Organic Photosensor in Elgraphy—Part III Enhancement of Spectral Sensitivity by Addition of Fluorescent Charge Transport Material

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The authors are engaged in developing a novel image acquisition system called Elgraphy, which is a combination of electrophotography and liquid crystal technology. One desirable property that the photosensor used for Elgraphy (Elgraphic photosensor) should have is sensitivity over a wide range of the visible spectrum in order to accurately capture color images. The authors found that, in the Elgraphic photosensor, which exhibits photocurrent amplification, the addition of a special charge transport material (CTM) to the charge transport layer (CTL) has the effect of enhancing the sensitivity in the blue light region. This effect is attributable to the following mechanism: Blue light that has passed through the charge generation layer (CGL) is absorbed by the CTM, where it excites the CTM to fluoresce in the absorption band of the CGL. The CGL absorbs the fluorescence, which induces the generation of photocarriers inside the CGL, thus giving rise to photocurrent amplification similar to the photoconduction mechanism that occurs in the green and red light regions.

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Introduction

The authors have been working on the development of a novel image capture and output system called Elgraphy,[1–3] which is a dry process featuring high resolution and high sensitivity. The intermediate storage medium consists of two parts: an organic photosensor layer (Elgraphic photosensor) and a polymer-dispersed liquid crystal memory layer (Fig. 1). The photosensor exhibits current amplification by trapping space charges generated at the interface between the electrode and photosensor layers.[4–7] When a photosensitive material consisting of a CGL and a CTL in a stack is used for electrophotography, the CTL side is commonly illuminated. However, this scheme often reduces the sensitivity of the photosensor to blue light due to the screening effect of the CTL. In Elgraphy, illumination comes from the glass substrate side, which means that the photoabsorption characteristics of the CGL directly determine the spectral characteristics of the photosensor.

The bis-azo pigments used for the charge generation material (CGM) in the Elgraphic photosensor are fairly sensitive over a relatively wide spectrum in the visible region, but the sensitivity in the blue region is insufficient. Since light is first broken down into its RGB components before striking the Elgraphic photosensor, low sensitivity in any of the R, G, and B regions can cause a problem with color balance. To avoid this, interference filters are used to adjust the intensity of the R and G components. Due to this adjustment process, the main factor determining the overall spectral characteristics of the photosensor is the sensitivity in the blue region. This report describes how the sensitivity in the blue region can be enhanced through the use of a fluorescent CTM.

Experimental

Fabrication of Photosensor

Figure 2 shows the configuration of the Elgraphic photosensor. Two charge conducting layers, a CGL,

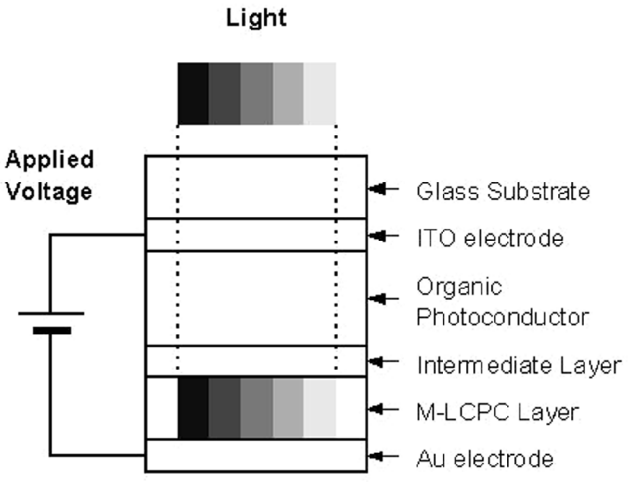

Figure 1. Structure and configuration of image receptor.

