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Electrochemical Properties of Electrochemically Polymerized Polypyrrole Film in the Dark and under Light Irradiation

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Polypyrrole films prepared on Pt or SnO_2 through electrochemical oxidative polymerization of pyrrole were characterized with respect to electroconductivity by photoelectrochemical measurements. Redox reactions of solution species such as methyl viologen, hydroquinone, oxygen, Cu^{2+}, I^-, and Br^- occur on these electroconductive films. Light excitation of the film with wavelengths shorter than 550 nm results in observable cathodic photocurrent at the potential region more negative than 0.0 V *vs.* Ag. The polypyrrole film is a p-type semiconductor with a bandgap energy of *ca.* 2.2 eV and is stable during redox reactions.

Many works on photoelectrochemical processes have recently been carried out from the standpoint of solar energy conversion to electrical energy and/or chemical energy. There have been intensive studies on semiconductor transducers such as photoelectrodes, composed of TiO_2, CdS, GaP, GaAs, Si, *etc.*, for electrochemical photocells.[1–7]

Thin-layer-coated semiconductor electrodes with dyes,[8,9] metal complexes,[10–12] and organic polymers[13–15] such as Rhodamine B, thiacyanine, chlorophyll, Cu-phthalocyanine, $Ru(bpy)_3{}^{3+}$, and polypyrrole have been developed as photoelectrodes for electrochemical systems. Fan *et al.*,[13] Simon *et al.*,[14] and Skotheim *et al.*[15] have reported that an Si electrode coated with polypyrrole film is stabilized against photodegradation by the SiO_2 layer formation on Si surface so as to provide an electrochemical photocell capable of supplying stable photocurrent for a long period.

Organic polymers such as polyacetylene $(CH)_x$, poly(sulfur nitride) $(SN)_x$, and polypyrrole $(Pyr)_x$ have been synthesized as promising electrical conductors and their electrical and optical properties have been investigated.[13–21] Diaz *et al.*[17] have reported on electrochemical preparation and behavior of polypyrrole films on a Pt electrode. The polypyrrole films show a metallic conductivity and redox reactions of ferrocene, nitrobenzene, and chloranil occur on the surface of these films.

This paper describes spectral observations during polypyrrole film formation, redox reactions of methyl viologen, hydroquinone, oxygen, Cu^{2+}, I^-, and Br^-, and photocathodic reactions under light irradiation. The polypyrrole film shows an electrical conductivity like a metal or semiconductor electrode. Especially, under light irradiation with wavelengths shorter than 550 nm the polypyrrole film shows cathodic photocurrent under cathodic polarization, so that the film is considered to have a p-type semiconducting property with a bandgap energy of *ca.* 2.2 eV. The polypyrrole film is discussed from the viewpoint of the traditional theory of semiconductors.

Experimental

A Pt electrode and an optically-transparent SnO_2 electrode were employed as substrate electrode for pyrrole polymerization. For the pretreatment of the Pt electrode, the potential of Pt was scanned several times between −0.2 and 1.3 V *vs.* SCE in order to get a clean Pt surface. The SnO_2 electrode was rinsed with a dilute H_2SO_4 aqueous solution and methanol before use.

