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Electron irradiation effects of radiochromic PCDA vesicle gel dosimeters*

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The gel dosimeter has the uniquely capacity in recording radiation dose distribution in three dimensions (3D), which has the specific advantages in dosimetry measurements where steep dose gradients exist. In this study, a novel radiochromic gel dosimeter was developed by dispersing nanovesicles self-assembled by 10, 12-pentacosadiynoic acid (PCDA) into the tissue equivalence gel matrix. The characteristics of radiochromic PCDA vesicle gel dosimeters were evaluated. Results indicate that these radiochromic gel dosimeters have good linear response to 1.7 MeV electron beam irradiation in the dose range of 0.32–6.36 kGy. In addition, the radiochromic gel dosimeters overcome the limitations of the existing gel dosimeters such as diffusion effect, post-radiation effect, and poor forming ability. Hence, the radiochromic PCDA vesicle gel dosimeters developed could be generally applied to 3D dose distribution measurement with optical readout.

Keywords: Radiochromic gel dosimeter, PCDA nanovesicle, 3D dose distribution measurement, Post-radiation effect

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I. INTRODUCTION

In radiotherapy and radiation processing, measuring three-dimensional (3D) dose distribution within a certain space is often needed. Conventional dosimetry systems, such as calorimeter, ionization chamber, liquid chemical dosimeter (e.g. Fricke dosimeter), thermoluminescence dosimeter, radiochromic film [1–4], provide only point or two-dimensional dose distribution. Gel dosimeters, in which radiation sensitive chemicals are distributed uniformly, are capable of recording radiation dose distribution in three dimensions [5, 6]. Upon irradiation, the chemical yield of products is a function of the absorbed radiation dose [7, 8]. Due to the high spatial resolution and dosimetry accuracy, the gel dosimeter has specific advantages in dosimetry measurements where steep dose gradients exist [5].

Some types of gel dosimeters, however, have their performance limitations. Fricke gel dosimeters do not retain spatial stability a few hours after irradiation due to rapid diffusion of Fe^{2+} and Fe^{3+} ions [6, 9, 13]. Polymer gel dosimeters are troubled by reading deviations caused by oxygen contamination [5, 10, 14] (where oxygen quenches the free radicals generated in the irradiation process and inhibits the polymerization reaction), and post-radiation effect [5] (where the monomer continues to polymerize after irradiation). Micelle gel dosimeters (e.g., leuco dye micelle gel dosimeters) are temperature-sensitive during irradiation and tend to fade over time [11, 12]. They are of relatively low dose sensitivity and may depend significantly on dose rate [15]. Besides, due to their poor forming ability, these gel dosimeters must be in containers to keep their shape, reducing tissue equivalence of the dosimeters. The diacetylene 10,12-pentacosadiynoicacid (PCDA) is the reporter molecule in commercial Gafchromic film, which is used for 2D dosimetry [16–18]. With a hydrophilic carboxyl head group and a hydrophobic tail, PCDA molecules can self-assemble into vesicles in water [19, 20]. PCDA monomer can be polymerized upon radiation and generate blue phase PDA vesicles without any precipitation. In this study, a novel radiochromic gel dosimeter was developed for 3D dose distribution measurement by dispersing nanovesicles self-assembled by PCDA into the tissue equivalence gel matrix. This nanovesicle design significantly overcomes the dose image blurring caused by monomer diffusion. Also, it limits polymer chain growth within the vesicle and reduces the post-irradiation effect. With excellent tissue equivalence and elastic properties, the gel matrices do not need vessel wall, without optical problems associated with refractive index mismatches. They provide good space structure for 3D dose distribution measurement by molding into desired shape. Thus, the radiochromic PCDA vesicle gel dosimeters are better than existing gel dosimeters, and are generally suitable for 3D dose distribution measurement with optical readout.

II. MATERIALS AND METHODS

A. PCDA vesicles and gel preparation

The radiochromic gel is composed of the radiochromic system, i.e. the PCDA vesicles; and gel matrix system consisting of organic matter and about 85% water (hence good radiation

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tissue equivalence). Fabrication of the radiochromic PCDA vesicle gel dosimeter is shown schematically in Fig. 1.

