On the linearly and nonlinearly optical for the TiO\textsubscript{2}/rGO nanocomposite prepared by pulse Laser ablation in Liquid

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Abstract. A nanostructured film composed of TiO\textsubscript{2} and reduced graphite oxide (rGO), the graphene Flakes were prepared by reduction graphite oxide which was prepare use pulse laser ablation in double distilled and de-ionized water (DDDW) by (Q-switcher, Nd:YAG repetitive modified 6 Hz and the pulse duration 10ns) used wavelength 1064nm, 532nm, E=300mj and 1000pulses, The linear optical measurements showed that nanostructure (TiO\textsubscript{2} /rGO) thin films have direct energy gap. Morphology of the thin films was studied by characterized by means of X-ray diffraction (XRD). The particle size was calculated by using equation Debye – Scherer, The micrographs of scanning electron microscopy (SEM) showed that TiO2/G0 has a fluffy aggregation and the form of grapheme as a flakes, AFM results show that the grain size increase by increasing wavelength. Also in theses papers, the nonlinearity property on this nanocomposite, such as nonlinearly index and nonlinearly absorption coefficients have measured use means of the rings diffraction set-up Z-scan techniques. It is educe that this prepared composite has extreme nonlinearity owing to the two photon absorption (TPA) and optical limiter phenomenally.

Keywords. Nanocomposite, Graphene oxide (GO), laser ablation, Z-scan.

1-Introduction

Discovered the semiconductor was once of the most Scientists and technologically break during the 20th centuries. It has causes major economically changed, and has possibls changes civilization itself [1]. More importantly property of nano-porous materials, distinguisher them of the material and determining more of their application. Syntheses of nono-porous materials are usually based on template-assisted bottom-up processes, including soft and hard templating methods [2]. Nanotechnology refers to the studied manipulate and utilized of nanosize materials (sizes of atoms and molecules). Materials whose crystallite, particle size is small than 100 nm are common named nano-crystal, nanostructure, nano-size materials [3, 4]. Thru improve materials properly, found the application as varied as semi-conductor electronic, sensor, specially polymer, magnetite, advances ceramic , and membrane , should also exploring the field in which there are foreseeable applicable of nanophase materials to long standing materials problem [5,6]. Among the transition metal oxides, TiO\textsubscript{2} has received considerable attentive in the scope of nanotechnology because of the unique property ampersand novel applications [7]. Laser ablation is typical example of top-down approach to fabrication TiO2 nanoparticles in liquid media [8].Graphene is a rapid upward star on the horizons of materially sciences and condense matters physic, the better conductors of thermal at chamber degree ampersand also the better conductors of electric known .It have a tremendous property of absorbing white light [9, 10]. The oxygen's groups up to the graphene surfaces any are connecter to the Grapheneoxide (GO). The oxygen's groups lets the dispersals of GO in aquatic lotion in proper's form [11]. The rediscovering of graphene opening a promise aspect toward synthesize of elastomer nano-composite [12].
Metal oxide nano-particles and nano-composites have, in recent years, received significant attention because of the unique nonlinearly optic (NLO) property, such as two-photon absorptive (TPA), saturated absorptive (SA), reverse saturated absorptive (RSA), self-focus and self-defocus arising from nonlinearity refraction [13,14].

In this paper we prepared the nanocomposite TiO$_2$/rGO by laser ablation in a liquid medium used DDDW, then by the technique Z-scan to study the nonlinearity optic propertied of the nonlinearly refractivity index and the nonlinearly absorptive coefficient.

2- Materials and Methods

2-1 Target Materials Titanium oxide TiO$_2$

TiO$_2$ is a colorless inorganic color, resistant to chromatic change, does not dissolve in water or fat and is very difficult to dissolve in concentrated acids [15] shown figure (1).

![Figure 1](image1.png)

**Figure (1)** explain TiO$_2$ (A) powder (B) bulk (C) crystal structure

2-2 Double distilled and deionized water (DDDW)

Double distilled and deionized water is necessary to prepare samples as a solution in this work. Even pure water is contaminated with ions, dissolved gases and dissolved solvents. So it is re-distilled again to avoid contamination.

2-3 Graphene oxide (GO)

Graphene is a thin layers of pure carbon; it is tightly packer layers of carbons atoms which are bond in a hexagonal lattice [16]. Have a high surface area and a wide range of mechanical, electrical, thermal and optical characteristics, making it an ideal material to be used as practical filler in many nanocomposite overlays [17].