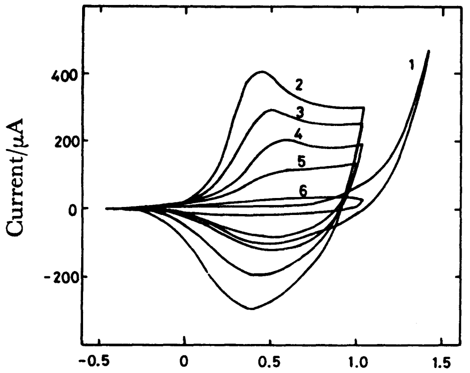
Polypyrrole film was formed on the electrode by electrochemical oxidation of pyrrole in an electrochemical glass cell with an Ag reference electrode and a Pt counter electrode, a potensiostat system (Hokuto Denko Co. Model HA301) being employed. The solution used for the polymerization was acetonitrile with 0.1 M (1 M=1 mol dm^{-3}) pyrrole and 0.1 M Bu_4NClO_4. As for the polymerization, the electrode potential was initially polarized at 1.3 V *vs.* Ag in order to produce a cationic radical[17] of pyrrole, pyrrole^{+}. Then to let the pyrrole^{+} polymerize with other pyrroles, the electrode potential was kept at 1.0 V for several minutes or scanned between −0.5 and 1.0 V *vs.* Ag. For the polypyrrole films in the photoelectrochemical study, the polymerization was carried out *via* oxidation with current charges from 10 to 100 milli coulombs (mC).

For the electrochemical measurement the light source was a 500 W Xe lamp (Ushio Electric Co.) with a glass cut-filter $\lambda(<350$ nm cut-off). Absorption spectra of polypyrrole films in the course of polymerization were measured with an SnO_2 electrode which was attached on the front of a box-type cell settled in the spectrometer. The light intensity dependence of cathodic photocurrents was measured with neutral density filters. Current-potential characteristics were observed by employing a potensiostat with a function generator. Measurements of action spectra of photocurrents were carried out by use of a synchrotrack lock-in amplifier and a light chopper (NF Circuit Design Block Co.). A grating monochromator (Nikon G-250) was employed for the wavelength selection on the light from the 500 W Xe lamp.

Chemicals used in this study were all of reagent grade and used without further purification. Electrolyte solutions were deaerated with a purified nitrogen purge during experiment.

Results and Discussion

Pyrrole was oxidized at the Pt electrode in the acetonitrile solution containing 0.1 M Bu_4ClO_4 (TBAP). Figure 1 shows the current-potential curves obtained in the course of the pyrrole polymerization. At first, the electrode was polarized at 1.2 V *vs.* Ag, where a pyrrole cationic radical was formed. Then the pyrrole was polymerized at the potentials above 1.0 V. In the first cycle of potential under the polarization between −0.5 and 1.0 V, the anodic (I_{pa}) and cathodic peak currents



(Potential *vs.* Ag)/V

Fig. 1. Current-potential curves in the course of the oxidative polarization of pyrrole in an acetonitrile solution with 0.1 M pyrrole and 0.1 M TBAP. Potential sweep rate is 30 s/V. 1; 1st sweep, 2; 3rd, 3; 5th, 4; 8th, 5; 10th, 6; 50th.

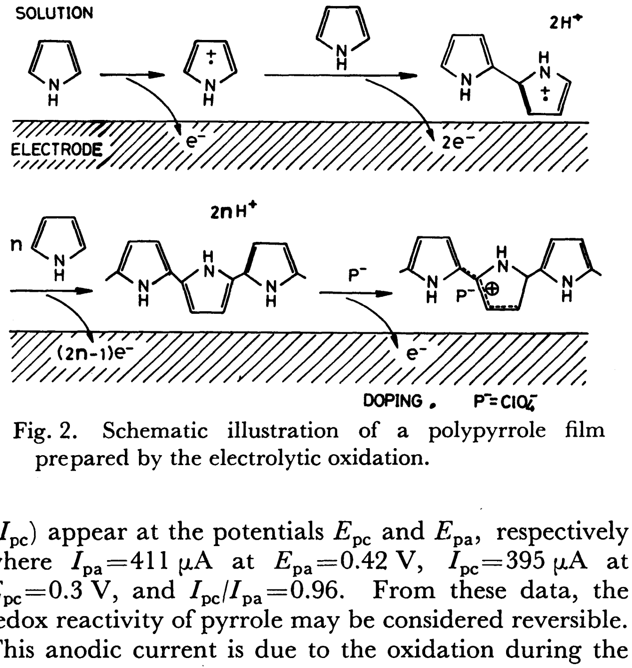
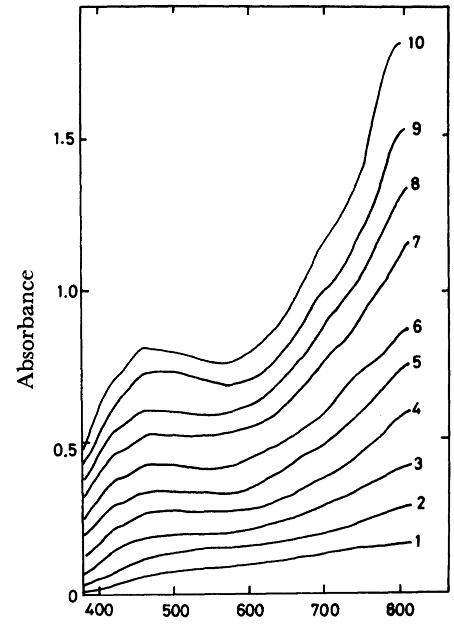


