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Graphene Oxides as Tunable Broadband Nonlinear Optical Materials for Femtosecond Laser Pulses

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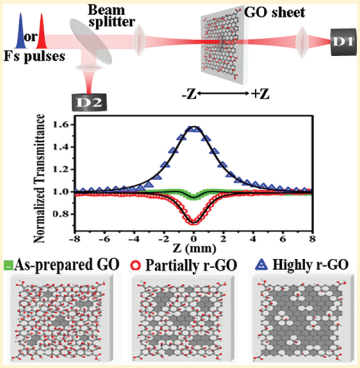
Supporting Information

ABSTRACT: Graphene oxide (GO) thin films on glass and plastic substrates were found to display interesting broadband nonlinear optical properties. We have investigated their optical limiting activity for femtosecond laser pulses at 800 and 400 nm, which could be tuned by controlling the extent of reduction. The as-prepared GO films were found to exhibit excellent broadband optical limiting behaviors, which were significantly enhanced upon partial reduction by using laser irradiation or chemical reduction methods. The laser-induced reduction of GO resulted in enhancement of effective two-photon absorption coefficient at 400 nm by up to ~19 times and enhancement of effective two- and three-photon absorption coefficients at 800 nm by ~12 and ~14.5 times, respectively. The optical limiting thresholds of partially reduced GO films are much lower than those of various previously reported materials. Highly reduced GO films prepared by using the chemical method displayed strong saturable absorption behavior.



SECTION: Kinetics, Spectroscopy

Since its invention in 1960,[1] laser has been widely used in many fields including electronics, medicine, information technology, entertainment, industries, and military.[2] There is significant interest in developing nonlinear optical materials (optical-limiting materials and saturable absorbers) to modulate the light intensity. Optical-limiting materials display a decreased transmittance at high input laser intensity, which can be utilized to protect eyes and senstive instruments from laser-induced damage.[3] In contrast, saturable absorbers display an increased transmittance at very high input laser intensity, which are useful for pulse compression, mode locking, and Q-switching.[4]

In the past decade, significant efforts have been devoted to develop ideal broadband optical-limiting materials.[5−8] Strong optical-limiting activity has been observed in carbon-based materials such as fullerenes,[2] carbon nanotubes,[9] and carbon black suspensions[2] and metal nanoparticles such as gold and silver.[6,10,11] These materials usually show saturable absorption at low input intensities and exhibit optical-limiting activity at very high input intensities. The primary contribution to the optical limiting effect is nonlinear scattering, which is due to formation of solvent microbubbles at high excitation intensities as a consequence of energy transfer from the dispersed material to the solvent. Optical-limiting materials for ultrashort (femtosecond or picoseocnd) laser pulses are less common than those for nanosecond laser pulses because nonlinear scattering for ultrashort laser pulses is usually much weaker than that for nanosecond laser pulses due to slow formation of microbubbles.[7,12] Thin film materials usually show worse optical-limiting performance than materials in solution due to lack of solvent to form microbubbles as scattering centers. An essential requirement for effective thin film optical-limiting materials is strong nonlinear absorption such as multiphoton absorption and excited state absorption.[13] π-Conjugated organic molecules such as porphyrins,[14] phthalocyanines,[14] and other large aromatic molecules are known to exhibit optical-limiting activity for femtosecond laser pulses due to strong multiphoton absorption or excited-state absorption. However, thin films of these materials exhibit femtosecond optical-limiting activity only over a very narrow wavelength range. Very recently, several research groups reported strong broadband optical limiting properties in graphene,[7] graphene oxide (GO),[5,15] and GO-polymer composite[16] in solutions for nanosecond laser pulses. They attributed the optical-limiting effects to nonlinear scattering. The femtosecond optical-limiting properties of GO have not yet been reported so far. GO sheets contain a mixture of electronically conducting sp^2 and insulating sp^3 carbon domains. Their electronic properties could be tuned by controlling the ratio of sp^2/sp^3 carbon domains,[17,18] which might have interesting implications on their nonlinear optical properties. The sp^2 domains in GO resemble π-conjugated organic molecules with strong nonlinear optical properties, which motivated us to investigate the nonlinear optical properties of GO. The investigation of

