Characterization and electrochemistry of interfacial self-assembled multi-manganese (III)-porphyrin arrays

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ABSTRACT

Electrochemical behaviors and catalytic oxidation of nitrite have been investigated by using the indium tin oxide (ITO) electrodes modified by the Langmuir–Blodgett (LB) films of manganese porphyrin and its palladium-mediated multiporphyrin arrays. The multiporphyrin arrays were prepared at the air–water interface. Surface pressure–area isotherms indicated that monolayers of the porphyrin of MnTPyP (TPyP: tetrapyridylporphyrin) could be stabilized on the sodium tetraphenylboron and K_2PdCl_4 subphase surfaces, but not on the pure water surface. These monolayers were transferred onto quartz and ITO substrate surfaces with the use of vertical dipping method, and characterized by using transmission electron microscope, UV–vis absorption and X-ray photoelectron spectra. For the electrodes modified by the porphyrin LB films, reversible $Mn^{(II)}TPyP \leftrightarrow Mn^{(III)}TPyP$ and $Mn^{(III)}TPyP \leftrightarrow Mn^{(IV)}TPyP$ redox couples were recorded, and centered at about -0.17 and 0.52 V vs. Ag/AgCl, respectively. A high-valent $Mn^{(V)}TPyP$ intermediate was detected when the cyclic voltammograms were measured in an electrolyte solution containing sodium nitrite. These multiporphyrin arrays modified electrode showed very strong stability and reproductivity, resulting in potential applications in the development for the nitrite sensors and molecular catalysts of organic compounds.

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1. Introduction

Manganese porphyrins have attracted growing interest because of their unique physical and chemical properties, such as mimicking the role of Mn complex in photosystem II and acting as electrocatalysts towards the oxidation of organic compounds and nitrite [1,2]. The manganese complex in photosystem II undergoes charge accumulation, which requires that the metal possesses a series of available redox states. Because the Mn porphyrins have been shown this requirement, they have been widely used in the study of biological electron-transfer processes in photosynthetic and mitochondrial membrane reactions [3,4]. Such kind of unique redox properties also results in the Mn porphyrins to be key ingredients in the chemically modified electrodes for the potential applications as sensors and efficient catalysts [5,6]. For instance, Mn porphyrins could catalytically oxidize nitric oxide and nitrite, resulting in potential applications as nitric oxide sensors [7]. In the past decades, the metalloporphyrins with the central metal ions of nickel, iron, cobalt, or manganese have been found to be able to act as effective catalysts for the oxidation of alkanes, alkenes, alcohols, ethers, and amines to a variety of products [8,9].

As one of the bottom-up techniques, we are currently investigating the design, preparation and opto-electrochemical properties for the monolayers or multilayers of metal-mediated multiporphyrin arrays on the solid surfaces and the immobilization of three-dimensional (3D) supramolecular porphyrin arrays at interfaces [10–12]. Because the porphyrins are connected by metal ions via coordination bond, the as-prepared films of the multiporphyrin arrays showed highly thermal, chemical, and structural stability as well as structural regularity and controllability. It was found that no significant change of the Soret absorption characters of the porphyrins could be observed when the multiporphyrin modified quartz substrates were immersed in solutions when the pH values were changed from 2 to 14 or when the modified substrates were heated up to 150 °C [13]. These features resulted in the multiporphyrin arrays acting as attractive molecular materials in the sensors and chemically modified electrodes.

