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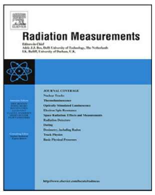

Luminescence enhancement in CeF_3/ZnO nanocomposites for radiation detection

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HIGHLIGHTS

- Energy transfer from CeF_3 to ZnO nanoparticles to enhance ZnO luminescence.
- The photoluminescence of ZnO nanoparticles due to energy transfer is 30 times.
- The enhancement in X-ray excited luminescence is more than 4 times.
- Energy transfer may improve the sensitivity for radiation detection.

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ABSTRACT

ZnO nanoparticles have a strong photoluminescence but weak scintillation luminescence which is an issue for their applications in radiation detection and dosimetry. To enhance their luminescence, ZnO nanoparticles were made into nanocomposites with CeF_3 nanoparticles. As a result of energy transfer from CeF_3 nanoparticles in the composites, the photoluminescence of ZnO nanoparticles is enhanced 30 times and their X-ray luminescence is enhanced 4 times. The combination of CeF_3 and ZnO nanoparticles makes CeF_3/ZnO nanocomposites promising scintillators for radiation detection.

1. Introduction

A good scintillator should have a fast decay time for time resolution, high light yield for energy resolution and high density for high stopping power (van Eijk, 2001; Moses, 2002; Shah et al., 2003). Extensive researches have been done on the scintillator development based on the application of Ce^{3+} ion as a luminescence center. The allowed *5d-4f* transition in Ce^{3+} ion makes Ce^{3+} doped luminescence materials fast and efficient scintillators (vanEijk, 1997). However most of the researches are done on the single crystals. Single crystals are expensive to grow in desire shape and size. Also most Ce^{3+} ion activated scintillators emit in the ultraviolet (UV) region at which the quantum efficiency of photomultiplier tubes (PMTs) is below 25% (Letant and Wang, 2006a,b). This could significantly reduce the light output and the detection sensitivity. Nanoscale luminescence materials are potential scintillators for radiation detection and preliminary investigations on several rare earth doped fluoride nanoparticles have indicated their potentials for radiation detection (Jacobsohn et al., 2011). It was also observed that the light yield was enhanced in nanophosphor cerium doped Y_2SiO_5 (YSO:Ce) compared to bulk powder under X-ray excitation (McKigney et al., 2007). The unique physical properties of Semiconductor nanocrystals (Quantum dots) have attracted tremendous interest in wide range of application from medical imaging (Bruchez , 1998; Byers and Hitchman, 2011), biosensing (Medintz et al., 2003), optoelectronic devices (Eberl et al., 2000) to solar cells (Zhang et al., 2012). Recently, radiation detection has emerged as an area of interest for quantum dots (QDs) application (Hossu et al., 2012). However, there have been very few published studies on the radiation detection based on colloidal QDs. For examples, It has been reported that scintillation performance of luminescent polymer has been improved in CdSe/ZnSe core–shell QDs/polymer composite under electron-beam excitation using cathodoluminescence (Campbell and Crone, 2006) and that the energy resolution of CdSe/ZnS core–shell QDs/glass

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nanocomposite is increase over a standard NaI scintillator by the factor of 2 when irradiated with 59 keV gamma ray (Letant and Wang, 2006). Quantum dots based nanocomposite materials could be a promising material for radiation detection because of their short luminescence life time and high quantum efficiencies as a consequence of quantum size confinement (Chen, 2008). Also, the emission of quantum dots is size dependent, so the output wavelength can be tuned to the sensitivity of the PMTs or avalanche photodiodes (APD). However, the stopping power of most QDs is low and their scintillation luminescence is very weak (Yao et al., 2010). The combination of high stopping power of inorganic scintillator with QDs could potentially lead to a new class of scintillator. Recently, we have reported that energy transfer based nanocomposites are new and promising scintillators for radiation detection (Yao et al., 2010; Hossu et al., 2012).

