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Nonlinear optical properties and optical limiting measurements of graphene oxide – Ag@TiO_2 compounds

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ABSTRACT

In this work Graphene Oxide (GO), Ag@TiO_2 core-shells and GO-Ag@TiO_2 compounds were prepared and experimentally verified. Using a low power laser diode with 532 nm wavelength, the magnitude and the sign of the nonlinear refractive index and nonlinear absorption were determined by the Z-scan technique. It was observed that the nonlinear absorption of GO-Ag@TiO2 mixture was higher than pure GO. The optical limiting effect of these samples was also investigated using the 2nd harmonics of a pulsed Nd-YAG laser at 532 nm. Our results showed that the sole Ag@TiO_2 didn't show any appreciable optical limiting effect, however after just mixing with graphene oxide the threshold of optical limiting was increased and the compound showed an enhancement of optical limiting behavior compared to GO itself. The presented results are discussed and compared with other literature reports.

1. Introduction

Nowadays nonlinear optical properties of materials are widely used in the industry. For this reason, measurement and evaluation of these properties are of importance which leads to identification of cheaper and more applicable materials. One of the most sensitive methods for measuring these properties is the z-scan method. In the z-scan method we can simultaneously measure nonlinear refractive index (n_2) and nonlinear absorption coefficient (β). Also the Optical limiting properties are investigated with evaluating the changes in material transmittance with changing the incident light power. These properties are mostly used in applications such as optical switches and protection of the sensors. Studying of different optical limiting mechanisms is possible through z-scan technique [1–3].

Graphene, reduced graphene oxide (rGO) and graphene oxide (GO) have been studied widely for their nonlinear optical properties (NLO) and their unique optical limiting behavior [4–8]. Reduced graphene oxide samples exhibited stronger NLO and optical limiting responses than their GO precursors because of their increased crystallinity and conjugation [8]. They have found that an unusually efficient nonlinear optical-limiting behavior that occurs in graphene and alkyl-functionalized sub-GO_x when they are dispersed as single sheets in appropriate solvents or film matrices. There are also reports on the optical limiting behavior of graphene oxide dispersed with organic solvents [3]. The research of Liaros et al. [9] on the broad band optical limiting of graphene oxide colloids has shown that the broad optical limiting behavior is comparable to C_{60} as well and dispersion in aqueous solution is an advantage of their report. There are also few reports on covalently bond graphene to metal oxide such as CuO [10], and $NaYF_4$:Yb^{3+}/Er^{3+} Nanoparticles [11]. Plasmonic materials such as Ag nanoparticles and its core-shells have been of great interest due to their novel optical behavior in visible range [12]. Among different core-shells of Ag nanoparticles, Ag@TiO_2 has been studied widely due to its unique optical, photochemical and electronic behaviors of TiO_2 which is widely used in many research areas such as solar cells and photonics [13–15]. Due to the production of electron–hole pairs on the surface of TiO_2 under photon excitation accompanied by near field plasmon resonance of Ag cores, it shows also nonlinear optical behavior [16]. Since electron–hole pair on the surface of TiO_2 is readily transferred to other materials with loosing bonds on their surface such as Graphene oxide, the proximity of Ag@TiO_2 and Graphene oxide possibly would result in interesting optical limiting behavior in visible range of light. Recently, Karimipour et al. [17] reported facile synthesis of Ag@SiO_2 core-shells

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using oleylamine with microwave irradiation. Thus, in this work we synthesized Ag@TiO_2 core-shells with a similar method and thereafter Graphene Oxide (GO) and GO-Ag@TiO_2 compounds were prepared and their nonlinear optical properties were investigated. Optical nonlinearity induced in samples by a CW diode laser at 532 nm was studied using Z-scan technique. The optical limiting effect was also investigated using the 2nd harmonics of a pulsed Nd-YAG laser at 532 nm.

2. Experimental

2.1. Fabrication of graphene oxide (GO)

Graphene oxide nanosheets (GONs) were prepared from purified natural graphite powder using an improved Hummer's method reported by Marcano et al. [18]. Briefly, 1 g of graphite flakes and 6 g of KMnO4 were added slowly over 1 h into a 150 ml mixture of H_2SO_4/H_3PO_4 with 9:1 volumetric ratio. The resulting mixture was stirred at 45–50 °C for 2 h. Then, 150 mL water was added, and the solution was stirred for 15 min at 95 °C. Additional 150 mL water was added and followed by a slow addition of 5 mL H_2O_2 (30%), turning the color of the solution from dark brown to yellow. The mixture was filtered and washed with 1:10 HCl aqueous solution (100 mL) to remove metal ions. The remaining solid was filtered over a PTFE membrane (0.45 μm pore size) and vacuum dried overnight at room temperature.

