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Super-paramagnetic and unusual nonlinear absorption switching behavior of an *in situ* decorated CdFe₂O₄-rGO nanocomposite

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A simple strategy based on electrostatic interaction was utilized to assemble in situ cadmium ferrite of various morphologies (nanoplatelets to nanorods) on reduced graphene oxide sheets using a one-step hydrothermal reaction. With ultrafast laser excitation (800 nm, 150 fs and 80 MHz), intensity dependent open aperture Z-scan data confirmed the presence of nonlinear absorption in pure GO [saturable absorption] and CdFe₂O₄ [reverse saturable absorption]. Surprisingly, the nanocomposite exhibited unusual switching of reverse saturable absorption at low peak intensities ($I_0 = 150 \text{ MW cm}^{-2}$) to saturable absorption behavior at high peak intensities ($I_0 = 250 \text{ MW cm}^{-2}$ and 350 MW cm $^{-2}$). This unusual nonlinear absorption switching suggests the contribution of the individual components of the nanocomposite with respect to the intensity of excitation. All the samples exhibited nonlinear selfdefocusing behaviour resulting from thermally-induced nonlinear refraction. High NLO coefficients were observed for the CdFe₂O₄⁻ (15 wt%) rGO nanocomposite which can be attributed to the synergetic effects stemming from the extent of conjugation with the graphene layers and 1D nanostructures of cadmium ferrite with a large reactive surface area for optical excitations. Earlier the different loadings and their respective morphologies were investigated by XPS, Raman, TGA, FESEM and TEM studies. Furthermore, the alteration in ground-state absorption and superparamagnetic properties with trimming was also analysed. Tunability of the thermal, magnetic, linear optical and NLO properties of the composites arises mainly due to tailoring the proportion of oxygen containing groups in the graphene layer and the CdFe₂O₄ loading on the graphene sheets, and the morphology of the CdFe₂O₄·CdFe₂O₄ (15 wt%) rGO nanocomposite exhibits excellent optical limiting action, implying the potential possibility of it being used in laser safety devices.

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1 Introduction

The interest in one-dimensional (1D) nanostructures stems from their intrinsic anisotropic nature, resulting from nanoscale confinement. These 1D nanostructures manifest themselves as a variety of structural motifs, including nanowires, nanorods, nanofibres, core–shell structures, nanoribbons/nanobelts, striped heterostructures, and hierarchical assemblies.^{1–9} Spinel ferrites (MFe₂O₄) are a small group of transition-metal oxide compounds having a face-centered cubic structure with a large unit cell in which Cd²⁺ (nonmagnetic) and Fe³⁺ (magnetic) cations coordinate with the oxygen atoms at tetrahedral and octahedral sites, respectively.¹⁰ It has been reported that when the bulk spinel ferrites are scaled down to a nanometer range, modifications transpire in the surface/interface, electronic states and magnetic interactions, which lead to tunable magnetic systems.¹¹⁻¹³ 1D nanostructure spinel ferrites continue to evoke interest in research on a wide range of applications such as high-density data storage, sensors, magnetocaloric refrigeration, heterogeneous catalysis, guided drug delivery, magnetic resonance imaging and hyperthermia of cancer cells.^{14–17} Also, these ferrofluids under an externally applied magnetic field exhibit unique magneto-optical properties, which can be utilized for applications such as optical shutters, switches, tunable polarizing or phase changing elements and most importantly optical limitation.¹⁸⁻²² Several spinel ferrite based systems, such as CdFe₂O₄,¹⁰ NiFe₂O₄, ZnFe₂O₄, CoFe₂O₄,²³ $(Zn_{1-x}Cu_x)(Al_xFe_{2-x})O_4^{24}$ and MgFe₂O₄, are reported to exhibit good nonlinear optical behaviour.25 Although the NLO action at different excitations was realized with these ferrite systems, the ability to deliver ultrafast pulses with controlled microjoules of energy through flexible fibres can open up a host of possibilities towards developing robust ultrafast laser microsurgery systems.²⁶

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To realize such superior third-order nonlinear optical (NLO) devices for clinical viability, enhancement of nonlinearity to scale down the onset limiting threshold to microjoules in these ferrite systems is ultimately required which can be achieved by hybrid nanocomposite formation of ferrites with layered carbonaceous materials.^{27–29}

In this aspect, trimming of graphene based complex metal oxides such as GO-Fe₂O₄,³⁰ GO-metal porphyrin composites,³¹ GO-ZnO,³² GO-HEG,³³ GO-bimetallic³⁴ and GO-metal phthalocyanine nanocomposites³⁵ etc., has received a great deal of attention due to their myriad of potential applications in laser safety devices. In the nanocomposites, graphene can serve as a high-performance support because of its good chemical stability and huge specific surface area.³⁶⁻³⁹ Deposition of a 1D complex metal oxide on the plane of graphene can yield hybrid materials that can show a synergistic effect to induce properties that are different from those of each individual component. Although different experimental techniques have been adopted for the synthesis of ferrite with different 1D morphologies like MnFe₂O₄ nanorods by a hydrothermal route,40 CuFe2O4 nanofibres by electrospinning,⁴¹ BaFe₁₂O₁₉ nanorods by sol-gel synthesis⁴² and NiFe₂O₄ nanorods via a PEG-assisted hydrothermal route,⁴³ there are some critical issues in constructing composites of ferrites and graphene nanosheets. Ferrite particles, due to their strong magnetic attractive forces, can aggregate on the surface of the graphene substrate and, hence, do not easily form 1D nanostructures. Therefore, the major challenge is to disperse the ferrite particles uniformly on the graphene nanosheets without any aggregation. Taking these issues into consideration, this article reports on the preparation of 1D nanorods of cadmium ferrite loaded on graphene sheets by a single step hydrothermal method through the formation of physical and chemical interactions, for the first time to the best of our knowledge. Since NLO studies of CdFe2O4-rGO nanocomposites are still scarce, investigation of these hybrids can lead to new generation nano-devices for optical limiting applications (at a microjoule scale of limiting threshold) in the IR regime towards protection against laser induced damage. Herein, we demonstrate the in situ preparation of CdFe₂O₄/rGO and its structural (Raman, FESEM and TEM), thermal (TGA), magnetic (VSM) and linear optical (UV-Vis) characterizations. Finally, their NLO properties were studied by means of the Z-scan technique under 150 fs laser excitation and the effect of CdFe₂O₄ nanorod loading on the NLO response of the nanocomposite is investigated.

