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Review

Optical limiting properties of (reduced) graphene oxide covalently functionalized by coordination complexes

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ABSTRACT

The nonlinear optical (NLO) and optical limiting (OL) properties of graphene oxide (GO), reduced graphene oxide (RGO), and particularly GO/RGO coordination complex hybrids are reviewed. A brief introduction to mechanisms of OL and a summary of the key measurement techniques for determining NLO/OL merit is provided. A summary of synthetic procedures to GO/RGO coordination complex hybrids is included.

Contents

Abbreviations: 2PA, two-photon absorption; 3PA, three-photon absorption; ESA, excited-state absorption; FCA, free carrier absorption; G, graphene; GO, graphene oxide; ISC, intersystem crossing; MPA, multiphoton absorption; MPc, metal phthalocyanine; NLA, nonlinear absorption; NLO, nonlinear optical; NLR, nonlinear refraction; NLS, nonlinear scattering; OL, optical limiting; Pc, phthalocyanine; PET, photo-induced electron transfer; RGO, reduced graphene oxide; RSA, reverse saturable absorption; SA, saturable absorption; ZnPc(DG)$_4$, 1,8,15,22-tetra-(3-[2-(2-hydroxyl)ethoxy]ethoxy)phthalocyanine zinc; ZnPc(TD)$_4$, 1,8,15,22-tetra(3-(5-hydroxyl)pentyloxy)phthalocyanine zinc.

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1. Introduction

Graphene oxide (GO) is a unique graphene-based material that possesses distinctive structural and electronic properties due to its oxygenated carbon backbone. GO has attracted attention as a versatile, solution-processable multifunctional carbon platform at which a variety of chemical transformations can be effected by modifying the oxygen-containing functional groups. GO exhibits third-order optical nonlinearities and interesting optical limiting (OL) responses that can be tuned by modifying the sp^2 and sp^3 carbon content. Specifically, it can be integrated with other complementary nonlinear optical (NLO) moieties via covalent or non-covalent surface functionalization strategies. The resultant hybrids have shown NLO and OL performance greater than the sum of the individual components or their physical blends.

This review is primarily focused on third-order NLO and OL properties of hybrids consisting of GO which have been covalently functionalized by coordination complexes. A summary of the fundamentals of OL and the third-order NLO effects contributing to OL is followed by a description of the Z-scan technique, the most popular approach to evaluate third-order NLO and OL properties. We then summarize some of the interesting NLO-based studies of GO-based materials, and report on the third-order NLO and OL properties of hybrids consisting of GO covalently functionalized by coordination complexes, concluding with suggestions for future profitable research in this contemporary interdisciplinary field.

2. Optical limiting processes and procedures

2.1. Passive optical limiting (OL)

Over recent years, the proliferation of laser technology in various research and technological fields has led to an extensive use of high-power laser sources operating at different power levels, pulse widths, repetition rates and a variety of wavelengths from the ultraviolet through the visible light spectrum to the infrared, so it is crucial to design appropriate laser protection devices that protect delicate optical sensors, especially the human eye, from accidental or deliberate exposure to detrimental laser sources, while allowing the sensor to operate under ambient light conditions [1–3].

Passive manipulation of laser beams (also known as passive optical limiting) is an effective strategy that can be applied to control the intensity or the fluence of laser beams, so as to avoid unacceptable levels of energy density on the sensor (Fig. 1). Passive optical limiting relies on intensity- or fluence-dependent third-order or higher-order NLO processes inherent to certain materials. These materials have the ability to control the intensity of the incoming laser in situ in a predetermined and predictable manner via nonlinear absorption, scattering, diffraction or blocking, as a response to the light-induced modifications in the nonlinear medium [1]. Thus, passive manipulation provides irradiance-dependent dynamic laser protection to the sensor by decreasing the output transmittance with increasing incident light intensity without the aid of an ancillary system to trigger the limiting action [2]. Hence, passive OL has great potential for integration into broadband sensor protection devices known as passive optical limiters, which operate at a wide range of power levels, wavelengths and pulse durations as well as with frequency-agile lasers. Besides controlling the optical fluence, optical limiters can be used in optical switches for pulse shaping, pulse smoothing and pulse compression [4,5].

