Mass ratio-dependently tunable enhancement of the optical nonlinearities of SnO$_2$/RGO composites

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Abstract

The composite of graphene and semiconductor nanoparticles has attracted increasing interest in the search for novel nonlinear optical materials. Herein, composites of reduced graphene oxide (RGO) and SnO$_2$ nanoparticles with different mass ratios were synthesized via a facile hydrothermal method. The structural morphology and basic physical properties of the SnO$_2$/RGO composites were characterized using TEM, SEM, XRD, Raman, XPS and UV–Vis spectra, indicating that SnO$_2$ nanoparticles were uniformly anchored on the surface of graphene nanosheets through covalent and partial-ionic bonds. The third-order optical nonlinearities of the composites were studied for the first time by the Z-scan technique using a picosecond laser at 532 nm. It was found that the composites demonstrated saturable absorption and positive nonlinear refraction properties, and both were significantly enhanced compared with pure SnO$_2$ nanoparticles and RGO nanosheets, and the enhancement was tunable with the variation of SnO$_2$:GO mass ratio. The maximum saturable absorption coefficient and the third-order susceptibility of the as-prepared SnO$_2$/RGO composites were obtained to be $-2.93 \times 10^{-11}$ m W$^{-1}$ and $2.25 \times 10^{-11}$ esu, respectively. The maximum saturable absorption modulation depth obtained was 10% with the corresponding saturation light intensity of 0.3 GW cm$^{-2}$. Moreover, the optimised third-order susceptibility of SnO$_2$/RGO was found much greater than many other materials ever studied. Several involved factors contributing to the nonlinearities were discussed. The results propose that the third-order optical nonlinearities of SnO$_2$/RGO and other similarly structured composites can be potentially tuned to meet certain application requirements of nonlinear optical devices by controlling the mass ratio of semiconductor to graphene.

1. Introduction

Two-dimensional materials have been extensively studied for applications in the field of optics, such as optical switches, optical signal processing, and optical communication [1–6]. In order to develop new optoelectronic materials, graphene, as a special two-dimensional material discovered a decade ago, has always been the focus of attention due to the unique structure and properties, such as broadband saturable absorption thanks to its zero band gap, large specific surface area of 2600 m$^2$·g$^{-1}$ and high electron mobility of $2.5 \times 10^5$ cm$^2$·V$^{-1}$·s$^{-1}$ at room temperature [7–11]. However, despite the advantages of broadband saturable absorption, the zero band gap also leads to the disadvantages of small nonlinear absorption coefficient and low modulation depth, which limits its applications in nonlinear optical devices. To solve this problem, a strategy of functionalizing graphene with semiconductor quantum dots has been proposed to improve the optical nonlinearities. For example, Zhu et al analyzed the synergistic mechanism between CdS and graphene which enhanced the nonlinear optical (NLO) response of CdS functionalized graphene composites [12]. Chen et al studied ZnSe size dependent enhancement of the third-order NLO effect of
ZnSe/graphene composites [13]. Zhao et al obtained superior optical limiting properties of graphene-PbS nanohybrid [14]. So far, this strategy has been applied in many studies and proved to be effective [15, 16].

Generally, the direct composite efficiency of graphene and semiconductor nanoparticles is very low, because the two-dimensional structure of graphene is only composed of sp² hybrid carbon atoms, thus there is no site on the surface of graphene that can be combined with nanoparticles. Whereas, graphene oxide (GO), an intermediate product of graphene prepared by graphite oxide reduction method, is composed of carbon atoms with sp² and sp³ hybrid structure. Compared with graphene, GO has a large number of various oxygen-containing groups on the surface. These oxygen-containing groups give GO not only many unique nonlinear optical properties [17–20], but also great potential for fabricating composite materials [21]. Hence, the graphite oxide reduction method is generally used to prepare graphene and its composites with other materials, which could provide a way to form a complex of graphene with semiconductor quantum dots, metal nanoparticles, etc., through covalency, hydrogen bonding, or electrostatic adsorption [22].

