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Photocatalytic Formations of Patterning Dye Films with TiO_2 Particles Based on Chromogenic Development of Photography

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Patterning dye films were obtained on a transparent polyester plate by ultraviolet (UV) light illumination of an alkaline suspension containing TiO_2 particles, methylviologen dichloride ($MVCl_2$), *N*,*N*-*p*-phenylenediamine (PPD), and coupler. The patterning films formed are of high resolution (10 μm). Influences of light intensity (Φ), amount of TiO_2 particles, solution acidity, and illumination time on the film formation were studied. Regeneration of MV^{2+} by oxygen was found to be important for film formation.

In recent years, in order to meet the needs for fast developing science and technology, research on thin films has been the subject of continuous interest.[1)] Various methods for preparing organic thin films have been presented[2—6)] among which thin films with special patterns have also been studied extensively.[7—9)]

Recently, we reported the preparation of thin films of dyes by electro- and photoelectro-chemical methods based on chromogenic development of photography.[10,11)] In the case of photoelectrochemical film formation, a yellow dye film with a photoimage was prepared by a coupling reaction of a dye forming coupler with quinonediimine (QDI), which was a photo-oxidized product of *p*-phenylendiamine in a particulate TiO_2 suspension. In this paper, we report the detailed study of this photoelectrochemical dye film formation and discuss the mechanism.

Experimental

2-Amino-5-(diethylamino) toluene monohydrochloride (PPD), acetoacetanilide, 1-phenyl-3-methyl-5-pyrazolone, 1-naphthol (α-), and methylviologen dichloride ($MVCl_2$) were purchased from Tokyo Kasei Kogyo Co., Ltd. Anatase TiO_2 powder (P25, 21 nm average particle size) was donated by Nippon Aerosil Co., Ltd. Twice distilled water was used. All the reagents were reagent grade and were used as received.

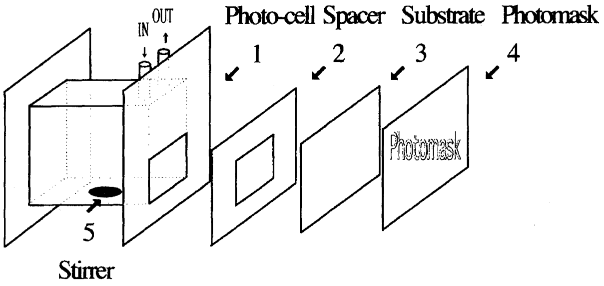
A 500 W Xenon lamp (Xenon short arc lamp UXL 500 D-O) was used as a light source. Hoya U-340 and HA-30 glass filters were used for delivering UV light. An irradiance tester (UNI METER UIT-101, sensor head: UVD-365PD, sensing range: 330—390 nm, Ushio Electric Co.) was used to measure the light intensity. Absorption spectra were recorded on a Hitachi U-3210 spectrophotometer. The scanning electron micrograph (SEM) was taken on a scanning microscope (JSM-T20, JEOL Technics Ltd.). A polyester plate was used as the substrate. This plate was cleaned by sonication in benzene for 10 min and rinsed with distilled water.

Film formation was done in a plexiglass cell (25 mL), equipped with an optical window to allow direct contact of the substrate with the solution and illumination of the incident light through a photomask and the substrate (Fig. 1). The area of the photomask's optical window was kept at 0.6 cm^2 when the amount of the dye deposited on the substrate was measured.

An aqueous suspension of TiO_2 containing the coupler was sonicated for 20 min, and then $MVCl_2$ was added. PPD was added to the suspension just before the illumination. During irradiation, moderate stirring was required to sustain a good suspension of TiO_2 particles. Buffer solutions were used to prepare suspensions.[12)] The amount of dye formed by the illumination was estimated by the absorption of methanolic solution obtained by dissolving the dye.[13,14)] For the dye deposited onto the substrate (film dye), the methanolic solution was prepared by dissolving the dye directly in methanol. For the dye deposited onto TiO_2 particles or dispersed in the suspension (non-film dye), the methanolic solution was prepared by the following procedures: a) separate the solid from the suspension by centrifugation; b) after drying, disperse the solid with methanol by sonication, followed by centrifugation.