In the present work, monolayers of the manganese(III) tetrapyridylporphyrin (MnTPyP) were stabilized on the $NaB(C_6H_5)_4$ subphase surface, and its metal-mediated multiporphyrin arrays were formed at the air–water interface. These monolayers were transferred onto substrate surfaces by using the Langmuir–Blodgett (LB) method, which provided facile ways to fabricate functional molecular materials [14], as well as to investigate two-dimensional kinetic processes, such as formation of organized aggregates and surface diffusion of ions [15,16]. Compositions and structural features for the LB films of MnTPyP multiporphyrin arrays were characterized by using the UV–vis absorption, transmission electron microscope (TEM) and X-ray photoelectron spectroscopy (XPS). Reversible $Mn^{(II)}TPyP \leftrightarrow Mn^{(III)}TPyP$ and $Mn^{(III)}TPyP \leftrightarrow Mn^{(IV)}TPyP$ redox waves were recorded for the indium

tin oxide (ITO) electrodes modified by the LB films. The electrodes modified with the multiporphyrin arrays showed catalytic oxidation properties for nitrite when the cyclic voltammeter measurements were done in an electrolyte solution of sodium nitrite. The present multiporphyrin arrays are of potential applications as molecular materials in the development of nitrite biosensors and catalysts for the oxidation of lots of organic compounds.

2. Experimental details

2.1. Materials

Manganese(III) 5,10,15,20-tetra(4-pyridyl)-21H,23H-porphyrin was purchased from Frontier Scientific Porphyrin Products. Sodium tetraphenylboron [NaB$(C_6H_5)_4$] was from Shanghai Chemical Reagent Co.; K_2PdCl_4 was from Wako Pure Chemicals, Ltd. Chloroform and methanol were from Fisher Chemicals Co. Poly(styrenesulfonic acid-o-maleic acid) (PSS) was from Aldrich Chemical Co. All chemicals were used as received without further purification. Double distilled water (firstly deionized) was used to prepare aqueous solutions.

2.2. Monolayers and Langmuir–Blodgett films of MnTPyP-B$(C_6H_5)_4$ and Pd-MnTPyP multiporphyrin arrays

Monolayers of MnTPyP were prepared by spreading a dilute ($\sim 5 \times 10^{-5}$ mmol/l) MnTPyP in a mixed methanol and chloroform (1:4, v/v) solution onto the pure water, 0.1–1 mg/ml PSS and 0.1 mol/l NaB$(C_6H_5)_4$ subphase surfaces. Multiporphyrin arrays of Pd-MnTPyP were prepared by spreading the dilute MnTPyP solution onto the 0.1–0.5 mmol/l K_2PdCl_4 subphase surfaces.

The surface pressure–area (π–A) isotherm measurements and LB film transfer were done with the use of a KSV 5000 minitrough (KSV Instrument Co., Finland) using a continuous speed for two barriers of 10 cm^2/min at room temperature. The accuracy of the surface pressure measurement was 0.01 mN/m. Transfer of monolayers of MnTPyP-B$(C_6H_5)_4$ and Pd-MnTPyP multiporphyrin arrays onto solid plates was done by vertical dipping method. For every transfer the dipping speed was 2 mm/min.

2.3. Characterization

UV–vis absorption spectra were measured with a Shimadzu UV-2550 UV–vis spectrophotometer. Transmission electron microscope images were taken on a Hitachi H-600 electron microscope operated at 75 kV. Monolayers of the Pd-MnTPyP multiporphyrin arrays were deposited on 230-mesh copper grid covered with formvar at different surface pressures by the LB method.

XPS spectra for the LB films on the quartz substrate surfaces were recorded using a VGESCALAB MKII multifunction spectrometer, with nonmonochromatized Mg–Kα X-rays as the excitation source. The system was carefully calibrated by Fermi-edge of nickel, Au 4f$_{2/7}$ and Cu 2p$_{2/3}$ binding energy. Pass energy of 70 eV and step size of 1 eV were chosen when taking spectra. In the analysis chamber pressures of $1-2 \times 10^{-7}$ Pa were routinely maintained. The binding energies obtained in the XPS analysis were corrected by referencing the C1s peak to 284.60 eV.

