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Incorporation of Dye Molecules in Polypyrrole Films in the Process of Photoelectrochemical Deposition

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Dye molecules were incorporated in polypyrrole films in the process of photoelectrochemical deposition. The concentration of the incorporated dyes depended on the charge of dye molecules and it was 5.1 mol dm^{-3} for Sodium Fluorescein and 1.3 mol dm^{-3} for Rose Bengal. Anionic dyes were most easily incorporated in the films.

It is well known that electrochemical deposition of polypyrrole is a convenient method to prepare functional films.[1,2] Thus prepared functional films are useful for sensors.[1,2] Besides electrochemical deposition process, the authors have reported that photoelectrochemical deposition process is highly useful for microfabrication.[3-5] This method enables us to fabricate microsensors. Thus, the present work deals the possibility of dye (functional molecule) incorporation in the process of photoelectrochemical deposition of polypyrrole.

Incorporation of dye molecules was carried out in a three electrode system using aqueous solutions of 0.1 mol dm^{-3} pyrrole containing 1×10^{-3} mol dm^{-3} dye. A titanium dioxide thin film electrode, which was prepared on a tin dioxide transparent electrode by a spray pyrolysis method, was used for the working electrode. A saturated calomel electrode (SCE) and a platinum electrode were used for the reference electrode and for the counter electrode, respectively. The TiO_2 electrode was attached to the cell as a window and was irradiated from the back side, i.e. the glass side by a mercury lamp. Absorption spectra of the films were measured in air as it is on the electrode surface using a bare substrate electrode as a reference.

Figure 1 shows the absorption spectrum of a polypyrrole film prepared photoelectrochemically using an electrolyte solution containing Rose Bengal (anionic dye). A spectrum for Rose Bengal in an aqueous solution is shown together. The broad peak between 500 and 600 nm clearly indicates the incorporation of Rose Bengal in the polypyrrole film. The broadening of the peak is observed presumably because dye molecules take different states in the film depending upon their interactions with polypyrrole matrix. Rough estimation of the dye concentration in the polypyrrole film can be carried out as follows.

(1) Absorption of polypyrrole film at 700 nm, where no absorption of Rose Bengal exists, was measured. (2) The thickness of the film was estimated from the absorbance using a relationship between the absorption and the thickness of the polymer film, which was obtained in separate experiments. (3) Absorption of the polypyrrole film at 570 nm, at which wavelength the absorption peak of Rose Bengal exists, was estimated from the absorption of the film at 700 nm using an absorption spectrum of a dye-free polypyrrole film. (4) The absorption of Rose Bengal at 570 nm was calculated by subtracting the estimated value of absorption of polypyrrole from the absorption of dye incorporated polypyrrole film. (5) Using thus obtained polypyrrole film thickness and absorption of dye, and assuming Lambert-Beer's law, the concentration of the dye in the polypyrrole film was calculated. Molar extinction coefficient of Rose Bengal obtained in aqueous solution was used for the calculation. Thus calculated value was 1.3 mol dm^{-3}, which means the condensation of dyes by the factor of 1300. Cyclic voltammetry of the dye incorporated polypyrrole film revealed that dye molecules are not released out of the film easily though small doping-undoping currents are observed during potential cycles.

Experiments using Sodium Fluorescein (anionic dye) and Rhodamine B (cationic dye) gave films with dye concentration of 5.1 mol dm^{-3} and 1.0 mol dm^{-3}, respectively. Therefore, both anionic and cationic dyes can be incorporated in the films in the process of the photoelectrochemical deposition. However, cationic dyes were poorly bound to the polymer matrix and washing with water or acetone caused loss of many dye molecules from the polymer film. The above data are those after washing with acetone. Anionic dyes are more easily incorporated in the films and more tightly bound to the polymer matrix probably because of the interaction between the negative charge of dyes and the positive charge of the polymer matrix; a similar conclusion has been made for the electrochemical deposition of polypyrrole.$^{1)}$

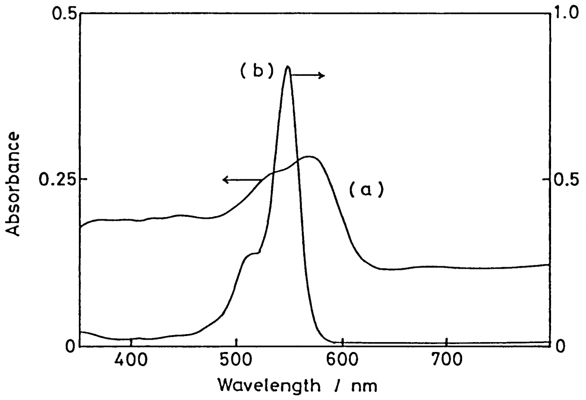

Fig. 1. An absorption spectrum of the polypyrrole film containing Rose Bengal and that of 1 x 10^{-5} mol dm^{-3} Rose Bengal aqueous solution (b).

References

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