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Effect of complex formation on nonlinear optical parameters of dye-graphene system

Sudhakara Reddy Bongu, Prem B. Bisht *, Basanth S. Kalanoor, Raman C.K. Namboodri, Pranati Nayak, Sundara Ramaprabhu

Department of Physics, Indian Institute of Technology Madras, Chennai 600036, India

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ABSTRACT

The effect of saturable absorption in a dye decreases significantly in the presence of functionalized hydrogen-induced exfoliated wrinkled graphene (f-HEG). The absorption spectra give strong evidence of complex formation in the ground state. The fluorescence spectra and nonlinear optical properties of the dye are affected by f-HEG and silver decorated graphene (Ag-f-HEG) by various degrees. The open aperture Z-scan and degenerate four wave mixing (DFWM) techniques have been used to record the drastic changes in the nonlinear optical parameters of dye in presence of f-HEG and Ag-f-HEG. The results indicate a reduction in the average value of the nonlinearity due to formation of the non-fluorescent ground-state charge-transfer complex. At high input irradiance the optical limiting capability of the dye-f-HEG system has been found to be enhanced. The pre-existing charge transfer between silver nanoparticles and f-HEG reduces the strength of dye-f-HEG complex formation.

1. Introduction

Graphene finds applications in various fields due to its superior mechanical, electronic, optical, magnetic, and thermal properties [1–3]. The zero band gap nature of graphene allows broadband absorption in the electromagnetic spectrum. Single layer of graphene can absorb 2.3% of incident light over a broad wavelength range [4]. It has been reported that graphene can interact with dyes through the π–π stacking resulting in the electron transfer [5]. Non-covalent functionalization of graphene with organic molecules has been found to tune its electronic structure [6]. Dye-graphene systems have found applications in resonance Raman spectroscopy [7], high-contrast visualization of graphene based sheets [8] and in photovoltaic cells [9]. Metal nanoparticles play significant role in spectroscopy due to their size, shape and localized surface plasmon resonances (LSPRs) [10]. The LSPRs have been used for surface enhanced Raman scattering [11], fluorescence modification [12,13] and bio-sensing [14]. It has been reported that when metal nanoparticles are in near proximity to the graphene surface, the bi-directional charge transfer takes place due to difference in the work function [15].

The semiconductor saturable absorber mirrors (SESAMS) used for the passive mode-locking need costly and complex fabrication technique [16]. Organic dyes have been used traditionally for lasers [17] and mode-locking [18], and also as model systems in nonlinear optics but undergo bleaching on prolonged use. Graphene in polyvinyl alcohol has been used for mode-locking at 1559 nm, based on its saturable absorption (SA) property [19]. Feng et al., have reported the broad band optical limiting behavior of graphene composites [20]. Enhancement in the SA behavior and low threshold optical power limiting has been observed in the presence of silver nanoparticles and dye than for the pristine graphene [21,22].

The combination of materials (graphene, nanoparticles and dyes) may lead to integration of the properties of the new hybrid materials those posses important features for industrial applications. The metal decorated graphene sheets have been used for heat transfer in nanofluids [23], gas sensing and optoelectronic devices [24,25]. An economical alternate for the SESAM technology [26] can be the binary dye-nanoparticles [27] or ternary systems including graphene in the visible and IR region. This is so as the adsorption of various organic molecules or metal nanopaticles on to the graphene surface results in increase in the number of either electrons or holes through molecular charge transfer [15]. Such an induced charge transfer in turn can change the electronic and optical properties.

In view of the above, to decipher the underlying mechanism of the charge transfer, the dye-graphene-nanoparticle system needs a detailed study of its spectroscopy and the nonlinear optical properties. Here, we have studied the effect of functionalized

* Corresponding author. Tel.: +91 4422574866.
E-mail address: bisht@iitm.ac.in (P.B. Bisht).

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hydrogen-induced exfoliated wrinkled-multilayer graphene (f-HEG) and its silver-decorated version (Ag-f-HEG) on the behavior of nonlinear absorption of a standard laser dye rhodamine 6G (R6G). It has been found that a strong non-fluorescent ground-state complex formation is responsible for the observed decrease of the luminescence as well as the SA effect. Graphene doped with silver nanoparticles gives reduced association constant with the dye due to the preexisting charge transfer in Ag-f-HEG. The energy dependent Z-scan profiles show that the system (R6G–f-HEG) can be tuned to exhibit the behaviour of saturable absorption (SA) at low energies to the optical limiting (OL) behavior at higher energies. The optical nonlinear parameters have also been measured with the degenerate four wave mixing technique to confirm the results.

