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Enhancement of white light generation from CdSe/ZnS core – shell system by adding organic pyrene molecules

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Abstract: The composite CdSe/ZnS core – shell mixed with pyrene molecules in polymethyl meth-acrylate (PMMA) polymer was used to generate intense white light when illuminated by InGaN/GaN UV LED. The addition of pyrene molecules in low concentration to the core – shell system tuned the chromaticity coordinates to (0.25, 0.34) and increased the intensity of the emit-ted white light. This improvement was attributed to the overlap of pyreneexcimer emission with the absorption spectrum of CdSe/ZnS core – shell which leads to a cold white light generation. The synthesis of core – shell nanoparticles, with the pyrene molecules in PMMA films, is pre-sented. The photoluminescence spectra of the pyrene, CdSe/ZnS core – shell and their mixture composite in PMMA were tested. The Gaussian fit was used to determine the chromaticity coor-dinate of the emitted white light.

Keyword: CdSe/ZnS core – shell; pyreneexcimer; energy transfer; white light generation.

1. Introduction:

Since 25% of the global electricity con-sumption is used for lighting, the white light generation has attracted great interest for sav-ing the electrical energy consumption in order to reduce the operating expense [1]. The solid state lighting (SSL) by using the tradition phosphor is not new and different schemes have been reported to generate white light [2, 3]. One of the most popular ways is the blend-ing of red, green and blue phosphors in ap-propriate ratio to generate the white light [4]. The importance of the SSL is not only due to its financial benefits, but because the SSL is predicted to reduce the carbon emission highly which leads to clean environment. The en-ergy efficiency of SSL in converting electrici-ty into light is about 50% whereas for tradi-tional lamp it’s around 1%. In addition, SSL offers ultra – long lifetimes for the lamps and the source becomes, ragged and compact.

The white nanoluminophors have attract-ed more attention for their potential use in solid-state lighting. Usually, the materials used in white nanoluminophors are semicon-ductors like CdS, CdSe, ZnS and ZnSe with size of the order of 1–10 nm [5]. Since the nanostructure have a large number of surface atoms compare with the bulk, the characteris-tics of the surface atoms have more effect onthe main physical and chemical properties of the material. It has been reported that nano-crystals synthesized with elemental sulfur have more surface defects acting as traps on the nanocrystal surface [6]. The formation of the surface defects increases the overlap of the electron and hole wave functions [7]. Cor-respondingly, the band gap recombination reduced, and the recombination to the surface states is dominated. Thus, abroad emission in the visible wavelength is observed due to charge recombination from the mid - gap states. Highly luminescent II-VI semiconduc-tor nanocrystals or colloidal quantum dots (QDs) are interesting materials because of their applications in optoelectronics, nonlinear optics, and biology. It is known that the photoluminescence (PL) efficiency of QDs can be significantly improved by growing a shell of a wide – band gap semiconductor around the QDs core by analogy with two-dimensional semiconductor heterostructures [8].

The white light emission from the trap – rich nanocrystalsCdS material was studied and the surface states formation was deter-mined [9]. The white light generated from the trap - rich nanocrystals requires a specific size distribution to generate the light in an accept-ed color index values under the UV illumina-tion. The specific size distribution technique required highly controlled reaction tempera-ture and reaction time.

The core – shell materials consist of a core structural domain covered by a shell do-main. The core and shell may be composed of variety of materials including polymers, inor-ganic solids, and metals; they have properties which may be different from the core or the shell materials [10]. One of the important characteristics of nanocrystallinesemiconduc-tors concerns the influence of the surface on the optical and electrical properties, and the need to embed semiconductors clusters in a passivating medium. It is well known that the photoluminescence (PL) emission intensity ofCdSe QDs increases several times when the CdSe cores are capped inside a shell of high band gap material like ZnS to form a CdSe/ZnS core – shell structure [11]. The generated white light from the CdSe/ZnS core – shell system was characterized by marginal chromaticity coordinates and with low exter-nal quantum efficiency.

