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Photoelectrochemical Properties of Orientation-Controlled Thin Film for 5,10,15,20-Tetraphenylporphyrin

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Dark- and photo-electrochemical properties of an orientation-controlled thin film of 5,10,15,20-tetraphenylporphyrin (TPP) were investigated in the indium-tin oxide(ITO)/TPP/I_3^-,I^-/Pt system. The oriented film exhibited a photocurrent quantum yield three times as great as the polycrystalline film. This enhancement in quantum yield may be attributable to the standing molecular orientation of TPP on the ITO substrate.

Thin solid porphyrin films have received an increasing interest as a functional material in solar energy conversion.[1)] Some porphyrin derivatives with various central metals[2)] and organic frameworks[3)] have been tailored in order to improve the photoelectric activity. The most efficient cells based on porphyrin films sublimed on Al electrodes have reached more than 20% in photocurrent quantum yield.[4)] In view of the fact that a crystallographically ordered system is integrated for an efficient energy transfer in photosystems of living organs, much attention should be paid to a molecular arrangement of porphyrins in solid films. However, most of photovoltaic and photoelectrochemical studies using organic materials have been done for amorphous or microcrystalline thin films deposited on metal electrodes.

In the present study, we show evidence that a thin epitaxial film of TPP can be prepared by vacuum-evaporation onto a KCl crystal. Furthermore, we describe that the photoelectrochemical cell sensitized by the orientation-controlled film is efficient more than that for the polycrystalline film in a respect of conver-

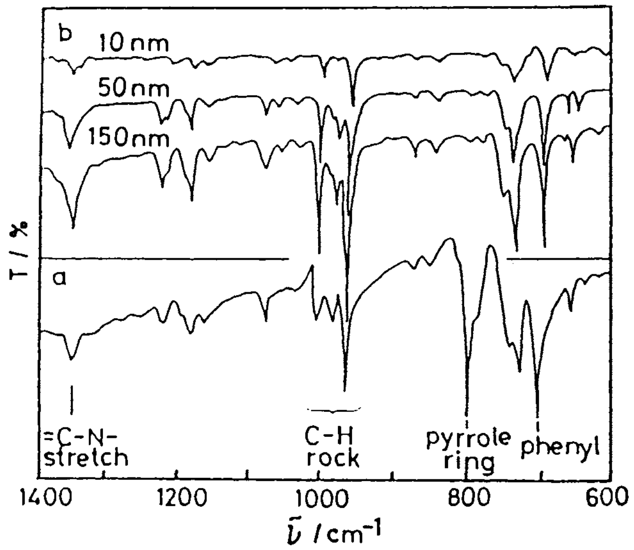

Fig. 1. Transmission infrared spectra of TPP: (a) KBr tablet of the vacuum-deposited powder and (b) crystalline films vacuum-deposited on KCl substrates at 10, 50, and 150 nm thicknesses.

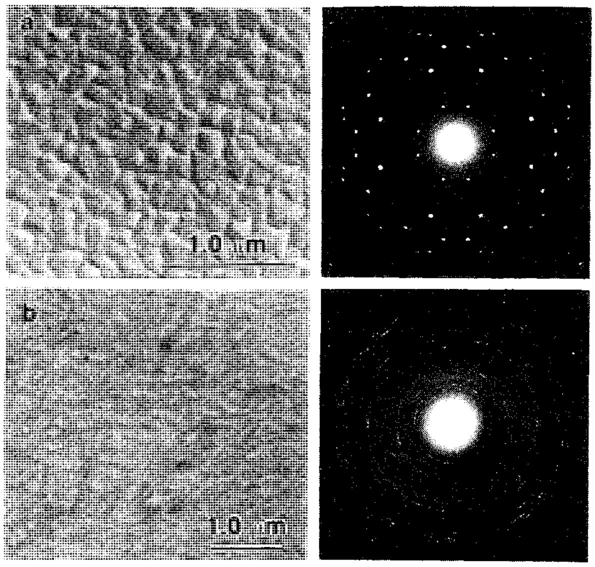

Fig. 2. Transmission electron micrographs and electron diffraction patterns of the TPP films deposited on cleavage surfaces of (a) KCl and (b) muscovite kept at 20°C.

sion efficiency. Improvement in photocurrent quantum yield for the porphyrin film is discussed in terms of the molecular orientation.

Figure 1 shows transmission infrared spectra of (a) the TPP powder in a KBr tablet and (b) the TPP films deposited on (001) cleavage surfaces of KCl crystals at various thicknesses. The transmission experiment, where the electric field vector is incident parallel to the substrate, gives intense bands with infrared active modes parallel to the substrate. The spectrum (a) shows all active vibration modes of TPP.5) In the spectra of the films (b) the C-H rocking vibration of pyrrole at 1003-966 cm^{-1} are dominant bands while the strong band at 799 cm^{-1} assigned to a vibration of the pyrrole ring disappears or becomes very weak. This suggests that the pyrrole rings, that is, the molecular planes of TPP stand perpendicular to the substrate surface.