2.4. Electrochemistry and catalytic oxidation of nitrite

The cyclic voltammograms (CVs) for the ITO electrodes modified with the LB films of MnTPyP-B$(C_6H_5)_4$ and Pd-MnTPyP multiporphyrin arrays were measured by using a CHI 601b electrochemical analyzer. A Pt wire and Ag/AgCl electrode were used as the auxiliary and reference electrodes, respectively, with 10 mmol/l KCl as the electrolyte. An initial potential of 1.2 V was applied for 2 s, and subsequently cyclic scans to a final potential of -0.8 V were done for 10 cycles. The curves

shown in the present work were the 10th cycle. The catalytic oxidation of nitrite was preformed by measuring the CV curves of the LB film-modified electrodes in the 10 mmol/l KCl electrolyte solutions containing 0.01–1 mmol/l sodium nitrite. All electrochemical measurements were done under an Ar atmosphere at room temperature.

3. Results and discussion

3.1. Monolayer behaviors of MnTPyP

It has been pointed out that monolayer behaviors (e.g., the π–A isotherms) of amphiphiles are closely related to the subphase conditions, especially when there exists an interfacial chemical reaction. This reaction often results in new products and/or different arrangement of the amphiphiles in the monolayers, such as formation of new structural molecular aggregates and polymeric network sheets, as well as nanostructural materials [17,18]. Here, we investigated the π–A isotherms for the MnTPyP monolayers on the surfaces of pure water, NaB$(C_6H_5)_4$, PSS and K_2PdCl_4, the results of which revealed that the monolayer properties of the MnTPyP were largely dependant on the subphase compositions.

Fig. 1 shows the π–A isotherms for the MnTPyP monolayers on the pure water and 0.1 mol/l NaB$(C_6H_5)_4$ subphase surfaces at room temperature. Very low surface pressure increase (10 mN/m) was recorded with the average MnTPyP molecular area of about 0.4 nm^2, when the MnTPyP was spread on the pure water surface (Fig. 1a). Both highest surface pressure and occupied average molecular area were much different from those we have observed for the monolayers of the metal-free tetrapyridylporphyrin (TPyP) or its zinc complex (ZnTPyP) on the pure water surface, where the surface pressure increased up to near 40 mN/m and the average (Zn)TPyP molecular area to about 0.65 nm^2 [10,12]. This difference may be attributed to that, different from TPyP and ZnTPyP, the MnTPyP is a kind of ionized porphyrin and can slightly dissolve into the water phase. Because of this solubility, the MnTPyP is difficult to form stable monolayer on the pure water surface. Although formation of three-dimensional aggregates can also lead to the difficulty for the stable monolayers formation [17], here, we suggest that the solubility is the main reason because the molecular structure of MnTPyP is very similar to that of (Zn)TPyP.

To improve the monolayer stability of the MnTPyP, following subphases were used instead of the pure water in our experiments; (1) the subphase containing larger anionic ions, (2) the subphase containing negatively charged polymer (PSS), and (3) the subphase containing metal or metal-complex ions which could react with MnTPyP and form multiporphyrin arrays at the interfaces. The former two ways have been often used to reduce the solubility of the ionic amphiphilic compounds or proteins. For instance, it has been previously found that the positively charged poly-L-lysine or CaCl$_2$ subphase could stabilize the monolayer formation of hydrogenase
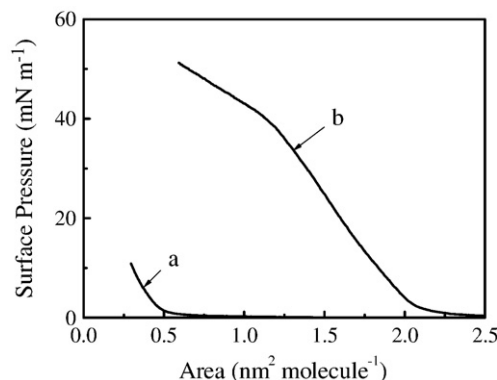

Fig. 1. Surface pressure–area isotherms for the monolayers of MnTPyP on (a) the pure water and (b) 0.1 mol/l NaB$(C_6H_5)_4$ subphase surfaces.