

LASER INTERACTION STUDIES ON NANO POWDER CALCIUM CARBONATE (CaCO_3)

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ABSTRACT: *The study of Nanoparticles with laser plays an important and major role in the material processing nowadays. In material processing the semiconducting materials with metal oxide have low cost. The effect of He-Ne laser and Diode laser irradiation of Calcium Carbonate (CaCO_3) nanoparticles were observed. 0.5 g of CaCO_3 nanoparticle powder with different laser exposures has been chosen as samples for investigation. The irradiation timings were 10 minutes and 20 minutes for each laser. Using UV-Vis Spectrometer, absorbance and transmittance has been measured. Also the energy band gap has been calculated. The band gap energy for the sample irradiated with He-Ne laser and Diode laser increases with increase in temperature. The functional groups for various peaks have been identified and the presence of CaCO_3 has been confirmed using FTIR Spectroscopy. Using DLS Spectra the particle size distribution of CaCO_3 nanoparticle has been revealed that the size ranges from 2.1nm to 268.9nm. From the Fluorescence Spectroscopy the emission and absorption spectrum of the sample has been recorded at room temperature with an excitation wavelength (λ_{exc}) from 569.60 nm to 570.36 nm. The crystalline size ranges 34.37 nm to 35.97 nm and Rhombohedral Structure of the samples has been determined by X-ray diffraction method. The Rhombohedral structure of the CaCO_3 nanoparticle has been revealed by SEM analysis also the particle size varies from 106.9nm to 122.9nm (without laser S1), 88.31nm to 101.6nm (He-Ne laser 20mins S3) and 64.66nm to 103.6nm (Diode laser 20mins S5).*

KEYWORDS: CaCO_3 nanoparticle, He-Ne laser, Diode laser, UV, FTIR, DLS, Fluorescence, XRD and SEM.

1. INTRODUCTION

LASER - Light Amplification by Stimulated Emission of Radiation. Starting with medicine to communications it has become a valuable tool in the variety of fields. It is very much different from many of light sources. With a narrow frequency range it produces a highly directional and high intensity beam. Rather than a light beam it is widely used as high power electromagnetic beam [1] [2]. In many ways it is a high technology device in our day today life [3]. Hence CaCO_3 has been irradiated with two different lasers for various applications. The nanoparticles of CaCO_3 have been used in fields of medical, industrial, agricultural and house hold uses [4] [5]. The important use in the industrial field as a building material, limestone aggregate for road building and ingredient of cement [6].

2. EXPERIMENTAL SECTION

Calcium Carbonate is a chemical compound. Its formula is CaCO_3 . It is a popular substance that is found in rocks. In rocks it is in the form of minerals, calcite and aragonite. It is also in the form of limestone – sedimentary rock contains calcite. This is the major material of pearls, shells of marine organisms, snails and eggs [7]. CaCO_3 is the mobile component in the agricultural lime. Agricultural lime is formed in hard water when ions of calcium react with ions of carbonate to produce limescale. It is dangerous on external consumption. From calcium oxide it has been prepared that calcium oxide [8] is transferred through the solution of calcium hydroxide (calcium oxide + water = calcium hydroxide).

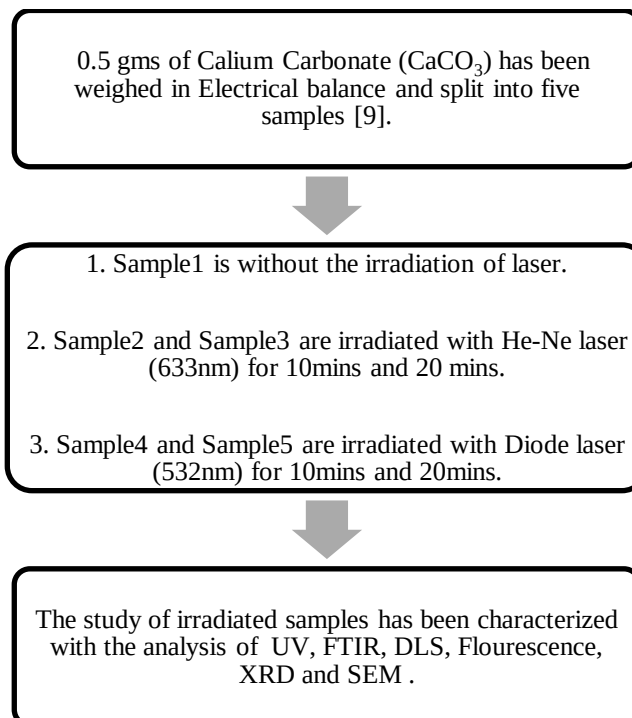
2.1. LASER IRRADIATED CaCO_3

Calcium carbonate powder split into five samples. The amount of each sample is 0.5 gram. Each sample is treated with He-Ne laser and Diode laser as per the Table1.

