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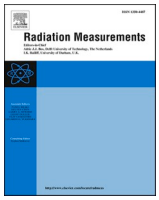

Radiochromic reactions in repetitive X-ray irradiations of a novel gel complex composed of polyvinyl alcohol, iodide, and silica nanoparticles (PAISiN)

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ABSTRACT

Radiochromic materials have good potentials for the prompt on-site detection of accidental high-dose exposure. One of the drawbacks of using these materials on various occasions is that they cannot generally be reused after coloration. In the present study, a recently developed radiochromic complex composed of polyvinyl alcohol, iodide, and silica nanoparticles named "PAISiN," was repeatedly annealed at 40 °C for 3 h and irradiated with X-rays (160 kV, 6.3 mA) at 8, 4 and 2 Gy(H_2O) each up to a total dose of 24 Gy. RGB color images of the PAISiN samples were acquired with a flatbed scanner and analyzed using image processing software. As results, PAISiN showed reproducible responses in all fractionated dose levels. Additionally, it was confirmed that the PAISiN samples annealed after repetitive irradiation maintained a stable white color for 12 days at room temperature. From these findings, it is expected that PAISiN could be used repeatedly and effectively for personal monitoring of accidental high-dose exposure under normal indoor conditions.

1. Introduction

Contemporary radiation monitoring is generally based on a dosimeter worn on the chest or abdomen, which provides an estimate of the whole-body personal dose. Meanwhile some of those who handle radiation in medical and industrial settings are at risk of significant radiation exposure of their extremities, particularly their hands (Zargan et al., 2007; Vanhavere et al., 2008; Parikh et al., 2017; ARPANSA, 2017; Adlienea et al., 2020). The local doses received by extremities could be much higher than the skin dose limit recommended by the International Commission on Radiological Protection (ICRP) (ICRP, 2007), even though whole-body doses were recorded to be insignificant (Parikh et al., 2017, ARPANSA, 2017). As work often necessitates a complex posture and movement of the body, it is difficult to determine the precise dose distribution in the extremities. Although some of the small luminescence dosimeters can be used for local dose monitoring at a specific location of the extremities, these dosimeters need special, exclusive readers and thus would not be able to meet the need for on-site monitoring.

To resolve these issues, the authors have investigated the application of radiochromic materials for routine extremity dosimetry. Some of these gels have good potentials, as they autonomously change color immediately after radiation exposure. The size and shape of a gel material can be flexibly adjusted to fit the purpose of monitoring. Workers could wear small gel dosimeters on their fingers while at risk of accidental exposure, so that they could confirm the radiological safety of the extremities in real time without any other instrument. In particular, under the circumstance of rescue or clean-up efforts in a nuclear accident, or when handling radioisotopes for nuclear medicine, the ability for a worker to immediately realize high-dose radiation exposure by just looking at her/his hands could enable safer work. Radiochromic materials cannot generally be reused after coloration, thus increasing the amount of waste, which may require special handling and additional costs. This has been a serious drawback of gel dosimeters in light of

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human health and environmental safety, which are high-priority issues in the current world.

To meet this need, the authors have considered using a recently developed radiochromic gel composed of polyvinyl alcohol (PVA), iodide (I) and silica nanoparticles (SiNP) (Miyoshi et al., 2016), named "PAISiN." The PAISiN autonomously changes color after several Gy γ-ray exposure which can cause tissue reactions, such as skin erythema and burn, and this color change from white to red was easily detected by the naked eye (Yasuda and Miyoshi, 2022). In addition, we consider that PAISiN is a preferable material in light of the United Nations' concept of sustainable development goals (SDGs) (Pizzi et al., 2020), as it is composed of non-toxic ingredients and can be easily produced by anyone without special equipment. Regarding reusability, it was reported that the radiation-induced coloration of PAISiN was returning to an uncolored state in hours or days depending on the dose and temperature (Yasuda and Miyoshi, 2022), which indicates that PAISiN could be reused at least one time. However, it remains unclear whether PAISiN can be reused twice or more. Thus, in the present study, the reusability and stability of this novel complex are comprehensively examined through repetitive irradiations.

