ZnO/PEG Nanocomposite material is synthesized by laser ablation of pure Zn target in the mix solution of PEG and water in different compositions. Synthesized Nanocomposite materials are characterized by using UV-visible absorption, Transmission electron microscope (TEM) and Photoluminescence (PL) spectroscopic techniques. TEM investigation illustrates synthesis of few 2-5 nm quantum dots with very narrow size distribution. UV-visible absorption spectrum of quantum dots (QDs) synthesized in 30 ml water and 10 ml PEG (3:1 v/v) have small intensity of SPR peak corresponding to ZnO as compared to the peak corresponding to core transition electron. As the PEG concentration increases SPR peak corresponding to ZnO raises. It insures that PEG helps in the oxidation of Zn clusters to make ZnO. Possible synthesis mechanism is also discussed.

1. INTRODUCTION

Metal oxides have been incorporated into polymers as a means of altering electrical and other properties while attempting to maintain high optical transmission [1]. Metal oxide/polymer Nanocomposite materials have wide range of applications in optoelectronic industry in the fabrication of LEDs, Photo detectors, Displays etc due to their composition dependent electroluminescence (EL) and photoluminescence (PL) properties. As a wide band gap semiconductor, wurtzite ZnO with band gap energy of 3.37 eV at room temperature and exciton binding energy of 60 meV is one of the best fluorescent nanomaterial with photo stable, and solution processable behavior [2,3]. The optical properties of different structured ZnO have extensively been studied for several decades. With the rapid developments in nanotechnology, many interesting nanostructures of ZnO have been fabricated by different synthetic methods, such as chemical vapor deposition (CVD), thermal evaporation of oxide powders, polymerization, ion implantation and template assisted growth [4-6].

In the present study, Zinc oxide quantum dots are synthesized in the solution of PEG and water in different compositions by pulsed laser ablation of Zn rod in the aqueous solution of Polyethylgylcol (PEG) with different PEG water ratio. UV-visible absorption, TEM and PL characterizations of synthesized semiconductor polymer nanocomposite are done. The possible mechanism of the synthesis of the Nanocomposite materials is also discussed.

2. EXPERIMENTAL

Experimental arrangement for the synthesis of colloidal solution of Nanocomposite using pulsed laser ablation in aqueous media is described elsewhere [7], briefly high purity zinc target (99.99 %, Johnston Mathey, U.K.), placed on the bottom of glass vessel containing aqueous media of PEG with water in different ratio, was allowed to irradiate with focused output of 1064 nm from pulsed Nd:YAG laser (Spectra Phys., Quanta Ray, USA) operating at 40 mJ/pulse energy, 10 ns pulse width and 10 Hz repetition rate for 2 hours.

UV-VIS absorption spectra of as synthesized colloidal solutions were recorded by PerkinElmer, Lambda-35. One drop of colloidal solution of nanoparticles were placed on the carbon coated copper grid and dried. TEM images of the composite material on the grid were recorded using Technai G²0 Transmission electron microscope working at 200kV. Photoluminescence spectrum of as synthesized colloidal nanoparticles was recorded by PerkinElmer, LS-55.

3. RESULTS

3.1 UV-VIS Absorption

UV-visible absorption spectra of Nanocomposite synthesized mix solution of water and PEG with different ratio have shown in figure 1. Composite material synthesized in solution of 10 ml PEG with 30 ml of water has small intensity of SPR peak corresponding to ZnO as compared to the peak corresponding to core transition electron. As the PEG concentration increases SPR peak corresponding to ZnO raises. It insures that PEG helps in the oxidation of Zn clusters to make ZnO. For the equal volume of water and PEG ratio of SPR to intra-band transition peak is maximum. Position of SPR peak also shifted towards right, which shows that particle size increases with the addition of PEG.
The optical band gap, $E_g$, is determined from the absorbance spectra [8], where a steep increase in the absorption is observed because of band – band transition, from the general relation $(\alpha h \nu)^n = B(E-E_g)$, where $B$ is the constant related to the effective masses of charge carriers associated with valance and conduction bands, $E_g$ is the band gap energy, $E = h \nu$ is the photon energy, and $n= \frac{1}{2}$ or 2, depending on whether the transition is indirect or direct respectively. The intersection of the slope of $(\alpha h \nu)^2$ verses $h \nu$ curve on the x- axis provide band gap energy of the sample.

Figure 2: Toue’s plot for determining optical band gap of the ZnO/polymer nanocomposite.