Figure 2 shows electron micrographs and electron diffraction patterns of the TPP films deposited on cleavage surfaces of crystals for (a) KCl and (b) muscovite. The film deposited on KCl is composed of the TPP crystals which grow epitaxially, and its electron diffraction pattern consists of a superposition of four singlet net patterns corresponding to the four-directional orientation. On the other hand, the TPP film deposited on muscovite is composed of randomly oriented polycrystals as is obvious from the ring diffraction pattern. The orientation of

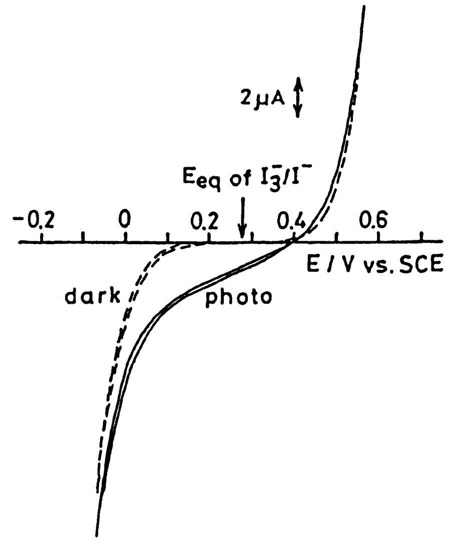

Fig. 3. Current-voltage curves of ITO/-TPP electrode in the dark and under illumination at 10 mW cm^{-2} in 0.5 mM I_2 and 0.1 M KI (pH 4.6).

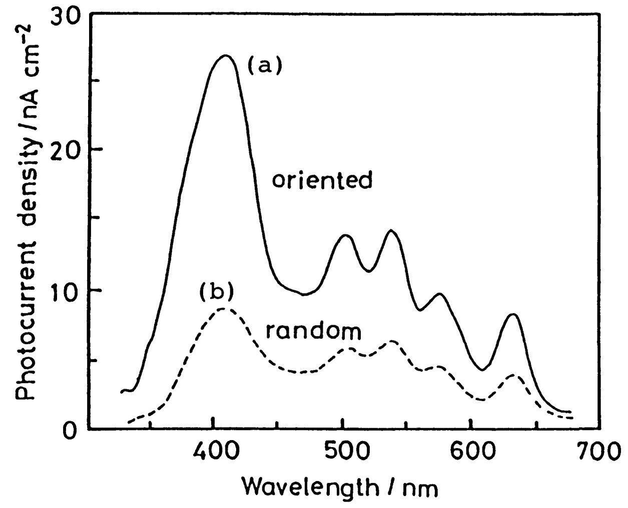

Fig. 4. Short-circuit photocurrent action spectra of ITO/TPP/I_3^-,I^-/Pt cells using (a) epitaxial and (b) polycrystalline TPP films deposited on KCl and muscovite, respectively.

TPP molecules on the (001) surface of KCl was confirmed further by a high-resolution electron microscopic observation.

The epitaxial TPP film on ITO electrode was prepared by dipping up the TPP film (about 150 nm in thickness) onto an ITO glass after separating the film from the KCl substrate in water. Figure 3 shows current-voltage characteristics of the TPP electrode thus prepared in the dark and under illumination with white light of 10 mW cm^{-2}. The dark-current-voltage curve indicates a rectifying behavior due to a p-type conductance of the TPP film. The cathodic photocurrent is observed at potentials more negative than 0.4 V vs. SCE. From the short-circuit photocurrent, open-circuit photovoltage and fill factor (≈0.25), the energy conversion efficiency was calculated to be 2.5×10^{-6}.

Figure 4 shows photocurrent action spectra of (a) epitaxial and (b) polycrystalline TPP films of about 150 nm in thickness, prepared by deposition on KCl and muscovite cleavage surfaces, respectively. The photocurrent was normalized to have a constant light intensity of 10 μW cm^{-2} incident on the TPP film electrode. Both of the action spectra correspond well in shape to the absorption spectrum of a TPP film, suggesting that charge carriers are generated via the excited states of TPP molecules. The epitaxial film electrode generates a photocurrent three times as great as the polycrystalline film electrode. The maximum photocurrent quantum yield for the epitaxial TPP film was estimated as 0.32% at around 410 nm.

The molecular arrangements in both film electrodes and the molecular packing in the epitaxial film are schematically shown in Fig. 5. The polycrystalline film is composed of granular and needle-like crystallites which take random orientation. In the epitaxial film, on the other hand, the TPP molecules slip and pile up with holding the molecular planes perpendicular to the substrate surface. In this packing, the π-electron conjugated rings overlap partly each other and electrically conducting pathways are extended through the film.

The improved photoresponse observed with the orientation-controlled TPP films may be attributable to the following reasons: (i) the decrease of electrical resistivity due to the extending π-π overlap between the TPP molecules, (ii) the low probability of electron-hole recombination at the grain boundaries and structural defects, etc.

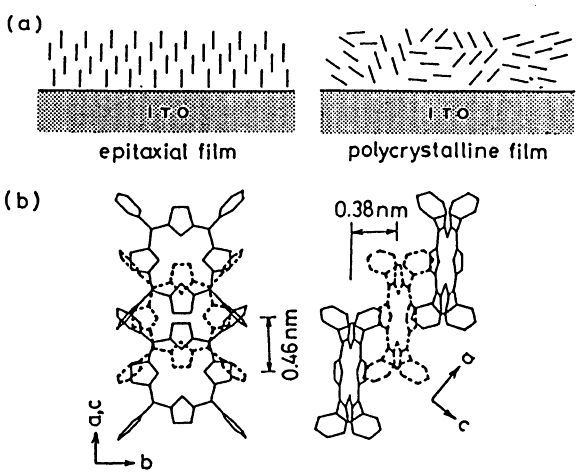

Fig. 5. Schematic diagrams of (a) molecular arrangements in the epitaxial and polycrystalline film electrodes and (b) molecular packing in the epitaxial film.

References

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