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Blue-Red Tuning Emission of ZnO: Europium Quantum Dots with Different Excitation Wavelengths

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Abstract

Optoelectronic applications require the development of new fluorescent and efficient luminescent materials, free of toxicity, low in cost, and easy to produce. In this way the synthesis of zinc-oxide (ZnO) quantum dots (QDs) has recently received special attention due to their good optical, electrical and chemical properties with low production costs and blue light emission. In this work ZnO QDs were successfully doped with europium in order to obtain a tunable emission luminescence from blue emission of ZnO to red emission of europium as a function of wavelength excitation. Results show an efficient blue to red tuning when the excitation wavelength was changed from 317 nm to 395 nm, respectively. This opens the possibility of having new optical devices to produce different color emission using the same material.

Keywords

Chromaticity Diagram, Emission Spectra, Europium Luminescence, Red-Blue Tuning, ZnO Quantum Dots, White Light

1. Introduction

Quantum dots (QDs) are crystalline particles nanometer-sized composed of lanthanide semiconductors which have highly efficient optical properties. QDs have many applications due to their strong and stable fluorescence with tunable light emission and absorption. Their main applications are efficient lighting, photovoltaic energy, and training of biological images [1]. On the other hand, ZnO QD has high quantum yield, quantum size effects, broad absorption and narrow emission spectrum. ZnO QDs are environmental friendly, nontoxic, less expensive, and biocompatible compared to traditional QDs semiconductors such as CdS, CdTe, and CdSe [2] [3] [4]. Besides, ZnO is a wide and direct band-gap n type (3.37 eV) semiconductor, and shows a large exciton binding energy of 60 meV [5]-[12] which has recently attracted considerable interest for applications in optical and optoelectronic devices such as blue light-emitting diodes covering the absorption of the entire ultraviolet range. Moreover, the ZnO QDs exhibit a hydrophilic character since they show great stability in water without a decrease in their luminescent properties. In a recent paper, it is reported that the incorporation of ZnO QDs enhance the optical performance of the grating [7].

Different methods have been proposed to the synthesis of ZnO QDs, like radio frequency magnetron sputtering, molecular-beam epitaxy, pulsed laser deposition, chemical-vapor deposition and sol-gel process [13] [14]. The sol-gel method has been proposed, since presents several advantages like: high purity, ultra-homogeneity, low processing temperature and the possibility to incorporate lanthanide ions into an oxide host. In this regard, the red light emission of Eu^{3+} lanthanide ions are well known when they are used as light activators of ZnO QDs.

In this regard, the present work reports a photoluminescence study of europium-doped ZnO QDs as possible tunable material from blue emission arising from the ZnO host to the red emission coming from Eu^{3+} ions by exciting at different wavelengths (317 - 395 nm). The results show different emission spectra when the wavelength excitation was changed in order to analyze the emission of de ZnO and Europium ions for different intensity ratios.

2. Experimental

2.1. QDs Preparation

For the preparation of ZnO nanoparticles doped with europium (Eu), europium chloride ($EuCl_3$) and zinc acetate ($Zn(C_4H_6O_4)$) were chosen as precursors. As solvents, methanol (CH_3OH) and glycerol ($C_3H_8O_3$) were used. Acetic acid (CH_3COOH) was employed as modifier, and distilled water was used for washing.

The synthesis of the sample consisted of mixing and dissolving 0.164 g of zinc acetate (98% Sigma Aldrich), 0.05 g of europium chloride (99.9% Sigma Aldrich), 2.5 g of glycerol and 2 g of methanol. Then, the sample was heated to 120˚C under vigorous stirring and the colloidal solution was kept at that temperature for 1 h. During the process, at 30 min the solution took a yellow color and around 45 min the nanoparticles began to nucleate and grow, taking a white color in short time. After 1 h, 100 μl of acetic acid was added in order to evaporate the highest amount of solvents used in the synthesis and until the final obtainment of 5 ml of colloidal solution. The ZnO nanoparticles exhibited a hydrophilic character since they showed great stability in water without a decrease in their luminescent properties. In a recent paper, it is reported that the incorporation of ZnO QDs enhance the optical performance of the grating [7].

2.2. Photoluminescence Characterization

Photoluminescence spectra were recorded by means of a Horiba Jobin Yvon Fluorolog Spectrofluorometer equipped with a 150 W ozone-free Xenon lamp for the steady state mode. All the measurements were carried out at room temperature.

