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Wavelength-Dependent Nonlinear Optical Absorption and Broadband Optical Limiting in Au-Fe₂O₃-rGO Nanocomposites

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S Supporting Information

ABSTRACT: Broadband optical limiting and wavelength-dependent nonlinear absorption studies of Au-Fe₂O₃-(15, 25, 40 wt %)rGO (reduced graphene oxide) nanocomposites were investigated using the Z-scan technique and excited with femtosecond (700-900 nm, 80 MHz, 150 fs) laser pulses. A reduction in the graphene perfect (L_a) domain and $I_{\rm D}/I_{\rm G}$ ratio observed in the Raman data and the appearance of a Au 4f and Fe 2p singlet along with a shift in the C 1s state toward higher energy in the XPS data, peak broadening in the XRD data, and different mass residues left out with respect to content of rGO in the TG-DTA data strongly indicated the incorporation of Au-Fe₂O₃ nanostructures on solar exfoliated reduced graphene oxide. Selected aread electron diffraction data ascertained the presence of Au and Fe₂O₃ as a composite, and transmission electron microscopy (TEM) data revealed that the nano-



octahedra Au-Fe₂O₃ turned themselves into nanospindles during incorporation of rGO. Ground state absorption spectra illustrated a pure and composite system possessing a broad absorption in the UV-visible spectral region which suffered band structure alteration with respect to its morphology. All the samples exhibited reverse saturable absorption (RSA) and broadband optical limiting action. The RSA has been attributed to the presence of a two-photon absorption (2PA) process. As wavelength increased, the 2PA coefficient also increased and was found to be varying in the order of Au-Fe₂O₃-rGO > Au-Fe₂O₃ > rGO. The higher 2PA coefficient ($16.0 \times 10^{-10} \text{ m/W}$) and lower onset-optical limiting threshold ($22.01 \mu \text{J/cm}^2$) of Au-Fe₂O₃-(15 wt%)rGO is attributed to the higher loading content of Au-Fe₂O₃, extent of conjugation due to reduction, higher $I_{\rm D}/I_{\rm G}$ ratio and 1D (nanospindle) structure. Our results suggest that the Au-Fe₂O₃-(15 wt %)rGO nanocomposite is promising for broadband optical limiting applications to protect sensitive detectors (including human eyes) from high-power, near-infrared, ultrafast, laser-pulse-induced damage.

KEYWORDS: optical limiters, Au-Fe₂O₃-rGO nanocomposites, wavelength dependent, femtosecond, two-photon absorption

1. INTRODUCTION

The rapid development in the technology of ultrafast nearinfrared (NIR) lasers has imparted revolutionary changes not only to the scientific community but also to our social life.¹ The undesirable aspect that the ultrafast laser technology has contributed to society includes the threat of irreversible damage to human eyes and skin through accidental exposure to intense laser pulses.² This is because NIR lasers (700-1400 nm) readily passes through the cornea and the lens focuses the laser on the retina at a smaller spot size.³ As a result, light entering the pupils gets amplified by $\sim 10^6$ which produces a very high peak of intensity on the retina that can result in permanent damage leading to blindness. Likewise, as the penetration depth increases with wavelength, an illumination of the skin with NIR laser having sufficiently high exposure levels results in burns.^{4,5} This has enthused many material scientists and chemists to explore novel materials exhibiting strong and broadband passive optical limiting, high linear transmittance, fast response time, and higher laser damage

thresholds.^{6,7} Although plenty of optical limiting materials have been identified in the past few decades, the rapid development of laser technology in the UV-visible-IR spectrum proposes a serious challenge to identify a broadband optical limiter that offers limiting action under different wavelengths. One feasible way to achieve broadband optical limiting is induced energyabsorbing based optical limiters that employ nonlinear optical (NLO) properties such as multiphoton absorption (MPA) to reduce the transmission of input laser pulses at high input peak intensities.^{8–10} The preparation of novel nonlinear absorption active materials that offers excellent broadband optical limiting characteristics still presents a significant challenge. Various strategies were employed recently to advance the optical limiting performance of existing materials including (a) doping, (b) optical limiting material incorporation in a solid-

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Figure 1. Schematic diagram of the experimental procedure used for preparing the rGO composite.

state matrix, and (c) preparation of novel composites and nanocomposites. Among them composites are a convenient way to modify band structure that opens up the possibility to achieve reverse saturable absorption/two-photon absorption (RSA/2PA) for different excitation sources. In this sense graphene-based nanostructures are extensively studied for their broadband ultrafast nonlinearity as they possess a large specific surface area, remarkable mechanical strength, and exceptional tunable band structure.¹¹ Particularly reduced graphene oxides (rGOs) are promising for creating new nanocomposites and can act as a material which can support dispersions of either monometallic or metal oxide systems. Considerable efforts have been made to use graphene as building blocks, and several graphene hybrid nanocomposites such as Au nanodots decorated on α -Fe₂O₃@rGO nanocomposites,¹² nitrogen sulfur codoped rGO-Ag nanohybrids, ¹³ α -Fe₂O₃/rGO composites,¹⁴ and Ag-graphene based nanocomposites¹⁵ demonstrated superior photonic applications. Particularly metal incorporated graphene nanocomposites exhibit exciting NLO and optical limiting properties owing to the amalgamation of different NLO mechanisms.^{16–19} Thus, by attaching metal nanoparticles to a single rGO sheet, it is possible to achieve selective NLO properties at different sites. In the process of designing a rGO based nanocomposite that delivers broadband optical limiting against most utilized ultrafast pulse NIR lasers, gold nanoparticles and ferric oxide are chosen as functionalization materials. This is because gold nanoparticles possesses plasmonic behavior that can be used to transduce heat from light absorption,²⁰ which is the most important requirement for broadband optical limiting against high-repetition NIR lasers. Similarly, Fe₂O₃ is a well-known semiconductor that exhibits size/shape dependent NLO properties.²¹ Further, these magnetic fluids assist in tuning magneto-optic properties and, therefore, are attractive for broadband NLO applications. These Au-Fe₂O₃-rGO nanocomposites are expected to possess tunable band structure and, hence, offer flexibility to invoke varying types and amounts of nonlinear absorption depending

