CHAPTER II

CHARACTERIZATION TECHNIQUES

The nanoparticles can be characterized by various techniques, which provide important information for the understanding of their optical, morphological and structural properties. This chapter gives an introduction to techniques like UV-visible absorption spectroscopy, photoluminescence spectroscopy, Fourier transform infrared spectroscopy, surface enhanced Raman spectroscopy, nonlinear optical transmittance measurement using Z-scan, transmission electron microscopy, energy dispersive X-ray analysis and X-ray diffraction technique.

2.1 Introduction

The properties and improved performance exhibited by nanomaterials are strongly dependent on their composition, size, surface structure and interparticle compositions. Hence, characterization of these properties is of immense importance in the development of nanomaterials and in understanding structure-function relationship. This requires the use of a range of analytical tools including spectroscopic and microscopic methods suitable for the investigation of nanostructures. The characterization techniques used in the present investigations are discussed in this chapter.
2.2 UV-visible absorption spectroscopy

Ultraviolet and visible (UV-vis) absorption spectroscopy is the measurement of the attenuation of a beam of light after it passes through a sample or after reflection from a sample surface. Absorption measurements can be at a single wavelength or over an extended spectral range. Ultraviolet-visible (UV-vis) spectroscopy is widely utilized to quantitatively characterize organic and inorganic nanosized molecules. It deals with the study of electronic transitions between orbitals or bands of atoms, ions or molecules in gaseous, liquid and solid state. A sample is irradiated with electromagnetic waves in the ultraviolet and visible ranges and the absorbed light is analyzed through the resulting spectrum. It can be employed to identify the constituents of a substance, determine their concentrations, and to identify functional groups in molecules. Size dependent properties can be observed in a UV-vis spectrum, particularly in the nano and atomic scales. These include peak broadening and shifts in the absorption wavelength.

The schematic representation of a typical UV-vis spectrometer is shown in the figure 2.1. The functioning of this instrument is relatively straight-forward. A beam of light from a visible and/or UV light source is separated into its component wavelengths by a prism or diffraction grating. Each monochromatic (single wavelength) beam in turn is split into two equal intensity beams by a half-mirrored device. One beam, the sample beam, passes through a small transparent container (cuvette) containing a solution of the compound being studied in a transparent solvent. The other beam, the reference beam, passes through an identical cuvette containing only the solvent. The intensities of these light beams are then measured by electronic detectors and compared. The intensity of the reference beam, which should have suffered little or no light absorption, is defined as $I_0$. The intensity of the sample beam is defined as $I$. Over a short period of time, the spectrometer automatically scans all the component wavelengths in the manner described. The ultraviolet (UV) region scanned is normally from 200 to 400 nm, and the visible portion is from 400 to 800 nm.

If the sample compound does not absorb light of a given wavelength, $I = I_0$. However, if the sample compound absorbs light then $I$ is less than $I_0$, and this difference may be plotted on a graph versus wavelength. Absorption may be presented as
transmittance \( (T = I/I_0) \) or absorbance \( (A = \log I/I_0) \). If no absorption has occurred, \( T = 1.0 \) and \( A = 0 \). The wavelength of maximum absorbance is a characteristic value, designated as \( \lambda_{\text{max}} \). Different compounds may have different absorption maxima and absorbance. Intensely absorbing compounds must be examined in dilute solution, so that significant light energy is received by the detector, and this requires the use of completely transparent (non-absorbing) solvents. Since the absorbance of a sample will be proportional to its molar concentration in the sample cuvette, a corrected absorption value known as the molar absorptivity is used when comparing the spectra of different compounds.

This is defined as: Molar Absorptivity, \( \varepsilon = \frac{A}{cl} \)  

(2.1)

where \( A \) is the absorbance, \( c \) is the sample concentration in moles/liter and \( l \) is the length of light path through the cuvette in cm (Alford et al., 2007).

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Figure 2.1 Schematic representation of a dual beam UV-visible spectrophotometer.

In the present study UV-vis spectra were recorded using Jasco V-550 UV-vis and Cary 5000 UV-vis-NIR spectrophotometer.
2.3 Photoluminescence spectroscopy

Photoluminescence spectroscopy is a contact less, nondestructive method of probing the electronic structure of materials. Photoluminescence (PL) is the spontaneous emission of light from a material under optical excitation. PL depends on the nature of the optical excitation. The excitation energy selects the initial photoexcited state and governs the penetration depth of the incident light. When light of sufficient energy is incident on a material, photons are absorbed and electronic excitations are created. Eventually, these excitations relax and the electrons return to the ground state. If radiative relaxation occurs, the emitted light is called PL. The energy of the emitted light (photoluminescence) relates to the difference in energy levels between the two electron states involved in the transition between the excited state and the equilibrium state. This light can be collected and analyzed to yield a wealth of information about the photoexcited material. The PL spectrum provides the transition energies, which can be used to determine electronic energy levels. The PL intensity gives a measure of the relative rates of radiative and nonradiative recombination. Electromagnetic radiation in the UV and visible ranges is utilized in PL spectroscopy. PL emission properties of the samples are characterized by intensity, emission wavelength, bandwidth of the emission peak and the emission stability. As the dimensions are reduced to the nanoscale, PL emission properties can change, in particular a size dependent shift in the emission wavelength can be observed. PL spectroscopy can be utilized to study material properties such as band gap, recombination mechanisms and impurity levels.

