 2D region of the Raman spectra (Fig.S2 a,b), which is typical for the samples with a high defect density.

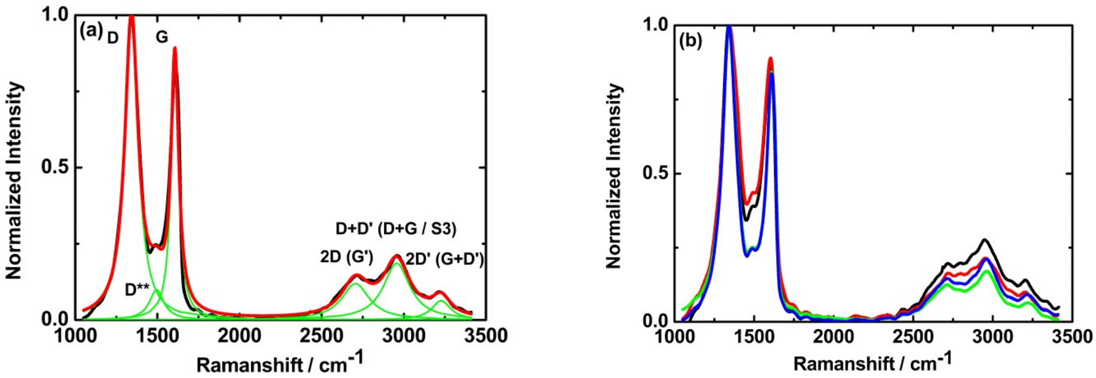

Figure S2. (**a**) Raman spectrum of reduced CT-GO obtained after 222 nm treatment of CT-GO dispersion at natural pH (black) and the deconvoluted (green) and fitted (red) spectra; (**b**) comparison of Raman spectra of CT-GO samples: non-treated (black) and reduced with hydrazine (red), photochemically (blue) and via EB-treatment (green). All presented Raman spectra are normalized taking the intensity of D band as unity.

The intensity ratio of I_D/I_G, a very often-used parameter in Raman analysis of graphene and graphene like materials such as rGO, did not showed any changes for rGO obtained by three different methods compared to starting GO. Therefore, the more sensitive ratio of the integrated areas of the peaks, corresponding to the D and G bands (A_D/A_G) was taken into considerations. This parameter is equal to 1.74 for non-treated sample and is only slightly larger (in the range of $A_D/A_G = 1.99 \pm 0.05$, i.e. at most 17 % more) for rGO obtained via hydrazine, EB- or photoreduction methods. A larger difference has been observed for the ratio of A_{2D}/A_G which increased from 0.26 for non-treated GO to about 0.7 for all kinds of treated GO. According to [5] such a trend indicates for the increased graphitization in rGO. In this regard photoreduced (using 2-PrOH/acetone system) GO can be considered as a material of (at least) similar quality as obtained by the conventional reduction with hydrazine.

Table S1. Results of Raman analysis for CT-GO and reduced CT-GO obtained by different methods.

Probe	I_D/I_G	A_D/A_G	A_{2D}/A_G	Γ_D, cm^{-1}	Γ_G, cm^{-1}	A_{S3}/A_{2D}
non-treated	1.16	1.74	0.26	128	75	1.92
hydrazine treated	1.17	1.94	0.72	113	55	1.79
EB-reduced*	1.17	2.03	0.63	105	51	0.99
Indirect** photoreduction	1.18	1.99	0.73	98	56	1.46

* - reduction with EB generated hydrated electrons and $(CH_3)_2C{\bullet}(OH)$ radicals [2]

** - reduction with photochemically (254 nm) generated $(CH_3)_2C{\bullet}(OH)$ radicals.

Another ratio, namely of integrated intensities of S3 and 2D peaks, has an obvious trend to decrease starting with a value of 1.92 for non-treated GO and ending at 0.99 for rGO obtained by EB treatment. The corresponding value for photoreduced GO lies in between (1.46) exceeding one for hydrazine method (1.76). According to Ref. [6], a lower value of A_{S3}/A_{2D} ratio indicates a reduced concentration of the defects at the rGO surface. This parameter is similar for the starting GO and the rGO obtained by hydrazine treatment. Significantly smaller A_{S3}/A_{2D} values have been obtained for UV-light and EB rGO's. Since the latter two reduction methods (UV-light and E-beam) are based on free-radical GO reduction, it must be concluded that free-radical mediated GO reduction gives rGO with less topologic defects compared to one obtained via hydrazine treatment. Another interpretation based on Ref [7, 8] is that the lowering of A_{S3}/A_{2D} ratio reflects an increase of the number of graphitic domains. This is another confirmation of a higher quality of the rGO obtained by indirect UV-light photoreduction compared to the well-established methods like hydrazine one.

