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Broadband electromagnetic response and ultrafast dynamics of few-layer epitaxial graphene
Broadband near infrared optical power limiting of few layered graphene oxides

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The transient nonlinear optical response of few layered graphene oxide dispersed in different organic solvents was studied and its nonlinear optical properties were determined under visible and infrared, nanosecond laser excitation. Few layered graphene oxide was shown to possess important and broadband optical limiting action under infrared laser wavelengths up to 1.8 \( \mu \)m, comparable to that observed for visible wavelengths. Finally, its nonlinear optical response and optical limiting efficiency was compared with that of single layer graphene oxide and it was found to be significantly superior. © 2014 AIP Publishing LLC. [http://dx.doi.org/10.1063/1.4878660]

The recent advances in nanotechnology offer a wide range of opportunities and open directions in the design and synthesis of materials suitable for optical limiting (OL) applications. Optical limiters constitute an important class of materials/devices used for controlling powerful laser beams employed in a variety of applications ranging from laser pulse shaping and compression1 to the protection of expensive devices (e.g., detectors) and/or the human eye.2,3 An ideal optical limiter is expected to exhibit some linear transmittance for low incident radiation intensities, which, above certain threshold incident intensity, remains constant, the response deviating from the Beer-Lambert law.

So far, various organic and inorganic materials have been considered and have been extensively studied, including phthalocyanine,4,5 porphyrins,6 fullerenes,7 carbon nanotubes,8 metal and metal oxide nanoparticles,9 metal complexes and clusters,10 and more recently graphene and its derivatives.11–19 Moreover, several photo-response mechanisms leading to OL behavior have been identified and investigated for their efficiency, as, for example, reverse saturable absorption (RSA), two- or multi-photon absorption (TPA/MPA), nonlinear scattering (NLS), nonlinear refraction (NLR), and thermal lensing.

In most of the cases, the studies of OL action are referring to visible and/or near infrared (NIR) laser radiation, usually extending up to 1064 nm, while investigations concerning laser radiations above this wavelength are rather scarce. As an example, significant OL at 1300 nm has been reported for some chromophores,20 while composites of fullerene-doped polyimides have been also found presenting OL at 1315 nm.21 More recently, OL has been reported for some chromophores,22 while composites of fullerene-doped polyimides have been also found presenting OL at 1300 nm (for bis-dioxaborine polymethine-based materials,23 at the spectral region 1200–1400 nm (in the case of fused azulene and oligomeric porphyrins)24 and between 1200 and 1580 nm (for nickel bis(dithiolene) complexes).25 Nevertheless, this spectral region is quite interesting since it includes the so-called “telecommunication wavelengths.”

Recently, graphene has been reported to exhibit OL only at high fluencies due to nonlinear scattering.11 In contrast, GOs and GOs linked with metal/organic complexes have both been reported to exhibit strong OL at much lower fluencies than graphene, both in the nanosecond and picosecond regimes, owing to the operation of RSA or RSA/TPA mechanisms.18 Moreover, in a recent work regarding some reduced GO films, having different degree of reduction, it has been shown that greater the ratio of \( sp^2/sp^3 \) domains, better the OL achieved.26 Likewise, in another report studying sub-GOx, a graphene sheet oxidized by about 1/3 to 1/2, having the \( sp^2 \) carbon atoms well organized into 2D \( \pi \)-electron nanographene domains, it was found that these nanographene domains can switch from a broadband photo-induced bleaching to a RSA mechanism, giving rise to larger nonlinear absorption than that in the heavily oxidized GOx.27 More recently, it has been shown by our group that few layered GO exhibits superior nonlinear absorption, and thus better OL efficiency, than single layer GO under 532 nm 4 ns laser excitation, due to the larger fraction of \( sp^2 \) clusters, the corresponding mechanism responsible for the OL behavior being RSA.19 A similar observation has been reported in an earlier study comparing the nonlinear optical (NLO) response of some nanodiamonds and onion-like nanocarbons, where the latter having more \( sp^2 \) carbons exhibited larger NLO response.28

In the present work, the OL action of few layered GOs is investigated, the emphasis given in the broadband OL action in the NIR spectral region upon nanosecond laser excitation. GO was prepared according to a modified Hummers’ method,29,30 using purified natural graphite powder (Alfa Aesar) and it was dispersed in various organic solvents, where, as it has been reported, its maximum dispersibility depends both on the solvent and the extent of surface functionalization imparted during oxidation, with typical values of the order of 0.5–4 mg/ml in water as well as in other

