Chapter 8

Summary and scope for future work
8.1. Summary

Development of nonlinear optical devices having ultrafast nonlinearity is a very relevant field of research which finds applications in optical limiting. The demand for protection of eyes of laser operators and various types of optical sensors attached to the laser optics systems from laser pulses has resulted in search for optical limiting devices. In order to prevent the accidental entrance of the laser pulses into the eyes, the laser operators must use goggles which are transparent at low intensity of light but non-transparent towards high intensity of light. Since the optical limiting devices are transparent at low intensity of light but non-transparent towards high intensity of light, they can be effectively used as a preventor of the laser pulses.

In the present study, we have succeeded in fabricating nanostructures based polymeric nonlinear optical limiting devices. The most striking character of our method is that the excellent compatibility between NPs and polymers is obtained via modifying the surface of the NPs to ensure the homogeneous distribution of NPs in the polymer matrix. The existence of the polymer network can stabilize the NPs, which act as cross-linking points. The structure of such NP/polymer composite network can stabilize the NPs for a long term, which is important for the protection of their function. The high device flexibility will render them to be actively used in any desired shapes. These superior optical limiting devices may be used as eye protection goggles or as protectors of sensors.
A completely automated Z-scan setup for the nonlinear optical characterization was fabricated in the laboratory. The automated setup made the data acquisition and data analysis quite easy. A better communication between the instruments and PC was achieved by the use of the LAB VIEW programming tools in conjunction with devices such as NI PCI 7332, UMI 7764. The micro step motion of the sample cell enabled to acquire very fast and error free data compared to manual data acquisition. The interfacing and automation saved lots of time and even could measure the full set of data in a few minutes.

The next step was the fabrication of the flexible nonlinear optical device having good mechanical strength based on metal and semiconductor nanostructures encapsulated polymeric optical limiting devices. All the devices gave comparatively good optical limiting characteristics and a few among them give good self defocusing type refractive nonlinearity.

ZnO nanoparticles in the present investigation were synthesized by room temperature wet chemical methods. The size of the quantum dots were tuned by varying the concentration of the NaOH in the precursor solution. The size of the nanoparticles was found to be increasing with increase in the concentration of the NaOH as observed from the broadening of the XRD spectra and blue shift in the absorption edge in the UV-visible absorption spectra and then confirmed by the TEM analysis. The nonlinear optical studies show an optical limiting type absorptive nonlinearity and self defocusing type refractive nonlinearity. The nonlinear absorption was due to the two photon absorption in ZnO. The values of
nonlinear absorption coefficient $\beta$ as well as refractive index $n_2$ are found to be increasing with increase in particle size. The enhancement in the $n_2$ and $\beta$ is attributed to the enhanced oscillator strength in bigger nanoparticles. The ZnO nanoparticles are very stable inside the polymer matrix and will work efficiently for long term optical applications.

ZnS:Cu nanoparticles were prepared by chemical route in aqueous media. ZnS nanoparticles with the sphalerite structure were formed as observed from the XRD pattern and as confirmed from the TEM characterization. The ZnS:Cu nanoparticles displayed a regular increase in the band gap with increase in the copper doping concentration. Copper doped ZnS samples showed green luminescence which resulted from the transition between the sulphur vacancy donor levels and the copper acceptor levels. These ZnS:Cu nanoparticles were embedded in PVA matrix and the Z-scan analysis performed with Ti-Sapphire laser (800nm with pulse width of 100 fs) showed a reduction in transmission which was due to three photon absorption process occurring in multiple steps. An increase in the value of the nonlinear absorption coefficient with increase in the doping concentration was found which was due to the increase in the density of intermediate defect levels which played a supplementary role in the enhancement of the rate of multi step transition enhanced three photon absorption. These Cu doped ZnS nanoparticles in the polymer matrix could be used as an effective sample material for optical limiting device fabrications at slightly different laser wavelengths.
Nanoparticles of gold and silver were synthesized by LP-PLA in water media by varying the laser ablation fluence using second harmonic of Nd:YAG laser at 532nm. The size of the Au and Ag nanoclusters was found to be increasing with increase in the ablation fluence as observed from the UV-visible absorption spectra and TEM studies. The silver nanoparticles prepared at higher laser fluence were found to be less stable as compared to those prepared at lower laser fluence. The optical limiting efficiency of Au and Ag nanoparticles increased with decrease in the nanoparticles size which is due to the size dependent enhancement in the oscillator strength in the nanoparticles associated with the intra band contribution to the nonlinear absorption. The Au nanoparticles showed self focusing type refractive nonlinearity. The lower sized Au and Ag nanoparticles showing maximum nonlinearity were embedded in PVA matrix and casted into thin film having approximate thickness of 1µm by spin coating. Such nanoparticles embedded polymeric films showing very good optical limiting were used for fabricating flexible limiting device having good mechanical strength. Also in the case of silver nanoparticles, it was observed that when the duration of ablation was increased keeping the incident laser fluence fixed, the size of the nanoparticles was decreased which was attributed to the efficient radiation absorption by the previously ablated nanoparticles.

Gold nanoparticles were successfully attached on to the surface of MWCNT's. Synthesis and attachment of homogenously distributed Au-NPs on to the surface of CNTs, especially through a simple and cost-effective route without using any surfactant or polyelectrolyte to functionalize the
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CNT's was introduced. Au nanoparticles of different concentrations were synthesized by LP-PLA in deionised water using third harmonic of Nd:YAG laser source by varying the duration of ablation keeping the laser fluence constant and minimum. A low value of laser fluence was maintained to obtain smallest sized nanoparticles. The attachment was achieved by the addition of a small amount of ethanol into MWCNT added Au colloidal solution in order to decrease the interfacial tension between the hydrophobic MWCNT and water. Au-NPs were distributed uniformly on the walls of MWCNTs as found from the XRD and as confirmed from the TEM studies. Au-nanoparticles attached MWCNTs were embedded in PVA films. The films showed optical limiting nature, which was attributed to the nonlinear scattering in MWCNTs. An increase in the optical limiting property was observed with increasing the concentration of Au-NPs on the surface of MWCNTs which was due to the additional contribution from the nonlinear absorption caused by the SPA processes at 532nm in Au-NPs. Thus highly stable and flexible optical limiting device was fabricated using MWCNTs with attached Au-NPs in a polymer matrix.