2. Materials and methods

2.1. Formation of the complex

A solution of 12 nm diameter silica nanoparticles (SiNP) was prepared from an aqueous agent of SiO_2 nanoparticles (LUDOX HS-40, Sigma-Aldrich Co., Ltd., St. Louis, Michigan, United States) by washing three times using ultrafiltration with distilled water. The final SiNP solution had a density of 1.10 g cm^{-3}. In parallel, 6 ml aqueous solution of PVA (polymerization degree: 500; average saponification: 88 mol%) with concentration of 43.3 mg ml^{-1} was prepared, and mixed with 900.4 mg of potassium iodide (KI) followed by a complete dissolution using a magnetic stirrer at room temperature, creating a PVA-KI aqueous solution. Then, 12 ml of the SiNP aqueous solution was poured into 6 ml of the PVA-KI aqueous solution and thoroughly mixed. Through this process, PVA is considered to be absorbed onto the SiNP surface because of hydrogen bonding between the hydroxyl groups and those in the PVA chains.

After mixing, pH of the suspension was measured using a pH meter (Accumet Research AR50, FisherScientific) before the mixture was solidified. Each 3.6 ml of that mixed solution was poured using a dispenser into a quartz cuvette with dimensions of 12.5 × 12.5 × 58.0 mm^3 coupled with a screw-type airtight cap. The density was calculated from the measured weight and inner volume of the cuvette. Eleven samples were prepared for the present study. The selected physicochemical properties of the PAISiN samples are summarized in Table 1. The effective atomic number was derived from the atomic numbers and weight fractions of the constituent elements (Murty, 1965). Each sample became whitened and solidified in 1 h at room temperature.

2.2. Methods of irradiation

The samples of the PAISiN complex were heated at 40 °C for 3 h for annealing (i.e., to make the coloration return to an initial uncolored state) and gradually cooled to the room temperature in the oven. Three samples for each dose level were irradiated with X-rays (160 kV, 6.3 mA) at three levels: 8 Gy, 4 Gy, and 2 Gy for water (H_2O) at a dose rate of 1.25 Gy min^{-1} using a commercial X-ray irradiator (CP160 Cabinet X-ray System, Faxitron X-ray LLC, Illinois, United States). The irradiated samples were measured occasionally for approximately 5 h, and then annealed again. This annealing-irradiation-measurement cycle was repeated several times to achieve a total dose of 24 Gy for three irradiation patterns: 3 times at 8 Gy, 6 times at 4 Gy, and 12 times at 2 Gy. This total dose level was determined in accordance with the fact that the exposure to the dose greater than 20 Gy causes a serious damage to any organ/tissue for which any medical treatment could hardly work effectively (ICRP, 2007). While repetitive irradiations at 8 Gy and 4 Gy were performed in parallel using different samples, the experiment with 2 Gy irradiations was conducted using the same samples used for 8 Gy or 4 Gy irradiation after they were annealed and stored for several weeks at room temperature (around 20 °C). During this period, the stability of the background color intensity of all the samples annealed after 24 Gy X-ray irradiation was observed over 12 days.

Table 1
Selected physico-chemical properties of PAISiN.

Elemental composition[a]	K:1, Si:1, C:2, H:6, O:4, I:1
pH	8.6
Density	1.10 g cm^{-3}
Effective atomic number	38.8

[a] Si was dispersed as silica nanoparticles.

2.3. Post-irradiation analyses

Following X-ray irradiation followed by prompt scanning of color images, the PAISiN samples were stored at 25 °C in an oven (MOV-112S, Sanyo Electric Biomedical Co., Ltd., Osaka, Japan) between measurements. The color images of the PAISiN samples were acquired in reflection mode using a flatbed scanner (GT-X900, Seiko Epson Corp., Nagano, Japan) five or six times at certain time intervals for up to 5 h after irradiation. It should be noted that the use of such a common, commercially available scanner is considered beneficial for the practical application of PAISiN in various settings for routine dosimetry in laboratory, medical, and industrial facilities.

The scanned images were then analyzed using ImageJ which is an image-processing freeware developed by the National Institutes of Health and the Laboratory for Optical and Computational Instrumentation (Rasband, 2024). The original RGB images were separated into three 8-bit images of blue, green and red components using the color split function of ImageJ, as described in our previous study (Yasuda and Miyoshi, 2022). Color intensities were quantified as an average of 8-bit color values (on a scale of 0 to 255) taken from three spots with an area of less than 0.3 cm^2 each around the center of the active radiochromic part from which the background (pre-irradiation) values at the corresponding areas were subtracted. As each sample was measured in three areas, and three samples were measured for each condition, we were able to determine variation both within and between samples.

3. Results and discussion

3.1. Decolorization process for repetitive irradiations

It was confirmed that the PAISiN samples turned red when exposed to X-rays and the color became thicker with increasing dose levels (2, 4 and 8 Gy), as shown in Fig. 1. These colorations were easily detected by the naked eye, and observed to return gradually to the initial white state in a few days.

