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Graphene and its derivatives for laser protection

Yu Chen [a,*], Ting Bai [a], Ningning Dong [b], Fei Fan [a], Saifeng Zhang [b], Xiaodong Zhuang [a,e], Jie Sun [c,d], Bin Zhang [a], Xiaoyan Zhang [b], Jun Wang [b,1,*], Werner J. Blau [d]

[a] Key Laboratory for Advanced Materials, School of Chemistry and Molecular Engineering, East China University of Science and Technology, 130 Meilong Road, Shanghai 200237, China
[b] Key Laboratory of Materials for High-Power Laser and State Key Laboratory of High Field Laser Physics, Shanghai Institute of Optics and Fine Mechanics, Chinese Academy of Sciences, Shanghai 201800, China
[c] Institute of Chemical Materials, China Academy of Engineering Physics, Mianyang 621900, Sichuan, China
[d] School of Physics and the Centre for Research on Adaptive Nanostructures and Nanodevices (CRANN), Trinity College Dublin, Dublin 2, Ireland
[e] Department of Polymer Science and Engineering, College of Chemistry and Chemical Engineering, Shanghai Jiao Tong University, 800 Dongchuan Road, Shanghai 200240, China

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ABSTRACT

The development of functional materials for laser protection is an extremely important research field for the safety and security of users. To achieve simultaneous protection against both pulsed and continuous wave (cw) or quasi-cw lasers, significant research effort has been invested into state-of-the-art broadband optical limiting (OL) materials and processes in an attempt to achieve some measure of protection from such laser beams in the past decades. As the first truly two-dimensional material, graphene is being considered as an ideal material for modern photonic, optoelectronic and electronic devices because of its fantastic physical properties. Graphene shows ultrafast carrier relaxation dynamics and ultra-broadband resonate nonlinear optical (NLO) response due to their

Abbreviations: 0D, zero dimensional; 1D, one dimensional; 2D, two dimensional; 3D, three dimensional; A, acceptor; Ag NPs, Ag nanoparticles; ACN, acetonitrile; APTES, 3-aminopropyl- triethoxysilane; B-AGNRs, B terminated armchair GNRs; Be-AGNRs, Be terminated armchair GNRs; BM, benzyl mercaptan; h-BN, hexagonal boron nitride; BPC, graphene-biphenyl carbon; CB, chlorobenzene; CdS QDs, cadmium sulfide quantum dots; CMC, carboxymethyl cellulose; CN, 1-chloronaphthalene; CNTs, carbon nanotubes; Cu-ZGNRs, Cu terminated zigzag GNRs; CW, continuous wave; Cz, carbazole; C_{60}-PVK, C_{60} chemically modified poly(N-vinylcarbazole); D, donor; DCC, N,N′-dicyclohexylcarbodiimide; DFT, density functional theory; DMF, N,N′-dimethylformamide; ESA, excited state absorption; ET, electron transfer; FCA, free-carrier absorption; fG, functionalized multilayer graphene; F–GO, partially fluorinated GO; f-HEG, acid functionalized hydrogen exfoliated graphene; fs, femtosecond; GNRs, graphene nanoribbons; GNSs, graphene nanosheets; GO, graphene oxide; GO-Cz, GO covalently functionalized with carbazole; GONRs, graphene oxide nanoribbons; GONSs, graphene oxide nanosheets; GO-P, porphyrins covalently modified GO derivatives; GO-PcGa, GO-axially functionalized gallium phthalocyanine; GO-PcZn, GO covalently functionalized with unsymmetrically substituted zinc phthalocyanine; GO–PTPP, graphene hybrid materials incorporating phosphorus- cored porphyrin; GOQDs, GO quantum dots; GO–SnTPP, graphene hybrid materials incorporating dihydroxotin (IV) tetraphenylporphyrin; GO-TPP, GO-poly[2-(3-thienyl)ethoxy-4-butylsulfonate]; GQDs, graphene quantum dots; h-BN-GNRs, hexagonal boron nitride hybrid graphene nanoribbons; HEG, hydrogen exfoliated graphene; HPG, hydrogenated porous graphene; M-GNRs, metal terminated GNRs; MPA, multi-photon absorption; MWNTs, multi-walled carbon nanotubes; NIR, near infrared; NLA, nonlinear absorption; NLO, nonlinear optical; NLR, nonlinear refraction; NLS, nonlinear scattering; NMP, N-methyl-2-pyrrolidone; NPs, nanoparticles; o-DCB, 1,2-dichlorobenzene; OL, optical limiting; OPE, oligo(phenylene ethenylene); Ormosil, methyltriethoxysilane modified silicate; Pac, polyacetylene bearing a quaternary ammonium pendant; PANI, polyaniline; PcGa, gallium phthalocyanine; PCF, poly(9,9′-diheylfluorene carbazole); Pcs, phthalocyanines; PcZn, zinc phthalocyanine; PEG, poly(ethylene glycol); PET, photoinduced electron transfer; pf, picosecond; PIPT, photo-induced photon transfer; PMMA, poly(methyl methacrylate); $PNP^{+}GO^{-}$, fluorescence-quenched charge-transfer complex formed by PNPB and GO; PNPB, 4-(1-pyrenylvinyl)-N-butylpyridinium bromide; PTPP, phosphorus-cored porphyrin; PVA, poly(vinyl alcohol); PVK, poly(N-vinylcarbazole); QDs, quantum dots; RGO, reduced graphene oxide; RGO-PCF-i, poly(9,9′-diheylfluorenecarbazole)-covalently func- tionalized reduced graphene oxide hybrids; RSA, reverse saturable absorption; S_1, lowest excited singlet state; SA, saturable absorption; SC, sodium cholate; SiC, silicon carbide; SnTPP, dihydroxotin(IV) tetraphenylporphyrin; SSPM, spatial self-phase modulation; SWNTs, single-walled carbon nanotubes; T_1, lowest excited triplet state; THF, tetrahydrofuran; THz, terahertz; TPA, two photon absorption; URENs, upconversion rare-earth nanomaterials; UV, ultraviolet; UV/Vis, ultraviolet/visible.

