Recent Advances in Optical Limiting Properties of Fluorinated Graphene Oxides

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ABSTRACT

There is a substantial interest in finding materials with high nonlinear optical (NLO) properties of materials because of its attractive applications in optical limiting for safety protections. In an effort to develop highly performing optical limiting materials, recently we have found that fluorination of graphene oxides leads to improvement in their NLO properties.

KEYWORDS: Fluorination, Photoacoustic, Z-scan, localized sp^2 domains, Graphene Oxide, Optical limiting.

1. INTRODUCTION

With the aid of rapid theoretical and experimental developments in nanoscience and nanotechnology, a number of novel nanomaterials with exceptional physical and chemical properties have been synthesized. One of the well-known nanomaterials is the family of carbon allotropes. Before the advent of nanotechnology only two

allotropes of carbon were known: graphite and diamond. However, several allotropes of carbon have been subsequently found. These materials differ not only in their atomic structures but also in their physical properties.

Nanomaterials can be categorized by their dimensionality, which ranges from zero dimension (0D) to three dimension (3D). In the case of carbon the common structures are, for example, 0D fullerene, 1D carbon nanotube, 2D graphene, and 3D graphite. Interestingly, one can think of 2D graphene as a building block to form the other dimensional structures of carbon allotropes. Graphene is a monolayer of carbon atoms densely packed into a two-dimensional honeycomb lattice. Graphene can be wrapped up to form 0D fullerene, rolled to form 1D nanotube, and stacked to form 3D graphite¹, as illustrated in Figure 1. Graphene possesses excellent electrical properties, mechanical flexibility, optical transparency, thermal conductivity and low thermal expansion coefficient²⁻⁶. There are several ways to synthesize graphene; for example, exfoliation of natural graphite⁷, un-zipping of carbon nanotube⁸, chemical vapor deposition⁹, and reduction of graphene oxide (GO)¹⁰. Among these processes, reduction of GO to form graphene has attracted significant attention¹¹⁻¹⁵ since this method can offer cost effective, large scale production of graphene based materials.

Figure1. Graphene is a basic building block of fullerene, carbon nanotube and graphite.

GO is an electrically hybrid material between the conducting π -states of sp^2 carbon sites, which contribute to the bandgap formation of the material, and the σ -states of sp^3 carbon sites. Chemical reduction can transform GO from an insulator to semiconductor and also to a metal-like state, in the form of graphene. Besides the excellent properties of its final product graphene, the GO precursor has interesting properties by itself. Unlike graphene, GO

has several types of oxygen containing functional moieties such as hydroxyl, epoxide, diol, ketone and carboxyl. These functional groups allow GO to interact with a wide range of materials, both organic and inorganic, which results in the high processability of GO. Functionalization of GO, both covalently and non-covalently, also allows manipulation of GO properties. For example, cross-linking polyallylamine with GO results in improved stiffness and strength¹⁶. Grafting a polymer to GO can improve dispersibility of the material in liquid media^{17, 18}. Chitosan-grafted GO exhibits excellent biocompatibility¹⁹. Optical limiting property of GO also greatly enhances with both organic and inorganic decorations²⁰⁻²². Therefore, due to its versatility, functionalized-GOs are promising candidates in various applications, for instance drug delivery^{23, 24}, magnetic resonance imaging (MRI)²⁵, memory devices²⁶, supercapacitor^{27, 28}, and optoelectronic devices^{29, 30}.

Fluorination of carbon nanomaterials has many advantages due to the unique nature of the carbon-fluorine (C-F) bond. For instance, the C-F bond demonstrates excellent oxidative and thermal stability³¹. Fluorine atoms being the most electronegative element in the periodic table, C-F bonds have high polarity and low surface free energy. F-GO will be an attractive material in many applications such as super amphiphobic surfaces, multimodality imaging and photonic devices.

Optical limiting is a nonlinear optical process in which the transmittance of a material decreases as the input light intensity increases. Materials with optical limiting property can be used to fabricate laser protection devices. In this paper we investigate the effect of fluorination on the optical limiting (OL) properties of GO dispersed in water, for nanosecond laser pulses at the excitation wavelength of 532 nm

2. EXPERIMENTAL SECTION

All Graphene oxide (GO) based samples were synthesized. Sample characterization and synthesis methods can be found in our previous reports^{32, 33}. We measured optical limiting of three samples namely, graphene oxides (GO), fluorinated graphene oxide (F-GO), and highly fluorinated graphene oxides (HF-GO). While the first two are dispersed in water, HF-GO is dispersed in N-methyl-2-pyrrolidinone (NMP) due to its high polarity. The open aperture Z-scan technique³⁴ was used to measure optical limiting properties at 532nm wavelength and 5ns laser pulse for these samples. All samples were prepared to have a linear transmission of 50% at the excitation wavelength

of 532nm. A photodiode was mounted near the sample at an angle to the beam axis to monitor linear and/or nonlinear light scattering. The obtained z-scans curves for an input energy of $30 \mu J$ are shown Figure 2(a). All samples show an optical limiting (OL) property since the transmission decreases with increase in input fluence.

