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Photochemical Biofuel Cells

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Abstract

A photobioelectrochemical Fuel Cell (PBEC-FC) relies on the synergic effect of electroactive and photo-electroactive microorganisms with or without photosensitive electrode to degrade organic matter for diverse bioelectrochemical application. In addition to wastewater treatment, PBEC-FC is also versatile in producing bioelectricity, biofuel, and pollutant degradation. PBEC-FC can come with a different configuration to accommodate for various applications under specific reaction. As a result of continuous research, there are three developing configurations which are: photosynthetic-BFC (PS-BFC), photovoltaic BFC (PV-BFC), and photoelectrode-BFC (PE-BFC). Studies have demonstrated that light-driven BFC has improved the substrate oxidation in the anode and concurrent bioelectrochemical reaction in the cathode as compared to dark conditions. Motivated by the increasing number of publications for this technology, the various configurations of PBEC-FC that suit different applications and their performance will be discussed in this chapter. Although the current performance of PBEC-FC remains low, but, with a continuous advancement to develop a durable and high photoactive material, this green technology will be realized into practicality in the future.

***Keywords*:** Photobioelectrochemical cell, photosynthetic biofuel cell, photovoltaic-biofuel cell, photoelectrode-biofuel cell

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9.1 Introduction

The term photobioelectrochemical refers to the exploitation of phototrophic microorganisms or photocatalyst to convert solar energy to electrical energy or fuels. Technically, when phototrophic/photocatalyst-integrated MFCs are shone with light, their current density increases higher than the current generated under the dark condition. Various types of light supported-MFC have been reported in the literature. However, the documented studies related to this topic is still lacking (2–3%), as compared to what has been widely known for MFC. A light driven MFC can be dependent specifically on the biological system, but normally it comprises biotic anode or cathode with an abiotic electrode. The abiotic electrode can be photoelectrode that deposited with photocatalyst on the electrode surface. Although MFC is powered by light, it maintains as MFC given that one of the electrodes is dwelled by the microbe. The integration of MFC with light energy is very promising if the target is to producing hydrogen with the assistance of a microbe. A standalone MFC could not afford to produce a higher potential than 0.135 V, which typically needed for hydrogen evolution reaction (HER) under microbial electrolysis condition [1]. Considering light as a source of energy, hydrogen can be spontaneously produced if the light-absorbing microorganism and/or electrodes such as photobioanode and platinum cathode are used [2].

Pocaznoi *et al.* have calculated that the highest theoretical power density that can be generated from a typical MFC mode can reach up to 8.98 W m^{-2} [3]. However, reported experimental data had never climbed to such high performance, which regularly in the range of 1–3 W m^{-2}; the highest ever reported was 6.9 W m^{-2} [4]. Since the past few years, the effort for enhancing the MFCs with high power generation is still scarce and the development of larger-scale is proven challenging due to demanding factors influencing MFC's power output. Certainly, a depth investigation is needed. The most practical way to address this low power generation is to provide light-sensitive microorganisms or photo-active electrodes under MFC mode with light. However, it is still arguable that light energy adds up the microbial power density. Thus, a detailed study is required. If more power can be generated through the combination of light and MFC, a new application can be introduced. These include more efficient wastewater treatment [5], biofuel production [6], and chemical synthesis [7]. Several authors have reviewed the light driven-MFC using photosynthetic microorganisms [8–12]. In addition to pure electricity generation, fuel generation from MEC has also been the subject of interest and reviewed

by some authors [6, 13]. Studies have shown that cyanobacteria are commonly worked as bioanode, whereas microalgae are considered to be more functional in the cathodes [14–16].

This chapter will present and discuss the combination of photoelectrochemical (PEC) cells and MFC. The layout of this chapter is initiated with the introduction of various cell configurations, followed by the discussion on photosynthetic biofuel cell, photovoltaic-assisted biofuel cell, and photoelectrode-integrated biofuel cell. In response to progressive research in this area, the next discussion is directed to the potential of fuel generation from PBEC/PBFC and their performance.

9.1.1 Various Configuration of PBEC-FC

Microbial fuel cells (MFCs) take advantage of the potential of microorganisms as bio-catalysts to oxidize substrate and liberate electrons. The generated electrons are ferried towards anode by the electroactive biofilm which formed during the acclimatization step. From anode, electrons are then transported to the counter electrode through external circuit to reduce oxygen into H_2O or H_2O_2 through $4e^-$ or $2e^-$ pathway, respectively [17, 18]. MFCs have been demonstrated to simultaneously treat wastewater and electricity generation. Currently, MFCs are capable of generating potential and maximum power density in the range 0.5–0.8 V and 1–3 W m^{-2}, respectively [19]. It is worth noting that, under open circuit potential, 1 V was attainable from several small-scale MFCs under optimal conditions [20], which merely 0.14 V lower than what has been theoretically calculated [21]. To be able to break through the theoretical performance of MFC, it is idealistic to couple MFC with photosynthetic microorganisms and/or light-sensitive material that can harvest light and convert it into electrical or chemical energy. Notably, sunlight is the biggest source of energy in the universe, in fact, it is free.

The integration of photosynthetic microorganisms into MFC has been demonstrated by exploiting cyanobacteria in the anode [22, 23] or microalgae in the cathode [15, 24, 25]. Screening on the literature, microalgae has been widely exploited for MFC than cyanobacteria due to microalgae's simple structure of being a unicellular species, thus they harvest solar energy more efficiently via photosynthesis reaction. The main reason microalgae are suitable for the MFC system is their nature of producing their own food; all they need is sunlight and CO_2. More importantly, microalgae liberate oxygen during their respiration. These privileges can help to convert CO_2 into a valuable product and provide aeration for MFC cathode chamber to realize the oxygen reduction reaction (ORR).

Another option than microalgae is the employment of photosensitive semiconductors that able to convert solar energy into chemical or electrical energy. A typical example of a photosensitive semiconductor is the photovoltaic (solar panel) which has a unique structure called a *p*–*n* junction. Briefly, illumination on the photovoltaic cell generates electron and proton in *p* and *n* junction, respectively. When the negative and positive pole of semiconductors are connected with any load by wiring, the photo-excited electron in the positive pole will be transported to a negative pole, thus generating electrical current. Replacing the load with MFC, the PV cells provide the external power supplement into MFC for various kinds of reactions in microbial electrosynthesis (MEC) mode. As a proof of concept, a photovoltaic-integrated biofuel cell system was introduced [26]. The investigation showed that the highest power density achievable was 275 mW m^{-3}, which equivalent to almost double than that of typical MFC. The integration of PV cells with MFC can enhance electron acceptance in the cathode and improve the electron donation in the anode, hence escalates the power generation of MFC.

Cutting down the capital cost for cell construction is always the prime concern in developing a cost-effective MFC system. A direct replacement of one of the electrodes with the photosensitive semiconductor or called photoelectrode can significantly reduce the capital cost since the presence of a PV cell is unnecessary. Having photoelectrode installed either in anode or cathode chamber, despite the cost reduction, enhances the charge transfer

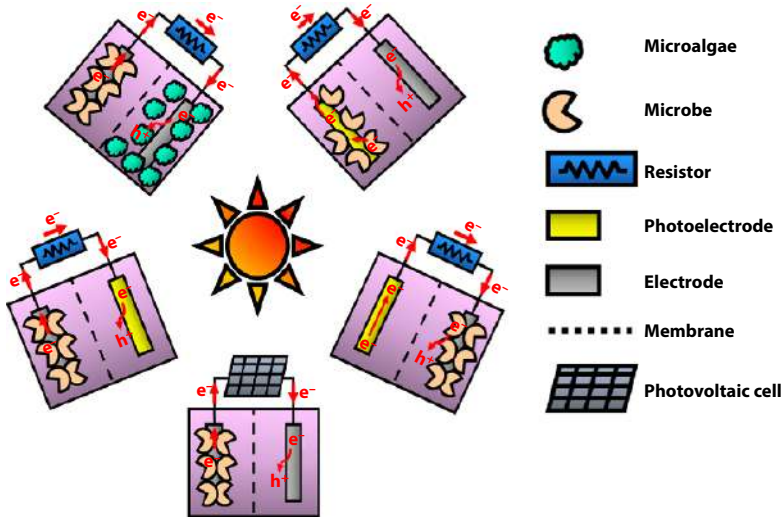

Figure 9.1 Various cell configuration of PBEC-FC.

efficiency owing to the direct illumination on the electrode [27]. However, this is not the case for PV cells where a potential loss is high and a resistive multistage electron transfer can occur [28]. The direct integration of photoelectrode in MFC can come into a different type of configurations (Figure 9.1), namely the photobioanode with metal electrode [29, 30], bioanode with photocathode [31], and anode with photobiocathode [15].