on the excitation wavelength. Consequently, appropriate design of an NLO compound/composite based on graphene provides versatility in performing selective nonlinear absorption and broadband optical limiting action. The novelty aspect of this article is that wavelength dependent nonlinear absorption and optical limiting action of Au-Fe₂O₃ decorated rGO nanocomposites using NIR laser pulses (700-900 nm, 80 MHz, and 150 fs) is reported for the first time, to the best of our knowledge. Although plenty of optical limiting materials have been identified and reported in the literature in the past few decades, the rapid development of laser technology in the UV-visible-IR spectrum proposes a serious challenge to identify broadband optical limiters that offer limiting action at these diverse wavelengths. This article reports one such broadband optical limiter capable of limiting the ultrashort NIR pulses (700-900 nm, 80 MHz, and 150 fs) at the millijoule level. Employing the Z-scan technique, the tunability of wavelength dependent nonlinear absorption and origin of 2PA due to the contribution of various individual components such as the sp² domain of rGO (700 nm), $n-\pi^*$ transition of rGO (800 nm), and plasmon resonance state of Au nanoparticles (900 nm) is discussed in detail. From the Sheik-Bahae formalism, a relation between the wavelength of excitation and nonlinear absorption coefficient was obtained as $\beta \propto A\lambda^2 \pm C.$

2. EXPERIMENTAL SECTION

2.1. Material Preparation. Gold Fe_2O_3 decorated reduced graphene oxide was prepared by a cost-effective and environmentally friendly procedure via a three-step process (Figure 1). As graphene is expensive, few-layer graphenelike systems called rGO that have characteristics close to that of graphene are in high demand. Oxidizing the naturally abundant inexpensive graphite flakes yields graphene oxide which, upon reduction, can produce graphenelike reduced graphene oxide. As a first step GO was achieved from graphite using a modified Hummers method.²² Preparing reduced graphene oxides via chemical treatments has the risk of handling the explosive reducing agent along with the major drawback of the attenuation in optical



Figure 2. XPS survey scans of rGO and Au-Fe₂O₃-(15 wt %)rGO (a). C 1s XPS spectra of rGO nanosheets (b) and Au-Fe₂O₃-(15 wt %)rGO (c). Au 4f core level spectrum (d). Fe 2p core level spectrum (e). The peaks of Figures 2b and c were fitted with Gaussian curves, and the green lines represent the components of the Gaussian fit made on the C 1s XPS spectrum. The units for intensity in all of the graphs are arbitrary units (a.u.).

properties.^{23,24} In this context, an express and green synthesis technique called as solar exfoliation was recently reported.^{25,26} This technique is capable of producing few-layer graphene at huge scales and with excellent quality. The method encompasses the usage of solar radiation for GO reduction/exfoliation. In the second step rGO was prepared through exfoliation of GO in the presence of focused sunlight $(f = 100 \text{ cm}, t = 2 \text{ s}).^{27}$ The incorporation of Au-Fe₂O₃ nanostructures on various rGO content (15, 25, 40 wt %) was achieved through a hydrothermal reaction of HAuCl₄·3H₂O and FeCl₃·6H₂O in the presence of rGO. In the third step of the experiment, 40 wt % of rGO in 60 mL ethanol was dispersed followed by sonication treatment for 60 min to obtain a homogeneous dispersion. HAuCl₄·3H₂O and FeCl₃·6H₂O were both dissolved in ethanol (20 mL) in a 1:2 molar ratio. This was added to the rGO dispersion solution and followed by constant stirring for \sim 30 min, at a temperature of 32 °C. The final solution was then transferred into Teflon-lined autoclave (150 mL capacity). Later, this was placed in an oven (at 180 °C) for about 12 h under autogenous pressure. Subsequently, the suspension was allowed to cool to room temperature. The product obtained through centrifugation was then oven-dried (at 60 °C) for about 24 h. For obtaining the other Au-Fe₂O₃-rGOs (25 and 15 wt % of rGO content) a similar procedure was adapted. Pure Au-Fe₂O₃ nanoparticles were prepared through analogous treatment without the use of rGO.

2.2. Instruments and Measurements. The carbon and other metals electronic states in the prepared complex systems were studied by employing X-ray photoelectron spectroscopy. Further confirmation on the products was achieved through powder XRD studies (Cu K α , 1.54 Å, 0.02 s⁻¹, 10–80°). The morphologies of the prepared materials were investigated by high-resolution transmission electron microscopy [TEM, TECNAI F (S-Twin)]. A thermogravimetric analyzer (PerkinElmer) was used to measure the thermal stability of the samples under air in atmosphere in the temperature range of 30–740 °C at a heating rate of 15 °C min⁻¹. Raman spectra of Au-Fe₂O₃

decorated rGO along with its individual counterparts were obtained using a Raman spectrometer (Renishawin Via Raman Microscope) at room temperature (30 °C) using a 532 nm laser. Ground state and wavelength dependent nonlinear absorption of the samples dispersed in ethylene glycol (5 mg/5 mL) were recorded using a JASCO Corp., V-570, spectrophotometer and Z-scan setup with a Ti:sapphire (700– 900 nm, 80 MHz, and 150 fs) excitation source, respectively.

