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Optical limiting properties of *in situ* reduced graphene oxide/polymer nanocomposites

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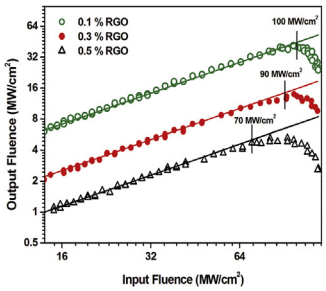
HIGHLIGHTS

- Developed reduced graphene oxide/polymer nanocomposite optical limiters.
- They exhibited high nonlinear absorption and low optical limiting threshold.
- Can be used to protect human eyes and delicate sensors from powerful lasers.
- Optical limiting behavior can be tuned by adjusting the filler concentration.

GRAPHICAL ABSTRACT



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ABSTRACT

Reduced graphene oxide/polymer nanocomposites are prepared by the *in situ* reduction of graphene oxide in the polymer matrix. Graphene oxide is dispersed in an aqueous solution of poly(vinyl alcohol) and is chemically reduced within the polymer matrix followed by solution casting to form the composite films. The nonlinear absorption characteristics and the optical limiting behaviour of the composite films are studied using z-scan technique. The composites exhibit excellent optical limiting behaviour along with improved thermal characteristics. The nonlinear absorption characteristics and the optical limiting properties are found to increase with increasing concentration of reduced graphene oxide in the polymer matrix. This clearly provides an opportunity to tune the optical limiting behaviour to attain a desired limiting threshold intensity by adjusting the concentration of the filler and hence these composites can find practical applications in many devices as potential optical limiters.

1. Introduction

The last few decades have witnessed many revolutionary developments in the areas of photonics and optoelectronics. As a result, lasers and laser based devices are finding more and more applications every day. Protection from powerful lasers is one of the greatest concerns in the modern optoelectronic era and this makes the development of optical limiting materials extremely important.

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Human eyes and delicate optical sensors can be protected from powerful lasers by the use of optical limiting materials which transmit light at low intensities and limit the transmission above certain threshold input intensity [1]. In most of the materials, optical limiting is caused by various nonlinear light–matter interactions, especially nonlinear absorption, nonlinear refraction and nonlinear scattering [2]. In the recent past, enormous work has gone in to the study of optical limiting behaviour of various materials such as carbon black suspensions, semiconductor nanoparticles, organic nanocrystals, fullerenes, carbon nanotubes, organic chromophores, metal nanostructures and polymer materials [3–14]. However, for practical device applications, use of a single material or limiting mechanism cannot meet all the stringent application requirements and hence investigations on new material systems for optical limiting applications would be a noteworthy attempt.

Graphene, a single atom thick layer of sp^2 hybridized carbon atoms in a two dimensional structure, has emerged as one of the most promising material for optoelectronics [15]. Graphene exhibits extraordinary thermal, mechanical, electrical and optical properties owing to its unique structure. Recently, the nonlinear optical properties of materials in the graphene family including graphene oxide, graphene nanosheets and graphene nanoribbons have been studied extensively by many researchers [1,16–22]. Most of the studies reported excellent optical limiting properties of graphene materials when dispersed in a liquid medium. However, graphene materials dispersed in liquids always suffer agglomeration over a period of time restricting its use in practical device applications. From a device integration perspective, finding a suitable solid matrix for uniformly dispersing the graphene material is very significant. In this context, graphene/polymer composites, which combine the optical properties of graphene and structural properties of polymers, have the potential to emerge as a new class of optical limiters. Works in this direction had already been initiated by a few researchers [23–26]. However, the solubility and processability are the major issues for many prospective applications of graphene/polymer composites. In many cases, chemical functionalization of graphene is required to improve the solubility and processability to make polymer composites [23–26]. Nevertheless, the chemical functionalization can definitely alter the optical properties of graphene. On the other hand, Graphene Oxide (GO), obtained through the chemical oxidation of graphite, is strongly hydrophilic and highly dispersible in water due to the presence of oxygen containing functional groups. GO is also a proven optical limiting material. The optical limiting properties of GO can be significantly improved by the partial reduction of GO [27,28]. The composites of GO with water soluble polymers can be easily processed using simple solution processes like spin coating or drop casting. Hence, the *in situ* reduction of GO dispersed in the polymer solution combines the advantages of a uniformly dispersed composite with improved optical limiting properties, offered through a simple processing technique.

