Fluoro-graphene: nonlinear optical properties

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Abstract: In the present work, we report on the investigation of the third-order nonlinear optical response of graphene fluoride dispersed in DMF and also of fluorosurfactant-stabilized graphene fluoride dispersed in water under visible (532nm) and infrared (1064nm), picosecond and nanosecond laser excitation. Both graphene derivatives were found to exhibit large nonlinear optical response, while significant differences on their nonlinear optical response have been observed (e.g. different sign of nonlinear refraction and absorption). These findings highlight the important role of the degree of fluorination of the graphene sheets on their optical and electronic properties. Furthermore, DMF dispersed graphene fluoride was found to exhibit important broadband optical limiting action under nanosecond laser excitation, making it promising candidate for optical limiting applications.

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OCIS codes: (160.4330) Nonlinear optical materials; (160.4670) Optical materials; (160.4760) Optical properties; (160.4890) Organic materials; (190.4400) Nonlinear optics, materials; (190.4710) Optical nonlinearities in organic materials.

References and links:

During the last years, the nonlinear optical properties of different carbon allotropes such as fullerene, carbon nanotubes, graphene and various kinds of carbon nanoparticles have greatly attracted the attention of the scientific community [1–4]. This research interest has been boosted by the several potential applications of these systems in photonic and optoelectronic technologies, ranging from optical limiters and optical data storage to optical computing, solar cells and several others [5–7]. Concerning the different carbon allotropes,
the most recent discovery is graphene, the two dimension lattice of π-conjugated carbon atoms [8].

Although graphene’s discovery is very new, it has already been established as a promising material for future electronics and optoelectronics [9]. In optoelectronics, the ability to tailor the optical and electrical properties of graphene is of crucial importance, especially the engineering of its band gap. In particular, the efforts of scientists led to the discovery of new graphene-based materials possessing tunable band gap, mostly through chemical modification of graphene via oxidation or hydrogenation or even decoration with metal/organic nanostructures [10–12]. An important member, in the already large family of graphene derivatives, is Graphene Fluoride (GF) [13]. GF is a two dimensional wide band gap semiconductor, being optically transparent in the visible. The stronger the fluorination is, more the carbon bonds of graphene that are transformed from $sp^2$ to $sp^3$ hybridization. Therefore, the ability of tuning the ratio between the $sp^2$ and $sp^3$ fractions can be a powerful tool for continuous tuning of graphene fluoride band gap, thus modifying the behavior of the material from conductor to insulator [14].

Recently, we have reported on the preparation, the characterization and the third-order nonlinear optical response under visible 35 ps laser pulses of aqueous dispersions of graphene fluoride (GF) sheets stabilized through non-covalent functionalization with perfluorooctanoate units [13,15]. In the present work, we present new results, concerning the detailed investigation of the third-order nonlinear optical response of graphene fluoride (GF) sheets dispersed in dimethylformamide (DMF) and of aqueous dispersions of graphene fluoride (GF) sheets stabilized by a fluorosurfactant, under both nanosecond and picosecond, visible and infrared laser excitation conditions. In both cases, the initial graphene fluoride (GF) sheets have been obtained by the liquid-phase exfoliation technique. The two graphene fluorides were found to exhibit important third-order nonlinear optical response, however their nonlinear optical properties (i.e. nonlinear absorption and refraction) were found to be very different suggesting the possibilities offered by such systems to engineer their nonlinear optical response and simultaneously revealing the potential of graphene fluoride as a promising material for photonic and optoelectronic applications.