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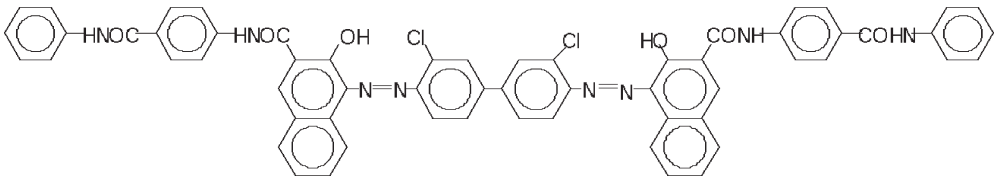


CGM: bis-azo pigment

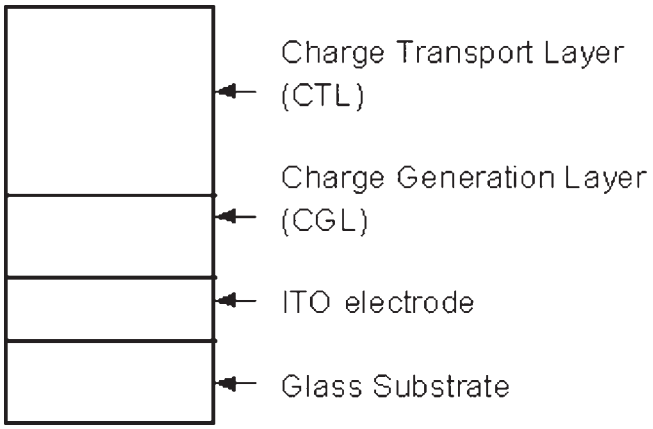


Figure 2. Structure of photosensor.

followed by a CTL, are stacked on a transparent electrode formed on a glass substrate. The CGL generates photocarriers and the CTL transports them.

The fabrication steps are as follows. The electrodes (ITO) were made on cleaned glass substrates**.** After ITO surface is cleaned, it is coated with a CGL layer by spreading an ink consisting of CGM, bisazo pigment material (Dainichiseika Color and Chemicals MFG. Co., Ltd., Japan), shown above, dispersed in polyvinylformal resin (3:1 by weight) to a thickness of 0.3 μm, and drying for an hour at 100°C.

A CTL layer is formed on top of the CGL layer. Several types of CTMs shown in Scheme 1,were mixed with polycarbonate resin (Eupiron Z400: Mitsubishi Gas Chemicals, Japan) in a ratio of 3:1 by weight. The mixtures were dissolved in a solvent mixture consisting of dichrolomethane and 1,1,2-trichloroethane, and were then spin coated on the substrate, and dried for two hours at 80°C in a clean oven. The amount applied was such that the final thickness was 10 μm after drying. Measurements were made after storing the sensor unit for three days in the dark.

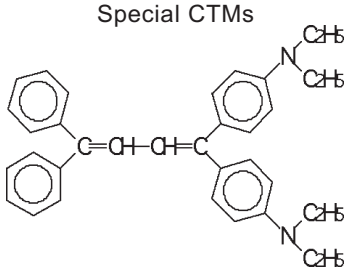
Measurement of Photocurrent

A measuring cell was made by evaporating a 4 mm × 4 mm Au electrode on the CTL surface. The circuit shown in the previous article[3] was used to measure the photocurrent and dark current. A constant DC voltage was applied across the cell, and light with a monochromatic light from a monochromator illuminated the cell while the photocurrent was monitored on an oscilloscope. All measurements were made at room temperature.

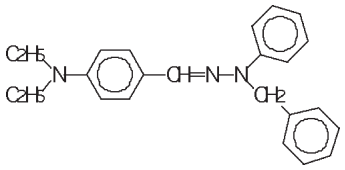
Calculation of Quantum Yield

The photoinduced current is defined to be the current obtained by subtracting the dark current from the photocurrent. The quantum yield η(t) is defined to be the ratio of the number of photogenerated electrons to the number of incident photons, and is estimated from the magnitude of the photoinduced current. The incident light had a wave-

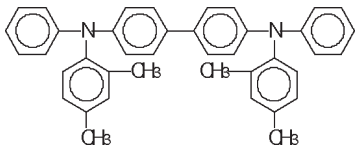
Scheme 1
Special CTMs



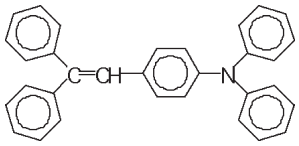
Butadiene derivative (BTD)



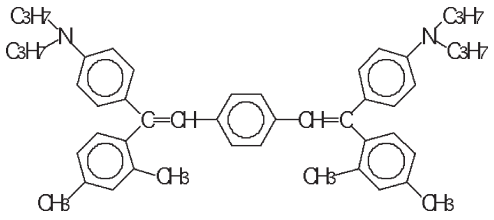
Hydrazone derivative (HDZ)



