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Optical limiting and nonlinear optical properties of gold-decorated graphene nanocomposites

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ABSTRACT

Metal nanoparticle-decorated low dimensional materials can synergistically combine the nonlinear optical properties of metallic/inorganic nanostructures for enhancing the optical limiting performance. While many materials exhibit excellent optical limiting performance at a relatively higher fluence (>9 J/cm^2), there is a still a dearth of optical limiting materials for protecting low damage threshold (<1 J/cm^2) photonic devices. Although metal nanoparticle-decorated graphene hybrids are expected to resolve this issue, the rehybridization of metal d-orbitals and graphene p-orbitals often lead to undesirable changes in graphene's electronic structure which adversely affect the nonlinear optical performance. Here, we demonstrate that d-orbitals of Au nanoparticles exhibit little or no rehybridization with graphene and result in an enhanced optical limiting behavior at a low fluence of ~0.4 J/cm^2, which is lower than most metal decorated graphene, carbon nanotube nanocomposites and metal nanoparticles. This optical limiting performance at a lower fluence is attributed to the excellent photo-absorption of Au nanoparticles combined with rapid thermalization of excited carriers by graphene.

1. Introduction

The wide spread use of lasers in applications ranging from modern defense weaponry to biomedical treatment necessitate safety limits on laser exposure to avoid undesired laser-induced damage [1]. The unavailability of ideal optical limiters to protect detectors and imaging devices and sensor (in particular, the human eye) with a low damage threshold exacerbates the probability of irreversible physical damage during intentional or accidental exposure to unsafe levels of laser radiation [2]. Nanostructured nonlinear optical (NLO) materials [3–11] have been used as *passive and effective optical limiters* to reduce the optical transmittance of the incident laser radiation by virtue of their intrinsic optical properties (e.g., multi-photon absorption in C_{60}). Of specific interest to this work is the use of noble metal nanoparticle-decorated low dimensional materials that can synergistically combine the NLO properties of metallic/inorganic nanostructures (e.g., Au, Ag, Pd & Pt nanoparticles (NPs)) and carbon nanomaterials (e.g., graphene, carbon nanotubes) for realizing efficient optical limiting (OL) materials for low fluence radiation (~0.4 J/cm^2). Previously, it has been demonstrated that nanohybrids such as graphene/Ag_2S organic glasses [4], Pt/Pd decorated on graphene [5], Ag decorated graphene [6], graphene/ZnO organic glasses [7], fullerene or graphene–metal porphyrin composites [8,9] and graphene-oligothiophene hybrids [10] exhibit enhanced OL performance. Although these studies demonstrated an improved OL threshold (the input fluence at which the transmittance falls to 50% of its initial value) at higher input fluences >9 J/cm^2, they exhibited poor OL capability in the low fluence regime (<1 J/cm^2), which is critical for practical realization of OL devices [2,11]. Metal nanoparticle (NP)–decorated graphene, e.g., graphene/Pt NPs, are expected to resolve the issue of OL in the low fluence regime. However, the rehybridization of metal d-orbitals and graphene p-orbitals often lead to undesirable changes in graphene's electronic structure, which adversely affect the NLO performance [13]. Unlike in the case of Pt NP-decorated graphene, the electronic/optical properties of graphene are not significantly perturbed because the d-orbitals of Au NPs are more than 2 eV below graphene's Fermi energy level [13]. Indeed, Sun et al., have recently proposed that addition Au nanoparticles (NPs) to graphene could enhance the OL performance [12].

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Here, we present a facile one-pot synthesis of Au NP-decorated chemically exfoliated graphene (Au–graphene) using the laser ablation technique for improved OL performance in low fluence regime. Our synthesis approach is unique in that it obviates the need for reducing and capping agents that are essential for preparing highly stable aqueous suspension of Au–graphene. Our results show that the absence of rehybridized orbitals between Au and graphene and increased electrostatic interaction between charged Au NPs and oxygen functionalities on chemically modified graphene, enhanced OL performance. Notably, the OL threshold of our Au–graphene system is lowered from 9 J/cm^2 (OL for bare Au NPs) to 0.4 J/cm^2 – a major improvement in low-fluence nanomaterials.

2. Material and methods

2.1. Synthesis of Au–graphene

In our method, the Au–graphene is prepared using the so-called functionalized hydrogen exfoliated graphene (referred henceforth as exf-graphene) as the starting material. The detailed synthesis of exf-graphene can be found in Ref. [14]. Briefly, exf-graphene was prepared by the reduction and hydrogen gas induced exfoliation of graphite oxide (GO) (rather than the conventional thermal exfoliation method [15]). The GO used in this study was prepared by a modified Hummers' method [16]. Exf-graphene is hydrophilic in nature due to the presence of –COOH and –OH functional groups. Such hydrophilic groups are important in the preparation of homogenous and stable dispersions of Au–graphene in water. An aqueous dispersion was prepared by first ultrasonically dispersing 1 mg of exf-graphene in 25 ml of millipore water. Next, a high purity Au strip (purity ~99.99%) of dimension (2 cm × 1 cm) was ultrasonically cleaned in 5 ml piranha solution and placed in a 25 ml glass beaker containing 3 ml of aqueous solution of exf-graphene. A Nd:YAG (Surelite III, 50 mJ, rep. rate of 10 Hz) with its fundamental harmonic at 1064 nm and 15 ns pulse–width was used to ablate the Au strip to generate Au NPs which decorated the suspended exf-graphene yielding Au–graphene [17–20]. The laser beam was focused into a 30 micron diameter spot onto the Au strip using a convex lens of focal length 10 cm (Fig. 1a). A similar procedure was followed for preparing pristine/bare Au NPs in plain millipore water. The weight of the gold strip was determined before and after the laser ablation process to assess the net amount of gold released into the solution (~0.3 mg).

