

Graphitic carbon nitride, a saturable absorber material for the visible waveband

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For the first time to our knowledge, graphitic carbon nitride ($g\text{-C}_3\text{N}_4$) nanosheets are found to be an excellent saturable absorber material in the visible waveband. $g\text{-C}_3\text{N}_4$ exhibits much stronger saturable absorption in this region than in the near-infrared region, unlike other two-dimensional materials such as graphene and black phosphorus. By the Z-scan method, the nonlinear absorption coefficient β of the material is first measured at three visible wavelengths, and for $g\text{-C}_3\text{N}_4$ it is -2.05 , -0.34 , and $-0.11 \text{ cm} \cdot \text{GW}^{-1}$ at 355, 532, and 650 nm, respectively. These are much larger than $-0.06 \text{ cm} \cdot \text{GW}^{-1}$ at 1064 nm. © 2018 Chinese Laser Press

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1. INTRODUCTION

The exploration of new two-dimensional (2D) materials, such as graphene [1–3], topological insulators [4], and transition-metal dichalcogenides [5] has attracted wide attention in recent years because of their exceptional chemical and physical properties. These layered materials exhibit a common characteristic of possessing strong atomic forces between the atoms within a layer and weak van der Waals forces between adjacent atomic layers. This results in their special electronic and optoelectronic properties. Because of the large nonlinear optical (NLO) susceptibility, high carrier density, and mobility, they have been utilized as multiple optical components such as passive saturable absorbers for Q-switching and mode-locking, optical limiters, and photodetectors [6–12].

Graphitic carbon nitride ($g\text{-C}_3\text{N}_4$), a metal-free 2D conjugated semiconductor, has attracted research attention since 2009 because of its sustainable photocatalytic ability [13,14]. $g\text{-C}_3\text{N}_4$ possesses highly stable chemical, thermal, and photochemical properties for its tri-s-triazine ring structure and a high degree of polymerization [13]; therefore it can be used in photocurrent, photoreactivity, electrocatalysis, and bioimaging applications [13,15,16]. Compared with the chemical properties, the optical characteristics of $g\text{-C}_3\text{N}_4$ have received less attention. In the last two years, due to the saturable absorption (SA) property of $g\text{-C}_3\text{N}_4$, researchers have realized its applications in passive Q-switching and mode-locking of infrared lasers at wavelengths 1, 1.3, 2.84, and 2.95 μm [17–20].

However, SA in the visible waveband has never been observed for pure $g\text{-C}_3\text{N}_4$ [21,22].

In this study, we used the Z-scan method to investigate the NLO properties of $g\text{-C}_3\text{N}_4$ at different wavelengths, with picosecond laser pulses as the excitation source. For the first time to our knowledge, strong SA was observed in a $g\text{-C}_3\text{N}_4$ dispersion in the visible waveband. At the same time, under long wavelength (650 and 1064 nm) excitation, two opposite absorption phenomena, namely, SA and optical limiting (OL), were found when we changed the input intensity. The nonlinear absorption coefficient β and the nonlinear refractive index n_2 were calculated from the experimental results of open aperture (OA) and closed aperture (CA) Z-scan measurements. For a $g\text{-C}_3\text{N}_4$ dispersion with 60% initial transmittance, the β values are -2.05 , -0.34 , -0.11 , and $-0.06 \text{ cm} \cdot \text{GW}^{-1}$ at 355, 532, 650, and 1064 nm, respectively. This illustrates that the SA ability of $g\text{-C}_3\text{N}_4$ is stronger at shorter wavelengths. Currently, diode-pumped continuous-wave visible solid-state lasers that can generate various colors are undergoing rapid development [23]. By directly inserting nanomaterial produced saturable absorbers, such as Au nanorods, MoS_2 , or Bi_2Se_3 , visible laser pulses can be obtained conveniently [24–26]. Besides, 2D nanomaterials have also been applied to the passive Q-switching of visible fiber lasers [27,28]. As a new, powerful SA material, $g\text{-C}_3\text{N}_4$ is hoped to produce pulsed visible lasers with the advantages of high efficiency, affordability, and compactness with potential applications in medical treatment, material processing, microscopy, and scientific research, etc.

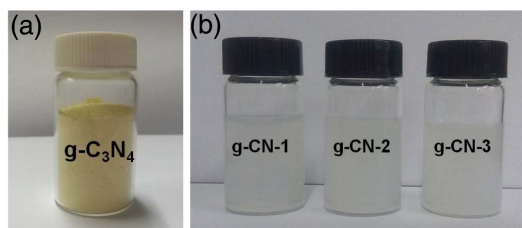


Fig. 1. Photographs of (a) g-C₃N₄ powder and (b) prepared g-C₃N₄ dispersions.

2. EXPERIMENT

A. Sample Preparation

Bulk g-C₃N₄ was synthesized by direct heating of dicyandiamide [29]. First, dicyandiamide was heated at 550°C for 4 h in static air at a ramp rate of 2.3°C/min. Then, it was cooled down to the room temperature at a cooling rate of 1°C/min. The resultant yellow agglomerate was finely ground to powder, as shown in Fig. 1(a).

The g-C₃N₄ dispersion was prepared by the liquid exfoliation method. The as-obtained powder was dispersed in deionized water with ultrasonic pulverization for 2 h. Then the suspension was allowed to settle for two days to deposit the undispersed particles. The final supernatant g-C₃N₄ dispersion was used in the Z-scan experiment. The g-CN-1, g-CN-2, and g-CN-3 samples [as shown in Fig. 1(b)] had different g-C₃N₄ contents, and their linear optical transmittances at 532 nm were 75%, 60%, and 43.5%, respectively. The samples prepared were stable and could be stored without any change in appearance for more than one month. This feature makes them suitable for time-consuming measurements and is also advantageous for future applications.

