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Study of photoanode kinetics at metal-free phthalocyanine in an organic p/n bilayer with respect to the pH conditions employed

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ABSTRACT

Using an organic p/n bilayer comprised of 3,4,9,10-perylenetetracarboxyl-bisbenzimidazole (PTCBI, an n-type semiconductor) and *29H,31H*-phthalocyanine (H_2Pc, a p-type semiconductor) as a photoanode in the presence of $Fe^{II}(CN)_6^{4-}$ (an electron donor), the oxidation kinetics on the H_2Pc surface was investigated with respect to the pHs employed (i.e. pH = 4, 7, and 10). The kinetic analysis of the rate-limiting charge transfer between H_2Pc and $Fe^{II}(CN)_6^{4-}$ was conducted by assuming the Langmuir adsorption equilibrium at the H_2Pc/water interface. In addition to a demonstration of the PTCBI/H_2Pc photoanode under the weakly acidic–alkaline conditions, the present work evidently shows that the photoanodic reaction is kinetically independent of the pH conditions employed.

1. Introduction

The study of molecule-based photoelectrodes has been extensively conducted to target the efficient uptake of visible-light energy into output [1,2]. Although organic p/n bilayer has been recognized as a photovoltaic material in dry state [3], we have recently shown its novel function as a photoelectrode in the water phase [4–9]. For example, when applying the organic bilayer to a photoanode, there is evidence of photo-induced oxidation occurring at the solid (p-type semiconductor)/water interface (Scheme 1). This photoelectrochemical event originates in the photophysical characteristics in the p/n interior (i.e. light absorption, dissociation of exciton into carrier, and carrier conduction); in addition, we also confirmed that a built-in-potential was formed at the p/n interface under an equivalent condition [9]. The organic bilayer of 3,4,9,10-perylenetetracarboxyl-bisbenzimidazole (PTCBI, an n-type semiconductor)/*29H,31H*-phthalocyanine (H_2Pc, a p-type semiconductor) can work as a stable and efficient photoanode [6–9], according to the Scheme 1. The most advanced characteristic of the PTCBI/H_2Pc bilayer is the fact that the entire visible-light energy less than 750 nm in the wavelength is available for chemical reactions at the H_2Pc/water interface, which is based on the action spectrum for photocurrent (cf. few examples of such a photodevice featuring inorganic materials have been appeared in literature [10,11]). To date, the photoelectrode characteristics of PTCBI/H_2Pc have been studied only in alkaline solutions and to the best of our knowledge, the acid–base behavior of H_2Pc particularly in its solid state has not been clarified. If the surface of H_2Pc changes with the conditions of the pH employed, there is the possibility that the photoanodic output due to charge transfer at the solid surface may vary in terms of kinetics. In the present work, the kinetics of the organic photoanode was examined with respect to pH, particularly in order to evaluate an applicable range of the photoelectrode in the water phase.

2. Experimental

PTCBI was synthesized and purified according to a previously described procedure [12]. H_2Pc (Tokyo Kasei Co., Ltd.), which was commercially available, was purified by sublimation prior to use (cf. thermal control was conducted for the vessel exterior at 510 °C). Potassium hexacyanoferrate (II) trihydrate ($K_4[Fe^{II}(CN)_6]\cdot 3H_2O$) was obtained from Kanto Chemical Co., Inc. and an ITO-coated glass plate (resistance = 8 Ω cm^{-2}; transmittance = more than 85%; ITO thickness = 174 nm) from Asahi Glass Co., Ltd.

The PTCBI/H_2Pc bilayer was prepared by vapor deposition (degree of vacuum = approx. 5.0×10^{-4} Pa; deposition

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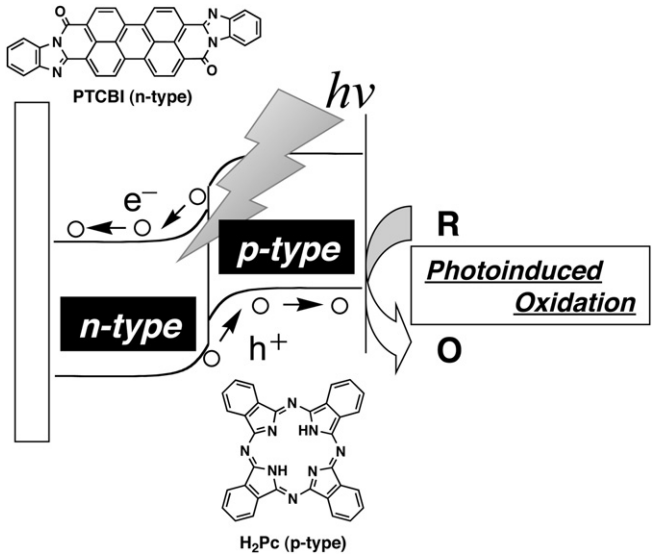

Scheme 1. Schematic illustration of oxidation taking place at ITO/PTCBI/H_2Pc.

speed = 0.03 nm s^{-1}), which comprised PTCBI coated on an ITO and H_2Pc coated on top of the PTCBI layer (denoted as ITO/PTCBI/H_2Pc). During vapor deposition, the temperature at the ITO plate was not controlled. An absorption spectral measurement was conducted using a spectrophotometer (Hitachi, U-2010). The resulting absorption spectra of both PTCBI and H_2Pc were identical to those reported earlier [13], and their absorption coefficients indicated the thickness of each film (cf. the aggregation structure of the H_2Pc single layer was also identifiable from the absorption spectrum; namely, the polymorph of H_2Pc was assignable to the α phase, which is also supported by earlier findings [14]). Since the additivity of the absorption coefficients is considered to be held on the visible-light absorption spectrum of the bilayer, the two unknown parameters – the thicknesses of both layers – were estimated by solving simultaneous equations based on absorbance at two distinct wavelengths.

