A Solar-driven Microbial Electrolysis Cell for Hydrogen Production from Acetate with Minimal CO₂ and CH₄ Emission Using p-Type Cu₂O Nanoparticles

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The microbial electrolysis cell (MEC) is a new, environmentally friendly technology to produce hydrogen from various organic substances. The microbial biofilm formed on the anode surface breaks down organics generating protons and electrons which are combined at the cathode upon application of external voltage bias. Since even wastewater can be treated by MECs with simultaneous H₂ production, this technology is regarded as sustainable. Another advantage is that MECs are not limited by fermentation, for example, maximum 12 moles of H₂ could be produced by MEC while only four moles are possible through fermentation when acetate is a final product.

Since H₂ is produced at the cathode, overall performance is quite dependent on cathode materials. Platinum, despite its excellent catalytic activity toward proton reduction, is very expensive and easily poisoned. Many cathodic materials have therefore been developed in an effort to replace Pt. For example, Selendo et al. reported 1.3 m³H₂/m³/day rate with a Ni powder cathode at 0.6 V. Chen et al. in the meantime reported the use of polyaniline/multicapped carbon nanotube and achieved 0.67 m³H₂/m³/day rate at 0.9 V. But H₂ production rate is still not sufficient. Another problem is the production of CH₄ instead of H₂ particularly when an MEC is operated in a single-chamber mode. The initial high rate of H₂ production is soon taken over by CH₄ production. At the anode, in the meantime, acetates are oxidized by bacteria generating protons and electrons. Electrons are transferred to the VB of the cathode. This process continues as long as acetate is oxidized and the light illuminates Cu₂O.

Here we report that a solar-driven MEC with a p-type semiconductor Cu₂O as a photocathode is a promising method to achieve high H₂ production rate and high H₂ yield along with minimal amount of CH₄ and CO₂ emission.

Synthesis of Cu₂O nanoparticle was done according to the literature. Prepared Cu₂O nanoparticles were of nearly monodispersed sphere shape having an average diameter of 130 nm (Figure S1(a)). X-ray photoelectron spectroscopy showed a characteristic Cu 2p peak at 932.4 eV for Cu₂O (Figure S1(b)). Bandgap energy (Eg) was determined by Tauc equation, [α(hν)]² = (hν - Eg), where α(hν) is the absorption coefficient. From the plot of [α(hν)]² vs. hν, an x-intercept gave 2.0 eV for Eg consistent with a reported value (Figure S2(a)).

The valence band (VB) position could be determined by Mott-Schottky equation (Eq. (1))

\[
\frac{1}{C^2} = \frac{2}{\varepsilon\varepsilon_0A^2CN_A}(V - V_{fb} - k_BT/e)
\]

where C, N_A, and k_B are interfacial capacitance, hole acceptor concentration, and Boltzmann constant, respectively. Other symbols have their usual meanings. By plotting C⁻² vs. V, the flat band potential V_{fb} which can be approximately equated to VB position was determined to be 0.55 V vs. NHE (Figure S2(b)).

The conduction band position was then determined to be -1.45 V vs. NHE (≈0.55–2.0 V). Energy levels and charge transfer processes are represented by the Figure 1.

Absorption of visible light excites electrons to CB leaving behind holes in VB in the Cu₂O cathode. Electrons move to the surface and react with H⁺ in the electrolyte to produce H₂. At the anode, in the meantime, acetates are oxidized by bacteria generating protons and electrons. Electrons are transferred to the VB of the cathode. This process continues as long as acetate is oxidized and the light illuminates Cu₂O.

Figure 2 shows the gas composition (a) and hydrogen production rate (Q_H₂) per unit reactor volume per day and overall H₂ recovery (r_H₂) (b) as a function of applied voltage. Generally more gases and hydrogen percentage increase as the voltage bias increases. Produced gases are mainly H₂, CH₄, and CO₂. At -0.8 V, hydrogen takes 98.70% with 1.3% CH₄ in Cu₂O cathode MEC. Essentially no CO₂ was produced. At lower voltages, the portion of H₂ was still very high. At -0.4 V, H₂, CH₄, and CO₂ take 87.6, 11.6, and 0.8%, respectively. Significance is that CH₄...
production was quite suppressed. It has been well known that CH4 production in a single-chamber MEC is very difficult to avoid due to methanogenesis. Logan et al., for example, reported that initial H2 was rapidly converted to CH4 in an acetate-fed MEC.\textsuperscript{13} It is therefore mandatory to solve this problem in order that MECs find an application in a real world. Several methods suppressing methanogens have been suggested which include chemical treatment or heat shocking.\textsuperscript{10,11} Our solar-driven MEC system, however, does not require those treatments.

QH2 and rH2 (\(=V_\text{collect}/ V_\text{theory}\)) are also important parameters to assess MECs. Our QH2 value of 1.2 m^3H2/m^3/day is favorable comparable to reported ones with Pt cathode and shows higher performance than the similar system using polyaniline nanofiber cathode.\textsuperscript{14} rH2 is the ratio of produced H2 volume with respect to the theoretical value. rH2 increased from 11.2% at 0.4 V to 29.2% and 66.8% at 0.6 V and 0.8 V, respectively. Chae et al. reported 55% with a Pt-coated Ti plate and Xiao et al. only 34.8% with a carbon/iron-based nanorod at \(-0.8\) V.\textsuperscript{15,16} Under much higher voltage of 1.1 V, 89% was achieved by Kadier et al.\textsuperscript{17}

Here we demonstrated that a solar-driven MEC with a p-type Cu2O semiconductor cathode could produce H2 at very high percentage under visible light illumination upon external potential bias. It is hoped that this method may be extended to the H2 production from real wastewater.

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Supporting Information. Additional supporting information is available in the online version of this article.

References