УДК 620.3

REVIEW: PHOTOLUMINESCENCE PROPERTIES OF UNDOPED AND Eu^{3+} DOPED CdS NANOMATERIALS

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During past several decades PL properties of II-VI group semiconductor binary compounds have been investigated. These group materials are doped with rare earth metal ions for determine of improvement in the luminescence intensity. In these review article look over influence of different parameters of PL properties of pure CdS nanomaterials and doped CdS nanomaterials.

Keywords: luminescence properties, doped, cadmium sulfide, nanomaterials.

1 INTRODUCTION

Semiconductor materials have been great attention due to their unique optic, electric and optoelectronic properties. Inorganic binary materials doped with rare earth metal ions for improvement luminescent properties and as a result using of luminescent material in the industry. When these pure nanomaterials doped with rare earth elements, the electronic states are change. Therefore, a possible influence of quantum size effect on the luminescence properties is expected for II–VI semiconductor nanocrystals due to the inclusion of rare earth (RE) metal ions [1]. Various semiconductors, ceramics and dielectrics doped with rare earth elements are used in solid-state lasers, fiber amplifiers [2, 3], biomarkers [4–6], solar cells [7], and in other optoelectronic devices [8, 9]. The effects of the reduced dimensionality on the electronic relaxation and the phonon density-of states of semiconductor and insulating nanocrystals has been extensively investigated by both theoretical and experimental approaches.

Europium doped CdS nanomaterials have been much investigated in the literature. In these research, we have been studied PL properties of doped materials by changing different parameters of reactions. As a result of research by many researchers can be sad that, the PL properties of Eu^{3+} doped CdS nanomaterials is better than PL properties of pure CdS nanomaterials. And due to changing parameters, the influence on PL properties have been studied. At present, the elucidation of the conditions for incorporation of Eu^{3+} ions into quantum dots (QDs) and the establishment of the mechanism responsible for the excitation of their intense luminescence are challenging fundamental problems [10–19]. The effects of the quantum-confinement size of the semiconductor nanoparticles not only create photogenerated carriers, which may have an interaction with f-electrons but also significantly influence the optical properties. Excitonic transition in the host material and an improvement in the luminescence intensity are also expected for the semiconductor nanostructures after the rare earths doping. The effects of the reduced dimensionality on the electronic relaxation and the phonon density-of-states of semiconductor compounds and insulating nanocrystals have been extensively investigated by both theoretical and experimental approaches. There are different synthesis method for Eu doped CdS nanomaterials. In here, we are analysis how the luminescence properties of nanomaterials synthesized by different methods have changed.

2 PL PROPERTIES OF PURE CdS AND Eu^{3+} DOPED CdS

2.1 Co-precipitation method

In here, two different solvent were used for synthesis of Eu doped CdS nanoparticles: Isopropyl alcohol (IPA) and ethylene glycol (EG) and they mixed with deionized water [1]. The emission peaks of pure cadmium sulfide nanocrystals were observed at 405 nm and 425 nm. For Eu^{3+}doped CdS nanocrystal the intense emission peaks are observed at 430, 475 and 574 nm. The emission peak at 574 nm due to 4f transition of rare earth element Eu^{3+} ions. $^5D_0 \rightarrow ^7F_1$ correspond to the magnetic dipole transition. $^5D_0 \rightarrow ^7F_2$ is a hypersensitive forced electric–dipole transition being allowed only at low symmetries with no inversion center. The electronic dipole transition, $^5D_0 \rightarrow ^7F_2$ is hypersensitive to Eu^{3+} symmetry. Due to quantum coefficient effect, the PL peak positions of the band-edge emission at 350–500 nm can be related with the size of the CdS crystallites. The surface-defect emission was caused, such as sulfur vacancies and sulfur dangling bonds created by doping, in the wavelength range 500–700 nm. The emission peak at 430 nm was due to CdS nanostructures. The maximum incense of emission peak at 750 nm due to blue shifted of CdS nanocrystal. The maximum incense of emission peak observed at 750 nm due to surface defect of host CdS nanocrystal and blue shifted. As shown from the results, the energy can be significantly transferred from the CdS to Eu^{3+}.