Figure2. (a) Z-scan curves of the samples. (b) Transmission vs input fluence (c) Output fluence vs input fluence (d) Scattering signals.

The z-scan data can be used to plot the variation of sample transmission with input laser fluence, because for a spatially Gaussian beam, the light fluence $F_{in}(z)$ at any position z can be calculated from the corresponding beam radius $w(z)$ and the input laser pulse energy E_{in} . The plot of sample transmission versus input fluence is shown in Figure 2(b), and that of output fluence versus input fluence is shown in Figure 2(c).

It is found that optical limiting efficiencies of all fluorinated graphene samples are higher than that of GO in water. The optical limiting threshold (input fluence at which transmission decreases to 50% of the linear transmission due to the nonlinearity) of F-GO/water and H-FGO/NMP are at 0.8 and 1.5 J/cm^2 respectively. The optical limiting properties of F-GO in (N-methyl-2-pyrrolidinone) NMP were also studied to find out the solvent

contribution to the optical limiting performances when comparing F-GO/water to HF-GO/NMP dispersions. It is found that F-GO in NMP also has better optical limiting efficiency than HF-GO in NMP.

Optical limiting behavior can arise from nonlinear absorption and/or nonlinear scattering. For example, carbon particle suspensions (CS) show strong optical limiting due to NLS caused by thermally induced microplasma,³⁵ whereas fullerenes (C_{60}) exhibit robust limiting due to large RSA.³⁶⁻³⁸ In addition, multiwalled and single walled carbon nanotubes (CNTs) exhibit broadband optical limiting due to NLS^{39, 40} while GO exhibits limiting due to RSA.⁴¹

By measuring the scattered light from our samples, it is found that all fluorinated graphene oxide samples have strong nonlinear scattering whereas there is no nonlinear scattering present in GO, Figure 2(d). This finding suggests that there is a significant enhancement in nonlinear scattering due to the presence of C-F bonds in the fluorinated samples. This enhancement, as a result, contributes to better optical limiting properties.

However, when comparing the z-scan and scattering data, it is found that, for fluorinated graphene oxide samples, the onsets of the optical limiting start earlier than the onsets of nonlinear scattering. This observation suggests that the optical limiting action of fluorinated graphene oxide in the *ns* excitation regime is not exclusively due to nonlinear scattering. In fact, Photoacoustic measurement technique is employed to verify this assumption.

Photoacoustics (PA) is a well-known sensitive method for measuring low level absorptions in materials.⁴²⁻⁴⁶ In our PA measurements, an in-house fabricated PA cell was used. The detail of the setup can be found elsewhere³³. The normalized PA signal plotted against input energy is shown in Figure 3. According to the plot, the PA signal is the highest in F-GO while GO has the lowest PA signal and HF-GO assumes an intermediate value. This observation renders the fact that, besides NLS, NLA also plays a significant role in the optical limiting of fluorinated GO samples.

Figure3. Normalized photo acoustic signals

X. F. Jiang et al. reported significantly enhanced nonlinear absorption of GO upon partial reduction.⁴² This enhancement in nonlinear absorption was attributed to localized sp^2 domains. By studying X-ray Photoelectron Spectroscopy (XPS) data of these samples³³, it is found that the degrees of the sp^2 localizations in our GO and F-GO samples are similar, while HF-GO has lowest number of sp^2 to sp^3 carbons. This renders the significance of fluorine sp^3 sites in the enhancement of nonlinear optical properties of fluorinated samples.

3. CONCLUSIONS

In conclusion, it is found that the optical limiting efficiency of F-GO was significantly greater than of GO. Nonlinear scattering measurements reveal that scattering is higher in F-GO when compared to GO, while photoacoustic measurements indicate that nonlinear absorption is also superior in F-GO. The limiting threshold of F-GO is an order of magnitude higher than of GO. These observations suggest that F-GO dispersions are potential candidates for optical limiting applications.

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