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# Tailoring the structural and non-linear optical properties of TiO<sub>2</sub> nanoparticles via solvent-directed green synthesis

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## Abstract

The development of materials with tunable structural and optical properties stands at the forefront of contemporary scientific research, given their broad applicability. In this study, we report the solvent-directed green synthesis of titanium dioxide nanoparticles (TiO<sub>2</sub> NPs) using *Nyctanthes arbor-tristis* (Night Jasmine) leaf extract as an eco-friendly reducing and capping agent. Synthesis was conducted employing both deionized (DI) water and ethanol as solvents to investigate their influence on the resulting nanoparticle properties. Comprehensive characterization using Field Emission Scanning Electron Microscopy (FESEM), Energy Dispersive X-ray Spectroscopy (EDX), Dynamic Light Scattering (DLS), X-ray Diffraction (XRD), UV-Vis spectroscopy, photoluminescence (PL), Fourier Transform Infrared (FTIR) spectroscopy, and Raman spectroscopy provided deep insight into structural, morphological, chemical, and optical variations imparted by solvent selection. FESEM analysis revealed solvent-dependent differences in nanoparticle size and morphology, while XRD patterns confirmed crystalline structures with solvent-induced changes in crystallinity and phase distribution. Optical analyses (UV-Vis, PL, and Raman) demonstrated notable shifts in band gap energy and emission behavior, attributable to the solvent medium. The non-linear optical (NLO) properties, evaluated by Z-scan technique, further underscored the effect of solvent choice on TiO<sub>2</sub> NP functionality. This study highlights solvent-mediated modulation of TiO<sub>2</sub> NP characteristics through a sustainable green synthesis approach, offering promising avenues for photocatalytic and environmental remediation applications.

**Keywords** TiO<sub>2</sub> NPs, Green synthesis, Solvent treated, NLO properties, Optical properties

## 1 Introduction

In recent years, research in nanotechnology has seen a rapid surge, leading to its widespread application across various fields, including material science [1, 2], device manufacturing [3, 4], sensing [5], catalysis [6], energy [7], and material synthesis [8] among others. Nanomaterials with their large surface to volume ratio offer advantages in sensing technology and catalytic activity [5–8]. Among the various types of nanomaterials,



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metal-oxide nanoparticles such as MgO [9], CuO [10], CdO, MnO [11], NiO [12], ZnO [13], Cr<sub>2</sub>O<sub>3</sub> [14], TiO<sub>2</sub> [15], Fe<sub>2</sub>O<sub>3</sub> [16] need special mention. These metal oxides stand out for their remarkable optical and chemical properties [17]. Out of all the metal-oxide nanoparticles, TiO<sub>2</sub> NPs possess unique properties that makes it an interesting prospect in current research. Titanium (Ti) is a lightweight and corrosion resistant metal. It ranks as the fourth most abundant element on earth, predominantly occurring in its oxide form, titanium dioxide (TiO<sub>2</sub>), also referred to as titania or titanium (IV) oxide [17]. TiO<sub>2</sub> is chemically, thermally, structurally stable and highly durable compound characterized by a wide band gap of approximately 3.2 eV [17]. It is a polymorphic material with three allotropic forms namely anatase (tetragonal, I<sub>4</sub>/amd), rutile (tetragonal, P<sub>4</sub><sub>2</sub>/mnm) and brookite (orthorhombic, Pbca) [18, 19]. Due to these properties, it is widely used in various semiconductor-based applications such as photocatalytic degradation [20], solar cells [21], anti-reflective coatings [22], luminescent materials [23], fiber optics [24], microwave absorption technologies [25], electrochemical sensing [26], super capacitors [27] are to name a few. Depending on the solvent media and synthesis methods, TiO<sub>2</sub> NPs possess unique optical and photocatalytic characteristics. They are also known for their excellent anti-inflammatory, antifungal, antimicrobial and other biological applications [28]. TiO<sub>2</sub> NPs are extensively utilized across various industries due to their versatile properties. They are commonly employed in the paint industry, plastic and rubber manufacturing and as a catalyst. Additionally, it is used in food colorants, food packaging, the automotive sector, adhesives, and a wide range of personal care products including body lotions, ointments, toothpaste, and cosmetics [29, 30]. Moreover, TiO<sub>2</sub> NPs exhibit biodegradability and biocompatibility, in addition to their environmental safety. Their distinctive nonlinear optical (NLO) properties also make them promising candidates for the development of advanced biosensors [31].

Conventional methods like hydrothermal synthesis, sol-gel, precipitation, chemical vapor deposition (CVD), plasma techniques, and microwave irradiation have commonly been applied for the synthesis of TiO<sub>2</sub> NPs [32]. However, these methods often rely on expensive reagents, toxic chemicals and high-temperature conditions thereby posing environmental and safety concerns. To address these issues, researchers are increasingly adopting green synthesis approaches, which offer a more sustainable, eco-friendly, and energy-efficient alternative for TiO<sub>2</sub> NPs synthesis [33]. This approach is environmentally benign, produces zero toxic waste, and utilizes renewable resources, making it a sustainable alternative [33]. Recently, Nabi et al. synthesized TiO<sub>2</sub> NPs using the lemon extract to study their optical and photocatalytic properties [34]. Lusvardi et al. synthesized TiO<sub>2</sub> NPs and reported their potential application in the remediation of water pollutants [35]. Basavaraja et al. demonstrated a sustainable combustion process to synthesize TiO<sub>2</sub> NPs using Aloe Vera latex as reducing agent to investigate the photodegradation of AR-88 dye and electrochemical sensing of paracetamol and D-glucose. They achieved impressive 98.6% dye degradation in 120 min and LOD of  $1 \times 10^{-3} \text{ mol L}^{-1}$  [36]. The morphological and chemical properties of these synthesized NPs differ based on the concentration of phytochemicals such as flavonoids, polyphenols, alkaloids present in each extract [37]. Bilal et al. studied the change in structural properties of the TiO<sub>2</sub> NPs by altering the solvent media [38]. But there are still very few published reports on the in-depth analysis of the influence of solvents on the morphological, chemical, optical and structural properties of green synthesized TiO<sub>2</sub> NPs.

In the present work, we employed the leaf extract of the *Nyctanthes arbor-tristis* plant for the green synthesis of  $\text{TiO}_2$  NPs, popularly known as Night Jasmine (NJ). The extract is rich in bioactive compounds (phenolics, alkaloids, flavonoids, ascorbic acid, tannins, proteins, terpenoids), which facilitate the reduction of  $\text{Ti}^{4+}$  ions to  $\text{TiO}_2$  NPs. Simultaneously, the functional groups  $-\text{OH}$ ,  $-\text{COOH}$ ,  $-\text{NH}_2$ , and  $-\text{C}=\text{O}$  present in these phytochemicals serve as capping and surface stabilizing agents, rendering the synthesis process both environmentally benign and economically viable [39]. The primary objective is to evaluate the influence of different solvents (DI water and ethanol) on the NPs by analysing the resulting alterations in physicochemical and optical characteristics. Furthermore, this study investigates the nonlinear optical (NLO) properties of  $\text{TiO}_2$  NPs using the closed-aperture Z-scan technique. The primary objective is to evaluate the influence of different solvents on the NPs by analysing the resulting variations in their physicochemical and optical characteristics. This research aims to contribute to the development of environmentally friendly synthesis approaches and highlight their potential advantages in a variety of applications [33, 40].

## 2 Experimental procedure

This current work contains several important steps, and these are detailed below.