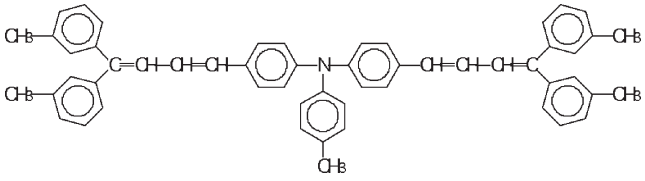
Triphenylamine derivative (TPD)



Stilbene derivative (STL)



di-butadienylbenzene derivative (DBB)



di-butadienyltriphenylamine derivative derivative (DBTPA)

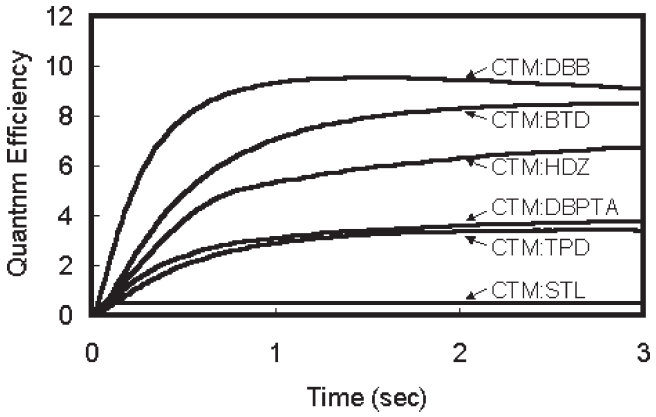


Figure 3. Change of quantum yield by light exposure (560 nm, 10 μW/cm²) at 150V applied.

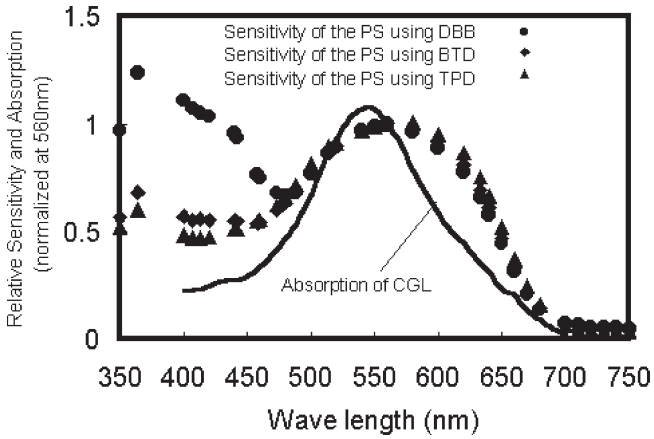


Figure 4. Absorption spectra of CGL and spectral sensitivity of photosensor (PS)**.** Spectral sensitivity curve was made by taking photo-current density measurement three seconds after exposure to monochromatic light of each wavelength under application of 120V across the photo sensor. The current density is then divided by light intensity of each wavelength, and the curve was normalized in reference to the spectral sensitivity at 560 nm.

length of 560 nm and an intensity of 10 μW/cm² (2.82×10^{13} photons/cm² sec). The quantum yield is given by:

$$\eta(t) = \frac{6.24 \times 10^{18} \times \int_0^t I(t)dt}{2.82 \times 10^{13} \times t} \quad (1)$$

where t is the exposure time (sec.), and I(t) is the induced current (A/cm²).

Measurement of Absorption and Fluorescence Spectra

Absorption spectra were measured with a Shimazu UV-240 spectrometer, and fluorescence spectra were measured with a Hitachi F4010 spectrometer.

Results and Discussion

Transient Characteristics of Quantum Yield

The transient characteristics of the photocurrent were measured for various types of Elgraphic photosensors employing BTD, HDZ, TPD, STL, DBB, or DBTPA for the CTM. All the photosensors contained measurement cells consisting of a Au electrode 4 mm × 4 mm in size, and were illuminated (560 nm, 10 μW/cm²) under an applied voltage of 120 V. The photoinduced current, which is calculated by subtracting the dark current from the photocurrent, was used to obtain the quantum yield (η). The time-wise change in η in Fig. 3 reveals that, for all the CTMs except STL, the quantum yield exceeded unity, which means that photocurrent amplification occurred. The differences in the photocurrent amplification characteristics of the various CTMs are attributable to differences in their ionization potential.[4]

Absorption Spectra of CGM and Spectral Sensitivity

The spectral response of the six Elgraphic photosensors described above was measured. The spectral sensitivity was calculated by measuring the intensity of the photoinduced current 3 s after the start of illumination with monochromatic light under an applied voltage of 120 V, and normalizing the current by the intensity of the illumination at the given wavelength.