XPS characterization of reduced CT-GO

According to the literature it is possible to quantitatively convolute the spectra according to six different carbon species.[9] C–C (284.5 eV); C–C/C–H (285.5 eV); C–O/epoxy (286.5 eV); C=O (287.7 eV); O–C=O (289.0 eV); π–π* interaction (290.7 eV). In the case of starting CT-GO the fitting was performed without fixation of the position of the peaks, otherwise the fitting procedure was not giving reasonable results. Therefore, the content of hydroxyl/epoxy and carbonyl functionalities could not be distinguished and only their combined content has been determined. In all systems the contribution of π–π* interaction was found to be negligible.

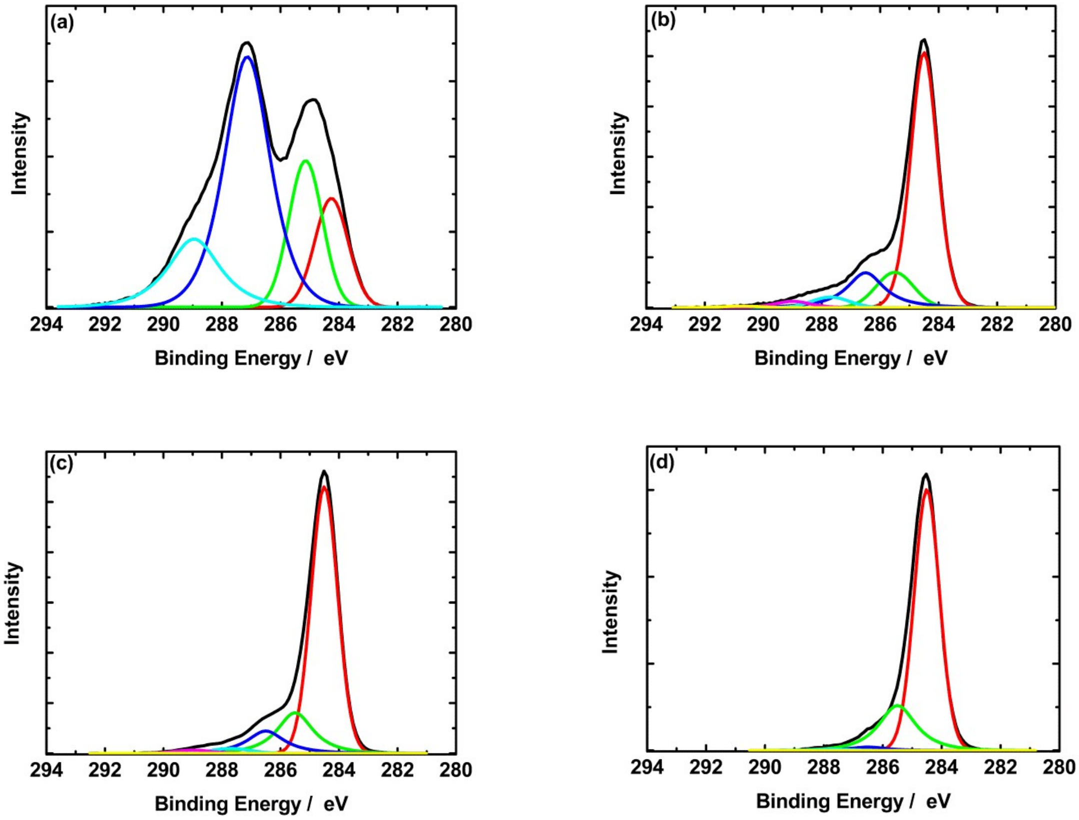

Figure S3. High-resolution C1s XPS spectra for CT-GO (a) and reduced CT-GO obtained by hydrazine (b), EB (c) and indirect photochemical reduction (d).

