



Original Article

The Role of Cu^{2+} Concentration in Luminescence Quenching of $\text{Eu}^{3+} / \text{Cu}^{2+}$ Co-doped ZrO_2 Nanoparticles

Pham Van Huan¹, Phuong Dinh Tam^{1,2}, Nguyen Thi Ha Hanh³,
Cao Xuan Thang¹, Vuong-Hung Pham^{1,*}

¹*Advanced Institute for Science and Technology (AIST), Hanoi University of Science and Technology (HUST), 01 Dai Co Viet, Hanoi, Vietnam*

²*Faculty of Material Science and Engineering, Phenikaa University, Yen Nghia, Hanoi, Vietnam*

³*School of Chemical Engineering, Hanoi University of Science and Technology (HUST), 01 Dai Co Viet, Hanoi, Vietnam*

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Abstract: This paper the role of Cu^{2+} concentrations in luminescence quenching of $\text{Eu}^{3+} / \text{Cu}^{2+}$ doped ZrO_2 nanoparticles synthesized by co-precipitation method. The synthesized $\text{Eu}^{3+} / \text{Cu}^{2+}$ doped ZrO_2 nanoparticles were observed to have sphere morphology with a diameter of ~ 25 nm. The XRD patterns of the nanoparticles revealed the peaks that were to be crystalline tetragonal ZrO_2 . The addition of Cu^{2+} to the Eu^{3+} doped ZrO_2 nanoparticles resulted in a significant suppress luminescence in $\text{Eu}^{3+} / \text{Cu}^{2+}$ doped ZrO_2 nanoparticles, which was attributed to the spectral overlap occurs between Cu^{2+} absorption and Eu^{3+} emission (${}^5\text{D}_0 \rightarrow {}^7\text{F}_2$ transition).

Keywords: Zirconia; luminescence; precipitation; quenching, nanoparticles.

1. Introduction

Zirconia (ZrO_2) nanoparticles have received considerable attention in optoelectronic materials because of its high refractive index, optical transparency, corrosion resistance, photothermal stability, high thermal expansion coefficient, low thermal conductivity, high thermomechanical resistance, and

*Corresponding author.

E-mail address: vuong.phamhung@hust.edu.vn

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catalysis [1, 2]. In addition, the stretching energy of ZrO_2 is very low that opens up the possibility of higher efficient luminescence of activator ions incorporated into host ZrO_2 matrix [3, 4]. While it is generally accepted that doping Eu^{3+} and Er^{3+} ions into ZrO_2 nanoparticles tailors the luminescence of ZrO_2 nanoparticles [5, 6]. An alternate approach to producing luminescence with tailoring the light emission capabilities is to manipulate the matrix to control energy transfer [7, 8]. Previous studies reported that luminescence quenching for Eu^{3+} emission was obtained by doping Cu^{2+} in ZnO [9] and glass matrix [10]. In particular, in our knowledge, there are no reports on the luminescence quenching for $\text{Eu}^{3+} / \text{Cu}^{2+}$ doped ZrO_2 nanoparticles. Therefore, this study proposes a report for suppressing luminescence in Eu^{3+} emission (${}^5\text{D}_0 \rightarrow {}^7\text{F}_2$ transition) by introducing Cu^{2+} into ZrO_2 matrix. The microstructure and crystal structure of the $\text{Eu}^{3+} / \text{Cu}^{2+}$ doped ZrO_2 nanoparticles were characterized by X-ray diffraction (XRD, D8 Advance, Bruker) and field emission scanning electron microscopy (FE-SEM, JEOL, JSM-7600F, JEOL Techniques), respectively. Light emission of nanowire was also determined by photoluminescence spectrometer (NANO LOG spectrofluorometer, Horiba).

