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Research article

Frequency doubling by nonlinearity of TiO_2 nanomaterial

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ABSTRACT

We reported titanium dioxide nanoparticles solution (TiO_2 NPS) preparation by the sol-gel method. The produced NPS was employed as a liquid crystal to generate the second harmonic (SH) of one part of the pumping Nd: YAG laser at different pumping intensities. The remaining part of the pumping laser was focused on a stander nonlinear material (NPP63) to produce another SH pulse (to be used as a reference). Then the two SH pulses (one from TiO_2 and one from NPP63) were used to calculate the nonlinear coefficient (β) of the synthesized TiO_2 Nano solution. The suggested method represents a simple and inexpensive setup for calculation β by excluding the very expensive femtosecond laser used in previous studies. The results reveal that β for the prepared TiO_2 nanoparticles is very large (5.3×10^{-26} esu).

1. Introduction

Nonlinear optics is the study of light interactions with materials when there is a considerable amendment of the optical responsiveness of the material by the exciting light beam. NL transitions produce new wavelengths that are not available in nature or through the usual interactions. Therefore, NL interactions became the basis for photonics and their applications [1]. The materials respond non-linearly only to high-intensity light, which requires using a laser [2].

An important phenomenon in the nonlinear optics is the Second Harmonic Generation (SHG), where the medium re-emits a photon at double the excitation frequency. The produced SH is coherent unless the re-emission occurs spontaneously in the isotropic media. In both cases, the newly generated wave or what is called Frequency Doubled (FD) has its applications in hyper photonics [3], diabetes test [4], NL spectroscopy [5], optical computing and others. The FD is greatly used in nonlinear analysis of films and interfaces. For NLO analyses of species in solutions, the SHG technique called harmonic light scattering (HLS). Currently, this is the most effective and versatile technique in the determination of first order hyperpolarizabilty values [6, 7], both for nanoparticles and molecules.

Although the production of the second harmonic followed the discovery of laser in a short time, most of the research still relied on using a special type of materials which are the nonlinear crystals, such as KTP, and KDP [8, 9, 10, 11]. Since the generation efficiency is influenced by the amount of non-linear coefficient of the crystal, the geometrical arrangement of the setup, the incidence angle, and the damage threshold of the crystal, it became necessary to search for alternatives to crystals. After the discovery of nanomaterials, work began on its experiment in generating harmonics, starting from the second and up to higher orders. Favaretto et al. produced the SH by an organic thin film. They found that the designed V-shape benzo [b] thiophene film has a high nonlinear coefficient comparable to that of $LiNbO_3$ single crystal [12]. Che et al. studied experimentally the surface SH generation from several of metal and semiconductor thin films. They developed a calibration system for these films [13].

The nonlinear coefficient (β) was first measured by Maker et al. Their technique was known as the Maker-Fringe Technique (MFT) [14]. They rotated the crystal to change the coherence lengths. The second harmonic waves generated at the input face of the crystal and that generated inside the crystal have in general different speeds. Rotating the crystal gives rise to interference fringes in the harmonic power of these two waves. Then they calculated the second harmonic power as a function of the rotation angle and used it in the calculation of β. The MFT technique is an accurate method; it was used successfully and is still being used [15, 16, 17], but it is applicable only for crystals and thin films. Morozov et al. measured β for a powder sample by scaled it to those of a reference crystal such as KDP. They put the sample and the reference crystal alternately in the same experiment and they measured the relative SH energies [18]. The disadvantage of this technique is that it becomes inapplicable when the

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standard reference crystal is unavailable. Joulaud et al. prepared colloidal suspensions of five nanocrystals (NC). The nonlinear coefficient is then derived by comparison with the measured from a reference solution containing molecules of known β. They used femtosecond Ti:sapphire laser to excite the reference solution and generate the SH [19]. The main limitation of using this method is the high cost of the ultra-short pulse durations' lasers.

Over the last few years, enormous studies of different synthesis methods and characterization of TiO_2 nanoparticles have been made due to its special optic properties, chemical sustainability, and environment adaptation [20]. In this proposal, we employ the nonlinearity of TiO_2 nanomaterial for frequency doubling of Nd:YAG laser and then we use the generated harmonics to measure β of the TiO_2 colloid solution. The work aims to provide a simple and inexpensive system for measuring the nonlinear coefficient of any nanomaterial by excluding the femtosecond laser used in the literature. The suggested setup is an improved and costless measuring technique useful in studying materials with desired structural features and properties.