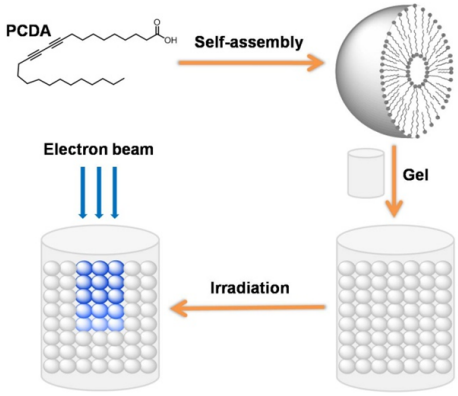


Fig. 1. (Color online) Schematic illustration of the fabrication and application of radiochromic PCDA vesicle gel dosimeter.

The 10,12-pentacosadiynoic acid (PCDA, 98+% purity, Alfa Aesar Chemical Co. Ltd., China), was used as the reporter molecule in the radiochromic gel. It was dissolved in acetone (CH_3COCH_3) and PCDA vesicles were made using the injection method. Monomers acrylamide (AA) and crosslinking agent N,N'-methylene-bis-acrylamide (BIS), were dissolved in the PCDA vesicles solution. They were polymerized together and crosslinked under the catalytic action of ammonium persulfate $(NH_4)_2S_2O_8$, to form radiochromic gel. The Acetone, AA, BIS and $(NH_4)_2S_2O_8$ were all analytically pure and purchased from Chengdu Kelon Chemical Reagent Factory, China. Deionized water was used in all experiments.

1. *PCDA nanovesicles preparation*

PCDA nanovesicles are prepared using the injection method. PCDA crystalline powder was dissolved in acetone of 20 mmol/L concentration. The solution was injected into a certain volume of deionized water at temperatures above the boiling point of acetone (56 °C). The solution was placed in warm water bath to maintain the temperature and supersonic vibrated for 10 minutes. The solution was left to cool to room temperature before placing it in a 4 °C fridge for over six hours to get the PCDA vesicle solution. The final concentration of PCDA was 1 mmol/L. To observe the morphology, the vesicle solution was air dried on silicon slice and copper grid, and characterized by scanning electron microscopy (SEM) and transmission electron microscopy (TEM).

2. *Radiochromic gel preparation*

AA and BIS were added into the vesicle solution prepared in Sec. II B 1 and dissolved by ultrasound at concentrations of 2×10^3 mmol/L and 65 mmol/L, respectively. The solution was heated to 50–60 °C by water bath, and then the ammonium persulfate (catalyst) was added and stirred to keep mixture uniform. The concentration of ammonium persulfate in the solution was 6 mmol/L. The temperature of solution was maintained until the AA monomer was completely polymerized to form a transparent gel.

B. Irradiation and test

The samples were irradiated by electron beams of 1 or 1.7 MeV from a JJ-2 model Van de Graaff accelerator, at the ambient temperature (25 °C) and relative humidity of 60%.

1. *The color change in response to irradiation of radiochromic gel*

Linearity of the irradiation response is a main technical indicator of gel dosimeter, which should be calibrated before its use in dose measurement. The gels prepared in one batch were irradiated by 1.7 MeV E-beams for 6.25, 12.50, 25.00, 37.50, 50.00, 62.50, 75.00, 93.75 and 125.00 s, in a fluence rate of 10^{11} cm^{-2} s^{-1}. The electron fluences were converted to absorb doses in gels using Monte Carlo (M-C) method. The absorption spectra of gel are tested with spectrophotometer (Shimadzu Corp., Japan) two hours after irradiation. The net optical density (net OD) referred in this paper is the difference of the optical density between irradiated and non-irradiated gel samples. The net OD-dose curve was plotted, and the fitting function and root mean square error were calculated.

2. *Post radiation effect*

Optical densities of absorption peak at 680 nm of the gel samples were measured at 0.1, 0.5, 1, 1.5, 2, 12, 24, 48, 72 and 168 h after 1.7 MeV EB irradiation of 5×10^{12} cm^{-2} at fluence rate of 10^{11} cm^{-2} s^{-1}.

