Enhanced nonlinear absorption and efficient power limiting action of Au/Ag@graphite core-shell nanostructure synthesized by laser ablation

Shiju E, Siji Narendran N K, Narayana Rao D and Chandrasekharan K

1 Laser and Nonlinear Optics Laboratory, Department of Physics, National Institute of Technology Calicut, Kozhikode 673601, Kerala, India
2 T K Madhava Memorial College, Nangiarkulangara, Alappuzha, 690513, Kerala, India
3 School of Physics, University of Hyderabad, Gachibowli, Hyderabad, 500046, India

E-mail: csk@nitc.ac.in

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Abstract

Here we report a drastic enhancement of nonlinear absorption behaviour and exceptional optical limiting action of two core-shell systems (Au@graphite and Ag@graphite) prepared by adopting a fairly easy way in which we did not use any graphitic substrate. We carried out pulsed laser ablation of Au and Ag targets in toluene, monosubstituted benzene from which graphite layers of nanometer thickness has emerged as a result of photochemical reactions. The prepared samples were characterized and analyzed by UV/Vis spectroscopy, Raman spectroscopy, and TEM. Theoretical simulations of the core-shell nanostructures were done by the finite-difference time-domain method underlined the quenching of SPR in the case of both Au and Ag NPs by the graphitic layers evolved from toluene. Au and/or Ag@graphite core-shell structure exhibited a huge improvement in the nonlinear absorption behaviour and the optical limiting efficiency of these systems is found to be better than that of many benchmark optical limiters. The enhancement in nonlinear absorption property and the limiting actions of these systems were attributed to the enhanced excited-state absorption as well as free-carrier absorption arose as a result of the modification in the electronic structure of graphite on core-shell formation. Moreover, the metallic NPs also enhances nonlinear absorption through free-carrier absorption free-carrier absorption. So we believe these results are quite useful for guiding the characterization, monitoring the synthesis of similar nanostructures and for, the development of nanohybrids with desired properties for nonlinear optical, optoelectronic and photocatalytic applications.

Introduction

Carbonaceous materials are one of the superior materials due to their excellent thermal and chemical stability, corrosion resistance, low cost, and lightweight and have attracted tremendous research interest from many technologically advanced countries during the last few years due to its versatile electronic, mechanical, and optical properties. Graphene, graphite, carbon nanotube, carbon dots, and fullerenes are a few of the allotropes, which offer excellent device efficiency [1–3]. These well-known multifunctional materials are found to be useful in applications such as catalysis [4], energy storage [5], microwave absorption [6], and biomedicine [7]. By surface modification or intercalation with nanoparticles, it is possible to enhance the properties of these materials [8–10]. Optical limiters are materials which exhibit a constant transmittance at lower intensities and a reduced transmittance at elevated intensities. Substantial research work has been focused in the direction of developing efficient optical limiting (OL) materials for protecting the delicate optical components and even human eyes etc from intense beams [11–15]. These materials can effectively attenuate intense light in a wide
spectrum of wavelengths via nonlinear absorption and nonlinear scattering. Among the carbonaceous materials, graphene is getting much research attention owing to its exceptional electronic, optical, and mechanical properties [16, 17]. As the incident light wavelength does not influence the interband transitions in graphene over a wide range, it has shown exclusive nonlinear optical properties [10, 18]. A number of studies on different materials like organic, inorganic, semiconductors and metal complexes, etc have been carried out to find an ideal optical limiter, as the existing optical limiters are short of ideal capabilities [19–22]. Research is still going on to develop a practical ideal optical limiter, which should be highly stable and suitable to use in an un-favoured atmosphere [19–22].

Since it was first studied by Wang et al [23], some works have been conducted to understand the OL properties and the underlying mechanisms of carbonaceous materials, like graphene, graphene oxide (GO) and graphene nanocomposites [24, 25]. The key mechanism behind the limiting action is attributed to the nonlinear scattering effect, where solvent microbubbles and/or microplasmas were produced as a result of interaction with intense light fluence, causing the attenuation of the incident light beams.