9.2 Photosynthetic Biofuel Cell (PS-BFC)

Photosynthetic Biofuel Fuel Cell (PS-BFC) uses electroactive bacteria (EAB) in the anode to form bioanode and photoautotrophic microorganism as a biocatalyst in the cathode site. While EAB is capable of oxidizing organic matter with the simultaneous release of electrons and protons, the photoautotrophic microorganism performs oxygenic photosynthesis in the cathode, a light-driven reaction that transforms CO_2 and H_2O into biomass. The PS-BFC involved a photosynthetic process carried out by the microalgae or cyanobacteria that utilize anode or cathode as the terminal electron [32, 33]. Studies suggested that cyanobacteria and microalgae are appropriate to be cultured in the anode and cathode, respectively [13]. Interestingly, PS-BFC offers cost reduction owing to the use of biocatalyst instead of noble metal co-catalyst, which is not economical and sometimes poisonous.

Figure 9.2 illustrates the basic mechanism of PS-BFC. Briefly, bioanode in the p-BFC anode chamber oxidized biomass to carbon dioxide (CO_2), proton (H^+), and electron [15]. In the anode chamber, cations such as protons (H^+), are transported from the anode to the cathode chamber via a proton ion exchange membrane (PEM) [34]. In the cathode, the biocatalyst reduced oxygen via ORR by receiving electrons and combined with a proton (H^+) to produce water and electrical current.

The advantage of using microalgae in the PS-BFC is mainly to produce metabolic oxygen and to be reduced by H^+ to form water [35]. Conventionally, MFC used mechanical air stirring to enhance the oxygen reduction reaction in the cathode chamber. However, in PS-BFC, air sparging is not needed because the algae produce metabolic oxygen during their respiration (Figure 9.2) [36]. Another benefit of PS-BFC as compared to the conventional MFC is the replacement of an expensive phosphate buffer with the microalgae in the cathode chamber [15]. It is intriguing to know that all nutrients can be reused in the same PS-BFC [37]. Research finding also revealed that PS-BFC afford to convert CO_2 into fuel and other valuable alkanes compound [38, 39]. Although CO_2 can be harnessed from the

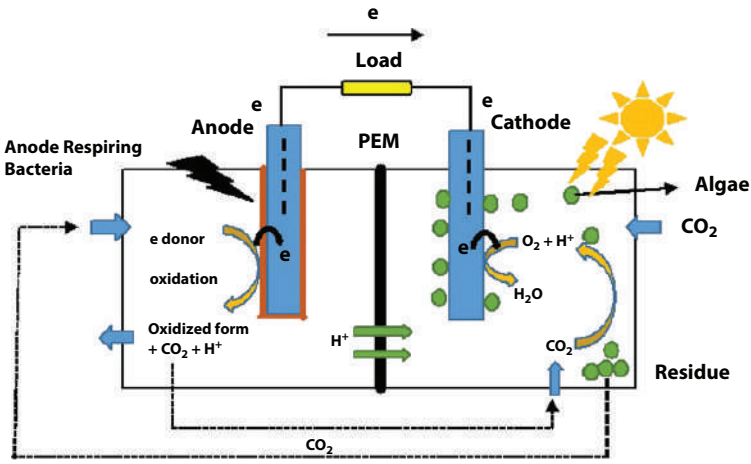

Figure 9.2 Working principle of dual chamber PS-BFC with biocatalyst on the cathode's surface.

atmosphere, its concentration is considerable low and exacerbated by the energy-intensive recovery process [40]. Alternatively, the production of non-toxic concentrated CO_2 gases from biological oxidation process in the anode can be channelled into the cathode to fuel the microalgae (Figure 9.2); a smart way of reducing CO_2 content in the atmosphere [37].

9.2.1 Various Configurations of PS-BFC

Cell configuration is among the main factors governing the generation of power output, durability, and cost-effectivity of the bioelectrochemical system (BES), which equally applies to the PS-BFC system. Four different configurations of PS-BFC were introduced and tested in the laboratory, namely coupled PS-BFC [41], single chamber PS-BFC [42], dual-chamber PS-BFC [43] and sediment PS-BFC [44]. Typically, the PS-BFC employs bioanode, which enclosed photosynthetic microorganisms at anode or cathode, in which photosynthesis is carried out [36]. The electrode in the PS-BFC system can either be enriched by the biofilm that formed on or near the electrode surface or replaceable with planktonic cells [36].

In a coupled PS-BFC, the anodic chamber is connected to an autotrophic photobioreactor (PBR), where CO_2 is transported directly from the PS-BFC to the PBR reactor (Figure 9.3) [45]. This configuration was developed without the use of an expensive ion exchange membrane; however, it was replaced with glass wool in which a simplified and cost-effective

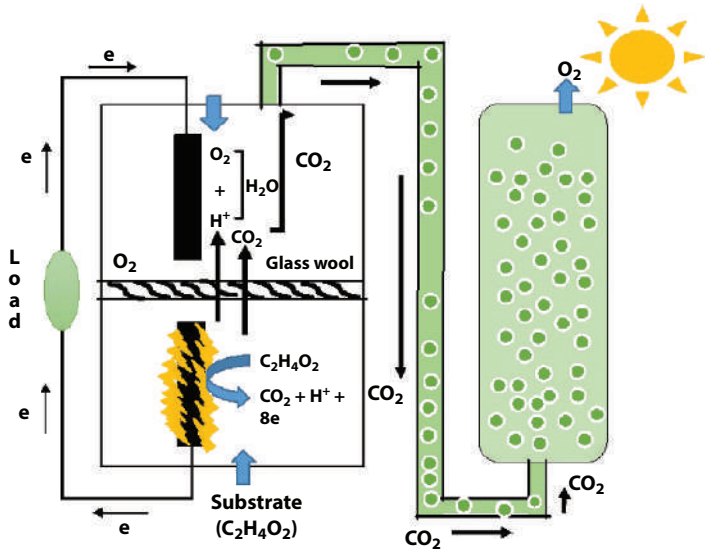

Figure 9.3 A coupled p-BFC with cathodic PBR half-cell.

cell structure was fabricated, therefore scalable [46]. Previously, *Chlorella vulgaris* microalgae were used in a photosynthetic microbial cathodic half-cell as the direct electron acceptor by introducing the half-cell into anodic yeast fermentation, producing a newly developed coupled PS-BFCs [47]. The cathodic half-cell PS-BFC was tested in an existing bioethanol fermentation plant acting as anodic half-cell. As a result, the integrated system was able to generate electricity to power the existing bioethanol plant, while the microalgae consumed the metabolic CO_2 for their growth through photosynthesis process in the cathodic photobioreactor half-cell [48].

