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Spectra Responsibility of Quantum Dot Doped Organic Liquid Scintillation Dosimeter for Radiation Therapy

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The aim is to investigate the spectra responsibilities of QD (Quantum Dot) for the innovation of new dosimetry application for therapeutic Megavoltage X-ray range. The unique electrical and optical properties of QD are expected to make it a good sensing material for dosimeter. This study shows the spectra responsibility of toluene based ZnCd QD and PPO (2.5-diphenyloxazol) mixed liquid scintillator. The QDs of 4 sizes corresponding to an emission wavelength (ZnCdSe/ZnS:440±5 nm, ZnCdSeS:470, 500, 570±5 nm) were utilized. A liquid scintillator for control sample was made of toluene, PPO. The Composition of QD loaded scintillators are about 99 wt% Toluene as solvent, 1 wt% of PPO as primary scintillator and 0.05, 0.1, 0.2 and 0.4 wt% of QDs as solute. For the spectra responsibility of QD scintillation, they were irradiated for 30 second with 6 MV beam from a LINAC (Infinity™, Elekta). With the guidance of 1.0 mm core diameter optical fiber, scintillation spectrums were measured by a compact CCD spectrometer which could measure 200~1,000 nm wavelength range (CCS200, Thorlabs). We measured the spectra responsibilities of QD loaded organic liquid scintillators in two scintillation mechanisms. First was the direct transfer and second was using wave shifter. The emission peaks from the direct transfer were measured to be much smaller luminescent intensity than based on the wavelength shift from the PPO to QDs. The emission peak was shifted from PPO emission wavelength 380 nm to each emission wavelength of loaded QD. In both mechanisms, 500 nm QD loaded samples were observed to radiate in the highest luminescence intensity. We observed the spectra responsibility of QD doped toluene based liquid scintillator in order to innovate QD dosimetry applicator. The liquid scintillator loading 0.2 wt% of 500 nm emission wavelength QD has most superior responsibility at 6 MV photon beam. In this study we observed the spectra responsibilities for therapeutic X-ray range. It would be the first step of innovating new radiation dosimetric methods for radiation treatment.

Keywords: Quantum Dot, Organic Liquid Scintillator

Introduction

Radiation is extensively used in various industrial, research and medical applications. Accurate radiation dose measurement is essential in the field of radiation therapy to increase the therapeutic effect of cancer patients, minimize the incidence of side effects and identify radiation exposure of medical personnel. From these reasons, various kinds of radiation dose measurement applications, a scintillation detector, an ionization chamber, a semiconductor detector and a radiochromic film, are commonly used in the field of radiation therapy according to the radiation measurement mechanism. However, these dosimetry applications have difficulties in clinical usage, consume an installing time, pre- and post-processing, using high voltage electricity and couldn't measure at time of radiation irradiate. So, there is a necessary to overcome the difficulties of commonly used dosimetry applications. These efforts focus on altering the sensing material properties and improving manufacturing technologies in order to enhance application performance.

Quantum Dots (QD), small size (2~10 nm) semiconducting crystals, have tremendous potential for developing new radiation dosimetry application in recent years because of their extraordinary optical characteristics.[1] Due to their small size, quantum confinement effects dominate, and the optical and electrical properties of the QDs are directly proportional to their size. As a result, these QDs exhibit ultra-narrow optical transitions, with high optical absorption levels and high quantum fluorescence efficiencies. Using the size effect, the optical absorption and emission spectra of the QDs can further be conveniently tuned.[2,3]

The organic scintillation material has great advantages of interaction properties that are similar to those of water and human tissues, especially in the Compton scattering dominated energy range of the photon beams which used in radiation therapy. These properties make QD doped organic scintillator as excellent candidate for the radiation dosimetry application.[4,5]

In this work, we focus on the designing and fabricating the prototype QD dosimetry application with organic solvent, as well as characterizing the applications in terms of scintillation intensity according to doped QDs composition ratio and other factors that influence the application's performance under therapeutic X-ray exposure.

