



The charge transfer characteristic of porphyrin Langmuir–Blodgett films[☆]



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ABSTRACT

The ordered porphyrin Langmuir–Blodgett (LB) films were prepared under different surface pressures. The UV–vis absorption spectrum, infrared spectrum, cyclic voltammetry and constant potential jump were used for testing. UV–vis spectra showed that under the surface pressure of approx. 10 mN/m, the ordered porphyrin LB films formed were demonstrated by infrared spectra. With the order degree of LB films strengthened, the charge transfer and storage of porphyrin LB films enhanced. And it was measured by electrochemical method. IR spectrum proves that both the interaction of porphyrin rings (the rings can form the head-to-head structure) and that of hydroxyl groups (the groups can form the feet-to-feet structure) in porphyrin LB ordered films can affect the charge transfer characteristics of porphyrin films.

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1. Introduction

Recently, the electrochemical [1–3] and electrocatalytic properties [4–7] of porphyrin and its derivatives have attracted a lot of attention. The electrode modified by porphyrin LB film has become the focus. Compare with spin-coating and self-assembly method, the thickness of films can be accurately controlled by LB technology and the defects of the molecular irregular arrangement can be decreased. The porphyrin LB films have been widely applied [8–12] in catalytic, sensor, and photochemistry because of its unique π conjugated system and the ordered arrangement. Porphyrin compounds have good absorption in the UV–vis with open axial coordination [13]. When porphyrin compounds are arranged in an ordered structure, the absorption spectra will change correspondingly. And UV–vis absorption spectrum can identify the change. From the perspective of the group interactions, the infrared absorption spectrum further confirms this change and the order of molecular of LB film, which is important for the study on the interaction between molecules [14]. In addition, that, the study of the structure of molecular ordered LB film [15] and charge transfer characteristics [16], has the practical significance for understanding the interaction of molecules and the surface performance change of LB film.

In this paper, porphyrin LB film is modified on the ITO electrode. Its characteristics of charge transfer and storage were studied by cyclic voltammetry (CV) and the constant potential jump. The results show that the ordered porphyrin films have an important effect on the charge transfer characteristic. The amount of transfer charges and the diffusion coefficient of charges of porphyrin film change regularly with the order degree of porphyrin molecular and the increase of the number of layers of porphyrin film. UV–vis absorption spectra and infrared spectra identified the formation of ordered structure of porphyrin LB films.

2. Experimental methods

2.1. Materials and instruments

The porphyrin ($C_{34}H_{34}N_4O_4$) was prepared from the further purified chloride iron porphyrins ($C_{34}H_{32}ClFeN_4O_4$, >98% purity, Hetianlong Biotechnology Co., Ltd., China) [17]. The porphyrin is dissolved in DMSO with the concentration of 3×10^{-5} mol/L for tests. Fiber optic spectrometer (AvaSpec-2048, Netherlands) was used for testing UV–vis absorption spectrum. Electrochemical workstation (CS350, Wuhan Corrtest Instrument Co., Ltd., China) was used for testing the CV and the constant potential jump. Fourier transform infrared spectrometer (NICOLET 6700, U.S.A.) was used for testing infrared spectrum.

2.2. Preparation and electrochemical test of LB films

The hydrophobic treated ITO glass was chosen as a base. Cleaned it by distilled water, treated it with ultrasonic treatment for

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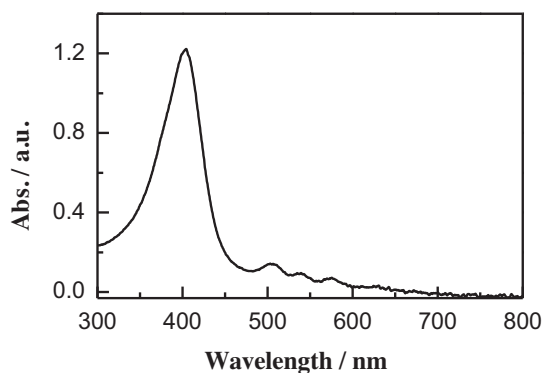


Fig. 1. UV–vis spectrum of porphyrin which is dissolved in DMSO with the concentration of 3×10^{-5} mol/L.

5–10 min in a mixed solution of acetone and ethanol (the volume ratio is 1:1) and dried it. The porphyrin LB films were prepared as follows. Utilizing a syringe, the DMSO solution of porphyrin was spread on the water sub-phase. The porphyrin film formed on the water surface after natural evaporation for 30 min, vertically stretched at the pulling speed of 1 mm/min (LB method), the porphyrin LB films were fabricated on ITO glass. The samples were prepared and named as follows. Under the surface pressure 0 mN/m [18], the film stretched by 2 times was named as sample A and the one stretched by 4 times was sample B. Similarly, under the surface pressures 5 mN/m, one was sample C and the other was sample D, under the surface pressures 10 mN/m, one was sample E and the other was sample F. A three electrodes system was used in electrochemical test. An ITO conductive glass modified by porphyrin LB films was used as a work electrode. A graphite electrode was used as auxiliary electrode and an Ag/AgCl electrode was used as reference electrode. A KCl solution with concentration of 0.1 mol/L was the supporting electrolyte for test. The scan range of CV measurements was -0.8 to 0.8 V and the scanning speed was 30 mV/s for two circles. The initial potential of constant potential jump and jump potential were -0.6 V and 0 V, respectively. And the jump time was 250 ms.

