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Photoelectric conversion of photosynthetic reaction center in multilayered films fabricated by layer-by-layer assembly

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Abstract

Multilayered protein films which contained ordered layers of photosynthetic reaction center (RC) from *Rhodobacter Sphaeroides* (RS601) were assembled by means of alternate electrostatic adsorption with positively charged poly(diallyldimethylammonium chloride) (PDDA). The assembly of RC was monitored by spectrometry and photocurrent measurement. Linear film growth was observed up to about 20 cycles of adsorption. For the monolayer film, the photocurrent was about 8.5 nA cm^{-2}. For the multilayered film, the total photocurrent was about 77 nA cm^{-2} for the 24-layer RC film, while the average photocurrent increment per adsorption cycle was about 3.2 nA cm^{-2}. The overall light-to-electricity conversion efficiency for a 24-layer film was about eight times higher than that for the monolayer one. The effects of electrode potential and pH on the photocurrent were also measured to illustrate the light-to-electric converting mechanism.

Keywords: Photocurrent; Photosynthetic reaction center; Layer-by-layer; Self-assembled monolayer

1. Introduction

Photosynthesis is the biological process by which light is converted into chemical energy. Two main classes of organisms perform photosynthesis: green plant and photosynthetic bacteria. The photosynthetic reaction center (RC) separated from purple bacteria, *Rhodobacter Sphaeroides*, is a trans-membrane protein complex and it is also minimum structure unit capable of producing the charge separation [1]. The sequence of photoinduced electron transfer (ET) inside the RC has been widely studied, and a very high quantum efficiency (ca. 100%) of the photoinduced charge separation of the RCs has been evaluated [1,2]. The conversion of photons light energy into electrical energy of separated charges in RC occurred with a high energy efficiency (up to 50%). Therefore, it was obvious that its application as an element of biomimic photoelectrochemical converter was promising [3].

Preparation of ultra-thin films based on spontaneous molecular assembly was one of the powerful approaches to create novel supramolecular systems [4]. Alternative adsorption of a polycation and a polyanion was readily achieved by excessive adsorption of polyelectrolytes on oppositely charged surfaces, and it had become a quite general technique for build up molecularly defined layers [5–7]. Many polymeric materials from biopolymers, such as proteins [8,9], to inorganic macromolecules [10] had been assembled with this technique. In our previous work [11], we reported the direct ET for RC embedded in polycation sandwiched films on the gold (Au) electrode modified by 3-mercaptopropionic acid. In this manuscript, multilayered thin ordered films, up to 24 layers, were firstly prepared by alternate absorption of poly(dimethyldiallylammonium chloride) (PDDA) and RC on Au electrodes. The photoelectric responses for the films and the effects of potential and pH on photocurrent were investigated. The mechanism for the light-to-electric converting was also discussed.

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2. Materials and methods

The RCs were prepared from RS601, which was one of *Rb. Sphaeroides* strains, following our previous procedures [12]. 2-Mercaptoacetic acid (MAA, Sigma, USA) and PDDA chloride (Aldrich, USA) were used as purchased. The sodium dithionite was purchased from Dong-Huan United Chemical Plants (Beijing, China) and other reagents were of analytical grade and used without further purification. The Tris–HCl buffer solution for pH 8.0 consisted of 50 mM tris(hydroxymethyl)-aminomethane (Tris) and 50 mM KCl. Deionized water obtained by ion exchange and filtration with a specific resistance of better than 18 MΩ cm was used.