Results and Discussion

Yellow, magenta, and cyan films were prepared by UV illumination of the suspensions containing TiO_2, PPD, and the corresponding coupler under alkaline and open air conditions. Figure 2 shows the absorption spectra of these films, which agree with those of dyes previously reported.[10)] As an



Plexiglass Photo-cell for Film Formation

Fig. 1. Photo-cell for film formation. 1, cell; 2, spacer; 3, substrate; 4, photomask.

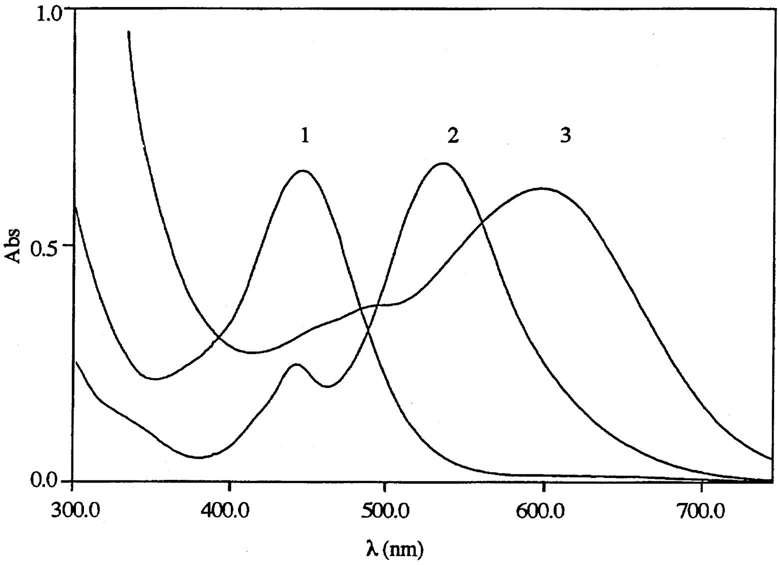


Fig. 2. Absorption spectra of dye films. 1, yellow film; 2, magenta film; 3, cyan film. Suspension conditions: 10 mM PPD, 20 mM coupler, 10 mM $MVCl_2$, and 3.0 g L^{-1} TiO_2; pH: 11; Light intensity: 2.0 mW cm^{-2}; Illumination time: 30 min; 1 M = 1 mol dm^{-3}.

example, the results for yellow dye formation will be discussed in detail. Figure 3 shows a typical photograph of the patterning yellow film. The resolution is about 10 μm. Typical SEM micrographs of the yellow film are shown in Fig. 4, which indicates that this film is composed of many islands in contact with each other. The thickness of the films is within 1 μm.

When oxygen in the suspension was purged with N_2, the color of the suspension changed to violet with illumination due to the formation of MV^+, and the film was not formed. Introduction of air resulted in rapid disappearance of the violet color, which means that oxygen is necessary for obtaining the film.

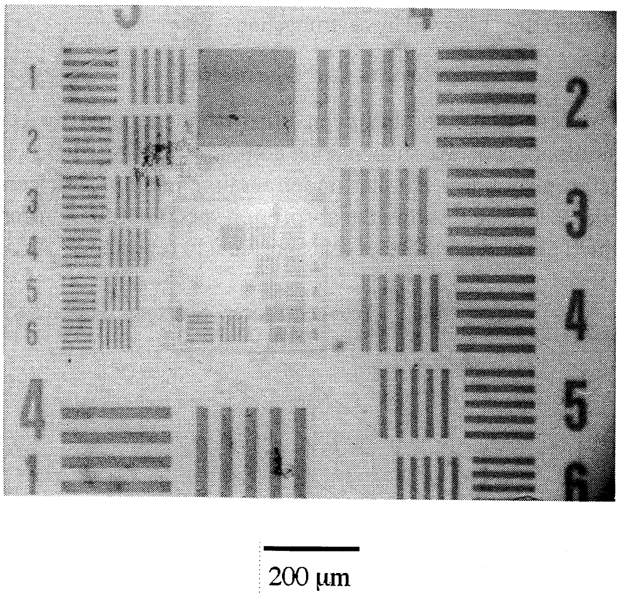


Fig. 3. Photograph of the patterned yellow film. Suspension conditions: 8 mM PPD, 5 mM coupler, 10 mM $MVCl_2$, and 3.0 g L^{-1} TiO_2; pH: 11; Light intensity: 2.0 mW cm^{-2}; Illumination time: 30 min.

