Role of defects in optical nonlinearity of CuS quantum dots

A nontoxic, green, one-pot synthesis method developed for the preparation of water dispersible CuS quantum dots (2-4 nm) and nanoparticles (5-11 nm) is discussed. Optical and microstructural studies indicate the presence of surface states and defects (dislocations, stacking faults and twins) in the quantum dots. Optical nonlinearities at near resonant excitonic band (532 nm, 5 ns excitations) and plasmonic band (800 nm, 100 fs excitations) were investigated in CuS nanoparticles and quantum dots. The fluence-dependent transmittance measurements from open-aperture z-scan reveal that CuS quantum dots are better ultrafast optical limiters compared to the nanoparticle counterparts. In addition to optical and microstructural studies, nonlinear optical characterizations provide further evidence for the presence of surface states and defects in CuS quantum dots.
4.1 Introduction

Design and fabrication of efficient miniaturized devices requires nanoscale functional materials with excellent properties. Semiconductor nanoparticles are promising candidates for solar and photovoltaic cells [1-2], optical data storage [3], and nonlinear optics [4-7] owing to their enhanced and tunable optical properties. During the last few years, intense research activities in preparing atomically precise and ultra small quantum dots (QDs) of metal sulfides are progressing at an increasing pace, not only from an application point of view, but also for understanding the fundamental scientific concepts at reduced dimensions. Recently, Ag:Se QDs with tunable NIR fluorescence for in vivo imaging [8], photoelectrochemical immunosensor based on water-soluble CdS QDs [9], photophysical and redox properties of CdSe nanoclusters [10], magnetic properties of ZnO nanoparticles [11] and size dependent properties of ZnS nanoclusters [12] have been widely studied. Furthermore, investigations of defect concentration dependent phase transition are interesting to determine crystal growth kinetics and microstructure formation in crystallography. The phase transformation related development of defect microstructures, size dependent phase transformation kinetics and the role of oriented attachment (OA) crystal growth have been reported in nanocrystalline ZnS [13,14]. However, relatively less attention has been paid to the preparation of CuS QDs; though phase transformation from rhombohedral Cu$_{1.8}$S nanocrystals to hexagonal CuS clusters and corresponding phase and composition dependent plasmonic absorption properties are reported [15].
Nevertheless, detailed investigations on defect related optical and nonlinear optical properties of cubic–hexagonal phase have been rarely reported. Presence of donor-acceptor levels and surface traps originating from vacancy and interstitial states, or associated with dislocations, stacking faults, and nonstoichiometric defects in semiconductors is advantageous in tailoring luminescent and nonlinear optical properties. Effects of various defect levels on the luminescent behavior of ZnS nanoparticles [16] and emissions originated from surface or grain-boundary defects, vacancy and interstitial states in ZnO nanostructures [17] are previously reported.

In nanomaterials, light matter interactions are related to the collective oscillations of charge carrier density, the so called surface plasmons, in response to the external electromagnetic field. The coupling of light to surface plasmons results in enhanced optical properties and the urge to explore new plasmonic materials is still continuing. While metallic nanostructures of Au [18, 19] and Ag [20] are well known plasmonic materials for visible region with applications in photovoltaics, sensing and tissue imaging, doped semiconductor nanostructures [21] are important for NIR plasmonics with a significant role in NIR detectors [22] and deep tissue imaging [23]. Moreover, through careful attachment of metal nanostructures, the nonlinear optical coefficients of semiconductor nanomaterials are tailored, and improved optical limiting efficiency is achieved due to effective surface plasmon interaction [24,25]. However, nonlinear optical properties of semiconductor nanomaterials having NIR plasmonic applications are not well explored yet. Copper chalcogenides are known to exhibit NIR absorption and localized surface
plasmon resonances (LSPR). CuS is an intermediate compound having a strong NIR absorption due to self doped p-type carriers, having potential applications in photocatalytic activity [26], DNA sensing [27] and photothermal therapy [28]. Considering the photonic applications of semiconductor plasmonic materials, in addition to exploring their SPR properties, it is crucial to understand how the nonlinear optical properties evolve from quantum dots to nanoparticles. In this background, the present chapter deals with the synthesis of CuS QDs (2-4 nm) and NPs (5-11 nm) through a soft chemical route, by using polyvinylpyrrolidone (PVP) as the capping agent. Their structural, crystalline and optical properties are investigated in detail and the dependence of NIR absorption on the surrounding solvent medium is studied. We also investigate the mechanism and efficiency of nonlinear optical absorption of CuS QDs and NPs using open aperture z-scan technique at the near resonant LSPR wavelength of 800 nm (100 fs ultrafast laser pulses), and near resonant excitonic wavelength of 532 nm (5 ns laser pulses).

