Research on ITO/PEN electrodes modified by organic dyes and their photoelectrochemical properties

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Introduction. The ITO/PET and ITO/PEN electrodes have been successfully utilized as the most transparent, light and flexible electrodes since their first report in 1974[1]. By adsorbing organic dyes on these electrodes, oxidation and reduction reactions can be induced by irradiation of light. In order to carry out photoelectrochemical reactions in a flow system, it is necessary to fix the dye firmly on the electrode. In this study, we tried fixation our kinds of porphyrin carboxylic acid derivatives (**1-4**) on the ITO/PEN electrode.

Synthesis. The porphyrin derivatives with one or two carboxy groups (**1**, **2**) were prepared according to the literature procedure.[2] These carboxylic acids were coupled with β-alanine ethyl ester and hydrolyzed, to give the carboxylic acids with β-alanine spacer units (**3**, **4**).

Adsorption Studies. For the pretreatment, the ITO/PEN electrodes were immersed in base-piranha solution (30% H_2O_2 : 30% NH_3 : H_2O = 1:1:5) at room temperature for about 1 hour. Using a stronger solution (H_2O_2:NH_3:H_2O = 1:3:5) resulted in the deterioration at the border of the electrode. There were 3 methods to For modification of the ITO/PEN surface with the porphyrins, three methods (A-C) were examined: (A) direct chemisorption, (B) modification of the ITO/PEN surface with APTMS followed by the formation of ionic bonds, and (C) formation of amide bonds with APTMS. The adsorption density of porphyrin on ITO/PEN electrode was evaluated through the UV-Vis absorption spectrum. As a result, the adsorption density of the porphyrins **2**, **4** was higher than that of the porphyrins **1**, **3**.

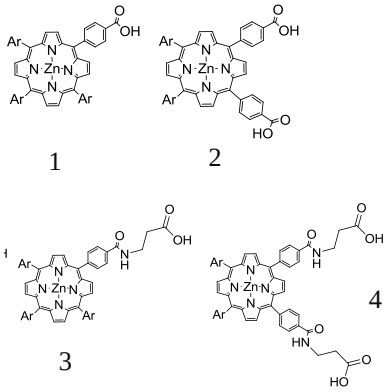

Table 1: The adsorption density of Porphyrin on ITO/PEN electronde

Porphyrin	Adsorption density ($\times10^{-11}$ mol cm^{-2})		
	A	B	C
1	1.5	0.73	0.81
2	3.3	10	11
3	2.1	2.4	4.1
4	19	55	51

1) T. Yatabe, *J. Vac. Soc. Jpn*., **2003**, *46*, 28.

2) H. Tamiaki et al. *Bull. Chem. Soc. Jpn.* **1993,** *66*, 2633.