B. Characterization

Atomic force microscopy (AFM) and X-ray diffraction (XRD) were used to analyze the morphology and structure of the g-C₃N₄ sample. Before the AFM measurement, the sample was deposited on a Si/SiO₂ substrate and dried for 12 h. As shown in Fig. 2, the thickness of the g-C₃N₄ nanosheets is about 4–6 nm. Assuming an interplanar stacking distance of 0.326 nm [30] for the aromatic units, this thickness corresponds to a packing of 12–18 layers.

The XRD result was obtained on a Bruker D8 advance X-ray diffractometer under Cu-K α radiation ($\lambda = 0.15418$ nm). As presented in Fig. 3, there are two primary diffraction peaks located at 13.1° and 27.6°. The (100) peak at 13.1° reveals

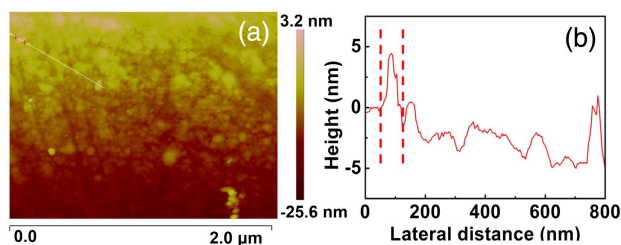


Fig. 2. (a) AFM image and (b) corresponding height profile of prepared g-C₃N₄ nanosheets.

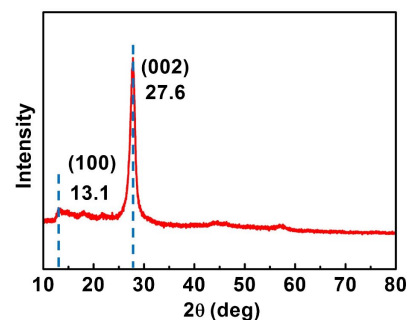


Fig. 3. XRD pattern of g-C₃N₄ nanosheets.

the in-plane structural packing motif, and the (002) peak at 27.6° shows typical graphite-like stacking of the conjugated aromatic C-N segments [30,31]. The result reflects the graphite-like structure of the g-C₃N₄ powder and confirms that the influence of amino on the structure of g-C₃N₄ can be neglected.

Using 1064 nm light as the excitation source, the Raman spectrum of g-C₃N₄ powder was recorded. As shown in Fig. 4, the peak at 707 cm⁻¹ attributes to the heptazine ring breathing mode. The peaks around 1232 cm⁻¹ correspond to the stretching vibration mode of C-N heterocycles [32]. The 1566 cm⁻¹ fingerprint peak of the NH₂ bending mode does not appear, which proves the high purity of the g-C₃N₄ powder.

Figure 5(a) shows the transmission spectrum of the g-C₃N₄-2 sample in the range of 250–1750 nm. It can be seen that the ultraviolet (UV) absorption cutting edge of g-C₃N₄ is shorter than 250 nm. The UV absorption peak at 300 nm is

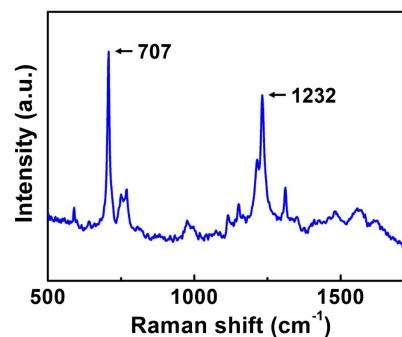


Fig. 4. Raman spectrum of g-C₃N₄ powder.

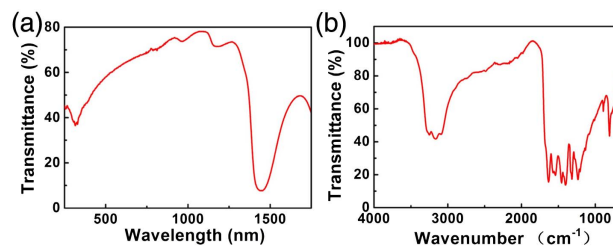


Fig. 5. Transmission characteristic of g-C₃N₄. (a) UV–near infrared spectrum from 250 to 1750 nm. (b) FTIR spectrum from 2.5 to 15.4 μm (4000 – 650 cm⁻¹).

due to the π bond transition of $g\text{-C}_3\text{N}_4$. The absorption bands around 965, 1180, and 1450 nm are attributed to the O—H bond vibrations of water in $g\text{-C}_3\text{N}_4$ dispersion. Figure 5(b) is the Fourier transform infrared (FTIR) transmission spectrum of $g\text{-C}_3\text{N}_4$ powder in the range of 2.5–15.4 μm measured with a Perkin Elmer 100 FTIR spectrophotometer. In the infrared direction, the cutting edge extends beyond 15.4 μm (650 cm^{-1}). This result means that a wide waveband from visible to infrared is available for optical applications. The broad absorption band from 3000 to 3300 cm^{-1} originates from the stretching vibration of the N—H bond, associated with uncondensed amino groups [33]. The other broad absorption bands in the 1200–1600 cm^{-1} region are assigned to the typical stretching vibration modes of C—N heterocycles. The sharp peak at 810 cm^{-1} attributes to the breathing vibration of triazine units [34,35].

3. NONLINEAR OPTICAL MEASUREMENT

The Z-scan method is a popular technique for characterizing the NLO properties of materials, including nonlinear absorption, scattering, and refraction [36]. Based on different materials and absorption mechanisms, the nonlinear absorption can be multiphoton absorption, reverse saturable absorption (RSA), and free-carrier absorption, etc. In this study, a Z-scan apparatus was used to study the NLO behavior of $g\text{-C}_3\text{N}_4$ dispersions at four wavelengths, namely, 355, 532, 650, and 1064 nm.

