Solid Film Device to Visualize UV-Irradiation

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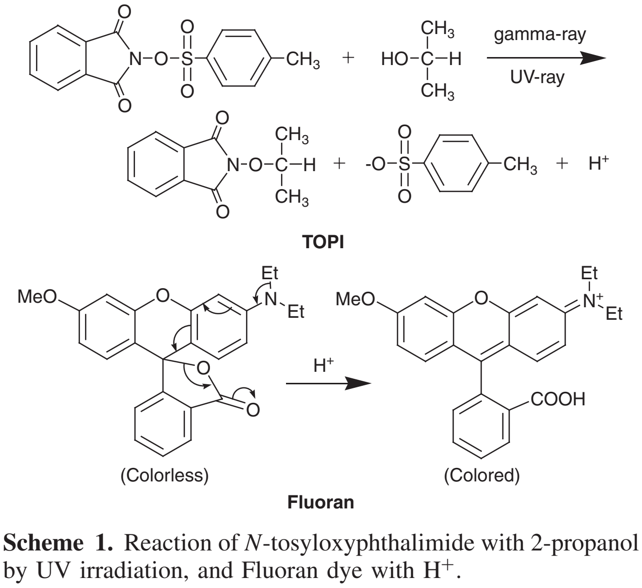
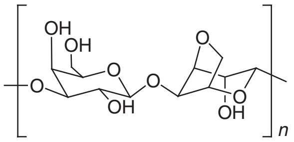
A solid film device capable of visualizing ultraviolet ray irradiation was created using a nanohetero-structured polysaccharide solid containing acid generator, dye and 2-propanol medium.

It is important to detect harmful UV- and γ-rays, for which it is preferable to visualize such irradiation to judge in situ the degree of exposure. It is also of importance to design a solid state device rather than a delicate detector comprising a solution. There have been solid films for visualizing the degree of γ-rays. However, their sensitivity was only low, and the detection with high sensitivity has been only possible with a solution system. One of the authors reported a highly sensitive detection system composed of a 2-propanol solution containing a dye (3′-methoxy-6′-diethylamino-spiro[isobenzofuran-1(3*H*),9′-[9*H*]xanthene]-3-one, Fluoran dye) and an acid generator (*N*-tosyloxyphthalimide, TOPI) for γ-ray (Scheme 1).[1] We have investigated to make a solid state device based on this detection by solution. At first, we performed trials to make a solid state device from the dye and acid generator adsorbing the reactants onto silica gel, porous glass, or cellulose paper. One of the authors has reported that a cellulose paper can be used as a matrix for a photochemical reaction to occur.[2] However, these trials to use dry solid state materials were unsuccessful showing that alcohol liquid is essential for the reaction. We have reported an interesting tight and elastic polysaccharide solid containing excess liquid wherein chemical reactions can take place the same as in a solution.[3] In the present paper we have succeeded in utilizing this solid to construct a film device to detect visually UV irradiation.



Scheme 1. Reaction of *N*-tosyloxyphthalimide with 2-propanol by UV irradiation, and Fluoran dye with H$^+$.



1 (agarose)

The solid was prepared from agarose[4] (**1**). 2-wt % agarose powder (from Acros Organics) was put in pure water, heated on a hot plate, and then irradiated very carefully by a high frequency wave (2.45 GHz) in an electric oven to entirely solubilize the material. This 2-wt % agarose/water solution was poured into a mold (20 × 10 × 2-mm size) made of glass. After cooling the clear solution to room temperature, an agarose solid film containing excess water was prepared. This agarose solid was soaked in 2-propanol to exchange water by 2-propanol, and this procedure was repeated three times in three days. Then, this solid containing excess 2-propanol was soaked in a 2-propanol solution containing the dye (0.3 mmol dm^{-3}) and acid generator (1.5 mmol dm^{-3}) to substitute the 2-propanol liquid by the solution, and this procedure was repeated three times in two days. This solid film (thickness; 1.85 mm) containing the dye and acid generator was put in a case (15 × 5 × 2-mm size) made of nonfluorescent slide glass and adhesive resin. This film was irradiated with UV-ray from black-light (366 nm, 1.54 mW cm^{-2}: MINERALIGHT® LAMP MODEL UVGL-58), and UV-vis spectrum was measured (HITACHI U-2000). The UV-vis spectral change of the agarose film is shown in Figure 1 during UV