Another type of configuration is a single chamber PS-BFC where the cathode was coated or layered on a cation exchange membrane (CEM) which placed in contact with outside air, resembling air cathode configuration, as shown in Figure 9.4 [36]. Under mixotrophic nutritional mode, microalgae were exploited to produce anodic biofilm with the presence of a carbon source from atmospheric CO_2 [36]. The advantage of using single chamber PS-BFC is the accessibility of various environments such as atmospheric CO_2 and organic source in a similar system. Thus, it improves the cooperation between heterotrophic and autotrophic metabolism in the same system. Several photosynthetic microorganisms such as *S. platensis* which capable of directly transfer electrons to the electrode without the assistance of mediator was applied in the co-existence with photo-synthetic

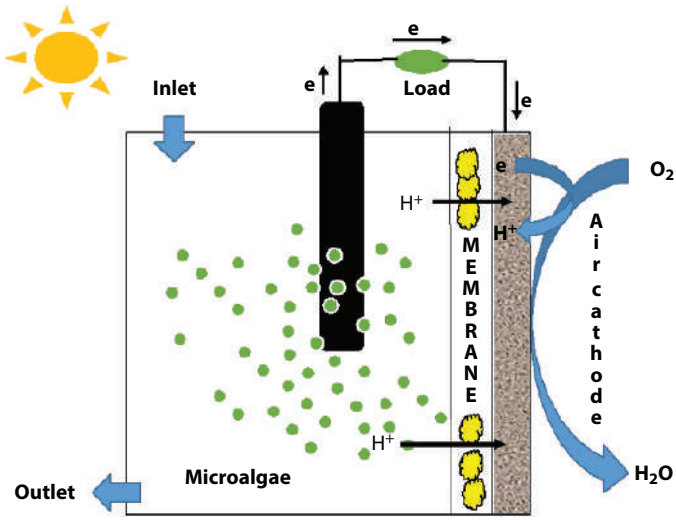

Figure 9.4 Single chamber p-BFC.

bioanode in a membrane-less single chamber PS-BFC [46]. Synergic interaction can be achieved by mixing the culture of microalgae and bacteria, which was proven effective to improve the efficiency of PS-BFC [49]. It was suggested that the microalgae could metabolize the organic substrate such as acetate to produce electricity. A similar design can be utilized as a portable bio-battery PS-BFC by illuminating the bionaode to activate the photosynthetic reaction, along with the intermittent light and dark condition; providing a rechargeable reaction for a longer usage [36].

Generally, a dual-chambered PS-BFC is a design which placed anode and cathode in the individual chamber separated by PEM, as illustrated in Figure 9.2 [34]. The difference between phototrophs-containing PS-BFC and heterotroph-containing MFC system is the source of electron donor in the anode chamber (Figure 9.2). A dual-chamber PS-BFC has been commonly used for carrying out microalgae photosynthesis as the oxygen producer in the cathode chamber [50]. For example, a study used an activated sludge as the influent for the anodic chamber under the dark condition to prevent the presence of microalgae, while the microalgae were cultured in the cathodic chamber under 12 h illumination per day [36]. The production of CO_2 as a result of microbial oxidation of organic in the anode was channelled into the cathode chamber, which benefits the microalgae growth through photosynthesis process.

In a different configuration, microalgae were also applied for anodic biocatalyst, accompanied by a chemical cathodic catalyst in a CEM-separated

dual-chamber PS-BFC [46]. The dual-chamber was programmed with a direct-three level: 1) the separation of microalgae and bacteria culture, 2) the replacement of the mechanical aeration method by the biological aeration derived from microalgae culture, and 3) lastly, the adjustment of the light exposure from continuous into periodic light and dark condition [38].

Inspired by the practicality of benthic MFC and the sunlight as a sustainable source of energy, a sediment PS-BFS was proposed [51, 52]. The motivation for the development of a sediment PS-BFC relies on the conventional potential differences generated between anode which concealed in the sediment of deep or shallow water and a cathode laying on top of the sediment (Figure 9.5). The cathode chamber which submerged in water is exposed to sunlight to realize the photosynthesis process. For the production of electricity, sediment PS-BFC relies on the ability of EAB oxidizing organic matter or the redox reaction of reduced complexed, along with ORR of dissolved oxygen in water [53]. The system can be driven by the privilege of an *in-situ* generation of CO_2 from bioanodic metabolic activity, which can be harnessed as a substrate for microalgae growth, and simultaneously generating current.

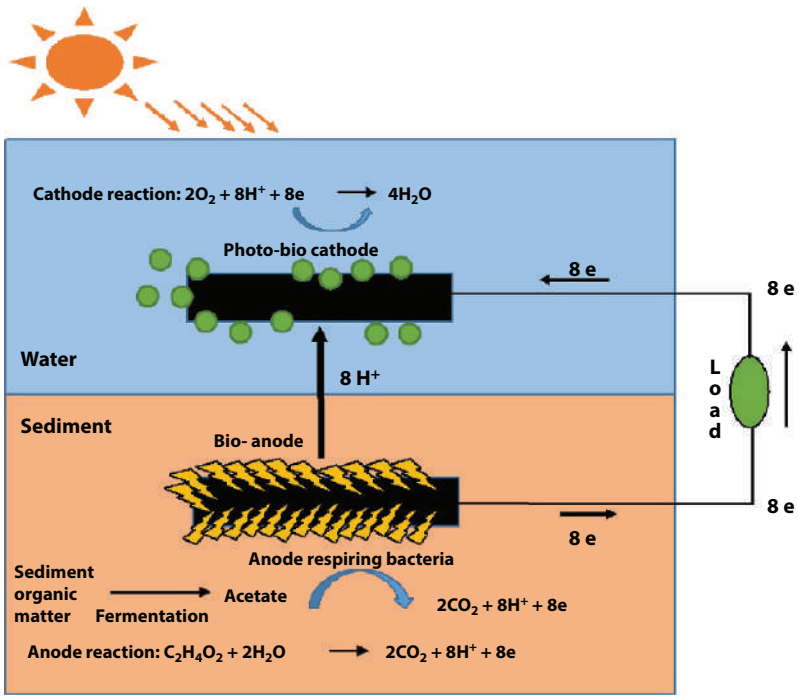

Figure 9.5 The diagram of sediment PS-BFC.

9.3 Photovoltaic-Biofuel Cell (PV-BFC)

Photovoltaic-biofuel cell (PV-BFC) is composed of two integrated components, which consist of a solid-state photovoltaic cell or so-called solar cell that is connected to the bio-fuel cell or commonly known as a microbial fuel cell. In general, photovoltaic cells consist of two semiconductors which formed a p–n heterojunction semiconductor either in a monocrystalline or polycrystalline material. The most popular semiconductor material that made photovoltaic to function is p-type silicon (Si) and n-type Si. The p and n-type Si can easily be tuned by introducing a doping element within its crystalline structure. For instance, the p-type Si can be obtained by introducing an element that possessed less one electron at their outer energy shells, such as boron (B) or gallium (Ga). Meanwhile, the n-type silicon can be obtained by introducing an element with an extra one electron than Si at their outer energy shell, such as phosphorus (P). It should be noted that the fabrication of photovoltaic is quite complex, where it consists of several layers which electrode, electron transport layer, hole transport layer, and photoactive layer (the essential layer) [53]. Up until today, various solar cell types have been fabricated, such as cadmium telluride (CdTe), copper zinc tin sulfide (CZTS), dye-sensitized solar cells (DSSCs) and perovskite solar cells [54].

The working principle of the photovoltaic cell can be briefly explained as follows: (1) under light irradiation, the top layer will be induced electron excitation; (2) The excited electron at the n-type layer will be attracted to the holes of the positive layer (p-type layer); (3) As a result, the depletion zone is formed where the electron and holes transport layer forces the electron to travel continuously within the cell; (4) The depletion zone that possessed an internal electric field drives the electron from the n-type layer and holes move to the p-type layer and ejected out from the cell; (5) Finally, the electrons are then returned to the n-type layer via external wires, which resulted in continuous electric current flow.

If the PV cell is externally connected to a biofuel-cell, the photo-induced electron holes obtained from steps 1–5 will be transfered to the existing electrode available within the biofuel-cell. In this event, the photo-induced electrons flow toward the biocathode while the photo-induced holes flow towards bioanode in the biofuel cell. The phenomena could enhance the redox capability in both bioanode and biocathode of the biofuel-cell via excellent electron-transfer capability. Additionally, the photo-induced electron-pairs obtained from PV cells can be enhanced via designing a holographic lens to increase the spectrum-splitting capacity optical

efficiency, and energy conversion efficiency [55]. Figure 9.6 shows the example of the integration of the photovoltaic-fuel cell system for hydrogen generation and carbon dioxide conversion into value-added products.

