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A Novel Photo-Induced Patterned Film Formation of Organic Pigments Using Tris(2,2'-bipyridine)ruthenium(II) and Surfactant with Ferrocenyl Moiety

Hironobu MIZUNO, Katsuyoshi HOSHINO, Jun-ichi HANNA, and Hiroshi KOKADO*†
Imaging Science and Engineering Laboratory, Tokyo Institute of Technology, 4259,
Nagatsuta, Midori-ku, Yokohama 227
† Department of Imaging Science, Faculty of Engineering, Chiba University, 1-33,
Yayoi-cho, Chiba 260

When an acidic aqueous dispersion of an organic pigment containing a ferrocene attached surfactant, a ruthenium(II) photocatalyst, and a sacrificial agent, was illuminated with light of wavelength 450 nm through a photo-masked indium tin oxide (ITO)-coated glass substrate, photo-induced reaction occurred and it deposited pigment layers not onto the illuminated region, but onto the unilluminated area of the substrate.

The film preparation of functional organic materials is an increasingly important issue, since those materials have been proposed for various electronic devices mostly in form of films. A number of methods for fabricating organic thin films have been presented.

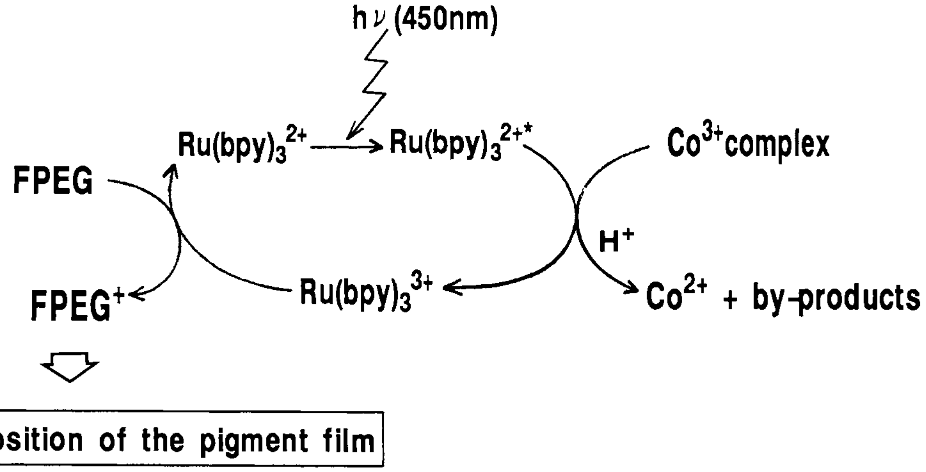
In recent years, the micellar disruption method (MD method)[1,2] has been proposed as an outstanding film-forming technique for organic materials. The MD method utilized a special surfactant with a ferrocenyl moiety. The film-formation is initiated by electrochemical oxidation of the surfactant, and subsequent desorption of the surfactants from film-forming materials leads to the deposition of the materials on a whole surface of the anodic electrode.[3] The key reaction of the MD method is the oxidation of the ferrocenyl group attached to the surfactant. If this surfactant undergoes oxidation by any compound photochemically produced in the vicinity of the substrate, the film deposition may occur according to the same scheme of the micellar break-up as the MD method but without passing electricity. This idea for film-formation motivated us to investigate a new system in this study. As a result, we succeeded in it with an unexpected effect - positive patterning. In this letter, we report this unique deposition phenomenon as well as detailed experimental procedures.

In our experiment, the surfactant used was (11-ferrocenylundecyl)polyoxyethylene glycol (FPEG, Dojin Chemical Co.).[4] The main film-forming pigment used was alfa form of metal-free phthalocyanine (H_2Pc, Tokyo Kasei Co.). In order to demonstrate the practicability of this method for wide use, pigments, such as various types of copper phthalocyanine derivatives and a perylene derivative were also examined. As the photocatalyst, tris[2,2'-bipyridine]ruthenium(II), $Ru(bpy)_3^{2+}$, having an intense absorption band at 452 nm in water was used. It was obtained as chloride from Strem Chemical Company. As the quenching sacrificial agent, chloropentaamminecobalt(III)chloride, $[Co(NH_3)_5Cl]Cl_2$, was prepared according to the conventional method.[5]

The indium tin oxide (ITO)-coated glass plate was obtained from Matsuzaki Shinku Co. (10 Ω / square) and used as a substrate. A Xe lamp (Ushio Electronics, UXL-500D0) was used as a light source. Monochromatic light at wavelength of 450 nm was obtained by using appropriate band-pass and interference filters.

Preparation of the pigment dispersion was as follows. At first, 360 milligrams (7 mM) of H_2Pc powder was dispersed in a 100 ml of aqueous solution containing FPEG (2 mM). The dispersion was sonicated for 30 min and stirred for several hours. The resultant dispersion was centrifuged at 1500 rpm for 15 min and the supernatant dispersion was used. The supernatant could be preserved for a few weeks. Secondly, $Ru(bpy)_3^{2+}$ (10 mM) and $[Co(NH_3)_5Cl]Cl_2$ (10 mM) were added to 10 ml of the supernatant dispersion which was acidified with dilute hydrochloric acid while stirring vigorously. The resulting dispersion (at about pH 1.6 to 2.0) was subjected to use as the standard solution.

The reaction cell was very simple. It consisted of two ITO-coated glass plates,[6] a spacer and a clip. The dimensions of the plate were 30 mm x 30 mm x 1.1 mm. The inner size of the spacer which was sandwiched between two plates were 20 mm x 20 mm x 1.5 mm, so that the area of the substrate (ITO plate) exposed to the pigment dispersion was 20 mm x 20 mm. A photo-induced reaction scheme which should fulfill the oxidation of FPEG is shown in scheme 1.[7,8] The validity of this reaction scheme will be discussed in a separate paper with the film-formation mechanism.