The experimental setup is shown in Fig. 6. The fundamental light source is a mode-locked Nd:YAG dye laser (PY61C-10, Continuum Inc, USA), which can operate at a near-infrared wavelength of 1064 nm. After frequency doubling and third harmonic generation with NLO crystals, 532 nm and 355 nm excitation wavelengths can be obtained. Further, after stimulated Raman scattering of pure water to the 532 nm output, the 650 nm excitation wavelength is obtained. Thus four representative wavelengths, namely, deep violet (355 nm), green (532 nm), red (650 nm), and near infrared (1064 nm), can be used for the Z-scan experiments. The pulse widths are 20, 30, 35, and 40 ps for 355, 532, 650, and 1064 nm, respectively. The pulse repetition rate is 10 Hz. The focal length of the focusing lens is 40 cm. The experimental samples, i.e., the $g\text{-C}_3\text{N}_4$ dispersions with different concentrations, were transferred to quartz cuvettes of 1 mm thickness. During the

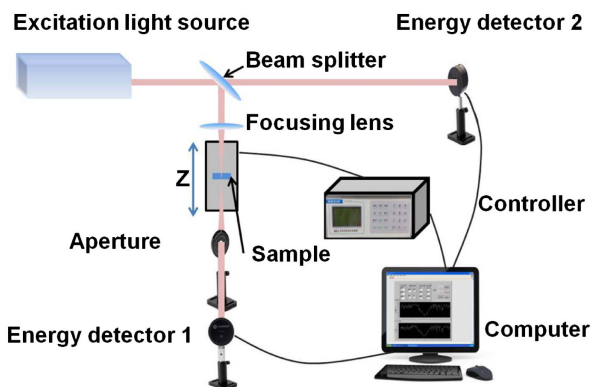


Fig. 6. Schematic of the Z-scan experimental setup.

experiments, each Z-scan for the $g\text{-C}_3\text{N}_4$ dispersions was accompanied by a reference scan for the quartz substrate with deionized water. The final Z-scan results were obtained by dividing the $g\text{-C}_3\text{N}_4$ data by the quartz substrate with deionized water data. In this way, the thermal effects, nonlinear effects from the quartz substrate, and the deionized water were removed.

Figure 7 presents the OA Z-scan results of $g\text{-C}_3\text{N}_4$ dispersions ($g\text{-C}_3\text{N}_4\text{-1}$, $g\text{-C}_3\text{N}_4\text{-2}$, and $g\text{-C}_3\text{N}_4\text{-3}$) at the excitation wavelengths of 355, 532, 650, and 1064 nm. The linear optical transmission values of $g\text{-C}_3\text{N}_4\text{-1}$, $g\text{-C}_3\text{N}_4\text{-2}$, and $g\text{-C}_3\text{N}_4\text{-3}$ are 55%, 43.6%, and 30% at 355 nm; 75%, 60%, and 43.5% at 532 nm; 81.8%, 65.5%, and 50% at 650 nm; and 82.4%, 73.5%, and 65% at 1064 nm, respectively.

Figures 7(a)–7(d) show the variation of normalized transmission as a function of the incident pulse energy density ($\text{J} \cdot \text{cm}^{-2}$) for different $g\text{-C}_3\text{N}_4$ samples. All samples exhibit a gradual increase in the transmittance with increasing incident energy at 355 and 532 nm, indicating typical SA. This is the first time that SA is observed in the visible waveband for $g\text{-C}_3\text{N}_4$. Furthermore, for the same sample, the strongest SA response is seen at the shortest excitation wavelength, 355 nm. Normalized transmittance T_N is used to scale the output

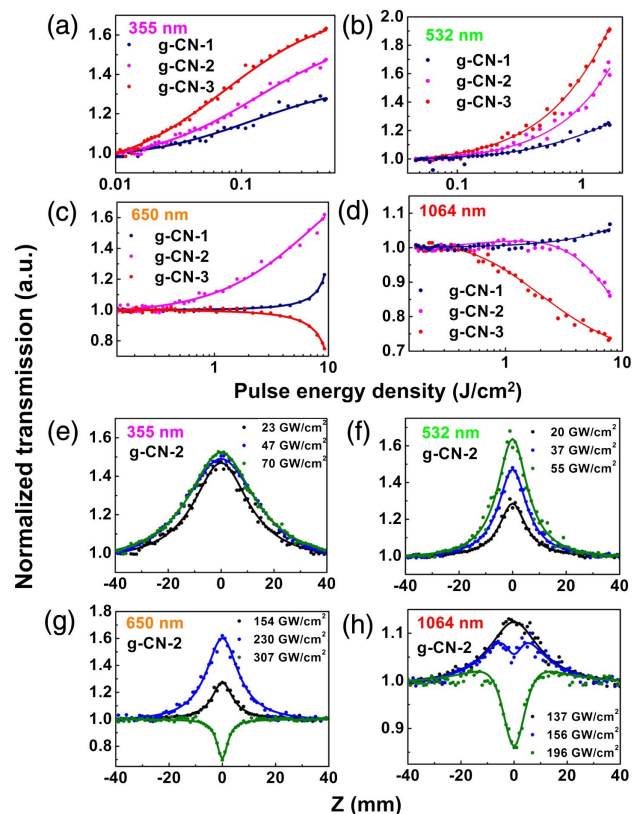


Fig. 7. OA Z-scan results of $g\text{-C}_3\text{N}_4$ nanosheets. (a) Different $g\text{-C}_3\text{N}_4$ samples at 355 nm. (b) Different $g\text{-C}_3\text{N}_4$ samples at 532 nm. (c) Different $g\text{-C}_3\text{N}_4$ samples at 650 nm. (d) Different $g\text{-C}_3\text{N}_4$ samples at 1064 nm. (e) $g\text{-C}_3\text{N}_4\text{-2}$ sample at different 355 nm excitation intensities. (f) $g\text{-C}_3\text{N}_4\text{-2}$ sample at different 532 nm excitation intensities. (g) $g\text{-C}_3\text{N}_4\text{-2}$ sample at different 650 nm excitation intensities. (h) $g\text{-C}_3\text{N}_4\text{-2}$ sample at different 1064 nm excitation intensities.

