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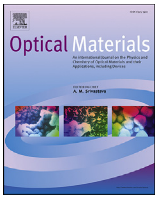

Barium borate nanorod decorated reduced graphene oxide for optical power limiting applications

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ABSTRACT

By simple hydrothermal method, nanorods of barium boate were successfully loaded on reduced graphene oxide sheets. Powder XRD confirms the incorporation of barium borate ($2\theta = 29^\circ$, (202)) along with the transition of graphene oxide ($2\theta = 12^\circ$, (001)) into reduced graphene oxide ($2\theta = 25^\circ$, (002)). In the FTIR spectra, presence of characteristic absorption peaks of rGO (1572 and 2928 cm^{-1}) and barium borate (510, 760 and 856 cm^{-1}) further evidences the formation of BBO:rGO nanocomposite. FESEM images potray the existence of graphene sheets as thin layers and growth of barium borate as nanorods on the sheets of reduced graphene oxide. Ground state absorption studies reveal the hypsochromic shift in the absorption maxima of the graphene layers due to reduction of graphene oxide and hypochromic shift in the absorbance intensity due to the inclusion of highly transparent barium bortae. The photoluminescence of BBO:rGO shows maximum emission in the UV region arising from the direct transitions involving the valence band and conduction band in the band gap region. Z-scan technique using CW diode pumped Nd:YAG laser (532 nm, 50 mW) exposes that both nanocomposite and individual counterpart possess saturable absorption and self-defocusing behavior. Third-order nonlinear optical coefficients of BBO:rGO nanocomposite is found to be higher than bare graphene oxide. In particular the nonlinear refractive index of nanocomposite is almost four times higher than GO which resulted in superior optical power limiting action. Strong nonlinear refraction (self-defocusing) and lower onset limiting thershold makes the BBO:rGO nanocomposite preferable candidate for laser safety devices.

1. Introduction

The major concerns of the electro-optical sensors that are widely used in laser applications are its susceptible to overexposure leading to permanent optical damage. Since the invention of laser in 1960, the protection of human eyes and sensors against intended or unintended damage by laser radiation has been an ongoing research field. Laser protection measures are typically realized using conventional optical filters based on linear absorption or interference effects. Unfortunately, these filters work only for predefined wavelength, but not beyond [1]. So a laser beam of high intensity can easily damage the retina and hence significant research effort has been invested on optical power limiting (OL) materials to achieve some measure of protection from such high intense laser beams. An efficient optical limiting material exhibits high transmittance for low intensity ambient light, while strongly attenuating intense and potentially dangerous laser beams [2]. Layer structured carbonaceous materials like graphene oxide (GO) stand high in this domain due to their stronger nonlinear optical response. However the basic requirement of high linear transmittance limits the possible usage as power limiter. Improvement of linear transmittance along with enhanced nonlinear action can be achieved through nanocomposite formation. The availability of several types of oxygen-containing functional groups on the basal plane (epoxide groups) and the sheet edge (ketone groups) allows GO to interact with a wide range of inorganic materials so that functional hybrids and composites with unusual properties can be readily synthesized. In the choice of inorganic materials, barium borate (BBO) nanostructures can be an interesting candidate as it possesses have unique characteristics like wide transparency, large birefringence, high laser damage threshold and excellent mechanical properties. In the wide variety of morphologies, 1D

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nanostructures provides an opportunity to understand both functional behavior in ultra low dimension and to develop high performance next generation devices. Efficient transport of optical excitations due to two dimensional confinements arising from intrinsic anisotropic nature also makes fabrication of 1D nanostructures promising route [3,4]. The origin of large nonlinear optical susceptibility in BBO arises from the anionic structural units and as boron atoms has two kind of co-ordination, a boron atom coordinate with three oxygen atom to form triangle [BO_3] unit and with four oxygen atom to form tetrahedral [BO_4] unit. The network of interconnected [BO_3] and [BO_4] forms infinite chains of [B_3O_6], [B_3O_3] anionic groups whose negative charge is compensated by the Ba^{2+} cations and hence resulting in diversity of structures. Hence most of research is focused on β-BBO nanostructures and reports show that nanorods, nanoplatelets and network like structures of β-BBO exhibits higher SHG performance than bulk form. Also γ-BBO (rich in BO_3 unit) nanostructure exhibited higher third order nonlinearities in the continuous wave (CW) regime demonstrating maximum thermal stability against intense laser radiations among the known NLO materials and hence rendering them ideal for optical limiting applications [5]. Based on these facts, this article reports the optical limiting performance of γ-BBO nanorod decorated rGO with CW laser pulses at a wavelength of 532 nm. It is found that BBO: rGO nanocomposite possesses stronger nonlinear refraction which are beneficial for power limiting applications.

2. Material preparation

Hydrothermal method is an elegant technique to prepare and incorporate barium borate upon graphene sheets. Preparation of barium borate: reduced graphene oxide nanocomposite involves a three step process. In the first step, graphene oxide (GO) was prepared from graphene flakes by Modified Hummer's method [6]. In the second step, the obtained GO was reduced to reduced graphene oxide (rGO) by using ascorbic acid as reducing agent [7]. In the third step of employed experimental procedure, 10 mmol of $BaCl_2 \cdot 2H_2O$, 15 mmol of H_3BO_3 and 20 mmol of NaOH were dissolved in 60 ml distilled water and used as starting precursor to obtain barium boate [5]. To the above mentioned solution, 20 mg of rGO was added and continuously stirred for 8 h to attain homogenous mixing. The solution was then transformed to 100 ml autoclave setup and placed in an oven at 120 °C for 24 h. The obtained slurry was washed with water and ethanol for several times to remove the suspended impurities and other byproducts. Finally the obtained powder was dried at 60 °C for 12 h resulting in the formation of ash colored powder. In each step, the obtained powders were taken out and indexed as GO, rGO and BBO: rGO for further characterization.