2. Experimental

The cadmium selenideCdSe nanoparticles were prepared as a colloidal from reaction of Na2SeSO3 and CdCl2 with gelatin solutions at 1:2 molar ratio. The ratio is adjusted by changing the volume of CdCl2 with gelatin solution while the Na2SeSO3 solution was maintained fixed. The two solutions were mixed in a three – neck flask at a temperature of about 25 ºC with continuous flowing of argon gas for about 30 minutes, until the CdSe nanostructures were formed. The result-ingCdSe nanoparticles were obtained by add-ing ethanol followed by centrifugation.

The Zinc Sulfide ZnS nanoparticle was prepared by mixing two 0.1 M chemical solu-tions from ZnCl2 and Na2S. The two solutions were mixed in a three – neck flask and were left on magnetic stirrer at room temperature with continuous flowing of argon gas for about one hour until the ZnS nanoparticles were formed.

The CdSe/ZnS core – shell nanostructures were prepared by the reaction of CdCl2 with gelatin solution and Na2SeSO3 solution at a molar ratio of 2:1 in three – neck flask, fol-lowed by the addition of 20 ml of ZnSsolu-tion. The solutions mixed in the three – neck flask were left on magnetic stirrer at 50 ˚C temperature with continuous flowing of argon gas for about one hour until the CdSe/ZnS core – shell nanostructures were formed and then, isopropyl alcohol was added followed by centrifugation.pyrene and PMMA were prepared by mixing different molarities of pyrene (0.1 – 1 M) in PMMA and adding CdSe/ZnS core – shell in a beaker. The mixture was magnetically stirred until a complete dissolution. A homog-enous mixture was obtained by ultrasoni-cation. Nanofilms of about 800 nm thickness from this mixture were prepared by spin coat-ing technique.

The X – ray diffraction pattern of CdSe/ZnS nanoparticle powder was recorded by SHIMADZU XRD – 6000 diffractometer. The system works with Cu-Kα radiation line of wavelength of 1.54 in range of 10 -70 degrees.

The UV-VIS absorption spectrum of the samples was recorded by OPTIMA SP – 3000 UV -VIS spectrophotometer within the range 200 – 1100 nm. The photoluminescence (PL) spectrum was registered by SL 174 spectrofluorometer covering a range of 300 – 900 nm.

3. Results and discussion

The X – ray diffraction pattern of the yield CdSe/ZnS core – shell nanoparticles is illustrated in Figure 1. The pattern shows three peaks centered around 28.15˚ for (111) plane whereas the other two peaks were centered around 47.15º and 56.6º. The appear-ance of the three mentioned peaks was observed by several other authors [8, 12, 13]. The broadening of the apparent X – ray diffraction peaks indicates that the CdSe/ZnS core – shells are in nanodimension. In order to estimate the size of the formed core – shell nanocrystals, Scherrer equation (1) was used; [14-17]:

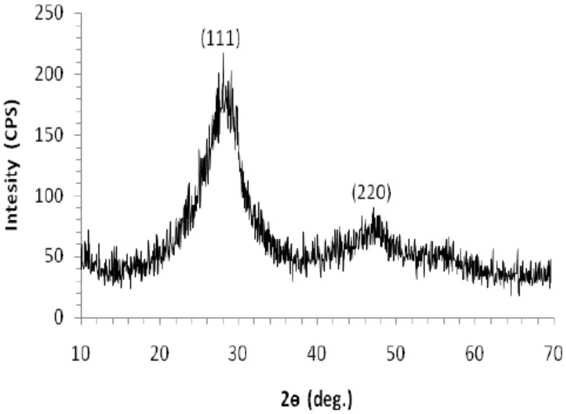

Figure 1: The XRD pattern of CdSe/ZnS core – shell nanoparticles.

$$D = 0.9\lambda/\beta\cos\theta \qquad (1)$$

Where D is the grain size, λ is the Cu - kα radiation line wavelength, β represents the full width at half maximum (FWHM) of the (111) peak in degree and θ is the diffraction angle. Using β value of about 7 degrees and as mentioned before, the size of the formed core – shell nanoparticle was found to be about 1.22 nm. The UV-VIS absorption spectrum of the CdSe/ZnS core –shell nanoparticles in PMMA is shown in Figure 2.

The spectrum shows that the sample is highly absorbed in the UV region whereas it shows low absorption between 450 – 550 nm and it is transparent above this wavelength.

