Giant broadband nonlinear optical absorption response in dispersed graphene single sheets

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Under intense laser excitation, thin films and suspensions of graphite and its nanostructure, including carbon black, nanotubes, few-layer graphenes and graphene oxides, exhibit induced transparency due to saturable absorption. This suggests that a number of graphitic nanostructures share similar NLO behaviour.

Preparation of functionalized graphene

Solvant-dispersible graphenes were prepared from sub-stoichiometric graphene oxide (sub-GOx) by half-oxidizing graphite and then grafting the sub-GOx with octadecylamine surface chains to give organic-solvent dispersible sheets in the range of 300–500 nm (ref. 17). It is important to distinguish between these sub-GOx and the heavily oxidized GOx that can be obtained by exhaustive oxidation of graphite18,19, although this distinction is often lost in the literature20,21. The fully oxidized stoichiometric GOx does not have π-electrons, but sub-GOx has a significant fraction of sp2...
carbon atoms retained in the basal plane which gives it semiconducting and optical properties.

For sub-GOx that is about one-third to half oxidized, the sp² carbon atoms are organized into nanographene domains, which are quite large 2D π-electron systems with diameters of ~10 nm (estimated by Raman and infrared spectroscopies; Supplementary Section 1), separated by boundaries comprising a network of epoxy and/or hydroxyl-bonded sp³ carbon atoms (Fig. 1). These domains exhibit broadband electronic absorption that is similar to that of ‘perfect’ graphene. Furthermore, in contrast to heavily oxidized GOx, sub-GOx can undergo facile thermal re-graphenization by extending the nanographene domains into a ‘graphenite’ network that shows band-like field-effect transport despite disorder. The sp³ carbon atoms in the domain boundaries provide sites for chemical functionalization with a variety of alkyl chains and groups. These sub-GOx can therefore be regarded as functionalized graphenes that can be dispersible as single sheets in a variety of solvents and film matrices.

The octadecylamine-functionalized sub-GOx nanosheets can be repeatedly isolated in the dry state, and re-dispersed in a variety of organic solvents (up to 15 mg ml⁻¹) and polymer matrices. The alkyl chains prevent the re-stacking of these sheets, and therefore promote their dispersability in various matrices. From here onwards, ‘sub-GOx’ will refer to this functionalized form. For comparison, we have also prepared and functionalized a heavily oxidized and oxygenated GOx, sub-GOx can undergo facile thermal re-graphenization that can be dispersible as single sheets in a variety of solvents and film matrices.

NLO characteristics were measured using an open-aperture nanosecond Z-scan technique (Fig. 2b). The transmittance of the sample was measured as a function of the incident laser fluence, which was varied by translating the sample through the focal plane along its propagation (Z) axis. A Q-switched Nd-YAG laser was frequency-doubled to produce 3.5 ns, 532 nm pulses, which were loosely focused by f/30 optics to a diameter 2w₀ of 20 μm (1/e² intensity) with a Rayleigh length z₀ of 600 μm. This Rayleigh length was similar to or much larger than the thickness of the sample (1.0 mm liquid cell, or 2-μm-thick films). Measurements were also made at the fundamental 1.064 nm wavelength.

Figure 2c presents a plot of output fluence F_out versus input fluence F_in for the sub-GOx/PC film measured in air for 3.5 ns, 1.064 nm pulses. Data were measured over ten spots and averaged. No significant spot-to-spot variation was found. The F_out/F_in ratio in the limit of zero fluence gives the linear transmittance T of the film. At high fluences, the limiting slope dF_out/dF_in gives the limiting differential transmittance T'. For this film with T’ = 0.85, the non-linearity onset fluence F_on occurs at 10 μJ cm⁻², and the half-transmittance fluence F_50 (where transmittance falls to 50% of T) occurs at 100 μJ cm⁻². Above this, the film exhibits good output clamping characteristics with T’ = 0.17.