3. RESULTS AND DISCUSSION

3.1. Structure Characterization. 3.1.1. XPS Studies. The XPS survey scan of rGO and Au-Fe₂O₂-(15 wt %)rGO is as shown in Figure 2a. In the XPS survey spectrum of rGO, only two main peaks were observed at 285.3 and 529.7 eV which correspond to the carbon and oxygen environment of the molecule. As shown in Figure 2b, the C 1s XPS spectrum confirms the presence of C=C, C-O, and C=O groups in rGO through the peaks observed at 284.5, 285.8, and 288.6 eV, respectively. In the XPS survey scan of the nanocomposite (2a), apart from the two main peaks around 285.3 and 529.8 eV that correspond to the C 1s and O 1s species of rGO, six peaks of Au $4f_{5/2}$, Au $2p_{3/2}$, Au $2p_{1/2}$, Fe 3p, Fe $2p_{3/2}$, and Fe $2p_{1/2}$ of Au-Fe₂O₃ were observed. Appearance of Au 4f and Fe 2p singlets along with rGO in the survey scan of Au-Fe₂O₃rGO indicate that Au and Fe₂O₃ were functionalized on the surface of the rGO. The C 1s, Au 4f, and Fe 2p core level spectra of the nanocomposite are shown in Figures 2c-e. The deconvoluted spectrum of the nanocomposite clearly depicted the 284.9 (C=C), 285.8 (C-O), 288.9 (C=O), 84.0, 87.8 (Au 4f), 710.6, and 724.0 eV (Fe 2p) peaks. Here the peak values corresponding to C 1s state are shifted to higher energy



Figure 3. Raman spectra of rGO, Au-Fe $_2O_3$, and the Au-Fe $_2O_3$ -(15, 25, and 40 wt %)rGO nanocomposite.

which is due to the effect of further reduction of rGO upon functionalization.

3.1.2. XRD Studies. XRD measurements (data shown in Figure S1a, SI) were performed for preliminary confirmation of nanocomposite formation and to investigate the crystal phases of the typical product. XRD of the product obtained from Hummer's method⁷ shows a peak at $2\theta = 10.6^{\circ}$ that represent the (001) plane of GO. The absence of any peak at a $2\theta = 26^{\circ}$ revealed the completion of the oxidization process and the formation of GO devoid of any graphite. The XRD of solar exfoliated graphene oxide gives the first confirmation of the complete reduction of GO, through the missing peak at 2θ = 10.6°, and the formation of a new weak and broad peak at 2θ = 24° represents the (002) plane of rGO. A broadening of the graphene peak in the XRD spectra of the exfoliated sample corresponds to short domain of layers. Under solar irradiation, due to quick heating, the rate of decomposition of functional groups in GO is higher than the diffusion rate of the evolved gases returning back to the material, thus yielding pressure that surmounts the van der Waals force holding the graphene sheets. In the XRD pattern of products from hydrothermal reaction the presence of an rGO peak $(2\theta = 24^{\circ}, (002))$ is accompanied by many distinct crystalline peaks arising from the incorporated elements. The representative diffraction peaks that emerged at $2\theta = 33.34^{\circ}$, 35.76° , 49.65° , 54.10° , 62.76° , and 77. 58° were indexed as (104), (311), (024), (116), (214), and (036) crystal planes of the rhomb-centered Fe₂O₃ [JCPDS: 89-8104] respectively. Similarly, the peaks observed at $2\theta = 38.34^{\circ}$, 44.56° and 64.86° correspond to the (111), (200), and (220) crystal planes of the face-centered cubic Au [JCPDS: 65-2870], respectively. This clearly shows that the Au-Fe₂O₃-rGO nanocomposites form themselves with Au metal Fe₂O₃ metal oxide and rGO. It is to be noted that the peak positions of individual counterparts get shifted in the nanocomposite due to intermolecular interactions with respect to the content of (15-40 wt %)rGO.

3.1.3. TGA Studies. TGA studies were performed primarily to evaluate the thermal stability of the composite and content of loading upon graphene sheets. Under thermal treatment, rGO decomposes completely near 700 °C and the left-out residue will provide information about the loaded inorganic content (Au-Fe₂O₃) upon rGO. The profile of the TGA curves



Figure 4. TEM and SAED images of pure rGO (a), Au-Fe₂O₃-(15, 25, and 40 wt %)rGO nanocomposite (b–g), and pure Au-Fe₂O₃(h and i).

of rGO, Au-Fe₂O₃, and Au-Fe₂O₃-rGO is shown in [Figure S1b, SI]. Pure rGO, starts losing its weight below 100 °C and the observed weight loss of 10% represents the loss of water molecules. This is followed by an exothermic peak at 204 °C (almost 15%) due to the pyrolysis of oxygen-containing functional groups left out after exfoliation. The thermal profile of pure Au-Fe₂O₃ does not show any major weight loss in the





Figure 5. UV–visible absorption spectra of pure rGO, Au-Fe₂O₃-(15, 25, and 40 wt %)rGO nanocomposite, and pure Au-Fe₂O₃.

temperature range of 30–800 °C, and the observed small variation arises due to adsorbed water molecule vaporization. The thermal decomposition pattern of nanocomposite follows a similar trend of rGO with the variation in the mass of left out residue. Here the observed weight loss at lower temperature corresponds to vaporization of water molecules, followed by the decomposition of graphene layers. It is to be mentioned that the thermal stability of Au-Fe₂O₃-(15 wt %)rGO is higher than all other composites due to the dominant contribution from the Au-Fe₂O₃ system. The masses of residue left out at 700 °C (where rGO decompose completely) were 77%, 54%, and 42% for Au-Fe₂O₃-(15, 25, and 40 wt %)rGO, respectively. This corresponds to the amount of Au-Fe₂O₃ loaded upon rGO, and it clearly shows that content of loading varies with rGO content.

