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Electrochemical properties of protoporphyrin IX zinc(II) films

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Abstract

The electrochemical properties of protoporphyrin IX zinc(II) (ZnPP) films on indium–tin oxide (ITO) substrate have been studied for three types of films with different arrangements, which were an adsorbed film of ZnPP and LB films of ZnPP and its hybrid with hexadecyltrimethylammonium bromide. Cyclic voltammetry (CV) measurement showed that, as the adsorbed amount of ZnPP increases, an irreversible oxidation peak of ZnPP film is intensified. This reveals that electrochemical properties depend on the adsorbed amount rather than the orientation of porphyrin molecules. It was also supported from CV measurement and ultraviolet–visible absorption spectroscopy that porphyrins adsorbed on ITO substrate were desorbed after the single scan of potential. Additionally, photoresponse of these ZnPP films was investigated by photocurrent measurement. The photocurrent generation is due to carboxylic acid moieties but not ZnPP macrocycles.

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Keywords: Porphyrin; Protoporphyrin; Hexadecyltrimethylammonium bromide; Langmuir–Blodgett film; Cyclic voltammetry; Photocurrent; ITO electrode

1. Introduction

The organization of porphyrins and their intentionally designed derivatives on solid substrates is of current interest due to their important roles in making functional materials and devices, such as catalysts [1] and sensors [2], and also as a model for some biochemical processes [3–5]. In particular, mono- or multilayer films of porphyrins may provide not only a template for their catalytic and biopolymer-binding properties but also a component in molecular devices. These properties greatly depend on the structure of the porphyrin derivatives, the environment surrounding the porphyrin, and the distance between porphyrin units [6,7]. Ultrathin films with a controlled orientation on solid substrates can be achieved by means of the self-assembled monolayer (SAM) [6–13] and Langmuir–Blodgett (LB) [5,14] techniques. For the preparation of porphyrin SAMs, two methods have been reported. One is chemical binding of the porphyrin functional groups to the substrate [6–11], and the other is axial coordination of the porphyrin central metal on a ligand covalently bound to the substrate [12,13].

Previous works [10,11] have reported that a stable multilayer was fabricated from self-assembly of protoporphyrin IX zinc(II) (ZnPP) (Fig. 1 insert), a natural porphyrin with two carboxy groups, onto an Au surface by the adsorption from a ZnPP solution. Furthermore, Li and Imae [15] investigated the formation of ordered molecular assembles of ZnPP and its hybrids with surfactants, *N*-hexadecylethylenediamine, hexadecyltrimethylammonium bromide ($C_{16}TAB$), and didodecyldimethylammonium bromide, by using LB technique and comparing with SAMs. As a result, the band positions of ultraviolet–visible (UV–vis) spectra are different, indicating that the orientation of porphyrin differs, depending on the fabrication method [16]. However, effects of such arrangement on the fundamental properties of ZnPP films have not been understood.

In the present study, we focus on the construction of ZnPP films (ZnPP SAM and LB films of ZnPP and its hybrid with $C_{16}TAB$). The electrochemical properties of these films are investigated, based on cyclic voltammetry, UV–vis spectroscopy, and photoelectrochemistry, and the influence of orientation of ZnPP is compared and discussed.

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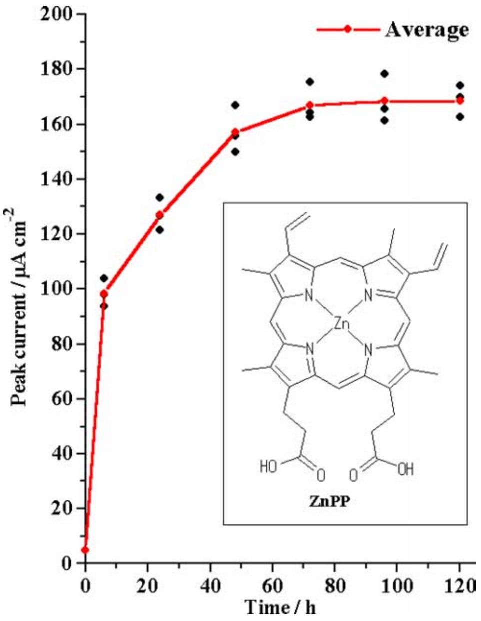


Fig. 1. Anodic peak intensity of CV wave depending on time of ITO electrode immersion into a solution (ethanol/DMF = 4:1) of ZnPP with a concentration of 0.2 mM. Closed red circles denote average values of measurements (three times). Insert is a chemical structure of ZnPP.