clamping characteristics of different g-C₃N₄ samples. A larger T_N implies better SA. When the 355 nm input fluence at the focal point ($Z = 0$) is fixed at $0.47 \text{ J} \cdot \text{cm}^{-2}$ (corresponding to an intensity of $23 \text{ GW} \cdot \text{cm}^{-2}$), the T_N values of g-C₃N₄-1, g-C₃N₄-2, and g-C₃N₄-3 samples can reach 128%, 147%, and 162%, respectively. This indicates that the SA ability increases with decreasing linear optical transmission. Under the same experimental conditions, the T_N value of black phosphorus can only reach 115% at a much higher incident intensity of $115 \text{ GW} \cdot \text{cm}^{-2}$. For 532 nm excitation, contrary to earlier reports on OL phenomena [21,22], all of the three g-C₃N₄ samples exhibit the SA effect under picosecond pulses. When the input fluence at the focal point is fixed at $1.66 \text{ J} \cdot \text{cm}^{-2}$ (corresponding to an intensity of $55 \text{ GW} \cdot \text{cm}^{-2}$), the T_N values of g-C₃N₄-1, g-C₃N₄-2, and g-C₃N₄-3 samples are 125%, 163%, and 192%, respectively. Similarly, for 355 nm excitation, the SA ability increases with decreasing linear optical transmission. At 650 nm, the g-C₃N₄ dispersions exhibit two opposite NLO phenomena, SA and OL. When the input fluence at the focal point is fixed at $9.23 \text{ J} \cdot \text{cm}^{-2}$ (corresponding to an intensity of $230 \text{ GW} \cdot \text{cm}^{-2}$), the T_N values of g-C₃N₄-1, g-C₃N₄-2, and g-C₃N₄-3 samples are 123%, 160%, and 75%, respectively. With decreasing linear optical transmission, the NLO responses of g-C₃N₄ dispersions shift from SA to OL. This means that the nonlinear absorption parameters of the g-C₃N₄ nanosheets have changed significantly with the changing initial linear optical transmission, or in other words, the concentration of the g-C₃N₄ dispersion. Meanwhile, at the wavelength of 1064 nm, no obvious SA behavior is shown by the three g-C₃N₄ dispersions. After increasing the fluence of the 1064 nm laser to $7.83 \text{ J} \cdot \text{cm}^{-2}$, the samples show two different NLO phenomena, namely, weak SA and strong RSA. The T_N values of g-C₃N₄-1, g-C₃N₄-2, and g-C₃N₄-3 are 105%, 86%, and 74%, respectively. Furthermore, the NLO absorption properties of g-C₃N₄ shift from SA to RSA with decreasing initial transmission. Such behavior indicates that g-C₃N₄ is highly suitable for the protection of infrared lasers. Overall, with increasing concentration, the g-C₃N₄ dispersion shows a lower initial linear transmittance, larger transmission variation magnitude, and more significant NLO absorption. Therefore, the g-C₃N₄-3 sample shows the strongest SA effect at low excitation energy densities (355 and 532 nm) and the strongest RSA effect at high excitation energy densities (650 and 1064 nm). As a layered material, g-C₃N₄ is based on tri-s-triazine building blocks, and the van der Waals forces between each layer lead to the π - π stacking [17]. It possesses higher charge carrier density due to an obvious increase of state density at the conduction band edge with respect to the bulk counterpart [37]. Its SA feature comes from the Pauli blocking effect of the conduction band and the depletion of the valence electrons under intense laser field.

Figures 7(e)–7(h) present the OA Z-scan results of the g-C₃N₄-2 sample at different excitation wavelengths and different energy intensities. At 355 nm, the values of T_N are 147%, 149%, and 152% for the energy intensities ($Z = 0$) of 23, 47, and $70 \text{ GW} \cdot \text{cm}^{-2}$, respectively. At 532 nm, the T_N values are 128%, 147%, and 163% when the energy intensities are 20,

37, and $55 \text{ GW} \cdot \text{cm}^{-2}$, respectively. It can be seen that at these two wavelengths the SA ability of g-C₃N₄ dispersion grows with increasing incident intensity. Under the excitation of 650 and 1064 nm lasers, the g-C₃N₄-2 dispersion exhibits SA and OL behaviors at different incident intensities. Therefore, in the near-infrared waveband, g-C₃N₄ can serve as an optical modulation material depending on the practical working conditions. From the excited state nonlinear absorption theory [38,39], it can be known that at 355 and 532 nm, $\sigma_1 > \sigma_2$ for g-C₃N₄-2, where σ_1 and σ_2 are the absorption cross sections of the first and the second excited states, respectively. Under such conditions, only the SA effect occurs [Figs. 7(e) and 6(f)]. At 650 and 1064 nm, $\sigma_1 < \sigma_2$. Under this condition, the SA effect will change to the RSA effect when the incident intensity reaches a certain threshold, which is inversely proportional to the value of $\sigma_2 - \sigma_1$. Figure 5(a) reveals that for g-C₃N₄-2, σ_1 (650 nm) $>$ σ_1 (1064 nm), so if σ_2 is assumed to be unchanged from 650 to 1064 nm, then $\sigma_2 - \sigma_1$ at 650 nm will be smaller than that at 1064 nm and correspondingly the SA \rightarrow RSA inversion intensity threshold at 650 nm will be larger. This is in accordance with the experimental phenomena: the inversion threshold at 650 nm is larger than $230 \text{ GW} \cdot \text{cm}^{-2}$ [Fig. 7(g)], while the one at 1064 nm is between 137 and $156 \text{ GW} \cdot \text{cm}^{-2}$ [Fig. 7(f)].

