Optical Materials 79 (2018) 120–128

Contents lists available at ScienceDirect

Optical Materials

journal homepage: www.elsevier.com/locate/optmat

Third-order optical nonlinearity of N-doped graphene oxide nanocomposites at different GO ratios

Salimeh Kimiagar [a], Fahimeh Abrinaei [b, *]

[a] Nano Research Lab (NRL), Department of Physics, Central Tehran Branch, Islamic Azad University, Tehran, Iran
[b] Department of Physics, East Tehran Branch, Islamic Azad University, Tehran, Iran

ARTICLE INFO

Article history:
Received 17 January 2018
Received in revised form
20 February 2018
Accepted 18 March 2018

Keywords:
Nonlinear optical response
Nitrogen-doped graphene oxide nanocomposites
Z-scan technique

ABSTRACT

In the present work, the influence of GO ratios on the structural, linear and nonlinear optical properties of nitrogen-doped graphene oxide nanocomposites (N-GO NCs) has been studied. N-GO NCs were synthesized by hydrothermal method. The XRD, FTIR, SEM, and TEM results confirmed the reduction of GO by nitrogen doping. The energy band gaps of N-GO NCs calculated from UV–Vis analyzed by using Tauc plot. To obtain further insight into potential optical changes in the N-GO NCs by increasing GO contents, Z-scan analysis was performed with nanosecond Nd-YAG laser at 532 nm. The nonlinear absorption coefficient, β, and nonlinear refractive index, n_2, for N-GO NCs at the laser intensity of 113 MW/cm were measured and an increase was observed in both parameters after addition of nitrogen to GO. The third-order nonlinear optical susceptibilities of N-GO NCs were measured in the order of 10^{-9} esu. The results showed that N-GO NCs have negative nonlinearity which can be controlled by GO contents to obtain the highest values for nonlinear optical parameters. The nonlinear optical results not only imply that N-GO NCs can serve as an important material in the advancing of optoelectronics but also open new possibilities for the design of new graphene-based materials by variation of N and GO ratios as well as manufacturing conditions.

1. Introduction

Researchers have shown that doping of graphene with heteroatoms like nitrogen, boron, and phosphorus can lead to great evolutions in its electronic, chemical, optical, and magnetic properties [1–4]. Among heteroatoms, nitrogen can be more beneficial for two reasons. First, the atomic radii of nitrogen and carbon are close to each other. Second, nitrogen can form the strong valence bonds with carbon atoms due to the presence of 5 valence electrons [5].

Doping of graphene with nitrogen can greatly improve its electrical properties [6]. It can be introduced into the hexagonal carbon network as the graphitic nitrogen (substitution a single C atom by N), the pyridinic nitrogen (substitution by a vacancy as a neighbor, contribution of one p electron to the π system both with sp^2 hybridization) and the pyrrolic nitrogen (contribution of two p electrons to the π system) [7,8].

In general, doping of graphene by nitrogen can transform its applications in various fields, such as photocatalyst, lithium battery, molecular sensing and fuel cells [9–12]. Recently, the employment of nitrogen-doped graphene for the nonlinear optical applications has attracted the attention of researchers [13,14].

This paper presents a glance of the nonlinear optical (NLO) properties of N-GO NCs prepared by using the hydrothermal method. UV–Vis absorption spectroscopy is utilized to calculate the optical band gap (E_g) and the linear absorption coefficient (α) of N-GO NCs. X-ray diffraction (XRD) illustrates the formation of the structure for N-GO NCs. Also, the Fourier transform infrared (FTIR) spectra and scanning electron microscopy (SEM) are measured. The NLO properties of N-GO NCs are investigated using a single beam Z-scan technique at a wavelength of 532 nm. The measurements are performed for both open and closed-aperture Z-scan setup.

2. Experimental detail

2.1. Materials synthesis

All materials were bought from Merck Company. GO was prepared using modified Hummers method which has been described

* Corresponding author.
E-mail address: f.abrinaei@iauet.ac.ir (F. Abrinaei).

https://doi.org/10.1016/j.optmat.2018.03.030
0925-3467/

in the previous report [15].

N-GO NCs were synthesized by hydrothermal method. In this regards, 80 mg GO was dissolved in 50 ml of the DI water with magnetic stirring at room temperature for 10 min. Then 5 g of urea ($(NH_2)_2CO$) was slowly added to the obtained solution and stirred for 30 min. The solution was then transferred to a Teflon-lined autoclave and heated at 180 °C for 6 h. After the reaction, the autoclave was naturally cooled down to room temperature. The N-GO NCs were collected by centrifugation, followed by washing with deionized water several times. The resulted material was dried in vacuum at 80 °C for 3 h. The obtained powder tagged N-GO80. The same process was repeated for two other samples with 90 and 100 mg of GO and labeled N-GO90 and N-GO100, respectively.

