The effect of Ag on the structural, dielectric, linear and third-order nonlinear optical properties of Graphitic carbon nitride nanosheets

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Abstract

In this work, prepared g-C_3N_4 and Ag/g-C_3N_4 nanomaterials was employed to explorer to the optical nonlinearity. The UV–Vis spectrophotometry, XRD pattern, FESEM image, FTIR spectroscopy, KK method and Z-scan measurements was applied to characterize the obtained nanomaterials. The Z-scan method was used to analyze third-order nonlinearity studies such as the nonlinear refractive (NLR) index, n_2, and nonlinear absorption (NLA) coefficient, β by using Nd: YAG laser with 50 mW power at 532 nm under different concentration of Ag/g-C_3N_4 nanostructure. The impact of concentration on the nonlinear optical (NLO) properties have been investigated in detail. NLO properties of the Ag/g-C_3N_4 nanostructure are enhanced, reaching values of 2.99×10^{-8} cm^2/W and 6.53×10^{-4} cm/W for the third-order NLR and NLA coefficients, respectively. In addition, this material possesses large optical characteristics in the IR region. The complex refractive index and dielectric coefficient of Ag/g-C_3N_4 nanostructure is investigated. Moreover, the Ag/g-C_3N_4 nanostructure's IR light responsiveness has significantly improved. The red shifts of longitudinal and transversal frequencies for Ag/g-C_3N_4 is more visible than g-C_3N_4. This research might lead to fresh ideas and a new way to make high-stability supported Ag optical devices.

Keywords: Ag/g-C_3N_4; Nanomaterials; Third-order nonlinearity; Z-Scan; Dielectric coefficient; KK method

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1 Introduction

The optical properties of nanostructures are crucial in the development of modern optoelectronic devices comprised of solar cells, light detector, light emitter and thin- film transistor displays [1]. Nonlinear optics is an area of physics concerned with the interaction of light with matter in situations when the linear superposition principle is broken [2]. Looking nonlinear optical (NLO) properties for new applications is nowadays relevant [3]. In optical modulation and optical confinement, materials with exceptional NLO characteristics are definitely required [4]. Especially, Because of their novel modes of operation displayed in ultrafast optical switching/limiting and photonic devices, third-order NLO materials attract researchers in the field of optics [5]. Until now, the explorer of NLO response of nanostructures, particularly on carbon nanomaterials which included of sp^2 hybridization, have been conducted by many researchers [6]. On the other hands, due to the abundant of delocalized π-electrons in sp^2 hybridized carbon atoms, carbon nanomaterials evaluated as possible options for NLO applications [7]. In comparison between graphitic carbon nitride (g-C_3N_4) and graphene nanomaterials, researchers have been more interested in g-C_3N_4 owing to the strong covalent C-N bonds in place of C-C graphene bonds, considerable thermal stability, and interesting electrical characteristics [8]. Despite the similarity of the structure of graphene and g-C_3N_4, many reports indicated that the NLO characteristics of the two carbon compounds differ. Furthermore, the investigation shows that the synergic effect of some elements such as silver and g-C_3N_4 can be enhanced considerably optical properties by decreases of band energy because of the modification of conduction band (CB) and valence band (VB) potentials [9].

X-ray diffraction (XRD), field emission scanning electron microscopy (FESEM), UV–Vis absorption, and FTIR spectroscopy were used to analyze the synthesized samples. The main purpose of this study is to find out how Ag affects the linear and NLO responses of g-C_3N_4 nanosheets. In the present study, the third-order optical nonlinearity of g-C_3N_4 and Ag/g-C_3N_4 nanostructures has been examined using Z-scan measurements in the continuous wave (CW) regimes, which has shown the significant nonlinear behavior in the samples, making it appropriate for optoelectronic applications.

2 Experimental section

2.1 Materials and Methods

16.2 mmol melamine and 32.8 mmol urea were blended in a mortar and then place in a crucible to synthesize g-C_3N_4. The prepared mixture was putted in a muffle furnace and heated according to a set of instructions: with the rate of 8 °C min^{-1} from 25 to 300 °C, with the rate of 2 °C min^{-1} from 300 to 500 °C, with the rate of 1 °C min^{-1} from 500 to 550 °C, finally heating at 550 °C for 2 h. Then, the cooling of crucible was performed to 25 °C. The substances were gathered and was in powder form. Ag/g-C_3N_4 was organized as a same process used for g-C_3N_4 expect that 2.2 mmol of $AgNO_3$ was added to the melamine and urea mixture [10].