Table S2. Atomic percentage of different carbon bonds identified by high-resolution XPS in CT-GO and differently obtained reduced CT-GO.

Method / bonds and energies	-C=C- 284.5 eV	C-H/C-C 285.5 eV	C-OH /epoxy 286.5 eV	C=O 287.7 eV	O-C=O 289.0 eV	π-π* 290.7 eV
Non-treated	16.0	18.5	49.5 [a]	[a]	16.0	n.d.
Hydrazine	66.1	12.4	15.1	3.7	2.2	0.5
EB	70.1	16.8	10.0	1.9	1.2	0
UV	75.7	22.0	1.7	0.6	0	0

[a] combined content of C-OH/epoxy and carbonyl functionalities

After the reduction, the content of sp^2-carbon (peak at 284.6 eV) increased from about 16 % to about 66%, 70% and 76% for hydrazine, EB- or photoreduced CT-GO, respectively. The contribution of sp^3-carbon (C–C/C–H bonds) did not change as dramatically as one for sp^2-carbon. The content of the hydroxyl/epoxy functionalities is strongly reduced for hydrazine (~15%) or EB treatment (~10%), but especially dramatic decrease had been observed for photoreduced CT-GO (1.7%). Removal of carbonyl moieties in the case of EB is better than for the hydrazine treatment. Photoreduced CT-GO possesses almost no carbonyls. In contrast to hydrazine or EB treatment, a complete disappearance of the carboxyl functionality has been determined for photoreduced CT-GO.

The calculated C/O ratios for both types of GO reveals a significant degree of deoxygenation, starting from the same value of 2.3 for both non-treated GO's and ending with 7.4 ± 0.5 for reduced CT-GO's and 9.5 ± 1.4 for reduced oxo-G_1. There is a trend for a slightly higher C/O ratio for reduced oxo-G_1 compared to reduced CT-GO, when the values for one particular treatment are taken (some more difference had been seen for the EB reduction).

Calculations for energy consumption:

Energy consumption in pulsed 248 nm KrF excimer laser GO reduction experiment[10] at frequency of 5 Hz, laser energy of 200 mJ and reaction time of 5 min (300 s) is calculated as: 0.2 J x 5 x 300 = 300 J. This energy was absorbed by 15 ml of 0.1 g/l GO, i.e. 20 J is needed for the reduction of 1 ml of 0.1 g/l GO. In the case of oxo-$G_1$and 254 nm treatment, 5.8 J of energy is absorbed by 3 ml of 0.05 g/l ai-GO dispersion, hence ca. 3.9 J is needed for the reduction of 1 ml of 0.1 g/l oxo-G_1. Thus, the energy input in the case of direct pulsed laser reduction of GO is at least 5 times higher than for the described in this work indirect photoreduction of GO.

UV-vis criterion of rGO quality

The quality of the rGO obtained by direct laser-induced reduction is much lower. The final product, is in fact, only partly reduced GO. It follows from the UV-vis spectra of the starting GO and the end product (5 min of laser beam irradiation) presented in Fig. 2 of [10]. Recently we have proposed a simple UV-vis criterion to determine the reduction degree of GO (see Ref 2). It was found that the ratio of the maximal absorbancies of rGO (at ca. 265-270 nm) and GO (at ca. 230 nm), when a dispersion of the latter is stable and no other strongly absorbing components are present, should be in the range of 1.6-1.7. These values can be indeed calculated from the published UV-vis spectra published. Since they were obtained with different starting GO's by hydrazine[11,12] and EB method[2], one can conclude that i) the nature of starting material and ii) reduction method do not play a significant role on the above mentioned ratio, when a maximal possible reduction degree is achieved.

However, in the case of Ref [10] the A_{rGO}/A_{GO} ratio is equal to 1.1 only. Also, the shape of the obtained rGO spectrum does not have a prominent maximum at 260-270 nm, as it is reported for hydrazine[11,12] or EB-reduced GO[2].

The same is even more relates to the spectra of the "rGO" obtained via femtosecond laser treatment of GO (see Fig. 2 in [13] where the maximal absorbance of rGO is lower, than one for starting GO. It is unclear, why the absorption maximum of the obtained rGO is situated at ca. 230 nm, but not at 260-270 nm as it is well-established. Finally, it is difficult to judge on the GO reduction degree, since no data on conductivity/sheet resistance was presented.

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