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A photo-assisted microbial electrolysis cell for the exclusive biohydrogen production using a MoS_2-coated p-type copper oxide

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HIGHLIGHTS

- MoS_2-coated p-type Cu_2O is used as photocathode for hydrogen production in PAMEC.
- H_2 is exclusively produced at −0.8 V under visible light with no CH_4 and CO_2.
- Energy efficiency of 225% and hydrogen yield of 3.4 are achieved.

GRAPHICAL ABSTRACT

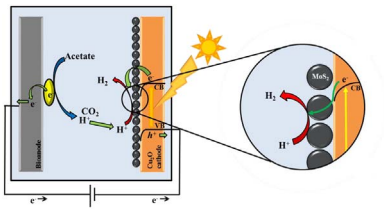

Photo-assisted microbial fuel cell

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ABSTRACT

A microbial electrolysis cell (MEC) has been regarded as an emerging new technology for the biohydrogen production from various organic substances, even from wastewater. One major problem is, however, that methane dominates produced gases in a long-term operation. Here we report that a photo-assisted MEC (PAMEC) is an efficient way to produce hydrogen with a p-type semiconductor cathode. When Cu_2O coated with MoS_2 as cocatalyst (MoS_2/Cu_2O) is employed, only hydrogen with essentially no methane and carbon dioxide was produced from acetate at −0.8 V bias under visible light illumination at a rate of 2.72 m^3H_2 $m^{-3}d^{-1}$. No appreciable performance degradation is observed over 50 days of operation. At lower bias voltage, methane and carbon dioxide begins to be produced. Energy efficiency based on input electricity and hydrogen yield are 225% and 3.4, respectively. This excellent feature of PAMEC is attributed to p-type semiconductor characteristics of Cu_2O and proton reduction activity of MoS_2. Electrons generated from acetate oxidation at the anode are photoexcited to the conduction band at the Cu_2O acquiring enough reduction potential to reduce protons. The concept of PAMEC can be extended to wastewater treatment for the hydrogen production.

1. Introduction

Having specific energy of 142 MJ per kilogram, molecular hydrogen is superior to any other energy carriers from a viewpoint of energy content and environmental impact. Leaving only water after combustion, hydrogen has been considered as an ideal future energy source. Much effort has therefore been poured on the hydrogen production and numerous methods have been proposed, among which are fossil fuel reforming [1,2], water electrolysis [3,4], fermentation [5,6], and photocatalytic water splitting [7,8].

Among various microbe-based electrochemical technologies [9], a microbial electrolysis cell (MEC), a relatively new technology developed a couple of decades ago, is unique in a sense that it can produce hydrogen from a variety of organics [10,11]. In the anodic compartment of an MEC, microbial biofilms function as catalysts to degrade organic substances, generating electrons and protons which are then transported to the cathode through the external circuit and electrolyte, respectively [12]. Under the anaerobic condition and a certain external

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voltage bias, electrons and protons are combined on the cathode surface to produce hydrogen. Since various forms of substrates, even those contained in wastewater, can be utilized by microbes, an MEC is recognized as sustainable and environmentally friendly technology for hydrogen production.

Another merit of MEC is that it is not limited by the fermentation barrier [13]. For example, while maximum four moles of hydrogen are possible by fermenting one mole of glucose leaving acetate as a final product, theoretically 12 mol of hydrogen could be produced in an MEC. However, a thermodynamic barrier exists in the hydrogen production by MECs. Since the formal potential of H^+/H_2 at pH 7 (-0.42 V vs. NHE) is more negative than those of CO_2/organic matters which lie around -0.3 V, external energy input is required to overcome this potential barrier. Practically external bias of -0.4 V or more is applied because of overpotentials and internal resistance. Despite these advantages, methane production instead of hydrogen has been recognized as a major problem in a single-chamber MEC particularly at low applied voltage or in a long-term operation [14,15]. Logan and coworkers, for example, reported that initial H_2 production was soon converted to CH_4 in their winery wastewater-fed MECs [16]. For the MEC to find applications in a real word, this problem needs to be solved.

Recently some attempts have been made to provide additional voltage to an MEC from solar energy. If p-type semiconductor is used as a photocathode and its conduction band level lies at more negative potential than -0.42 V, in principle H_2 can be produced by the photoexcited electrons. This concept has been proven by several researchers using oxide semiconductors such as Cu_2O [17] and TiO_2 [18]. However, the performances were quite poor giving hydrogen production rate below 0.01 $m^3H_2\ m^{-3}d^{-1}$. External voltage bias is needed to enhance H_2 production rate. For example, 0.26 $m^3H_2\ m^{-3}d^{-1}$ was achieved using a microbial fuel cell as a voltage source when a silicon nanowire was used as a photocathode [19]. H_2 production rate still being low, solar-driven MECs are inefficient to find their application in a real world.

In this study, we report that much more efficient hydrogen production was made possible by a photo-assisted MEC (PAMEC) in which MoS_2-coated p-type Cu_2O was used as a photocathode. Under external voltage of -0.8 V and visible light illumination, the maximum rate of 2.72 $m^3\ H_2\ m^{-3}d^{-1}$ was achieved. We observed essentially exclusive H_2 production from acetate without CH_4 and CO_2 at -0.8 V. Performance was maintained without appreciable degradation over 50 days of operation.