2.2 Instruments

The employed instruments for the characterization of prepared nanomaterials are demonstrated according to Fig. 1.

2.3 Third-order NLO

Third-order NLO properties were performed by a Z-scan method for its simplicity, by means of Nd: YAG laser at 532 nm. The spatial distortion of the transmitted beam (both amplitude and phase) at the sample exit is the fundamental concept behind the Z-scan method [11]. This study's experimental setup is similar to that described in Ref [12]. Using a photodetector with closed aperture (CA), a sample is moved along the focal length of the lens while the transmitted light is used to measure a far field [13]. The focal length of employed lens is f = 50 mm. A cell of 1 mm of thickness was applied for satisfying the condition of thin sample approximation was allowed to move in steps of 1 mm by means of step motor over a distance of 40 mm along the axis of the laser beam. The calculated Rayleigh length in this case is $z_0 = k\omega_0^2 / 2 = 4.63$ mm. The focal plane input intensity is calibrated to 4062.13 W/cm^2. The distance *ΔZ* between the transmission peak and valley values is linked by the spatial characteristics of focused radiation in the focal plane based on the expression [14]:

$$\Delta Z \cong 1.7 z_0 \tag{1}$$

As a result of the normalized transmission's dependence on Z during scanning the sample, the spatial characteristics of focused radiation may be determined with high precision.

The NLA coefficient, β and NLR index, n_2 of g-C_3N_4 and Ag/g-C_3N_4 nanomaterials are derived by fitting the following equations to normalized transmittance (T(z)) with regards to the position of sample (Z, assessed from the focal plane), respectively:

$$T(z) = Ln(1 + q_0(z,t))/q_0(z,t) \tag{2}$$

$$\Delta T_{p-v} = 0.406(1-S)^{0.25}\left(\frac{2\pi}{\lambda}\right) n_2 I_0 L_{eff} \tag{3}$$

Where $q_0(z,t) = \beta I_0 L_{eff}/(1 + z^2/z_0^2)$, $L_{eff} = (1 - e^{-\alpha L})/\alpha$, $I_0 = 2P_{in}/\pi\omega_0^2$, $S = 1 - \exp\left(\frac{-2r_0^2}{\omega_0^2}\right)$ is the aperture linear transmittance, r_0 indicates the aperture radius and ω_0 indicates the beam radius at the aperture [5] obtained about 28 µm, α is the linear absorption coefficient and ΔT_{p-v} is the difference between the normalized peak and valley transmittance in pure CA curve.

Ground state absorption cross section σ_0 was determined from the equation for linear absorption coefficient,

$$\alpha = \sigma_0 N_A C \tag{4}$$

where N_A stands for the Avogadro's number and C for the concentration in mol/cm^3 [15]. The obtained parameters are tabulated in Table 1.

3 Results and Discussion

3.1 Characterization

Fig. 2 shows the XRD results of g-C_3N_4 and Ag/g-C_3N_4 nanosheets. As Fig. 2 shows, no considerable peaks of any other phases or impurities can be distinguished in the prepared nanomaterials, indicated the crystal structure of prepared g-C_3N_4 was not affected by introducing of Ag species. The observed peaks at 12.9° and 27.7° in g-C_3N_4 was ascribed to the g-C_3N_4 nanomaterials as reported in literatures [16-18]. The most and less intense peak at 27.7° and 12.9°, which is assigned to (002) and (100) planes in g-C_3N_4, is as a result of conjugated aromatic layers stacking and to the tri-s-triazine units layered packing structure in JCPDS 87–1526 card, respectively [16, 19]. The observed planes named as (311), (220), (200) and (111) in the Ag/g-C_3N_4 pattern was indexed to the Ag cubic structure. However, the observation of graphitic structure was confirmed by existence of (002) plane at 27.7°. Comparing the g-C_3N_4 and Ag/g-C_3N_4 patterns, we concluded that the high intensity of the Ag peaks has caused the (100) peak in the Ag/g-C_3N_4 patten to disappear. As shown in Fig. 2, Ag species had sharp diffraction peaks, which might be attributed by two factors: initially, the considerable numbers of Ag species introduced and high dispersion in the produced nanomaterials, and secondly, high uniform distribution and Ag plasmonic properties in Ag/g-C_3N_4 nanomaterials [20, 21].