2. Materials and method

2.1. Synthesis of TiO_2 nanoparticles

The titanium dioxide nanopowder was prepared using the sol-gel method. Titanium tetrachloride ($TiCl_4$) was added dropwise to 50:50 water to alcohol mixture. The mixture was immersed in an ice bath to calm the reaction. After vigorous stirring, a $TiCl_4$: H_2O solution of PH = 1 resulted. Then the hydrolysis precursor solution condenses subsequently to a gel product. Adding dropwise of sodium hydroxide solution (NaOH) reduces the Cl-concentration and increases the PH to about 2.5. This step

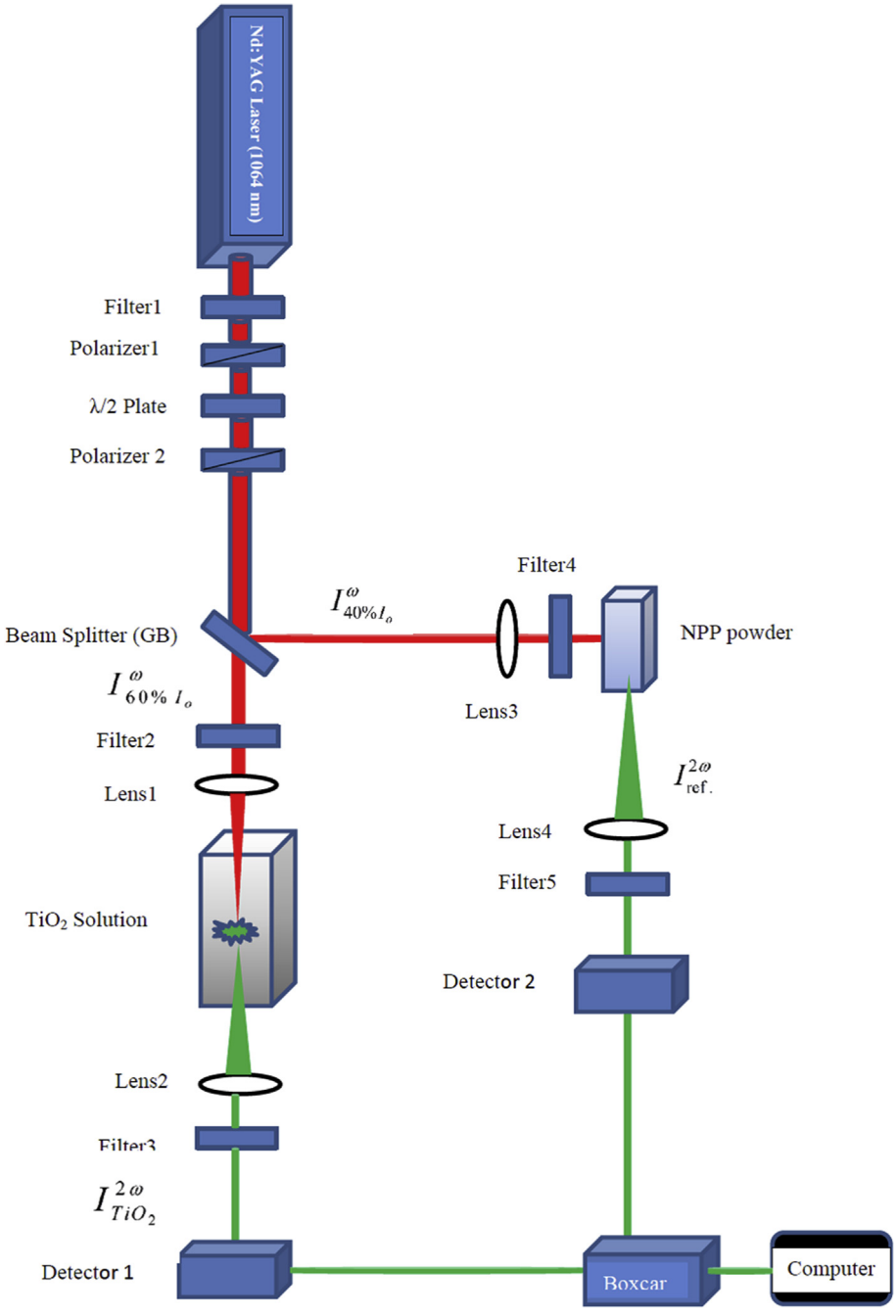

Figure 1. A scheme of the experimental Setup of producing the second harmonic of Nd:YAG laser from TiO_2 nanoselution.