Figure 2.2 shows a schematic representation of a general purpose spectrofluorometer. This instrument uses a Xenon lamp as a source of exciting light. The instrument shown is equipped with monochromators to select both the excitation and emission wavelengths. The excitation monochromator in this schematic diagram contains two gratings which decreases stray light, that is, light with wavelengths different from the chosen one. In addition, these monochromators use concave gratings, produced by holographic means to further decrease stray light. Both monochromators are motorized to allow automatic scanning of wavelength. The fluorescence is detected with photomultiplier tubes and quantified with the appropriate electronic devices. The
output is usually presented in graphical form and stored digitally. The instrument also shows the components of the optical module that surrounds the sample holder. Shutters are provided to eliminate the exciting light or to close off the emission channel. A beam splitter is provided in the excitation light path. This splitter reflects part of the excitation light to a reference cell, which generally contains a stable reference fluorophore. The beam splitter consists of a thin piece of clear quartz, which reflects about 4% of the incident light. The intensity from the standard solution is typically isolated with a bandpass filter and is proportional to the intensity of the exciting light. Changes in the intensity of the arc lamp may be corrected for by division of the intensity from the sample by that of the reference fluorophore. Polarizers are present in both the excitation and emission light paths. The polarizers are removable and accurate measurement of fluorescence anisotropies requires accurate angular positioning of the polarizers. The polarizer mounts must be accurately indexed to determine the angular orientation. The PL emission intensities and wavelengths are dependent on particle size. Hence, PL spectroscopy directly enables particle size effects, in particular those in nanoscale, to be observed and quantified (Lakowicz 2006).

Figure 2.2 Schematic representation of a spectrofluorophotometer.
In the present work, photoluminescence measurements are done using Flurolog III spectrofluorophotometer.

### 2.4 Fourier transform infrared spectroscopy

Fourier transform infrared spectroscopy (FTIR) spectroscopy is the study of the interaction of infrared (IR) radiation with matter. It is an analytical technique used to identify organic and inorganic materials. This technique measures the absorption of infrared radiation by the sample material versus wavelength. When a material is irradiated with infrared radiation, absorbed IR radiation usually excites molecules into a higher vibrational state. The wavelength of light absorbed by a particular molecule is a function of the energy difference between the at-rest and excited vibrational states. The wavelengths that are absorbed by the sample are characteristic of its molecular structure.

Schematic diagram showing working of FTIR spectrometer is given in figure 2.3. There are three basic spectrometer components in an FTIR system: radiation source, interferometer and detector. The interferometer is used to differentiate and measure the absorption component frequencies. The interferometer divides radiant beams and generates an optical path difference between the beams. Further it recombines them for producing repetitive interference signals measured as a function of optical path difference by a detector. The interferometer produces interference signals, which contain infrared spectral information generated after passing through a sample. When IR beam is directed through the sample, the amplitude of set of waves are reduced by absorption if the frequency of set of waves is same as one of the characteristics frequencies of the sample. The interferogram is the record of the interference signals recorded in time domain. It contains information over the entire IR region to which the detector is responsive. A mathematical operation known as Fourier transformation converts the interferogram to the frequency domain spectrum showing intensity versus frequency or wave number (Zadeh et al., 2008).
Figure 2.3 Schematic diagram showing the working of FTIR spectrometer.

FTIR measurements in the present work were carried out using Jasco 6300 FTIR spectrophotometer.

2.5 Surface enhanced Raman spectroscopy

Surface enhanced Raman spectroscopy (SERS) is a vibrational spectroscopy that is able to identify analyte substances by their vibrational bands and is useful when identification of the analyte is important. SERS is both a selective and a sensitive method. The instrument includes a laser for excitation, a spectrograph and a detector for recording the spectra obtained. It can be a very sensitive spectroscopy that allows the detection of organic molecules adsorbed on noble metal surfaces at submicro molar concentration. Although now a widely accepted and utilized technique, the first SERS experiment was performed in 1974. The initial discovery by Fleischmann reported very intense spectra for pyridine on a roughened silver electrode. The two phenomena believed to be responsible for SERS are large increases in the electric field near the surface (electromagnetic effect) and specific adsorbate-surface interactions (chemical effect). The electromagnetic mechanism takes place only when the localized surface plasmons on the metal get excited. These localized surface plasmons are excited when the incident light strikes the metal surfaces. When the plasmon frequency is in
resonance with the radiation, the field enhancement is seen to be the greatest. Scattering of light takes place when the plasmon oscillations are perpendicular to the metal surface. This effect is strongest where the particle has the highest curvature. As a result, the magnitude of SERS enhancement is highly affected by the adsorption of the analyte on the long or narrow axis of an ellipsoid or spheroid shaped metal particle.