SnO₂ is a typical wide band gap semiconductor material. Its preparation process is simple, non-toxic and low cost. Due to the excellent electrochemical properties, it has been used as a battery electrode material [23, 24]. Moreover, because of the large response range, fast response speed, high repeatability to special gases and excellent conductivity, it also has been used in sensors and capacitors [25–29]. Nevertheless, its application in NLO devices has rarely been found since the less research on the NLO properties of SnO₂ and its composites with graphene.

The main motivation of this work is to explore the third-order optical nonlinearities of graphene functionalized by SnO₂ quantum dots. The samples of SnO₂/GO composites with different mass ratios of SnO₂:GO were synthesized by a facile hydrothermal method, in which GO was first prepared from graphite powder and then SnO₂/GO were prepared. Due to the presence of hydroxyl and carboxyl groups in GO, SnO₂ were less aggregated and uniformly distributed on the surface of RGO nanosheets via covalent and partial-ionic bonds, which was confirmed by morphology and structure characterizations. The nonlinear absorption and the third-order susceptibility of the samples were studied using open aperture and closed aperture Z-scan technique with the excitation of a picosecond pulsed laser at 532 nm. The as-prepared SnO₂/GO composites exhibited significantly enhanced saturation absorption and nonlinear refraction index compared to the individual components, and the enhancement was tunable with the mass ratio of SnO₂:GO. Furthermore, the SnO₂/GO composites had larger modulation depth and smaller saturable intensity compared to the individual components. The mechanism of the nonlinear enhancement was discussed based on the synergistic effect and charge transfer process between SnO₂ and RGO.

2. Experimental methods

2.1. Preparation of GO

The modified Hummers method was used to prepare GO from graphite powder [30]. First, 90 ml of H₂SO₄ and 10 ml of H₂O₂ were poured successively into a three-port flask. Second, a small amount of graphite powder was mixed with potassium permanganate, and the mixture was slowly added into the flask, heated to 60 °C, and stirred for 24 h. Then, the reactants were cooled to room temperature and poured into hydrogen peroxide diluted with distilled water. And then, the resultant of reaction was washed once with hydrochloric acid and five times with deionized ultrapure water. Finally, the product was vacuum freeze-dried for 24 h for later use.

2.2. Preparation of SnO₂/GO

The schematic diagram of SnO₂/GO preparation is depicted in figure 1. In the first place, 15 mg GO was dissolved in 30 ml deionized water, and ultrasonic treatment was performed for 10 min to make GO completely dissolved and the solution gradually turned brown. In the next place, a certain amount of SnCl₄·5H₂O was added to the GO solution and stirred until they were thoroughly mixed. Thirdly, the above aqueous solution was poured into a 50 ml Teflon-lined stainless steel autoclave and placed in a vacuum drying oven at 180 °C for 12 h of hydrothermal reaction. Finally, the reactants were washed three times alternately with deionized water and absolute ethanol, further purified by centrifugation at 5000 rpm for 5 min, and then stored in ultrapure water.

In this experiment, SnO₂/GO composites with SnO₂:GO mass ratios 0.5:1, 1:1, 1.5:1 and 2:1 were prepared by changing the dosages of SnCl₄·5H₂O and GO. The corresponding samples prepared were marked as S1, S2, S3 and S4, respectively. For comparative study, the same experimental process was conducted to prepare pure RGO without adding SnCl₄·5H₂O, and pure SnO₂ nanocrystals without adding GO.

2.3. Characterizations

The surface morphology, element information and structure of the samples were characterized by scanning electron microscopy (SEM) and energy dispersive x-ray spectroscopy (EDS) (JSM-7610F Plus, JEOL Ltd., Tokyo,
Japan), transmission electron microscopy (TEM) (JEM-2100, JEOL Ltd., Tokyo, Japan), and x-ray diffraction (XRD) pattern (Bruker D8 Advance, Bruker Inc., Germany). Raman spectra were measured using Renishaw inVia Raman spectrometer (Renishaw Co., Ltd., Britain). The x-ray photoelectron spectroscopy (XPS) was measured using Thermo ESCALAB 250XI (Thermo Fisher Scientific Inc., USA). The absorption properties of the samples were measured using CARY 5000 UV–vis spectrometer (Agilent Corporation, USA).

