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Preparation of a microalgal photoanode for hydrogen production by photo-bioelectrochemical water-splitting

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ABSTRACT

In this study, a microalga *Tetraselmis subcordiformis* (synonym: *Platymonas subcordiformis*)-based photoanode was prepared by a novel method developed in our lab. The optimal photocurrent density of microalgae photoanode, 37 μA/cm^2, was achieved under illumination of 145 μmol s^{-1} m^{-2} at anode potential of 0.5 V vs Ag|AgCl|sat. KCl, immobilized cell density of 2.08 × 10^6/cm^2 and BQ concentration of 300 μmol/L. The results of measurements showed that oxygen evolution peak, hydrogen evolution peak and photocurrent response were all synchronous to light impulse in a three-electrode system. It revealed that there occurred a process of photo-bioelectrochemical water-splitting. Hydrogen can be produced by the method. The investigation for whole photo-bioelectrochemical process also indicated that the electrons for hydrogen evolution had two sources, microalgal metabolic process in dark condition and photosynthetic water oxidation. The photo-hydrogen evolution was twice more than hydrogen evolution in dark condition.

1. Introduction

Oxygenic photosynthesis, biological water-oxidation, is considered as the most important process among all energy converting processes on earth [1]. The high-energy electrons produced from water oxidation in the photosystems could be potentially transferred to electrodes through exogenous mediators to generate a photocurrent. Some studies have been done to investigate photo-bioelectrochemical anodic reactions [2,3].

Photoelectrochemical (PEC) water-splitting, which was first demonstrated by Fujishima and Honda [4], provides us one particularly promising approach [5]. In the method, water oxidation (producing O_2) and hydrogen reduction (producing H_2) are spatially separated by having each process occur at a separate electrode. Meanwhile, an applied (electrical or

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chemical) bias is needed to compensate for insufficient PEC cell voltage and overcome slow kinetics [5]. Similar to photoelectrochemical (PEC) water-splitting, we can suppose that there should be photo-bioelectrochemical water-splitting based on microalgal photoanode, in which absorption of visible light provides driven energy for water-splitting with the assistance of an applied bias.

In our lab, we developed a novel method to prepare microalgal photoanode, which can be applied to eukaryotic and prokaryotic alga, and investigated photoinduced electron transfer and photosynthetic oxygen evolution based on microalgal photoanode [6,7]. More than 60% of the electrons coming from water-oxidation in PS II could be extracted to generate photocurrent.

In this study, a microalga *Tetraselmis subcordiformis* (synonym: *Platymonas subcordiformis*)-based photoanode was prepared. By investigating effects of anode potential, cell density and BQ concentration on the photocurrent of microalgal photoanode, the preparation process of microalgal photoanode was optimized. In order to investigate the whole photo-bioelectrochemical process, dissolved oxygen near anode and dissolved hydrogen near cathode was measured by O_2 and H_2 microsensors respectively during electrochemical investigation of microalgal photoanode.

2. Materials and methods

2.1. Green microalga

T. subcordiform, a marine green microalga, was kindly presented by the Institute of Aquaculture of Liaoning Province, Dalian, China. The cells were grown in the airlift tubular photobioreactor bubbling with N_2 containing 2% (v/v) CO_2 at 27 °C in the following growth medium: 0.5 g KNO_3, 0.05 g KH_2PO_4, 0.81 g Tris, 0.33 mL glacial acetic acid, 1 mL of modified Walne medium, 1000 mL seawater from Yellow Sea in Dalian. Modified Walne Medium contained 0.8 g $FeCl_3$, 0.4 g $MnCl_2{\cdot}4H_2O$, 33.6 g H_3BO_3, 45.0 g EDTA·2Na, 20.0 g $NaH_2PO_4{\cdot}2H_2O$, 100.0 g $NaNO_3$, 0.021 g $ZnCl_2$, 0.02 g $CoCl_2{\cdot}6H_2O$, 0.009 g $(NH_4)_6Mo_7O_{24}{\cdot}4H_2O$, 0.002 g $CuSO_4{\cdot}5H_2O$, 1000 mL of water (Synergy water purification system, Millipore) [8]. The photon flux density focused on the airlift tubular photobioreactor was fixed at 200 μmol s^{-1} m^{-2} unless otherwise noted.