Of the two mechanisms, the chemical effect is believed to contribute only one or two orders of magnitude towards the surface enhancement. The molecule adsorbed onto the roughened surface of the substrate interacts with the surface of the metal particles. Due to this interaction, metal-adsorbate complexes are formed. These complexes produce charge-transfer intermediates that have higher Raman scattering cross sections than the analyte that is not adsorbed on the surface. Substrates can include a range of materials and structures. The roughness of the surface is important for large surface enhancements for molecules adsorbed at noble metal surfaces.

As Raman scattering is governed by the relationship $\mu = E\alpha$, then SERS must involve an increase in either or both of the terms 'E', amplitude of the electric field and '\(\alpha\)', the molecular polarizability. The electromagnetic theory essentially addresses the enhancement of E, and the charge transfer model is concerned with the enhancement of '\(\alpha\)'. One common feature between these two theories is that both require surface roughness for spectral enhancement to occur.

**Raman signal enhancement**

In order to estimate the SERS enhancement, the intensities of the SERS signal are compared with that of the normal Raman intensities. It is the ratio of the Raman intensities normalized by the analyte concentration in samples with and without the presence of colloids.

$$E_{\text{SERS}} = \frac{I_{\text{SERS}}}{I_{\text{NORMAL}}} C_{\text{SERS}}$$

(2.2)

where $E_{\text{SERS}}$ is the Raman signal enhancement

$C_{\text{SERS}}$ is the concentration of the analyte solution with gold/silver colloids (molarity)
$C_{NORMAL}$ is the concentration of analyte in solution without any gold/silver colloid (molarity)

$I_{SERS}$ is the SERS intensity (counts)

$I_{NORMAL}$ is the Raman intensity (counts)

Figure 2.4 shows the schematic representation of micro Raman spectrometer. The micro Raman spectrometer combines both the aspects of microscope and the Raman spectrometer. It is a fully integrated instrument that can do Raman spectroscopy and digital imaging of microscopic samples. The Raman spectrometer portion of the micro Raman spectrometer is an optical instrument for measuring the intensity of light relative to its Stokes shift from the wavelength of the exciting laser light. A beam of light collected from the sample, enters the device and is separated into its Stokes shifted frequencies by a diffraction grating. The separated light is then focussed onto a CCD array detector where the intensity of each frequency is then measured by an individual pixel on the array. The CCD is then read off to a computer and the result is a spectrum which displays the intensity of the inelastically scattered light in wavenumbers relative to the wavelength of the exciting laser. The greatest advantage of micro Raman spectroscopy are its high resolution, the simplicity of the equipment set up and the short time required for obtaining data (Eric et al., 2009).
In the present study the SERS spectra were collected with a Renishaw invia micro Raman spectroscopy system with 785 nm and 514 nm laser as excitation source. The laser beam was focused on the samples through a 20X objective and the Raman signals were collected through the same objective in the back scattering geometry. The laser power used was 50 mW and the acquisition time was 30 s. The SERS spectra were also measured using FT Raman Bruker RFS100/S spectroscopy system with 1064 nm Nd:YAG as excitation source. The laser power used was 200 mW with a resolution of 4 cm\(^{-1}\). The acquisition time used was 30 s. Horiba JY microRaman spectroscopy system employed with 514 nm laser as excitation source was also employed in the present study.

### 2.6 Nonlinear optical transmission

Depending on the characteristic response of a medium to the frequency of light, the transmission of light gets affected by the scattering, refraction or absorption by the medium. For instance, when the intensity of the input light is such that the corresponding electric field is sufficient to evoke the otherwise small nonlinear terms in the dipole oscillation, it modifies the properties of the medium, affecting light transmission. The change in transmittance of a medium as a function of the input light intensity or fluence is referred to as nonlinear light absorption or nonlinear light transmission. At sufficiently high intensities, the probability of an absorber absorbing more than one photon before relaxing to the ground state can be enhanced. A few major mechanisms that control nonlinear light transmission are saturable absorption, two photon absorption (2PA), three photon absorption (3PA), reverse saturable absorption, free carrier absorption and nonlinear scattering.