Temporal changes in the measured color intensity of the RGB components (i.e., red, green, blue, and RGB) after 8 Gy X-ray irradiation are shown in Fig. 2. The 'Run' in these plots means each repetition cycle including annealing, X-ray irradiation, and subsequent measurements. The results of the first irradiation (Run 1) were notably different from those of the subsequent irradiations (Runs 2 and 3); this reason is unclear at present. In comparison among the color intensities of different color components, the blue component consistently showed a stronger and steadier intensity than the other color components. While the higher sensitivity of the blue component was accompanied by higher sample-to-sample variation in our recent study (Yasuda and Miyoshi, 2022), here the blue component showed lower variation between samples in addition to higher sensitivity. In another study, the light absorbance of a thin

Fig. 1. A photograph of PAISiN samples; from the left, unirradiated one and those in few minutes after irradiation with X-rays (160 kV, 6.3 mA) at 8 Gy, 4 Gy, and 2 Gy, respectively.

sample of PAISiN showed a peak around 495 nm, which was a boundary wavelength between the blue light (450–495 nm) and green light (495–570 nm) ranges. Considering these findings, the blue component was selected for subsequent analyses in the present study.

The observed patterns of decolorization of the PAISiN samples irradiated repeatedly with 8 Gy, 4 Gy and 2 Gy X-rays until the total dose reached 24 Gy are shown in Fig. 3, in which the curves correspond to three levels of cumulative dose: 8 Gy, 12 Gy, and 24 Gy for all graphs (i.e., Runs 2, 4, and 6 for 4 Gy-irradiated samples and Runs 4, 8 and 12 for 2 Gy-irradiated samples). At 8 Gy, the initial colorations (the levels of radiation-induced color immediately after irradiation) and decolorization patterns for up to 5 h were almost the same for all three runs. At 4 Gy, although the initial sensitivity was comparable for all six runs, the decolorization speed was slightly faster for the first two runs than for the subsequent runs. This implies that exposure to ionizing radiation can affect the chemical property related to the radiochromic reactions. No changes in sensitivity were observed after repetitive irradiations at these dose levels (8 and 4 Gy), as expected from the one-time repetition data in our previous study (Yasuda and Miyoshi, 2022). At 2 Gy, the sensitivity was found to be progressively lower with repetitive irradiation of up to 12 times, which implies that the dosimetric property of PAISiN gradually changes in this repetition experiment carried out over a period of several weeks. This issue of long-term stability is discussed in the following subsection.

3.2. Reusability of PAISiN

The blue color intensities measured soon after annealing and also immediately after X-ray irradiation are plotted in Fig. 4 for three dose levels: 8 Gy, 4 Gy and 2 Gy. For repetitive irradiation with higher doses (4 Gy and 8 Gy), both the initial color levels and post-annealing background levels were reproducible, with less than 2% change between runs, and thus PAISiN is expected to be reused effectively in this dose range (4–8 Gy).

On the other hand, in the case of 2 Gy irradiation, the background levels gradually increased with the repetition number along with the lowering of sensitivity in radiochromic reaction, as indicated in Fig. 3c also. The background color measured soon after annealing was 7.8% higher in Run 12 than in Run 1, while the increase of coloration induced by 2 Gy irradiation was relatively smaller (2.7%). It is presumed that this trend observed in only the 2 Gy samples was caused by changes in the chemical property of PAISiN over the relatively longer period (several