8.2. Scope for future studies

8.2.1. Fabrication of eye protection goggles and sensor protecting boxes based on in-situ polymerized nanoparticles

As regarding the protection of sensors attached to the lasers, sensors should be kept in boxes made up of these optical limiting materials. In a device and industrial point of view, we should use materials with high
mechanical strength and ease of flexibility so that they can be moulded easily into any shape needed for the application. The development of optical limiters based on metal and semiconductor nanoparticles incorporated into the polymer matrix via insitu polymerization can improve the performance of the optical limiter. The insitu polymerization will diminish the minute chance of agglomeration inside the polymer matrix and loss of transparency and thus keeps the stability and functionality of the device well, even though the chance of agglomeration is not relevant for ultrafine nanoparticles below 10nm. Subsequently they are molded into desired shape for making laser preventing goggles and sensor protecting boxes. For this purpose we can prepare the nanoparticles of gold [1], silver [2] and ZnO [3] embedded in the polymer matrix through in-situ polymerization tools.

8.2.2. Luminescent ZnS quantum dots for the cancer cell attachment

One of the most exciting applications of nanotechnology in medicine is the use of luminescent quantum dots (QDs) for bio-medical imaging [4]. Further, quantum dots can be made very effective for targeted imaging by attaching them with disease specific ligands such as proteins, vitamins, monoclonal antibodies and peptides. Despite the fact that there have been significant developments in anti cancer technology such as radiotherapy, chemotherapy and hormone therapy, cancer still remains as one of the leading cause of death all over the world. In all these methods, normal cells are also destroyed along with the tumor cells since the cell killing is proportional to the region of exposure [5, 6]. This lack of tumor
specific treatment is one of the main hurdles of the current cancer treatment technology.

An ideal solution to these limitations is to deliver a biologically effective concentration of anti-cancer agents with high specificity. Luminescent quantum dot (QD) based on doped zinc sulfide (ZnS), conjugated with a cancer-targeting ligand, folic acid (FA), is presented as a promising bio-friendly system for targeted cancer imaging [7]. Folic acid has specific attachment to the cancer cells due to the presence of the Folate Receptor (FR) alpha protein [8], which is more prominent in the cancer cells such as FR positive human nasopharyngeal epidermoid carcinoma, KB cells as compared to the normal cells. Folate Receptor alpha protein is encoded by the FOLR1 gene [9]. The FR, a tumor associated glycosyl phosphatidylinositol anchored protein, can actively internalize bound folates and folate conjugated compounds via receptor-mediated endocytosis [10, 11]. The protein encoded by this gene is a member of the Folate Receptor (FOLR) family. The members of this family have a special affinity to folic acid and for several reduced folic acid derivatives.

Luminescent centers in doped QDs could be excited using bio-friendly visible light >400 nm by directly populating the dopant centers, leading to bright emission. Specific attachment of Folic acid attached ZnS quantum dots synthesized through wet-chemical route to the FR+ cancer cell line has been reported earlier [7]. However, these chemical methods produce byproducts, which contaminate and affect the stability of the nanoparticles and as regarding biological applications only contamination
free nanoparticles have real relevance. It is very tedious to synthesise extra stable nanoparticles with extremely small size using the chemical route. In therapeutic applications of the nanoparticles, kidney can filter only those nanoparticles with extremely small size after the specified cancer targeting is achieved. In this situation the safe and practically simple methods like laser ablation of solid targets [12] has been introduced which produces homogenous dispersion of extremely small sized nanoparticles devoid of impurities with maximum stability in a transparent aqueous media.

Luminescent ZnS:Cu nanoparticles can be prepared by liquid phase pulsed laser ablation technique (LP-PLA) in water media. As synthesised nanoparticles can be attached to folic acid after the preparation and these ZnS:Cu nanoparticles will show green luminescence under UV illumination. The cytotoxicity of bare and FA conjugated QDs can be tested. The attachment of the nanoparticles to the cancer cells may be checked by fluorescence microscopy where in ZnS:Cu nanoparticles will show specific luminescence in the green region. Hence it will be easy for tracing out the cancer cells from the normal cells, and thus the drug delivery becomes quite easy thereby the cancer cells may be destroyed without affecting the normal cells.
8.3. References


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Introduction to nanostructured materials

Figure 1.1. Wurtzite Crystal structure of ZnO.

It is predicted that the gas sensing, photon to electron conversion efficiency and photonic performance would be enhanced by reducing the dimensions of ZnO because of the surface area increase and the quantum confinement effect. Therefore, extensive research on the fabrication of ZnO nanostructures, such as nanowires, nanobelts, nanocables and nanotubes, has been carried out recently [7]. The fabrication method of the 1D ZnO nanostructures are mainly focused on the vapour transport including chemical vapor deposition (CVD), metal organic chemical vapour deposition (MOCVD), metal organic vapor phase epitaxy (MOVPE) or pulsed laser deposition. The growth of ZnO nanorods on Au-coated ITO substrates using a low temperature wet chemical process has been reported earlier [22].
calculated from geometry and ionic radii of 0.074 nm (Zinc) and 0.184 nm (Sulfide). It forms ABCABC layers. The hexagonal analog is known as the wurtzite structure.