Figure 3: TEM image of nanocomposite synthesized in (a) 10ml PEG with 30ml water and (b) 20ml PEG and 20ml water have shown in figure 3. The ZnO/polymer composite synthesized in 10ml PEG has 4-5 nm average size while in that of 20ml PEG has particles lying in the range of 6-8 nm with 7 nm average size and 2 nm dispersion. Most of the particles are spherical in shape along with some of the elongated particles with low aspect ratios. Size of the particles is larger as compared to those synthesized in the solution of 10 ml PEG in 30 ml water. HRTEM image shows that nanocomposite contains different planes of ZnO Nanocrystals. It is evident that particle size increases with the increase of PEG concentration. Therefore according to the band gap theory, band-gap of materials synthesized in low PEG concentration should be higher than that of synthesized in higher PEG concentration.
3.3 Photoluminescence (PL)

Figure 4 shows the photoluminescence spectra of the ZnO/polymer nanocomposite synthesized in the solution of 20ml water and 20ml PEG by different excitation. There is low absorbance at 225 and 250 nm, therefore it shows low emission efficiency corresponding to these excitations. With the variation of excitation wavelength one can determine bandgap energy and presence of defect levels. Excitation of the ZnO/Polymer composite material with 225 and 250 nm light emits PL in the range of 370-580 with bands at 320 and 400 nm. The band intensity and width at 400 nm produced by excitation of 250 nm light, is stronger as compared to that originates by excitation of sample by 225 nm. There is also emission band in the red region at 615 nm for 225 nm excitation, which shifted towards longer wavelength, with slightly decreased intensity, and falls at 630 nm for excitation by 250 nm light. Excitation of the sample with 275 and 325 nm have enhanced violet (342-600 nm) and near IR (λ>700 nm) emissions, which may have profitable applications in the fabrication of visible and IR LEDs.

4. DISCUSSIONS

We have observed blue emission as well as red emission from the composite nanostructures. Weak blue emission from ZnO nanostructures including their different shape and size are reported by several researchers. Recently Zeng et al. have reported blue emission from ZnO nanoparticles is due to interstitial Zn present in ZnO nanoparticles i.e. Zn/ZnO core/shell synthesized by pulsed laser ablation of Zn in liquid media. Emission peak at 300 nm corresponds for the wide band-gap of the polymer semiconductor Nano-composite particles having 4.0 eV gap. Size of the quantum dots are below 5 nm in diameter, therefore they are exhibiting quantum confinement effect.

Laser ablation in active liquid media, causes high non-equilibrium processing, which allows synthesis of novel phases of materials and, is of particular interest. Synthesis of nanomaterials by laser ablation in liquid media is under developing stage. Laser ablation at solid liquid interface, interaction between laser light and target creates local high temperature and pressure plasma plumes above target surface. It is reported that laser ablation of graphite\cite{48} target in water using 70 mJ/pulse energy of laser and detecting emission spectra and simulation, it was found that pressure and temperature inside plasma plume was 1Gpa and 6000 K respectively. At this high temperature and pressure several chemical reactions and physical processes, that are not possible at normal conditions, will take place among ablated species, solvent and surfactant molecules, which induces formation of particles in the solution. The structure, morphology, size, distribution and hence properties of nanoparticles are highly dependent on laser wavelength, irradiance, surfactant concentration, nature of solvent and other ablation parameters. Therefore properties of materials can be tuned by tuning ablation parameters.

Production of active metallic oxide polymer nanocomposite involves following processes in their formation (a) Generation of high temperature and high-pressure plasma at solid-liquid interface, after interaction between pulsed laser light and solid target. (b) Cluster formation by adiabatic and supersonic expansion leads to cooling of plasma plume. (c) Interaction of theses reactive clusters with species in aqueous media and reactive oxygen. Polymer is highly viscous therefore it strongly confines laser produced zinc plasma expansion. The more the confinement, more will be the pressure and temperature of ablated species inside the plasma. High pressure and high temperature induces and induces several reactions between laser induced plasma plume and ablating media. With the increase of Polymer/water ratio confinement of the laser ablated plasma plume increases, which induces more oxidation and reaction of laser ablated zinc plasma and aqueous media, therefore oxidation of ablated particles increases with the polymer concentration.

CONCLUSIONS

Size of synthesized polymer /ZnO Nanocomposite material increases with the increase of polymer water ratio. PL spectra have Strong UV-visible and near IR emissions applicable to LEDs and lasing applications. Size of the synthesized quantum dots are below 5 nm in diameter.

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