

Structural, Morphological & Optical Study of Eu-doped CDS Nanocrystals

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Abstract- In this section that we have stated that the solution of ethylene glycol has been employed as a solvent in the solvothermal approach to yield CdS: Eu nanocrystals with a bright white emission. It can be determined by high resolution transmission electron microscopy (HRTEM) and X-ray diffraction (XRD) examination that the CdS:Eu nanocrystals have an average diameter of 5.8 nm. The functional groups absorbed on CdS:Eu nanocrystals were confirmed via FT-IR spectra. From photoluminescence (PL) studies at $\lambda_{ex} = 398$ nm, the PL emission intensity of CdS: Eu nanocrystals enhanced by doping Eu³⁺ ions. Furthermore, the optical characteristics of CdS:Eu nanocrystals are influenced by the chemical reaction parameters, such as the concentration of doped Eu³⁺ ions. The structural, morphological & optical properties of CdS:Eu nanocrystals were also investigated.

Keywords- Nanocrystals, Doped, CdS:Eu, FT-IR spectra, Photoluminescence characteristics.

I. INTRODUCTION

In past years, due to their superior qualities over conventional fluorescent labels, including broader absorption spectra, more symmetric emission spectra, and improved photostability, semiconductor nanocrystals have generated a lot of attention [1]. They have vast variety of applications such as in light emitting diodes (LEDs) [2], lasers [3] and biological labels [4]. Furthermore, it is a common approach for tuning the electronic, optical, mechanical and magnetic properties of materials [5]. A member of the most significant II–VI compound semiconductors is CdS, which has a room-temperature direct bulk band gap of 2.4 eV. Because of its ability to tune emission in the spectrum of visible light with shapes and sizes that vary, it is widely utilized in optoelectronic devices [6]. The rare earth property possessed by Eu³⁺ ions has the potential to elevate CdS:Eu nanocrystals to a prominent class of emissive substances, as of recent. Several authors report that luminescence of Eu³⁺ ions can be highly enhanced by interaction with CdS nanocrystals. The role of dopant

concentration and surface coating of CdS:Eu nanocrystals on the modification of crystal structure and studied their optical properties [7].

In this article, we reported the preparation of CdS:Eu nanocrystals by solvothermal method. To the best of our knowledge, there is little information is available on white emission from CdS:Eu nanocrystals. The obtained nanocrystals have been characterized thoroughly by XRD, HRTEM, FT-IR and PL analysis. Moreover, influence on PL properties of the CdS:Eu nanocrystals were investigated including the concentrations of Eu³⁺ ions.

II. EXPERIMENTAL SECTION

1. Used Chemicals

CdCl₂•5H₂O (99%), thiourea (99%), ethylene glycol (99%), Eu (NO)₃•6H₂O (99%), and High-purity nitrogen (99.9995%) was used as a precursor material. No additional purification needed to be performed for any of the reactants. Every experiment's water was deionized.

2. Preparation of CdS:Eu nanocrystals

The formation of CdS:Eu nanocrystals, which were made via a modified synthesis, was done in a single step. This approach uses a simple one-pot procedure that saves time and is simpler. A typical procedure is as follow: CdCl₂•5H₂O and Eu(NO₃)₃•6H₂O were mixed ethylene glycol and stirred strongly with 6:30 min under the protection of N₂, and then thiourea was added in the mixture solution. After continuous stirring for 15 min at room temperature, the reaction mixture was transferred into a Teflon-lined stainless-steel autoclave with a volume of 30 ml.

The autoclave was sealed and maintained at 150°C for 2:30 hr and then cooled to room temperature by a hydrocooling process to terminate the growth of nanocrystals immediately for the purpose of recording their optical spectra. After mixing acetone and ethanol to the concentrated reaction mixture, the resulting CdS:Eu nanocrystals were precipitated, concentrated, and then separated and purified through centrifugation and the decantation process many times.