2.4. Z-scan measurement

The NLO properties of the samples were tested using the Z-scan technique [31]. The optical path of the Z-scan experimental apparatus is shown in figure 2. The Z-scan principle is briefly summarized here:

The laser beam is split into two by a beam splitter. One beam of light is probed by the detector D1 as a reference light, and the other beam is focused on the moving sample through a lens. The beam passing through the sample passes fully or partly through the aperture located in the far field and is detected by detector D2. Whether it passes wholly or partly through the aperture depends on the linear transmittance $S$ of the aperture, which is defined as $S = 1 - \exp(-2r_a^2/w_0^2)$, where $r_a$ represents the radius of the aperture and $w_0$ represents the beam radius at the aperture in the linear regime. Thus, a transmittance signal ratio $D_2/D_1$ is recorded. A Z-scan starts from a distance $(-z)$ far away from the focus, where the nonlinear refraction and absorption are negligible since the beam irradiance is low, hence, the transmittance $D_2/D_1$ remains relatively constant. As the sample moves near the focal plane, the intensity of light hitting the sample is stronger than in the far-field due to the beam narrowing, and varies with the change of the sample position from $-z$ to $+z$. In this case, the nonlinear response of the sample occurs due to strong irradiance, and the transmittance $D_2/D_1$ is thus recorded as a function of the sample position. As the sample moves far away from the focus in the $+z$ direction, the beam irradiance is low again, hence, the transmittance $D_2/D_1$ becomes a constant again, and the Z-scan is completed. If the $D_2/D_1$ constant measured far away from the focus is taken as 1, then the full Z-scan result is the normalized transmittance as a function of the sample position $z$. In other words, the normalized transmittance is obtained through dividing the entire Z-scan data by the transmittance measured at a distance far from the focal point.

An open-aperture (OA) Z-Scan is performed to measure nonlinear absorption by fully opening or removing the aperture. A closed-aperture (CA) Z-scan is performed to measure nonlinear refraction by setting a certain linear transmittance of the aperture. However, the result of CA Z-scan generally includes nonlinear refraction
together with nonlinear absorption. In order to obtain only nonlinear refraction, the CA z-scan result is usually divided by the OA Z-scan result to remove the nonlinear absorption. In the case of saturated absorption, the OA Z-scan curve is a peak at the focal plane, but for the reverse saturated absorption, the OA Z-scan curve is a valley. In addition, if the CA/OA Z-scan curve is a valley-peak shape symmetrical up and down, the nonlinear refraction of the sample is positive (the sample has a self-focusing property), and if CA/OA Z-scan curve is a peak-valley shape symmetrical up and down, the nonlinear refraction is negative (self defocusing property).

In this study, a picosecond pulsed laser (EKSPLA, PL2251, Lithuania) with the wavelength 532 nm, pulse duration 30 ps and repetition rate 10 Hz is utilized as the light source. The spatial profile of the laser beam is Gaussian TEM₀₀ mode, with the pulse energy of 10 μJ and the beam waist of 10.6 μm. The optical path of the Z-scan measurement system was calibrated using CS₂ as a standard reference nonlinear material. All the as-prepared RGO, SnO₂, and SnO₂/RGO composites were tested by OA and CA Z-scans, and all the Z-scan data were normalized, through which the regulated nonlinear absorption and refraction properties were deduced.

3. Results and discussion

3.1. Morphology and structure

The surface morphology and element information of the RGO, SnO₂, and SnO₂/RGO composites were characterized by SEM, EDS and TEM, which are shown in figure 3. As can be seen from figure 3(a), flaky RGO prepared by graphite oxide reduction method presents the commonly seen human skin-like structural wrinkles [32] with overlapping edges which were formed by the oxygen-containing groups on GO sheets. Figures 3(b)–(c) are SEM images of SnO₂/RGO composites with the increase of SnO₂ concentration from S1 to S4, in which the wrinkled morphology of RGO was maintained, but the surface was rougher than RGO, indicating that SnO₂ nanoparticles were compounded on the surface of RGO, and the distribution of SnO₂ were becoming denser with the increase of SnO₂ concentration. EDS and elemental mappings in figures 3(d)–(g) containing C, O and Sn further demonstrate that SnO₂ nanoparticles were successfully hybridized on the surface of RGO. Figure 3(h) indicates that pure SnO₂ nanoparticles were easy to agglomerate and uneven in distribution. However, after compounding with GO, as shown in figures 3(i)–(j), the agglomeration was effectively alleviated and the
distribution was more uniform, which was due to the effect of hydroxyl and carboxyl groups in GO [33, 34]. GO could change the nucleation process of SnO$_2$, resulting in changes in the morphology and distribution of SnO$_2$ nanoparticles on RGO sheets. The structure of the modified RGO and the distribution of SnO$_2$ would affect the NLO performance of the composites.