Figure 2d shows the F_out versus F_in characteristic at a wavelength of 532 nm, and Fig. 2e the corresponding transmittance versus F_in characteristic. At this wavelength, the film shows T = 0.73, with F_on at 10 μJ cm⁻² and F_50 at 80 μJ cm⁻², and even better output clamping with T’ = 0.055. These F_on, F_50 and T’ values for both wavelengths greatly surpass those of CNT dispersed in poly(methyl methacrylate) (PMMA) measured under similar conditions, by a factor of ~5–10. Note that CNT in PMMA is not stable to repeated laser shots, in contrast to these sub-GOx nanocomposites. A more precise comparison will therefore have to be made in liquid dispersions, as presented below. Note also that the PC film does not show any optical limitation, and the heavily oxidized GOx/PC film with the same T gives a considerably weaker optical-limiting effect (F_50 = 300 μJ cm⁻² and T’ = 0.25) (Fig. 2d,e). This shows that the giant NLO response in the sub-GOx/PC film is related to the nanographene domains.

It is clear that the mechanism for this giant optical-limiting effect does not involve the material breakdown that is known to occur at much higher fluences in CBS³,⁵, CNT¹³,²⁶, and even in graphite.²⁷ No black spots or pinholes were found by optical microscopy on the films after more than 100 shots at the highest fluences. Moreover, the Z-scan characteristic (Fig. 2f) is symmetric before and after traversal through the focus. No irreversible change in the film optical properties occurred due to heating or induced chemical transformation.

Giant optical-limiting effect in graphene–polymer film

Figure 2a shows the UV-vis-NIR transmittance spectrum of a 2.0-μm-thick film of sub-GOx dispersed in bisphenol-A polycarbonate (PC) at a weight ratio of 2.9 w/w%: the film quality is good (inset, Fig. 2a). Differential scanning calorimetry reveals the glass transition temperatures of the polymers in these nanocomposites to be generally upshifted, so the nanosheets are well-dispersed in the film matrices (Supplementary Section 2). The transmittance spectrum of a 2.0-μm-thick film of heavily oxidized GOx in PC at a weight ratio of 4.5 w/w% is also shown for comparison, together with that of sub-GOx dispersed in chlorobenzene (CB, 80 μg ml⁻¹) and ultrasonically exfoliated graphene in 1,2,4-trichlorobenzene (TCB, 30 μg ml⁻¹) in 1.0 mm path length cells.

The absorption of sub-GOx increases towards shorter wavelengths, with a profile that is nearly identical to that of graphene down to the mid-infrared region. The nanographene domains in the sub-GOx therefore have an optical joint density-of-states that is similar to graphene. Curiously, sub-GOx in both chlorobenzene and PC shows an absorption cross-section per basal carbon atom of 2.2 × 10⁻¹⁸ cm² at a wavelength of 532 nm, which is also similar to graphene. In contrast, the heavily oxidized GOx has a much lower absorption cross-section (by a factor of two) and shows discernible structures in the short-wavelength region that are characteristic of small π-electron systems.

Strong solvent/matrix effect on NLO response of graphene

Figure 3a reveals that the NLO characteristics of sub-GOx using 3.5 ns pulses at 532 nm exhibit an unusual and strong dependence on the film matrix. A neat film of the sub-GOx does not in fact give any optical limitation in the measured fluence range. It shows nearly perfect saturable absorption with T’ = 0.97 above 10 μJ cm⁻². The absence of optical limitation in this film is consistent with the behaviour of graphite at similar fluences, over which the photoexcited electron–hole gas relaxes to the K-point and recombines
over a picosecond timescale, during which the joint density-of-states is blocked and absorption saturates\(^28,29\). A similar behaviour has also been found in multilayer graphenes\(^30,31\).

The optical-limiting effect emerges when the sub-GOx is dispersed into PMMA, and becomes even stronger in PC. It is therefore clear that the giant optical-limiting effect is not an intrinsic feature of the nanographene domains, but depends on interaction with their environment. To clarify an aspect of this interaction, we conducted the following experiments in liquid cells. These offer a wider range of solvent matrices, and better stability to intense laser pulses due to continuous regeneration of the probe volume.