In this work, reduced graphene oxide (RGO)/poly(vinyl alcohol) (PVA) nanocomposites are prepared through the *in situ* reduction of GO dispersed in PVA solution. Uniformly dispersed RGO/PVA composite films are formed by simple solution casting method. PVA was selected as the polymer matrix because of its good mechanical properties, excellent film forming nature and very good solubility in water. Moreover, the use of water alone as the solvent makes the whole process environmentally friendly. The nonlinear absorption properties and the optical limiting behaviour of RGO/PVA nanocomposites are studied using z-scan technique. The effect of laser power and the RGO content on the nonlinear absorption and optical limiting properties are also investigated. The thermal properties are also examined to understand their usability in practical applications.

2. Experimental

2.1. Materials

Graphite flakes were received from Hind minerals, India (94.1% C). Poly(vinyl alcohol) (PVA, Mw 1,25,000) was purchased from SD Fine Chemicals, India. Sulphuric acid (H_2SO_4, 98% GR), ortho phosphoric acid (H_3PO_4, 85% pure), potassium permanganate ($KMnO_4$, 99% GR), hydrogen peroxide (H_2O_2, 30% GR) and hydrazine monohydrate were purchased from Merck, India and were used as received.

2.2. Synthesis of graphene oxide (GO)

GO was synthesized from natural graphite flakes using a highly oxidizing mixture of concentrated sulphuric acid, orthophosphoric acid and potassium permanganate as suggested by Marcano et al. but with a new modified synthesis protocol [29,30]. 3 g of graphite flakes were mixed with concentrated H_2SO_4 (360 ml) and H_3PO_4 (40 ml). 18 g of $KMnO_4$ was added slowly while keeping the reaction mixture in an ice bath and stirred for 2 h. Then the mixture was heated at 50 °C in a water bath for 45 min and stirring was continued at room temperature. After 24 h, 400 ml of ice water was added slowly to the reaction mixture which results in an increase of temperature of the system to about 98 °C. The stirring was continued for another 2 h and then, hydrogen peroxide (10 ml) was added. The solid collected from the reaction mixture was washed few times with 5% HCl solution followed by distilled water. For each washing, solid was suspended by ultra-sonication and was collected by centrifugation. The resultant graphite oxide was then readily exfoliated to completely water dispersed graphene oxide (GO) by ultra-sonication.

2.3. Preparation of GO/PVA and RGO/PVA nanocomposites

GO was dispersed in 10 mL of distilled water by ultrasonication for 2 h to make a homogeneous brown dispersion. PVA powder was dissolved in distilled water at 90 °C and the solution was subsequently cooled to room temperature. The GO aqueous dispersion was gradually added to the PVA solution and sonicated at room temperature for 15 min and stirred to obtain homogeneous GO/PVA solutions which were cast in glass dishes and kept at 40 °C for film formation until its weight equilibrated. For preparing RGO/PVA nanocomposites, to the mixture of GO dispersion in PVA solution, 35% hydrazine monohydrate (1 μL/3 mg GO) was added and heated at 80 °C for 3 h with stirring. Hydrazine, which is a strong reducing agent, removes the oxygen containing functional groups of the GO within the polymer solution and results in a black coloured solution of RGO/PVA which was cast into composite film. RGO/PVA nanocomposite films with 0.1, 0.3 and 0.5 wt% of RGO were prepared.

2.4. Characterization

The X-ray diffraction (XRD) analysis of graphite, GO and the composite films was carried out using Cu Kα radiation ($\lambda = 0.154$ nm, Bruker AXS D5005, Germany). The Scanning Electron Microscopic (SEM) images were acquired using Hitachi SU 6600 field emission scanning electron microscope. The absorption spectrum was taken in the wavelength range 200–2000 nm using a UV–Vis–NIR spectrophotometer (JascoV-570, USA). Thermal analysis of the composites were carried out using TG/DSC analyzer (SDT Q600, TA Instruments, USA) at a heating rate of 10 °C min^{-1} under nitrogen atmosphere.

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