Applied Energy 113 (2014) 164–168

Contents lists available at ScienceDirect

Applied Energy

journal homepage: www.elsevier.com/locate/apenergy

Hydrogen production in a light-driven photoelectrochemical cell

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HIGHLIGHTS

- A microbial photoelectrochemical cell system is constructed for hydrogen production.
- The photocathode was prepared with carbon paper and TiO_2 for hydrogen production.
- Continuous hydrogen production is achieved under UV irradiation.

ARTICLE INFO

Article history:
Received 6 December 2012
Received in revised form 5 July 2013
Accepted 12 July 2013

Keywords:
TiO_2
Hydrogen production
Microbial photoelectrochemical cell
Photocathode
UV irradiation

ABSTRACT

Conversion of organic matter to hydrogen in a microbial electrolysis cell (MEC) is one of promising ways for hydrogen generation. However, the lack of efficient and cost-effective cathode catalysts and the need of additional electricity input make it less attractive. To resolve these problems, in this work a light-driven microbial photoelectrochemical cell (MPC) system, which consists of a TiO_2 photocathode and a microbial anode, was constructed to utilize light energy and harvest electrons respectively. In this MPC system, continuous hydrogen production was achieved without external applied voltage under UV irradiation, and it had worked well continuously over 200 h in a batch-fed mode under light illumination. An average hydrogen production rate of 3.5 μmol/h was obtained. The results are useful for designing new hydrogen-harvesting systems.

1. Introduction

Hydrogen is considered to be one of the most promising energy carriers, because it has high energy content and could avoid the emissions of green house gases. Numerous studies have been made to explore hydrogen generation, such as fermentative biohydrogen [1], photocatalytic hydrogen generation [2], electrochemical hydrogen generation [3], as well as some integrated systems [4]. In all these approaches, microbial electrolysis cell (MEC) holds a great promise to produce hydrogen and remove organic pollutants simultaneously [5–7]. In the anode chamber of an MEC, organic matters are utilized by microbes, and in the cathode chamber, hydrogen is generated when the protons in solution react with electrons released from the anode [5]. Such a system has several advantages, e.g., high hydrogen yields and great ability to use many different types of substrates including fermentable and non-fermentable organics [8–11]. Therefore, MEC is recognized as an environmentally friendly approach for hydrogen generation. However, from a thermodynamic point of view, an additional energy input is required to overcome the energy barrier in the formation of hydrogen from protons and electrons [12], which makes MEC less attractive. To improve the economic applicability of MEC, considerable efforts have been made, such as MEC system optimization, electrode design, and catalyst selection [5,6,13].

Alternatively, obtaining the required energy from a renewable energy source (such as solar energy) could sort out the energy barrier problem. The thermodynamics of the semiconductor-based solar water splitting is well established [14], and numerous catalysts have been used to catalyze hydrogen production since the first report by Honda and Fujishima in 1972 [15,16]. However, in most cases, hydrogen generation by semiconductor catalysis needs chemical sacrificial agents to provide electron for the hole of catalysts [17,18], or brings difficulty for separating hydrogen and oxygen, which cause chemical pollution or suffer high costs. These drawbacks make photocatalysis less attractive.

To resolve the two problems mentioned above, here we propose a solar-assisted microbial photoelectrochemical cell (MPC), an integration of microbial anode and semiconductor photocathode. In the microbial anode, electrons are produced by electrochemically active microorganisms from organic matters and are transferred to cathode; and in the photocathode, semiconductor absorbs photon to produce electrons at its conduction-band (CB) and holes at its valence-band (VB). Then, hydrogen is revolved at the CB of the photocathode, while holes at the VB of the

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http://dx.doi.org/10.1016/j.apenergy.2013.07.020

photocathode are filled by the electrons from the anode. In such a PEC system, with the high conduction-band position of semiconductor, the extra energy input is no longer needed. Meanwhile, the electrons transferred from anode fill holes in catalyst to replace sacrificial reagents, which make this system environmentally friendly and cost-effective. TiO_2 is one of the model photocatalysts because of its stability and low cost. It has been used for hydrogen generation in many systems [19,20]. The conduction of TiO_2, $E_{cb} = -0.5$ V at pH = 7 [21], is feasible to drive H^+ reduction to H_2, $E^0(H^+/H_2) = -0.41$ V at pH = 7. Moreover, the electrons supplied from the anode can combine with the photo-generated holes on the TiO_2 surface, and suppress the reoxidation of H_2. To explore the feasibility of this PEC system, its performance and the effects of pH in cathode and substrate of catalysts on hydrogen generation were also examined in the present work.

2. Methods and materials

2.1. Reactor setup and operation

The hydrogen-producing MPC had a two-chamber configuration with an anode and a cathode, separated by a proton exchange membrane (PEM) (GEFC-10N, GEFC Co., China). Each chamber had a volume of 200 mL. On one side of the cathode chamber, a quartz plate with a diameter of 6 cm was used to allow UV penetration. Bioanode was cultivated in another air–cathode microbial fuel cell with anaerobic sludge as inoculum and acetate as substrate. After 2-month incubation, a consortium of electrochemically active microorganisms was well enriched on the carbon felt. The anode chamber was filled with 200 mL of fresh medium as described previously and with 1 g L^{-1} $NaAc{\cdot}3H_2O$ as substrate [13]. All solutions were prepared with distilled water. The cathode chamber was filled with 200 mL phosphate buffer (50 mM, pH 7.0). The photocathode was prepared by painting TiO_2 (P25) on a carbon paper or indium tin oxide (ITO) (5 × 5 cm) as described previously [22]. The prepared electrodes had 0.163 g of TiO_2 loaded on their surface. A 30-W low-pressure mercury lamp was fixed outside of the reactor against photocathode surface with a distance of about 5 cm. The anode chamber was covered with tinfoil to protect electrochemically active microorganisms. At the end of each cycle, the medium in anode and PBS buffer and N_2 in cathode were replaced with new one.