Scheme 1. Schematic representation of photo-induced oxidation of FPEG.

Figure 1 shows two different photomasks used and deposited H_2Pc pigment patterns prepared by the present method. Surprisingly, deposition of pigment occurred exclusively onto the masked area of the ITO substrate, not onto the illuminated area. At the present stage, clear-contrast film-patterns with line width of about 100 μm have been obtained.

Figure 2 shows the illumination-time dependence of the H_2Pc film thickness using photomask 1. During the illumination, light intensity was kept constant at 0.1 mW/cm^2. The film thickness was determined by both the usual stylus (Talystep) method and the UV-vis absorption measurements. It was revealed that there were three stages in the growth process of the film, i.e., incubation, rapid growth and slow growth. The existence of the incubation period (ca. 20 min) may suggest that the deposition to occur requires a distribution of a certain intermediate state of the pigment assembly in the vicinity of the unilluminated area of the substrate. As for the long-time illumination, the coalescence of the pigment assembly was also observed in the dispersion.

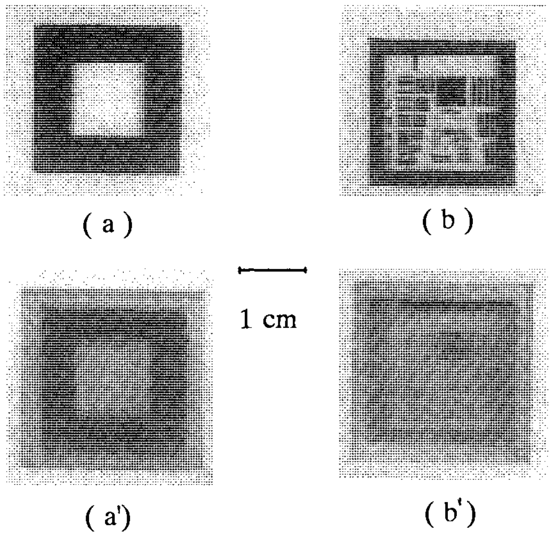


Fig. 1. Two different photomasks used and obtained H_2Pc pigment patterns deposited onto ITO-coated glass plates :
(a) photomask 1;
(a') pigment film pattern using photomask 1;
(b) photomask 2;
(b') pigment film pattern using photomask 2

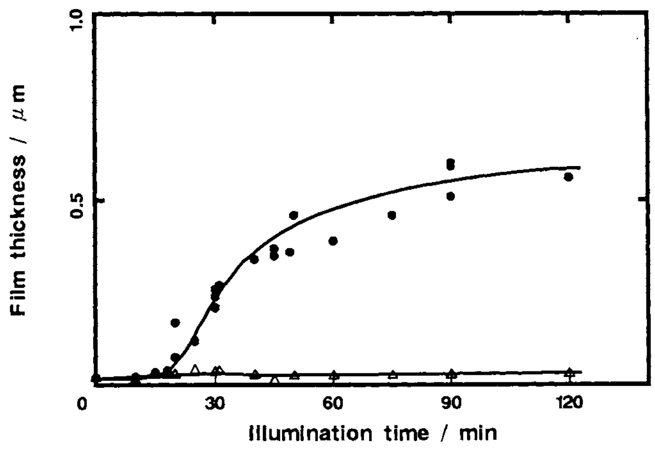


Fig. 2. Film growth during the illumination (light intensity = 0.1 mW/cm^2) by use of the photomask 1.
● : Masked area,
△ : Illuminated area

Figure 3 shows the dependence of the H_2Pc film thickness on light intensity using photomask 1 under the condition of constant illumination time (30 min). With increasing light intensity, film thickness increased until the light intensity reached about 0.1 mW/cm^2, while film thickness decreased with the light intensity above 0.1 mW/cm^2. This peculiar result suggests that there exists an optimum rate for the photo-induced deposition and that too rapid photo-induced reaction (light intensity » 0.1 mW/cm^2) does not effectively contribute to the deposition of the pigment.

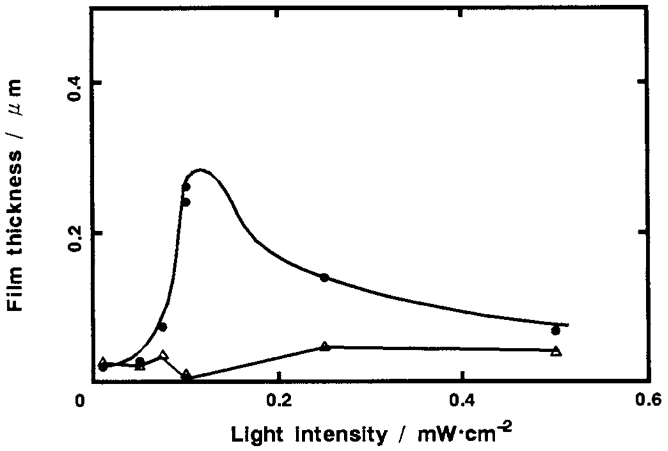


Fig. 3. Light intensity dependence of film thickness using photomask 1 under the condition of constant illumination time (30 min).
● : Masked area,
△ : Illuminated area

By use of this method, not only the hereto described H_2Pc pigment but also other pigments, such as various forms of copper phthalocyanines, halogenated copper phthalocyanine (Pc Green), and perylene derivative (Perylene Red) were found to be suitable for a clear-cut pattern formation.

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