Tunable Nonlinear Optical Properties of ZnO-Cu Nano Composites Due to the Impact of Self Assembly

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Abstract— **In the present work, we compare the nonlinear optical properties of ZnO-Cu colloid and self-assembled film by z scan technique. ZnO and Zno-Cu 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 weak free-carrier absorption and interband absorption mechanisms.Zno-Cu 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.ZnO–Cu is a potential nanocomposite material for the light emission and for the development of nonlinear optical devices with a relatively small limiting threshold.**

Index Terms: **Nanocomposites, Self-assembly, ZnO-Cu, 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-Cu colloid and self-assembled film employing the technique of single beam z scan. ZnO-Cu 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 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 0.025M 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 wateris 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 copper nanocolloids are prepared by a hydrolysis method (5). The method of preparation involves the hydrolysis of copper sulphate in H2O near boiling temperature. The solution is kept boiling for 1 hour to get a monodisperse stable colloid. The molar concentration of the precursor solution is 0.025 M. The ZnO–Cu nanocomposites are prepared by colloidal chemical synthesis by mixing a certain amount of Cu colloid to ZnO colloid at 120 °C during its preparation stage and stirred for 1 hour at that temperature. The volume fraction of Cu is changed keeping the volume of ZnO constant. The samples having ZnO–xCu composition with (x) 0.1%, 0.5%, 1%, 1.5%, 2%, and 5% are named as ZnO–0.1Cu, ZnO–0.5Cu, ZnO–1Cu, ZnO– 1.5Cu, ZnO–2Cu, and ZnO–5Cu, respectively. Self-assembled films are then produced from the ZnO-Cu colloid by the technique of drop casting onto a preheated glass substrate maintained at a temperature of 1200C.

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

3. RESULTS AND DISCUSSION

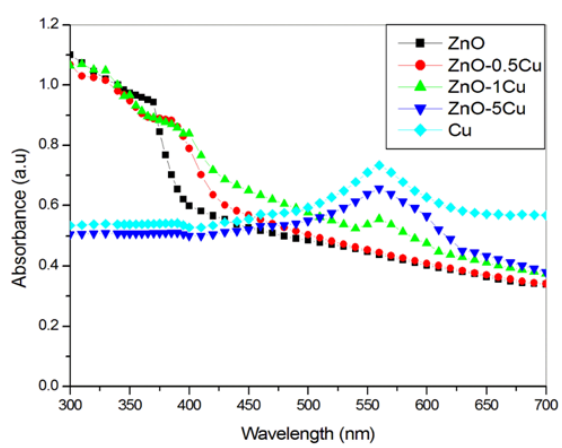

Figure 1: Absorption spectra of ZnO-Cu nanocomposites

Figure 1 shows the room temperature absorption spectra of ZnO-Cu 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. For Cu nanocolloid,the surface plasmon absorption band(SPA) lies in the 560 nm region. For small volume fraction of Cu, the composite exhibits the characteristics of ZnO with a red shift in the excitonic peak. When the volume fraction of Cu increases, the surface plasmon peak of Cu appears at 560 nm and it has been established that the plasma band of Cu observed is a result of the accumulation of excess electrons on the ZnO/Cu particles which leads to equalization of the potentials of the conduction zones of the semiconductor and the metallic components of the nanocomposites.

Figure 2 shows the open aperture z-scan traces of ZnO-Cu nanocomposites at an intensity of 300MW/cm2 for an irradiation wavelength of 532nm. The normalized transmittance valley indicates the presence of induced absorption in the colloids. Interestingly, ZnO and Cu colloids show a minimum nonlinearity, while the ZnO–Cu nanocomposites clearly exhibit a larger induced absorption behavior. It is reported that the nonlinear absorption coefficient increases in the bimetallic and core-shell nanocomposites, as compared to pure metals(6).