2.1. Au electrode cleaning and modification

The Au disk electrodes were polished successively with 0.3 and 0.05 μm Al_2O_3 powders and washed with deionized water. The electrochemical characteristics of bare Au electrode were estimated from the background current of cyclic voltammetry ($\leq 2 \times 10^{-7}$ A in pH 8.0 Tris–HCl buffer, scanning rate: 200 mV s^{-1}). The electrode was ultrasonicated in deionized water and ethanol for 10 min, and then rinsed thoroughly with deionized water and ethanol, respectively. The cleaned Au electrode was immersed in 1 mg cm^{-3} MAA ethanol solution for 24 h, following rinsed carefully with ethanol and dried by nitrogen, then immersed in 1 mg cm^{-3} PDDA solution for 6 h, following rinsed carefully with deionized water and dried by nitrogen. For quartz slide, it was ultrasonicated in acetone, ethanol and deionized water for 20 min and dried by nitrogen, respectively.

2.2. Alternate assembly RC multilayers

The protein assembly by the alternate electrostatic adsorption was previously reported for the adsorption of negatively charged poly(sodium styrenesulfonate) and positively charged myoglobin [8]. The RC (negatively charged) and PDDA (positively charged) layers were prepared [11] by immersing the substrate (quartz slide and Au disk electrode) in 0.5 mg cm^{-3} RC Tris–HCl buffer (pH 8.0) and 1 mg cm^{-3} PDDA aqueous solution for 2 h alternatively with intermediate water-washing. Sufficient washing of substrate after adsorption was necessary for reproducible results. After removing the substrate from the wash solution, a stream of nitrogen was blown over the film surface until the adhering water layer was completely removed. The process for the fabricated complex films was shown in Fig. 1.

2.3. Characterization of the composite films

Absorption spectra for the RC films prepared on quartz slides were measured with SM-240 CCD spectrophotometer (CVI spectral instruments, Putnam, CT, USA). The photocurrents were measured in a three-electrode cell with an RC-modified electrode as the working electrode, a saturated calomel electrode as the reference one and a platinum flake as the auxiliary electrode. The solution consisted of 5 cm^{-3} Tris–HCl buffer (pH 8.0) and 50 mm^{-3} 0.1 M sodium dithionite. All potentials quoted in this paper were versus standard hydrogen electrode (SHE). The working electrode was illuminated with an incandescent lamp (60 W) through a filter ($\lambda > 600$ nm, 10^{-2} W cm^{-2}). The photoelectric signals given in this paper were recorded by CHI-660A electrochemistry workstation with technology of amperometric i–t curve, and the IR compensation was 100% during testing. The electrode potential was set at its open-circuit voltage before each testing (0−−0.1 V), and the background dark current was less than 1.0 nA.

3. Results and discussion

The successful self-assembly of a large number of repeating sandwich units of substrate/$(PDDA/RC)_n$/PDDA was monitored by absorption and photocurrent measurement. The absorption spectrum for RC films on a transparent quartz slide was observed as shown in Fig. 2. The absorbance at 802 nm versus the number of sandwich units (n) in substrate/$(PDDA/RC)_n$/PDDA was plotted in the inset. The observed good linearity in multilayered PDDA/RC film indicated the uniformity of the sandwich units that were self-assembled. The similar results were also obtained for RC multilayers with Langmuir–Schaefer method [13]. At pH 8.0, RC is negatively charged and the PDDA is positively charged. Thus, RC protein could be immobilized effectively on the electrode by using interlayer polyion 'glue' (PDDA). The average thickness of the layers (0.7 nm for PDDA and 5.7 ± 0.6 nm for RC) was estimated on the dry film with a quartz crystal microbalance following the previous procedures [11].

Fig. 3 showed the photoelectric responses of the multilayered PDDA/RC films on the Au electrode prepared by self-assembly method. When the actinic light was subsequently switched on and off, a series of almost identical electric signals could be obtained. The photocurrent responses were very similar to those of multilayered films prepared by Langmuir–Schaefer method [13]. The short-circuit photocurrent behavior for the multilayered films was also similar to the one-layer results reported by other labs [18,19]. For the monolayer film ($n = 1$), the photocurrent was about 8.5 nA cm^{-2}. The inset in Fig. 3 showed a linear increase in the photocurrent of the electrode with the number of adsorption cycles. The integral photocurrent response