2 Experimental details

2.1 Material preparation and confirmation

Synthesis of graphene oxide. Graphite oxide (GO) was obtained by a modified Hummers method.⁴⁴ Firstly, 1.0 g of graphite and 1.0 g of NaNO₃ were dissolved in 46 ml of H_2SO_4 in an ice bath (0–5 °C). After stirring the mixture for 15 minutes, 6.0 g of KMnO₄ was added to the solution and the rate of addition was controlled to maintain the temperature well below 20 °C. Then the temperature of the solution was increased to

98 °C and maintained for 15 minutes. Finally, 200 ml of distilled water and 6.0 ml of H₂O₂ (30%) were added to the solution and then filtered using Whatman filter paper, followed by washing with HCl (5%) and distilled water several times. The graphite oxide suspension was centrifuged at 8000 rpm for 10 minutes and dried at 60 °C for 12 hours to obtain graphene oxide powder. To confirm the molecular formation, the synthesized powders were subjected to XPS and Raman studies. The XPS and Raman spectrum of GO is as shown in Fig. 1. In the XPS survey spectrum of GO (Fig. 1a), only two main peaks were observed at 284.6 eV and 530.0 eV which correspond to the carbon and oxygen environment of the molecule. As shown in Fig. 1b, the C 1s XPS spectrum of GO can be de-convoluted into three peaks centered at 284, 286 and 287 eV, corresponding to the C=C bond, the C-O bond and the carbonyl C=O groups of graphene oxide, respectively. These data further indicate the existence of various oxygen-containing functional groups on the GO surface. Furthermore, in the Raman spectra of GO (Fig. 1c), peaks at 1301 cm^{-1} (D-band) and 1597 cm^{-1} (G-band), also confirmed the formation of GO. Here the D peak is associated with the vibrations of carbon atoms with dangling bond in plane terminations of disordered graphite and is a breathing mode or k-point phonons of A1g symmetry, whereas the G peak corresponds to the first-order scattering of the E_{2g} mode and is related to the vibration of sp²-bonded carbons atoms in a 2-D hexagonal lattice.

Synthesis of CdFe₂O₄-rGO nanocomposites. Trimming of cadmium ferrite with various graphene oxide contents (40, 25, 15 wt%) was performed by a one-step hydrothermal reaction. Briefly, 40 wt% of GO was dispersed in 60 ml of ethanol through sonication for 1 h. Then, Fe(NO₃)₃·9H₂O and Cd(NO₃)₂·6H₂O (the molar ratio of Cd/Fe was 1:2) were dissolved in ethanol (20 ml) and stirred for 30 min. Then, the mixture was transferred into a 150 ml Teflon-lined stainless-steel autoclave and kept at 180 °C for 12 h. Then the mixture was left to be cooled to room temperature naturally. The obtained CdFe₂O₄/ rGO powder was filtered, rinsed with distilled water several times, and dried in an oven at 60 °C for 24 h. In a typical reaction, the functional groups on graphene were reduced on aqueous dispersion and the incorporated inorganic species evolve themselves into Cd²⁺ ions. Through electrostatic interactions, cadmium undergoes nucleation on the layer of GO and then develops into cadmium ferrite. The positively charged complex metal oxide nanoparticles can then be intimately mixed with aqueous dispersions of negatively charged GO through electrostatic attraction. Furthermore, the π - π interactions between the GO sheets support the selfassembly process. Although GO materials can be reduced to form reduced graphene oxide (rGO) in reducing/inert environments at elevated temperatures, and/or under alkaline conditions, here, hydrothermal reaction was used for the reduction of the GO contents, as similarly reported by others.45 In fact, as an advantage, the hydrothermal reaction not only results in an easy one-pot reaction for the synthesis of the composite, but also efficiently reduces the GO sheets that are incorporated into the composite. The pure CdFe2O4 nanoparticles were synthesized using the same method as mentioned above, without adding any graphite oxide.



Fig. 1 (a) XPS survey spectra, (b) C 1s XPS spectra and (c) Raman spectra of GO confirming the attachment of oxygen functional groups on the graphene layers.

The recorded XPS spectra of decorated rGO are shown in Fig. 2. In the XPS spectra of the nanocomposite, apart from the two main peaks around 284.6 eV and 530.0 eV which correspond to the C 1s and O 1s species of GO, three additional peaks of Cd 3d, Cd $3p_{3/2}$ and Fe $2p_{3/2}$ of CdFe₂O₄ were observed. The relative peak intensity ratio of C 1s to O 1s for the decorated

rGO hybrids was obviously larger than that of GO. Furthermore, a substantial loss of oxygen-containing functional groups was apparently observed in the XPS spectrum (Fig. 2b-d) of C 1s for $CdFe_2O_4^-$ (40 wt%, 25 wt% and 15 wt%) rGO, which strongly indicated the reduction of GO and interfacial contact of CdFe₂O₄ and GO after hydrothermal treatment. The recorded Raman spectra of the decorated rGO are shown in Fig. 3. The Raman spectrum of pure $CdFe_2O_4$ shows four peaks positioned around 213, 272, 385 and 778 cm⁻¹ which are all characteristic bands of CdFe₂O₄. Assignments of these phonon modes were carried out in accordance with the work performed by Reitz et al.46 The phonon modes at lower frequencies (213, 272 and 385 cm^{-1}) were due to the metal ion in the octahedral void and correspond to the symmetric and anti-symmetric bonding of the oxygen atom M–O bond (E_g and T_{2g}). Other phonon modes at higher frequencies (peak maxima at 778 cm⁻¹) were due to the A1g mode involving symmetric stretching of the oxygen atom with respect to the metal ion in the tetrahedral void. Furthermore, the Raman spectra of the decorated rGO system show peaks at 1301 cm⁻¹ (D-band), 1597 cm⁻¹ (G-band), 213, 272, 385 cm⁻¹ (E_g and T_{2g}) and 778 cm⁻¹ (A_{1g}) which confirms the trimming of rGO with CdFe₂O₄. All these results indicated the successful incorporation of CdFe2O4 into the reduced GO material (40 wt%, 25 wt% and 15 wt%).

