Chapter 2

Material preparation and characterization techniques

This chapter gives an overview on the synthesis of the photonic materials and their characterization techniques used in the present work. Reflux and microwave irradiation methods are used for the synthesis of CdSe QDs. Structural and linear optical characterization methods used for the study are explained. Thermal lens and photo acoustic methods are the selected thermo-optic techniques applied on the material while Z-scan method is used for the nonlinear-optical characterization. Experimental methods along with the theory of these techniques are discussed. Basic ideas of solar cell and random lasers are given as the applications of CdSe QDs.
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2.1 Introduction

Nanotechnology represents the design, production and application of materials at atomic, molecular and macromolecular scales, in order to produce new nanosized materials. Advances in nanophotonics devices have proceeded rapidly for the last 10 years. It causes an enormous increase in number and diversity of photonic applications which have resulted from significant advances in the computational design tools and their accessibility, the emergence of new nanofabrication technique and realization of new optical and structural characterization methods. The selection of appropriate method for the preparation of nanoparticles (NPs) depends on the physical, chemical character of the material to be loaded. Synthesis of NPs using microwave heating has been on the increase in recent years. Fabrication of high quality NPs can be achieved by simple operations compared with the more conventional NP synthesis methods. Applications of NPs in various fields require an inexpensive and simple process of synthesizing high quality shaped NPs. In this regard, recent years have witnessed significant research being done in the use of microwave radiation in NP synthesis. Although various techniques have been applied for the synthesis of NPs, there are some features to consider that are common to all the methods. That is, the synthesis of NPs requires the use of a device or process [1, 2] that fulfills the following conditions:

- Control of particle size, shape, size distribution, crystal structure and composition distribution.
- Improvement of the purity of NPs.
- Control of aggregation.
- Stabilization of physical properties, structures and reactants.
- Higher reproducibility.
- Higher mass production, scale-up and lower costs.
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2.2 Preparation methods of nanoparticles

Methods of preparation of NPs can be divided into physical and chemical methods based on whether or not there exist resonant chemical reactions. On the other hand, these methods can be classified into solid phase synthesis, liquid phase synthesis, gas phase synthesis and vapour phase synthesis. Solid phase method includes thermal decomposition, solid state reaction, spark discharge and stripping and milling methods. Liquid phase method for synthesizing NPs includes mainly precipitation, hydrolysis, spray, solvent thermal, solvent evaporation pyrolysis, oxidation reduction, emulsion, radiation, chemical synthesis and sol-gel processing. The gas phase method includes gas-phase evaporation method, chemical vapor reaction, chemical vapor condensation and sputtering method. In our work we emphasize synthesis of NPs in the liquid phase. A brief description of the other methods like gas phase synthesis and vapour phase synthesis [3] are also given.

2.2.1 Liquid phase synthesis

- Co-precipitate method: It is a method of carrying down of substances by a precipitate, normally soluble under the conditions employed. It involves simultaneous occurrence of nucleation, growth, coarsening or agglomeration process.

- Sol-gel processing: In materials science, the sol-gel process is a method for producing solid materials from small molecules. The method is used for the fabrication of metal oxides.

- Microemulsion: Microemulsion method is one of the recent and ideal techniques for the preparation of inorganic NPs. Oil and water are immiscible and they separate into two phases when mixed, each saturated with traces of the other component. An attempt to combine the two phases requires energy that would establish water-oil association replacing the water-water/oil-oil contacts[4,5].

- Sonochemical synthesis: Sonochemistry is the application of ultrasound to chemical reactions and processes. The mechanism causing sonochemical effects in liquids is the phenomenon of acoustic cavitation.
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- Template synthesis: Template-assisted electrodeposition is an important technique for synthesizing metallic nanomaterials with controlled shape and size. Arrays of nanostructured materials with specific arrangements can be prepared by this method, employing either an active or restrictive template as a cathode in an electrochemical cell.

- Biomimetic synthesis: Biomimetic synthesis is a branch of natural product synthesis that aims to synthesize a target molecule through a series of reactions, and passing through intermediate structures, that are closely related to those that occur during biosynthesis in its natural source.

- Hydrothermal/Solvothermal: Solvothermal synthesis is a method for preparing a variety of materials such as metals, semiconductors, ceramics, and polymers. The process involves the use of a solvent under moderate to high pressure and temperature that facilitates the interaction of precursors during synthesis. If water is used as the solvent, the method is called hydrothermal synthesis.

Reflux method for the synthesis of nanophotonic materials

Reflux method is one of the hydrothermal methods which is used to apply thermal energy to a chemical reaction. In this method, a liquid reaction mixture is placed in a vessel open only at the top and is connected to a condenser such that any vapours given off are cooled back to liquid, and fall back into the reaction vessel. To thermally accelerate the reaction, it is carried out at an elevated temperature. The main advantage of this technique is that it can be left for a long period of time without the need to add more solvent or fear of the reaction vessel boiling dry as any vapour is immediately condensed in the condenser. In order to boil the given solution at a certain temperature, one can be sure that the reaction will proceed at a constant temperature always. The choice of solvent is an important factor through which, one can control the temperature within a very narrow range. This technique is also useful for performing chemical reactions under controlled conditions that require substantial time for completion [6, 7]. Figure 2.1 shows a typical reflux apparatus for supplying thermal energy for the chemical reactions. It includes an optional beaker of water between the reactants.
and the heat. In our experiments we used a two necked flask with one neck to keep the thermometer inside and the condenser is fit in the other neck. Inlet and outlet for water are included. Furthermore, a high boiling, thermally stable silicone oil is an option to immerse the reaction vessel, rather than water which evaporates too readily to be useful for lengthy reactions. Using an oil bath, temperatures of up to several hundred degrees can easily be achieved, which is higher than the boiling point of most commonly used solvents. If even higher temperatures are required, the oil bath can be replaced with a sand bath.

**Microwave synthesis**

In recent times, a microwave-assisted method has been widely applied in chemical reactions and synthesis of nanomaterials. It is an attractive method to promote reactions by effective heating compared to conventional heat conduction methods due to the direct heating of the reaction mixture. In conventional heating methods, the vessel is heated and subsequently transfers the heat by convection. In other words microwave heating is more efficient in terms of the energy used, produces higher temperature homogeneity, and is considerably more rapid than conventional heat sources. Microwave heating is a transfer of electromagnetic energy to thermal energy, and is an energy conversion phenomenon rather than the heat transfer. The electric component of an electromagnetic field causes heating by two main mechanisms, dipole
interaction mechanism and ionic conduction mechanism. Main features of these interactions between materials and microwaves are based on:-

- Both require effective coupling between target material and rapidly oscillating electromagnetic field of microwaves.
- Dipole interaction occurs with polar molecules.
- Polar end of the molecules reorient themselves and oscillates in steps with the oscillating electric field of microwaves.
- Heat is generated by molecular collision and friction.
- Generally, more polar the molecule the more effectively it will couple with microwave field.
- Nanostructures with smaller size distribution and higher degree of crystallization are obtained under microwave heating than in conventional heating.

In dipole interaction mechanism, for a substance to generate heat when irradiated with microwaves it must possess a dipole moment, as in water molecule which possess a very high dipole moment. The greater the polarity of a molecule, the more pronounced the microwave effect with regard to the rise in temperature [8, 9]. A dipole is sensitive to external electric fields and will attempt to align itself with the field by rotation. The applied field offers the energy for the molecules to collide with one another and heats the sample. High and low frequency radiation does not give rise to effective heating because in the first case, the field oscillates so well that there is no random motion generated and in the second case, the molecules follow the field so closely that there is no random motion generated [10, 11]. Second mechanism is the conduction process which is a much stronger interaction than the dipolar mechanism with regard to the heat-generating capacity. In this case mobile charge carriers like electrons, ions, etc. move relatively easily through the material under the influence of the microwave electric field. These induced currents will cause heating in the sample due to electrical resistance. In the same way as visible light, infrared irradiation, and UV irradiation, microwave energy is also delivered directly to the material through molecular interaction with the electromagnetic field. Since microwaves
can penetrate the material and supply energy, heat can be generated throughout the volume of the material resulting in volumetric heating [12]. Additionally, the method shows acceleration in reaction rate, yield improvement, short reaction time, small particle size, narrow particle size distribution, high purity materials, and enhanced physical-chemical properties [13-15].

2.2.2 Gas phase synthesis

This process involves super saturation achieved by vaporizing material into background gas and then cooling the gas. The gas phase method includes gas-phase evaporation method, chemical vapour reaction method, chemical vapor condensation and sputtering method. It can also be classified with the precursors used as:

- Methods using solid precursors
  1. Inert gas condensation
  2. Pulsed laser ablation
  3. Spark discharge generation
  4. Ion sputtering

- Methods using liquid or vapour precursors
  1. Chemical vapour synthesis
  2. Spray pyrolysis
  3. Laser pyrolysis/photo chemical synthesis
  4. Thermal plasma synthesis
  5. Flame synthesis
  6. Low temperature reactive synthesis
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2.2.3 Vapour phase synthesis

This involves same mechanism as liquid phase reaction. Here, elevated temperature with vacuum is used for the reaction process. Vapour phase mixture rendered thermodynamically is unstable relative to formation of desired solid material.

Characterization techniques

Characterization techniques of materials are important to researchers as they are the basic tools in identifying the structure and thereby properties of materials synthesized, which help in determining whether the designed materials are suitable for particular applications. We present the experimental techniques to find out the structural, thermal, linear and nonlinear optical properties of samples and its applications as photonic materials.

2.3 Structural characterization techniques

X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR), Dynamic light scattering (DLS) method for particle size analysis, Transmission electron microscopy (TEM) and Scanning electron microscopy (SEM) are the main techniques used for the structural characterization of our samples in this thesis.

2.3.1 X-ray diffraction spectroscopy (XRD)

X-ray diffraction, often abbreviated as XRD, is extensively used to characterize the crystalline form of nanoparticles to estimate the crystalline sizes and for the study of crystal structures and atomic spacing. Since this method often utilizes X-ray diffraction from nanoparticles in powder form, it is called powder diffraction. This rapid analytical technique can provide information on unit cell dimensions and the crystalline nature of the sample. Max von Laue, in 1912, discovered that crystalline substances act as three-dimensional diffraction gratings for X-ray wavelengths similar to the spacing of planes in a crystal lattice. The basic principle behind XRD is the constructive interference of monochromatic X-rays from a crystalline sample. The interaction of the incident rays
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with the sample produces constructive interference and a diffracted ray when conditions satisfy Bragg’s Law [16].

\[ 2d \sin(\theta) = n\lambda \]  \hspace{1cm} (2.1)

This law relates the wavelength of electromagnetic radiation to the diffraction angle and the lattice spacing in a crystalline sample. These diffracted X-rays are then detected, processed and counted. By scanning the sample through a range of \( 2\theta \) angles, all possible diffraction directions of the lattice could be attained due to the random orientation of the powdered material. Conversion of the diffraction peaks to d-spacing allows identification of the mineral because each mineral has a set of unique d-spacing. If a material does not show this diffraction peaks it confirms that the material is not a crystal and must be non-crystalline or amorphous. We used a Bruker AXS D8 Advance X-ray diffractometer with Ni-filtered Cu K\( \alpha \) (1.5406 Å) source to investigate the structural properties of the samples.

2.3.2 Fourier transform infrared spectroscopy (FTIR)

This non-destructive techniques provide extensive information about the structure and vibrational properties along with the characterizing covalent bonding information. FTIR is used to gather information about the structure of a compound and as an analytical tool to assess the purity of a compound. In the experimental section of IR spectroscopy, an organic molecule is exposed to infrared radiation and when the radiant energy matches the energy of a specific molecular vibration, absorption occurs. The wavenumber, plotted on the X-axis, is proportional to energy; therefore, the highest energy vibrations are on the left. The percent transmittance (%T) is plotted on the Y-axis. Absorption of radiant energy is therefore represented by a trough in the curve: zero transmittance corresponds to 100% absorption of light at that wavelength [17]. IR source emits an IR beam which is split into two identical beams; one goes through the sample and the other through a reference cell. IR spectroscopy is used to measure the amount of energy absorbed when the frequency of the infrared light is varied. In our works the FTIR spectra of the samples were recorded using Thermo NICOLET 380 FTIR Spectrometer by means of KBr pellet procedure[18].
2.3.3 Dynamic light scattering analysis (DLS)

DLS method is a well-established technique for measuring the size of particles and macromolecules typically in the sub micron region down to below 1 nanometer. It is sometimes referred to as Photon correlation spectroscopy (PCS) or quasi-elastic light scattering (QELS) method and is suitable to measure samples which consist of particles suspended in a liquid or emulsions. The basic mechanism behind is that, particles in suspension undergo Brownian motion caused by thermally induced collisions between the suspended particles and solvent molecules. If the particles are illuminated with a laser, the intensity of the scattered light fluctuates over very short time scales at a rate that is dependent upon the size of the particles; smaller particles are displaced further by the solvent molecules and move more rapidly. Analysis of these intensity fluctuations yields the velocity of the Brownian motion and hence the particle size using the Stokes-Einstein relationship.

The term hydrodynamic diameter is used to indicate the diameter measured in DLS method which refers to the way a particle diffuses within a fluid. This means that the particle size will be larger than measured by electron microscopy, and it is important to note that DLS produces an intensity weighted particle size distribution, which means that the presence of over sized particles can dominate the particle size result.

A conventional DLS instrument consists of a laser light source, which converges to a focus in the sample using a lens. Light is scattered by the particles at all angles and a single detector, traditionally placed at 90° to the laser beam, collects the scattered light intensity. Laser diffraction measures particle size distributions by measuring the angular variation in intensity of light scattered as a laser beam passes through a dispersed particulate sample. Large particles scatter light at small angles relative to the laser beam and small particles scatter light at large angles. The angular scattering intensity data is then analyzed to calculate the size of the particles responsible for creating the scattering pattern, using the Mie theory of light scattering. The particle size is reported as a volume equivalent sphere diameter[19]. We have used nanoparticle analyzer SZ-100 (Horiba) for the particle size measurement.
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- **Measurement of Zeta potential**

  It is one of the fundamental parameters known to affect dispersion stability. It is a measure of the magnitude of the electrostatic or charge repulsion or attraction between particles in a liquid suspension. It can also be done with Dynamic light scattering instrument system described above. Its measurement brings detailed insight into the causes of dispersion, aggregation or flocculation and can be applied to improve the formulation of dispersions, emulsions and suspensions [19, 20].

2.3.4 **Transmission electron microscopy (TEM)**

TEM is a tool utilized to analyze the structures of very thin specimens through which electrons as probes are transmitted. TEM image provides reliable information about the size and shapes of nanoparticles. The principle of operation in this instrument is similar to an optical microscope, where an electron beam, like light in a transmission microscope, travels through the sample and is affected by the structures in the specimen. Transmitted electron beam is projected onto a phosphor screen for imaging. A TEM consists of the following components:

1. An electron gun that produces a stream of monochromatic electrons
2. Electromagnetic condenser lenses that focus the electrons into a small beam
3. A condenser aperture to restrict the beam by eliminating the high-angle electrons
4. A sample stage on which the sample is placed
5. An objective lens to focus the transmitted beam
6. Optional objective and selected area metal apertures to enhance the contrast by blocking out high-angle diffraction, as well as to obtain electron diffraction
7. Subsequent intermediate and projector lenses to enlarge the image
8. Optical recording of the image carried by the transmitted electron beams
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As the high energy electrons pass through the thin specimen, scattering occurs at the atoms because of Coulomb interactions. The degree of scattering depends on the constituent atoms of the specimen. The intensity distribution of the electrons reaching the fluorescent screen is determined by the number of electrons transmitted. This results in a relative darkness in the specimen image area, which is rich in heavy atoms and thus, TEM image provides reliable information about the size and shapes of nanoparticles. The electron micrograph images of our samples in colloidal form were obtained using transmission electron microscope of Philips Technai G2 at 120 kV [21].

2.3.5 Scanning electron microscopy (SEM)

SEM is a technique to obtain the image of a sample, by scanning of an electron beam across the surface of specially prepared specimens. It provides a greatly enlarged and highly resolved three-dimensional view of the specimen’s exposed structure. An electron beam from an electron gun is focused onto the specimen surface by condenser lenses and this electron beam spot size determines the resolution of the image, which is finally obtained by scanning. A set of scanning coils deflects the electron beam which allows scanning of the surface in a grid fashion. There are several types of signals which are produced when the focused electron beam impinges on a specimen surface, to form an SEM image. They include back-scattered electrons, secondary electrons, cathode luminescence, and low-energy characteristic X rays generated by the impinging electrons. The signals obtained from specific emission volumes within the sample are used to measure composition, surface topography, crystallography, magnetic or electric character, etc. The secondary and back-scattered electrons are captured by a detector and are primarily responsible for topographic images. Thus, in principle, every point spot on a specimen is transposed to a corresponding point on the CRT and the brightness of a spot in a SEM image is a measure of the intensity of secondary electrons, which critically depends on the local surface topography. The advantage of SEM over TEM is that, it provides tremendous depth of focus [21]. Scanning electron microscopy (SEM) of our samples are performed on JEOL Model JSM-6390LV.
2.4 Linear Optical characterization

2.4.1 Absorption spectroscopy

JASCO V-570 UV/VIS/NIR Spectrophotometer was used for the absorption, transmission and reflectance measurements of the samples. The spectrometer consists of an optical system with single monochromatic, UV/VIS region (1200 lines/mm plane grating) and NIR region (300 lines/nm plane grating) of Czerny-Turner mount double beam type. The resolution is of 0.1 nm (UV/VIS region) and 0.5 nm (NIR region). Light source used are 30 mW deuterium discharge tube in 190 nm to 350 nm region and 20 W tungsten iodine lamp in 330 - 2500 nm region. The total wavelength range for the analysis is 190 nm - 2500 nm. The beam from the light source is converged and enters into the monochromator. It is dispersed by the grating in the monochromator and the light passes out through the exit slit. This light is split into two light paths by a sector mirror, one incident on the sample to be measured and the other on the reference sample such as solvent. The light that has passed through the sample or reference sample is incident on the photomultiplier tube and PbS photo conductive cell which act as the detectors.

In the reflectance measurement, the setup has to be changed. The Model SLM-468 single reflection attachment is designed to measure the relative reflectance of sample using the forward reflected light from the aluminum-deposited plane mirror as reference. It permits the measurement of the reflectance of metal deposited film, metal plating etc. The wavelength range is 220 nm to 2200 nm with a beam port diameter of 7 mm and angle of incidence approximately $\sim 5^\circ$[17]. For each wavelength of light passing through the spectrometer, the intensity of the light passing through the reference cell is measured as $I_0$. The intensity of the light $I$ passing through the sample cell is also measured for that wavelength. If $I$ is less than $I_0$, then obviously the sample has absorbed some of the light. By Beer-Lambert Law [22], the relationship between $A$ (the absorbance) and the two intensities are given by $A = \log \frac{I_0}{I}$ and the absorption coefficient, $\alpha = A/d$, $d =$ thickness of the sample where $\alpha$ is given by the Taucs [23] relation to obtain the absorption edge as,

$$\alpha(\omega) = \beta \left( \frac{\hbar \omega}{4\pi} - E_{opt} \right)^n$$  \hspace{1cm} (2.2)

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where, $\beta$ is a constant and $n$ is an index which takes values of 2 and 1/2 for direct and indirect transitions. Band gap of CdSe QDs are calculated for direct transitions, using Tauc plot, with $(\alpha h\nu)^2$ along y-axis and $E_{opt}$ along x-axis.

2.4.2 Fluorescence spectroscopy

The fluorescence excitation and emission spectrum of the samples were carried out using Cary eclipse fluorescence spectrophotometer of VARIAN [17]. It has a single cell holder for liquid sample analysis and a solid sample holder accessory to perform fluorescence measurements on solid samples. The solid sample holder accessory provides both rotational and translational adjustment of the sample. The angle of incidence of the excitation may be varied from $20^\circ\text{C} - 35^\circ\text{C}$. This is the angle between the exciting light and a line perpendicular to the surface of the sample mounting slide. The source of excitation is xenon lamp.

2.5 Photo-thermal characterization methods

Thermo-optic or photothermal (PT) spectroscopy belongs to a class of highly sensitive techniques, which can be used to measure optical absorption and thermal characteristics of a sample based on the change in thermal state of the sample resulting from the absorption of radiation. The basic principle of PT spectroscopies is the detection of the heat produced in the sample due to non-radiative de-excitation processes resulting from the absorption of intensity-modulated light by the sample. PT signals will not be affected by scattered or reflected light unlike conventional optical signal detection. Hence PT spectroscopy measures optical absorption more precisely in scattering solutions, solids and at interfaces. The large signal to noise ratio of thermo-optic techniques makes it an effective tool to study the surface and absorption properties of materials, particularly for solids. There are different PT mechanisms that can be used for the physical and chemical analyses of materials, such as photo acoustic spectroscopy, PT deflection, PT lens spectroscopy etc. Measurements of the temperature, pressure, and/or density changes that occur due to optical absorption are ultimately the basis for these PT spectroscopic measurements. Each of these has a name indicating
the specific physical effect measured [24]. These are briefly described in the following sections.

1. Photo acoustic spectroscopy (PAS) is an indirect method for measuring optical absorption. Indirect methods do not measure light transmission or emission but rather measure an effect of sample absorption.

2. Photothermal lens spectroscopy (PTL) measures the thermal blooming that occurs when a beam of light heats a transparent sample. It is typically applied for measuring minute quantities of substances in homogeneous gas and liquid solutions.

3. Photothermal deflection (PTD) spectroscopy or the mirage effect measures the bending of light due to optical absorption. This technique is particularly useful for measuring surface absorption and for profiling thermal properties of layered materials.

4. PT diffraction, a type of four wave mixing, monitors the effect of transient diffraction gratings written into the sample with coherent lasers. It is a form of real time holography.

5. PT emission measures an increase in sample IR radiance resulting from absorption. Sample emission follows Stefan’s law of thermal emission. These methods are used to measure the thermal properties of solids and layered materials.

2.5.1 Thermal lens effect

Thermal lens (TL) spectroscopy was the first PT spectroscopic method to be applied for sensitive chemical analysis. The TL effect was discovered by Gordon et al. in 1965. In this technique the sample is illuminated using a Gaussian beam having intensity distribution across the beam as

\[ I_r = I_0 e^{-2r^2/\omega^2} \]  

(2.3)

where \( \omega \) is the beam radius. When energy from a laser beam passes through a sample, a part of the incident radiation is absorbed by the sample and subsequent nonradiative decay of excited state population results in local heating of the medium along the beam path. Heating
caused by absorption of a Gaussian beam has radial symmetry along the laser path which creates a corresponding radial temperature gradient in the sample and a blooming occurs, which is proportional to this temperature changes. Modification in refractive index causes the medium to mimic a lens, called thermal lens (TL). This lens causes beam divergence or convergence with the change in refractive index and the signal is detected as a time dependent decrease in power at the center of the beam. The thermal lens generally has a negative focal length since most materials expand upon heating and hence have negative temperature coefficient of refractive index which causes beam divergence and the signal is detected as a time dependent decrease in power at the center of the beam at far field using a probe beam.

**Theory of thermal lens effect**

Several experimental conditions have to be applied to derive TL theoretically [25-31]. Under pulsed and continuous wave (CW) excitation conditions, different pump or probe beam geometries and different sample conditions are some of the models applied. The theoretical procedure can be divided into three parts.

1. The heat equation must be solved for the particular boundary conditions of the system to generate a temperature distribution within the sample.
2. Temperature distribution must be converted into a refractive index profile.
3. Interaction of the beam with the refractive index profile is used to predict a change in the beam intensity profile.

The different models differ primarily in the last step. A simple paraxial approximation theory is also usually used to predict changes in the beam center intensity and in the beam spot size [32, 33]. This paraxial approximation is a closed-form solution of ray tracing through a parabolic temperature rise near the beam axis. Following assumptions are involved in the model of the thermal lens.

- Beam cross section should be Gaussian and the spot of the laser beam remains constant over the length of the sample cell.
- The thermal conduction is the main mechanism of heat transfer
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while the sample is homogeneous and satisfies Beer’s law.

- Intensity profile of the laser beam detection is undertaken in the far field from the sample
- The strength of the thermal lens is not sufficient to induce a change in the beam profile within the sample where the refractive index change of the sample with temperature is constant over the sample.

Consider a Gaussian beam passing through an element of an absorbing sample in which the heat flow is radial and the beam is turned on during the time interval $0 \leq t \leq t_o$.

The heat generated per unit length \([34]\) is given by

$$Q(r)dr = \frac{2\alpha E_0}{\pi \omega^2} e^{\left(-\frac{2r^2}{\omega^2}\right)}$$  \hspace{1cm} (2.4)

where $\alpha$ is the absorption coefficient of the medium. $E_o$ is the total energy in each laser pulse and $\omega$ is the beam radius at time $t = 0$. The temperature rise of the laser-irradiated region \([35, 36]\) is obtained as

$$T(r, t) = \frac{2\alpha E_0}{\pi \rho c_p (\omega^2 + 8Dt)} e^{\left[-\frac{2r^2}{\omega^2 + 8Dt}\right]}$$  \hspace{1cm} (2.5)

Then thermal diffusivity $D$ of the sample can be calculated from the equation

$$t_c = \frac{\omega^2}{4D}$$  \hspace{1cm} (2.6)

where $\omega$ is the beam radius at the sample position and $t_c$, the time response to attain the steady state focal length. The solution of equation(2.5) for CW excitation is given as \([29, 30]\)

$$T(r, t) = \frac{2\alpha P (1 + \cos \omega t)}{\pi \rho c_p (\omega^2 + 8Dt)} e^{\left[-\frac{2r^2}{\omega^2 + 8Dt}\right]}$$  \hspace{1cm} (2.7)

Due to non-uniform radial temperature distribution, time dependent refractive index gradient formed inside the sample can be expressed as

$$n(r, t) = n_0 + \left(\frac{\partial n}{\partial t}\right) T(r, t)$$  \hspace{1cm} (2.8)

where $n_o$ is the refractive index at time $t=0$. Consequently, the irradiated sample acts like a lens, which affects the laser beam intensity.
profile by altering the radius. The relative change in the beam intensity is proportional to the relative changes in power of the beam reaching the detector and hence is a direct measure of the thermal lens strength. The PT lens signal is obtained by monitoring the probe laser power that passes through a pinhole placed far from the sample. The photo TL will either focus or defocus the probe laser beam so that the power at the center of the beam will either increase or decrease.

**Measurement approach of TL technique**

- Single beam thermal lens configuration

In single-beam TL spectrometer, the same laser is used to excite the sample and to probe the thermal lens created. In single beam TL spectrometer, the laser beam is focused with a lens and modulated with a chopper or a shutter. After passing through the sample, the beam center intensity is usually measured in the far field with a photodiode.

- Dual beam thermal lens configuration

In this method the pump beam is used to generate the thermal lens in the medium and another laser of low intensity is used to probe the lens formed. Separate lenses are used to focus pump and prob beam on to a dichroic mirror. There are two types of dual beam instrumentation: Collinear and transverse configuration. In collinear configuration, good spatial overlapping of both beams is necessary for optimal sensitivity. In transverse thermal lens experiment, the excitation beam is focused on to the sample perpendicular to the probe beam[37]. This alignment is useful for samples, which are available in very low concentration and in small volume and for chromatographic detection. Prism can be used to ensure a good overlap and counter propagation between the pump and probe beams. Dual beam technique is more advantageous since only a single wavelength (probe) is always detected and no correction for the spectral response of the optical elements and detector are required.

**Experimental methods**

Schematic experimental set up for thermal lens study is shown in figure 2.2. The excitation source used is a CW, 532 nm diode pumped solid
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Figure 2.2: TL experimental setup using pump-probe method.

state(DPSS) laser with a maximum power of 150 mW. The power at the sample is suitably adjusted using attenuators so that the probe beam spot is free from aberrations. A 2mW He-Ne laser emitting at 632.8nm used as the probe and is arranged to be collinear with the pump using a dichroic mirror. The two beams are focused into the sample cell such that the beam area at the sample plane is the same for both pump and probe resulting in a mode matched TL arrangement. Sample was taken in a cuvette of 1 cm×1 cm path length for making the measurements. A low frequency mechanical chopper with 3 Hz is used to modulate the intensity of the pump, until the TL peak-to-peak signal is maximum. This also enables one to determine the thermal recovery of the sample. In the TL experiment the excitation laser must have Gaussian profile, so that when sample absorbs the beam with Gaussian intensity profile, the temperature distribution has a radial dependence. The temperature gradient causes refractive index gradient which behaves like a converging or diverging lens depending on whether rate of change of the refractive index with respect to temperature is positive or negative [38, 39]. The TL signal was collected using an optical fiber, which serves as the finite aperture and the same is mounted on an xyz translator. It is positioned at the center of the probe beam spot and connected to a photo detector-Digital Storage Oscilloscope (DSO) system. A filter to cut off 532 nm was used before the detector to remove the residual pump. The probe beam from the He-Ne laser which passes collinearly with pump beam experiences divergence and the beam shape expands in the presence of
a diverging thermal lens. The change in intensity of the probe beam is measured using a fast photodetector from which the relative intensity and initial slope is measured. The data are analyzed using the procedure described before[40]. Time dependent probe beam intensity follows the expression [41, 42]

\[ I(t) = \frac{I_0}{1 - \theta(1 + \frac{\rho}{\pi})^{-1} + \frac{1}{2} \theta^2 (1 + \frac{\rho}{\pi})^{-2}} \]  

(2.9)

Here, the parameter \( \theta \) is related to the thermal power radiated as heat and can be obtained with

\[ I = \frac{I_0 - I_\infty}{I_\infty} \]  

(2.10)

and

\[ \theta = 1 - \sqrt{1 + 2I} \]  

(2.11)

where \( I_0 \) is the initial intensity and \( I \) is the intensity after the steady state. A detailed curve fitting of this experimental data to equation (2.9) gives the time constant \( t_c \) of the thermal decay process. Finally the thermal diffusivity \( D \) of the sample can be calculated from the equation

\[ t_c = \frac{\omega^2}{4D} \]  

(2.12)

where \( \omega \) is the beam radius at the sample position and \( t_c \), the time response to attain the steady state focal length.

**Advantages of thermal lens spectrometry**

1. Linear PT signals are relatively independent of excitation and probe laser beam focus geometries.
2. Excitation energy or power dependent signals may be easily measured.
3. Yielding information regarding ground and excited state absorption cross sections and relaxation rate constants.
4. Data is complimentary to relaxation kinetic measurements but yield more information.
5. Sensitivity allows the use of thin optical cells.
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2.5.2 Photo acoustic spectroscopy

Photo acoustic spectroscopy (PAS) is the oldest form of PT spectroscopy [43, 44]. To get a quantitative spectrum of a sample, the wavelength of excitation is scanned and the corresponding magnitude of the acoustic signal normalized by the excitation pulse energy is measured to provide an excitation spectrum called a PA spectrum [45]. This technique, called photo acoustic spectroscopy or PAS, is different from the conventional techniques. Even though the incident energy is in the form of optical photons, the interaction of these photons with the material under investigation is studied not through the subsequent detection and analysis of some of the photons, but rather through a direct measure of the energy absorbed by the material as a result of its interaction with the photon beam. The PA spectrum complements the fluorescence excitation spectrum in that, it responds to that part of the absorbed energy which is not radiated. The phase of the PA signal with respect to the phase of the input modulation can give information both on the lifetime of the excited state and on the heat energy transfer [46, 47].

Principle behind photo acoustic spectroscopy is that, when light of appropriate energy falls on a sample, a part of the absorbed energy will be degraded to random translational motion of the molecules which is in the form of heat, thus leading to a temperature rise in the cell. The absorbing sample warms and cools in a cycle if the incoming light is modulated. If the cycle is so fast that the sample does not have time to expand and contract in response to the modulated light, a change in pressure develops through the ideal gas equation PV = nRT for n moles of gas. This pressure wave can lead to the production of a sound wave. These sound waves can be detected by a sensitive microphone, piezoelectric devices, or optical methods. These techniques are more properly called PA techniques.

The magnitude of the acoustic signal depends on such properties of the sample as the absorption coefficient, the duration of the processes of conversion of absorbed radiation to heat, the thermo-physical properties, and the geometry [48, 49]. The acoustic oscillations also acquire a certain phase shift relative to the incident modulated radiation, mainly because of a considerable time lag of heat transfer processes [49-51].
Historical outlook

The PA effect in both non-gaseous and gaseous matter was first reported by Alexander Graham Bell in 1880 [50, 52]. According to him the PA effect in solids was dependent on the absorption of light and that the strength of the acoustic signal was in turn dependent on the strength of the absorption of incident light by the material in the cell. The earlier works on PA were done by Tyndall [53], Rntgen [51], Rayleigh [54] and Preece [55] et. al. The PA effect was completely undeveloped for nearly 50 years, until the advent of the microphone. The Rosencwaig-Gersho (RG) theory of the PA effect for a sample in PA cell provided a comprehensive theoretical framework which led to the rapid development and application of the effect. This led to the invention of numerous other detection schemes and to the current wide spread interest in PT science [56, 57].

General theory of the PA effect using CW excitation source in condensed media

The main source of a photo acoustic signal from a condensed sample, as measured by the gas-microphone method, arises from the periodic heat flow from the sample to the surrounding gas with the consequent change in the gas pressure within the cell. In the case of gas-microphone technique, it is often treated as an "indirect" PA generation method due to the measurements of the acoustic signals generated in the sample which are not "directly" observed.

Rosencwaig and Gersho formulated a general theory for the PA effect in condensed media [58, 59], now commonly referred to as the RG theory. It shows that in the gas-microphone measurement of a PA signal, the signal depends both on the generation of an acoustic pressure disturbance due to the periodic temperature of the sample-gas interface and on the transport of this disturbance through the gas to the microphone. The RG theory derives exact expressions for this temperature, while it considers the transport of the disturbance in the gas in an approximate experimental manner, which is, however, valid for most experimental conditions. In the following section we outline a simplified version of the salient features of the RG theory.
Indirect PA generation

Indirect PA generation is very valuable when the optical absorption is so strong that no light passes through the sample. It requires acoustic detection in a coupling fluid in contact with the sample. The main advantage of such experiment is that, spectra of totally opaque or highly light scattering materials can be measured.

- Experimental verification of the RG theory

One of the most obvious and important predictions of the RG theory is that the photo acoustic signal is linearly proportional to the power of the incident photon beam, irrespective of the sample or cell geometry. So it is possible to construct optical power meters based on the PA effect, and several of these have been described by various authors [60-62]. The variation of the PA signal amplitude as a function of sample thickness and modulation frequency for thin polymer films has been found to obey the RG theory except at very low modulation frequencies such as 10 Hz [63]. Wetsel and McDonald [64] have shown that the chopping frequency dependence of the PA signal is in agreement with the RG theory, and the predicted PA saturation has been demonstrated in aqueous solutions of the dye Methylene blue by HCClelland and Kniseley [65].

Direct PA generation by pulsed laser

Conventional PA spectroscopy utilizes a gas phase microphone which is in thermal contact with the sample of condensed matter that senses the heating and cooling of a gas layer. The acoustic signal generated in the sample with irradiated chopped light plays only a minor role in this case. Hence this technique has an inherently low sensitivity [66, 67] and is often only useful for observing absorptions typically exceeding 1%. The low coupling efficiency can be partially compensated for, however, by the use of high efficiency gas-phase microphones. It is also possible to improve the sensitivity by using piezoelectric transducers in contact with solid samples or liquid samples.

Attempts to use a pulsed laser source instead of CW modulation method seems to have been undertaken for the first time by Bonch-Bruevich et. al. [68]. However, the potential of pulsed PA spectroscopy has been
brought out and demonstrated by the pioneering work of Patel and Tam, wherein they have shown that pulsed PA spectroscopy technique, involving the use of pulsed lasers, a piezoelectric transducer in direct contact with the sample, and gated detection can have very high detection sensitivities. This technique is truly PA in character, because the original acoustic pulse generated in a condensed sample is directly detected by a piezoelectric transducer, where good acoustic impedance matching is also ensured.

**Advantages of photo acoustics**[48, 69]

- The main advantage of this method is that, it can be performed on all states of matter.

- Transmitted, reflected or elastically scattered light by the sample is not detected rather a direct measure of the energy absorbed by the material as a result of its interaction with the photon beam is measured [70, 71]. This is of crucial importance when one is working with essentially transparent media, such as pollutant-containing gases, that have few absorbing centers [56] of the order of parts per trillion[48, 69].

- Optical absorption spectra of completely opaque materials can be obtained as PAS, which does not depend on the detection of photons [56]. So it can be applied to samples which are difficult to examine by conventional spectroscopic methods.

- PAS is a non-destructive method as the samples can be used as it is and depth profiles of analytes can be performed in optically transparent media.

- This non-destructive depth-profile analysis of absorption as a function of depth into a material is a unique advantage of the PAS.

- The PA effect resulting from nonradiative energy conversion process is a simple and sensitive spectroscopic tool for studying the phenomena of fluorescence and photo sensitivity in matter and is therefore complimentary to radiative and photochemical processes.
2. Material preparation and characterization techniques

- Since the sample itself constitutes the electromagnetic radiation detector, no photoelectric device is necessary and a wide range of optical and electromagnetic wavelengths are possible for study.
- A direct measurement of non-radiative relaxation, lifetimes and the ability to gather information from sub-surface layers is possible in the method.
- One of the important advantages of this method is the scope for obtain information on thermal parameters like thermal diffusivity, thermal conductivity and thermal effusivity of the sample.
- An increase in S/N ratio with increase in input power is obtained in this method [72].

Basic requirements and experimental methods

The basic requirements of the PA detection technique are the light source, means of modulating light, appropriate photo acoustic cell, detection schemes and processing electronics equipments like DSO or lock in amplifier.

- The light source:
  Two major classes of light sources that have been used for PA studies are the CW light sources and pulsed wave light sources. These sources can be xenon arc lamps or lasers. CW sources should possess broad wavelength output from UV to far IR and fast modulation capability while laser sources have high intensity, narrow spectral line width and modulation capability[72].

- Modulation techniques:
  Several methods have been employed to execute a temporal variation of the optical energy applied to a sample. The simplest form of modulating the light is using a chopper in the path of the light beam. It offers 100% modulation depths for frequencies from a few Hz to 5-8 kHz. The electro-optic modulation involves the changing of the plane of polarization of the incoming polarized laser beam in a non-linear crystal with the application of electric field on it. Acousto-optic (AO) modulation involves the spatial modulation of the laser by acoustic diffraction of the light in a crystal.
2. Material preparation and characterization techniques

- **Photo acoustic cell:**
  PA cell contains the samples, and a fabricated piezoelectric transducer chamber to detect the acoustic signals [73]. The cell is of stainless steel body with an inner diameter of 2 cm and length 5 cm. Glass windows are fixed with flanges and O-rings to the cell for the entry and exit of the laser beam. One side of the cell has an opening in which the transducer chamber is fixed. A Lead Zirconate-Titanate -PZT- disc of 4 mm thickness and 15 mm diameter is the piezoelectric transducer that is contained in this chamber. The PZT disc is spring-loaded against the thin front diaphragm, with a thin layer of silicon grease applied between them to ensure good acoustic coupling. The PA signal is taken out through the BNC connector. Due to its high sensitivity a few µV of electrical signal could directly be obtained from the transducer with absorbing sample in the cell [73].

![Figure 2.3: (a) Schematic representation and (b) Photograph of the PA cell used in the experiment.](image)

- **Detection schemes and processing electronic equipments:**
  PA signal detection techniques employ either a gas condenser microphone for the detection of the pressure variations in air or a piezoelectric transducer for the detection of thermo-elastic waves in solid or liquid media[72,74]. For periodic modulation, phase-
2. Material preparation and characterization techniques

Sensitive detection (lock-in-amplifier) can be utilized to process the detected signal. The technique is extremely efficient for extracting very weak signals associated with noise. With pulsed laser sources, digital storage oscilloscope is used to store the data signal.

Experimental methods

1. CW laser source for excitation

Experimental set up for PA measurements in continuous wave light source as input is shown in figure 2.4. It consists of a light beam from a standard solar irradiation of 1000W Xe lamp (Oriel 6269). A water column kept after the Xenon lamp will effectively filter out the infrared portion of the spectrum. Light coming out of the Xe lamp is intensity modulated using a mechanical chopper (Ithaco HMS 230) and is focused on the sample within the PA cell. The acoustic signals generated are detected by the PZT, and processed on a lock in amplifier (Stanford Research Systems SR 510). The description of the PA cell is same given above. PA cell contains the samples, and a fabricated piezoelectric transducer chamber to detect the acoustic signals. In the

![Figure 2.4: Experimental set up for PA study using Xe- lamp.](image)

experimental section, the sample is taken in the PA cell which is firmly held on a holder, and properly aligned with the laser beam axis. After taking readings corresponding to one sample, it is pipetted out and the next sample is filled, without moving the PA cell. The experiment is repeated for sample at different wavelengths.
2. Material preparation and characterization techniques

2. Pulsed laser source for excitation

In pulsed PA signal generation, Nd-YAG laser operating at 532 nm, at a pulse repetition frequency of 10Hz with 1 joule pulse energy is used as the excitation source, where signal detection was done with a digital storage oscilloscope (DSO-Tektronix; TDS 220, digital real time oscilloscope). Same PA cell was used for both the continuous wave and pulsed measurements. Here the synchronizing pulse from the laser is given as the reference signal to the DSO. The experimental setup is shown in figure 2.5.

![Figure 2.5: Experimental setup for PA signal generation by pulsed Laser.](image)

2.6 Nonlinear optical studies by Z-Scan technique

For many photonic and optoelectronic applications like optical limiting and switching, the knowledge of the nonlinear optical properties of materials is necessary. There are a number of nano sized organic nonlinear optical materials and semiconductor structures of low dimension which have got new entry into the field of NL optics. There are many methods to study the NL properties of materials. Z-Scan is a fairly accurate and convenient method to study transparent samples.
2. Material preparation and characterization techniques

2.6.1 Z-Scan technique

The Z-scan technique is a simple and effective experimental method to measure intensity dependent nonlinear optical susceptibilities of materials. Z-scan technique was originally introduced by Sheik Bahae et.al. [75]. In this method, the sample is translated in the Z-direction along the axis of a focused Gaussian beam, and the far field intensity is measured as function of sample position. This technique helps us to measure the sign and magnitude of both real and imaginary part of the third order nonlinear susceptibility coefficient $\chi^{(3)}$ of materials. When an incident beam propagates inside a NL medium it induces a self-phase change there by producing a wave front distortion of the beam. This can be studied by Z-Scan technique. Thus a laser beam propagating through a nonlinear medium will experience both amplitude and phase variations. Measurement of the transmission intensity of the focused laser beam as a function of distance from the sample, give information about nonlinear refraction and nonlinear absorption by the medium.

This technique has several advantages, some of which are:

- No complicated alignment except for keeping the beam centered on aperture.
- Simultaneous measurement of both sign and magnitude of nonlinearity.
- Data analysis is quick and simple except for some particular conditions.
- Possible to isolate the refractive and absorptive parts of nonlinearity unlike in DFWM.

Some of the disadvantage include:

- Requirement of high quality Gaussian beam for absolute measurements
- For non-Gaussian beams the analysis is completely different.
- Relative measurements against a standard samples allows relaxation on requirements of beam shape.
- Beam walk-off due to sample imperfections, tilt or distortions.
2. Material preparation and characterization techniques

2.6.2 Theory of Z-scan technique

Two techniques employed in Z-Scan studies are:

1. Open aperture Z-Scan
2. Closed aperture Z-Scan.

In the open aperture Z-scan measurements nonlinear absorption of the sample is evaluated. For example, if nonlinear absorption like two-photon absorption (TPA) is present, it is manifested in the measurements as a transmission minimum at the focal point [76,77]. On the other hand, if the sample is a saturable absorber, transmission increases with increase in incident intensity and results in a transmission maximum at the focal region. A straight-line Z-scan graph is obtained in the case of samples with linear absorption. In closed aperture Z-scan technique the transmitted light is measured through an aperture placed in the far field with respect to focal region[75, 78]. In this case, the transmitted light is sensitive to both nonlinear absorption and nonlinear refraction. In a closed aperture z-scan experiment, phase distortion suffered by the beam while propagating through the nonlinear medium is converted into corresponding amplitude variations. If transmitted light is measured without an aperture, the mode of measurement is referred to as open aperture z-scan and with an aperture it is closed aperture Z-scan [78]. Closed and open aperture Z-scan graphs are always normalized to linear transmittance i.e., transmittance at large values of $|z|$ and the real part and imaginary part of nonlinear susceptibility $\chi^{(3)}$ are obtained from the closed and open aperture z-scan methods respectively. Usually closed aperture Z-scan data is divided by open aperture data to cancel the effect of nonlinear absorption contained in the closed aperture measurements [78]. In a Z-scan measurement, it is assumed that the sample thickness is much less than Rayleighs range $z_0$ (diffraction length of the beam), defined as

$$z_0 = \frac{k\omega_0^2}{2} \quad (2.13)$$

where $k$ is the wave vector and $\omega_0$ is the beam waist radius given by

$$\omega_0 = \frac{f\lambda}{D} \quad (2.14)$$
2. Material preparation and characterization techniques

where $f$ is the focal length of the lens used, $\lambda$ is the wavelength of the source and $D$ is the beam radius at the lens. Z-scan technique is highly sensitive to the profile of the beam and also to the thickness of the sample. The sample thickness should always be kept less than the Rayleighs range for ensuring that the beam profile does not vary appreciably inside the sample. The sensitivity of this z-scan method is used to monitor nonlinear refraction at low irradiance levels, where a third order nonlinearity attributed to $n_2$ caused by bound electrons can be observed. At higher irradiance levels, the refraction caused by two photon absorption induced free charge carriers becomes significant. Thus the electronic Kerr effect will be dominant at low irradiance levels whereas TPA induced free carrier absorption (FCA) will be dominant at high irradiance levels. These are represented graphically in figure 2.6 where, nonlinear absorption like two-photon absorption (TPA) is present. It is manifested in the measurements as a transmission minimum at the focal point for reverse saturable absorption (RSA). On the other hand, if the sample is a saturable absorber, transmission increases with incident intensity and results in a transmission maximum at the focal region and the process is saturable absorption (SA). Both the curves are normalized to give a transmittance of one in the linear region (i.e. regions of large $|z|$). Sample positions are presented in units of $z/z_0$ where $z_0$ is the diffraction length.

**Open aperture Z-scan technique**

In the case of an open aperture z-scan, the transmitted light measured by the detector is sensitive only to the intensity variation. Therefore the phase variations of the beam can be neglected safely. The theory of Z-scan experiment outlined below is same as that given by M Sheik Bahae et.al. [75]. The intensity dependent nonlinear absorption coefficient $\alpha(I)$ can be written in terms of linear absorption coefficient $\alpha$ and TPA coefficient $\beta$ as [75]

$$\alpha(I) = \alpha + \beta(I) \quad (2.15)$$

The irradiance distribution at the exit surface of the sample can be written as

$$I_r(z, r, t) = \frac{I(z, r, t)e^{-\alpha_0 L}}{1 + q(z, r, t)} \quad (2.16)$$

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2. Material preparation and characterization techniques

\[ q(z, r, t) = \beta I(z, r, t) L_{\text{eff}} \]  \hspace{1cm} (2.17)

\[ L_{\text{eff}} = \frac{1 - e^{-\alpha l}}{\alpha} \]  \hspace{1cm} (2.18)

For a pulse of Gaussian temporal profile, equation (2.16) can be integrated to give the transmission as

\[ T(Z, S = 1) = \frac{1}{\sqrt{\pi q_0(z,0)}} \int_{-\infty}^{+\infty} \ln[1 + q_0(z,0)e^{-\tau^2}]d\tau \]  \hspace{1cm} (2.19)

Nonlinear absorption coefficient is obtained from fitting the experimental results to the equation (2.19). If \( q_0 < 1 \) equation can be simplified as

\[ T(z, S = 1) = \sum_{m=0}^{\infty} \frac{[-q_0(z,0)]^m}{(m + 1)^{3/2}} \]  \hspace{1cm} (2.20)

where \( m \) is an integer. The imaginary part of third order susceptibility (\( \text{Im} \chi^3 \)) determines the strength of the nonlinear absorption.

\[ \text{Im}(\chi^{(3)}) = \frac{n_0^2 c^2 \beta}{240\pi^2 \omega} (\text{esu}) \]  \hspace{1cm} (2.21)
where \( \lambda \) is the excitation wavelength, \( n_0 \) is the linear refractive index, 
\( \epsilon_0 \) is the permittivity of free space and \( c \) the velocity of light in vacuum.

Closed aperture z-scan technique

The basis of closed aperture z-scan is the self-refraction and self-phase modulation effects. The technique relies on the transmittance measurement of a nonlinear medium through a finite aperture in the far field as a function of the sample position \( z \) with respect to the focal plane using a single Gaussian beam in a tight focus geometry. Consider, for instance, a material with a negative nonlinear refraction and thickness smaller than the diffraction length

\[
z_0 = \frac{\pi \omega_0^2}{\lambda} \quad (2.22)
\]

of the focused beam being positioned at various points along the \( z \)-axis where

\[
k = \frac{2\pi}{\lambda} \quad (2.23)
\]
is the wave vector. This assumption implies that the sample acts as a thin lens of variable focal length due to the change in refractive index at each position (\( n = n_0 + n_2 I \)). Suppose that the sample is kept at a distance far away from the focus (-\( z \)). The irradiance is low and there is negligible nonlinear refraction. Hence the transmittance characteristics are linear. As the sample is moved close to the focus, the beam irradiance increases, leading to self-lensing in the sample. A negative self-lensing prior to focus will tend to collimate the beam, causing a beam narrowing at the aperture which results in an increase in the measured transmittance. As the scan in \( z \) direction continues and passes the focal plane, the sample which acts as a negative lens increases the defocusing effect thus increasing the beam divergence, leading to beam broadening at the aperture. Hence the transmittance decreases. Thus there is a null as the sample crosses the focal plane (\( z_0 \)). The z-scan is completed as the sample is moved away from focus (+\( z \)) such that the transmittance become linear since the irradiance is again low. A pre-focal transmittance maxima (peak) followed by a post focal transmittance minima (valley) is the z-scan signature of negative refraction nonlinearity. The curves for closed z-scan in the case of positive nonlinearity
and negative nonlinearity shows opposite effects as depicted in figure 2.7. This is the case of purely refractive nonlinearity where nonlinear absorption is absent. In the presence of multiphoton absorption, there is a suppression of the peak and enhancement of the valley, whereas the opposite effect occurs if there is a saturation of absorption [78]. In a cubic nonlinear medium the index of refraction (n) is expressed in terms of nonlinear index $n_2$ through

$$n = n_0 + n_2 I$$

(2.24)

where $n_0$ is the linear index of refraction, $n_2$ the intensity dependent refractive index and I denotes the irradiance of the laser beam within the sample [78]. Assume a TEM$_{00}$ beam of waist radius $\omega_0$ travelling in the $+z$ direction. E is the peak electric field and can be written as

$$E(r, z) = E_0 \frac{\omega_0}{\omega(z)} e^{-\frac{r^2}{\omega^2} + i \frac{4\pi}{\lambda} \frac{\nabla^2 |\omega(z)|^2}{2\omega(z)^2} e^{-i\psi(z)}$$

(2.25)
2. Material preparation and characterization techniques

\[ E(0, z) e^{-\frac{kz^2}{2}} \]

where \( \omega^2(z) = \omega_0^2 (1 + \frac{z^2}{z_0^2}) \) \hspace{1cm} (2.26)

is the beam radius and

\[ R(z) = z(1 + \frac{z^2}{z_0^2}) \] \hspace{1cm} (2.27)

is the radius of curvature of the wave front at \( z \).

\( E_0(t) \) denotes the radiation electric field at the focus and contains the temporal envelope of the laser pulse. The term \( e^{i\phi(z,t)} \) contains all the radially uniform phase variations. For calculating the radial phase variations \( \Delta \phi(r) \), the slowly varying envelope approximation (SVEA) is used and all other phase changes that are uniform in \( r \) are ignored. In the case of cubic nonlinearity and negligible nonlinear absorption, equation (2.28) and equation (2.29) can be solved to get the phase shift \( \Delta \phi \) at the exit of the sample and is given by

\[ \Delta \phi(z, r, t) = \Delta \phi(z, t) e^{i \frac{2r^2}{\omega^2(z)}} \] \hspace{1cm} (2.28)

with

\[ \Delta \phi(z, t) = \frac{\Delta \phi_0(t)}{(1 + \frac{z^2}{z_0^2})} \] \hspace{1cm} (2.29)

where \( \Delta \phi_0(t) \) is the on axis phase shift at the focus which is defined as

\[ \Delta \phi(t) = k \Delta n_0(t) L_{eff} = \frac{2\pi}{\lambda} n_2 I_0(t) L_{eff} \] \hspace{1cm} (2.30)

Where \( I_0(t) \) is the on axis irradiance at focus (i.e. at \( z=0 \)). The complex electric field exiting the sample \( E \) now contains the nonlinear phase distribution

\[ E(z, r, t) = E(z, r, t) e^{\frac{\alpha_l}{2} e^{i \Delta[z, r, t]}} \] \hspace{1cm} (2.31)

By virtue of Huygens principle and making use of Gaussian decomposition method one can show that

\[ \exp^{i \Delta[z, r, t]} = \sum_{k=0}^{\infty} \frac{[i \Delta \phi_0(z, r, t)]^m}{m!} e^{- \frac{2mr^2}{\omega^2}} \] \hspace{1cm} (2.32)
Each Gaussian beam can be simply propagated to the aperture plane and they will be resumed to reconstruct the beam. After including the initial beam curvature for the focused beam, the resultant electric field pattern at the aperture is

\[ E(r, t) = E(z, r = 0) e^{-\frac{\alpha l}{2}} \sum_{k=0}^{\infty} \frac{[i \Delta \phi_0(z, r, t)]^m}{m!} \frac{\omega_{m0}}{\omega_m} e^{\frac{-r^2}{\omega_m^2} + i \theta_m} \tag{2.33} \]

For a cubic nonlinearity, the peak and valley of the -scan transmittance can be calculated by solving the equation

\[ \frac{d}{dz} T(z, \Delta \phi_0) = 0 \tag{2.34} \]

Solution to this equation (2.34) yields the peak valley separation as

\[ \Delta \phi_0 = 1.7 z_0 \tag{2.35} \]

Then the peak valley transmittance change is

\[ \Delta T_{p-v} = 0.406 \Delta \phi_0 \tag{2.36} \]

for \( \Delta \phi_0 \leq \pi \), where \( S \) is the linear transmittance of the far field aperture. From the closed aperture Z-scan fit, \( \Delta \phi_0 \) can be obtained. Then the nonlinear refractive index \( n_2 \) can be determined using equation (2.30) and is given by

\[ n_2(\frac{m^2}{w}) = \frac{\lambda}{2\pi I_0 L_{eff}} \Delta \phi_0 \tag{2.37} \]

\[ n_2(e.s.u) = \frac{cn_0 \lambda}{40\pi 2\pi I_0 L_{eff}} \Delta \phi_0 \tag{2.38} \]

The \( n_2 \) is related to Re( \( \chi^{(3)} \)) by the relation

\[ Re\chi^{(3)} = \frac{n_0 n_2}{3\pi} (e.s.u) \tag{2.39} \]

From the real and imaginary part of \( \chi^{(3)} \), the modulus of third order nonlinear susceptibility can be found out as.

\[ |\chi^{(3)}| = \sqrt{[Re(\chi^{(3)})]^2 + [Im(\chi^{(3)})]^2} \tag{2.40} \]

The magnitude of \( \chi^{(3)} \) is significantly affected by the molecular orientation and it determines the strength of nonlinearity of the material.
Experimental methods

In the present investigation, we have employed the single-beam z-scan technique with nanosecond laser pulses to measure the nonlinear optical absorption properties of samples. A Q-switched Nd: YAG laser (Spectra Physics LAB-1760, 532 nm, 7 ns, 10 Hz) is used as the light source. The sample is moved in the direction of the light incidence near the focal spot of the lens which have a focal length of 20 cm. The beam waist $\omega_0$ is calculated to be $42.56 \mu$m. The Rayleigh length, $z_0 = \pi \omega_0^2 / \lambda$, is estimated to be $10.06 \text{ mm}$, much greater than the thickness of the sample, which is an essential prerequisite for Z-scan experiments. The transmitted beam energy, reference beam energy, and their ratio are measured simultaneously by an energy ratio meter (Rj7620, Laser Probe Corp.) having two identical pyroelectric detector heads (Rjp735). The experimental set-up is shown in figure 2.8.

![Diagram](image)

Figure 2.8: Experimental set-up of open/closed aperture Z-scan method.

The sample was moved along the z-axis by a motorized translational stage. The effect of fluctuations of laser power is eliminated by dividing the transmitted power by the power obtained at the reference detector[77]. Z-scan technique is highly sensitive to the profile of the beam and also to the thickness of the sample. Any deviation from Gaussian profile of the beam and also from thin sample approximation will give rise to erroneous results. For ensuring that the beam profile does not vary appreciably inside the sample, the sample thickness should always
be kept less than the Rayleighs range. The sensitivity of the Z-scan method is used to monitor nonlinear refraction at low irradiance levels, where a third order nonlinearity attributed to $n_2$ caused by bound electrons can be observed. At higher irradiance levels the refraction caused by two photon absorption induced free charge carriers becomes significant.

**Optical limiting**

To study the optical limiting property of the sample, the nonlinear transmission of the sample is measured as a function of input fluence. Optical power limiting is effected through the nonlinear optical processes of the sample. A schematic representation of transmission through an ideal optical limiter is shown in figure 2.9.

![Schematic representation of transmission through an ideal optical limiter.](image)

Figure 2.9: Schematic representation of transmission through an ideal optical limiter.

An important term in the optical limiting study is the optical limiting threshold. Optical limiters are essentially those systems which transmit light at low input fluence or intensities, but become opaque at high inputs. The optical limiting property is mainly found to be absorptive nonlinearity, which corresponds to the imaginary part of third order susceptibility [79, 80]. From the values of fluence at focus, the fluence values at other positions could be calculated using the standard equations for Gaussian beam waist. Such plots give a better comparison of the nonlinear absorption or transmission in the sample and are generated from z-scan trace. There are three basic requirements for a material to be good optical limiter: (1) An excited state absorption cross-section that exceeds the ground state absorption cross-section, (2) Fast response and
(3) High damage threshold. This phenomenon is exploited in passive optical power limiting to protect optical sensors, including human eye, from intense laser pulses.

2.7 Solar cells as the photonic material application of CdSe QDs

Traditional photovoltaic devices suffer from high costs of manufacturing and installation. Low-cost and high-performance solar cells are the main challenge to replace fossil for sustainable energy sources[81-83]. Semiconductor QD-sensitized solar cells (QDSSCs) have attracted considerable attention recently due to their cost-effective alternative to silicon-based photovoltaics, and have shown promising developments for the next generation of solar cells[83-88]. QDSSCs can be regarded as a derivative of dye-sensitized solar cells (DSSCs), which were first reported by O’Regan and Grätzel in 1991 [89]. The sensitizer commonly used in dye sensitized solar cells are organic dyes. To increase the efficiency, the light harvesting property in the visible region has to be increased, and have been made the focus on the development of high-performance sensitizers as quantum dots [89-92]. Narrow-band-gap semiconductor QDs, such as CdS [93, 94], CdSe[95, 96], PbS [97] and InAs [98] have been used as the photo sensitizers instead of organic dyes due to their versatile optical and electrical properties [99-101].

Background of three generations of solar cells

- Silicon solar cell

It is one of the most widely used solar cells which have efficiencies up to 24.4% reported for a commercial product[102]. But the main disadvantage of such solar cells are their relatively high cost for production. Even though amorphous silicon solar cell can be produced at lower temperature, this cell tends to degrade on longer duration of light exposure and hence efficiency decreases. Silicon solar cell can absorb a certain amount of energy greater than band gap and it can’t absorb entire solar spectra, which is required to knock out an electron. Since silicon is a very shiny material having very high reflectance an anti-reflective coating is needed to reduce reflection losses.
2. Material preparation and characterization techniques

- Polymer solar cells

These are flexible photovoltaic devices which are made of electron- donor and electron- acceptor materials. The main advantage of polymer solar cells over silicon cell-based devices are that they are being light weight [89,103], easily disposable and inexpensive. They acquire lower negative environmental impact, but are relatively unstable towards photochemical degradation. The photo induced charge transfer at polymer fullerene interfaces takes place within 15 fs [104]. The created charges have to be transported selectively to the contacts.

- Dye sensitized solar cells

DSSC [89, 105], a third generation photovoltaic cell, represents one of the most promising one that has been offered to challenge conventional silicon cells [106] over the past decade. These offer the lowest cost input and has an easy manufacturing process[107, 108]. The reported maximum overall power conversion efficiency is nearly 12.3%[109]. However, the main disadvantage of such types of cells is that, it absorbs light only in a particular region of solar spectrum.

- Quantum dot sensitized solar cell (QDSSC)

QDSSC is a third generation solar cell, with narrow band gap semiconductor quantum dots (QDs) as the sensitizer material used. The size-tunable band gap property of the QDs particularly makes this as attractive sensitzers. Several semiconductor QDs, such as PbS, CdS, CdSe and CdTe have been successfully verified as visible light sensitizers for Titanium Dioxide (TiO₂)-based working electrodes[95, 97, 110, 111]. In QDSCs the QDs generate excitons under illumination with sunlight and the excited electrons then are injected from the CB of QDs into the CB of TiO₂. At the same time, the photogenerated holes are donated to the electrolyte and thus the QDs are restored. The oxidation species of the electrolyte diffuses to the counter electrode and is reduced by the migrated electrons from the external circuit. The advantages of such types of solar cells are large QD extinction coefficients, the multiple exciton generation phenomenon and short excitonic path length which would lead to the enhancement of the conversion efficiency in QDSSCs[112].
2.7.1 Working principles of QDSSCs

The structure of a QDSSC consists of a wide-band-gap mesoporous oxide film (a photo electrode, such as the commonly used TiO$_2$ or ZnO), QDs (the sensitizer), an electrolyte, and a counter-electrode. During operation, photons are captured by QDs, yielding electron-hole pairs that are rapidly separated into electrons and holes at the interface between the nanocrystalline oxide and QDs. The electrons jump into the oxide film, and the holes are released by redox couples in the electrolyte for regeneration at the counter electrode. However, electron transport within the mesoporous TiO$_2$ film is slower than that of electron and hole transfers. So the recombination losses become a major factor in limiting the overall efficiency[81, 113]. Principle of operation of the QDSSCs is shown in figure 2.10.

![Figure 2.10: Principle of operation of the QDSSCs.](image)

Photo excitation of the sensitizer is followed by electron injection into the conduction band of the wide-band-gap semiconductor. The sensitizer is regenerated by the redox system, which itself is regenerated at the counter electrode (cathode) by electrons passing through the load.
Methods of preparation of QDSSC

The synthesis of QDs and their incorporation into the QDSSC photoactive electrode as sensitizers is carried out by several techniques:

- **Chemical Bath deposition**
  This technology is based on the slow controlled precipitation of the desired compound from its ions in a reaction bath solution [114].

- **Successive ionic layer adsorption reaction (SILAR)**
  SILAR method is mainly focused on the adsorption and reaction of the ions from the solutions and rinsing between every immersion with deionized water to avoid homogeneous precipitation in the solution[115].

- **Deposition of Ex-Situ-Grown QDs**
  In this method, mono disperse QDs are synthesized using organic capping ligands to control the shape and size of the QDs and are separated from the excess organic ligands and dissolved in an organic solvent; they are then ready to be attached to the TiO$_2$ electrodes with the help of a functional molecular linker [116, 117].

2.7.2 Factors influencing conversion efficiency of QDSSC

1. *Sensitizer materials*
   It is very important to select the appropriate materials to be not only cost-effective but also long lasting. The use of these quantum dots, which may produce more than one electron-hole pair per single absorbed photon (also known as multiple exciton generation (MEG)), is a promising solution to enhance power conversion efficiency. Furthermore, the creation of a type-II heterojunction greatly enhances charge separation, exciton concentration, quantum yield, and lifetime of hot electrons and therefore, the performance of QD-sensitized solar cells. [90, 118]

2. *The inherent triple junction of TiO$_2$/QDs/electrolyte*
   The mechanisms of charge-transfer processes occurring at the complex interfaces formed among the nanostructured Ti O$_2$, the sensitizing QDs, energy-level alignment among the materials constructing the triple junction and the aqueous electrolyte are the impor-
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tant factors determining the overall performance of QDSSCs[113, 119, 120].

3. Redox electrolyte
An efficient electrolyte solution, which is able to transfer electrons rapidly to regenerate the oxidized QD sensitizers while having good long-term stability under working conditions, constitutes one of the major challenges in the field of QDSSCs. It is because the $V_{oc}$ of a QDSSC is determined by the energy difference between the $TiO_2$ Fermi level and the electrolyte redox potential.

4. Counter electrode
Highly efficient counter electrode (CE), is able to catalyze the regeneration of the oxidized charge carrier ions, so as to maximize the performance of QDSSCs[121, 122].

Other main features of QDSSCs

- **Quantum confinement effect for QDSSCs**
QDs are extremely small semiconductor nanocrystals with a size comparable to the Bohr radius of an exciton [123]. For most semiconductors, the Bohr radius of an exciton is in the range of 1-10 nm. Due to the dimension effect, the behavior of electrons in QDs differs from that in the corresponding bulk material, which is called the quantum confinement effect. Because of the quantum confinement effect, the band gap energy ($E_g$) of QD increases with the decrease of particle size [124, 125]. So a range of optical absorption wavelengths of QD can be tuned by controlling the size of QD. Such a feature of QDs with tunable $E_g$ has led to their application in LEDs for full-color displays [126], and in QD-sensitized solar cells for the generation of optical absorption at desired wavelengths [127, 128].

- **The multiple electron generation effect for QDSSCs**
The multiple electron generation (MEG) effect is that two or more electron-hole pairs (excitons) are generated by one photon excitation, in contrast to the conventional case where one photon excitation can produce only a single exciton. In theory, the MEG effect requires a photon with energy at least twice that of the band gap.
of the QDs. The possible reasons for the MEG effect, which can be achieved easily in QDs, have been attributed to the following [129]:
1) the electron- hole ($e^- - h^+$) pairs are correlated and thus exist as excitons rather than free carriers.
2) The rate of hot electron and hole cooling can be slowed because of the formation of discrete electronic states.
3) Momentum is not a good quantum number, and thus the need to conserve crystal momentum is relaxed.
4) Auger processes are greatly enhanced because of the increased $e^- - h^+$ Coulomb interaction.
So the production of multiple exciton pairs in QDs can be enhanced in comparison with bulk semiconductors. So the utilization of high-energy photons to generate multiple excitons or capture hot electrons before their thermalization can boost the operational efficiency of QDSSC[130].

2.7.3 Experimental methods

Current-voltage (J-V) characteristics of the cells were examined using a standard solar irradiation of 1000W Xe arc lamp (Oriel 6269) as the light source. The J-V curves were measured with a digital multimeter. Input intensity was measured using light meter (METRAVI 1332). In all the cases, input intensity was in the range of 1-10 Klux [131, 132]. The performance of a QSSC is assessed by determining the parameters such as the short-circuit current density ($J_{sc}$), the open-circuit voltage ($V_{oc}$), the fill factor (FF), and the overall power conversion efficiency ($\eta$).

I-V curve of a typical solar cell in figure 2.11 shows the current drawn from a photovoltaic cell when illuminated.
The efficiency of a solar cell is defined as the ratio of maximum electrical power extracted to the incident radiation power illuminating the solar cell surface,

$$\eta = \frac{P_{max}}{P_{min}} = \frac{J_{sc}V_{oc}FF}{P_{in}}$$

The IPCE parameter of a QSSC is defined as the ratio of the number of electrons generated by light in the external circuit to the number of
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Figure 2.11: I-V curve of a typical solar cell.

incident photons, which can be expressed as

\[ IPCE\% = \frac{1240I_{sc}}{P_{in}\lambda} \]  

(2.42)

where \( P_{(in)} \) is the incident power and \( \lambda \) is the incident photon wavelength.

2.8 Random Lasers

Random Lasers (RL) differ from other conventional types of laser in that its cavity is formed not by mirrors but by multiple scattering in a disordered gain medium. In other words, a random laser is a non-conventional laser for which feedback mechanism is based on disorder-induced light scattering. The laser is random in the sense that the feedback for the photons generated in the dye is provided by the random multiple scattering of light from the particles. Fabry-Perot cavity is the
most common laser cavity made of two mirrors with one partially trans-
mitting, and are placed on either side of the gain medium. Amplification
of light occurs when it is bounced back and forth between two mirrors
through the gain medium. Light that remains in the cavity interferes
constructively after traveling a round trip between the mirrors and re-
turning to its original position. When the population inversion occurs or
the optical amplification is large enough to compensate the loss caused
by mirror leakage and material absorption etc., lasing oscillations occur
at cavity resonant frequencies. The laser light transmitted through the
partially reflecting mirror has well defined frequency, good direction-
ality and a high degree of coherence. However, in RL, inside the cavity
there are scatterers and the light can be scattered in other directions
as well[133-137]. This results in additional loss and increases the lasing
threshold. Therefore, in conventional laser cavities optical scattering is
considered detrimental and we have to minimize the amount of scatter-
ing. In random lasers a disordered medium that contains a number of
scattering centers scatter light many times before it escapes the gain
medium [138, 139]. Multiple scattering increases the dwell time of light,
enhancing light amplification. Light in the gain medium is trapped in
the absence of mirrors as the scattering can do the job on its own[139-
141]. Thus strong scattering in a disordered media can give rise to laser
operation and produces random laser. The word random has been used
to describe lasers that operate on the basis of these properties[142-145].

2.8.1 Classifications

The two classifications of random lasers:

1. **Random laser with incoherent feedback**
   In this case the feedback is used simply to return part of energy
   or photons to the gain medium, i.e. it is energy or intensity feed-
   back. Thus, in a laser with incoherent feedback or non resonant
   feedback the only resonant element is the amplification line of the
   gain medium. The mean frequency of emission does not depend
   on the dimensions of laser cavity but only on the center frequency
   of the amplification line[141].

2. **Random laser with coherent feedback**
   In the case of RL with coherent feedback, the light can return to
its origin position in the disordered medium from which it was scattered. The process of making closed loops by light is called recurrent light scattering. When the amplification of light along each of the loop exceeds the loss, lasing oscillation occurs and this loops can serve as cavity analogous to ring cavity of conventional laser. If scattering light forms several loops, disordered medium lases at some determined frequencies and we receive some modes of coherent random laser very similar to that of a conventional laser. The major difference of coherent random laser from that of the normal laser is that the output is multi directional and the direction of each individual mode is different in coherent random laser while directional output is obtained in conventional laser.

2.8.2 Some salient features of random laser are:

- The output of random laser modes are multi directional, which means the modes have spatial distribution.
- When the pump intensity increases the output of modes and the number of modes increases with spectral narrowing of the emission lines.
- There is a mode competition between the random laser modes that results in the photon hopping effect, i.e. the hop of photon from one mode to the other modes and the field interaction effect between side modes.

2.8.3 Experimental methods

A Q-switched Nd: YAG laser (Spectra Physics LAB-1760, 532 nm, 7 ns, 10 Hz) emitting pulses of 7 ns duration at 532 nm and 355 nm, at a repetition rate of 10 Hz is used as the light source. A cylindrical lens is used to focus the beam through the filter into the sample kept in a cuvette of 1 mm thickness. To collect the output a monochromatic-CCD system (Spectra Pro) with a resolution of 0.03 nm is used. The experimental setup for random laser study is shown in figure 2.12.
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![Diagram of experimental setup](image)

Figure 2.12: The experimental setup is shown with Nd-YAG Laser, L- cylindrical lens, F - filter, S- sample in cuvette, CCD spectrometer.

### 2.8.4 Applications of random lasers

- Lasing in a wide spectral regime from ultra-short wave (γ-ray, X-ray) to optical and radio waves obtained with random lasers and the construction of lasing is certainly cheaper and easier than conventional laser.

- Moreover multidirectional output of a random laser can be used in displays because a thin layer of random medium doped with emitter can be used to coat an arbitrarily shaped display panel.

- In the medical area, the random laser has potential application in photo dynamic therapy and tumor detection.

- The micro random laser may play the crucial role of an active element or miniature light source in integrated photonic circuit.

- It is possible to monitor the flow of liquids by adding a small number of nanoparticle clusters to the liquid and detecting their random laser emission over a large flow distance.

- Fast switching on and off of random laser can be used to create high speed display[142, 146].
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2.9 Conclusion

- Preparation methods of the samples are discussed briefly along with the basic principle of microwave and reflux methods.
- Structural characterization methods including XRD, TEM, SEM, DLS and FTIR techniques are discussed.
- Linear optical characterization methods like U-V visible absorption and fluorescence methods have been discussed.
- Thermo-optic characterization methods - Thermal lens and Photo acoustic methods have been explained along with the basic theory.
- Nonlinear-optical studies using Z-scan methods - open and closed aperture are discussed along with the theory.
- Applications of the nanophotonic materials in the field of solar cell and random laser are discussed.

2.10 References

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