In either structure, the nearest neighbor connections are similar, but the distances and angles to further neighbors differs. Zinc blende has 4 asymmetric units in its unit cell whereas wurtzite has 2. To recap, zinc blende is best thought of as an fcc array of anions and cations occupying one half of the tetrahedral holes. Each ion is 4-coordinate and has local tetrahedral geometry. Unlike wurtzite, zinc blende has its own antitype, that means we can switch the anion and cation positions in the cell and it doesn't matter (as in NaCl). In fact, replacement of both the Zn and S with C gives the diamond structure. In Figure 1.2 shown below for the Sphalerite structure, notice that how only half of the tetrahedral sites (i.e. four of the eight octants of the cube) are occupied by Zn$^{2-}$ (Blue).

Figure 1.2. Shalerite structure of ZnS.
In detail, the surface plasmons (surface plasmon polaritons) are surface electromagnetic waves that propagate in a direction parallel to the metal/dielectric (or metal/vacuum) interface as shown in figure 1.4. Since the wave is on the boundary of the metal and the external medium (air or water for example), these oscillations are very sensitive to any change of this boundary, such as the adsorption of molecules on to the metal surface. SPs have lower energy than bulk (or volume) plasmons which quantise the longitudinal electron oscillations about positive ion cores within the bulk of an electron gas (or plasma). The charge density oscillations and associated electromagnetic fields are called surface plasmon-polariton waves. These waves can be excited very efficiently with light in the visible range of the electromagnetic spectrum. The excitation of a surface plasmon is one of the energy loss interactions that take place within the energy levels.

Figure 1.4. Schematic representation of an electron density wave propagating along a metal-dielectric interface.

The energy of the surface plasmon $E_p$ may be estimated using the free electron model (eqn.(1.20), where $n$ is the conduction electron density, $e$
The melting point of pure gold is 1064°C, although when alloyed with other elements such as silver or copper, the gold alloy will melt over a range of temperatures. The boiling point of gold, when gold transforms from the liquid to gaseous state is 2860°C. Gold is dense, soft, shiny and the most malleable and ductile pure metal known. Pure gold has a bright yellow colour and lustre traditionally considered attractive, which it maintains without oxidizing in air or water. Chemically, gold is a transition metal and can form trivalent and univalent cations in solutions. Compared with other metals, pure gold is chemically least reactive, but it is attacked by aquaregia (a mixture of acids), forming chloroauric acid, but not react with the individual acids and with alkaline solutions. Gold dissolves in mercury, forming amalgam alloys, but does not react with it. Gold demonstrates excellent biocompatibility within the human body (the main reason for its
The property of SPR in the metal nanoparticles causes enhanced light absorption at frequencies very close to the SPR frequency which comes under the category of nonlinear absorption that find application in "optical limiting". The nonlinear absorption may be of multi photon absorption type occurring in a single step or may be an excited state absorption process which is a multi step process. That means the nonlinearity may be a spontaneous nonlinearity or a cascaded nonlinearity. Gold nanoparticles in a colloidal form or gold nanoparticles embedded dielectric matrices were selected widely for optical limiting application. Optical limiters are those materials whose transmittance falls with increase in incident light fluence.
One nanomaterial that is having an early impact in healthcare products is nano-silver. Nanoparticles are used because they obviously exhibit enhanced or different properties when compared with the bulk material. Nano-silver is: highly efficacious, fast acting, non poisonous, non stimulating, non allergic, tolerance free and hydrophilic. Sharp surface plasmon absorption of silver nanoparticles \[74\] makes them very attractive for optics and bioscience applications. Silver nanoparticles are advantageous compared with nanoparticles of other noble metals (in particular, gold and copper) because the energy of the surface plasmon resonance (SPR) of silver lies far from the energy corresponding to inter band transitions. The latter means that, in composite materials with silver nanoparticles, it becomes possible to study optical nonlinearities associated with the SPR of silver.
X-ray diffraction studies give a whole range of information about the crystal structure, orientation, average crystalline size and stress in the sample material. Experimentally obtained diffraction patterns of the sample are compared with the standard powder diffraction files published by the international centre for diffraction data (ICDD). The average grain size $D$ of the sample can be calculated using the Scherrer's formula [37],

$$D = \frac{0.9 \lambda}{\beta \cos \theta} \quad (2.7)$$

where, $\lambda$ is the wavelength of the X-ray and $\beta$ is the full width at half maximum intensity in radians. The lattice parameter values for different
Figure 2.3. Schematic of a transmission electron microscope.
of the grating, only monochromatic light (single wavelength) successfully passes through a slit. A filter is used to remove unwanted higher orders of diffraction. The light beam hits a second mirror before it gets split into half (half of the light is reflected, the other half passes through). One of the beams is allowed to pass through a reference cuvette (which contains the solvent only), the other passes through the sample cuvette. The intensities of the reference light beam ($I_0$) as well as the transmitted beam ($I$) are then measured at the end using detector 1 and 2. From the value of $I_0$ and $I$ the absorption coefficient ($\alpha$) and band gap ($E_g$) of the sample material can be found out.

Figure 2.4. The schematic diagram of UV-visible spectrophotometer.
PMT) ranging from 180-850nm. The reference detector monitoring the Xenon lamp - a UV enhanced Si photodiode - requires no external bias and has good response from 190-980nm. The signal from the detector is reported to a system controller and host computer where the data can be manipulated and presented using special software.

Figure 2.5. The schematic block diagram showing the components of spectrofluorometer.
(the power) put into the flame is known and the quantity remaining at the other side (at the detector) can be measured, it is possible, from Beer-Lambert law, to calculate how many of these transitions took place, and thus get a signal that is proportional to the concentration of the element being measured. The schematic of an atomic absorption spectrometer is shown in figure 2.6. The components are described below.

