Light Image Formations on Deprotonated Polyaniline Films Containing TiO_2 Particles

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Formation of novel light images of high resolution in polyaniline films containing TiO_2 particles is described. The light images are produced by scanning the third harmonic of a Nd:YAG laser on the polyaniline films or by exposing the polyaniline films to lights from a xenon lamp through patterned masks. The keys for the light image formation are (1) to incorporate the semiconductor particles into polyaniline, (2) to convert highly conductive polyaniline into insulating one by utilizing deprotonation which is induced to occur by immersing the conducting polyaniline in aqueous neutral solutions or by anodically polarizing in aliphatic alcohol solutions such as methanol and ethanol solutions, and (3) to use a hole scavenger capable of releasing protons on its oxidation such as above alcohols. The quantum efficiency for the light image formation determined at 355 nm under a low illumination intensity was ca. 10%. The mechanisms of the formation of light images are discussed.

Introduction

The formation of erasable light images has been attracting great interests in recent years. Achievements of this by electrochemical means have been published for prussian blue films on titanium(IV) oxide,[1] for molybdenum(VI) oxide,[2,3] and for conducting polyaniline films containing methylene blue and $Ru(bpy)_3^{2+}$.[4] Furthermore, photoelectrochemical deposition of metals and metal oxides on semiconductor electrodes has been successfully used for the light image formations.[5,6] In this paper, a novel method utilizing electrochromism of polyaniline is described.

Electrically conductive polymers have wide utilities in electrochemical applications such as conducting supports for fixing electrocatalysts,[7-10] active materials for lithium batteries,[11-13] and electrochromic display devices.[14-16] We have been studying incorporation of oxide particles into polypyrrole and polyaniline to widen their functionalities.[17-21] Polypyrrole films containing WO_3 exhibit dual electrochromisms due to the polymer and the incorporated oxide,[19] those containing TiO_2 exhibit photosensitivities,[17] and those containing MnO_2 work as electroactive materials of high-energy densities for lithium batteries.[20] The incorporation of WO_3 and TiO_2 particles into polyaniline is also useful to attach apparent photoactivities to polyaniline films.[21] Furthermore, since as-grown polyaniline films are in an oxidized state, the incorporated oxide particles serve as the photosensitizer to reduce the polyaniline in the presence of appropriate hole scavengers. Recently, we have discovered that light images of high resolution are produced on polyaniline films containing TiO_2 particles (PAn/TiO_2) in neutral phosphate buffer solutions containing methanol.[22]

If we attempt to produce light images of high resolution by using photoinduced electrochromic reactions, the following two contrary requirements must be fulfilled. One is that the polymer film must have a very low conductivity to prevent spreading of the light image from the illuminated area. If films of high conductivity are used, they allow two-dimensional diffusion of electrons in the films, resulting in light images of low resolution in the polymer films. The other requirement is that the high-resistivity film must have a high electrochemical activity for its photoreduction. It is very common that films of high resistivities possess very low electrochemical activities. Accordingly, some trick must be undertaken to induce the electrochemical reaction in the resistive films. It will be shown in this paper how such contrary requirements are solved at the PAn/TiO_2.

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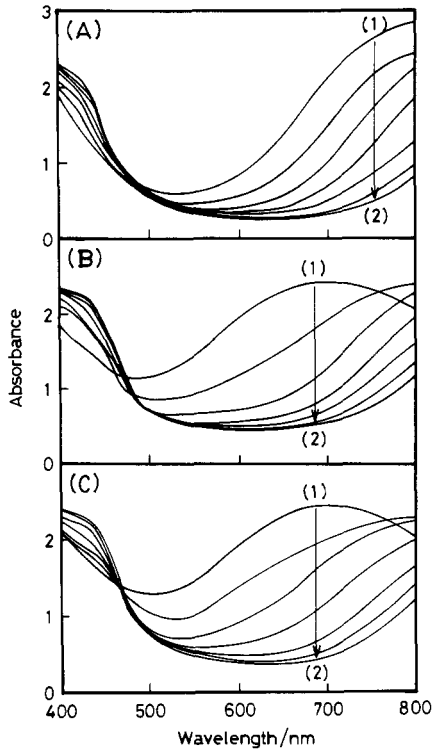