Table1 Laser Processing Parameters of the Samples

Samples	Laser Irradiation	Weight (G)
1	Without Laser	0.5
2	He-Ne Laser (10mins)	0.5
3	He-Ne Laser (20mins)	0.5
4	Diode Laser (10mins)	0.5
5	Diode Laser (20mins)	0.5

2.2. PROCEDURE



3. RESULTS AND DISCUSSION

3.1. Uv-Visible Spectrometer Studies

The band gap energy for the sample irradiated without laser (Fig 1a and 1b), with He-Ne laser (Fig 1c, 1d, 1e and 1f) increases with increase in temperature and with Diode laser (1g, 1h, 1i and 1j) also it increases with increase in temperature. It ranges (Table5) from 5.90ev to 6.30ev. Because of UV radiation the photoluminescence spectra is expected to be strong [10].

Fig 1a, 1b Sample1 (CaCO_3 Without laser irradiation - UV)

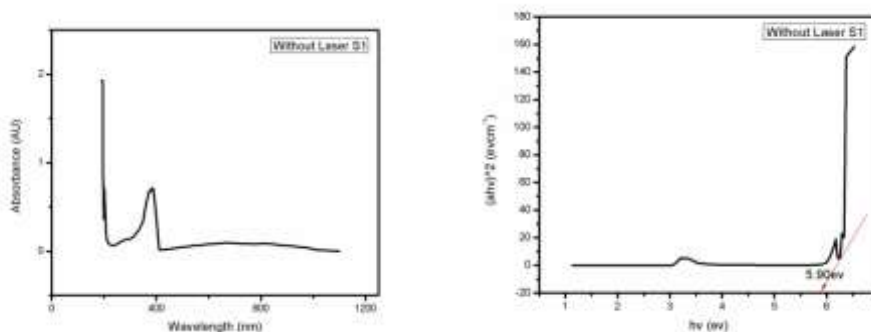


Fig 1c, 1d Sample2 (CaCO_3 with He-Ne 10mins - UV)

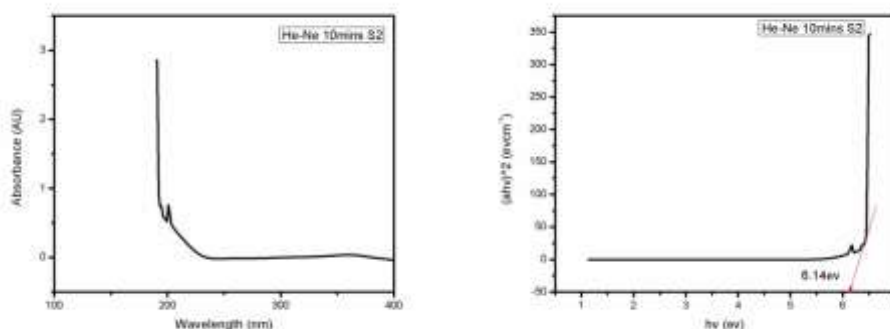


Fig 1e, 1f Sample3 (CaCO₃ with He-Ne 20mins - UV)

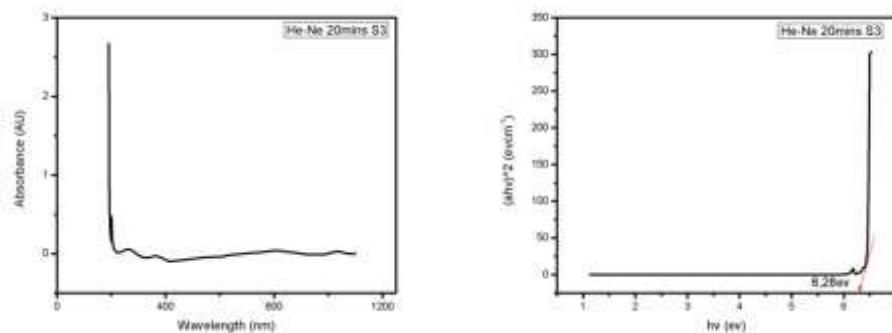


Fig 1g, 1h Sample4 (CaCO₃ with Diode 10mins - UV)

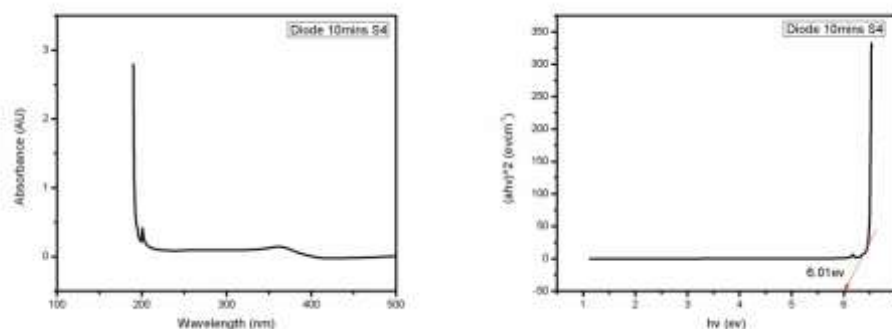


Fig 1i, 1j Sample5 (CaCO₃ with Diode 20mins - UV)