3.1.4. FTIR Studies. The IR spectra of rGO, Au-Fe₂O₃, and Au-Fe₂O₃-rGO nanocomposite are shown in Figure S2 of the SI. For GO, the presence of various functional groups like hydroxyl and carboxylic units is confirmed from the bands at 3420 and 1712 cm⁻¹, respectively. The peak at 1682 cm⁻¹ is associated with skeletal vibrations of aromatic C=C bond, and other bands at 1367 and 1051 cm⁻¹ correspond to C-O-H deformation of C-O (alkoxy) stretching vibration.^{28,29} These confirm the availability of various oxygenous groups in the surface of rGO and thus open the sites for decoration/ functionalization. For pure Au-Fe₂O₃, the absorption peak in the lower wavenumber corresponds to the heavy metal vibrations of Au-Fe-O. And for the composite, it is interesting to observe that the intensity of functional group (C=O stretching, 1712 cm^{-1}) decreased while the intensity of skeletal vibrations (C=C, 1628 cm^{-1}) of graphene increased. This provides evidence of the interaction between Au-Fe₂O₃ nanoparticles and the oxygen-containing functional groups (i.e., -COOH) of rGO nanosheets through chemical or electrostatic attractions.

3.1.5. Raman Analysis. Raman spectroscopy was used to analyze the formation of the Au-Fe₂O₃-rGO nanocomposite. Figure 3 shows the Raman spectra of rGO, Au-Fe₂O₃, and Au-Fe₂O₃-rGO. The bands at 1580 and 1350 cm⁻¹ represent the G and D bands of the GO sample. During exfoliation, double bonds of rGO become conjugated which is confirmed from the shift in G band (1580–1607 cm⁻¹). The change in the I_D/I_G ratio of 0.99 (GO) to 0.78 (rGO) indicates the removal of



Figure 6. Open aperture patterns of pure rGO, Au-Fe₂O₃, and Au-Fe₂O₃-(15, 25, and 40 wt %)rGO nanocomposite at (a) 700, (b) 800, and (c) 900 nm. Symbols are experimental data, and the solid lines represent the theoretical fits.

most of the oxygen containing functional groups. The peaks at 140, 218, 344, and 385 cm⁻¹ are consistent with vibration modes of the hematite phase of iron oxide (Fe_2O_3). In the nanocomposite, the presence of both characteristic peaks of rGO and Au-Fe₂O₃ also confirms the formation of the



Figure 7. Probable excitation mechanisms for 2PA in pure rGO, Au-Fe₂O₃, and Au-Fe₂O₃-rGO nanocomposite.

Table 1. NLO Coefficients of the Pure rGO, Au-Fe₂O₃, and Au-Fe₂O₃-rGO Nanocomposite Excited with NIR Wavelengths

		Nonlinear 2PA Coefficient $(\beta_{2PA} \times 10^{-10} \text{ m/W})$				
excitation wavelength of Ti:sapphire laser (150 fs, 80 MHz)	rGO	Au- Fe ₂ O ₃	Au-Fe ₂ O ₃ - rGO (40 wt %)	Au-Fe ₂ O ₃ - rGO (25 wt %)	Au-Fe ₂ O ₃ - rGO (15 wt %)	
700 nm	1.3	5.6	3.4	5.8	6.5	
800 nm	2.1	6.3	6.0	9.0	9.3	
900 nm	3.2	6.6	7.6	14.1	16.0	

composite. Here the I_D/I_G ratio of the composite varies as 0.73, 0.67, and 0.64 which ensures the further reduction of rGO during incorporation of Au-Fe₂O₃ upon (15, 25, and 40 wt %)rGO, respectively. It is worth noting that the strength of the Au-Fe₂O₃ peaks are comparatively higher in (15 wt %)rGO which confirms the dominance of Au-Fe₂O₃ in the composite. The perfect graphene domain (L_a) was estimated using the well-known formula³⁰ L_a (nm) = $\frac{560}{E_{\lambda}^4} \left(\frac{I_D}{I_G}\right)^{-1}$ where E_{λ} is the excitation energy (eV). Perfect graphene domains of rGO (L_a = 8.96 nm) increase upon decoration to 9.57, 10.42, and 10.92 nm for Au-Fe₂O₃-(15, 25, and 40 wt %)rGO, respectively. This change adheres to the higher defect density of in-plane graphitic crystallite sp² domains upon rGO.

During the composite formation, the average in-plane crystallite size of sp² carbon nanoislands decreases which is evidence of the decrease of L_a from 10.92 nm of rGO to 8.96 nm of Au-Fe₂O₃-(40 wt %)rGO. The possible reason for the decrease of the L_a (which reflects the lateral dimension of the sp² carbon cluster) may be that, during hydrothermal reaction, the existing sp² carbon cluster does not grow large and instead only a few sp² configurations are created during the functionalization process. In fact, the decxygenation of rGO reduced the I_D/I_G ratio which confirms the functionalization.

Thus, the Raman data further supports XPS and XRD analyses, indicating the successful synthesis of the Au-Fe₂O₃-rGO nanocomposite through the hydrothermal treatment.

3.1.6. Morphological Analysis. Figure 4 shows the TEM image of rGO, and the curvy and wrinkled sheets can be attributed to the graphene layers attained through the solar exfoliation process. This expended morphology is essential in the synergic effect process as it maximizes the surface area available for incorporation of Au-Fe₂O₃. TEM images of Au- Fe_2O_3 show a nano-octahedra-like structure with a size of 196 $nm \times 174$ nm, and the corresponding selected area electron diffraction (SAED) pattern represents the (111), (311) planes of Au and Fe₂O₃ respectively. This ascertains that metallic Au and metal oxide Fe₂O₃ form themselves as individual components. During synthesis, the left-out oxygen-functional moieties act as sites of nucleation and promote the incorporation of functionalization units in graphene sheets (Figure S3, SI). The nucleation of the Au-Fe₂O₃ NPs may be attributed to the interaction of Au⁺ and Fe⁺ ions with the negatively charged carboxylic acid groups, which act as locations for anchoring and growth of the Au-Fe₂O₃-rGO. It is interesting to observe that Au-Fe₂O₃ appear as bright spots upon the slightly wrinkled and folded rGO sheets. Nanospindlelike structures were observed which arise due to aggregation and cohesion and later grow as stacks because of the Ostwald ripening effect.^{31,32} The corresponding SAED pattern of the composite also resembles the pure Au-Fe₂O₃ and thus confirms the incorporation as Au-Fe₂O₃ in nanocomposites.