2.2 Growth mechanism and morphology studies

Understanding the morphology and its growth mechanism is a crucial step for estimating the structure-property relationship of a material. The formation of GO, reduction to rGO and incorporation of cadmium ferrite were confirmed through XPS and Raman analysis. As a continuation of structural characterization, textural arrangements were analysed through FESEM and TEM analysis. Fig. 4 illustrates the FESEM images of pure and decorated rGO samples. The image of the bare GO indicates the presence of layered sheets with some crumples arising due to the strong oxidation process. Recent reports demonstrate that improved photocatalytic47 and high sensitive gas detection48 can be achieved with wrinkled and crumpled graphene sheets. Therefore, the presence of wrinkled graphene layers has provided the ability to improve the optical performance due to the increased area density of active materials over the planar film. Pure CdFe₂O₄ particles form nanoplatelet structures with severe aggregation arising due to strong magnetic attractive forces between nanoparticles. The trimming of CdFe₂O₄ on GO was confirmed through the FESEM image in which bright spots represent cadmium ferrite and dark shades corresponds to graphene layers. The loading and morphology of cadmium ferrite were found to vary with increasing graphene content. The formation of nanoplatelets (CdFe₂O₄⁻ (40 and 25 wt%) rGO) and nanorods (CdFe₂O₄⁻ (15 wt%) rGO) of cadmium ferrite was observed. EDS analysis was performed to determine the chemical compositions of the samples and is given in the inset of the FESEM figures. The EDS compositions of the samples are presented in Fig. 4f. As expected, the atomic percent of Cd and Fe was found to increase with a decrease in the graphene content attaining a maximum atomic percent of inorganic species along with the



Fig. 2 XPS survey spectra of (a) $CdFe_2O_4^-$ (40 wt%, 25 wt% and 15 wt%) rGO and C 1s XPS spectra of (b) $CdFe_2O_4^-$ (40 wt%) rGO, (c) $CdFe_2O_4^-$ (25 wt%) rGO and (d) $CdFe_2O_4^-$ (15 wt%) rGO assuring the reduction of functional groups to form reduced graphene oxide.



Fig. 3 Raman spectra of $CdFe_2O_4$ and $CdFe_2O_4$ -rGO nanocomposites with fundamental vibrational modes of cadmium ferrite and graphene.

lowest carbon for $CdFe_2O_4^{-}$ (15 wt%) rGO. The morphology and growth mechanism of the CdFe_2O_4-rGO composite nanostructure was further elucidated by TEM. Fig. 5a shows that GO displayed a wrinkled paper like structure of the ultra-thin sheets with multiple stacking arising due to vigorous oxidation involved

in the reaction mechanism. The SAED pattern [inset of Fig. 5a] of GO showed only diffraction rings, which represent the amorphous nature of GO sheets. The recorded TEM images (Fig. 5) depict the formation of $CdFe_2O_4$ nanoplatelets of diameter 38 nm, 19 nm, and 144 nm for pure $CdFe_2O_4$, (40 wt%) rGO, and (25 wt%) rGO respectively. However, with (15 wt%) rGO, $CdFe_2O_4$ forms nanorods with a diameter of 328 nm and a length of ~a few µm. The corresponding SAED pattern [inset of Fig. 5(b–e)] also shows diffraction rings along with a bright spot which signifies the polycrystalline nature of the pure $CdFe_2O_4$ and $CdFe_2O_4$ -rGO nanocomposites. In general, hydrothermal methods do not facilitate controlling the particle size and loading of cadmium ferrite. However, in the present case, loading of cadmium ferrite was altered by varying the GO content and this also led to a change in shape from nanoplatelets to nanorods.

The involved growth mechanism (Fig. 6) can be explained as follows: GO exhibits a thin sheet structure with wrinkled, folded and silk-like morphologies. Furthermore, the GO nanosheets appear as an isolated lamellar structure with a random distribution, which is convenient for the magnetic particle to anchor on the large surface of GO. Under the experimental conditions chosen, $CdFe_2O_4$ grows into nanoplatelets as the hydrothermal reaction is carried out in an autoclave chamber. It is to be noted that in the trimming process, the morphology of



Fig. 4 FESEM with corresponding EDS (inset) spectrum of (a) GO, (b) $CdFe_2O_4$, (c) $CdFe_2O_4^-$ (40 wt%) rGO, (d) $CdFe_2O_4^-$ (25 wt%) rGO and (e) $CdFe_2O_4^-$ (15 wt%) rGO, and (f) table of atomic percentages ensuring the controlled loading of cadmium ferrite on rGO.

metal oxides relies on the nucleation and growth process. Under appropriate reduction of metal precursors, the quantity of aromatic conjugated domains (number of graphene layers) and the number of oxygen containing functional groups that act as electron donating sources decide the number of nucleation sites. Thereafter the nuclei grow into complex ferrites and their shape is determined by the intrinsic energy of the crystallographic surface. Accordingly, the route to anchoring $CdFe_2O_4$ nanoparticles onto the GO sheets may be proposed as the intercalation and adsorption of cadmium and iron into layered GO sheets, followed by the nucleation and growth of $CdFe_2O_4$ crystals. Then the clusters serve as seeds for further growth to



Fig. 5 TEM images of (a) GO (layered structure), (b) $CdFe_2O_4$ (nanoplatelets), (c) $CdFe_2O_4^-$ (40 wt%) rGO (nanoplatelets of cadmium ferrite upon thin graphene layers), (d) $CdFe_2O_4^-$ (25 wt%) rGO (nanoplatelets of cadmium ferrite upon thin graphene layers) and (e) $CdFe_2O_4^-$ (15 wt%) rGO (nanorods of cadmium ferrite upon thin graphene layers) and the corresponding SAED pattern (inset).



Fig. 6 Schematic diagram of the growth mechanism of CdFe₂O₄-rGO nanocomposites.

form larger nanostructures. In the present case, with an increase in the content of GO (15 to 40 wt%), the number of nucleation sites varies and hence the growth also varies.

For 40 wt% and 25 wt% GO content, the high density of oxygen moieties and graphene layers promotes more nucleation than growth and thus $CdFe_2O_4$ preferred its natural growth into nanoplatelets due to the availability of a large surface area. However, at (15 wt%) rGO, the surface area is limited and, therefore, $CdFe_2O_4$ nanoparticles accumulate themselves and grow into nanorods. Here with 15 wt%, the number of nucleation sites is restricted due to the reduced number of graphene layers (limited surface area) and the growth process is promoted to attain a nanorod structure through natural magnetic attractive forces.