It has been reported that the first integration of PV cell and fuel cell system had increased the hydrogen generation as renewable energy with solar to hydrogen efficiency of 30% over 48 h of operating system [56]. Even though the performance of the system is significantly high, but in term of cost productivity of hydrogen fuel generation by the system (Figure 9.6(a)), it needs to be reanalyzed. In other development, the biofuel cell

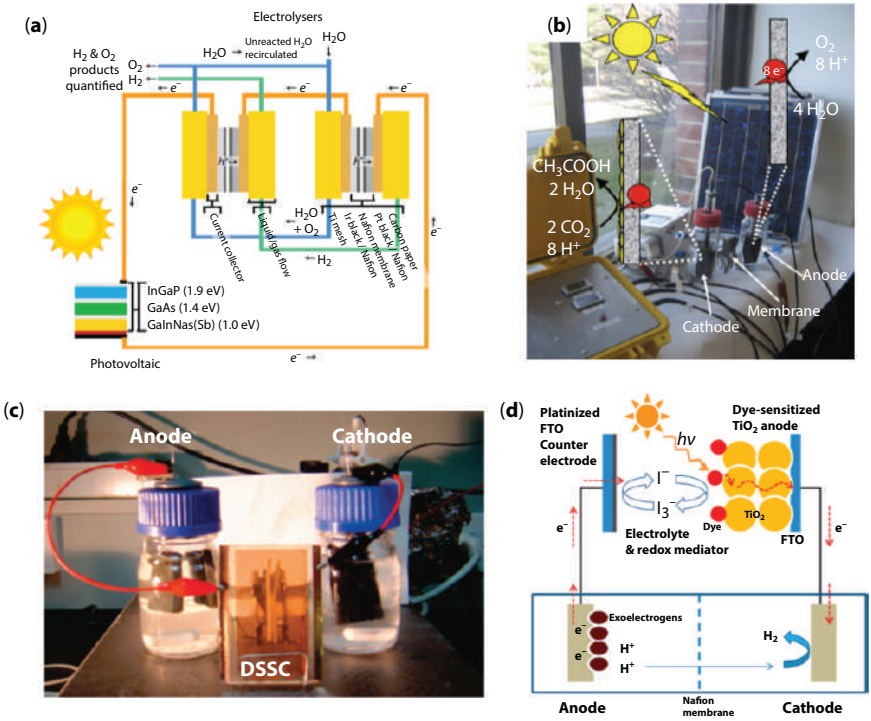

Figure 9.6 (a) Photovoltaic (PV)-electrolysis device schematic for solar water splitting. The PV-electrolysis system consists of InGaP/GaAs/GaInNAsSb triple-junction solar cells and two polymer electrolyte membrane (PEM) electrolyzers connected in series. *Reproduced with permission from Ref.* [56]. *Copyright 2016 Springer Nature.* (b) H-cell device for supplying cathode biofilms of *S. ovata* electrons derived from water. The solar-powered option is illustrated. *Reproduced with permission from Ref.* [57]. *Copyright 2010 American Society for Microbiology.* (c) Solar-powered microbial electrolysis cell for hydrogen production. (c) Photograph. (d) Schematic diagram. *Reproduced with permission from Ref.* [58]. *Copyright 2009 American Chemical Society.*

has been integrated with PV cells to accelerate the production of a value-added organic compound from CO_2 reduction reaction (Figure 9.6(b)) [57]. The study has highlighted the utilization of *S. ovata* as a biofilm for the fabrication of the cathode electrode in the system with long-term viability. By the concept of microbial electrosynthesis, *S. ovata* revealed a significant capability in converting the CO_2 to acetate by utilizing the supplied electrons by the PV cells into the biofuel cell. Inspired by this encouraging finding, Chae and co-workers have developed PV-BFC based on a dye-sensitized solar cell (DSSC)-powered microbial electrolysis cell (MEC) for hydrogen evolution as shown in Figure 9.6(c) [58]. This work highlighted the excellent hydrogen conversion efficiency, 71.3–77.0%, which comparable with the PV-BFC system that used Pt as a cathode at 79.3–82.0%. Interestingly, the finding is promising to overcome the drawback of conventional MECs, especially the expensive use of Platinum. However, the role of microbes to improve the system's performance was not discussed in detail.

Therefore, it can be stated that the presence of a PV cell can be considered as a complementary system to boost the electrochemical potential of the biofuel cells. Consequently, a high electrocatalytic redox reaction can be realized. However, research for the PV-BFC system is not progressive throughout the year because of the intermittent solar energy. Besides, the efficiency of solar to energy conversion of the PV cell is limited by the type of material used. Even though DSSC has been chosen as a cost-effective PV, the performance of solar to energies conversion is still not up to the satisfactory level.

9.4 Photoelectrode Integrated-Biofuel Cell (PE-BFC)

In general, the BFC electrode has to be coated with a biofilm of electroactive bacteria (EAB) to drive the electron and proton productions [59]. However, BFC remains problematic due to low power output and efficiency, which need to be solved. When the conventional BFCs are light supported, the electrical power and efficiency will increase above what is possible with the dark reaction. Usually, a light assisted BFC is exclusively depend on the microbial communities at the anode and catalytic activity at the cathode. The bioanode obtained power from EAB that digest the available nutrient in the wastewater. Based on the theoretical calculation, the highest achievable electrical power was measured to be 8.98 Wm^{-2}. However, based on the experimental report, the highest electrical power was obtained to be 6.9 Wm^{-2} [29, 60].

So far, not much progress has been made to improve the BFC performance. There are many factors need to be investigated to improve the system. The electrode performance is among the most important factor which always associated with the characteristic of the material and the presence of co-catalysts (bio- or chemical catalysts). Although PV cell-assisted BFC has shown a feasible technology to carry out the MECs system, the application of PV cell incur additional cost and proven ineffective with respect to the resistive electrons transportation between PV cell and BFC [29]. Concerning the issue, the use of photoelectrochemical cell (PEC) stands as a promising alternative approach. When semiconductor or photoelectrode is illuminated, it can directly drive the oxidation or reduction reactions in the aqueous phase as shown by many [61–65]. Motivated by the concept, photoelectrode (PE) can be integrated into BFC to generate a high-power output and enhance the light conversion efficiency of the overall cell. Chamousis *et al.* [30] have proven that the p-BFC can generate 0.73 $mWcm^{-2}$ of power density, which corresponds to 3-folds higher than that obtained by conventional BFC. In the next sub-chapter, discussion on this topic will be extended to elucidate the working principle of photoelectrode (PE) followed by PE-integrated BFC, the various configuration of the PE-BFC, systems and material used in PE-BFC.

9.4.1 The Basic Mechanism of Photoelectrochemical (PEC) Reaction

A PEC system is comprised of photoelectrode, which has been used to harvest light energy and convert it to electrical current. Types of photoelectrode are divided into *n*-type and *p*-type, which are used as photoanode and photocathode, respectively (Figure 9.7). The *n*-type semiconductor has a valence band (VB) edge positioned at sufficiently positive potential to conduct organic substrate oxidation. Meanwhile, the *p*-type semiconductor has a conduction band (CB) edge positioned at higher negative potential than the water reduction potential to realize hydrogen production. It should be noted that the photoanode must has the lower Fermi level compared to that of photocathode. When the light strikes the photoelectrode, electrons at the VB will be excited and jump to the CB of the semiconductor materials. The photoexcited electrons leave holes for oxidation reaction; such progression spontaneously produces photocurrent. The photoexcited electrons then move from the photoanode (*n*-type) towards the outer circuit and combine with a proton (H^+) at the counter electrode or photocathode to complete the circuit [66, 67]. Hence, the photoexcited electrons and holes can contribute to organic subtrates degradation and water reduction [68, 69].