Characterization

All optical measurements of as-prepared samples were performed at room temperature. All photoluminescence (PL) spectra of QDs suspension were measured using a Shimadzu RF-5301 fluorescence spectrometer with both the excitation and the emission spectrum. PL spectra were taken at the excitation wavelength $\lambda_{ex} = 398$ nm.

The morphologies and dimensions of the products were observed by high resolution transmission electron microscopy (HRTEM) taken on a JEOL 100CX-II electron instrument at an acceleration voltage at 100 kV. Powder X-ray diffraction (p-XRD) analysis was obtained on a Bruker Advanced D8 X-ray diffractometer equipped with graphite monochromatized high-intensity Cu-K α radiation ($\lambda = 1.54178\text{\AA}$). FT-IR spectra over the range 500–4000 cm⁻¹ were performed on a Bruker Alpha FT-IR Spectroscopy. The CdS: Eu nanocrystals mixed with solid KBr power was ground to a fine powder.

III. RESULTS AND DISCUSSION

The XRD patterns of the CdS: Eu nanocrystals are shown in Fig. 1. It is obvious that all the peaks in the XRD patterns are consistent with JCPDS data (No. 10-0454) [8] of the face centered cubic structure of CdS. The peaks in the XRD patterns at 26.6°, 42.8° and 51.7° for CdS nanocrystals correspond to crystal planes (111), (220), and (311). There is no shift in the peaks due to the dopant incorporation, because of the low europium concentration. The width of the diffraction pattern is strongly broadened due to the small size of the crystallites.

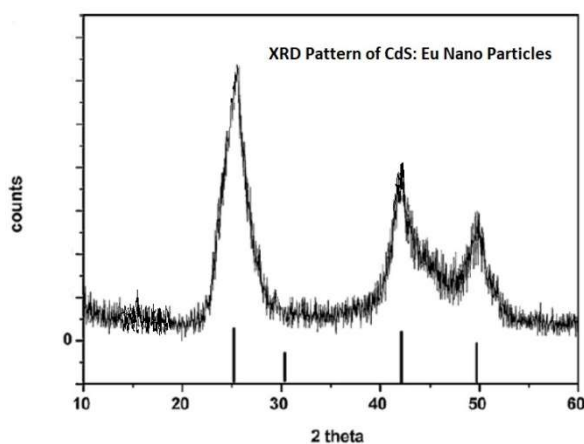


Fig. 1 The XRD pattern of CdS: Eu nanocrystals

The average nanocrystallite size [D] was calculated in according to Debye–Scherrer formula [9]:

$$D = k\lambda / \beta \cos\theta$$

where k is a constant, λ is the X-ray wavelength (1.5405 Å), β is the full width at half maximum (FWHM) of the main diffraction line, and θ is the diffraction angle. The calculated result indicates that the mean crystalline size of CdS: Eu QDs sample is approximately 5.8 nm.

TEM Micrographs

The morphology of the synthesized CdS: Eu nanocrystals were determined by HRTEM as shown in Fig. 2. It is quite evident that these nanocrystals are close to spherical with excellent monodispersity. The nanocrystals with an average diameter of approximately 5.8 nm and this value are almost in agreement with the one obtained

from XRD result. The existence of well-resolved lattice planes in TEM images further confirms the excellent crystalline structures of the as-prepared CdS: Eu nanocrystals.