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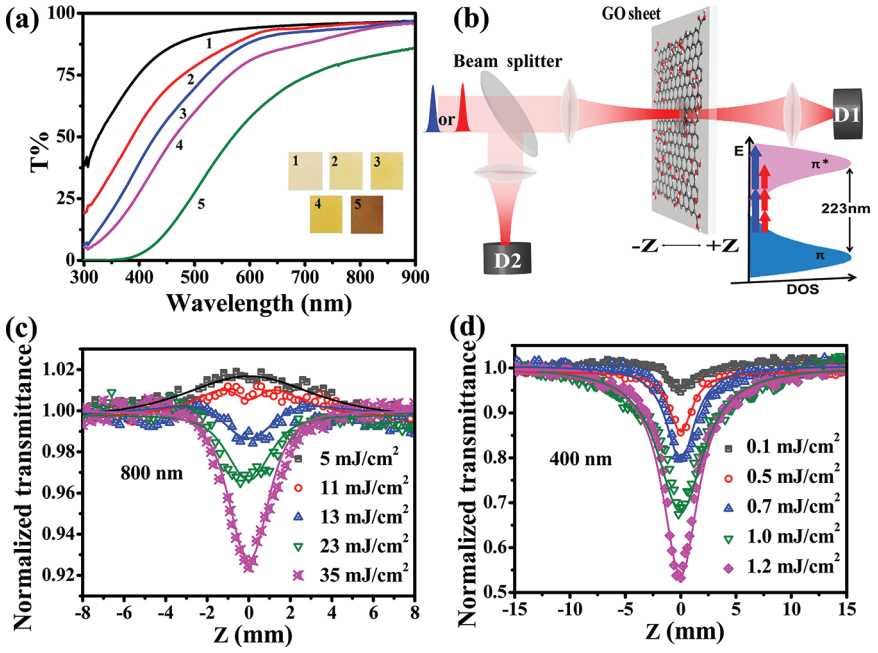

Figure 1. (a) UV−vis transmittance spectra and photographs (inset) of GO films of different thicknesses on glass substrates (Samples 1−5). (b) Schematic experimental setup of the Z-scan measurements. D_1 and D_2: photodiodes (Inset: the band structure of GO). (c,d) Open aperture Z-scan results of a GO film (Sample 4) at 800 (c) and 400 nm (d) under different input fluences.

femtosecond nonlinear optical properties of GO is vital for the development of future graphene-based ultrafast optoelectronic applications.

Here we report exceptional broadband nonlinear optical properties of GO and partially reduced GO thin films for femtosecond laser pulses. The as-prepared GO films on glass substrates displayed exceptional optical limiting effects for femtosecond laser pulses at both 400 and 800 nm, with a huge effective two-photon absorption coefficient of ∼41 000 cm·GW^{-1} at 400 nm, effective two- and three-photon absorption coefficients at 800 nm of ∼31 cm·GW^{-1} and ∼0.47 cm^3·GW^{-2}, respectively. Most interestingly, their optical-limiting performances were found to be significantly enhanced upon partial reduction of GO. The partially reduced GO could be prepared by laser-induced reduction or chemical reduction by exposure to the hydrazine vapor. The laser-induced reduction of GO could result in enhancement of effective two-photon absorption coefficient at 400 nm by up to ∼19 times and effective two- and three-photon absorption coefficients at 800 nm by ∼12 and ∼14.5 times, respectively. The optical-limiting thresholds of a 380 nm thick, partially reduced GO film for femtosecond laser pulses at 800 and 400 nm were found to be as low as 37 and 0.12 mJ·cm^{-2} respectively, which are much lower than those of various previously reported materials.[5,6,19,20] The limiting thresholds of these films could be further reduced by increasing the film thickness. The chemically reduced GO film displayed complicated nonlinear optical properties. Slightly reduced GO films displayed enhanced nonlinear absorption, whereas highly reduced GO films displayed saturable absorption. These GO films can also be deposited onto a plastic substrate to fabricate flexible broadband optical limiters with excellent performance for femtosecond laser pulses.