### 4.1.1 Quantum dots and nanoparticles

Generally, the commonly used terms to describe ultrasmall particles are nanoparticles, nanocrystals and quantum dots, “zero-dimensional” structures having diameters <100 nm. They are the simplest building block used for nanomaterials design, fabrication and application. The term nanoparticle is generally used to encompass all 0D nanometer-sized building blocks (regardless of size and morphology). For semiconductor nanoparticles smaller in size (i.e., 1–10 nm), smaller
than exciton bohr radius with a narrow size distribution, the term quantum dot is more appropriate. A nanomaterial that is crystalline in nature can be referred to as nanocrystal. Usually, this term is used for single crystalline materials and is characterized by the presence of an ordered lattice array of the constituent subunits.

4.1.2 Surface plasmon resonances

Surface Plasmon polaritons (SPPs) are surface electromagnetic waves that propagate parallel to the interface between a metal and a dielectric material. The electromagnetic (em) radiation can couple to the free electron excitations near the surfaces. Surface plasmon resonance (SPR) is a phenomenon taking place at metal surfaces when an incident beam of light at a particular wavelength strikes the surface. The collective oscillations of the conduction electrons in resonance with the driving electromagnetic field result in wavelength selective absorption and scattering of incident radiation.

![Figure 4.1: Localized surface plasmon resonance (LSPR) frequency dependence on free carrier density and doping constraints [29].](image-url)
To achieve SPRs in the visible region, carrier densities in the range $10^{22}$ - $10^{23}$ cm$^3$ is required for the common plasmonic metals, namely, gold, silver, and copper. For SPRs in infra-red region free electron densities in the range $10^{19}$ - $10^{22}$ cm$^3$ is needed which is achievable by controlled doping of semiconductor nanocrystals (Figure 4.1) [29]. More than the size and shape tunability as metals, the free carrier concentration in self doped semiconductors can either be tuned by doping or with temperature. In addition to this, the localized surface plasmon resonance (LSPR) frequency can be tuned by the local medium or capping layer of nanomaterials. This makes them more compactable plasmonic materials, as dynamic control over operation can be achievable within the running device. First and foremost, all this tunability is chiefly influenced by the free carrier concentration in the material.

4.2 Experimental

4.2.1 Synthesis of CuS nanoparticles and quantum dots in PVP

Synthesis of CuS QDs was carried out with PVP and copper acetate as starting materials. 0.2mM copper acetate was added to 0.5mM PVP solution in distilled water under magnetic stirring. The mixture was heated to 70 °C and kept for 30 minutes with constant stirring to get a homogeneous solution. Aqueous solution of 0.2 mM thiourea was added to the mixture in drops. Addition of this sulfur precursor into the mixture led to immediate sequential color changes through green, dark green, dark brown and finally black. The reaction was maintained at 70
Chapter 4

°C for 1 hour before cooling to room temperature. The solid precipitate obtained was separated by centrifugation. It was washed several times with distilled water and ethanol to remove impurities and excess capping agents, and finally dried overnight in a hot air oven at 50 °C. The reaction procedure for CuS nanoparticles is similar to that for CuS QDs except that the sulfur precursor used is thioacetamide. The synthesis of the CuS - PVP nanocrystals is similar to the method reported previously for metal sulfide nanoparticles such as PbS [30], ZnS [31] and CuS [32].

4.2.2 Optical and morphological characterization:

The X-ray diffraction patterns obtained from PANalytical X'Pert PRO X-ray diffractometer with Cu-Kα radiation were interpreted to know the crystalline structure of samples. The transmission electron micrographs (TEM) and SAED pattern acquired from JEM 2100 electron microscope were used to determine the morphological and crystalline nature of the samples. Elemental analysis was done from the energy dispersive X-ray (EDX) spectra recorded using JEOL J SM 6390 scanning electron microscope. UV-Vis-NIR absorption spectra were measured using a Varian Cary 5000 spectrophotometer. The FT-IR spectrum was recorded using a Shimadzu 8400S Spectrophotometer to analyze the effect of capping agents.