Fig. 2. Schematic illustration of a polypyrrole film prepared by the electrolytic oxidation.

(I_{pc}) appear at the potentials E_{pc} and E_{pa}, respectively where $I_{pa}=411$ µA at $E_{pa}=0.42$ V, $I_{pc}=395$ µA at $E_{pc}=0.3$ V, and $I_{pc}/I_{pa}=0.96$. From these data, the redox reactivity of pyrrole may be considered reversible. This anodic current is due to the oxidation during the polymerization of pyrrole accompanying a ClO_4^- doping into the polypyrrole film matrix.[18] The anodic and cathodic currents decrease with increasing number of potentials cyclings, due to increase in film thickness.

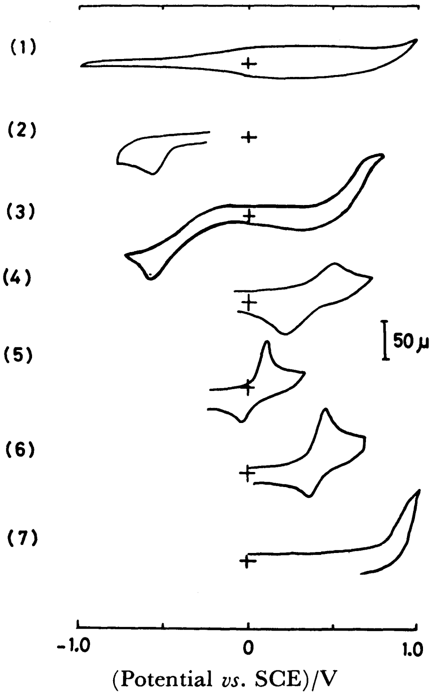
The polymerization reaction under an anodic polarization of an electrode can take place accompanying a doping of ClO_4^- anion, leading to the formation of pyrrole cation radical-ClO_4^- pair, and is controlled by the charge amount of anodic current. That is, the concentration of ClO_4^- as a dopant controls the electrical conductivity of the film from 0.1 to 10 Ω^{-1} cm^{-1}. The polypyrrole film formation is schematically illustrated in Fig. 2.

The thickness of polypyrrole was increased and its blue color deepened with increasing electrolytic charge amount. Absorption spectra of the polypyrrole film on an optically transparent SnO_2 electrode in the course of the polymerization are shown in Fig. 3 as a function of the electrolytic charge amount. The absorbance in



Wavelength/nm

Fig. 3. Absorption spectra of the polypyrrole films prepared on a SnO_2 electrode as a function of the oxidation charges. 1; 12.4 mC/cm², 2; 19.1, 3; 26.0, 4; 35.5, 5; 43.0, 6; 47.3, 7; 66.1, 8; 75.2, 9; 83.2, 10; 97.0.