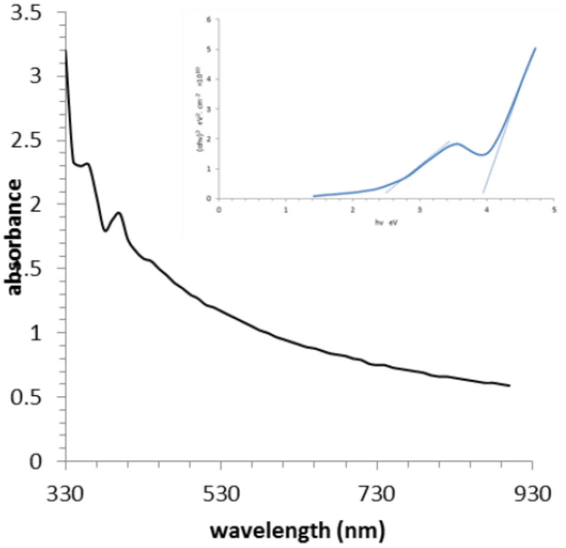

Figure 2: UV-VIS absorption spectrum of CdSe/ZnS core-shell nanoparticle.

It can be noticed from the figure that there are two inflection points; the first one around 360 nm and the other one is around 400 nm. The relation between (αhν)2 and (hν) is plotted to determine the energy gaps of CdSe and ZnS using Kosek and Tauc relation for the direct energy gap [18]. The energy gaps of the CdSe and ZnS were found to be 2.43 eV and 3.87 eV respectively. The dependence of the ener-gy gap on the nanocrystal size was used to estimate the prepared Q – dots dimension as in equation (2) [19]:

$$\Delta E = \frac{\hbar^2 \pi^2}{2R^2}\left[\frac{1}{m_e} + \frac{1}{m_h}\right] - \frac{1.786\, e^2}{\varepsilon R} - 0.248E^* \qquad (2)$$

where R is the Q – dots radius, and E* is the effective Rydberg energy. The size of CdSe (2.43 eV) and the ZnS (3.87 eV) where found to be 1.24 nm and 2.1 nm respectively. These values were not far away from the value extracted from Scherrer relation as mentioned previously.

The room temperature emission spectrum of the CdSe/ZnS core – shell nanoparticles in PMMA sample is shown in Figure 3. The fig-ure shows a peak centered around 320 nm which is related to the band to band transition of ZnS. Several peaks were observed around 375, 410 and 460 nm, respectively. This may be attributed to the formation of the surface states related to the uncompleted covering of the CdSe core by the ZnS shell. Similar ob-servation was reported by Denzler et al [20]. The peak centered around 505 nm may repre-sent the band to band transition of the CdSe core.