High density and good stability that yields a small radiation length makes CeF_3 as one of the most promising for high rate-calorimetry (Lecoq, 1994). Zinc Oxide (ZnO), a wide band gap (3.37 eV) semiconductor with large exciton binding energy (60 meV) has been known as a fast scintillator (Simpson et al., 2003). However it has relatively low light yield (Bourret-Courchesne et al., 2006) and low density. The nanocomposite scintillators based on energy transfer from Ce^{3+} doped nanoparticles proposed by us (Yao et al., 2010, Hossu et al., 2012) could overcome these shortcomings. Here we report the enhancement in the photoluminescence and X-ray luminescence from ZnO nanoparticles in CeF_3/ZnO nanocomposites. The enhancement observed not only improve ZnO nanoparticles for applications in radiation detection, dosimetry, solid state lighting, biological sensing but also their applications in photodynamic activation for cancer treatment as well as in solar cell enhancement (Chen and Zhang, 2006; Chen, 2008; Liu et al., 2008; Zhang et al., 2008; Liu et al., 2010; Fakhar-e-Alam et al., 2012).

1.1. Experimental details

CeF_3/ZnO nanocomposite scintillators were prepared using a two-step wet chemistry synthesis. Firstly, the colloidal ZnO nanopaticles were synthesized in methanol using similar method reported by Sun et al. (2007). To synthesize ZnO nanoparticles, 0.08 M potassium hydroxide in methanol is refluxed and stirred for 30 min at 60 °c. After refluxing, 0.04 M Zinc acetate dihydrate (ZAD) in methanol is added dropwise while stirring. The ZnO sol was then aged at 60°c for 2 h with continuous stirring and refluxing. The colloidal ZnO nanoparticles appear clear under room light but emit green under UV-light.

Secondly, the Cerium Fluoride (CeF_3) nanoparticles were prepared using similar method reported by our group (Sun et al., 2009). In this approach, 2 mmol of cerium nitrate hexahydrate [$Ce\ (NO_3)_3 \cdot 6H_2O$] is dissolved in 40 ml DI water. 400 µl Poly (ethylene glycol) bis(carboxymethyl) ether is added as a surfactant to the $Ce(NO_3)_3 \cdot 6H_2O$ solution and then stirred at room temperature for 15 min. In another beaker 1 ml hydrofluoric acid is mixed with 39 ml of DI water and then added dropwise to the above slurry and then kept stirring at room temperature for 30 min. After 30 min of stirring, the mixture is heated for 2 h and 30 m at 95 °c. CeF_3 nanoparticles were then centrifuged, washed with DI water for several times and dried overnight at 45 °c under vacuum.

Finally, the as prepared CeF_3 nanoparticles were added to the colloidal ZnO nanoparticles and ultrasonicated for 10 min. Hexane and isopropanol were added to the CeF_3/ZnO sol and kept it in refrigerator overnight to precipitate. The volume ratio of colloidal ZnO nanoparticles: isopropanol: hexane was 1:1:5. The product was centrifuged and then dries at 45 °c under vacuum.

After drying for overnight, ZnO nanoparticles, CeF_3 nanopartcles and CeF_3/ZnO nanocomposites were examined by X-ray diffraction. The particles size was estimated using Scherer's equation. Optical absorption of colloidal ZnO nanoparticles was recorded with SHIMADZU UV-2450 spectrophotometer. Photoluminescence emission (PL) and excitation (PLE) were taken on a SHIMADZU RF-5301 PC Spectrofluorometer. X-ray luminescence was measured in a light-proof X-ray cabinet equipped with optic fiber connection to an outside detector. X-ray irradiation (90 kV and 5 mA) was performed using a Faxitron RX-650 X-ray cabinet (Faxitron X-Ray Corp, IL, USA). The luminescence spectra were recorded using a QE65000 spectrometer (Ocean Optics Inc, Dunedin, FL), connected to the X-ray chamber using a 600 µm core diameter, P600-2-UV-Vis fiber optic (Ocean Optics Inc, Dunedin, FL).

