Light-writing in Polyaniline Film Containing WO₃ Particles

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Light-writing in polyaniline film containing WO₃ particles as a photosensitizer has been studied. The polyaniline film is first deprotonated by applying anodic potentials in several kinds of alcohol solutions, and then illuminated with a 500 W xenon lamp to permit photoreduction of the film at the illuminated area alone, giving a light image. The resulting light image is erasable with application of anodic potentials, allowing renewable light writing. The mechanism for the light-writing is discussed.

1 INTRODUCTION

Recently, we have discovered the means of incorporating metal oxides into the conducting polymers¹⁻⁴⁾ to widen their original functions. For example, polypyrrole films incorporated with WO₃ possess dual electrochromic properties due to polypyrrole and the oxide,²⁾ and those containing MnO₂ have very high energy densities as an active material for lithium batteries.⁴⁾ Furthermore, we have found that WO₃ particles can be incorporated into polyaniline films, and the resulting films (PAn/WO₃) are reduced by illumination in electrolyte solutions containing hole scavengers such as methanol.⁵⁾ In the present paper, we report the achievement of light-writing in the PAn/WO₃. We have recently demonstrated at PAn/TiO₂ that a light image can be produced in the film with the use of appropriate solution.⁶⁾

2 EXPERIMENTAL

Aniline was purified by distillation under reduced pressure. Methanol, ethanol, 1-propanol, and 2-propanol were distilled under N₂ prior to use. WO₃ particles used were anhydrous and the

average diameter was *ca.* 0.2 μm , as determined by observation with a scanning electron microscope (Hitachi S-800). As the electrode substrate, an indium-tin-oxide coated glass (ITO) and a glassy carbon plate were used for absorption spectra and electrochemical measurements, respectively. A saturated calomel electrode (SCE) served as a reference electrode.

PAn/WO₃ films were prepared by electrolysis at 1 mA cm⁻² for 200 mC cm⁻² of 1 mol dm⁻³ aniline dissolved in aqueous 2 mol dm⁻³ HCl solution containing 100 g dm⁻³ of suspended WO₃ particles under N₂. The deposition bath was stirred during the course of polymerization. The WO₃ particles are incorporated into PAn due to specific adsorption of Cl⁻ ions on the particles. The prepared film was washed with acetonitrile in an ultrasonic bath, followed by drying in vacuo before measurements. It was found that the amount of the incorporated WO₃ was 45 wt% of the resulting film.⁵⁾

Absorption spectra of the film were measured *in situ* under illumination and polarization of the film using a diode array spectrophotometer (Hewlett Packard 8452A). A 500 W xenon lamp (Ushio Electric UXL-500D-O) was used as a light source. The light-writing in the PAn/WO₃ film was performed by illumination of the film through a patterned mask.

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3 RESULTS AND DISCUSSION

The PAN/WO₃ film lost its electrochemical activities with potential sweep cyclings between -0.6 and 1.0 V vs. SCE in methanol containing 1 mol dm⁻³ LiClO₄, as shown in Fig. 1, and the color of the film was changed from green to blue, as

Fig. 1 Cyclic voltammograms of PAN/WO₃ film taken in methanol containing 1 mol dm⁻³ LiClO₄.

noticed from comparison of spectrum (1) of Fig. 2 (A) and (B), which give the spectrum of the green and blue film, respectively. Such changes are observed when PAN is deprotonated by anodic polarization in weak acid solutions, as reported in our previous paper.⁷⁾ When the blue film was immersed in 1 mol dm⁻³ HCl solution, the color was changed into green, and the redox activity was completely recovered. Similar behaviors were observed for blue PAN films prepared in the other alcohol solutions. These results strongly suggest that polyaniline is deprotonated by anodic polarization in the alcohol solutions. The reaction scheme for the deprotonation is shown in Fig. 3. Details of the anodic deprotonation reactions of polyaniline in alcohol solutions will be reported elsewhere.

It was found that both green and blue films were reduced to yellow by illumination with a 500 W xenon lamp. Figure 2 shows changes in absorption spectra of an as-grown green film caused by illumination with a 500 W xenon lamp in aqueous 1 mol dm⁻³ HCl solution containing 20 vol% of methanol (A) and those of the blue film

Fig. 2 Changes in absorption spectra of PAN/WO₃ films caused by illumination with a 500 W Xenon lamp under open circuit, taken at 10 sec intervals in aqueous 1 mol dm⁻³ HCl solution containing 20 vol% of methanol (A) and methanol solution containing 1 mol dm⁻³ LiClO₄ (B). The films were polarized at 0.6 V vs. SCE before illumination, resulting in the spectrum given by curve (1). Photo-reduced films gave the spectrum (2). Broken lines show absorption spectra obtained by succeeding polarization at 0.5 V vs. SCE for 5 sec.

