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# Ultrafast and short pulse optical nonlinearity in isolated, sparingly sulfonated water soluble graphene

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## ABSTRACT

We report the nonlinear optical properties of graphene oxide (GO), reduced graphene oxide (rGO), sulfonated graphene oxide (S-rGO), and sparingly sulfonated water soluble graphene (WSG), measured under ultrafast (100 fs) and short pulse (300 ps, 50 ns) laser excitations at 800 nm, employing the open aperture Z-scan technique. The samples exhibit typical third order nonlinear optical behaviour including two-photon absorption (2 PA), reverse saturable absorption (RSA), and saturable absorption (SA). A significant variation in the nature of nonlinear absorption is seen when the laser pulse duration is changed. For example, RSA is prominent under nanosecond (ns) excitation, 2 PA is prevalent under femtosecond (fs) excitation, and SA is dominant under picosecond (ps) excitation. For comparison purposes the measurements are repeated using 5 ns laser pulses at 532 nm. RSA is enhanced in WSG in the nanosecond excitation domain, which can be attributed to the covalent bonding between p-phenyl-$SO_3H$ groups and $sp^2$ graphitic planes. WSG exhibits a switching behaviour from SA to RSA upon increasing the excitation intensity under fs excitation. Results show that these graphene derivatives are potentially useful for saturable absorber and optical limiter device applications.

## 1. Introduction

Materials capable of nonlinearly transmitting light as a function of the input light intensity have a number of applications including optical limiting and saturable absorption [1,2]. Optical limiters (OL) are materials that can attenuate intense laser pulses by limiting the output fluence to a safe range so that delicate optical instruments, optical sensors and human eyes can be saved from accidental or hostile exposure. Various materials such as carbon allotropes, carbon composites, graphene oxide hybrids, organics, glasses, quantum dots and metal nanoparticles are known to exhibit strong optical power limiting [3–15]. Large nonlinear optical response, minimal loss at the operational wavelength, good optical quality, and mechanical stability are desirable for practical optical limiters. Saturable absorbers, on the other hand, allow the transmission of more light at higher intensities, making them suitable for Q-switching and mode-locking applications [16,17]. It has been shown that a tandem arrangement of an optical limiter with a saturable absorber can yield optical diode action [18].

Graphene, which is the 2D monoatomic building block of carbon, is known to be a nonlinear optical (NLO) material [19]. This is primarily because of its large π-electron conjugation, owing to which the interband optical transitions are dependent only on the fine-structure constant [20]. Physical methods for the fabrication of high quality graphene sheets are expensive, and its poor solubility due to the highly cohesive Van der Waals energy (5.9 kJ $mol^{-1}$) usually limits its applicability [21]. On the other hand, chemical synthesis of graphene through the exfoliation of reduced graphene oxide is a cheaper alternative. However, graphene sheets stored in solution after exfoliation suffer from agglomeration. Similarly, graphene sheets synthesized by the exfoliation of graphene oxide

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are found to lose their water dispersibility, and they aggregate as the oxygen containing functional groups are removed during the reduction process. Therefore, it is technologically important to find a suitable liquid medium which can hinder graphene agglomeration. Such a medium will allow for the study of its properties in the solution phase, and also help transfer it on to a substrate for the fabrication of practical devices. Towards this end, the long term stability of graphene oxide in a mixture of water and non-aqueous solvents such as DMF, methanol and acetone has been investigated in the past [22]. On the other hand, a facile technique for the synthesis of stable, water soluble graphene was demonstrated by Si et al. through sulfonation of graphene oxide and subsequent reduction [23].

In this work we report the optical limiting properties of graphene oxide (referred hereafter as GO), reduced graphene oxide (referred hereafter as rGO), sulfonated graphene oxide (referred hereafter as S-rGO) and sparingly sulfonated water soluble graphene (referred hereafter as WSG) dispersions synthesized inhouse, determined by using the open aperture Z-scan technique in the nanosecond (ns), picosecond (ps) and femtosecond (fs) excitation domains. Results indicate that the NLO properties of these materials vary substantially with the laser pulse duration, based on which they can be employed either for saturable absorption (SA) and/or optical limiting applications, at a given excitation wavelength of interest.

## 2. Experimental

GO prepared by oxidizing graphite flakes with acid was used as the starting material for the preparation of S-rGO and WSG [24]. WSG was prepared from GO using the following three steps: (1) pre-reduction of GO with sodium borohydride at 80 °C for 1 h to remove the majority of the oxygen functionality, (2) sulfonation with the aryl diazonium salt of sulfanilic acid in an ice bath for 2 h, and (3) post-reduction with hydrazine (100 °C for 18 h) to remove oxygen functionality. The synthesis details and the sulfonation mechanism can be found elsewhere [23].