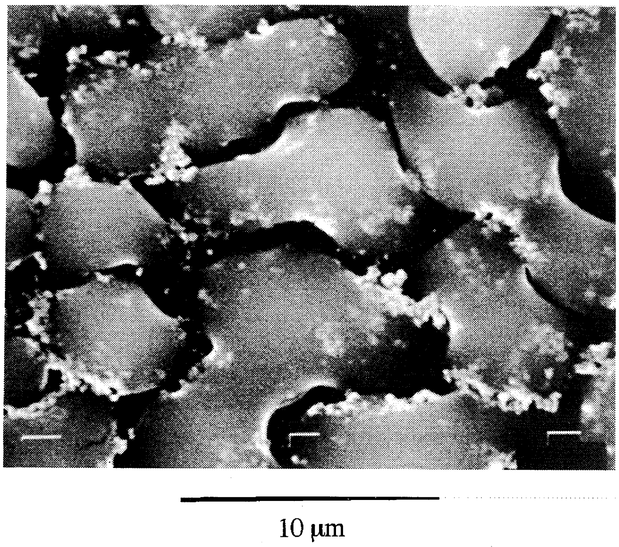


Fig. 4. SEM photographs of the surface of the yellow film. Suspension conditions: 10 mM PPD, 20 mM coupler, 10 mM $MVCl_2$, and 3.0 g L^{-1} TiO_2; pH: 11; Light intensity: 4.5 mW cm^{-2}; Illumination time: 40 min.

In a chromogenic developing process, a dye is formed by the coupling reaction of the oxidized PPD with a coupler.[15] In our research, PPD is oxidized to quinonediimine (QDI) by photo-generated holes which have a more positive potential than that of the QDI/PPD couple (−0.06V vs. SCE[11]). QDI reacts with the coupler to form dye molecules. While most of the dye molecules may deposit immediately on the surface of TiO_2 particles or disperse in the suspension, the remaining dye molecules may diffuse to the surface of the substrate and deposit on it to form the film. The role of MV^{2+} may be the removal of excess electrons in TiO_2 to prevent e^-–h^+ from recombination as itself being reduced to MV^+. An oxygen molecule reoxidizes MV^+ to MV^{2+}, thus maintaining a continuous supply of electron scavengers and preventing a back reaction between MV^+ and h^+. The following processes are reasonable:

$$\mathrm{TiO_2}+h\nu \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \mathrm{TiO_2(e^-h^+)} \tag{1}$$

$$\mathrm{TiO_2(e^-h^+)}+\mathrm{PPD} \xrightarrow{k_2} \mathrm{TiO_2(e^-)}+\mathrm{QDI} \tag{2}$$

$$\mathrm{QDI}+\mathrm{Coupler} \underset{k_{-3}}{\overset{k_3}{\rightleftharpoons}} \mathrm{I} \xrightarrow{k_4} \mathrm{Dye} \tag{3}$$

$$\mathrm{TiO_2(e^-)}+\mathrm{MV^{2+}} \xrightarrow{k_5} \mathrm{TiO_2}+\mathrm{MV^+} \tag{4}$$

$$\mathrm{MV^+}+\mathrm{O_2} \xrightarrow{k_6} \mathrm{MV^{2+}}+\mathrm{O_2}^- \tag{5}$$

I is the leuco dye intermediate, k_1, k_{-1} are the generation and recombination rate constants of photo-generated e^- h^+ pairs in TiO_2, k_2, k_3, k_{-3}, and k_4 are the rate constants of QDI formation, of I's forward and backward reactions, and of the final dye formation. The coupler dissolved in water partially dissociated to a coupler anion.[11,16]

The influence of light intensity (Φ) on the amounts of film dye and the non-film dye is shown in Fig. 5. With an increase in Φ, the amount of film dye increases linearly up to about 0.5 mW cm^{-1} and then increases gradually. On the other hand, the amount of the non-film dye increases rapidly and then increases gradually. When there was no light illumination, some amount of the dye was still formed, but the film and the photoimage were not formed on the substrate. That means that PPD was oxidized to QDI slowly by oxygen in the air. The ratio of the film dye to the non-film dye is shown in Fig. 6, which increases with the increase in light intensity, meaning that higher light intensity improves the efficiency of film deposition.