2. Experimental procedure

$\text{Eu}^{3+} / \text{Cu}^{2+}$ doped ZrO_2 nanoparticles were synthesized through a co-precipitation method, as follows: $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$ (99 % purity, Aldrich, Saint Louis, US), $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ (99.9 %, Aldrich, Saint Louis, M \ddot{y}), and CTAB (99.9 %, Merck) was dissolved in distilled water (DW) under vigorous stirring at 25 °C for 30 min to obtain A solution. $\text{Eu}(\text{NO}_3)_3$ were obtained by dissolving stoichiometric Eu_2O_3 (99 % purity, Aldrich) in dilute HNO_3 with vigorous stirring. Various amount (0, 1, 3, 5, 7, 10 and 15 % mol Cu^{2+}) were used in all the set of the experiments, whereas, the sample was prepared according to the above procedure with the fixed amount of 5 % mol Eu^{3+} . The reaction mixture was further stirred for 0.5 h at 80 °C and pH was adjusted to 11 by using aqueous ammonia solution (Duc Giang Chemicals, Hanoi, Vietnam). The resulting precipitates were washed three times and then dried at 600 °C for 2 h. The crystalline structures of the $\text{Eu}^{3+} / \text{Cu}^{2+}$ doped ZrO_2 nanoparticles were characterized by X-ray diffraction (XRD, D8 Advance, Bruker, Germany). The microstructure and chemical composition of the $\text{Eu}^{3+} / \text{Cu}^{2+}$ doped ZrO_2 nanoparticles were determined by field emission scanning electron microscopy (JEOL, JSM-7600F, JEOL Techniques, Tokyo, Japan) and energy dispersive X-ray spectroscopy (EDS, Gatan, UK). To investigate the absorption properties of $\text{Eu}^{3+} / \text{Cu}^{2+}$ doped ZrO_2 nanoparticles, spectra were recorded in the wavelength of 200 to 800 nm using UV-Vis spectroscopy (Cary 5000, Varian). Photoluminescence (PL) tests were performed to evaluate the optical properties of $\text{Eu}^{3+} / \text{Cu}^{2+}$ doped ZrO_2 nanoparticles. NANO LOG spectrofluorometer (Horiba, USA) equipped with 450 W Xe arc lamp and double excitation monochromators was used. The PL spectra were recorded automatically during the measurements.

3. Results and discussions

Figure 1 shows the typical XRD patterns of the $\text{Eu}^{3+} / \text{Cu}^{2+}$ doped ZrO_2 nanoparticles synthesized by co-precipitation with different Cu^{2+} concentrations in the reaction solution. All the $\text{Eu}^{3+} / \text{Cu}^{2+}$ doped ZrO_2 nanoparticles showed several strong peaks at $2\theta = 30.2^\circ$, 35.4° , 50.3° , 60.2° , and 62.7° associated with the (001), (200), (112), (121) and (202) plane of the crystalline tetragonal ZrO_2 (JCPDS 50-1089, (Fig 1 (b) - (e)). However, the Eu^{3+} doped ZrO_2 nanoparticles synthesized without the addition of Cu^{2+} showed peaks attributed to the crystalline tetragonal ZrO_2 structure (JCPDS (50-1089) with additional peak at $2\theta \approx 28.4^\circ$ corresponded to the (-111) planes of the crystalline monoclonal ZrO_2 structure (JCPDS 37-1484), (Fig 1 (a)). These results indicate that the Eu^{3+} doped

ZrO₂ nanoparticles synthesized with the addition of Cu²⁺ via a co-precipitation method had the preferential formation of tetragonal phase. It is also can be seen that XRD patterns obtained for all of Eu³⁺ / Cu²⁺ doped ZrO₂ nanoparticles do not reveal the presence of any phases related to europium and other copper species, suggesting the successful preparation of Eu³⁺ / Cu²⁺ doped ZrO₂ nanoparticles.