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studied solvents. In the present work, GO suspensions were prepared using six different solvents, namely, DMF (Dimethylformamide), THF (Tetrahydrofuran), NMP (N-Methyl-2-pyrrolidone), CB (Chlorobenzene), o-DCB (1,2-Dichlorobenzene), and CN (1-Chloronaphthalene). The dispersions were prepared by a 2 h sonication (Elma S 30 H Elmasonic) of the GO powder. Longer sonication times were avoided, since they can damage the GO sheets. Finally, the sheet size and the numbers of the layers were controlled through the centrifugation procedure.

The GO sheets were characterized by FESEM (Field Emission Scanning Electron Microscopy), XRD, FTIR and Raman spectroscopy. The size of the GO sheets was determined by FESEM to range between 1 and 1.2 μm, while their thickness was deduced from the FWHM of the XRD peak to be about 12 nm. Using Scherrer’s equation, an average number of 16 layers was determined for the GO sheets. Furthermore, a Lc/Ld ratio of 0.9 was determined from the Raman spectra. The smaller value of this ratio compared to that reported for single layer GO (ca. 1.15) should be attributed to the number of the layers, since the intensity of the D-band is not only associated with the amount of the disorder but also tends to decrease with the number of layers as well. Finally, the strong degree of oxidation of the graphene oxide was verified from the FTIR spectra exhibiting the characteristic features at 3430 cm\(^{-1}\) (O-H stretching vibrations), at 2854 and 2922 cm\(^{-1}\) (C-H stretching), at ~1715 cm\(^{-1}\) (C = O), and the graphitic domains of C-C at ~1577 cm\(^{-1}\).

In order to study the OL behavior, the few layered GO dispersions were placed in 1 mm thick quartz cells. Then, their OL was investigated by means of the Z-scan technique, both at 532 and 1064 nm, employing 4 ns pulses from a Q-switched Nd:YAG laser. Moreover, simple transmission measurements were performed at 1250, 1520, and 1750 nm, using 4ns pulses delivered from an Optical Parametric Oscillator (OPO) pumped from the same Nd:YAG laser. In all cases, the laser was focused into the sample by means of a 20 cm focal length plano-convex lens. During the measurements, the samples were continuously stirred, while measurements were performed with the laser running at different repetition rates between 1 and 10 Hz, in order to check for any thermal/cumulative effects. However, the Z-scan recordings did not show any significant differences, thus confirming the absence of such effects. Furthermore, the UV-Vis-NIR absorption spectra of the samples were measured prior and after the irradiation of the suspensions in order to ensure that no photo-degradation effects had occurred.

In Figure 1, the UV-Vis optical absorption spectra of the few layered GO dispersions in the different solvents used are presented. The concentration of the different dispersions was adjusted to about 1 mg/ml of GO, so that all dispersions exhibit similar linear transmission (ca. 50%) at 532 nm. For comparison, the absorption spectrum of a similar linear transmission 2.48 mg/ml C\(_{60}\)-toluene solution is also presented, C\(_{60}\) being considered as a benchmark material for optical limiting.

In Figures 2(a) and 2(b), some representative “open-aperture” Z-scans of the few layered GO dispersed in CN are presented, as obtained under 532 and 1064 nm laser excitation, respectively. Since CN, as the other solvents used as well, did not exhibit any NLO response under ns excitation, the obtained Z-scans reveal straightforwardly the response of few layered GO. As can be seen, it was found to exhibit SA at low incident laser intensity, changing to RSA at higher incident laser intensity. In Figures 2(c) and 2(d), similar “open-aperture” Z-scans corresponding to aqueous dispersions of single layer GO are given. As shown, single layer GO exhibited RSA at much higher laser intensity, indicating significantly lower nonlinear absorption than the few-layered GO. It should be noted at this point, that under ns excitation the NLO response of a material is rather a transient response than an instantaneous one, being influenced by its photophysical parameters as it has been shown elsewhere.