GO was prepared from graphite using the Hummers method. (See the Supporting Information.)[21] The prepared GO sheets were dispersed in water to a concentration of 5 mg·mL^{-1}. The UV−vis absorption spectrum of GO shows an absorption maximum at 223 nm (Figure S1 of the Supporting Information), which is due to the $\pi-\pi^*$ transition. The AFM images showed that the prepared GO is polydisperse with sizes ranging from 300 nm to a few micrometers. The GO films were prepared by spin-coating the solution onto oxygen plasma-treated glass slides at a speed of 1000 rpm. Thicker GO films were prepared by increasing number of layers. The films were dried at 70 °C after each layer of spin-coating. Figure 1a shows the transmittance spectra of GO films of different thickness on glass substrates (thickness of 32, 73, 100, 140, and 380 nm for Samples 1−5). These GO films are highly transparent in the near-IR region, and the transmittance decreased toward shorter wavelengths. The transmittance of these GO films decreases with increasing film thickness.

Nonlinear optical properties of these GO films were characterized by using an open-aperture femtosecond Z-scan technique (Figure 1b). The Z-scan measurements were performed by using a mode-locked Ti:sapphire oscillator-seeded regenerative amplifier, which gives output laser pulses with a central wavelength of 800 nm, pulse duration of ∼100 fs, and repetition rate of 1 kHz. The laser beam was focused onto the sample with a beam waist of ∼20 μm. The transmittance of the GO films was measured as a function of input fluence, which was varied by moving the samples in and out of beam focus along the z axis. Z-scan measurements have also been performed by using laser pulses of 400 nm, which were generated by frequency-doubling the 800 nm beam. Experiments on different samples have been done, and the results of Sample 4 were chosen for illustration purpose.

Figure 1c,d shows the excitation fluence dependent open-aperture Z-scan measurement results of a GO film (Sample 4) at 800 and 400 nm respectively. At the lowest excitation fluence at 800 nm (Figure 1c), the normalized transmittance was found to increase as the sample moved into the beam focus (z = 0), indicating an optically induced transparency or saturable

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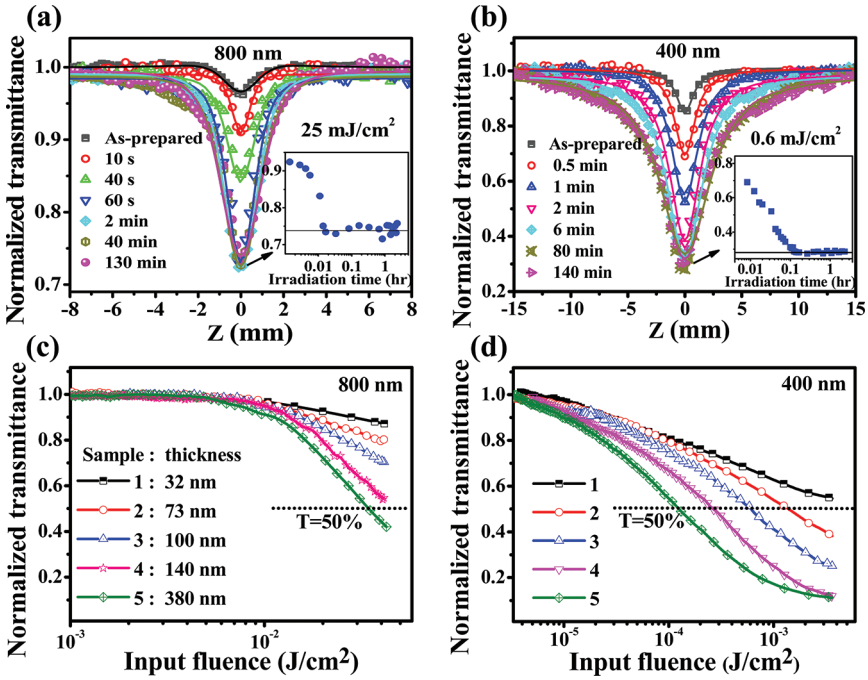

