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EFFECT OF SELF ASSEMBLY ON THE NONLINEAR OPTICAL PROPERTIES OF ZnO-CdS NANOCOMPOSITES

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Abstract:
In the present work, we compare the nonlinear optical properties of ZnO-Cds colloid and self-assembled film by z scan technique. ZnO and Zno-Cds colloid clearly exhibit a negative nonlinear index of refraction at 532 nm and the observed nonlinear refraction is attributed to two photon absorption followed by free carrier absorption. Zno-Cds colloid exhibit reverse saturable absorption whereas the self-assembled film exhibits saturable absorption. These different nonlinear characteristics in the self-assembled films can be mainly attributed to the saturation of linear absorption of the ZnO defect states.

Key words
Nanocomposites, Self-assembly, ZnO-CdS, z-scan, Saturable absorption, Reverse saturable absorption

1. INTRODUCTION

Both from a research and an industry perspective, interest is growing in the hunt for new nonlinear optical materials with high optical nonlinearities. Wide band gap semiconductors have been the topic of in-depth research in recent years because to the rising demand for new nonlinear optical materials with potential uses in integrated optics (1). A fascinating wurtzitic II-VI wide band gap semiconductor, ZnO possesses a 3.3 eV band gap at ambient temperature, along with a high excitonic gain and a significant excitonic binding energy (2). As a result of the industrial demand for optoelectronic devices that might work at short wavelengths, there is currently a significant amount of research being done on the optical characteristics of this material. Thin film nonlinear optical materials that can be incorporated into an optoelectronic device are in high demand. Recent research has shown that ZnO thin films have substantial nonlinear second order susceptibilities, making them suitable for second harmonic generation (3). Due to its significance in applications including quick optical switching, self-focusing, damage to optical materials, and optical limiting in semiconductors, the third order susceptibility is of interest.

In the present investigation, we focus on the third order nonlinear optical properties of ZnO-Cds colloid and self-assembled film employing the technique of single beam z scan. ZnO-Cds colloid clearly exhibit a negative nonlinear index of refraction, however there is a change in the sign of the absorptive nonlinearity of the self-assembled films at 532 nm. The colloid exhibit reverse saturable absorption whereas the self-assembled film exhibits saturable absorption.

2. EXPERIMENT

Colloids of ZnO are synthesized by a modified polyol precipitation method (4). The monodisperse ZnO colloidal spheres are produced by a two-stage reaction process. The method of preparation involves the hydrolysis of zinc acetate dihydrate ZnAc in diethylene glycol DEG medium. Among the different polyols, the DEG is chosen because it is reported to give particles with uniform shape and size distributions. The size of the particles and hence the stability of this colloidal suspension depend on the concentration of zinc acetate as well as on its rate of heating. The molar concentration of precursor solution is 0.025*M* and a heating rate of 4 °C/min is employed for the formation of ZnO at a temperature of 120 °C. The product from the primary reaction is placed in a centrifuge and the supernatant DEG, dissolved reaction products, and unreacted ZnAc and water is decanted off and saved. A secondary reaction is then performed to produce the monodisperse ZnO spheres. Prior to reaching the working temperature, typically at 115 °C, some volume of the primary reaction supernatant is added to the solution. After reaching 120 °C, it is stirred for 1 h to get a monodisperse stable colloid.

The CdS nanocolloids are prepared by chemical method (5). $CdNO_{32}$ $4H_2O$ Merck, India and NH_2CSNH_2 Merck, India are used as the precursors for the incorporation of Cd and S, respectively. These precursors are dissolved in 2-propanol and distilled water under stirring. The solution is kept on stirring for 1 h to get a monodisperse stable colloid. The molar concentration of the precursor solution is 0.025*M*.