**Light source:** The light source is usually a hollow-cathode lamp of the element that is being measured. The radiation source chosen has a spectral width narrower than that of the atomic transitions. Inside the lamp, filled with argon or neon gas, is a cylindrical metal cathode containing the metal for excitation and an anode. When a high voltage is applied across the anode and cathode, gas particles are ionized. As voltage is increased, gaseous ions acquire enough energy to eject metal atoms from the cathode. Some of these atoms are in an excited state and emit light with the frequency characteristic
The major factors which limit the accuracy of stylus measurements are [59]:

1. Stylus penetration and scratching of films (makes problem in very soft films).
2. Substrate roughness: Excessive noise is introduced into the measurement as a result of substrate roughness and this creates uncertainty in the position of the step.
3. Vibration of the equipment: Proper shock mounting and rigid supports are essential to minimise background vibrations.
Generally speaking, an optical switch is the unit that actually switches light between fibers and a photonic switch is one that does this by using nonlinear optical properties of the material to steer light. Usually refractive nonlinearity is responsible for photonic switching [71]. The response time of the nonlinearity depends on the mechanism of evolution of nonlinearity. Optical switching by third order effects such as optical Kerr effect (as shown in figure 3.3) has special advantages over the linear electro optic effect. The former has instantaneous response (response time around
The automated Z-scan set-up contains the following major components.

1. Nd:YAG Laser

The pulsed laser used here for the experiment is an electro-optically Q-switched Nd:YAG laser having a fundamental output of 1.06\,\mu m (Quantum Ray GCR 150). Nd:YAG is the acronym used for Neodymium doped Yttrium Aluminum Garnet. The diffraction coupled resonator cavity delivers a ‘doughnut’ shaped beam profile at energies of the order of 650 mJ at \approx 8-
file for fitting the experimental data to the theoretical equations. Proper fitting of the data will give the value of the nonlinear refractive index and nonlinear absorption coefficient. The front panel for automating the energy ratiometer is shown in figure 3.10.

![Front panel for automation programme of energy ratiometer.](image)

**Figure 3.10.** The front panel for the automation programme of energy ratiometer.

**5. Automated micro stepper**

The microstepping motion of the translation stage in the focused region of the lens (varying intensity region) is very significant to get error less data. The pulse width of the laser source used is very narrow of the
order of 6ns and the frequency of the pulsed laser is 10Hz. The nonlinear response induced by the high peak power of the laser pulses is ultrafast that requires an ultrafast data acquisition for the detection. Also sample motion should be highly precise of the order of microns and reproducible such that the output signal measured will be highly accurate while the microstepping motion of the sample cell. The microstep motion of the sample cell can be achieved by using stepper motor and its translation stage. The front panel of the programme developed for the stepper motor movement is shown in figure 3.11.

Figure 3.11. The front panel for the automation programme of stepper motor.
was stirred for 1 hour. 3ml of the ZnO solution is added drop wise to the PMMA solution (10ml) and stirred again for one hour. The resulting viscous solution was spin coated on glass plate at a rotation speed of 1500rpm so as to get a thin film of thickness 1μm. The UV-visible absorption spectra of the as prepared ZnO colloids and ZnO: PMMA thin films were recorded using Jasco V 570 spectrophotometer.

The nonlinear optical properties were analyzed using single beam Z-scan technique. The experimental setup for the nonlinear study is shown in figure 4.1.

![Figure 4.1. Schematic of closed aperture Z-scan setup.](image)

The experimental setup consists of Nd:YAG laser working at 532nm operating at a repetition rate of 10Hz which function as the light source. The incident beam is splitted into two, one is taken as the reference beam and the other beam is allowed to transmit through the sample. The laser
Figure 4.2. XRD pattern of bulk ZnO and the ZnO nanoparticles prepared at various NaOH concentrations.

The high resolution TEM (HRTEM) image of ZnO nanoparticles prepared with 0.075M of NaOH is shown in figure 4.3. The selected area electron diffraction (SAED) pattern of ZnO nanoparticles prepared at 0.075M (the inset of figure 4.3(b)) exhibits a concentric diffused ring pattern due to the nanocrystalline nature of ZnO [10]. TEM analysis of the ZnO
reveals the formation of hexagonal nanoparticle with size as 6 nm. Atomic scale images of ZnO nanoparticles prepared with 0.075M in the reaction mixture (figure 4.3(b) shows parallel lines of atoms at regular intervals of 0.28nm which coincides the d spacing corresponding to (100) planes of ZnO. The d values obtained from the SAED confirms the formation of (102) and (103) planes of ZnO.

Figure 4.3 (a) HRTEM image of ZnO nanoparticles prepared at 0.075 M NaOH and (b) HRTEM images of ZnO nanoparticles prepared at 0.075 M showing parallel lines of atoms at regular intervals (inset shows SAED pattern).

Figure 4.4(a) shows the TEM image of the ZnO nanoparticles prepared at 0.2M NaOH showing an average particle size of 10nm ; and figure 4.4(b) shows the HRTEM image showing parallel lines of atoms: the interplanar spacing observed d=0.28nm corresponds to the (100) plane of
ZnO. The inset of figure 4.4(b) shows the SAED pattern showing the (102) and (100) planes of ZnO.

Figure 4.4 (a) TEM and (b) HRTEM images of ZnO nanoparticles prepared at 0.2M NaOH showing parallel lines of atoms at regular intervals (inset shows SAED pattern).

The transmission spectrum of the ZnO:PMMA films are compared with that of pure PMMA film (figure 4.5). It shows the transparency of the ZnO:PMMA film is above 60% in the visible region. Inset of the figure 4.5 shows the photograph of the ZnO:PMMA thin films with the writing beneath it.
Figure 4.5. The transmission spectra of ZnO:PMMA and pure PMMA thin films (inset shows the photograph of ZnO:PMMA films with the writing beneath the film).

The UV-visible absorption spectra of the ZnO nanoparticles in methanol are shown in figure 4.6. The absorption in the ZnO above $\lambda=370\text{nm}$ corresponds to the band-to-band transition. An increase in the band gap with decrease in particle size is observed which is attributed to the quantum size effect [11]. The band gap of ZnO nanoparticles prepared with various NaOH concentration increases as the concentration of NaOH
(figure 4.7) decreases in the reaction mixture. Second peaks at 420nm are
sub-band transition due to the interstitial zinc and zinc vacancy [12].