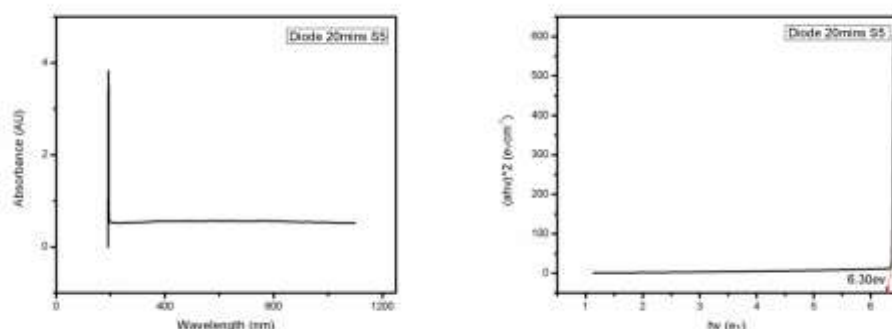


Table2 Band gap energy variation of the samples (UV)

Samples	Time Duration Of Laser Irradiation [Sec]	Band Gap Energy [ev]
1	Without Laser Irradiation	5.90
2	10mins (He-Ne Laser Irradiation)	6.14
3	20mins (He-Ne Laser Irradiation)	6.28
4	10mins (Diode Laser Irradiation)	6.01
5	20mins (Diode Laser Irradiation)	6.30

3.2. FTIR Spectroscopy Studies:

For various peaks (Fig 2a, 2b, 2c, 2d and 2e), the functional groups (Table 3a, 3b, 3c, 3d and 3e) for all the samples have been determined [11] [12].

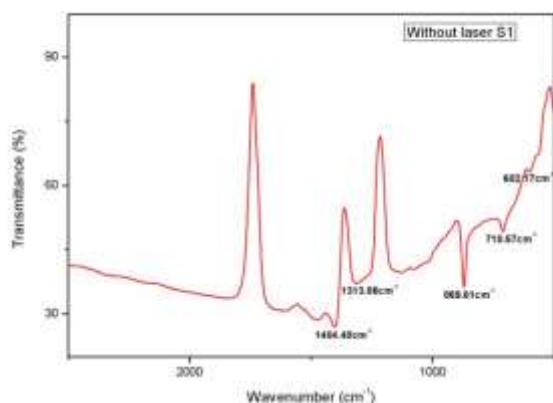


Fig 2a Sample1 (FTIR)

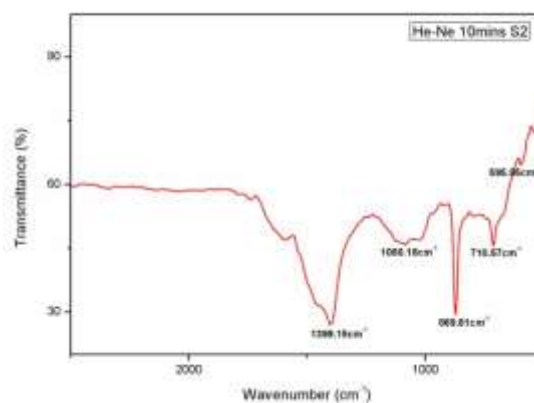


Fig 2b Sample2 (FTIR)

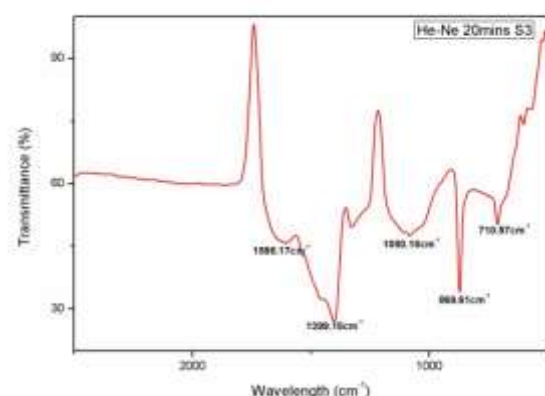


Fig 2c Sample3 (FTIR)

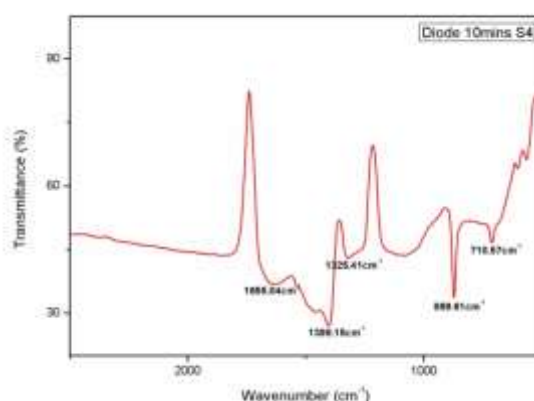


Fig 2d Sample4 (FTIR)

