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Improved Microbial Electrolysis Cell Hydrogen Production by Hybridization with a TiO₂ Nanotube Array Photoanode

Ki Nam Kim [†]^(D), Sung Hyun Lee [†], Hwapyong Kim^(D), Young Ho Park and Su-II In ^{*}

Department of Energy Science and Engineering, DGIST, 333 Techno Jungang-daero, Hyeonpung-myeon, Dalseong-gun, Daegu 42988, Korea; kaizer1354@dgist.ac.kr (K.N.K.); mattlee@dgist.ac.kr (S.H.L.); khp911@dgist.ac.kr (H.K.); nano.e.park@dgist.ac.kr (Y.H.P.)

* Correspondence: insuil@dgist.ac.kr; Tel.: +82-053-785-6417

+ These authors contributed equally to this work.

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Abstract: A microbial electrolysis cell (MEC) consumes the chemical energy of organic material producing, in turn, hydrogen. This study presents a new hybrid MEC design with improved performance. An external TiO₂ nanotube (TNT) array photoanode, fabricated by anodization of Ti foil, supplies photogenerated electrons to the MEC electrical circuit, significantly improving overall performance. The photogenerated electrons help to reduce electron depletion of the bioanode, and improve the proton reduction reaction at the cathode. Under simulated AM 1.5 illumination (100 mW cm⁻²) the 28 mL hybrid MEC exhibits a H₂ evolution rate of 1434.268 ± 114.174 mmol m⁻³ h⁻¹, a current density of 0.371 ± 0.000 mA cm⁻² and power density of 1415.311 ± 23.937 mW m⁻², that are respectively 30.76%, 34.4%, and 26.0% higher than a MEC under dark condition.

Keywords: microbial electrolysis cell; hydrogen production; TiO₂ nanotube

1. Introduction

To curtail global heating, or 'warming' as it is commonly called, and its associated potentially catastrophic climate changes, anthropogenic carbon dioxide emissions should be near zero [1]. Hydrogen is a potential substitute for fossil fuels, and upon combustion produces only water. Hydrogen possesses an energy density of \approx 120 MJ kg⁻¹, which compares quite favorably to gasoline at 45.7 MJ kg⁻¹. However, if hydrogen is to be used as a carbon-neutral fuel it must be made on a renewable basis [2], not by the common technique of steam methane reforming (SMR) of natural gas [3]. One approach to carbon-neutral generation of hydrogen is by the use of microbial electrolysis cells (MECs), which convert the chemical energy inherent in wastewater organics into hydrogen. The chemical energy inherent to the organic materials in wastewater is substantial, \approx 9.3 times greater than the energy utilized for conventional wastewater treatment [4,5]. MECs offer the dual benefits of both renewable hydrogen generation and wastewater treatment.

A MEC can be viewed as a modified microbial fuel cell (MFC), using the metabolic energy of the inherent organic matter to reduce protons and produce hydrogen [6–8]. MFC exoelectrogens, a type of microorganism, metabolize organic materials of wastewater and generate CO₂, H⁺, and electrons. These electrons can be transferred to the anode in various ways: by an electron mediator [9], direct electron transfer [10], and microbial nanowire [11,12]. The electrons flow through the electrical circuit to reach the air cathode, where they react with atmospheric oxygen and protons to produce water through the oxygen reduction reaction [13,14]. To improve MFC performance, recent studies



have investigated the combination of MFCs with external photocurrent sources, such as photosynthetic microorganisms [15,16], a copper oxide photocathode [17], a PtO_x -TiO₂ composite photocathode [18], a CuInS₂ photocathode [19], or a TiO₂ nanotube (TNT) array photoanode [20].