Recently, nanocomposites made of noble metal nanoparticles with graphene and its other allotropes are getting much consideration owing to its enhanced linear and nonlinear optical properties [26, 27]. Vincenzo Amendola has already shown it in 2005, Au nanoparticle prepared by laser ablation in toluene was not exhibiting characteristic surface plasmon absorption, and they also observed that these nanoparticles are included in the graphitic matrix, which prevents the formation of bigger particles and thus suppresses the surface plasmon absorption [28]. Moreover, a similar result is reported by the same group in 2016 based on the discrete dipole approximation method, the surface plasmon resonance (SPR) of Au and Ag NPs are seriously affected in the proximity of graphene [29]. By calculations they could show that the SPR of Ag nanoparticles is quenched in nanohybrids, whereas surface plasmon quenching or enhancement can be found with Au nanoparticles, depending on the configuration accepted. However, Au/Ag-based core-shell structure can enhance the optical limiting properties by charge/energy transfer and local field effects. For example, a good enhancement in nonlinear optical property is observed in GO when it is decorated with Au NPs and it is found that efficient charge and/or energy transfer and synergistic coupling between the GO and Au NPs is the mechanism behind the improved NLO properties [30]. Similarly, graphene decorated with Ag NPs is found to exhibit strong saturable absorption behaviour and it is attributed to the electronic interaction among the system [31]. Carbonaceous core-shell materials with metallic core may alter the electronic properties with an excellent NLA effect [32]. Good photo-stability along with exceptionally well NLA activity renders these core-shell nanostructures an outstanding candidate for short pulse optical limiting applications. Though such composites score well in terms of nonlinear optical parameters, the preparation part is usually cumbersome, especially with certain core-shell type composites. Here we synthesis Au/Ag core-based graphitic core-shell structure by laser ablation of Au/Ag target in toluene and its detailed NLA analysis is provided. The NLA analysis of this kind of system is not reported by anyone to the best of our knowledge. The excellent NLA behaviour of the studied system makes them be quite suitable candidates for optical limiting applications.

**Experimental**

**Synthesis of Au/Ag @graphite core-shell nanostructures**

Laser ablation is one of the easiest and cleanest ways to produce nanoparticles in vacuum or liquids. It has many advantages over other nanoparticle synthesizing techniques [32, 33]. Here, particle size is depending on laser wavelength, fluence, pulse width, and dielectric constant of the surrounding medium [33]. Au@graphite and Ag@graphite core-shell structures were synthesized by laser ablation technique using an Nd: YAG laser of wavelength 532 nm, 7 ns pulse width, and 10 Hz repetition rate. Au/Ag (>99%) target of 1 mm thickness was taken in a glass beaker, which contains a 10 ml solution of toluene solution. The laser beam was tightly focused on the target using a convex lens of 10 cm focal length with a laser fluence of 20 mJ cm$^{-2}$ and the ablation process is carried out for 7 min. The transparent solution turns into a yellowish colour which confirms the formation of core-shell structures. The mechanism behind the NPS formation by pulsed laser ablation is reported elsewhere [32, 33]. Interaction of the laser beam with toluene produces the graphene layer which further leads to the formation graphitic layer around the NP with few nanometer thicknesses which is schematically shown in figure 1. Ag and Au NPs were prepared separately in diacetone alcohol under the same experimental conditions for comparing the results (SI-1 is available online at stacks.iop.org/NANOX/1/030026/mmedia).

**Optical and morphological characterization**

Morphology of the prepared sample was analyzed using high-resolution transmission electron microscopy ((HR-TEM) JEOL, JEM-2100). Absorption spectra in the range of 200 to 1100 nm of the samples were taken
using UV-Visible spectrophotometer (Shimadzu-UV 2450). Raman analysis of the sample is conducted using LabRam HR micro Raman spectrometer with an excitation wavelength of 600 nm and collection time of 1 s. The possibility of local field effect by the Ag/Au NPs on the samples was studied using Lumerical finite-difference time-domain (FDTD) solutions software.