2.3 Physical measurements

The surface composition and carbon state of the products were determined by X-ray photoelectron spectroscopy (XPS, MULTI-LAB 2000). The Raman spectra of pure GO and spinel ferrite decorated GO were obtained using a Raman spectrometer (Horiba-Jobin, Lab RAM HR) at ambient temperature using a 632 nm excitation wavelength. The morphologies of the samples were investigated using a field emission scanning electron microscope (FEI-QUANTA-FEG 250) and a high-resolution transmission electron microscope [TECNAI F (S-Twin)]. A thermogravimetric analyzer (Perkin Elmer) was used to measure the thermal stability of the samples in air in the temperature range of 25–740 °C and at a heating rate of 15 °C min⁻¹. A magnetic hysteresis study of spinel ferrite decorated graphene oxide was

carried out using a vibrating sample magnetometer (VSM; Lake Shore: model: 7404) in the magnetic field range of -1.5 Tesla to +1.5 Tesla. UV-visible absorption spectra of the samples were recorded using a JASCO Corp., V-570 spectrophotometer. The third-order nonlinear optical properties were determined by Z-scan measurements using a Ti:sapphire laser having a pulse width of 150 fs at 800 nm with peak intensities of 150, 250 and 350 MW cm⁻². The laser was focused with a plano-convex lens with a focal length of 100 cm while the input beam diameter was 2 mm.

3 Results and discussion

3.1 Thermal (TG/DTA) and magnetic (VSM) studies

The obtained hybrid material is expected to possess improved thermal and peculiar magnetic behaviour compared to the individual counterparts. Also, the employed hydrothermal method has provided an opportunity to alter the loading of cadmium ferrite which can be estimated through TG/DTA analysis. Hence thermogravimetric analysis was carried out to reveal the thermal stability and percentage composition of CdFe₂O₄ in the nanocomposite. The recorded TG and DTA curves are shown in Fig. 7(a and b). For pure GO, a weight loss of $\sim\!18\%$ was observed between 32 and 100 $^\circ\!\mathrm{C}$ and this can be attributed to the vaporization of absorbed water along with various functional groups anchored during Hummer's treatment. With further increase in temperature, the material suffered a large weight loss of 58% which corresponds to the decomposition of graphene layers leaving almost no residue at 300 °C. For bare CdFe₂O₄, first an exothermic peak at 296 °C with 5% weight loss was observed due to the removal of atmospheric water. The second exothermic peak at 380 °C represents the removal of excess nitrate absorbed during the reaction (11%) and the residue left at 730 °C was 83%. For (15 wt%) rGO, the TG/DTA curve almost resembles the pattern of pure CdFe2O4 with two exothermic peaks at 298 °C (7%) and 380 °C (15%) attributed to the removal of the absorbed functional groups and decomposition of GO respectively. For higher content (25 and 40 wt%) rGO samples, the exothermic peaks shift to higher temperatures due to the functional groups observed. Here the first exothermic peak at 371 °C (12%) and 372 °C (15%), and the second exothermic at 449 °C (21%) and 453 °C (27%) was due to the decomposition of GO for the 25 wt% and 40 wt% decorated rGO samples respectively. From the residues left in the nanocomposites, the percentage composition of CdFe₂O₄ was found to be about 76%, 72% and 65% for (15, 25 and 40 wt%) rGO respectively. This further confirms that the hydrothermal method has successfully loaded different contents of cadmium ferrite onto the graphene layers. Although the pattern of degradation is the same for the pure and decorated samples, the degradation temperature of the CdFe₂O₄-rGO composite is higher than that of GO. This was due to the weakening of interactions among the GO sheets which was achieved by the introduction of CdFe₂O₄. The attenuation of absorption among the GO sheets (due to the absorbed Cd²⁺ and Fe³⁺ ions on the surface) and the destruction



Fig. 7 (a) TG and (b) DTA curves of pure GO, $CdFe_2O_4$ and $CdFe_2O_4$ -rGO nanocomposites.

of regularity of the GO sheets (anchored $CdFe_2O_4$ nanoparticles) has destroyed the interactions among GO sheets. This resulted in the improved degradation temperature of the $CdFe_2O_4$ -rGO composite compared to GO.

Combinations of nonmagnetic GO with magnetic CdFe₂O₄ yield peculiar magnetic properties for the composite. Accordingly, the isothermal magnetization M(H) curves of pure CdFe₂O₄ and the rGO nanocomposites with cadmium ferrite were obtained at room temperature and are shown in Fig. 8. All the samples exhibit a nonlinear and reversible 'S' behavior with an almost immeasurable magnetic hysteresis loop. The curves do not get saturated up to +15 000 Gauss with coercivity and remanence values approaching zero suggesting the presence of superparamagnetic behavior. Also, a similar superparamagnetic behavior was observed for graphene/ZnFe2O4 nanocomposites.49 The magnetic remanence of CdFe₂O₄, and CdFe₂O₄⁻ (40, 25, and 15 wt%) rGO was found to be 0.0444, 0.0238, 0.0213, and 0.0074 emu g^{-1} , which shows that there was almost no magnetization left after the removal of the external magnetic field. There is no sign of saturation in magnetization due to the disordered surface-spin structure and the saturation magnetization at the maximum applied field is 0.227, 0.090, 0.084 and 0.007 emu g^{-1} for CdFe₂O₄ and CdFe₂O₄⁻ (40, 25, and 15 wt%) rGO respectively. A lower value of saturation magnetization was Paper



Fig. 8 Room temperature M-H curves of the pure CdFe₂O₄, CdFe₂O₄⁻ (40 wt%) rGO, CdFe₂O₄⁻ (25 wt%) rGO and CdFe₂O₄⁻ (15 wt%) rGO.