2. Experimental

2.1. Chemicals

ZnPP was purchased from Aldrich Chemical Co., $C_{16}TAB(CH_3(CH_2)_{15}N(CH_3)_3Br)$ was a product from Tokyo Chemical Industries Co. Ltd., and arachidic acid was purchased from Wako Pure Chemical Industries, Co. Ltd. All chemicals were used as received without further purification. Other reagents used in the experiment were all commercially available and in analytical grade. Milli-Q ultrapure water (Millipore Co., 18.3 MΩ) was used throughout the experiment.

2.2. Substrate

The ITO electrode plate was donated by Professor Osamu Takai, Nagoya University. It was cleaned by exposing it to UV/ozone (Nippon Laser & Electronics Laboratory).

2.3. Fabrication of the adsorbed films

The ITO electrode plate was immersed at room temperature into an ethanol/DMF (4:1 in volume) solution of ZnPP with a concentration of 0.2 mM. After immersion, the plate was rinsed with an ethanol/DMF (4:1 in volume) mixed solvent and sonicated in the mixed solvent for 3 min. Finally it was rinsed again with the mixed solvent and water and dried overnight in vacuo. Fig. 1 shows a plot of the anodic peak intensity of the CV wave against immersion time. This result confirmed that 70 h is enough to reach the adsorption equilibrium. Following this experiment, we fixed on immersing for 72 h.

2.4. Preparation of LB films

The preparation of the LB film was carried out on an LB film deposition apparatus (Nippon Laser & Electronics Laboratory). ZnPP and its hybrid with $C_{16}TAB$ at a molar ratio of 1:2 were dissolved in chloroform/DMF (4:1 in volume). The concentration of ZnPP in these two systems was commonly 57.5 μM. For the fabrication of LB film, following the immersion of the ITO electrode in the subphase, a small amount of solution was spread with a microsyringe on the water subphase at $25 \pm 0.5\,^{\circ}C$. The solvent was allowed to evaporate for 20 min, and the floating film was then compressed to 25 $mN\,m^{-1}$ at a rate of 10 $mm\,min^{-1}$. Twenty minutes were spent to establish equilibrium of the monolayer. The monolayer was then transferred onto a clean ITO electrode by the vertical transfer method at a rate of 2 $mm\,min^{-1}$. The multilayer LB films were prepared by successive upstroke and downstroke accumulation. All the LB films were dried overnight in vacuo.

2.5. Apparatus

UV–visible transmission spectra were recorded at room temperature on a Shimadzu UV-2200 spectrometer. The reference used was a blank ITO electrode. All electrochemical measurements were performed on a computerized electrochemical measurement system (HZ-3000, Hokuto Denko). A three-electrode cell was used. A saturated calomel electrode (SCE) and a platinum wire were used as the reference and counter electrodes, respectively. The supporting electrolyte used was 0.1 M Na_2SO_4 in water, which was degassed by nitrogen bubbling. During the photocurrent measurements, the light irradiation was carried out by a UV irradiation light source (EX-250, HOYA–SCHOTT Co.). The UV light (<370 nm) was cut with a S76-L37 filter (Suruga Seiki Co. Ltd.).

