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

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CdTe quantum dots have intense photoluminescence but exhibit almost no x-ray luminescence. However, intense x-ray luminescence from CdTe quantum dots is observed in LaF₃:Ce/CdTe nanocomposites. This enhancement in the x-ray luminescence of CdTe quantum dots is attributed to the energy transfer from LaF₃:Ce to CdTe quantum dots in the nanocomposites. The combination of LaF₃:Ce nanoparticles and CdTe quantum dots makes LaF₃:Ce/CdTe nanocomposites promising scintillators for radiation detection. © 2012 American Institute of Physics. [doi:10.1063/1.3674313]

For radiation detection, the sensitivity, response time, and energy resolution are important.^{1,2} 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.² Ce^{3+} is a great activator exhibiting a very fast response in radiation detectors of medical imaging systems employed in diagnostic radiology.³⁻⁶ Currently, Ce³⁺ doped scintillators meet most of the requirements and have become popular scintillators for radiation detection and dosimetry.³⁻⁶ 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. For practical applications, this is potentially an issue. For example, when the nanoparticles are embedded into polymers for radiation detection, the sensitivity might be reduced because the UV emission cannot penetrate most polymers. Quantum dots such as CdTe and CdSe can have very high quantum efficiencies as a consequence of quantum size confinement,^{7–9} up to 98% (Ref. 10) and short luminescence lifetimes in the nanosecond range.^{11–13} 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.¹⁴ The combination of high stopping power and sensitivity of LaF₃:Ce nanoparticles with the high emitting rate as well as the emission tenability of CdTe quantum dots may overcome the shortcomings of Ce³⁺ doped scintillators and semiconductor quantum dots; therefore, they can provide improved properties for radiation detection. The possible energy transfer from Ce³⁺ doped scintillation nanoparticles to semiconductor quantum dots is the key for the design of these new materials and the energy transfer rate could be very high because the absorption maximum of the quantum dots can be tuned by size to have a large overlap with the emission peak of LaF₃:Ce nanoparticles. These energy transfer based nanocomposites may be promising for radiation detection. In this communication, we report the observation of x-ray luminescence from CdTe quantum dots in LaF3:Ce/CdTe nanocompo-

CdTe/LaF₃:Ce nanocomposites were prepared by a wetchemistry 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 mole) was added to the solution, and the pH value was adjusted to \sim 11 by the addition of 0.1 M 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 0.5 M sulfuric acid in an inert atmosphere (nitrogen) and was combined with the above solution containing Cd^{2+} ions using the setup as described.¹⁵ After the completion of the reaction a yellow solution of CdTe nanocrystal 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 (DEG) was added to the mixture solution as a surfactant. Ce(NO₃)₃ was used at a concentration of 0.1 M to provide the Ce³⁺ dopant. The chemicals were mixed thoroughly, and then 20.1 mmol of NH₄F water solution with a volume of 5 ml added drop wise to the mixture solution was stirred at room temperature. The reaction solution was heated to 50 °C for different reaction times up to 3.5 h under protection of nitrogen. The product was centrifuged, washed with de-ionized water three times, and dried at 40 °C in a vacuum atmosphere.

The identity, crystalline structure, size, and shape of the nanoparticles were observed by high-resolution transmission electron microscopy (HRTEM). The HRTEM images of the particles were obtained with a JEOL JEM-2100 electron microscope with accelerating voltage of 200 kV. X-ray luminescence was measured in a light-proof x-ray cabinet equipped with optic fiber connection to an outside detector. X-ray irradiation (60 kV and 5 mA) was performed using a Faxitron RX-650 X-ray cabinet (Faxitron X-Ray Corp., IL,

sites and investigate their potential application as a new kind of scintillators for radiation detection.

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FIG. 1. Transmission electron microscope images of LaF₃:Ce/CdTe nanocomposites. The low magnification image (top) shows the shape and size distribution of the nanoparticles in the composites, and high resolution image (bottom) identified the lattice spacing for LaF₃ nanoparticles (0.39 nm lattice spacing) and CdTe quantum dots (0.36 nm lattice spacing).