2.2 Chemical route method

In this synthesis method, the samples preparation was carried out at two stage [20]. Firstly, the CdS quantum dots were synthesis by simple chemical route. The thioglycolic acid (TGA) were used at coating agent. After obtaining of CdS quantum dots, Eu ions were added. For this purpose, 3 different ratio of samples were synthesized: CdS:Eu (3:1), CdS:Eu (1:1), CdS:Eu (1:3). The luminescence spectra at 300 K, excited by the radiation with a wavelength of 375 nm, for colloidal

CdS/TGA and CdS:Eu^{3+}/TGA QDs for various concentrations of introduced Eu^{3+}:TTA. For all samples of colloidal CdS: Eu^{3+}/TGA QDs, there are several luminescence bands in the spectra. The first one is a broad band with a maximum at about 540 nm; it corresponds to colloidal quantum dots. Given the considerable width of the band at its half-maximum (160 nm) and its noticeable red-shift with respect to the ground state exciton absorption, this band can be attributed to the trap state recombination [21, 22]. The other bands correspond to the transitions between the levels of europium ions: the band at 592 nm to $^5D_0$-$^7F_1$, at 615 nm to $^5D_0$-$^7F_2$, and the bands at 653 nm and 702 nm to $^5D_0$-$^7F_3$ and $^5D_0$-$^7F_4$, respectively. It is also known [16] that when europium ions are embedded in semiconductor crystals of A_2B_6, europium ions can be present as Eu^{2+} and Eu^{3+} charge states. In this case, the luminescence of Eu^{2+} ions is located in the blue-green spectral region and represents a wide band. In the luminescence spectra of the samples studied by us there are no luminescence bands that can be correlated with Eu^{2+} ions.

2.3 "One-Pot" sol–gel method

In this work, Eu^{3+} doped CdS–SiO_2 monoliths were prepared by simple pot method [23]. In here, two samples were prepared. The PL properties of non-doped CdS: SiO_2 and Eu^{3+}-doped SiO_2 samples were investigated. In Eu^{3+} species, absorption bands corresponding to the forbidden 4f–4f transitions are usually weak. In the prepared samples, a small absorption located at 394 nm was observed which related to $^7F_0$-$^5L_6$ transition. Generally, the photoluminescence excitation spectra of the samples $^5D_0$-$^7F_2$ transition at 615 nm, $^7F_{0,1}$-$^5D_1$ excitation band at 525–535 nm which related to dipolar magnetic were observed. It is reported by the author that, these transitions are beyond to CdS nanoparticles. In non-annealed sample 1 and 2, the emission spectra are found belong to Eu transitions which at 362 nm ($^7F_1$-$^5D_4$), 380 nm ($^7F_0$-$^5G_3$), 394 nm ($^7F_0$-$^5L_6$), 414 nm ($^7F_0$ -$^5D_3$), 465 nm ($^7F_0$ - $^5D_2$), 526 nm ($^7F_0$-$^5D_1$), 534 nm ($^7F_1$ - $^5D_1$) were observed. The emission occurs from ^5D_J levels towards ^7F_J manifolds and when CdS nanoparticles crystallization, the excitation bands lying in the absorption range of CdS nanoparticles drastically reduce in intensity and almost vanish were reported. From the results, the disappearance of excitation bands from multiplets in resonance with the CdS absorption could be attributed to an energy transfer from Eu^{3+} ions to CdS nanoparticles which supported by the $^5D_0$ dynamics study. Furthermore, the observation of the CdS absorption in the excitation spectra of Eu^{3+} means that back transfer CdS-Eu^{3+} is efficient [24]. The emission spectra of the raw and annealed Eu-doped samples recorded at 535 nm ($^5D_1$ level). All spectra were normalized to the band associated to $^5D_0$-$^7F_1$ (located at 590 nm. A broad spectrum of lanthanoids is observed at 580, 595, 613, 652 and 703 nm, which corresponds to the radiative emissions from the $^5D_0$ initial state to the ^7F_J final state (J = 0, 1, 2, 3 and 4). The $^5D_0$ - $^7F_0$ transition at around 580 nm and the high intensity of the electric dipole transitions (D_J = 2, 4) denote a very low symmetry of the Eu^{3+} surroundings is explained low symmetry such as those of Cnv, Cn or Cs symmetry groups [25]. Generally, the intensity of the so-called "hypersensitive" related to electric dipolar transition ($^5D_0$-$^7F_2$), and the magnetic dipolar transition is called the "asymmetry" of the Eu^{3+} site. Based on the results, in the emission spectra, there are no significant variations are observed between annealed samples, where most of the OH groups must be removed, and as-prepared Eu-doped CdS–SiO_2 samples. This could indicate that the disorder and the high asymmetry in the Eu^{3+} surroundings control the fluorescence features. Furthermore, another author states that organic moieties can still be present in the annealed sample, as suggested [26].