Materials and Methods

1. Design and fabrication of Quantum Dot doped liquid scintillator

QD samples were obtained from PlasmaChem (Berlin, Germany). The 4 sizes of ZnCdSe based QDs corresponding to an emission wavelength (ZnCdSe@ZnS:440±5 nm, ZnCdSeS:470, 500, 570±5 nm) were utilized. 8 kinds of QD doped scintillator samples were designed according to the mixing ratio of QD, solvent and wavelength shifter. The Composition of each QD loaded scintillators are about 99 wt% Toluene as solvent, 1 wt% of PPO (2, 5-diphenyloxazole) as primary scintillator and 0.05, 0.1, 0.2 and 0.4 wt% of QDs as solute, which shown in Table 1. The fabricated samples were placed in 1.1 cm diameter and 4 cm height glass vials and irradiated. The optimal efficiency for therapeutic X-rays were observed by analyzing the spectral responsibility of each samples. A toluene was used as an organic solvent due to the electron density is similar to the tissue, low polarity and high signal ratio. Efficient (high rate) energy transfer from the solvent molecules to the solutes (PPO and/or QDs) is crucial for a high light yield because the direct emission of light from toluene undergoes strong self-absorption and subsequent light loss, the solutes can emit light at higher wavelengths where the scintillator is more transparent.[5,6] A wavelength shifter is often used to match the wavelength to the response characteristics of the scintillation detector like PMT (Photo Multiplier Tube). A PPO has been proposed as a wavelength shifter to minimize absorption losses and increase the emission spectrum signals in this study.[7]

Table 1. Composition of 8 type of QD doped liquid scintillator samples.

Samples	QD doped toluene	QD doped toluene with PPO
Toluene	>99 wt%	99 wt%
QD (440 to 540 nm wavelength)	0.05, 0.1, 0.2, 0.4 wt%	0.05, 0.1, 0.2, 0.4 w%
PPO	-	1 wt%

2. Spectra responsibility of radiation measurement

To characterize the spectra responsibility of QD scintillator at therapeutic X-ray, they were irradiated for 30 second with 6 MV beam from a LINAC (Infinity™, Elekta), shown in Fig. 1. The scintillation spectrums were measured by a compact CCD spectrometer which could measure 200~1,000 nm wavelength ranges (CCS200™, Thorlabs). An applicator using 3D printing technique was used to concentrate optical signals. Standard SMA 905, 1.0 mm

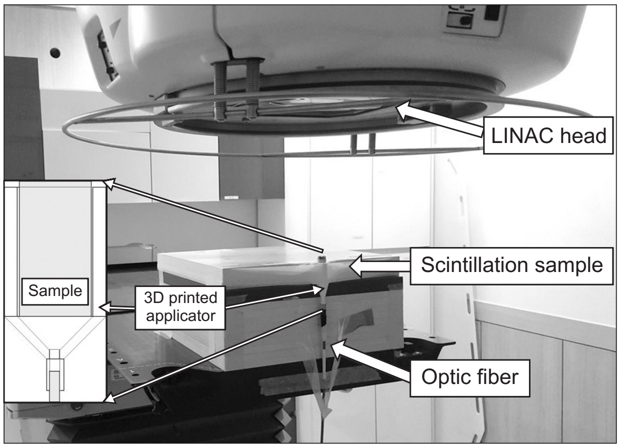

Fig. 1. Direct measurement of x-ray induced scintillation spectrum set-up from a LINAC (Infinity™, Elekta) at National Medical Center. The applicator and optic fiber connection design is at the left bottom side. A 3D printed applicator was used to concentrate the scintillation signals and SMA 905 connector was used to connect optic fiber with applicator.

core diameter optical fiber was connected to the 3D printed applicator. The pure spectra responsibility of QD was obtained by excluding the spectra response of toluene and toluene with PPO signal from the QD doped scintillator signal. Stability of the emission intensity over time was also measured on the same QD scintillator samples in June 2016 and June 2017. The acquisition data was analyzed using homemade code of CERN library.

