



Scintillation properties of quantum-dot doped styrene based plastic scintillators

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ABSTRACT

We fabricated quantum-dot doped plastic scintillators in order to control the emission wavelength. We studied the characterization of the quantum-dots (CdSe/ZnS) and PPO (2, 5-diphenyloxazole) doped styrene based plastic scintillators. PPO is usually used as a dopant to enhance the scintillation properties of organic scintillators with a maximum emission wavelength of 380 nm. In order to study the scintillation properties of the quantum-dots doped plastic scintillators, the samples were irradiated with X-ray, photon, and 45 MeV proton beams. We observed that only PPO doped plastic scintillators shows a luminescence peak around 380 nm. However, both the quantum-dots and PPO doped plastic scintillators shows luminescence peaks around 380 nm and 520 nm. Addition of quantum-dots had shifted the luminescence spectrum from 380 nm (PPO) toward the region of 520 nm (Quantum-dots). Emissions with wavelength controllable plastic scintillators can be matched to various kinds of photosensors such as photomultiplier tubes, photo-diodes, avalanche photo-diodes, and CCDs, etc. Also quantum-dots doped plastic scintillator, which is irradiated 45 MeV proton beams, shows that the light yield of quantum-dots doped plastic scintillator is increases as quantum-dots doping concentration increases at 520 nm. And also the plastic scintillators were irradiated with Cs-137 γ -ray for measuring fluorescence decay time.

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1. Introduction

Due to the low cost, easy fabrication and fast response time, plastic scintillator materials have been widely used as detectors in nuclear, particle physics, and homeland security applications. Plastic scintillators have a fast decay time of 2–3 ns and high light output [1–3]. Most of the plastic scintillators are composed with solvents and primary solutes like p-terphenyl (1, 4-Diphenylbenzene), PPO (2, 5-diphenyloxazole) and butyl PBD (2–4(biphenyl)-5-(4-tert-butylphenyl)-1, 3, 4-oxadiazole) [4,5]. In order to match the emission wavelength of plastic scintillators to the quantum efficiency of a photomultiplier tubes (PMTs), secondary solutes like POPOP (5-phenyl-2-[4-(5-phenyl-1, 3-oxazol-2-yl) phenyl]-1, 3-oxazole) are used as wavelength shifters. Thus, most of the secondary solutes have an emission wavelength around 400 nm [1,4,6].

Many photosensors like PMTs, photo-diodes, avalanche photo-diodes and CCDs detect scintillation light. Each sensor has different properties such as quantum efficiency, detection mechanism, etc. Most of the PMTs have maximum quantum efficiency around 400 nm but photo-diodes and CCDs have theirs around 600 nm. Due to the different quantum efficiencies of photosensors, it is

important to match the emission wavelength of the scintillator with the photosensor.

Colloidal semiconductor nano-crystals, quantum-dots (QDs), have been used as light emitting diodes (LEDs) and sensors for bio-imaging. One of the properties of QDs is their size effect. It is known that an increase in the size of the QDs causes a red shift. Thus, as the size of the QDs increase, the color of the light emission changes from blue to red [7,8].

Plastic scintillators are easy to mix with other dopant materials. Thus it is possible to fabricate the QDs doped plastic scintillators. By using different size QDs, the emission wavelength of the plastic scintillator could be controlled to match with various photosensors.

At this paper, we present the scintillation properties of QDs doped styrene based plastic scintillators. In order to study the luminescence property, the samples were irradiated with Cs-137 γ -ray, X-ray, photon and 45 MeV proton beams.

2. Fabrication of quantum-dot doped plastic scintillators

2.1. Materials

We fabricated styrene based scintillators with PPO, POPOP and QDs as the dopants. The monomer styrene was obtained from the SAMCHUN Chemical. Primary solute PPO and secondary solute

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Table 1
Concentrations of styrene based plastic scintillators.