2.4 Chemical bath deposition method

In this study, Eu doped CdS thin film were synthesis by chemical bath deposition method at the reservoir temperature of 70±2°C varying the synthesis time in a wide range (80 to 135 min) [27]. At the same time, the concentration of Eu was selected in the range of $0.0 \leq x \leq 3.47$. CdS were synthesis at four different synthesis time. Here, were discussed the results of the CdS synthesized within 65 minutes which had best luminescence spectra. The radiative bands are observed at 434 nm (2.86 eV) (violet), 523 nm (2.37 eV) (green), 565 nm (2.19 eV) (orange), 659 nm (1.88 eV) (red) and 898.21 nm (1.38 eV) (infrared) eV. The violet band is associated a radiative transition band-to-band, which is higher than the single CdS band gap for 358 meV. This is explained by quantum confinement associated with grain size since it is less than the exciton Bohr radius. The green band were observed at 523 nm and explained by optical signature of interstitial oxygen [28]. In the observed luminescence spectra, the relative intensity increased with the increase in the synthesis duration, with a maximum value was observed at 65 minutes, followed by a decrease in intensity with increasing of synthesis time. The orange band, the effect of oxygen is different since the use of oxygen during the growth leads to the appearance of a band at 563 nm (2.2 eV) [28]. The spectrum observed at 574 nm is related to form CdO during the nucleation of layer [29]. The broad emission peak was observed at 659 nm (1.88 eV) which called "orange band". But in the literature, orange band is observed at range of 610 to 596 nm (2.03-2.08 eV) [30, 31]. It is possibly associated to a donor-acceptor pair (DAP) radiative transition between a donor level related to interstitial cadmium and an unidentified acceptor level [32]. The ionization energy of this donor has estimated to be between 120 and 206 meV, which corresponds to interstitial cadmium [28]. If we look at the spectrum at 892 nm, the broad and weak peaks disappear with increasing synthesis time. These spectra are indicative of the deep impurities along with located in the infrared region. Among all bands, orange band is dominant for 65 minutes and very weak for other times. The photolumine-

scence spectra of the Eu^{3+} doped CdS samples. As written above, the absence of the optical signature of interstitial oxygen at 523 nm (2.37 eV) indicates that the incorporation of rare earth- Eu in CdS lattice decreases the concentration of interstitial oxygen. Between the luminescence spectra of Eu doped CdS, which doping time is 135 min have the best luminescence spectra. There are four main radiative transitions at 431 nm (2.88 eV), 576 nm (2.15 eV), 683 (1.81 eV) and 840 (1.48) nm (eV). The dominant radiative peak at 576 nm (2.15 eV) which has been related to the intra-4f radiative transitions of Eu^{3+} ions that compatible to the magnetic dipole transition ($^5D_0 \rightarrow ^7F_1$). Compared to literature, observed peak have been blue shifted [28, 33]. In Eu^{3+}-doped CdS, the $^5D_0 \rightarrow ^7F_1$ transition is mainly magnetically allowed magnetic-dipole transition. Due to the surface-defect radiative transitions are caused by surface states. These sulfur vacancies or sulphur dangling bonds created by doping are in the wavelength range from 700–500 nm (1.77–2.48 eV) [34]. Therefore, the peak at 683 nm (1.81 eV) is associated with surface defects of the CdS nanocrystals. The luminescence spectra at 840 nm is due to deep residual impurities. In generally, the results showed that a part of Eu ions are contained in CdS nanocrystal and the host CdS transfer the energy to Eu ions significantly. There are also explanations in the literature. Upon excitation, the energy from non-radiative recombination of electron-hole pairs can be transferred to the high energy levels of the Eu ions [35, 36].