Results

We measured the spectra responsibilities of QD loaded liquid scintillators in two scintillation mechanisms. Fig. 2 shows the direct transfer of luminescence energy from toluene to QDs. The emission peaks from the direct transfer were measured to be much smaller than those of the second, which shows in Fig. 3, in based on the wavelength shift from the PPO to QDs. The emission peak

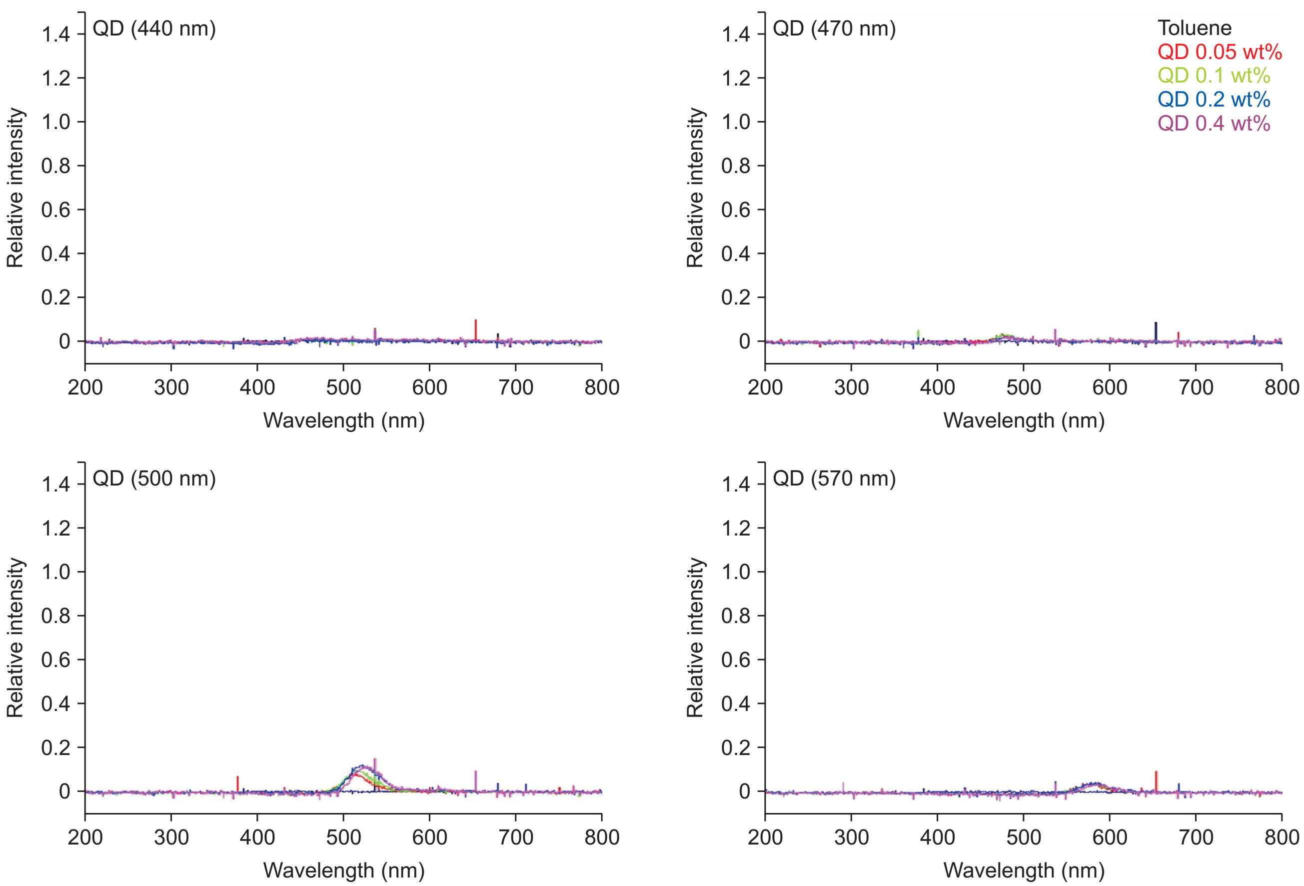

Fig. 2. Scintillation spectrum comparison of QD doped organic liquid scintillator as loaded QD size and composition ratio. At 500 nm emission wavelength size of QD shows most high luminescent intensity.