In MFC and MEC operation, exoelectrogens attached to the bioanode surface catabolize the organic matter, acetate in this experiment, and generate electrons and protons, and the generated electrons from bioanode flow in the external circuit and reach the cathode [7]. In the MFC, the electrons arrive at the air cathode to react with protons and atmospheric oxygen to produce water, i.e., the oxygen reduction reaction. In a MEC the cathode is not exposed to air, in order to suppress the oxygen reduction reaction, and an external electrical bias is applied to promote proton reduction and thus hydrogen formation [6,21]. The required potential of MEC (>0.2 V) is much lower than the required potential for conventional water electrolysis (1.23 V). Because of this lower required potential, well-controlled MEC can produce hydrogen gas with 2–4 times higher energy than supplied electric energy [22]. There are both single chambered and double chambered MEC, but single chambered MEC without proton exchange membrane has a higher hydrogen production [23]. Recent studies of bioelectrochemical systems have extended to full biological MFC (FB-MFC) [24-26] and full biological MEC (FB-MEC) [27–29], which is composed of biocathode. This replaces expensive chemical catalysts such as Pt, and effectively treats wastewater [30–32]. MEC gets noticeable attention as a sustainable wastewater treatment system with energy recovery [33], and many research teams built pilot scale MEC facilities to validate that MEC can be utilized in real industry [34–39]. In recent studies, various modified MEC structures are suggested for different applications, such as microbial electrodialysis cell (MEDC) [40], microbial reverse-electrodialysis electrolysis cell (MREC) [41,42], microbial electrolysis struvite-precipitation cell (MESC) [43–45], microbial electrolysis desalination and chemical-production cell (MEDCC) [46–49], and microbial saline-wastewater electrolysis cell (MSC) [50–52].

TiO₂ is one of the important material for photocatalysis, because of its stability, low cost, and nontoxicity [53]. There is correlation between anatase crystallinity of TiO₂ and its photocatalytic activity, especially in nanoparticles [54,55]. In TiO₂ photocatalyst, photocatalytic activity is proportionate to the fraction of crystallized anatase [56]. This is because anatase TiO₂ has longer carrier lifetimes [57,58] and faster electron transfer rates [59] than amorphous or rutile TiO₂. To achieve a maximum photocatalytic efficiency of TiO₂, maximizing surface area is important, therefore nanoparticulated TiO₂ is widely utilized. 1D nanostructure TiO₂ such as nanotube has crucial advantages over other nanostructures, because we can control its physical properties, specifically diameter and length, which results in an improved and effective system [60]. In a previous study on a MFC coupled with an external TNT array photoanode, we confirmed that supplementary electrons accelerate the oxygen reduction reaction at air cathode, improving overall MFC performance [20].

In this study, we couple an external TNT array photoanode, made by electrochemical anodization of Ti foil, with a single chamber MEC. Under simulated 1.0 sun solar light (AM 1.5, 100 mW cm⁻²) the 28 mL hybrid MEC demonstrates, in comparison with a MEC under dark, a significantly greater rate of H₂ evolution rate (1434.268 \pm 114.174 mmol m⁻³ h⁻¹), current density (0.371 \pm 0.000 mA cm⁻²), and power density (1415.311 \pm 23.937 mW m⁻²). It appears that the additional photoelectrons from the TNT array photoanode significantly reduce electron depletion of the bioanode, and accelerate the proton reduction reaction at the cathode, and hence overall MEC performance.

2. Materials and Methods

2.1. Chemicals and Materials

The Pt-catalyzed cathode was made using: Carbon cloth (Fuel Cell Earth LLC, Woburn, MA, USA), polytetrafluoroethylene (PTFE, 60 wt.% dispersion in H₂O, Sigma-Aldrich, St. Louis, MO, USA), Pt on Vulcan XC-72 (10%, Premetek Co., Wilmington, DE, USA), carbon vulcan powder (Premetek, Wilmington, DE, USA), Nafion perfluorinated resin solution (15–20%, Sigma-Aldrich, St. Louis, MO, USA), and 2-propanol (99.5%, Sigma-Aldrich, St. Louis, MO, USA). A carbon brush (mill-rose,