3. Results and discussion

3.1. Oxidation of ZnPP films

The cyclic voltammetric measurements of ITO electrodes, which were a bare film, coated with LB films of arachidic acid, ZnPP, and ZnPP/$C_{16}TAB$ and an adsorbed film of ZnPP in an aqueous 0.1 M Na_2SO_4 solution, were performed with a sweep rate of 50 $mV\,s^{-1}$ and shown in Fig. 2. It is evident that the current intensity was suppressed after the bare ITO electrode was coated with the arachidic acid LB film. This implies that the ITO surface is completely shielded from the aqueous solution by a nonconductive LB film. Moreover, for both bare ITO electrode and ITO electrode coated with arachidic acid LB film, the first

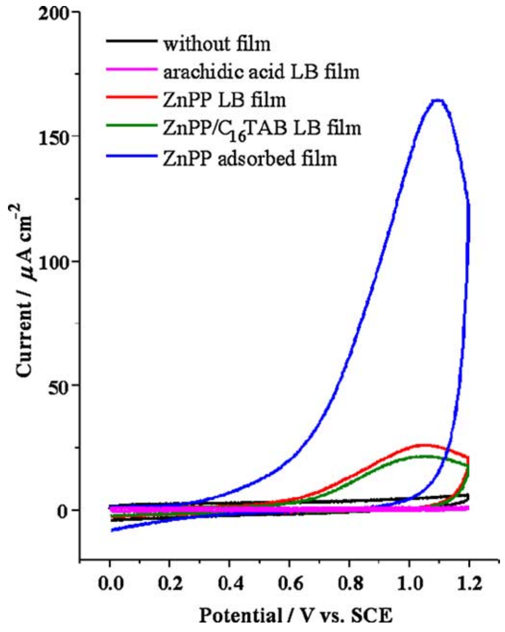
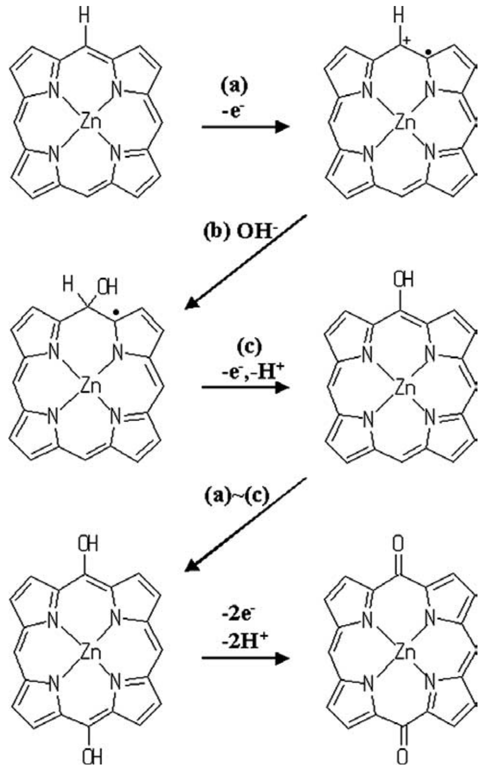


Fig. 2. Cyclic voltammograms of ITO electrodes, which are bare, coated with LB films of arachidic acid, ZnPP and ZnPP/C_{16}TAB, and adsorbed ZnPP, in an aqueous 0.1 M Na_2SO_4 solution. The sweep rate is 50 mV s^{-1}.

and successive scans between 0 and 1.2 V vs SCE remained approximately the same, indicating the stability of the electrodes. On the other hand, the LB films, including ZnPP, showed well-defined oxidation peaks, though the films are closely packed and make the ITO surface isolate from the aqueous solution. Similar redox behavior was also observed for the ZnPP adsorbed film. Though the similarity of the coverage of adsorbed film to that of LB film is unknown, the influence of coverage of adsorbed film must be considered, as discussed later, because peak intensities are incomparably large. CVs observed on three films, including ZnPP, show a well-defined oxidation peak but no reduction peak, indicating an irreversible reaction, and the electroactivity was lost after a single scan (data are not shown).