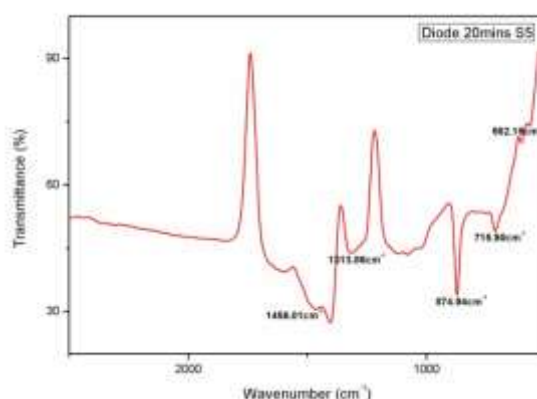


Fig 2e Sample5 (FTIR)

Table 3a CaCO₃ Without laser irradiation - FTIR (Sample1)

Functional Groups	Frequency (cm ⁻¹)	Vibrations	Intensity
O-H (carboxylic acid)	1404.48	Bending	Medium
C-N (aromatic amine)	1313.86	Stretching	Strong
C-Cl (halo compound)	869.61	Stretching	Strong
C=C (alkene)	710.57	Bending	Strong
C-Br (halo compound)	602.17	Stretching	Strong

Table 3b CaCO₃ with He-Ne laser 20mins – FTIR (Sample2)

Functional Groups	Frequency (cm ⁻¹)	Vibrations	Intensity
O-H (carboxylic acid)	1399.15	Bending	Medium
C-O (primary alcohol)	1080.18	Stretching	Strong
C-Cl (halo compound)	869.61	Stretching	Strong
C=C (alkene)	710.57	Bending	Strong
C-Br (halo compound)	595.95	Stretching	Strong

Table 3c CaCO₃ with He-Ne laser 20mins – FTIR (Sample3)

Functional Groups	Frequency (cm ⁻¹)	Vibrations	Intensity
N-H (amine)	1598.17	Bending	Medium
O-H (carboxylic acid)	1399.15	Bending	Medium
C-O (primary alcohol)	1080.18	Stretching	Strong
C-Cl (halo compound)	869.61	Stretching	Strong
C=C (alkene)	710.57	Bending	Strong

Table 3d CaCO₃ with Diode laser 10mins – FTIR (Sample4)

Functional Groups	Frequency (cm ⁻¹)	Vibrations	Intensity
C=C (alkene)	1655.04	Stretching	Medium
O-H (carboxylic acid)	1399.15	Bending	Medium
C-N (aromatic amine)	1325.41	Stretching	Strong
C-Cl (halo compound)	869.61	Stretching	Strong
C=C (alkene)	710.57	Bending	Strong

Table 3e CaCO₃ with Diode laser 20mins – FTIR (Sample5)

Functional Groups	Frequency (cm ⁻¹)	Vibrations	Intensity
C-H (alkane)	1456.01	Bending	Medium
C-N (aromatic amine)	1313.86	Stretching	Strong
C=C (alkene)	874.94	Bending	Strong
C=C (alkene)	715.90	Bending	Strong
C-Br (halo compound)	562.19	Stretching	Strong

3.3. DLS (Dynamic Light Scattering) Studies

The particle size [13] distribution has been measured (Table4) and observed by graphical (Fig 3a, 3b, 3c, 3d and 3e) pattern using DLS studies for with and without laser treated samples.

Fig 3a Sample1 (CaCO₃ Without laser - DLS)

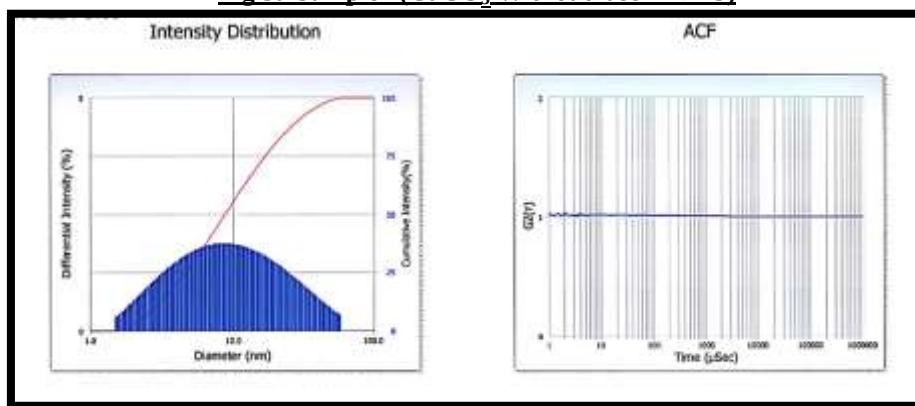


Fig 3b Sample2 (CaCO₃ He-Ne laser 10mins - DLS)