Figure 4(a) depicts XRD spectra of GO, SnO$_2$ and SnO$_2$/RGO (S2). The diffraction peak of GO at angle of 2$\theta$ = 9.3° is owing to the characteristic (002) crystalline plane [35], which disappeared in SnO$_2$/RGO, indicating that GO was well reduced to graphene. The main characteristic diffraction peaks of SnO$_2$ at angles of 2$\theta$ = 26.55°, 34.01°, 37.66°, 51.67°, and 65.04° conform to the standard tetragonal rutile SnO$_2$ colorimetric card (JCPDS Card no. 41–1445) [36, 37], which are retained in SnO$_2$/RGO but with relatively weak strength, indicating that both SnO$_2$ and RGO phase components coexisted and there was a strong interaction in between.

Figure 4(b) shows Raman spectra of GO and SnO$_2$/RGO composites S1–S4 to investigate the interaction between SnO$_2$ and RGO. The Raman spectra of all samples have two characteristic peaks at 1344 and 1598 cm$^{-1}$, corresponding to D-band and G-band, respectively. The D-band was caused by the defect states of graphene, and the graphite band (G-band) originated from the stretching of C–C bonds in the graphene plane. The intensity ratio I$_D$/I$_G$ of D-band and G-band represents the sp$^2$/sp$^3$ carbon atom ratio, which is used to evaluate the defects of graphene materials [38, 39]. The calculated I$_D$/I$_G$ ratios of S1–S4 were 0.89, 0.91, 0.88 and 0.92, respectively, which were much higher than 0.67 of GO, indicating that the surface defects of the composites increased after the introduction of SnO$_2$. The interaction between SnO$_2$ and graphene may lead to the breakage and formation of chemical bonds.

Figure 5 depicts the composition and valence information of elements of SnO$_2$/RGO composite (ex. S2). Figure 5(a) shows the full spectral valence information of Sn, O and C in sample S2. In figure 5(b), there are two peaks in the Sn 3d spectrum, located at 486.9 eV and 495.4 eV, respectively, which were caused by the binding energy of Sn 3d$_{5/2}$ and Sn 3d$_{3/2}$ in the Sn$^{4+}$ oxidation state [34]. As can be seen from figure 5(c), due to the presence of the C–C/C=C, C–O and C=O bonds, the C 1s spectrum has three peaks, which are located at 284.6, 286 and 288.7 eV, respectively, and three main peaks can be fitted according to the binding energy [34, 40]. The presence of C–O and C=O bonds indicated that there were still a few oxygen functional groups in the SnO$_2$/RGO composite. Figure 5(d) depicts O 1s spectra, which can be fitted into two peaks at 530 and 531.5 eV and assigned to the Sn–O and Sn–O–C bonds, respectively [41, 42]. The existence of Sn–O–C bonds indicates that SnO$_2$ and RGO were connected in the form of chemical bond, which not only enhanced the interaction between them, but also may affect the NLO properties of the composite.

3.2. UV–Vis absorption

Figure 6(a) depicts UV–vis absorption properties of SnO$_2$, RGO and SnO$_2$/RGO (S1–S4) composites. The absorption characteristic peaks of RGO and SnO$_2$/RGO (S1–S4) composites occurred at 233 nm and 259 nm, respectively. Based on the Tauc relation [43]: $\alpha h\nu = A(h\nu - E_g)^n$, where $\alpha$ is the absorption coefficient, $h\nu$ is the photon energy, $A$ is a constant, $E_g$ is the band gap, and $n$ is the exponent determined by the transition type ($n$ is half for direct transition SnO$_2$ [43]), the band gaps of SnO$_2$ and SnO$_2$/RGO (S1–S4) were figured out to be 3.58,
1.90, 2.16, 2.29 and 2.36 eV, respectively, and shown in figure 6(b), which indicates that the band gaps of SnO2/RGO (S1–S4) composites increased with the increase of SnO2 concentration, but all smaller than SnO2, which provided evidence of chemical bond connection between RGO and SnO2. The ionic and covalent bonds may be used as a bridge for charge transfer between the components of the nanohybrids. The presence of these
bonds will change the transfer rate and efficiency of the charge transfer process when the laser illuminates the material, and then affect the photophysical properties of the material.