Mentor, OH, USA) was used to make the bioanode. Disodium phosphate (anhydrous, for molecular biology, Applichem, Darmstadt, Germany), potassium chloride (Sigma-Aldrich, St. Louis, MO, USA), sodium phosphate monobasic monohydrate (ACS reagent, \geq 98%, Sigma-Aldrich, St. Louis, MO, USA), ammonium chloride (for molecular biology, suitable for cell culture, \geq 99.5%, Sigma-Aldrich, St. Louis, MO, USA), and sodium acetate (anhydrous, for molecular biology, \geq 99%, Sigma-Aldrich, St. Louis, MO, USA) were used to make the MFC and MEC medium. Titanium foil (0.1 mm thickness, 99.5%, Nilaco Co., Tokyo, Japan), carbon paper (CNL energy, Seoul, Korea), ammonium fluoride (98.0%, Alfa Aesar, Haverhill, MA, USA), and ethylene glycol (Spectrophotometric grade, 99%, Alfa Aesar, Haverhill, MA, USA) were employed to synthesize the TNT array photoanode. Titanium wire (1.0 mm diameter, 99.5%, Nilaco Co., Tokyo, Japan) was used to connect the cathode with the external electric circuit. A 100 W Xenon solar simulator (LCS-100, Oriel[®] Instruments, Irvine, CA, USA) with an AM 1.5 filter was employed as the light source in an otherwise dark room. External bias application, and electrical and electrochemical characterizations were implemented by use of a potentiostat (Bio-Logic, VSP model, Seyssinet-Pariset, France).

2.2. Synthesis of TNT Array Photoanodes

The TNT array photoanode was synthesized by electrochemical anodization of Ti foil $(6.0 \text{ cm} \times 4.0 \text{ cm})$. Prior to anodization the Ti foil sample was washed by sonication in acetone, ethanol, and DI water (deionized water), for 10 min each. Electrochemical anodization was conducted by a two-electrode cell using Ti foil as working electrode and carbon paper as counter electrode and interval between both electrodes was 2 cm. The anodization electrolyte was ethylene glycol with 0.5 wt.% NH₄F and 2.0 vol.% DI water. Anodization was performed at 40 V for 30 min, as previously reported [20,61]. With anodization, Ti⁴⁺ ions are generated (Ti \rightarrow Ti⁴⁺ + 4e⁻) and driven from Ti substrate to the electrolyte by electric field. Also, hydroxyl ions (OH⁻) and O²⁻ anions are formed due to water of the anodic oxide film in the electrolyte [62]. These anions form TiO_2 oxide through several reactions (Ti⁴⁺ + 2O²⁻ \rightarrow TiO₂; Ti⁴⁺ + 4OH⁻ \rightarrow Ti(OH)₄; Ti(OH)₄ \rightarrow TiO₂ + 2H₂O). F⁻ ions of electrolyte can combine with Ti^{4+} ions to generate $\text{Ti}F_6{}^{2-}$ ($\text{Ti}^{4+} + 6F^- \rightarrow \text{Ti}F_6{}^{2-}$). Because Gibb's free energy of TiF₆²⁻ ($\triangle G^{\circ}_{298} = -2118.4 \text{ kJ mol}^{-1}$) is much lower than Gibb's free energy of TiO₂ $(\Delta G^{\circ}_{298} = -821.3 \text{ kJ mol}^{-1})$ [63], F⁻ ion can also dissolve the oxide and hydrated layer, which results as etching of the foil (TiO₂ + 6F⁻ + 4H⁺ \rightarrow TiF₆²⁻ + H₂O; Ti(OH)₄ + 6F⁻ \rightarrow TiF₆²⁻ + 4OH⁻). Through competition between oxidation reactions of Ti and dissolution reactions of Titanium oxide, TiO₂ nanotube array structure is produced [64,65]. The anodized Ti foil was sonicated in ethanol for 2 min to wash contaminants and debris off the anodized Ti foil surface and then annealed at 450 °C for 2 h. Through annealing process, the amorphous anodized TiO_2 nanotube array is converted to crystalline anatase phase [64,66]. The crystallinity of the TNT array was investigated by X-ray diffraction spectroscopy (XRD, Empyrean, Panalytical, Almelo, The Netherland) with Cu K α radiation $(\lambda = 1.54 \text{ Å})$ as an X-ray source, operating at 40 kV and 30 mA, scanned in the range of $2\theta = 20-80^{\circ}$ with a rate of 2.5° min⁻¹. Morphological analysis was performed by field emission scanning electron microscope (FE-SEM) (S-4800, Hitachi, Tokyo, Japan). The TNT array sample was cut into circular form with a diameter of 3.0 cm (7.0 cm^2 area) for attaching with the MEC. We measured the stability of TNT array by changes in photocurrent changes with respect to time. The photocurrent was measured by potentiostat (Bio-Logic, VSP model, Seyssinet-Pariset, France), with TNT array serving as the working electrode, the reference electrode was Ag/AgCl reference electrode (3.0 M KCl, EC-frontier, Kyoto, Japan), and Pt wire was used as the counter electrode. Electrolyte was composed of phosphate buffer solution with sodium acetate, which has been used as MFC and MEC medium (Composition is mentioned in Section 2.3). A potential of 0.40 V was applied and the TNT array was illuminated by a 100 W Xenon solar simulator (AM 1.5) for 60 h.