2-4 Nd-YAG Laser

Q-switcher Nd-YAG laser systemic type (HUAFEI) made in china (shown in figure(2)) providing pulses of 1064nm & 532nm (frequency doubled) wavelength with maximum energy per pulse of 1000mJ, pulses view of 10 ns, tentatively 6 Hz and beam diameter of 0.8 mm, was used for laser ablation. The laser is applied with a lens with 10 cm focal length this work was prepared in (Advanced Laser Lab/ College of Education / University of AL-Qadisiyah).

2-5 Z-Scan devices
In this work, performed using 650 nm (CW) diode lasers, (max power is 50 mW, Ac: 220-240 volt, Frequency: 50-60 Hz 250mA. beam diameter 1.5 mm, which was focus by 30 cm focal length lens. The laser beam waist $\omega_o$ at the focus is measured to be 0.015 mm and detector. This work was prepared in (College of Education / University of Qadisiyah).

3- Experimental Work

TiO2 NPs were prepared by using laser ablation in liquid by Nd:YAG, used wavelength (1064& 532) nm, frequency (6 Hz), beam diameter 0.8 nm, energy per pulse of 300 mJ and numbers of laser pulses (1000) at room temperature. TiO$_2$ nanoparticles target of (Ti) (purity of 99.99%) immersed in DDDW and fixed at bottom of glass vessel container are ablation surface of target and TiO$_2$ colloidal this explain in figure (2). The suspension of (0.13g) high-purity commercially available microstructures (99.9%, Sigma Aldrich) in 10 ml of (DDDW) was made and this suspension was mixed with (2ml) of TiO$_2$NPs (to get homogeneous solution, a speed magnetic stirrer was used during the experiment) then further subjected to the laser irradiated by a focused laser beam (532 nm, energy 300 mJ, and 1000 pulse) During this process, GO gets reduced and becomes rGO. The schematic diagram of the synthesis procedure is depicted in figure (3). After then, the crystallographic structure of the films was investigated by X-ray (XRD) system Shimatzu (6000) using Cu Ka radiation. The optical transmittances of TiO2/rGO films on glass substrate prepared by PLAL were measured by UV-VIS (SP8001) Shimatsu double beam spectrophotometer. The surface morphologies of the films were investigated by using an atomic force microscope (AFM) (Shimatsu AA3000 Scanning Probe Microscope).

![Figure (2) experimental setup of TiO2 nanoparticles synthesis by PLA method.](image-url)
Figure (3) the schematic for the synthesis of, TiO$_2$NP and rGO-TiO2 by pulsed laser ablation in liquids method. TiO$_2$ NPs, RGO, reduced graphene oxide

4- Resulting and discussing

4-1 X-ray diffract (XRD)

X-ray diffract (XRD) variable of TiO2 NPs prepared by pulsed laser ablation in (DDDW) on glass substrates at room temperature. Figure(4) appear three peaks with (2θ) values of 27.2, 45.66 and 54.29 degree, corresponding to TiO2 crystal planes of (110), (210), and (211) respectively at 1000 pulses in DDDW solvent, and figure (5) the X-ray diffraction test showed a high-intensity high peak for the Graphene oxide at the surface (001) and angle (2θ=11.85°) this agree with card (JCPDS Card NO.75-1621) this agree with researcher[10,17,18].

Figure (4) X-ray diffract of TiO$_2$NPs

Figure (5) X-ray diffract of GO
4-2 Surface Morphology

Bumpy structures with flat area exhibit height of 0.4–0.9 nm, and some high region show a par height of 1.7 nm [19]. AFM images shown in figures (6) and (7) disparate in homogenous of grains' surfaces of films graded different regions, and yonder embeds in colour. Ice species beckons pills growing is sequential then these colures commences hierarchy to the darkerer colour, so this colour represent the formation of agglomerate pills one on the above of the other. From table (1) the indicated that granuler size and RMS increases when laser beam wavelength increases [20].

![AFM photo of TiO$_2$/rGO at (E=300mj, 1000 pulse, $\lambda=1064$nm)](image)

**Figure (6)** AFM photo of TiO$_2$/rGO at (E=300mj, 1000 pulse, $\lambda=1064$nm)

![AFM photo of TiO$_2$/rGO at (E=300mj, 1000 pulse, $\lambda=532$nm)](image)

**Figure (7)** AFM photo of TiO$_2$/rGO at (E=300mj, 1000 pulse, $\lambda=532$nm)

**Table (1)**. The root mean square roughness surface (RMS) and grain size

| Wavelength (nm) | Sample structure | Grain size (nm) | RMS (nm) |
|-----------------|------------------|----------------|---------|
| 532             | TiO$_2$/rGO      | 54.49          | 2.02    |
| 1064            | TiO$_2$/rGO      | 65.76          | 7.12    |