#### 2.6.1 Saturable absorption

Saturable absorption is a property of materials where the absorption of light decreases with increasing light intensity. At sufficiently high incident light intensity, atoms or molecules in the ground state of a saturable absorber material become excited into an upper energy state at such a rate that there is insufficient time for them to decay back to the ground state before the ground state becomes depleted, and the absorption
subsequently saturates. A simple kinetic model can often be used when the saturation is considered in terms of depletion of the ground state concentration. Thus, under the steady state,

\[ \frac{dN}{dt} = \frac{\sigma I}{h\nu} (N_g - N) - \frac{N}{\tau} = 0 \]  

(2.3)

where \( N \) is the concentration of excited state molecules, \( N_g \) is the undepleted ground state concentration, \( \sigma \) is the absorption cross section, \( h\nu \) is the photon energy, and \( \tau \) is the lifetime of the excited state population. Assuming that the absorption coefficient \( \alpha \) is proportional to the ground state population, \( \alpha = \sigma (N_g - N) \), the equation describing the saturation,

\[ \alpha = \alpha_0 \frac{1}{1 + \left( \frac{\tau \sigma I}{h\nu} \right)} = \alpha_0 \frac{1}{1 + \left( \frac{I}{I_s} \right)} \]  

(2.4)

where \( I_s = h\nu/(\sigma \tau) \) is the saturation intensity and \( \alpha_0 = \sigma N_g \) is the linear absorption coefficient. The case described by the above equation is often referred to as homogeneous saturation.

In the case of a two-level system with inhomogeneously broadened states and hole burning, it has been found that the saturation can be described by,

\[ \alpha = \alpha_0 \frac{1}{\left( 1 + \left( \frac{I}{I_s} \right)^{0.5} \right)} \]  

(2.5)

The main applications of saturable absorbers are in passive mode locking and Q-switching of lasers, i.e., in the generation of short pulses. The key parameters for a saturable absorber are its wavelength range (where it absorbs), its dynamic response (recovery time), and its saturation intensity and fluence (at what intensity or pulse energy it saturates). Saturable absorbers are also useful for purposes of nonlinear filtering.
outside laser resonators, e.g., cleaning up pulse shapes, and optical signal processing (Siegman 1986).

2.6.2 Two-photon absorption (2PA)

The process of the transition of a system from the ground state to a higher level by the simultaneous absorption of two photons from an incident radiation field is termed two-photon absorption. Two photons of frequency $\omega$ of the incident field are simultaneously absorbed by the system to make the transition to a state that is approximately resonant at $2\omega$. A schematic representation of two-photon absorption can be found in figure 2.5.

The intermediate level being virtual, the two photons should be simultaneously absorbed making the process sensitive to the instantaneous optical intensity of the incident radiation.

![Figure 2.5 Schematic representation of two-photon absorption.](image)

The two-photon absorption process is proportional to the square of the input intensity. The propagation of laser light through the system describing the optical loss is given by,

$$\frac{dl}{dz} = -\alpha I - \beta I^2$$

(2.6)
where $\alpha$ is the linear absorption coefficient (which can be very small) and $\beta$ the two-photon absorption coefficient (Hercher 1967).

Since the physical quantity that is measured is the transmitted energy in a typical light transmission measurement, the transmittance is conveniently defined as the ratio of the transmitted and incident energies. For a pulsed laser beam that is spatially and temporally Gaussian, the transmittance $T$ in the presence of two-photon absorption is given as,

$$T = \frac{(1-R)^2 \exp(-\alpha L)}{\sqrt{\pi q_0}} \int_{-\infty}^{\infty} \ln[1 + q_0 \exp(-\tau^2)] d\tau$$  \hspace{1cm} (2.7)

where $R$ is the Fresnel reflection at the interface of the material with air, $\alpha$ the linear absorption coefficient and $L$ the length of the medium. $q_0$ is given by,

$$q_0 = \beta(1-R)I_0L_{\text{eff}}$$  \hspace{1cm} (2.8)

where $I_0$ is the peak on-axis intensity incident on the material and $L_{\text{eff}}$ is the effective length of the medium given as,

$$L_{\text{eff}} = \frac{1-\exp(-\alpha L)}{\alpha}$$  \hspace{1cm} (2.9)

### 2.6.3 Three-photon absorption (3PA)

The process of the transition of a system from the ground state to a higher level by the simultaneous absorption of three photons from an incident radiation field is termed as three-photon absorption (3PA). The schematic representation is given in figure 2.6.
3PA is a fifth-order nonlinear process, and the propagation equation for a medium having significant three-photon absorption is given as,

$$\frac{dl}{dz} = -\alpha I - \gamma I^3$$

(2.10)

where \(\alpha\) is the linear absorption coefficient, which can be typically small, and \(\gamma\) is the three-photon absorption coefficient.