The crystal structures of the prepared samples were measured using an X-ray diffractometer (PANalytical, *X'PertPRO*) with Cu-K$\alpha$ radiation ($\lambda = 0.154$ nm, 40 kV, 100 mA). UV–Vis absorption spectra were recorded using a Shimadzu, *UV-1800* spectrophotometer. Raman spectra of the samples were recorded using *Labram-HR 800* spectrometer at an excitation radiation of wavelength 514.5 nm obtained from an argon ion laser with a spectral resolution of about 1 $cm^{-1}$. Infrared spectra was recorded using *Perkin Elmer Spectrum AX3* spectrometer. Optical nonlinearity of the as-synthesized samples were studied through the open-aperture Z-scan technique using various laser pulses generated from two different laser sources. Regeneratively amplified Ti:Sapphire laser (*TSA-10*, Spectra Physics) was employed for generating 50 ns, 300 ps and 100 fs (FWHM) laser pulses at the wavelength of 800 nm with a beam waist of ~22 μm for all three pulse widths. The laser beam was focused using a plano-convex lens of 10 cm focal length. The sample was taken in a 1 mm path length cuvette and translated along the beam (Z-axis) through the focal region by a stepper motor controlled linear translation stage. Maximum optical intensity is attained at the beam focus ($Z = 0$), and the intensity reduces as a Lorentzian away from the focal point (i.e., for $Z > 0$ and $Z < 0$). The transmitted laser energy for each position (Z) was measured using a pyroelectric energy probe (RjP-735). For measurements at 532 nm, the second harmonic output of an Nd:YAG laser (5 ns) with a beam waist of 15 μm was employed. The laser pulse repetition rate in all our measurements is very low, at approximately one pulse in 5 s. For 800 nm excitation this is achieved by using an electronically controlled fast mechanical shutter in the beam path, and for 532 nm by employing external triggering of the Q-switch.

## 3. Results and discussion

### 3.1. X-ray diffraction

XRD patterns of as-synthesized samples, the precursor, and pristine graphite are shown in Fig. S1 (supplementary content). The disappearance of the sharp diffraction peak of graphite at $2\theta = 26.5°$ and the appearance of a broad peak at $2\theta = 10.3°$ can be attributed to its oxidation to GO [25]. Likewise, the disappearance of the peak at $2\theta = 10.3°$ and the appearance of a broad peak at $2\theta = 24.4°$ confirms the reduction of GO to rGO [26]. Surprisingly, the XRD patterns of rGO, S-rGO and WSG looked similar. This indicates that the addition of p-phenyl-$SO_3H$ functional group does not have any effect on the structure of rGO. We therefore used infrared and Raman spectroscopy to analyse and detect the sulfonation of GO.

### 3.2. Infrared spectroscopy

Fig. 1 shows the FT-IR spectra of pristine GO compared with those of sulfonated GO (S-rGO and WSG). The vibrations observed in Fig. 1a at 1040, 1218, 1375 and 1710 $cm^{-1}$ correspond to C–O, C–O–C, C–OH and C=O in GO and the peak at 1612 $cm^{-1}$ can be attributed to the skeletal vibrations of un-oxidized graphitic domains in GO [27]. The FT-IR spectrum of S-rGO (Fig. 1b) indicates the presence of many other vibrations in addition to those observed for GO. The vibrations emerging at 1175, 1126 and 1040 $cm^{-1}$ in Fig. 1b for S-rGO can be assigned to two S–O groups and one S-phenyl group, respectively. Additionally, the peak formed at 841 $cm^{-1}$ (out-of-plane hydrogen wagging) is a characteristic vibration of the p-disubstituted phenyl group, confirms the sulfonation of GO.

On the contrary, the intensity of FT-IR vibrations at 1175, 1126 and 1040 $cm^{-1}$ in the spectrum of WSG (Fig. 1b) is slightly lesser compared to S-rGO, indicate the loss of sulfonic group due to post reduction reaction with hydrazine [23].

### 3.3. Raman spectroscopy

Raman spectra of GO, rGO, S-rGO and WSG plotted along with graphite (for comparison) are presented in Fig. 2. The two characteristic bands in the Raman spectra of graphite, GO and rGO appearing around 1355 $cm^{-1}$ and 1600 $cm^{-1}$ arise from the defects (D band) and first-order scattering of the $E_{2g}$ phonons from the $sp^2$ carbon lattice (G band), respectively [28]. When graphite is oxidized to GO the G band is red shifted due to the formation of $sp^3$ carbon atoms, while during the reduction of GO to rGO the G band is blue shifted due to the increased number of $sp^2$ carbon atoms. On the other hand, during the oxidation of graphite to GO the disorder induced D band broadens with a small blue shift and its intensity increases due to the reduced size of the $sp^2$ domains with the creation of defects and vacancies [29]. When GO is reduced to rGO, the intensity of the D band decreases slightly along with a small red shift [30].

Structural changes induced by the chemical processing of graphene can be evaluated by calculating the intensity ratio of the D and G bands ($I_D/I_G$) [31]. In the present case, sulfonation of GO is confirmed from the higher $I_D/I_G$ ratio of S-rGO (0.98) in comparison to rGO (0.93). During the sulfonation process excess p-phenyl-$SO_3H$ functional groups covalently link with the graphitic planes and create $sp^3$ defects, increasing the D band intensity. Hence the intensity ratio of S-rGO turns out to be higher than that of rGO. On the contrary, the intensity ratio of WSG (0.88) is lower owing to the