### 3.3. Nonlinear properties

All samples tested by Z-scan were dissolved in ultra-pure water with a concentration of 0.2 mg mL\(^{-1}\). At the same laser intensity of 532 nm, the nonlinear responses of ultra-pure water were found to be negligible, which was below the threshold of our detection system, indicating that the observed nonlinear phenomenon revealed directly the responses of RGO, SnO\(_2\), and SnO\(_2\)/RGO. To minimize the accidental uncertainty of measurement, all the samples were tested many times at different points on each sample, and the experimental results of each sample were averaged over multiple measurements. It could be seen from figure 7 that the slight deviation between the experimental data and the fitting line may be due to the system error from the laser source and signal receiver.

As shown in figure 7(a), OA Z-scan normalized transmittance of RGO, SnO\(_2\), and SnO\(_2\)/RGO (S1–S4) all have a symmetric peak at the focus, indicating that all samples have saturable absorption (SA) characteristics. These characteristics can be ascribed to that when the atoms of the samples were irradiated by laser, electrons absorbed photons and transitioned from the valence band to the conduction band, and with the increase of the incident irradiance, the rate of absorption transition was becoming greater than that of relaxation, due to Pauli’s incompatibility principle, the photon energy subbands of the valence band and the conduction band were gradually occupied by holes and electrons respectively, and thus the absorption reached saturation. Compared with single component, all SnO\(_2\)/RGO samples showed higher peaks meaning greater SA intensity, which can be attributed to the modification of SnO\(_2\) to the surface structure of GO and the presence of charge transfer between them. In addition, the CA/OA Z-scan curves of RGO, SnO\(_2\), and SnO\(_2\)/RGO (S1–S4) composites shown in figure 7(b) demonstrate a symmetric valley-peak trajectory, which means that all samples exhibited self-focusing characteristics due to the positive nonlinear refraction.

To quantitatively evaluate the NLO properties of all samples, the normalized Z-scan transmittance can be calculated as equation (1)\(^{[31]}\)
The imaginary part of the third-order nonlinear susceptibility can be obtained by
\[
\chi^{(3)}_{\text{Im}} = \frac{1}{\omega_{0}^{2}L_{\text{eff}}} \int P_{f}(t) \left( \Delta \Phi_{0}(t) \right) dt
\]
where \( P_{f}(\Delta \Phi_{0}(t)) = \frac{c_{0}n_{0} \pi}{\epsilon_{0}} \int_{0}^{\infty} |E_{\text{in}}(r, t)|^{2} dr \) is the transmitted instantaneous power through the aperture, \( c \) is the light speed in vacuum, \( c_{0} \) is the permittivity of vacuum, \( n_{0} \) is the linear index of refraction, \( E_{\text{in}}(r, t) \) is the electric field distribution at the aperture. \( \Delta \Phi_{0}(t) = k \gamma I_{0}(t)L_{\text{eff}} \) is defined as the on-axis phase shift at the focus \((z = 0)\), \( k = 2\pi/\lambda \) is the wave vector. \( \gamma \) (in \( m^{2}/W \)) or \( n_{2} \) (in esu) is the nonlinear index of refraction in different unit, they are related through the conversion formula \( n_{2}(\text{esu}) = (c_{0}n_{0}/4\pi) \gamma \) (in \( m^{2}/W \)). \( I_{0}(t) \) is the on-axis irradiance at the focus. \( L_{\text{eff}} = [1 - \exp(-\alpha_{0}L)] / \alpha_{0} \) is the effective length of the sample with the actual thickness \( L \) and the linear absorption coefficient \( \alpha_{0} \), which can be obtained from the UV–Vis absorption spectra. \( P_{f}(t) = \omega_{0}^{2}I_{0}(t)/2 \) is the instantaneous input power within the sample, \( \omega_{0} \) is the beam waist (10.6 \( \mu \)m), and \( S \) is the linear transmittance of the aperture.