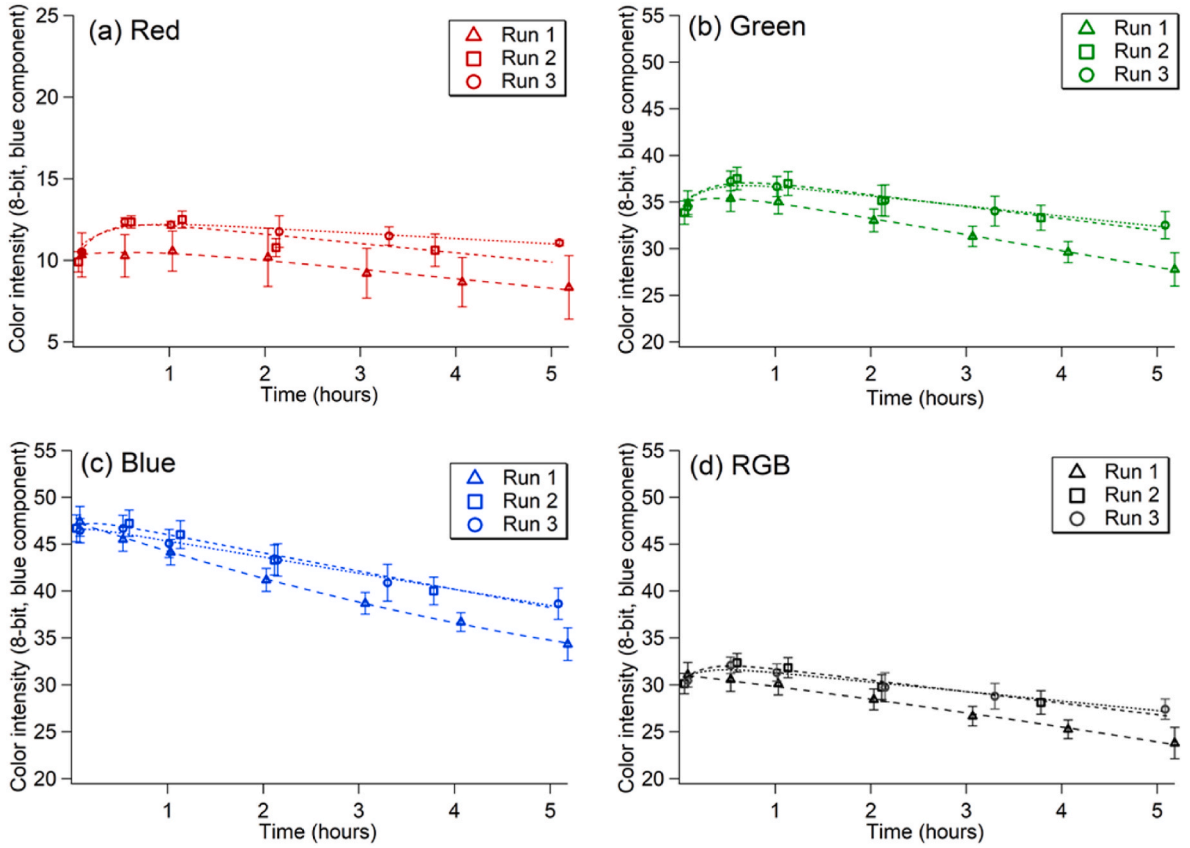

Fig. 2. Time changes of color intensity of PAISiN in three repetitive irradiations (Runs 1 to 3) with 8 Gy of X-rays regarding (a) red, (b) green, (c) blue and (d) RGB components. Error bars indicate the standard deviation of the three samples irradiated simultaneously. The samples were stored at 25 °C between measurements.

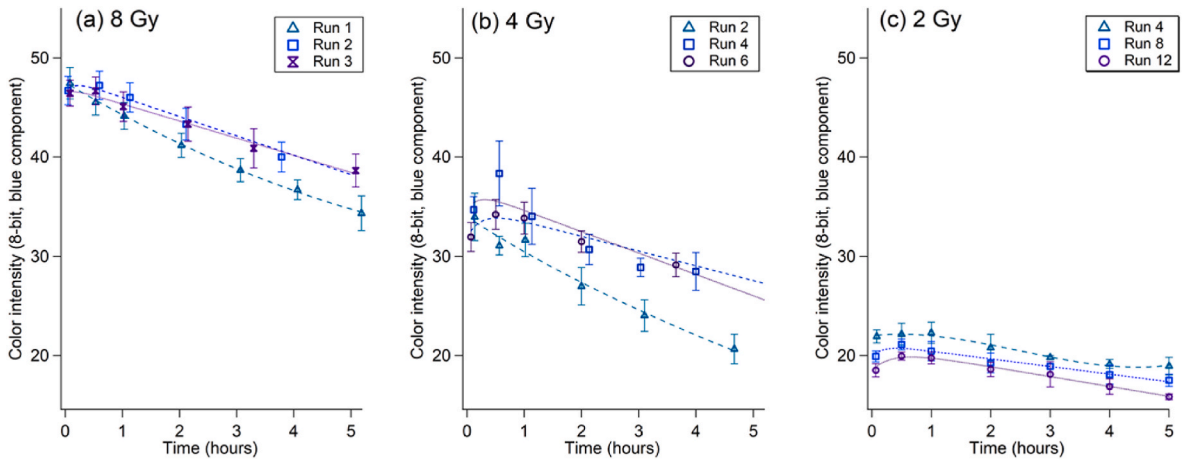

Fig. 3. Time changes of blue-component color intensity of PAISiN after 3, 6 and 12 repetitive cycles of annealing and X-ray irradiation at (a) 8 Gy, (b) 4 Gy and (c) 2 Gy, respectively. Selected data at the same cumulative doses (8, 16 and 24 Gy) are compared. The plots in (a) are the same as those in Fig. 2c. Error bars indicate the standard deviation of the three samples irradiated simultaneously.