3.2. Ground State Absorption. 3.2.1. Uv-VisibleAbsorption Spectra. Ground state absorption (Figure 5) clearly shows that both pure and decorated Au-Fe₂O₃-rGO composites possess broad absorption in the UV-visible-NIR region, which is the most essential condition for nonlinear absorption based broadband optical limiters. The absorption maximum at 230 and 260 nm represents the $\pi-\pi^*$ transition (C-C aromatic) and $n-\pi^*$ transition (C-O) of GO. The



Figure 8. Optical limiting behavior of pure rGO, Au-Fe₂O₃, and Au-Fe₂O₃-(15, 25, and 40 wt %)rGO nanocomposites at (a) 700 (b) 800, and (c) 900 nm. Symbols are experimental data, and the solid lines represent the theoretical fits.

restoration of sp² carbon atoms after reduction red shifts the absorption maximum to 272 and 390 nm. Detailed examination of the literature illustrates that the major transitions observed in Fe₂O₃ include (i) ligand to metal charge (200–400 nm), (ii) pair excitation processes and a ligand field (400–600 nm), (iii) d–d transitions (600–900 nm), and (iv) a broad absorption band due to plasmon resonance of Au nanoparticles (500–570 nm).³³ In the recorded Au-Fe₂O₃ absorption spectrum, the UV (272 nm)

Table 2. Onset Optical Limiting Threshold of the Pure rGO, Au-Fe₂O₃, and Au-Fe₂O₃-rGO Nanocomposite under NIR Wavelength Excitations

		onset optical limiting threshold ($\mu J/cm^2$)				
excitation wavelength of Ti:sapphire laser (150 fs, 80 MHz)	rGO	Au- Fe ₂ O ₃	Au-Fe ₂ O ₃ - rGO (40 wt %)	Au-Fe ₂ O ₃ - rGO (25 wt %)	Au-Fe ₂ O ₃ - rGO (15 wt %)	
700 nm	48.59	38.28	38.90	38.93	26.60	
800 nm	47.55	32.02	34.89	31.48	26.29	
900 nm	46.40	28.44	34.26	25.93	22.01	

peak arises due to ligand to metal charge transfer of Fe_2O_3 , and the peak at 572 nm represents the surface plasmon resonance (SPR) of Au nanoparticles. In the Au-Fe₂O₃ spectrum, the UV absorption peak at 272 nm arises due charge transfer from ligand to metal of Fe_2O_3 , and the peak at 572 nm represents the SPR of Au nanoparticles. As SPR absorption of Au is dominant, it has suppressed the absorption peaks (400–600 nm due to the pair excitation process) arising from Fe_2O_3 in the composite.

The optical properties of Au-Fe₂O₃ are evident individually and thus demonstrate that these materials are nanocomposite structures. For the nanocomposite, UV absorption (272 nm) arises due to the combined contribution of $\pi - \pi^*$ transition state of rGO and metal charge transfer of Fe₂O₃. And the SPR peak of Au nanoparticles arises at 599 (40 wt %), 560 (25 wt %), and 544 nm (15 wt %). This shift in peak position was due to formation of the composite between Au-Fe₂O₃ and graphene sheets. Thus, the electronic band structure gets strongly altered through composite formation, and the availability of energy states (due to Au, Fe₂O₃, rGO) provides the opportunity for the system to be used as broadband optical limiters.

3.3. Wavelength Dependent Nonlinear Absorption. Understanding the third-order nonlinearities is very crucial for identifying laser photonic devices that rely on ultrafast nonresonant NLO responses of materials. This can be achieved by employing Z-scan techniques using femtosecond mode locked lasers as excitation sources. Laser properties such as wavelength, pulse width, repetition rate, intensity, etc. to be employed in Z-scan were chosen considering the properties of the material such as laser damage threshold, linear absorption, and physical state. The open aperture (OA) Z-scan technique was used to estimate the nonlinear absorption (NLA) coefficients. The NLA in such materials has contributions from more than one mechanisms including (a) 2PA, (b) ESA, (c) free carrier absorption (FCA), etc.^{34,35} The NLA of pure and hybrids of Au-Fe₂O₃-rGO systems dispersed in ethylene glycol as a function of wavelength was measured. Definitive care should be taken in the choice of dispersing medium, and here, ethylene glycol is chosen since it offers (i) a high viscous nature to maintain the stability of dispersed system for longer time and (ii) solvents do not show any nonlinearity under excitation. For data reliability, the system must be highly stable during Z-scan measurement, and the stability of dispersed system as a function of time was tested. The recorded image is provided in the supplementary data (Figure S4, SI), and the system was found to be highly stable for 8 h. The complete details of Z-scan experimental details and measurements can be found elsewhere.³⁶ For obtaining the open aperture Z-scan data, a large aperture lens was used to collect the entire laser beam transmitted through the sample. While performing wavelength dependent NLO studies, it is to be noted that the diameter of laser pulses varies with wavelength, i.e., $\omega_0 = \frac{2f\lambda}{\pi d}$ In the present case, the input laser pulses diameter $(D = 2\omega_0)$ varied as 4.44 μ m (700 nm), 5.08 μ m (800 nm), and 5.72 μ m (900 nm), which resulted in slightly different Rayleigh range $[Z_0 = 2.2 \text{ mm} (700 \text{ nm}), 2.54 \text{ mm} (800 \text{ nm}), \text{ and } 2.86 \text{ mm}$ (900 nm)] for different scans. Hence, sufficient care was taken in fixing the thickness (L) of the samples so as to obtain Z-scan conditions for the thin sample limit, $L \ll Z_0$. For different wavelengths, typical input power of 3 mW was used corresponding to input peak intensities of 160 MW/cm² (at 700 nm), 122 MW/cm² (at 800 nm) and 96 MW/cm² (at 900 nm). This change in peak intensity with respect to wavelength of laser source is the most critical element that has resulted in different nonlinear absorption behavior of the materials as a function of wavelength.