also observed in superparamagnetic Fe₃O₄/PZS nanofibers.⁵⁰ The reduction and variation in magnetic coefficients of the nanocomposites compared to the bare cadmium ferrite can be attributed to a range of factors such as the interaction of nonmagnetic GO, size reduction, morphology and different loadings of cadmium ferrite. As observed in thermal analysis, different contents of CdFe₂O₄ (76% - 15 wt%, 72% - 25 wt% and 65% - 40 wt%) has varied the magnetic coefficients. This clearly suggests that the magnetic properties of the nanocomposites could be tuned by changing the ratio of cadmium ferrite to GO. It is also interesting to note that the cadmium ferrite prepared by a combustion method exhibits antiferromagnetic behavior¹⁰ which is quite different from the superparamagnetic behavior of cadmium ferrite synthesized by the hydrothermal method. This is because in the present case, the presence of isolated non-interacting particles with elementary magnetic moment dipoles arrange in a parallel direction and the magnetic moments of the particles arrange randomly with negligible magnetic interaction of particles resulting in superparamagnetism. The isolated lamellar structure with wrinkled, folded and silk-like morphologies provides an opportunity for the magnetic particles to anchor onto the large surface of rGO. Cadmium ferrite being the magnetization contributing entity, its morphology plays a significant role in deciding the ordering and magnetization of the sample. As nanorods were formed by the agglomeration of magnetic nanoparticles, the Bloch walls of the rods increase with the growth of grains. And as the energy of magnetic particles in an external magnetic field is proportional to the number of nanoparticles in a single magnetic domain, CdFe2O4-rGO (15 wt%) possesses stronger superparamagnetism than other samples. The coercivity of the samples was estimated to be 282, 276, 278, and 293 Gauss and the existence of nonzero coercivity with super-paramagnetism was due to anisotropy and size distribution. Among the samples, the CdFe₂O₄-rGO (15 wt%) nanocomposite has higher coercivity than the pure system arising from the contribution of the nanorod morphology. This is because one dimensional structures possess increased magnetocrystalline, large shaped anisotropy, higher aspect ratio, and low spin disorder on the surfaces, which exerts an influence on higher coercivity. Super-paramagnetism with higher coercivity was observed and reported for the Fe–Al₂O₃ system.⁵¹ By tuning the magnetic properties of the nanocomposites, the magnetic anisotropy of the magnetic ion at the interfaces can be reduced which leads to a strong nonlinear optical response. One of the advantages of using magnetic nanoparticles in optical devices is that it may be possible to control their optical properties through the application of external magnetic fields. The super-paramagnetic properties of the CdFe₂O₄–rGO composites are similar to those of Fe₃O₄ nanocrystals loaded on GN sheets⁵² and Ni nanoparticles, and thus they can be utilized for practical applications in the fields of bio-nanotechnology/controlled targeted drug delivery, field-modulated gratings, and optical switches.

3.2 Ground state and intensity dependent nonlinear absorption

Interaction of electronic states of GO and cadmium ferrite can alter the band structure of the composite. For complete realization of NLO applications, studying the linear and nonlinear absorption of the materials is very essential. Linear (ground state) and nonlinear (intensity dependent) optics of the samples were analysed under conventional and laser excitation. Fig. 9 shows the ground state absorption spectrum of pure and spinel ferrite decorated reduced graphene oxide dispersed in ethylene glycol. The characteristic absorption peaks of GO were observed at 230 nm and 292 nm which arise due to π - π * and π -n transition of graphene sheets respectively. The characteristic absorption peak of cadmium ferrite was observed at around 425 nm. The simultaneous appearance of peaks due to both graphene and CdFe₂O₄ in the absorption spectra of the decorated samples is a clear indication of the formation of the CdFe₂O₄-rGO nanocomposite. However, in the decorated graphene oxide, the peak at 425 nm got suppressed and the characteristic peak of GO suffered a bathochromic shift to 389 nm. This red shift was attributed to the deoxygenation of GO sheets and the formation of a composite between CdFe₂O₄ nanoparticles and graphene sheets.



Fig. 9 UV-visible absorption spectra of pure GO, $CdFe_2O_4$ and $CdFe_2O_4$ -rGO nanocomposites.

Upon increasing the GO content, a new absorption peak at 206 nm arises due to the decrease in functional groups and weak interlayer coupling between the layers, causing electrons to be easily excited at lower energy levels.

From the absorption tail, the optical band gap of the samples was estimated to be 2.92 eV and 3.19 eV for cadmium ferrite and decorated rGO respectively. Thus, the incorporation of inorganic species has significantly altered the electronic states of the compound which is a very essential criterion to demonstrate energy absorbing broad band optical limiters. Among all the samples, absorbance of pure GO was observed to be higher due to the presence of oxygen containing functional groups and due to the decrease in conjugation. Reduction of GO provides a highly restored conjugated network in rGO form and hence for decorated samples the absorbance hypochromically shifted due to the decoration of cadmium ferrite. The presence of higher linear transmittance in the NIR region (800 nm) and the varying electronic states suggest the suitability of the materials for third-order NLO applications like optical limitation against ultrafast IR lasers.

Intensity dependent nonlinear absorption of the samples was studied using an open aperture Z-scan experiment performed at different excitation powers using a Ti:sapphire laser. The recorded open aperture pattern for the pure and decorated system in the input intensity range of 150–350 MW cm⁻² is as shown in Fig. 10. The observed intensity dependent nonlinear absorption $\alpha(I)$ is governed by the equation⁵³

$$\alpha(I) = \frac{\alpha}{1 + I/I_{\rm s}} + \beta_{\rm eff}I$$

where the nonlinear absorption coefficient, β , relates to the twophoton absorption (2PA) or RSA occurring at low intensities, while I_s represents the saturation intensity related to the SA response. The intensity variation equation was solved numerically within the thin sample approximation, to calculate the laser beam intensity as a function of the propagation depth in the sample z' under the appropriate initial conditions⁵⁴

$$\frac{\mathrm{d}I}{\mathrm{d}Z'} = -\alpha(I) \cdot I$$

To find the nature and strength of nonlinear absorption we numerically fitted the measured data to the corresponding net transmission for open aperture data using the relation⁵⁵

$$T_{\rm OA} = \frac{1}{\sqrt{\pi} \left[\frac{\beta I_0 I_{\rm eff}}{(1+Z^2/Z_0^2)} \right]} \int_{-\infty}^{\infty} \ln \left[1 + \frac{\beta I_0 I_{\rm eff}}{(1+Z^2/Z_0^2)} \exp(-t^2) \right] dt$$

where *T* is the normalized transmittance; I_0 is the peak on-axis irradiance at the focus; Z_0 is the Rayleigh length; and l_{eff} is defined as $l_{\text{eff}} = [1 - \exp(-\alpha L)]/\alpha$ with α as the linear absorption coefficient, and *L* as the path length of the sample. Under ultrafast excitation, the presence of the peak at focus (*Z* = 0) for all input intensities (Fig. 10a) shows that GO exhibited saturable absorption (SA) characteristics similar to graphene.²⁸ Here under a high enough intensity of photoexcitation, a non-equilibrium population was formed and all the available states in the higher

energy state are occupied by photo-generated carriers which resulted in ground state bleaching and saturable absorption due to Pauli blocking. The estimated nonlinear absorption coefficient (Table 1) was found to increase with the input intensity and so saturable absorption behaviour depicting high linear transmittance at higher intensities was observed for pure GO. Thus, GO with its unique electronic band structure and energy dispersion being linear to the vicinity of the *k* point can act as an excellent saturable absorber that finds potential applications in optical switching, pulse shaping and mode-locking.⁵⁶