When OA Z-scan was performed (\( S = 1 \)), the transmittance was insensitive to beam distortion and is only a function of the nonlinear absorption. Therefore, the normalized energy transmittance can be ultimately derived from equation (1) through time integration for a temporally Gaussian laser pulse, and can be finally expressed in terms of the peak irradiance as a summation form more suitable for numerical evaluation [31]:

\[
T(z, S = 1) = \sum_{m=0}^{\infty} \left[ -q_{m}(z) \right]^{m} \left( 1 + m \right)^{1/2} \text{ for } |q_{m}| < 1
\]

where \( q_{m}(z) = (\beta L_{\text{eff}})/(1 + z^{2}/z_{0}^{2}) \), \( z_{0} = \pi \omega_{b}^{2}/\lambda \) is the diffraction length of the Gaussian beam, and \( \omega_{b} \) is the beam waist. Hence, the nonlinear absorption coefficient \( \beta \) can be derived as \( \beta = 2\sqrt{2}(1 - T_{x=0})(1 + z^{2}/z_{0}^{2})/I_{0}L_{\text{eff}} \) and the value of it can be obtained by fitting OA Z-scan data with formula (2). With \( \beta \) known, the imaginary part of the third-order nonlinear susceptibility can be obtained by \( \text{Im} \chi^{(3)} = n_{2}^{*} \lambda^{3} \beta/480\pi^{5} \), other nonlinear parameters, such as nonlinear refraction index \( \gamma \) or \( n_{2} \), the real part \( \text{Re} \chi^{(3)} \) of the third-order nonlinear susceptibility and consequently \( \chi^{(3)} \), can be deduced from CA Z-scan with \( S < 1 \).

When CA Z-scan is performed, if the far-field condition is satisfied, i.e. the distance between the aperture and the sample is much longer than the diffraction length \( z_{0} \), the normalized transmittance \( T(z) \) is geometry-independent and can be expressed as [31]

\[
T(z) = 1 - \frac{4\Delta \Phi_{0}x}{(1 + x^{2})(9 + x^{2})}
\]

where \( x = z/z_{0} \). The peak-valley difference \( \Delta T_{p-v} \) can be deduced by solving the differential equation \( dT(z)/dz = 0 \), and the result can be expressed within a \( \pm 2\% \) accuracy:

\[
\Delta T_{p-v} \approx 0.406(1 - S^{0.25})[\Delta \Phi_{0}]
\]

for \( |\Delta \Phi_{0}| \leq \pi \) (4)

From (4) and \( \Delta \Phi_{0}(t) = k\gamma I_{0}(t)L_{\text{eff}} \), the expression \( \gamma = \lambda \alpha_{0} \Delta T_{p-v}/[0.812\pi I_{0}(1 - S^{0.25})(1 - e^{-\alpha_{0}L})] \) is obtained and used to calculate the nonlinear refractive index \( \gamma \) and \( n_{2} \). As a result, from the fitted data of the CA/OA Z-scan curves, the nonlinear refractive index \( n_{2} \) is obtained, and the real part of the third-order nonlinear susceptibility \( \text{Re} \chi^{(3)} \) is calculated by \( \text{Re} \chi^{(3)} = n_{2}n_{1}/3\pi \). With \( \text{Re} \chi^{(3)} \) and \( \text{Im} \chi^{(3)} \) known, the third-order nonlinear susceptibility \( \chi^{(3)} \) is calculated by equation (5). All the calculated results are listed in table 1.

\[
\chi^{(3)} = [(\text{Re} \chi^{(3)})^{2} + (\text{Im} \chi^{(3)})^{2}]^{1/2}
\]

It is worth noting that in table 1, all the nonlinear parameters of the composites (S1–S4) are larger than those of the SnO2 and RGO, and have been regulated to varying degrees by SnO2:GO ratios. Specifically, with the increase of SnO2 content from S1 to S4, \( \beta \) and \( \text{Im} \chi^{(3)} \) were firstly increased and then decreased, reaching