USA). The luminescence spectra were recorded using a QE65000 spectrometer (Ocean Optics Inc., Dunedin, FL) connected to the x-ray chamber using a 600 μ m core diameter, P600-2-UV-Vis fiber optic (Ocean Optics Inc., Dunedin, FL). The fiber was positioned at a constant angle of 135° with its tip at 5 mm from the surface of the samples.

Figure 1 displays the HRTEM images of LaF₃:Ce/CdTe nanocomposites. Oval shaped nanostructures are observed which have an average dimension of about 18 nm long and 12 nm wide (see Fig. 1(top)). In the nanocomposites, there are two kinds of nanocrystallines that can be identified in the HRTEM images as shown in Fig. 1(bottom). In one kind of nanoparticles, the spacing between adjacent lattice planes is about 0.36 nm which corresponds to the (110) plane of the wurtzite CdTe lattice. The other nanoparticles that can be identified with the interplanar spacing of 0.39 nm which is similar to the interplanar spacing of (0001) planes in the hexagonal LaF₃ structure.¹⁶ The HRTEM observations demonstrate that CdTe and LaF3:Ce nanostructures are in close proximity in the composites. The inter-distance between these two kinds of nanoparticles is less than 3 nm; therefore, there is strong interaction among these nanoparticles.



FIG. 2. (Color online) Energy-dispersive x-ray spectroscopy (EDS) spectrum of LaF₃:Ce/CdTe nanocomposites.

In order to identify the compositions of the nanocomposite, the energy-dispersive x-ray spectroscopy (EDS) spectrum was measured and shown in Fig. 2. Significant signals of La, Te, Cd, and Ce were found from the sample. C and S can also be seen from the spectra coming from the stabilizer (TGA), and Cu that is from the sample holder grid. The results from EDS support the formation of LaF₃:Ce/CdTe nanocomposites.

CdTe quantum dots have intense photoluminescence and upconversion luminescence.¹¹ The decay lifetimes of CdTe quantum dots are very fast—in picosecond to nanosecond ranges.^{11,14} If these quantum dots have strong scintillation luminescence, they could be promising for radiation detection. However, in the setup we have for x-ray luminescence measurement, we could never measure any x-ray luminescence from CdTe solution samples. We could detect x-ray luminescence from CdTe solid samples but the luminescence is very weak. However, in LaF₃:Ce/CdTe nanocomposites, intense x-ray luminescence from CdTe quantum dots is observed as shown in Fig. 3. The x-ray luminescence of CdTe quantum dots in LaF₃:Ce/CdTe nanocomposites is more than 6 times stronger than the x-ray luminescence from CdTe solid samples.

The weak x-ray luminescence from CdTe quantum dots is most likely due to their low stopping power. The x-ray



FIG. 3. (Color online) X-ray luminescence spectra of CdTe solid powder (blue) and LaF₃:Ce/CdTe nanocomposites (red).



FIG. 4. (Color online) Photoluminescence spectra of LaF3:Ce nanoparticles (LaF3:Ce3+-PL), CdTe quantum dots (CdTe-PL), and optical absorption spectrum of CdTe quantum dots (CdTe-ABS).

luminescence enhancement in LaF₃:Ce/CdTe nanocomposites is attributed to the energy transfer from LaF3:Ce to CdTe quantum dots. This is similar to the photoluminescence enhancement already observed in LaF3:Ce/CdTe nanocomposites except that in the previous report the CdTe quantum dots were partially aggregated in nanowires.¹⁷ In the nanocomposites reported here most CdTe quantum dots remain spherical dots based on HRTEM observations. Therefore, the energy transfer from LaF₃:Ce to CdTe quantum dots is the only possible mechanism for the x-ray luminescence enhancement. The energy transfer from Ce³⁺ doped scintillation nanoparticles to semiconductor quantum dots can be very high because the emission of $\text{Ce}^{\tilde{3}+}$ ions and the absorption of quantum dots largely overlap, and this overlap can be simply adjusted by controlling the size of the quantum dots.¹⁸ The emission spectrum of LaF₃:Ce³⁺ nanoparticles (5 nm in size), the absorption, and emission of red CdTe quantum dots (8 nm in size) are shown in Fig. 4. As seen, the emission peak of $LaF_3:Ce^{3+}$ is largely overlapped with the absorption band of CdTe quantum dots. Therefore, the energy transfer from LaF3:Ce to the red CdTe is very efficient which is responsible for the x-ray luminescence enhancement.