The normalized transmittance for the OA Z-scan experiment can be expressed as [36]

$$T_{\text{OA}}(z) = \sum_{m=0}^{\infty} \frac{[-q_0(z, 0)]^m}{(m+1)^{1.5}}, \quad m \in N, \quad (1)$$

$$q_0(z, 0) = \frac{\beta I_0 L_{\text{eff}}}{1 + z^2/z_R^2}, \quad (2)$$

where β is the nonlinear absorption coefficient, I_0 is the peak intensity at the focus point ($z = 0$), $L_{\text{eff}} = (1 - e^{-\alpha_0 L})/\alpha_0$ is the effective length, L is the length of the sample, α_0 is the linear absorption coefficient, z is the position of the sample, and z_R is the Rayleigh length.

Taking the g-C₃N₄-2 sample as an example, the value of the nonlinear absorption coefficient β is fitted to be $(-2.05 \pm 0.4) \text{ cm} \cdot \text{GW}^{-1}$ under different 355 nm intensities [Fig. 7(e)]. At 532 nm, the β value is fitted to be $(-0.34 \pm 0.02) \text{ cm} \cdot \text{GW}^{-1}$ under different 532 nm intensities [Fig. 7(f)]. For 650 nm, the β value is $-0.11 \text{ cm} \cdot \text{GW}^{-1}$ at $230 \text{ GW} \cdot \text{cm}^{-2}$ and $0.014 \text{ cm} \cdot \text{GW}^{-1}$ at $307 \text{ GW} \cdot \text{cm}^{-2}$. At 1064 nm excitation [Fig. 7(h)], the fitted β value is $-0.06 \text{ cm} \cdot \text{GW}^{-1}$ at $137 \text{ GW} \cdot \text{cm}^{-2}$ and $0.016 \text{ cm} \cdot \text{GW}^{-1}$ at $196 \text{ GW} \cdot \text{cm}^{-2}$. The β values at all of the four wavelengths are listed in Table 1, as well as the corresponding saturation intensities I_s . I_s is defined as the optical intensity required to increase the saturable transmission to a half. For g-C₃N₄-2, the I_s values in Table 1 are obtained from Figs. 7(a)–7(c) and 7(h) (at $137 \text{ GW} \cdot \text{cm}^{-2}$), respectively. Based on a 30 ps, 532 nm laser, the I_s of g-C₃N₄-2 is $11.4 \text{ GW} \cdot \text{cm}^{-2}$, which is much larger than the values of graphene oxide ($0.86 \text{ GW} \cdot \text{cm}^{-2}$) [40], black phosphorus ($7.6 \text{ MW} \cdot \text{cm}^{-2}$) [41], and MoS₂ ($1 \text{ GW} \cdot \text{cm}^{-2}$) [42] under similar conditions. The large I_s represents high energy storage ability, which indicates that g-C₃N₄ will be a powerful Q-switcher material

Table 1. Nonlinear Optical Properties of g-C₃N₄-2 Sample at Different Visible Wavelengths

Wavelength/nm	$I_s/\text{GW} \cdot \text{cm}^{-2}$	$\beta/\text{cm} \cdot \text{GW}^{-1}$	$n_2/\text{cm}^2 \cdot \text{W}^{-1}$	$\text{Im}\chi^{(3)}/\text{esu}$	$\text{Re}\chi^{(3)}/\text{esu}$	$\text{FOM}/\text{m}^4 \cdot (\text{sW})^{-1}$
355	4.6	-2.05	0.87×10^{-15}	-4.00×10^{-12}	0.62×10^{-13}	2.19×10^{-22}
532	11.4	-0.34	1.42×10^{-15}	-6.62×10^{-13}	1.02×10^{-13}	5.44×10^{-23}
650	185	-0.11	0.40×10^{-15}	-4.03×10^{-13}	0.27×10^{-13}	1.69×10^{-23}
1064	60.3	-0.06	0.34×10^{-15}	-2.20×10^{-13}	0.23×10^{-13}	1.51×10^{-23}

Table 2. Nonlinear Absorption Properties of g-C₃N₄-2 Sample and Several Representative Nanomaterials at Visible Wavelength of 532 nm

Sample	Laser Pulse Duration/ps	$I_0/\text{GW} \cdot \text{cm}^{-2}$	Main NLO Response/nm	$\beta/\text{cm} \cdot \text{GW}^{-1}$	Reference
g-C ₃ N ₄ -2	30	20–55	SA	-0.34	This work
Graphene	30	12.8	RSA	0.4	[43]
Graphene oxide	35	0–34	RSA	2.2	[44]
	35	0–30	RSA	2.5	[40]
	35	20	RSA	2	[45]
	35	0.114	RSA	16	[41]
BP	30	0.114	RSA	16	[41]
MoS ₂	19	2.1	RSA	-0.0003–0.5	[42]
BCN	35	94	RSA	0.08–0.106	[46]
Carbon nanotubes	35	22	RSA	0–1	[44]

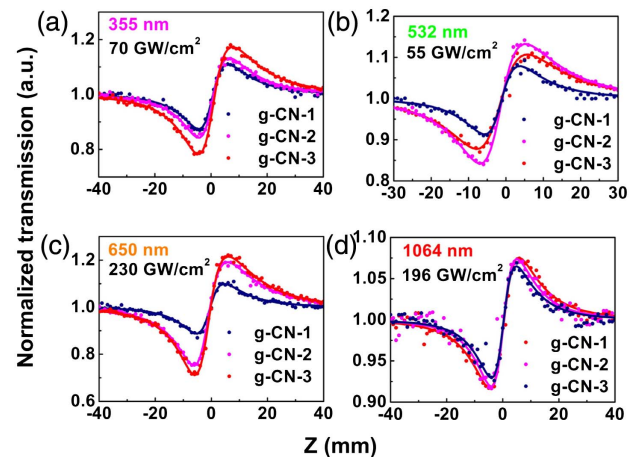
based on the theory of passively modulated pulsed lasers [47]. From Fig. 7(b), it can be known that g-C₃N₄-2 possesses a large saturable loss (36%) and a small non-saturable loss (4%). The other favorable characteristics includes short recovery time (4 ps) [48] and high laser damage threshold ($>8 \text{ MW} \cdot \text{cm}^{-2}$ for mid-infrared solid-state laser *Q*-switching) [19].