Figure 3b shows that the sub-GOx can exhibit saturable absorption or reverse saturable absorption depending on the solvent. We have previously established that our sub-GOx disperses as single sheets in these solvents\(^17\). The sub-GOx in chlorobenzene exhibits strong optical limitation \((F_{\text{out}}/F_{\text{in}} = 10 \text{ mJ cm}^{-2} \text{ and } T' = 0.10)\) that is comparable to the sub-GOx/PC film, and markedly superior to those of \(C_{60}\) (and also phenyl-\(C_{61}\)-butyrate methyl ester; data not shown) in toluene and single-walled CNTs in tetrahydrofuran (THF). The wavelength dependence of the optical-limiting response in chlorobenzene was measured using a tunable laser (Supplementary Section 3). The results confirm that this is broadband and extends over the 450–1,064 nm wavelength range, but with a gradual roll off above 700 nm.

This optical limitation effect increases marginally when the solvent is changed to bromobenzene (BB), 1,2-dichlorobenzene, etc.

Figure 2 | Linear and nonlinear transmittance characteristics of sub-GOx/PC film. 

- **a.** UV-vis-NIR spectra of sub-GOx/PC film. The solution spectra are collected in a 1.0 mm path length cell. Spectra of ultrasonically exfoliated graphene dispersed in TCB, sub-GOx in CB and heavily oxidized GOx in PC are also shown for comparison. Inset: photograph of film cast on fused silica disc (scale bar, 5 mm) showing 70% transmittance over the central region. 
- **b.** Schematic of the Z-scans. 
- **c,d.** Plot of output versus input fluence (red square) for 3.5 ns pulses at 1,064 nm and 532 nm wavelengths, respectively. \(T\) is the linear transmittance given by the \(F_{\text{out}}/F_{\text{in}}\) ratio in the limit of zero fluence and is 0.85 at 1,064 nm and 0.73 at 532 nm. The PC film is given in **d** as a reference, showing no optical limiting property. 
- **e,f.** Plot of transmittance versus input fluence for 3.5 ns pulses at 532 nm and its Z-scan characteristics. 

The characteristics of heavily oxidized GOx/PC film are also shown in **d** and **e**. All spectra and input fluences are corrected for reflection loss.

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(DCB) or TCB, but diminishes greatly in 1,3-difluorobenzene (DFB) and benzonitrile (BN). It disappears in N-methylpyrrolidinone (NMP), THF, anisole (ANS) and mesitylene (MES). This last is the strong solvent that is the least electronegative solvent. The possibility that the optical-limiting effect in BN (and DFB) than in bromobenzene, DCB, TCB is characteristic of a marked heavy-atom effect. This effect has been traditionally studied in molecular systems, where the heavy atom promotes intersystem crossing of the excited singlet state to the triplet state by spin-orbit coupling. Its emergence in the nanographene response here is therefore unexpected, and suggests that the excited states have become localized. Charge transfer can be ruled out as the dominant mechanism, because the sub-GOx shows a weaker optical-limiting effect in BN (and DFB) than in benzonitrile, which is the less electronegative solvent. The possibility that the solvent perturbs the ground state of the nanographene domains in different ways has also been ruled out. Raman spectroscopy shows no difference in the D and G bands of the sub-GOx in different solvents (Supplementary Section 4). Incidentally, the solvent microporosity phenomenon can also be ruled out for lack of dependence on the solvent boiling point (cf. TCB, DCB and CB).

Figure 4 shows that ultrasonically exfoliated graphene sheets in TCB give similar optical-limiting characteristics as sub-GOx in chlorobenzene, but the heavily oxidized GOx is decidedly inferior. It has been shown previously that these graphenes do not show optical-limiting effects in NMP and DMF over this fluence range. It is therefore clear that one aspect of the unusual optical-limiting behaviour of dispersed graphene sheets relates to the formation of localized and highly absorbing triplet-like states. In the following, we will use nanosecond pump–probe spectroscopy to measure the transient response of dispersed sub-GOx across the F\textsubscript{on} threshold to reveal further evidence of localized excited states.