Under intense laser interaction the intensity-dependent absorption coefficient will follow the relation $\alpha(I) = \alpha_o + \beta I$, where α_o is the usual linear absorption coefficient (cm⁻¹) and β is NLA coefficient (m/W). Employing the Sheik–Bahae formalism (SBF), the nature of nonlinearity and magnitude of the NLA coefficient can be estimated from the recorded OA Zscan curves and through theoretical fits given by³⁶

$$T_{\text{OA}}(z, s = 1) = \frac{1}{\sqrt{\pi q_o}(z, 0)} \int_{+\infty}^{-\infty} \ln[1 + q_o(z, 0)e^{-r^2}] dr$$
(1)

$$T_{\rm OA} = \frac{1}{1 + \beta L_{\rm eff} \left[\frac{I_0}{\left(1 + \left(\frac{z}{z_0} \right)^2 \right)} \right]}$$
(2)

Where $q_o(z, o) = \beta I_0 L_{\text{eff}}$, $I_0 = \frac{2\text{peak power}}{\pi \omega_0^2}$ is the peak intensity, $L_{\text{eff}} = \frac{[1 - \exp(-\alpha l)]}{\alpha}$ is defined as effective thickness of the sample, and L is the sample thickness. To understand the relation between wavelength and nonlinear absorption coefficient, the above equation can be rewritten in terms of wavelength by putting $Z_0 = \frac{\pi \omega_0^2}{\lambda}$

$$T_{\text{OA}} = \frac{1}{1 + \beta L_{\text{eff}} \left[\frac{I_0}{1 + \left(\frac{Z}{\pi \omega_0^2 / \lambda} \right)^2} \right]}$$
(3)

Rearranging the above equation

$$\beta L_{\text{eff}} I_0 + \left[1 + \left(\frac{Z^2}{\pi^2 \omega_0^4 / \lambda^2} \right) \right] = \frac{1 + \left[1 + \frac{Z^2}{\pi^2 \omega_0^4 / \lambda^2} \right]}{T_{\text{OA}}}$$
(4)
$$\beta = \frac{1}{L_{\text{eff}} I_0} \left\{ \frac{1 + \frac{Z^2}{\pi^2 \omega_0^4 / \lambda^2}}{T_{\text{OA}}} - 1 - \frac{Z^2 \lambda^2}{\pi^2 \omega_0^4} \right\}$$
(5)

 $L_{\text{eff}} l_0 \left(\begin{array}{cc} l_{\text{OA}} & n & \omega_0 \end{array} \right)$ (5) The above equation provides the following relation between

NLA coefficient and wavelength as

$$\beta \propto A\lambda^2 \pm C \tag{6}$$

It can be concluded from the above relation that NLA coefficient increases with increase in wavelength.

The recorded OA Z-scan data is as shown in Figure 6. The Z-scan data obtained for in pure ethylene glycol did not show any NLO contribution at these peak intensities. OA Z-scan measurements performed at different excitation wavelength exposes the presence of valley-like pattern suggesting the occurrence of nonlinear absorption in all the samples. For the chosen wavelengths, both pure and composite of Au-Fe₂O₃ decorated rGO demonstrates RSA action. Au-Fe₂O₃-rGO (in ethylene glycol) exhibited enhanced NLO behavior when compared to bare Au-Fe₂O₃ and rGO dispersions. This is evident from the higher depth of the valley pattern of Au-Fe₂O₃-rGO composite compared to its individual counterpart. All the experimental data were fitted with the theoretical transmittance equation.³⁷ The 2PA equation fitted well with the experimental data.

For wavelength-dependent nonlinear absorption studies, it is pertinent to note that as wavelength changes energy of the excitation also changes, from which the requirement of the material to possess broad energy states arises; thus, it is difficult to predict the origin of nonlinearity in a material. The open aperture Z-scan measurements obtained from pure rGO and Au-Fe₂O₃ nanoparticles are illustrated in Figures 6a and b. The fact that both of the samples exhibited interesting excitation wavelength dependent reverse saturable behavior is ascribed to the 2PA process. Furthermore, it has been established that the 2PA process occurs when the input photon energy is more than half of the band gap of the material $(hv > E_g/2)$. Therefore, with NIR excitation [700 nm (1.77 eV), 800 nm (1.55 eV), and 900 nm (1.38 eV)] the involved electronic transition requires energy states at 3.56 eV (700 nm), 3.10 eV (800 nm), and 2.76 eV (900 nm) to accomplish the 2PA process. As discussed earlier, rGO possesses absorption in a wide range of the UV-visible spectrum and thus opens up the possibility to promote NLA for different wavelengths. The NLO properties of rGO are generally associated with sp²/sp³ hybridization. The structural defects and functional groups with oxygen also participate and contribute to the overall NLO properties of rGO. It is well-established that rGO consists of sp² clusters, sp² domains, and an sp³ matrix.³⁸ Thus, the electronic energy structures in rGO exist in three states: the $\sigma - \sigma^*$ bandgap of the sp³ matrix is 6 eV, the semiconducting band structure of the sp² cluster is 0.5 eV, and the sp² domain energy with respect to size is 0.5-6 eV. All the chosen excitation wavelengths are well below the sp³ matrix bandgap and above the sp² cluster band gap, so $n-\pi^*$ transitions of the sp² domain of rGO are responsible for the observed 2PA process. Similar to rGO, the Au-Fe₂O₃ composite also portrays a broad absorption band in the UV-visible spectral region. The ground state absorption involves three transitions due to iron oxide in the 200-400 nm (ligand to metal charge transfer transition and partly due to Fe³⁺ ligand) range, 400-600 nm (pair excitation process due to ligand field transition) range, and 600-900 nm (d-d transition) range. Incorporation of Au leads to a broad absorption in the 500-570 nm spectral regime [due to surface plasmon resonance (SPR) of the Au nanoparticles]. Hence, the observed 2PA in Au-Fe₂O₃ composites can be thought of arising due to the electronic states of Fe₂O₃ for 700 nm (ligand to metal charge transfer) and 800 nm (ligand field transition) excitations.