At the same visible excitation wavelength of 532 nm, the nonlinear absorption properties of the g-C₃N₄-2 sample and several representative nanomaterials are compared in Table 2 [40–46]. It can be seen that at a similar laser pulse duration (~ 30 ps) and energy range of $10 - 100 \text{ GW} \cdot \text{cm}^{-2}$, only g-C₃N₄-2 presents an SA response ($\beta < 0$). At the same time, compared with other popular 2D materials, such as graphene [49], black phosphorus (BP) [41], and boron carbon nitride (BCN) [46], g-C₃N₄ exhibits a different SA characteristic, i.e., a larger SA coefficient in the visible waveband (355, 532, and 650 nm) than in the infrared region (1064 nm). All of these properties indicate that g-C₃N₄ is a powerful 2D SA material in the visible waveband. In earlier reports, nanosecond lasers were used to study the NLO effects of g-C₃N₄ at 532 nm. No NLO response was observed under a power intensity of $0.8 \text{ GW} \cdot \text{cm}^{-2}$, and the OL effect was observed under a power intensity of $4 \text{ GW} \cdot \text{cm}^{-2}$ [21,22]. We used picosecond lasers as the excitation light source; they can supply a much higher power intensity than what was produced from the nanosecond lasers in earlier works. Thus, the SA effect is easier to realize. Besides, the dispersion concentration has a positive influence on the NLO performance; the NLO phenomena are more remarkable at higher dispersion concentrations.

The nonlinear refractive index can be extracted by dividing the CA data by the OA data. The results are shown in Fig. 8. The valley-peak configurations reveal that the nonlinear refractive index is positive, which shows that self-focusing occurs in g-C₃N₄ dispersions when they are irradiated by high power laser pulses. The fitting formula is [38]

$$T_{C/O}(x) = 1 + \frac{4x\Delta\Phi}{(1+x^2)(9+x^2)} + \frac{4(3x^2-5)\Delta\Phi^2}{(1+x^2)(9+x^2)(25+x^2)} + \frac{32(3x^2-11)x\Delta\Phi^3}{(1+x^2)(9+x^2)(25+x^2)(49+x^2)}, \quad (3)$$

where $x = z/z_R$, $\Delta\Phi = kn_2I_0L_{\text{eff}}$ is the on-axis nonlinear phase shift at the focus, and k is the wavelength number. Using Eq. (3), we can obtain the nonlinear refractive index n_2 under different conditions. At 355 nm and an input fluence of $0.47 \text{ J} \cdot \text{cm}^{-2}$, the n_2 values of g-C₃N₄-1, g-C₃N₄-2, and g-C₃N₄-3 samples are 0.59×10^{-15} , 0.87×10^{-15} , and $1.52 \times 10^{-15} \text{ cm}^2 \cdot \text{W}^{-1}$, respectively. For 532 nm excitation, when the input fluence is $1.66 \text{ J} \cdot \text{cm}^{-2}$, the n_2 values of

**Fig. 8.** CA/OA Z-scan results of different g-C₃N₄ samples at (a) 355 nm, (b) 532 nm, (c) 650 nm, and (d) 1064 nm.

g-C₃N₄-1, g-C₃N₄-2, and g-C₃N₄-3 samples are 0.57×10^{-15} , 1.42×10^{-15} , and $1.44 \times 10^{-15} \text{ cm}^2 \cdot \text{W}^{-1}$, respectively. At 650 nm and an input fluence of $9.23 \text{ J} \cdot \text{cm}^{-2}$, the n_2 values of g-C₃N₄-1, g-C₃N₄-2, and g-C₃N₄-3 samples are 0.15×10^{-15} , 0.40×10^{-15} , and $0.51 \times 10^{-15} \text{ cm}^2 \cdot \text{W}^{-1}$, respectively. For 1064 nm excitation, when the input fluence is $7.83 \text{ J} \cdot \text{cm}^{-2}$, the n_2 values of the three samples are 0.27×10^{-15} , 0.34×10^{-15} , and $0.42 \times 10^{-15} \text{ cm}^2 \cdot \text{W}^{-1}$, respectively. A high dispersion concentration and short excitation wavelength result in a high nonlinear refractive index.

The imaginary part of the third-order NLO susceptibility, $\text{Im}\chi^{(3)}$, is related to the nonlinear absorption coefficient, and the real part, $\text{Re}\chi^{(3)}$, is related to the nonlinear refractive index. They can be expressed by the following equations [50]:

$$\text{Re}\chi^{(3)}(\text{esu}) = \frac{cn_0^2}{120\pi^2} n_2 \text{ (m}^2/\text{W)}, \quad (4)$$

$$\text{Im}\chi^{(3)}(\text{esu}) = \frac{c^2 n_0^2}{240\pi^2 \omega} \beta_2 \text{ (m/W)}, \quad (5)$$

where n_0 is the linear refractive index, and ω is the light frequency. The figure of merit (FOM) for the third-order optical nonlinearity is defined as $\text{FOM} = |\text{Im}\chi^{(3)}/\alpha_0|$. The $\text{Re}\chi^{(3)}$, $\text{Im}\chi^{(3)}$, and FOM values of the g-C₃N₄-2 sample are listed in Table 1 for different wavelengths.

