

Light-assisted Formation of Free Patterns of Colour Images on ZnO Film prepared by Ultrasonic Spray Pyrolysis

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Free patterns of graded multicolour images have been formed using ZnO films, prepared by ultrasonic spray pyrolysis, by illuminating the semiconducting films with UV light; an external bias to the ZnO electrode is not necessarily required.

Previously,¹ we have described a new film-formation technique called photoelectrolytic micelle disruption (PMD). In this proposed method, area-selective illumination of an *n*-TiO₂ thin film with UV light resulted in the formation of desired patterns of colour images based on organic pigments, although intense UV light was needed. To overcome this shortcoming, ZnO films prepared by ultrasonic spray pyrolysis have been examined.

Organic pigments such as di-antraquinone red (A2B) were dispersed with (11-ferrocenyl)undecyl tridecaethylene glycol ether (FPEG) (Dojindo Lab.) in a similar way as described previously.^{2,3} ZnO films were prepared on ITO-coated glasses kept at 250 °C by thermal decomposition of zinc acetate. Aqueous mists containing zinc acetate were generated by using a commercially available humidifier (Panasonic FE-05KYC); the concentration of the zinc acetate in water was determined to be 0.8% m/m so as to maximize the film growth rate. Several minutes were sufficient to cover the ITO surface completely with the ZnO layer. The ZnO electrode was illuminated from behind with UV light provided by a projector with a 150 W Hg–Xe lamp (Hamamatsu photonics). The irradiation system enabled enlargement or reduction of a projected image easily. A potentiostat (Hokutodenko HAB-151) was used in the photoelectrolysis experiment.

The photocurrent quantum yield of the ZnO electrode was *ca.* 20% for UV light at 365 nm when biased at +0.5 V *vs.* SCE in an aqueous solution of 0.5 mol dm⁻³ LiBr. The relatively high photoactivity of the ZnO electrode allowed photoelectrolysis experiments to be carried out under much lower intensities of light than for those on TiO₂. Fig. 1 shows a plot of the UV light intensity and the thickness of A2B films prepared by the PMD method, where the ZnO electrodes, biased at +0.5 V *vs.* SCE, were illuminated for 60 s. The plot shows that film formation is feasible even under UV light as weak as 50 μW cm⁻² and that the film thickness increases as the intensity of UV light increases. The latter finding implies that graded colour images can be obtained by illuminating the ZnO electrode with UV light with a different intensity at different positions of a projected area [see Fig. 3(b)]. Apart from the practical importance of the finding, it is of interest from a mechanistic viewpoint to note that a diffusion-con-

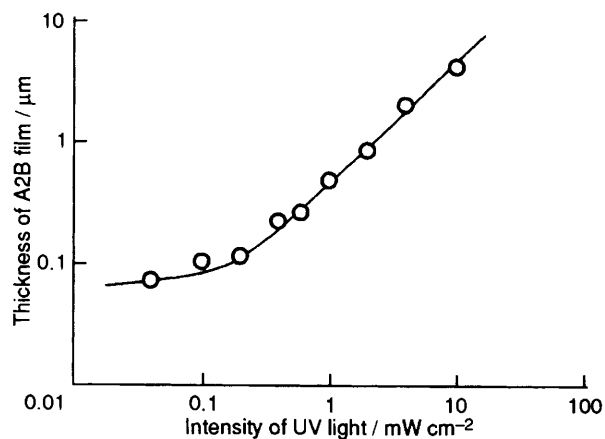


Fig. 1 Plot of intensity of UV light *vs.* thickness of A2B film prepared by the PMD method with the ZnO electrode

trolled oxidation of FPEG on the ZnO surface alone is unable to elucidate the observed light intensity dependence of the film thickness. In the electrolytic micelle disruption (EMD) method, the magnitude of a steady-state current in oxidizing FPEG at a metal electrode biased at a sufficiently positive voltage is controlled by diffusion of FPEG, which also limits the rate of film formation. In the PMD method, on the other hand, current at an illuminated semiconductor electrode can be greater than that in the EMD by increasing the light intensity. The photocurrent consists of the diffusion-limited current due to oxidation of FPEG and a current due to electrochemical oxidations of chemical species other than FPEG. Therefore, a larger photocurrent cannot necessarily lead to a higher rate of film formation. In fact, a similar light intensity dependence was not observed with the TiO₂ electrode. It appears that a photodissolution of ZnO yielding OH radicals⁴ is responsible for the above finding.

It was also found that an external circuit connected to the ZnO electrode was not needed. Illumination of the ZnO

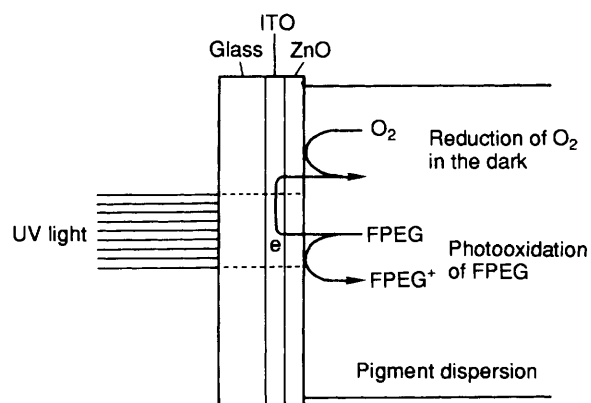


Fig. 2 Schematic illustration of the mechanism for photoelectroless formation of pigment film on the ZnO/ITO electrode

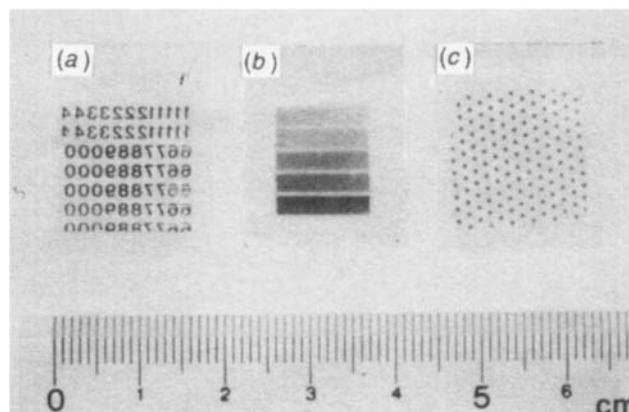


Fig. 3 Pigment filters of organic images of (a) copper phthalocyanine, (b) and (c) metal-free phthalocyanine prepared on ZnO electrodes using the PMD method for (a) and (b) and the photoelectroless method for (c). Intensity of UV light: (a) and (b) 0.5 mW cm⁻², (c) 10 mW cm⁻². Duration of illumination: (a) and (b) 3 min, (c) 10 min.

electrode, dipped in a dispersion of an organic pigment, with UV light led solely to a successful preparation of a pigment film on the semitransparent ZnO film. The above experiment required a more intense UV light than for the PMD experiments. Similar experiments were also made with TiO₂ electrodes. However, no film was formed, probably, because of the low photoresponses of our TiO₂ electrodes prepared as described previously.¹ The electroless formation of colour images on ZnO may be explained as illustrated in Fig. 2. Oxidation of FPEG will occur only at the illuminated part of the ZnO electrode and then electrons injected to the ZnO electrode will move through the ITO substrate to reach the dark part of the ZnO surface, where solute species, most likely O₂, will be reduced by the electrons from the conduction band of the *n*-ZnO electrode.

Fig. 3 illustrates pigment films prepared on the ZnO electrodes. Figs. 3(a) and (b) represent organic images

obtained by using the normal PMD method while Fig. 3(c) is an organic image prepared by the electroless method.

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