The Fig. 3(a) and (b) were presented the FESEM descriptions of the prepared g-C_3N_4 and Ag/g-C_3N_4 nanomaterials, respectively. In g-C_3N_4, a sheet-like structure with regular surface structure was obtained, as shown in Fig. 3(a). When g-C_3N_4 and Ag/g-C_3N_4 were considered (Fig. 3(a) and b), it was discovered that the presence of Ag in the structure of the Ag/g-C_3N_4 increased the number of active sites. Figs. 3(c-f) show the elemental mappings of the obtained Ag/g-C_3N_4 nanosheets. Also, EDX spectrum of the Ag/g-C_3N_4 nanosheet were presented in the Fig. 3(g). As Figs. 3(c-f) show, the existences of the elements including Ag, C, and N, specified effective preparation of the Ag/g-C_3N_4 nanosheets. The elemental mapping also confirms a uniform distribution of the present elements. Table 1 were presented the quantitative analyses of the EDX results of the prepared nanomaterials.

UV-Vis absorbance spectra were used to evaluate the optical absorption characteristics of produced nanomaterials, as shown in Fig. 4(a). The results show that, in the presence of Ag, the absorption intensity of the g-C_3N_4 improved particularly in the visible region. As Fig. 4(a) shows, two sharp and weak shoulders at region of 300 to 400 nm that ascribed to π–π^* and n–π^* transitions were observed for g-C_3N_4, respectively [22]. Because of the SPR effect, a new absorption peak arises in the visible-light range after adding Ag species into the g-C_3N_4 structure (Fig. 4(a)). As Fig. 4(a) presented, the SPR of Ag atoms caused of a sharp absorption peak at about 500 nm of Ag/g-C_3N_4 [23].

Tauc's equation was performed to calculate the energy band gap of the nanomaterials that had been synthesized (Fig. 4(b)). The Tauc’s equation was given at below [16, 24]:

$$\alpha h\upsilon = A(h\nu - E_g)^{n/2} \qquad (5)$$

where E_g, α, ν, A, and h, are band gap energy, absorption coefficient, light frequency, a constant, and, Planck’s constant respectively. The value of n for direct and indirect light transmission is 1 and 4, respectively. For both g-C_3N_4 and Ag/g-C_3N_4 nanomaterials the number 4 was preferred [16]. As Fig. 4(b) indicated, 2.86 and 2.25 eV were measured for g-C_3N_4 and Ag/g-C_3N_4 band gap values, respectively. As shown by this finding, adding Ag into the g-C_3N_4 structure reduces the band gap and enhances the absorption capability.

The rate of electron-hole pairs recombination of the prepared nanomaterials was evaluated by very helpful method named as PL characterization [25, 26]. As Fig. 4(c) show, the appearance of the main emission peak around 440 nm were observed for pristine g-C_3N_4 and Ag/g-C_3N_4, which in agreement with the reported literature [27, 28]. Compared to the g-C_3N_4, the PL intensity of Ag/g-C_3N_4 compounds was quenched remarkably and lead to the lower recombination rate of electrons and holes [29], which could increase the activity. The achieved results proposed that incorporated Ag in g-C_3N_4 structure acted as an electron trap, so the recombination process was effectively suppressed leads to enhanced efficiency of Ag/g-C_3N_4.

In order to show better illustration of Ag/g-C_3N_4 heterostructure, Fig. 5 presented the construction of this heterostructure schematically at the molecular scale. Fig. 5(a) and (b) indicated the relaxed rectangular g-C_3N_4 monolayer containing C and N atoms (composed from relaxed g-C_3N_4 unit cell) in the top and slide view. Fig. 5(c) show the one of the simple stable silver cluster (Ag_6) in the top and slide view [30]. As Fig. 5(d) presented, a relaxed rectangular g-C_3N_4 monolayer is placed on top of relaxed monolayer of Ag_6 cluster show in the top and slide view.