2. Experimental

Since the preparation of the aqueous dispersions of graphene fluoride sheets functionalized with perfluorooctanoate units has been reported elsewhere [15], only the preparation details of the newly synthesized graphene fluoride sheets dispersed in DMF will be presented here. In the second case, the dispersed GF sheets were obtained by the liquid-phase exfoliation technique. In detail, 250 mg of fully fluorinated graphite CF$_{1.2}$ (light gray powder from Alfa Aesar, Product code: 42543, LOT: H13M40) were directly suspended in 50 mL dimethylformamide (DMF) by sonication in an ultrasound bath (2h, 130 W). The mixture was left in rest for 1-2 days in order to settle down the insoluble particles and collect a clear supernatant. The obtained pale grey colloid gave an intense Tyndall effect with a laser pointer and contained dispersed graphene fluoride sheets based on TEM and AFM analyses, as shown in Figs. 1 & 2, respectively).
Fig. 1. TEM images of folded (left) and overlapped (right) graphene fluoride nanosheets. The inset depicts a thin sheet with a lateral size of 500 nm.

The thickness of the dispersed sheets was estimated between 0.6 and 0.9 nm by AFM measurements, i.e. quite close to the thickness of graphene fluoride (0.6 nm). Nevertheless, the presence of thicker nanosheets in the dispersion cannot be ruled out, as it is common for the liquid-phase exfoliation technique. In general, thick graphite fluoride plates (before exfoliation) show broad and quite low intensity G and D bands in their Raman spectrum as a result of fluorination [16]. In contrast, the Raman spectrum of exfoliated graphene fluoride nanosheets is featureless, e.g. the intensity of the broad lines seems to drop even more to cause practically their suppression [17]. In our case, using highly fluorinated graphite fluoride, Raman study of the samples gave no G and D bands, thereby suggesting the presence of thin nanosheets in the dispersions. EDX analysis based on SEM revealed carbon and fluorine X-ray peaks, in accordance with a carbon-fluorine composition. The dilute colloid was concentrated by evaporation to the particle content of 1.87 mg mL$^{-1}$ prior to the non-linear optical study.

Fig. 2. AFM image and height profile of a single graphene fluoride sheet with thickness of 0.6 nm. The white spots are from underlay mica which is partly affected by the DMF solvent.

The nonlinear optical response of the graphene fluoride sheets dispersed in DMF and of the functionalized sheets dispersed in water has been studied by means of the Z-scan technique [18], employing the fundamental and the second harmonic outputs, at 1064 and 532nm respectively, of two different Nd:YAG laser systems, namely a 4ns Q-switched laser and a 35ps mode-locked one. Z-scan technique has been used, because it allows the simultaneous determination of both the magnitude and the sign of the nonlinear refraction and absorption of a sample. According to this technique, the investigated sample is moving along...
the propagation direction of a focused laser beam thus experiencing different incident laser
intensity at each position, giving rise to nonlinear absorption and refraction, which on their
turn modify the transmission of the sample. The nonlinear absorption coefficient \( \beta \) can be
determined by measuring the transmitted through the sample laser light by means of e.g. a
PMT or a photodiode. Correspondingly, the nonlinear refractive index parameter \( \gamma' \) can be
obtained by measuring the transmitted through the sample laser light after it has passed
through a pinhole located after the laser beam focusing lens, at the far field. The former
transmission measurement is known as “open-aperture” (OA) Z-scan whiles the latter as
“closed-aperture” (CA) Z-scan. Since the “closed-aperture” Z-scan is sensitive to the
nonlinear absorption, the nonlinear refractive parameter \( \gamma' \) is more adequately obtained using
the so-called “divided” Z-scan, which is obtained from the division of the CA Z-scan by the
Corresponding OA one. The presence of a transmission minimum or maximum in the OA Z-
scan recording indicates reverse saturable absorption (RSA) or saturable absorption (SA)
respectively, while the shape of the “divided” Z-scan recording, exhibiting a valley-peak or a
peak-valley transmission configuration, indicates positive or negative sign nonlinear
refractive parameter respectively, corresponding to self-focusing or self-defocusing
behaviour. From the analysis of the OA and “divided” Z-scans, the magnitude of the
nonlinear absorption coefficient \( \beta \) (which is related to the \( \Im \gamma'^2 \)) and the nonlinear refractive
parameter \( \gamma' \) (which is related to the \( \Re \gamma'^2 \)) of the sample can be obtained according to the
procedures described in detail elsewhere [15,18].