Num.	Styrene (wt%)	PPO (wt%)	POPOP (wt%)	QDs (wt%)
1	~99	0.4	0.01	–
2		0.4	–	–
3		0.4	–	0.4
4		0.4	–	0.1
5		0.4	–	0.05
6		–	–	0.1
7		–	–	0.05

POPOP were purchased from the Lancaster Company. Home-made QDs were fabricated using the trioctylphosphine (TOP) and the trioctylphosphine oxide (TOPO) synthesis methods [9]. The QDs consisted of a core (CdSe) and shell (ZnS).

2.2. Preparation of styrene based plastic scintillators

Plastic scintillators were grown by using the thermal polymerization method [10,11]. Initial temperature was in the range of 100 °C during the first 24 h, followed by 120 °C during the next 72 h for the polymerization and then 80 °C during the last 24 h for the annealing. Whole growth process was carried out in glass bottles about 2.5 cm in diameter and 5 cm in length. Plastic scintillators were fabricated with different concentrations of QDs. Both POPOP and QDs were used as a wavelength shifter. Detailed dopant concentrations are given in Table 1. Fig. 1 shows the fabricated samples of plastic scintillators which are cut and polished to dimension of 2.5 cm × 2.5 cm × 0.6 cm. Plastic scintillator #1 consisted of styrene, PPO (0.4 wt%) and POPOP (0.01 wt%). Plastic scintillator #2 consisted of styrene and PPO (0.4 wt%). Plastic scintillator #3, #4 and #5 consisted of styrene, PPO and different concentrations of QDs with 0.4 wt%, 0.1 wt% and 0.05 wt%, respectively. Plastic scintillator #6 and #7 consisted of styrene and 0.1 wt% and 0.05 wt%, respectively.

3. Measurement system

In order to study the scintillation properties, all plastic scintillators were irradiated with X-ray, photon and 45 MeV proton beams. All luminescence measurements were made at room temperature. X-ray induced emission spectra were measured using a tungsten target X-ray generator, QE65000 spectrometer (Ocean Optics Co.) and optical fiber. The X-rays with an intensity of 100 kV and a current of 1.5 mA were irradiated to all plastic scintillators [12].

Photo-induced excitation and emission spectra were measured using a xenon lamp (HORIBA Jobin Yvon Inc., Fluorlog-3 Model FL3-21). The excitation and emission signal was detected using a PMT (Jobin Yvon Inc., R928P). The xenon source was placed at a right angle to the detector. The plastic scintillators were located at 45° from the excitation xenon source.

The proton-induced emission spectra of the plastic scintillators were measured at the Korea Institute of Radiological and Medical Sciences (KIRAMS). When the proton beam passed through the beam pipe, the proton beam energy changed from 45 MeV to 38 MeV [13]. The proton-induced scintillation light passed through an optical fiber and was detected using a USB4000 spectrometer (Ocean Optics Co.).

In order to fluorescence decay time, we used 2-in. Bi-alkali PMTs and 400 MHz flash analog to digit converter (FADC). The plastic scintillator was wrapped in 0.1 mm thick Teflon tape and attached to PMTs. All plastic scintillators were irradiated Cs-137 (661 keV) γ -ray source to measure fluorescence decay time.

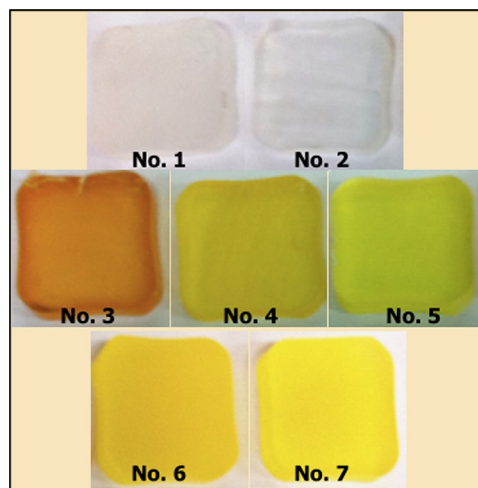


Fig. 1. Photograph of the styrene based plastic scintillators.