2. Experimental section

2.1. Anode preparation and MEC experiments

The anodes for the MEC experiments were prepared in an MFC mode as reported in the literature [20]. A single chamber MFC was constructed and run to form an electrochemically active bacterial biofilm on the anode surface. After the reproducible voltage-time curves were achieved (Fig. S1), anodes were removed and attached to the MEC reactors. A cubic-shaped single chamber MECs of internal volume of 15 mL was employed throughout the experiments. Bioanode and MoS_2/Cu_2O cathode having surface area of 9.6 cm^2 were facing each other at the opposite sides of the cell. On the top of the cell, a head space of 5 mL was glued for the temporary gas collection. Acetate solution (1 g L^{-1}) was used as substrate. The MEC operation was done in a batch mode in which an old batch was replaced with a new one after the gas production stopped. Three voltage biases of -0.4, -0.6, and -0.8 V were applied to the cathode with respect to the anode.

Produced gases were collected in a glass cylinder filled with water and the total volume was measured by the replaced water. Collected gases were analyzed using a gas chromatograph (DS 6200, DS science, Korea) equipped with a thermal conductivity detector. Ar was used as a carrier gas and a carbon molecular sieve column (Carbosphere™, Alltech, USA) was employed to separate gases. Percentages of produced gases were calculated by taking chromatogram areas of each gas after correcting its detector response.

A 100 W Xenon lamp (SOLAX XC-100, SERIC, JAPAN) with a UV cutoff filter was used as an artificial sunlight to irradiate the cathode. The measured light intensity at the cathode surface was adjusted to one sun (100 mW cm^{-2}). A Multi-channel potentiostat (WMPG 1000, WonAtech, Korea) was used to apply voltage and measure current.

2.2. Preparation and characterization of MoS_2-coated Cu_2O (MoS_2/Cu_2O) surface

A copper foil was treated in a solution containing 2.5 M NaOH and 0.125 M $(NH_4)_2S_2O_8$ for 30 min. A deep blue film known as $Cu(OH)_2$ was developed on the surface. Then the copper foil was taken, washed with deionized water, and dried in air. Heating this surface in air at 450 °C for 1 h turned $Cu(OH)_2$ to CuO. A suspension composed of MoS_2 (100 mg), deionized water (8.3 mL), isopropanol (33.3 mL), and 5% Nafion solution (0.67 mL) was sprayed over the CuO surface. Thus prepared MoS_2/CuO surface was dried in air for 24 h at room temperature. We tried different MoS_2 amount and found 2 mg cm^{-2} gave the best results. All the experiments have been done with this amount of MoS_2 coating. We found from XPS measurements CuO turned to Cu_2O after the MEC experiment. Therefore we denote our cathode as MoS_2/Cu_2O.

2.3. Bandgap energy and band position determination

Bandgap energies of Cu_2O and MoS_2/Cu_2O were optically determined from UV-vis absorption spectra by the Tauc equation (eq. (1)) [21],

$$\{\alpha(\nu)h\nu\}^2 = B(h\nu - E_g) \quad (1)$$

where $\alpha(\nu)$ is the absorption coefficient of the material as a function of light frequency and B is constant. Extrapolation of the linear part of the plot of $\{\alpha(\nu)h\nu\}^2$ vs. $h\nu$ into the x-axis gives E_g as an x-intercept.

The type and the flat band potential were determined by the Mott-Schottky equation (eq. (2)) [22],

$$\frac{1}{C^2} = \frac{2}{\varepsilon\varepsilon_0 A^2 e N_A}\left(V - V_{fb} - \frac{k_B T}{e}\right) \quad (2)$$

where ε, C, N_A, V, and V_{fb} are the dielectric constant, the interfacial capacitance, the number of acceptors, applied voltage, and flatband potential, respectively. Other symbols have their usual meanings. The plot of C^{-2} vs. V yields a straight line from which V_{fb} could be determined from x-intercept by correcting ca. 25 mV ($= k_BT/e$). V_{fb} is almost identical to the valence band (VB) position of p-type semiconductor. The conduction band (CB) position is then determined by subtracting E_g. In this study, a small ac (5 mV) of 1 and 2 kHz was superimposed on dc voltage to ensure the measurement certainty. The dc voltage was stepped by 50 mV interval from -0.1 V to 0.5 V with respect to SCE.

2.4. Bacterial community analysis

DNA was extracted from a microbial biofilm formed on the cathode using the Tissue Miniprep Kit (LaboPass, CME0111). The 16S rRNA gene was amplified by PCR using 16S rRNA universal primers 27F (AGAGTTTGATCMTGGCTCAG) and 1492R (GGTTACCTTGTTACGACTT) with G-Taq PCR Mastermix (LaboPass, CMT7001) as PCR solution. PCR products were purified and ligated using a Gel Extraction Kit (LaboPass, CMG0111) and pMD20-T kit (TAKARA, 3270). After overnight incubation at 16 °C, ligation samples were transformed into Top10 competent *E. coli*, and then smeared on the ampicillin (100 mg/mL)/IPTG/X-gal plate. The suitable colony was amplified by colony