The OA data recorded for $CdFe_2O_4$ (Fig. 10b) displayed a minimum transmittance at the focus (Z = 0) and this corresponds to the reverse saturable absorption (RSA) behaviour. To identify the involved nonlinear absorption mechanism, the experimental data were fitted with the standard equations and were found to be best fitting for the two-photon absorption equation. Furthermore, it is well known that the 2PA process can take place when the laser energy is larger than half of the band gap of the material ($h\nu > E_g/2$). Hence with NIR excitation (800 nm, 1.55 eV), the involved electronic transition is the simultaneous absorption of two photons to transit to a higher energy state of cadmium ferrite (425 nm, 2.92 eV). The very little absorption in the excitation region without any available electronic state at excitation (800 nm, 1.55 eV) suggests the nonlinear absorption to be a genuine 2PA process, rather than a two-step absorption process. Furthermore, the estimated nonlinear absorption coefficient of cadmium ferrite was independent of the input intensity which further confirms the involved nonlinear absorption as 2PA. A similar 2PA behavior of cadmium ferrite prepared by the combustion method¹⁰ under single shot excitation was reported whose 2PA coefficient was found to be lower than the present case, suggesting the superiority of CdFe₂O₄ obtained by the hydrothermal process.

The OA patterns [Fig. 10(c-e)] of the nanocomposite showed a peculiar combination of saturable and reverse saturable absorption patterns. At lower input intensity ($I_0 = 150 \text{ MW cm}^{-2}$), the decorated samples exhibited an RSA (valley) pattern and the experimental data were found to be best fitting for the two photon absorption equation. While for high intensities ($I_0 = 250$ MW cm⁻² and 350 MW cm^{-2}) the samples displayed SA (peak) behaviour. Although plenty of reports are available on the transition of SA to RSA with an increase in input intensity, very limited reports of RSA at low intensities and SA at high intensity are available in the literature.⁵⁷ The peculiar transition of RSA to SA may originate due to the involvement of different molecules in the composite under excitation. Here at low intensity, the nanocomposite exhibits an RSA pattern due to the 2PA process similar to the behaviour of pure cadmium ferrite. This suggests the involvement of σ -states (sp³) due to the incorporation of cadmium ferrite resulting in the 2PA process. At high intensity, the large numbers of photons are involved in the production of free carries in the graphene band structure which results in a strong one photon absorption process leading to SA. Therefore, the study of the SA pattern suggested the involvement of graphene like carbon sites (π -states, sp² hybridization). Unlike graphene, sp² and sp³ hybridization coexists in GO and here the carbon sites give rise

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Fig. 10 Intensity dependent OA Z-scan curve (scattered points are the experimental points and solid lines are 2PA theoretical fitting) of the pure (a) GO, (b) cadmium ferrite and (c-e) $CdFe_2O_4^-$ (40, 25 and 15 wt%) rGO.

Table 1 Estimated third-order NLO coefficients of the compounds in the present study

NLO parameters	800 nm, 150 fs, 80 MHz excitation				
	GO	$CdFe_2O_4$	CdFe ₂ O ₄ -rGO (40 wt%)	$CdFe_2O_4$ -rGO (25 wt%)	CdFe ₂ O ₄ -rGO (15 wt%)
$\beta \times 10^{-12} \text{ m W}^{-1}$ at $I_0 = 150 \text{ MW cm}^{-2}$	-3.7 (SA)	+9.3 (RSA)	+3.8 (RSA)	+11.0 (RSA)	+21.1 (RSA)
$\beta \times 10^{-12} \text{ m W}^{-1}$ at $I_0 = 250 \text{ MW cm}^{-2}$	-6.5 (SA)	+9.0 (RSA)	-0.4 (SA)	-0.9 (SA)	-1.1 (SA)
$\beta \times 10^{-12} \text{ m W}^{-1}$ at $I_0 = 350 \text{ MW cm}^{-2}$	-3.7 (SA)	+0.8 (RSA)	-1.7 (SA)	-2.2 (SA)	-1.3 (SA)
$n_2 \times 10^{-16} \text{ m}^2 \text{ W}^{-1}$ at $I_0 = 150 \text{ MW cm}^{-2}$	-9.92	-6.71	-1.48	-1.49	-4.29
$\chi^{(3)} \times 10^{-14}$ esu at $I_0 = 150$ MW cm ⁻²	4.86	3.02	6.71	2.10	7.12

to π -states and other functional groups result in σ -states. The observation of SA in all the three intensities of excitation suggested the dominance of sp² clusters in GO. Upon trimming, the sp²/sp³ ratios get altered and this resulted in the modification of the energy band gap. Here, although the conditions of 2PA were not completely satisfied as in the case of pure cadmium ferrite, the possibility of 2PA cannot be completely ignored. The obtained experimental data were fitted with theoretical equations and were found to be best fitting for SA along with a weak 2PA process. Although the π -state is responsible for SA, the presence of σ -states should also to be taken into account. This is the reason why a weak 2PA coexisted with strong SA in the nanocomposite at high intensities. As the band gap of the decorated rGO comes close to the vicinity of excitation, the presence of the real electronic near excitation states (1.55 eV) suggested the possibility of a sequential 2PA process. Hence, in the decorated samples the observed nonlinearity was due to effective 2PA (which is genuine 2PA for pure cadmium ferrite). A similar observation of this combined effect of SA with weak 2PA was already reported for SWCNTs.58 Furthermore it was observed that the 2PA co-efficient was found to increase with decreasing GO content. Due to the higher content of graphene, the 2PA co-efficient of the (40 wt%) rGO composite was lower than that of pure cadmium ferrite.