The fact that the oxidation reaction was not observed at the arachidic acid LB film shows that the irreversible oxidation reaction is due to porphyrin moieties. In general, metalloporphyrins are able to give rise to two-electron redox reaction of the porphyrin macrocycle as well as redox reaction of the central metal. It is noted that the first and second ring oxidation potential of ZnPP are 0.75 and 1.08 V, respectively [17]. In aqueous systems, however, methine bridges are known to be sites for nucleophilic attack, and provide meso-hydroxyporphyrin by following electron transfer to another radical or to the electrode. The meso-hydroxyporphyrin has a lower oxidation potential than the original porphyrin. Thus, the process is readily repeated at another methine bridge, and the resulting dihydroxyporphyrin can immediately be oxidized, in another two-electron step, to a quinoidal dioxoporphomethene, Zn (α,γ-dioxoporphomethene). For the reasons mentioned above, the oxidation potential was not observed around 0.75 V. It is therefore possible that the oxidation of the ZnPP film in contact with water leads to rapid formation of the dioxoporphomethene, via the scheme shown in Scheme 1, accounting for the anodic current on the initial cycle and subsequent loss of electroactivity.



Scheme 1. Oxidation of ZnPP film in an aqueous solution.

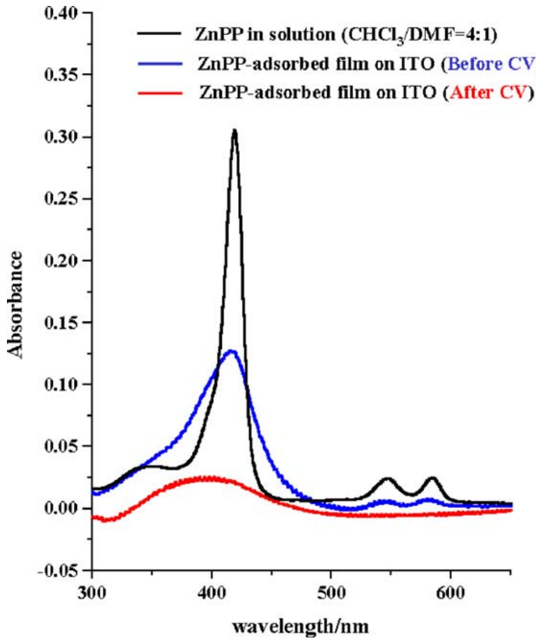


Fig. 3. UV–vis spectra of ZnPP in a solution ($CHCl_3$/DMF = 4:1) and of adsorbed films of ZnPP on ITO before and after oxidation.

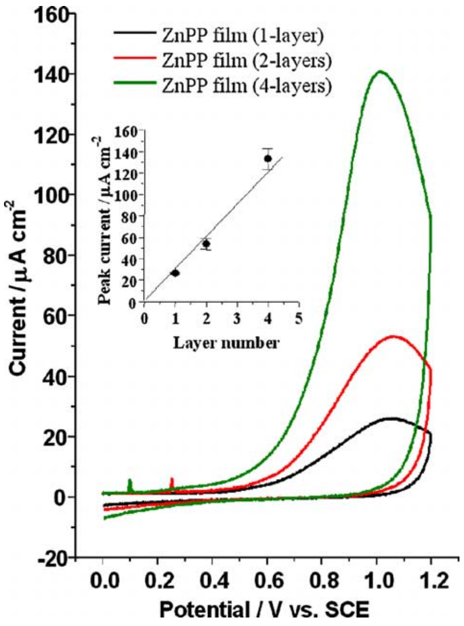


Fig. 4. Cyclic voltammograms of one, two, and four layers of ZnPP multilayer LB films. The insert is a plot of the anodic peak intensity against the layer number.