Figure 1. Changes in absorption spectra of PAn/TiO_2 films caused by illumination with a 500-W xenon lamp under open-circuit conditions. Each spectrum was taken at 4-s intervals in aqueous 1 mol dm^{-3} HCl solution (A) and in phosphate buffer solution adjusted to pH 7 (B) both of which contained 20 vol % methanol, and in methanol solution containing 1 mol dm^{-3} $LiClO_4$ (C). The PAn/TiO_2 film immersed in the methanol solution (C) was polarized at 0.7 V vs SCE for 5 min to deprotonate the film prior to illumination. The quantity of electricity used for polymerization was 100 mC cm^{-2}, and the light intensity on the film was 0.06 W cm^{-2}.

Experimental Section

Aniline was purified by distillation under reduced pressure, and methanol, ethanol, 1-propanol, and 2-propanol were purified by storing in the presence of sodium metal to eliminate dissolved water, followed by distillation. Twice distilled water was used to prepare aqueous electrolyte solutions. TiO_2 particles used in this study were anatase (Aerosil P-25) having an average particle size of 21 nm. Indium tin oxide-coated glass plates (ITO) were used as the electrode substrates. An electrical lead wire was attached to its round rim with silver epoxy and fixed with epoxy resin.

Polyaniline films containing TiO_2 (PAn/TiO_2) were prepared by electrolysis at 0.2 mA cm^{-2} under N_2 of aqueous 2 mol dm^{-3} HCl solution containing 1 mol dm^{-3} aniline and 30 g dm^{-3} TiO_2 particles. The deposition bath was magnetically stirred during the course of the electropolymerization. The amount of the incorporated TiO_2 was about 70 wt % of the resulting films.[22] TiO_2-free polyaniline films were also prepared under the same conditions except for the absence of the suspended TiO_2 particles in the deposition bath. Measurements of the film thickness and analyses of the incorporated electrolyte ions in the resulting films were carried out with the use of a scanning electron microscope (SEM; Hitachi S-800) and an energy-dispersive electron probe X-ray microanalyzer (EPMA; Horiba EMAX-1700) connected to the SEM, respectively.

For photoreduction experiments of the PAn/TiO_2 films, an electrolytic cell (40 × 10 × 60 mm) made of quartz was used. A saturated calomel electrode (SCE) served as a reference electrode. The cell was set in a diode array spectrophotometer (Hewlett-Packard 8452A), and lights from a 500-W xenon lamp (Ushio Electric UXL-500D-0) were irradiated onto the film. Changes in absorption spectra of the film caused both by illumination under open circuit conditions and by anodic polarization in the dark were measured in situ. The formation of light images on the PAn/TiO_2 film under open circuit conditions was undertaken by illuminating the film through a patterned mask using the xenon lamp as a light source. In the case of writing a narrow line in the film, focused third harmonic of a Q-switched Nd:YAG laser (Spectra-Physics GCR-11) was scanned on the film. After the formation of light images the films were washed with acetonitrile, followed by drying in air, and then the images were observed with a microscope (Nikon Model S).

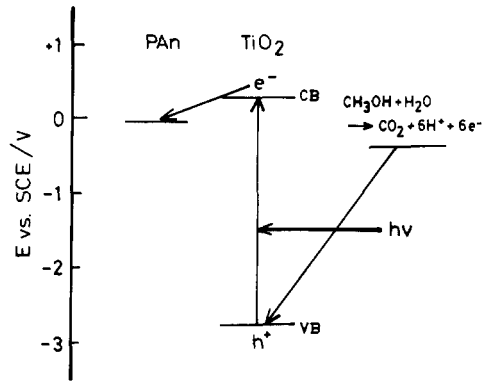

Figure 2. Energetic correlation between the redox potential of polyaniline, oxidation potential of methanol, and potentials of the bottom of the conduction bands (CB) and the top of the valence bands (VB) of TiO_2. The direction of the electrons in the photoreduction of polyaniline is given by arrows.

