Luminescence enhancement of CdTe nanostructures in LaF3 : Ce / CdTe nanocomposites
Mingzhen Yao, Xing Zhang, Lun Ma, Wei Chen, Alan G. Joly, Jinsong Huang, and Qingwu Wang

Citation: Journal of Applied Physics 108, 103104 (2010); doi: 10.1063/1.3506416
View online: http://dx.doi.org/10.1063/1.3506416
View Table of Contents: http://scitation.aip.org/content/aip/journal/jap/108/10?ver=pdfcov
Published by the AIP Publishing

Articles you may be interested in
Sodium chloride protected CdTe quantum dot based solid-state luminophores with high color quality and fluorescence efficiency

Nanocomposites of POC and quantum dots
AIP Conf. Proc. 1459, 151 (2012); 10.1063/1.4738427

Preparation, characterization and luminescence properties of polyaniline-CdS nanocomposites

X-ray luminescence of CdTe quantum dots in LaF3:Ce/CdTe nanocomposites

CdTe quantum dots and polymer nanocomposites for x-ray scintillation and imaging
Appl. Phys. Lett. 98, 181914 (2011); 10.1063/1.3589366
Luminescence enhancement of CdTe nanostructures in LaF₃:Ce/CdTe nanocomposites

Mingzhen Yao,¹ Xing Zhang,¹ Lun Ma,¹ Wei Chen,¹(a) Alan G. Joly,²(b) Jinsong Huang,³ and Qingwu Wang⁴
¹Department of Physics, The University of Texas at Arlington, Arlington, Texas 76019-0059, USA
²Pacific Northwest National Laboratory, Richland, Washington 99352, USA
³Department of Mechanical Engineering, University of Nebraska–Lincoln, Nebraska 68588-0656, USA
⁴Agiltron, Inc., Woburn, Massachusetts 01801, USA

(Received 8 July 2010; accepted 23 September 2010; published online 17 November 2010)

Radiation detection demands new scintillators with high quantum efficiency, high energy resolution, and short luminescence lifetimes. Nanocomposites consisting of quantum dots and Ce³⁺ doped nanophosphors may be able to meet these requirements. Here, we report the luminescence enhancement of LaF₃:Ce/CdTe nanocomposites which were synthesized by a wet chemistry method. CdTe quantum dots in LaF₃:Ce/CdTe nanocomposites are converted into nanowires, while in LaF₃/CdTe nanocomposites no such conversion is observed. As a result, the CdTe luminescence in LaF₃:Ce/CdTe nanocomposites is enhanced about five times, while in LaF₃/CdTe nanocomposites no enhancement was observed. Energy transfer, light reabsorption, and defect passivation are the likely reasons for the luminescence enhancement. © 2010 American Institute of Physics [doi:10.1063/1.3506416]