### 2.1 Chemicals and reagents

Titanium (IV) n-butoxide ( $\text{Ti}(\text{OBu})_4$ ) is used as a precursor and *Nyctanthes Arbor-Tristis* (Night Jasmine, NJ) leaf extract as a reducing and capping agent in the synthesis of  $\text{TiO}_2$  NPs.  $\text{Ti}(\text{OBu})_4$  with  $\geq 99\%$  purity was purchased from Sigma Aldrich, USA. Ethanol ( $\text{C}_2\text{H}_5\text{OH}$ , synthesis grade) was acquired from Mark. All the chemicals were used directly without further purification. All the aqueous solutions were prepared using Millipore de-ionized (DI) water.

### 2.2 Preparation of green extract

The proposed  $\text{TiO}_2$  NPs were synthesized using NJ leaf extract. The first step of the synthesis includes the preparation of the leaf extract. Healthy and mature leaves of the NJ plant were collected from the Tezpur University garden. The leaves initially rinsed with tap water to eliminate surface pollutants, followed by multiple washes with DI water to remove any residual dust particles [41]. The leaves were allowed to dry at room temperature for seven days and then manually cut into small sizes. 2 g of dried leaves were then mixed with 200 mL DI water and boiled at  $60^\circ\text{C}$  for 45 min until the color turns brown. The leaf extract was then filtered with filter paper with pore size  $0.22\ \mu\text{m}$  into a glass container and stored at a cold temperature for future use [41, 42]. The entire mechanism is schematically represented in Figure 1(A).

### 2.3 Preparation of $\text{TiO}_2$ NPs

To study the solvent variation of the nanoparticles, two separate solutions of  $\text{Ti}(\text{OBu})_4$  were prepared by dissolving 3.625 mL into 200 mL of DI water and ethanol separately. The mixture was then stirred for 1 h to ensure uniform distribution of the particles. Subsequently, 2 mL of leaf extract was added dropwise into the solution, which was continuously stirred at  $60^\circ\text{C}$  for 8 h at 1500 rpm using a magnetic stirrer. A colour change from colorless to yellowish, accompanied by the formation of a precipitate at the bottom of

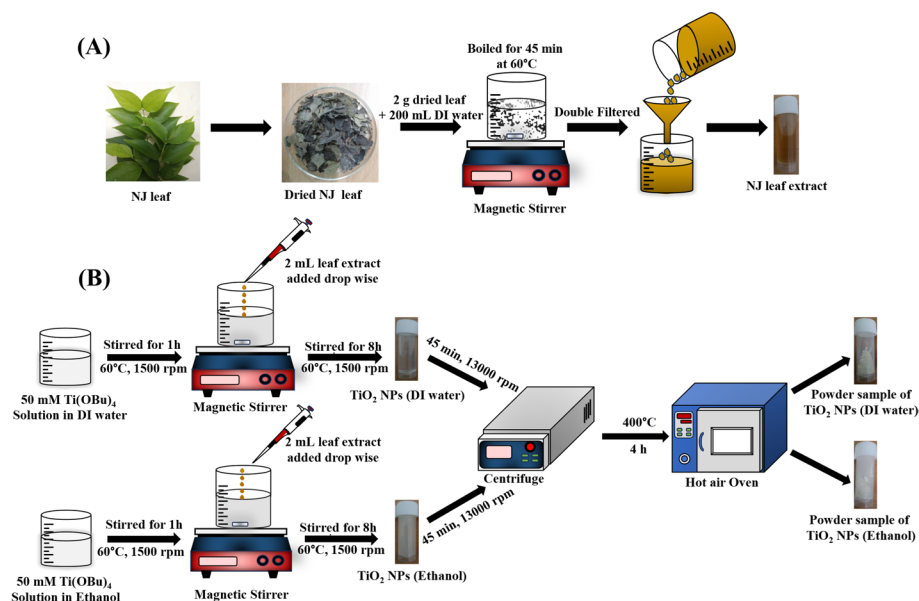


**Fig. 1** Schematic diagram of synthesis of  $\text{TiO}_2$  NPs (A) Preparation of NJ leaf extract, (B) preparation of  $\text{TiO}_2$  NPs.

the beaker, indicates the successful synthesis of nanoparticles. The final pH of the sample was measured to be 5.90. The solution was centrifuged at 13000 rpm for 45 min and subsequently passed through a syringe filter. The collected nanoparticles were then calcined at 400 °C for 4 h. Finally, we obtained the white  $\text{TiO}_2$  NPs powder, which was used directly for characterisation without further modification [42].

The entire process was repeated for ethanol and the final pH of the sample was found to be 6.19. The entire synthesis process is schematically described in Figure 1(B).

## 2.4 Material characterization

The morphological, structural, physiological, and optical properties of the as-synthesized  $\text{TiO}_2$  NPs were characterized by various sophisticated instruments. The morphology and particle distribution of the prepared  $\text{TiO}_2$  NPs were analysed by FESEM (JEOL, model: JSM7200F). The elemental composition of the nanoparticles was investigated using EDX spectroscopy (JEOL, model: JSM 6390LV from JAPAN). The optical absorption spectra of the nanoparticles were recorded using a UV–Vis spectrophotometer (SHIMADZU, Model: UV-2600i). For DLS analysis, Zeta sizer (Nano ZS90, Malvern) was utilised. Analytical crystalline size, phase and structure of the NPs were determined using X ray diffraction instrument (BRUKER AXS, model: D8 FOCUS from GERMANY) having Cu-K $\alpha$  radiation ( $\lambda = 1.5046 \text{ \AA}$ ). Also, the chemical structure, phase and molecular interactions of the samples studied using Raman spectrometer (Model: EZRaman-N-785-B1S developed by Enwave Optronics, USA) using a 785 nm diode laser. The functional groups involved in the formation of nanoparticles were identified using FTIR spectroscopy (PerkinElmer, Model: Frontier IR). The luminescence study was performed using a photoluminescence spectrometer (Horiba Instruments Incorporated, model: Flurolog-3 TCSPC). The non-linear optical properties of the synthesized  $\text{TiO}_2$  NPs were recorded using a Z-scan experimental setup (model: HO-IAD-ZS-01 A by Holmarc Opto-Mechatronics Ltd.) [33, 43].

### 3 Results and discussion

#### 3.1 Field Emission Scanning Electron Microscopy (FESEM) analysis

The morphology and particle distribution of the  $\text{TiO}_2$  NPs were evaluated using FESEM. Figures 2(A and B) depicts the FESEM images of the synthesized nanoparticles in both the solvents (DI water and ethanol). The FESEM micrographs confirmed that the particles are irregular in shape and sizes and show agglomerated morphology. In case of  $\text{TiO}_2$  NPs (DI water) sample, the agglomeration is more compared to ethanol mediated  $\text{TiO}_2$  NPs. This irregularity may be due to the presence of defects in grain boundaries and effect of solvents used in the synthesis process [44]. The particle size distribution histograms are given in Figures 2(C and D). The average particle sizes for both the  $\text{TiO}_2$  NPs (DI water) and  $\text{TiO}_2$  NPs (Ethanol) samples were around 19.77 nm and 23.07 nm. The standard deviation ( $\sigma_{s,d}$ ) of the histogram measuring size of the synthesized NPs are 2.74 nm and 2.94 nm respectively. These differences may arise due to interaction of different phytochemicals such as flavonoids, polyphenols, alkaloids and terpenoids with solvent media [44, 45]. Apart from that, we are also aware that the size of the synthesised nanoparticles greatly influenced by the nature and polarity of the solvents, as ethanol is less polar compared to DI water, the chances of defects and reduction in particle size is less in case of  $\text{TiO}_2$  NPs (Ethanol) sample compared to  $\text{TiO}_2$  NPs (DI water) sample [46].