However, at 900 nm 2PA requires lower energy states (450 nm, 2.76 eV) and thus involves the electronic state (SPR) of

the Au nanoparticles. For the entire wavelength (700-900 nm), the estimated nonlinear absorption coefficient of the pure Au-Fe₂O₃ composite is better compared to pure rGO. The OA Z-scan data (presented in Figure 6c) of the Au-Fe₂O₃-rGO nanocomposite showed a transmittance valley, indicating RSA behavior. A small absorption coefficient and the absence of any electronic state at the excitation wavelength clearly suggests the nonlinear absorption to be, predominantly, a result of the instantaneous 2PA process with minimal contribution from a two-step absorption process. The origin of 2PA involves the electronic states of rGO for 700 and 800 nm excitations and high probability of electronic transition in the states of surface plasmon resonance of Au metals favors 2PA in the case of excitation with 900 nm (Figure 7). More details on the involved electronic states responsible for 2PA and transient absorption properties can be obtained by performing fs/ns time-resolved transient absorption spectra measurements, which will be a subject of our future studies. As the rGO content level decreased from 40 to 15 wt %, the NLA improves significantly, which could be due to the contribution from Au- Fe_2O_3 . It is evident for TGA curve discussion that Au-Fe₂O₃-(15 wt %)rGO possesses higher Au-Fe₂O₃ content (\sim 75%), and thus, it possess stronger nonlinear absorption. From the numerical fit, the estimated β_{2PA} of the samples are tabulated in Table 1. It can be clearly evidenced that with increase in wavelength of excitation, nonlinear absorption coefficient also increases. The strong nonlinear absorption coefficient at 900 nm is not only due to involved longer wavelength exposure but also because of the contribution arising from the surface plasma resonance of Au metal nanoparticles. For all wavelengths (700-900 nm), the order of variation in nonlinear absorption coefficient is found to be Au-Fe₂O₃-rGO > Au-Fe₂O₃ > rGO. And here Au-Fe₂O₃-(15 wt %)rGO possesses higher 2PA coefficients compared to Au-Fe₂O₃-(25 and 40 wt %)rGO and many known materials excited with a similar laser. $^{39-42}$ The NLO properties of Au-Fe₂O₃ decorated rGO possibly have contribution from two different sources. The first could be a local field effect, and the second could be the large nonlinear response of the metal itself. The large extent of conjugation in the compound will lead to a higher rate of electron/energy transfer, thereby enhancing the NLO response. Furthermore, the enhancement in NLA perhaps occurs owing to the defect induced states. These states originate from the functionalization of rGO which enables interband transitions (as was discussed in Raman analysis, the $I_{\rm D}/I_{\rm G}$ ratios were 0.73, 0.67, and 0.64 for Au-Fe₂O₃-(15, 25, and 40 wt %)rGO, respectively). During the decoration process, the functional groups possessing oxygen (present on the surface of the rGO) were removed which also possibly resulted in the enhanced nonlinearity. Additionally, Au-Fe₂O₃ is a stronger 2PA system than rGO, and involvement of Au-Fe₂O₃ (SPR state of Au) in achieving 2PA at 900 nm resulted in the maximum 2PA coefficient not only with Au-Fe₂O₃-(15 wt %)rGO but also with other composites. Therefore, it can be established that loading has affected the overall performance.

Earlier works on the investigation of nonlinearity of individual components (Au, Fe_2O_3 , rGO) of chosen systems using different excitation sources include pure Fe_2O_3 (Nd:YAG laser, 532 nm, 30 ns and 30 ps),⁴³ gold clusters (Nd:YAG laser, 532 nm, 14 ns, and 1 Hz),⁴⁴ gold nanorods (Ti:sapphire, 800 nm, 220 fs, and 1 kHz),⁴⁵ Au (nanocubes and nano-octahedra-Ti:sapphire, 800 nm, 60 fs, and 1 kHz),⁴⁶ Au nanoparticles (Nd:YAG laser, 532 nm, 8 ns, and 1 Hz),⁴⁷ noble metal

(Nd:YAG laser, 532 nm, 1064 nm, and 8 ns),⁴⁸ graphene (Ti:sapphire laser, 800 nm, 36 fs and 80 MHz, 400 nm, 1 kHz, and 60 fs),⁴⁹ reduced graphene oxide (Ti:sapphire, 800 nm, 100 fs, and 10 Hz),³⁹ Ag nanoparticles (Nd:YAG laser 445-660 nm, 8 ns, and 10 Hz),⁵⁰ Au nanoparticles (Ti:sapphire, 800 nm, 50 fs, and 1 kHz), ⁵¹ graphene oxide-Pt complex (Nd:YAG laser, 532 nm, 4 ns, and 10 Hz),²⁸ Fe₃O₄-Ag nanocomposite (Nd:YAG laser, 532 nm, 7 ns, and 10 Hz), and reduced graphene oxide/silver nanoparticle hybrid (Nd:YAG laser, 532 nm, 5 ns and Ti:sapphire laser, 800 nm, 100 fs).⁵³ Although a direct comparison of the NLO coefficients obtained in all these cases is not possible due to their strong dependence on the excitation sources used, the densely decorated Au-Fe₂O₃ upon rGO (Au-Fe₂O₃-(15 wt %)rGO) showed higher NLA coefficients compared to rGO (10^{-12} cm/W) , Fe₂O₃ (10^{-13} cm/W) , CuO/GO hybrids (10^{-12} cm/W) , f-HEG (10^{-13} cm/W) , and BiFeO₃ (10^{-12} cm/W) W), which were obtained under similar experimental conditions to those presented in this work.³⁹⁻⁴²