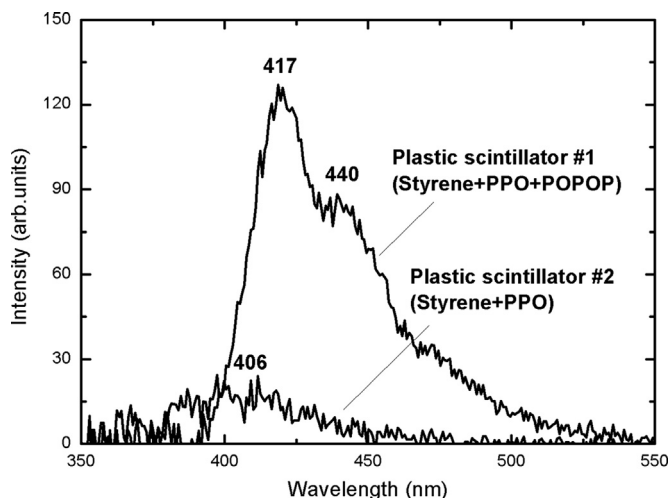


Fig. 2. The X-ray induced luminescence of plastic scintillators #1 (Styrene+PPO+POPOP) and #2 (Styrene+PPO).

The signals generated in the PMTs due to scintillation in the plastic scintillator were amplified. The signal from the PMTs was fed to 400 MHz FADC. The data is analyzed with a C++ based data analysis program, ROOT package [14].

4. Results and discussion

We had two ideas about the luminescence mechanism of the QDs doped plastic scintillators. One idea was wavelength shift from the PPO to QDs. Thus, we fabricated plastic scintillators #3, #4 and #5. Another idea was the direct transfer of luminescence energy from the styrene to the QDs. Therefore we fabricated plastic scintillators #6 and #7. Among the QDs doped plastic scintillators, plastic scintillators #3, #6 and #7 did not show any significant X-ray emission spectrum. Thus, in this paper, we present only the results on the QDs doped plastic scintillators #4 and #5.

4.1. X-ray induced luminescence

Figs. 2 and 3 shows the X-ray induced emission spectra of the fabricated plastic scintillators. Fig. 2 shows the emission spectra of plastic scintillators #1 and #2. The emission peaks of plastic scintillator #1 are located at 417 nm and 440 nm, whereas

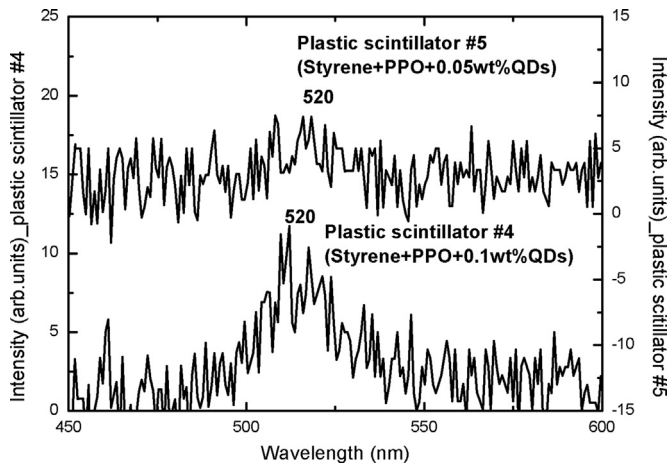


Fig. 3. The X-ray induced luminescence of the QD doped plastic scintillators. Upper trace: 0.05 wt% QD doped plastic scintillator. Lower trace: 0.1 wt% QD doped plastic scintillator.