3.2 Nonlinearity analysis

For investigation of nonlinearity, a 1 mm long quartz cell was filled with the samples as a solution in dimethyl formamide (DMF) at three distinct concentrations of 0.1, 0.01, and 0.001 mg/ml. The g-C_3N_4 and Ag/g-C_3N_4 nanomaterials were also exposed to Z-scan using a semiconductor CW laser with a wavelength of 532 nm and a power of 50 mW. In the case of open aperture (OA) that S=1, all transmitted light is gathered, and any nonlinear beam distortion induced by NLR have no effect [31]. The OA Z-scan curve given in Fig.6(a) is peak-shaped and symmetric about the beam focus, which declines progressively on both sides of the focal point, corresponding to saturable absorption (SA). In SA procedure, a high-energy laser beam collides with ground-state atoms, photons are absorbed and transferred to the excited state at such a rapid rate that there isn't enough time to come back to the ground state, and photon absorption by atoms becomes saturated [4, 32]. For Ag doped g-C_3N_4 nanosheets, with the addition of Ag content, the transmittance peak at the focus rises and the NLA coefficient values also increased.

Eq. 2 was used to calculate the value of β for normalized transmittance using the OA Z-scan data presented in Table 2. According to $L_{eff} = (1 - e^{-\alpha L})/\alpha$, The lower linear absorption coefficient of samples corresponds to a higher L_{eff}, which reduces the nonlinear absorption coefficient, β according to Eq. 2 [33].

Under CW excitation, the CA Z-scan's pre-focal valley and post-focal peak pattern indicates positive nonlinearity (self-focusing ability) [11] depicted in Fig. 6(b). This nonlinearity is due to photothermal effects, and it suggests that g-C_3N_4 and Ag/g-C_3N_4 nanomaterials might be used as optical limiters in the CW regime [34]. The value of NLR index can be obtained by Eq. 3 listed in Table 2. The reduction in peak-to-valley transmittance differential ($\Delta \mathrm{T}_{\mathrm{p-v}}$) (in Fig. 6(b)) causes the NLR index n_2 to decrease based on Eq. 3 [33].

Because the samples were irradiated with a CW Nd:YAG laser, thermally generated optical nonlinearity overcomes electronic nonlinearity [35]. Under CW lasers, thermal effects can have a significant impact on the nonlinear refractive index [36, 37]. The thermal effect causes heated electrons to thermalize, and the consequent dissipation of their energy induces the ambient temperature to rise, leading the refractive index to alter. The thermal lens diverges and the fluctuation in refractive index as a function of temperature thermally induced stress, implies that the nanostructures achieve clear positive nonlinearity, i.e. self-focusing. [36]. Because of the high phase shift and the laser heating effect, the measurement curve is asymmetric, similar to normal Z-scan curves [31]. As it can be seen from the Table 2, Ag/g-C_3N_4 nanostructure reveal the larger NLA and larger NLR than that of g-C_3N_4 nanosheets.

However, Fig. 7 shows normalized transmittance curves of (a) pure CA Z-scan and (b) OA Z-scan, which are obtained at different concentrations of Ag/g-C_3N_4 nanostructure and an input laser power of 50 mW. The third-order NLO values of Ag/g-C_3N_4 nanostructure vs. the concentration are summarized in Table 3.

The higher third-order nonlinearity of Ag/g-C_3N_4 nanostructure was obtained for the lower concentration. Because of the interactions between the nanoparticles, NLO values rise with increasing nanoparticle concentration. The contact between nanoparticles grows as the distance among them reduces, resulting in more absorption and refraction. When the concentration of nanoparticles is increased more, the size of the nanoparticles can also grow, eventually resulting in a reduction in nonlinear characteristics [38, 39].

The findings imply that the Ag/g- C_3N_4 nanostructure has strong third-order NLO characteristics and might be a suitable material for nonlinear optical device applications [14].

3.3 FTIR analysis

Fig. 8 shows the FTIR spectra of the g-C_3N_4 and Ag/g-C_3N_4 samples, respectively. In FTIR spectrum of g-C_3N_4 and Ag/g-C_3N_4 samples, three important absorption regions were observed.