Figure 4 shows the absorption spectra of the CGL and the sensitivity for three types of Elgraphic photosensors (namely, those with a CTM of BTD, TPD, or DBB) relative to the spectral sensitivity at 560 nm. The spectral sensitivity of photosensors with a CTM of BTD or TPD showed a reasonable correlation with the spectrum of the CGL, with a slight shift in the peak sensitivity toward longer wavelengths. However, the photosensor with a CTM of DBB exhibited enhanced sensitivity in the blue region (350–450 nm). No such enhancement was observed in photosensors with a CTM of HDZ or STL, but it was again observed when the CTM was DBPTA. These results indicate that the material used for the CTM affects the spectral distribution of sensitivity of the photosensor.

Possible Mechanism of Blue Sensitivity Enhancement

Enhanced sensitivity was observed in the region of the spectrum where the CGL does not absorb light, and the enhancement characteristics were different for the various CTMs. Based on this observation, it is thought that the blue component of the incident light that is not absorbed by the CGL reaches and is absorbed by the CTM, and the following three phenomena occur (Fig. 5).

(1) The CTM fluoresces and the CGL absorbs the fluorescence and generates photocarriers, which are trapped in the CGL, thus giving rise to photocurrent amplification.
(2) Energy is transferred from the CTM in the excited state to the CGM, and photocarriers are generated in the CGL. The electrons thus generated are trapped in the CGL, giving rise to photocurrent amplification.
(3) The CTM produces photocarriers, and these electrons are injected into the CGL, where they are trapped, thus inducing photocurrent amplification.

Photoconductivity of CTM

One possible mechanism that explains the enhanced spectral sensitivity in the blue region is the generation of photocarriers by DBB and DBPTA by light in that region of the spectrum. To examine the photoconductivity

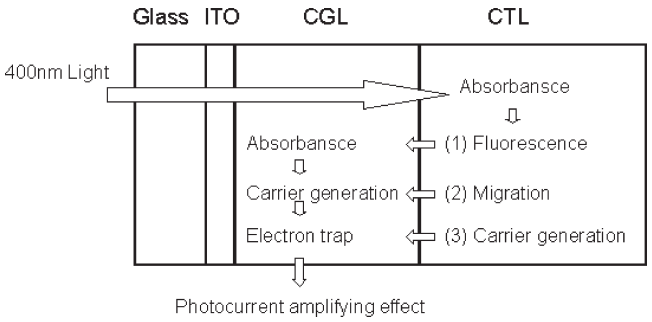


Figure 5. Mechanism by which spectral sensitivity is enhanced in blue region

of DBB and DBTPA, we made test cells by coating an ITO electrode with a CTL layer (DBB or DBTPA; thickness: 10 μm) without a CGL, and then forming a Au electrode on top by vapor deposition to make a sandwich structure. Monochromatic light with a wavelength of 400 nm and a much higher intensity (100 μW/cm²) than for normal spectral measurements, and an applied voltage of 150 V were used. Under these conditions, no generation of photocurrent was observed. From these results, it can be concluded that the enhanced sensitivity in the blue region is not attributable to the photosensitivity of DBB or DBTPA in that region of the spectrum.

Absorption and Fluorescence Spectra of CTM

The absorption and fluorescence spectra of six types of CTL with a CTM of BTD, HDZ, TPD, STL, DBB, or DBTPA were measured. In these samples, there was no binder in each CTL to eliminate the effect of binder. The thicknesses of CTLs without binder were also 10 μm. The fluorescence spectra were measured using an excitation wavelength of 380 nm, at which the enhancement of the spectral sensitivity was the largest. Figures 6(a)-(c) show absorption and fluorescence spectra for BTD, TPD, and DBB, respectively. Absorption band for CGL is also shown here. Table I lists the peak absorption wavelength (λ_{abs}), the peak fluorescence wavelength (λ_{lum}), and the maximum relative fluorescence intensity (I) of the different CTMs. It also shows the ratio of the spectral sensitivity at 400 nm to that at 560 nm (S_{400}/S_{560}) for photosensors with the various CTMs without binder.