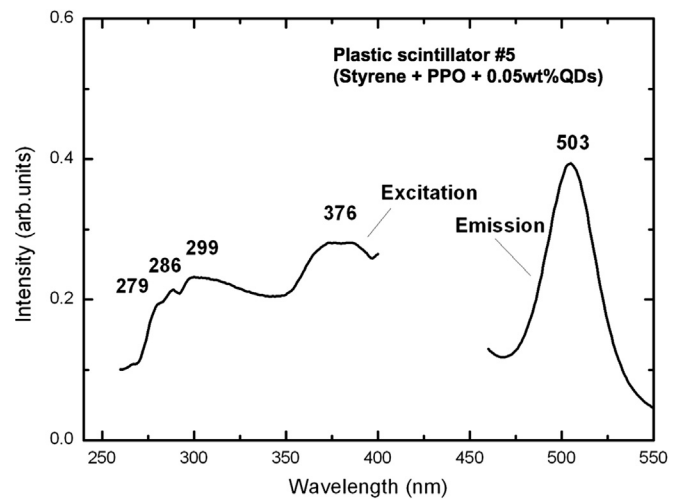


Fig. 5. Photo-induced excitation spectrum (under 503 nm) and emission spectrum (under 380 nm) of plastic scintillator #5 (Styrene+ PPO + 0.05 wt% QDs).

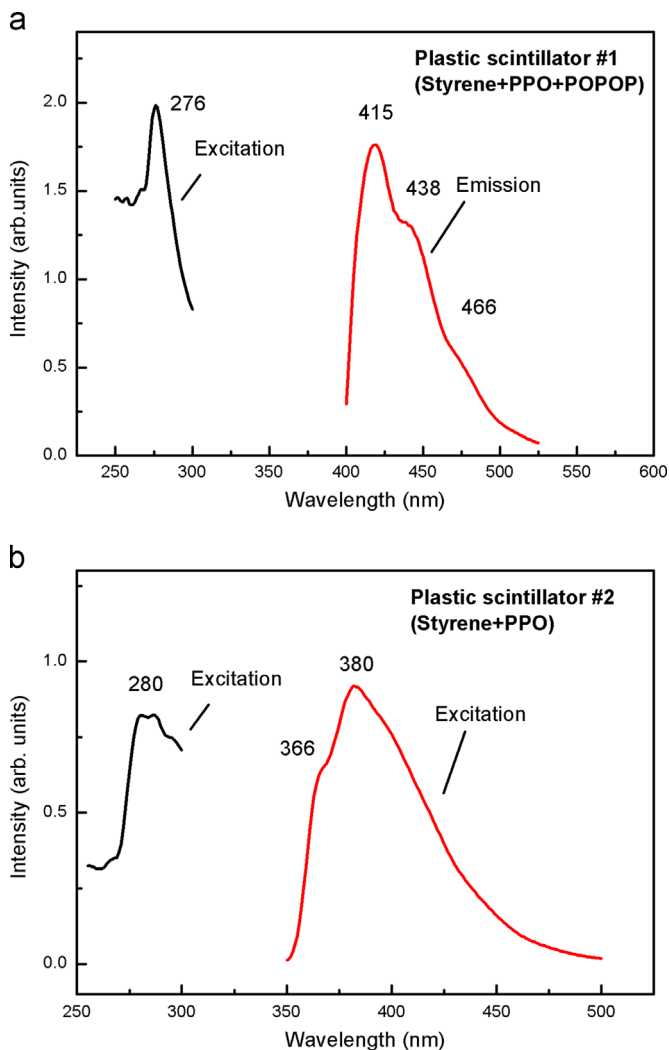


Fig. 4. Photo-induced excitation and emission spectrum of (a) plastic scintillator #1 (Styrene+ PPO+POPOP) and (b) plastic scintillator #2 (Styrene+ PPO).

scintillator #2 is at 406 nm. Fig. 3 shows the X-ray induced emission spectra of the QDs doped plastic scintillators #4 and #5. Both samples have shown emission peaks at 520 nm. Comparing the luminescence intensities of QDs doped plastic scintillators #4 and #5 in Fig. 4, it was observed that luminescence intensity of

0.1 wt% showed higher than 0.05 wt%. Moreover, no luminescence was observed for 0.4 wt% QDs sample (not shown), which might be due to the concentration quenching effect of the QDs in the plastic scintillator. Generally, the primary scintillator PPO emits luminescence at 380 nm and the secondary scintillator POPOP emits at 410 nm [15]. Thus, plastic scintillator #1 had emission peaks at 417 nm and 440 nm and #2 at 406 nm. However, since the QDs (CdSe/ZnS) had an emission peak at 520 nm, the QDs doped plastic scintillator had emission peaks at 520 nm.