Fig. 3 compares UV–visible absorption spectra of a ZnPP adsorbed film on the ITO electrode, before and after CV measurement, with that of ZnPP in a chloroform/DMF (4:1 in volume) solution. ZnPP molecules in the solution exhibit three bands, due to the Soret band (419 nm) and two Q-bands. For the ZnPP film before measurement, the band position is almost the same as the ZnPP in solution (Soret band: 416 nm). After measured CV, however, there was no well-defined band from the ZnPP film. Macor and Spiro [17] have reported that the absorption spectrum of Zn (α, γ-dioxoporphomethene) was very similar to that of the unoxidized ZnPP film in point of band position and molar absorption coefficient. Therefore, after a single scan, most of the ZnPP molecules coated on ITO electrode are probably desorbed by the oxidation. It is possible that desorption of ZnPP results from increasing hydrophilicity due to a keto group caused by oxidation.

Fig. 4 shows cyclic voltammograms obtained from one, two, and four layers of ZnPP multilayer LB films, and the insert is a plot of the anodic peak intensity against the layer number. It is obvious that the intensities of the anodic current increase in proportion to an increase of layer number. In other words, there was a linear relationship between the intensity of the anodic current and the amount of adsorption.

In general, the cyclic voltammogram of a working electrode coated by the redox substance differs from that of a free electrode in solution containing a redox substance. In the case where redox-activated species are immobilized on an electrode surface, the redox reaction is unaccompanied by a mass-transfer process such as diffusion but produces redox-activated species on the electrode surface,

$$\mathrm{Ox_{ad}} + ne^- \rightleftarrows \mathrm{Red_{ad}}, \tag{1}$$

where n is the number of electrons exchanged per molecule. Furthermore, quantity of electricity Q (C) is ordinarily gained from the integration of an oxidation peak or a reduction peak, and in this case especially, it is also in proportion to the adsorbed amount Γ (mol cm^{-2}) of the redox-activated species,

$$|Q| = nFA\Gamma, \tag{2}$$

where F is the Faraday constant and A the area of the electrode. Therefore, Γ is calculated by using Eq. (2). In the meantime, in the cases where the molecules adsorb onto the electrode according to the Langmuir monolayer adsorption isotherm and react fast and reversibly on the electrode, the CV wave must have no difference between oxidation and reduction peak potentials and become axial symmetry. The intensities of peak current should be in proportion to sweep rate. However, in practice, adsorbates and electrodes were influenced by several factors such as temperature, interaction between adsorbates, electron transfer rate, solvent and supporting electrolyte, revealing waves far from the ideal behavior.

In the present work, upper limit of sweep potential was set at 1.2 V, because ITO electrodes work in the region from −0.6 to 1.2 V. Oxidation of ZnPP proceeds incompletely in this region. Hence, it is indefinite that CV waves are axial symmetry. If the CV wave was asymmetric, Q could not be calculated from the integration of the anodic peak intensity, and therefore it is difficult to decide the adsorbed amount of ZnPP. In this speculation, we touch only on proportionality between layer number and intensity of the anodic peak. Using this linear relation to estimate layer thickness, the ZnPP-adsorbed film shown in Fig. 2 was estimated to be 5–6 layers, that is, multilayer. This result is consistent with the AFM observation of ZnPP adsorption on gold substrate [18]. The layer formation is due to the π–π interaction of porphyrin macrocycles in the lateral direction and hydrophobic interaction or hydrogen bonding in the normal direction.

3.2. Photoirradiation and photocurrent generation

Photoelectrochemical measurements were carried out in an aqueous 0.1 M $\mathrm{Na_2SO_4}$ solution using an ITO working electrode, a platinum counter electrode, and a SCE. Fig. 5 displays current produced by on-and-off illumination of visible light. The films show an anodic photoelectronic response at an applied potential of 0.5 V vs SCE when the light is switched on and off. The photocurrents observed at electrodes covered with films are much higher than those of the bare electrode. The anodic photocurrent generation implies electron transfer from adsorbates to the ITO electrode. In general, if ITO electrodes modified with photoreactive dyes are used, the anodic photocurrent is generated by electron transfer between the electrode and dyes, which are excited from ground state to exited state. However, as seen in Fig. 5, the photocurrent was also observed at the arachidic acid LB