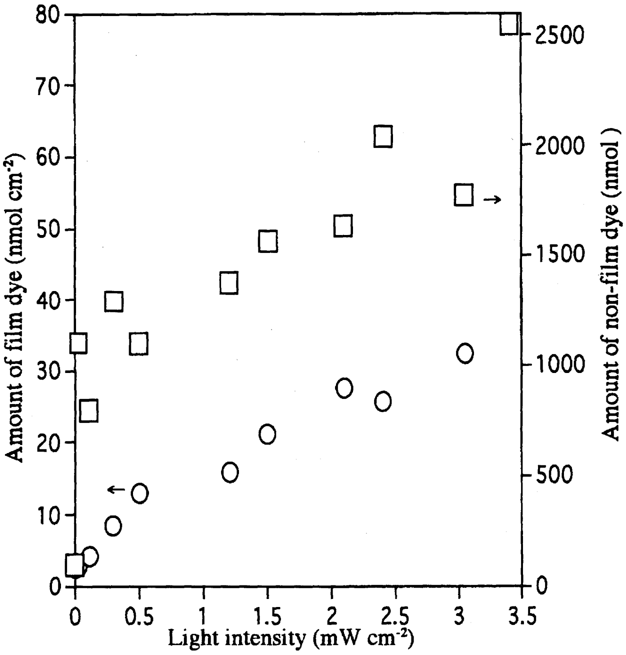


Fig. 5. Influence of light intensity on the amount of film dye and non-film dye. Suspension conditions: 10 mM PPD, 20 mM coupler, 10 mM $MVCl_2$, and 4.8 g L^{-1} TiO_2; pH: 11; Illumination time: 20 min.

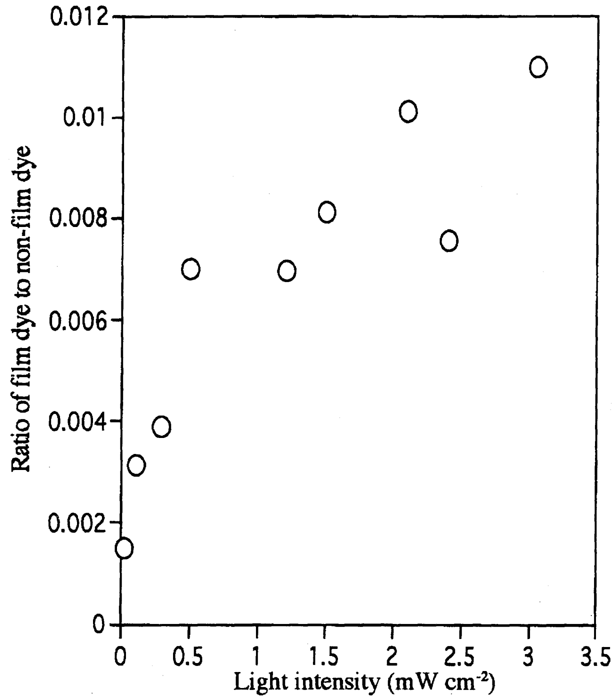


Fig. 6. Influence of light intensity on the ratio of film dye to non-film dye. Suspension conditions: 10 mM PPD, 20 mM coupler, 10 mM $MVCl_2$, and 4.8 g L^{-1} TiO_2; pH: 11; Illumination time: 20 min.

From reactions (2) and (3) and by the steady-state approximation that the net rate of formation of QDI is zero and other side reactions are assumed to be negligible, the following equations are obtained:

$$[\mathrm{QDI}]=k_2[\mathrm{PPD}][\mathrm{h^+}]/k_c[\mathrm{C^-}] \tag{6}$$

$$\mathrm{d}[\mathrm{Dye}]/\mathrm{d}t=k_c[\mathrm{QDI}][\mathrm{C^-}]. \tag{7}$$

The parameters $k_c=k_4k_3/(k_{-3}+k_4)$,[16] [PPD], [QDI],[C$^-$], [Dye], and [h$^+$] are the concentrations of PPD, QDI, dissociated coupler anion, dye, and photogenerated holes at the TiO_2 surface, respectively.

When an n-type semiconductor's depth of space charge layer and energy barrier height are constant, [h$^+$] is proportional to the intensity (Φ) of the incident light.[17] By introducing Eq. 6 into Eq. 7, we obtain Eq. 8:

$$\mathrm{d}[\mathrm{Dye}]/\mathrm{d}t=k_2k_\Phi[\mathrm{PPD}]\Phi, \tag{8}$$

where k_Φ is a constant relating [h$^+$] to Φ.