3. *Diffusion effect*

The PCDA nanovesicles self-assembled by PCDA monomers can prevent the diffusion of monomer molecules. To test the diffusion effect of radiochromic gel, gel slice of ϕ4.5 cm was irradiated 1.7 MeV E-beams of ϕ2 cm beam spot, along the axial direction with a fluence of 5×10^{12} cm^{-2} and fluence rate of 10^{11} cm^{-2} s^{-1}. Photos were taken in a dark room at 0.5 h and 96 h after irradiation, where the gel samples were placed on a white plane back light source with the digital camera (Nikon D90, Japan) fixed right above the gel. A bandpass filter ((680 ± 20) nm) was connected to the camera lens through a connecting tube. The distance between gel surface and camera lens was 32 cm. The camera parameters were as follows: shutter speed, 1/2 s, focal length, 105 mm, aperture, 5.6, ISO 1000, and pixels, 4288×2848. The filtered photos were converted to gray-level images with Image-Pro Plus software. The gray

levels analyzed were converted into net OD using Eq. (1),

$$\begin{aligned}\Delta\overline{OD} &= \overline{OD}_{\text{irr}} - \overline{OD}_{\text{blank}} \\ &= \lg(\text{GL}_{\text{light}}/\text{GL}_{\text{irr}}) - \lg(\text{GL}_{\text{light}}/\text{GL}_{\text{blank}}) \\ &= \lg(\text{GL}_{\text{blank}}/\text{GL}_{\text{irr}}),\end{aligned} \quad (1)$$

where $\overline{OD}$ = 660–700 nm is optical density; $\Delta\overline{OD}$ is net mean optical density; and GL stands for gray level. The radial net OD distribution figures derived from the two gel slice images (0.5 and 96 h) were compared.

4. *Depth OD distribution test*

Two cylindrical gels of $\phi 4.5\,\text{cm} \times 2\,\text{cm}$ were prepared. They were irradiated by $\phi 2$ cm E-beams of 1 and 1.7 MeV, respectively, along the axial direction with a fluence of $5 \times 10^{12}\,\text{cm}^{-2}$ and fluence rate of $10^{11}\,\text{cm}^{-2}\,\text{s}^{-1}$. Then, the gels were cut into $\phi 4.5\,\text{cm} \times 0.3\,\text{cm}$ slices, which were placed with a gap of 0.15 cm for photographing with a digital camera of the same settings as those in Sec. II B 3. The filtered photo was converted to gray-level image with Image-Pro Plus software. The gray levels were converted into net OD using Eq. (1). The depth-net OD distribution curve derived from the gel gray-level image was plotted.

III. RESULTS AND DISCUSSION

A. Morphology of the PCDA nanovesicles

SEM and TEM images of the PCDA vesicles prepared in Sec. II B 1 are shown in Fig. 2. The vesicles are globular or ellipsoidal in shape, of about 60 nm in diameter, with an obvious hollow structure. These indicate that the PCDA monomers in aqueous solution can self-assemble into hollow vesicles using the injection method, which is advantageous in its simpler operation and higher yield, than the other methods of vesicle preparation, such as membrane method and reverse evaporation. It is suitable for batch preparation of PCDA vesicle gel dosimeters.

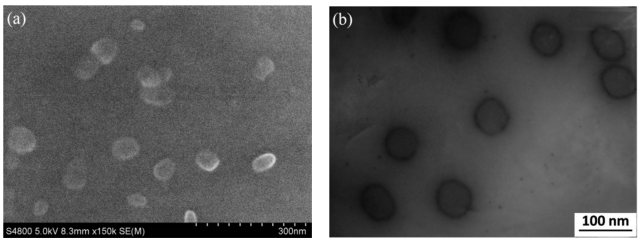


Fig. 2. SEM (a) and TEM (b) images of PCDA nanovesicles.

B. Response of PCDA vesicle gel samples to different electron doses

The PCDA nanaovesicles were evenly distributed in the radiochromic gel matrix. Upon irradiation, the PCDA monomer molecules in the vesicles reacted to form blue phase polydiacetylene (PDA) that have conjugated double and triple bonds [19] as shown schematically in Fig. 3. After the gels were irradiated by electron beams with the fluences of 0.625×10^{12}–$12.500 \times 10^{12}\,\text{cm}^{-2}$ (0.32–6.36 kGy, as calculated with M-C method), the polymerization reaction yield of monomers is approximately proportional to the absorbed dose. Figure 4 shows that the gel samples change in color gradually, from being colorless to dark blue as the absorbed dose increases.