#### 3.2 Energy dissipative X-ray spectroscopy (EDX) study

The EDX analysis reveals the elemental composition and purity of the as-synthesized nanoparticles. Figures 3(A and B) depict the EDX spectra of sample  $\text{TiO}_2$  NPs (DI water) and  $\text{TiO}_2$  NPS (Ethanol) respectively. The study shows the strong peaks of titanium (Ti) and oxygen (O) (at 4.4 to 5 KeV) for both the cases, confirming the purity of the synthesis. The atomic and weight% of the elements are shown in the inset. The elemental mapping of the sample  $\text{TiO}_2$  NPs (DI water) and  $\text{TiO}_2$  NPs (Ethanol) are plotted in Figures 3(C, E, D, F) respectively [47, 48].

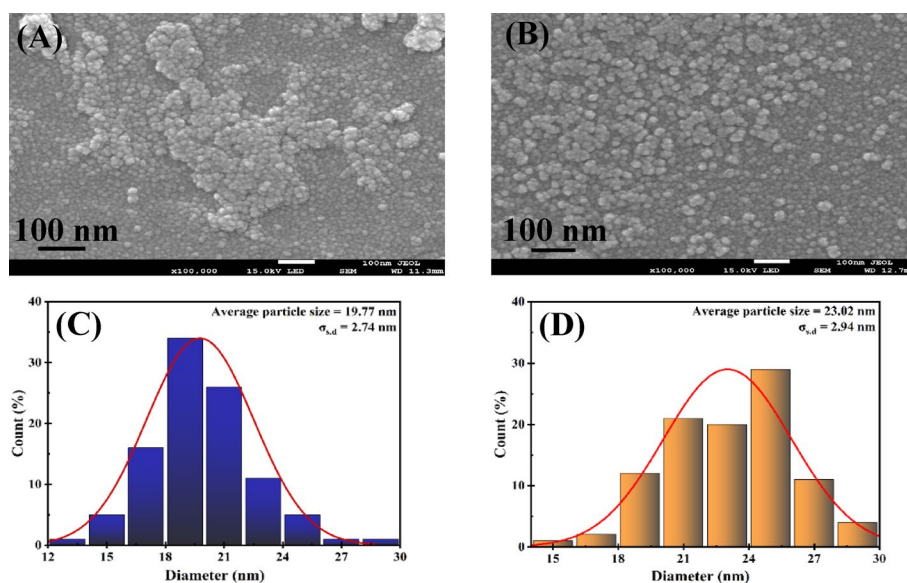


**Fig. 2** FESEM images and particle size distribution (A) & (C)  $\text{TiO}_2$  NPs (DI water) and (B) & (D)  $\text{TiO}_2$  NPs (Ethanol) respectively.

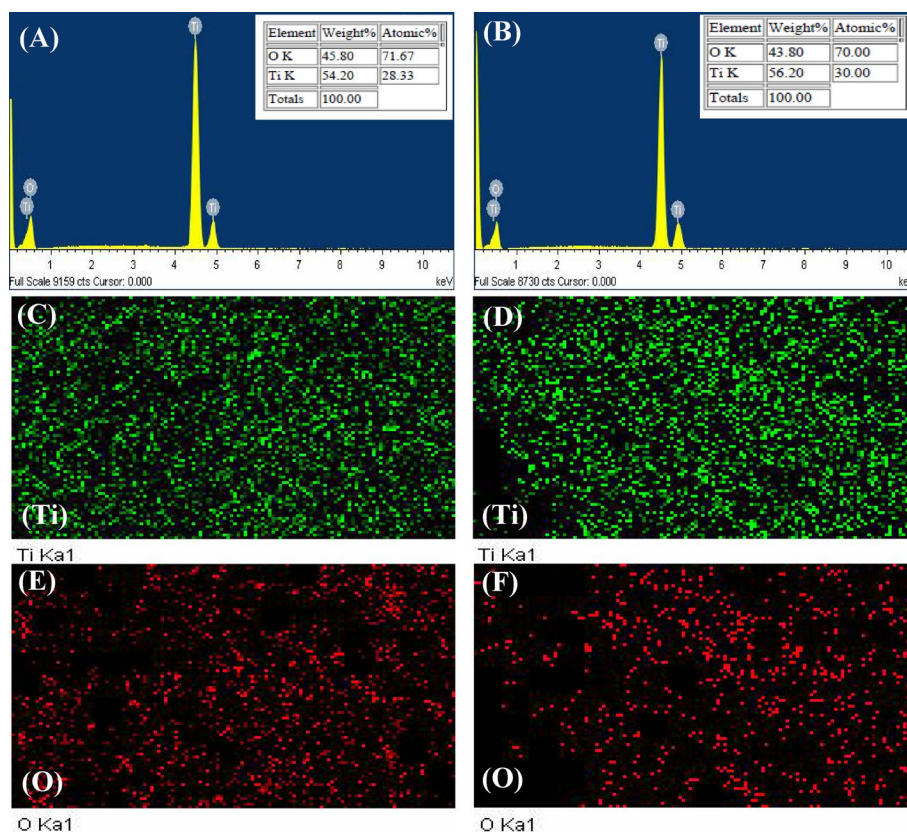


**Fig. 3** EDX spectra of samples (A)  $\text{TiO}_2$  NPs (DI water), (B)  $\text{TiO}_2$  NPs (Ethanol); EDX elemental mapping for  $\text{TiO}_2$  NPs (DI water) sample- (C) Titanium & (E) Oxygen and for  $\text{TiO}_2$  NPs (Ethanol) sample- (D) Titanium & (F) Oxygen.

### 3.3 Size and stability analysis by dynamic light scattering (DLS) method

DLS analysis, also known as photon correlation spectroscopy, gives the hydrodynamic size and the approximate surface zeta potential value of the samples. Figures 4(A, B, C, D) shows the DLS and Zeta Potential value for both the synthesized nanoparticles. It was found that for  $\text{TiO}_2$  NPs (DI water), the hydrodynamic size is 12.37 nm but for  $\text{TiO}_2$  NPs (Ethanol) it resulted in two distinct peaks at 0.71 nm and 155.70 nm as obtained in Figures 4(A and B) respectively. This increase in the hydrodynamic size may be due to the quantum size effect and solvent effect of the nanoparticles. Further, the zeta potential values are  $-10.9$  mV and  $-3.26$  mV respectively, which is more than  $-30$  mV, confirming the stability of synthesized nanoparticles [49]. Since the zeta potential value is more negative in the case of  $\text{TiO}_2$  NPs (Ethanol) compared to  $\text{TiO}_2$  NPs (DI water), the stability of the former sample is higher, this is further affirmed by larger particle size as obtained from FESEM analysis and low values of  $\epsilon$  and  $\delta$  obtained from XRD analysis shown in Table 1.