2.3. MFC Operation for Bioanode Preparation

The MEC bioanode was obtained by enriching an electroactive biofilm of exoelectrogen on the surface of a carbon brush anode, using a single chamber MFC (cylindrical reaction chamber of 4 cm length, 7 cm² cross section, 28 mL volume) [67], comprised of a Pt-catalyzed cathode, carbon brush anode, and external resister (1000 Ω), see Figure S1. To make Pt-catalyzed cathode, used air cathode of MFC and cathode of MEC, in which one side of carbon cloth, contact with MFC and MEC medium, was coated with a mixture of Pt on Vulcan XC-72 and Nafion resin (0.5 mg cm⁻² Pt), and the other side of carbon cloth, contact with air in MFC, was coated with a layer of 40% PTFE (polytetrafluoroethylene) with carbon black and four layers of 60% PTFE [68]. To make the ammonia treated carbon brush anode, carbon brush was washed with acetone and DI water, each, to remove contaminants prior to ammonia gas treatment. Later, the carbon brush was treated in 5% NH₃ (He base) at 700 °C for 60 min to improve the performance of bioanode [69].

The MFCs were charged with sludge of an anaerobic reactor, source of the exoelectrogen, collected from Daegu Environmental Corporation Seobu sewage treatment plant (Daegu, Korea). The medium contains sodium acetate (2 g L⁻¹) as a substrate and a 50 mM phosphate buffer solution (PBS), the composition of which is 4.58 g L⁻¹ Na₂HPO₄; 0.13 g L⁻¹ KCl; 2.45 g L⁻¹ NaH₂PO₄·H₂O; 0.31 g L⁻¹ NH₄Cl; trace vitamins (5 mL L⁻¹) and minerals (12.5 mL L⁻¹) stock solutions [70]. The MFC medium was replaced by fresh medium every two days. The MFC was operated for 10 weeks for the formation of a mature exoelectrogenic biofilm on the carbon brush anode and to show stable performance.

2.4. Hybrid MEC Fabrication and Operation

The schematic design of the hybrid MEC is shown in Figure 1. The following steps were taken to convert the MFC to a MEC: (1) The Pt-catalyzed cathode of the MFC was covered with an acrylic plate to prevent oxygen from reaching the cathode. With the oxygen reduction reaction blocked, hydrogen is evolved from the Pt-catalyzed cathode. (2) The carbon brush bioanode was separated from the reactor and exposed to air for 40 min to suppress methanogen growth [7]. After aerial exposure, the bioanode was re-assembled into the reactor. (3) The reactor chamber was filled with medium, and the whole purged with ultra high purity (UHP) nitrogen for 35 min. The external resistor of the MEC was 10 Ω . (4) The TNT array photoanode was electrically connected, see Figure 1, to the bioanode of the MEC.



Figure 1. Schematic illustration of the hybrid microbial electrolysis cell (MEC) with external TiO₂ photoanode.