2.5 Sol-gel method

In this work, F. Ben Slimen et. all were investigated the effect of co-doping with CdS nanoparticles on the photoluminescence properties of Eu^{3+} doped silicophosphate glass prepared via the sol gel method [37]. The enhancement of Eu^{3+} emission induced by CdS nanocrystals and thermal annealing was assigned to either an energy transfer via defect states or structural alteration of the glass network around the rare earth ions. In order to study the energetic interaction between CdS nanocrystals and Eu^{3+} within the SiO_2–P_2O_5 sol gel glass heated at 250 ^{0}C and co-doped with different CdS concentrations, the emission spectra of the different samples were recorded upon excitation at either 355 nm or 375 nm, which corresponds to the semiconductor absorption detected in the UV-visible spectra. At these wavelengths, Eu^{3+} ions have negligible absorption [38]. Under an excitation at 375 nm, the PL spectra of the sample doped only with CdS exhibits a narrow emission band in the UV region centered at 406 nm, which is Stokes-shifted from absorption onset of CdS nanocrystals together with a weak and large band peaking at 647 nm. These two emissions are ascribed respectively to shallow traps and deep traps states in the band gap of CdS nanocrystals. However, for samples containing both CdS and Eu^{3+} ions, the spectra show the tail of a narrow peak attributed to shallow traps together with a large band extending in the range of 450 to 600 nm and a weak structure in the low energy side. Indeed, it is well established that for nanosized CdS particles, the emission involves surface states due to the presence of native defects, such as cadmium interstitials and vacancies as well as sulfur interstitials and vacancies [39]. The ratio between deep traps and shallow traps emission varies depending on the amount of defects inside CdS nanoparticles or on their surface. Therefore, conclude by comparing the spectra that Eu^{3+}, codoping generates novel trap states within the gap of CdS nanoparticles, which results in the intense emission in the range between 450 and 600 nm. Indeed, Eu^{3+} ions may be inserted inside or at the surface of CdS nanoparticles by substituting cadmium cation. Additionally, the small blue shift in the shallow traps emission indicates that Eu^{3+} codoping affect slightly the processes of nucleation and growth of CdS nanocrystals within the silica matrix. The deep traps band overlap with most of the excitation lines of Eu^{3+}, which may be favorable for an efficient CdS/Eu^{3+} energy transfer. Co-doping with Eu^{3+} ions partially quenches this broad emission band and additionally produces the structure in the low energy side, which is assigned to transitions inside the 4f shell of europium ions. When the excitation wavelength is turned to 355 nm, each of the PL spectra displays only wave emission peaks at about 579, 592, 611, 651, and 700 nm, which are associated to the transitions from $^5D_0$ to ^7F_J (J j 0, 1, 2, 3, 4), respectively. Since the lifetime of CdS fluorescence is so much shorter than that of europium emission, CdS emission is not seen in all the PL spectra of the co-doped samples. As compared to the reference sample doped only with Eu^{3+} ions, we can see a drastic improvement of the Eu^{3+} emission with the introduction of CdS nanoparticles in the glass matrix. The enhancement of the emission intensity of europium ions may be accomplished via profound modification of the glass network around rare earth ions and/or efficient energy transfer from CdS to Eu^{3+} ions [40]. Therefore, this ratio is dependent on the glass host composition, activator concentration and heat-treatment, and it is widely used to investigate the local environment of the rare element. In the case of the present study, the relative intensity of the $^5D_0$ / $^7F_2$ and $^5D_0$ / $^7F_1$ transitions was obtained by measuring the area under the corresponding emission bands. The obtained values for the different concentration are between 2.4 and 3.1, which are characteristic for Eu^{3+} ions in highly asymmetric sites. However, these values are lower than those estimated for sol–gel silica glasses [41]. Similar to the effect of aluminum [42], the addition of phosphorous in a convenient concentration, makes the glass structure less rigid, the local structure less distorted, and Eu^{3+} ions tend to occupy more symmetric sites with a more homogeneous distribution. Since no quenching of the emission was observed for the used CdS concentrations, we believe that silicophosphate glass is more suitable to disperse great amount of either CdS or Eu^{3+} ions than only one-component silica glasses [40]. This may be due to the role of phosphorus, which is known to preclude rare earth clustering. Moreover, CdS nano-