### 3.4 X-ray Diffraction (XRD) analysis

The XRD pattern depicts the phase, crystallinity, lattice parameter, average crystal size and planes of the samples. The XRD graph of DI water and ethanol mediated green synthesized  $\text{TiO}_2$  NPs were recorded in the room temperature having  $2\theta$  range of  $10^\circ$ – $80^\circ$  as shown in Figure 5(A). The  $\text{TiO}_2$  NPs can be found in anatase, brookite, rutile and amorphous phase depending on the conditions such as temperature, pressure, solvent media,

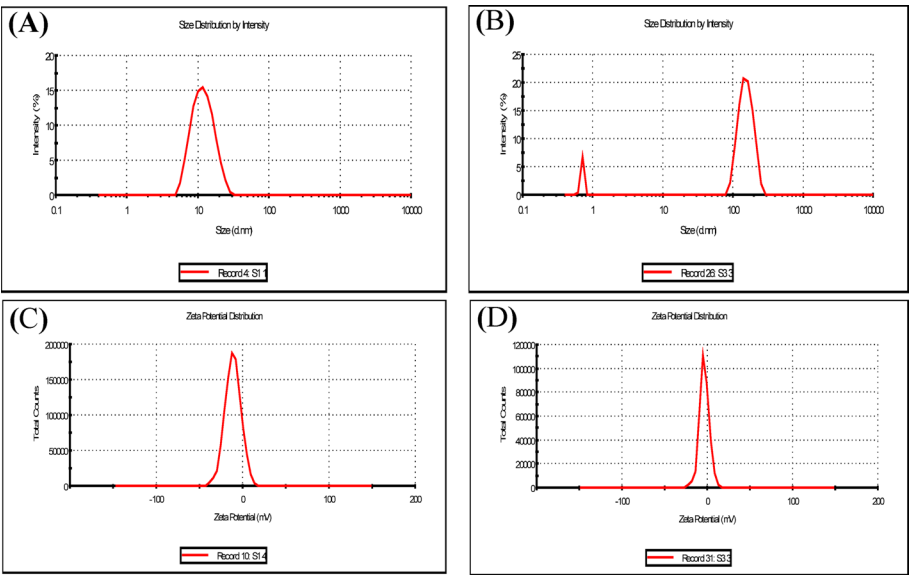


**Fig. 4** The hydrodynamical size and zeta potential (A) & (C) TiO<sub>2</sub> NPs (DI water) and (B) & (D) TiO<sub>2</sub> NPs (Ethanol) respectively.

**Table 1** Structural parameters of synthesized nanoparticles.

| Parameters                                                                  | TiO <sub>2</sub> NPs (DI water) | TiO <sub>2</sub> NPs (Ethanol) |
|-----------------------------------------------------------------------------|---------------------------------|--------------------------------|
| Phase                                                                       | Anatase                         | Brookite                       |
| Crystal structure                                                           | Tetragonal                      | Orthorhombic                   |
| Space group                                                                 | I41/amd                         | Pbca                           |
| Space group number                                                          | 141                             | 61                             |
| Lattice parameter (Å)                                                       |                                 |                                |
| a                                                                           | 3.73                            | 5.43                           |
| b                                                                           | 9.37                            | 5.13                           |
| c                                                                           | 90°                             | 90°                            |
| α=β=γ                                                                       |                                 |                                |
| Unit cell volume Å <sup>3</sup>                                             | 130.36                          | 255.86                         |
| Density ρ (g/cm <sup>3</sup> )                                              | 3.90                            | 4.14                           |
| Crystalline size D (nm)                                                     | 4.84                            | 5.73                           |
| Particle size (nm)                                                          | 19.77                           | 23.02                          |
| Lattice strain ε × 10 <sup>-3</sup>                                         | 8.01                            | 6.52                           |
| Dislocation densities δ (lines/nm <sup>2</sup> )                            | 0.04                            | 0.03                           |
| Specific surface area S <sub>a</sub> × 10 <sup>5</sup> (cm <sup>2</sup> /g) | 31.78                           | 25.29                          |

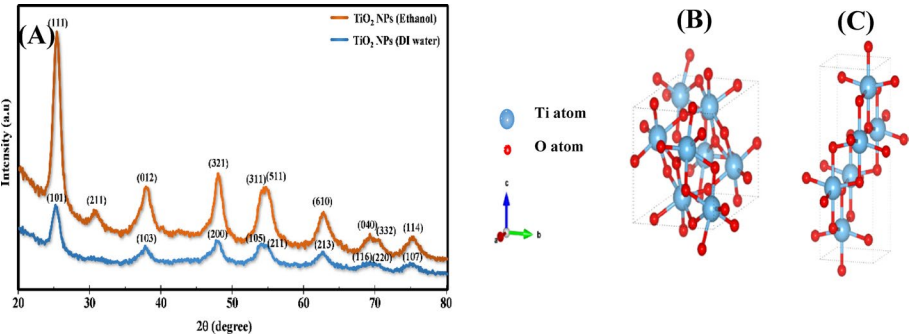


**Fig. 5** (A) XRD patterns of synthesized TiO<sub>2</sub> NPs; crystal structure of (B) Brookite, (C) Anatase TiO<sub>2</sub> NPs obtained from VESTA software.

pH, precursor concentration and synthesis method [33, 49]. The diffraction peaks of TiO<sub>2</sub> NPs (DI water) have a prominent peak at the 2θ value of 25.16° and other peaks at 37.70°, 47.64°, 53.92°, 55.11°, 62.58°, 69.17°, 70.35° and 74.77° corresponding to lattice plans (101), (103), (200), (105), (211), (213), (116), (220) and (107) respectively. All these peaks closely matched with anatase TiO<sub>2</sub> NPs (ICDD card no.00–001–0562). On the other hand for TiO<sub>2</sub> (Ethanol), the predominant peak is found at 25.36° and other minor peaks at 30.75°, 37.84°, 47.91°, 54.30°, 55.00°, 62.89°, 69.18°, 70.37° and 75.26° corresponding to the Bragg's diffraction plans (111), (211), (012), (321), (131), (511), (610), (040), (332) and (114) respectively. The results align with the brookite phase (card no 00–002–0514) of TiO<sub>2</sub> NPs [33, 50]. The 3D crystal structures of the nanoparticles are drawn using VESTA software given in Figures 5(B and C) [51]. Furthermore, the crystalline size of as prepared nanoparticles is estimated using Debye-Scherrer's equation [52], which is expressed as,

$$D = \frac{k\lambda}{\beta_{hkl}\cos\theta}$$

Also, the lattice strain (ε), dislocation densities (δ), surface area (S<sub>a</sub>), and density (ρ) of the as-synthesized nanoparticles are calculated using the formulas given below,

$$\epsilon = \frac{\beta \cos\theta}{4}$$

$$\delta = \frac{1}{D^2}$$

$$\rho = \frac{nM}{NV}$$

$$S_a = \frac{6}{D \times \rho}$$

$$S_f = \frac{2\pi^2}{45\sqrt{3}\tan\theta}$$

where λ is the wavelength of incident X-ray (1.504 Å), β<sub>hkl</sub> is the full width at half maximum (FWHM), k is the shape factor, n is the number of atoms per unit cell (for anatase, n = 4, for brookite, n = 8), D is the crystalline size, θ is the Bragg's angle of diffraction, N is Avogadro's number, V = a<sup>3</sup> and M is the molecular weight of the material [33, 53]. The calculated values are tabulated in Table 1.

From Table 1, it was found that there is a significant decrease in the unit cell volume, density, and crystalline size of TiO<sub>2</sub> NPs (DI water), which can be attributed to the small particle size and quantum size effect of the nanoparticles. Also, the increased values of ε and δ in the TiO<sub>2</sub> NPs (DI water) sample indicate an increase in defect centers, and the large value of S<sub>a</sub> implies an increase in the number of active sites compared to TiO<sub>2</sub> NPs (Ethanol) sample [49, 53].