Equation 8 means that the dye formation rate is proportional to Φ if the concentration of PPD is much higher than that of the dye formed.

The decay of light caused by the dye film deposited on the substrate with illumination time is shown in Fig. 7. This indicates that Φ first decayed rapidly and then leveled off with illumination time. During the illumination, Φ may decay owing to the absorption of the light by the dye film depositing on the substrate, the dye molecules dispersing

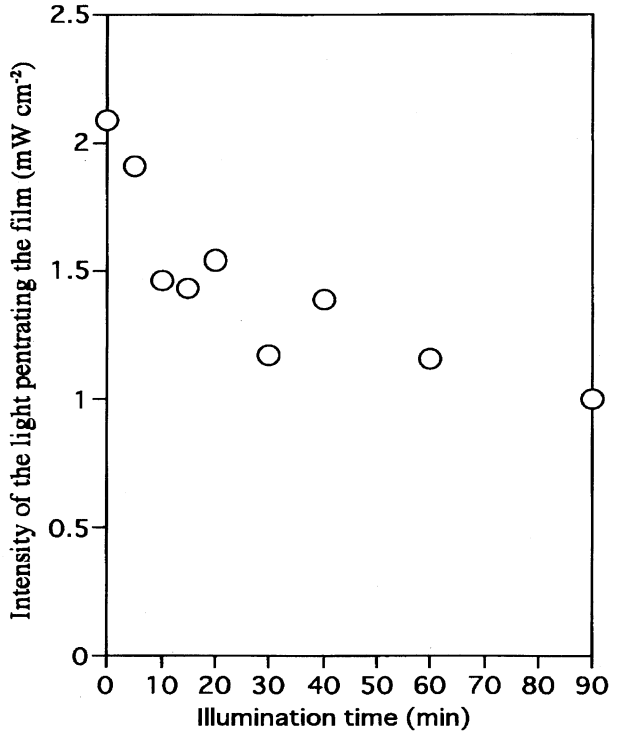


Fig. 7. Intensity variation of the light penetrating the yellow dye film. Suspension condition: 8 mM PPD, 5 mM coupler, 10 mM $MVCl_2$, and 3.0 $g\,L^{-1}$ TiO_2 at pH 11.

in the suspension, and the dye adsorbing on the surface of TiO_2 particles. As is known, most of the dye molecules deposited on the surface of the TiO_2 particles and dispersed in the suspension which resulted in decay of Φ of the light reaching "naked" TiO_2. Besides, the decrease in the effective reaction area owing to the insulating dye film formed on TiO_2 may also result in the decrease in photo-generated e^- h^+ pairs in TiO_2 particles. The changing tendencies of dye formation with the increase in Φ are explained by the above discussion.

Figure 8 shows the influence of the amount of TiO_2 on dye formation When the amount of TiO_2 is increased, the amount of film dye first increases linearly and then increases gradually. The amount of the non-film dye first increases rapidly and then increases gradually. The changing tendency in Fig. 8 is similar to that in Fig. 5. The influence of the amount of TiO_2 on the ratio of the film dye to the non-film dye is plotted as Fig. 9. The plot shows that there is little influence on the ratio of the film dye to the non-film dye when the amount of TiO_2 is larger than 1.5 $g\,L^{-1}$.

The amounts of both the film dye and the non-film dye increased rapidly with UV illumination time within 50 min (Fig. 10), then this increasing tendency slowed down. The amount of non-film dye increased sharply, especially in the first 5 min. In the early period of the illumination, the dye formation rate was very fast owing to the large "naked" surface area of TiO_2 particles. Therefore most of the dye molecules formed may deposit immediately on TiO_2 to form an insulating film. After some time, the dye formation rate decreased owing to the decrease in "naked" surface area of TiO_2. The influence of the UV light absorption by the