particles act as network modifier producing non-bridging CdS–O groups, which can coordinate with europium ions. As a result, the Eu–Eu interaction is diminished and the europium emission is increased. The presence of CdS nanocrystallites may be also responsible for an increase of both the covalency and the polarization of the local vicinities of the Eu^{3+} ions, which can be affected by reaction with sulfur [43]. The increase of the asymmetry factor R for the higher concentration of CdS is an indication for an important distortion in the glass network due to the filling of more pores by semiconductor nanoparticles. In the other hand, the increase of the Eu^{3+} emission intensity may be due to an energy transfer between the CdS nanoparticles and Eu^{3+} ions. So that, this process occurs only when the distance between CdS nanoparticles and Eu^{3+} ions becomes sufficiently short. However, owing to the fast radiative and non-radiative decay of excitons in CdS, direct energy transfer from semiconductor nanoparticles to Eu^{3+} ions is physically impossible. Indeed, for achieving efficient energy transfer, the emission spectrum of the nanoparticles has to spectrally overlap an absorption band of the rare-earth ions. This is not the case for the exciton energy level of CdS nanoparticles. However, efficient energy transfer to Eu^{3+} ion may be achieved when defect states at the semiconductor nanocrystals surface are abundant. As it is well known, these defects give rise to trap levels within the gap of the semiconductor nanoparticles, and their corresponding emission overlap well with the absorption bands of Eu^{3+}. When excitation light is absorbed mostly by CdS nanocrystals, it generates electron–hole pairs. Photo-generated electrons will be first trapped at these levels before interacting with the Eu^{3+} ions located close to the surface of CdS. Then, the electron trapped at the surface recombines with a valence band free hole or trapped hole at the nanocrystal surface before transition energy being non-radiatively transferred to the Eu^{3+} ions. Increasing CdS concentration will reduce the distance between semiconductor quantum dots and rare earth ions enhancing thus the energy transfer rate between CdS and Eu^{3+}. However, when these species are spatially close, a diminution of the total emission and lifetime values is usually observed, which is assigned to back energy transfer from the Eu^{3+} ions to CdS nanoparticles [40]. Further, the fact that the europium emission did not appear clearly in the PL spectra recorded under an excitation wavelength of 375 nm as they were obtained under 355 nm excitation, may be connected to the effect of energy transfer in the emission process of Eu^{3+} ions. Indeed, when using 355 nm wavelength, which is confidently matched with the bandgap energy of the nanoparticles, the number of excited CdS nanoparticles, which contribute to energy transfer to Eu^{3+} is greater than that reached when 375 nm is used. Therefore, the emission of Eu^{3+} ions will be so weak in the latter case. Similar behavior was observed in SiO_2 gel doped with Eu^{3+} and ZnO nanocrystals [44]. Additionally, the fact that no luminescence from CdS nanocrystals was observed under 355 nm excitation wavelength indicates that energy transfer from a nanocrystal to Eu^{3+} is so fast. Indeed, when CdS are coupled to Eu^{3+}, any generated exciton will immediately recombine non-radioactively by exciting Eu^{3+} ions [45]. To investigate the effect of annealing temperature on the luminescence properties of our material, we have reproduced the PL spectra for differently heat-treated samples having the same starting composition. Over this temperature, a significant decrease of the emission of Eu^{3+} ions is observed. This is the reason why the annealing temperature for samples doped with different CdS concentrations was chosen to be 250 °C. In fact, several structural modifications of the glass network, which have a great influence on the Eu^{3+} emission, may occur during heat-treatment. In particular, annealing may reduce considerably the density of hydroxyl groups, which are known to be luminescence quenchers. This leads to an efficient enhancement of emission. Additionally, various defect centers are formed by the hydrolysis and condensation reactions of the initial precursors. Since energy transfer takes place via surface defects at CdS nanocrystals surface, this will enhance the emission of trivalent rare earth ions. However, for sufficiently high temperature, defect concentrations may decrease in the network of the xerogel matrix, which inhibits the energy transfer between the defects and RE ions [40]. Moreover, heat treatment leads to an increase in the homogeneities of the local environment, owing to the cross-linking between silica chains and consequent shrinkage. Due to change in the geometry of silica, annealing at higher temperature produces an increase in the concentration of both Eu and CdS, which could results in the aggregation of Eu–Eu and emission quenching due to energy migration amongst Eu^{3+} ions. To clarify the effect of annealing on the local environment around Eu^{3+} ions, we have estimated again the ratio R for different annealing temperatures. Above this temperature, R remains almost constant, which could be due to a rearrangement of the network and an increase of the symmetry around rare earth ions [46].