### Table 1. The nonlinear optical parameters of the samples.

| Sample | \( \beta/10^{-11} \text{ m W}^{-1} \) | \( n_{2}/10^{-12} \text{ esu} \) | \( \text{Im} \chi^{(3)}/10^{-12} \text{ esu} \) | \( \text{Re} \chi^{(3)}/10^{-12} \text{ esu} \) | \( \chi^{(3)}/10^{-12} \text{ esu} \) |
|--------|---------------------------------|----------------------------|---------------------------------|---------------------------------|----------------------------|
| RGO    | -1.03                           | 30.87                      | -2.13                           | 14.38                           | 14.54                      |
| SnO2   | -1.26                           | 19.78                      | -0.54                           | 4.20                            | 4.23                       |
| S1     | -1.78                           | 41.87                      | -3.69                           | 19.51                           | 19.85                      |
| S2     | -2.08                           | 44.73                      | -4.31                           | 20.83                           | 21.28                      |
| S3     | -2.93                           | 45.00                      | -6.05                           | 20.96                           | 21.82                      |
| S4     | -1.92                           | 47.57                      | -3.95                           | 22.16                           | 22.51                      |


Table 2. Nonlinear absorption parameters of RGO, SnO₂ and S1–S.

| Sample | λ nm | \( \beta \) cm/GW | \( \Delta T \)% | \( I_s \) GW cm\(^{-2} \) |
|--------|------|-----------------|----------------|-----------------|
| RGO    | 532  | -1.03           | 4.7            | 0.86            |
| SnO₂   | 532  | -1.26           | 5.5            | 0.5             |
| S1     | 532  | -1.78           | 7.1            | 0.22            |
| S2     | 532  | -2.08           | 8.2            | 0.15            |
| S3     | 532  | -2.93           | 10             | 0.3             |
| S4     | 532  | -1.92           | 7.4            | 0.23            |

maximum values in sample S3, but the other parameters, such as \( n_2 \), \( \text{Re} \chi^{(3)} \) and \( \chi^{(3)} \), were all gradually enhanced and reached maximum values in sample S4. Numerically, the maximum nonlinear absorption coefficient \( \beta \) of the composites was calculated to be \(-2.93 \times 10^{-13} \text{ (m/W)}\) which was more than 2.8 times that of RGO and 2.3 times that of SnO₂, respectively. The maximum third-order nonlinear susceptibility \( \chi^{(3)} \) of the composites was \( 22.51 \times 10^{-12} \text{ (esu)} \) which was more than 1.5 times that of RGO and 5.3 times that of SnO₂, respectively.

The modulation depth and saturable intensity are important parameters in the application of saturable absorbers. These parameters of as-prepared SnO₂, RGO and SnO₂/RGO composites can be deduced from the plotting of the normalized transmittance \( T \) obtained in OA Z-scan against the incident light intensity \( I_z \) of each sample at different positions from \(-z\) to the focus. The average light intensity of Gaussian beam can be described as \( I_z = I_0/(1 + z^2/z_0^2) \) due to the relation of \( w_z^2 = w_0^2(1 + z^2/z_0^2) \), where \( w_z \) is beam radius at \( z \), \( I_0 \) is the average intensity at the focus (\( z = 0 \)). The normalized transmittance \( T \) against the incident light intensity \( I_z \) was then plotted in figures 7 (c) and (d) respectively, and was fitted using the following formula [44]:

\[
T = 1 - \frac{\Delta T}{1 + I_z/I_s} - T_{ns}
\]

where \( \Delta T \) is the modulation depth, \( T_{ns} \) is the nonsaturable loss, \( I_s \) is the saturation intensity. The fitting results are listed in table 2, which indicates that SnO₂/RGO composites have larger modulation depth and smaller saturable intensity than both SnO₂ and RGO. Therefore, the SnO₂/RGO composites are better saturable absorbers.