The laser beam of each laser system employed for the measurements, was focused into the
samples by means of a 20cm focal length plano-convex lens, while the beam spot radii at
focus (i.e. half width at 1/e^2 of the maximum of irradiance) were determined using a CCD
camera. They were found to be 17.5 and 30 \( \mu \)m, for the 532 and 1064nm laser beams
respectively.

During the experiments, the samples were continuously stirred while in order to check for
thermal and/or cumulative effects, measurements at repetition rates of 1 and 10Hz have been
performed. However, no sizeable differences have been observed in the Z-scan recordings
ruling out the presence of such effects. Furthermore, in order to search for the presence of
nonlinear scattering, a sensitive photo-diode has been positioned at a fixed angle of about 30°
with respect to the laser beam propagation axis and it was recording systematically any
scattered laser light. For all laser energies used, no significant scattered light has been
detected.

3. Results and discussion

The UV-Vis-NIR absorption spectra of a DMF dispersion of GF sheets and an aqueous
dispersion of perfluorooctanoate-functionalized GF placed in 1mm thick quartz cells are
presented in Fig. 3 together with a similar spectrum of a graphene oxide (GO) dispersion to
facilitate comparison between the fluorinated graphene sheets and graphene oxide ones.

In Figs. 4(a) and 4(b), some representative OA Z-scan recordings of a 1.87mg/ml GF
suspension in DMF are presented obtained under 4ns, 532nm laser excitation. As can be seen,
the obtained OA Z-scans using low incident laser intensity [Fig. 4(a)] were found to exhibit a
transmission maximum, indicative of saturable absorption (SA) behavior, while as the laser
intensity was increasing, a valley was progressively formed within the transmission
maximum, becoming finally a transmission minimum at higher laser intensity [Fig. 4(b)],
indicating reverse saturable absorption (RSA) behavior.

A similar behavior has been observed under 4ns, 1064nm laser excitation as shown in
Figs. 4(c) and 4(d). Interestingly, the aqueous dispersions of the fluorosurfactant stabilized
GF did not exhibit any nonlinear absorption under either visible or infrared nanosecond laser
excitation.
Fig. 3. UV-Vis-NIR absorption spectra of a GF dispersion in DMF, an aqueous dispersion of fluorosurfactant stabilized GF and of a GO water suspension for comparison.

In order to determine the nonlinear absorption coefficient $\beta$ of the samples taking into account the observed bleaching of the transmission of the GF dispersions exhibited at low incident laser intensity, the corresponding OA Z-scan recordings were fitted using the intensity variation equation and adopting an intensity dependent absorption coefficient [19]. In this case, the intensity absorption coefficient $\alpha_0$ can be written in the following form:

$$\alpha(I) = \frac{\alpha_0}{1 + I/I_s} + \beta \cdot I$$  \hspace{1cm} (1)

where the nonlinear absorption coefficient $\beta$ corresponds to the two-photon absorption (TPA) or RSA occurring at high intensities, while $I_s$ represents a saturation intensity introduced to account for the SA response exhibited at the low intensity regime. The nonlinear absorption coefficient $\beta$ is a concentration dependent parameter while the saturation intensity $I_s$ should be a concentration independent term. Then, the intensity variation equation was solved numerically within the thin sample approximation, in order to calculate the laser beam intensity as a function of the propagation depth in the sample $z'$ using the appropriate initial conditions:

$$\frac{dI}{dz'} = -\alpha(I) \cdot I$$  \hspace{1cm} (2)