### 3.5 Fourier transform infrared spectroscopy (FTIR) measurement

FTIR measurements were conducted in the wavenumber range of 4000–400 cm<sup>−1</sup> to investigate the chemical bonds and identify the functional groups present in the

synthesized nanoparticles. As shown in Figure 6, both samples exhibited absorption peaks within the range of 400–800  $\text{cm}^{-1}$ , corresponding to Ti-O and Ti-O-O vibrational modes associated with the  $\text{TiO}_2$  lattice. This confirms the formation of  $\text{TiO}_2$  NPs [33]. The distinct sharp peaks at 1631  $\text{cm}^{-1}$  and 1604  $\text{cm}^{-1}$  for both the samples are characteristic bending vibrations of -OH group [54]. The peaks identified at 2380 and 3475  $\text{cm}^{-1}$  for  $\text{TiO}_2$  NPs (Ethanol) are associated with C-H stretching and O-H stretching vibrations. The decrease in the bending vibrations for  $\text{TiO}_2$  NPs (DI water) sample indicates increased crystallinity and particle growth [55].

### 3.6 UV-visible spectroscopy (UV-Vis) analysis

We have utilized UV-Vis spectroscopy in the range of 200–800 nm to investigate the optical properties and elucidate the transitions of the synthesized nanoparticles. Figure 7(A) shows the UV absorption spectra of as prepared ethanol and DI water mediated  $\text{TiO}_2$  NPs at room temperature. 266 nm and 332 nm are the absorption maxima ( $\lambda_{\text{max}}$ ) corresponding to  $\text{TiO}_2$  NPs (DI water), whereas for  $\text{TiO}_2$  NPs (Ethanol), it was found to be 262 nm and 345 nm. A slight variation in the absorption peaks was observed mainly due to differences in particle size [56]. The optical bandgap of the nanoparticles was determined using the Tauc plot method, as given by the following relation,

$$(\alpha h\nu)^n = k(h\nu - E_g)$$

where,  $\alpha$  is absorption coefficient,  $h$  is Planck's constant,  $\nu$  is the frequency of the absorbed light,  $k$  is the proportionality constant, the optical band gap energy is denoted by  $E_g$  and  $n$  represents the nature of the transition (2 for direct band gap and  $\frac{1}{2}$  for indirect band gap). The band gap is calculated by plotting  $(\alpha h\nu)^n$  along Y-axis and energy  $h\nu$  along X-axis and a tangent is drawn to the curve which intersects the X-axis. This intersection point is the value of band gap. Figures 7(B and C) shows Tauc plot for direct and indirect transitions. For DI water mediated  $\text{TiO}_2$  NPs, the direct and indirect band gaps were determined to be 3.28 eV and 2.87 eV, respectively. In contrast the nanoparticles synthesized with ethanol showed slightly lower band gaps of 3.23 eV and 2.84 eV

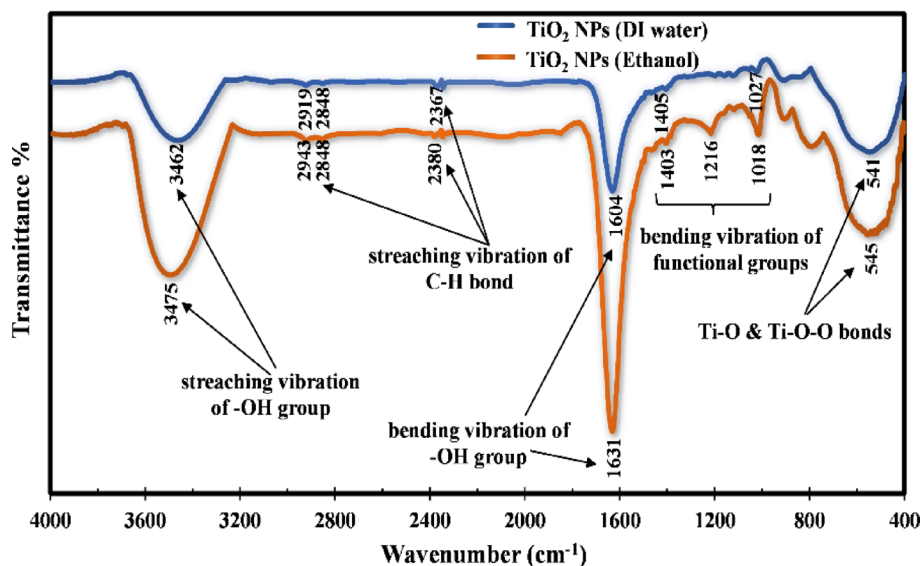


**Fig. 6** FTIR spectra of synthesized  $\text{TiO}_2$  NPs.

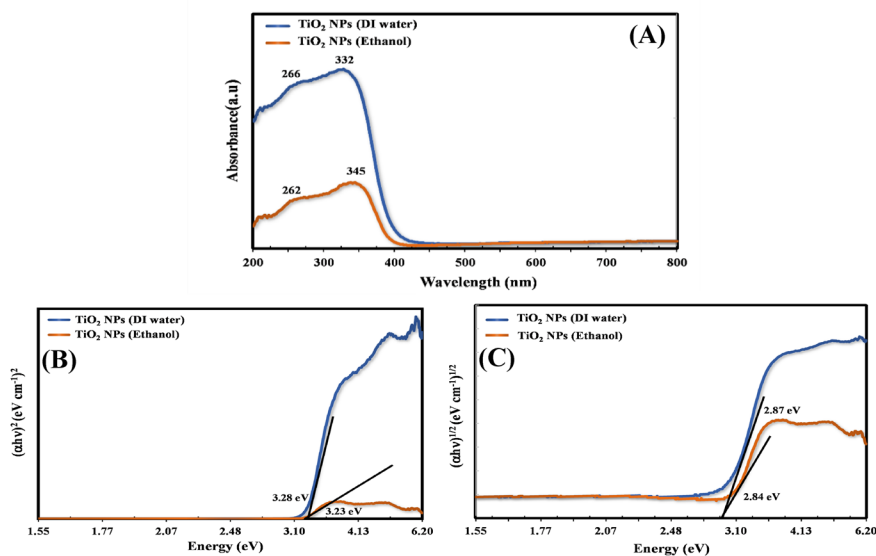


**Fig. 7** (A) UV-Vis spectra of TiO<sub>2</sub> NPs; Tauc plot of (B) direct band transition, (C) indirect band transition.

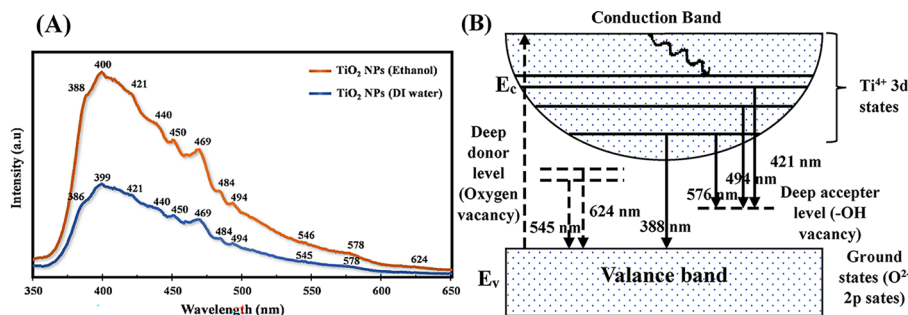
for direct and indirect band gap respectively. These values correspond to the electronic transition from O-2p state to Ti-3d state. In both the cases it was observed that the value of band gap for ethanol-mediated TiO<sub>2</sub> NPs is less as compared to DI water-mediated TiO<sub>2</sub> NPs [56]. This variation in band gaps in different solvent media can be explained based on factors such as particle size, crystallinity, solvent polarity, quantum confinement effects etc. Since the crystalline as well as particle size of DI water mediated TiO<sub>2</sub> NPs is less (which is consistent from FESEM and XRD analysis) so there is a possibility that the size becomes comparable to or smaller than the Bohr radius, which confines the movement of electrons and holes. This confinement causes the energy levels in the valence and conduction bands to split, resulting in a wider energy separation, or a larger band gap [33]. Also, polarity plays a key role on how precursor ions dissolve, how reducing agents interact, and how stabilizers/capping agents bind to the growing particles ultimately influencing nanoparticle size. The high polarity of DI water compared to ethanol offers strong electrostatic stabilisation, rapid precursor reduction leading to small and uniform nanoparticles [40, 41]. To further investigate the band-to-band transitions in the as-synthesized nanoparticles, the Brus equation was employed, which describes the relationship between excitonic energy (in eV) and the radius of the nanoparticle ( $R_0$ ),