(Potential *vs.* SCE)/V

Fig. 4. Current-potential curves at the polypyrrole film electrode in the aqueous solution (0.1 M $NaClO_4$) with various redox agents. (1) without redox agent, (2) 1 mM MV^{2+}, (3) 1 mM H_2Q, (4) *ca.* 1 mM O_2, (5) 1 mM Cu^{2+}, (6) 1 mM I^-, (7) 1 mM Br^-.

the visible region, especially at wavelengths longer than 600 nm, increases with increase in the oxidation charge amount.

Figure 4 shows current-potential curves which were

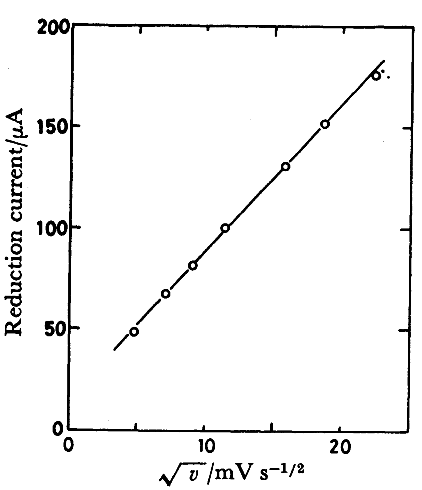


Fig. 5. Cathodic peak currents of MV^{2+} as a function of potential sweeping rate (v).

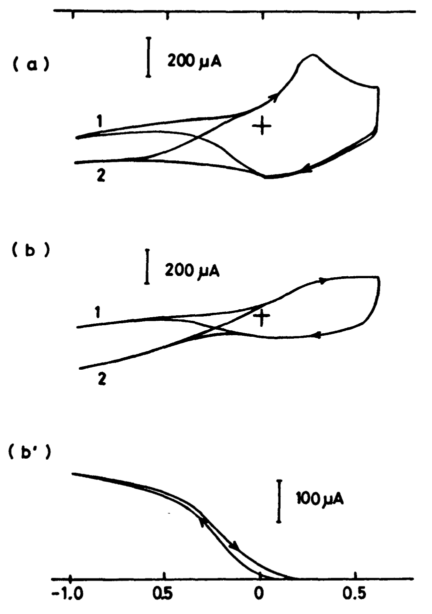


Fig. 6. Current-potential curves at the polypyrrole film in a solution with 0.1 M TBAP in the dark (1) and under light irradiation (2). (a) At the film prepared with the charge of 23.4 mC (1200 Å thickness), (b) at the film prepared with the charge of 30.0 mC (1500 Å thickness), (b′) a photocurrent-potential curve at the film (b).

obtained with the Pt electrode with the polypyrrole film in the presence or absence of various redox agents such as methyl viologen (MV^{2+}), hydroquinone (H_2Q), O_2, Cu^{2+}, I$^-$, and Br$^-$ in solution. The presence of redox agents brings about increase in the anodic and cathodic currents. Especially, the redox agents H_2Q, Cu^{2+}, and I$^-$ can exchange electrons with the polypyrrole electrode surface, resulting in reversible voltammograms. Oxygen can be reduced on this film surface. Therefore, the polypyrrole film doped with ClO_4^- can be considered to have electrical conducting characteristics which are similar to those of metallic electrodes. Diaz *et al.*[17,18] have reported that redox agents such as ferricinium and that redox reactions for these redox agents are reversible on this film electrode.

Figure 5 shows cathodic peak currents as a function of the sweeping rate of potential. The linear relationship of the plot indicates that the charge transfer reaction is controlled by the MV^{2+} diffusion toward the polypyrrole electrode surface. The diffusion constant of MV^{2+} in Fig. 5 is 4.8×10^{-6} cm^2 s^{-1}, a little smaller than the value of 1.38×10^{-5} cm^2 s^{-1} obtained with a Pt electrode in an acetonitrile solution.[22] This discrepancy between the diffusion constants may result from surface constitution of the polypyrrole film.