2.6 Straightforward one-pot process

H.Q. Chen, J. Fu, L. Wang and et all. Were investigated with the biomolecule glutathione as a capping ligand, Eu^{3+}-doped cadmium sulfide composite nanoparticles were successfully synthesized through a straightforward one-pot process [47]. The fluorescence spectra were performed using a Hitachi F- 4500 spectrofluorometer (Hitachi, Japan) equipped with a plotter unit and a quartz cell (1cm×1 cm). The emission spectrum of Eu^{3+} (1), CdS nanoparticles (2) and Eu^{3+} CdS composite nanoparticles (3) were recorded. The characteristic peaks of Eu^{3+} located at 592, 614 and 698nm under the excitation wavelength of 395 nm, the three weak peaks are attributed to $^5D_0$-^7F_J. The fluorescence intensity at 614 nm is stronger than that at 592 nm and 698 nm. From the results, it can be say that the strong emission wavelength occurs at 510 nm. After doping with Eu^{3+} ions, the fluorescence of Eu^{3+} ion can be enhanced remarkably, which indicates

that CdS nanoparticles has the enhancement effect on the luminescence of Eu^{3+}, so the reaction between CdS nanoparticles and Eu^{3+} was studied. They found that the characteristic fluorescence intensity of Eu^{3+} enhanced with the amount of Cd^{2+} increased. Obviously, there was a fluorescence energy transfer process between CdS nanoparticles and Eu^{3+}. The fluorescence intensity of the Eu^{3+} only changed a little, when the concentration of the Cd^{2+} raised to a certain value. The reason might be that the fluorescence energy transfer efficiency reached to maximum. It is known that, upon excitation of the CdS host, the energy from non-radiative recombination of electron–hole pairs can be transferred to the high-lying energy levels of the Eu^{3+} [48]. When the trace amounts of Hg^{2+} were added to the Eu^{3+}-doped CdS nanoparticles solution, the wavelength of excitation and emission were unchanged, but the intensity of the peak decreased, the possible mechanism for the fluorescence quenching effect of Eu^{3+} is that the energy transfer system was destroyed upon combining with Hg^{2+}, thus reducing the fluorescence quantum efficiency of the composite nanoparticles. Although the fluorescence intensity of the CdS nanoparticles and Eu^{3+} both decreased in the present of Hg^{2+}, they found that the sensitivity and detection limit of using the characteristic fluorescence of Eu^{3+} for Hg^{2+} detection is better than CdS nanoparticles. Furthermore, the Eu complex has a very large Stoke's shift that permitted more sensitive fluorescence detection, so we chose the characteristic fluorescence of Eu^{3+} ion for the detection of Hg^{2+}.