4.2.3 Nonlinear transmission experiments:

The nonlinear optical properties of PVP capped CuS NPs and QDs were investigated through sensitive single beam z-scan technique [33]. For the open aperture z-scan experiments 5 ns laser pulses at 532
nm wavelength from a frequency-doubled Q-Switched Nd:YAG laser and 100fs laser pulses at 800 nm wavelength from a Ti:Sapphire laser were used as the excitation sources. Samples dispersed in distilled water were taken in a 1mm quartz cuvette, and mounted on a stepper motor controlled translation stage. The incident laser pulse energy was set to a suitable low value of 10 µJ by inserting a set of neutral density filters. Laser pulses were focused using a converging lens and samples were scanned along the beam axis through the beam focus. The transmitted energy as a function of the sample position was measured using a pyroelectric energy detector (Rjp735, Laser Probe Corp.) placed in the far field. Laser was run at a repetition rate of 10 Hz for energy stability, but the experiment was in effect done in the single-shot mode by using a synchronized fast mechanical shutter in the beam path, which could allow single pulses from the pulse train to pass through as desired. The experiment was automated using a LabVIEW program.

4.3 Results and discussion

4.3.1 Powder X-ray diffraction (XRD)

The diffraction peaks obtained from powder XRD (p-XRD) patterns (Figure 4.2) of CuS NPs are at the 2θ values of 29.53°, 31.96°, 32.71°, 48.19°, 52.69° and 58.93°. Their position and relative intensities can be perfectly indexed as the (102), (103), (006), (110), (108) and (116) reflections of the pure hexagonal phase of CuS (ICDD No. 65-3561) with (110) as the preferential crystalline direction. The absence of impurity peaks from other crystalline phases and stoichiometric phases of copper sulfide in the XRD pattern confirms the formation of pure covellite CuS.
from the synthesis route. But in the case of CuS QDs, the XRD pattern of CuS quantum dots is more broadened suggesting the formation of smaller crystallites. Moreover, the characteristic peaks in powder XRD patterns are found to have contributions from the face centered cubic phase of CuS (ICDD No.89-2073), in addition to diffraction intensities from its hexagonal phase. As there is a large resemblance between the cubic and hexagonal phases, the existence of the cubic phase can be inferred from the diffraction peaks at the 2θ values of 27.96°, 47.34° and 56.58°, corresponding to the (111), (220) and (311) lattice planes of cubic CuS nanocrystals respectively. No such peaks were observed in the CuS Nanoparticles sample. The diffraction peak at the 2θ value of 58.86° corresponding to the (116) plane of hexagonal CuS is somewhat suppressed in CuS QDs.

![Figure 4.2. XRD spectra of CuS nanoparticles (NPs) and CuS Quantum dots (QDs) in PVP.](image)
4.3.2 Fourier transform infrared spectroscopy (FTIR)

The presence of the capping agent (PVP) can be confirmed from the FTIR spectra of the samples (Figure 4.3). The observed peaks are in agreement with previous FTIR investigations of PVP based materials. It is known that for PVP, the absorption peak located at 1652 cm$^{-1}$ is due to the C=O stretching vibrations [34]. In CuS/PVP NPs and QDs, this peak is slightly red shifted to 1642 cm$^{-1}$ and 1640 cm$^{-1}$ respectively, indicating strong interaction between the nanoparticles and the C=O of PVP. The strong interaction of Cu with C=O of PVP by transferring nonbonding electrons of the O-atom leads to a decrease in the force constant (k) of the bonds. In addition to this, the increased reduced mass due to the higher atomic weight of Cu leads to a decrease in vibration frequencies as observed for the C=O stretching vibrations. The C-H bending mode and C-N stretching mode result in peaks at 1469 cm$^{-1}$ and 1277 cm$^{-1}$ respectively. As reported for PbS/PVP nanocomposites, the C-H bending mode is coupled with the C-N stretching mode and the peaks appeared in this region are significantly weakened and slightly red shifted due to the interaction of CuS NPs/QDs with N of C-N bond in PVP [34]. The absorption band peaking at 1070 cm$^{-1}$ can be attributed to cyclic C-C stretching mode vibrations. The broad vibration band observed between 2930 cm$^{-1}$ and 3490 cm$^{-1}$ is associated with the stretching vibration of the –OH group of physically adsorbed H$_2$O molecules in the samples. This spectral evidence confirms that the nanocrystals are encapsulated by the capping layer in spite of thorough washing.
4.3.3 Energy dispersive X-ray spectroscopy (EDX)