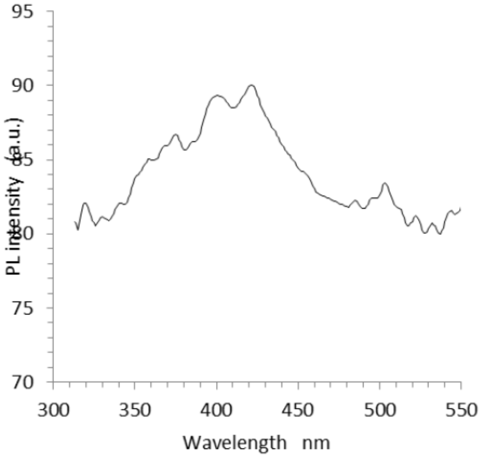

Figure 3: Photoluminescence emission spectrum of CdSe/ZnS core-shell in PMMA

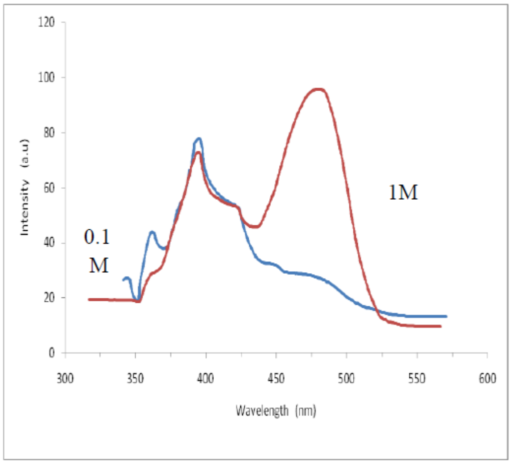

Figure 4: The fluorescence spectra of 0.1M and 1M of pyrene in PMMA films

The fluorescence spectra of 0.1 M and 1 M of pyrene in PMMA films are shown in Figure 4. It can be noticed from the figure that the fluorescence of 0.1 M does not show ex-cimer formation whereas the 1M shows the broad band excimer emission centered around 485 nm. The appearance of the excimer at 1M concentration is attributed to the aggregation of the pyrene molecules at high concentration in polymer.

In this work, an intense pyreneexcimer peak was observed even at low concentration (0.1 M) of pyrene mixed with the CdSe/ZnS core – shell. This may be interpreted to the fact that the prepared CdSe/ZnS core – shell nanoparticles of dimension (1-3 nm), which were measured through this work, behave likea seed for the pyrene molecules (0.3 nm) to be aggregated around it leading to excimer for-mation which emits a radiation at 485 nm.

The overlap between the pyreneexcimer emission around 485 nm and the absorption spectrum of CdSe/ZnS core – shell is shown in Figure 5.

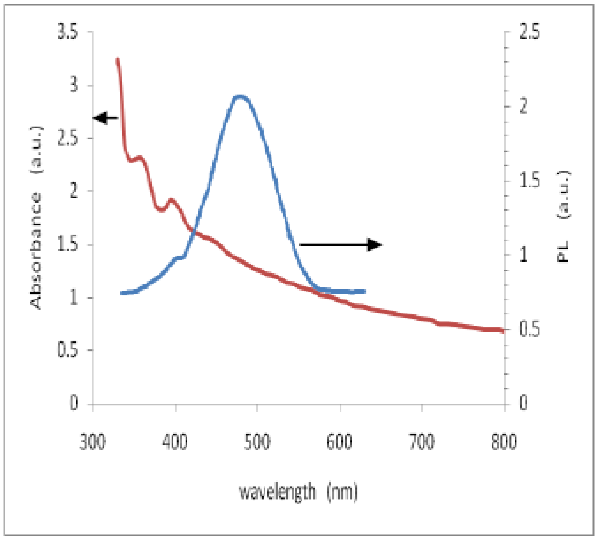

Figure (5): Photoluminescence of pyrene and absorbance of CdSe/ZnS core-shell.

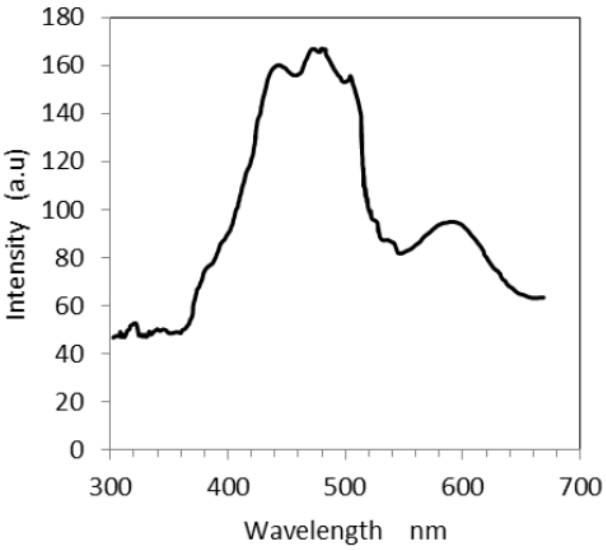

Figure (6): The fluorescence spectrum of core-shell and pyrene mixture in PMMA film.

Since the CdSe/ZnS core – shell quantum dots are efficient luminoophores and the py-rene is an efficient excimer harvester, the en-ergy transfer from the excimer to the quantum dots is possible. The overlap of pyrene ex-cimer fluorescence and the CdSe/ZnS quan-tum dots spectrum enhances the possibility of efficient energy transfer. The energy transfer mechanism leads to the observed quenching of pyrene excimer photoluminescence (PL) and the associated enhancement of the core – shell PL.