The fluorescence peak is at 499 nm for BTD and 493 nm for HDZ. However, both of these peaks are more than one order of magnitude less intense than those of DBB and DBTPA, and no enhancement of the spectral sensitivity was observed in the blue region for those materials. TPD and STL exhibit strong fluorescence peaks at 405 and 467 nm, respectively; but neither of them exhibits enhanced spectral sensitivity in the blue region. These results can be attributed to the fact that, as is shown in Figure 6(b), the fluorescence regions do not overlap the absorption band of the CGL. On the other hand, DBB and DBTPA emit strong fluorescence at 497 nm and 491 nm, respectively, which are within the absorption band of the CGL. Enhanced sensitivity was observed in the blue region with these materials, and the values of S_{400}/S_{560} were twice as large as those of the other CTMs. In these samples there were no binders in CTMs, therefore, the values of S_{400}/S_{560} were smaller than that of Fig. 4, because of a self-quenching effect.

Based on these observations, it seems that the sensitivity is enhanced by the following mechanism: The CTM

Table I. Absorption and Fluorescence Characteristics of Various Types of CTMs.

CTM	λ_{abs} (nm)	λ_{lum} (nm)	I	S_{400}/S_{560}
BTD	402	499	14.7	0.22
HDZ	403	493	19.9	0.23
TPD	350	405	820	0.20
STL	374	467	1730	0.21
DBB	400	497	311	0.39
DBPTA	416	491	770	0.41

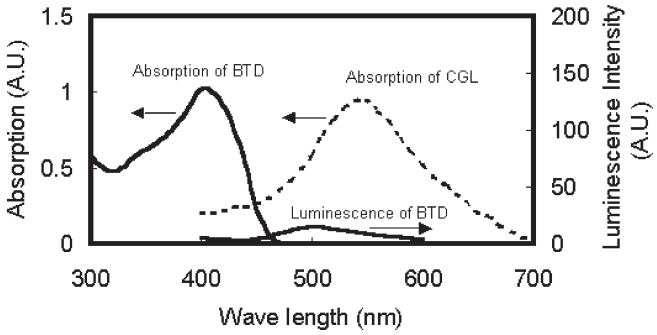


Figure 6(a). Absorption and fluorescence spectra of CTL with a CTM of BTD. The fluorescence spectra were measured at an excitation wavelength of 380 nm.

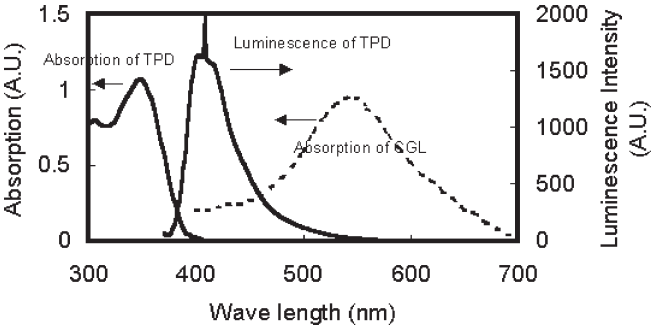


Figure 6(b). Absorption and fluorescence spectra of CTL with a CTM of TPD. The fluorescence spectra were measured at an excitation wavelength of 380 nm.

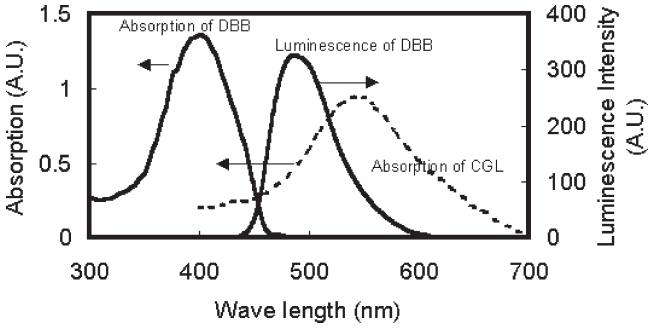


Figure 6(c). Absorption and fluorescence spectra of CTL with a CTM of DBB. The fluorescence spectra were measured at an excitation wavelength of 380 nm.