I. INTRODUCTION

Luminescent nanoparticles have many potential applications including medical labeling, imaging, photodynamic activation, and radiation detection.¹⁻⁴ For radiation detection, the sensitivity, response time, and energy resolution are important.⁵⁻⁶ To meet these requirements, a scintillator must have a high luminescence quantum efficiency, a short luminescence lifetime, high stopping power as well as high carrier mobility-lifetime products.⁶ Ce³⁺ is a great activator exhibiting a very fast response in radiation detectors of medical imaging systems employed in diagnostic radiology.⁷⁻¹⁰ Currently, Ce³⁺ doped scintillators meet most of the requirements and have become popular scintillators for radiation detection and dosimetry.⁷⁻¹⁰ However, Ce³⁺ doped scintillators have their own shortcomings. For example, some Ce³⁺ doped scintillators such as LaBr₃:Ce³⁺ have very high quantum efficiency and energy resolution, but they are hygroscopic, making them impractical for many applications. In addition, most Ce³⁺ doped scintillators have emission in the ultraviolet (UV) range. This is an issue as UV light is often limited in detection systems and many materials are not transparent in the UV range. Quantum dots such as CdTe and CdSe can have very high quantum efficiencies as a consequence of quantum size confinement.¹¹⁻¹³ Indeed, quantum dots have very high luminescence quantum efficiency up to 98%¹⁵ and short luminescence lifetimes in the nanosecond range.¹⁴⁻¹⁶ Therefore, in principle, semiconductor quantum dots could be promising for radiation detection because of their short lifetimes and high sensitivities. However, the stopping power of most II-VI quantum dots is low and their scintillation luminescence is very weak.¹⁷ Nanocomposites composed of CdTe quantum dots and LaF₃:Ce³⁺ nanoparticles may overcome the shortcomings of Ce³⁺ doped scintillators and semiconductor quantum dots, therefore, they can provide improved properties for radiation detection. This combination may solve these problems because Ce³⁺ doped scintillators have high stopping power and high scintillation efficiency. The possible energy transfer from Ce³⁺ doped scintillation nanoparticles to semiconductor quantum dots may be very high because the emission of Ce³⁺ ions and the absorption of the quantum dots can be made to largely overlap by simply adjusting the size of the quantum dots. In this paper, we report the synthesis and luminescence enhancement of CdTe nanostructures in LaF₃:Ce/CdTe nanocomposites, and explore their potential application as a new kind of phosphor for radiation detection and solid state lighting.

II. EXPERIMENTAL DETAILS

CdTe/LaF₃:Ce nanocomposites were prepared by a wet chemistry method in two steps. In the first step, CdTe quantum dots coated with thioglycolic acid (TGA) surfactant were synthesized. In the second step, LaF₃:Ce nanoparticles were attached to CdTe quantum dots to form LaF₃:Ce/CdTe nanocomposites. To synthesize CdTe quantum dots, Cd²⁺-containing solution was prepared by dissolving 0.7311 g of Cd(ClO₄)₂·H₂O in 125 ml of water. Then, TGA (0.396 mol) was added to the solution and the pH value was adjusted to ~11 by the addition of 0.1M NaOH. The solution was then purged with nitrogen for at least 30 min. H₂Te gas was generated by the chemical reaction of excess aluminum telluride with 0.5M sulfuric acid in an inert atmosphere (nitrogen) and was combined with the above solution containing Cd²⁺ ions using the setup as described.¹⁸ After the completion of the reaction a yellow solution of CdTe nano-
crystal nuclei was obtained. This solution was then refluxed at 100 °C to promote crystal growth with the particle size controlled by the reaction time.

To form LaF3:Ce/CdTe nanocomposites, 6.3 mmol of La(NO3)3 and 0.7 mmol of Ce(NO3)3·6H2O were first dissolved in 15 ml of deionized water and then mixed with 10 ml of the CdTe nanoparticle solution prepared in step-1, 1 ml diethylene glycol was added to the mixture solution as a surfactant. Ce(NO3)3·6H2O was used as the dopant to provide Ce3+ with doping concentration of 0.1M. The chemicals were mixed thoroughly, and then 20.1 mmol of NH4F water solution with a volume of 5 ml was added drop wise to the mixture solution under stirring at room temperature. The reaction solution was stirred at room temperature for 0.5 h and subsequently was heated to 50 °C for different reaction times up to 3.5 h under protection of nitrogen. The product subsequently was heated to 50 °C for different reaction times.