The transmittance of a system with three-photon absorption, when the incident laser is spatially and temporally Gaussian, is given as,

$$T = \frac{(1-R)^2 \exp(-\alpha L)}{\sqrt{\pi} p_0} \int_{-\infty}^{\infty} \ln[\sqrt{1 + p_0^2 \exp(-2\tau^2)} + p_0 \exp(-\tau^2)] d\tau$$

(2.11)

where \(p_0 = \sqrt{2\gamma(1-R)^2 l_0^2 L_{\text{eff}}^2}\), \(l_0\) is the peak on-axis intensity incident on the material and \(L_{\text{eff}}\) is the effective length in the medium given as,

$$L_{\text{eff}} = \frac{1 - \exp(-2\alpha L)}{2\alpha}$$

(2.12)

### 2.6.4 Reverse saturable absorption

Reverse saturable absorption (RSA) is a two-step, sequential one-photon absorption process as shown schematically in figure 2.7. In this case the medium has a resonant linear absorption for the incident laser beam, and some of the molecules in the
ground state are excited to an excited state 2. For a properly chosen medium, it is possible that the excited molecules make another transition from the excited state 2 to a higher excited state 3 via another one-photon absorption (Sutherland 2003).

![Figure 2.7 Schematic representation of reverse saturable absorption.]

The possibility of this process depends on the number of molecules \( N_2 \) at the first excited state 2, the incident intensity \( I \), and the excited state absorption cross section \( \sigma_{23} \). On the other hand \( N_2 \) is related to \( N_1 \) and \( I \) by the relation,

\[
N_2 \propto \sigma_{12} N_1 I
\]  

(2.13)

where \( \sigma_{12} \) is the cross-section of the transition from the ground state to state 2. As can be seen from this relation, the number of molecules in state 2 (\( N_2 \)) continuously grows with the incident intensity \( I \) and the one-photon sequential absorption from state 2 to state 3 becomes more significant, provided that the cross section \( \sigma_{23} \) of this transition is considerably larger than \( \sigma_{12} \). Under the steady-state condition, the intensity change of the laser beam in the nonlinear medium along its propagation direction can be expressed as,

\[
\frac{dI}{dz} = -\sigma_{12} (N_1 - N_2) I - \sigma_{23} N_2 I
\]  

(2.14)

In the simplest case, it can be assumed that \( N_1 \gg N_2, N_3 = 0 \), and \( N_1 = N_0 \), where \( N_0 \) is the number density of the absorbing molecules. Then, the above equation can be rewritten as,
where $b$ is a proportionality coefficient, and the linear absorption coefficient $\alpha_0$ and nonlinear absorption coefficient $\beta'$ are defined as,

$$\alpha_0 = \sigma_{12} N_0$$

(2.17)

$$\beta' = b\sigma_{12} \sigma_{23} N_0$$

(2.18)

### 2.6.5 Free carrier absorption

Once free carriers are generated by linear absorption in semiconductors, they may experience phonon-assisted absorption to higher-lying (lower-lying) states in the conduction (valence) band. This process is called free carrier absorption. In the weak absorption regime, the attenuation may be described by,

$$\frac{dl}{dz} = -\alpha l - \beta' l^2$$

(2.15)

or

$$\frac{dl}{dz} = -\alpha_0 l - \beta' l^2$$

(2.16)

where $N_c(I)$ is the intensity dependent carrier density, and $\sigma_c$ is the free carrier absorption cross-section. $\sigma_c$ is related to the electronic properties via the relation,

$$\sigma_c = \frac{e^2}{\varepsilon_0 n_0 c m^* \omega^2 \tau}$$

(2.20)

where $m^*$ is the effective carrier mass and $\tau$ is the free carrier life time (mean collision time). Note that it has the $1/\omega^2$ dependence of a high-frequency conductivity and thus is
most important for infrared radiation in semiconductors. The free carrier density is governed by a rate equation given by,

\[
\frac{\partial N_c}{\partial t} = \frac{\alpha I}{\hbar \omega} \frac{N_c}{\tau_c}
\]

(2.21)

where \( \tau_c \) is the free carrier relaxation time due to electron–hole recombination and carrier diffusion. When the incident pulse is short compared to the carrier relaxation time, the latter term may be neglected and these equations may be integrated over time to obtain the fluence attenuation equation,

\[
\frac{\partial F}{\partial z} = -\alpha \left( 1 + \frac{F}{2F_s} \right) F
\]

(2.22)

where \( F_s = \hbar \omega / \sigma_c \) is the saturation fluence. For excitation with a pulsed Gaussian beam, the transmittance is given by,

\[
T = \frac{(1-R)^2 \exp(-\alpha L)}{q} \ln(1+q)
\]

(2.23)

where \( q = (1-R)[1-\exp(-\alpha L)]F_0/2F_s \). The value of \( F_s \) can be found out from the appropriate theoretical fit to the experimental data, from which the free carrier cross section can be calculated (Close 1966).