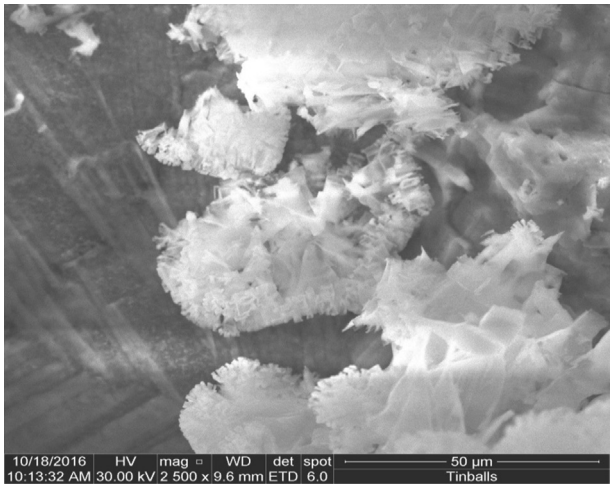

Figure 2. SEM image of TiO_2 nanoparticles prepared by sol-gel method and annealed at a 200 °C.

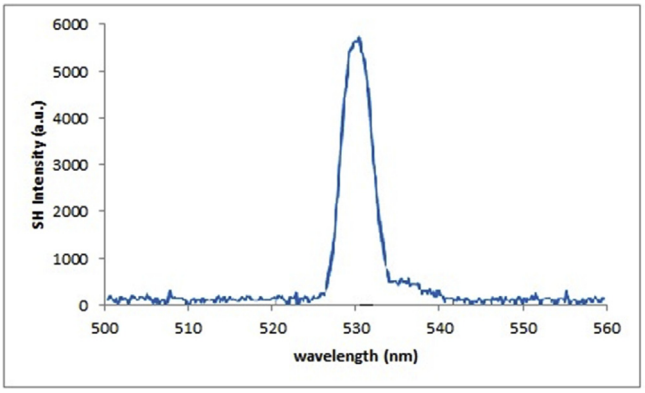

Figure 3. Power spectrum of the generated second harmonic pulse from TiO_2 nanoselution.

was necessary to obtain a more stable suspension. The vigorous stirring was continuous until the gel precipitated from the suspension. The resulting product was put in a centrifuge and washed many times to get the pure TiO_2 nanopowder. The following steps describe the whole reaction process

$$TiCl_4 + 2H_2O \rightarrow TiO_2 + 4H^+ + 4Cl^- \quad (1)$$

$$4NaOH \rightarrow 4Na^+ + 4OH^- \quad (2)$$

$$TiCl_4 + 4NaOH \rightarrow TiO_2 + 4NaCl + 2H_2O \quad (3)$$

Finally, the nanopowder was dissolved by DMSO and then the TiO_2 solution was used as a nonlinear medium to double the frequency of the pumping laser.

2.2. Frequency doubling generation

A pumping Nd: YAG laser beam (1064nm, 6Hz pulse repetition rate, 10 ns, up to 800mJ) was divided by a glass plate (GP) into two parts. The first (60% of the incident intensity, $I^{\omega}_{60\%I_o}$) was focused into the center of the sample by a suitable converging lens to ignite the nonlinearity of the TiO_2 nano solution and generate the desired FD pulse. The remaining part (40%, $I^{\omega}_{40\%I_o}$) was sent into a highly nonlinear material (NPP63 powder) to produce the reference FD signal. The experimental setup is shown in Figure 1.

The generated FD photons (at 532 nm) was collected and focused on the detector by a lens of 5 cm diameter and 5cm focal length. The variation of the generated SH intensity ($I^{2\omega}_{TiO_2}$) from the TiO_2 solution was recorded on the computer as a function of the reference SH ($I^{2\omega}_{ref.}$) provided by the NPP powder. The values of ($I^{2\omega}_{TiO_2}$) for two-component system (the DMSO solvent and the TiO_2 nano solution) is given by Eq. (4) [7].

$$I^{2\omega}_{TiO_2} = G(N_{sol}\langle\beta^2_{sol}\rangle + N_{TiO_2}\langle\beta^2_{TiO_2}\rangle)(I^{\omega}_{60\%I_o})^2 \quad (4)$$

where: G is the instruments' constant, N_{sol} and N_{TiO_2} is the density per unit volume of solvent and the nano solution respectively.

3. Results and discussion

3.1. Characterization of TiO_2 nanoparticles

The titanium oxide nanopowder was annealed at a 200 °C for 120 min for obtaining homogeneous particles of size and shape. The prepared nanoparticles show less aggregation which can be attributed to the annealing effect. TiO_2 nanoparticles were suspended in a DMSO solvent instead of water, this ensures that the solution remains homogeneous for a longer time. The structure and surface characteristics of the product were investigated by Scanning Electron Microscope (SEM) and the result illustrated in Figure 2.