The identity, crystalline structure, size, and shape of the nanoparticles were observed by x-ray diffraction and high-resolution transmission electron microscopy (HRTEM). The x-ray powder diffraction (XRD) patterns of LaF3:Ce/CdTe nanocomposites were recorded in the range of 20° ≤ 2θ ≤ 80° using a Siemens Kristalloflex 810 D-500 x-ray diffractometer operating at 40 kV and 30 mA with a radiation beam of λ=1.5406 Å. The nanocomposites in solution were brought onto holey carbon covered copper grids for HRTEM observations. The HRTEM images of the particles were obtained with a JEOL JEM-2100 electron microscope with accelerating voltage of 200 kV. The excitation and emission spectra were measured using a Shimadzu RF-5301PC fluorescence spectrophotometer. Luminescence lifetimes were collected using the frequency-doubled output of a synchronously-pumped picosecond dye laser operating at 610 nm. The doubled output was focused onto the samples and emission collected at right angle to the input. The emission was spectrally filtered and the lifetime measured using time-correlated single photon counting. The instrument resolution was determined to be about 50 picoseconds full-width at half maximum (FWHM) using a standard scattering material.

III. RESULTS AND DISCUSSION

A. XRD

Figure 1 shows the XRD patterns of LaF3:Ce/CdTe and LaF3:Ce. The results of the XRD are in good agreement with the trigonal tysonite LaF3 structure as described in the reports, and from bulk LaF3 and CeF3 crystals (Joint Committee on Powder Diffraction Standards Card 32-0483 and 08-0045). No XRD signals were observed for CdTe in LaF3:Ce/CdTe nanocomposites which most likely due to its low concentration. The particle size can be estimated from the Scherrer equation, \(D = \frac{0.90\lambda}{\beta \cos \theta}\), where \(D\) is the average crystallite size, \(\lambda\) is the x-ray wavelength (0.154-0.155 nm), and \(\theta\) and \(\beta\) are the diffraction angle and FWHM of an observed peak, respectively. The strongest peak (111) at \(2\theta\) =27.8° was used to calculate the average crystallite size (\(D\)) of the nanoparticles, providing an average size estimated at about 15 nm. No XRD signals were observed for impurity phases indicating that Ce3+ is likely doped into the LaF3 crystal lattice. The ionic radius of Ce3+ (1.034 Å) is very close to that of La3+ (1.061 Å), therefore, Ce3+ can easily substitute for La3+ ions in LaF3 crystals.

B. TEM

Figure 2 displays the HRTEM images of LaF3:Ce/CdTe nanocomposites. Oval shaped nanostructures are observed with an average dimension of about 22 nm long and 10 nm wide, which consistent with the XRD results. In the nanocomposites, there are two kinds of nanostructures in the HRTEM images, nanowires and nanoparticles. In the nanowires, the spacing between adjacent lattice planes is about 0.39 nm shown in Figs. 2(a) and 2(b). The spacing corresponds to the (110) plane of the wurtzite CdTe lattice. In the nanoparticles, the interplanar spacing is about 0.36 nm which is similar to the interplanar spacing of (0001) planes in the hexagonal LaF3 structure. The HRTEM observations demonstrate that CdTe and LaF3:Ce nanostructures are in close proximity in the composites. During the synthesis, CdTe quantum dots have been converted to nanowires in the composites.