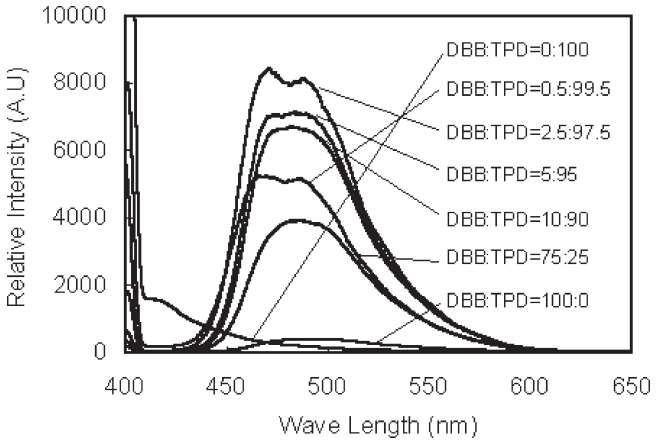


Figure 7. Fluorescence spectra of CTM consisting of a mixture of DBB and TPD. The fluorescence spectra were measured at an excitation wavelength of 380 nm.

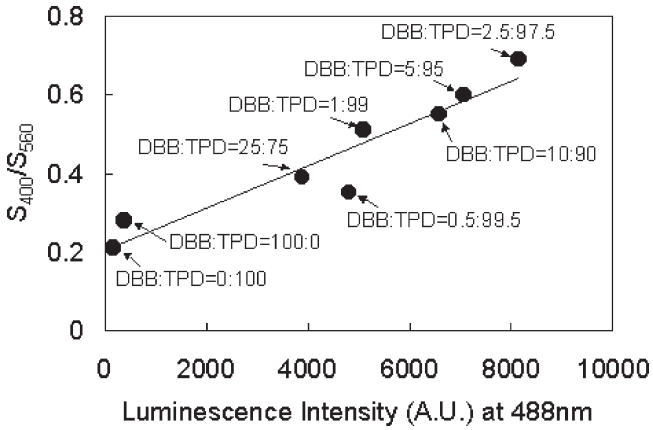


Figure 8. Relationship between fluorescence intensity and S_{400}/S_{560}. The fluorescence intensity was measured at an excitation wavelength of 380 nm.

is excited by blue light and fluoresces, and the CGL absorbs the fluorescence and generates photocarriers.

Enhancement of Spectral Sensitivity by Using Mixtures of CTMs

CTL layers were formed on glass substrates using mixtures of DBB and TPD at various ratios and illuminated at a wavelength of 380 nm. At this wavelength, DBB luminesces in the absorption band of the CGL, while TPD does not. No binder components were used in the CTLs. The results of fluorescence measurements on these CTLs are shown in Fig. 7.

Making a CTL by mixing TPD with pure DBB has the effect of increasing the intensity of the fluorescence peak at 497 nm, which is the strongest peak for DBB. The largest enhancement in peak intensity was observed at the ratio DBB : TPD = 2.5 : 97.5. A new peak emerged at 465 nm when these materials were mixed. This can be attributed to two factors: reduced extinction effects due to the lower DBB concentration, and the creation of new fluorescent sites due to the interaction between DBB and TPD.

Elgraphic photosensors were fabricated with various types of CTLs and their spectral sensitivities were measured. The graph of S_{400}/S_{600} versus fluorescence intensity in Fig. 8 shows a clear correlation between the fluorescence intensity of the CTL and spectral sensitivity, indicating that the enhanced spectral sensitivity in the blue region can be attributed to the fluorescence of the CTM. It was also confirmed that a mixture of DBB and TPD was effective in enhancing the spectral sensitivity in the blue region.