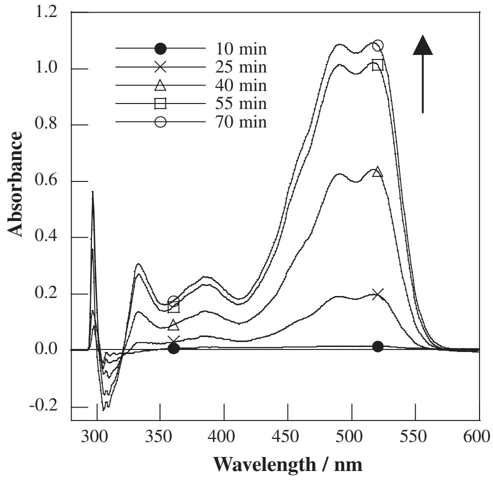


Figure 1. Absorption spectral change of Fluoran dye under UV irradiation ($\lambda = 366$ nm) in the agarose solid. Irradiation time = 10 min (●), 25 min (×), 40 min (△), 55 min (□), 70 min (○). Base line, 0 min. Optical path length, 1.85 mm.

irradiation (25, 40, 55, and 70 min). The device has shown coloration by UV irradiation with the appearance of the absorption at 518 nm ($\lambda_{\max}$ for Fluoran dye). In the dark the device was not colored. However, when the film was left without sealing, it got colored quickly probably because of humidity from the air. Since the film is sealed for the measurement in the Figure 1, coloring by other factors such as solvent evaporation and disturbance by humidity was not observed.

The absorbance increase with time in Figure 1 did not show a linear relation, but showed an induction period in the first stage of the irradiation typical for a chemical amplitude reaction, and then the absorbance was saturated. The saturated value is about one half of that estimated when assuming that the Fluoran dye concentration in the film is the same as that in the exchange solution, so that the concentration in the film would be one half of that of the exchange solution. The details are now under investigation.

Diffusion of solutes in the solid is an important factor. In order to study the diffusion of the solute in this solid, cyclic voltammogram (CV) was measured for this solid film containing Fluoran dye and coated on a basal-plane pyrolytic graphite (BPG) electrode, and is shown in Figure 2. This modified electrode was prepared by the following procedure. A 2-wt % agarose/water hot solution was at first cast onto a BPG (0.21 cm^2) electrode. After cooling to room temperature, an agarose solid film containing excess water coated on a BPG electrode was prepared. This agarose solid film electrode was soaked in 2-propanol to exchange water by 2-propanol, and this procedure was repeated three times in one day. Then, this solid film (Film thickness; 1 mm) containing excess 2-propanol coated on a BPG electrode was soaked in a 2-propanol solution containing 0.3-mmol dm^{-3} Fluoran dye and 0.1-mol dm^{-3} $LiClO_4$ (as an electrolyte) to substitute the 2-propanol liquid by the solution, and this procedure was repeated three times in one day. This modified BPG (BPG/Agarose[Fluoran + $LiClO_4$ + 2-propanol]) working, platinum counter, and Ag/AgCl reference electrodes were soaked in a 0.3-mmol dm^{-3} Fluoran dye and 0.1-mol dm^{-3} $LiClO_4$ 2-propanol solution. The voltammogram shows a feature similar to that of a non-modified BPG electrode. Apparent diffusion coefficient (D_{app}) of the Fluoran dye in the agarose solid film was estimated from the peak currents of the CV to be 6.1×10^{-7} cm^2s^{-1} in the solid. Although this value was lower than that in a 2-propanol solution (3.1×10^{-6} cm^2s^{-1}), it is evident that the Fluoran dye can diffuse in the solid similarly as in a solution.

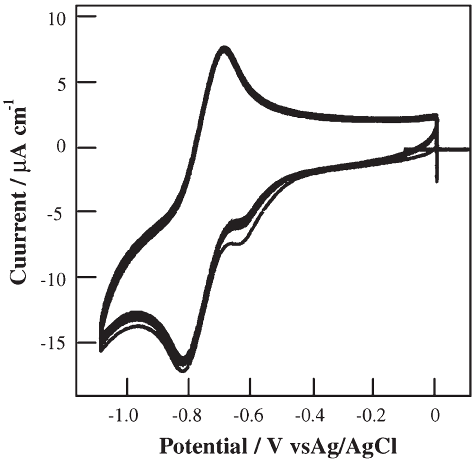


Figure 2. Cyclic voltammogram of Fluoran dye (0.3 mmol dm^{-3}) at a coated agarose solid film containing 0.1 mol dm^{-3} $LiClO_4$ electrolyte. Reference electrode, Ag/AgCl. Counter electrode, Pt wire. Scan rate, 10 mVs^{-1}. Under Argon.

Thus, a film state visualization device for the UV-ray was obtained by using the photo-acid-generating reaction in the solid made of polysaccharide.

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