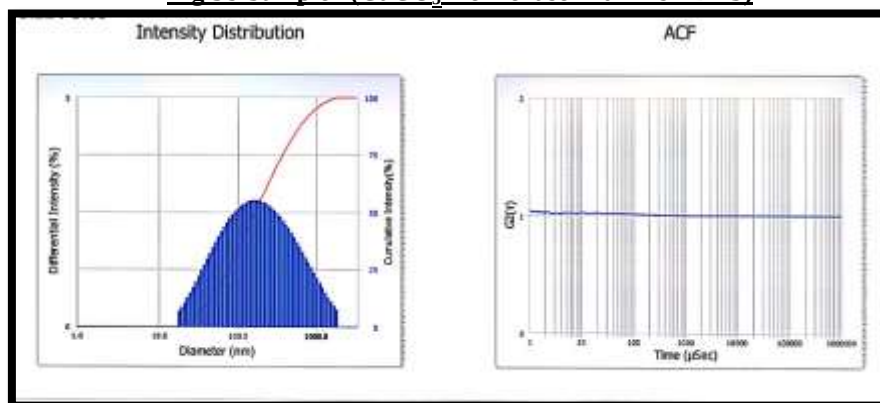


Fig 3c Sample3 (CaCO₃ He-Ne laser 20mins - DLS)

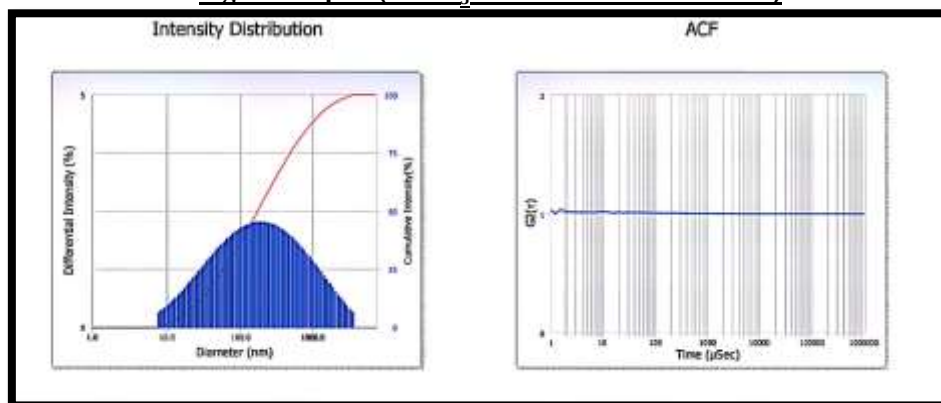


Fig 3d Sample4 (CaCO₃ Diode laser 10mins - DLS)

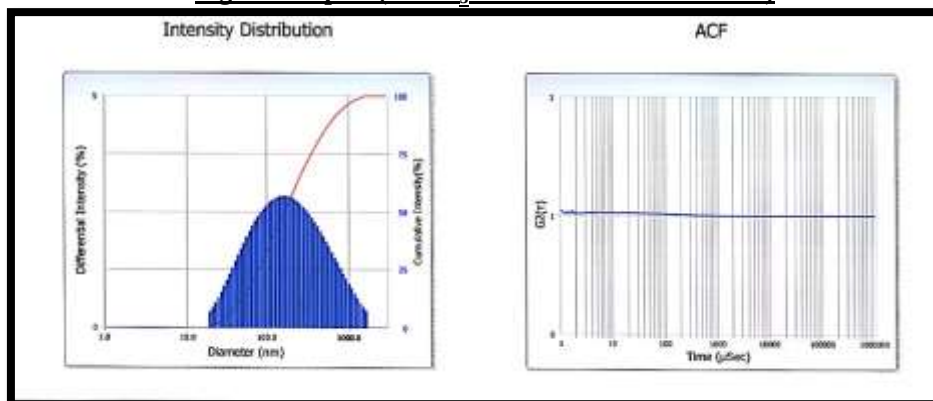


Fig 3e Sample5 (CaCO₃ Diode laser 20mins - DLS)