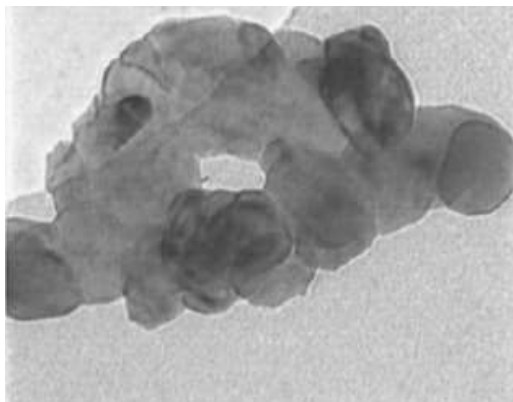


Fig. 2. HRTEM image of CdS:Eu nanocrystals

Fourier Transform Infrared (FT-IR) Analysis

The FT-IR spectrum of CdS:Eu nanocrystals is shown in Fig. 3. The peak at 2924 cm^{-1} is attributed to the bending vibrating mode of C-H, the presence of characteristic peak at 1632 cm^{-1} assign to O-H stretching vibrations, the peak at 1415 cm^{-1} is mainly due to C-O stretching vibrations, the presence of characteristic peak at 1096 cm^{-1} corresponds to C-C stretching. The weak peak around 690 cm^{-1} in the spectrum indicates the presence of Cd-S bond. There are two O-H bonds in ethylene glycol molecules. The peak at 3172 cm^{-1} is due to the inter H-bonding and the peak at 3289 cm^{-1} is due to O-H stretching vibrations, which is bonding with CdS:Eu nanocrystals.

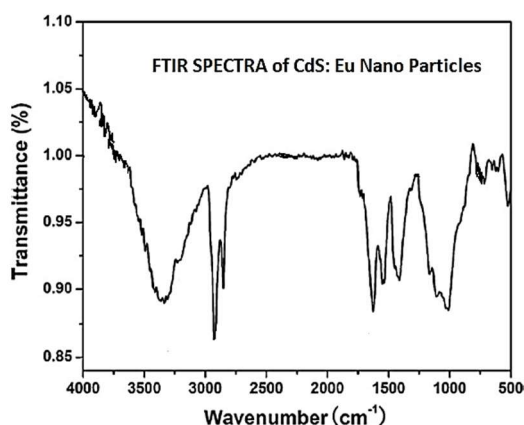


Fig. 3 FTIR spectra of traces on CdS: Eu nanocrystals.

Photoluminescence Analysis Excitation & Emission Spectra

Fig. 4 shows the PL emission spectra of CdS:Eu nanocrystals. After excitation at 398 nm, the emission of CdS:Eu nanocrystals show the strong emission band at 451 nm, which was blue shifted compared to the earlier reports [10]. For the CdS:Eu nanocrystals, emission peaks at 451, 592 and 617 nm are observed. The characteristic peak of Eu^{3+} ions at 592 nm observed due to the intra-4f transitions of Eu^{3+} ions and correspond to the magnetic dipole transition (${}^5\text{D}_0 \rightarrow {}^7\text{F}_1$). The other characteristic peak of Eu^{3+} ions at 617 nm correspond to electronic dipole transition (${}^5\text{D}_0 \rightarrow {}^7\text{F}_2$), which is hypersensitive to Eu^{3+} ions symmetry. We observed that when CdS nanocrystals doped with Eu^{3+} ions, the corresponding PL emission peak shows a slight blue shift, which indicates that a part of Eu^{3+} ions are contained in CdS nanocrystals and the energy can be significantly transferred from the host CdS to Eu^{3+} ions. In addition, the PL emission intensity of CdS:Eu nanocrystals can be enhanced after doping with Eu^{3+} ions, which indicated that Eu^{3+} ions have the enhancement effect on the characteristic luminescence of CdS nanocrystals. It is obviously that the sample of CdS:Eu nanocrystals is well-dispersed in solution. Under UV excitation, the sample displays strong white emission, which is consistent with the result of the PL emission.