2.2. Synthesis of Ag@TiO_2

2.2.1. Synthesis of Ag nanoparticles

The microwave synthesis of Ag nanoparticles was performed using Shikoku Keisoku SMW 064, with a 2.45 GHz working frequency, attached with a refluxing system. This system had a maximum power of 1000 W and a built-in magnetic stirring system. The temperature was controlled using a feedback system with a thermocouple. Ag (NO_3) (Merck) was used as the starting material. Polyvinylpyrrolidone (PVP-40) (Sigma–Aldrich) was applied as stabilizer and capping agent and also to reduce Ag ions and ethanol (96%) was used as solvent. To synthesis Ag nanoparticles, 0.05gr Ag (NO_3) was dissolved in 40 ml of ethanol and stirred for 5 min. Then, 1gr PVP was added to the initial solution and stirred for another 10 min. The prepared transparent solution was exposed to microwave irradiation at 360 W for 1 min. Then the yellow solution was centrifuged and the Ag nanoparticles were dispersed in ethanol for further use.

2.2.2. Preparation of Ag@TiO_2 core-shells

The prepared Ag nanoparticles with 1 mg/ml concentration in ethanol were used as starting solution for the preparation of core-shells. 100 μl Oleylamine injection was used for functionalization of Ag nanoparticles and the solution stirred for 1 h. Thereafter a subsequent 50 μl titanium isopropoxide was injected directly to the above solution and stirred for 5 min. Then, the solution was transferred to a refluxing flask and placed in the microwave oven. It was exposed to irradiation at the power of 360 W for 20 min until a brown solution was obtained. The irradiated solution was left to be cooled naturally. Thereafter a mixture of acetone, and toluene (1:1 in volume ratio) was added to the solution to obtain a brown precipitation. Then, the core–shell nanoparticles were centrifuged and the obtained powder was washed with ethanol, and re-dispersed again in 20 ml ethanol for further analysis.

2.3. Preparation of GO-Ag@TiO_2 compound solution

To study the nonlinear optical and optical limiting of GO-Ag@TiO_2 compounds, 0.003 g GO powder was dispersed in 40 ml absolute ethanol and sonicated for 1 h. 2 ml of the prepared Ag@TiO_2 was diluted in GO solution and the GO-Ag@TiO_2 mixture was sonicated for 20 min.

2.4. Characterizing Ag and Ag@TiO_2 nanoparticles characteristic

Plasmon resonance of Ag and Ag@TiO_2 nanoparticles was confirmed by UV–Vis spectroscopy using AvaSpec-ULS3648TEC in the wavelength range of 200–1100 nm. Fourier transformed infrared (FTIR) data were collected using an AVATAR-370-FTIR THERMONICOLET spectrometer using two separate procedures. The sample was unpacked into a tablet shape and put onto a polished silicon wafer before analysis. To obtain transmission electron microscope (TEM) images, a LEO912 AB electron microscope operating at the bias voltage of 200 kV was employed. Crystalline structure of the particles was recorded by D8-Advance Bruker X-ray diffractometer using Cu-Ka radiation (λ = 1.54056 Å) in the range of $2\theta = 5^{o}$–80°.

2.5. Nonlinear optical properties

The measurements of the nonlinear optical properties of our samples were performed using the standard Z-scan technique and the thermal lens model [19,20]. The prepared dispersions were placed in 10 mm and 1.2 mm thick quartz cells. The laser beam was focused onto the samples through a 6.29 cm and 15 cm focal length Plano-convex lens, the respective beam spot radius at focus obtained by a knife-edge scan method were 19.3 μm and 40 μm at power of 9.3 mW and 35 mW. In this technique, the sample is translated along the propagation axis (e.g. z-axis) of a focused laser beam while its transmission is recorded at each position.

Briefly, form the "open-aperture" (OA) Z-scan recording, to find the nonlinear absorption coefficient, the experimental data are analyzed by a model related to both SA (saturation absorption) and RSA (reverse saturation absorption). The total absorption coefficient $\alpha(I)$ can be expressed as [21]:

$$\alpha(I) = \frac{\alpha_0}{1 + I/I_s} + \beta I \tag{1}$$

I and I_s are laser radiation intensity and saturation intensity, respectively. β is positive nonlinear absorption coefficient. Therefore the modified normalized transmittance using Eq. (1) can be written as [21,22]:

$$T(z) = \frac{Q(z)}{\sqrt{\pi} q(z)} \int_{-\infty}^{+\infty} \ln\left[1 + q(z)\exp\left(-\tau^2\right)\right] d\tau \tag{2}$$

where

$$\begin{aligned} Q(z) &= \exp\left(\alpha_0 \frac{LI}{I + I_s}\right) \\ q(z) &= \beta I_0 l_{eff} \Big/ \left(1 + \frac{z^2}{z_0^2}\right) \end{aligned} \tag{3}$$

Here, the first term describes the SA, and second term describes two photon absorption (TPA).

And form the "close-aperture" (CA) Z-scan recording, the normalized transmittance was plotted versus position and was analyzed by fitting the Sheik-Bahae formalized and thermal lens model as follows [20]: