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## Emission image of X-ray-irradiated CR-39 stick doped with methylviologen-encapsulated silica nanocapsules using LED light

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Light-emitting diode (LED)-light-excited emission images of 6 MeV-X-ray (10 Gy)-irradiated CR-39 doped with methylviologen-encapsulated silica nanocapsules (MV @SiO<sub>2</sub> NCs) were observed using an iPhone 5S for the first time. The excitation and fluorescence spectra were also observed, and the emission peak at 580 nm produced by the X-ray irradiation was confirmed. Emission intensities of 80 kV-X-ray (0.5, 1, 1.5, and 2 Gy)-irradiated CR-39 doped with MV @ SiO<sub>2</sub> NCs could be measured using a portable fluorometer (FC-1), and a good linear relationship between their emission intensity and dose was clearly observed.

**Keywords:** X-ray irradiation; dose; CR-39; emission image; LED light; emission intensity; iPhone 5S; transparent; silica nanocapsule

### 1. Introduction

Our goal is to measure an exposure dose of the lens of the eye directly and easily in a clinical setting such as in interventional radiology (IVR), which is evaluated as an equivalent dose. For this purpose, the dosimeter should be close to the surface of the eye and must be transparent.

A CR-39 plate, which is composed of polyallyldiglycol carbonate (PADC), is transparent and can be used as glass. Generally, CR-39 itself is used as a plastic nuclear track detector (PNTD) of neutrons and  $\alpha$ -particles after treating with NaOH [1]. Therefore, we have synthesized CR-39 doped with methylviologen-encapsulated silica nanocapsules (MV @ silica NCs). After the doped CR-39 plate was irradiated with X-rays (80 kV), its emission image after excitation with the laser light of an FLA-9000 imager (Fuji Film Co., Ltd.) was obtained [2]. In the range from 3 to 0 Gy, the dose of X-rays (80 kV) has a linear relationship with the intensity of the emission image [3]. However, in the clinical setting, the FLA-9000 imager having a laser and photomultiplier tube (PMT) cannot be used because of its large size [1180 (W) x 780 (D) x 480 (H) mm, 160 kg].

In this study, a CR-39 stick doped with MV @ silica NCs was fabricated. Light-emitting diode (LED) light in a compact case [65 (W) mm x 100 (D) mm x 35 (H) mm,

80 g] with cutoff filters to only transmit light with wavelengths longer than 550 nm was used to excite the X-ray-irradiated doped CR-39 stick, and an emission image of the stick was successfully recorded using an iPhone 5S. The effect of LED light on the emission intensity of X-ray-irradiated parts was analyzed to detect low doses.

### 2. Experimental

#### 2.1. Preparation of CR-39 stick doped with MV @ silica NCs

Methylviologen-encapsulated silica NCs were prepared by a core-shell method [4] as follows. A 0.8 mM methylviologen aqueous solution was added to a 0.5 mM Au nanoparticle (NP) aqueous suspension as a core, followed by stirring for 1 h. Then, 0.8 mM 3-aminopropylorthosilicate (APS) was added to the aqueous suspension, followed by stirring for 15 min. Finally, a 0.27 wt% silicate solution was added to them, followed by stirring for 3 days. Silica-covered methylviologen-adsorbed Au NPs were obtained. After a 0.4 M sodium cyanide solution was added to them to dissolve the Au NPs, they were washed with water. Ultrafiltration was performed with a 10 kDa membrane filter to remove Au(CN)<sub>2</sub><sup>-</sup> and excess NaCN, and the solvent was changed from an aqueous solution to ethyl alcohol.

An approximately 10 mm<sup>2</sup> and 40-mm-long CR-39

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stick doped with MV @ silica NCs was synthesized using MV @ silica NCs dispersed in ethyl alcohol and provided by SUN•LUX Optical Co., Ltd. [2]. **Figure 1** shows a CR-39 plate (a) and stick (b) doped with MV @ silica NCs. They are clearly transparent as shown in the figure.

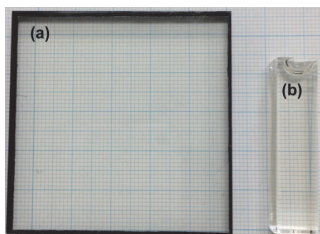


Figure 1. Photoimages of CR-39 doped with MV @ silica NCs: plate (a) and stick (b).

### 2.2. Irradiation of X-rays to CR-39 sticks doped with MV @ silica NCs

The stick was irradiated up to a height of 1 cm from the bottom with 6 MV X-rays for 2 min (Varian Novaris TX) at Tokushima University Hospital. The absorbed dose was about 10 Gy.

80 kV X-rays (Allura Xper FD20/20 biplane neuro X-ray system, Philips Electronics Co., Ltd.), whose doses were 0.5, 1, 1.5, and 2 Gy, were irradiated to the region above 2 cm from the bottom of CR-39 sticks doped with MV @ silica NCs at Tokushima University Hospital. The dose was measured using an Accu-Pro control unit and a 10X6-6 ion chamber (Radcal Co., Ltd.) These sticks were shielded using a 1-mm-thick Pb plate to demarcate an X-ray-irradiated area and a nonirradiated area.

### 2.3. Emission image of X-ray-irradiated CR-39 sticks doped with MV @ silica NCs using LED light

Each irradiated stick was excited by 24 LED lights (NCSB119T, Nichia Co., Ltd.) arranged in a compact case [65 mm (W) x 100 mm (D) x 35 mm (H)], whose peak wavelength was 525 nm, and its emission image was recorded using the camera of an iPhone 5S with two optical filters to obtain emission light of more than 550 nm wavelength.

ImageJ software installed in a Mac Air or Mac mini was used to decompose the obtained images into each color component. The intensity of a region of interest (ROI) positioned in each emission image was measured.

### 2.4. Measurement of fluorescence intensity of X-ray-irradiated CR-39 sticks doped with MV @ silica NCs as a function of dose

The fluorescence and excitation spectra of each irradiated stick were measured using a Shimadzu RF-5300PC fluorophotometer with a 200 W xenon lamp. The emission intensity at 525 nm was recorded using an FC-1 portable fluorometer (TOKAI OPTICAL Co., Ltd.), whose size is 130 mm (W) x 140 mm (D) x 62 mm (H), with a 525 nm filter for excitation and a >550 nm filter for emission. LED light was used as an

excitation light.

## 3. Results and discussion

### 3.1. Emission image of 6 MeV-X-ray-irradiated CR-39 stick doped with MV @ silica NCs using LED light

**Figure 2** shows an emission image of the 6 MeV-X-ray (10 Gy)-irradiated CR-39 stick doped with MV @ silica NCs. The image clearly shows the X-ray-irradiated parts with a high emission intensity in the lower part of the stick in the original image using LED light. This emission image was obtained easily using the camera of an iPhone 5S. The colors of the emission image were decomposed to the red, green, and blue components using ImageJ software. The red image showed a high emission intensity, whose color is white, indicating that the emission mainly comprised the red component.

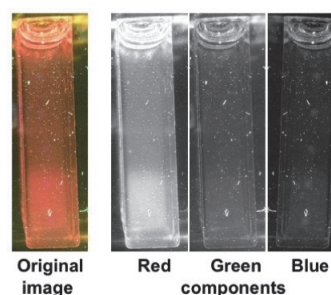


Figure 2. Emission and decomposed images of CR-39 stick doped with MV @ silica NCs irradiated by 10 Gy of 6 MeV X-rays.

**Figure 3** shows that the fluorescence (Em) and excitation (Ex) spectra of the X-ray-irradiated CR-39 stick doped with MV @ silica NCs have a peak at 580 nm upon 525 nm excitation (red solid curve), as can be seen by comparing the red dashed curve with the spectra for a nonirradiated stick. Consequently, the emission peak at 580 nm agreed with the red component in Figure 2.

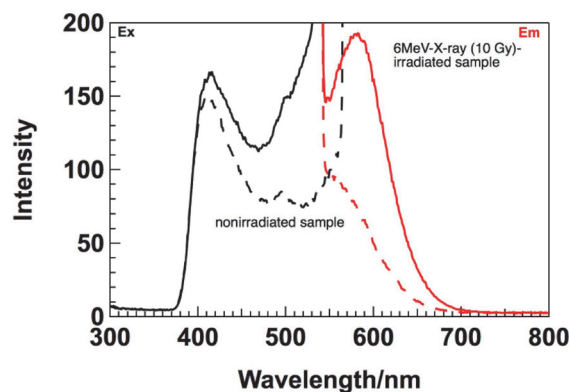


Figure 3. Emission and excitation spectra of 10 Gy- and 0 Gy- X-ray-irradiated (—) and nonirradiated (----) CR-39 sticks doped with MV @ silica NCs. The slits for both excitation and emission are 10 nm.

These results indicate that the quantitative visualization and counting of 10 Gy X-rays are possible using LED light and by recording on an iPhone 5S.

**3.2. Emission images of 80 kV-X-ray-irradiated CR-39 sticks doped with MV @ silica NCs using LED light**

Figure 4 shows emission images of the 80 kV-X-ray-irradiated CR-39 sticks doped with MV @ silica NCs subjected to doses of 0.5, 1, 1.5, and 2 Gy for the area up to 2 cm from the bottom. The irradiation area of the 24 LED lights arranged in a compact case was 55 mm (W) x 90 mm (D), and two optical filters were used to obtain emission light of more than 550 nm wavelength. As shown in Figure 4, it was difficult to distinguish a difference between each dose by eye. This indicates that the LED light intensity may be insufficient to detect the difference between such low doses by eye. Using the image of the red component obtained with ImageJ software, an ROI (a circle of area 14.2 mm<sup>2</sup>) was set in both the X-ray-irradiated area and the nonirradiated area at each dose. Then, the intensity of each ROI was measured (n=3), the mean and standard deviations were calculated, and the net intensity was calculated by subtracting the mean intensity of the nonirradiated area from that of the X-ray-irradiated area. Finally, the net intensity per mm<sup>2</sup> in the ROI was obtained.

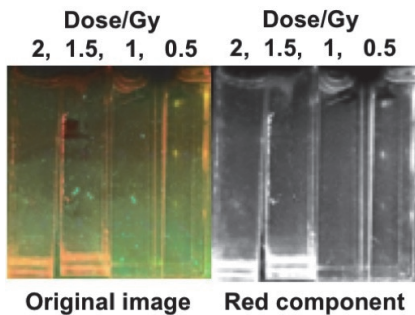


Figure 4. Emission and red-component images of CR-39 sticks doped with MV @ silica NCs irradiated by 0.5, 1, 1.5, and 2 Gy of 80 kV X-rays.

Figure 5 shows the relationship between the net intensity per mm<sup>2</sup> and the dose along with the standard deviations (n=3). It was found that the intensity increased linearly with the dose from 0 to 2 Gy. Equation (1) was obtained by approximating the net intensity as a linear function of the dose.

$$[\text{Net intensity per mm}^2] = 1.94 \times [\text{dose}] - 0.04, \quad R^2=0.98643 \quad (1)$$

However, the relative standard deviation increased from about 15 to 62% when the dose decreased from 2 to 0.5 Gy as shown in Figure 5. This result indicates that the use of emission images obtained by an iPhone5S with 24 LED lights arranged in a compact case is unsatisfactory for detecting doses of less than 0.5 Gy. This appears to be due to the light transmitted from the 24 LED lights in

addition to the background emission light from the CR-39 sticks. Therefore, a portable fluorometer was used to eliminate the light transmitted from the LEDs.

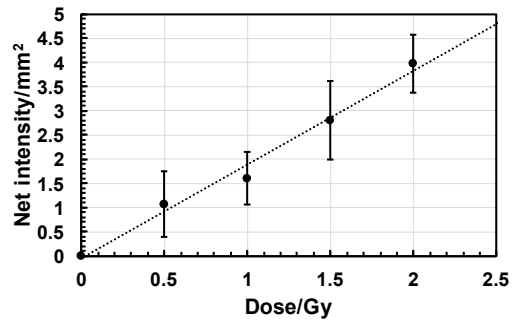


Figure 5. Relationship between intensity of the 80-kV-X-ray-irradiated ROI of the stick and dose.

**3.3. Relationship between emission intensity measured by a portable fluorometer (FC-1) and dose**

Figure 6 shows the relationship between the emission intensity measured (n=4) by a portable fluorometer (FC-1) and the dose. The stick subjected to 1 Gy irradiation exhibited some cracks, suggesting that the emission light may have been scattered. A good linear relationship was observed between them, except at 1 Gy, given by

$$[\text{Emission intensity}] = 20.857 \times [\text{dose}] + 148.86, \quad R^2=0.98612. \quad (2)$$

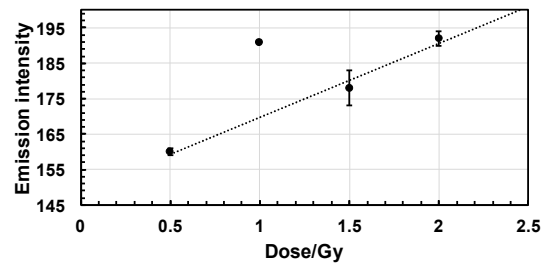


Figure 6. Relationship between emission intensity measured by a portable fluorometer (FC-1) and dose. 80 kV X-rays were irradiated to the CR-39 sticks doped with MV @ silica NCs.