4.2. Photo-induced luminescence

In order to study in greater detail the luminescence properties of the plastic scintillators, we measured the photo-induced excitation and emission spectra. Fig. 4 (a) shows the excitation and emission spectra of plastic scintillator #1. Under the excitation peak 280 nm, plastic scintillator #1 had emission peaks at 415 nm, 438 nm and 466 nm. The excitation spectrum of plastic scintillator #1 was measured under the emission peak at 419 nm and found to be 280 nm shown in Fig. 4 (a) [16]. Fig. 4 (b) shows the excitation and emission spectra of plastic scintillator #2. Plastic scintillator #2 had emission peaks at 366 nm and 380 nm. The peak of excitation was 280 nm [1]. As shown in Fig. 5, QDs doped plastic scintillator #5 had a luminescence peak around 503 nm under an excitation peak at 380 nm. The excitation peaks were 280 nm, 288 nm, 299 nm and 380 nm, respectively, under an emission peak at 503 nm. Fig. 6 shows the emission spectrum of the QDs under an excitation peak at 365 nm. The emission peak of the QDs was at 520 nm. QDs have the characteristic that they have a broad excitation peak and the maximum luminescence intensity of the QDs is around the excitation wavelength of 365 nm [17]. The three results are based on three Stokes shifts. The wavelength change between excitation and emission of plastic scintillator #1 was 135 nm, plastic scintillator #2 was 100 nm, and plastic scintillator #5 was 127 nm. Based on the results of the photo-induced luminescence, the transfer relationship between PPO and QDs was studied. As shown in Fig. 4 (b) and Fig. 6, the emission wavelength of the PPO was similar with the excitation wavelength of the QDs. Thus, QDs were able to be excited by the PPO emission energy [18]. In other words, energy transfer took place from the PPO to the QDs.

4.3. Proton-induced luminescence

Plastic scintillators were irradiated with 45 MeV proton beams of 10 nA for 10 s. Fig. 7 shows the proton induced spectrum of

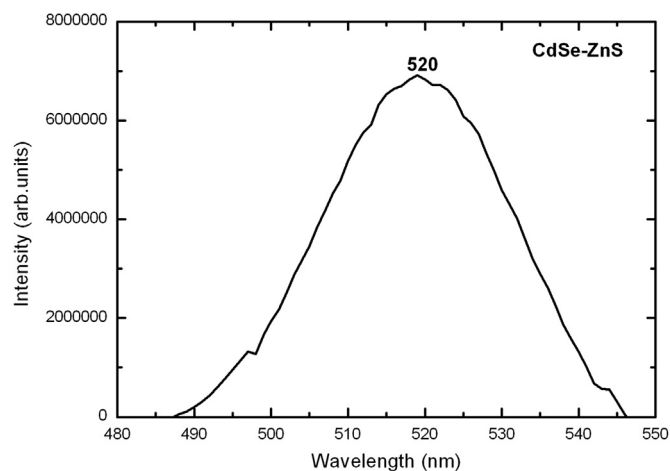


Fig. 6. Emission spectrum of QDs (CdSe-ZnS) under an excitation peak at 365 nm.