The ZnO–CdS nanocomposites are prepared by colloidal chemical synthesis by mixing a certain amount of CdS colloid to ZnO colloid and stirring for 1 h. The volume fraction of CdS is changed keeping the volume of ZnO constant. The samples having ZnO–*x*CdS composition with *x*= 0.1%, 0.5%, 1%, 1.5% 2%, and 5% are named as ZnO–0.1CdS, ZnO–0.5CdS, ZnO–1Cds, ZnO–1.5CdS, ZnO–2CdS, and ZnO–5CdS, respectively. Self-assembled films are then produced from the ZnO-CdS colloid by the technique of drop casting onto a preheated glass substrate maintained at a temperature of 120^0C.

The ZnO–CdS nanocomposites are characterized by optical absorption measurements recorded by using a spectrophotometer

3. RESULTS AND DISCUSSION

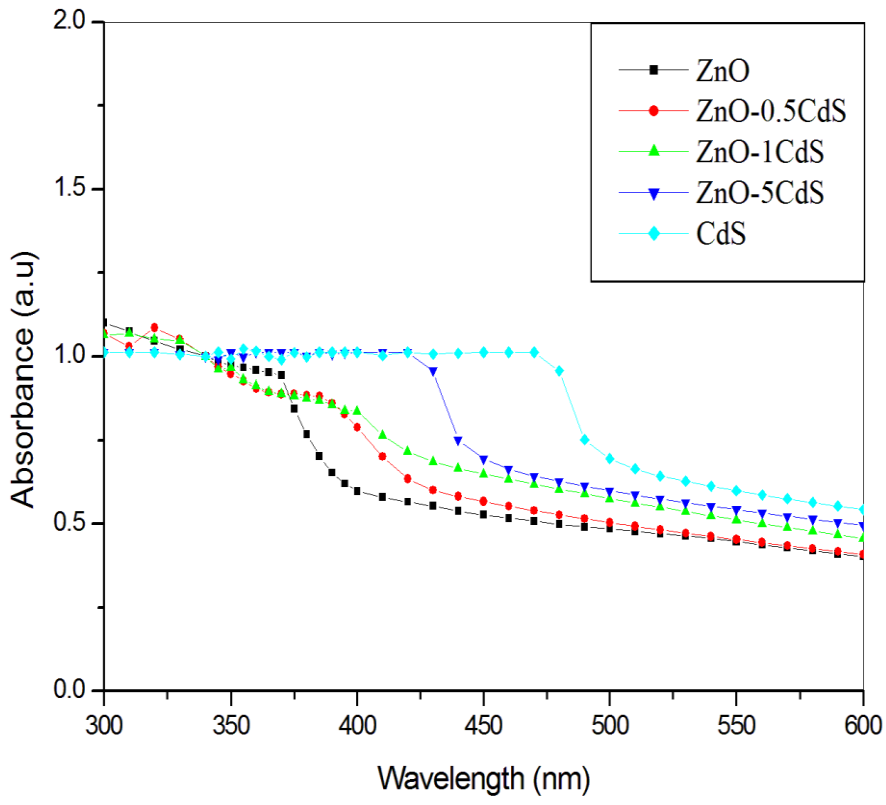

Figure : Absorption spectra of ZnO-CdS nanocomposites

Figure 1 shows the room temperature absorption spectra of ZnO-CdS nanocomposites. The excitonic peak is found to be blue shifted with decrease in particle size with respect to that of bulk and this could be attributed to the confinement effects. The presence of excitonic peak itself indicates that the composites are of nanometer in size. It is seen that the absorption edge corresponding to the nanocomposites gets red shifted as a function of the CdS content.