The quantum efficiency for photoinduced reduction of the PAn/TiO_2 was obtained in the following way. An as-grown PAn/TiO_2 film prepared with 100 mC cm^{-2} was reduced electrochemically at 0.1 mA cm^{-2} in a phosphate buffer solution of pH 3 containing 20 vol % methanol. During the course of the reduction, lights from a He–Ne laser (=632.8 nm), whose energy is insufficient to photoexcite the incorporated TiO_2, was irradiated onto the PAn/TiO_2 film, and the intensity of transmitted light was monitored using a power meter (Japan laser JPL-03) to obtain an intensity of transmitted light vs reduction charge relation. The photoreduction of an as-grown PAn/TiO_2 film was carried out with illumination of a pulsed laser beam of the third harmonic of a Nd:YAG laser (355 nm) at 10 Hz. The intensity of transmitted light was monitored with the same way as that mentioned above for the electrochemically reduced PAn/TiO_2 films. On the basis of the transmittance at 632.8 nm, the amount of charges involved in the photoreduction was evaluated. The quantum efficiency was then determined as the ratio of this charge to the amount of irradiated photons determined with the use of the power meter.

Results and Discussion

Photoreduction Behavior of Polyaniline Films Containing TiO_2 in Aqueous and Alcohol Solutions. Figure 1 shows changes in absorption spectra of the PAn/TiO_2 film caused by illumination with a 500-W xenon lamp, taken at 4-s intervals under open-circuit conditions. The electrolyte solutions used were aqueous 1 mol dm^{-3} HCl (Figure 1A) and 0.1 mol dm^{-3} phosphate buffer solution adjusted to pH = 7 (Figure 1B), both of which contained 20 vol % methanol, and a methanol solution containing 1 mol dm^{-3} $LiClO_4$ (Figure 1C). When an as-grown PAn/TiO_2 film was immersed in the HCl solution, a spectrum (1) of Figure 1A was obtained. The color (green) of the film was unchanged in that case, whereas it was changed from green to blue by immersing in the phosphate buffer solution, as noticed by a blue shift from a large absorption band given by the spectrum (1) of Figure 1A to that of Figure 1B. In the case of using the methanol solution, the PAn/TiO_2 film was prepolarized prior to the illumination to cause changes in the film color from green to blue. It will be shown in another paper that the blue shift of the

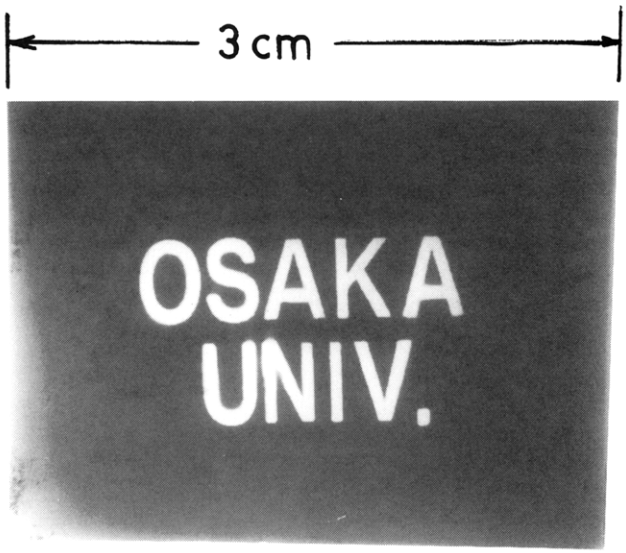

Figure 3. Light image formed on the PAn/TiO_2 film immersed in methanol containing 1 mol dm^{-3} $LiClO_4$. The image was obtained by illumination with a 500-W xenon lamp through a mask for 10 s. The film was polarized at 0.7 V vs SCE before the illumination.

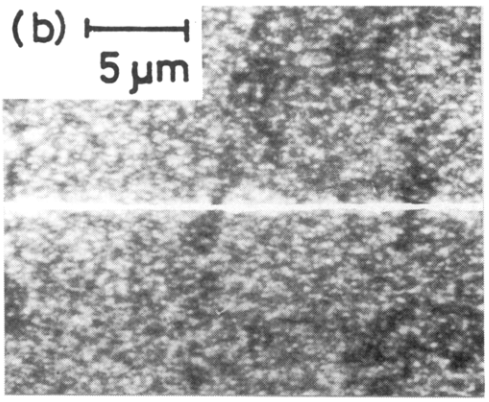

Figure 4. Light image produced by scanning laser beam on the PAn/TiO_2 film immersed in 0.1 mol dm^{-3} phosphate buffer solution (pH 7) containing 20 vol % methanol. The laser beam of focused third harmonic of a Nd:YAG laser (355 nm) of 0.3 mW was scanned on the PAn/TiO_2 at 0.1 mm s^{-1}.

