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Electroluminescence in Nanocrystals and Nanocomposites

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Introduction

Nanometer sized semiconductor clusters are representative of a state of matter intermediate between molecules and bulk matter. These have attracted growing interest of material scientists, physicists, chemists as well as biologist during last two decades due to their novel characteristics and size dependent properties. It has been demonstrated by several groups that nanocrystalline materials of II-VI semiconductors can be used as light emitting material for preparation of electroluminescence devices. Semiconductor nanocrystals exhibit many unique properties, which are promising for the improvement of electroluminescence (EL) devices. Combination of polymer and semiconductor nanocrystals allows the fabrication of flexible and lightweight EL devices. The incorporation of nanocrystals in polymer is expected to increase the life of the device and enhance the brightness of emission. In present work II-VI semiconductor nanoparticles and their nanocomposites in polymers have been synthesized by chemical route. The samples have been characterized and their electroluminescence has been investigated.

Experimental

1. Preparation of samples

Nanocrystals of CdS and ZnS doped with Mn, Ag or Cu are synthesized by chemical precipitation method using mercaptoethenal as capping agent. Aqueous solutions of $CdCl_2$ or $ZnCl_2$ with CuCl, $MnCl_2$ or AgCl in adequate quantity for doping, was mixed with solution of Na_2S in presence of mercaptoethenol capping agent to give doped and undoped nanocrysals. CdSe nanocrysals were prepared by reacting cadmium acetate with sodium selenosulfate using mercaptoacetic acid as capping agent. The resulting precipitate was washed, centrifuged and then air dried to obtain nanocrystalline powder.

Nanocrystal-polymer sample of ZnS or CdS have been prepared with different loading of nanocrystals. For preparation of composites, the polymer granules were dissolved in suitable solvent. Then proper amount of zinc or cadmium acetate was added to it and H_2S was passed. PVA/CdSe polymer nanocomposite films were prepared by reacting cadmium chloride with sodium selenosulfite (Na_2SeSO_3) in polyvinyl alcohol (PVA) solution at proper pH. The solution was cast on glass substrates; upon solvent evaporation, nanocomposite films were obtained. For characterization, films were deposited on plane glass plates and for EL studies, these were deposited on SnO_2 coated conducting glass plates.

2. Characterization

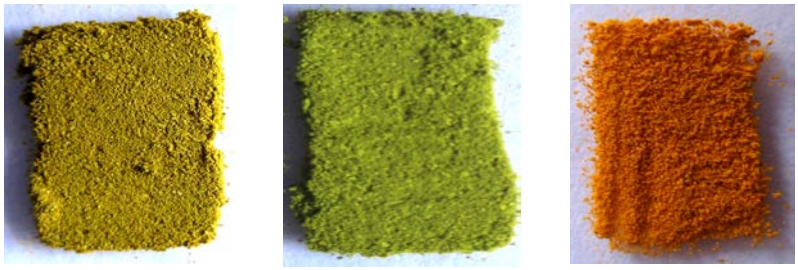
The samples have been characterized for their morphology and structure by scanning electron microscope (SEM), atomic force microscope (AFM), transmission electron microscope (TEM) and X-ray diffraction (XRD). Size of nanocrystals is determined from broadening of XRD peaks. The absorption spectra of the sample have been studied by Perkin Elemer spectrometer. The increase in the effective band gap has been estimated from the absorption edge or peak and the particle size is computed using effective mass approximation model.

3. *Electroluminescence measurements*

For EL investigations, the emission material layer is placed between conducting glass and aluminium electrodes. In case of nanocrystalline powder samples, a piece of mica sheet having a window of 2x2 mm is placed over the conducting glass and the sample powder is placed within this window and fixed with adhesive. In case of composite films, mica sheet with window was placed over the film layer deposited on the conducting glass plate. An aluminum strip is fixed over the sample along with conducting gel in order to obtain good contact. Voltage is applied at the conducting glass and the aluminum and light emitted from the sample is viewed through the conducting glass side. The EL was studied at different voltages and frequencies.

Results and Discussion

The change in colour of samples has been observed by changing the nanoparticle size by varying preparation conditions (Fig.1).



Small particles Largerer particles Large particles

CdSe nanoparticles prepared at different pH

Fig.1

The morphology of the sample is seen by SEM, TEM and AFM images. In nanocrystalline powder specimens, agglomeration of particles is observed. A typical AFM image of ZnS nanoparticles is shown in Fig.2. The TEM images reveal the nanoparticles more clearly. Fig.3 shows such an image for ZnS nanoparticles. The particle size is of the order of a few nm.