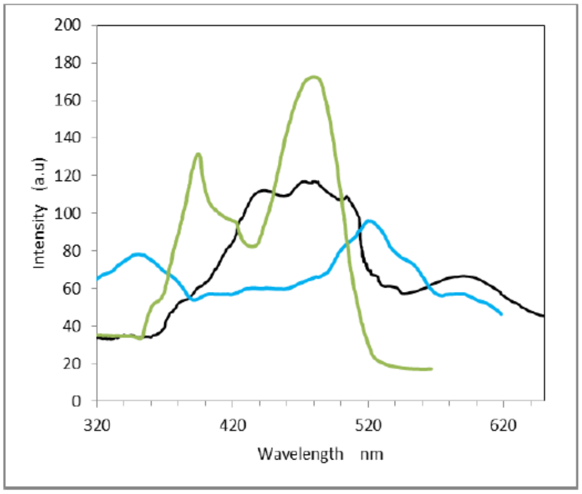

Figure 7: The photoluminescence spectra of the pyreneexcimer, CdSe/ZnS core – shell and the core – shell with pyrene in PMMA.

It can be noticed from the figures 6 and 7 that the radiation in the range 280 – 300 nm is efficiently absorbed by the composite, where-as the intensity of the fluorescence peaks around 440, 460 and 480 nm, respectively, are highly increased and there is an appearance of a peak at around 600 nm. The low intensity red peak observed in the fluorescence spec-trum of the CdSe/ZnS core – shell was referred to the formation of surface states due to non-perfect coating of CdSe core by ZnS shell. These results give a good evidence of the energy transfer from pyrene to the core – shell system.

A simple schematic energy levels diagram representing the energy transfer between the CdSe/ZnS core – shell and the pyreneexcimer level is shown in Figure 8. The energy level diagram shows that the ZnS shell emission absorbed by the pyrene molecules in the ground state. The excited pyrene molecule $^1M^*$ (monomer $^1M^*$) with energy of about 3.35 eV and a lifetime of 450 ns, may interact within 1 ns time with another pyrene molecule in the ground state to form the pyreneexcimerof energy around 2.55 eV and of lifetime of the order of 113 ns at room temperature [21]. The excimer energy may be transferred to the CdSe core of 2.43 eV energy. This mechanism leads to quenching of the fluorescence intensity below 400 nm, and increases the emission within the range 420 – 550 nm with the appearance of fluorescence peak around600 nm. This behavior may be supported by carrier localized model. The band gap of ZnS (3.87 eV) is much higher than that of CdSe (2.43 eV for the nanoparticles). The generated carriers in CdSe core are strongly localized in the ZnS shell. This prevents the carriers from being captured in the nonradiative recombination centers. This mechanism helps in recy-cling the excitation of CdSeexcitons which are excited by pyreneexcimer emission, lead-ing to more intense radiation in the 420 – 550 nm spectral range. The suggested energy transfer mechanism can be represented by the following relations (3 – 5) [22]:

$$(ZnS)^* + {}^1M \xrightarrow{Energy\ transfer} (ZnS) + {}^1M^* \qquad (3)$$

$$^1M^* + {}^1M \xrightarrow{Excimer\ formation} {}^1D^* \qquad (4)$$

$$^1D^* + (CdSe) \xrightarrow{Energy\ transfer} {}^1M + {}^1M + (CdSe)^* \qquad (5)$$

The illumination of the composite CdSe/ZnS core – shell and pyrene dispersed in PMMA by UV- LED of 5 mW generates an intense white light as shown in Figure 9. The figure shows that the illuminated part of the slide covered with CdSe/ZnS-pyrene in PMMA emits the white light, whereas the un-coated part was transparent to the UV radia-tion. The brightness of the emitted white light from the core – shell / pyrene composite dispersed in PMMA is much higher than that observed from CdSe/ZnS core – shell in the same polymer.