Figure 4.4 shows Energy Dispersive X-ray spectroscopy images (EDX) of PVP modified CuS QDs and CuS NPs which demonstrate the presence of Cu and S. The ‘O’ peak may have originated from the PVP polymer, which is used as the capping agent.
4.3.4 Transmission electron micrographs (TEM)

The crystal structure and morphology of nanoparticles can be elucidated from SAED patterns and Transmission electron micrograph (TEM) images shown in Figure 4.5. For QDs, the size of the nanocrystallites is in the range of 2 - 4 nm, while for NPs, the average particle size is in the range of 5 - 11 nm. The SAED patterns (inset of Figure 4.5) obtained for NPs match well with the hexagonal CuS structure, with prominent rings corresponding to diffraction peaks of (102), (103), (006), (110), (108) and (116) planes with the corresponding d-spacings as 3.046 Å, 2.871 Å, 2.718 Å, 1.868 Å, 1.718 Å, and 1.535 Å respectively (ICDD No. 65-3561). For QDs the d-spacings of 3.117 Å, 1.917 Å, and 1.589 Å obtained from the SAED pattern are consistent with the (111), (200) and (311) lattice planes of the face centered cubic phase of CuS (ICDD No.89-2073). The occurrence of a prominent ring with d=2.810 Å corresponds to the (103) hexagonal plane in addition to cubic CuS.

HRTEM images of CuS QDs and NPs are shown in Figure 4.6. While QDs show randomly oriented crystallites with sharp edges, NPs exhibit spherical shapes and smooth edges. The darker region of the observed image results from the thickness variation of overlapped (102) and (103) hexagonal lattice planes of the NPs. As clearly seen from the HRTEM image, the grains stacked over one another with different interplanar distances give rise to modulated fringes known as Moire interference. This effect has been previously observed in hexagonal CuS nanodisks [35], graphene [36] and silicon [37].
Figure 4.5 TEM image of CuS–PVP NPs (a) and QDs (b). Corresponding SAED pattern is given (inset).

Figure 4.6 HRTEM image of CuS–PVP NPs (a) and QDs (b).

In addition to the occurrence of grain boundaries, CuS QDs possess a considerable number of planar defects which can be seen from Figure 4.7. The nanocrystal shown in Figure 4.7 (a) does not have a definite shape but has abrupt edges, similar to many nanocrystals in the
sample which contain dislocations (DL), twins (T) and stacking faults (SF). Details are illustrated in Figure 4.7 (b). While nanocrystal A consists of many stacking faults and a twin boundary, nanocrystal B contains edge dislocations and stacking faults. These defects are the active sites for the nonradiative recombination of absorbed radiation.

Figure 4.7. HRTEM image of CuS-PVP QDs showing abrupt edges (a). Dislocations, twins and stacking faults are illustrated in (b).

Figure 4.8. HRTEM image of nanocrystal in CuS QDs. The stacking sequence determined follows cubic and hexagonal phases as indicated.

From the SAED patterns it is evident that CuS QDs consist of both cubic and hexagonal phases suggesting the possible formation of wide variety of microstructures. Wherever the cubic arrangement
ABCABC or the hexagonal stacking sequence ABABAB is disrupted by the introduction of a new layer or the absence of a layer, a stacking fault (ABCABABC) is created. If it does not correct itself immediately and continues over a few more atomic spacings, a twin defect is formed. A twin region formed between the cubic and hexagonal phases of CuS is illustrated in Figures 4.8 (a) and 4.8 (b). The close-packed-layer-stacking sequence is determined as ABCABABCAB as indicated by the arrow.