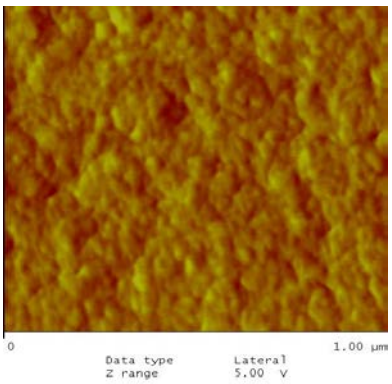


Fig. 2 Typical AFM Image of ZnS Nanoparticles

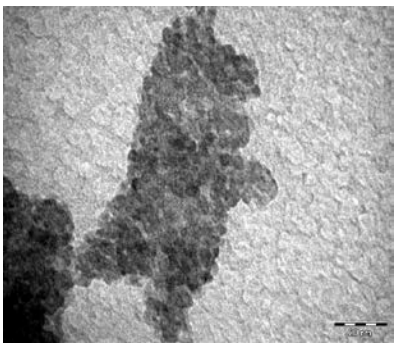


Fig.3 Typical TEM Image of ZnS Nanoparticles

a) *X-ray diffraction studies*

The XRD studies indicate that most of the samples are cubic in nature. The broadening of peaks is indicative of small particle size. The sizes have been computed busing Dubey-Scherrer formula and obtained in the range of 2 to 10 nm.

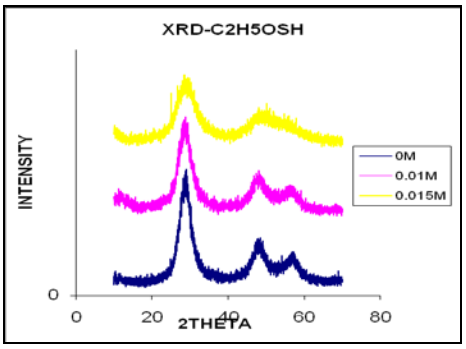


Fig.4 XRD Patterns of ZnS Nanocrystals

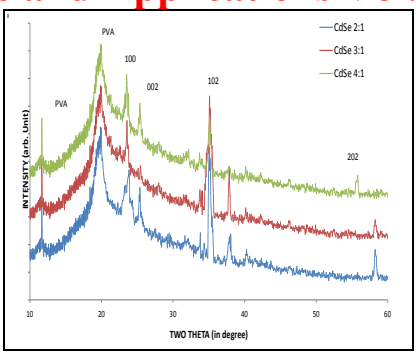


Fig.5 XRD patterns of CdSe/PVA Nanocomposite film

It is observed that smaller particles are obtained by increasing capping agent concentration or pH value, or reducing temperature or reaction time. Fig.4 shows XRD patterns of ZnS nanocrystals. In nanocrystal /polymer composites, XRD shows halo due to polymer and peaks superimposed on it due to the nanocrystallites. CdSe as well as its polymer composite and CdS/PVA composite have found to contain hexagonal crystals (Fig.5). The lattice constants have been found in close agreement with the standard ones.

b) Absorption studies

Absorption spectra of nanocrystals have shown blue shift in absorption edge or first absorption peak, as compared to their bulk counterpart indicating increased band gap energy. The absorption edge or peak is found to shift towards higher energies for smaller particles. Fig.6 shows the absorption spectra of CdSe nanocrystals prepared with different capping agent concentrations. No effect of doping has been observed on the absorption spectra. The effective band gap energy has been determined from the absorption spectra and particle size is computed from the effective mass approximation (EMA) model. The particle sizes obtained by this method are in agreement with those from XRD.

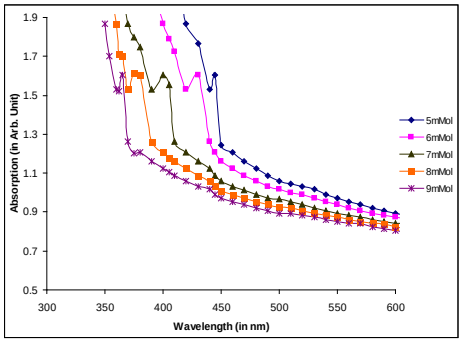


Fig.6 Absorption Spectra of CdSe nanocrystals

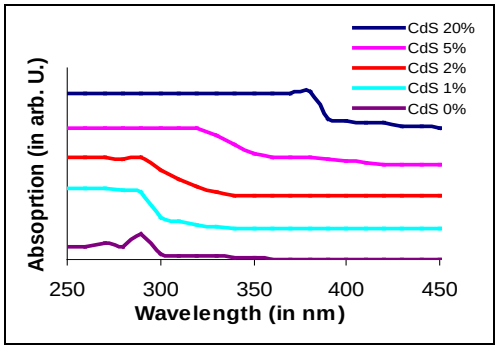


Fig7 Absorption Spectra of CdS/PVK Nanocomposites

In case of nanocomposites, pure polymer is found to be transparent in visible region and absorption peak is obtained inultraviolet region. When CdS, ZnS or CdSe nanocrystals are incorporated in it, their absorption is superimposed. In case of CdS, absorption edge is obtained in visible region and shift towards higher wavelengths by increasing nanocrystalline loading from 0 to 20% as shown in Fig.7. This indicates that crystal size increases with increasing nanocrystalline loading.

c) Electroluminescence studies

The EL studies on nanocrystalline powder samples and nanocrystal/polymer composites have shown that the light emission starts at certain threshold voltage, different for

different specimens, and then usually increases rapidly with increasing voltage (Fig.8). It is found that for smaller nanocrystals, threshold voltage is lower and EL brightness (B) increases rapidly with voltage. The relationship between applied voltage (V) and current is found to be linear indicating ohmic nature. In general higher brightness is obtained at higher frequencies.