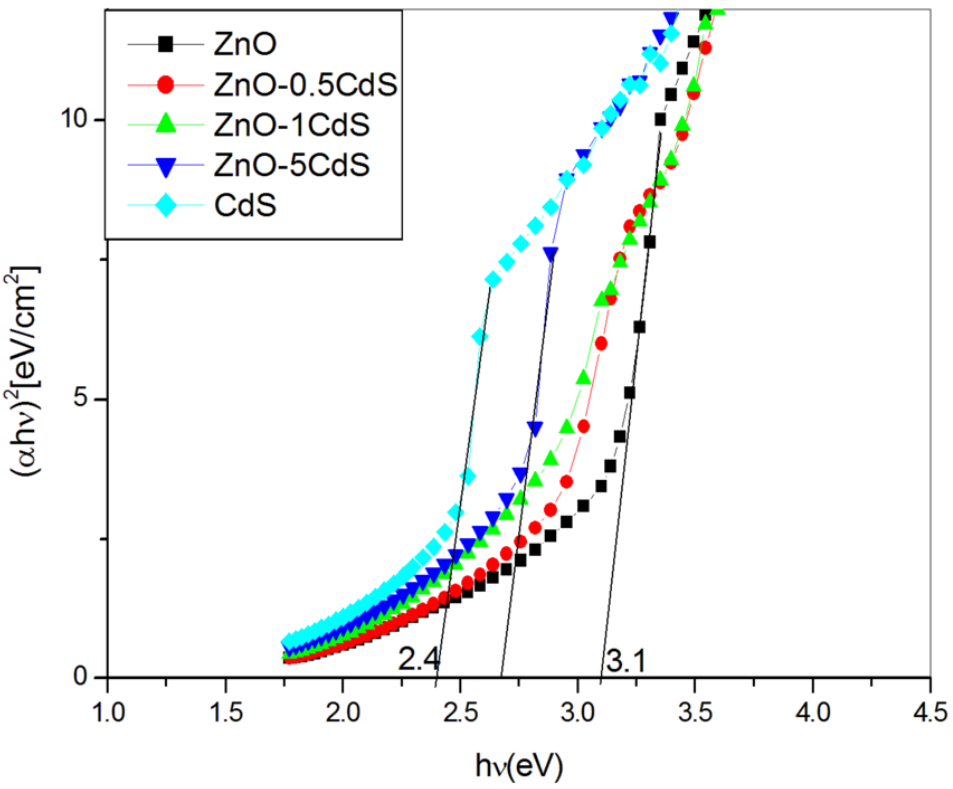

Figure 2: Optical band gap of ZnO-CdS nanocomposites

The direct band gap of ZnO–CdS nanocomposites is estimated from the graph of $h\nu$ versus $(\alpha h\nu)^2$for the absorption coefficient that is related to the band gap E_g as $(\alpha h\nu)^2 = k(h\nu - E_g)$, where $h\nu$ is the incident light energy and k is a constant. The optical band gap E_g is found to be dependent on the composition, and there is a decrease in the band gap of the semiconductor with an increase in volume fraction of CdS in the nanocomposites, as shown in Figure 2. E_g changes from 3.1 eV for ZnO to 2.4 eV for CdS almost in proportion to the composition of CdS. The total change in the band gap of the material is contributed by the shifts of the valence band as well as that of the conduction band edges away from each other.

Figure 3 shows the open aperture z-scan traces of ZnO-CdS nanocomposites at an intensity of 300MW/cm^2 for an irradiation wavelength of 532nm. The normalized transmittance valley indicates the presence of induced absorption in the colloids. Interestingly, ZnO and CdS colloids show a minimum nonlinearity, while the ZnO–CdS nanocomposites clearly exhibit a larger induced absorption behavior. The nonlinear absorption coefficient increases substantially in the nanocomposites, as compared to pure ZnO and CdS colloids due to the enhancement of exciton oscillator strength (6).