**Nonlinear absorption measurements**

Nonlinear optical absorption analysis of the prepared samples was carried out by the Z-scan technique using a Q-switched Nd:YAG laser at 532 nm wavelength, 7 ns pulse width and 10 Hz repetition rates. The details of the experimental setup are described elsewhere [32, 34]. However, a brief description and useful parameters are given below. The incoming beam is divided into two by a beam splitter; the reflected beam was used as the reference beam and the transmitted beam was focused on the sample through a convex lens (focal length 15 cm). The beam waist at the focus ($w_0$) and Rayleigh range of the laser beam were calculated as 17 $\mu$m and 1.7 mm respectively. The sample was taken in a 1 mm thick quartz cuvette to guarantee the validity of thin sample approximation analysis. The experiment was conducted by moving the sample over a distance of 40 mm across the focus in steps of 1 mm under constant input pulse energy with the help of a computer-controlled translational stage. Both the transmitted light from the sample and the reference beam was monitored simultaneously using two similar pyroelectric detectors (RjP-735, Laser Probe Corp., USA) and the ratio was taken by an energy ratio meter (Rj-7620, Laser Probe Corp., USA). Collective thermal effect was reduced by functioning laser pulse in single-shot mode. For comparative analysis, Z-scan studies of all the samples were conducted at a linear transmittance of around 80%.

**Results and discussions**

**TEM analysis towards morphology**

To understand the size, structure, and morphology, of the prepared sample, transmission electron microscopy analysis is carried out. Sample for TEM characterization was prepared by putting a drop of the sample solution onto a carbon covered copper grid and dried out before the examination. TEM image of the hybrid system was shown in figure 2. From the TEM images, it is clear that graphitic nanocrystals enclose Au/Ag NPs with different sizes varies from a fraction of nanometer to tens of nanometers. The contours of graphite are not well-defined around small particles. This indicates their attachment in an amorphous carbon matrix which also stops their growth, though the interparticle separation is very small. The carbon matrix prevents the formation of larger particles and therefore, indirectly, the presence of the SPR peak. The formation of the graphitic carbon matrix can be elucidated by recalling the synthesis reported in the literature, where graphitic materials are produced from the pyrolysis of benzene [35]. The graphitic structure which is surrounded by Au/Ag NPs in our sample is of a similar kind reported by Chieu et al since the Raman spectra obtained for graphitic material in our case is very similar to the one obtained from the pyrolysis of benzene. Hence, we can infer that the process is of the same nature [36]. It is clear from the literature that the carbon matrix can not only control the growth of nanoparticles but also suppress the surface plasmon absorption of bigger particles [28].

UV/Visible absorption spectra of the prepared samples are shown in figures 3(a) and (b). The absorption spectra of both samples Au@graphite and Ag@graphite core-shell show almost similar absorption, with
absorption maxima located around 286 nm. We expect the surface plasmon peak of Au as well as Ag in the absorption spectrum in addition to the graphitic peak which is missing. The theoretical model predicts (figures 4(a) and (b)) that if it is Au NPs alone in the toluene solution there should be SPR absorption with maximum absorbance around 530 nm for the nearly same size of the particles which we obtained, it is true also in the case of Ag, where SPR maximum located around 400 nm (black lines in figures 4(a) and (b)). The presence of Au/Ag NPs in the system is confirmed from EDS and XRD studies (SI-II). A core-shell structure model based on Au/Ag core with nanometer thickness graphitic layer as shell, we could see that the intensity of 530 nm SPR peak of Au/400 nm SPR peak of Ag start decreasing and at the same time a new peak at 280 nm formed as we introduce graphite layer 0.1 nm thicknesses. This SPR peak is completely diminished when the shell thickness became 1.5 nm for Au and 3 nm for Ag. These facts are completely in agreement with the transmission electron spectroscopy results, where we found that Au and Ag nanoparticles having a size less than 5 nm is formed and a thin layer of graphite surrounds it. Since the absorption peaks are similar for both Au@graphite and Ag@graphite core-shell systems, and the absorption maxima is located around 286 nm, the heterostructure shows the absorption spectrum of graphitic carbon.