2.2. Analysis

Scanning electron microscopy (SEM; FEI Co., the Netherlands) was used to characterize the morphology of the prepared TiO_2 photocathode, and X-ray diffraction (XRD; X' Pert PRO, Philips Co., the Netherlands) was used to examine its crystal structure.

The photochemical response of the TiO_2 photocathode was measured by a CHI 660 electrochemical workstation (Chenhua Co., China) with a Pt counter electrode and an Ag/AgCl reference, in a 0.1 M Na_2SO_4 aqueous solution. The electrolyte solution was purged with high-purity nitrogen for 20 min prior to measurements to ensure an anaerobic environment of the solution in the measurement. The photopotential vs time curve (E–t) was collected with light on/off cycles vs Ag/AgCl, and photocurrent vs time curve (I–t) was collected respectively at 0 V and −0.4 V (vs Ag/AgCl) with light on/off cycles. Electrochemical impedance spectroscopy (EIS) was measured at the open circuit voltage over a frequency range of 100 kHz to 0.01 Hz with a potential amplitude of 5 mV.

The hydrogen produced from the MPC was measured using a gas chromatograph (SP-6800A, Lunan Co., China). A blocking valve was used to maintain the same pressure with that in the cathode, and the hydrogen volume was estimated through upper volume of the cathode and composition of the gas mixture. A total hydrogen recovery based on total added substrate was estimated. The current across a 10 Ω resistor was recorded every 60 min using a data acquisition device (UT39A, UNIT Inc., China).

3. Results and discussion

3.1. Preparation and observation of the photocathode

Because of its low cost, chemical inertness, and photo-stability, TiO_2 has been considered to be one of the most promising

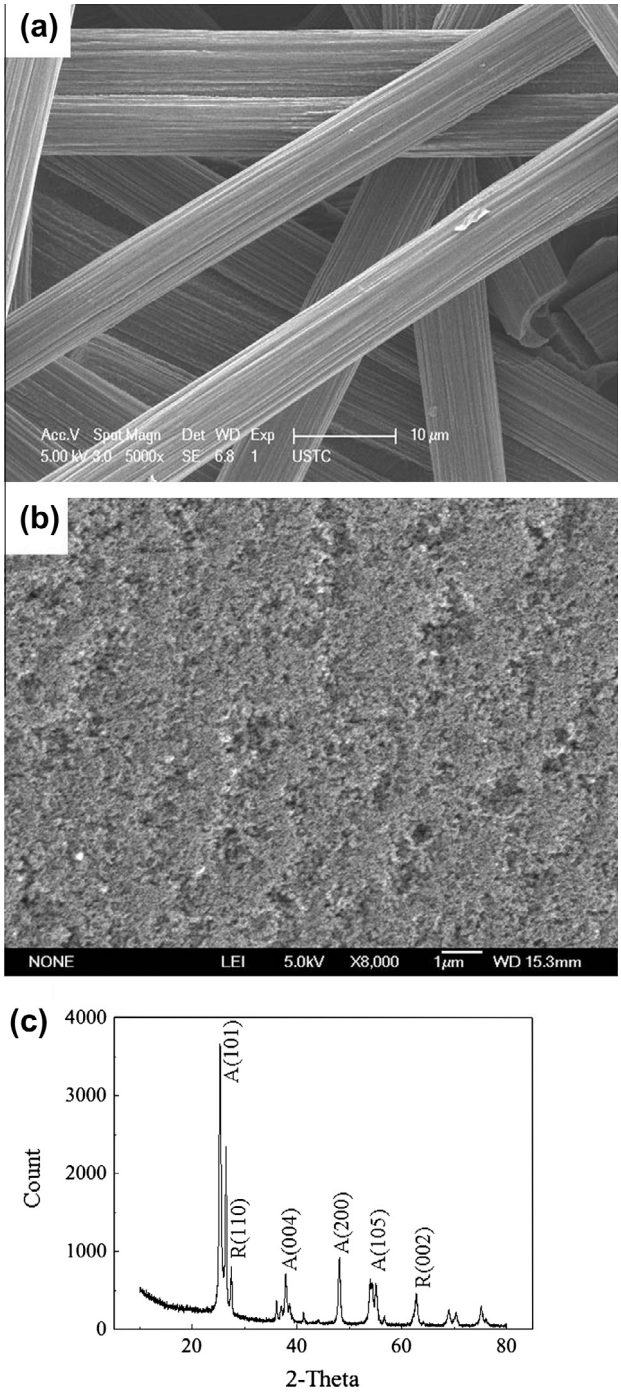

Fig. 1. SEM images of: (a) the raw carbon paper electrode; (b) the photocathode coated with TiO2 and (c) XRD spectrum of the TiO_2 on the photocathode.