The chlorophyll content was estimated spectrophotometrically. The photosynthetic capacity of algal cell was measured by a chlorophyll fluorometer (Water-PAM WALZ, Germany) with the pulse-amplitude-modulation (PAM) [9].

2.2. Chemicals and instruments

All chemicals used in this study were of analytical reagent grade quality. Toray carbon fiber paper (TGP-H-060) was purchased from Toray Industries Inc. P-benzoquinone (BQ) was used as the exogenous artificial electron acceptor.

All electrochemical measurements in a single compartment cell containing a three-electrode configuration were carried out using electrochemical workstation (CS300, Wuhan Corrtest Instrument Co., Ltd, China). Microalgal photoanode was used as the working electrode and platinum electrode (2 mm × 7 mm) and Ag|AgCl|sat. KCl electrode was used as the counter and reference electrode, respectively. The electrochemical cell system was placed in an illumination incubator, and the fluorescent lamp was used as light source. Illumination by visible light was added from all directions of the cell. The light intensity focused on the fixed position of working electrode was fixed at 145 μmol s^{-1} m^{-2} unless otherwise noted. Electrolysis solution was 100 mL of sea water. The solution was deaerated by passing pure nitrogen gas before and during measurements. All measurements were carried out at room temperature.

2.3. Preparation of microalgal electrode

The porous silica sol was obtained by the hydrolysis followed by the condensation of tetraethoxysilane (TEOS) [10,11]. Briefly, silica sol was prepared as follows: 10 mL of TEOS, 60 mL of H_2O and 30 mL of 0.01 M HCl were violently stirred for 48 h at ambient temperature resulting in an acidic nanosol. Then the pH value of silica sol was adjusted to 7.5 by adding 1 M of NaOH. The silica sol was violently stirred for 48 h continuously.

The microalgal electrode was prepared as follows: cells were harvested by centrifugation at the speed of 500 g for 2 min. The algal cells pellet was uniformly dispersed in the 2 mL of silica sol. Then, 50 μL of resulting mixture was well coated on the paper carbon (1.2 cm × 2.0 cm) forming the thin layer, which was subsequently air-dried for 2 min.

2.4. Measurements of dissolved oxygen concentration and dissolved hydrogen concentration

The concentration of dissolved oxygen near anode and dissolved hydrogen near cathode was measured by O_2 and H_2 microsensors connected to a picoammeter (UniSense A/S, Aarhus, Denmark) respectively while electrochemical investigation of microalgal photoanode was carried out.

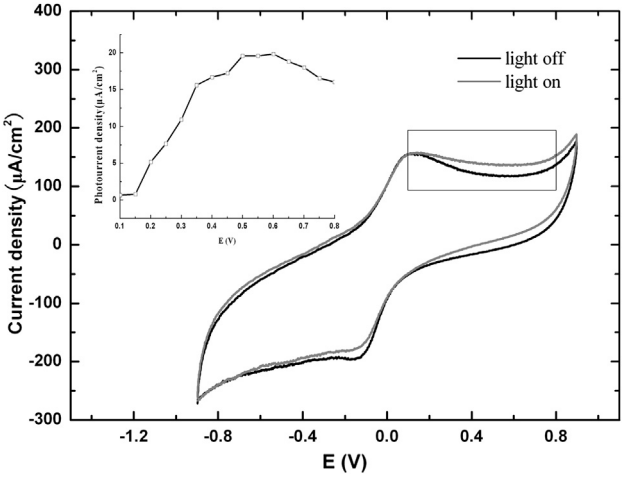

Fig. 1 – Cyclic voltammogram of microalgal photoelectrode without and with illumination. The scan rate was 50 mV s^{-1} with solution deaerated by nitrogen.