Figure 4.6. UV-visible absorption spectra of ZnO colloidal solution
prepared at various NaOH concentrations.

The average particle size can be deduced from the absorption
spectra using eqn.(4.1). Here the pronounced dependence of the band gap
on the size of ZnO nanocrystals is used to determine the particle size [13].
The band gap is calculated from the point of inflection of the first derivative
curve of the absorption spectra. The difference in the value of band gap of the ZnO nanoparticles with respect to bulk ZnO, $\Delta E_x$ is found. From the $\Delta E_x$ the particle size, $d$, is determined [13] using eqn. (4.1),

$$\Delta E_x = 100(18.1d^2 + 41.4d - 0.8)^{-1}$$  \hfill (4.1)

The particle size shows a progressive decrease from 10nm to 2.9nm with the decrease in concentration of NaOH from 0.2M to 0.025M (figure 4.7).

![Graph showing dependence of band gap and particle size of ZnO nanoparticles on NaOH concentration](image)

Figure 4.7. Dependence of band gap and particle size of ZnO nanoparticle on the NaOH concentration in the reaction mixture.
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The figure 4.8 shows that the concentration of the ZnO nanoparticles synthesized decreases with increase of the concentration of NaOH in the reaction mixture. Therefore the lower concentration of ZnO nanoparticles results in lower absorption at higher wavelengths in larger sized nanoparticles.

![Graph showing concentration of ZnO nanoparticles vs NaOH concentration](image)

Figure 4.8. Variation in the concentration of ZnO nanoparticles produced at various NaOH concentrations.

Generally the PL spectra of ZnO contains one emission peak in the UV region attributed to the free excitons and one or more emission peaks in
Figure 4.9. PL emission spectra of ZnO:Na nanoparticles prepared at various concentration of NaOH (inset shows the energy level and transition of PL emission in ZnO, where Zn$_i$, O$_i$, V$_o$, V$_{Zn}$ represents zinc interstitial, oxygen interstitial, oxygen vacancy and zinc vacancy respectively).

Optical nonlinearities of ZnO:PMMA films were measured using single beam Z-scan technique. Figure 4.10 gives the open aperture Z-scan traces of ZnO:PMMA films (which contains ZnO nanoparticles having different particle sizes and hence different band gap) at laser irradiance of 0.325 J/cm$^2$ which shows that the samples can be best used for optical limiting applications. That means all films show a decrease in transmission with increase in the input laser fluence.
Figure 4.10. Open aperture Z-scan traces of the ZnO:PMMA films containing ZnO nanoparticles having different band gap (E_g) at laser irradiance of 0.325 J/cm².

Here the optical limiting curve fits to a two photon absorption transition between the valence and conduction band given by the theoretical eqn.(4.2) using Shake Bahae formalism,
in particles prepared with larger concentration of NaOH. However detailed studies are needed to evaluate the exact phenomena behind the curve broadening.

Figure 4.11 gives the closed aperture Z-scan curves at laser irradiance of 0.325 J/cm².

Figure 4.11. Closed aperture Z-scan traces of the ZnO: PMMA films containing ZnO nanoparticles having different band gap (E_g) at laser irradiance of 0.325 J/cm².
HRTEM shows parallel lines of atoms at regular intervals of 2.7Å which coincides with the d spacing corresponding to the (200) planes of ZnS. The d values obtained from the SAED confirm the formation of (200) and (222) planes of ZnS.

The band gap for the ZnS:Cu nanoparticles is found from the Kubelka-Munk plots as shown in figure 5.3. Compared to the band gap of bulk sphalerite ZnS (3.67eV) [21], the synthesised ZnS:Cu nanoparticles displayed an increase in the band gap which indicates the formation of the nanocrystals. Also a systematic increase in the band gap (3.88eV to 4.25eV) with increase in the copper doping concentration is observed which is attributed to the shifting apart of the valence and conduction bands, due to
the formation of impurity levels in between. This kind of increase in band gap with increase in the copper doping concentration has been reported by Manzoor et al [22].

Figure 5.3. The Kubelka-Munk plots reduced from the diffused reflectance spectra.

Figure 5.4 schematically illustrates the band gap widening associated with Cu$^{2+}$ doping, and the electronic transitions involved in the excitation and emission processes.

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Figure 5.4. Schematic diagram showing the band gap widening in Cu doped ZnS nanoparticles.

The photoluminescence emission of the pure ZnS nanoparticles is shown in figure 5.5 and inset shows the PL excitation spectra. The undoped ZnS shows excitation peak at 318nm corresponding to the band-to-band electronic excitation. PL emission from the pure ZnS ($\lambda_{\text{ex}}=318\text{nm}$) shows a blue emission peak at 434nm which is attributed to the sulphur vacancies. For low concentrations of sulfide ions during precipitation, the ZnS nanoparticles formed will have a large number of sulfur vacancies ($V_S^{2+}$) [22]. Bearing a charge of 2+, the $V_S$ sites can effectively trap excited electrons from the conduction band and act as a doubly ionized donor by forming a shallow energy level below the conduction band (CB) edge. Subsequent electron–hole (e–h) recombinations at the valence band lead to blue emissions, referred to as ‘self-activated’ emission in nanosized ZnS.
In doped nanoparticles a larger numbers of dopant centers are situated near the surface than in the interiors, and therefore nanoparticles are expected to have better luminescent emission efficiencies compared to their bulk counterparts. The photoluminescence emission of the ZnS:Cu nanoparticles is shown in figure 5.6. The green photoluminescence emission ($\lambda_{em}=375\text{nm}$) arises from the recombination between the shallow donor level (sulphur vacancy) and the $t_2$ level of Cu$^{2+}$.
Figure 5.6. PL emission of Cu doped ZnS nanocolloids (Inset shows the green luminescence from ZnS:Cu nanocolloids).