4. CONCLUSIONS

g-C₃N₄ nanosheets were fabricated from bulk C₃N₄ by mechanical exfoliation. The nonlinear absorption and nonlinear refractive properties of g-C₃N₄ nanosheets were investigated at the wavelengths of 355, 532, 650, and 1064 nm with the Z-scan technique. For the first time to our knowledge, SA behavior in the visible waveband is observed from g-C₃N₄. At the same time, we found that the SA effect would change to the OL effect with increasing excitation intensity. It indicates that g-C₃N₄ can be used for different applications and be altered depending on the practical working conditions. In summary, this research shows that g-C₃N₄ is an excellent and promising wide waveband NLO material, whose applicable waveband includes the visible region.

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REFERENCES

- E. McCann, "Asymmetry gap in the electronic band structure of bilayer graphene," *Phys. Rev. B* **74**, 161403 (2006).
- K. S. Novoselov, A. K. Geim, and S. V. Morozov, "Two-dimensional gas of massless Dirac fermions in graphene," *Nature* **438**, 197–200 (2005).
- Q. Bao, H. Zhang, and B. Wang, "Broadband graphene polarizer," *Nat. Photonics* **5**, 411–415 (2011).
- J. E. Moore, "The birth of topological insulators," *Nature* **464**, 194–198 (2010).
- Q. H. Wang, K. Kalantar-Zadeh, and A. Kis, "Electronics and optoelectronics of two-dimensional transition metal dichalcogenides," *Nat. Nanotechnol.* **7**, 699–712 (2012).
- G. Zhao, S. Han, and A. Wang, "'Chemical weathering' exfoliation of atom-thick transition metal dichalcogenides and their ultrafast saturable absorption properties," *Adv. Funct. Mater.* **25**, 5292–5299 (2015).
- J. Hou, G. Zhao, and Y. Wu, "Femtosecond solid-state laser based on tungsten disulfide saturable absorber," *Opt. Express* **23**, 27292–27298 (2015).
- Y. Chen, G. Jiang, and S. Chen, "Mechanically exfoliated black phosphorus as a new saturable absorber for both Q-switching and mode-locking laser operation," *Opt. Express* **23**, 12823–12833 (2015).
- Z. Zheng, C. Zhao, and S. Lu, "Microwave and optical saturable absorption in graphene," *Opt. Express* **20**, 23201–23214 (2012).
- M. Feng, H. Zhan, and Y. Chen, "Nonlinear optical and optical limiting properties of graphene families," *Appl. Phys. Lett.* **96**, 033107 (2010).
- Q. Ouyang, K. Zhang, and W. Chen, "Nonlinear absorption and nonlinear refraction in a chemical vapor deposition-grown, ultrathin hexagonal boron nitride film," *Opt. Lett.* **41**, 1368–1371 (2016).
- Y. Xie, B. Zhang, and S. Wang, "Ultrabroadband MoS₂ photodetector with spectral response from 445 to 2717 nm," *Adv. Mater.* **29**, 1605972 (2017).
- X. Wang, K. Maeda, and A. Thomas, "A metal-free polymeric photocatalyst for hydrogen production from water under visible light," *Nat. Mater.* **8**, 76–80 (2009).
- S. Cao, J. Low, and J. Yu, "Polymeric photocatalysts based on graphitic carbon nitride," *Adv. Mater.* **27**, 2150–2176 (2015).
- J. Liu, Y. Liu, and N. Liu, "Metal-free efficient photocatalyst for stable visible water splitting via a two-electron pathway," *Science* **347**, 970–974 (2015).
- J. Duan, S. Chen, and M. Jaroniec, "Porous C₃N₄ nanolayers@N-graphene films as catalyst electrodes for highly efficient hydrogen evolution," *ACS Nano* **9**, 931–940 (2015).
- X. Gao, S. Li, and T. Li, "g-C₃N₄ as a saturable absorber for the passively Q-switched Nd:LLF laser at 1.3 μm ," *Photon. Res.* **5**, 33–36 (2017).
- Y. Zhou, M. Zhao, and S. Wang, "Developing carbon-nitride nanosheets for mode-locking ytterbium fiber lasers," *Opt. Lett.* **41**, 1221–1224 (2016).
- M. Fan, T. Li, and G. Li, "Graphitic C₃N₄ as a new saturable absorber for the mid-infrared spectral range," *Opt. Lett.* **42**, 286–289 (2017).
- M. Fan, T. Li, and G. Li, "Passively Q-switched Ho, Pr:LiLuF₄ laser with graphitic carbon nitride nanosheet film," *Opt. Express* **25**, 12796–12803 (2017).
- K. Sridharan, T. Kuriakose, and R. Philip, "Transition metal (Fe, Co and Ni) oxide nanoparticles grafted graphitic carbon nitrides as efficient optical limiters and recyclable photocatalysts," *Appl. Surf. Sci.* **308**, 139–147 (2014).
- K. Sridharan, P. Sreekanth, and T. J. Park, "Nonlinear optical investigations in nine-atom silver quantum clusters and graphitic carbon nitride nanosheets," *J. Phys. Chem. C* **119**, 16314–16320 (2015).
- C. Kränkel, D. T. Marzahl, and F. Moglia, "Out of the blue: semiconductor laser-pumped visible rare-earth doped lasers," *Laser Photon. Rev.* **10**, 548–568 (2016).
- S. Wang, Y. Zhang, J. Xing, X. Liu, H. Yu, A. Di Lieto, M. Tonelli, T. Sum, H. Zhang, and Q. Xiong, "Nonlinear optical response of Au nanorods for broadband pulse modulation in bulk visible lasers," *Appl. Phys. Lett.* **107**, 161103 (2015).
- Y. Zhang, H. Yu, R. Zhang, G. Zhao, H. Zhang, Y. Chen, L. Mei, M. Tonelli, and J. Wang, "Broadband atomic-layer MoS₂ optical modulators for ultrafast pulse generations in the visible range," *Opt. Lett.* **42**, 547–550 (2017).
- S. Luo, X. Yan, B. Xu, L. Xiao, H. Xu, Z. Cai, and J. Weng, "Few-layer Bi₂Se₃-based passively Q-switched Pr:YLF visible lasers," *Opt. Commun.* **406**, 61–65 (2018).
- D. Wu, J. Peng, Z. Cai, J. Weng, Z. Luo, N. Chen, and H. Xu, "Gold nanoparticles as a saturable absorber for visible 635 nm Q-switched pulse generation," *Opt. Express* **23**, 24071–24076 (2015).
- H. Lin, W. Li, J. Lan, X. Guan, H. Xu, and Z. Cai, "All-fiber passively Q-switched 604 nm praseodymium laser with a Bi₂Se₃ saturable absorber," *Appl. Opt.* **56**, 802–805 (2017).

