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Effect of gamma irradiation on optical properties of CdSe/ZnS quantum dots embedded in PDMS

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Abstract: The optical properties of CdSe/ZnS quantum dots (QDs) embedded in polydimethylsiloxane (PDMS) flexible materials after irradiated with γ-rays were studied. As an embedding matrix, PDMS exhibits the advantage of high radiation hardness. The luminescence spectra and fluorescence lifetime of the irradiated and unirradiated samples were tested. The fluorescence intensity of QDs decreases with the increase of the irradiation dose according to the result of luminescence spectra. The fluorescence intensity of the QDs decreases by 80% after irradiation with a dose of 1 kGy, but the position of the emission peak and the spectral shape of the QDs remain consistent before and after irradiation. In addition, the fluorescence lifetime of QDs is shortened after irradiation. Based on the fluorescence response of QDs to the irradiation of γ-rays and combined with flexible materials, our work provides a theoretical basis for the application of QDs as a new wearable dosimeter.

Key words: CdSe/ZnS quantum dots; γ irradiation; polydimethylsiloxane (PDMS); dosimetry

0 Introduction

Semiconductor nanocrystalline quantum dots (QDs), as a kind of ideal fluorescent material[1], have been studied and widely-used in light-emitting diodes[2-3], lasers[4-5], solar cells[6-8], optoelectronics, electronic devices, photocatalysis and biomedicine[9], due to their outstanding optical properties such as broad-band excitation and narrow-band photolumine scence (PL) emission, continuously adjustable emission peak, long fluorescence lifetime, stable fluorescence intensity[10], and relatively high quantum yield. Meanwhile, the QDs are used for radiation dosimetry and ionizing radiation detection owing to the good properties of optical and scintillation[11].

Letant et al. reported on the use of QDs for detecting α particles[12-13]. Lecavalier et al. studied the effects of γ-ray irradiation on the luminescence properties of multilayer CdSe/CdS/CdZnS/ZnS QDs dispersed in aqueous solution, providing a research basis for real-time dose detection[14]. At present, the optical properties of colloidal QDs dispersed in different solutions are studied under different irradiation environments. In our work, CdSe/ZnS QDs were embedded in the polydimethylsiloxane (PDMS) medium. Compared with other organic polymers, PDMS as a kind of embedded matrix has advantages of good transparency, good stability, high elasticity, high radiation hardness, and non-toxicity[15-17]. The effects of different doses of γ-ray irradiation on the PL properties of QDs were studied, and the defects induced by radiation were explained in terms of luminescence intensity and fluorescence lifetime by using the steady-state and time-resolved PL measurement methods by comparing them with unirradiated samples. In our work, combination with flexible materials and usage of fluorescence response of QDs to radiation provide a theoretical basis for the development of wearable dosimetry devices based on

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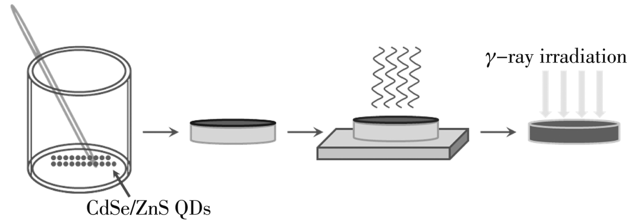
QDs.

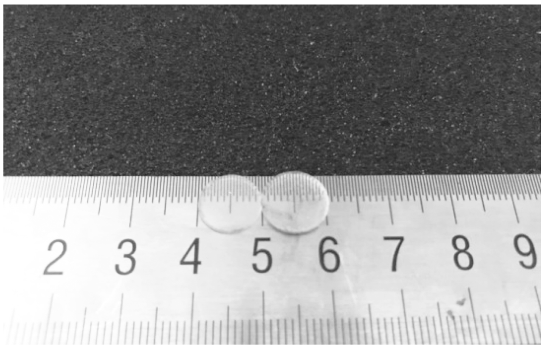
1 Sample preparation and experiment

1.1 Sample preparation

In the experiment, the colloid CdSe/ZnS QDs were dissolved in toluene solution (purchased from Suzhou Xingshuo Nano Technology Co., Ltd.) with an emission peak of 622 nm, and the dispersion concentration was 10 g/L. PDMS and curing agent were mixed in the ratio of 10 : 1, then the QD solution was dropped into the mixture and stirred evenly. The QDs and PDMS were mixed uniformly after ultrasonic treatment for 15 min. The concentration of QDs in the mixture was 1 g/L. Then, the mixture solution was evenly dispersed in six circular molds with a diameter of 1 cm and a thickness of 1 mm. Afterwards, six samples were placed on a heating plate with the temperature of 60 ℃ for 1 h, then cooled down to room temperature for overnight. Finally, the PDMS samples embedded with CdSe/ZnS QDs were prepared, as shown in Fig. 1. Fig. 1(a) shows the preparation procedures, and Fig. 1(b) shows the as-prepared samples. In order to facilitate the comparison of the effects of γ-ray irradiation and non-irradiation on the samples, five of the samples were irradiated with different doses of γ-ray irradiation, and one of the samples was not irradiated as the control sample.