2.6.6 Nonlinear scattering (Induced thermal scattering)

Optically induced scattering can also have an effect on the nonlinear transmission in a system. This is a common nonlinear phenomenon associated with nanomaterials. The scattering process can spread the incident light into a larger spatial dimension thereby reducing the intensity of the direct transmitted beam. There are three major mechanisms that are believed to be responsible for the nonlinear scattering of incident light in a system. The first possibility is the generation of solvent bubbles (in a liquid sample). In this case, the sample absorbs the incident photons and transfers the generated thermal energy to the surrounding solvent. The solvent in turn evaporates to form
bubbles. There will be a large refractive index discontinuity at the vapour–solvent interface, and hence the vapour bubbles scatter the incident light effectively. The scattering cross section increases significantly with increasing size of the vapour bubbles and it is an intensity-dependent quantity since the size of the gas bubbles is non-linearly related to the incident energy density. Since the evaporation time of typical solvents is generally of the order of nanoseconds, this process is more effective for excitation with nanosecond laser pulses. In some cases, the refractive index of the surrounding solvent or the interface between the particles and the surrounding liquid may vary due to the absorption of laser radiation and the subsequent thermal energy transfer. Such dielectric constituents with a refractive index discontinuity or mismatch, formed in the nanosecond excitation time scales, can play the role of scattering centers as well. The difference of this process with the first one is the absence of bubble formation. This type of a process is more likely to happen in samples dissolved in non-volatile solvents (Wang et al., 2009).

The third possibility is the direct ionization of the sample and the subsequent production of microplasmas in the focal region. The microplasmas formed will strongly scatter the input radiation from its normal transmission path, thereby resulting in a nonlinear decrease in the measured transmitted light. Especially for metal nanoparticles, if the wavelength of the incident beam is in the surface plasmon absorption band, strong photon absorption can make the particles form microplasma states, and hence serve as scattering centers. Compared with the long formation time of the other two processes, the sublimation of particles can be completed in the sub-nanosecond range, resulting in a faster nonlinear transmission response. However this process needs much higher incident intensity than solvent evaporation (Tutt et al., 1993).

2.6.7 Open aperture Z-scan technique

The open aperture Z-scan technique has become quite popular for nonlinear transmission measurements. In the open aperture Z-scan experiment, a laser beam is first focused using a lens. The direction of beam propagation is taken as the z-axis, and the focal point is considered as \( z = 0 \). The z value increases towards either side of the focal point, but the sign will be negative on one side and positive on the other (similar to a number line). The sample is now placed in the beam at a position (z) between the lens
and the focal point, and the transmitted laser energy is measured. Then the sample is moved in small steps towards the focus and beyond, and the transmission is measured at each step. At each of these positions the sample will experience different laser intensity, and the intensity will be a maximum at the focus. Thus the open aperture z-scan is essentially a sample transmission measurement, the data being continuously taken while the sample is slowly translated from a position before the focus to a position after the focus. A schematic of the open aperture z-scan setup is given in figure 2.8.

If a spatially Gaussian laser beam is used, then each z position will correspond to an input laser energy density (fluence) of 
\[ 4\ln(2)^{1/2}E_{\text{in}}/\pi^{3/2}\omega(z)^2 \]
where \( E_{\text{in}} \) is the input laser pulse energy, and \( \omega(z) \) is the beam radius. \( \omega(z) \) is given by 
\[ \omega(0)(1+(z/z_0)^2)^{1/2} \]
where \( \omega(0) \) is the beam radius at the focus and \( z_0 = \pi\omega(0)^2/\lambda \) is the Rayleigh range (diffraction length), where \( \lambda \) is the excitation wavelength. Thus from the open aperture z-scan data, it is possible to draw a graph between the input laser fluence and the sample transmission. The nature of this graph will reveal the absorptive nonlinearity of the system.

![Figure 2.8 Schematic representation of open aperture z-scan setup.](image)

In the present study, a plano-convex lens of 20 cm focal length was used to focus the laser beam. Samples were taken in a 1 mm glass cuvette (Hellma GmBH) and were loaded as such on a programmable linear translation stage. The input energy reaching the sample and the energy transmitted by the sample were measured using two pyroelectric...
energy probes (RjP 735, Laser Probe Inc.). The laser pulse-to-pulse energy fluctuations were generally less than +5% and were monitored by the reference energy probe. The interval between successive laser pulses was kept sufficiently large (about one second) to allow complete thermal relaxation of the excited sample between adjacent laser pulses. The energy meter outputs were digitized with the help of a digital storage oscilloscope, which was interfaced to a PC using the serial port (RS-232). The experiment was automated using a program written in LabView. The stepper motor was controlled through the parallel port of the PC using appropriate drivers developed in-house. The nonlinear scattering in the samples was measured with the help of a third photo detector (UDT 10 - photo diode), kept at an angle of about 45 degrees and 4 cm away from the front surface of the sample.