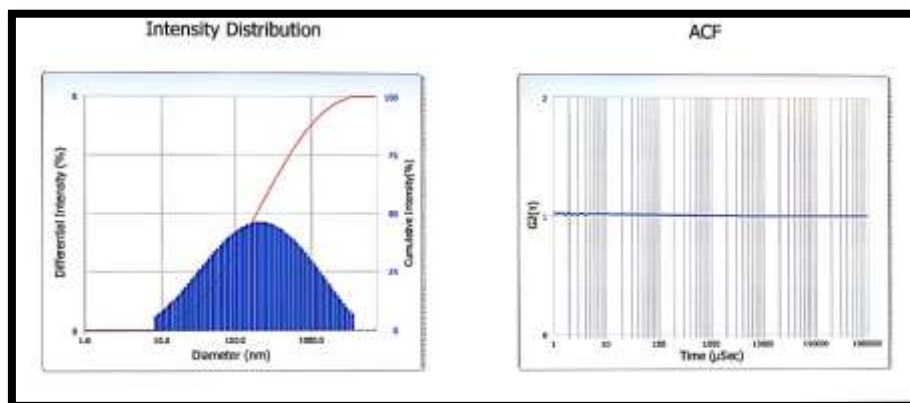


Table4 The particle size distribution of CaCO₃ nanoparticle (DLS)

Sample	Lasers Used	Time duration of laser irradiation	Diameter (nm)
1	Without Laser		2.1
2	He-Ne Laser	10 minutes	107.4
3		20 minutes	241.9
4	Diode Laser	10 minutes	112.0
5		20 minutes	268.9

3.4. Fluorescence Spectroscopy Studies

The photoluminescence [14] spectrum (Fig 4a, 4b, 4c, 4d and 4e) of the samples has been recorded.

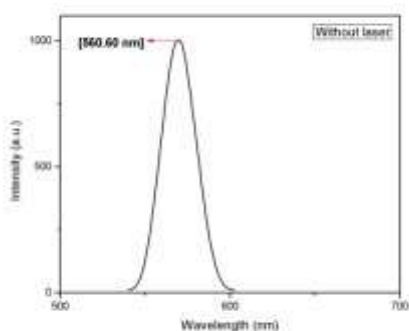


Fig 4a Sample1 (FLS)

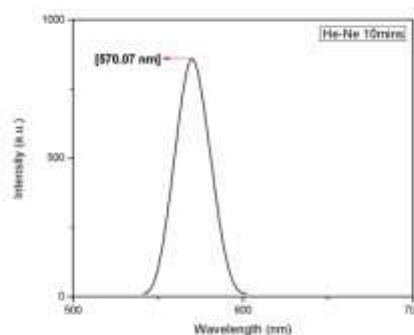


Fig 4b Sample2 (FLS)

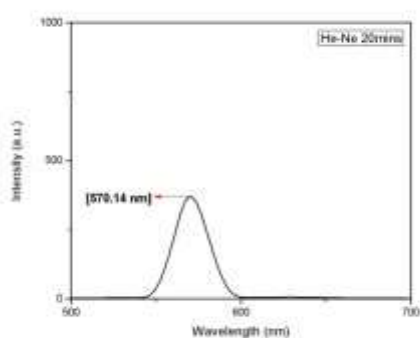


Fig 4c Sample3 (FLS)

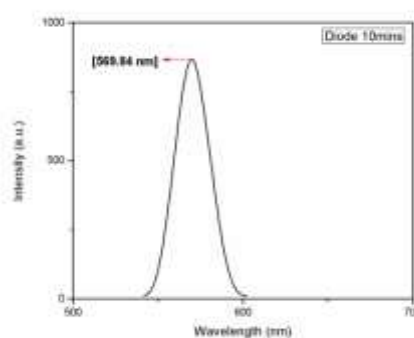


Fig 4d Sample4 (FLS)

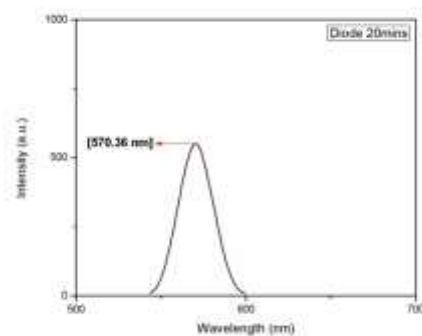


Fig 4e Sample5 (FLS)

Table5 Variation of Excitation wavelength (FLS)

Sample	Lasers Used	Time duration of laser irradiation	Excitation wavelength (λ_{exc}) (nm)
1	Without Laser		569.60
2	He-Ne Laser	10 minutes	570.07
3		20 minutes	570.14
4	Diode Laser	10 minutes	569.84
5		20 minutes	570.36

The photoluminescence spectral studies of the CaCO_3 nanoparticle are strong [9] [10] [14] and have been determined as greenish yellow colour spectrum at the room temperature with an (Table5) excitation wavelength (λ_{exc}).

3.5. XRD Studies

To analyze the structure and particle size of the CaCO_3 nanoparticles, the sample has been undergone with XRD studies. Also the average particle size (D) was determined using Scherer's equation.

$$D = K\lambda / \beta \cos\theta$$

D → Crystalline size

K → Shape factor (=0.9)

λ → X-ray wavelength

β → Full width

θ → Bragg's diffraction angle

The analyzed samples of CaCO_3 nanoparticle [11] [13] [15] exhibits the results (Fig 5a, 5b and 5c) in the form of graphical pattern.