absorption band results from deprotonation of polyaniline.[23]

When the PAn/TiO_2 films were illuminated under open-circuit conditions in 1 mol dm^{-3} HCl solution, the film color was changed from green to yellow, and absorption at wavelengths longer than 500 nm was decreased, as shown in Figure 1A, where changing behaviors of a spectrum (1) of the green film toward a spectrum (2) of a yellow film are given. Similarly the blue PAn/TiO_2 film was changed its color into yellow when the film was illuminated under open-circuit conditions both in the phosphate buffer solution containing 20 vol % methanol and in the 0.1 M $LiClO_4$ methanol solution, as shown in Figure 1B,C, respectively. The original green or blue of the PAn/TiO_2 was easily recovered by anodically polarizing the yellow film at 0.5 V vs SCE in each solution. Since TiO_2-free PAn film did not show any photoactivity under open circuit conditions in the above described three kinds of solutions, it is of no doubt that the observed photoinduced color change of the PAn/TiO_2 is caused by the incorporated TiO_2.

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Table I. Photoreduction Behavior of PAn/TiO_2 in Several Kinds of Solutions

solution	color of oxidized film	film color after illumin.	light image formation
methanol (1 M $LiClO_4$)	green	yellow	no (spreading)
methanol (1 M $LiClO_4$)[a]	blue	yellow	yes
ethanol (1 M $LiClO_4$)[a]	blue	yellow	yes
1-propanol (1 M $LiClO_4$)[a]	blue	yellow	yes
2-propanol (1 M $LiClO_4$)[a]	blue	yellow	yes
acetonitrile (1 M $LiClO_4$)[b]	green	yellow	no (spreading)
1 M HCl[b]	green	yellow	no (spreading)
phosphate buffer (pH 3)[b]	green	yellow	no (spreading)
phosphate buffer (pH 3)[a,b]	blue	yellow	yes
phosphate buffer (pH 4)[a,b]	blue	yellow	yes
phosphate buffer (pH 5)[b]	blue	yellow	yes
phosphate buffer (pH 7)[b]	blue	yellow	yes

[a] The PAn/TiO_2 film was polarized at 0.7 V vs SCE for 5 min before light illumination. [b] 20 vol % of methanol was contained in the solution.

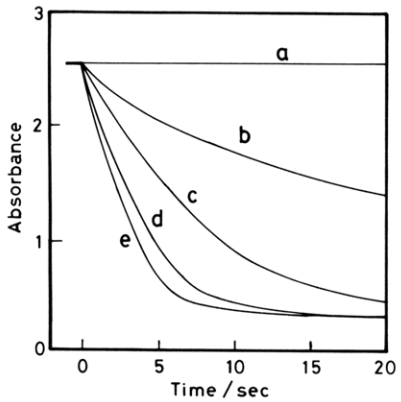

Figure 5. Time course of changes in absorbance at 600 nm of a blue PAn/TiO_2 film caused by illumination with a 500-W xenon lamp in methanol containing 1 mol dm^{-3} $LiClO_4$. The light intensity on the film was 0 (a), 0.02 (b), 0.06 (c), 0.18 (d), and 0.22 (e) W cm^{-2}. The quantity of electricity used for polymerization was 100 mC cm^{-2}. The film was polarized at 0.7 V vs SCE before illumination to cause the deprotonation of polyaniline.

Figure 2 shows energetic correlations at pH 0 between the redox potential of the polyaniline film, the oxidation potential of methanol, and the incorporated TiO_2 in aqueous solutions. It is easily recognized from this figure that polyaniline in an oxidized state is reduced by the conduction band electrons. The photogenerated positive holes in the TiO_2 particles are involved in oxidation of methanol. It has been reported that the deprotonated polyaniline is electrochemically inactive.[24] Nevertheless, it is photoreduced in the solutions given in the figure captions of Figure 1. Then, the photoreduction mechanisms of the deprotonated polyaniline is a matter of discussion and will be described in the next section.