C. Optical properties

Figure 3 displays the optical absorption spectra of LaF3:Ce nanoparticles, CdTe quantum dots, and LaF3:Ce/CdTe nanocomposites. In the measurement, the concentration of CdTe quantum dots is kept constant between the CdTe quantum dots and LaF3:Ce/CdTe nanocomposites samples. Similarly, the concentration of LaF3:Ce nanoparticles is the same in the LaF3:Ce and LaF3:Ce/CdTe nanocomposite samples. The absorption spectrum of CdTe quantum dots is similar to those reported in literature. The absorption spectrum of LaF3:Ce is similar to that of the LaF3:Ce/CdTe nanocomposites with the main absorption band attributed to the LaF3:Ce nanoparticles. The absorption from CdTe quantum dots is very weak and barely observed.
This may be due to the conversion of the quantum dots to nanowires as observed by TEM as shown in Fig. 2. The change in three dimensionally quantified quantum dots to two dimensionally quantified nanowires can reduce the nanostructure absorption coefficient.\textsuperscript{12} Fig. 4 shows emission spectra from LaF\textsubscript{3}:Ce nanoparticles, CdTe quantum dots, and LaF\textsubscript{3}:Ce/CdTe nanocomposites. The CdTe quantum dots have a green emission at 547 nm. The emission peak at around 342 nm in LaF\textsubscript{3}:Ce is attributed to the 5\textit{d} \rightarrow 4\textit{f} transition of Ce\textsuperscript{3+} from the lowest 5\textit{d} excited state to the spin-orbit split ground \textit{f} state.\textsuperscript{21,22} Two emissions peaking at 368 and 541 nm are observed from LaF\textsubscript{3}:Ce/CdTe nanocomposites, which are attributed to the LaF\textsubscript{3}:Ce nanoparticles and CdTe quantum dots, respectively. Compared with the emissions in pure CdTe quantum dots and LaF\textsubscript{3}:Ce nanoparticles, the emission from CdTe quantum dots shifts to shorter wavelength and the emission from Ce\textsuperscript{3+} shifts to longer wavelength. As compared to pure CdTe quantum dots and LaF\textsubscript{3}:Ce nanoparticles, the emission from LaF\textsubscript{3}:Ce nanoparticles decreases in intensity while the emission from CdTe quantum dots increases in intensity in the nanocomposites. The excitation wavelength is 265 nm for the luminescence measurement in Fig. 4, and the absorbance at 265 nm is almost identical for the two LaF\textsubscript{3}:Ce and LaF\textsubscript{3}:Ce/CdTe samples. This indicates that the luminescence quantum efficiency of CdTe in LaF\textsubscript{3}:Ce/CdTe nanocomposites is higher than in pure CdTe nanoparticles.

Figure 5 shows the LaF\textsubscript{3}:Ce/CdTe nanocomposite emission spectra prepared at room temperature and followed by heating at 50 °C for 1 h, 2.5 h, and 3.5 h, respectively. As the annealing time lengthens, the LaF\textsubscript{3}:Ce nanoparticle emission decreases and the CdTe quantum dot emission increases gradually. We note that the CdTe quantum dot emission shifts to longer wavelengths at longer reaction time while the Ce\textsuperscript{3+} emission in LaF\textsubscript{3}:Ce nanoparticles remains at the same position. This emission color change is visible to even the naked eye as shown in Fig. 6. By eye the nanocomposites are significantly brighter than the quantum dots. As observed by TEM, CdTe nanoparticles are converted to nanowires during the heating process during the formation of the nanocomposites. The mechanism for the change in the quantum dots to nanowires is not yet clear but it is likely that the redshift in the emission wavelength is due to the formation of nanowires as previously reported in the literature.\textsuperscript{23}
As the heating time increases, more nanowires are formed. This is perhaps also the reason for the increase in CdTe emission with increasing reaction time.

D. Lifetime measurement

One possible mechanism for the CdTe luminescence enhancement in LaF₃:Ce/CdTe nanocomposites is energy transfer from LaF₃:Ce nanoparticles to CdTe nanowires. The decrease in the Ce³⁺ emission along with the increase in CdTe emission in intensity is a good indication that energy transfer from Ce³⁺ to CdTe takes place in the nanocomposites. To reveal if there is energy transfer between them, the Ce³⁺ luminescence lifetimes in LaF₃:Ce and LaF₃:Ce/CdTe as well as the CdTe lifetime in LaF₃:Ce/CdTe were measured as shown in Fig. 7 and collected in Table I. For the fast component, the lifetime of Ce decreases from 3.2 ns in LaF₃:Ce to 1.5 ns in LaF₃:Ce/CdTe, and for the slow component, the lifetime of Ce decreases from 24.5 ns in LaF₃:Ce to 12.5 ns in LaF₃:Ce/CdTe (Table I). The reduction in the Ce³⁺ lifetime is consistent with energy transfer from Ce³⁺ to CdTe which would lead to an observed luminescence enhancement in the LaF₃:Ce/CdTe composites. According to the Förster resonance energy transfer (FRET) theory, FRET efficiency is related to the quantum yield and the fluorescence lifetime of the donor molecule as follows:

\[ E = 1 - \frac{\tau_D}{\tau_D} \quad (1) \]

where \( \tau_D \) and \( \tau_A \) are donor fluorescence lifetimes in the presence and absence of an acceptor, respectively. Based on this formula, the energy transfer efficiency from LaF₃:Ce to CdTe were calculated as 53% for the fast component and 49% for the slow components, respectively.