To explore the plasmonic effects of Au@graphite and Ag@graphite core-shell nanostructures, near-field intensity distributions around the nanostructures and absorption property of nanostructures were simulated using the finite-difference time-domain method. Near field intensity distribution of Ag NPs (SPR ~ 400 nm) in toluene is shown in figure 5, and it is clear that there is a strong local field enhancement on the near-surface of the nanoparticle. It is also observed that the near field intensity of Ag NP completely vanishes when it forms a core-shell structure with graphite. A similar result is observed in the case of Au NPs.

Raman spectrum analysis
Figure 6 shows the Raman spectra of the samples. Toluene alone did not show any Raman peak whereas laser irradiated toluene exhibited Raman peaks similar to that of graphite when excited at 600 nm. Mainly two broad
Figure 4. Simulated Absorption spectra of (a) Au and (b) Ag NPs in toluene (black); SPR peak is located around 530 nm for Au NPs and 400 nm for Ag NP. Coloured lines are a variation of the absorption spectrum when it is simulated as (a) Au@graphite and (b) Ag@graphite layer with different layer thickness.

Figure 5. Normalized near-field intensity distributions around (a) Ag nanoparticles (b) Ag@graphite core-shell structure.

Figure 6. Raman spectra of pure toluene (blue), irradiated toluene (red), Au@graphite (black) and Ag@graphite (green) formed as a result of pulsed laser ablation of respective targets in toluene.
peaks were observed in the Raman spectrum which is characteristic of the graphitic carbon spectrum: one at 1355 cm\(^{-1}\) (D band) and another one at 1592 cm\(^{-1}\) (G band). Vincenzo Amendola reported similar Raman results when they ablated Au NPs in toluene using a 1064 nm laser source [28]. Both Au and Ag targets ablated in toluene exhibit Raman peaks correspond to graphitic carbon and the Raman signal intensity is found to be enhanced in the case of both silver and gold, in which gold compound shows maximum enhancement. Since the SPR of NP is absent in this core-shell structure the enhancement in Raman signal intensity is due to charge/energy transfer between the nanoparticles and graphite nanostructures [32].

**Nonlinear optical analysis**

To investigate the potential of the prepared sample to work as a good third-order NLO material under ns excitation regime and to understand the mechanism responsible for the nonlinearity, Z-scan analysis of the samples was carried out. When the intensity of the interacting light is sufficiently strong the chances of absorbing more than one photon in a single event increases resulting in nonlinear optical behaviour. There is a probability of occurring many nonparametric phenomena due to the presence of a real excited state, which is reachable through multiphoton and/or excited state absorption within the time duration of the interacting beam. These phenomena are taken place through different processes like multiphoton absorption, excited-state absorption, free carrier absorption, etc depending on the excitation wavelength, intensity, and pulse width. Figure 7 shows the open aperture Z-scan signatures of the samples at 0.14 GW cm\(^{-2}\). Z-scan traces represented by solid spheres in the figure were fitted numerically using equation (1) and the value of nonlinear absorption coefficient $\beta_{eff}$ has been extracted [32, 34]. The results are summarized in table 1.