Relationship between Photocurrent Amplification and Enhancement of Spectral Sensitivity

An Elgraphy photosensor requires several days of storage at atmospheric pressure before it exhibits photocurrent amplification. During storage, the dark current and photoinduced current gradually increase. One possible explanation for this phenomena is that space charges gradually accumulate when thermally generated electrons are trapped in the CGL, thus lowering the barrier to hole injection in the photosensor. The barrier is thought to be further lowered by the accumulation of space charges due to the trapping of photogenerated electrons.[4,5]

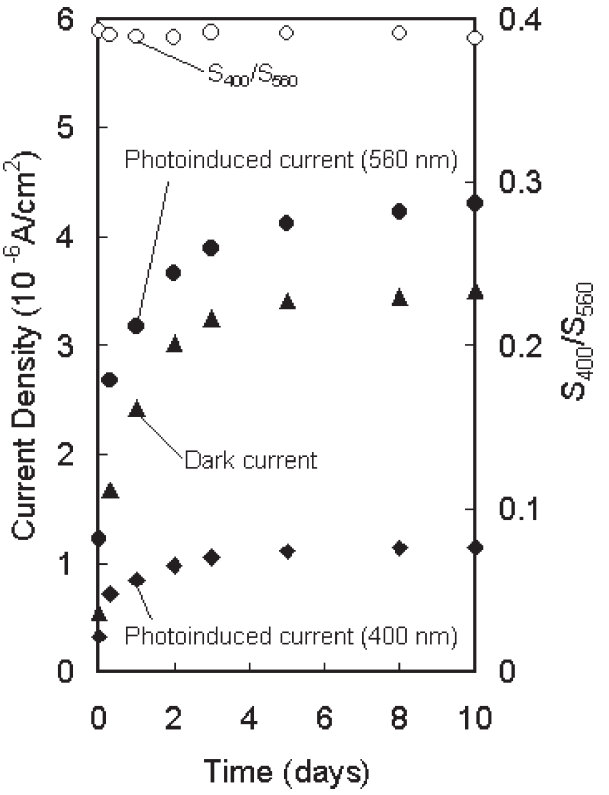


Figure 9. Time-wise change in dark and photo-induced current densities. In this experiment, the CTM was DBB. The photocurrent density was measured at wavelengths of 560 nm (10 μW/cm^2) and 400 nm (6.89 μW/cm^2). The voltage applied to the photosensor was 120 V.

To further investigate the relationship between photocurrent amplification and spectral sensitivity, a photosensor with DBB in a binder-free CTL was illuminated at wavelengths of 560 nm (10 μW/cm^2) and 400 nm (6.89 μW/cm^2) for 33 msec. Figure 9 shows how the photoinduced current, S_{400}/S_{560}, and the dark current vary over time. In this experiment, the voltage applied to the photosensor was 120 V. It can be seen that, although the

TABLE II. Enhancement of Sensitivity in Elgraphy Photosensor

Enhancement effect	Mechanism
1. Increased efficiency of photo- and thermal carrier generation	Reaction of photoinduced electrons at CGM/CTM interface
2. Amplification of photoinduced current	Electron trapping near the interface between the electrode and the photoconductive layer
3. Enhancement of spectral sensitivity in blue region	Photoabsorption and fluorescence of CTM

spectral sensitivity does not change, both the photoinduced current and the dark current increase over time in similar ways at both wavelengths. This indicates that, in the blue light region where enhancement of the spectral sensitivity is observed, and also in the red and green regions, photocarriers are generated and trapped as space charges, resulting in the flow of a photoinduced current.

Conclusions

An investigation of the Elgraphic photosensor has revealed that the mechanism by which the spectral sensitivity is enhanced in the blue light region involves the following steps: Blue light incident on the photosensor passes through the CGL and is absorbed by the CTM, which fluoresces in the absorption band of the CGL. The fluorescence absorbed by the CGL induces the generation of photocarriers, with the overall result being enhanced sensitivity in the blue region. In addition, this effect is accompanied by the generation of a photoinduced current by the same photocurrent amplification mechanism as that for green and red light, thus enabling photocurrent amplification in the blue region.

After studying various Elgraphic photosensors, the authors have discovered the three sensitivity enhancement mechanisms listed in Table II. The first enhancement effect is a photoinduced electron reaction arising from the contact between the CGM and the CTM,[6] which boosts the efficiency with which both photocarriers and also thermal carriers are generated. This increases the number of space charges inside the photoconductive layer. The second enhancement effect arises from the trapping of electrons near the interface between the electrode and the photoconductive layer, which lowers the barrier to hole injection at the interface,[4] resulting in an increase in the photoinduced current. The third enhancement effect, detailed in this article, is caused by the fluorescence of the CTM. This enhances the spectral sensitivity in the blue light region.

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