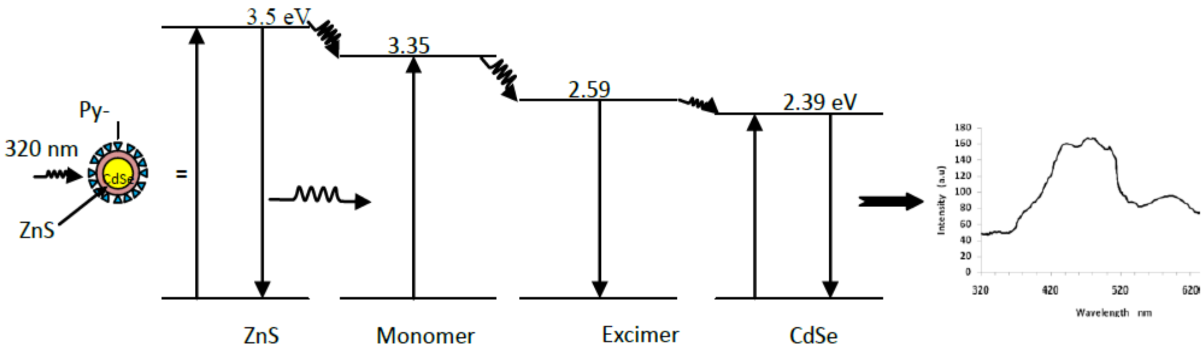

Figure 8: Simple schematic energy levels diagram represent the energy transfer between the CdSe/ZnS core-shell and the pyrene excimer level

Figure (9): The photo of slide covered with CdSe/ZnS core – shell with pyrene in PMMA illuminated by UV LED.

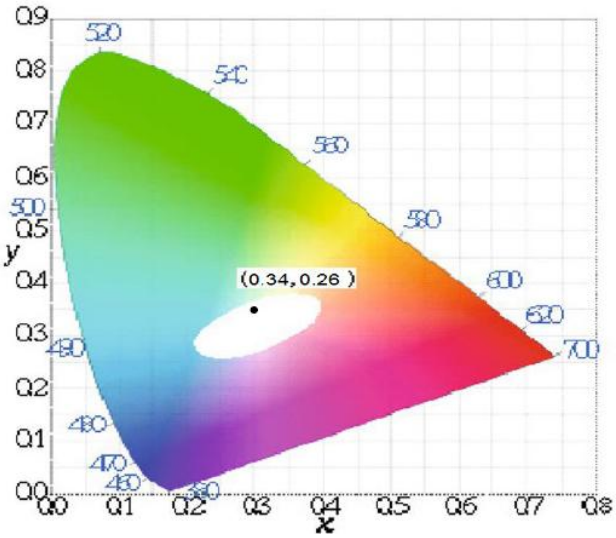

Figure (10): chromaticity coordinates of CdSe/ZnS core-shell nanoparticles (x=0.25, y=0.34) on the CIE in 1931 chromaticity diagram.

Since the color of light is expressed by the CIE colorimetric system, the CIE in 1931 chromaticity diagram is shown in Figure 10. The spectrum of a given light is weighted by the XYZ color matching function [23]. The resultant of the three weighted integral values of X , Y, and Z representing the red, green and blue are calculated from the photoluminescence spectrum by finding the area under the curve for the three peaks in red , green and blue centered around 350, 520 and 600 nm. The chromaticity coordinates x, y can be found from equation (6) as written below:

$$\left.\begin{array}{l} x = \dfrac{X}{X+Y+Z} = 0.26 \\ y = Y/(X+Y+Z) = 0.34 \end{array}\right\} \quad (6)$$

The location of the above coordinates shows that the generated white light from the CdSe/ZnS core – shell with the pyrene molecules is in the cold region with Tc=10304 K.

Conclusions

The CdSe /ZnS core – shell nanoparticles were prepared by chemical method with di-mension 1.3 – 3 nm. The core – shell formation was confirmed by the structure study and the optical properties measurements. The addition of pyrene molecules to the core – shell system alters its photoluminescence spectrum leading to enhancement of the emit-ted white light. The emitted white light was characterized by the new color chromaticity coordinates and the high intensity of the recorded light. The enhancement was attributed to the energy transfer between the pyrene excimer and the core – shell exciton system, and it was explained by a proposed energy levels schematic diagram. The appearance of the pyreneexcimer at low pyrene concentration in the presence of CdSe/ZnS nanoparticles in PMMA was referred to the possibility of pyrene aggregation on the CdSe/ZnSnanoparti-cles.

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