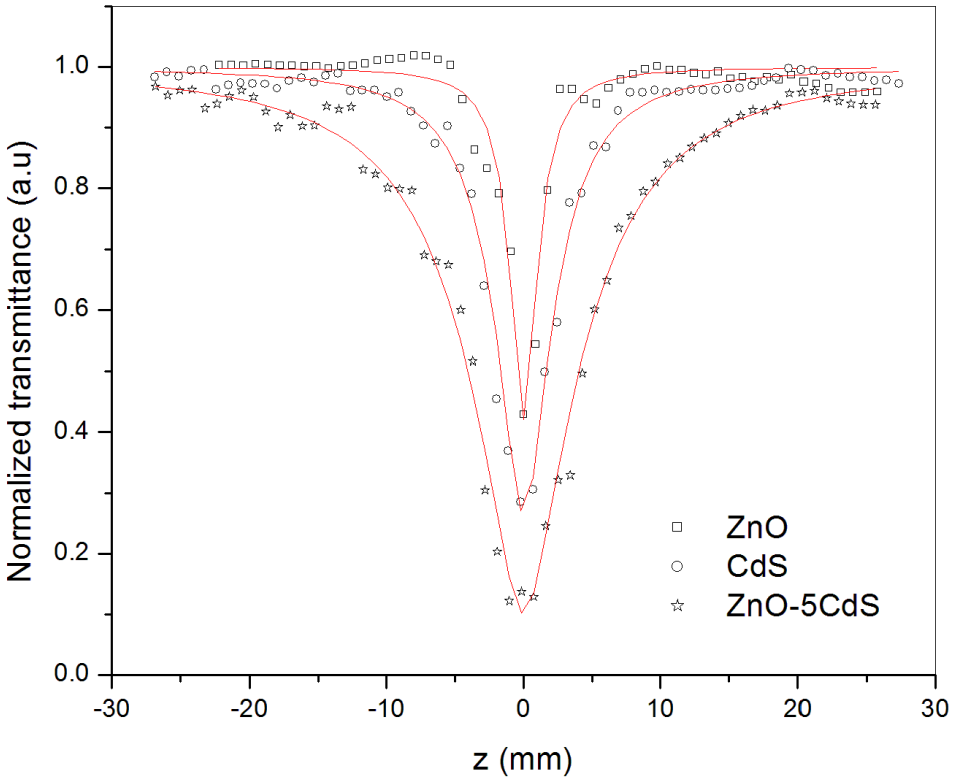

Figure 3. Open aperture z scan traces of ZnO-CdS nanocomposites at an intensity of 220 MW/cm^2 for an irradiation wavelength of 532 nm

In general, many different processes can lead to induced absorption. The theory of the two-photon absorption process (TPA) agreed well with the experimental curve, and the fact that two photons of 532 nm radiation lie below the absorption band-edge of the samples under investigation suggests that TPA is the fundamental mechanism. Induced absorption may be influenced by higher order nonlinear processes like free carrier absorption (FCA). The free carrier lifetime of ZnO is reported to be 2.8 ns [7]. Thus, there is a good chance that the rising edge of the 7 ns pulses utilised in the current investigation is stimulating the accumulated free carriers produced by TPA. Considering all these factors and the fact that we employed nanosecond excitation pulses, it is plausible to assume that TPA and FCA are the key mechanisms causing induced absorption in ZnO-CdS colloids.

Figure 4 shows the open aperture z-scan plot of ZnO-CdS Colloid and Film. ZnO-CdS colloid shows Reverse Saturable Absorption (RSA) whereas the film shows Saturable Absorption (SA). The self-assembled film exhibits saturation of absorption and bleaching and possesses a larger absorption coefficient and may have been even more susceptible to thermal effects. For semiconductor materials, heat tends to reduce the fermi energy level and thereby, increase the number of carriers in the conduction band. This, in turn, depletes the ground level and induces bleaching in the ground state absorption, which results in SA process.