Figure 2. (a,b) Open-aperture Z-scan curves of a partially reduced GO film (Sample 4, film thickness = 140 nm) at 800 nm (fluence of 25 mJ·cm^{-2} at the focal point) and 400 nm (fluence of 0.6 mJ·cm^{-2} at the focal point) by laser irradiation of different periods of time (Insets: normalized transmittance at the focus (z = 0) versus laser illumination time). (c,d) Optical-limiting response of laser-induced partially reduced GO films of different thickness to femtosecond laser pulses at 800 and 400 nm.

absorption behavior. As the excitation fluence increased, reverse saturable absorption was observed instead, indicating existence of strong nonlinear absorption. When 400 nm laser pulses were used, the GO films showed systematical reverse saturable absorption even at very low excitation fluence (Figure 1d) despite the high linear absorbance at 400 nm (Figure 1a), indicating the existence of very strong nonlinear absorption at 400 nm.

The observed saturable absorption behavior at 800 nm under low excitation fluences can be ascribed to ground-state bleaching. 800 nm is located at the edge of absorption band of GO (Figure 1a). Ground-state bleaching will be caused by increasing pump fluence as the sample moves into the beam focus. When the excitation fluence further increases, nonlinear absorption starts to play a dominant role because it is more sensitive to the excitation fluence. Reverse saturable absorption was observed instead at high excitation fluences. There are generally two types of nonlinear absorption: excited state absorption and multiphoton absorption, both of which lead to a decrease in transmittance with increasing input fluence. Observation of reverse saturable absorption at very low excitation fluences (Figure 1d) suggests very large nonlinearity at 400 nm, which dominates the ground-state bleaching at all excitation fluences used here.

The plots of $\ln(1 - T)$ versus $\ln(I_0)$ (I_0: input intensity) at 400 and 800 nm gave slopes of ~0.79 and ~1.75, respectively (Figure S2 of the Supporting Information), indicating coexistence of one- and two-photon absorption processes at 400 nm and coexistence of two- and three-photon absorption at 800 nm.[22] The Z-scan measurement results at 400 and 800 nm were fitted by considering one- and two-photon absorption at 400 nm and one-, two- and three-photon absorption at 800 nm using equations $\alpha = \alpha_0/(1 + I/I_S) + \beta_{eff}I$ and $\alpha = \alpha_0/(1 + I/I_S) + \beta_{eff}I + \gamma_{eff}I^2$, respectively, where α and α_0 are total absorption coefficient and linear absorption coefficient, respectively, and I and I_S are laser intensity and saturation intensity, respectively. Because it is difficult to distinguish the contributions of excited-state absorption and multiphoton absorption using the Z-scan technique, the fitting results give effective two- and three-photon absorption coefficients (β_{eff} and γ_{eff}). An average value of ~41 000 ± 1000 cm·GW^{-1} was obtained for effective two-photon absorption coefficient (β_{eff}) at 400 nm. The effective two- and three-photon absorption coefficients (β_{eff} and γ_{eff}) at 800 nm were calculated to be ~31 ± 2 cm·GW^{-1} and ~0.47 ± 0.03 cm^3·GW^{-2}, respectively.