Finally, by integrating the intensity distribution at the exit surface of the sample, the transmittance was calculated at each $z$ position.
Following this procedure, the OA Z-scan recordings have been fitted and the parameters $I_s$ and $\beta$ have been determined. The imaginary part ($\text{Im}\chi^{(3)}$) of the third-order susceptibility $\chi^{(3)}$ was then easily calculated from the following equation:

$$\text{Im}\chi^{(3)}(\text{esu}) = \frac{c^2 (m/s)^2 n_0^2 \beta (m/W)}{960 \pi^2 \alpha(s^{-1})}$$  \hspace{1cm} (3)

In Figs. 5(a) and 5(b), some representative “divided” Z-scans are presented, obtained using 4ns, 532nm and 1064nm laser excitation respectively. As depicted, the DMF suspensions of the GF sheets were found to exhibit a valley-peak transmission configuration at both excitation wavelengths, suggesting positive nonlinear refraction (i.e. positive Re$\chi^{(3)}$ or $n_2$), corresponding to self-focusing behavior, while the aqueous dispersions of the fluorosurfactant stabilized GF sheets exhibited a peak-valley transmission configuration under visible excitation, indicative of negative nonlinear refraction, corresponding to self-defocusing behavior [Fig. 5(c)], while they exhibited negligible nonlinear refraction under infrared excitation.

Fig. 5. “Divided” Z-scans of a 1.87mg/ml GF suspension obtained under (a) 4ns, 532nm, and (b) 1064nm laser excitation and (c) a “divided” Z-scan of a 0.5mg/ml fluorosurfactant stabilized GF, obtained under 4ns, 532nm laser excitation.
From the analysis of the “divided” Z-scans, the nonlinear refractive parameter $\gamma'$ of the samples was deduced using the following relation:

$$
\gamma' = \frac{\lambda \alpha}{1 - e^{-\alpha l}} \frac{\Delta T_{p-v}}{0.812 \pi l_0 (1 - S)^{0.25}}
$$

(4)

where $\lambda$ is the laser wavelength, $\alpha$ is the linear absorption coefficient, $\Delta T_{p-v}$ is the difference between the peak and the valley of the normalized transmission of the “divided” Z-scan curve, and $S$ is the transmittance of the aperture defined as: $S = 1 - \exp\left(-2r_a^2/w_a^2\right)$, with $r_a$ being the radius of the aperture and $w_a$ denoting the beam radius on the aperture.

Then, the real part, $\text{Re} \chi^{(3)}$, of the third-order nonlinear susceptibility, was calculated using the following relation:

$$
\text{Re} \chi^{(3)} (\text{esu}) = \frac{10^{-6} c (\text{cm/s}) n_a^2}{480 \pi^2} \gamma' (\text{cm}^2/\text{W})
$$

(5)

Then, similar Z-scan experiments were performed under a different excitation regime, namely using 35ps laser pulses. Under these conditions, the GF sheets dispersions in DMF were found to exhibit negligible nonlinear absorption, both for visible and infrared excitation, for laser energy up to about 70 and 85 GW/cm² respectively, while the fluorosurfactant-stabilized GF aqueous dispersions exhibited measurable nonlinear absorption, at both excitation wavelengths, as shown in Figs. 6(a) and 6(b). Interestingly, the shapes of their OA Z-scans were relatively narrower (see e.g. Figures 6(a) and 6(b)) compared to those of other similar OA Z-scan recordings, being evidence that multiphoton processes might occur [20–23]. In fact, multiphoton processes can occur at the high incident laser intensity employed to obtain the corresponding OA Z-scan recordings.