The formation of dislocations, twins and stacking faults are often direct consequences of oriented attachment (OA) based crystal growth. The surface features of CuS QDs depict the fact that several primary particles act as building blocks, whose aggregation by sharing a common crystallographic orientation results in the development of QDs with irregular shapes. Under hydrothermal treatment, crystal growth occurs through collision and coalescence involving primary particles and secondary particles or multilevel particles. The reduction in surface energy due to the removal of nanocrystal interfaces acts as the driving force for the mechanism to continue. This is similar to that reported earlier for H$_2$O-ZnS and mercaptoethanol-capped ZnS samples [38,39]. At the same time, CuS NPs are almost spherical in shape with smooth edges, and do not have any dislocations and planar defects. This suggests that the crystal growth mechanism is possibly classical Ostwald ripening (OR) in which larger particles grow at the expense of smaller particles. The coalescence of particles often happens through the accumulation of ions on to the particle surface from the solution, and the driving force for this growth mechanism is the reduction in the total surface free energy. The crystal growth of hydrothermally treated PbS
Role of defects in optical nonlinearity of CuS quantum dots

nanoparticles, for instance, is reported to occur through the Ostwald ripening mechanism [40]

The synthesis conditions are similar for both QDs and NPs in terms of the temperature, duration of the reaction, surface adsorption of anions (CH$_3$COO$^-$), capping ligands, and concentration. The difference is in the source of sulfur, which seems to be the crucial factor for OA during crystal growth. Addition of copper ions into an aqueous solution of PVP results in the formation of the Cu-PVP complex, through donor-acceptor interactions from the unshared electron pairs of $-\text{O}^-$ and N-$\text{O}$ of the PVP chain to the Cu ions. Thiourea used for preparing CuS QDs has two amine groups and hence it can be effectively adsorbed, whereas CuS NPs are prepared from thioacetamide which has a methyl group instead of the amine groups. The decomposition of thiourea is faster in the presence of Cu ions [41] and the metal removes sulfide as metal sulfide from the Cu-PVP complex. These strongly capped primary particles undergo OA crystal growth at suitable crystallographic phases. On the contrary, thioacetamide is an efficient sulfur donor and tends to release sulfide ions directly in the solution by hydrolysis [41]. The free sulfide ions react directly with the copper species in the solution to form CuS nanocrystals. Crystal growth continues through the OR mechanism by the accumulation of ions on to the particle surface.

2.1.1 UV-Visible absorption spectra

The steady state absorption spectrum of CuS measured in distilled water exhibits a 300 - 500 nm absorption band which is slightly blue shifted from the bulk band gap due to quantum confinement effects
This low energy absorption peak arises from the $1S_n-1S_e$ excitonic transition found in semiconductor nanoparticles. From the Tauc plot obtained by the extrapolation of $(\alpha h\nu)^2$ versus $h\nu$, the band gaps of the NPs and QDs are calculated to be 2.4 eV and 2.1 eV respectively (Figure 4.9 (a)). The slight increase observed in the band gap energy of NPs compared to the values reported in literature can be attributed to quantum confinement effects [29]. The presence of surface states and traps in and around the band gap of the densely capped CuS–PVP QDs can be the reason for the lower band gap of the QDs. Different stoichiometric phases of Cu$_{2-x}$S QDs have characteristic absorption bands, and the observed absorption band corresponds to pure covellite CuS.

![Figure 4.9.](image)

**Figure 4.9.** (a) Tauc plot calculated from the absorption spectrum (Inset) of CuS-PVP in distilled water. (b) SPR observed from the absorption spectra of CuS-PVP in water and chloroform as solvents.

In addition to these excitonic features, CuS also exhibits an SPR mode in the near-infrared range. Evolution of this NIR band is related to
copper vacancies which contribute to free carrier absorption from excess holes in the valence band. The spectral properties of copper chalcogenide nanocrystals in the NIR region showing carrier concentration dependent plasmonic absorption, and the possible non-stoichiometry between copper and sulfur, have been studied in detail by Zhao et al. [42,43]. Wavelength tuning of the SPR mode has been previously achieved by actively controlling carrier density concentrations by varying the size, shape and stoichiometry of the Cu$_{2-x}$S nanocrystallites [44,45]. In addition to the size, shape and stoichiometry dependence of this NIR signature, the surrounding dielectric medium also has an influence on the plasmonic behavior of the nanocrystals. For typical plasmonic behavior, the absorption band will blue-shift when the refractive index of the surrounding medium decreases. To examine the effect of the solvent on the SPR band, we compared the absorption spectra of CuS-PVP measured in water (refractive index 1.33) with that measured in chloroform (refractive index 1.44) (Figure 4.9 (b)). The band shifts to a higher wavelength for CuS/chloroform owing to its higher refractive index, in accordance with the findings of Luther et al [29].