(a) Processing steps of the sample



(b) PDMS samples of doped and undoped CdSe/ZnS QDs

Fig. 1 Samples of CdSe/ZnS QDs embedded in PDMS

1.2 Experiment

In this study, CdSe/ZnS QDs embedded in PDMS were irradiated by γ-ray produced by ^{60}Co irradiation source with an energy of 1.25 MeV. The samples were irradiated at room temperature with a total dose of 0.1 Gy, 1 Gy, 10 Gy, 100 Gy and 1 000 Gy, respectively.

The radiation dose rate was 0.6 Gy/min. In order to separate irradiation-induced phenomena from the possible effects of natural degradation such as oxidation processes, all samples were processed in the same batch. It is also assumed that both irradiated and unirradiated samples stored at room temperature undergo the same natural aging process and respond in the same way to environmental changes. The luminescence spectra of QD before and after irradiation were measured by laser optical device and Horiba HR520 fluorescence spectrometer. The 532 nm laser with stable power in the optical device is provided by a diode pumped solid-state laser. The laser is reflected to the objective lens (reflection wavelength 380 nm—550 nm, transmission wavelength 584 nm—700 nm) through the dichroscope, and focused on the sample through the objective lens. Then the photoluminescence was generated when 532 nm laser excited the QDs. The fluorescence lifetime measurements were performed using the same optical device equipped with a photomultiplier tube (PMT) and a Horiba monochromator. The test system of luminescence spectrum and fluorescence lifetime is shown in Fig. 2.

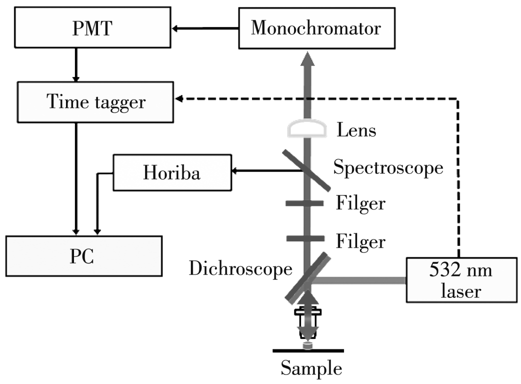
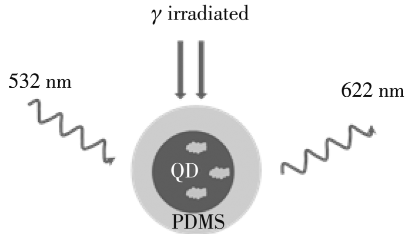


Fig. 2 Test system of luminescence spectrum and fluorescence lifetime

1.3 Irradiation principle of CdSe/ZnS QDs embedded in PDMS

Due to the γ-ray irradiation, the quenching centers are introduced at the QDs surface, which will decrease the average QDs fluorescence intensity and affect the fluorescence lifetime of QDs. Fig. 3 shows the irradiation principle of CdSe/ZnS QDs embedded in PDMS. Fig. 3(a) shows the luminescence emission peak of unirradiated sample is 622 nm which is excited by 532 nm laser. Fig. 3(b) shows the appearance of quenching centers at the QDs surface.

(a) Unirrated sample



(b) Sample irradiated by γ-rays with different doses

Fig. 3 Irradiation principle of CdSe/ZnS QDs embedded in PDMS

2 Analysis and discussion

2.1 Test of luminescence spectrum

The luminescence spectra of CdSe/ZnS QDs embedded in PDMS irradiated with different doses are shown in Fig. 4.

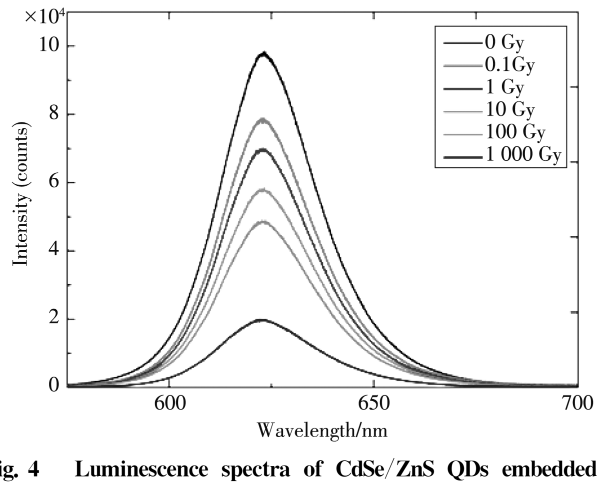


Fig. 4 Luminescence spectra of CdSe/ZnS QDs embedded in PDMS irradiated with different doses

The fluorescence intensity of QDs changes after irradiation with a dose of 0.1 Gy, and the fluorescence intensity of QDs gradually decreases with the increase of irradiation dose. The fluorescence intensity of QDs decreases by 80% after irradiated with a dose of 1 kGy. Similar observations were reported by Wither[18] and Robert[2] et al. Fig. 4 also shows that the position of QDs emission peak and the shape of the spectrum do not change after irradiated with different doses, and the position of emission peak is $\lambda=622$ nm. For the new quenching centers introduced by γ-ray irradiation, the density of quenching centers increase with the increase of irradiation dose, which leads to the decrease of fluorescence intensity of QDs. In Fig. 5, the percentage variation of the main peak intensity is reported as a function of the irradiation doses.