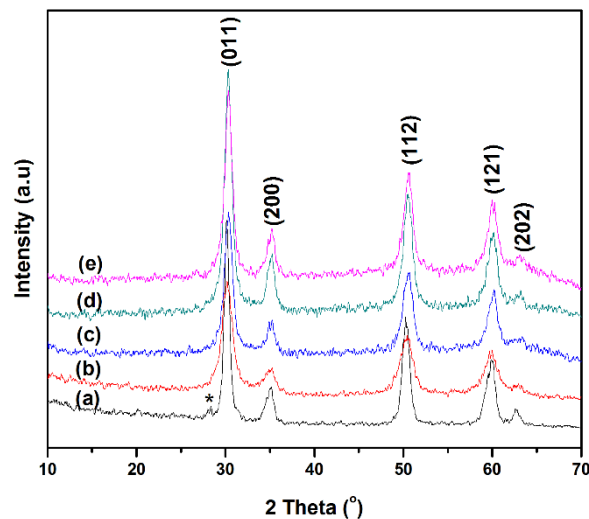


Figure 1. XRD patterns of Eu³⁺ / Cu²⁺ doped ZrO₂ nanoparticles with different Cu²⁺ concentrations in the reaction solution. (a) 0 %, (b) 1 %, (c) 5 %, (d) 10 %, (e) 15 % Cu²⁺ in the reaction solution, * monoclinal ZrO₂.

The microstructures variation in Eu³⁺ / Cu²⁺ doped ZrO₂ nanoparticles synthesized co-precipitation method with different concentrations of Cu²⁺ in the solution was examined by FE-SEM as shown in Figs. 2 (a)–(b). The Eu³⁺ / Cu²⁺ doped ZrO₂ nanoparticles synthesized with and without Cu²⁺ dopants showed spheres nanoparticles with the diameter of ~ 25 nm.

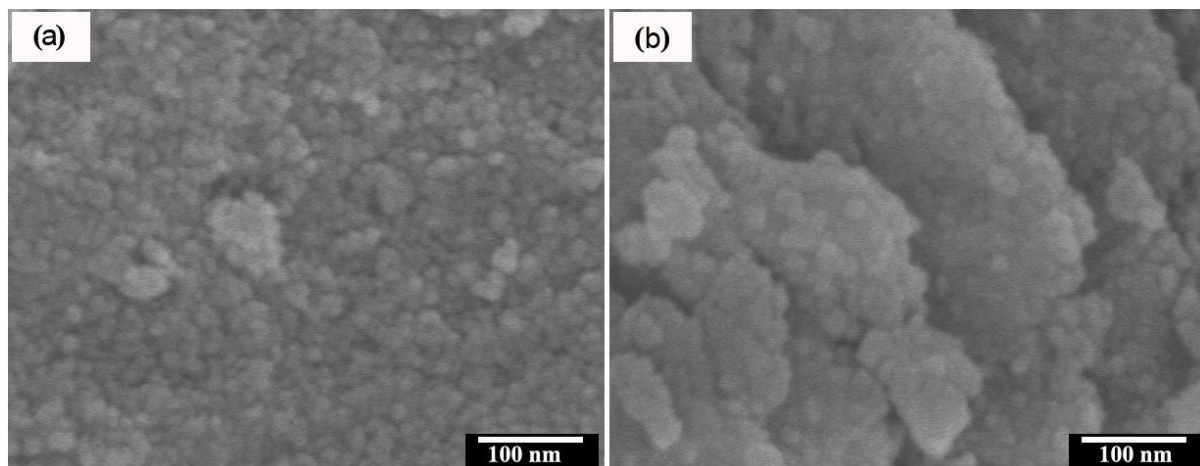


Figure 2. FE-SEM image of Eu³⁺ / Cu²⁺ doped ZrO₂ nanoparticles synthesized by co-precipitation method with various Cu²⁺ concentrations in the reaction solution. (a) 15 % Cu²⁺, (b) 0 % Cu²⁺ at 100000 X magnification.