Fig. 3 Schematic illustration of anodic deprotonation of polyaniline. A = electrolyte anion.

caused by the illumination in methanol containing $1 \text{ mol dm}^{-3} \text{ LiClO}_4$ (B). Both films gave absorption spectra given by curve (2) when they were photoreduced. The resulting yellow films recovered the original green or blue when they were anodically polarized at 0.5 V vs. SCE for 5 sec in the dark, as shown by broken lines in Fig. 2. The photoreduction is energetically feasible as shown in Fig. 4 for the case of photoreduction in aqueous solutions containing methanol. Photo-

Fig. 4 Energetic correlations between redox potentials of polyaniline, oxidation potential of methanol, and potential of the bottom of the conduction band (CB) and the top of the valence band (VB) of WO_3 in aqueous solution of pH 0.

generated positive holes are involved in oxidation of methanol, and photogenerated electrons in reduction of polyaniline.

Figure 5 shows changes in absorbance of the blue PAn/WO_3 film at 680 nm with the repetition of a cycle of illumination under open circuit and the succeeding anodic polarization at 0.5 V vs. SCE in the dark. As suggested from this figure, the photoreduction and electrochemical reoxidation of the PAn/WO_3 film took place reversibly.

It was found that focused illumination of a center of the PAn/WO_3 film caused reduction in the illuminated area alone if the methanol solution was used as the electrolyte solution, but not so if aqueous $1 \text{ mol dm}^{-3} \text{ HCl}$ containing $20 \text{ vol\%}$ of methanol was used. In the former case, photoreduction was restricted to the illuminated

Fig. 5 Response behavior of the absorbance at 680 nm of PAn/WO_3 obtained in methanol solution containing $1 \text{ mol dm}^{-3} \text{ LiClO}_4$ with repetition of illumination under open circuit and polarization at 0.5 V vs. SCE in the dark.

area, allowing the light-writing in the blue PAn/WO_3 films, as shown in Fig. 6 as an example, while in the latter case the reduced area spreaded beyond the illumination area with progress in illumination time. The light images given in Fig. 6 was produced by illumination through a patterned mask for 70 sec . The resulting image was stable even when the film was allowed to stand in air for 3 days , although a gradual fading of the image was noticed for exposure to air for much longer time. If the film was kept in N_2 -purged solution or in N_2 atmosphere, no appreciable fading of the image

Fig. 6 A Light image produced in PAn/WO_3 immersed in methanol containing $1 \text{ mol dm}^{-3} \text{ LiClO}_4$ with illumination by a 500 W Xenon lamp for 70 sec . The film was polarized at 0.6 V vs. SCE before illumination.

Table 1 Photoreduction behaviors of PAn/WO₃ in several kinds of solutions

Solution	Color of oxidized film	Film color after illumination	Light-writing
aqueous 1 mol dm ⁻³ HCl ^{a,b)}	green	yellow	no (spreading)
methanol ^{c)}	green	yellow	no (spreading)
methanol ^{b,c)}	blue	yellow	yes
ethanol ^{b,c)}	blue	yellow	yes
1-propanol ^{b,c)}	blue	yellow	yes
2-propanol ^{b,c)}	blue	yellow	yes

a) The solution contained 20 vol% of methanol.

b) The film was polarized at 0.6 V vs. SCE for 5 min before illumination.

c) The solution contained 1 mol dm⁻³ LiClO₄.

was noticed at least for 2 weeks. The light image formation in the PAn/WO₃ was investigated in several kinds of other electrolyte solutions. The obtained results are summarized in Table 1. The photoreduction of PAn took place in all electrolyte solutions, but in order to obtain images of high resolution, polarization at 0.6 V vs. SCE in alcohol solutions were essential.

Since the deprotonated polyaniline film shows null redox activities, protonation seems essential to form light images in the deprotonated films. As noticed from comparisons of absorption spectra given in Fig. 2 (A) and (B), the blue film changed its color into green in an initial stage of the photoreduction, getting electrochemical reactivities in the methanol solutions. The protonation in that case must occur with the use of protons that are produced on the oxidation of alcohol by the valence band holes in the incorporated WO₃ particles. Since the oxidation of alcohols preferentially occurs on the illuminated area of the PAn/WO₃ films, the protonation is limited to polyaniline in the illuminated area, allowing the reduction by the conduction band electrons to give light-writing of high resolution. In contrast, since the protonated polyaniline possesses a high conductivity which allows easy diffusion of photo-

generated electrons in the WO₃ particles beyond the periphery of the illuminated area, the photoreduction spreads over the illuminated area, not allowing the light-writing.

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