Figures (8)(A,B,C) exposes the scanning electron microscopy (SEM) photo show that the TiO$_2$ NPS were well uniform anchored on the surf of the rGO sheet. The SEM photos of the small particle sizes TiO2/rGO demonstrate the homogenies' of the composites in larger scales. More of rGO sheet was cover wield the TiO2 nanoparticle owing this enuresis the efficient electron collect via the rGO sheet through the extract processes [21, 22]. The SEM photo of TiO2/rGO reveals that the particles were in an aggregate state shrubbery.
Figure (8). SEM photo of the (A) GO (B) TiO₂ (C) TiO₂/rGO

5- Optical properties

Figure (9) shows the spectral absorbance for (TiO₂/rGO) colloid. It is shown that the TiO₂ absorptive in ultra-violet region is the mainly objective of additional of rGO to increases the light absorptive efficient of TiO₂ in the visible spectral region. The value of the optical band gap that obtain off the linearly parts of the $(\alpha h\nu)^2$ as a functions of the photon energy $h\nu$, as shown in figure (10) it is find that the band gap energy $(E_g)$ decreases with increases wavelength.

Figure (9). Optical absorbance spectra of TiO₂/rGO

Figure (10) optical band gap function to photon energy for TiO₂/rGO

6- Nonlinear optics

The nonlinear optical properties for (TiO₂/rGO) are explained through Z-scan measurements to determine the nonlinear refraction index and the nonlinearly absorptive
The sample put in quartz cell was scanned using transition system along direction Z-axes through the focusing area. Z- Scan experiment illustrates in the figures (11-A) (11-B). In closed Aperture (CA) calculated the nonlinearly refractivity index by the peaky to valley difference of the normalized transmission (experimentally). If the phase shift is positive (self-focus) and then the peaky will trails the valley and if the phase shift is negative then the valley will trail the peak (self-defocus) [23]. The magnet of the phase shift can be computed by the changed in normalization transmitting between peaky and valley used following formulas

\[ n_2 = \frac{\Delta \Phi_o}{I_0 L_{eff} k} \]  
\[ \Delta \Phi_o = \frac{\Delta T_{p-v}}{0.406} \]  
\[ L_{eff} = \left(1 - e^{-\alpha_o t}\right) / \alpha_o \]  
\[ \alpha_o = \frac{1}{L} \ln \frac{1}{T} \]  

Where: \( \Delta \Phi_o \): nonlinear phase shift, \( \alpha_o \): linear absorption coefficient

\[ I_0 \] is the intensity at the focal spot given by \( I_0 = \frac{2P_{peak}}{\pi \omega_o} \) where, \( \omega_o \) is the beam radius at the focal point, \( P \): power.

The nonlinear absorptivity coefficients (\( \beta \)) can be easily calculated in opened Aperture (OA) from the transmittance curves [13].

\[ \beta = \frac{2\sqrt{2}}{I_0 L_{eff}} \Delta T \]  

Figure (11). Z- Scan Technique Experimental (A) Open Aperture (B) Closed Aperture

Figure (12A) show the normalized transmission curves obtained using close aperture set up for TiO2/rGO sample the Normalized peak and valley transmittance \( \Delta T_{p-v} \) was calculated to be (-0.27). Consequently, laser beam widening the media operates as a concave lens to beam and it is called self-defocusing and indicates refraction index as a negative value (-2.8*10^-9 cm/W) and non-linear absorption coefficient exhibits the behavior of two photon absorption calculated (1.44*10^-3 cm/W). The values of \( \beta \) and \( n_2 \) depend on the spotlight issue interact that occurring when a laser of sufficient hefty intensity is faller on a sampled, and thus the interplay can changed the optic property of the heartland can be shown in Figure (12B).
Figures (12) Z-Scan Technique Experimental (A) Closed Aperture (B) Open Aperture

Conclusions

TiO2/rGO nanocomposite was synthesized by laser ablation method at different wavelengths (532nm, 1064nm), 1000 pulses and 300mj, the Surface Morphology RMS and grain size increase when wavelength increases. The SEM images of TiO2/rGO reveal that the particles were in an aggregate state shrubbery. The UV–VIS absorbance spectrally in ultraviolet region, the values of the optical band gap decrease with increasing wavelength. Z-scan teaching used to study nonlinear optical properties result negative nonlinearity for refraction (self-defocusing) and absorption coefficient two photon absorption (TPA). This applicability availability photo-catalyst TiO2/rGO nanocomposites that double working near UV light, as well as an interface layer to reduce the rearer-transportation reactions in dye-sensitivitiy sunshade cells.

Acknowledgments.

The authors thank Advanced Laser Lab/ College of Education / University of AL-Qadisiyah).

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