X-ray visualization and quantification using fibrous color dosimeter based on leuco dye

Phu Phong Vo¹, Hoan Ngoc Doan¹ Kenji Kinashi^{2*}, Wataru Sakai², Naoto Tsutsumi², and Dai Phu Huynh³

¹ Doctor's Program of Materials Chemistry, Graduate school of Science and Technology, Kyoto Institute of Technology, Matsugasaki, Sakyo, Kyoto 606-8585, Japan.

² Faculty of Materials Science and Engineering, Kyoto Institute of Technology, Matsugasaki, Sakyo, Kyoto 606-8585, Japan.

³ Polymer Research Center, Faculty of Materials Technology, HoChiMinh City University of Technology, Vietnam National University, HoChiMinh City 700000, Vietnam.

AUTHOR INFORMATION

Corresponding Author

*E-mail: kinashi@kit.ac.jp

ORCID

Kenji Kinashi: 0000-0003-4342-3516

Wataru Sakai: 0000-0002-0255-0861

Naoto Tsutsumi: 0000-0001-8835-1347

Phu Phong Vo: 0000-0002-6957-8519

Hoan Ngoc Doan: 0000-0001-5473-6628

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The X-ray radiation dose rate of continuous X-ray radiation from an X-ray radiation source (HW-100W, Hitex Co., Japan) with W target under operating at 70 kV and 7 mA was determined by a Fricke dosimeter. The Fricke dosimeter was prepared with 0.392 g of (NH₄)₂Fe(SO₄)₂·6H₂O, and 0.058 g of NaCl, in a 12.5 mL of 0.4 mol·L⁻¹ H₂SO₄ solution. Dilute to 1 L in a volumetric flask with air-saturated 0.4 mol·L⁻¹ sulfuric acid at 25 °C[1,2,3]. The Fricke dosimeter was content in a transparent cuvette with a 10 mm pathlength. The cuvette was exposed 60 min under an X-ray beam in the X-ray radiation system (HW-100W, Hitex Co., Japan). The exposed procedure was performed with three samples. The X-rays absorbance dose of each sample was calculated by the net absorbance of the sample. The absorbance spectrums were record by UV-Vis spectroscopy (UV-2101 PC, Shimadzu Co., Japan). The absorbed dose of the Fricke solution was calculated by the equation below:

$$D_F = \frac{\Delta A}{\epsilon \cdot \mathbf{G} \cdot \rho \cdot \mathbf{d}} \tag{1}$$

where D_F is the absorbed dose of Fricke solution (Gy), ΔA is a net absorbance at the optimum wavelength (302 to 305 nm), $\rho = 1.024 \cdot 10^3$ Kg·m⁻³ is a density of the dosimetric solution, $\epsilon = 219$ m²·mol⁻¹ at 25 °C is a molar linear absorption coefficient of their ferric ions (Fe³⁺), $G = 1.61 \cdot 10^{-6}$ mol·J⁻¹ at 25 °C is a radiation chemical yield of the ferric ion (Fe³⁺), mol·J⁻¹ and d is an optical pathlength of the dosimetric solution in the cuvette m[3]. The change of absorbance spectrum is shown in Figure S1. The system was exposed to estimated X-ray dose rates of 0.71 Gy min⁻¹.



Figure S1: Absorbance spectra of the Fricke dosimeter before and after X-ray exposure.

The FTIR spectra of each component and fibers composite were determined by an FTIR spectrophotometer (FTIR-4700 with ATR PRO ONE equipped with a diamond prism, Jasco Co., Japan) were shown in Figure S2. As shown in Figure S2, the ATR-FTIR spectrum of the composite fibers shows transmittance at 3370, 3020, 2924, 1775, 1175, and 830 cm⁻¹. These bands are assigned to aromatic C–H stretching (3025 cm⁻¹), terminal methylene C–H stretching (2924 cm⁻¹) of PS in composite fibers, N–H stretching (3370 cm⁻¹) and C = O stretching in lactone rings (1775 cm⁻¹) of Black305 in composite fibers, C–O stretching (1175 cm⁻¹) and C–Cl stretching (830 cm⁻¹) of MBTT in composite fiber[4]. The composite fibers consist of the MBTT and Black305 after the centrifugal spinning process.



Figure S2: ATR-FTIR spectra of the composite fibers, MBTT (photoacid), leuco dye Black 305, and PS fibers.

To analyze the thermal properties of the fibrous color dosimeter, the fibrous color dosimeter prepare from PS/THF 10.0/35.5 w/w consists of MBTT/Black305 3.0/3.0 and each component were used for TGA analysis. The result of the fibrous color dosimeter, and each component are shown in Figure S3. As shown in Figure S3, all the TGA curves showed no weight loss up to 230 °C. The fibrous color dosimeter can be used under high temperature. Due to the wearable-dosimeter, the effect of thermal on the sensitivity of the fibrous color dosimeters made of the composite fibers was also investigated at 20, 40, and 60 °C



Figure S3: TGA thermograms of the fibrous color dosimeter with MBTT/Black305 ratio at 3.0/3.0 w/w, Black305, MBTT, and PS fibers in air.

Three fibrous color dosimeters made of the composite fibers (MBTT/Black 305 3.0/3.0 w/w) were prepared. These samples were exposed under X-ray with 20, 40, and 60 °C. Dose-response curves for the fibrous color

dosimeters made of the composite fibers irradiation at different temperatures were obtained by plotting the chromaticity difference (ΔE) against the exposure dose at an exposure rate of 0.71 Gy min⁻¹. These plots are shown in Figure S4.



Figure S4. Dose-response curves of the fibrous color dosimeters made of the composite fibers consist of MBTT/Balck305 3.0/3.0 by weight at different temperatures (a) 20, (b) 40, (c) 60 °C. The color bar signifies the color tone corresponding to ΔE . The black broken line indicates the point at which color change can be visually observed.

As shown in Figure S4, the sensitivities (absorbed dose at $\Delta E = 10$) increased when the increasing temperature. The sensitivities were 15.36, 14.92, 10.00 Gy at 20, 40, 60 °C, respectively. In the reaction scheme, the first step is a fast photolysis step, and the rate constant is not affected by temperature. However, the second and the third steps are slow thermodynamic processes and control the colored form of Black305 that contributes to the chromaticity difference ΔE . At higher temperatures, the thermodynamic processes are faster, and the fibrous color dosimeters made of the composite fibers more sensitive.

REFERENCES

(1) Tsuchida, H., Nakamura, R., Kinashi, K., Sakai, W., Tsutsumi, N., Ozaki, M., & Okabe, T. Radiationinduced colour changes in a spiropyran/BaFCl:Eu2+/polystyrene composite film and nonwoven fabric. *New Journal of Chemistry*, **2016**, *40*(*10*), 8658–8663.

(2) Kinashi, K., Iwata, T., Tsuchida, H., Sakai, W., & Tsutsumi, N. Composite Resin Dosimeters: A New Concept and Design for a Fibrous Color Dosimeter. *ACS Applied Materials and Interfaces*, **2018**, *10*(14), 11926–11932.

(3) ASTM, Standard and E1026-04e1, "Standard Practice for Using the Fricke Reference-Standard Dosimetry System," ASTM International, West Conshohocken, PA, 2004, www.astm.org.

(4) Iwata, T., Kinashi, K., Doan, H. N., Vo, P. P., Sakai, W., & Tsutsumi, N. Leuco-Based Composite Resin Dosimeter Film. *ACS Omega*, **2019**, *4*(6), 9946–9951.