![Figure 7.](image-url)
which leads to the depletion of the ground state population. Under sufficient two-photon absorption. The strong contribution of ESA comes from the availability of real intermediate states, NLA can be discussed like this; the metallic system normally exhibits NLA through FCA since the availability of intermediate levels became highly populated and photons are further absorbed from this level. Enhancement in NLA coefficient of toluene to graphene or graphitic layer upon laser irradiation. It is well known that carbonaceous materials are shows significantly enhanced NLA at a particular on-axis input intensity. We checked the NLA property of pure toluene, toluene irradiated with different materials will improve the NLO properties significantly. Moreover, it is also reported that forming composite, core-shell structures, under nanosecond excitation regime and found that the modification of the electronic structure of graphite on core-shell formation plays a crucial role in improved nonlinearity. This modification leads to the accessibility of dopant state within the bandgap which results in an enhanced NLA through free-carrier absorption and excited-state absorption. Here, in our case, the formation of Au/Ag/graphite core-shell leads to the formation of new defects and it will modify the electronic structure within the bandgap of the graphite layer as a result of interaction between Au/Ag NPs. Accessibility of new defect states improves the NLA significantly via Excited-State absorption (ESA) and free-carrier absorption (FCA). [29]. The schematic energy level model represents the different transitions towards the observed NLA is shown in figure 7(b). Here VB and CB are the valence band and conduction band of graphite carbon and metal nanoparticles. On exciting the system with the laser beam, the electrons get excited to the excited state of graphite carbon and from there it can easily transfer to the lower-lying vacant d orbitals of metal nanoparticles. It is also possible to transfer the electrons from the excited state to the valence band of metal nanoparticles. From there absorption of another photon leads to the transition of an electron to higher-lying excited states. Further absorption of the photon moves the electron to the continuum via free carrier absorption. The quality/degree of the graphitization has a significant role in the observed nonlinear absorption. An optimal degree of graphitization is essential for improving the NLA strength. The degree of graphitization increases the defects that modify the energy band structure of the system. In other words, the formation of defects state within the bandgap region modifies the bandgap as a result of altering the electronic structure associated with the energy bands. It strongly influences the linear and nonlinear optical properties of the system. Moreover, The interaction between the energy levels of graphitic layers and Au/Ag NPs in Au/Ag@graphite core-shell will lead to the formation of complex energy level which is visible in the Raman spectra, where we observed a significant enhancement in Raman intensity, even though the core-shell system did not exhibit SPR, and the enhancement could be attributed to energy/charge transfer. It is noteworthy to mention that the $\beta_{eff}$ is strongly influenced by, FCA, ESA, and comparatively less contribution from direct two-photon absorption. The strong contribution of ESA comes from the availability of real intermediate states, which leads to the depletion of the ground state population. Under sufficiently strong input intensity the real intermediate levels become highly populated and photons are further absorbed from this level. Enhancement in NLA can be discussed like this; the metallic system normally exhibits NLA through FCA since the availability of free electrons enables the absorption of energy via Ohmic conduction. The coexistence of the metallic core and

| Sample               | On-Axis Intensity GW cm$^{-2}$ | Limiting threshold J cm$^{-2}$ | $\beta_{eff}(\text{cm GW}^{-1})$ |
|---------------------|-------------------------------|-------------------------------|---------------------------------|
| Toluene             | 0.14                          | —                             | 0.14                            |
| Toluene (laser irradiated) | 0.14                          | —                             | 1.30                            |
| Au (diaceton alcohol) | 0.14                          | —                             | 48.0                            |
| Au@graphite         | 0.14                          | 0.38                           | 305.0                           |
| Ag (diaceton alcohol) | 0.14                          | —                             | 55.0                            |
| Ag@graphite         | 0.14                          | 0.33                           | 320.0                           |
| C$_{40}$            | 3                             |                               |                                 |
| GO + Porphyrin      | 1.9                           |                               |                                 |
| Au + Porphyrin      | 4.3                           |                               |                                 |
| Pt/f-HEG            | 13.7                          |                               |                                 |
| Pd/f-HEG            | 8.8                           |                               |                                 |
| CuO/f-HEG           | 4.4                           |                               |                                 |
| GO-Ag               | 6.4                           |                               |                                 |

$$T(z) = \frac{1}{\sqrt{\pi q(z)}} \int_{\infty}^{\infty} \ln \left[ 1 + q(z)e^{-r^2} \right] dr$$  \hspace{1cm} (1)$$

$q(z) = \frac{\beta_{eff}L_0}{(1 + z^2/\omega_0^2)}$ and $L_0 = (1 - e^{-\alpha L})/\alpha$, where $L$ is the sample thickness and $\omega_0$ is the Rayleigh range and $\omega_0$ is the beam waist radius at the focus and $\lambda$ is the wavelength of the laser source.