2.7 Transmission electron microscopy

Transmission electron microscopy (TEM) is an imaging technique whereby a beam of electrons is transmitted through a specimen, 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 sensor such as a CCD camera. It is capable of displaying magnified images typically with a magnification in the range of $10^3$ to $10^6$. The first practical transmission electron microscope was built by Albert Prebus and James Hiller at the University of Toronto in 1938 using concepts developed earlier by Max Knoll and Ernst Ruska. TEM is used to investigate the morphology, crystallographic structure, particle size distribution and composition of a specimen, either of biological or non-biological (inorganic, organic) origin, up to the atomic scale.

The schematic of a typical TEM is given in figure 2.9. It consists of (1) an electron gun, which emits a beam of monochromatic electrons as the illumination source, (2) a set of condenser lenses to focus the illumination onto the specimen, (3) an objective lens used to form the first image of the specimen, and (4) a series of magnifying lenses to create the final magnified image. The electron gun produces a beam of monochromatic electrons along the optical axis of microscope. An intense electron beam is required for imaging at high magnification. Electrons are emitted by heating a filament (thermionic
emission, tungsten or LaB$_6$ filament) or from an unheated filament that has an extremely high potential gradient placed across the filament (field emission, fine-tipped single-crystal tungsten). The passage of electrons through the TEM column requires an ultra-high vacuum in the column. This vacuum level minimizes the contamination that occurs when the beam interacts with the specimen. The sample and the photographic plates are introduced into the high vacuum through separate evacuated load locks without breaking the vacuum. The electron beam is focused into a thin, coherent beam with the use of the first and second condenser lenses. The first lens controls the beam-spot size and dictates the general size range of the final spot that illuminates the sample. The second lens controls the intensity and the size of the spot on the sample. A user-selectable, condenser aperture removes high-angle electrons (those far from the optic axis) and allows for a collimated beam down the optical axis.

Figure 2.9 Schematic representation of a typical TEM components.
The beam strikes the specimen, and a portion of the beam is transmitted through the sample and other parts of the beam are diffracted. The transmitted portion of the beam is focused by the objective lens into an image. The electron image is focused by adjusting the objective focal length. The objective aperture and selected area diffraction aperture can both restrict the beam. The objective aperture enhances image contrast by blocking out high-angle diffracted electrons. The selected area aperture enables the user to image the electron diffraction pattern from a specific portion of the TEM sample. The image is passed down the column through the intermediate and projector lenses. There the image of the sample is magnified onto the viewing screen. Upon selection of the appropriate control, the projector system magnifies the image of the electron diffraction pattern from the rear focal plane of the objective lens. It is the projection lens setting that defines the camera length. The electrons that form the image strike a fluorescent screen (typically coated with a fine grain ZnS). When the electrons strike the screen, fluorescence occurs and results in the formation of a visible image, allowing the user to see the image.

In the bright field (BF) mode of the TEM, an aperture is placed in the back focal plane of the objective lens, allowing only the transmitted or direct beam to pass. The diffracted beams are blocked. In this case, diffraction contrast contributes to image formation. Crystalline regions that are oriented so as to strongly diffract intensity away from the transmitted beam will appear dark. In the dark field (DF) images, a selected diffracted beam is allowed to pass through the objective aperture. The aperture blocks the direct beam. In contrast to direct beam, the diffracted beam has interacted strongly with the specimen, and very useful information is often present in DF images, e.g., about planar defects, stacking faults or particles. The TEM has the capability to create both electron microscope images (information in real space) and diffraction patterns (information in reciprocal space) for the same region by adjusting the strength of the magnetic lenses. By inserting a selected area aperture and using parallel incident beam illumination, selected area electron diffraction (SAED) pattern from an area as small as several hundreds to a few nm in diameter is obtained. In diffraction imaging, an image of the diffracted beams is brought into focus at the back focal plane of the objective lens. Once this real image is formed, it can be projected onto the viewing screen by the intermediate and projection lens system. For obtaining crystallography information about a specific area of the sample, SAED requires an intermediate aperture placed at the
first intermediate image focal plane to specify the area from which the diffraction image is acquired. A single crystal sample produces spot patterns associated with a specific zone axis for that crystal. Under diffraction conditions, polycrystalline samples give rise to ring patterns, which are the superposition of many single crystal patterns. Crystal structures can also be investigated by high resolution transmission electron microscopy (HRTEM) where the images are formed due to differences in phase of electron waves scattered through a thin specimen (Egerton 2005).