$$E(R_0) = E_g + \frac{\hbar^2 \pi^2}{2R_0} \left( \frac{1}{m_e} + \frac{1}{m_h} \right) - \left( \frac{1.8e^2}{\epsilon} \right) \frac{1}{R_0} + \text{smaller terms}$$

The first term,  $E_g$  is the band gap (we used indirect band gap) energy of the bulk material, second term is the energy term due to quantum confinement effect, and the third term corresponds to the energy shift due to coulombic attraction between electrons and holes.  $e$  is the electronic charge (C),  $m_e$  and  $m_h$  are the effective masses (kg) of electrons and holes respectively,  $\hbar$  is Planck's constant (Js) and  $\epsilon$  is the dielectric constant (C<sup>2</sup> N<sup>-1</sup> m<sup>-2</sup>) of the bulk system [57, 58]. Further, we can also study the refractive index variation of the nanoparticles using Herve-Vandamme relation,

**Table 2** Experimentally and theoretically obtained values of band gaps of TiO<sub>2</sub> NPs.

| Samples                         | Direct band gap (eV) | Indirect band gap (eV) | Refractive index (n) | Band gap (eV) (Brus Method) |
|---------------------------------|----------------------|------------------------|----------------------|-----------------------------|
| TiO <sub>2</sub> NPs (DI water) | 3.28                 | 2.87                   | 2.38                 | 3.16                        |
| TiO <sub>2</sub> NPs (Ethanol)  | 3.23                 | 2.84                   | 2.40                 | 3.17                        |

**Fig. 8** (A) PL spectra of TiO<sub>2</sub> NPs; (B) Electronic transition mechanism of TiO<sub>2</sub> NPs.

$$n^2 = 1 + \left( \frac{A}{E_g + B} \right)^2$$

where,  $n$  denotes refractive index,  $E_g$  is energy band gap,  $A$  and  $B$  represents Cauchy's constant given by (13.6 eV) and (3.4 eV) respectively [59]. Table 2 summarizes the optical analysis of TiO<sub>2</sub> NPs synthesized using different solvent media. A comparative study has been provided in the Supplementary Information (Table T) to analyze the optical and morphological properties of the current work in relation with the other already reported literature.

### 3.7 Photoluminescence (PL) study

Figure 8(A) depicts the photoluminescence spectra of the synthesized nanoparticles recorded at room temperature over a range of 350–650 nm at an excitation wavelength of 340 nm. PL spectra are useful for investigating the recombination of electron (e<sup>-</sup>)-hole (h<sup>+</sup>) pair, charge transfer and surface defects [60]. It is mostly regarded as a surface phenomenon. The emission spectra of the TiO<sub>2</sub> NPs (Ethanol) and TiO<sub>2</sub> NPs (DI water) consist of several emission peaks at different wavelengths with very minor change in the peak position. The observed peaks are positioned approximately at 388 nm, 400 nm, 421 nm, 440 nm, 450 nm, 469 nm, 484 nm, 494 nm, 545 nm, 574 nm and 620 nm. The emission spectra for small wavelengths are due to excitonic emissions and for large wavelength, surface state emission [60, 61]. The first emission at 388 nm is due to excitonic emission. The predominant UV emission peak at 400 nm corresponds to phonon-assisted indirect transition (M→Γ) in the Brillouin zone [40, 61, 62]. These emission peaks originate from the recombination of electron-hole pairs associated with surface dangling bonds of the nanoparticles [63, 64]. The broad emission peak observed at 469 nm is likely attributed to a charge transfer transition from Ti<sup>3+</sup> to O<sup>2-</sup> within the TiO<sub>6</sub><sup>2-</sup> octahedral structure [63]. The emissions at 421 nm, 494 nm and 578 nm are due to the deexcitation from lower vibronic levels in Ti<sup>3+</sup> 3d states to the deep acceptor levels created by the hydroxyl group (-OH). Also, the emission peaks at 545 nm and 624 nm are due to deexcitation from deep vibronic levels formed by oxygen vacancy to the

ground state [64]. The mechanism of the emission process is depicted in Figure 8(B). The PL spectroscopy in general depends on factors such as size, shape, excitation wavelength, synthesis method, temperature and defects [63, 64]. The PL emission efficiency ( $\eta$ ) depends on the contributions from both radiative and non-radiative transitions, and is given by the following relation [63].

$$\eta = \frac{I_r}{I_r + I_{nr}}$$

where  $I_r$  and  $I_{nr}$  represents the radiative and non-radiative transition probabilities respectively.

### 3.8 Raman spectroscopy analysis

Raman spectroscopy is a powerful non-destructive technique for probing the structural quality, crystallinity, size effects and phase composition of nanoparticles. The Raman spectra of both TiO<sub>2</sub> NPs samples were analysed over the frequency range of 100–1000 cm<sup>−1</sup> at an excitation wavelength of 532 nm [44, 59]. Here we have studied the Raman vibrational modes for both TiO<sub>2</sub> NPs samples based on their phase structures, i.e. anatase (TiO<sub>2</sub> NPs (DI water)) and brookite (TiO<sub>2</sub> NPs (Ethanol)) as investigated from XRD analysis. According to factor group analysis, anatase TiO<sub>2</sub> has 6 (six) Raman active modes ( $A_{1g} + 2B_{1g} + 3E_g$ ). The characteristic Raman spectra of anatase TiO<sub>2</sub> NPs (DI water) exhibit five vibrational modes positioned at 152, 204, 402, 516 and 616 cm<sup>−1</sup> as shown in Figure 9(A). The peak shift from the traditional anatase TiO<sub>2</sub> is due to the presence of defect sites and impurities [65]. Among these modes, the peaks at 152, 204, and 616 cm<sup>−1</sup> correspond to the  $E_g$  vibrational mode, the peak at 402 cm<sup>−1</sup> is assigned to the  $B_{1g}$  mode, and the peak at 516 cm<sup>−1</sup> corresponds to a combination of  $A_{1g} + B_{1g}$  modes. These characteristic vibrational modes confirm the presence of the anatase phase in the as-synthesized nanoparticles [65]. It can be observed that the strongest and sharpest peak appears at 152 cm<sup>−1</sup>, which corresponds to the symmetric stretching vibration of Ti–O bonds [66]. The peak obtained at 204 cm<sup>−1</sup> corresponds to the symmetric bending vibration of Ti–O bonds. The peak at 404 cm<sup>−1</sup> is associated with the antisymmetric bending vibration of O–Ti–O bonds. The mixed symmetric stretching and antisymmetric bending vibrations of O–Ti–O bonds are related to 516 cm<sup>−1</sup>. The 616 cm<sup>−1</sup> peak is related to bending vibration of Ti–O–Ti bonds [33, 67].