From the signature, it is clear that the sample produced by ablating Au/Ag in toluene exhibits exceptionally well NLA at a particular on-axis input intensity. We checked the NLA property of pure toluene, toluene irradiated (same time and intensity used for ablating Au/Ag in toluene) to confirm the contribution from the solvent. It is found that toluene alone did not show any nonlinearity at this intensity, whereas irradiated toluene shows significant nonlinear absorption. Observed NLA of irradiated toluene could be attributed to decomposing of toluene to graphene or graphitic layer upon laser irradiation. It is well known that carbonaceous materials are good NLO materials. Moreover, it is also reported that forming composite, core-shell structures, or doping with different material will improve the NLO properties significantly. Considering the NLO properties of core-shell systems, both the samples exhibited good nonlinear absorption with a very high NLA coefficient. R. Kumar et al. [29] reported the enhancement in Fe$_3$C@graphite core-shell nanostructures under nanosecond excitation regime and found that: The modification of the electronic structure of graphite on core-shell formation plays a crucial role in improved nonlinearity. This modification leads to the accessibility of dopant state within the bandgap which results in an enhanced NLA through free-carrier absorption and excited-state absorption. Here, in our case, the formation of Au/Ag@graphite core-shell leads to the formation of new defects and it will modify the electronic structure within the bandgap of the graphite layer as a result of interaction between Au/Ag NPs. Accessibility of new defect states improves the NLA significantly via Excited-State absorption (ESA) and free-carrier absorption (FCA). The schematic energy level model represents the different transitions towards the observed NLA as shown in figure 7(b). Here VB and CB are the valence band and conduction band of graphite carbon and metal nanoparticles. On exciting the system with the laser beam, the electrons get excited to the excited state of graphite carbon and from there it can easily transfer to the lower-lying vacant d orbitals of metal nanoparticles. It is also possible to transfer the electrons from the excited state to the valence band of metal nanoparticles. From there absorption of another photon leads to the transition of an electron to higher-lying excited states. Further absorption of the photon moves the electron to the continuum via free carrier absorption. The quality/degree of the graphitization has a significant role in the observed nonlinear absorption. An optimal degree of graphitization is essential for improving the NLA strength. The degree of graphitization increases the defects that modify the energy band structure of the system. In other words, the formation of defects state within the bandgap region modifies the bandgap as a result of altering the electronic structure associated with the energy bands. It strongly influences the linear and nonlinear optical properties of the system. Moreover, The interaction between the energy levels of graphitic layers and Au/Ag NPs in Au/Ag@graphite core-shell will lead to the formation of complex energy level which is visible in the Raman spectra, where we observed a significant enhancement in Raman intensity, even though the core-shell system did not exhibit SPR, and the enhancement could be attributed to energy/charge transfer. It is noteworthy to mention that the $\beta_{eff}$ is strongly influenced by, FCA, ESA, and comparatively less contribution from direct two-photon absorption. The strong contribution of ESA comes from the availability of real intermediate states, which leads to the depletion of the ground state population. Under sufficiently strong input intensity the real intermediate levels became highly populated and photons are further absorbed from this level. Enhancement in NLA can be discussed like this; the metallic system normally exhibits NLA through FCA since the availability of free electrons enables the absorption of energy via Ohmic conduction. The coexistence of the metallic core and
graphitic shell contribute NLA through ESA and FCA besides a small contribution of TPA. There is a synergistic relationship between the metal core and defective graphitic carbon in improving NLA.

The open aperture Z-scan studies were conducted for different input intensities to further confirm the underlying mechanism behind the NLA. Figure 8 shows the $\beta_{\text{eff}}$ plot as a function of the on-axis intensity of Au@graphite and Ag@graphite respectively. From the signatures, it is clear that $\beta_{\text{eff}}$ is decreasing with increasing on-axis intensity and it is the characteristic property of ESA, where at higher input intensities significant depletion occurred in the ground state population that results in reduced $\beta_{\text{eff}}$ value. If it is genuine TPA, the $\beta_{\text{eff}}$ remains unchanged even if we increase the input intensity [32].