Then, the nonlinear absorption coefficient \(\beta\) corresponds to an effective quantity, namely, \(\beta_{\text{eff}}\). In order to determine \(\beta_{\text{eff}}\), the “open-aperture” Z-scan recordings were fitted by the following intensity dependent absorption coefficient \(\alpha(I)\):

\[
\alpha(I) = \frac{\alpha_0}{1 + I/I_s} + \beta_{\text{eff}} I,
\]

where \(\alpha_0\) is the linear absorption coefficient, and \(I_s\) is a saturation intensity related to the SA response. The continuous lines shown in Figures 2(a)–2(d) correspond to the fitting of the “open aperture” Z-scan transmission curves with the above equation. Similar fittings have been performed for all GO dispersions. The determined values of \(\beta_{\text{eff}}\) and the corresponding \(\text{Im}\beta^{(3)}\) are given in Table I. As shown, the values of \(\beta_{\text{eff}}\) of the few layered GO, obtained in the different solvents were found to exhibit important variations. In particular, the use of CN and o-DCB was found resulting in larger NLO response, a behavior that can be attributed to the larger value of the local field correction factor \(L\).

In general, and particularly in the case of solutions, it is known that the NLO response of a solute can be considerably affected by its environment, i.e., the solvent, through the modification of the macroscopic electric field \(E\) experienced by the solute, due to the polarization induced on the solvent by the incident electromagnetic field (i.e., the laser light). In the case of isotropic medium and for optical frequencies, the local electric field \(E_{\text{loc}}\) interacting with the...
solute molecules is related to the incident electric field $E$ by the following equation:

$$E_{\text{loc}} = L\, E,$$

where $L = \frac{1}{3} (n_0^2 + 2)$ is the so-called Lorentz-Lorenz local field correction factor and $n_0$ is the linear refractive index of the solvent.

Moreover, the solvent may affect both the geometry and the electronic distribution of the solute molecules, since these molecules are not isolated and are not in an unperturbed state. These changes are normally evidenced in the absorption spectra, through the spectral shifting of bands (solvatochromic effect) and/or the modification of vibronic structure as well. In the present study, since the NIR excitation wavelengths (i.e., 1–1.8 $\mu$m) used are far from any absorption band, solvatochromic effects do not matter and therefore cannot affect the NLO response. Usually, the influence of the solvent is introduced in terms of the Lorentz-Lorenz local field correction factor $L$. Since the refractive index of the solvents is given at 589 nm,\textsuperscript{40} this was calculated at 532 and 1064 nm using the Kramers-Kronig (K-K) dispersion analysis\textsuperscript{41}

$$\eta(\omega) - 1 = \frac{2}{\pi} P \int_0^{\infty} \frac{\omega' k(\omega')}{\omega'^2 - \omega^2} d\omega',$$

$$k(\omega) = -\frac{2\omega}{\pi} P \int_0^{\infty} \frac{\eta(\omega') - 1}{\omega'^2 - \omega^2} d\omega',$$

where $\eta(\omega)$ and $k(\omega)$ are the real and imaginary parts of the refractive index, respectively.

The absorption coefficient $\alpha(\omega)$ was obtained from the UV-Vis-NIR spectra of the solvents measured from 200 to

| TABLE I. Local field correction factor $L$, nonlinear absorption coefficient $\beta_{\text{eff}}$, and imaginary part of the third-order susceptibility, $\text{Im} \chi^{(3)}$, of few layered GO dispersed in different solvents. The concentration was about 1 mg/ml. |
|----------------|----------------|----------------|----------------|----------------|----------------|----------------|----------------|
|                | 532 nm          | 1064 nm         |                |                |                |                |                |
|                | $n_D$ | $n_0$ | $L$ | $\beta_{\text{eff}}$ (x cm/GW) | $\text{Im} \chi^{(3)}$ ($\times 10^{-13}$ esu) | $n_0$ | $L$ | $\beta_{\text{eff}}$ (x cm/GW) | $\text{Im} \chi^{(3)}$ ($\times 10^{-13}$ esu) |
| GO in CN       | 1.633 | 1.6448 | 1.5685 | 530 | 367.1 | 1.5992 | 1.5192 | 215 | 306.2 |
| GO in o-DCB    | 1.551 | 1.5569 | 1.4747 | 410 | 256.4 | 1.5341 | 1.4512 | 175 | 200.0 |
| GO in CB       | 1.524 | 1.5301 | 1.4471 | 320 | 193.2 | 1.4973 | 1.4140 | 155 | 216.7 |
| GO in NMP      | 1.47 | 1.4734 | 1.3903 | 320 | 179.8 | 1.4499 | 1.3674 | 137 | 158.7 |
| GO in DMF      | 1.430 | 1.4337 | 1.3518 | 220 | 116.7 | 1.4165 | 1.3355 | 130 | 142.5 |
| GO in THF      | 1.407 | 1.4089 | 1.3263 | 140 | 72.1 | 1.3932 | 1.3137 | 120 | 127.8 |
| Single layer GO in H$_2$O | 1.33 | 1.26 | 108 | 49.7 | 16.7 | 15.91 |

