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Effect of reduction time on third order optical nonlinearity of reduced graphene oxide

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ABSTRACT

We report the influence of reduction time on structural, linear and nonlinear optical properties of reduced graphene oxide (rGO) thin films synthesized by spin coating method. We observed that the structural, linear and nonlinear optical properties can be tuned with reduction time in GO is due to the increased structural ordering because of the restoration of sp2 carbon atoms with the time of reduction. The nonlinear absorption studies by open aperture Z-scan technique exhibited a saturable absorption. The nonlinear refraction studies showed the self de focusing nature of rGO by closed aperture Z scan technique. The nonlinear absorption coefficient and saturation intensity varies with the time for reduction of GO which is attributed to the depletion of valence band and the conduction band filling effect. Our results emphasize duration for reduction of GO dependent optical nonlinearity of rGO thin films to a great extent and explore its applications Q switched mode locking laser systems for generating ultra short laser pulses and in optical sensors. The rGO coated films were characterized by X-Ray diffraction method (XRD), Fourier transform infrared spectroscopy (FTIR), Raman spectroscopy, UV–Vis absorption spectroscopy (UV–Vis), Photoluminescence (PL) and Scanning electron microscope (SEM) measurements.

1. Introduction

Graphene, is an eminent two-dimensional carbon nanomaterial, shows remarkable linear and nonlinear optical properties and has potential applications in photonics and optoelectronics [1–3]. Since graphene consists of large number of sp2 hybridized carbon atoms and π -conjugated structures, enhances its nonlinear optical properties (NLO) and make it possible for significant applications in optical limiters, optical storage, optical computing and optical communication [4,5]. Graphene oxide (GO) is the main precursor for the production of graphene, also possesses NLO properties due to the co existence of sp3 matrix and sp2 hybridized carbon domains [6,7]. Restoration of the physical structure of pristine graphene can almost possible by the reduction of GO by any suitable reducing agents and the effect of reduction time on GO can tune the nonlinear optical property of the reduced graphene oxide (rGO) material to a great extent [8]. Nonlinear optical phenomena like nonlinear absorption (NLA) effects involving saturable absorption, reverse saturable absorption, two photon absorption, optical limiting and four wave mixing can be observed in both GO and rGO carbon based materials [5–8]. The band filling effect of graphene makes it a promising saturable absorber (SA) for mode locking application of ultra short pulse generation in laser cavities and optical switching [9,10]. The fast response time, low saturation intensity and the maximum change in the absorption induced by the incident light makes it an excellent saturable absorber [10,11]. Two photon absorption is another nonparametric process occurring in graphene that has attracted research interest due to its numerous applications in the area of optoelectronics [9–12]. Nonlinear absorption (NLA) and nonlinear refraction (NLR) have been examined systematically to explore various technological and industrial applications in the field of nonlinear optics [13–17].

The goal of the present research work is to investigate and develop reduced graphene oxide material presenting large optical nonlinearities and simultaneously satisfying different technological and cost-effective requirements. Although some studies of GO and rGO have been reported in the field of nonlinear optics [18–21], the

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dependence of the time of reduction of GO on the progression of nonlinear optical properties of rGO has not been reported thus far. In this paper, we report the reduction of GO using hydrazine hydrate at two different reaction temperatures (70 and 100 °C) for the same duration of reduction (12 h). Spin coated rGO thin films with various thicknesses were synthesized for each of these reaction temperatures. Our experimental results confirmed that rGO synthesized at higher temperature showed fewer defects. Structural properties were found to improve with reaction temperature and thickness of rGO thin film. By keeping these two parameters (temperature and thickness) at the best values, we tried to study the synthesis of rGO on the basis of reduction time (12 h, 24 h). It was found that the increased reduction time of GO helps to enhance the quality of rGO and the mechanism behind the dependence of reduction time on nonlinear optical properties with respect to saturable absorption behavior are also explained.

2. Experimental

2.1. Synthesis of reduced graphene oxide (rGO)

All the chemicals used in the synthesis of GO and rGO were of analytical grade. Graphene Oxide was synthesized from graphite oxide powder by modified Hummers' method [22,23]. 2.0 g of graphite oxide powder mixed with 500 ml of distilled water. The solution was ultrasonicated for 40 min 10 ml of hydrazine hydrate was added to the solution and heated at 70 °C in a condenser mantle for 12 h. The resulting rGO powder was dried at 55 °C for 18 h.

2.2. Synthesis of reduced graphene oxide thin film

The rGO thin film was prepared on a glass substrate by spin coating technique. 0.05 g of rGO was suspended in 10 ml of di methyl formamide (DMF). A part of the rGO suspension was then spin coated on the glass slide through ultra violet light (UV) curing by using Spectrospin 10 K-Table top spin coating unit with online IR curer at 3000 rpm for 30sec. The UV curing enhances the adsorption of the material and to ease better bonding. This increases the quality of the film and allow for greater stability. Samples were prepared by taking an appropriate volume of sonicated suspension, keeping the rpm and rotation time a constant. The glass substrates for the film deposition were washed with acetone, ethanol and deionized water for 20 min successively under the assistance of ultrasonication. The rGO thin film was obtained after drying at room temperature for 12 h.