The morphology of the particles in the present study were determined using high resolution transmission electron microscopy (HRTEM) using JEOL 3010 and FEI TECNAI 30 G² S-TWIN equipped with selected area electron diffraction (SAED).

2.8 Energy dispersive X-ray analysis (EDX)

Energy-dispersive X-ray spectroscopy (EDS or EDX) is an analytical technique used for the elemental analysis or chemical characterization of a sample. It is based on the investigation of a sample through interactions between electromagnetic radiation and matter, analyzing X-rays emitted by the matter in response to being hit with charged particles. Its characterization capabilities are due in large part to the fundamental principle that each element has a unique atomic structure allowing X-rays that are characteristic of an elements atomic structure to be identified uniquely from one another. To stimulate the emission of characteristic X-rays from a specimen, a high-energy beam of charged particles such as electrons or protons or a beam of X-rays, is focused into the sample being studied. At rest, an atom within the sample contains ground state (or unexcited) electrons in discrete energy levels or electron shells bound to the nucleus. The incident beam may excite an electron in an inner shell, ejecting it from the shell while creating an electron hole where the electron was. An electron from an outer, higher-energy shell then fills the hole, and the difference in energy between the higher-energy shell and the lower energy shell may be released in the form of an X-ray. The number and energy of the X-rays emitted from a specimen can be measured by an energy-dispersive spectrometer. As the energy of the X-rays are characteristic of the difference in energy between the two shells, and of the atomic structure of the element

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from which they were emitted, this allows the elemental composition of the specimen to be measured (Alford 2007). The principle of EDX is given in figure 2.10.

![Figure 2.10 Principle of EDX.](image)

In the present study an energy-dispersive spectrometer attached to the TEM system FEI TECNAI 30 G² S-TWIN was used.

### 2.9 X-ray diffraction

X-ray diffraction (XRD) involves monitoring the diffraction of X-rays after they interact with the sample. It is a crystallographic technique used for identifying and quantifying various crystalline phases present in solid materials and powders. In XRD the crystal structure as well as the size of the grains and nanoparticles can be determined. When X-rays are directed at a regular crystalline sample, a proportion of them are diffracted to produce a pattern. From such a pattern the crystal phases can be identified by comparison to those of internationally recognized databases that contain reference patterns. From the diffraction patterns, the uniqueness of nanocrystal structure, phase
purity, degree of crystallinity and unit cell parameters of the nanocrystalline materials can be determined. X-ray diffraction technique is nondestructive and does not require elaborate sample preparation, which partly explains the wide use of XRD methods in material characterization. In crystallography, the solid to be characterized by XRD has a space lattice with an ordered three dimensional distribution of atoms. These atoms form a series of parallel planes separated by a distance \( d \), which varies according to the nature of the material. For any crystal, planes have their own specific \( d \)-spacing. When a monochromatic X-ray beam with wavelength \( \lambda \) is irradiated onto a crystalline material with spacing \( d \), at an angle \( \theta \), diffraction occurs only when the distance travelled by the rays reflected from successive planes differs by an integer number \( n \) of wavelengths to produce constructive interference. Such constructive interference patterns only occur when incident angles fulfill the Bragg condition such that \( n\lambda = 2dsin\theta \). Condition for constructive interference is given in figure 2.11.

![Figure 2.11 Condition for constructive interference.](image)

By varying the angle \( \theta \), the Bragg law condition is satisfied for different \( d \)-spacings in polycrystalline materials. Plotting the angular positions versus intensities produces a diffraction pattern, which is characteristic of the sample. When a mixture of different phases is present, the resultant diffractogram is a superposition of the individual patterns. In a typical XRD pattern, the diffracted intensities are plotted verses the detector angle \( 2\theta \). Each peak is then assigned a label indicating the spacing of a crystal plane. Bragg’s
law states the condition for sharp diffraction peaks arising from crystals which are perfectly ordered. Actual diffraction peaks have a finite width resulting from imperfections, either the irradiation source or the sample. As the crystallite dimensions enter the nanoscale the peaks broaden with decreasing crystal size. The widths of the diffraction peaks allow the determination of crystallite size. The size of the crystallites can be determined using Debye–Scherrer equation; \( D = \frac{k \lambda}{\beta \cos \theta} \), where \( D \) is the size of the nanocrystal, \( k \) is a constant which depends on the crystallite shape, \( \lambda \) = wavelength of X-rays, \( \beta \) is the full width at half maxima of the broadened peak (Cullity 1978).

In the present study the structure and crystallinity of the films were analyzed by X’per PRO diffractometer (PANalytical), operated with CuK\( \alpha \) radiation source (\( \lambda = 0.15406 \) nm, 40 kV, 30 mA). The phases were identified by comparing the data obtained with the JCPDS data.