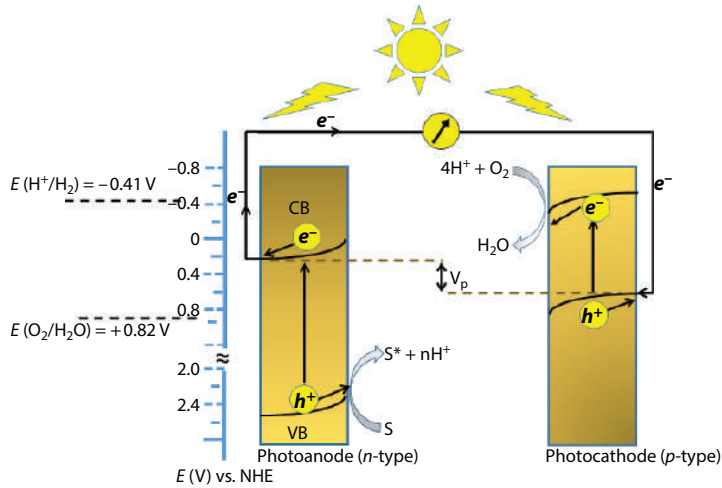

Figure 9.7 Mechanistic illustration of photoelectrode reactions under illumination. Whereas substrate (S) is oxidized to S* along with the liberation of a proton (H^+) and electrons (e^-) at the photoanode, the oxygen is reduced to water by accepting electron at the photocathode. *This illustration was modified and adapted with permission from Ref.* [68]. *Copyright 2012 American Chemical Society.*

9.4.2 Photoelectrode-Integrated BFC

PE can be applied either to the anode and/or cathode in the BFC system. When both anode and cathode are illuminated, they are called as photobioanode and photocathode, respectively. The schematic of energy for the promotion and delivery of electrons from the electroactive bacteria (EAB) to the photoelectrode is shown in Figure 9.8. The anode (photobioanode) is exposed to light to generate protons and electrons (Figure 9.8a), while the cathode material which coated with co-catalysts (i.e., Pt) reacts with oxygen to produce water (Figure 9.8b).

In the PE-BFC, the photobioanode oxidizes the substrate (i.e., wastewater) to release carbon dioxide, protons, and electrons (Equation (9.1)). Then, protons and electrons at the photobioanode are transferred to the cathode to reduce oxygen and produce water (Equation (9.2)). The performance of PE-BFC is determined by the ability of photoelectrode materials to absorb light energy, oxidize wastewater, and overcome the oxygen reduction overpotentials. In PE-BFC, the photogenerated holes and the EAB at the photoelectrode oxidized the organic substrate at the anode compartment. The overall reaction for the PE-BFC can be described in Equation (9.3). The PE-BFC can convert the substrate into electricity with the presence of light and air. In general, open circuit potential (V_{OC}) of +0.82 V can be achieved in PE-BFC systems.

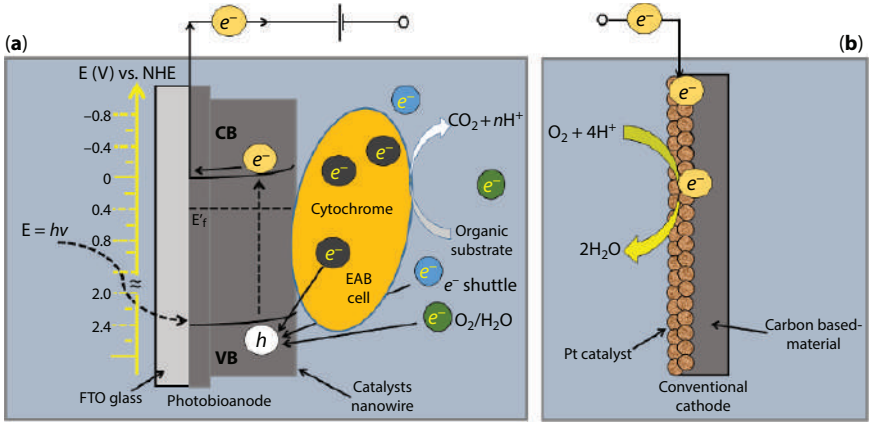

Figure 9.8 (a) Energy diagram for the promotion and delivery of electron from microbes (EAB) to photoelectrode. (b) the oxygen reduction reaction with Pt as a co-catalyst electrode.

$$\text{Anode reaction; } C_nH_{2n}O_n + nH_2O \xrightarrow{PV,hv} n\,CO_2 + 4n\,H^+ + 4n\,e^- \tag{9.1}$$

$$\text{Cathode reaction; } n\,O_2 + 4n\,H^+ + 4n\,e - \xrightarrow{PV,hv} 2n\,H_2O \tag{9.2}$$

$$\text{Overall reaction; } C_nH_{2n}O_n + n\,O_2 \xrightarrow{PV,hv} n\,CO_2 + n\,H_2O \tag{9.3}$$

In addition to the photobioanode, the photocathode materials have also demonstrated with enhanced BFC performance [68]. Photobioanodes improved the EAB biofilm thickness owing to the enhanced respiration under illumination, which then accelerates the transfer of electrons from microbe to electrode [70]. Thicker biofilm is the desired characteristic because it helps to reduce the internal resistance of anode, thus generate greater power output from BFC [70]. Meanwhile, the photocathode improved the catalytic activity of oxygen reduction to water [68]. Photobioanode and photocathode will be discussed in detailed the next subtopic.

9.4.3 Various Configuration of PE-BFC

The configuration of PE-BFC is categorized into a single and dual chamber PE-BFC. In a single chamber PE-BFC, the photoanode (photobioanode) and photo/cathode are placed at a distance between each other in the same

chamber, and no membrane separating them (Figure 9.9). During the PE-BFC operation, the photobioanode chamber must be fully controlled under anaerobic condition because the EAB activities are very sensitive to the presence of oxygen. The single-chamber PE-BFC using photobioanode and the conventional cathode is as shown in Figure 9.9a. The illumination should be performed at the anode side while the cathode (usually using Pt as co-catalyst) is exposed to oxygen. To enhance the cell performance, conventional cathode could be replaced with photocathode materials such as TiO_2 or Cu_2O/Cu [64, 69, 71]. Both photobioanode and photocathode were illuminated to drive the oxidation and reduction reactions simultaneously (Figure 9.9b). As a result, the performance of the PE-BFC was higher than the BFC using conventional electrode.

Contrastingly, the photobioanode in a dual-chamber PE-BFC must be operated under anaerobic conditions, while the photo/cathode chambers performed under aerobic conditions. Therefore, the photobioanode

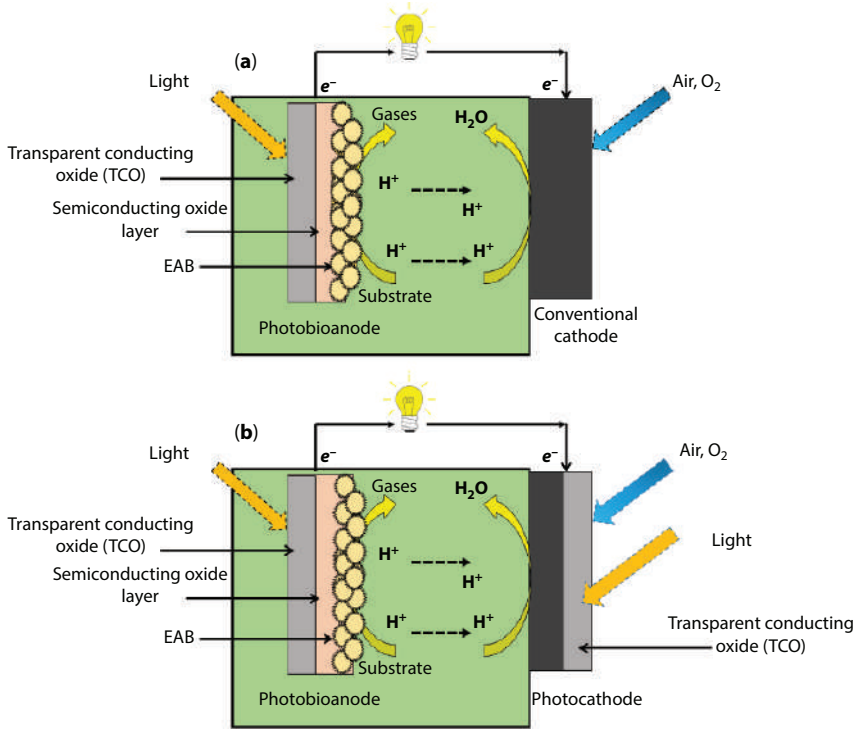

Figure 9.9 (a) Schematic diagram of a single chamber PE-BFC with the phtobioanode-conventional cathode and (b) photobioanode-photocathode. The cell was operated under anaerobic conditions.