29. P. Niu, L. Zhang, and G. Liu, "Graphene-like carbon nitride nanosheets for improved photocatalytic activities," *Adv. Funct. Mater.* **22**, 4763–4770 (2012).
30. Q. Huang, J. Yu, and S. Cao, "Efficient photocatalytic reduction of CO₂ by amine-functionalized g-C₃N₄," *Appl. Surf. Sci.* **358**, 350–355 (2015).
31. S. Hu, L. Ma, and J. You, "Enhanced visible light photocatalytic performance of g-C₃N₄ photocatalysts co-doped with iron and phosphorus," *Appl. Surf. Sci.* **311**, 164–171 (2014).
32. S. Tonda, S. Kumar, S. Kandula, and V. Shanker, "Fe-doped and -mediated graphitic carbon nitride nanosheets for enhanced photocatalytic performance under natural sunlight," *J. Mater. Chem. A* **2**, 6772–6780 (2014).
33. S. Yan, Z. Li, and Z. Zou, "Photodegradation performance of g-C₃N₄ fabricated by directly heating melamine," *Langmuir* **25**, 10397–10401 (2009).
34. J. Ran, T. Ma, G. Gao, X. Du, and S. Qiao, "Porous P-doped graphitic carbon nitride nanosheets for synergistically enhanced visible-light photocatalytic H₂ production," *Energy Environ. Sci.* **8**, 3708–3717 (2015).
35. H. Lan, L. Li, X. An, F. Liu, C. Chen, H. Liu, and J. Qu, "Microstructure of carbon nitride affecting synergetic photocatalytic activity: hydrogen bonds vs. structural defects," *Appl. Catal. B* **204**, 49–57 (2017).
36. M. Sheik-Bahae, A. A. Said, and T. H. Wei, "Sensitive measurement of optical nonlinearities using a single beam," *IEEE J. Quantum Electron.* **26**, 760–769 (1990).
37. X. Zhang, X. Xie, H. Wang, J. Zhang, B. Pan, and Y. Xie, "Enhanced photoresponsive ultrathin graphitic-phase C₃N₄ nanosheets for bioimaging," *J. Am. Chem. Soc.* **135**, 18–21 (2012).
38. C. Li, J. Si, and M. Yang, "Excited-state nonlinear absorption in multi-energy-level molecular systems," *Phys. Rev. A* **51**, 569–575 (1995).
39. X. Deng, X. Zhang, S. Liu, and C. Li, "The theoretical analysis of critical conditions for several nonlinear absorptions," *Acta Photon. Sin.* **27**, 1077–1090 (1998).
40. N. Liaros, P. Aloukos, A. Kolokithas-Ntoukas, A. Bakandritsos, T. Szabo, R. Zboril, and S. Couris, "Nonlinear optical properties and broadband optical power limiting action of graphene oxide colloids," *J. Phys. Chem. C* **117**, 6842–6850 (2013).
41. F. Zhang, Z. Wu, Z. Wang, D. Wang, S. Wang, and X. Xu, "Strong optical limiting behavior discovered in black phosphorus," *RSC Adv.* **6**, 20027–20033 (2016).
42. K. Zhou, M. Zhao, M. Chang, Q. Wang, X. Wu, Y. Song, and H. Zhang, "Size-dependent nonlinear optical properties of atomically thin transition metal dichalcogenide nanosheets," *Small* **11**, 694–701 (2015).
43. F. Zhang, Z. Wang, D. Wang, Z. Wu, S. Wang, and X. Xu, "Nonlinear optical effects in nitrogen-doped graphene," *RSC Adv.* **6**, 3526–3531 (2016).
44. Z. Liu, Y. Wang, X. Zhang, Y. Xu, Y. Chen, and J. Tian, "Nonlinear optical properties of graphene oxide in nanosecond and picosecond regimes," *Appl. Phys. Lett.* **94**, 021902 (2009).
45. A. B. Bourlinos, A. Bakandritsos, N. Liaros, S. Couris, K. Safarova, M. Otyepka, and R. Zbořil, "Water dispersible functionalized graphene fluoride with significant nonlinear optical response," *Chem. Phys. Lett.* **543**, 101–105 (2012).
46. F. Ma, M. Wang, and Y. Shao, "Thermal substitution for preparing ternary BCN nanosheets with enhanced and controllable nonlinear optical performance," *J. Mater. Chem. C* **5**, 2559–2565 (2017).
47. U. Keller, "Recent developments in compact ultrafast lasers," *Nature* **424**, 831–838 (2003).
48. Z. Chen, Q. Zhang, and Y. Luo, "Determining the charge-transfer direction in a p-n heterojunction BiOCl/g-C₃N₄ photocatalyst by ultrafast spectroscopy," *ChemPhotoChem* **1**, 350–354 (2017).
49. J. Wang, Y. Hernandez, and M. Lotya, "Broadband nonlinear optical response of graphene dispersions," *Adv. Mater.* **21**, 2430–2435 (2009).
50. G. Yang, W. Wang, and L. Yan, "Z-scan determination of the large third-order optical nonlinearity of Rh: BaTiO₃ thin films deposited on MgO substrates," *Opt. Commun.* **209**, 445–449 (2002).