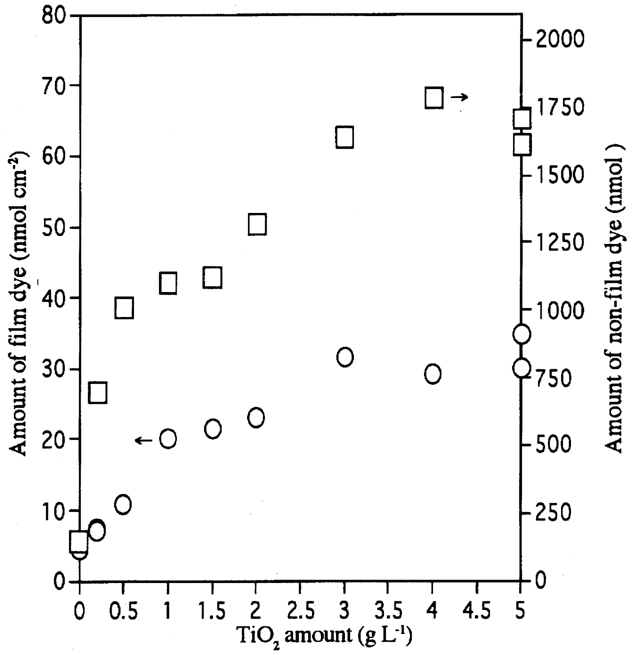


Fig. 8. Influences of TiO_2 amount on film dye and non-film dye formation. Suspension conditions: 10 mM PPD, 20 mM coupler, 10 mM $MVCl_2$, and x $g\,L^{-1}$ TiO_2; pH: 11; Light intensity: 2.0 $mW\,cm^{-2}$; Illumination time: 20 min.

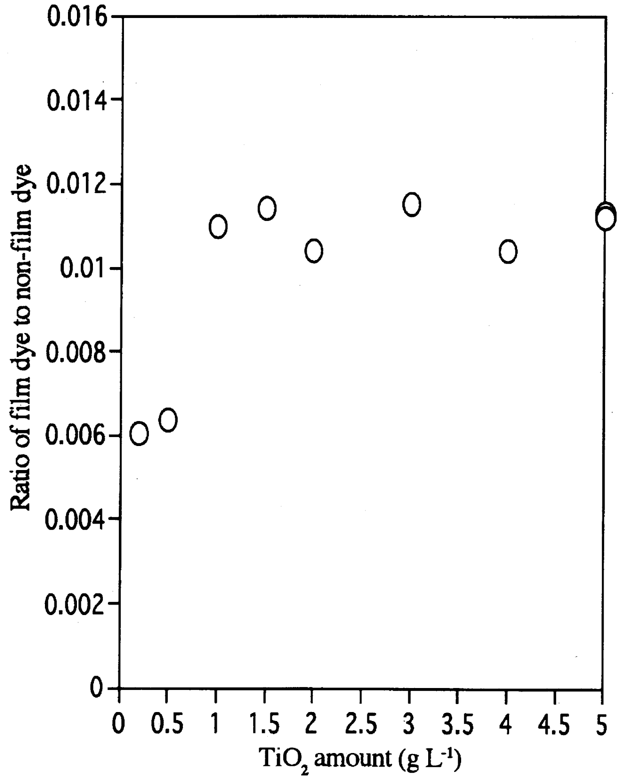


Fig. 9. Influences of TiO_2 amount on the ratio of film dye to non-film dye. Suspension conditions: 10 mM PPD, 20 mM coupler, 10 mM $MVCl_2$, and x $g\,L^{-1}$ TiO_2; pH: 11; Light intensity: 2.0 $mW\,cm^{-2}$; Illumination time: 20 min.

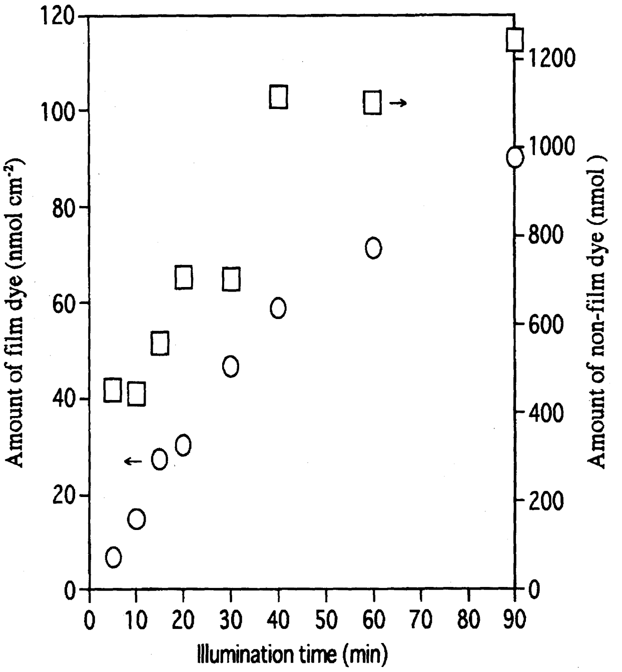


Fig. 10. Variation of the amount of film dye and non-film dye with illumination time. Suspension conditions: 8 mM PPD, 5 mM coupler, 10 mM $MVCl_2$, and 3.0 g L^{-1} TiO_2; pH: 11; Light intensity: 2.09 mW cm^{-2}.