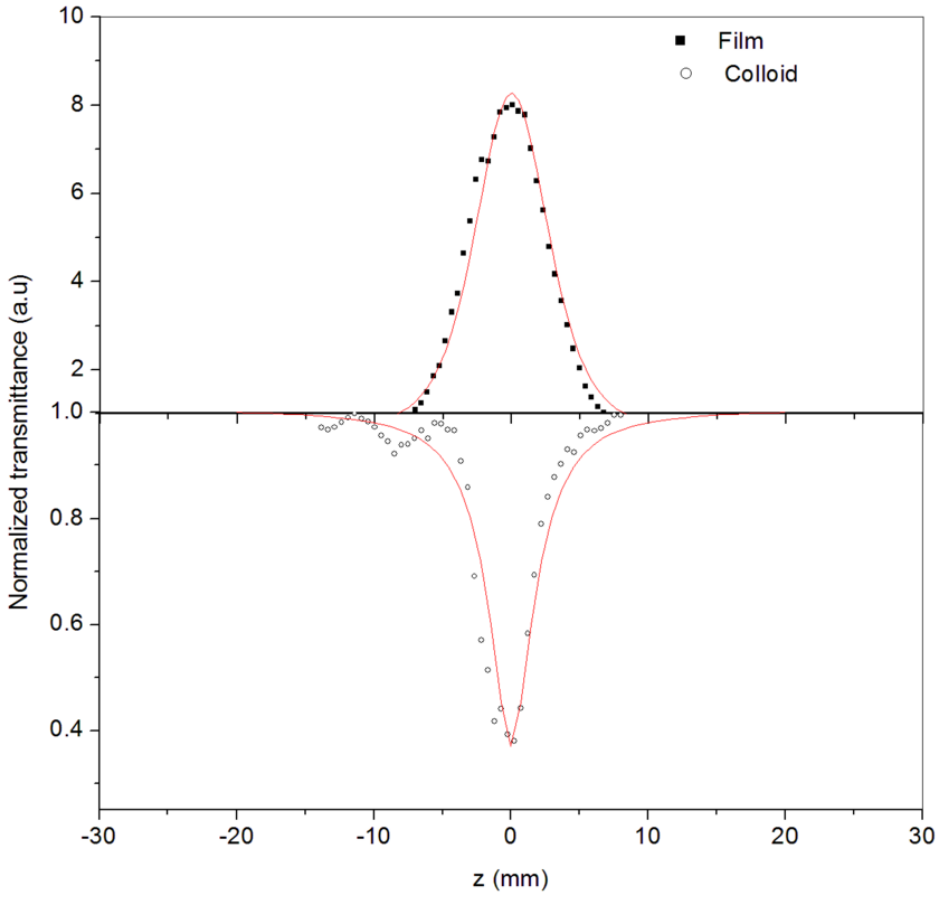

Figure 4 : Open aperture z-scan plot of ZnO-CdS Colloid and Film

The sensitivity of ZnO to impurities as well as native defects with respect to electronic properties is well known [8]. Thus we propose the mechanism behind the saturable absorption in self-assembled films can be attributed to saturation of linear absorption of the ZnO defect states. During the preparation of self-assembled films, unwanted particles may get trapped in the interstitial spaces which lead to point defects. The absorption of these defect states leads to the saturable absorption by the films.

Generally, ZnO exhibits reverse saturable absorption. An interesting phenomena that can be employed for optical pulse compression, optical switching, and laser pulse narrowing is the saturable absorption behaviour in self-assembled ZnO-CdS self-assembled films [9, 10]. The z scan data shows that, along with moving the self-assembled film towards the focus, the increase in the laser intensity induces bleaching in the ground state absorption, which results in SA process. The substantial SA and lack of RSA in the self-assembled film indicate that the ground state absorption cross section is significantly larger than the excited state absorption cross section. At the wavelength of the excitation radiation, all RSA materials have a greater excited state absorption cross section than the ground state. It's interesting to note that they will also provide a positive value for the imaginary component of susceptibility, which is really a measure of the induced absorption. A saturable absorber, on the other hand, has a negative value for the imaginary part of susceptibility. These materials' most significant uses are for optical limiting and as saturable absorbers. Thus, the ZnO-CdS nanocomposites investigated here show good nonlinear optical response and might be considered as suitable candidates with potential applications in nonlinear optics

4. CONCLUSION

We have investigated the nonlinear optical properties of ZnO-CdS colloids and films developed by self-assembly. ZnO- CdS colloids clearly exhibit a negative nonlinear index of refraction at 532 nm and the observed nonlinear refraction is attributed to two photon absorption followed by free carrier absorption.

There is a change in absorptive nonlinearity of the colloids and films. The colloids exhibit reverse saturable absorption whereas the self-assembled film exhibits saturable absorption. This behaviour can be attributed to the saturation of linear absorption of the ZnO defect states.

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