2.2. Material characterization

We studied the morphology and distribution of Au NPs on exf-graphene using a high resolution transmission electron microscopy (HRTEM – TECNAI F–20, S–TWIN, 200 kV). In order to probe the electronic structure of the as- synthesized nanostructures, we measured their optical density using UV–Visible absorption spectroscopy (*Shimadzu 2450*), and in-plane crystallite size (L_a) from the ratio of the so-called D & G band intensities using micro-Raman spectroscopy (*Dilor X–Y*, 514 nm excitation wavelength) [21].

3. Experimental

To gauge the NLO performance of Au NPs, exf-graphene, and Au–graphene, we used a conventional open aperture Z-scan technique [22] which allows for the measurement of nonlinear absorption (NLA) and nonlinear scattering (NLS) of the incident intensity. In our automated Z-scan experimental set-up, we used the second harmonic (532 nm) of a high power Nd:YAG laser (*Surelite III, Continuum Lasers*) with 15 ns pulse width at a repetition rate of 1 Hz. In the Z-scan experiment, a converging lens with a focal length of 20 cm was used to focus the incident laser beam on to the stable dispersion that was held in a 1 mm quartz cuvette and translated across the focal plane in the beam direction. At each Z position, the position dependent transmittance was measured using a calibrated photodetector (PIN10D, UDT sensor). The NLS intensity was measured simultaneously by another identical photodetector that was placed behind the focal plane at an angle of 45° relative to the beam axis. The linear transmittance of each suspension (held in quartz cuvette of 1 mm path length) was adjusted to 70% at 532 nm.

4. Results and discussion

4.1. Morphological characterization and UV–Vis spectroscopic studies

Representative high-resolution transmission electron microscope (HRTEM) images of exf-graphene prior to the laser ablation of the Au strip, Au–graphene, and bare Au NPs are shown in Fig. 1b–d, respectively. The average diameter of Au NPs generated by the laser ablation process was found to be ~22 ± 5 nm (Fig. 1e). The Au NPs were observed to be highly crystalline with a (1 1 1) lattice fringe spacing of ~0.24 nm (Fig. 1d). As expected, the optical absorption spectra of as-synthesized Au NPs (green spectrum in Fig. 1f) exhibited the localized surface plasmon resonance (LSPR) peak at ~520 nm (2.38 eV). The absorption bands at 224 nm are attributed to the presence of Au clusters (Au^{3+} or Au^{+} ions) [23]. Likewise, the exf-graphene (red spectrum in Fig. 1f) exhibited the 273 nm (4.5 eV) peak which arises from the π to π^* transitions in graphene [24]. The black spectrum in Fig. 1f in which the LSPR and plasmon peaks are evident at ~523 and 275 nm, respectively, is indicative of the formation of the Au–graphene, and consistent with the HRTEM image in Fig. 1c.

4.2. Raman spectroscopy

Fig. 2 shows the Raman spectra of exf-graphene and Au–graphene, which show the presence of the D (~1350 cm^{-1}), G (1585 cm^{-1}) and 2D (~2700 cm^{-1}) bands. A Lorentzian line shape analysis of the experimental Raman data yielded I_D/I_G ratios of 0.4 and 0.9 for exf-graphene and Au–graphene, respectively, where I represents the integrated area of a Raman band. These ratios correspond to an average crystallite size (L_a) of 42 and 18 nm, respectively [21]. In addition, the D and G band frequencies are slightly upshifted by ~3 and ~4 cm^{-1} respectively, which is indicative of a plausible absence of charge transfer between the laser generated Au NPs and exf-graphene. Indeed, such a small shift in the G band frequency confirms our hypothesis that there is very little or no rehybridization between Au d-orbitals and exf-graphene p-orbitals. Furthermore, the presence of a broader 2D band (Fig. 2b) in Au–graphene compared to exf-graphene also may imply possible stress in graphene sheets due to the loading of Au NPs.

4.3. Z-scan and optical limiting measurements

The open aperture Z-scan data contains information from different kinds of NLA processes (e.g., multi-photon absorption (MPA) and excited state absorption (ESA)), which can be elicited, from numerical analysis as described below. At times, both of these processes compete and contribute collectively to the OL response. Accordingly, we fitted the Z-scan data in Fig. 3 to nonlinear transmission equations involving two-photon absorption (2PA), three-photon absorption (3PA) and saturable absorption (SA).