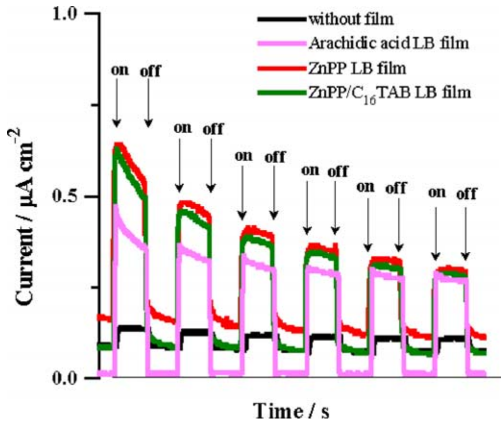
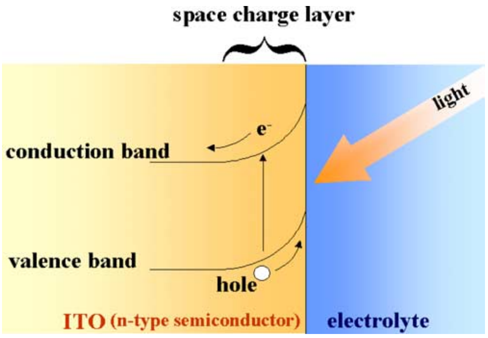


Fig. 5. Photoelectrochemical response of ITO electrodes, which are bare, coated with LB films of arachidic acid, ZnPP, and ZnPP/C$_{16}$TAB, at applied potential of 500 mV vs SCE in an aqueous 0.1 M Na$_2$SO$_4$ solution.

film, which has no chromophore to be absorbed in the visible region. Photocurrent of arachidic acid film is comparable to those of ZnPP and ZnPP/C$_{16}$TAB LB monolayer films, indicating that this photocurrent is due not to porphyrin macrocycles but to carboxy groups, which interact with the ITO electrode surface.

Molecular adsorption onto the surface of a metal oxide such as the ITO electrode is more complicated than the adsorption onto a noble metal surface, because the cleaning method on the ITO electrode influences the work function [19]. Therefore, the photocurrent generation can be attributed to changes worked in the surface energy gap by the existence of films on the ITO electrode.

In this experiment, since hydrophilic moieties of porphyrin and surfactant contact the substrate, the adsorbed surface is hydrophobic. After measurements, the electrode surface, which is contacted once by electrolyte, carried hydrophilicity. This implies that the hydrophilic group was generated by the degradation. Otherwise, ITO surface was naked by desorption. In the former case, it is necessary for the degradation of organic materials to irradiate with the vacuum ultraviolet laser. Therefore, visible light irradiation cannot cause the degradation. For the latter, there are three possibilities; (i) photo Kolbe reaction, (ii) removal from electrode as R-COO$^-$, (iii) removal from electrode as R-COO$^-$M^{n+}. For the photo Kolbe reaction, irradiation for semiconductor electrodes poses decarboxylation of carboxy group, producing the hydrophobic film on the electrode surface. This is inconsistent with the result. Removal of the R-COO$^-$ anion from the electrode to the bulk leads to a cathodic current, which is also in conflict with the result. Finally, in view of (iii), the electrical double layer, so-called space charge layer, was formed at the interface between the ITO (n-type impurity semiconductor) surface and the electrolyte solution, as shown in Scheme 2. Electron–hole pairs are created by the irradiation, and then the holes move from the metal bulk to its surface along the band gradient. The holes collected on the surface may make the semiconductor elute to the electrolyte as metal ions. This phenomenon occurs in most n-type impurity semiconductors. We infer that the carboxy groups contacted on the electrode surface make ITO easy to elute, because a carboxy group is able to make a pair with a metal ion of ITO. On the assumption that the photocurrent generation comes from the carboxy group, the intensities of photocurrent depend on the number of carboxy groups on the electrode surface.



Scheme 2. Formation of space charge layer and separation to photoinduced electron–hole pair at ITO (n-type semiconductor)/electrolyte solution interface.

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