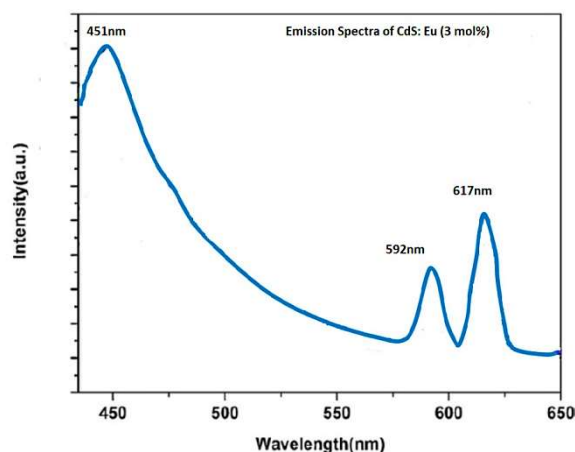


Fig. 4 The PL emission of CdS:Eu nanocrystals with 3 mol % doping concentration of Eu^{3+} ions.

Effect of the Eu^{3+} ions concentration

To investigate the effect of doping concentration of Eu^{3+} ions on the optical properties of CdS:Eu

nanocrystals. Fig. 4 shows the PL emission of CdS:Eu nanocrystals with 3 mol % doping concentration of Eu^{3+} ions. On the other hand, the PL emission intensities of CdS:Eu nanocrystals were gradually enhanced with increasing the doping concentration of Eu^{3+} ions, the strongest PL emission intensity could be reached when the doping concentration of Eu^{3+} ions was 3 mol%. Furthermore, the PL emission intensity of ${}^5\text{D}_0\text{--}{}^7\text{F}_2$ transition is stronger than ${}^5\text{D}_0\text{--}{}^7\text{F}_1$, which indicates the sites symmetry of Eu^{3+} ions in host CdS are low symmetry [9].

IV. CONCLUSION

In summary, the XRD and HRTEM analyses verified that the CdS:Eu nanocrystals were produced in a single pot method, and their approximate size was determined to be 5.8 nm. Investigations using X-ray diffraction were used to carry out the structural investigation. There were no further impurity peaks seen in either sample, suggesting that the dopant ions were integrated into the nanocrystal lattice. Every chemical bond is visible in the FT-IR spectra. FT-IR measurements were recorded using the resulting powder to verify that encapsulating compounds were bound to the surface of CdS:Eu nanocrystals. 3 mol% doping concentration of Europium ions was found to yield the maximum photoluminescence intensity. For the CdS:Eu nanocrystals, emission peaks at 451, 592 and 617 nm are observed. As the doping concentration of Eu^{3+} ions increase, the PL emission intensities steadily decrease.

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REFERENCES

1. S.W. Jung, J.H. Kim, H. Kim, C.J. Choi, K.S. Ahn, *Journal of Applied Physics* 110 (2011) 044313.
2. J.L. Zhao, et al., *Nano Letters* 6 (2006) 463–467.

3. V.I. Klimov, A.A. Mikhailovsky, S. Xu, A. Maklo, J.A. Hollingsworth, C.A. Leatherdale, H.J. Eisler, M.G. Bawendi, *Science* 290 (2000) 314–317.
4. D. Jan´ czewski, N. Tomczak, M.Y. Han, G.J. Vananocrystalso, *Nature Protocols* 6 (2011) 1546–1553.
5. Y. Louyer, L. Biadala, J.B. Trebbia, M.J. Fernee, Ph Eamarat, B. Lounis, *Nano Letters* 11 (2011) 4370–4375.
6. H.L. Qiu, G.Y. Chen, R.W. Fan, C. Cheng, S.W. Hao, D.Y. Chen, C.H. Yang, *Chemical Communications* 47 (2011) 9648–9650.
7. S. Sadhu, P.S. Chowdhury, A. Patra, *Journal of Luminescence* 126 (2007) 387–392.
8. JCPDS data (Pdf File No. 10-0454).
9. P.S. Chowdhury, A. Patra, *Journal of Physical Chemistry Chemical Physics* 8 (2006) 1329–1334.
10. A.Chahbouna, A.G. Roloa, S.A. Filonovicha, M.J.M. Gomes, *Solar Energy Materials and Solar Cells* 90 (2006) 1413–1419.