The observed activity of the deprotonated polyaniline for photoreduction is very useful in producing light images of high resolution, because the insulating properties of the deprotonated polyaniline does not allow the photoreduction beyond the periphery of the illuminated area. One example of a yellow light image in the blue film is given in Figure 3. In Figure 4 is given a light image produced by a scanning focused third harmonic (355 nm) of a Nd:YAG laser beam at 0.1 mm s^{-1}. Although the size of the beam spot was not determined, the picture shown here seems enough to demonstrate high resolution of the light image produced. In this picture, very fine white spots due to the incorporated TiO_2 particles are seen, but to the

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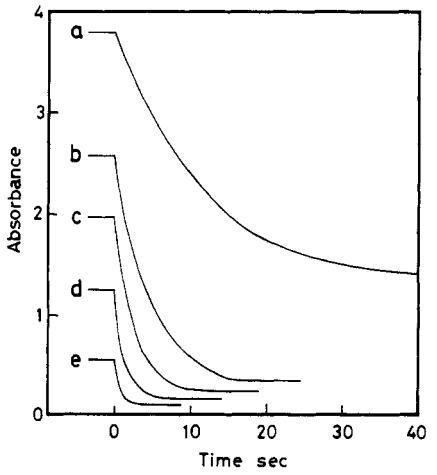

Figure 6. Time course of changes in absorbance at 600 nm of PAn/TiO_2 film prepared with the polymerization charges of 150 (a), 100 (b), 80 (c), 50 (d), and 25 (e) mC cm^{-2}, caused by illumination with a 500-W Xe lamp in methanol solution containing 1 mol dm^{-3} $LiClO_4$. The light intensity on the film was 0.22 W cm^{-2}.

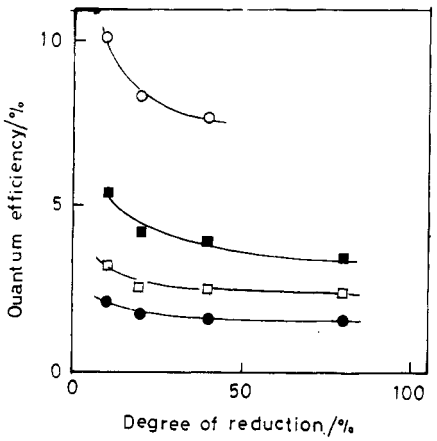

Figure 7. Quantum efficiency of the PAn/TiO_2 film for photoreduction caused by illumination with third harmonic of a Nd:YAG laser (355 nm) in potassium phosphate buffer solution (pH 3) containing 20 vol % methanol. Illumination intensity: (○) 0.05 mW, (■) 0.2 mW, (□) 0.5 mW, (●) 1.0 mW. The PAn/TiO_2 used was prepared with the same electrolysis condition as that given in the caption of Figure 5.

naked eyes they were not seen and the yellow line only was observed. It was found that the use of the phosphate buffer solution and of the methanol solution gave the same light images if they were formed under the same conditions. The contrast of the obtained images was not changed at least for 1 month if the film was kept under open circuit in the N_2-purged solutions or in N_2 atmosphere. The images were easily erased by polarizing the films at 0.5 V vs SCE in the methanol solution or in the phosphate buffer solution.

The formation of light-images on the PAn/TiO_2 film was attempted using various kinds of aqueous and non-aqueous solutions. The results are summarized in Table I. The light images could be produced on the blue films regardless of the preparation methods but not on the green films, as expected. When the green films were used, the photoreduction easily spreaded beyond the illuminated area due to high conductivities of the green films, the degree depending on the illumination time.

