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# Electro- and Photoelectro-chemical Formations of Dye Films Based on Chromogenic Development of Photography

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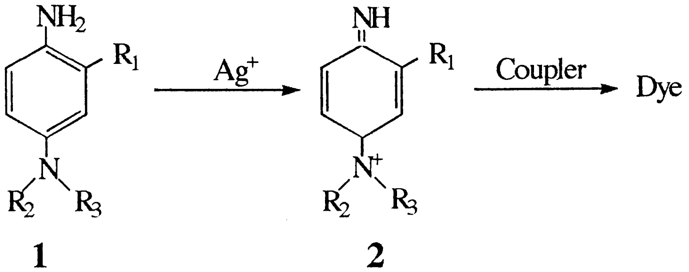
A dye thin film was prepared on an indium tin oxide (ITO) electrode by controlled potential electrolysis (oxidation) of 1,4-benzenediamine derivative (**1**) following reaction with a coupler. Photoelectrochemical oxidation of **1** with $TiO_2$ particle in the presence of methyl viologen ($MV^{2+}$) also gave a dye film and a photo image.

Thin films of dyes are important subject due to their potential application to many devices. However, technique for preparation of these films is limited to a few methods.[1] Recently, we have presented two novel techniques for the preparation of a wide variety of dye thin films.[2,3]

In color photography, following chromogenic developing process has been used.[4]



a: $R_1$=H, $R_2$=$R_3$=$CH_3$
b: $R_1$=H, $R_2$=$R_3$=$C_2H_5$
c: $R_1$=$CH_3$, $R_2$=$R_3$=$C_2H_5$
d: $R_1$=H, $R_2$=$C_2H_5$, $R_3$=$C_2H_4OH$
e: $R_1$=$CH_3$, $R_2$=$C_2H_5$, $R_3$=$C_2H_4NHSO_3CH_3$

In this paper, we report other new methods for the preparation of a thin film of dye by electro- and photoelectro-chemical oxidation of **1** following coupling reaction between quinonediimine (**2**) and coupler (**3**).

The cyclic voltammogram (CV) of an aqueous solution containing 1 mM (**1a**) at pH 11 ($NaHCO_3$ and NaOH buffer solution) at glassy carbon electrode showed an irreversible step with a peak potential at +0.01 V vs. SCE and one rereduction peak at -0.18 V. The rereduction peak may be assigned to reduction of 4-imino-2,5-cyclohexadien-1-one produced by deamination of **2a**.5) At higher scan rate (1 V $s^{-1}$), a reversal rereduction peak of **2a** was observed at -0.02 V, and the rereduction peak current at -0.18 V decreased (Fig. 1). The CV of same solution at the ITO electrode with rate 0.1 V $s^{-1}$ showed one irreversible broad peak at +0.6 V. This shift of the peak potential is ascribable to large over potential for oxidation of **1**. The results of CV of **1b-e** were similar to those of **1a**.

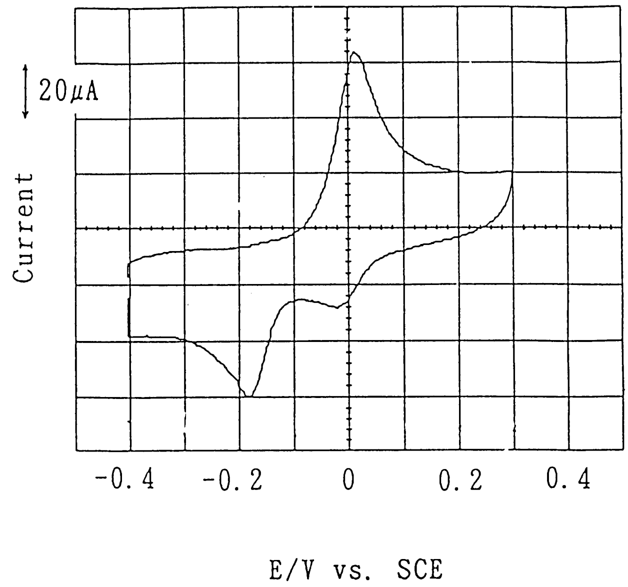
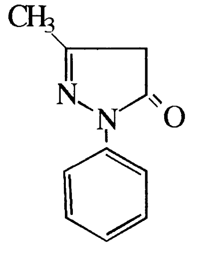
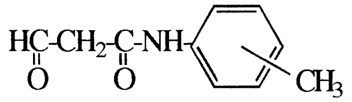


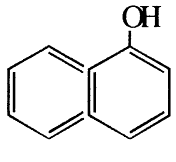
Fig. 1. Cyclic voltammogram of an aqueous solution containing 0.5 mM **1a** at pH 11.2. Scan rate: 1 V $s^{-1}$. Working electrode: Glassy carbon (0.080 $cm^2$).



**3a**



**3b**



**3c**

Film formations were tried by controlled-potential electrolysis of an aqueous solution containing **1**, **3**, and 0.1 M NaOH at +0.7 V at ITO electrode. As a typical example, preparation of a magenta film will be described. Concentration of **3a** was kept to be twice of **1a**. A transparent magenta film was formed by electrolysis of an aqueous solution containing more than 4.0 mM **1a** for 4 min. A short life time may account for the failure of film formation in the lower concentration of **1**.