2. Experimental

2.1. Sample preparation and characterization

The synthesis procedure for f-HEG is given elsewhere [23]. R6G was purchased from Aldrich chemicals and was used as received. Deionized water was used as the solvent. The absorption spectrum of water was recorded to check its purity in the spectral range. The stock solutions of the samples (1 mg/ml) were prepared by dispersing the f-HEG and Ag-f-HEG in water using a sonicator. The samples were taken from the sonicator just before the measurement. The quality of dispersion was checked by dividing a sample into 4 parts and observing that the absorbance remains unchanged for all. R6G–graphene solutions were prepared by adding different amounts of f-HEG to the dye solution of 1 mM. In all the cases, the dye concentration was kept the same.

The absorption and fluorescence spectra of samples were recorded by using the UV–vis dual beam spectrophotometer (Jasco, V-570) and fluorimeter (Jasco, FP-6600), respectively. For fluorescence studies, the excitation wavelength was 510 nm. Fluorescence lifetime measurements were carried out with the time-correlated single-photon counting technique (TCSPC). Here, the excitation was done with a 470 nm picosecond diode laser (1 MHz, Advanced Photonics). X-ray diffraction (XRD) studies were done with the X-ray diffractometer (Panalytical X'pert Pro). Raman spectra were recorded with a Jobin Yvon model HR-300 equipped with a He–Ne laser (632.8 nm). The electron microscopy imaging studies were done with a field emission scanning electron microscope (FEI Quanta) and transmission electron microscope (Jeol JEM-2010F).

2.2. Z-scan

The measurements on the nonlinear absorption coefficient (β) and third order nonlinear susceptibility ($\chi^{(3)}$) of R6G in presence of f-HEG and Ag-f-HEG were carried out by the open aperture (OA) Z-scan technique (Fig 1(A)). The second harmonic wavelength (532 nm) of a picosecond Nd:YAG laser (Continuum, ~40 ps, 10 Hz) was used for exciting the sample. The sample (with a thickness of 1 mm) was scanned in the focal plane of a lens of focal length of 5 cm. The transmitted light was detected by a photodiode (Becker and Hickle, PDI-400l). The data were recorded using the LabView software in a PC.

2.3. Degenerate four wave mixing (DFWM)

The phase conjugation geometry of the DFWM technique was used with a ps laser as the pump source (Fig. 1(B)). Two strong counter propagating laser pulses are incident on the sample and are known as forward and backward pump, respectively. A third weaker beam acts as the probe beam. The angular separation between the forward pump and the probe is about 8^0 at the sample cell of thickness 1 mm. The phase conjugate (PC) beam that retraces the path of the probe beam is separated by introducing a beam splitter on the path of probe beam. The signal was measured by using a photodiode (Becker and Hickl, PDI-400) and was averaged over 100 pulses using a digital oscilloscope (Tektronix, TDS 220).

3. Theoretical considerations

3.1. Ground state complex formation

The apparent association constant in the ground state (K_g) between R6G and quencher (Q) can be obtained by using the Benesi–Hildebrand equation [28].

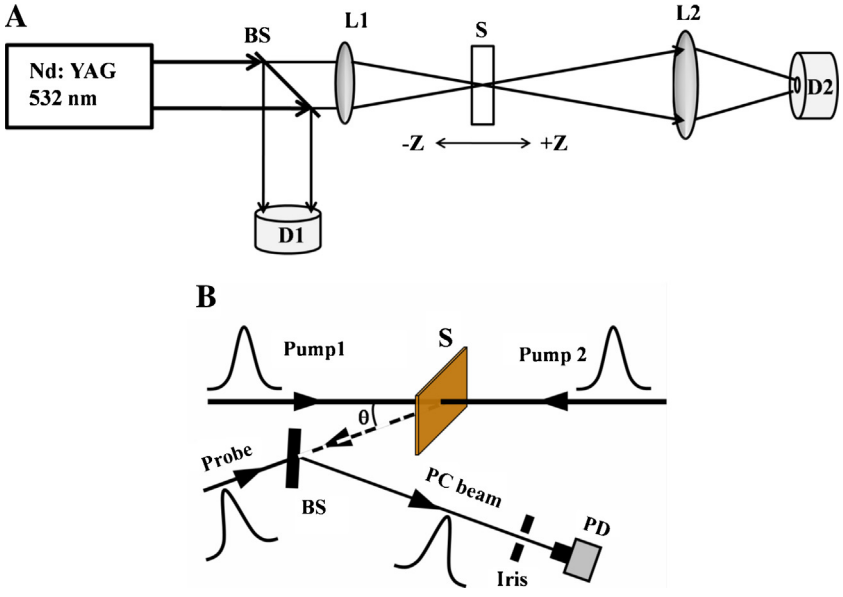

Fig. 1. Schematic representation of open aperture Z-scan setup (Panel A). BS is the beam splitter, L1, L2 are the double convex lenses, S is the sample and D1, D2 are the reference and signal photodiodes, respectively. Panel B shows the phase conjugation geometry of DFWM technique. Pump1, Pump2 indicate the forward and backward pump beams, respectively meeting at the sample (S). PC beam is phase-conjugate beam when the Probe beam is incident on the sample. PD is the phitodiode.