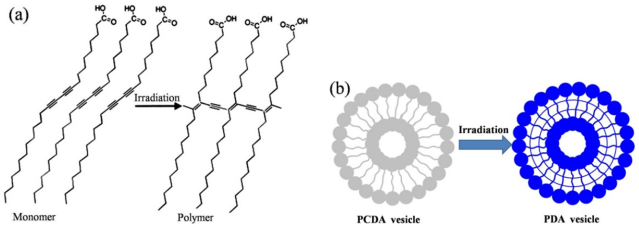


Fig. 3. (Color online) Reaction schmatics of PCDA before and after irradiation. (a) PCDA monomer react to form PDA polymer and (b) PCDA vesicle react to generate blue phase PDA vesicle.

Figure 5(a) shows the absorption spectra of the gel samples irradiated to different doses. The main absorption peak of the gel samples is located at 680 nm, with a minor absorption peak near 625 nm. Amplitude of the absorption peaks increase with the dose. Figure 5(b) shows net OD of the main absorption peak as function of the dose. Gel discoloration has a good linear response to doses of 0.32–6.36 kGy with $R^2 = 0.9992$. Note that the linear range of the dose response is 6.36 kGy.

C. Post radiation effect

The net OD of the PCDA vesicle gel samples measured at different hours after irradiation is shown in Fig. 6. One sees a 1.76% increase at 2 h, and a further increase of 1.09% at 48 h, but no increase at all from 48 to 168 h. Therefore, the post radiation effect of gel response proceeded quickly within 2 hours after irradiation, and continued in a slower pace in 48 hours, where the post-radiation effect halted. Reading the optical density 2 h after irradiation can effectively increase the dosimetry accuracy of the PCDA vesicle gel dosimeters. While other polymer gel dosimeters have serious post-radiation effect because of free radical polymerization, polymer gels undergo rapid polymerization reaction in the first a few hours after irradiation. In terms of practical dosimetry, it is recommended that the users shall wait 10 hours before reading the irradiated PAG gel, and 30 hours for the MAGIC gel [14]. The time for a stable response of PCDA vesicle gel

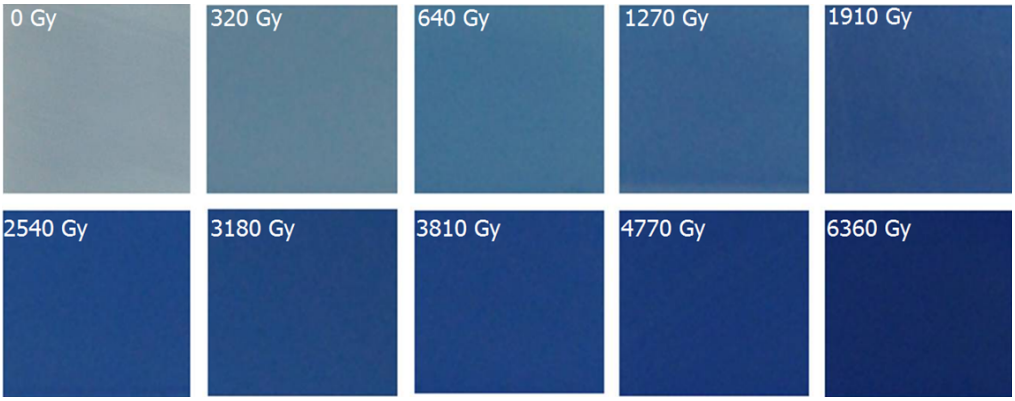
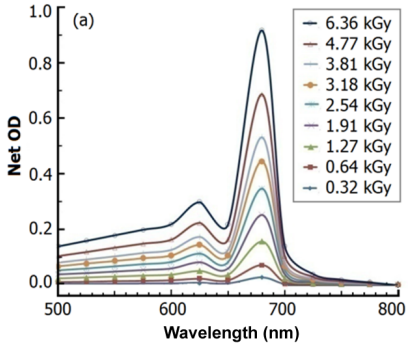


Fig. 4. (Color online) The photos of gels irradiated by 1.7 MeV electron with different doses.