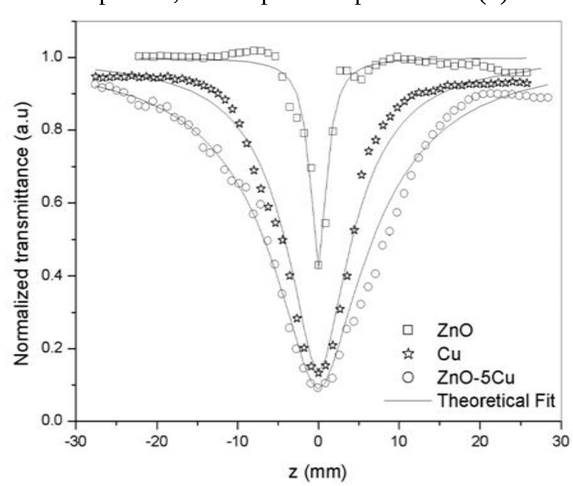

Figure 2. Open aperture z scan traces of ZnO-Cu nanocomposites at an intensity of 220 MW/cm2 for an irradiation wavelength of 532 nm

Different processes, such as two-photon absorption (TPA), free-carrier absorption (FCA), transient absorption, interband absorption, photoejection of electrons, and nonlinear scattering, are reported to be operative in nanoclusters. In general, induced absorption can occur due to a variety of processes. The theory of two-photon absorption process fitted well with the experimental curve and infers that TPA is the basic mechanism. There is the possibility of higher order nonlinear processes such as FCA contributing to induced absorption. The free carrier lifetime of ZnO is reported to be 2.8 ns (7). Hence, the 7 ns pulses used in the present study can excite the accumulated free carriers generated by TPA by the rising edge of the pulse. The FCA is weak compared to TPA and hence the corresponding contribution in the z-scan curves is relatively less. Copper nanoparticles are well-known materials for nonlinear optical applications because of their subpicosecond time response of third-order optical nonlinearity. Transient absorption and nonlinear absorptive mechanisms are reported to lead to optical limiting in the case of metal nanoparticles (8).

A laser pulse can cause an intraband or interband absorption in the metal nanoparticle system, depending on the excitation wavelength and incident intensity. The electrons thus excited are free carriers possessing a whole spectrum of energies, both kinetic and potential, immediatelyafter the absorption leading to the bleaching of the ground state plasmon band. This process is accompanied by the nascent excited state showing a transient absorption due to the FCA (9). The possibility of photoejection of electrons, which is an ultrafast phenomena occurring by a two photon or multiphoton absorption process, should also be considered as a contributing factor leading to nonlinear absorption, since the excitation photons in the visible region are usually not energetic enough for monophotonic electronic ejection. In our case, the excitation energy (532 nm or 2.3 eV) is higher than the interband threshold of copper from d-level to p-level (571 nm or 2.17 eV) and hence interband absorption accompanied by the absorption of free carriers generated in the conduction band is possible. Strong optical limiting properties because of interband absorption are reported in different nanoparticle systems (10). Thus, we propose that the observed nonlinearity is caused by two-photon absorption and weak FCA with a contribution from interband absorption occurring in the nanocomposites.

Figure 3 shows the open aperture z-scan plot of ZnO-Cu Colloid and Film. ZnO-Cu 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.

The sensitivity of ZnO to impurities as well as native defects with respect to electronic properties is well known [11]. 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-Cu self-assembled films [12, 13]. 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-Cu nanocomposites investigated here show good nonlinear optical response and might be considered as suitable candidates with potential applications in nonlinear optics

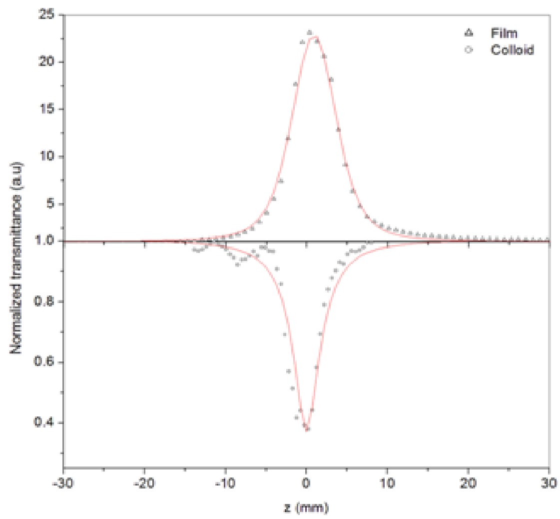

Figure 3: Open aperture z-scan plot of ZnO-Cu Colloid and Film

4. CONCLUSION

We have investigated the nonlinear optical properties of ZnO-Cu colloids and films developed by self-assembly. ZnO- Cucolloidsclearly 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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