3. Results and discussion

3.1. The absorption spectra

Fig. 1 shows the UV–vis absorption spectrum of porphyrin which was dissolved in DMSO (3×10^{-5} mol/L). The five characteristic absorption peaks of porphyrin molecules are a Soret band peak (403 nm) and four Q band peaks (505 nm, 539 nm, 574 nm and 630 nm, respectively).

Fig. 2 shows the UV–vis absorption spectra of samples A–F. There are no obvious differences on shape for the curves (a)–(c) and (e). Compared with Fig. 1, the characteristic absorption peaks width of porphyrin molecules increase. It shows that despite of the impact of the interaction between porphyrins and ITO, porphyrins still maintained the molecular characteristics. The peak positions and peak ranges of the absorption spectra of sample D (curve in Fig. 2(d)) and F (curve in Fig. 2(f)) change significantly, which suggests that the characteristics of single-molecule porphyrin disappeared.

3.2. The electrochemical characteristics of porphyrin LB films

3.2.1. CV curves

Fig. 3 shows CV curves of porphyrin LB films. Each sample was scanned twice. The oxidation peaks of all samples appear around -0.6 V. The oxidation current value of (e) curve is significantly higher than those of (a) and (c) curves. It indicates that the

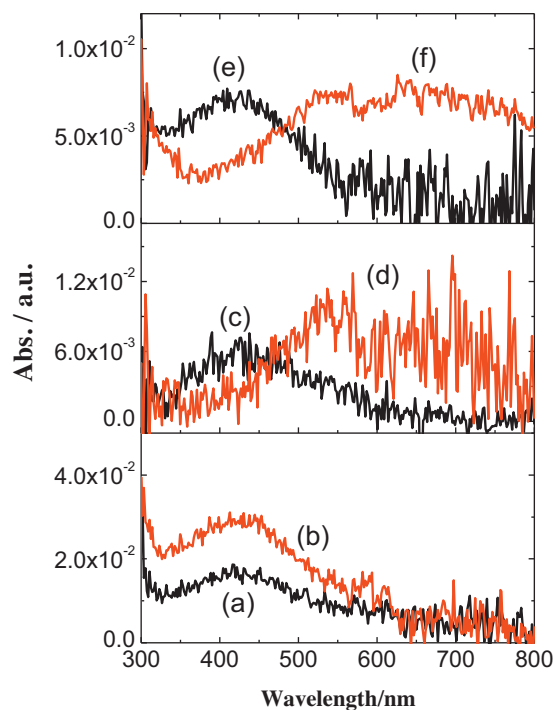


Fig. 2. UV–vis spectra of porphyrin LB films. The corresponding curves of the samples A–F are (a)–(f), respectively. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

conductivity and charge transfer ability of porphyrin LB films increase with the increasing of surface pressure. The CV current values of samples B, D and F are greater than samples A, C and E, respectively. In other words, as the number of LB films increases, the

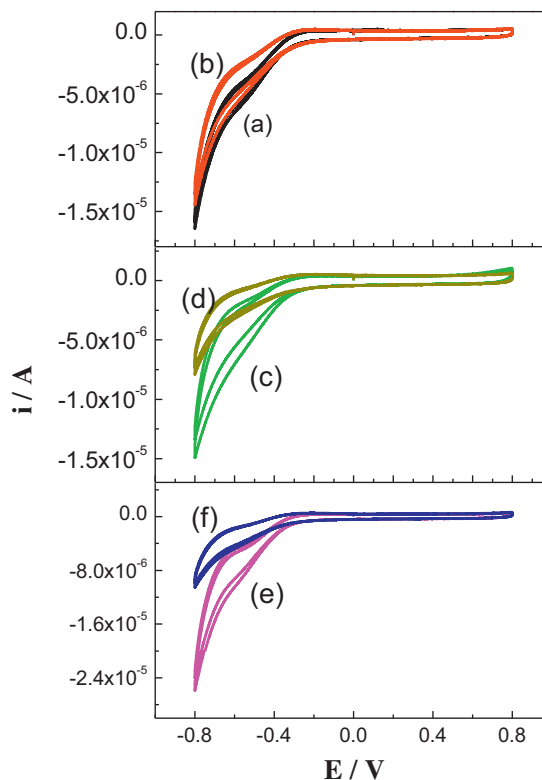


Fig. 3. The CV graph of porphyrin LB films. The corresponding curves of the samples A–F are (a)–(f), respectively.

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