Figure 6 shows current-potential curves obtained under light irradiation for the polypyrrole films which were prepared by applying charge amounts of (a) 23.4 mC and (b and b′) 30.0 mC for oxidative polymerization with resulting film thicknesses of *ca.* 1200 and 1500 Å, respectively; in these preparations cathodic photocurrents were observed at cathodic potentials more negative than 0.0 V *vs.* Ag. Cathodic photocurrents at the potential of −1.0 V were 120 μA for (a) and 260 μA for (b), reaching a maximum value with the film corresponding to *ca.* 40 mC, as established from variation in the relationship between light absorption and resistance of the film with film thickness. Hysteresis of photocurrent is observed during cyclic potential scanning, as shown in Fig. 6(b′). This may be explained in terms of the concentration of the dopant, that is, the film composition depends on the flow of dopant ClO_4^- which directs from the polypyrrole film into the solution at the cathodic current observed and in the reverse direction at the anodic current.

In the aqueous solution with 0.1 M $NaClO_4$, current-potential characteristics of the redox agents are similar to those in the acetonitrile solution; the non-Faradaic current is a little larger in the former solution than in the latter. The onset potential for cathodic photocurrent is 0.3 V *vs.* SCE.

For interpretation of the electrochemical behavior and photoresponse of polypyrrole film, the following physical properties need to be taken into account: The electrical property of organic polymers such as polyacetylene, polypyrrole, and poly(sulfur nitride) is controlled by the π-electron distribution for polymer, as schematically illustrated in Fig. 7. A polymer film with perfectly localized π-electrons (Fig. 7(1)) has no or a low conducting property because the π-electrons over the polymer are trapped in deep wells of electronic potential in double bonds. According to the traditional semiconductor theory, the energy diagram can be represented as being equal to the one for an intrinsic semiconductor with a large bandgap energy E_g. On the contrary, the polymer film with fully delocalized π-electrons (Fig. 7(2)) has a high conducting property because the π-electrons are distributed over the polymer chain.

For the film involved in the charge transfer doping of an anion (P$^-$) (Fig. 7(3)), an acceptor is induced to appear removal of one π-electron from one π-bond of the polymer under the requirement of electrical neutrality and causes localized distortion of the π-electrons on the polymer. The nonlinear wave function of the positively-charged localized region is called a soliton.[23,24]

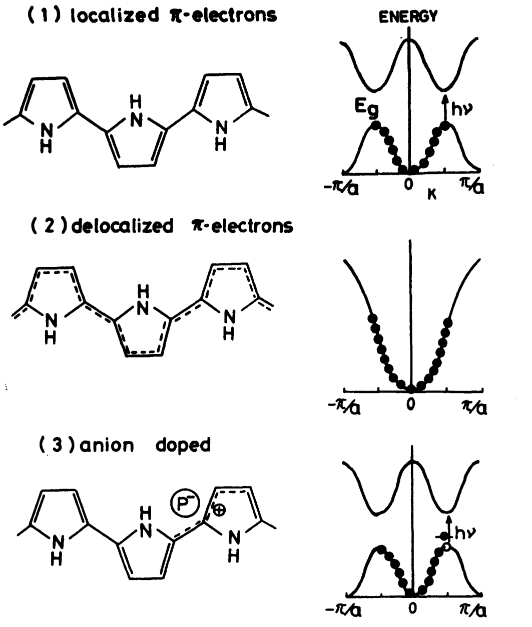


Fig. 7. Schematic diagram of the energy bands of the polypyrrole film where the energy diagram is governed by the electron distribution spreading over the polypyrrole linkage. Electroconductivity of the film with localized π-electrons is quite low because of the large bandgap energy E_g, on the contrary, that of the film with delocalized π-electrons is high because of no bandgap energy. A dopant forms a state within the bandgap resulting in an increase in the conductance.