**Transient absorption spectroscopy**

The probe pulses were prepared by broadband non-collinear parametric amplification seeded by a 1 kHz, 800 nm, 90 fs output of a Ti:sapphire (Solstice) regenerative amplifier. The pump pulses (532 nm, 0.5 ns) were the frequency-doubled output of a Q-switched Nd:YVO\textsubscript{4} laser, triggered electronically by the Solstice Ti:sapphire (Solstice) regenerative amplifier. The pump pulses are for 3.5 ns pulses at 532 nm collected in a 1.0 mm path length cell. The increase in the optical-limiting response across the solvent series DBF << CB < BB, DCB, TCB is characteristic of a marked heavy-atom effect. This effect has been traditionally studied in molecular systems, where the heavy atom promotes intersystem crossing of the excited singlet state to the triplet state by spin-orbit coupling. Its emergence in the nanographene response here is therefore unexpected, and suggests that the excited states have become localized. Charge transfer can be ruled out as the dominant mechanism, because the sub-GOx shows a weaker optical-limiting effect in BN (and DFB) than in benzonitrile, which is the less electronegative solvent. The possibility that the solvent perturbs the ground state of the nanographene domains in different ways has also been ruled out. Raman spectroscopy shows no difference in the D and G bands of the sub-GOx in different solvents (Supplementary Section 4). Incidentally, the solvent microporosity phenomenon can also be ruled out for lack of dependence on the solvent boiling point (cf. TCB, DCB and CB).

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of fluence in the Z-scan. This was varied between 2 and 90 mJ cm\(^{-2}\) by varying the incident power and focusing optics.

Figure 5a–d show the \(\Delta T/T\) spectra of sub-GO\(_X\) in chlorobenzene for different probe delays and pump fluences. Zero delay corresponds to coincidence of the centres of the pump and probe pulses. For a pump fluence of 2 mJ cm\(^{-2}\), which is well below the nonlinearity onset, the transient response is a spectrally flat photo-induced bleaching (that is, positive \(\Delta T/T\)). This is characteristic of blocking of the optical joint density-of-states by the photo-excited electron–hole plasma, which indicates that the electrons and holes are substantially delocalized within the nanographene domains. There is an unusually long tail with a lifetime of \(\sim 20\) ns, which suggests trapping. Similar results have been obtained in other solvents including mesitylene and anisole.

At a higher fluence of 20 mJ cm\(^{-2}\), the photo-bleaching is still present, but is attenuated by induced absorptions that emerge within the first 0.2 ns (instrument-limited), with dips at 2.1, 1.9 and 1.75 eV. At 30 mJ cm\(^{-2}\), the photo-absorption dips become more pronounced and dominate the response after \(\sim 2\) ns. At 90 mJ cm\(^{-2}\), the transient response is firmly photo-induced absorption across the entire spectral window, beginning at the sub-nanosecond timescale. There is a roll-off of the absorption beyond 700 nm, as found also in the wavelength-dependent optical-limiting data. Absorption bands are again found at 2.15, 1.95 and 1.80 eV. The dynamics is complicated by the presence of slow-rise components with rise times of 1–3 ns, and multiple decay lifetimes from 6 to 45 ns.