On the other hand, the brookite TiO<sub>2</sub> has 36 (3 acoustic + 33 optical) Raman active modes ( $9A_{1g} + 9B_{1g} + 9B_{2g} + 9B_{3g}$ ). However, only a limited number of distinct peaks are typically observed due to overlapping and weak intensity [68]. Figure 9(B) shows the

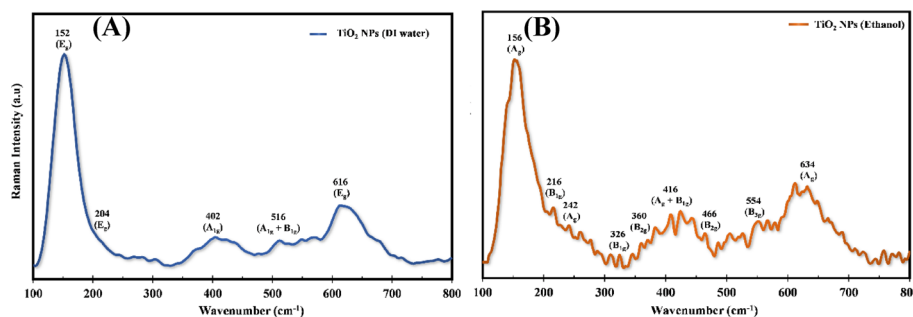


**Fig. 9** Raman spectra of (A) anatase TiO<sub>2</sub> NPs (DI water), (B) brookite TiO<sub>2</sub> NPs (Ethanol).

Raman modes observed for brookite  $\text{TiO}_2$  NPs (Ethanol) are 156, 216, 242, 326, 360, 416, 466, 554,  $634 \text{ cm}^{-1}$  which shows a slight blue shift from the theoretical values [69]. The most intense peak,  $156 \text{ cm}^{-1}$  ( $A_g$ ) corresponds to the translational vibration of Ti and O atoms, the peak 242 ( $A_g$ ) corresponds to symmetric stretching vibration of O-Ti-O bonds, 326 ( $B_{1g}$ ) describes the symmetric stretching of Ti-O bonds within distorted  $\text{TiO}_6$  octahedron, the 416 ( $A_g + B_{1g}$ ) antisymmetric bending of Ti-O bonds, 554 ( $B_{3g}$ ) peak stands for twisting or shearing vibration of  $\text{TiO}_6$  octahedra and 634 ( $A_g$ ) represents asymmetric stretching of Ti-O bonds within distorted  $\text{TiO}_6$  octahedra [69, 70]. The peaks obtained at  $513 \text{ cm}^{-1}$ , which is not the characteristic peak for brookite  $\text{TiO}_2$  NPs may arise due to the mixed anatase-brookite phase present in the sample, also there are some unexplained peaks at higher wavenumbers that are due to impurities or defects in the sample. These characteristic peaks of both samples at specific wavelengths provide valuable insight about the structural properties of  $\text{TiO}_2$  NPs [69–71].

The phonon lifetime for the sharpest and strongest peaks ( $148 \text{ cm}^{-1}$  and  $156 \text{ cm}^{-1}$ ) of both the samples can be calculated using time- energy uncertainty relation given by,

$$\frac{1}{\tau} = \frac{\Delta E}{\hbar} = 2\pi c\Gamma$$

where,  $\tau$  denotes phonon lifetime,  $\Delta E$  is the uncertainty in energy,  $c$  is the velocity of light in vacuum, ( $\hbar = \frac{h}{2\pi}$ )  $h$  denotes Planck's constant and  $\Gamma$  represents the FWHM value of Raman peak in  $\text{cm}^{-1}$  [59].

From the Table 3, the calculated phonon life times for both the samples are 0.12 ps and 0.09 ps for  $\text{TiO}_2$  NPs (DI water) and  $\text{TiO}_2$  NPs (Ethanol), respectively. The value of phonon life time is directly proportional to crystalline size of nanoparticles. Hence, bigger crystalline size in  $\text{TiO}_2$  NPs (Ethanol) should lead to higher phonon distribution and increased phonon life time, which is not the case observed here. But crystalline size alone doesn't determine phonon lifetimes, it also depends on crystal quality, phase purity, internal strain, and phonon-phonon interactions [72].

### 3.9 Non-linear optical (NLO) property study using z-scan measurement

The closed-aperture (CA) Z-scan measurement of  $\text{TiO}_2$  NPs is recorded using a 100 MW, 532 nm solid state diode pump (SSDP) laser. The schematic diagram of closed aperture Z-scan is shown in Figure 10. The CA Z-scan is used to study non-linear refraction of materials. Presence of transmittance peak (maximum) and valley (minimum) in the characteristic of CA scans relative position with respect to  $z = 0$  determines the type of the non-linear refractive index ( $n_2$ ). When valley precedes the peak as in the present case, it is indicative of a positive  $n_2$  and self-focusing of the beam about  $z = 0$ . The laser beam was focused using a lens of 45.9 cm focal length. Both the samples were translated using a motorized translation stage. The focused beam has a waist of  $52 \mu\text{m}$  and a Rayleigh length ( $Z_R$ ) of 0.0255 m. The graphs obtained from the CA Z-scan measurement

**Table 3** Calculation of phonon life-times of  $\text{TiO}_2$  NPs.

| Samples                       | Peak position ( $\text{cm}^{-1}$ ) | FWHM $\Gamma$ ( $\text{cm}^{-1}$ ) | Phonon life-time $\tau$ ( $\times 10^{-14}$ s) |
|-------------------------------|------------------------------------|------------------------------------|------------------------------------------------|
| $\text{TiO}_2$ NPs (DI water) | 152                                | 43.38                              | 12.25                                          |
| $\text{TiO}_2$ NPs (Ethanol)  | 156                                | 53.35                              | 9.95                                           |