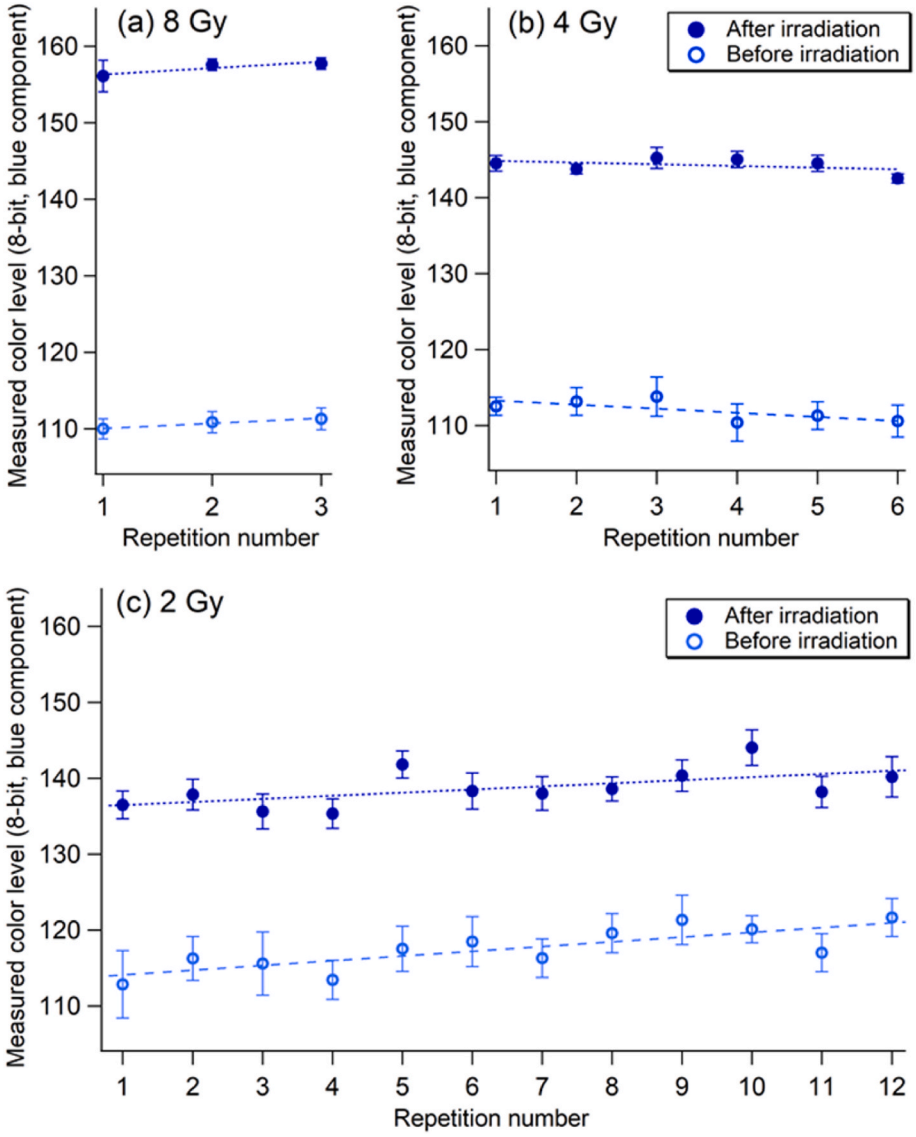

Fig. 4. The blue-component color intensities of PAISiN measured before and immediately after irradiation in repetitive cycles of annealing at 40 °C for 3 h and irradiation with X-rays (160 kV, 6.3 mA): (a) 3 times at 8 Gy, (b) 6 times at 4 Gy, and (c) 12 time at 2 Gy. Error bars indicate the standard deviation of the three samples irradiated simultaneously.

weeks) of this experiment, compared to the shortly performed experiments at 8 and 4 Gy. The authors recognize that this subject (i.e., the long-term stability of the dosimetric properties of PAISiN) should be carefully investigated in future studies using newly made PAISiN samples under rigorously controlled handling conditions.