4.3.5 Emission spectrum

For the QDs, room temperature photoluminescence (Figure 4.10) was obtained for an excitation wavelength of 266 nm. When CuS QDs and NPs are coated with PVP polymer, there is strong interaction between Cu and the C=O and C–N bonds of PVP, as evident from FTIR measurements. Due to the smaller size of nanocrystallites in CuS QDs, the unsaturated sp$^3$ hybridized orbitals of surface S atoms may dangle
out of the crystal surface as higher proportion of the total number of atoms will be located on the surface. In other words, a larger number of unsaturated S dangling bonds will be present. Moreover, QDs having abrupt edges and imperfect surfaces can have active electron and/or hole traps upon optical excitation. Consequently, at excitation energies as high as 4.66 eV (266 nm), CuS QDs in such a small size regime will have strong luminescence. The broad photoluminescence emission peaked at 339 nm, similar to that observed by Shailaja and coworkers in ZnS quantum dots [16], can be attributed to traps originating from the unsaturated sp$_3$ orbitals of surface S atoms. Moreover, the observed emission is in agreement with the strong fluorescence appeared at 364 nm in CuS hollow spheres, resulting from recombination of electrons and holes in the surface states at an excitation wavelength of 256 nm [46].

![Figure 4.10 Emission spectra of CuS QDs](image)

**Figure 4.10 Emission spectra of CuS QDs**
4.3.6 Ultrafast optical nonlinearity of CuS NPs and QDs

We investigated the effect of plasmon resonance on the nonlinear optical properties in CuS nanoparticles by employing the open aperture z-scan configuration. For CuS nanoparticles and quantum dots, nonlinear transmission curve measured for 100 fs laser pulse excitation of 10 µJ energy at 800 nm wavelength [Figure 4.11(a)] is in their NIR plasmonic absorption regime.

![Figure 4.11](image)

Figure 4.11 (a) Open aperture z-scan curves measured in CuS-PVP NPs and QDs for 800 nm, 100 fs excitation, at laser pulse energy of 10 µJ. (b) Nonlinear transmission as a function of input intensity, calculated from the z-scan curves

Solid lines give the best theoretical fits to the measured data, based on the model discussed below. Samples used were dispersed in distilled water to the appropriate dilution so that when taken in 1 mm cuvettes the linear transmission was 75% at 800 nm. The two peaks seen in the z-scan of CuS NPs (flanking the central valley) indicate absorption
saturation, whereas the valleys seen for both QDs and NPs indicate reverse saturable absorption (RSA). Nonlinear transmission as a function of input intensity and fluence, calculated from the z-scan data, are plotted in Figure 4.11 (b). Both z-scan curves exhibit valleys with reduced normalized transmission near the beam focus, indicating optical limiting behavior at the higher intensities used. Optical limiting efficiency is found to be higher for CuS QDs at 800 nm, 100 fs excitations.

4.3.7 Optical nonlinearity of CuS NPs and QDs with short laser pulse excitations (ns)

![Graph showing normalized transmission as a function of input intensity and fluence for CuS NPs and QDs.](image)

Figure 4.12 (a) Open aperture z-scan curves measured in CuS-PVP NPs and QDs for 532 nm, 5ns excitation, at laser pulse energy of 60 µJ. (b) Nonlinear transmission as a function of input intensity, calculated from the z-scan curves.