The surface morphology gives an indication of formation of fine structures with small grain size reaches 79.55 nm. Comparing with

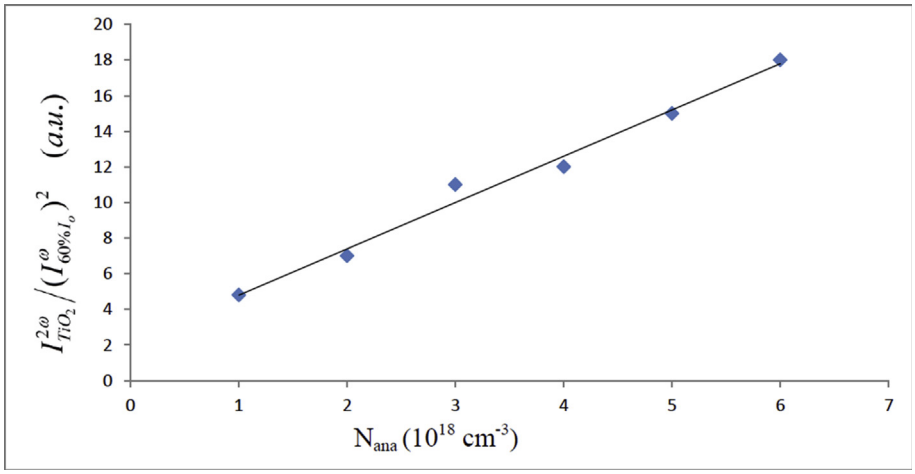

Figure 4. The ratio of the produced second harmonic intensity to the pumping intensity as a function of the TiO_2 nanoparticles density.

previous studies, the results of the SEM test showed regular structures of nano flower shape, unlike to the amorphous structures which obtained by A.S Bakri and his group at the same annealing temperature [21].

3.2. Characterization of FD pulse

A simple experimental setup has used to generate the second harmonic of Nd: YAG laser, where the fundamental laser beam has split into two parts. The first part was used in inducing nonlinearity in TiO_2 nano solution, while the second part was used to generate the reference second harmonic. In contrast to previous studies that used a femtosecond laser in generating the reference beam. Figure 3 represents the power spectrum of the generated second harmonic.

As shown by Figure 3, the curve is not a smooth bell form which gives indicative of the contribution of nonlinear behavior in the spectrum. Nonlinear behavior in nano solutions results from the random fluctuating orientation of particles density where the movement of atoms affects the charge polarization induced by the strong electric field of the laser.

3.3. Calculation of the second order nonlinearity (β value)

The generated harmonic pulse can be used in studying the second order NL property (β) of the nano solution. A plot of $I^{2\omega}_{TiO_2}/(I^{\omega}_{60\%I_o})^2$ as a function of density (N_{TiO_2}) is shown in Figure 4.

From Figure 4 and depending on Eq. (4), β_{TiO_2} can be obtained by dividing the slope ($G\langle\beta^2_{TiO_2}\rangle$) on the intercept ($GN_{sol}\langle\beta^2_{sol}\rangle$). DMSO was used as an internal standard with β_{sol} equal to 15.8×10^{-30} esu thus, the calculated β_{TiO_2} for TiO_2 nanoparticles was 5.3×10^{-26} esu. For comparison with other materials, the current method has been applied to measure the non-linear coefficient of chloroform. The result ($\beta = 0.49 \times 10^{-30}$ esu at 1064 nm) was in a good agreement with ref. [22].

4. Conclusions

The TiO_2 nanoparticles produced by the sol-gel method showed good nonlinear behavior. This was demonstrated by the high value of the nonlinear coefficient (β). It can, therefore, be used in photonics and optoelectronic applications without determinants such as phase matching and walk -off angle as in solid crystalline materials. Also, the results have revealed that the intensities of the generated second harmonic have moderate values and can be increased by increasing the pumping intensity or concentration of the nanoparticle. We have presented a simple, efficient, and inexpensive setup in generating the second harmonic and calculating β. The current setup is inexpensive in β measurement compared with earlier studies that used the expensive femtosecond laser.

Declarations

Author contribution statement

Rabea Q. Nafil: Conceived and designed the experiments; Performed the experiments; Analyzed and interpreted the data; Wrote the paper.

Munaf S. Majeed: Performed the experiments; Analyzed and interpreted the data.

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Competing interest statement

The authors declare no conflict of interest.

Additional information

No additional information is available for this paper.

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