The TNT array photoanode was illuminated by a 100 W Xenon solar simulator with an AM 1.5 filter for 24 h. A potentiostat (Bio-Logic, VSP model, Seyssinet-Pariset, France) was used to apply a 0.40 V bias between bioanode and Pt-catalyzed cathode. The electrode potential was measured using a three-electrode system against an Ag/AgCl reference electrode (3.0 M KCl, EC-frontier, Kyoto, Japan). A conical tube with a water-filled rubber septum was connected to the MEC for capturing generated gas which, after 24 h MEC operation, was analyzed using a gas chromatograph (Agilent, 6890N, Santa Clara, CA, USA) using a 19095-MOSE column (30 m × 0.53 mm i.d., 50.0 μ m film thickness). GC data to evaluate the hydrogen evolution were taken three times (*n* = 3) for the hybrid MEC under illumination and the MEC under dark.

2.5. Hybrid MEC Performance Evaluation

The MEC performance was evaluated by polarization curves and power density curves. To measure the current density of MEC, potentiostat (Bio-Logic, VSP model, Seyssinet-Pariset, France) was set in chronopotentiometry mode, and the working electrode was connected with cathode, the reference electrode and the counter electrode were connected with bioanode. The applied current started from $-200 \ \mu$ A and was increased by $-200 \ \mu$ A until potential went lower than 0 V. There were no external resistance and any external bias; a similar condition for measuring the current density of MFC. MEC current density (mA cm⁻²) and power density (mW cm⁻²) were normalized to the cathode area (7 cm²). Power Density = I · V · A⁻¹, where I = current, V = voltage, and A = cathode area. The MEC polarization curve was measured with the TNT array photoanode illuminated (100 W Xenon solar simulator, AM 1.5 filter). All measurements were taken three times (*n* = 3) for evaluating the hybrid MEC under illumination and the MEC under dark.

3. Results and Discussion

The TiO₂ photoanode, fabricated by oxidation of Ti foil, is a self-organized array of nanotubes resting upon the underlying Ti foil substrate [71,72]. Figure 2a is a FE-SEM image of the top surface, with Figure 2b showing sample cross-section. As seen, the TiO₂ photoanode is comprised of well-aligned nanotubes of $4.04 \sim 4.35 \mu m$ length.



Figure 2. (a) Surface and (b) cross-sectional field emission scanning electron microscope (FE-SEM) images of TiO₂ nanotube (TNT).

The crystal structures of Ti foil and TNT arrays revealed by X-ray diffraction (XRD) patterns are shown in Figure 3. The Ti foil showed peaks at 2θ values of 40.16° , 52.98° , 70.63° and 76.19° [73,74]. The unannealed TNT array sample showed peaks similar to those of the Ti foil, but also a slight

peak at $2\theta = 62.75^{\circ}$, which can be referred to (204) plane of anatase TiO₂. The annealed TNT arrays showed 2θ peaks at 25.39° , 36.91° , 37.97° , 48.13° , 54.10° , 55.13° , 62.75° , 68.86° and 75.12° . These peaks are corresponding, respectively, to (101), (103), (004), (200), (105), (211), (204), (116) and (215) planes of anatase [75]. It proves that the annealing process makes amorphous unannealed TNT array as crystalline anatase phase.



Figure 3. XRD patterns of Ti foil (black), unannealed (blue) and annealed (red) TNT array.

The photocurrent measurement of TNT array's photoanode with respect to time is shown in Figure S2. After illuminating for 2 min, the photocurrent of TNT array photoanode increased rapidly and reached a maximum photocurrent density of 0.11088 mA cm⁻². This was followed by a fall in photocurrent density to 0.10212 mA cm⁻²; a value obtained after 13 min of illumination. Beyond this, a gradual decrease in the photocurrent was observed ($-0.00391 \text{ mA cm}^{-2} \text{ h}^{-1}$ to $-0.00049 \text{ mA cm}^{-2} \text{ h}^{-1}$). Photocurrent density reaches 90% (0.10077 mA cm⁻²), 80% (0.08877 mA cm⁻²), 75% (0.08322 mA cm⁻²), and 50% (0.055578 mA cm⁻²) with respect to maximum photocurrent density in 45 min, 6.2 h, 12.4 h, 52.4 h after illumination, respectively. Photocurrent density after 24 h illumination is 66.3% (0.07351 mA cm⁻²) of maximum value.