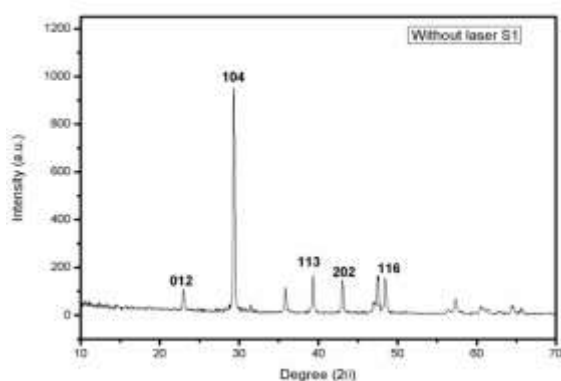


Fig 5a Sample1 (XRD)

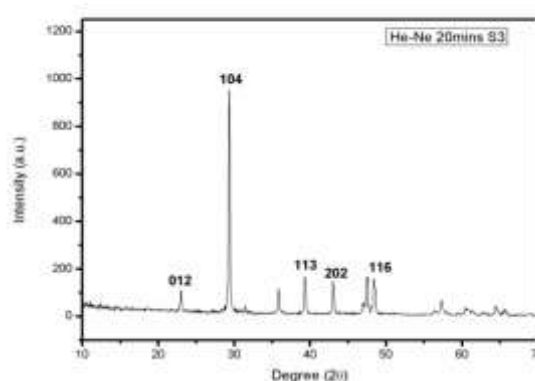


Fig 5b Sample3 (XRD)

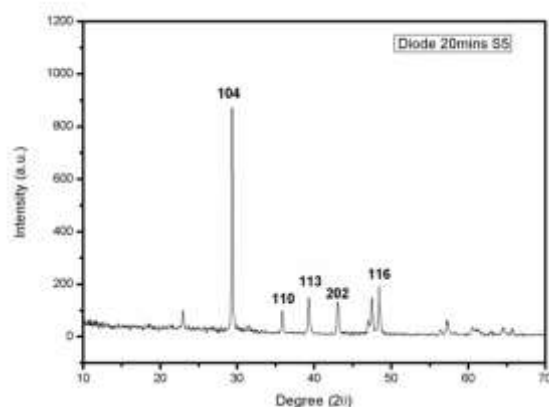


Fig 5c Sample5 (XRD)

Table 6a Sample1 (Without laser irradiation - XRD)

Position(2θ)	hkl	FWHM(2θ)	d-spacing(A°)	Particle Size(nm)
22.98	012	0.25529	3.86585	31.75547
29.36	104	0.21692	3.86585	37.85900
39.33	113	0.23528	2.29068	35.85746
43.07	202	0.23035	2.10061	37.07616
48.46	116	0.29701	1.87941	29.33192

Table 6b Sample3 (He-Ne laser 20minutes - XRD)

Position(2θ)	hkl	FWHM(2θ)	d-spacing(A°)	Particle Size(nm)
22.98	012	0.24949	3.86585	32.49359
29.37	104	0.22177	3.86585	37.03248
39.36	113	0.22913	2.29068	36.82259
43.09	202	0.25746	2.10061	33.84195
48.49	116	0.24914	1.87941	34.28231

Table 6c Sample5 (Diode laser 20minutes - XRD)

Position(2θ)	hkl	FWHM(2θ)	d-spacing(A°)	Particle Size(nm)
29.35	104	0.19759	3.04221	41.56222
35.86	110	0.23924	2.50554	34.90154
39.31	113	0.23665	2.29182	35.64718
43.05	202	0.23629	2.10099	36.14268
48.44	116	0.27561	1.87972	31.60763

The average particle sizes of the samples are tabulated (Table 6a, 6b and 6c) and the size are as follows:

Sample 1: 34.38 nm

Sample 3: 34.89 nm

Sample 5: 35.97 nm

3.6. SEM Analysis

The Surface morphology of the CaCO_3 nanoparticles has been determined [11] [13] [15] and tabulated (Table7) using SEM analysis and the nanosize has been (Fig 6a, 6b and 6c) confirmed.