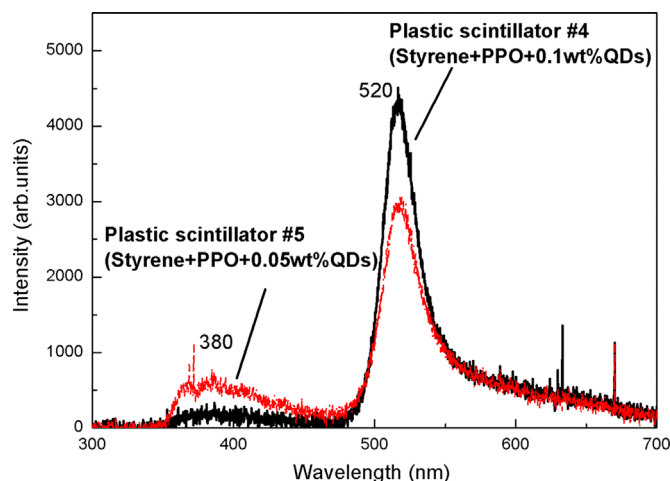


Fig. 7. Proton induced emission spectra of QD doped plastic scintillator #4 (solid line) and #5 (dash line).

plastic scintillators #4 and #5. Both scintillators had the same emission peaks at 380 nm and 520 nm. However, the luminescence intensities of each peak were different. The light yield of plastic scintillator #5 was 3.5 times stronger than that of plastic scintillator #4 at 380 nm. However, the luminescence intensity of plastic scintillator #4 was 1.3 times stronger than that of plastic scintillator #5 at 540 nm. The total light yield of both samples was similar. Since the doping concentration of the QDs was different, the light yield of both samples was different at each peak. As shown in Fig. 7, we observed that the increase of the 520 nm peak with a higher concentration of QDs was due to the higher energy transfer from the PPO to the QDs. Maximum quantum efficiency of photo-sensors is different. Thus, to match the emission wavelength with the quantum efficiency of photo-sensors, we need to use special scintillators. Moreover, most scintillators need to be doped with different materials for changing emission wavelength in order to match with photo-sensors. However, QDs have size dependent emission wavelength. Thus just using same dopant material, which is different in size, is able to change emission wavelength. By tuning the emission wavelength of QDs, plastic scintillator can be made to match well with photo-sensor.

4.4. Fluorescence decay time

The fluorescence decay time spectrum of the plastic scintillator was recorded at room temperature under Cs-137 γ -ray excitation.

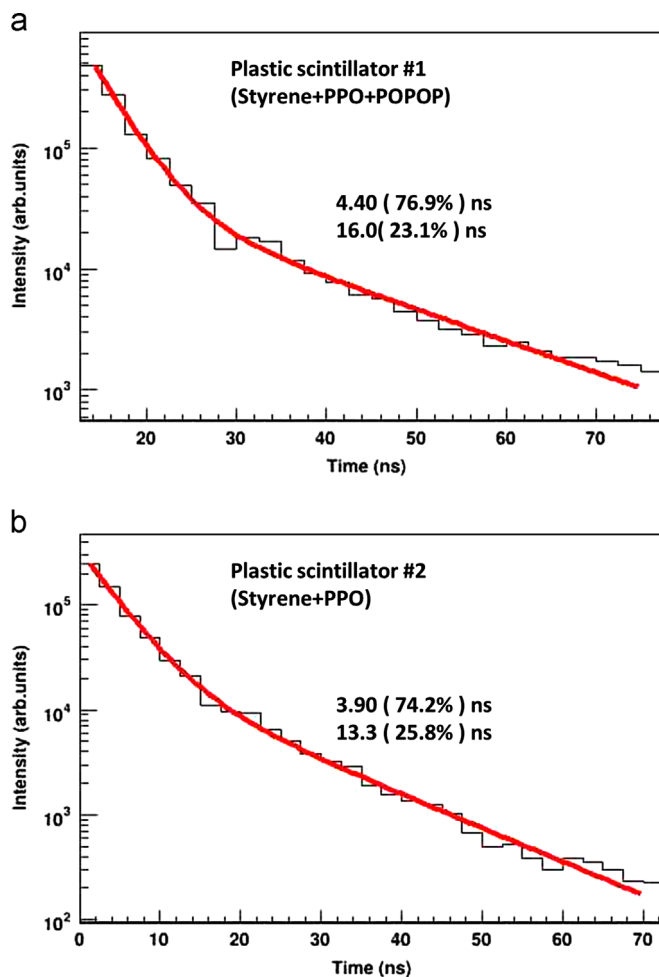


Fig. 8. Fluorescence decay time spectrum in (a) plastic scintillator #1 (Styrene+PPO+POPOP) and (b) plastic scintillator #2 (Styrene+PPO).