The corresponding “divided” Z-scans of the GF dispersed in DMF were found to exhibit a valley-peak configuration under 532nm laser excitation, indicative of positive nonlinear refraction, corresponding to self-focusing behavior. In particular, the $\Delta T_{p-v}$ values of these dispersions were found to be larger than those of neat solvent (i.e. DMF), as shown in Fig. 7(b), suggesting that the GF sheets and DMF possess same sign (i.e. positive) nonlinear refraction. Remarkably, the aqueous dispersions of the fluorosurfactant-stabilized GF were found to exhibit opposite behavior, i.e. a peak-valley transmission configuration (see e.g. [15]) under both visible and infrared laser excitation, indicative of negative nonlinear refraction, corresponding to self-defocusing [Fig. 7(a)]. Interestingly, the dispersions of the GF sheets in DMF were found to exhibit negligible nonlinear optical response under 1064nm laser excitation, at least for the range of incident laser energies employed.

Fig. 6. OA Z-scans of a 0.5mg/ml aqueous dispersion of fluorosurfactant stabilized GF sheets obtained under 35ps, 532nm (a) and 1064nm (b) laser excitation.
Finally, the determined parameters: nonlinear absorption coefficient ($\beta$), nonlinear refractive parameter ($\gamma'$), the corresponding third-order nonlinear susceptibility $\chi^{(3)}$, the saturation intensity ($I_s$) and the nonlinear refractive index ($n_2$), resulting from the analysis of the experimental Z-scan data, under nanosecond and picosecond laser excitation conditions, both at visible and infrared, are all summarized and presented in Tables 1 and 2, respectively. For comparison purposes, the corresponding values of C$_{60}$ toluene solution and of graphene oxide solution are also included.

![Fig. 7. “Divided” Z-scans of (a) a 0.5mg/ml fluorosurfactant stabilized GF and (b) a 1.87mg/ml GF dispersion in DFM obtained under 35ps, 532nm laser excitation. The solid lines represent the best fits of the experimental data.](image)

Table 1. Third-order NLO parameters of GF dispersions in DMF, aqueous dispersions of fluorosurfactant stabilized GF, aqueous dispersions of graphene oxide and a C$_{60}$ toluene solution under 4ns laser excitation.

<table>
<thead>
<tr>
<th>$\lambda_{\text{exc}}$ (nm)</th>
<th>Sample</th>
<th>Conc. (mg/ml)</th>
<th>$\beta$ ($\times 10^{-9}$ cm/W)</th>
<th>$\gamma'$ ($\times 10^{-18}$ m$^2$/W)</th>
<th>$\chi^{(3)}$ ($\times 10^{-13}$ esu)</th>
<th>$\chi^{(3)}/I_0$ ($\times 10^{-13}$ esu/cm$^2$)</th>
<th>$I_s$ (GW/cm$^2$)</th>
<th>$n_2$ ($\times 10^{-12}$ esu)</th>
</tr>
</thead>
<tbody>
<tr>
<td>532</td>
<td>GF in DMF</td>
<td>1.87</td>
<td>20.71 ± 1.23</td>
<td>22.19 ± 3.20</td>
<td>30.83 ± 4.17</td>
<td>22.67 ± 3.07</td>
<td>0.02</td>
<td>75.82</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.94</td>
<td>13.37 ± 1.13</td>
<td>16.44 ± 2.78</td>
<td>21.48 ± 3.63</td>
<td>23.87 ± 4.03</td>
<td>0.03</td>
<td>56.17</td>
</tr>
<tr>
<td></td>
<td>GF in H$_2$O</td>
<td>0.50</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>58.77</td>
</tr>
<tr>
<td>*GO in H$_2$O</td>
<td>1.20</td>
<td>130.10 ± 11.12</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>0.03</td>
<td>-</td>
</tr>
<tr>
<td>**C$_{60}$</td>
<td>0.72</td>
<td>100.67 ± 8.33</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>301.40</td>
</tr>
<tr>
<td>1064</td>
<td>GF in DMF</td>
<td>1.87</td>
<td>12.53 ± 1.35</td>
<td>14.09 ± 3.25</td>
<td>22.86 ± 4.46</td>
<td>49.69 ± 9.70</td>
<td>0.04</td>
<td>48.17</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.94</td>
<td>7.49 ± 1.03</td>
<td>7.09 ± 2.18</td>
<td>12.28 ± 3.07</td>
<td>39.12 ± 9.12</td>
<td>0.05</td>
<td>24.23</td>
</tr>
<tr>
<td></td>
<td>GF in H$_2$O</td>
<td>0.50</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>*GO in H$_2$O</td>
<td>0.72</td>
<td>20.01 ± 1.97</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>0.02</td>
<td>-</td>
</tr>
<tr>
<td>**C$_{60}$</td>
<td>0.72</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