Fig 6a Sample1 (CaCO_3 Without laser irradiation - SEM)

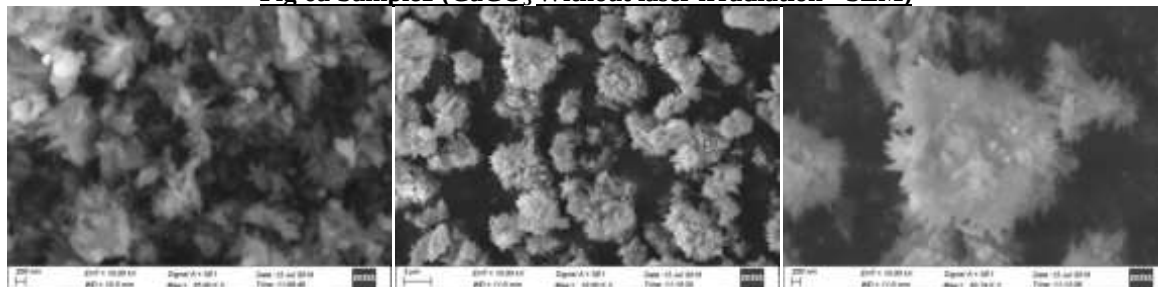


Fig 6b Sample3 (CaCO_3 He-Ne laser 20mins - SEM)

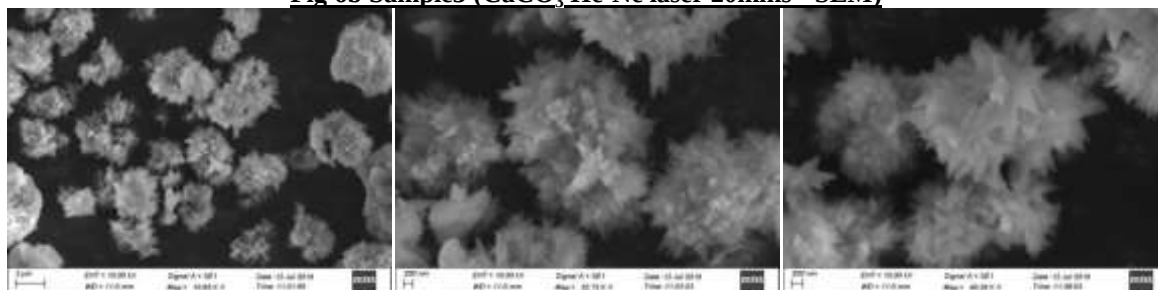


Fig 6c Sample5 (CaCO_3 Diode laser 20mins - SEM)

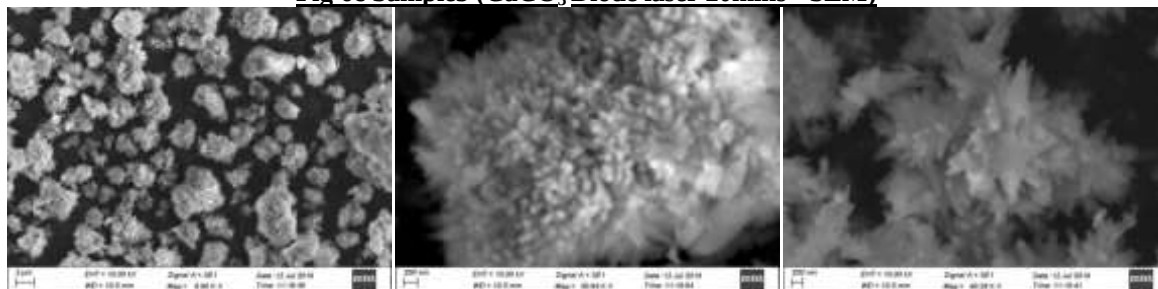


Table7 Particle size variation (SEM)

Sample	Laser Irradiation (sec)	Particle size (nm)
1	Without laser	106.9 – 122.9
3	He-Ne laser (20mins)	88.31 – 101.6
5	Diode laser (20mins)	64.66 – 103.6

4. CONCLUSION

The effect of He-Ne laser and Diode laser were induced in the nanoparticles of calcium carbonate. We observed the variation in band gap energy for different laser treated samples from UV spectrum ranges from 5.90ev to 6.30ev. From FTIR spectrum studies, the various peaks for synthesized samples were analyzed in order to each functional group. The DLS studies exhibited that the particle size distribution of CaCO_3 nanoparticle ranges from 2.1nm to 268.9nm. With an excitation wavelength (λ_{exc}) ranges from 569.60nm to 570.36nm, the photoluminescence spectra has been recorded at room temperature using Fluorescence Spectroscopy. From XRD studies, we observed that the structure of calcium carbonate nanoparticles is Rhombohedra phase structure. The crystalline grain size were determined as 34.37nm (without laser), 34.89nm (He-Ne laser 20mins) and 35.97nm (Diode laser 20mins). Using SEM analysis the nanosize are in the range about 106.9nm to 122.9nm (without laser S1), 88.31nm to 101.6nm (He-Ne laser 20mins S3) and 64.66nm to 103.6nm (Diode laser 20mins S5) has been confirmed. Generally there will be improved result in the band gap energy as well as in grain structure when the laser power is increased with time exposures. Because of these applications it can be used further in medical and industrial applications.

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