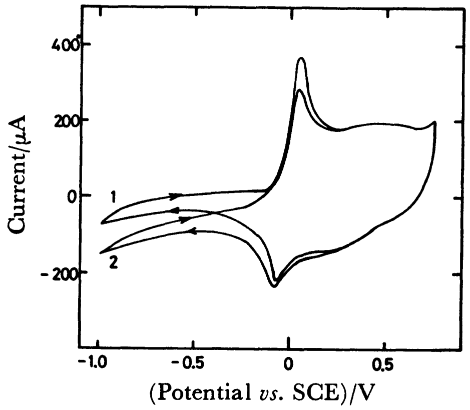


Fig. 8. Current-potential curves at the polypyrrole film of 1000 Å thickness in a 0.1 M $NaClO_4$ solution with 1 mM $CuCl_2$. 1; in the dark, 2; under light irradiation.

The spreading mode of a soliton determines the electrical conductivity of polymer. The soliton density increases with increase in the dopant concentration, enhancing the electrical conductivity of polymer. The polypyrrole film with ClO_4^- anions doped may be considered to be a p-type semiconductor with positive acceptor sites in its bandgap.

The dopant transfer into and out of polymer, allowed to occur by anodic and cathodic polarization, respectively, in the course of potential cycling, can change the acceptor density in the polymer; under cathodic polarization the polymer has a high conductivity. The hysteresis illustrated in Fig. 6(b′) is presumed to be due to a conductivity difference between the anodic and cathodic polarizations.

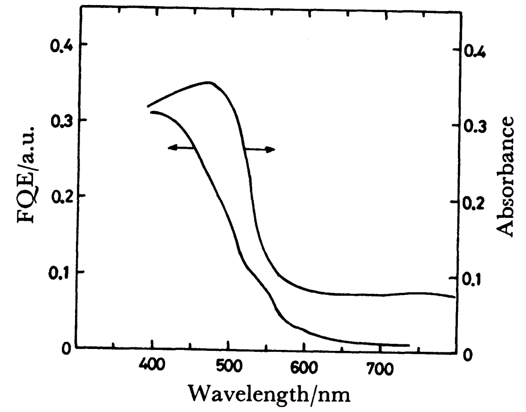


Fig. 9. Actionspectrum of the formal quantum efficiency (FQE) of cathodic photocurrents observed at the polypyrrole film electrode at −1.0 V *vs.* Ag in an acetonitrile solution and the absorption spectrum of the polyrrole film polarized at −1.0 V. FQE denotes the current efficiency against the amount of the incident photons.

Figure 8 shows current-potential curves for the polypyrrole electrode in an aqueous solution with 0.001 M $CuCl_2$ and 0.1 M $NaClO_4$ under light irradiation. The current-potential curve in the dark (a) has a couple of anodic and cathodic current peaks around 0.0 V *vs.* SCE, representing an occurrence of the reversible redox reaction of Cu^{2+}/Cu^+

$$Cu^{2+} + e^- \rightleftharpoons Cu^+. \qquad (1)$$

When the polypyrrole electrode is irradiated with light, cathodic photocurrent appears at negative potentials than 0.3 V. For curve (b) in Fig. 8, the anodic current peak for the oxidation of Cu^+ to Cu^{2+} is larger than the one in the dark (a). The photoinduced increase in anodic current is attributed to the increase in the Cu^+ concentration on the surface due to the reduction by photogenerated conduction band electrons. Because an electron-hole pair produced in a photoexcited polypyrrole film can be separated by the electric field generated by the cathodic polarization, the electron produced reduces the oxidized form (Cu^{2+}) on the film surface. Therefore, it is inferred that the polypyrrole film electrode can act as an active photocathode for the redox reaction of solution species.