The power density and I–V polarization curves of a hybrid MEC, illuminated and in the dark (equal to a MEC without photoanode) are shown in Figure 4a. It can be observed that under simulated solar light the hybrid MEC showed a current density of 0.371 ± 0.000 mA cm⁻² (n = 3) and power density of 1415.311 ± 23.937 mW m⁻² (n = 3), while in the dark exhibited a current density of 0.276 ± 0.010 mA cm⁻² (n = 3) and power density of 1122.848 ± 32.664 mW m⁻² (n = 3). Coupling of a TNT array photoanode to the MEC resulted in a 34.4% improvement in current, and 26.0% increase in power density.

The open circuit and working electrode potential of the hybrid MEC, under illumination and under dark, are shown in Figure 4b. The cathode polarization curves of both hybrid MECs under illumination/under dark have similar slopes, while for the anode polarization curves there is considerable difference. For the MEC under dark, the slope of the anode potential curve rapidly increases after 0.295 ± 0.019 mA cm⁻² (n = 3), while in the hybrid MEC under illumination the slope of the anode potential curve remains almost constant until 0.533 ± 0.053 mA cm⁻² (n = 3). This sudden change in the anode potential curve of the MEC under dark is similar with "power overshoot" behavior [76,77]. Generally, power overshoot occurs when the anodic overpotential caused by electron depletion overruns the cathodic overpotential [78]. However, in our case, this sudden change arises because of electron depletion at the bioanode as given in Figure 4b. Nonetheless, this lack of electrons at the bioanode is compensated by additional electrons supplied by the TNT array photoanode and thus the overall electron production of the anodes (TNT photoanode + bioanode)

exceeds electron reduction at the cathode. This delays the electron depletion at bioanode, and results in increased power density. Figure S3 shows the power density, I–V polarization, and electrode potential curves for hybrid MEC under illumination and MEC under dark in order to check reproducibility.



Figure 4. (**a**) Power density (open symbol), I–V polarization (solid symbol), and (**b**) electrode potential of hybrid MEC under simulated solar light and under dark (equal to a MEC without photoanode).

The quantity of hydrogen produced, measured by the GC, in ppm h^{-1} and μ mol h^{-1} was calculated as shown:

$$H_2[] = \frac{\mu \text{mol } of \ H_2 \ produced}{\text{mol } of \ gaseous \ mixture} \times \frac{1}{t[h]}$$
(1)

$$H_2 \ [\mu \text{mol } h^{-1}] = \frac{\mu \text{mol } of \ H_2 \ produced}{\text{mol } of \ gaseous \ mixture}} \times \frac{1}{t[h]} \times \frac{1}{V[\text{mL } \text{mol}^{-1}]} \times \text{Total produced } gas \ [\text{mL}]$$
(2)

where "V" is the molar volume (22,400 mL mol⁻¹) of gas at STP and "t" is total reaction time.

$$H_2\left[\text{mmol }\text{m}^{-3}\text{ }\text{h}^{-1}\right] = \frac{H_2\left(\mu\text{mol }\text{h}^{-1}\right)}{V_R\left[\text{mL}\right]} \times \frac{10^{-3}\text{ }\text{mmol}}{1\,\mu\text{mol}} \times \frac{1\,\text{mL}}{10^{-6}\,\text{m}^3} \tag{3}$$

where " V_R " is volume of reactor (28 mL).

Under simulated solar light the hybrid MEC displayed an H₂ evolution rate of $40.159 \pm 3.197 \,\mu\text{mol}\,\text{h}^{-1}$ (n = 3), while MEC under dark showed $30.711 \pm 0.431 \,\mu\text{mol}\,\text{h}^{-1}$ (n = 3). By normalizing against reactor volume, H₂ evolution rate is translated as $1434.268 \pm 114.174 \,\text{mmol}\,\text{m}^{-3}\,\text{h}^{-1}$ (n = 3) and $1096.809 \pm 15.388 \,\text{mmol}\,\text{m}^{-3}\,\text{h}^{-1}$ (n = 3), as shown in Figure 5.