2.2. Characterization of synthesized materials

The optical absorbance of N-GO NCs was carried out with a high-resolution UV–Vis spectrophotometer, Perkin–Elmer. Fourier transform infrared spectra were taken in the range of 500–4000 cm^{-1} by jasco FTIR-410 spectrophotometer. The structural properties of the sample were analyzed by a Philips Xpert-MPD Model 3040 X-ray diffractometer (XRD) with Cu Ka radiation with $\lambda = 1.5406$ Å. Transmission electron microscope (Philips CM120 model) was applied to characterize the morphology of the N-GO NCs. Furthermore, scanning electron microscope (SEM, VEGA/TESCAN-XMU) was also applied to characterize the morphology of the samples.

2.3. Z-scan technique

A simple and pleasant technique for measurement the NLO properties of materials is the Z-scan experiment, developed by Sheik-Bahae and co-workers [16]. The schematic experimental setup used for the Z-scan technique is presented in Fig. 1.

In the Z-scan experiment, a polarized Gaussian laser beam was focused using a lens. The sample was moved along the path of the laser beam between + z and -z positions and the transmitted intensity through the sample was measured. In the closed-aperture Z-scan setup, an aperture was placed at the far field and in front of the detector. During the moving the sample through the focus of the beam at $z = 0$, self-focusing or self-defocusing phenomena alter the wavefront phase, therewith modify the detected intensity which recorded by detectors. In this work, Z-scan experiments were performed by using a Q-switched Nd: YAG laser (Ekspla NL640 model, 532 nm, 10 ns, 200 Hz). The laser beam was focused to a spot size of 80 μm and the Rayleigh length z_0 of 37.8 mm [17].

3. Results and discussion

3.1. Structural investigations

The X-ray diffraction (XRD) analysis was used to illustrate the effect of GO content on the structural properties of N-GO NCs. Fig. 2(a–d) show the XRD spectra of the GO, N-GO80, N-GO90 and N-GO100 samples synthesized by hydrothermal method with various GO ratios. As shown in Fig. 2 (a) which belongs to the XRD spectra of GO, a strong reflection peak was observed at around $2\theta = 26.63°$ which was related to the characteristic peak of hexagonal pristine graphite and corresponds to the coherent and parallel stacking of graphene. This peak corresponds to (002) plane of GO and equivalent to an interlayer distance of 3.34 Å calculated using Bragg's law, $2d\sin\theta = n\lambda$. At the angle $2\theta = 43.3°$, (100) peaks were observed which corresponds to the honeycomb structure which is formed by sp^2 hybridized carbons [18].

Fig. 2(b–d) show the XRD pattern of N-GO NCs with 80, 90 and 100 mg GO, respectively. By adding nitrogen to GO, it can be seen a broadening for (002) peak. This broadening that is centered at around 24° is observed for all N-GO NCs samples, confirming the reduction of GO due to the restoration of van der Waals' interaction between the carbon frameworks on the graphene sheets upon reduction [19]. The comparing of XRD pattern of N-GO NCs shows that by increasing GO contents, the broadening increases

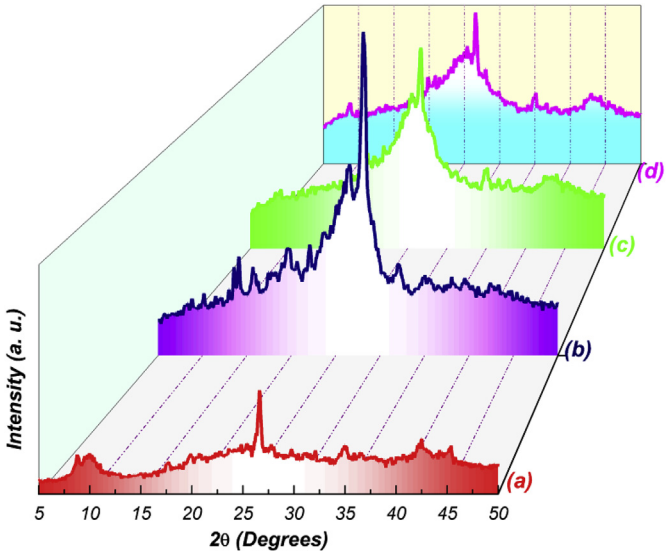

Fig. 2. 3-D plot of XRD spectra for the GO (a), N-GO80 (b), N-GO90 (c) and N-GO100 (d) samples.

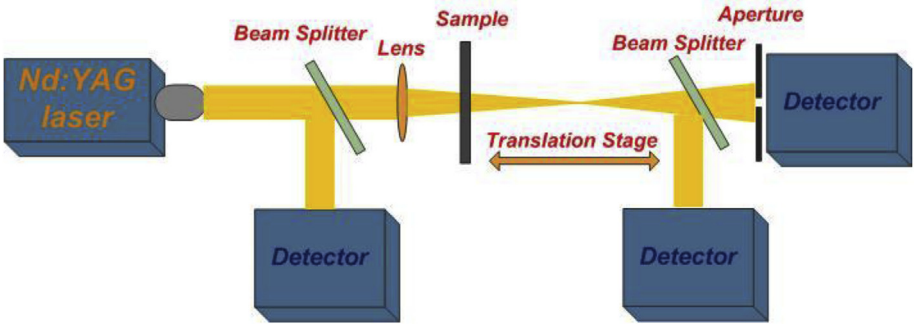

Fig. 1. The experimental setup for measurement of NLO parameters of GO and N-GO NCs.