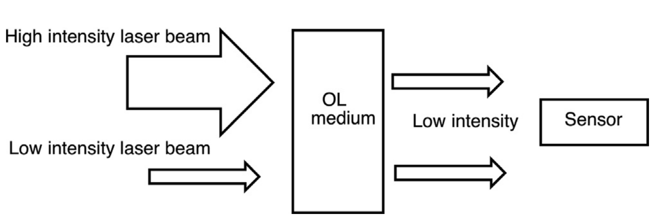

Fig. 1. Passive optical limiting for sensor protection with different laser intensities.

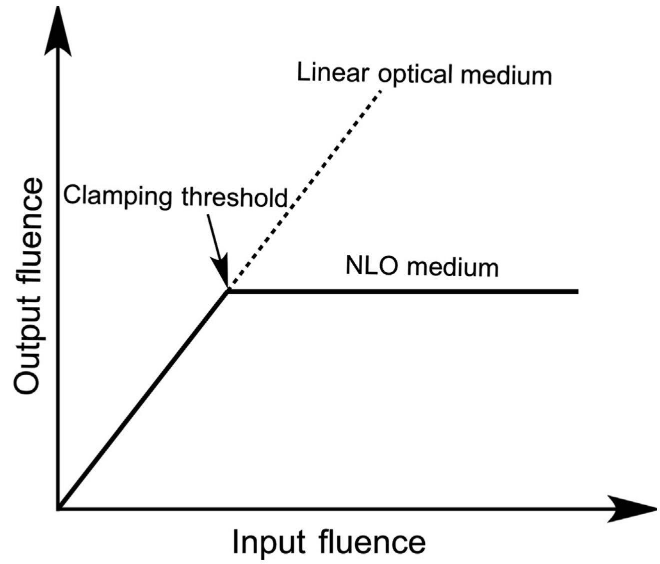

Fig. 2. Schematic output vs input fluence plot showing optical limiting response of an ideal optical limiter.

An ideal optical limiter shows high linear transmittance for low input intensities up to a certain threshold value known as the clamping threshold (Fig. 2). Upon further increase in input laser intensity above the clamping threshold, the optical limiter starts to attenuate the incoming radiation via energy absorption- or energy spreading-type NLO mechanisms as discussed in detail later [6]; thus, the output transmittance starts to clamp at a constant value that depends on factors such as the concentration of the active species, the geometry of the experimental laser set-up, etc. As a result, the amount of radiation reaching the sensor is limited while the sensor is allowed to function optimally under normal light intensities. However, the OL ability of the medium may be lost after exposure to a particular maximum input fluence known as the damage fluence because of laser-induced irreversible optical damage.

In designing a practical optical limiter with high OL efficiency, certain primary requirements need to be fulfilled, such as high linear transmittance at low laser intensities, large nonlinear optical susceptibilities, low optical limiting threshold, and high damage threshold, which collectively give a large dynamic range, fast response time, quick recovery, etc. Besides these requirements, some secondary requirements such as low cost, light weight, ease of processing and robustness (good mechanical and thermal stability) are important [1]. A vast catalogue of NLO materials with different degrees of OL efficiency have been reported to date [2,7–10]. However, none of the materials have been demonstrated to possess all the requisites for an ideal optical limiter: each candidate material has one or more shortcomings that can override their favorable OL merits. For example, some materials show promising low limiting thresholds, but low damage thresholds narrow their dynamic range; finding suitable NLO materials with extended dynamic ranges to function optimally at high laser intensities is imperative.

The OL ability of a NLO medium originates from a diverse range of intensity- or fluence-dependent third-order or higher-order