3. Results and Discussion

Photoluminescence Emission Spectra

Figure 1 shows the emission luminescence characterization. As the wavelength excitation was increased the emission of ZnO was changed from 405 nm to 450 nm. One interesting feature presented is that at 405 nm the transition of Europium ions is diminished. When the wavelength was increased to 392 nm the transition of Europium ions is highly increased, and the maximum emission was obtained at 395 nm of excitation wavelength, showing that the ZnO emission is singly decreased for an energy transfer process. Europium presented the characteristic transitions $^5D_0 \rightarrow {}^7F_1$, $^5D_0 \rightarrow {}^7F_2$ and $^5D_0 \rightarrow {}^7F_3$.

Figure 2 shows the CIE (Commission Internationale de lÉclairage) chromaticity diagram at different wavelengths of excitation. It can be appreciated that the emission color moves from blue to red as the wavelength excitation changes from 317, 320, 392, 393 and 395 nm. This is because the ZnO emission moves from 405 nm to 450 nm and also because the emission intensity of europium was increased. These results confirm the tunable color of the emission when the wavelength is changed.

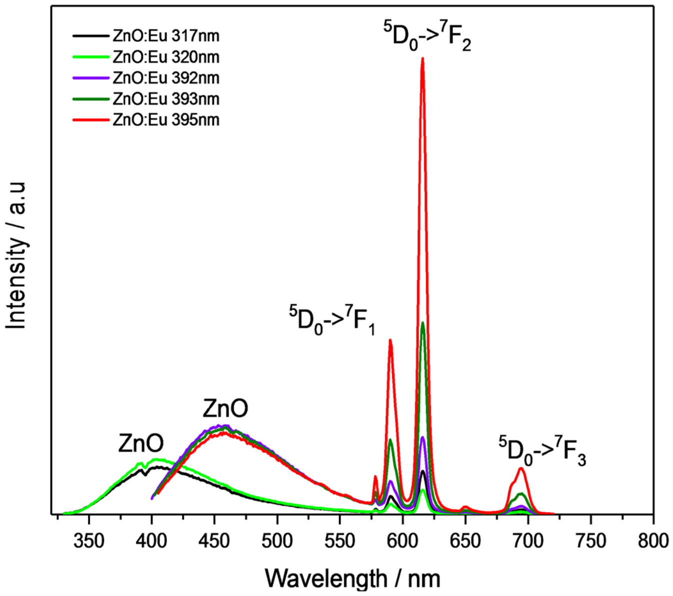

Figure 1. Emission spectra of ZnO:Eu QDs at different wavelengths of excitation.

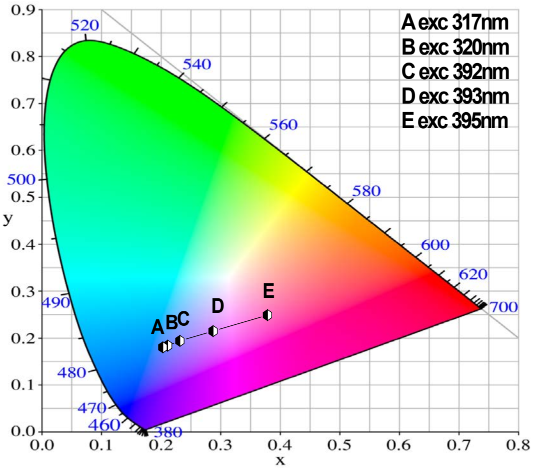

Figure 2. CIE chromaticity diagram of the emission color at different wavelengths of excitation.

4. Conclusion

The synthesis of europium doped zinc oxide quantum dots were successfully carried out. The broad blue emission centered at 405 nm arising from ZnO host is recorded at a wavelength excitation of 317 and 320 nm, while the characteristic transition of Eu^{3+} ions ($^5D_0 \rightarrow {}^7F_2$) was low compared to the ZnO emission. However, the excitation at 392 nm changes the emission of the ZnO host at 455 nm and the emission of Eu^{3+} is lightly increased. Finally, the occurrence of a highly emission of Eu^{3+} ions is recorded by exciting at 393 and 395 nm. This last result allows tuning the color emission from blue to red.

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Conflicts of Interest

The authors declare no conflicts of interest regarding the publication of this paper.

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