The peculiar transition of nonlinear absorption (RSA to SA) in the nanocomposite can possibly be attributed to the contribution of individual counterparts (CdFe₂O₄–RSA and GO–SA) with respect to the intensity of excitation. It is known that sp² and sp³ hybridization coexists in GO and here the carbon sites give rise to π -states and other functional groups result in σ -states. At low intensities, the nanocomposite exhibits an RSA pattern due to the 2PA process and interaction occurs at the band states of CdFe₂O₄ (which comes at proximity to excitation). This suggests the involvement of σ -states (sp³) due to the incorporation of cadmium ferrite resulting in the 2PA process. At high intensity, a strong one photon absorption process occurs at the graphene band structure (π -states, sp² hybridization) leading to SA. Although the π -state is responsible for SA, the chance of σ -state involvement has resulted in the coexistence of weak 2PA with strong SA. The maximum 2PA coefficient of 21.1×10^{-12} m W⁻¹ for (15 wt%) rGO with two-fold increase compared to pure cadmium ferrite was due to the involvement of high content and one-dimensional morphologies of cadmium ferrite which resulted in shortening of the path of carrier transportation, enhancing the carrier collection ability and function as an electron expressway in the axial direction in a 1D structure. Intensity dependent variation of the effective 2PA coefficient of 3×10^{-14} m W⁻¹ by using fs laser pulses at 800 nm laser radiation for GO dispersions in water was reported earlier by Ran et al.⁵⁹ Under similar experimental conditions (800 nm, 100 fs), the 2PA coefficients of CdO $(7.1 \times 10^{-15} \text{ m W}^{-1})$,⁶⁰ NF-RGO/Ag (6.7 \times 10⁻¹⁵ m W⁻¹),⁶¹ sulfonated graphene oxide $(2.0 \times 10^{-14} \text{ m W}^{-1})$,⁶² Bi₂S₃ and Bi₂S₃@Au nanocomposites $(0.0016 \text{ and } 0.6 \text{ cm GW}^{-1})$,⁶³ and Ni-Ag NPs $(6.3 \times 10^{-15} \text{ m W}^{-1})$ ⁶⁴ were found to be lower than that of the cadmium ferrite-rGO nanocomposite. Thus CdFe₂O₄-rGO (15 wt%) with the maximum 2PA coefficient guarantees a stronger nonlinear absorption leading to effective limiting action (in the order of μ J cm⁻²) against highly intense short pulse lasers.

3.3 Nonlinear refraction and optical limiting action

Apart from nonlinear absorption, understanding the nonlinear refraction of the material helps to evaluate the ultrafast thermal nonlinearity. To evaluate the NLO refraction of the pure $CdFe_2O_4$ and nanocomposites, the recorded closed aperture pattern at lower intensity ($I_0 = 150 \text{ MW cm}^{-2}$) is shown in Fig. 11. The CA Z-scan of the pure and decorated system dispersion was found to exhibit a peak-valley configuration, characteristic of self-defocusing behaviour, *i.e.*, negative non-linear refraction. The n_2 value was obtained by fitting the normalized transmittance *versus* the sample position with the theoretical equation given by⁴⁹

$$T_{\rm CA} = 1 + \Delta \phi \frac{4(Z/Z_0)}{\left(1 + (Z/Z_0)^2\right) \left(9 + (Z/Z_0)^2\right)}$$



Fig. 11 (a) CA Z-scan pattern of pure GO and CdFe₂O₄-rGO. (b) Optical limiting properties of CdFe₂O₄ and CdFe₂O₄⁻ (40 wt%, 25 wt% and 15 wt%) rGO (scattered points are the experimental points and solids are the theoretical fitting) at an intensity of 150 MW cm⁻².

where (Z/Z_0) is the diffraction length, $\Delta \phi = kn_2I_0L_{\rm eff}$ is the on-axis phase shift at focus, *k* is the wave number, $Z_0 (= n\pi\omega_0^2/\lambda)$ is the Rayleigh range and ω is the beam spot radius at focus. The estimated value of nonlinear refractive index is given in Table 1.

It is to be observed that the nonlinear refractive index was found to be maximum for bare GO and minimum for CdFe₂O₄. This interesting combination has resulted in the varying of the n_2 value between these two extremes with the GO content. The high n_2 value of GO suggests the dominance of optical Kerr nonlinearity (thermal) due to the stronger thermal conducting properties of the planar structure. Because of the high repetition rate of the laser involved, thermal contribution was found to be more dominant. As the samples have layered carbon structures the thermal diffusion is very high for GO and hence it possesses a higher n_2 value. The formation of negative thermal lensing with different nonlinear refractive indexes is an interesting parameter to achieve optical limiting action with tunable threshold. As nonlinear refraction is stronger than nonlinear absorption, $\chi^{(3)}$ variation follows a similar trend of n_2 change. Here GO possesses maximum $\chi^{(3)}$ and it is found to be lower for the (40 wt%) rGO composite.

As graphene is dispersed in solution, π -electrons, reorientation, alignment of the graphene sheets and thermal effects from solution dispersions can also contribute to nonlinear refraction. Thus, unlike the case of single layer or few-layer graphene on substrates, the NLR response and n_2 value of graphene sheets or GO sheet dispersions is the sum of NLR signals from many sheets interacting with the laser pulse. The obtained n_2 and $\chi^{(3)}$ values are presented in Table 1. Upon decoration, the values of n_2 and $\chi^{(3)}$ are observed to vary with the content of CdFe₂O₄ on the GO sheets. It is well known that the estimated third-order NLO properties strongly depend on the input laser properties used for excitation. Gnoi et al.65 and Makhal et al.66 demonstrated that the cumulative thermal effects contribute to the overall nonlinearity when excited with high-repetition-rate laser pulses. In addition, owing to the heat conduction process, the thermal nonlinear response presents a nonlocal behaviour, which can be exploited in the investigation of several nonlocal nonlinear phenomena, such as spatial soliton propagation and shock waves. The thermally induced nonlinearity denotes temporal variation of optical parameters due to linear and nonlinear absorption in the medium followed by a non-radiative relaxation down to the ground state. Furthermore, the laser heating leads to the generation of an acoustic wave that changes the medium density followed by a variation in the refractive index. The presence of self-defocusing along with the observed 2PA makes the pure cadmium ferrite and nanocomposites suitable for optical limiting action under given laser excitation. The variation in the third-order NLO behaviour and its coefficients arises mainly due to the contribution from the following factors: (i) tailoring the proportion of oxygen containing groups in the graphene layer, (ii) the CdFe₂O₄ loading on the graphene sheets and (iii) the morphology of CdFe₂O₄. The exact reason for the change in the nonlinear optical behaviour with morphology is not clearly understood, however there are some literature studies suggesting that the size and the shape of the nanoparticles will strongly affect the nonlinear optical behaviour. Furthermore, 1D nanostructures tend to retain

