Electronic Supplementary Information (ESI)

1. Sample preparation

Graphene oxide (GO) was synthesized using a modified Staudenmaier method.\(^1\) 1 g graphite (Fluka, 50870) was dispersed in 20 mL HNO\(_3\) 65 wt% (Riedel-de Haën, 30709) and 40 mL H\(_2\)SO\(_4\) 96 wt.% (Merck, 100731) in a 100 mL spherical flask. Solution was stirred for 30 min at \(\sim 273 \text{ K}\) with an ice-bath. 20 g KClO\(_3\) 99+% (Alfa-Aesar, A17075) were gradually added and stirring was continued for 20 h at room temperature (RT). The solution was then added to 200 mL H\(_2\)O and GO\(_1\) was obtained by 6 centrifugations (2700 rcf, 5 min) with interval rinsing with H\(_2\)O until the pH value of the supernatant solution surpassed 6. GO\(_1\) was air-dried at RT. The same oxidation process was followed for the preparation of sample GO\(_2\) by using 1 g of GO\(_1\) instead of graphite. Oxidation was repeated once more for sample GO\(_3\) by using 0.5 g of GO\(_2\) and half quantities of the rest chemicals as well. The preparation of the GO colloids was performed following our previous method.\(^2\) Freeze-dried powder from each sample (2 mg) was inserted in a 2 ml polypropylene vial and dispersed in H\(_2\)O (0.8 ml) which was pre-adjusted at pH=12.5 (NaOH, 1M). The amount of NaOH used was recorded in order to be taken into consideration later during the determination of the concentration of GO colloids (with TGA). The samples were sonicated (20 min, Branson 2510, 100W, 45 kHz) and left under mild agitation (48 h). Then, the vials were left to stand still and an aliquot from the supernatant was removed (see Table 3 for sampling time) in order to isolate only the fine particles. The sampling times varied, since the GOs with different oxidation degree exhibit different colloidal stability. The lower the oxidation, the less stable the colloid, thus sampling no later than 10 min was necessary for GO\(_1\). For GO\(_3\), sampling at 3 h was sufficient to produce a fine colloid, and in fact with higher concentration than GO\(_1\) (Table S1).

<table>
<thead>
<tr>
<th>Sampling time</th>
<th>Concentration of GO colloids [mg/ml]</th>
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<tbody>
<tr>
<td>GO(_1)</td>
<td>10 min</td>
</tr>
<tr>
<td>GO(_2)</td>
<td>1 h</td>
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<tr>
<td>GO(_3)</td>
<td>3h</td>
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The third-order nonlinear optical (NLO) properties and the optical limiting (OL) performance of graphene oxide suspensions have been investigated by means of the Z-scan technique,\(^1\) using a 35 ps mode locked Nd:YAG laser and a 4 ns Q-switched Nd:YAG laser delivering visible (532 nm) and infrared (1064 nm) laser pulses. The advantage of this technique relies not only on its experimental simplicity (single beam technique), but also because it allows the simultaneous determination, from a single measurement, of the sign and magnitude of the nonlinear absorption and refraction of a sample, which are related to the imaginary and real parts of the third-order susceptibility, \(\chi^{(3)}\), respectively. In the Z-scan, the transmittance (T) of a sample is measured as it moves along the propagation direction of a focused Gaussian beam. The sample experiences different light intensity in each position, while around the focal point the intensity is large enough to induce the nonlinear optical response of the material. The measurement of the transmittance of a sample, as it moves along the laser propagation direction of a focused laser beam, is performed by two different ways: (i) just after the sample, where the entire transmitted laser light is collected and measured, or (ii) after the transmitted laser beam has passed through a small aperture placed in the far field. The former measurement is known as “open-aperture” Z-scan while the latter one as “closed-aperture” Z-scan. From the former measurement, the magnitude of the nonlinear absorption coefficient \(\beta\) of the sample, which is related to the imaginary part of the third-order susceptibility \((\text{Im}\chi^{(3)})\), can be determined by fitting the “open-aperture” Z–scan recording with the following equation:

\[
T = \frac{1}{\sqrt{\pi}} \left[ \frac{\beta I_0 L_{\text{eff}}}{1 + z^2 / z_0^2} \right] e^{-\beta I_0 L_{\text{eff}}} \left[ 1 + \frac{\beta I_0 L_{\text{eff}}}{1 + z^2 / z_0^2} \exp\left(-\frac{2r^2}{w_a^2}\right) \right] \exp\left(-\frac{2r^2}{w_a^2}\right) \quad \text{(1)}
\]

where \(T\) is the normalized transmittance, \(I_0\) is the peak on-axis irradiance of the laser beam at the focus, \(z_0\) is the Rayleigh length and \(L_{\text{eff}} = (1 - \exp[-a_d L]) / a_0\) with \(a_0\) being the linear absorption coefficient at the laser wavelength and \(L\) denoting the physical length of the sample (i.e. the thickness of the cell which was 1 mm). In addition, the presence of a transmittance minimum or maximum at the “open-aperture” Z-scan recording indicates the sign of the nonlinear absorption coefficient \(\beta\), corresponding to reverse saturable absorption (RSA, \(\beta > 0\)) or saturable absorption (SA, \(\beta < 0\)) respectively.

From the “closed-aperture” Z-scan, the nonlinear refractive parameter \(\gamma\) of the sample (related to the real part of the third-order susceptibility \((\text{Re}\chi^{(3)})\)) can be determined. A “closed-aperture” Z-scan can exhibit either a pre-focal transmission minimum (valley) followed by a post-focal maximum (peak) or a pre-focal maximum (peak) followed by a post-focal minimum (valley), indicating positive or negative \(\text{Re}\chi^{(3)}\), with the sample acting as positive (focusing) or negative (defocusing) lens respectively. The nonlinear refractive parameter \(\gamma\) can thus be obtained using the following equation:

\[
\gamma = \frac{\lambda a_0}{1 - e^{-a_0 L}} \frac{\Delta T_{\text{p-v}}}{0.812 \pi L_0 (1 - S)^{1/2}} \quad \text{(2)}
\]

where \(\lambda\) is the laser wavelength, \(\Delta T_{\text{p-v}}\) is the difference between the peak and the valley of the normalized transmittance, \(S\) is the linear transmittance of the aperture (defined as \(S = 1 - \exp(-2r_a^2 / w_a^2)\)); with \(r_a\) being the radius of the aperture and \(w_a\) being the beam radius at the aperture). The quantities \(a_0\), \(L_0\) and \(L\) as previously defined.

The NLO parameters \(\gamma\) and \(\beta\) having been determined, the real and imaginary parts of the third-order susceptibility \(\chi^{(3)}\) can be easily calculated according to the following equations:

\[
\text{Re} \ \chi^{(3)} (\text{esu}) = \frac{10^{-6} c n_o^2}{480 \pi^2} \gamma (\text{cm}^2 / \text{W}) \quad \text{(3a)}
\]

\[
\text{Im} \ \chi^{(3)} (\text{esu}) = \frac{10^{-7} c^2 n_o^2}{96 \pi^2 \omega} \beta (\text{cm} / \text{W}) \quad \text{(3b)}
\]
where \( \omega \) (in s\(^{-1}\)) is the frequency of the laser light.

3. UV-Vis-NIR absorption spectra

![Graph showing UV-Vis-NIR spectra of aqueous GO suspensions with different degrees of oxidation.]

**Fig. S1.** UV-Vis-NIR spectra of the aqueous GO suspensions with the different degree of oxidation used for the NLO measurements.
4. Dynamic light scattering (DLS) measurements

Fig. S2. Autocorrelation functions of several DLS measurements from the stable colloid formed by the highly oxidized GO₃ and the respective results from its reduced derivatives through UV irradiation (RGOs). The latter show faster decay rates manifesting smaller hydrodynamic sizes, i.e., smaller aggregates.

References

