Chapter 5

Preparation and Characterization of Anatase TiO₂ Nanoparticles

5.1 Introduction

In last two decades, with the introduction of many innovative routes, there has been great revolution to prepare nanocrystals of different sizes, size distributions and morphologies, e.g. zero-dimensional (0-D) nanocrystals, 1-D nanowires and nanorods, hollow structures, superlattice materials etc. [1]. Owing to its unique optical and chemical properties, titanium dioxide (TiO₂) has received considerable attention towards commercial applications, such as, in chemical and material science ranging from pigment, sunscreens, paints, ointment, toothpaste etc. [2], as well as in basic research, particularly in the area of condensed matter physics. Since the discovery of phenomenon of photocatalytic splitting of water on a TiO₂ electrode under ultraviolet (UV) light by Fujishima and Honda in 1972, enormous efforts have been developed to the research of TiO₂ material. This not only led to many promising applications but also to the different methods.

TiO₂ occurs in nature in three distinct crystallographic phases; anatase, brookite and rutile, [3] and various forms of TiO₂ have found many important technological applications [4]. Among these polymorphs, TiO₂ in the anatase form has been used as an excellent photocatalyst for photodecomposition and solar-energy conversion due to its high photoactivity [5, 6]. Recent studies by Almquist et al. [7] and Vorontsov et al.
[8] have demonstrated that the photoactivity of anatase nanoparticles is strongly particle size dependent. Anatase is one of the metastable phase (another known example is pure tetragonal or cubic ZrO$_2$ nanoparticle [9]) that can be fully stabilized into the nanoscale regime at ambient conditions and in the absence of stabilizer dopants. It is also a model compound that can provide information on the thermodynamics of phase transitions in many oxide materials driven by high-temperature coarsening [10]. Furthermore, as demonstrated in other nanoscale systems [11,12], surface absorbents can play a significant role in the stabilization of nanophases and in the control of chemical reactions and properties. Consequently, obtaining anatase nanoparticles with high purity and precisely controlled particle size is the key to understand these potential applications.

Anatase nanoparticles have been synthesized primarily by solution chemistries involving titanium sulfates and by hydrolytic reactions of titanium (IV) chloride or organic titanium [13-15]. These methods suffer from the demerit of providing the product which is often contaminated with residual chemical impurities or minor accessory phases. For example, a frequently employed method uses a sulfate process in which pure anatase can be obtained by adding a titanium sulfate solution into hot water under controlled conditions. This hydrolysis reaction on heating leads to anatase nanoparticles contaminated with 3 wt% sulfite species which remain strongly bonded to the noncrystalline surface and cannot be removed by washing [13]. Hydrolysis of TiCl$_4$ has extensively been reported for the synthesis of anatase nanocrystals at temperatures lower than 100°C [14(d-g)], but the reaction is sensitive to many factors such as pH, concentration of reactants in the reaction medium, molar ratio of reactants, and the types of mineralizers and additives (such as SO$_4^{2-}$, NH$_4$Cl, NaCl, SnCl$_4$, etc.). Taken together,
these factors make it very difficult to precisely control the particle size and composition of the prepared nanocrystals and result to drastic reduction in phase purity. In the case of organic hydrolytic reactions, TiO$_2$ nanoparticles obtained are crystallized primarily in the anatase phase but a minor phase of brookite cannot be eliminated by tuning the reaction conditions [15]. The presence of trace amount of brookite has been reported to significantly enhance the transformation kinetics from anatase to rutile phase [16 (a)]. Since impurities often appear during the formation of anatase nanoparticles, some workers have questioned [16-21] the inherent structural stability of anatase TiO$_2$ nanocrystals. This raises a concern over the application of anatase nanoparticles in photocatalytic reactions and other chemical processes.

The relevant questions, then, are as follows:

1. Can high purity anatase be synthesized without the accessory second phase of brookite or rutile [15-19]?

2. Do anatase nanoparticles contain OH$^-$ groups as a part of the lattice?

3. Does anatase become more stable in the nanoscale regime?

Banfield et al. [20] performed a thermodynamic analysis and concluded that anatase becomes more stable relative to rutile at particle sizes smaller than approximately 14 nm. However, this conclusion may be drawn into question because systematic studies on size effects in pure anatase nanoparticles are unavailable. Recently, Rao et al. [22] have synthesized anatase nanocrystals, where they soaked as-prepared precursor into different ionic salt solutions for one week. In this treatment at relatively low temperature (~120$^\circ$ C), anatase TiO$_2$ nanocrystals had been formed with crystallite size of around 10 to 25 nm, and the particle size was observed to be controlled by varying acid and base
concentrations and reaction time. In the sol-gel technique [23], as-prepared amorphous precursor was calcinated to achieve crystalline phase at around $450^\circ C$ or higher. With the increase in calcination temperature, crystalline size increased from 20 to 100 nm and anatase phase transformed to rutile.

Therefore, it is essential that a systematic study be performed on the synthesis of high purity anatase nanocrystals and on the control of the particle size, keeping in view the grain growth kinetics. Until now, such a study has not been reported, most likely due to the difficulties associated with the preparation of pure anatase phase. In this work, we have prepared high purity anatase nanocrystals and explored the kinetic control of the particle size using a near room-temperature wet chemical method and low-temperature calcination methods.

### 5.2 Experimental

There are various methods available now days such as mechanical method, which includes solid-state reaction, chemical vapor deposition, electrodeposition, chemical temperature calcination methods etc. to achieve quality product with respect to purity, homogeneity, reactivity particle size etc., each method find its own advantages and disadvantages. In the present study we use different chemical methods to produce TiO$_2$ nanoparticles in the range of 8 to 16.5 nm by setting up the annealing temperature and time. Amorphous titania has been prepared by using wet chemical and low temperature calcination methods [24,25]. We have followed three different routes, varying temperature and reaction time designated as, methods I, II and III to obtain amorphous titania. For this study, analytical grade titanium tetrachloride (TiCl$_4$), ethylene glycol,
polyethylene glycol and sodium acetate are procured from S. D. Fine Chemicals, Mumbai. Ammonium hydroxide solution (NH$_4$OH; 35%) is purchased from Merck Ltd., Mumbai. The reagents were used as received, without any further purification. The samples are characterized by means of x-ray diffraction, transmission electron microscopy, Raman scattering and differential scanning calorimetry (DSC).

5.2.1 Wet Chemical Method

Analytical grade TiCl$_4$ is used to prepare nanocrystalline titanium dioxide particles [24]. Titanium chloride (2 ml) is mixed drop wise to ethylene glycol under vigorous stirring and the stirring is continued for 10 min. The reaction is exothermic and carried out in 100 ml beaker. This mixed precursor is heated to 333 K under reflux. This resulted into appearance of white precipitates of titanium which is collected by centrifugation. In order to remove chlorine impurities from the precipitate, it is washed several times with warm water. The product is finally washed with acetone and dried under reduced pressure.

5.2.2 Low Temperature Calcination Methods

5.2.2.1 Method I: Initially, TiCl$_4$ (1.5 ml) and NH$_4$OH (20 ml) are diluted with cold distilled water up to 10 ml and 80 ml, respectively. Amorphous titania is precipitated by slow addition of titanium chloride into ammoniated water under vigorous stirring. The reaction temperature is increased and maintained at 60$^\circ$C for 30 minutes. Precipitated particles are collected by centrifugation. Chlorinated and other impurities are removed by three times washing of the particles with warm distilled water. Final washing and drying of the precipitated powder is performed with acetone to achieve white titania powder. It is labeled as TN0. Further, this dried powder is annealed at
350\degree C for three different annealing times, i.e., 20, 120 and 240 minutes. The particles annealed at 350\degree C for 20, 120 and 240 minutes are designated as TN2, TN12 and TN24, respectively.

5.2.2.2 Method II: TiCl\textsubscript{4} (2 ml), ethylene glycol (40 ml), sodium acetate (3.6 gm) and polyethylene glycol (0.9 ml) are used in this method. With vigorous stirring, TiCl\textsubscript{4} is added drop wise into ethylene glycol until solution became transparent. To this solution, sodium acetate and polyethylene glycol are added at room temperature and stirring is continued for another 30 minutes. Now, the temperature of the reaction mixture was allowed to increase until condensation started which is marked by change of color of the reaction mixture from violet to dark blue and subsequently to whitish yellow. This condensation reaction is continued up to 4 hrs, following which the precipitated powder is collected through centrifugation and warm distilled water is used for removal of impurities. Finally, water is removed from the powder by performing dehydration with acetone and the sample is designated as TE40. Later, TE40 is annealed at 300\degree C for 60 minutes and is designated as TE46.

5.2.2.3 Method III: This method is similar to method II, except the condensation time, which is extended to eight hours in order to study the effect of digestion time on the particle characteristics. The as-prepared sample and powder annealed at 300\degree C for 60 minutes are designated as TE80 and TE86, respectively.

The solubility of titanium chloride is different in ammonium hydroxide and ethylene glycol. So product formation takes place through different mechanisms. Formation of TiO\textsubscript{2} through the above-described methods has been summarized below;
In case of method I, the following reaction takes place:

$$\text{TiCl}_4 + 4\text{NH}_4\text{OH} \xrightarrow{\Delta} \text{Ti(OH)}_4 + 4\text{NH}_4\text{Cl}$$  \hspace{1cm} (1)

$$\text{Ti(OH)}_4 \rightarrow \text{TiO}_2$$  \hspace{1cm} (2)

In the case of method II and III, reaction proceeds as per the sequence provided here under:

$$\text{TiCl}_4 + 2\text{CH}_3\text{COONa} \xrightarrow{\Delta} \text{TiCl}_2 (\text{CH}_3\text{COO})_2 + 2\text{NaCl}$$  \hspace{1cm} (3)

$$\text{TiCl}_2 (\text{CH}_3\text{COO})_2 + 5\text{H}_2\text{O} \rightarrow \text{Ti(OH)} + 2\text{CH}_3\text{COOH} + 2\text{HCl} + 2\text{O}_2$$  \hspace{1cm} (4)

$$\text{Ti(OH)} \rightarrow \text{TiO}_2$$  \hspace{1cm} (5)

It is evident from the equations (2) and (5) that since the intermediate product is different for method I as compared to II and III, the annealing temperature required for the phase transformation will not be the same. Other impurities obtained during the reaction are soluble in water and hence could be removed easily.

### 5.3 Results and Discussion

#### 5.3.1 X-ray Diffraction (XRD) Properties of TiO$_2$ Nanoparticles

X-ray diffraction (XRD) is a powerful non destructive technique for the structural analysis of a material. Powder x-ray diffraction is a very common tool to determine the crystalline phase present in a material. It also provides information on structures, preferred crystal orientation and other structural properties such as average crystallite size (i.e. coherently scattered domains), crystallinity, lattice strain and crystal defects [26]. XRD pattern is widely used to establish the atomic arrangement or structure of the material because the inter-planer spacing ($d_{hkl}$) of diffraction planes are of the order of x-
ray wavelength [27, 28]. Consequently, diffraction measurement by XRD is an excellent tool for compound identification when a material has atomic-scale periodicity or crystallinity. There are several softwares such as Powdmult, Powder X, Mond, Fullprof, Crys Fire etc., available for XRD data analysis. However, the Rietveld refinement procedure [29, 30] has revolutionized the application of powder x-ray diffraction. Structural characterization of the prepared samples of TiO$_2$ nanoparticles was performed by using an advanced model powder x-ray diffractometer (Bruker D8, Germany). The powder diffractometer is configured with a graphite monochrometor. The x-ray source used was CuK$\alpha$ ($\lambda=1.5406$ Å). The operating voltage and current of x-ray tube are 35 keV and 20 mA respectively. The measurements have been carried out for very fine powder samples over a wide range of Bragg angles ($2\theta \leq 70^0$) at a scanning rate of $2^0$/min. The powder diffractometer records the intensity with scattering angle scan. Before recording the intensity distribution (XRD pattern), the diffractometer must be calibrated against a certified standards material (silicon powder). The glass slide having the powder specimens are placed at the center of the instrument.

Fig. 5.1: XRD of sample 1 and 2.
Fig. 5.1 shows XRD pattern of the sample prepared by wet chemical method (Samples 1 and 2). It shows broad hump in the 2θ range of 200 to 370, which is indicative of amorphous nature of the material. In order to convert amorphous form of the sample into its crystalline phase, it was annealed at 623 K for 2 hours, and henceforth this sample is designated as sample 2. XRD pattern of sample 2 showed all the lines corresponding to anatase crystalline phase and has been indexed accordingly. Particle size was calculated using Debye-Scherrer formula given by:

\[ D_x = \frac{0.9 \lambda}{B \cos \theta} \]  

Where, \( \lambda \) is x-ray wavelength, here 1.5414 Å, 0.9 is the Scherer factor, \( B \) is full width at half maxima and \( \theta \) is the Bragg angle. Calculated crystallite size for Sample 2 is \(~15\) nm. Fig. 5.2 shows XRD patterns of the as-prepared and annealed samples TN2, TN12 and TN24. As prepared sample showed amorphous nature. However, phase transformation process is observed to be completed upon annealing. The diffraction pattern corroborated well with the JCPDS data for anatase phase of TiO\(_2\).
The particle size of samples TN2, TN12 and TN24 as estimated using Debye-Scherrer formula, is found to be 13.6, 15.3 and 16.5 nm, respectively. Figures 5.2(b) and 5.2(c) show the diffraction pattern of as-prepared and annealed samples, synthesized using methods II and III, respectively. In the as-prepared samples, two diffracted lines correspond to the anatase phase which is indicative of commencement of phase transformation process. However, the process is completed only when the samples are subjected to annealing. The particle size estimated for samples TE46 and TE86 are 9.1 and 8 nm, respectively.

5.3.2 Differential Scanning Calorimetric (DSC) Properties

Differential scanning calorimetry (DSC) is an experimental technique for measuring the energy necessary to establish a nearly-zero temperature difference between a test substance S (or its reaction products) and an inert reference material R, where the two samples are subjected to an identical (heating, cooling or constant) temperature programme. This technique is used to determine temperature of the phase transitions like melting point, solidification onset, re-crystallization onset, evaporation temperature etc.

Two types of DSC systems are commonly in use: Power-compensation DSC and Heat flux DSC. In the power-compensation DSC, the specimen (TS) and reference (TR) temperatures are controlled independently using separate (identical) ovens. The temperature difference between the sample and reference is maintained to zero by varying the power input to the two furnaces. This energy is then a measure of the enthalpy or heat capacity changes in the test specimen S (relative to the reference R). The heat flux DSC consists the test specimen S and reference material R (usually an empty sample pan+lid) in the same furnace together with a metallic block with
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high thermal conductivity that ensures a good heat-flow path between S and R. The enthalpy or heat capacity changes in the specimen S lead to temperature differences relative to R. This results in a certain heat-flow between S and R, because of the good thermal contact between S and R. The temperature difference $\Delta T$ between S and R is recorded and further related to the enthalpy change in the specimen using calibration experiments. The DSC instrument used in the present experiment is a heat-flux type Shimadzu DSC-50. Sample was sandwiched in aluminum-sealed cell. Samples were scanned in the temperature range of 317 K to 890 K with scan rate of 10 K/min.

![DSC thermogram](image)

**Fig. 5.3(a):** DSC thermogram of samples 1 and 2.

Fig. 5.3(a) shows the differential scanning calorimetric thermograms of Samples 1 and 2. Thermogram of Sample 1 shows two major peaks at around 405 K and 666 K, which indicated the endothermic and exothermic reactions, respectively. Its precise exothermic peak is indicative of the phase transformation from amorphous to crystalline. Thermal
energy corresponding to endothermal and exothermal peak area is found to be -6.18 kJ/gm and 2.15 kJ/gm, respectively. They represent the energy required for the phase transformation process. In sample 2, a typical endothermic peak is observed, however no any other impurity and/or secondary phase could be observed. Thermal energy involved in the process is -694.25 J/gm, which is one order to magnitude less than the sample 1. It is, therefore, concluded that phase formation process is completed in sample 2. These results of sample 1 and 2 are in agreement with the XRD results. The peak crystallization temperature was found to be 666 K. As the sample 2 is already in the crystalline state, it did not exhibit any peak corresponding to crystallization. Other noteworthy features in the DSC thermograms of these two samples are the endothermic events occurring at 405 K and 365 K for samples 1 and 2, respectively.

Fig. 5.3 (b): DSC thermogram of samples TN0, TN12 and TE40

Fig. 5.3(b) shows the typical DSC thermogram of TiO₂ powder samples TN0, TN12 and TE40. In TN0 sample, a broad endothermic peak exists at 130° C which could be
attributed to the desorption of water molecules. Since the reaction is carried out in the aqueous media, there is a strong likelihood of partial presence of water molecules on to the surface of precursor. A strong exothermic peak observed at around $393^\circ$ C is indicative of the first temperature induced phase transition from amorphous to crystalline anatase phase. The process started around $350^\circ$ C and continued up to $400^\circ$ C. Beyond this temperature, phase transition is not observed until a temperature of $550^\circ$ C is reached. Taking into account this temperature range, TN0 sample is annealed at $350^\circ$ C for 120 minutes to form TN12. DSC thermogram of the sample TN12 exhibits an endothermic peak at around $90^\circ$ C which corresponds to desorption of moisture from the surface of particles. In this case, temperature induced phase transition is not observed even upon increasing the temperature, which is suggestive that the temperature chosen for annealing is sufficient for the formation of anatase phase. For sample TE40, an endothermic peak is observed around $115^\circ$ C, owing to desorption of water and organic molecules from the sample. Temperature induced phase transition is observed in the range of $260^\circ$ C to $330^\circ$ C. However, a maxima is observed at $292^\circ$ C. The endothermic peak observed at $400^\circ$ C could be attributed to the decomposition of polyethylene glycol from the surface of nanoparticles. The phase transformation energy associated with the TN0 and TE40 is found to be 2.15 kJ/gm and 2.34 kJ/gm, respectively. We can conclude on the results of DSC thermogram, that the pure anatase structure could be produced through the annealing of as-prepared samples.

It is noticeable here that the temperature required for phase transformation is different for method I and II. Besides, variation in the properties of nanoparticles prepared with different synthesis routes could be attributed to the change in solubility
product, reaction rate, dissolution crystallization, nucleation formation, growth rate, etc. Hence, it could be concluded that even if we use the same solute in different solvents, the characteristic properties of final or intermediate product may be different.

5.3.3 Fourier Transformed Infrared Spectroscopy (FTIR)

![FTIR spectrum of TiO₂ nanocrystals sample 1 and 2.](image)

**Fig.5.4:** FTIR spectrum of TiO₂ nanocrystals sample 1 and 2.

As shown in Fig. 5.4, Fourier transform infrared transmittance is used to analyze the samples 1 and 2. The main peak observed around 1384 cm⁻¹ is attributed to the Ti-O bond in both the samples. FTIR spectra provided us the evidence that upon increasing the annealing temperature, sample became more crystalline, hence a small shoulder appearing in sample 1 at around 1353 cm⁻¹ is converted into a well-formed peak in sample 2. The broad hump observed > 2000 cm⁻¹ could be attributed to the presence of OH⁻ ion on the surface of the prepared nanoparticles.

5.3.4 Transmission Electron Microscopic (TEM) Studies

Transmission electron microscopy (TEM) is a technique whereby a beam of electrons
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is transmitted through a sample, then an image is formed, magnified and directed to appear either on a fluorescent screen or layer of photographic film, or to be detected by a CCD camera. The morphology and size characteristics of TiO$_2$ nanocrystals are measured by transmission electron microscope (TEM). The high-resolution transmission electron microscopy (HRTEM) images was recorded using JEOL JEM 2100 200-kV transmission electron microscope (TEM) with a resolution of 50 x to 1.5 Mx.

**Fig. 5.5:** TEM image of sample TN2. Inset shows selected area diffraction pattern.

TEM image of TE86 sample acquired after suspending it in ethanol has been shown in Fig. 5.5. All the particles were nearly spherical. The average size of particles is found to be 8 nm. This result is in agreement to the size determined from the XRD studies. The diffracted ring pattern with the dotted line is indicative of high crystallinity of the particles.
5.3.5 Raman Vibrational Properties of TiO$_2$ Nanoparticles

The challenge for the so-called nanotechnology is to achieve perfect control of nanoscale related properties. This obviously requires correlating the parameters of the synthesis process (self-assembly, microlithography, sol-gel, polymer curing, electrochemical deposition laser ablation, etc.) with the resulting nanostructure. Not every conventional characterization technique is suitable for that purpose but Raman spectroscopy (RS) has already been proven to be. For quite a long time this technique is mainly devoted to fundamental records, but instrumental progress (laser miniaturization), CCD detection, notch filters and data processing softwares have rendered it a general characterization method.

![Raman Spectroscopy Setup](image)

**Fig. 5.6:** Scheme of experimental Raman setup.

Not only can it provide basic phase identification but also subtle spectra alteration can be used to assess nano-scale structural changes and characterize micromechanical
behaviour. RS is thus a unique tool for probing or mapping nanophases dispersed in a matrix [31], precipitates in a fiber coating [32], surface formed nanophases [33] and solid state devices [34]. Some specific features can even be used to study size of cluster [35], polymerization [36], Gruneisen parameter [36] etc.

Fig. 5.6 shows the principles of Raman spectrometer. Up to date equipment would include holographic gratings, for improved excitation, light rejection, a set of monochrometers and a CCD for detection. The laser source is often built-in but light coming from an external excitation source can also be used.

The translational symmetry of crystalline materials is broken at grain boundaries, which results in the appearance of specific surfaces, and interface vibrational contribution [37]. Besides, the outer atomic layers of grains often react with neighboring species (lattice reconstruction, passivation/corrosion layers, contamination) and experiences steep thermo-chemical gradients during processing, which generates new phases with their own spectral contribution. These two factors are often neglected in RS but we can expect them to become very significant in nanocrystals, where the concentration of grain boundaries is very high. In many nanomaterials, the RS remains sufficiently similar to that of the corresponding single crystal to facilitate direct identification of the phases [37, 38]. Once Raman spectra are known, phase transition can be characterized (transition temperature, transition pressure, transition order) through mode variation, much the same way as in bulk materials. Besides, the observation of any theoretical mode is a very sensitive probe of lattice distortions [39].

Barborini et al. [40] showed with RS that the structure of gas phase-deposition TiO$_2$ clusters turned from rutile to anatase whenever they reached 5 nm in diameter, due to
difference in surface energies. As the size of TiO₂ nanoparticles decreases, the featured Raman scattering peaks become broader [41, 42]. The size effect on the Raman scattering in nano-crystalline TiO₂ is interpreted as originating from phonon confinement [41, 42, 43], nonstoichiometry [44] internal stress/surface tension effects [45]. Among these theories, the most convincing is the dimensional confinement of phonons in nanocrystals [41, 43]. The phonon confinement model is also referred to as the spatial correlation model or q-vector relaxation model. It links the q-vector selection rule for the excitation of Raman active optical phonons with long-range order and crystallite size [46, 47]. In a perfect “infinite” crystal, conservation of phonon momentum requires that only optical phonons near Brillouin zone (BZ) centre (q=0) are involved in the first order Raman scattering. In an amorphous material lacking long-range order, the q-vector selection rule breaks down and the Raman spectrum resembles the phonon density of states. For nanocrystals, the strict “infinite” crystal selection rule is replaced by a relaxed version (as large as Δq≈1/L (L=diameter)) due to the uncertainty principle. Raman spectra of all the nanocrystalline samples and as-prepared (TN0) sample have been shown in Fig. 5.7. Due to its amorphous nature, TN0 did not show any peak. The crystalline samples showed similar spectral lines to that of the bulk anatase. The anatase TiO₂ has six Raman-active fundamentals in the vibrational spectrum: three E₉, two B₁g, and an A₁g mode. However, crystalline samples exhibited blue shifts and broadening of peaks. Raman lines at 142, 196, 397, 517 and 636 cm⁻¹ could be assigned to E₉, E₂g, B₁g, B₁g + A₁g, and E₉ modes of the anatase phase, respectively.
The strongest \( E_g \) mode at 142 cm\(^{-1} \) is from the external vibration of the anatase structure and was observed to be well resolved. This was suggestive of formation of anatase phase which is possessed with a certain degree of long-range ordering. As the particle size decreases, the Raman peaks show increased broadening and systematic frequency shifts. The most intense mode (\( E_g \) at 142 cm\(^{-1} \)) shows the maximum blue shift and significant broadening with decreasing particle size. The small blue shift is seen for other \( E_g \) modes, while the \( B_{1g} \) (1) and \( B_{1g}(2)+A_{1g} \) modes show very small blue shift and red shift respectively. Whereas the frequency shifts for the \( A_{1g} \) and \( B_{1g} \) decreasing particle size is clearly seen for these modes. The \( E_g(3) \) mode shows significant broadening and red shift with decreasing size. Weak broader peak in the high wavenumber region indicated that there was a lack of short-range order in the anatase phase [49, 50]. This observation was favored by the XRD results also. In fact, the XRD spectra are used to determine average structural information within several unit cells and also, it reveals the long-range ordering within the material. On the contrary, Raman scattering, as a local probe, is
very sensitive to crystalline and microstructures of material. As a result, Raman lines become weak and broad when the samples have local lattice imperfections. It is evident from the Fig. 5.7 that the intensity of all Raman lines increased with the increasing annealing time for the samples TN2, TN6 and TN12. A similar behavior of frequency shift has been reported in TiO$_2$ nanocrystals synthesized by other techniques such as sol-gel [49], gas condensation [50] and solution chemical process [51]. Moreover, the size dependent variation in Raman peak and FWHM has been explained using modified phonon confinement model considering the log-normal distribution function.

5.3.6 Photoluminescence Properties of TiO$_2$ Nanoparticles

In contrast to Raman scattering, photoluminescence is directly related to the electronic structure and transitions. Differences in the electronic behavior between bulk and low dimensional semiconductors arise due to the difference in the electron density of states, g(E). For example, g(E) of a bulk semiconductor has a continuous dependence g(E)$\propto E^{1/2}$, whereas in two-dimensional semiconductors it has a step-like dependence on energy. In one-dimensional semiconductor structures it diverges as $E^{-1/2}$ and for zero-dimensional semiconductor it is a delta function of energy. In semiconductors, the electrons in the valence band absorb photons and are lifted into the conduction band, leaving holes in the valence bands. In a bulk sample, this excitation of the valence electrons occurs provided that $\hbar\omega_i \geq E_g$ where $E_g$ is the band gap of the semiconductor and $\omega_i$ is the frequency of the incident photon. Some of these excited electrons lose their energy by nonradiative transitions. It also is possible for an electron to fall from the conduction band into the holes in the valence band by a radiative transition process. Usually the lowest levels are
seen in the photoluminescence spectrum and the emitted photoluminescence frequency satisfies $\omega_{PL} < \omega_i$. Thus, the photoluminescence peak of a bulk semiconductor corresponds to its band gap. Because of the quantization of energy levels in the conduction and valence bands in low-dimensional systems, the frequency of photoluminescence emission, $\omega_0$, corresponds to the transition of excited electrons from the lowest state in the conduction band, $E_{C1}$, to the lowest state in the valence band, $E_{V1}$. Because $\omega_{PL} < \omega_0$, the photoluminescence peak in low dimensional systems blueshifts from that in the corresponding bulk materials (see Fig 5.8). The characteristic change of the band gap with decrease in size of the nanostructures can be studied from the blueshift in the photoluminescence peak position. Thus, photoluminescence is useful in the study of quantum confinement of electrons in low dimensional materials. Due to the change in the band gap, some nanomaterials can have tunable light emission, where the tuning depends on the size of the system. Photoluminescence spectroscopy also yields information on the surface state density from the intensity variations [52] and the width of the spectrum. Surface states are caused by the interruption of the periodic arrangement of the atoms and by the deposition of impurities at the surface. Because of the large surface to volume ratio, these effects are more pronounced in nanoparticles. Thus, photoluminescence spectroscopy offers a tool for improving our understanding of the compound semiconductor surface. Photoluminescence spectroscopy also gives information on band bending [53], surface related transitions, [54] and near-surface bulk properties [55].
Fig. 5.8: (a) The electronic transition between the quantized levels $E_{c1}$ to $E_{v1}$ in a semiconductor low dimensional system in comparison with PL energy of the bulk system (b) corresponding photoluminescence intensity as a function of frequency for low dimensional system (dotted line) and for the bulk system of same material (solid line).