Figure 5 shows the effect of the illumination intensity on the response of the photoreduction of the blue PAn/TiO_2. As expected, the rate of the photoreduction

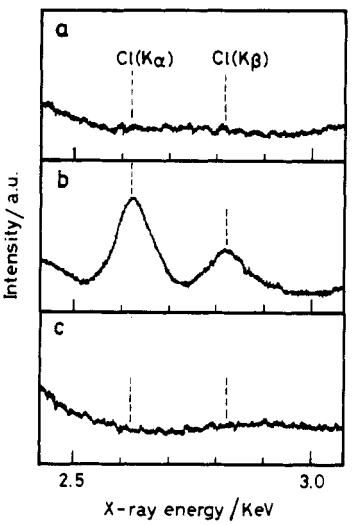

Figure 8. EPMA spectra of the PAn/TiO_2 film prepared by polarization of an as-grown film at 0.7 V vs SCE for 5 min in methanol containing 1 mol dm^{-3} $LiClO_4$ (a), those taken after illumination of the blue film for 4 s in the methanol solution (b), and after illumination for 24 s in the same solution to give a yellow film (c). The PAn/TiO_2 film was prepared with the same condition as that given in the caption of Figure 5.

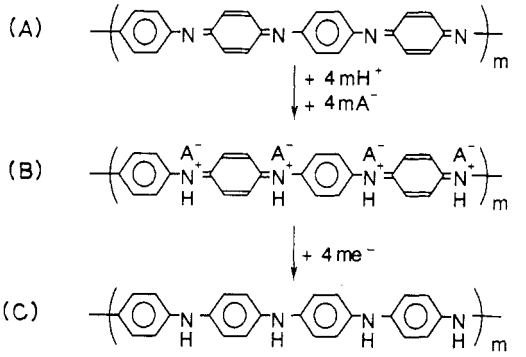

Figure 9. Schematic illustration of compositional changes in deprotonated polyaniline in its photoreduction: (A) deprotonated blue film, (B) as-grown and/or green film, and (C) reduced yellow film. A^- denotes an monovalent electrolyte anion.

increased with increasing the light intensity. It was found by comparing the results obtained by the different kinds of alcohols used that the rate of the photoreduction of the blue PAn/TiO_2 was a little influenced by the kind of alcohols. Apparently, the use of alcohol molecules having the smaller size (methanol) is feasible to get the higher rate of the photoreduction, suggesting that the rate of diffusion of alcohol molecules in the interior of the PAn/TiO_2 film as a hole scavenger determines the rate of photoreduction. The same conclusion can be derived from results shown in Figure 6, which were obtained by using different thickness of the PAn/TiO_2 films prepared by changing the polymerization charges of polyaniline. The thickness of the PAn/TiO_2 films prepared with 25, 50, 80, 100, and 200 mC cm^{-2} was 0.3, 0.5, 0.7, 0.9, and 1.7 μm, respectively. The photoreduction of the thinner film was completed in the shorter time, indicating that the time needed for methanol molecules to diffuse to all TiO_2 particles present in the film becomes short with decreasing the film thickness.

Figure 7 shows the quantum efficiency for photoreduction of the PAn/TiO_2 film, obtained under different illumination intensities of the monochromatic light at 355 nm, as a function of the degree of its reduction. The quantum efficiency of about 10% was obtained in an initial

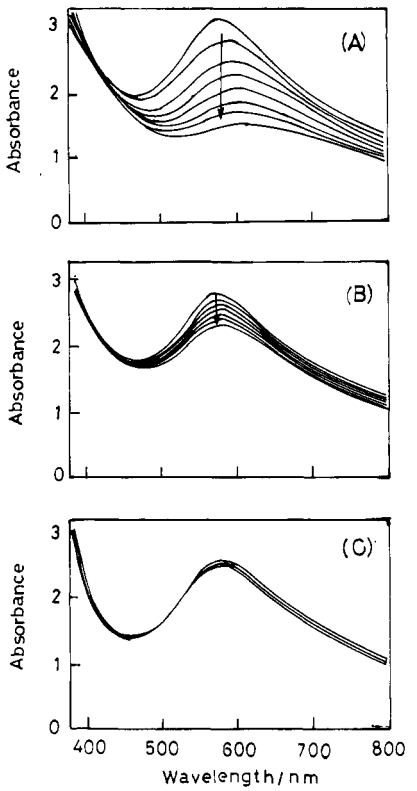

Figure 10. Changes in absorption spectra of deprotonated PAn/TiO_2 films caused by illumination with a 500-W xenon lamp in 0.1 M potassium phosphate buffer solution containing 20 vol % methanol. Solution pH: (A) pH 9, (B) pH 10, and (C) pH 11. The PAn/TiO_2 was prepared with the same condition as that given by the caption of Figure 5.