Further among the investigated samples, a maximum nonlinear absorption coefficient of 16.0 \times 10^{-10} m/W was observed with Au-Fe₂O₃-(15 wt %)rGO at an excitation wavelength of 900 nm. The reason for this enhancement in the nonlinearity can be explained as follows: the I_D/I_G ratio increased with decrease in the graphene content of $\operatorname{Au-Fe_2O_3}$ functionalization and this suggests the possibility of an upsurge in the defects in the case of decorated systems. Consequently, an increase in the $\beta_{\rm 2PA}$ of Au-Fe₂O₃-rGO nanocomposite is expected due to the functionalization. The maximum 2PA coefficient is also due to the one-dimensional morphologies (nanospindles as demonstrated by the TEM images) of Au-Fe₂O₃. This has been observed earlier in CdFe₂O₄-rGO nanocomposites,⁵⁴ which resulted in (a) shortening of the carrier transportation path, (b) enhanced carrier collection ability, and (c) functionalization of an electron pathway in the axial direction of the 1D (spindle) structure. This clearly suggests the superiority of densely decorated Au-Fe₂O₃ upon rGO (Au-Fe₂O₃-(15 wt %)rGO) for broadband optical limiting applications.

3.4. Broadband Optical Limiting. One of the prime motivations to investigate the wavelength dependent NLA is to understand and explore the broadband optical limiting capability of the material under investigation. Optical limiting is an NLO process in which beyond a particular fluence (the onset limiting threshold) the transmittance gets attenuated by an NLO process providing the possibility to avoid induced laser damage. From the OA Z-scan data it is conceivable to plot the optical limiting curve in which the sample transmission versus input laser fluence can be obtained. The input fluence, $F_{in}(z)$, can be estimated from the beam radius $[\omega(z)]$ and the input laser pulse energy $[E_{in}]$ using the following relation.^{55,56}

$$\omega(z) = \omega(0) [1 + (z/z_0)^2]^{1/2}$$

The Z-dependent fluence is provided by

$$F(z) = 4\sqrt{\ln 2} \left(\frac{E_{\rm in}}{\pi^{3/2}}\right) \omega(Z)^2$$

As the equation emphasizes, position dependent input fluence also depends upon wavelength and change in wavelength of excitation has direct impact on fluence, even though input energy (E_{in}) is maintained. Unlike a conventional

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plot of the optical limiting curve for specific wavelength, here the wavelength influence Rayleigh range was chosen which in turn alters the position-dependent fluence. Hence for every chosen wavelength, it is essential to plot the optical limiting curve to identify the potential material for broadband optical limiting applications.

Figure 8 shows the OL curves of all samples excited under different wavelengths, 700–900 nm. All the samples exhibited a similar behavior wherein the transmittance remained constant at low input fluences and gradually decreased with fluences for all wavelengths 700–900 nm, clearly signifying the presence of a broadband OL effect. It is established that the OL behavior of decorated systems excited with femtosecond laser pulses (700–900 nm) can be accredited to the effects such as RSA, 2PA, and/or thermal processes. In the present study, the contribution of the two last mechanisms (2PA and thermal processes) has been examined. In contrast to metals in the bulk/nanoparticle form, the decorated systems demonstrated a broad optical absorption in the chosen IR region, which prompted us to investigate the broadband OL behavior.

Many of the OL materials reported in the literature are referred to as "broadband devices". However, to the best of our knowledge, there is no detailed report on an Au-Fe₂O₃-rGO based optical limiter which is actually a broad band, that is capable of limiting the input laser beams over the entire NIR region. In the composite, the origin of broadband OL action has been ascribed to the 2PA process, arising from the contribution of individual components such as sp² domain of rGO (700 nm), $n-\pi^*$ transition of rGO (800 nm), and the plasmon resonance state of Au nanoparticles (900 nm). A trend in the limiting threshold followed the same variation of the NLA coefficient (see Table 2). Among all the samples investigated, the lowest onset limiting threshold was observed for Au-Fe₂O₃-(15 wt %)rGO for all the chosen wavelengths. The lowest limiting threshold of 22.01 μ J/cm² recorded for Au-Fe₂O₃-(15 wt %)rGO with 900 nm excitation is lower than recently reported OL thresholds for other oxygenated carbon nanomaterials, suggesting the superior properties of the HEG graphene composite.³⁸

4. CONCLUSIONS

In summary, Au-Fe₂O₃-rGO nanocomposites with superior NLO properties have been directly synthesized from rGO through a simplistic, effectual, and hydrothermal method that is scalable. We have demonstrated wavelength dependent tunable NLA and broadband OL activity related with $n-\pi^*$ transition of graphene and surface plasmon state of Au NPs of Au-Fe₂O₃-rGO nanocomposite. The NLA coefficient increased with increase in the excitation wavelength, and the higher NLO coefficients obtained at 900 nm are not only due to involved longer wavelength exposure but also because of the contribution arising from the SPR of Au metal nanoparticles. The tunability of NLO properties was achieved by varying the content of rGO, and the Au-Fe₂O₃-(15 wt %)rGO nanocomposite possesses a stronger nonlinear absorption coefficient and low onset optical limiting threshold under the chosen NIR (700-900 nm) wavelength. This arises from the contribution from densely decorated Au-Fe₂O₃, increase in the number of defects due to Au-Fe₂O₃ functionalization, and onedimensional nanospindle morphology of Au-Fe₂O₃. Accordingly, Au-Fe₂O₃-(15 wt %)rGO nanocomposites have been demonstrated as promising candidates for broadband ultrafast optical limiters.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsanm.8b01544.

Figure S1: XRD and TGA pattern of pure and Au- Fe_2O_3 -rGO nanocomposite. Figure S2: FTIR pattern of pure and Au- Fe_2O_3 -rGO nanocomposite. Figure S3: Synergic effect and nucleation growth. Figure S4: photograph showing the stability of the sample in a dispersed state (PDF)

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V.R.S. and T.C.S.G. designed and planned the experiments. T.C.S.G. and M.S. performed the experiments and analyzed the data. All authors were involved in writing the manuscript and have given approval to the final version of the manuscript.

Notes

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