The representative chemical composition of the $\text{Eu}^{3+} / \text{Cu}^{2+}$ doped ZrO_2 nanoparticles was characterized by EDS, as shown in Figs. 3. It can be seen that peaks corresponding to the Cu and Eu elements were observed, indicating the presence of the Cu and Eu in the ZrO_2 . In addition, a calculated atomic concentration of the Cu and Eu incorporated into ZrO_2 was $\sim 3.6\%$ and 2.4% , respectively, which would be suggested to the successful doping of Cu and Eu into the host ZrO_2 .

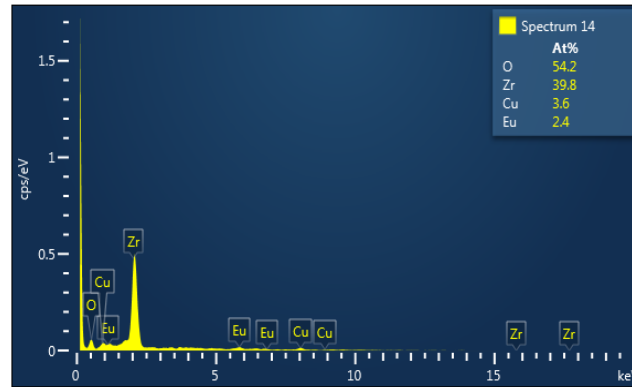


Figure. 3. EDS analysis of chemical composition of $\text{Eu}^{3+} / \text{Cu}^{2+}$ doped ZrO_2 nanoparticles prepared by co-precipitation method with 10 % Cu^{2+} in the reaction solution.

Figure 4 shows the UV-VIS absorption spectrum of $\text{Eu}^{3+} / \text{Cu}^{2+}$ doped ZrO_2 nanoparticles synthesized by co-precipitation with different Cu^{2+} concentrations in the reaction solution (0-15 %). The $\text{Eu}^{3+} / \text{Cu}^{2+}$ doped ZrO_2 nanoparticles synthesized with 0 % Cu in the reaction solution showed an absorption peak at ~ 250 nm, Fig. 4 (a). On the other hand, when a certain concentration of Cu^{2+} was doped, a broad absorption peak at $\sim (250-280)$ nm was observed attributing for the contributions of $\text{O}^{2-} - \text{Cu}^{2+}$ charge transfer transitions on the ZrO_2 with an additional broad peak at $\sim (550 \text{ nm} - 800 \text{ nm})$ was assigned to the ${}^2\text{E} \rightarrow {}^2\text{T}_2$ (d – d) transition of Cu^{2+} , Fig. 4 (b) - (f) [11, 12].

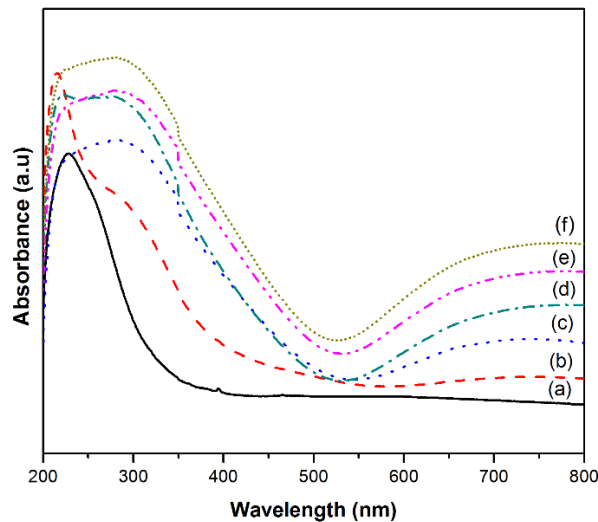


Figure 4. UV-VIS spectra of $\text{Eu}^{3+} / \text{Cu}^{2+}$ doped ZrO_2 nanoparticles with various Cu^{2+} concentrations in the reaction solution. (a) 0 %, (b) 1 %, (c) 5 %, (d) 7 %, (e) 10 %, (f) 15 % Cu^{2+} .