Yellow and cyan films were formed using corresponding coupler (**3b** (yellow) and **3c** (cyan)), respectively. The absorption spectra of these magenta, yellow, and cyan films showed peaks at 507, 433, and 598 nm, respectively. The absorption spectra of methanol solutions prepared by washing these films were similar to those reported by earlier workers.[6]

Similar films were prepared by using **1b-e** instead of **1a**. Typical SEM micrographs of the magenta film are shown in Fig. 2, which indicate that this film is uniform with thickness of approximately 0.4 μm.

Growth of the film stopped within 2 min. The cessation of the growth may be due to coverage of electrode with the film of electric insulation.

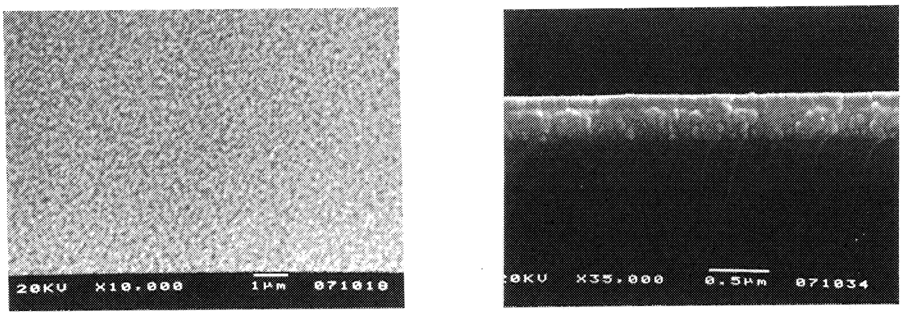


Fig. 2. Scanning electron micrographs of surface and cross section of the film prepared by the electrolysis of an aqueous solution containing 12 mM **1b**, 24 mM **3a**, and 0.1 M NaOH at ITO electrode maintained at +0.50 V vs. SCE for 2 min.

Instead of the electrolysis for oxidation of **1**, photoelectrochemical method was used. 500 W Xenon lamp was used as a light source. HOYA HA-30 glass filter was used for cutting infrared light. A yellow film was prepared on a transparent nylon slide by illumination of a suspension containing 10 mM **1b**, 20 mM **3b**, 10 mM $MVCl_2$ and 4.8 g $dm^{-3}$ $TiO_2$ at pH 11 ($NaHCO_3$ and NaOH buffer solution). Under deaeration condition, the film was not formed. Figure 3 shows a typical photograph of the film formed by this photochemical method, which indicates that the film is uniform and the photo image is clear. The thickness of the film was 0.4 μm for the illumination for 40 min.

Such film formations may be explained by the following process: In the photoelectrochemical case, $TiO_2$ particles within the penetrating depth of incident UV light were excited to generate electron-hole pairs. The holes oxidized **1**. Electrons were trapped by $MV^{2+}$ which changed to $MV^+$. Oxygen may help to prevent back reaction between hole in $TiO_2$ particle and $MV^+$ by oxidation of $MV^+$.[7] In both of the electro- and photoelectro-chemical cases, the oxidized **1** reacted with **3** to form a dye. This dye molecule finally deposited on the substrate.

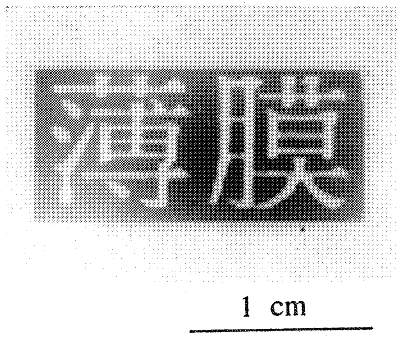


Fig. 3. Photograph of the film prepared by illumination of an aqueous solution containing 10 mM **1b**, 20 mM **3b**, 10 mM $MV^{2+}$, and 4.8 g $dm^{-3}$ $TiO_2$ at pH 11 for 40 min.

New electro- and photoelectro-chemical procedures were used to prepare the thin films of dyes based on chromogenic development of photography. These films were smooth and adhered well to the substrate. Present experiments show that such methods serve as techniques for preparing thin films of a wide variety of dyes.

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## References

1) For a review, see: P.S. Vincett and G.G. Roberts, *Thin Solid Films*, **68**, 135 (1980).
2) T. Saji, K. Hoshino, Y. Ishii, and M. Goto, *J. Am. Chem. Soc.*, **113**, 450 (1991).
3) T. Saji, Y. Yamada, and H. Tani, *Chem. Lett.*, **1992**, 2091.
4) R. Fisher and H. Siegrist, *Photogr. Korresp.*, **51**, 18 (1914).
5) K. Kobayashi, B. Xu, T. Ohno, and S. Mizusawa, *Nihon Shashin Gakkaishi*, **48**, 175 (1985); L. K. J. Tong, *J. Phys. Chem.*, **58**, 1090 (1954).
6) R. L. Bent, G. H. Brown, M. Carolyn Glesmann, and D. P. Harnish, *Photogr. Sci. Eng.*, **8**, 125 (1964); G. H. Brown, J. Figueras, R. J. Gledhill, C. J. Kibler, F. C. McCrossen, S. M. Parmerter, P. W. Vittum, and A. Weissberger, *J. Am. Chem. Soc.*, **79**, 2919 (1957)
7) M. D. Ward, J. R. White, and A. J. Bard, *J. Am. Chem. Soc.*, **105**, 27 (1983).

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