*From [24].
**From [25]. $^1 n_2$ (esu) = $\frac{c n_0}{40\pi} \gamma (m^2/W)$
Table 2. Third-order NLO parameters of GF dispersions in DMF, aqueous dispersions of fluorosurfactant stabilized GF, aqueous dispersions of graphene oxide and a C\textsubscript{60} toluene solution under 35ps laser excitation.

<table>
<thead>
<tr>
<th>(\lambda) (nm)</th>
<th>Sample</th>
<th>Conc. (mg/ml)</th>
<th>(\beta) (\times 10^{-9}) cm/W</th>
<th>(\gamma) (\times 10^{-15}) m(^2)/W</th>
<th>(\chi^{(3)}) (\times 10^{-13}) esu/cm(^3)</th>
<th>(\chi^{(3)}/\alpha_0) (\times 10^{-13}) esu/cm(^3)</th>
<th>(I_s) (GW/cm(^2))</th>
<th>(n_2) (\times 10^{-12}) esu</th>
</tr>
</thead>
<tbody>
<tr>
<td>532</td>
<td>GF in DMF</td>
<td>1.87</td>
<td>-</td>
<td>0.35 ± 0.03</td>
<td>0.45 ± 0.04</td>
<td>0.33 ± 0.03</td>
<td>-</td>
<td>1.20</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.94</td>
<td>-</td>
<td>0.14 ± 0.02</td>
<td>0.19 ± 0.02</td>
<td>0.22 ± 0.02</td>
<td>-</td>
<td>0.48</td>
</tr>
<tr>
<td></td>
<td>GF in H\textsubscript{2}O</td>
<td>0.50</td>
<td>0.42 ± 0.04</td>
<td>-0.58 ± 0.04</td>
<td>0.69 ± 0.05</td>
<td>0.35 ± 0.03</td>
<td>-</td>
<td>1.84</td>
</tr>
<tr>
<td></td>
<td>*GO in H\textsubscript{2}O</td>
<td>1.20</td>
<td>2.50 ± 0.25</td>
<td>-</td>
<td>1.15 ± 0.15</td>
<td>0.16 ± 0.02</td>
<td>0.86</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>**C\textsubscript{60}</td>
<td>0.72</td>
<td>1.03 ± 0.12</td>
<td>-</td>
<td>0.60 ± 0.07</td>
<td>0.09 ± 0.01</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>1064</td>
<td>GF in DMF</td>
<td>1.87</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
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<tr>
<td></td>
<td></td>
<td>0.94</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
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<td>-</td>
</tr>
<tr>
<td></td>
<td>GF in H\textsubscript{2}O</td>
<td>0.50</td>
<td>0.22 ± 0.03</td>
<td>-0.45 ± 0.04</td>
<td>0.55 ± 0.06</td>
<td>0.82 ± 0.09</td>
<td>1.43</td>
<td></td>
</tr>
<tr>
<td></td>
<td>*GO in H\textsubscript{2}O</td>
<td>0.72</td>
<td>0.12 ± 0.02</td>
<td>-</td>
<td>0.11 ± 0.02</td>
<td>0.25 ± 0.05</td>
<td>3.7</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>**C\textsubscript{60}</td>
<td>0.72</td>
<td>-</td>
<td>0.09</td>
<td>0.12</td>
<td>0.12</td>
<td>-</td>
<td>0.31</td>
</tr>
</tbody>
</table>

*From [24].  
**From [25].