With the incorporation of Cu$^{2+}$ pairs, the V$_{S}$-related 434 nm peak is completely quenched at the expense of green emissions, indicating the formation of impurity-related new energy levels within the band-gap of nanoparticles. The PL emission maxima shows a blue shift in wavelength with increase in the dopant percentage indicating widening in the separation between the copper acceptor levels and the V$_{S}$ donor levels; which also supports the widening of band gap with increase in the copper doping.
When the doping concentration is increased, the luminescence intensity observed to be diminished which is caused by the formation of CuS, though the XRD measurement did not detect the existence of the copper sulfide phase [23, 24]. The reason for the reduced emission is that the formation of CuS particles will effectively reduce the number of Cu$^{2+}$ optically active luminescent centers in ZnS nanoparticles. The formation of CuS can be detected with the change in colour observed for the powder from white to grey when the Cu doping percentage is increased. The schematic energy level diagram of ZnS:Cu nanoparticles and the mechanism of PL emission is depicted in Fig. 5.7.

![Schematic energy level diagram showing the emission mechanism in ZnS:Cu nanoparticles.](image)

Figure 5.7. Schematic energy level diagram showing the emission mechanism in ZnS:Cu nanoparticles.
The excitation spectra of ZnS:Cu nanophosphors recorded for the green emission (Figure 5.8) also reveal a new excitation band at 375 nm, indicating that, characteristic intra-band gap electronic transitions are associated with Cu$^{2+}$ substitution for Zn ($\text{Cu}_{\text{Zn}}$). As the Cu doping percentage is increased a blue shift in the excitation peak is observed. This suggests widening in the band gap in ZnS nanoparticles doped with higher Cu$^{2+}$ concentrations.

![Figure 5.8. The PL excitation spectra of the Cu doped ZnS nanocolloids.](image)

The open aperture Z-scan traces taken using ultrafast (100fs) laser pulses at 800nm at an average energy of 17 μJ are shown in figure 5.9(a).
Figure 5.9. Ultrafast (a) open aperture Z-scan traces and (b) optical limiting plots of copper doped (Cu At% varied from 0.01 to 0.03) ZnS nanoparticles.
Figure 5.10. Variation of the three photon absorption coefficient $\gamma$ with the dopant concentration.

Frequency-degenerate three photon absorption is a process wherein three photons, whose energies are the same, are absorbed by the nanoparticle simultaneously through two virtual states to reach the excited state which is strongly band gap dependent. The frequency-degenerate three photon absorption coefficient has been found to decrease with increase in the band gap of the undoped quantum dots (inversely proportional to the 7\textsuperscript{th} power of band gap) as reported earlier [25]. However in the present case, both the band gap (figure 5.3) and the three photon absorption coefficient
Figure 6.3. TEM (a, c) and size histogram (b, d) of Au nanoclusters prepared at 1.2 J/cm² (top row) and 3.8 J/cm² (bottom row).
Figure 6.4. HRTEM (a, c) and SAED (b, d) of Au nanoclusters prepared at 1.2 J/cm² (top row) and 3.8 J/cm² (bottom row).

Au nanoclusters in water prepared at fixed laser fluence of 1.9 J/cm² for different durations 1 hour, 2 hour and 3 hour show SPR peak at the same position 520 nm (Figure 6.5) indicating an almost constant size of the nanoparticles irrespective of the duration of ablation. It has been reported in the literature that during the growth of nanoparticles with nanosecond lasers, a reduction in particle size will be observed due to the efficient radiation absorption by the previously ablated particles [15]. No such a
A reduction in particle size was observed in our study. Only an enhancement in the absorbance is observed in the UV-visible spectrum which is due to the increased nanoparticle density of the samples with increase in ablation duration. Therefore absorption spectra indicate an almost constant size (around 4nm) for the Au nanoparticles prepared at 1.9J/cm² independent of the ablation duration.

Figure 6.5. UV-visible absorption spectra of Au nanoclusters prepared at a laser fluence of 1.9J/cm² for different ablation duration.
Figure 6.6. Open aperture Z-scan traces of gold nanoparticles prepared at various laser ablation fluences.

Experimental data fit well with the theoretical eqn.(6.4) for normalized transmittance $T(z, S=1)$ corresponding to nonlinear absorption [19],

$$T(z, S=1) = \frac{1}{\sqrt{\pi q_0(z,0)}} \int \ln \left[ 1 + q_0(z,0)e^{-r^2} \right] dr$$

(6.4)

where $q_0(z,0) = \beta I_0 L_{\text{eff}}$ and $\beta$ is the nonlinear absorption coefficient, $L_{\text{eff}}$ is given by

$$\frac{(1-e^{-\alpha L})}{\alpha}$$

where $L$ is the sample length, $\alpha$ linear absorption coefficient $I_0$ is the incident intensity. The experimental data points are fitted
with the theoretical eqn.(6.4) with \( \beta \) taken as the fitting parameter and the value of \( \beta \) corresponding to the best theoretical fit is taken. The optical absorptive nonlinearities of the samples prepared at lowest (1.2J/cm\(^2\), 4nm) and highest (3.8J/cm\(^2\), 6nm) laser ablation energy shows that a better absorptive nonlinearity is obtained for smallest nanoparticles (4nm). The nonlinear absorption coefficient \( \beta \) corresponding to 4nm and 6nm are \( 4.737 \times 10^{-10} \) m/W and \( 4.37 \times 10^{-11} \) m/W respectively; i.e. a decrease in the value of \( \beta \) with increase in size of nanoparticles. The optical limiting plots corresponding to 4nm and 6nm is shown in figure 6.7 which clearly shows the reduction in transmission as the size of the nanoparticles decreases.

![Figure 6.7](image-url)

Figure 6.7. Optical limiting characteristic of the Au nanoclusters of particle size 4nm and 6nm (the solid line represents theoretical fitting to the experimental data).