However, energy transfer may also change the lifetime of the acceptor if the lifetimes of the donor and acceptor are different. For example, if the donor lifetime is significantly longer than the acceptor lifetime, in the energy transfer system, the lifetime of the acceptor should be the same or similar to that of the donor as observed in BaFBr:Eu²⁺/CdTe nanocomposites. Here, in the LaF₃:Ce/CdTe nanocomposites, it is noted that the CdTe nanowire lifetime is almost the same as in pure CdTe quantum dots and is about a factor of two shorter than the donor (Ce³⁺) lifetime. This cannot exclude energy transfer from Ce³⁺ to CdTe in LaF₃:Ce/CdTe nanocomposites but it indicates that the energy transfer rate is not high and energy transfer is not the only reason for the

<table>
<thead>
<tr>
<th>Sample</th>
<th>Excitation/emission</th>
<th>Lifetime T1 (ns)</th>
<th>Lifetime T2 (ns)</th>
<th>Curve</th>
</tr>
</thead>
<tbody>
<tr>
<td>LaF₃:Ce</td>
<td>300 nm/350 nm</td>
<td>1.9</td>
<td>22.0</td>
<td>a (Ce³⁺)</td>
</tr>
<tr>
<td>LaF₃:Ce/CdTe</td>
<td>285 nm/375 nm</td>
<td>1.5</td>
<td>12.5</td>
<td>b (Ce³⁺)</td>
</tr>
<tr>
<td></td>
<td>285 nm/520 nm</td>
<td>0.6</td>
<td>5.2</td>
<td>c (CdTe)</td>
</tr>
</tbody>
</table>
enhancement. In addition, as the Ce$^{3+}$ emission peak effectively overlaps the CdTe nanowires absorption, emitted light from Ce$^{3+}$ can be reabsorbed by the CdTe nanowires in the nanocomposites. This could also be another factor responsible for the luminescence enhancement.

**E. Possible mechanism for enhancement**

Energy transfer is one possibility for the luminescence enhancement observed. In addition to energy transfer, there must be other factors such as surface modification by annealing that increase the CdTe luminescence efficiency. LaF$_3$ coating and the configuration conversion from quantum dots to nanowires also could have an effect. To determine whether annealing is responsible for the enhancement, pure CdTe quantum dots were annealed at 50 °C for 1, 2, and 3.5 h under the same conditions as for LaF$_3$:Ce/CdTe nanocomposites. The results indicate that the CdTe quantum dot emission increases about 5% in intensity for 1 h annealing, and then decreases in intensity for 2.5 and 3.5 h annealing. Therefore, enhancement by annealing can be excluded. To determine if coupling with pure LaF$_3$ nanoparticles is the reason for the luminescence enhancement, LaF$_3$ nanoparticles and LaF$_3$/CdTe nanocomposites were prepared and compared with both LaF$_3$:Ce nanoparticles and LaF$_3$:Ce/CdTe nanocomposites. Surprisingly, Ce$^{3+}$ emission was detected in pure LaF$_3$ nanoparticles but its intensity is nine times weaker than in LaF$_3$:Ce nanoparticles (Fig. 8). The Ce$^{3+}$ emission is likely due to Ce$^{3+}$ contamination in the La(NO$_3$)$_3$ precursor. In the LaF$_3$/CdTe nanocomposites, the emissions of Ce$^{3+}$ and CdTe quantum dots are five times weaker than the emission of Ce$^{3+}$ and of CdTe quantum dots in LaF$_3$:Ce/CdTe nanocomposites (Fig. 9). After annealing at 50 °C for 1 h, the Ce$^{3+}$ emission in LaF$_3$/CdTe nanocomposites increases slightly but the CdTe emission is almost the same. After annealing for 2 h, both the Ce$^{3+}$ and CdTe quantum dot emissions are quenched in intensity (Fig. 10). These observations exclude the contributions of annealing and LaF$_3$ coating to the CdTe luminescence enhancement in the LaF$_3$:Ce/CdTe nanocomposites.