While conducting Z-scan measurements under very high excitation fluences, such as 58 mJ·cm^{-2} at 800 nm or 4.1 mJ·cm^{-2} at 400 nm, asymmetric and nonrepeatable Z-scan curves (Figure S3 of the Supporting Information) were observed. These results indicated the occurrence of laser-induced change in the GO films under strong laser illumination. It has been previously reported that femtosecond laser irradiation can partially reduce the GO.[23] We also noticed a change of color from yellow to brown in the illuminated area, which is consistent with increased extent of conjugation and ratio of sp^2/sp^3 carbon domains in the GO film after the reduction. The absorption of GO (Figure S5 of the Supporting Information) increases upon laser illumination due to restoration of sp^2 π-conjugated network by deoxygenation of GO. The change in Raman spectra of GO before and after laser illumination (Figure S6 of the Supporting Information) is consistent with partial reduction of GO.[24]

The asymmetric shape of the Z-scan curves under very high excitation fluences (Figure S3 of the Supporting Information) suggested that laser induced reduction of GO caused an enhancement in their nonlinear absorption. To further confirm and understand the laser-induced enhancement of nonlinear optical properties of GO, we intentionally irradiated a small

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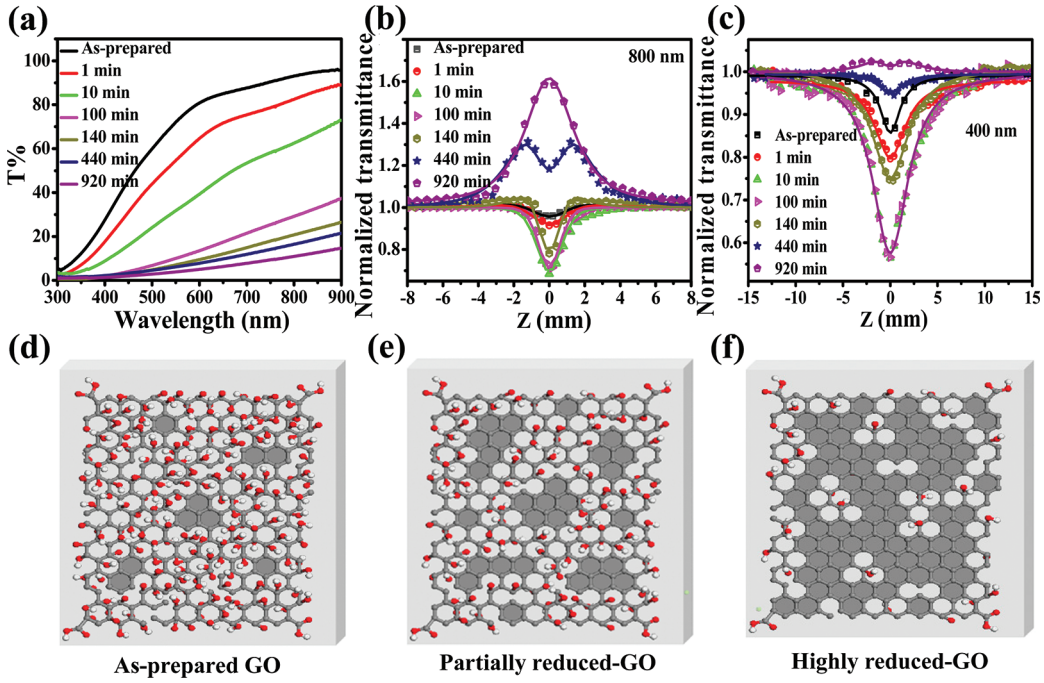

Figure 3. Linear transmittance (a) and Z-scan measurement results at 800 nm (fluence of 25 mJ·cm^{-2} at the focal point) (b) at 400 nm (fluence of 0.6 mJ·cm^{-2} at the focal point) (c) of a GO film (Sample 4) upon exposure to hydrazine vapor for different periods of time. (d–f) Schematic structures of GO at different stages of reduction: as-prepared (d), partially reduced (e), and highly reduced (f).