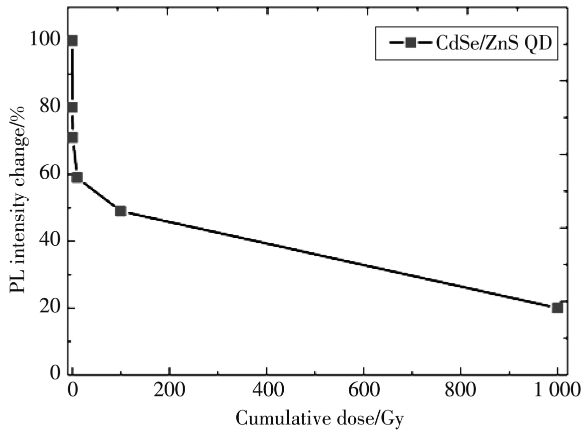


Fig. 5 Relative change of QDs luminescence intensity plotted in percentage as a function of irradiation doses

The result of luminescence spectra show that QDs are sensitive to γ-ray radiation. The irradiation dose is characterized by the relative change of QDs photoluminescence intensity and combined with flexible materials, which provides a basis for the application of wearable dose detector.

2.2 Test of fluorescence lifetime

In order to further study the relationship between irradiation doses and fluorescence intensity, the photoluminescence lifetime of CdSe/ZnS QDs embedded in PDMS irradiated with different doses are tested, the corresponding results are shown in Fig. 6. In general, the luminescence decay of colloidal QDs has multiexponential properties. More specifically, it has been demonstrated that it typically follows a biexponential function[19]. In fact, it has been assessed that the surface of colloidal QDs plays an important role in carrier relaxation and recombination processes due to the large surface-to-volume ratios. In fact, the luminescence decay curve approached a single exponential function as the QDs surface structure was improved[20].

In Fig. 6, the fluorescence lifetime of QDs is shortened with the increase of irradiation dose. The shortening of fluorescence lifetime is attributed to the quenching center generated by irradiation capturing excited state carriers and reducing the overlap between electron and hole wave functions, enhancing the irradiation path of non radiative recombination of exciton states.

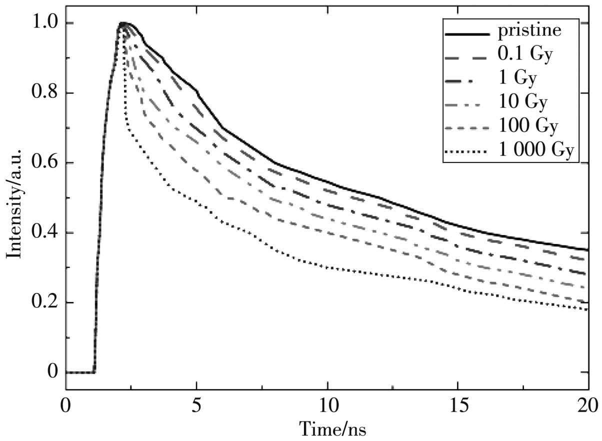


Fig. 6 Fluorescence lifetime of CdSe/ZnS QDs embedded in PDMS irradiated with γ-rays at different doses

3 Conclusions

In conclusion, the optical properties of CdSe/ZnS QDs embedded in PDMS are changed under irradiated with γ-ray at different doses. These obvious changes can be obtained when the irradiation dose of γ-ray is as low as 0.1 Gy or as high as 1 000 Gy. And the luminescence intensity of the QDs embedded sample decreases with the increase of irradiation dose. The luminescence intensity decreases by 80% and the fluorescence lifetime shortens after irradiation with a dose of 1 000 Gy. The detection of irradiation dose is realized by the change of luminescence intensity of QDs after irradiation by combining with flexible material PDMS, which provides a theoretical basis for the irradiation monitoring system based on QDs as the nano sensing elements.

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伽马辐照对嵌入 PDMS 的 CdSe/ZnS 量子点光学特性的影响

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摘　要： 将 CdSe/ZnS 量子点与具有高辐射硬度优点的聚二甲硅氧烷（Polydimethylsiloxane，PDMS）柔性材料结合，研究了不同辐照剂量的 γ 射线对嵌入 PDMS 中的 CdSe/ZnS 量子点光学特性的影响，并对辐照样品与未辐照样品进行了发光光谱与荧光寿命测试。结果表明，随着辐照剂量的增加，量子点的发光强度降低，1 kGy 剂量辐照后荧光强度降低了 80%，但量子点的发光峰位置与光谱形状在辐照前后保持一致；同时辐照后量子点的荧光寿命也发生缩短。研究得出了量子点对辐射的荧光响应规律，并与柔性材料结合，为量子点在新型可穿戴式剂量计中的应用提供理论依据。

关键词： CdSe/ZnS 量子点；γ 辐照；聚二甲硅氧烷；剂量计

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