All the above regulation of NLO properties of the composites may be attributed to the interaction of several mechanisms. Firstly, for the case of saturable absorption, the transfer of charge between the two components of the composite competed with the recombination of electron-hole pairs, which affected the saturable absorption. At first, with the increase of the concentration of SnO₂, the possibility of the formation of electron donor-acceptor pairs between SnO₂ and RGO increased, which facilitated the charge transfer rate and efficiency, and delayed the recombination of electron-hole pairs, resulting in an increase in saturable absorption. Later, as the concentration increased further, probability of the recombination of electron-hole pairs increased significantly, which weakened the saturable absorption. Therefore, the saturation absorption had an inflection point, a maximum, as the concentration of SnO₂ increased. Calculation based on the experimental data indicated that the saturable absorption coefficient reached the maximum at the mass ratio of 1:5:1.

Secondly, for the case of the third-order nonlinear susceptibility, in addition to the type of material itself, the local field generated by SnO₂ nanoparticles and the uniformity of its distribution were also factors affecting the nonlinear refraction. At first, with the increase of the concentration of SnO₂, the local field was enhanced because the hydroxyl and carboxyl groups in graphene alleviated the agglomeration of SnO₂ and made its distribution more uniform, which favored the increase of the nonlinear refractive index \( n_2 \) that played a dominant role in the third-order nonlinear susceptibility. And then, as the concentration increased further, the uniformity became worse, which made the nonlinear refractive index become less, resulting in the decrease of the susceptibility. According to the experimental data and calculation, the nonlinear refractive index reached the maximum at the ratio of 2:1.

The above factors including charge transfer, recombination, local field and distribution were also affected by the band gaps of SnO₂ and RGO which have been modified by their combination. All the factors resulted in enhanced tunable nonlinear absorption and tunable third-order nonlinear susceptibility of SnO₂/RGO composites with the mass ratio of SnO₂:GO. With the variation of the mass ratio of SnO₂:GO, the charge transfer rate and efficiency between them, the synergistic effect, and the local field centered on SnO₂ on the graphene surface have all changed, resulting in the change of the nonlinear optical properties of the composites. Therefore, the nonlinear optical properties could be tuned by controlling the mass ratio.

It was found that the maximum value of the third-order nonlinear susceptibility of SnO₂/RGO composite was much higher than that of many other materials. Comparing with previous studies, the maximum third-order susceptibility \( \chi^{(3)} \) of SnO₂/RGO (22.51 × 10^{-12} esu) was found two times larger than that of MoSe₂/G composite (8 × 10^{-12} esu) [45], six times larger than rGO-Au@CdS composite (3.43 × 10^{-12} esu) [46],

\[
\chi^{(3)} = \frac{\Delta T}{\Delta I}
\]

where \( \Delta T \) is the modulation depth per unit change in intensity, \( \Delta I \) is the change in intensity, and \( \chi^{(3)} \) is the third-order nonlinear susceptibility.
forty-four times larger than MWCNTs-Au-ZnS composite (5.1 \times 10^{-15} \text{ esu}) [47], and seventy times larger than Ni-ZnS/RGO composite (3.2 \times 10^{-13} \text{ esu}) [48], indicating that SnO_2/RGO exhibited outstanding NLO properties and potential applications in nonlinear optics.

4. Conclusions

In conclusion, SnO_2/RGO composites with different mass ratio SnO_2:GO were synthesized for the first time by using a facile hydrothermal method. The prepared composites were confirmed to be hybridized by covalent and partial-ionic bonds. The nonlinear absorption and nonlinear refraction of the prepared composites were all enhanced compared to the components, and the enhancement was mass ration-dependently tunable. At the ratio of 1.5:1, the nonlinear absorption coefficient reached the maximum which was 2.8 times that of RGO and 2.3 times that of SnO_2, respectively. Meanwhile, the maximum modulation depth was obtained to be 10% corresponding to the saturable intensity 0.3 GW cm^{-2}. In addition, at the ratio of 2:1, the third-order nonlinear susceptibility of the SnO_2/RGO composite achieved the maximum which was found to be much greater than many other composites studied previously. The tunable nonlinearity was attributed to the contribution of several mechanisms. The results of this study provide a reference for the further research and application of SnO_2/RGO composites.

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Data availability statement

All data that support the findings of this study are included within the article (and any supplementary files).

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