2. Results and discussion

Fig. 1 shows the XRD pattern of the as synthesis ZnO nanoparticles and CeF_3 nanoparticles along with CeF_3/ZnO nanocomposite. The XRD pattern of the ZnO nanoparticles sample matches with the ZnO microparticle. The peaks are identified as (100), (002), (101), (102), (110), (103) and (112) crystal planes of the wurzite ZnO. Peak broadening is due to the small size of the particles. The average size of the ZnO nanoparticles is estimated to be about 5 nm by the (101) peak using the Scherer's equation, $D = 0.9\ \lambda/\beta\ \mathrm{Cos}\theta$, where D is the average size of the particles, λ is the X-ray wavelength (1.5406 Å), θ is the diffraction angel and β is FWHM of an observed peak. In the XRD pattern of as synthesis CeF_3 nanoparticles, the diffraction peaks at 2θ values of 24, 28, 35, 44, 45, 51, 53 and 65° are corresponding to the (002), (111), (112), (300), (113), (302), (221) and (214) reflecting planes, respectively, and can be indexed to the hexagonal phase of CeF_3. The particle size is estimated to be about 10 nm using the (300) peak.

Fig. 2 shows the optical absorption spectrum of as synthesis colloidal ZnO nanoparticles and emission spectrum of CeF_3 nanoparticles measured at room temperature. ZnO nanoparticles show the absorption peak at around 335 nm which is blue shifted compared to that of bulk ZnO as a result of quantum size confinement (Woo et al., 2008). The emission peak in CeF_3 nanoparticles at around 334 nm is attributed to the *5d-4f* transition of Ce^{3+} ion (Feller et al., 2011). As shown in Fig. 2, the emission peak of CeF_3 is overlapped largely with the absorption peak of ZnO nanoparticles. Thus, it may expect that there would be efficient energy transfer from CeF_3 to ZnO in CeF_3/ZnO nanocomposites. Fig. 3 shows the photoluminescence emission of ZnO QDs and CeF_3/ZnO

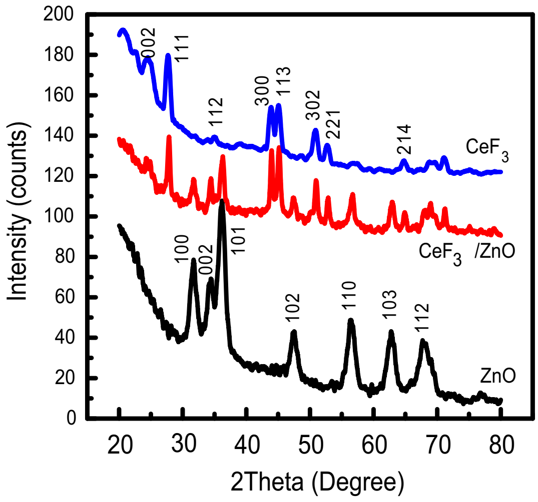

Fig. 1. XRD patterns of ZnO nanoparticles, CeF_3 nanoparticles and CeF_3/ZnO nanocomposites.

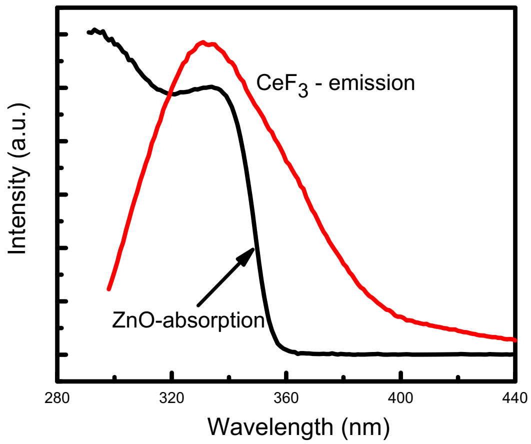

Fig. 2. Emission spectrum of CeF_3 nanoparticles excited by 290 nm and absorption spectrum of ZnO nanoparticles.

nanocomposites, both excited by 290 nm excitation wavelength. ZnO nanoparticles have an emission peak at 366 nm and defect emission at 510 nm. Emission peak at 366 nm is attributed to the band edge excitonic emission and green emission is due to the oxygen vacancies (Vanheusden et al., 1996) in ZnO. Due to the quantum confinement, the excitonic peak is significantly shifted to shorter wavelength as compared with that in bulk ZnO (Irimpan et al., 2007). CeF_3/ZnO nanocomposites show a large enhancement in the photoluminescence of ZnO nanoparticles as compared to ZnO nanoparticles only. The enhancement for the excitonic emission is almost 30 times and the enhancement for the defect green emission is more than 10 times. In CeF_3/ZnO nanocomposites, the emission from CeF_3 nanoparticles is not observed. The quenching of CeF_3 emission and the enhancement of ZnO emission in CeF_3/ZnO nanocomposites indicate that there is energy transfer from CeF_3 to ZnO nanoparticles. As the quenching of CeF_3 emission is almost 100% and this might indicate that the energy transfer efficiency is almost 100%. This high transfer efficiency is due to the large overlap of CeF_3 emissions with the ZnO absorption, as well as the two kinds of nanoparticles are closely together in the nanocomposites.