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For nonlinear optical applications, it will be better to incorporate the nanoparticles immobilized in a suitable matrix like polymer or glass. The ease of flexibility that the polymer matrix offers as compared to a rigid fragile matrix like glass makes it best to incorporate Au nanoparticles in polymer matrix for fabricating devices. Lower size (4nm) nanoparticles having high value of $\gamma$ as well as $\beta$ are embedded inside the poly vinyl alcohol (PVA) matrix so as to achieve a stable optical limiting device.
The UV-visible absorption spectra of the Au/PVA film as well as pure PVA film are shown in figure 6.9, which show the presence of strong SPR bands peaked at 520nm indicating the incorporation of Au NPs in the matrix. A slight shift (2nm) in the SPR compared to the colloidal solution in water is due to a change in the dielectric constant of the medium used. Inset of the figure 6.9 show the photograph of the Au/PVA thin film with the writing beneath it.

![Figure 6.9. UV-visible absorption spectra of Au/PVA films (inset shows the photo of Au/PVA film).](image)

The open as well as closed aperture Z-scan traces of the Au/PVA films are recorded using Z-scan technique. Figure 6.10(a) shows the optical limiting curve of Au/PVA films where as figure 6.10(b) gives the closed aperture curve showing negative refractive index type nonlinearity. The
optical limiting property of Au nanocrystals in polymer film is similar to the Au colloids but the nonlinear refraction in Au/PVA is found to be better compared to the Au/water colloidal solution. The deviation of the experimental plots from the theoretical fit may be attributed to the contribution from thermally induced nonlinear scattering produced by the generated hot plasma in the solid polymer matrix [36].

The nonlinear refraction may contain electronic as well as thermal contributions. However the enhancement in the refractive index may be attributed to thermally induced lensing in the Au/PVA as compared to the Au/water colloidal solution. Thermal lensing arises from the excited hot electrons which are thermalized by dissipating the excess heat energy through scattering process [33]. The excess thermal energy increases the surrounding temperature and generates a temperature gradient which leads to a variation in refractive index which is called a thermal lens [34]. Phase
6.3.2. Silver nanoparticles by LP-PLA

(a). Silver nanoparticles prepared at 532nm

Figure 6.11 shows the UV-visible absorption spectra of the silver nanoparticles prepared at 1.2/J/cm², 2.2/J/cm² and 3.8/J/cm² laser fluences at laser ablation wavelength 532nm. The absorption spectra shows strong surface plasmon bands peaked around 400nm indicating the presence of the silver nanoparticles [39]. The plasmon band around 400nm is attributed to the longitudinal surface plasmon resonance of the free electrons in the silver nanoparticles. The absorption peak is found to shift from 403nm to 406nm with increase in the ablation laser fluence indicating a small increase in the particle size [39] as confirmed by TEM analysis.

![Figure 6.11. UV-visible absorption spectra of silver nanoparticles prepared at different laser fluences.](image)

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Figure 6.12(a) and figure 6.12(b) shows the HRTEM images of the silver nanoparticles prepared at 1.2J/cm² and 3.8J/cm² respectively, the size of the silver nanoparticles are found to be 4nm and 6nm respectively. Figure 6.12(c) and figure 6.12(d) gives the selected area electron diffraction (SAED) pattern of silver nanoparticles showing the (111) and (200) planes of silver.

Figure 6.12. The TEM image of nanoparticles prepared at (a) 1.2J/cm² and (b) 3.8J/cm² (c) SAED pattern of nanoparticles prepared at 1.2J/cm² and (d) 3.8J/cm².
Figure 6.13(a) and figure 6.13(b) show HRTEM images showing parallel lines of atoms of the silver nanoparticles prepared at 1.2J/cm² and 3.8J/cm² respectively where the observed inter planar spacing 2.35Å is in well agreement with (111) plane of silver.

![HRTEM images of silver nanoparticles prepared at (a) 1.2J/cm² and (b) 3.8J/cm² showing parallel lines of atoms.](image)

The absorption spectra of the colloidal solutions prepared at 1.2J/cm² and 3.8J/cm² taken just after the synthesis, after 5 days and after 15 days are shown in figure 6.14(a) and 6.14(b) respectively. From figure 6.14(a) and 6.14(b), it is found that the SPR band is diminished after 15 days for the nanoparticles prepared at ablation fluence 3.8J/cm² (7nm) where as the SPR band is present even after 15 days for nanoparticles prepared at ablation fluence 1.2J/cm² (4nm). It shows the extra stability of silver.
nanoparticles prepared at lower ablation fluence. This fast decay of SPR band of silver nanoparticles prepared at 3.8 J/cm² is attributed to the increased nanoparticle concentration and particle size for the colloidal solutions prepared at higher laser fluence, which lead to the agglomeration of the nanoparticles in the colloidal solution.

Figure 6.14. The effect of ageing on the UV-visible absorption spectra of silver nanoparticles prepared at (a) 1.2 J/cm² and (b) 3.8 J/cm².

The open aperture Z-scan plots for silver colloidal solutions (measured with Nd:YAG laser at 532nm operating at a repetition rate of 10Hz at a laser irradiance I₀=0.521 J/cm²) are shown in figure 6.15.
Figure 6.15. Open aperture Z-scan curves of silver nanoparticles prepared at 532nm for various laser ablation fluence.
Figure 6.16. The UV-visible absorption spectra of Ag/PVA film.

The open aperture Z-scan traces of the Ag/PVA film showing good nonlinear absorption is given in figure 6.17. Ag nanocrystals in polymer film display almost the same limiting efficiency as the Ag/water colloidal solution which can be used effectively for the fabrication eye protection goggles for laser operators and for protecting sensors attached to laser optics.
Figure 6.17. Open aperture Z-scan traces of the Ag/PVA film.