$^a$n$_D$ is the refractive index at 589 nm (at the sodium D lines wavelength).\textsuperscript{40}

$^b$n$_0$ is the calculated refractive index following Kramers-Kronig dispersion analysis.\textsuperscript{41}
2700 nm, while the imaginary parts of the refractive index \( k(x) \) were then calculated from \( k(x) = c \omega / 2 \alpha \). Next, from Eq. (3), the refractive index was deduced. The calculated values at 532 and 1064 nm are given in Table I. The dispersion of the refractive index for the six solvents used is shown in Figure 3(a), while in Figure 3(b), the variation of \( \beta \) versus the local field correction factor \( L \) are presented for the solvents used, at 532 and 1064 nm. In both cases, a good correlation was found to hold between \( \beta_{\text{eff}} \) and \( L \).

The OL action of the few layered GO dispersions under 532 nm and 1064 nm laser light is presented in Figures 4(a) and 4(b), respectively. As shown, strong and broadband OL were clearly observed. In all cases, a deviation from the linear response was observed above an onset fluence, \( F_{\text{on}} \), while the OL efficiency was found to depend strongly on the solvent used according to the previous discussion. Interestingly, the \( F_{\text{on}} \) was found to be slightly lower at 1064 nm, ca. 0.1–0.2 J/cm\(^2\), than at 532 nm, depending on the solvent. Furthermore, few layered GOs were found to exhibit OL efficiency comparable to that of the benchmark optical limiter \( C_{60} \) at 532 nm, while, at 1064 nm, OL was observed only in few layered GOs, the response of \( C_{60} \) being negligible.\(^7\)

In order to extend our OL investigation to other infrared wavelengths, few layered GO dispersions in NMP (polar) and CN (non-polar) were studied and transmission experiments were conducted. In Figure 5, the corresponding absorption spectra are depicted up to 1800 nm, together with the absorption spectrum of an aqueous dispersion of single layer GO. As shown, the few layered GO exhibited significant absorption in the NIR spectral region, in contrast to the single layer GO, which is highly transparent for wavelengths greater than 800 nm. This situation, which also implies a lowering of the optical band-gap, is attributed to the larger fraction of graphene-like conducting \( sp^2 \) domains, since in the case of few layered GO, the oxidized groups exist mostly at the edges of the graphene sheet, leaving the interlayers with considerable number of \( \pi \)-conjugated localized electrons.\(^{35}\)

In Figure 6, the OL of the CN and NMP suspensions of few layered GO for the NIR wavelengths is presented. The dashed lines correspond to the linear transmittance of each dispersion at the wavelength where the measurement was performed. The corresponding onset for optical limiting \( F_{\text{on}} \) was found to be about 0.1 J/cm\(^2\) for 1064, 1250, and 1520 nm laser radiation, while it dropped to half at 1750 nm. It should be noted at this point, that single layer GO suspensions did not display any OL at NIR wavelengths, exhibiting only some OL under 1064 nm laser radiation, at fluencies much higher than those required for few layered GOs.\(^{18}\)

Comparing the OL of few layered GO dispersions in CN and NMP, at 1064, 1250, and 1520 nm, the CN dispersions were found to exhibit clearly stronger OL that in the NMP dispersions. However, the opposite trend has been observed for 1750 nm irradiation. As it is known, the OL behavior of GO under nanosecond 532 and 1064 nm laser pulses can be attributed to RSA, TPA, NLS, and thermal/cumulative effects.\(^{12,13,18}\) In this study, the role of the two last mechanisms has been examined. However, no significant contributions were found. Hence, the observed OL can be attributed to RSA and/or TPA mechanisms. For a more detailed and quantitative description of the broadband NIR optical limiting of few layered GO, more information about its excited state(s) absorption (RSA mechanism) or TPA cross sections is needed.
In conclusion, the OL of few layered GO dispersed in a variety of solvents has been studied under nanosecond laser pulses at different wavelengths. In particular, few layered GO suspensions in CN and NMP at different NIR wavelengths.

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