Then, the optical limiting action of the GF dispersions has been investigated under both excitation regimes. In Fig. 8, the variation of the normalized transmittance of a 1.87mg/ml GF dispersion in DMF as a function of the laser fluence for visible and infrared 4ns laser pulses is shown. As can be seen, the GF dispersion in DMF exhibited important optical limiting both for visible and infrared laser pulses, thus exhibiting an efficient broadband optical limiting action. In particular, the optical limiting onset (defined as the laser fluence \(F_{\text{in}}\) at which the transmittance of the sample starts to depart from its normalized linear transmittance value) was found to be at about 0.3 and 0.4J/cm\(^2\) for visible and infrared laser excitation, respectively, i.e. low enough making these dispersions very interesting for potential applications. The relatively higher OL onset determined for the 1064nm laser pulses is due to the relatively lower linear absorption of the GF dispersions at this wavelength range compared to the visible, as can be seen from the UV-Vis absorption spectrum presented in Fig. 3.

It has to be noted at this point, that the GF sheets dispersions in DMF were found to exhibit a broadband optical limiting action very similar to that observed in GO, in [24] under ns laser pulses. This is also supported by the \(\chi^{(3)}/\alpha_0\) values shown in Table 1, where GF (in DMF) and GO exhibited similar values, significantly larger than that of the aqueous fluorosurfactant-stabilized GF dispersions. Furthermore, it is interesting to underline that they both exhibit larger values in the IR than in the visible. In GO, the \(sp^2\) and \(sp^3\) hybridizations coexist, with the \(\pi\)-states arising from graphene-like carbon sites and the \(\sigma\)-states arising from the carbons bonded with several oxygen containing functional groups such as hydroxyls, carboxyls, ketones etc [26]. In a perfect graphene sheet, only \(sp^2\) hybridization exists, while in GO a mixture of \(sp^2\) and \(sp^3\) hybridizations coexist, the \(sp^2\) carbon atoms forming small clusters within the \(sp^3\) network. In addition, in GO, optical transitions in \(sp^2\) clusters and \(sp^3\) domains are independent, the former giving rise to SA at low laser intensities, while the latter leading in MPA/RSA at relatively higher intensities. Using reduction chemistry, the \(sp^2/sp^3\) ratio of a GO sheet can be altered, resulting in modification of the energy band gap, which on its turn can greatly affect the NLO response explaining the observation of the transition from SA to RSA [27].

In a similar way, in GF, the defects created by the fluorine atoms can give rise to the formation of a \(sp^3\) network. So, both in GF and GO, the \(sp^3\) domains continue to exist since
there is no way of creating an exclusively $sp^3$ hybridization network by oxidation/fluorination through chemical modification. In this sense, the mechanism of the transition from SA to RSA response in GF seems to be of the same origin as in GO.

Recently, in a study concerning the optical limiting properties of some fluorinated graphene oxides, it was found that the fluorination of GO resulted to great enhancement of the optical limiting efficiency [28]. This enhancement has been attributed to the $sp^3$ defects created by the highly electronegative atom, i.e. the fluorine atom, which can give rise to larger nonlinear absorption and therefore more efficient optical limiting than the corresponding $sp^2$ sites created by the oxygen rich functional groups in GO. The present work, although has not particularly investigated this aspect, it confirms the important nonlinear absorption resulted from the fluorine atoms. The above findings make obvious that oxidation and/or fluorination of graphene can constitute efficient strategies in order to modify the NLO properties of graphene thus opening new ways for potential applications of graphene and its derivatives. In fact, the chemical modification of graphene (e.g. oxidation, hydrogenation, fluorination etc.) has been employed as an efficient strategy to modify the band gap of graphene and/or its derivatives. So, through chemical route, the adsorbed atoms or groups on graphene surface could strongly affect the band structure of $\pi$-electrons. As a matter of fact, the attached atoms forming covalence bonding with graphene, transform the $sp^2$ hybridization into $sp^3$ one, making the relevant $\pi$ bands crossing at the Dirac point, to be significantly perturbed, creating a band gap. This band gap can be then further tuned widely, e.g. by controlling the density of adsorbed atoms. This provides an extraordinary degree of freedom in order to tailor the electronic structure and thus the linear and nonlinear optical properties as well of graphene in view of specific applications.