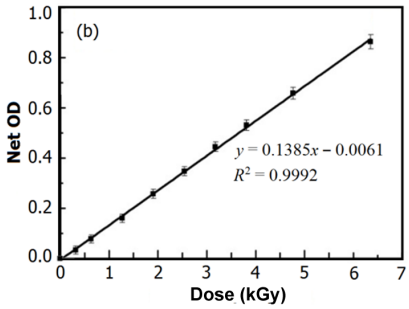


Fig. 5. (Color online) Absorption spectra of PCDA vesicle gel samples measured two hours after irradiating them to different doses (a), and net OD of the main absorbtion peak (680 nm) response to irradiation doses (b).

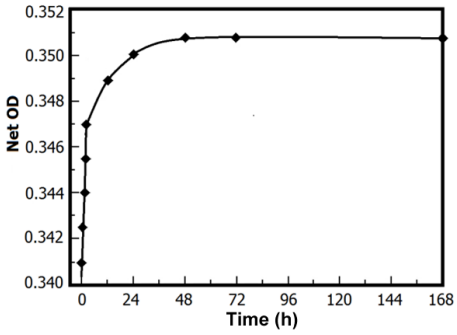


Fig. 6. Post-radiation effect of PCDA vesicle gel: net OD at 680 nm measured at different hours after irradiation.

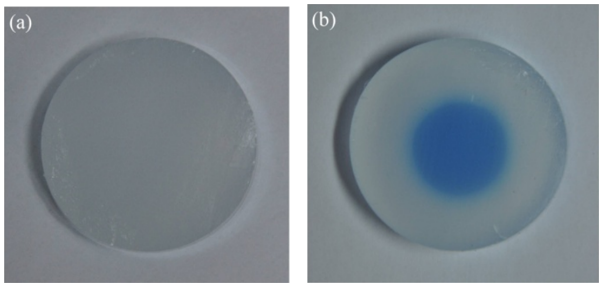


Fig. 7. (Color online) The gel slices before (a) and after (b) irradiation by ϕ2 cm E-beams.

to irradiation is far less than the above polymer gels. The reduced post-radiation effect may be due to that the polymer chain growth is limited within vesicles.

D. Diffusion effect

Figure 7 shows gel slices before and after 2.54 kGy irradiation of ϕ2 cm electron beams. The irradiated area changed into blue, in sharp contrast with the non-irradiated surrounding area. The filtered photos of the gel slice were taken at 0.5 and 96 h after irradiation (Figs. 8(a) and 8(b)), and were converted into gray-level images with Image-Pro Plus software. The gray levels of the points on the lines in the images were obtained and converted into the net OD using Eq. (1). Figure 8(c) shows the radial net OD distributions derived from the two gel slice images (0.5 and 96 h). Due to post-radiation effect, the 96 h gel sample is slightly larger in net OD in the irradiated area than that of the 0.5 h sample. However, the half height width of OD distribution curve keeps the same ($\pm$9.9 mm. This indicates that assembling PCDA monomers into nanovesicles prevents effectively the diffusion of monomer molecule. No diffusion effects were observed in the high dose gradient area of PCDA vesicle gel samples, and the dose distribution image is clear.

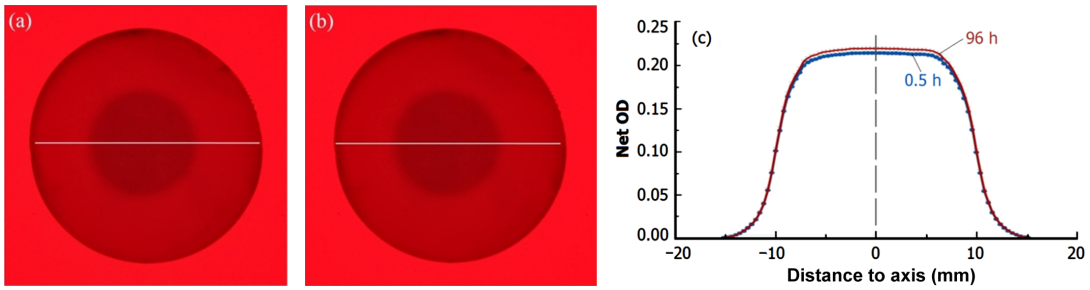


Fig. 8. (Color online) Filter (680 nm) photos of gel slices taken at 0.5 h (a) and 96 h (b) after irradiation, and their radial net OD distribution (c).