stage of photoreduction for the lowest illumination intensity of 0.05 mW, but with increasing the illumination intensity the quantum efficiency was decreased. With increasing the illumination intensity, the recombination of photogenerated charge carriers becomes serious by the reason that the supply of methanol to the incorporated TiO_2 surfaces in the film by diffusion cannot follow the rate of photogeneration of charge carriers. In addition, scattering and penetration of the irradiated photons through the PAn/TiO_2 film must become great with increasing the illumination intensity. As shown in Figure 7, the quantum efficiency tended to decrease with progress in the reduction of the PAn/TiO_2 as a result of decrease of the fraction of the conducting polyaniline.

Photoreduction Mechanisms of Deprotonated Polyaniline Films Containing TiO_2 Particles. As already reported, the deprotonated polyaniline film shows no redox activity, but when it is protonated, the same remarkable electrochemical activities as those of the as-grown polyaniline appear.[25,26] Accordingly, the protonation of the blue polyaniline films must occur when the blue films are photoreduced. By comparing the changing behaviors of the absorption spectrum of the green film given by Figure 1A with those of the blue films given by Figure 1B,C, it is noticed that an absorption peak of the blue film observed at around 700 nm is red-shifted by illumination of its initial stage. The spectrum obtained after 4-s illumination was almost the same as that obtained for the green film in the same illumination time. In fact, it was observed to naked eyes that the blue of the deprotonated film became greenish in that time period in the alcohol solution or in the phosphate buffer solution containing methanol. The protonation of the blue films was further confirmed by changes in the film composition before and after the occurrence of such color change.

Figure 8 shows results obtained by electron probe X-ray microanalysis of the PAn/TiO_2 taken at three different stages in its photoreduction; a blue film prepared by anodic polarization of the green film at 0.7 V vs SCE in the methanol solution, and a film whose color became greenish with illumination for 4 s in the same alcohol solution, and a yellow film prepared by illumination for 24 s. The deprotonated blue film did not contain chloride anions, but when the color was changed into greenish one, chloride anions were incorporated from the solution. The protonation of the deprotonated polyaniline results in generation of positive charges, which must be compensated by the incorporated chloride anions. When the resulting greenish film was photoreduced, the chloride anions were dissolved out, as well-established.[25] Then the reaction mechanisms of polyaniline of the PAn/TiO_2 in the formation of light images are given by Figure 9.

Photoexcitation of the incorporated TiO_2 results in generation of positive holes and electrons in it. The photogenerated positive holes react with alcohols in solution to release protons. Presently it is not known what is the major oxidation product of alcohols. However, the oxidation must accompany the release of protons, as several reactions for the case of oxidation of methanol suggest:

$$CH_3OH + 2p^+ \rightarrow HCHO + 2H^+$$

$$CH_3OH + 4p^+ \rightarrow CO + 4H^+$$

$$CH_3OH + 6p^+ + H_2O \rightarrow CO_2 + 6H^+$$

Since the proton release takes place in the illuminated area, the attachment of the released protons to the deprotonated polyaniline must occur in the illuminated area only if the protonation takes place so rapidly as not to allow the escape of the released protons beyond the illuminated area by diffusion. The experimental results show that such situations were valid in the light image formation on the blue PAn/TiO_2. When the protonated polyaniline of high electrochemical activities is produced, it is reduced by the photogenerated electrons left in the TiO_2 particles.

Figure 10 shows the effect of pH on the photoreduction behavior of the blue polyaniline. It is seen that the rate of photoreduction becomes slow down if the solution pH exceeds pH 9. There seems to be two different interpretations for this finding. One is that with an increase in the concentration of hydroxide ions in solution, protons generated by photooxidation of alcohols by the valence band holes must easily react with hydroxide ions rather than with the deprotonated polyaniline, leaving the polyaniline in the electrochemically inactive state. The other is that the protonation of blue polyaniline may occur, but the resulting protonated polyaniline will be quickly deprotonated under high concentrations of hydroxide ions, giving no appreciable changes in absorption spectrum.

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