This result indicates that the CR-39 sticks doped with MV @ silica NCs can be used with an FC-1 fluorometer in a clinical setting. This is because the measurement by the FC-1 fluorometer only obtained the emission intensity from the X-ray-irradiated area based on the dose without any light transmitted from the LEDs.

However, the dose used for measurement should be minimized for practical use at hospitals. For example, the equivalent dose limit was recommended as 100 mSv per 5 years and not to exceed 50 mSv per year by the International Committee on Radiological Protection (ICRP) Publication 2007 [5].

Our proposed method of detection with a minimized dose is as follows. Table 1 shows emission intensities in emission slits with widths of 10 and 15 nm for different doses measured with a Shimadzu RF-5300PC

fluorophotometer. A 1.5-fold increase in the emission slit width led to  $2.1 \pm 0.1$ -fold higher emission intensities. Also the slopes of the straight lines approximating the relationship between the emission intensity and the dose obtained from the doses of 2, 1.5, and 0.5 Gy were  $8.1 \pm 0.7$  and  $27 \pm 4$  for slit widths of 10 and 15 nm, respectively, equivalent to emission intensities of  $0.81 \pm 0.07$  and  $2.7 \pm 0.4$  per 0.1 Gy. The emission intensity for a slit width of 15 nm was about three that for a slit width of 10 nm, and the relative standard deviations were about 9 and 15% for the slit widths of 10 and 15 nm, respectively. These values are lower than that in the case of LED irradiation (about 62% for 0.5 Gy). Therefore, it was found that excitation by intensive light irradiation using a slit width of 15 nm is better than that using a slit width of 10 nm for detecting a dose of 0.1 Gy.

This result indicates that an increase in the LED light intensity will lead to the visualization of doses lower than 0.1 Gy and will enable the evaluation of doses by measurement of the emission intensity.

Table 1. Emission intensities in emission slits with widths of 10 and 15 nm for different doses.

Dose/Gy	Slit (Ex/Em)=10/10 nm	Slit (Ex/Em)=10/15 nm
2	73	149
1.5	70	141
1	50	110
0.5	61	128

### 3.4. Reusability of CR-39 sticks doped with MV @ silica NCs for X-ray irradiation

X-ray-irradiated CR-39 sticks doped with MV @ silica NCs can be reused after erasing the emission images using 525 nm LED light irradiation. This is because the emission intensity at 580 nm decreased up on the long-term irradiation of 24 LED lights with a wavelength of 525 nm arranged in a compact case, for example, 2 h irradiation of the 24 LED lights led to a 36% decrease in the emission intensity at 580 nm.

The mechanism of the emission phenomenon for X-ray-irradiated CR-39 sticks doped with MV @ silica NCs that allows the sticks to be reused is as follows. When the sticks were subjected to X-ray irradiation, charge separation ( $e^-$  and  $h^+$ ) occurred in the sticks. It has been found from electron spin resonance (ESR) studies that the  $MV^{2+}$  molecules in doped MV @ silica NCs act as trap sites for the electrons generated by the X-ray irradiation of the CR-39 sticks [2,3]. When the trapped electrons were excited and released by the excitation of 525 nm LED light, an emission peak at 580

nm was observed. Moreover, long-term irradiation of the X-ray-irradiated CR-39 sticks doped with MV @ silica NCs by LED light (525 nm) led to a decrease in the emission intensity at 580 nm. This indicates that the trapped electrons were released and the trap site became empty upon excitation with 525 nm light.

Therefore, CR-39 sticks doped with MV @ silica NCs can retrap the electrons generated in CR-39 by X-ray irradiation, enabling their reuse.

## 4. Conclusion

The emission image of a 6 MeV-X-ray (10 Gy)-irradiated CR-39 stick doped with MV @ silica NCs excited by LED light was clearly observed using an iPhone 5S. Those of 80 kV-X-ray (0.5, 1, 1.5, and 2 Gy)-irradiated sticks excited by LED light were not observed using the iPhone 5S. The emission intensities of these sticks were measured using a portable fluorometer (FC-1) and a linear relationship with the dose was observed.

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