In summary, $LaF_3:Ce/CdTe$ nanocomposites were successfully synthesized using a two-step wet chemistry method. The x-ray luminescence of CdTe quantum dots in LaF₃:Ce/CdTe nanocomposites is more than six times stronger than in pure CdTe quantum dot solid samples. No x-ray luminescence is detected at all from CdTe quantum dot solutions. The enhancement of x-ray luminescence is attributed to the energy transfer from LaF₃:Ce to CdTe quantum dots. These energy transfer based nanocomposites are potentially promising for radiation detection and can find applications as radiation probes for public safety and radiation treatment.

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- ¹G. F. Knoll, *Radiation Detection and Measurement*, 3rd ed. (John Wiley & Sons, Inc., New York, 2000).
- ²S. E. Derenzo, M. J. Weber, E. Bourret-Courchesne, and M. K. Klintenberg, Nucl. Instrum. Methods Phys. Res. A 505, 111 (2003).
- ³M. D. Birowosuto, P. Dorenbos, C. W. E. v. Eijk, K. W. Kramer, and H. U. Gudel, IEEE Trans. Nucl. Sci. **52**, 1114 (2005).
- ⁴N. M. Khaidukova, S. K. Lamb, D. Lob, and V. N. Makhov, Opt. Commun. 205, 415 (2005).
- ⁵E. Radzhabov, Radiat. Eff. Defects Solids **158**, 203 (2003).
- ⁶M. S. Zhang, J. Yu, W. C. Chen, and Z. Yin, Prog. Crystal Growth Charact. **40**, 33 (2000).
- ⁷B. O. Dabbousi, J. R. Viejo, F. V. Mikulec, J. R. Heine, H. Mattoussi, R. Ober, K. F. Jensen, and M. G. Bawendi, J. Phys. Chem. B **101**, 9463 (1997).
- ⁸W. Chen, J. Z. Zhang, and A. G. Joly, J Nanosci. Nanotechnol. 4, 919 (2004).
- ⁹W. Chen, J. Nanosci. Nanotechnol. 8, 1019 (2008).
- ¹⁰Y. He, L.-M. Sai, H.-T. Lu, M. Hu, W.-Y. Lai, Q.-L. Fan, L. H. Wang, and W. Huang, Chem. Mater. **19**, 359 (2007).
- ¹¹A. G. Joly, W. Chen, D. E. McCready, J.-O. Malm, and J.-O. Bovin, Phys. Rev. B 71, 165304 (2005).
- ¹²W. Chen, A. G. Joly, and D. E. McCready, J. Chem. Phys. **122**, 224708 (2005).
- ¹³J. Ouyang, J. A. Ripmeester, X. Wu, D. Kingston, K. Yu, A. G. Joly, and W. Chen, J. Phys. Chem. C 111, 16261 (2007).
- ¹⁴W. Chen, J. Zhang, S. L. Westcott, A. G. Joly, J.-O. Malm, and J.-O. Bovin, J. Appl. Phys. 99, 034302 (2006).
- ¹⁵N. Gaponik, D. V. Talapin, A. L. Rogach, K. Hoppe, E. V. Shevchenko, A. Kornowski, A. Eychmuller, and H. Weller, J. Phys. Chem. B 106, 7177 (2002).
- ¹⁶H. Hu, Z. Chen, T. Cao, Q. Zhang, Mengxiao Yu, F. Li, T. Yi, and C. Huang, Nanotechnology **19**, 375702 (2008).
- ¹⁷M. Yao, X. Zhang, L. Ma, W. Chen, A. G. July, J. Huang, and Q. Wang, J. Appl. Phys. **108**, 103104 (2010).
- ¹⁸Y. Liu, W. Chen, A. G. Joly, Y. Wang, C. Pope, Y. Zhang, J. O. Bovin, and P. Sherwood, J. Phys. Chem. B **110**, 16992 (2006).