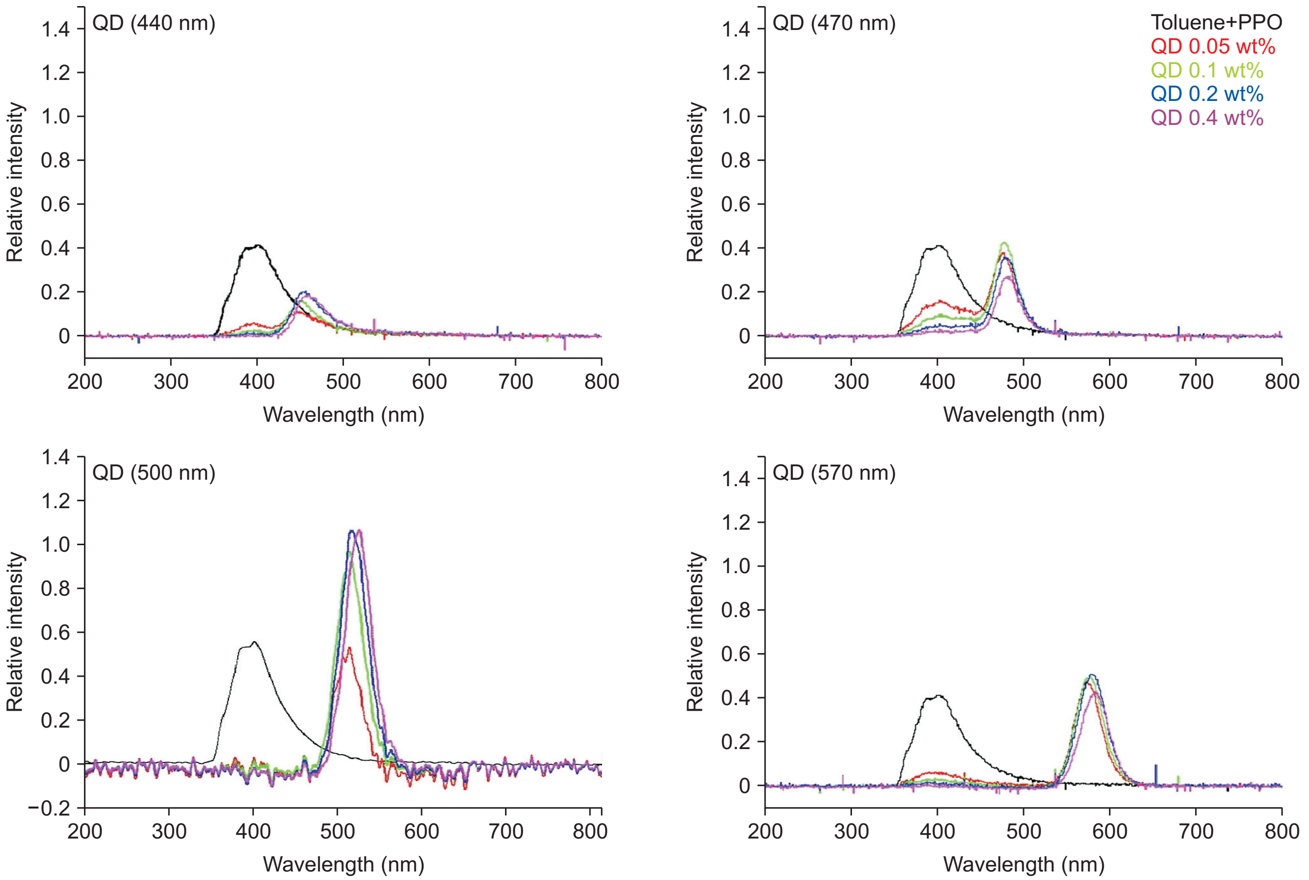

Fig. 3. Scintillation spectrum comparison of QD doped organic liquid scintillator with wavelength shifter as loaded QD size and composition ratio. At 500 nm emission wavelength size of QD shows most high luminescent intensity.

was shifted from PPO emission wavelength 380 nm to each emission wavelength of loaded QD. In both mechanisms, 500 nm QD loaded samples were observed to radiate in the highest luminescence intensity. And we confirmed that the luminescence intensity was reduced as the size of QD increase than 500 nm emission wavelength and the luminescent intensity was saturated over 500 nm emission wavelength size of QD. 0.2 wt% of QD doped scintillator was generates the most signal among the fabricated samples in our experiments set-up. The reproducibility over time for QD scintillator was shown in Fig. 4. An emission intensity of QD scintillators were degraded with passage of time. The scintillation process in the higher wt% QD loading was observed to be suppressed by color quenching effect.