2.7 Co-precipitation method

L. Deng, Y. Shan, J. J. Xu were investigated Eu^{3+} doped CdS nanocrystals which synthesized via a co-precipitation method [49]. The doping of Eu^{3+} ions caused a 4-fold enhancement in electrochemiluminescence intensity and more stable cathodic signals compared to pure CdS nanocrystals. Similar to the PL spectrum, the electrochemiluminescence spectrum is also a good tool to investigate energy transfer between host nanocrystals and metal ions dopants. They were analysis pure CdS nanocrystals, 1.5% and 5.0% Eu^{3+} doped CdS:Eu nanocrystals. The electrochemiluminescence spectrum of undoped CdS nanocrystals appeared only one broad emission peak from 480 nm to 600 nm, which belonged to the recombination emission of surface states. As for both Eu^{3+} doped CdS nanocrystals, a new emission peak around 620 nm was observed, which belongs to the $^5D_0$ / $^7F_2$ transition of Eu^{3+} ions, indicating successful energy transfer from host nanocrystals to Eu^{3+} ions in the electrochemiluminescence process. The energy transfer reached greatest efficiency when the Eu^{3+} doping level was 1.5%, and then reduced as the doping concentration continued rising. Comparing the electrochemiluminescence spectrum of 1.5% Eu^{3+} doped nanocrystals with that of undoped nanocrystals, the electrochemiluminescence emission intensity of doped nanocrystals from 450 nm to 550 nm belonging to the recombination emission of surface states was greatly enhanced. This electrochemiluminescence enhancement, together with a newly appeared intense emission around 620 nm, produced a total 4-fold electrochemiluminescence increase.

2.8 Sol–gel route by an in situ method

M. Bouazaoui and et. all were prepared semiconductor nanoparticles (CdS and ZnS) and Eu^{3+} co-doped zirconia thin films using the sol–gel route by an in situ method [50]. The principal purpose of this work is to study the energy exchange between semiconductor nanoparticles and europium ions. Hence, once the films doped with CdS or ZnS characterized, they introduced europium ions into the precursor sol in order to obtain co-doped systems. The characteristic absorption peaks of Eu^{3+} ions from the $^7F_0$ fundamental state are observed [51]. Energy transfer processes are known to be more efficient between species which present a large spectral overlapping of their optical transitions. In fact, the emission spectrum of the nanoparticles has to spectrally overlap an absorption band of the rare-earth ions. The transitions which could be involved in this process are $^7F_0$ - $^5D_2$ (electric-dipole character) at 466 nm and $^7F_0$ -$^5D_1$ (magnetic-dipole character) at 530 nm. Two zirconia co-doped films at 15% CdS–5% Eu^{3+} and 15% ZnS–5% Eu^{3+} have been elaborated. The PL (k_{exc} = 351 nm) of these films compared to the 5% Eu^{3+}-doped film. Energy transfer from CdS nanoparticles to Eu^{3+} ions has been reported in the literature [52]. The absolute measurements performed in our case, under excitation at k_{exc} = 351 nm, show that the intensity from 15% CdS–5% Eu^{3+} is only two times higher than for 5% Eu^{3+}. Moreover, the almost entire emission band of CdS nanoparticles covers wavelengths higher than the $^5D_2$ Eu^{3+} peak at 466 nm, indicating that a majority of the electrons occupy shallow traps (k > 466 nm). This location of defect levels is too low in energy to obtain an efficient spectral overlap with $^5D_2$ level (466 nm) of the europium ion. Hence, only a small part of nanoparticles (k < 466 nm) contribute to the energy transfer process. On the other hand, one can note that the $^5D_1$ level is situated at the maximum of the CdS emission. This determining involvement of the excited state $^5D_2$ of the Eu^{3+} ion in the transfer process can be explained by the Foerster model [53] based on the dipole–dipole interactions. This model considers the electric dipole generated by the optical wave within the nanoparticle and that of the rare-earth ion induced by the exciton of the particle. The interactions of a higher order, such as dipole–quadrupole or quadrupole–quadrupole, are neglected. Thus, if one supposes the same process for the CdS: Eu^{3+} interaction, only electric dipole transitions of the europium ion, such as the transition $^7F_0$-$^5D_2$, in resonance with the defect states, will contribute significantly to the energy transfer. The magnetic dipole transitions such as $^7F_0$-$^5D_1$, even when they are in resonance with the defect states of the nanoparticles, which is the case for CdS: Eu^{3+}, do not contribute to the energy transfer. This enhancement of the rare earth emission in a CdS: Eu^{3+} co-doped zirconia film when the sample is