As pointed out that ZnO is a promising material for radiation detection due to its high exciton binding energy, fast decay lifetime,

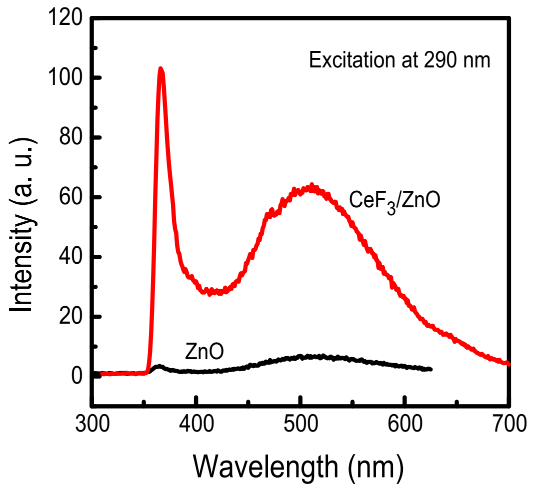

Fig. 3. Photoluminescence of pure ZnO nanoparticles and CeF_3/ZnO nanocomposite, both excited by 290 nm.

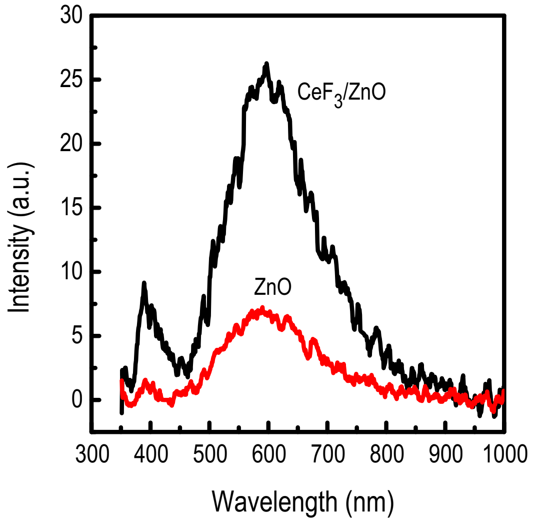

Fig. 4. X-ray luminescence of pure ZnO nanoparticles and CeF_3/ZnO nanocomposite.

good stability and environmentally friendly (Ozgur et al., 2005). The energy transfer in CeF_3/ZnO nanocomposites might enhance the X-ray excited luminescence or scintillation luminescence for radiation detection. For that, we investigated X-ray excited luminescence as shown in Fig. 4. Obviously, the X-ray excited luminescence of ZnO nanoparticles in CeF_3/ZnO nanocomposites were enhanced about 4 times both in the exciton and the defect emissions by comparing to that of X-ray excited luminescence from ZnO nanoparticles. Here we should point out that the exciton emission in the X-ray excited luminescence is weaker in intensity than the defect emission and both the exciton and the defect emissions are shifted about 20 nm to longer wavelength by comparing with their photoluminescence emissions. This is because the photodetector for the X-ray excited luminescence system has lower sensitivity in UV range. The other possibility is that the defect emission is stronger because more defects were created by X-ray irradiation during the measurement.