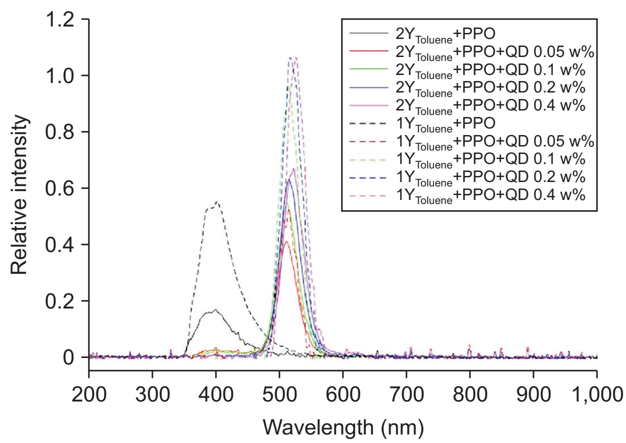

Fig. 4. The aging effect of fabricated QD doped liquid scintillator as sample composition changes. Dashed line shows a result of June of 2016 and solid line shows a result of June of 2017. The scintillation signals were degraded with passage of time.

Discussion

In this study, we fabricated an organic liquid scintillator using QD with semiconductor characteristics. Due to the semiconductor characteristics of the QD, pure and narrow spectrum range signals could be measured. Therefore, the fabricated scintillator could be used with low noise and precise application for radiation dosimetry. In addition, an optimized detector is needed to measure the scintillation signal from commonly used scintillators. However, the scintillator using QD could be tune the bandgap by changing the size of materials, this makes easy to fabricate an optimized scintillator for user's detector.

A concern when constructing liquid scintillator detectors is the degradation of the scintillator with age. For quantum dots, it is known that the organic molecules that allow the dots to be suspended in organic solvents or water can also lead to the clumping of dots and the degradation of their performance.[8] We measured same QD scintillator samples in June of 2016 and June of 2017. And we found the emission peaks of scintillator samples were same, but the signal intensities were degraded about 30% at 1 year after. We think that this issue was caused by the polarity of toluene, and we are going to carry out additional experiments by changing the polarity of the solvent.

Measuring the absorbed dose into the human body is the most important thing in the field of radiation therapy. In commonly used radiation energy range for treatment, the Compton scattering is dominant interaction with matter. The intensity of Compton scattered photons is directly proportional to the electron density of a substance. Thus, it is possible to measure the absorbed dose into the human body by measuring the absorbed dose into the organic tissue equivalent substance.[9,10]

In addition, the liquid organic scintillator has the advantage that it could be produced regardless of its shape. It is possible to measure the absorbed dose into the tumor or critical organs like volume under the same patient treatment condition. In the case of HDR brachytherapy using radioisotopes, it is difficult to measure the dose to be irradiated inside the patient. When the isotope is inserted into a patient, a scintillation applicator of the appropriate size connected to the flexible optic fiber and inserted into the patient's body to measure the radiation dose, thereby enabling a real time in-vivo dosimetry at outside of the treatment room.[10] Organic applications which could provide a various form are expected to great role in the field of radiotherapy for patient specific dosimetry.

The QD-doped scintillation dosimeter developed in this study could measure an absorbed dose in real time, does not require pre- and post-procedure to use, and does not require calibration constants such as temperature or pressure. These advantage of convenience of usage will improve the quality of life of the radiation worker by reducing the workload over the existing methods.

Conclusion

In this study, we fabricate the QD doped organic liquid scintillator for radiation dosimetry application and observed their spectra responsibility in order to innovate new convenient and accurate application for therapeutic X-rays. This new dosimeter has the advantages of real time dose measurement, without pre- and post-processing, easy to optimize the emission wavelength to high efficient absorption range of user's detector. The dose linearity, energy dependency, and aging issues will be proceeded in our further study.

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Conflicts of Interest

The authors have nothing to disclose.

Availability of Data and Materials

All relevant data are within the paper and its Supporting Information files.

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