H₂ production [mmol m⁻³ h⁻¹] CO₂ production [mmol m⁻³ h⁻¹] CO₂ Coulombic efficiency [%]

Figure 5. H₂ production rate, CO₂ production rate, and coulombic efficiency by the MEC under dark condition and hybrid MEC under simulated solar light for 24 h.

The coulombic efficiency (CE) of the MEC can be calculated as:

$$CE = \frac{C_P}{C_{Ti}} \times 100\%$$
(4)

where " C_P " is the total coulombs calculated by the amount of hydrogen produced, and " C_{Ti} " is the theoretical coulombs that can be produced from wastewater substrate. C_P and C_{Ti} can be calculated via following equations:

$$C_P(C) = n \times F \times H_2 \text{ evolution rate} \times Operation \text{ time}$$
(5)

$$C_{Ti}(C) = \frac{FbSv}{M} \tag{6}$$

where "*n*" is number of moles of electrons per mole of reduced hydrogen, "*F*" is Faraday's constant, "*b*" is number of moles of produced electrons per mole of oxidized substrate, "*S*" is substrate concentration

of medium, "v" is medium volume, and "M" is molecular weight of the substrate [67]. Considering substrate oxidation equation of bioanode ($C_2H_4O_2 + 2H_2O \rightarrow 2CO_2 + 8e^- + 8H^+$) and hydrogen reduction equation of cathode ($2H^+ + 2e^- \rightarrow H_2$), calculations of C_P and C_{Ti} of MEC appear as the following equation:

$$C_{P,illumination} = 2 \ electrons \times 96485 \ \frac{C}{mol} \times 40.159 \ \frac{\mu mol}{h} \times 24 \ h = 185.99 \ C \tag{7}$$

$$C_{P,dark} = 2 \ electrons \times 96485 \ \frac{C}{mol} \times 30.711 \ \frac{\mu mol}{h} \times 24 \ h = 142.23 \ C$$
(8)

$$C_{Ti} = \frac{96485 \frac{C}{mol} \times 8 \ electrons \times 2 \ \frac{g}{L} \times 0.028 \ L}{82.0343 \ \frac{g}{mol}} = 526.92 \ C \tag{9}$$

Under simulated solar light, the coulombic efficiency of the hybrid MEC is $35.30 \pm 2.81\%$ (n = 3), while that of the MEC under dark is $26.99 \pm 0.38\%$ (n = 3), shown in Figure 5.

4. Conclusions

Herein we combine a MEC with a TNT array photoanode to significantly improve H₂ production. The hybrid MEC design achieves a H₂ evolution rate of 1434.268 ± 114.174 mmol m⁻³ h⁻¹ (n = 3) and coulombic efficiency of 35.30 ± 2.81% (n = 3) under simulated 1.0 sun solar light (AM 1.5, 100 mW cm⁻²), values some 30.76% higher than a MEC under dark. The hybrid MEC achieved a current density of 0.371 ± 0.000 mA cm⁻² (n = 3) and power density of 1415.311 ± 23.937 mW m⁻² (n = 3) under illumination, values, respectively, 34.4% and 26.0% above those of a MEC under dark. We believe the enhanced performance is due to an increased quantity of electrons arriving at the bioanode that, in turn, accelerates the proton reduction reaction. We suggest this photocatalytic hybridization strategy will improve the efficiency of MEC hydrogen production and it will help to make hydrogen a true carbon-neutral energy source, which can solve anthropogenic carbon dioxide emission problem and global warming.

Supplementary Materials: The following are available online at http://www.mdpi.com/1996-1073/11/1/3184/s1, Figure S1: Schematic illustration of the MFC for preparing matured bioanode, Figure S2: Photocurrent dependent time of the TNT array photoanode under simulated solar light for 60 h, Figure S3: (a) Power density, I–V polarization, and (b) electrode potential curves for hybrid MEC under illumination and MEC under dark for checking reproducibility.

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