yellow dye formed on the substrate and the surfaces of the TiO_2 particles is not significant compared to other influences, because the yellow dye shows weak absorption in the range of 300 to 400 nm (Fig. 2). Figure 11 shows the change in the ratio of the film dye to the non-film dye with illumination time. This ratio first increased rapidly and then tended to saturate with UV illumination time. Within the experimental time, at most about 5% of the dye molecules could deposit on the surface of the substrate.

The photogenerated holes oxidized PPD in the dispersion to give QDI; the latter then reacted with the coupler to form dye molecules. In the early period, enough coupler molecules could diffuse to the surface of the TiO_2 particles. So the coupling reaction usually took place at the surface of the TiO_2 particles. With the continuation of illumination, coupler molecules diffusing to the surface of TiO_2 were not sufficient to exhaust all the QDI molecules formed. Some QDI molecules could move away from the TiO_2 surfaces and even reached the surface of the substrate to react with coupler molecules there, hence resulting in the deposition of dye molecules on the substrate as islands. As the illumination continued, these isolated islands grew, due to the consecutive deposition of dye molecules around them and finally contacted each other to form a patterning film. This implies that only after some dye molecules deposit on the surface of TiO_2 and disperse in the solution, in other words, only after some time can the dye molecules deposit on the substrate.

Figure 12 shows the plots of the amount of the film dye and that of the non-film dye vs. pH. In the pH range less than 6, the film was not formed and the color of the suspension changed from white to pink. At pH 7, a very small amount of dye adhered to the substrate, but no photoimage formed. In the pH range of 8—12, the film and photoimage were formed, and the amount of film dye was greatest at pH 11. At pH

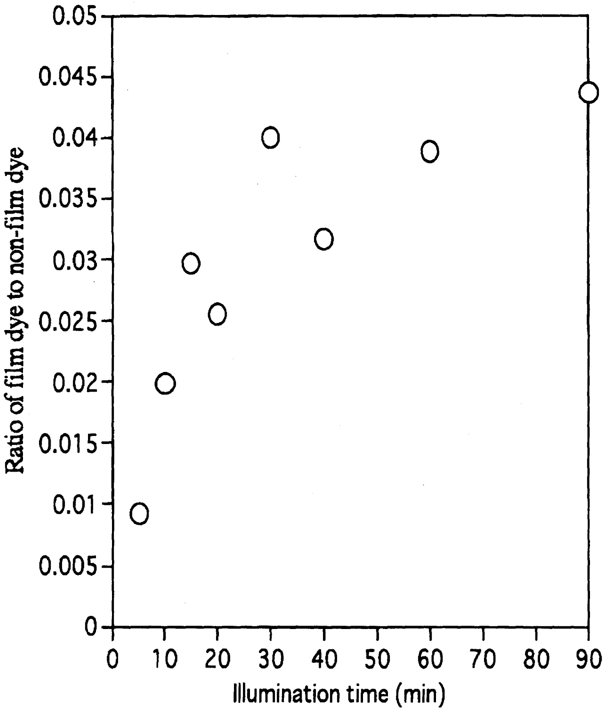


Fig. 11. Ratio of film dye to non-film dye. Suspension conditions: 8 mM PPD, 5 mM coupler, 10 mM $MVCl_2$, and 3.0 g L^{-1} TiO_2; pH: 11; Light intensity: 2.09 mW cm^{-2}.