high surface-to-volume ratios and large reactive surface areas and so they are capable of efficiently transporting electrons and optical excitation. Altogether CdFe₂O₄-rGO (15 wt%) possesses a higher 2PA coefficient, a stronger nonlinear refractive index and TONLO susceptibility. Generally, magneto-optical effects in magnetic fluids are believed to be the consequence of anisotropy in dielectric constant induced by the orientation of the suspended particles. When the particles form chains in the direction of an applied magnetic field a kind of mechanical anisotropy is induced. The induced anisotropy results in optical anisotropy in the refractive index, in the absorbance, or in both. Usually, superparamagnetism originates due to magnetic anisotropy in materials. The observed superparamagnetic behavior was mainly from the contribution of cadmium ferrite nanoparticles in which a fraction of Fe^{III} was distributed out of the preferred octahedral A sites to tetrahedral B sites leading to the coupling between the cations. During the synthesis of the CdFe₂O₄-rGO, some oxygen-containing groups on the surface of GO are partially removed by hydrothermal treatment, and the extent of conjugation is thereby further increased. The larger the extent of conjugation, the higher the chance of electron/energy transfers, leading to an enhanced nonlinear optical response. Hence functionalization of cadmium ferrite on GO has introduced more sp³ defect levels (enhanced NLO response) and led to the emergence of a localized magnetic moment (superparamagnetic nature). Tailoring of functional groups has varied the number of nucleation sites leading to different contents of cadmium ferrite with different morphologies. This interesting variation has brought about significant variation in the ordering of magnetic particles resulting in altering magnetic behavior. CdFe₂O₄⁻ (15 wt%) rGO with stronger superparamagnetic behavior and high coercively has attained the maximum nonlinear absorption coefficient. The next step of this investigation will be to determine the influence of the magnetic field on nonlinearity of the samples. Preliminary results indicate that the nonlinearity and optical limiting action can be tuned under the external magnetic field and research on the effects of the magnetic field is in progress.

It is to be noted that as short pulse lasers allow high precision microsurgery with minimal invasiveness, high repetition rate femtosecond laser are under prime utilization. Hence femtosecond laser microsurgery has emerged strongly in tissue ablation, studying neural injury, and cleaving microtubules which require energy pulses on the order of microjoules. As the intensity threshold to attain controllable photochemical damage with a high repetition rate femtosecond laser (800 nm, 10 fs) is \sim 3 \times 10¹¹ W cm⁻², safety measures of using optical limiters to control fluence (of the order of µJ cm⁻²) are ultimately required.⁶⁷ Optical limiting (OL) curves, illustrated in Fig. 11, were extracted from the corresponding open-aperture fs Z-scan data. The position dependent fluence was evaluated using the relation $F(z) = 4\sqrt{\ln 2} \left(\frac{E_{\text{in}}}{\pi^{3/2}}\right) \omega(Z)^2$ where F(z) is the input fluence, E_{in} is the laser energy and ω_0 is the laser beam radius at the focus.41 The transmittance decreases rapidly with increased input fluence for all the samples. The OL onset values, defined as the incident fluence at which optical limiting

activity starts, was calculated to be 0.90 μ J cm⁻², 3.23 μ J cm⁻², 2.00 μ J cm⁻² and 0.65 μ J cm⁻² corresponding to pure CdFe₂O₄ and CdFe₂O₄⁻ (40 wt%, 25 wt% and 15 wt%) rGO, respectively. In the case of trimming of rGO, it was observed that the sample exhibits strong two-photon absorption and therefore is responsible for the limitation reported here. The improved OL effect in CdFe₂O₄⁻ (15 wt%) rGO may be attributed to 2PA at lower intensity due to the presence of CdFe₂O₄ nanorods in the GO sheets. The delivery of limitation at microjoules open the utility of the composite in microsurgery applications with ultrafast IR laser like surgical excision of polyps, cysts, lesions, and tumors. However, it must be noted that still an intense experiment has to be carried out to realize such precise applications. With sufficient energies to overcome tissue scattering at a microjoule level, subsurface ablation *via* an endoscopic device also becomes a real possibility.²⁶

4 Conclusions

In summary, employing a simple one-step hydrothermal method, trimming of cadmium ferrite upon graphene layers was successfully performed. The formation of CdFe₂O₄-rGO with different contents and morphologies (nanoplatelets to nanorods) of cadmium ferrite was confirmed through the Raman, XPS, FESEM and TEM analysis. The nanocomposites possess superparamagnetic behavior with negligible remanence $(0.0238-0.0074 \text{ emu } \text{g}^{-1})$, saturation magnetization (0.090–0.007 emu g^{-1}) and non-zero coercivity (276-293 Gauss) due to disordered surface-spin structures. A hydrochromic shift in the NIR region and varying electronic states due to the incorporation of CdFe₂O₄ into rGO were observed in ground-state absorption studies. Intensity dependent nonlinear absorption Z-scans expose the interesting transition of RSA (150 MW cm⁻²) to SA (250, 350 MW cm⁻²) in the nanocomposite. This peculiar switching behavior arises due to the contribution of CdFe₂O₄ (RSA, sp³, σ -states) at low-intensity and graphene layers (SA, sp², π -states) at high-intensity. A closed aperture Z-scan confirms the presence of self-defocusing and the dominance of optical Kerr nonlinearity (negative lens effect). The nanocomposite exhibits optical limiting action at low-intensity of excitation and the onset-limiting threshold was found to be in the range of 3.23-0.65 μ J cm⁻². Among the nanocomposites, CdFe₂O₄⁻ (15 wt%) rGO exhibits stronger nonlinear absorption coefficients (21.1 \times $10^{-12} \text{ m W}^{-1}$) and lower onset-limiting threshold (0.65 µJ cm⁻²), making it a preferable candidate for optical limiting applications and most-particularly in microsurgery systems.

Conflicts of interest

There are no conflicts to declare.

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