Fig. 5.9: Photoluminescence record with laser line 457 nm with a power of 0.15 W/cm$^2$. 
The photoluminescence spectra are recorded at 0.15 W/cm² power using laser line of wavelength 457 nm and have been shown in Fig. 5.9. All the spectra have similar Gaussian-type distribution with a broad nanostructure band centered at 2.31, 2.32, 2.35 and 2.48 eV, respectively for TN2, TN12, TE46 and TE86. In general, photoconductivity increases with decrease in the particle size of the material. In our study, broad peak and minor change in conductance were observed in TN12 as compared to TN2. This could be attributed to the increase in particle size. It is known that, with increase in particle size results into decreased surface area and this, in turn, decreases the number of surface active sites. This leads to reduction in $e^-/h^+$ recombination process. In spite of being different systems, enhancement in luminescence efficiency with the decreasing grain size was observed in CdS and CuCl semiconductor nanocrystals [56, 57]. The effect could be attributed to the quantum size effect and to the confinement of electron and hole in a comparatively smaller volume. The large shift occurs because of the small effective masses of electron and hole, resulting from strong chemical bonding and this result into delocalization of valence and conduction band electrons. PL spectra of TN12 nanocrystals were recorded at 457 nm laser wavelength and at four different excitation powers, i.e. 50, 100, 150 and 200 mW. They have been shown in Fig. 5.10. All the spectra were observed to be centered around 2.32 eV; although their intensity increased with increasing the excitation power. In TiO₂, $e^-/h^+$ recombination may be grouped in two categories: (i) volume recombination – dominates in well crystalline larger size TiO₂, and (ii) surface recombination – dominates in smaller sized particles due to large surface area to volume ratio and presence of large number of surface active sites. With reduction in particle size the photonic efficiency increases due
to increase in interfacial charge carrier transfer rate. However, in nanocrystalline semiconductor particles, when particle size becomes extremely small (i.e. several nm in diameter),

![PL spectra of TN12 nanocrystals recorded at four different excitation power under 457 nm.](image)

**Fig.5.10:** The PL spectra of TN12 nanocrystals recorded at four different excitation power under 457 nm.

surface recombination becomes an important process [58]. In the region of ultrafine particle size, most of the e\(^{-}\)/h\(^{+}\) pairs are generated sufficiently close to the surface. They may quickly reach the surface and undergo rapid surface recombination mainly due to abundant surface trapping sites and the lack of driving force for e\(^{-}\)/h\(^{+}\) pair separation. Since the characteristic time for surface e\(^{-}\)/h\(^{+}\) recombination is much faster than that of the interfacial charge carrier transfer processes, the increase in the interfacial transfer rate will be outweighed by the increased surface recombination rate in ultrafine particles
beyond a certain size reduction. Therefore, an optimal particle size exists in the pure TiO$_2$ system for the maximum photocatalytic efficiency. The TiO$_2$ nanoparticle of 8nm size produces maximum photonic efficiency. Our finding is in agreement to the findings of Zhang and co-workers [59], who reported that about 10 nm is the optimum size for pure TiO$_2$, for the particles larger than this diameter, emission decay time increases.
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and therein