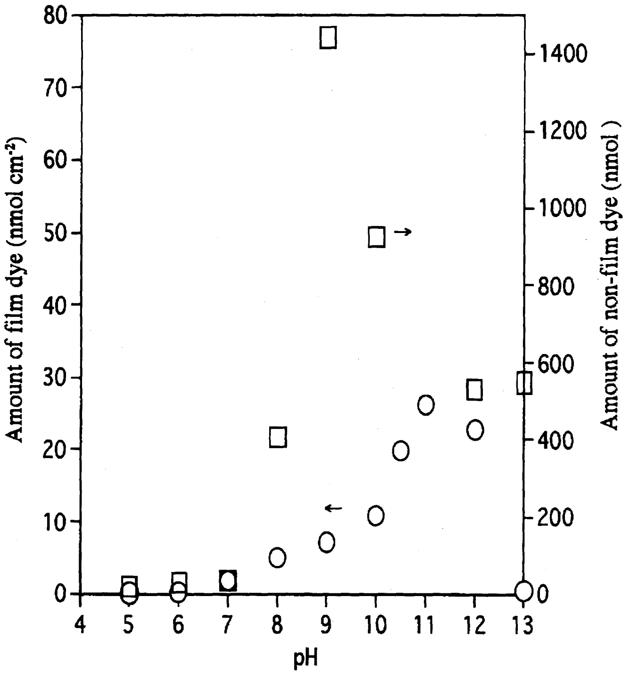


Fig. 12. Influences of pH on the amount of film dye and non-film dye. Suspension conditions: 10 mM PPD, 20 mM coupler, 10 mM $MVCl_2$, and 4.8 g L^{-1} TiO_2; Light intensity: 1.0 mW cm^{-2}; Illumination time: 20 min.

13, no film and photoimage formed. A similar dependence on pH was observed for the non-film dye except that the maximum point shifted to pH 9 and some amount of dye formed even at pH 13.

pH of the solution has a great influence on the flat band potential (E_{fb}) of TiO_2. The redox potential of the $\text{MV}^{2+}/\text{MV}^{+}$ couple (−0.69 V vs. SCE[18]) does not depend on pH. The flat band potential can be expressed as below:

$$E_{\text{fb}} = E_{\text{fb}}(\text{pH } 0) - 0.059 \text{ pH (V vs. SCE at 25 °C)} \quad (9)$$

E_{fb} (pH 0) was reported to be −0.29 and −0.38 V vs. SCE.[18,19] With an increase in pH, the driving force for the reduction of MV^{2+} also increases, owing to the negative shift of E_{fb} with respect to $E_{\text{MV}^{2+}/\text{MV}^{+}}$; hence e^- h^+ pairs are separated more effectively, which results in an increase in QDI and the amount of dye. On the other hand, the rate of the coupling reaction of the coupler with QDI also depends on pH. The following equation can be used to express dye formation rate:[11]

$$\text{d[Dye]}/\text{d}t = k_{\text{D}}[\text{QDI}] = k_3[\text{QDI}][\text{CH}]_0/(1 + 10^{\text{p}K_{\text{a}}-\text{pH}}) \quad (10)$$

Where k_3 is the rate constant of the leuco dye intermediate from the coupling reaction between coupler anions and QDI, $\text{p}K_{\text{a}}$ is the logarithm of the quotient of the acid electrolysis constant (for yellow dye, $\text{p}K_{\text{a}}=10.45$), and $[\text{CH}]_0$ and [QDI] are the concentrations of the coupler before dissociation and QDI, respectively.

From Eq. 10, the pH at which the maximum dye formation rate is reached is around 10.5. This is in accord with the experimental results. A further increase in pH resulted in a decrease in the dye forming amount. One reason may be that deamination of QDI to quinone monoimine or even quinone hindered the formation of the dye at high pH.[12,20]

Conclusions

The authors have succeeded in preparing patterning yellow, magenta, and cyan films by photoelectrochemical reactions in particulate TiO_2 suspensions. Most researchers studied the deposition of solid products onto the TiO_2 surface and photo patterning on a TiO_2 film.[21,22] This paper presents a novel method for obtaining a patterning film on a transparent and insulating substrate other than on TiO_2 surfaces. If the dye formation reaction is fast enough, all dye molecules formed would deposit on the nearest surfaces of TiO_2 or disperse in the suspension, and there would be no film formed on the substrate. In this film formation process, part of the QDI formed can still diffuse to the substrate and form dye molecules with the couplers. This is the reason why dye films and photoimages can be obtained. Such a film formation may be explained as follows: TiO_2 particles were excited to generate e^- h^+ pairs on illumination. Photogenerated h^+ oxidized PPD to QDI, while e^- was trapped by MV^{2+} to give MV^{+}, which was immediately reoxidized to MV^{2+} by O_2 in the solution. QDI reacted with the coupler dissolved in solution to form dye molecules. Dye molecules in the vicinity of the substrate were adsorbed onto its illuminated surface to form a patterning film.

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