The HRTEM images of LaF$_3$/CdTe nanocomposites with no Ce$^{3+}$ doping are shown in Fig. 11. By comparing the TEM results between LaF$_3$:Ce/CdTe (Fig. 2) and LaF$_3$/CdTe (Fig. 11), it is noted that in LaF$_3$:Ce/CdTe, the CdTe quantum dots are converted to nanowires, while this conversion does not occur in LaF$_3$/CdTe nanocomposites. The CdTe lifetime in LaF$_3$/CdTe nanocomposites before heating and after heating for one hour are shown in Fig. 12. The two samples show very similar emission spectra and lifetimes. This also indicates there is no conversion of the quantum dots into nanowires in LaF$_3$/CdTe nanocomposites. The conversion of CdTe quantum dots to nanowires likely is the reason for the redshift in the CdTe emission observed in LaF$_3$:Ce/CdTe because the increase in the dimensionality results in the narrowing of the energy gap. However, the conversion of quantum dots to nanowires does not likely contribute to the luminescence enhancement because the increase in the dimensionality reduces luminescence yield.

It is interesting that the luminescence enhancement seems correlated with the formation of nanowires. Rare earth ions such as Ce$^{3+}$ can have unique properties and have been used as catalysts for crystal growth. It has been reported that several rare-earth elements, including Y, Ce, Tb, La, Ho, Gd, and Pr, together with Ni form bimetallic catalysts for carbon nanotube synthesis. The addition of rare-earth ele-
ments can improve the nanotube yield and can affect the structure. In our experiments, we observe that when Ce³⁺ ions are added to the nanoparticle synthesis, the nanoparticle solubility and luminescence efficiency are enhanced. It is possible that Ce³⁺ ions work as catalysts for CdTe nanowire formation and also passivate defect sites. This would result in both luminescence enhancement and nanowire formation.

IV. CONCLUSION

In summary, LaF₃:Ce/CdTe nanocomposites were successfully synthesized using a two-step wet chemistry method. In LaF₃:Ce/CdTe nanocomposites the CdTe quantum dots were converted into nanowires, while in LaF₃/CdTe nanocomposites no such conversion was observed. The CdTe luminescence in LaF₃:Ce/CdTe nanocomposites is about five times stronger than in pure CdTe quantum dots. In LaF₃/CdTe nanocomposites no enhancement was observed. Energy transfer, light reabsorption and defect passivation are possible reasons for the luminescence enhancement. The LaF₃/CdTe nanocomposites with enhanced luminescence may find applications in radiation detection and solid state lighting.

ACKNOWLEDGMENTS

We would like to acknowledge the support from the startup funds from UTA, the NSF, and DHS joint ARI program (2008-DN-077-ARI016-03, CBET-1039068), DOD DTRA08-005, and the U.S. Army Medical Research Acquisition Activity (USAMRAA) under Contracts of W81XWH-10-1-0279 and W81XWH-10-1-0234. Part of the research described was performed at the W.R. Wiley Environmental Molecular Sciences Laboratory, a national scientific user facility sponsored by the Department of Energy’s Office of Biological and Environmental Research and located at the Pacific Northwest National Laboratory (PNNL). PNNL is operated by Battelle for the U.S. Department of Energy under Contract No. DE-AC06-76RL01830.