3. Structural confirmation

The prepared samples were subjected to powder X-ray diffraction using CuKα radiation (1.54 Å) in the angle of 10°–80°. Fig. 1 shows the recorded XRD patterns of GO, rGO and BBO: rGO. The characteristic peak (001) observed at $2\theta = 12°$ confirms the formation of graphene oxide in the modified Hummer's method. After reduction process no diffraction peaks of GO is observed and the presence of diffraction peak at $2\theta = 12°$ signatures the formation of rGO. Recorded XRD pattern of BBO: rGO forecast the diffraction peaks of both rGO with BBO and thus confirms the formation of nanocomposite. All the additional peaks were indexed and are found to be consistent with the values in the standard card of γ-BBO [JCPDS: 01-071-2501]. The peak at $2\theta = 24°$, 26°, 29°,32°, 34°, 40°, 42°, 47°, 53°, 61° and 68° represents planes (1 1 2), (0 2 1), (2 1 1), (1 0 4), (0 2 3), (0 1 5), (3 1 2), (3 1 3), (3 2 3), (2 1 7) and (4 2 4) of barium borate and thus formation of BBO:rGO nanocomposite is confirmed. As the samples were prepared at low temperature (120 °C), γ-BBO was obtained and thus expected to attain higher third-order NLO co-efficient [5]. The widths of the reflection peaks are considerably broadened, indicating the crystalline particles fall in the nanoscale range [8]. The average grain size of BBO:rGO composite is deliberated to be 17 nm from the Debye–Scherrer equation. No characteristic peaks that correspond to the possible byproducts and other impurities are identified.

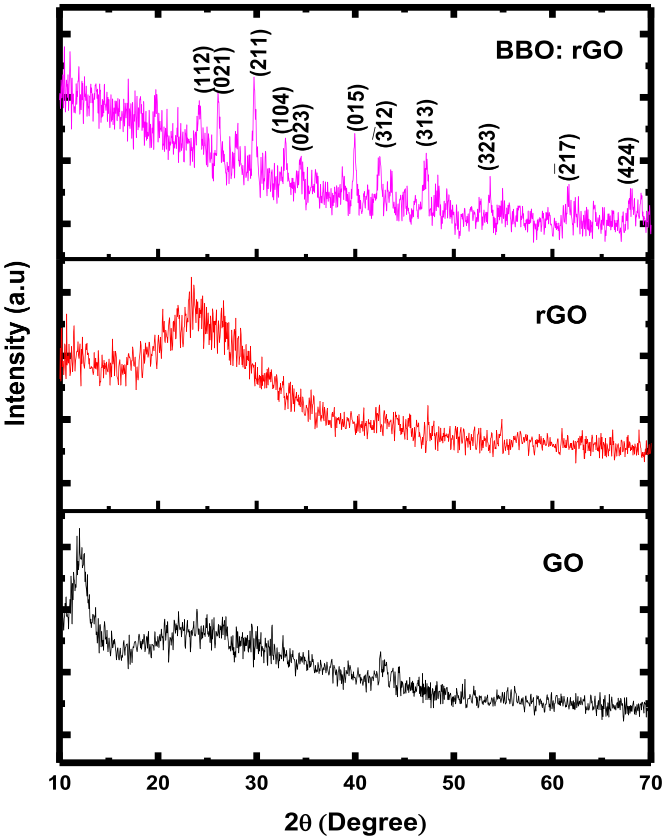

Fig. 1. XRD pattern of GO, rGO and BBO: rGO.

IR spectra were recorded with JASCO 460 PLUS FTIR spectrometer in the range of 400–4000 cm^{-1} with spectral resolution of 1 cm^{-1} to identify various functional groups and the available molecular vibration of the samples. The recorded FTIR spectra of the samples (Fig. 2) show strong absorption peaks which corresponds to the various vibrational modes of GO and BBO (Table 1). It is interesting to note that the in the modified Hummer's method, graphene sheets were successfully incorporated with various oxygen containing functional groups such as aromatic hydrocarbons (2825 cm^{-1}), hydroxyl (3442 cm^{-1}), carboxyl (2324 cm^{-1}), carbonyl (1738 cm^{-1}), epoxyl (1243 cm^{-1}) and alkoxy (1207 cm^{-1}) groups. Ascorbic acid being a mild reducing agent removes carboxyl groups during reduction and leaves most of the functional groups in the graphene sheets. It is interesting to note that, during incorporation of BBO upon graphene layers, some of the functional groups (namely carboxyl and epoxy) were effectively removed. Also in the FTIR spectrum of BBO: rGO, the additional absorption peaks at 510 and 760 cm^{-1} corresponds to the bending vibrations of B–O–B bond [9] and peak at 856 cm^{-1} is due to stretching vibration of B–O bond in BO_3 unit [5] of barium borate (γ-BBO), by which the formation of BBO: rGO composite is confirmed.

Morphologies of the samples were investigated by Field