The open aperture z-scan curves at nonresonant plasmonic absorption wavelength of 532nm, 5ns excitation and at the laser pulse energy of 60 µJ is shown in Figure 4.12 (a). Samples used are dispersed...
in distilled water taken in 1 mm cuvettes having linear transmittance of 60% at 532 nm. Both the samples have similar nonlinear transmission curve whereas CuS QDs possess a better dip in the z-scan curve. The incident fluence at which the transmittance drops to 50% of the normalized linear transmittance, termed as optical limiting threshold is calculated from optical limiting curve (Figure 4.12(b)) as 4 J/cm$^2$ and 6.5 J/cm$^2$ for CuS QDs and CuS NPs respectively. Thus the optical nonlinearity is found to be independent for different capping agents but is influenced by the crystallite size and cluster formation.

**4.3.8 Analysis and fitting of experimental data**

Optical nonlinearity in nanomaterials is found to have contributions from several processes such as saturable absorption (SA), multiphoton absorption, free carrier absorption (FCA) and excited state absorption (ESA). The normalized transmission curves having a dip may be due to multiphoton absorption or free carrier absorption and the occurrence of SA can be inferred from the peak in the transmittance-position graph. All the z-scan curves obtained shows combined phenomenon of SA and RSA. We find that the best numerical fits to the measured z-scan data can be obtained by considering a nonlinear absorption coefficient $\alpha(I)$ that includes saturable absorption, free carrier absorption, and two-photon absorption, as given by the equation

$$
\alpha(I) = \left( \frac{\alpha_0}{I_s} + \left( \frac{I}{I_s} \right) \right) + N_c(I) \sigma_c I
$$

where $\alpha_0$ is the linear absorption coefficient, $I$ is the input intensity and $I_s$ is the saturation intensity. The product of intensity-
dependent carrier density $N_c(l)$, with free carrier absorption cross section $\sigma_c$, can be written as $\beta_{\text{eff}}$, the effective nonlinear absorption coefficient. The effective nonlinear coefficient accounts for both genuine two photon absorption (2PA) and two step excitations or free carrier absorption taking place in the material. Considering this, the normalized transmittance for ns and fs excitation can be obtained by numerically solving the propagation equation

$$\frac{dl}{dz'} = - \left[ \left( \alpha_0/1 + \left( \frac{l}{I_s} \right) \right) + \beta_{\text{eff}}l \right] l$$

where $z'$ is the propagation distance within the sample. From the best numerical fits to the experimental data, the saturation intensity $I_s$ and nonlinear absorption coefficient, $\beta_{\text{eff}}$ are calculated. These values are listed in Table 4.1.

**Table 4.1: Nonlinear optical parameters calculated for the samples and reported in literature.**

<table>
<thead>
<tr>
<th>Material</th>
<th>100 fs, 800 nm excitation</th>
<th>5 ns, 532 nm excitation</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$I_s$ ($\times 10^{16} \text{ W/m}^2$)</td>
<td>$\beta_{\text{eff}}$ ($\times 10^{-15} \text{ m/W}$)</td>
</tr>
<tr>
<td>CuS NPs</td>
<td>2</td>
<td>6</td>
</tr>
<tr>
<td>CuS QDs</td>
<td>1</td>
<td>0.23</td>
</tr>
<tr>
<td>Au NCs [18]</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Se NPs [47]</td>
<td></td>
<td>1.7</td>
</tr>
<tr>
<td>Hydrogen exfoliated graphene [48]</td>
<td>0.1</td>
<td>1</td>
</tr>
</tbody>
</table>
The obtained values are comparable with the reported nonlinear coefficients for ns and fs time scales for the same experimental conditions. It may be noted that $\beta_{\text{eff}}$ is an order of magnitude larger in CuS QDs compared to the NPs, which makes the QDs better optical limiters. Similar size dependence in the optical limiting behavior and efficiency of nanoparticles and atomic nanoclusters of Au has been reported recently [18].