portion of the GO film (Sample 4) with femtosecond laser pulses of high fluences (fluence of 80 mJ·cm^{-2} at 800 nm and 8 mJ·cm^{-2} at 400 nm, see Supporting Information for detailed experimental procedures) for different periods of time. The Z-scan measurements were subsequently performed on the irradiated area at much lower excitation fluences (25 mJ·cm^{-2} for 800 nm and 0.6 mJ·cm^{-2} for 400 nm at the focus point), and the results are shown in Figure 2a,b. It can be clearly seen that exposure to strong femtosecond laser pulses resulted in a significant increase in nonlinear absorption of the GO films. The nonlinear absorption quickly increased to maximum within a few minutes (~1 min under irradiation at 800 nm and ~6 min at 400 nm) and remained nearly unchanged for up to 2 h (Figure 2a,b). The effective two-photon absorption coefficient (β_{eff}) at 400 nm of GO increased by ~19 times under strong irradiation at 400 nm. The effective two- and three-photon absorption coefficients (β_{eff} and γ_{eff}) at 800 nm increased by ~12 and ~14.5 times, respectively, after laser irradiation at 800 nm. The observed significantly enhanced nonlinear absorption can be ascribed to increased conjugation length and the formation of more and larger sp^2 domains in the GO sheets upon laser-induced reduction.

Similar laser irradiation treatments have been applied to GO films of different thickness (Samples 1–5), and their nonlinear optical properties were then characterized by using Z-scan measurements. The GO films were irradiated with strong femtosecond laser pulses for 10 min to ensure their nonlinear absorption reaching the maximum. The input fluence-dependent transmittance at 800 and 400 nm (Figure 2c,d) was extracted from the Z-scan measurement results. The transmittance of these laser-reduced GO films decreased with increasing input fluence, exhibiting promising optical limiting activity for femtosecond laser pulses at both 800 and 400 nm. The optical-limiting threshold values (F_{50}, defined as the incident fluence at which the transmittance falls to 50% of the linear transmittance) for different samples at 800 and 400 nm are summarized in Tables S1 and S2 of the Supporting Information. The F_{50} values of 77, 57, 46, 42, and 37 mJ·cm^{-2} at 800 nm and 6, 1.4, 0.6, 0.3, and 0.12 mJ·cm^{-2} at 400 nm were obtained for Samples 1–5, respectively. The optical-limiting threshold values (F_{50}) at both 800 and 400 nm decreased with increasing film thickness. The F_{50} values of these partially reduced GO films for femtosecond laser pulses are significantly lower than those of previously reported metal nanoparticles (26 000 mJ·cm^{-2} at 780 nm)[6] and conjugated organic molecules (117 mJ·cm^{-2} at 800 nm).[25] Most importantly, these partially reduced GO materials display huge nonlinear absorption at 400 nm with exceptionally low limiting thresholds for femtosecond laser pulses at 400 nm. So far, there is no report on femtosecond optical limiting materials at 400 nm.

GO can also be reduced via a chemical method by exposing the film to the hydrazine vapors, which can convert the insulating GO to a semimetal.[17,18] This method allows us to control the extent of reduction and ratio of sp^2 and sp^3 carbon domains in the GO sheets by controlling exposure time to the hydrazine vapor.[17] The gradual transformation of GO was monitored by the transmittance measurements after different periods of exposure time (Figure 3a). It can be seen that the transmittance gradually decreased with increasing exposure time to hydrazine. The decreasing transmittance is due to formation of larger sp^2 conjugated network upon chemical reduction.[17]

Nonlinear optical properties of the chemically reduced GO film after different periods of hydrazine exposure were measured by performing Z-scan measurements at 800 and 400 nm (Figure 3b,c). It can be seen that nonlinear absorption of the GO film at both 800 and 400 nm increased significantly upon a short period (10 min) of exposure to the hydrazine vapor. The results are consistent with enhanced nonlinear

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absorption upon laser-induced partial reduction of GO. However, this trend is reversed after extended exposure of the GO films to the hydrazine vapor. Longer exposure (>100 min) to the hydrazine vapor led to a decrease in nonlinear absorption, and the Z-scan profiles eventually switched to saturable absorption at both 800 and 400 nm.