A simple but not very accurate estimation of the energy band gap, can be obtained using the Tauc plots [29,30]. So, the energy band gap of the aqueous dispersions of the fluorosurfactant stabilized GF, of the GF dispersed in DMF and of the aqueous dispersions of GO were determined to be approximately 4.56 (~272nm), 3.68 (~337nm) and 2.35 eV (~527.5nm) respectively. Although these band gap values are not so accurate, they allow some comparison to be performed. In fact, in several recent theoretical works studying different fluorinated graphenes, the dependence of their key properties (e.g. optical, electronic, magnetic, etc.) on the degree of fluorination has been studied [31,32]. In all cases,
the results suggest the strong dependence of these properties upon the degree of fluorination. In this context, the stronger excited state absorption (ESA) exhibited by the GF dispersed in DMF to that of fluorosurfactant stabilized GF, becomes understandable considering the lower band gap of the former. Similarly, holds for GO which was found to exhibit even stronger ESA in [24].

Under ps laser excitation, the fluorosurfactant stabilized GF exhibited significant nonlinear absorption at both excitation wavelengths, oppositely to GF in DMF, which exhibited negligible nonlinear absorption. Semiconducting materials are assumed to exhibit 2PA when the photon energy, \( h\omega \), equals one-half the band gap [33]. In the case of the fluorosurfactant stabilized GF, as discussed previously, an energy gap of about 4.56 eV (~272 nm) has been determined. Therefore, the observed nonlinear absorption under 532 nm (2.33 eV) excitation, can be attributed to a 2PA mechanism, while for 1064 nm (1.17 eV) excitation a 4PA scheme might be operational due to the high laser intensity employed.

Concerning the origin of the observed nonlinear refraction of GF, it can be understood in terms of excitation of electrons from the valence band to the intermediate states of the linear absorption tail, leading to the generation of a large number of electrons and holes. Generally in semiconductors, the relaxation of free carriers occurs in a time window of few tens of picoseconds, which is comparable to the pulse duration of the laser employed. The reduction, therefore, of the valence band electron density and the accompanying increase of the electron density in the intermediate states results in a change of the refractive index, including nonlinear refraction [34].

4. Conclusion

In summary, in this work we have investigated in details the nonlinear optical response of graphene fluoride sheets dispersed in DMF and also functionalized by means of fluorosurfactant forming stable aqueous dispersions, employing visible (532 nm) and infrared (1064 nm), 4 ns and 35 ps laser pulses. It has been shown that the direct fluorination of graphene and/or the use of fluorosurfactant to stabilize the aqueous dispersions can importantly modify its nonlinear optical response thus allowing the effective tailoring of the nonlinear optical properties of GF in view of specific applications. In addition, it has been shown that DMF dispersed graphene fluoride sheets exhibit important broadband optical limiting action, making them interesting candidates for optical limiting devices for human eyes’ and detectors’ protection.

Acknowledgments

NL acknowledges partial support of this research by the European Union (European Social Fund – ESF) and Greek national funds through the Operational Program “Education and Lifelong Learning” of the National Strategic Reference Framework (NSRF) - Research Funding Program: HERAKLEITUS II. Investing in knowledge society through the European Social Fund. The support by the Operational Program Research and Development for Innovations-European Regional Development Fund (project CZ.1.05/2.1.00/03.0058) and Operational Program Education for Competitiveness (CZ.1.07/2.3.00/20.0017) is gratefully acknowledged.