An electrochemical glass cell was equipped with a modified ITO working electrode (effective area = 1 cm^2), a spiral Pt counter electrode, and an Ag/AgCl (in saturated KCl electrolyte) reference electrode. The entire photoelectrochemical study was conducted in an aqueous electrolyte solution containing a known concentration of $K_4[Fe^{II}(CN)_6]$ within an Ar atmosphere, where distinct conditions of pH were employed (pH = 4, 7, and 10). This study was carried out using a potentiostat (Hokuto Denko, HA-301) with a function generator (Hokuto Denko, HB-104), a coulomb meter (Hokuto Denko, HF-201), and an X-Y recorder (GRAPHTEC, WX-4000) under illumination. A halogen lamp was used as the light source. The light intensity of the lamp was measured using a power meter (Ophir Japan, Ltd., Type 2A). In the present study, the effect of incident light reflecting from the glass surface was not considered (i.e. the light intensity was not corrected).

3. Results and discussion

The time course of photocurrent was first measured to evaluate the characteristics of ITO/PTCBI/H_2Pc in kinetics terms. A typical example is shown in Fig. 1. An increasing current was found to exhibit an enhancement by on of illumination, where a spiky photocurrent (J_{in}) was initially observed, after which it attained a steady state (J_s represents a steady-state photocurrent).

The photoelectrode characteristics were investigated in terms of light intensity and reactant concentration (see Figs. 2 and 3). In all the cases studied, the resulting photocurrents exhibited the same response as shown in Fig. 1.

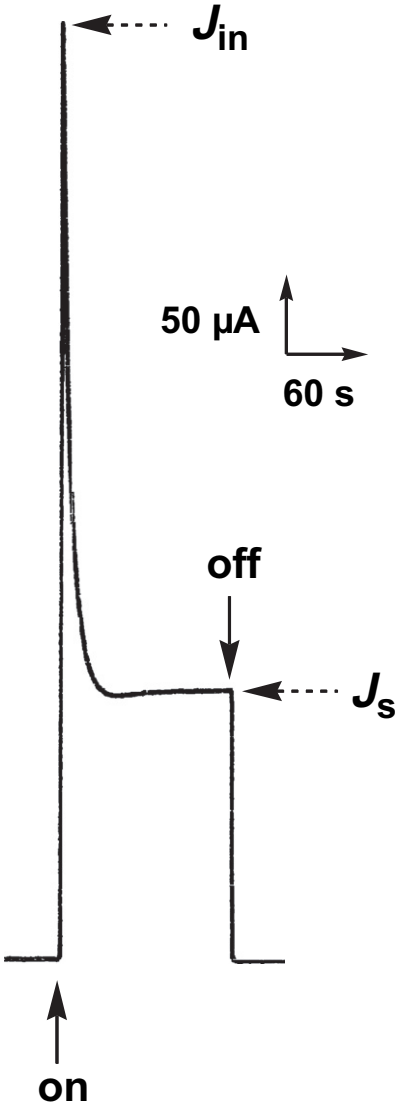

Fig. 1. A transient photocurrent generated at ITO/PTCBI/H_2Pc immediately after irradiation with white light (intensity, 112 mW cm^{-2}). Film thickness = 300 nm (PTCBI)/70 nm (H_2Pc); concentration of $Fe^{II}(CN)_6^{4-} = 5 \times 10^{-3}$ mol dm^{-3} (pH = 10); applied potential = +0.3 V.

Fig. 2 shows the photoanodic currents with a change in light intensity, which also shows that the photocurrents of both J_{in} and J_s attained constant values under irradiation conditions higher than 50 mW cm^{-2}. Also in a high concentration of $Fe^{II}(CN)_6^{4-}$ (10 mmol dm^{-3}), a similar dependence of photocurrent on the light intensity was confirmed, although the magnitude of the resulting photocurrents was relatively large in this case. If the photophysical process within the bilayer is rate-determining, the photocurrent should immediately attain a steady state without an overshoot (cf. Fig. 1). Those results indicate that the photoelectrode kinetics was not dominated by the carrier generation within the bilayer interior.

A measurement similar to that in Fig. 1 was also conducted with a change in the concentration of $Fe^{II}(CN)_6^{4-}$, which involved white-light irradiation administered under a high intensity condition (i.e. light intensity = 112 mW cm^{-2}). The results are summarized in Fig. 3. Saturation in the concentration was observed for both J_{in} and J_s, implying that the photo-induced oxidation is not kinetically controlled by the mass transfer of $Fe^{II}(CN)_6^{4-}$ (i.e. diffusion). As