These results indicated that partially reduced GO films act as good optical-limiting materials, whereas highly reduced GO films are good saturable absorbers. Previous studies revealed that GO underwent an insulator−semiconductor−semimetal transition depending on the reduction time.[18,26] This transition can be explained by the change in fraction of sp^2 domains in the GO sheet. Eda et al.[17] reported that blue photoluminescence (PL) of GO was enhanced upon partial reduction due to increased localized sp^2 domains. The PL signal was found to be quenched upon high reduction of GO due to the interconnectivity of the localized sp^2 domains, which resulted in increased nonradiative recombination rates.[17] As-prepared GO sheets contain mostly sp^3 domains and fewer sp^2 domains (Figure 3d). After a short period of exposure to hydrazine, the fraction of strongly delocalized semiconducting sp^2 domains increases (Figure 3e), which leads to a significant increase in nonlinear absorption. Further reduction of the GO films leads to the formation of larger sp^2 domains (Figure 3f).[17,18] Saturable absorption (due to strong linear absorption) may dominate over nonlinear absorption, and an overall saturable absorption would result. Nonlinear optical properties of GO can thus be controlled by varying the degree of reduction.

There are generally two mechanisms responsible for optical-limiting effects: nonlinear scattering and nonlinear absorption.[7,13] The development of thin film optical-limiting materials for femtoseond laser pulses with low thresholds is very challenging because of lack of contribution from nonlinear scattering. To the best of our knowledge, there is no report on femtosecond optical-limiting materials at 400 nm so far. Most materials generally display saturable absorption in the near-UV region. These GO films, in particular, the partially reduced GO films, display very strong two-photon absorption at 400 nm (with huge effective two-photon absorption coefficient of 768 000 $cm \cdot GW^{-1}$) and strong two- and three-photon absorption at 800 nm, which make them excellent candidates for broadband (from UV to near-infrared) optical-limitng materials for femtoseond laser pulses. It has to be noted that these GO films can also be prepared on a plastic substrate, which also displayed excellent optical-limiting effects (Figure S7 of the Supporting Information). Excellent flexible plastic optical-limiting materials could be developed using these partially reduced GO films.

In summary, we have investigated the broadband nonlinear optical properties of GO thin films and their optical limiting activity for femtosecond laser pulses at 800 and 400 nm, which could be tuned by the extent of reduction. The as-prepared GO films were found to exhibit strong broadband optical-limiting behaviors, which were significantly enhanced upon partial reduction by using laser irradiation or chemical reduction methods. The laser-induced reduction of GO could result in the enhancement of an effective two-photon absorption coefficient at 400 nm by up to ∼19 times and effective two- and three-photon absorption coefficients at 800 nm by ∼12 and ∼14.5 times, respectively. Highly reduced GO films prepared by using chemical method displayed strong saturable absorption behavior. The optical-limiting thresholds of these partially reduced GO films are significantly lower than those of previously reported π-conjugated organic molecules and metal nanoparticles. These thin films could be easily fabricated on glass and even plastic substrates by using solution processing methods on a large scale. Low cost, easy preparation, and excellent nonlinear optical properties make these GO materials promising candidates for practical applications as broadband femtosecond optical limiters or saturable absorbers.

■ ASSOCIATED CONTENT

Supporting Information

UV−vis absorption spectrum and AFM image of GO, plots of $\ln(1 - T)$ versus $\ln I_0$ (I_0: input intensity) at 400 and 800 nm and the corresponding data analysis, consecutive Z-scan measurements under high excitation intensities, absorption spectra of GO before and after laser irradiation, Raman spectra of as-prepared GO and laser-reduced GO film, UV−vis spectrum of a GO film on a plastic substrate (Sample 6) and its optical limiting properties at 800 and 400 nm after laser-induced reduction, linear transmittances (T), effective two- and three-photon absorption coefficients (β_{eff} and γ_{eff}), and optical limiting onsets (F_{on}) and thresholds (F_{50}) of laser- reduced GO films at 400 and 800 nm for Samples 1−6. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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