To compare the results, Au and Ag nanoparticles were ablated under a similar experimental condition in diacetone alcohol. The prepared NPs are found to exhibit SPR peak around 523 nm for Au NPs and 410 nm for Ag NPs (SI). Figure 9 shows the open aperture Z-scan signatures of Au and Ag NPs ablated in diacetone alcohol and toluene. The NLA parameter obtained for Au and Ag NPs ablated in toluene is exceptionally higher than that of Au and Ag NP formed in diacetone alcohol. A huge enhancement in the value of NLA coefficient is observed in the case of both Au and Ag. 6.4 times enhancement is observed in the case of Au NPs and a 5.8 times enhancement (Table 1) is observed in the case of Ag NPs.

Optical limiting is activated, when the interacting light alters the absorptive and refractive nonlinearity of the material, as a result of which the transmitted intensity is greatly attenuated. A number of nonlinear mechanisms like reverse saturable absorption, nonlinear scattering, and nonlinear refraction are responsible for the limiting action [37–41]. Optical limiting properties of the sample are studied by plotting normalized transmittance as a function of input fluence which can be expressed by equation (2).
Where $E_{\text{pulse}}$, $w(z)$, and $\tau$ are the energy of the incoming pulse, beam radius at a distance $z$ from the focus, and pulse width of the laser beam respectively. Optical limiting data is directly extracted from the open aperture Z-scan results. The fluence experienced by the sample is gradually varied which is maximum at the focus. From the OL signature of the compound (figure 10) it is clear that the curve deviates from the linear dependence of output transmittance on input fluence as the input intensity reaches a particular (onset) value. Here at this input intensity, pure toluene keeps the linear dependence of output transmittance as we increase the input fluence (Beer’s Law). The remaining samples deviate from Beer’s law and became more opaque as the input fluence increases. The optical limiting threshold value (input fluence at which output transmittance drops to 50% of the initial transmittance) is found to be one of the best ($0.38 \text{ J cm}^{-2}$ for Au@graphite and $0.33 \text{ J cm}^{-2}$ for Ag@graphite) and it is better than many benchmark results under similar study reported recently (table 1) [37–41]. The limiting mechanism in the case Au@graphite and Ag@graphite were attributed to the NLA mechanism discussed above and it is also obvious that the power limiting efficiency is significantly enhanced when it forms Au/Ag graphite core-shell structure.

Conclusion

In summary, we discuss the huge enhancement of the nonlinear absorption behaviour of Au and Ag NPs in preparing their core-shell structures with graphite by pulsed laser ablation of Au and/or Ag targets in toluene. The interaction of laser pulses with toluene, a mono-substituted benzene derivative, results in the formation of graphitic carbon layers. The quenching of SPR in the case of both Au and Ag NPs by the graphitic layer was confirmed from the theoretical simulations studies done by finite-difference time-domain software and it is experimentally verified from UV/visible spectroscopy, Raman spectroscopy, and TEM analysis. A drastic enhancement in the NLA on nanohybrid formation could be due to the interplay between the intermediate energy states of metal and graphite. Also, the photo-generated charge carriers in the conduction bands of Au/Ag or the increase in defect states during the formation of core-shells might also contribute to excited state absorption and free carrier absorption and thus the enhancement in nonlinear absorption. Since the integration of Ag and Au NPs with graphite is frequently sought for the realization of hybrid materials with optical, photoelectric, and photocatalytic applications, these results are useful to guide characterization and for monitoring the synthesis of similar nanostructures, as well as for the development of nanohybrids with desired optical properties.

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Conflicts of interest

There are no conflicts to declare.

ORCID iDs

Shiju E https://orcid.org/0000-0001-8489-0474

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