* Corresponding authors.
E-mail address: chentangyu@yahoo.com (Y. Chen).
[1] Co-corresponding author. Email address: jwang@siom.ac.cn.

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extended π-conjugate system and the linear dispersion relation holding for their electronic band structure. Almost all types of graphene-based materials described in this review exhibit strong broadband OL response. The dominant limiting mechanism of graphene is nonlinear scattering, which is very effective in liquid suspensions rather than in solid state hosts. In contrast to the pure graphene, the solubilized graphene and its derivatives optically limits through nonlinear absorption mechanism, nonlinear scattering as well as the photoinduced electron transfer and/or energy transfer between graphene and organic/polymeric species. This review describes systematically the OL mechanisms and the recent achievements on the graphene-based functional materials (i.e., graphene nanostructures, graphene composites, and covalently modified graphene) for OL applications. The future major ongoing areas of effort have also been suggested.

Contents

1. Introduction

Since the coming out of the first operational laser (light amplification by stimulated emission of radiation) in 1960 [1], new and improved laser technology for both civilian and military purposes has continued to be at the forefront of research activities over the world. Light from a laser source may be continuous or pulsed. Continuous laser light may possess power from 0.001 W to thousands of watts. Pulsed lasers may reach energy levels of up to millions of watts per fraction of a second. Because lasers are coherent, monochromatic and travel in only one direction, they are uniquely adapted for numerous important applications such as presentation pointers, medical cosmetology, sighting, scanning and ranging devices, materials forming and processing, surgery operation, laser weapons, laser guidance, and law enforcement as well. Aside from their numerous civilian applications, on the other hand, lasers have evolved into numerous modern battlefield weapons. Some are designed to dazzle or permanently disable humans by blinding, while others are used to destroy optical sensors, missiles, and other targets. A laser beam can be focused to an intensity on the retina which may be up to 2×10^5 times higher than at the point where the laser beam enters the eye. If the energy of a laser beam reaches a high level of intensity within a