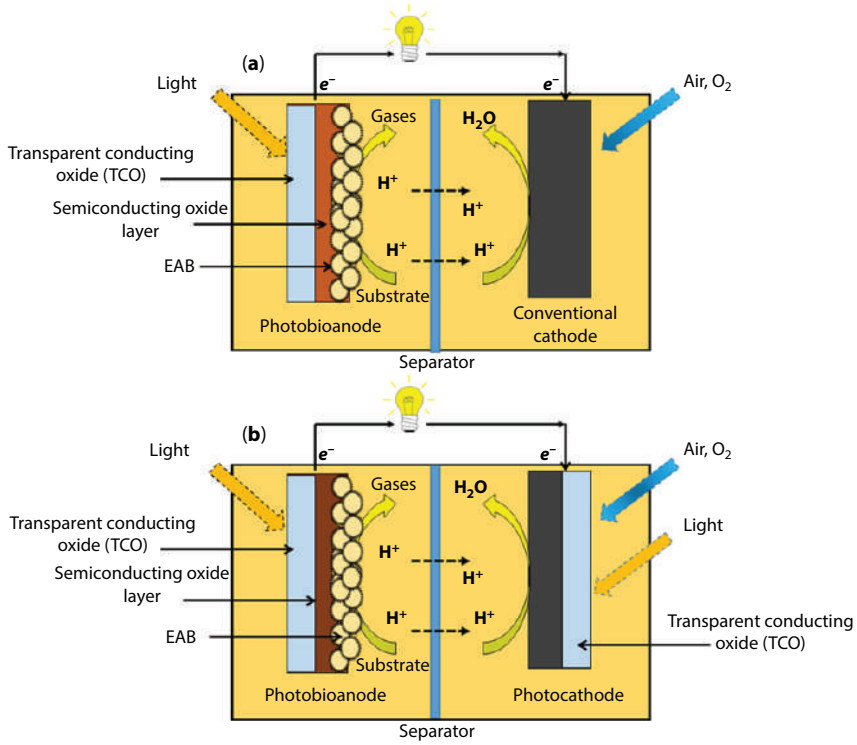

Figure 9.10 Schematic diagram showing (a) a dual-chamber PE-BFC with the photobioanode-conventional cathode, and (b) a photobioanode-photocathode.

and photo/cathode chambers must be separated using a separator such as Nafion (Figure 9.10). The presence of separator in dual-chamber PE-BFC can prevent the diffusion of gases, ionic concentration gradient and EAB migration from or to the photobioanode and the photo/cathode [72]. However, the presence of separator will reduce the amount of the protons that can be transferred from the photobioanode to the photo/cathode [73]. Consequently, the pH in the photobioanode chamber can be rapidly decreased, declining the EAB activity [74].

9.4.4 Materials Used in PE-BFC

The material used for an electrode in PE-BFC must offers for improving the interaction between light absorption, EAB biofilm, and materials surface [71]. Material of choice should be good in term of electrical conductivity, physically and chemically stable, commercially available, inexpensive, and environmentally friendly [71]. The example of material used for the

fabrication of electrode and photoelectrode in PE-BFC is tabulated in Table 9.1. The carbon-based and metal-based materials and conducting polymers have been widely used as an electrode in PEC applications. Among carbon-based electrodes, carbon nanotubes (CNTs) such as single-walled and multi-walled carbon nanotube (SWCNT and MWCNT) are the best option owing to the high conductivity. Metal-based electrodes such as TiO_2 and WO_3 doped onto SnO_2 [30], boron-doped ZnO, and CuO [71], fluorinated tin oxide/glass substrate [30] was used as photoelectrodes in PEC applications. In

Table 9.1 The material used for the fabrication of electrode and photoelectrode in PE-BFC.

Electrode material		**Ref.**
Anode/Photobioanode		
Carbon nanotubes	Single-walled carbon nanotube (SWCNT)	[71]
	Multi-walled carbon nanotubes (MWCNT)	[93]
	TiN-CNTs, 2D Graphene	[94]
Metal oxide thin film	TiO_2, WO_3, ZnO	[30, 68, 70, 71]
	WO_3/W	[82]
	$BiVO_4$, α-Fe_2O_3, WO_3, TaON and Ta_3N_5	[83]
	$SrTiO_3$, ZnO, and NbO_5	
Polymers	PCDTBT: $PC_{61}BM$ sealed with TiO_2/Al.	[75, 91]
	PTB_7 : PC71BM	[71]
	PCDTBT: PC71BM	[71]
Cathode/photocathode		
Carbon based materials	Pt/C	[30, 86]
	MnO_2/C	[92]
Metal oxide thin film	$LiTaO_3$	[85]
	Cu_2O/Cu	[68]
	NiS	[77]
	$CuInS_2$	[86]
	TiO_2	[29]

Note: PCDTBT: $PC_{61}BM$ = Poly[9-(1-octylnonyl)-9H-carbazol-2,7-diyl]-2,5-thiophenediyl-2,1,3-benzothiazol-4,7-diyl-2,5-thiophenediyl: Phenyl C61 butyric acid methyl ester; PTB_7 : PC71BM = Poly[4,8-bis(2-ethylhexyloxyl) benz[1,2-b:4,5-b'] dithiophene-2,6-diyl-alt-ethylhexyl-3-uoro thithieno[3,4-b] thiophene-2-carboxylate-4,6-diyl]:(6,6-phenyl-C71-butyric acid methyl ester.

addition, the conducting polymers such as poly 3,4-ethylenedioxythiophene (PEDOT) [71, 75], poly-styrenesulfonate (PSS), and poly-3-hexylthiophene (P3HT) and polyaniline (PANI) [71] have also been applied as electrodes. Generally, a photoanode (photobioanode) combines the photoactive material and EAB biofilm on the bifunctional quadratic two-sided electrode [76]. At one side of the glass substrate, the electrode surface is covered with transparent conducting oxide (TCO) and exposed to light. Meanwhile, the other side of the electrode surface is contacted and attached with EAB. A study has revealed that the power output and the light conversion efficiency of TiO_2 photobioanode was measured to be 0.73 mW cm^{-2} and 1.7%, respectively. Furthermore, the performance of TiO_2 photobioanode was improved by using a DSSC counter electrode [77]. Several strategies such as nanoarchitecture of semiconductor film, $TiCl_4$ post-treatment, interfacial engineering, doping, compositing and light scattering have been investigated to enhance the performance of photobioanodes [76]. The other photobioanode materials used were $BiVO_4$ [78], α-Fe_2O_3 [79], WO_3 [80, 81], TaON [82] and Ta_3N_5 [82], $SrTiO_3$ [83], ZnO [83], and NbO_5 [83].