We also noticed that the enhancement in photoluminescence is much higher than in X-ray luminescence. The reasons are not very clear yet. One possible reason is that the two luminescence processes excited by light and by X-ray are different. In photoluminescence, the UV or visible light excites the luminescence centers to higher energy states, then relax to the emitting state and

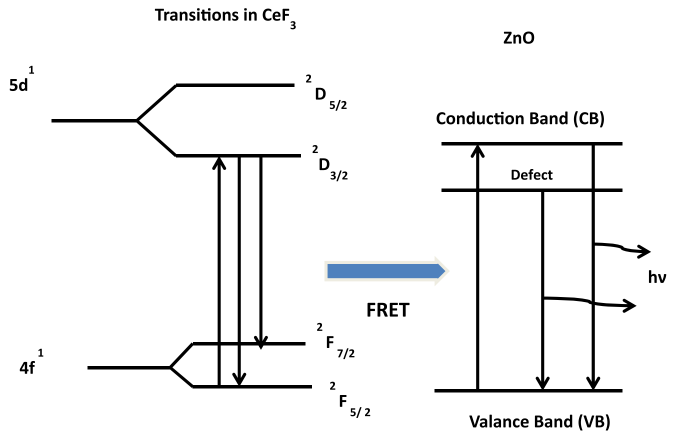

Fig. 5. A schematic diagram for energy transfer from cerium fluoride (CeF_3) to Zinc Oxide (ZnO) nanoparticles.

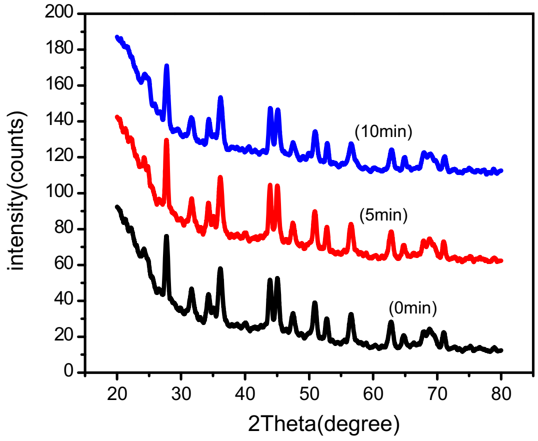

Fig. 6. XRD pattern of CeF_3/ZnO nanocomposites before (0 min) and after (5min and 10 min) X-ray irradiation.

return to the ground state to produce luminescence. In X-ray luminescence, absorption of X-ray photons produces energetic electrons and holes. These electrons and holes transfer their energy to the luminescence centers to excite them to higher energy states, then relax to the emitting state and return to the ground state to produce luminescence. Thus, the X-ray luminescence is more complicated than photoluminescence, and also involves electrons, holes and defects. In this case, it is understandable that energy transfer enhancement in X-ray luminescence is weaker than in photoluminescence.

The energy transfer mechanism from CeF_3 to ZnO nanoparticles can be explained through the energy level diagram as shown in Fig. 5. Under 290 nm excitation, CeF_3 nanoparticles emits light with peak at 334 nm due to *5d-4f* transition, which is in resonance with the excitation spectrum of ZnO nanoparticles. If the two nanoparticles come close together then CeF_3 nanoparticles transfer its energy to the ZnO nanoparticles through dipole–dipole transition. The energy transfer mechanism exited by X-ray should be similar but the efficiency might be different because some point defects or color centers are created by X-ray irradiation and these defects would influence the luminescence and energy transfer efficiencies (Chen et al., 1997; Chen et al., 1998; Bandyopadhyay et al., 1999; Chen and Su, 1999; Chen et al., 2002; Chen et al., 2005; Chen et al., 2006; Chen et al., 2007; Chen et al., 2008).

For radiation detection, the materials must be stable or have high radiation hardness. The XRD patterns of CeF_3/ZnO nanocomposites before and after X-ray irradiation for 5 and 10 min are displayed in Fig. 6. Their XRD profiles are almost identical and the diffraction line intensities are almost the same. This indicates that these nanocomposites are very stable under X-ray irradiation at the dose rate we have in the lab. The high radiation hardness of these materials means they are potentially good for radiation applications.

3. Conclusion

In summary, CeF_3/ZnO nanocomposites were successfully synthesized using a two-step wet chemistry method and large energy transfer was observed from CeF_3 to ZnO nanoparticles in the nanocomposites. Consequently, the photoluminescence of ZnO nanoparticles is enhanced more than 30 times and the X-ray excited luminescence is enhanced more than 4 times in the nanocomposites by comparing with that of ZnO nanoparticles only. The nanocomposites are very stable under X-ray irradiation. These energy transfer based nanocomposites are potentially promising for radiation detection, solid state lighting, biological sensing, and solar cell enhancement as well as light sources for photodynamic activation for therapeutic applications.

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