First, almost sharp peak at 809 cm^{-1} is attributed to the breathing mode of s-triazine units [40, 41]. Second, the broad peak at 3159 cm^{-1} is ascribed to the stretching vibration of N-H group [41, 42]. Finally, a series of strong absorption peaks in 1200–1650 cm^{-1} region is corresponded to the CN stretching vibration, indicating the presence of a typical CN structure such as aromatic C-N stretching vibration [42, 43]. As FTIR spectra of Ag/g-C_3N_4 shows, all observed FTIR peaks for g-C_3N_4 and suggest that the overall structure of g-C_3N_4 was not changed after Ag nanoparticles loading [44].

3.4 Kramers-Kronig method

The optical and dielectric constants of g-C_3N_4 and Ag/g-C_3N_4 were calculated using KK method. According to literature, reflectance function of samples R (ω) is a crucial key in detecting constants [45]. Both real and imaginary parts of $\tilde{N}(\omega)$ and $\tilde{\varepsilon}(\omega)$ based on using KK method can be calculated as follow [45, 46]:

$$\begin{aligned}\tilde{N}(\omega) &= n(\omega) + i\ k(\omega) = A\ \{(1 - R(\omega) + i\ \ (-2\sqrt{R(\omega)}\sin\varphi(\omega))\} \\ \tilde{\varepsilon}(\omega) &= \varepsilon_1(\omega) + i\ \varepsilon_2(\omega) = \{(n^2(\omega) - k^2(\omega)) + i\ 2n(\omega)k(\omega)\}\end{aligned} \tag{6}$$

Where $A = (1 + R(\omega) - 2\sqrt{R(\omega)}\cos\varphi(\omega))^{-1}$.

Fig. 9 indicates real and imaginary parts of $\tilde{N}(\omega)$ of g-C_3N_4/Ag/ g-C_3N_4 in the range of 1000-2500 cm^{-1}.

Adding Ag in $g - C_3N_4{}^+$, causes to increase the intensity of two parts of $\tilde{N}(\omega)$. The maximum intensity of $n(\omega)$ was 18.3 around 2121 cm^{-1} and for $k(\omega)$ was 13.1 around 2118 cm^{-1}. In different literatures, the similar findings confirm our results [47-55].

The Transversal Optical (TO) and Longitudinal Optical (LO) modes are detected by real and imaginary parts of $\tilde{N}(\omega)$ as intersection points of them (Fig. 10) [56]. TO (lower frequency) and LO (higher frequency) modes are depicted in Fig. 10.

The $\tilde{\varepsilon}(\omega)$ function of g-C_3N_4 and Ag/g-C_3N_4 nanostructure calculated using Eq (6) are in the range of 1000-2500 cm^{-1} shown in Fig. 10. Adding Ag to g-C_3N_4 increased the real and imaginary parts of dielectric coefficients. Inter-band transitions between the bands correspond to structural peaks in the imaginary component of the dielectric function (ε_2). Otherwise, when the ε_1 curves versus wavenumber turns positive to negative data, the turning point is TO frequencies. The turning point of negative to positive data of ε_1 curve is LO frequencies. Using each method, TO and LO frequencies of synthesized sample are equal. The real and imaginary parts of permittivity of synthesized samples increased by adding Ag to g-C_3N_4.

As it is obvious in Fig. 11, the overall value for the imaginary part of $(-1/\tilde{\varepsilon})$ at 1500-2500 cm^{-1} increased with adding Ag into g-C_3N_4. Additionally, LO frequency occurs at maximum in the imaginary part of $(-1/\tilde{\varepsilon})$ [57]. As to TO and LO frequencies of Ag doped g-C_3N_4, by Ag in matrix, TO and LO have red shifts. Al related frequencies (TO and LO) are tabulated in Table 4. Also, the materials with high ε_1 and ε_2 apply in sensing and actuating industries [48].

The complex dielectric function may be used to characterize the optical properties of solids generally. Sonali Saha [58] suggested that the dielectric function can be used as the basis of other optical properties [59]. The absorption coefficient $\alpha(\omega)$ is introduced in terms of dielectric function [60].