TiO_2 is a photosensitive material that can absorb UV light [63]. It is an inexpensive material, commercially available, and can be used as a photocathode in BFC application. TiO_2 is an *n*-type semiconductor. When TiO_2-coated graphite was used in PV-BFC, the power density was increased from 7.64 mW cm^{-3} (dark reaction) to 12.03 mW cm^{-3} (under light irradiation) which correspond to 1.57-fold enhancement [84]. Another material used as photocathode is lithium-tantalate ($LiTaO_3$), which was also used as a photocathode in biological fuel cell application. When $LiTaO_3$ photocathode was illuminated with a 500 W of UV/Vis intensity, it can deliver 3-folds higher of power (55 mW cm^{-2}) compared to that of the dark reaction (17 mW cm^{-2}) [85]. Copper indium sulfide ($CuInS_2$) has also been used as photocathode in a dual-chamber PE-BFC. The PE-BFC using $CuInS_2$ photocathode can generate 0.108 mWcm^{-2} of power density which was comparable to that of Pt/C (0.123 mW cm^{-2}) under the dark reaction [86]. The result demonstrated that expensive Pt/C is replaceable with low-cost $CuInS_2$ semiconductors.

9.5 Potential Fuels Generation and Their Performance From PEC-BFC

9.5.1 Hydrogen Generation

PEC-BFC technology is known as one of the methods of producing energy from wastewaters. The wastewaters from industrial, agricultural,

and municipal sources contain large amounts of dissolved natural matter which might be a potential resource for chemical and gasoline production. Principally under light condition, the organic compound is oxidized by the bacteria, producing CO_2 and electron in anode. The bioelectrochemical reaction occurs in the anode drive the transportation of electrons to the cathode in which they integrate with protons to generate hydrogen fuel with a minimum external voltage.

Ngaw *et al.* investigated the effect of different biofilm on term of the performance of photo-biofuel cell technology in terms of the ability to facilitate electron transfer (MFC) and photoelectrochemical (PEC) cell [87]. The combination of a graphene/carbon nanotube (G/CNT) in MFC and a gold/titanium dioxide (Au/TiO_2) in PEC cell, has producing a photocurrent density of ~0.758 mA cm^{-2} and an H_2 evolution rate (HER) of ~11.2 mmol h^{-1}. The enhancement was attributed to the stepped forward electron transfer of the G/CNT biofilm which relied on factors: (1) the large surface area of graphene sheets allows extra bacterial adhesion on the anode surface; a thick multi-layered biofilm was formed which referred to bacteria colonization on the electrode surface after 1-day operation (Figure 9.11(a)), (2) the incorporation of CNTs into the G-biofilm advanced the conductivity of the biofilm by facilitating the electron transfer between *Shewanella oneidensis* and the electrode, as indicated in linear sweep voltammograms (LSV) (Figure 9.11c). The hybrid device using the $Au–TiO_2$ photoanode and carbon felt anode ($AuTiO_2$/C-PEC–MFC) generated a photocurrent of ~0.294 mA cm^2 (orange line) at zero bias (0 V vs. Pt), which is ~5 times greater than that of the stand-alone $Au–TiO_2$ photoanode PEC cell (~0.056 mA cm^2, red line), at the same potential (Figure 9.11(c)). In order to understand the performance of different anodes on H_2 evolution, the HER which catalyzed from four combination materials were evaluated (Figure 9.11(b)). The combination which employed the G/CNT-biofilm exhibited the outstanding H_2 evolution rate (~11.2 mmol h^{-1}), 2.4 times higher compared to the lowest H_2 overall performance of carbon felt biofilm at zero bias.

The enhance overall performance was ascribed to the additional electrons provided by the MFC in the hybrid device. When both MFC and PEC cells were connected, bacteria at the MFC anode oxidized the organic compound to generate electrons, which then transferred to the Pt wire of the PEC cell via external circuit, resulting in improved photocurrent technology for the hybrid device. Notably, HER became strongly dependent on the photocurrent density generated by the hybrid devices. Thus, the employment of high performance anode is crucial in enhancing the overall performance of the system.

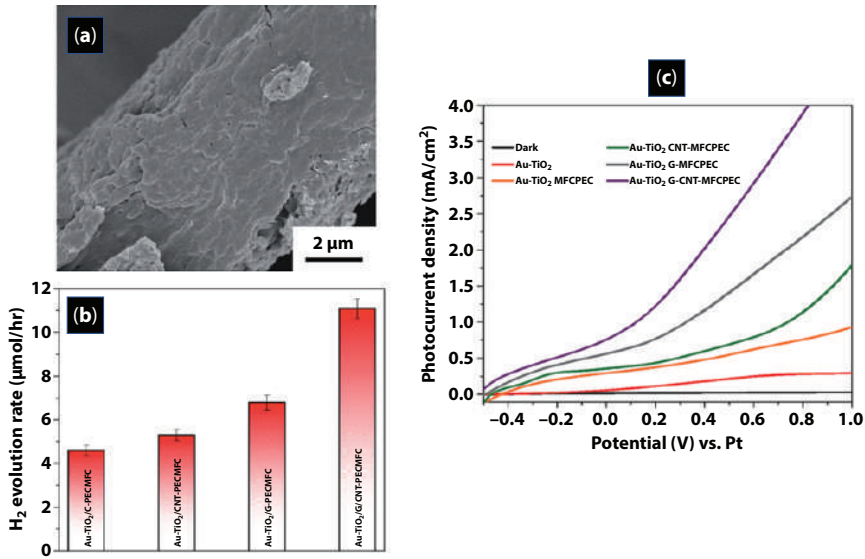

Figure 9.11 (a) FESEM image showing the G/CNT biofilm tightly attached to the carbon felt surface, (b) HER of the various hybrid systems employing different biofilm anodes (c) Linear sweep voltammograms of various hybrid systems employing different biofilms. *Reproduced with permission from Ref.* [87]. *Copyright 2017 The Royal Society of Chemistry.*

9.5.2 Contaminants Removal and Waste Remediation

Current processes for biological treatment of low intense wastewater are based on the power intensive-traditional technology which is not environmentally friendly. New procedures to wastewater treatment which enabling a large-scale energy recovery are the most effective technique to generate and supply a large amount of electricity into the conventional wastewater treatment. BES combines the benefit of wastewater treatment from various source for energy and resource recovery through the production of bioelectricity or other useful products.

Long *et al.* investigated the use of a single fabric for each anode and cathode as a high-performance electrode to treat pollutants in MFC [88]. Blue titania nanotube arrays (BTNA) as a bioanode, which fabricated by cathodic treatment has remarkably increased the electricity production from 3.64 ± 0.112 to 6.246 ± 0.135 mA. The application of blue titania nanotube arrays at both anode and cathode produced a complete photobiological catalyst of PBEC-FC, which successful to conduct a green photoelectrocatalytic degradation of azo dye. The degradation of the azo dye and its transitional products resulted from the electronic contraction of the

dye and oxidation of free radicals. Figure 9.12(a) shows an SEM image of the surface morphologies of the BTNA. The form of rod-shaped bacteria, 1-μm long and 0.1-μm wide have protected the nanotube arrays and the nanotubes were discovered between both bacteria and electrode, which has been proven to be an efficient morphology for extracellular electron transfer processes. Under illumination, when the potential increased to 0.6V, the photocurrent of the TNA increased to 1.25 mA while BTNA increased to 2.5 mA (Figure 9.12(b)), which correspond to two folds improvement of current output. The obtained result was due to the improve aggregation of Geobacter on BTNA anode and the resistance was significantly decreased after a cathodic treatment as compared to the TNA.