4.3.9 Evolution of optical nonlinearity - NPs to QDs

The present samples are excited resonantly at (2.33 eV), which results in excitons and free carrier generation due to interband and intraband absorption. Photon absorption by these free carriers will be strong at higher input intensities and fluences. For long pulse width excitations, after one photon or two photon excitations, other excitations and relaxations are possible within the pulse duration. This cumulative effect adds to the 2PA coefficient resulting in a higher value of effective two photon coefficient at ns excitations. The excited state absorption and free carrier absorption is found to be the main mechanisms for optical limiting effects in CuS hollow spheres [49]. Ground state bleaching with 3 ns relaxation and excited state absorption for 2.33 eV excitation is reported in Cu$_x$S nanocrystals from transient absorption spectroscopy [50,51]. The alignment of band structure of CuS is such that the valance band maximum is formed from occupied S 3p and Cu 3d states whereas unoccupied Cu 4p states contributes to conduction band minimum [52]. For both CuS NPs and CuS QDs, the nonlinear absorption coefficients are of the same order, whereas CuS QDs have a slightly lower optical
limiting threshold of 4.6 J/cm$^2$ than CuS NPs (limiting threshold - 6.3 J/cm$^2$). As clusters are ultra small particles, a large percentage of atoms are present on or near the surfaces. Furthermore, the presence of infinite interfaces between cluster and surroundings and occurrence of imperfect surfaces from OA crystal growth often creates electrons and/or holes traps [53]. The existence of surface states and traps in and around band edge can hold the higher excited state population by saturation of one photon and further excitation to higher states at higher input energies. Anand et.al. has shown that the formation of surface states and traps in and around the band edge in a system is conducive for nonlinear absorption [54]. Thus in addition to the information obtained from the UV-Vis absorption studies, increase in limiting efficiency for CuS QDs further confirms higher concentration of defect levels and surface states in the band edge following the crystal growth mechanism through OA.

The mechanism behind ultrafast optical limiting in the present case is two-photon absorption acting along with free carrier absorption. In CuS NPs the plasmon band is stronger compared to that in QDs, and absorption saturation is seen at moderate intensities as indicated by the two humps flanking the valley in the z-scan curves. Absorption saturation associated with SPR in metallic nanoparticles has been reported before [18,55]. Generally SPR will decay through the channels of radiative emission, interband excitation and intraband excitation. As CuS has no radiative emission around 800 nm (1.55 eV) and interband transition requires a relatively higher energy of 2.3 eV, plasmon excitation decays mainly through intraband excitation generating more free carriers. In addition, excess holes will be generated in the valence
Role of defects in optical nonlinearity of CuS quantum dots

band due to the copper vacancies (copper vacancy density increases with size, possibly due to the reducing surface/volume ratio [29]). Also NIR band formed in response to oxidative environment generates an additional level from unoccupied 3d-4s orbitals of CuII having electron acceptor character at 1.1 eV above valance band [52]. The two-photon energy of 3.1 eV for 800 nm excitation is greater than the band gap energy of CuS QDs and NPs. Thus the saturation of one photon absorption due to the presence of SPR, as well as the subsequent decrease in transmission due to free carrier absorption, can both be seen in CuS NPs. For CuS QDs, optical absorption has a broad and less intense plasmon resonance band. Thus the saturation of one photon absorption due to the bleaching of ground-state surface plasmon resonance (SPR) absorption is more in CuS NPs than QDs. As discussed earlier, the higher density of defects and surface traps renders a higher optical limiting efficiency for CuS QDs.

4.4 Conclusions

In summary, we prepared PVP capped copper sulfide nanoparticles and quantum dots through nontoxic, green, one-pot synthesis method. As evident from FTIR spectrum effective linkage between capping agent PVP and nanoparticles can be achieved. This makes nanoparticles highly dispersible in water making it relevant for biological applications and in vivo imaging. While their crystalline nature is studied from XRD patterns; the morphology, microstructural defects and internal crystallinity are confirmed from TEM and HRTEM studies. A pure hexagonal phase of CuS is observed in the NPs, whereas
the coexistence of cubic and hexagonal phases is seen in the QDs. In addition to grain boundaries, CuS QDs exhibit considerable amount of dislocations and planar defects such as twins and stacking faults. Growth process for CuS QDs is dominated by oriented attachment (OA) based crystal growth at suitable crystallographic phases, whereas for CuS NPs, crystal growth continues through the classical Ostwald ripening mechanism by accumulation of ions. Optical absorption in the linear as well as nonlinear regimes is examined for both QDs and NPs. The lower band gap energy in CuS QDs suggests the existence of electron/hole traps. The presence of defects and surface traps enhances free carrier absorption in CuS QDs resulting in a relatively higher optical limiting efficiency compared to the NPs.
Role of defects in optical nonlinearity of CuS quantum dots

References


Chapter 4


Role of defects in optical nonlinearity of CuS quantum dots


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