It is observed that CdS nanoparticles give bluish light emission where as purple-green emission has been obtained in case of ZnS nanoparticles. The EL brightness (B) is found to depend on the doping concentration. Fig.9 shows the variation of EL brightness in case of ZnS:Cu nanocrystals. It can be seen that maximum brightness is obtained at 0.01% Cu concentration. At higher concentration of dopent, the probability of nonradiative trasition increases due to decrease in the distance between two dopent ions.

Similar results are obtained for nanocrystal/polymer composites. By increasing nanocrystalline loading, EL starts at lower threshold voltages and higher intensity is observed.

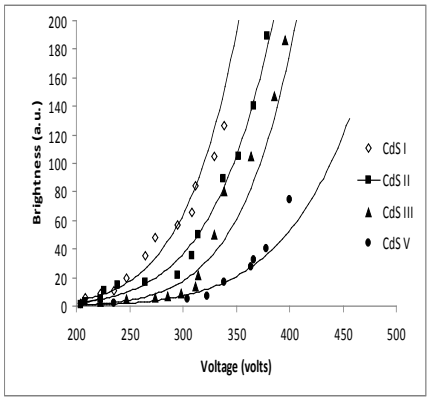


Fig.8 Electroluminescence Brightness of CdS nanocrystals

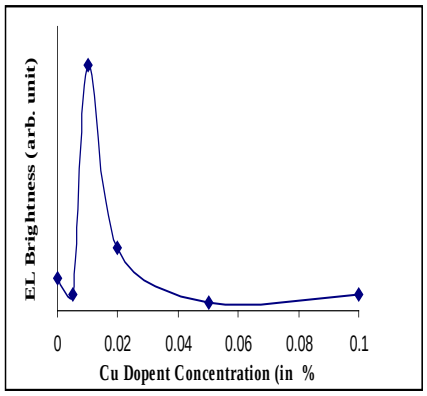


Fig. 9 Dependence of EL brightness on dopent concentration

Fig.10 shows the variation of EL brightness by increasing the CdS concentration in the nanocomposite (CdS/PVK). It can be seen that at higher voltages, saturation of EL intensity occurs for lower concentrations of nanocrystalline loading. This shows that such composites can be easily used for EL devices with advantage of better flexibility and good quality films.

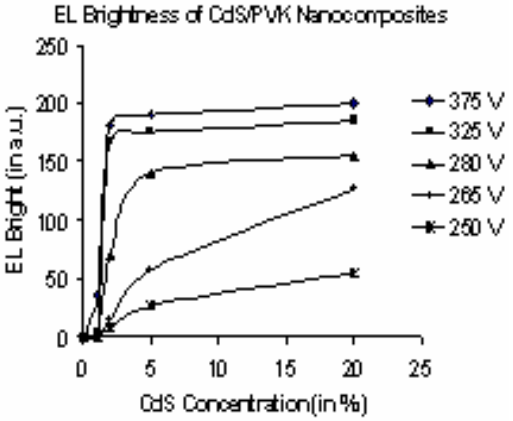


Fig. 10 EL Brightness vs Concentration Characteristics of CdS/PVK Nanocomposites

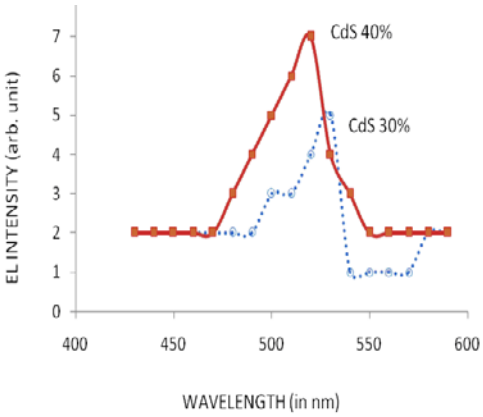


Fig. 11 Electroluminescence spectra of CdS/PVA nanocomposites

Fig.11. shows electroluminescence spectra of CdS/PVA nanocomposite film with CdS loading 30% and 40%. The emission peak is observed at 530 nm for 30% loading. In the EL spectrum, peak shifts towards lower wavelength increasing loading concentration. It has been speculated that the luminescent is due to recombination emission from electron trapped in the shallow defects and hole trapped in the deep defects, and shallowly trapped electron still posses small effective masses and therefore exhibit the quantum size effect.

From the EL investigations of nanocrystalline powder as well as nanocomposites, it is seen that Log B vs. $1/\sqrt{V}$ curve is a straight line with negative slope. This indicates that EL is produced by acceleration-collision mechanism. Low energy states are also populated by electrical excitation that can not be populated by optical process. Therefore EL emission is obtained at photon energies much less than the band gap of the material.

The investigations have revealed that EL is enhanced by reducing the size of nanocrystals. II-VI semiconductor nanocrystals embedded in polymer matrix improved the EL as compared to powder samples. Different materials or different sized nanoparticles in polymer matrix may be used for light emission of different colors.

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