We directly registered the pulse shape of the PMT output to the 400 MHz FADC and decay time spectrum of the QDs doped plastic scintillators. As shown in Fig. 8 (a), the decay times of the plastic scintillator #1 were 4.40 ns (fast component) and 16.0 ns (slow component). The Fig. 8 (b) showed that the fluorescence decay time spectrum in the plastic scintillator #2. The fast decay time was 3.90 ns and slow decay time was 13.3 ns. The fluorescence decay time spectrum of plastic scintillator #5 was shown in Fig. 9. The fast decay time was 2.40 ns and slow decay time was 11.4 ns.

4.5. Conclusion

We have fabricated QDs doped styrene based plastic scintillators. The QDs consisted of a core (CdSe) and shell (ZnS) and had emission peaks at 540 nm. In order to study the luminescence properties, the samples were irradiated with X-ray, photon, and proton beams. From the results of the X-ray induced luminescence of the QDs doped plastic scintillators, we found that only QDs doped plastic scintillators (Styrene+PPO+0.1 wt% and 0.05 wt% QDs) had a luminescence spectrum. Between two samples, the sample #4 (Styrene+0.4 wt% PPO+0.1 wt% QDs) was optimized for detecting radiation. The emission peak for both samples was 520 nm. From the results of the photo-induced luminescence of plastic scintillators, there are three different Stokes shifts. At case of standard plastic scintillator (Styrene+PPO+POPOP), large separation between excitation wavelength and emission wavelength showed about 135 nm. Wavelength change of QDs doped plastic scintillator (Styrene+PPO+0.05 wt% QDs) is 127 nm.

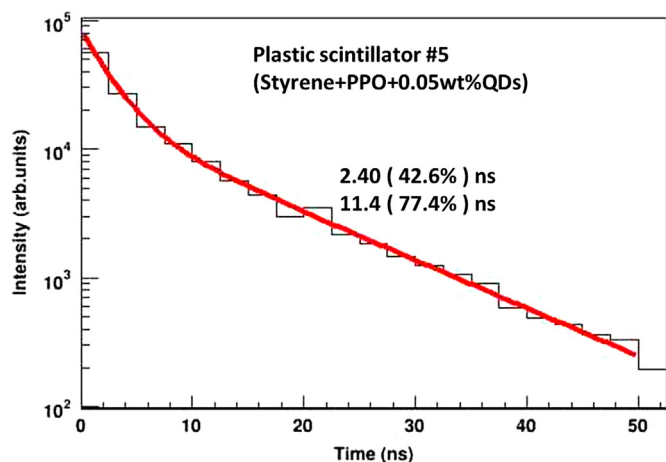


Fig. 9. Fluorescence decay time spectrum in plastic scintillator #5 (Styrene+PPO+0.05 wt% QDs).

When QDs doped plastic scintillators were irradiated with 45 MeV proton beams, we observed luminescence peaks at both 320 nm and 520 nm. We observed that the luminescence energy transferred from the PPO to the QDs. The QDs were able to use wavelength shifters such as POPOP. Thus, QD doped styrene based plastic scintillators can be matched with many photosensors such as PMTs, photo-diodes, avalanche photo-diodes, and CCDs. We also measured fluorescence decay time using Cs-137 γ -ray. Decay time of standard plastic scintillator (styrene+PPO+POPOP) is 4.40 ns (fast) and 16.0 ns (slow), and QDs doped plastic scintillator (styrene+PPO+0.05 wt% QDs) is 2.40 ns (fast) and 11.4 ns (slow). Because QDs doped plastic scintillators have few ns decay time, it can be used for radiation detection, nuclear and high energy physics application.

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