(b). Silver nanoparticles prepared at 266 and 355nm

The UV-visible absorption spectra of the Ag nanoparticles prepared at incident laser wavelength 355nm and 266nm at a fixed laser fluence 1.2J/cm² for different ablation durations are shown in figure 6.18(a) and 6.18(b) respectively. In both cases the amplitude of the SPR peak is found to increase with increase in the duration of laser ablation which is attributed to the increase in number of silver nanoparticles in water. Figures 6.18(a) and 6.18(b) shows that the SPR peak blue shifts with increase in the duration of laser ablation. This can be attributed to a reduction in particle size due to the efficient radiation absorption by the previously ablated particles [41].
Figure 6.18. UV-visible absorption spectra of silver nanoparticles prepared for different durations at laser wavelength (a) 355nm (b) 266nm at a laser ablation fluence 1.2J/cm².

The TEM image of the silver colloids produced at 266nm for 1 hour and 3 hour duration is shown in figure 6.19(a) and 6.19(b). It confirms the reduction in the average particle size and a more homogenous size distribution with increase in the laser ablation duration. Inset of figure 6.19(a) shows the HRTEM image of the silver nanoparticles produced at 1 hour duration which shows parallel lines of atoms at a separation of 2.35Å corresponding to the (111) plane of silver.
Figure 6.19. TEM image of the silver nanoparticles prepared at ablation fluence 1.2 J/cm\(^2\) for ablation duration (a) 1 hour (b) 3 hour (inset shows HRTEM image of silver nanoparticles).

6.4. Conclusions

Gold and silver nanoparticles of different sizes are produced by laser ablation of gold and silver target in deionised water. An increase in nanoparticle size is observed with increasing laser ablation fluence. The absorption spectrum of the nanocolloids is red shifted in wavelength with increase in particle size. The silver nanoparticles prepared at higher laser fluence are found to be less stable as compared to those prepared at lower laser fluence. The optical absorptive nonlinearity of the Au and Ag nanoclusters shows an optical limiting type nonlinearity which finds application in the fabrication of optical limiting devices. It is found that the efficiency of limiting increases with decrease in particle size. The nonlinear
where $E_L$ is the laser energy and here for Argon Ion laser $E_L = 2.41399\text{eV}$. And for our sample we got $I_D = 173$ and $I_G = 179$ leading to a crystalline size equal to $17.07\text{nm}$.

![Raman spectra of pure MWCNT](image)

**Figure 7.1.** Raman spectra of pure MWCNT.

The ICP-AES analysis shows that the concentration of the Au in the colloid is found to increase with increase in the duration of laser ablation. The concentration of the colloids prepared at laser ablation durations 1hr, 2hr and 3hr are 3.45ppm, 4.25ppm and 7.65ppm respectively. The UV-visible spectra (figure 7.2) shows strong surface plasmon resonance (SPR) band peaking at 520nm indicating the presence of Au-NPs.
The amplitude of the SPR peak is increasing gradually with increase of the duration of laser ablation indicating the increase in the concentration of the Au-NPs in the colloidal solution as observed from the ICP-AES analysis. The plasmon peak remains at almost the same wavelength which shows that the particle size remains unchanged with different ablation duration. The UV-visible absorption spectra of the supernatant solution after the filtration of the MWCNT/Au black powder is also shown in the figure 7.2. It is observed that the UV-visible spectra of the supernatant
Figure 7.3. The XRD pattern of pure MWCNT and MWCNT with attached Au-NPs.

The TEM image and size histogram of the Au-NPs in water produced at laser ablation energy $1.2\text{J/cm}^2$ for 1 hour duration is shown in figure 7.4(a) and 7.4(b) respectively which shows average size of Au-NPs to be 7nm. The high resolution TEM (HRTEM) (inset of figure 7.4(a)) shows parallel lines of atoms with interatomic spacing $2.35\text{Å}$ that corresponds to (111) plane of gold. Inset of figure 7.4(b) shows the selected area electron
diffraction (SAED) pattern which corresponds to atomic planes (111) and (220) of gold.

The TEM and HRTEM pattern of the MWCNT/Au are shown in figure 7.5(a) and 7.5(b) respectively. From TEM studies it is observed that the outer diameter of the MWCNT is around 15.6nm quite close to the value obtained from the Micro-Raman studies. TEM characterization confirms that all the Au-NPs were attached to the CNT walls. The attached Au-NPs have a narrow size distribution and are finely dispersed. From the TEM images of the MWCNT/Au, we can see the Au-NPs as dark spots on the CNT surface. Thus it can be noted that the hydrophobic CNT could be decorated uniformly with desired loading ratios of Au-NPs. Figure 7.5(b) shows the HRTEM image of MWCNT/Au, showing parallel lines of atoms.
The interplanar spacing of MWCNT as seen from figure 7.5(b) is 3.47\(\text{Å}\) which corresponds to (002) plane of MWCNT. The interplanar spacing of Au-NPs is found to be 2.35\(\text{Å}\), which corresponds to (111) plane of gold (Figure 7.5(b)).

The optical limiting characteristics of thin films containing pure MWCNTs as well as those with attached Au-NPs (containing different loading ratios of NPs) in PVA matrix has been taken by the automated Z-scan setup [34]. Second harmonics of Nd: YAG laser (532 nm, pulse width 6-7ns) having a repetition rate of 10 Hz was used as the light source for the nonlinear optical studies. The optical limiting plots (taken at laser irradiance \(I_0=0.15\text{J/cm}^2\)) of thin films containing pure MWCNTs and MWCNT/Au in
An increase in the optical limiting property has been observed (Figure 7.6) with increasing the gold loading ratio on the surface of MWCNTs. We propose that this improvement of the optical limiting performances in MWCNT/Au is mainly due to nonlinear scattering properties resulting from the surface plasmon absorption (SPA) processes in the Au NPs at 532 nm. This SPA band is due to the electromagnetic field-