The fast emergence of transient absorption demonstrates that the leading mechanism for the giant optical limitation effect in liquid cells is excited-state absorption. This absorption is characteristic of localized excited states typically associated with molecular \(\pi\)-electron systems. The average band spacing is 0.15–0.20 eV, which coincides with the Raman modes of graphene (\(G\) band, 0.195 eV; \(D\) band, 0.165 eV), and so we assign to the vibronic spacing of excitonic states. This interpretation receives support from (i) the heavy-\(D\) band, 0.165 eV), and so we assign to the vibronic spacing of exci-

In summary, we have found an unusually efficient nonlinear optical-limiting behaviour that occurs in graphene and alkyl-functionalized sub-GO\(_X\) when they are dispersed as single sheets in appropriate solvents or film matrices. As a result, practical broadband optical limiters in both liquid cells and thin films or coatings.
oxidized GOx (9.3 mg) was first dispersed in chlorobenzene (0.50 ml). To this was
off the solvent. on a fused silica disc (diameter, 13 mm), then baked at 90 
the nitrogen glovebox. Functionalized sub-GOx (6.0 mg) was separately dispersed in PC (400 mg ml
2)

...Graphene single sheet

Graphite or multi-layer graphene

Spin-orbit coupling via environment

Interacting e-h pairs

Polaron

Figure 6 | Schematic outlining new optical-induced absorption mechanisms. a, Electron-hole pairs. Further excitation causes the appearance of localized states such as (i) excitons (neutral excited state) or (ii) polarons (charged excited state) due to interactions. b, For comparison, graphite gives on electron-hole gas that is very short-lived due to fast cooling and recombination.

can now be constructed with performances exceeding those of other carbon nanostructures by a factor of 5–10. We have outlined a new phenomenon in which the initially delocalized electron–hole gas localizes at high excitation densities in the presence of heavy atoms, to give strongly absorbing excitons. The resultant excited-state absorption mechanism can therefore be very effective. In essence, the broadband absorption advantage of large π-electron systems has been combined with the intense excited-state absorption advantage of small π-electron systems.

Methods
Materials. Sub-GOx was prepared by oxidation of synthetic graphite (496596, Sigma Aldrich) using a modified Strudemaier oxidation17. The graphite was reacted with a mixture of concentrated sulphuric acid, fuming nitric acid and potassium chlorate at 0–5 °C (1 h), held at room temperature for seven days, then washed extensively with Millipore water to give a product with an empirical formula of C2xO2y (according to combustion analysis). This was functionalized by mixing sub-GOx (10 mg) with octadecylamine (ODA, 100 mg) and 1,3-diisopropylcarbodiimide (60 μl) in DCM (5 ml) and heating with intermittent ultrasonication to 80 °C (24 h) under a nitrogen blanket to give a homogeneous black dispersion. This dispersion (1 ml) was mixed with THF (5 ml), briefly ultrasonicated, then centrifuged (8,000 r.p.m., 5,580g) for 1 h to separate the sediment from the supernatant, which contains the functionalized sub-GOx. The functionalized sub-GOx was then purified by precipitation with ethanol (5 ml), centrifugation (1,000g, 1 h), and re-dispersion in THF (0.25 ml), repeated three times, and dried under vacuum at room temperature. This purified material had an empirical formula of C2xO2y–ODA0.085 (according to Supplementary Section 1). Heavily oxidized GOx was also prepared as above, but added the PC solution (0.5 ml) with ultrasonication to give 4.5 w%/w heavily oxidized GOx to total solids. A 2.0-μm-thick film was formed by spin-casting as above.

For functionalized sub-GOx dispersed in PMMA, a solution of PMMA (400 mg ml
2) in chlorobenzene) was prepared at 65 °C. Functionalized sub-GOx (12 mg) was added to this solution (1.0 ml) with ultrasonication to give 2.9 w%/w sub-GOx to total solids. A 2.0-μm-thick film was formed by spin-casting at 1,000 r.p.m. For neat sub-GOx film, functionalized sub-GOx dispersed in THF (0.3 mg ml
2) was drop-cast.

References

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Author contributions
G.K.L. and L.L.C conceived the idea, performed the experiment and analysed the data. J.C. performed the experiments and analysed the data. R.H.F and P.K.H.H. analysed the data. Z.L.C. and R.G.S.G. synthesized and characterized the graphene materials. W.H.N and H.W.T. contributed to Z-scan measurement setup. G.K.L, J.C., R.H.F., P.K.H.H. and L.L.C. contributed to writing the paper.

Additional information
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