In order to study the effect of reaction temperature on the reduction of graphene oxide, same synthesis process was repeated by changing the reaction temperature to 100 °C.For observing the effect of thickness on the properties of rGO, thin films with various thicknesses (150 nm, 350 nm) were prepared for each temperature (70 °C and 100 °C). Finally, to study the effect of reduction time on the structural and nonlinear optical properties, rGO thin films of 350 nm thickness were synthesized with the powder samples prepared at 100 °C for 12 h and 24 h reduction time.

2.3. Characterization techniques

The crystallographic structure of synthesized samples was analyzed with Bruker AXS D8 advance X-ray diffractometer by using Cu-Kα lines. Shimadzu IR Affinity-1 FTIR Spectrophotometer was used to record the Fourier transform infrared spectra in the range of 400–4000 cm^{-1}. With a Horiba JobinYvon Lab Ram HR system, Raman spectrum of the sample was recorded with Ar-ion laser (514.5 nm) as the excitation source with a resolution better than 3 cm^{-1}. The optical absorption of the samples are obtained using UV–Vis–NIR Spectrophotometer (Model-Varian, Cary5000). Photoluminescence (PL) spectra of the samples were traced using Horiba scientific Fluoromax-4C spectrofluorometer. The surface morphology of rGO samples were examined using JEOL JSM 7600F field Emission Scanning electron microscope. The thickness of rGO thin films was estimated by using stylus profilometer and it was found to be approximately 150 nm and 350 nm.

The nonlinear optical studies of the obtained rGO thin films were analyzed by closed and open aperture Z-scan technique based on the principle of spatial distortion of laser beam which offers high sensitivity and simplicity [24,25]. Light source used was a 532 nm diode pumped Nd:YAG laser beam (Coherent Compass™215M- 50). A 3.5 cm converging lens was used to focus the laser beam. The beam waist (ω_0) at the focus and Rayleigh length $Z_0 = \pi\omega_0^2/\lambda$ were calculated as 15.84 μm and 1.48 mm, respectively. Using a computer-controlled translation stage, the sample was moved across the focal region along the direction of propagation of the laser beam. The transmitted beam through the aperture (closed aperture Z-scan method) and without the aperture (open aperture Z-scan technique) was scanned a photo detector fed to the digital power meter (field master,GS-coherent). The detected signals were acquired, stored and processed by the computer. The nonlinear absorption coefficient and nonlinear refractive index was calculated by fitting the Z-scan plot with theoretical plot.

3. Results and discussions

3.1. XRD analysis

XRD patterns of Graphite, Graphene Oxide and spin coated rGO thin films (thickness 350 nm, reduction temperature 100 °C) for reduction time 12 h and 24 h are as shown in Fig. 1.

The strong and sharp peak at $2\theta = 28.67°$ of graphite indicates a higher ordered structure, with an interlayer spacing of d = 3.11A°. The absence of the diffraction peak at 28.67° and the emergence of the peak at 9.44° shows that the product is completely oxidized with an increase in d-spacing from 3.11 A° to 9.36A°. An increased interlayer distance between consecutive carbon basal planes is detected and it is due to the intercalation of oxygen functional groups and water molecules between the layers of graphite [23]. XRD study confirmed the reduction of graphene oxide with the

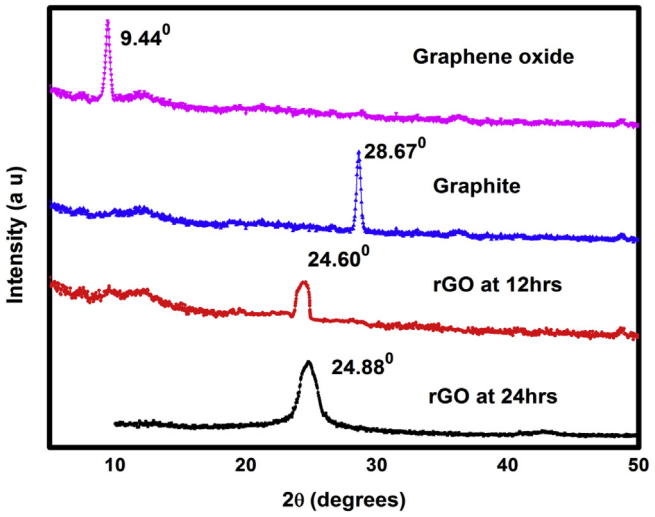

Fig. 1. XRD pattern of graphite, graphene oxide and rGO thin films with 350 nm thickness and reaction temperature 100 °C for different reduction time.