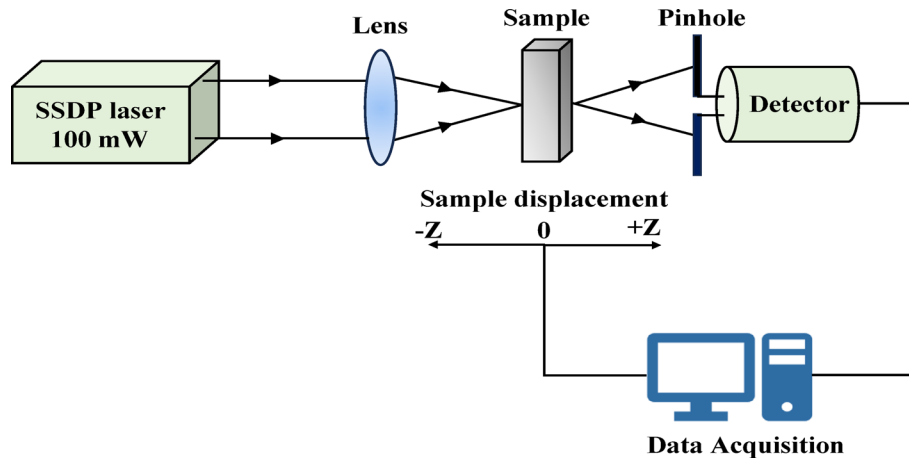


**Fig. 10** Schematic diagram of closed aperture Z-scan experimental set-up for NLO measurements.

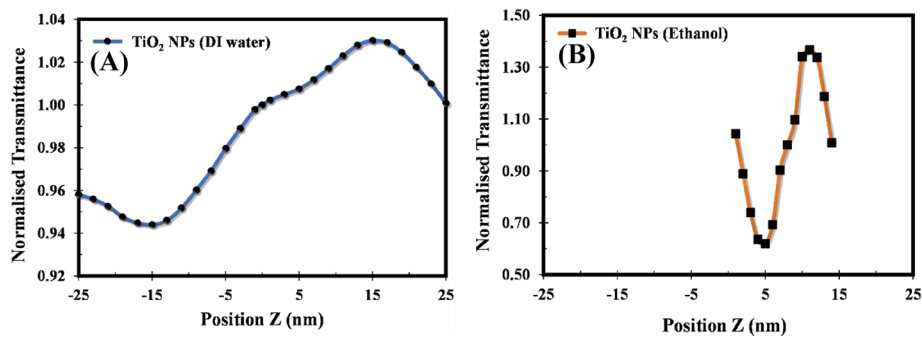


**Fig. 11** Closed aperture Z-scan measurement plot for synthesized (A) TiO<sub>2</sub> NPs (DI water) and (B) TiO<sub>2</sub> NPs (Ethanol).

for samples TiO<sub>2</sub> NPs (DI water) and TiO<sub>2</sub> NPs (Ethanol) were shown in Figures 11(A and B), respectively.

The intensity  $I_0$  (at  $z = 0$ ) is 1.96 KW/c.m<sup>2</sup>. Further, the separation between peak and the valley along the translation direction ( $Z_{p-v}$ ) is greater than  $1.7 Z_R$ , the Rayleigh length. It signifies that non-linearity in the samples is due to the thermal origin [73]. The positive  $n_2$  can be attributed to a positive temperature refractive index gradient in the medium [74]. Measuring peak-to-valley transmittance difference ( $\Delta T_{p-v}$ ) the on-axis phase shift ( $|\phi_0|$ ) may be calculated from the expression given below [75].

$$\Delta T_{(p-v)} = 0.406 \times (1 - S)^{0.25} \times |\phi_0|$$

where,

$$S = 1 - \exp\left(-2r_0^2/\omega_0^2\right)$$

with  $r_0$  as the aperture radius and  $\omega_0$  the beam radius at the aperture. The value of the phase shift  $|\phi_0|$  is then used to calculate the nonlinear refractive index  $n_2$  given by the expression,

**Table 4** Non-linear optical parameters of synthesized TiO<sub>2</sub> NPs.

| Sample                          | Concentration of the sample (mM) | Peak-to-valley transmittance $T_{P-V}$ | Phase shift ( $\Delta\phi$ ) in radian | Non-linear refractive index ( $n_2$ ) $\times 10^{-12}$ (m <sup>2</sup> /W) |
|---------------------------------|----------------------------------|----------------------------------------|----------------------------------------|-----------------------------------------------------------------------------|
| TiO <sub>2</sub> NPs (DI water) | 50                               | 0.0828                                 | 0.2224                                 | 0.98                                                                        |
| TiO <sub>2</sub> NPs (Ethanol)  | 50                               | 0.7734                                 | 2.0776                                 | 9.19                                                                        |

$$n_2 = \frac{|\phi_0| \times \lambda}{2\pi I_0 \times L_{eff}}$$

here,  $L_{eff} = \frac{1 - \exp(-\alpha L)}{\alpha}$ , is the effective length of the sample,  $\alpha$  is the linear absorption coefficient,  $L$  is the sample thickness, and  $I_0$  is the intensity at the focus. The calculated values are presented in the Table 4.

The observed variation in the values of  $n_2$  may be ascribed to the environmental factor (solvent) and can significantly influence design of solvent-specific optical limiters and photonic devices [31, 33].

#### 4 Conclusion

The present work highlights the multifaced advantages of biogenic TiO<sub>2</sub> NPs using NJ leaf extract as a reducing agent with DI water and ethanol as two solvent media. Although there are many ways to make nanostructures, it is important to stay away from hazardous chemicals and promote environmentally friendly synthesis methods. These methods can be used to produce nanoparticles in bulk due to their lower energy requirement, cost-efficient, straightforward mechanism. Major scalability issue with green synthesis are reproducibility issues, optimum reaction conditions, and effective supply. However, with future developments should take into account integration with machine learning and artificial intelligence for better scalability. The as-synthesized TiO<sub>2</sub> NPs was prepared following the same synthesis mechanism. The morphological, chemical and optical properties of these nanoparticles were extensively investigated to understand the effect of solvents to get the superior TiO<sub>2</sub> NPs combination. Results obtained from FESEM show that the particle size of TiO<sub>2</sub> NPs (DI water) sample is lower compared to TiO<sub>2</sub> NPs (Ethanol) sample, which indicates the stability of DI water mediated TiO<sub>2</sub> NPs over its counterpart. This result is also in accordance with DLS analysis. Further, from the XRD analysis the nanoparticles obtain two distinctive phases, anatase and brookite which significantly alter their chemical properties. The anatase TiO<sub>2</sub> NPs (DI water) sample having large value of dislocation density and lattice stain compared to brookite TiO<sub>2</sub> NPs (Ethanol) sample. This indicates the increase in defect centers and grain boundaries of the DI water mediated TiO<sub>2</sub> NPs over ethanol mediated TiO<sub>2</sub> NPs. The FTIR result showed presence of similar functional groups which confirms the similar chemical composition of the two samples. The optical band gap of the nanoparticles is calculated from the UV-Vis spectroscopy reveals that the value of direct and indirect bandgaps for TiO<sub>2</sub> NPs (DI water) sample is greater which adds the advantage of photocatalytic degradation and application in semiconducting materials over TiO<sub>2</sub> NPs (Ethanol). The Raman and PL spectroscopy analysis shows the structural and charge transfer properties of the nanoparticles. The phonon life-time of the TiO<sub>2</sub> NPs (DI water) sample is larger than the TiO<sub>2</sub> NPs (Ethanol). Moreover, The NLO properties of the nanoparticles were carried out with CA Z-scan experiment. From the study we obtained the

positive nature of non-linear refractive index ( $n_2$ ) value for both the samples. The reason for the increased value of  $n_2$  of TiO<sub>2</sub> NPs (Ethanol) is because of the presence of a higher number of oxygen vacancies and quantum size confinement.

Hence, based on our results, for application in photocatalytic degradation and sensing applications, TiO<sub>2</sub> NPs (DI water) sample will be suitable due to its large band gap, large surface area, increased defect sites and high phonon lifetime. On the other hand, for solar cell, photovoltaics, optoelectronics devices and battery technology applications, the TiO<sub>2</sub> NPs (Ethanol) will be a more promising candidate due to its narrow band gap which provides good electrical and thermal conductivity with efficient light absorption property in the visible and infrared spectrum.

### Supplementary Information

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Supplementary Material 1

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### Author contributions

Prakash Nandi: Conceptualization, synthesis, sample preparation, characterization and writing of original draft; Dimishree Neog: NLO characterization, analysis; Rajib Biswas: supervision of the entire research work, validation, reviewing and editing the manuscript. Nirmal Mazumder: Review and writing.

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### Data availability

Data for this research may be obtained upon reasonable request from the corresponding author.

### Declarations

#### Ethics approval and consent to participate

Not applicable.

#### Consent for publication

Not applicable.

#### Competing interests

The authors declare no competing interests.

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