BTNA was also tested as cathode in MFC to accomplish a photocatalytic degradation of active brilliant red X3(ABRX3) from Azo dye. High elimination of ABRX3 and the intermediary products was achieved, which sourced from the devaluation of photoelectrons and oxidation of the free radical. Interestingly, according to previous research, electrons from bioanode dissociate the azo bond under dark condition rather than degrading the aromatic compounds or their intermediate products [89]. In the case

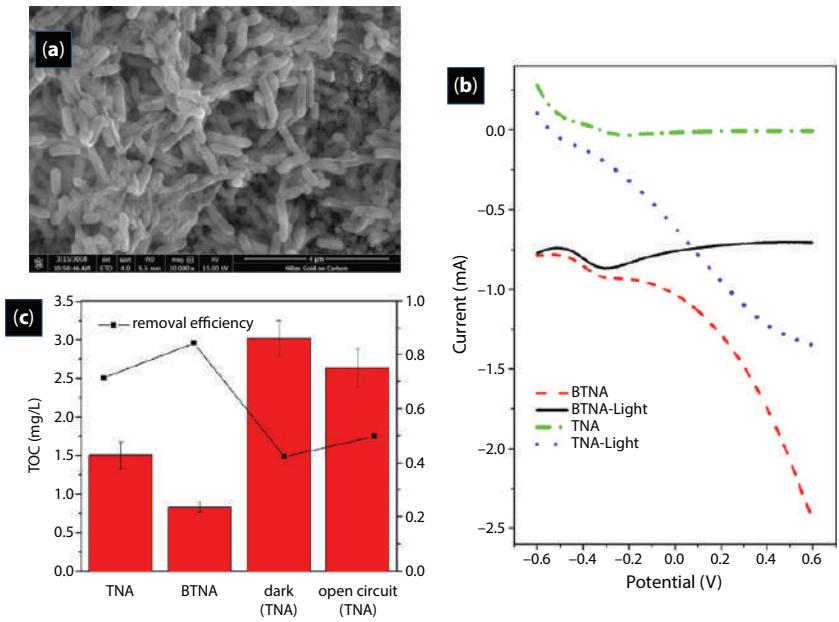

Figure 9.12 (a) The SEM image of BTNA, (b) photocurrent generation of BTNA and TNA under light or dark, (c) The TOC changes of the electrolyte after 6 h degradation. *Reproduced with permission from Ref.* [88]. *Copyright 2019 Elsevier.*

of PBEC-FC, further reduction of the ABRX3 intermediate products were induced by the superoxide free radicals effects at the photocathode. As shown in Figure 9.12(c), the total organic carbon (TOC) decreased to 3.0 ± 0.24 mg/L under dark condition, which is 3.75 times higher than BTNA and 2.0 times higher than TNA under illumination.

PBEC systems also have been efficiently tested to bleach dyes, although dyes are toxic, chemically durable, and hard to be degraded with natural microbial action [88]. Therefore, a highly conductive electrode is needed to boost the photobioelectrocatalytic activity.

9.5.3 Sustainable Power Generation

Photobioelectrochemical fuel cells are bioelectrochemical devices that permit the generation of electricity during anaerobic respiratory of selected bacterial species in light conditions. This technology shows promise in both wastewater treatment and sustainable bioenergy conversion applications. Bacterial respiratory occurs in the anaerobic anode compartment of the MFC generates electrons, which then transported through external circuit and electrochemically coupled with electron acceptors inside the aerobic cathode compartment.

Amao *et al.* developed a new PBEC-FC which functioned as a solar cell and has an ability to convert CO_2 to formic acid. The photoanode was prepared by immobilizing thylakoid membrane-possessing microalgae *Spirulina platensis* on a nanocrystalline TiO_2 film to develop TK/TiO_2|FDH$CH_3V(CH_2)_9COOH$ heterojunction, along with the large formate dehydrogenase (FDH) coating on the photoanode's surface. The corresponding SEM image of TK/TiO_2 and FDH-$CH_3V(CH_2)_9COOH$ electrode are shown in Figure 9.13(a). Figure 9.13(b) presents the light and dark current and potential (J–V) curves for TK/TiO_2|FDH-$CH_3V(CH_2)_9COOH$. The generated photocurrent was estimated to be 44.5 μA cm^{-2}, which is 5 times higher in the light as compared to the dark environment. Figure 9.13(c) shows the oxygen production catalyzed by the TK/TiO_2|FDH-$CH_3V(CH_2)_9COOH$, in time dependence of formic acid under continuous visible-light irradiation. By increasing irradiation time, the amount of formic acid and oxygen generation were increased accordingly. The photoexcited electrons from TiO_2 transported through the external circuit to the FDH-$CH_3V(CH_2)_9COOH$ electrode, where the viologen moiety of $CH_3V(CH_2)_9COOH$ was reduced and CO_2 was converted to formic acid due to the catalytic action of FDH. A continuous cycle was introduced to produce oxygen at the anode (TK/TiO_2) and the conversion of CO_2 to formic acid at the cathode (FDH-$CH_3V(CH_2)_9COOH$) [90].

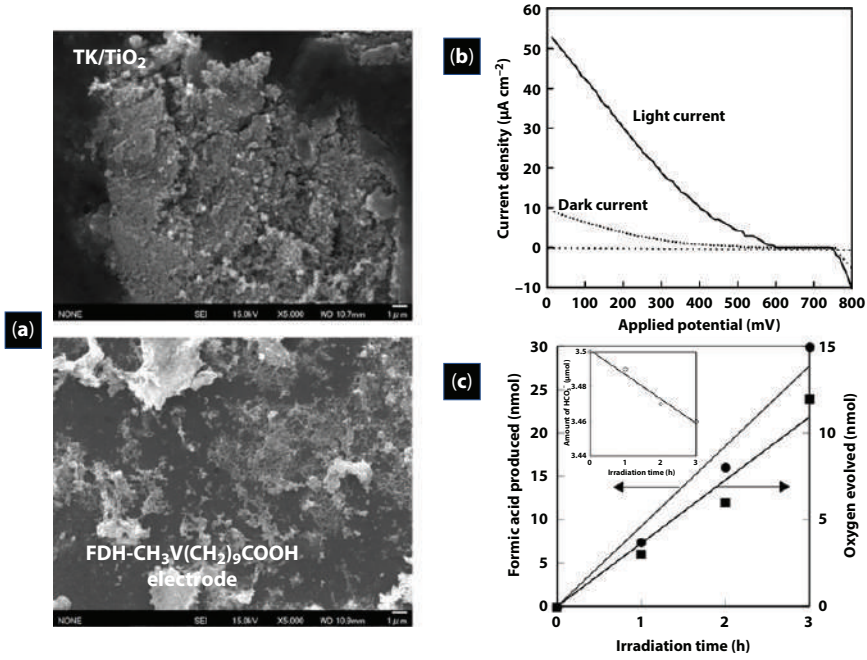

Figure 9.13 (a) The SEM images of TK/TiO_2 and FDH-$CH_3V(CH_2)_9COOH$ electrode, (b) Dark and light current and potential (J–V) curves of TK/TiO_2|$FDHCH_3V(CH_2)_9COOH$ with 100 $mWcm^{-2}$ light, (c) Time dependence of formic acid and oxygen production in the visible-light-driven electrochemical biofuel cell consisting of TK/TiO_2 and $FDHCH_3V(CH_2)_9COOH$ electrodes under continuous irradiation with 100 $mWcm^{-2}$ light. *Reproduced with permission from Ref.* [90]. *Copyright 2018. The Royal Society of Chemistry (RSC) on behalf of the Centre National de la Recherche Scientifique (CNRS) and the RSC.*

9.6 Conclusion

Obviously, the performance of versatile MFC technology to deliver multipurpose functions including wastewater treatment, power generation, fuel production, and a wide range of contaminant degradation can be improved by integrating a sustainable source of light energy from solar radiation. In contrast to cyanobacteria, microalgae as a biocatalyst in the cathode received wider research attention in line with the recycling concept of renewable energy sources. Despite water and light, the exploitation of microalgae needs CO_2 for respiration and produces O_2 during exhalation; thus reducing cost for mechanical aeration and make use of the emitted CO_2 in the anaerobic chamber for algae growth. Considering today's advancement of PV cell, its incorporation into BFC afford to expedite the PV-BFC towards industrialization. However, limited by the resistive

electron transfer in PV-BFC hybrid system and additional cost required for PV cell, PE-BFC can offer cost reduction and higher photoconversion efficiency owing to direct illumination on photoelectrode, hence direct charge transfer. However, the race to develop a high photoactive, durable, and cost-effective photoelectrode has been proven challenging. Thereby, a significant research effort should be directed to find a cost-effective and highly photoactive material which practical for all PBEC-FC configurations prior to field application.

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