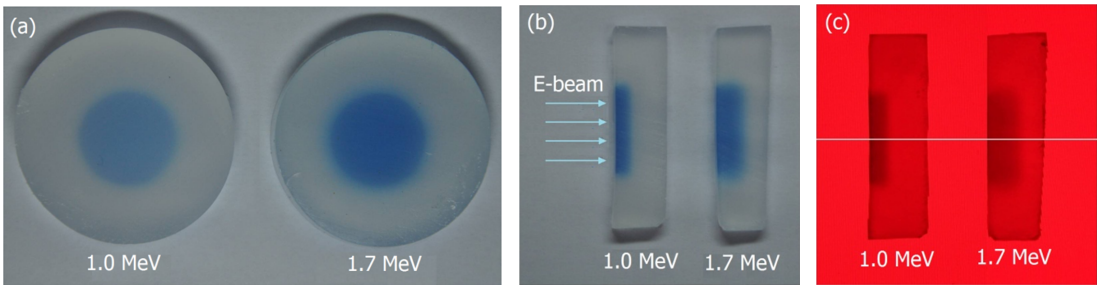


Fig. 9. (Color online) Cylindrical gels irradiated by ϕ2 cm E-beams (a), and normal (b) and filter (c) photos of the irradiated gel slices.

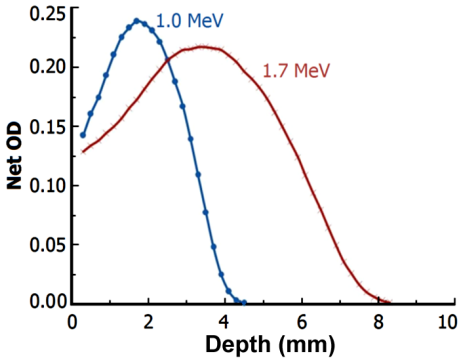


Fig. 10. (Color online) Depth-net OD distribution curves of gels.

E. Depth OD distribution test

Two cylindrical gels irradiated by 1.0 and 1.7 MeV E-beams are shown in Fig. 9(a). The highest absorb doses in gels calculated with M-Carlo methods were 2.80 kGy (at 1.7 mm depth) and 2.54 kGy (at 3.3 mm depth), respectively. The gel slices penetrated by the E-beams (Fig. 9(b)) are photographed by the digital camera with the same settings as in Sec. II B 3. The filtered photo (Fig. 9(c)) was converted to a gray-level image with Image-Pro Plus software and the gray levels of the points on the line in Fig. 9(c) were then obtained. The gray levels were converted into the net optical densities using Eq. (1). The depth profiling of net OD derived from the gel gray-level image is shown in Fig. 10. The energy deposition of electron beam in the gel is similar to that of a human soft tissue. When electron beams enter the gel sample, the energy deposition increases to a maximum value that is close to the secondary electron's maximum range in the gel sample, and then decreases gradually.

IV. CONCLUSION

Due to the high spatial resolution, dose accuracy, and tissue equivalence, gel dosimeters could potentially be applied to 3D dose distribution measurement of high dose gradient radiation field. The radiation polymerization process of PCDA monomers is not affected by oxygen, and the polymerization product exhibits intense color, leading to a response that is approximately proportional to absorbed dose [17]. In this study, nanovesicles self-assembled by PCDA monomers with amphiphilic surfactant structure, were dispersed into the tissue equivalence gel matrix to develop a novel radiochromic gel dosimeter. The design of the nanovesicles significantly overcomes the dose image blurring caused by the diffusion of monomer molecules, and at the same time limits the polymer chain growth within the vesicle which reduces the post-radiation effect. The gel matrices prepared in this study possess excellent tissue equivalence and elastic strength and could be arbitrarily shaped or cut. Hence, the radiochromic PCDA vesicle gel dosimeters developed within this work overcome the limitations of the existing gel dosimeters, and are generally suitable for 3D dose distribution measurement with optical readout.

In this work, all optical density data was acquired from gel slices with spectrophotometer or digital camera. How-

ever, the mechanical slicing technique is time-consuming and may decrease precision. In the further work, if non-destructive scanning techniques can be successfully applied to the radiochromic gel dosimeters, then the overall efficiency and precision of the dosimetry system will be effectively increased.

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