Shorie et al. determined the dielectric function spectrum for pure gCN and gCN including a Hg atom [61]. The intensity of peaks related to in-plane polarization status of gCN-Hg slightly increased than gCN ones, in which the reason of other peaks is reported plasmonic excitation [61]. Some researches were done theoretically on Au/g-C_3N_4 monolayer [60]. Accordingly, in the visible range, this substance has excellent optical characteristics. Furthermore, the insertion of Au into the cavity of a single layer of g-C_3N_4 saves energy [60].

Lin and his coworkers explored the optical characteristics of g-C_3N_4/TiO_2 via KK relation and the complex dielectric function [62]. They found that after forming a g- C_3N_4/TiO_2, the edge of absorption curve shifts to a higher λ, and the highest absorption activity of the g- C_3N_4/TiO_2 is above 330 nm in comparison with g- C_3N_4 and a TiO_2 (101) slab [62].

According to literature, our calculated results indicated the good agreement with related researches, in which the enhanced optical responses of Ag/g-C_3N_4 can be a key factor for improving the optical, electronic and photocatalytic activity.

4 Conclusion

The single beam Z-scan method was used to provide the results of an experimental investigation into the third-order NLO characteristics of materials. The SA and self-focusing capabilities were demonstrated in the prepared samples. The NLA performances and third-order NLR index of Ag/g-C_3N_4 nanostructures were higher than those of g-C_3N_4 nanosheets. The enhanced optical nonlinearity of Ag/g-C_3N_4 over g-C_3N_4 was attributed to a number of important factors, such as the combined consequence of the Ag's localized surface plasmon resonance (LSPR) effect and the hybrid effect of g-C_3N_4, resulting in a coupling interaction of improved light absorption intensity, significant separation capability of photoproduced electrons–holes, and prolonged charge carrier lifetime. Moreover, Ag/g-C_3N_4 nanostructure shows self-focusing nonlinearity and good NLA behavior at lower concentration. Besides, we investigated the optical and dielectric properties via KK method. Actually, Ag/g-C_3N_4 led to higher refractive index and dielectric coefficient than g-C_3N_4 in the range of IR wavelength. Moreover, the red shifts of Ag/g-C_3N_4 in TO and LO frequencies were more obvious than g-C_3N_4.

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Figure Captions

Fig. 1. Instrumentation of the present work.

Fig. 2. XRD diagram of prepared g-C_3N_4 and Ag/g-C_3N_4 nanomaterials.

Fig. 3. FESEM resalts of (a) g-C_3N_4, (b) Ag/g-C_3N_4 and the elemental mapping data of C (c), N (d), Ag (e), O (f), and EDX analysis of (g) the Ag/g-C_3N_4.

Fig. 4. (a) UV-Vis results of g-C_3N_4 and Ag/g-C_3N_4 nanomaterials and, (b) Tauc plot for g-C_3N_4 and Ag/g-C_3N_4 (c) PL spectra of prepared nanomaterials.

Fig. 5. Schematic illustration of Ag/g-C_3N_4 heterostructure including (a) The relaxed g-C_3N_4 unit cell to (b) construct rectangular g-C_3N_4 monolayer. After that, the relaxed rectangular g-C_3N_4 monolayer combined with (c) relax Ag_6 stable cluster to arrangement Ag/g-C_3N_4 heterostructure (d) The top and side views of relaxed Ag/g-C_3N_4 heterostructure. Values shown for bond distances were extracted from reference [30].

Fig. 6. (a) OA Z-scan curve and (b) pure CA Z-scan curve of g-C_3N_4 and Ag/g-C_3N_4 nanomaterials.

Fig.7. (a) OA Z-scan curve and (b) pure CA Z-scan curve of Ag/g- C_3N_4 nanomaterials at different concentrations.

Fig. 8. FTIR spectra of prepared nanostructures of g-C_3N_4 and Ag/g-C_3N_4 samples.

Fig. 9. The refractive index (solid line) and extinction coefficient (dash line) for g-C_3N_4 and Ag/g-C_3N_4 nanostructure.

Fig. 10. The real (solid line) and imaginary (dash line) parts of dielectric function for g-C_3N_4 and Ag/g-C_3N_4 nanostructures.

Fig. 11. The $\mathrm{Im}(-1/\varepsilon)$ of g-C_3N_4 and Ag/g-C_3N_4 nanostructures.