The action spectrum of cathodic photocurrents at the potential of −1.0 V *vs.* SCE is shown in Fig. 9, were the action spectrum coincides well with the absorption spectrum of polypyrrole film referring to a photoabsorption due to π-π^* transition at wavelengths shorter than 550 nm. From this result, the bandgap energy of the p-type semiconducting polypyrrole film is estimated to be about 2.2 eV. The action and absorption spectra of the film observed at −1.0 V are different from the absorption spectrum of the film observed at 1.0 V, as seen from Fig. 3. This electrochromic property of the polypyrrole film arises from conformation change of the polymer based on the ClO_4^- doping with electrode

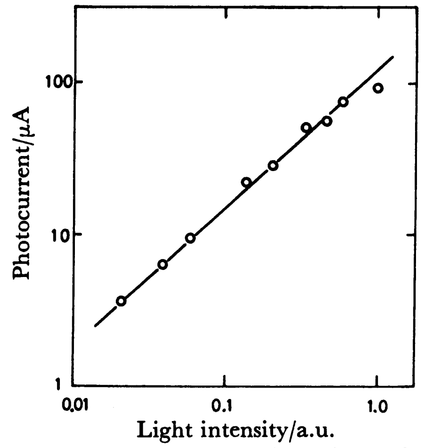


Fig. 10. Dependence of the light intensity on the cathodic photocurrents observed at the polypyrrole film electrode polarized at −1.0 V *vs.* Ag in an acetonitrile solution with 0.1 M TBAP and 2 mM MV^{2+} under light irradiation with wavelengths longer than 430 nm.

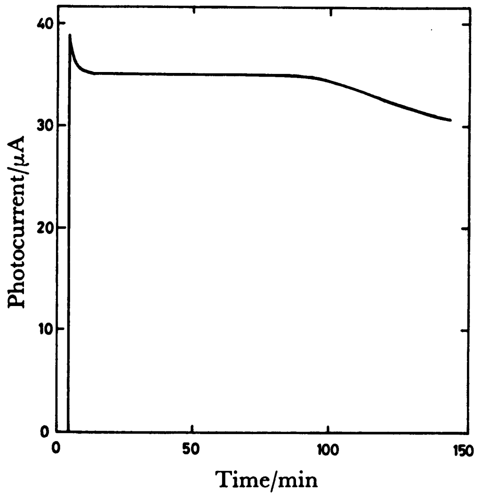


Fig. 11. Time dependence of the cathodic photocurrent observed at the polypyrrole film (500 Å thickness) polarized at −1.0 V *vs.* Ag in an acetonitrile solution with 2 mM MV^{2+}.

polarization.

Figure 10 shows the light intensity dependence of cathodic photocurrent which was observed at −1.0 V *vs.* Ag in an acetonitrile solution. The cathodic photocurrent increases in a linear relationship with a slope of *ca.* 0.9 with increasing light intensity. It follows that the carrier formation is of one photon. The quantum efficiency of the photocurrent is around 0.01.

Figure 11 shows the time dependence of cathodic photocurrent. Photocurrents flow with fair stability but decrease by 15% after a 120 min irradiation. The charge required for the polypyrrole film preparation and the photocurrent charge for 120 min are 10 and 250 mC, respectively. The result suggests that the polypyrrole film works stably under the restriction that the ratio of cathodic photocurrent charge to polymerization charge should be less than 20, although the photocurrent decreases gradually over about 2 h.

Conclusion

The polypyrrole film was formed on Pt and SnO_2 electrodes through an oxidation of pyrrole accompanying a radical linking and an anion doping. The polypyrrole film is capable of electrical conduction based on the solution effect that a doped anion (ClO_4^- in this study) affects the distribution of π-electron densities in the polypyrrole linkage.

Redox reactions of solution species occur on the polypyrrole film electrode. Under visible light irradiaton at $\lambda < 550$ nm, the polypyrrole film electrode shows a p-type semiconducting property, resulting in cathodic photocurrent evolution due to reduction of solution species.

p-Type semiconducting polypyrrole films with high conductance can be developed which are applicable to photoelectrodes in photoelectrochemical cells and to electrochromic devices.25)

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