Figure 5 shows the emission spectra of $\text{Eu}^{3+} / \text{Cu}^{2+}$ doped ZrO_2 nanoparticles with different Cu^{2+} concentrations in the reaction solution. All the $\text{Eu}^{3+} / \text{Cu}^{2+}$ doped ZrO_2 nanoparticles showed strong visible emission peaks appeared at about 590, 616, 650 and 700 nm and they can be attributed to the $^5\text{D}_0 \rightarrow ^7\text{F}_1$, $^5\text{D}_0 \rightarrow ^7\text{F}_2$, $^5\text{D}_0 \rightarrow ^7\text{F}_3$, $^5\text{D}_0 \rightarrow ^7\text{F}_4$ transitions within Eu^{3+} ion, respectively. However, it should be noted that the PL spectra of the $\text{Eu}^{3+} / \text{Cu}^{2+}$ doped ZrO_2 nanoparticles decreased with increasing Cu^{2+} concentrations. In particular, when the concentration of Cu^{2+} reach 10 %, they reached the significant decreasing the PL intensities and then decreased completely with further increasing Cu^{2+} concentrations to 15 %. This significant decreasing PL was mainly attributed to the achievement of Cu^{2+} dopants in the $\text{Eu}^{3+} / \text{ZrO}_2$ nanoparticles, which can be explained by considering the photo quenching effect. More specifically, a decreasing luminescent emission of $\text{Eu}^{3+} / \text{Cu}^{2+}$ doped ZrO_2 nanoparticles is due to the spectral overlap occurring between Cu^{2+} absorption and Eu^{3+} emission ($^5\text{D}_0 \rightarrow ^7\text{F}_2$ transition) [10, 13].

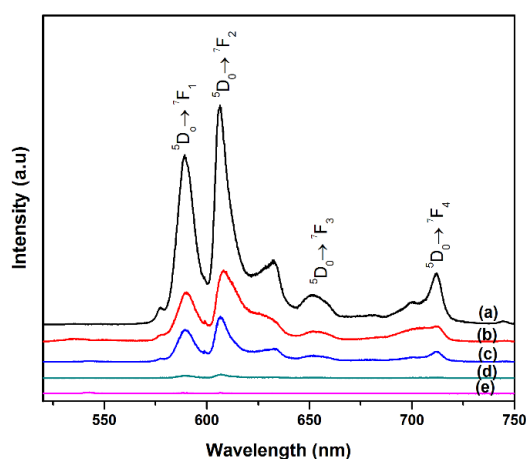


Figure 5. Luminescence spectra of $\text{Eu}^{3+} / \text{Cu}^{2+}$ doped ZrO_2 nanoparticles with various Cu^{2+} concentrations in the reaction solution. (a) 1%, (b) 5 %, (c) 7 %, (d) 10 %, (e) 15 % Cu^{2+} .

4. Conclusions

We herein demonstrated that the luminescence quenching of $\text{Eu}^{3+} / \text{Cu}^{2+}$ doped ZrO_2 nanoparticles could be obtained effectively by controlling the concentrations of Cu^{2+} dopants. In particular, the co-doped of Eu^{3+} and Cu^{2+} into ZrO_2 allows to achieve the tetragonal phase of ZrO_2 . The $\text{Eu}^{3+} / \text{Cu}^{2+}$ doped ZrO_2 nanoparticles synthesized without Cu^{2+} dopants showed typically visible emission peaks of Eu^{3+} . On the other hand, when a certain concentration of Cu^{2+} was doped, luminescence quenching $\text{Eu}^{3+} / \text{Cu}^{2+}$ doped ZrO_2 nanoparticles was achieved. This luminescence quenching of $\text{Eu}^{3+} / \text{Cu}^{2+}$ doped ZrO_2 nanoparticles was mainly attributed to the containing of Cu^{2+} in the nanoparticle which is a suppressing Eu^{3+} luminescence.

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