cooled down to 10 K, had been already observed by Morita et al. [52]. This exaltation is about 3.5 greater than the one calculated at 293 K (enhancement factor 12). There are two combined effects that could explain such behaviour at low temperature. The increase in the lifetime of the nanoparticle defect states responsible for the energy transfer to the excited levels of europium ion, allows an increasing population of these excited states [53], leading to the sensitization of a great number of Eu^{3+} ions. The increase in the lifetime of the nanoparticle defect states responsible for the energy transfer to the excited levels of europium ion, allows an increasing population of these excited states [54], leading to the sensitization of a great number of Eu^{3+} ions. The increase of the emission with decreasing the temperature was already reported in bulk semiconductor by Krustok et al. [55].

CONCLUSION

In the Eu^{3+} doped CdS, The results confirm that at least a part of the Eu^{3+} ions is effectively doped into CdS nanocrystals and the energy transfer occurs from CdS nanocrystals to Eu^{3+} ions. The results show that at least a part of the Eu^{3+} ions are effectively doped into CdS nanocrystals and the energy transfer occurs from CdS nanocrystals to Eu^{3+} ions. Generally in here $^5D_0 \rightarrow ^7F_2$ and $^5D_0 \rightarrow ^7F_1$ transitions in europium ions is observed which is due to electron dipole transition and magnetic dipole transition. At the same time, it is shown that from experiments Eu^{3+} emission is significantly dependent on concentration of CdS nanoparticles and annealing temperature. The using temperature must be selected optimal for reaction. Furthermore, the PL emission intensity could be influenced by changing several factors such as the concentration of doped Eu^{3+} ions, the reaction time, the reaction temperature, the charge compensation and the storage time and condition. The results suggest that these kinds of rare earth doped semiconductor nanoparticles can be used in many fields such as chemical sensors (especially in fiber optic coating platforms fluorescence probes, and other analytical applications. At the same time this material can be used as energy-transfer materials.

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ШОЛУ: ЛЕГИРЛЕНБЕГЕН ЖӘНЕ Eu^{3+}-ПЕН ЛЕГИРЛЕНГЕН CdS НАНОМАТЕРИАЛДАРЫНЫҢ ФОТОЛЮМИНЕСЦЕНТТІК ҚАСИЕТТЕРІ

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Соңғы бірнеше онжылдықта II-VI топтардың жартылай өткізгіш бинарлық қосылыстарының ФЛ қасиеттері зерттелді. Бұл топтық материалдар люминесценцияның қарқындылығын жақсартуды анықтау үшін сирек кездесетін металдардың иондарымен легирленген. Бұл шолу мақаласында таза CdS наноматериалдары мен легирленген CdS наноматериалдарының ФЛ қасиеттерінің түрлі параметрлерінің әсері қарастырылады.
Кілт сөздер: люминесценттік қасиеттері, легирлеу, кадмий сульфиді, наноматериалдар.

ОБЗОР: ФОТОЛЮМИНЕСЦЕНТНЫЕ СВОЙСТВА НЕЛЕГИРОВАННЫХ И ЛЕГИРОВАННЫХ Eu^{3+} НАНОМАТЕРИАЛОВ CdS

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В течение последних нескольких десятилетий были исследованы ФЛ свойства полупроводниковых бинарных соединений II-VI групп. Эти групповые материалы легированы ионами редкоземельных металлов для определения улучшения интенсивности люминесценции. В данной обзорной статье рассматривается влияние различных параметров ФЛ свойств чистых и легированных наноматериалов CdS.
Ключевые слова: люминесцентные свойства, легирование, сульфид кадмия, наноматериалы.