Fig. 5 shows the temporary change in the background (post-annealing) color levels of PAISiN samples at room temperature for 12 days after completion of repeated X-ray irradiations to the total of 24 Gy (3 times 8 Gy and 6 times for 4 Gy). According to these trends, PAISiNs are expected to maintain a stable background level for a few weeks under normal indoor conditions, while the effects of longer-term storage and more repetitive irradiations are to be rigorously examined in future studies. Although PVA-I-based radiochromic gels generally show natural, autonomous coloration during the storage (Fujino et al., 2020; Taño et al., 2021; Hayashi et al., 2022; Welti et al., 2022; Rabaeh et al., 2022), this problematic auto-oxidation behavior was not observed in PAISiN even at room temperature. It should be noted that the present study confirmed the validity of the annealing condition (i.e., heating at 40 °C for 3 h) adopted by the authors (Yasuda and Miyoshi, 2022), whereas aged PAISiN samples may require a higher temperature or longer hours of heating to erase the enhanced coloration.

The present study has limitations related to the uncertainty in the time change of the structure of PAISiN. As a major issue, we lacked a comprehensive analysis of the temporal changes in the physicochemical conditions of PAISiN, which could affect its radiochromic reactions. The observed increase in the background color level during repetitive irradiation with 2 Gy X-rays (Fig. 4c) indicates that the chemical properties of PAISiN could gradually change according to an unknown mechanism. In addition, the notable change in the decolorization pattern between the first irradiation and subsequent irradiations (Figs. 2 and 3) implies some radiation-induced changes in the radiochromic properties of PAISiN. These observations warrant further experimental and theoretical studies using other analytical techniques such as infrared spectroscopy (IR), X-ray diffraction (XRD) and scanning electron microscopy (SEM) (Bhat et al., 2005).

4. Conclusions

The present study indicated a reusable feature of the recently developed radiochromic complex, PAISiN, for repetitive irradiation with 2, 4 and 8 Gy(H_2O) X-rays. The post-annealing (background) color level at room temperature was stable even after receiving a cumulative exposure to 24 Gy. These findings provide additional advantages to this novel radiochromic complex for on-site, real-time monitoring of accidental high-dose exposure, which makes PAISiN more promising than other radiochromic materials currently under development.

Meanwhile, we are continuing this study to realize the practical application of PAISiN as a radiochromic dosimeter by achieving the highest levels of radiosensitivity and reusability. More specifically, we attempt to find ways to reduce the fluctuation in decolorization patterns after repetitive irradiation and to increase the long-term stability of the radiochromic reaction over months, while seeking alternative compositions that could solve the issues raised in this study.

CRediT authorship contribution statement

Sophia E. Welti: Writing – original draft, Visualization, Investigation. **Hirokazu Miyoshi:** Writing – review & editing, Validation, Resources, Methodology. **Hiroshi Yasuda:** Writing – review & editing, Supervision, Project administration, Funding acquisition, Conceptualization.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

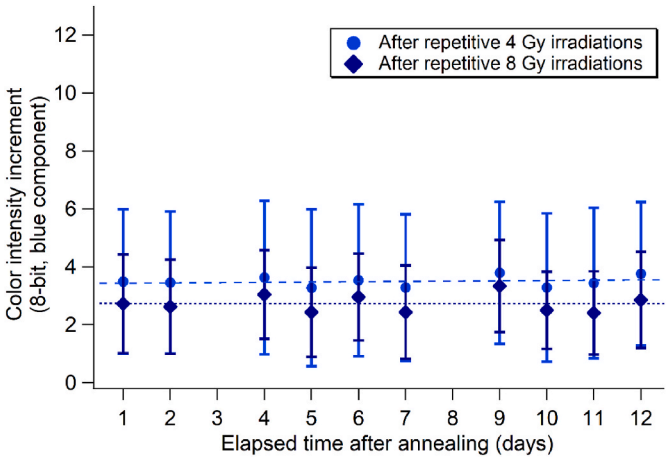

Fig. 5. Temporal change of blue color intensity over 12 days at room temperature for the PAISiN samples annealed at 40 °C for 3 h after irradiation with X-rays at 24 Gy in total (6 times at 4 Gy and 3 times at 8 Gy). Error bars indicate the standard deviation of the three samples handled under the same conditions.

Data availability

Data will be made available on request.

Acknowledgments

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