Light energy to bioelectricity: photosynthetic microbial fuel cells
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Here, we reviewed five different approaches that integrate photosynthesis with microbial fuel cells (MFCs) — photoMFCs. Until now, no conclusive report has been published that identifies direct electron transfer (DET) between a photosynthetic biocatalyst and the anode of a MFC. Therefore, most recent research has been performed to generate sufficient electric current from sunlight with either electrocatalysts or heterotrophic bacteria on the anode to convert photosynthetic products indirectly. The most promising photoMFCs to date are electrocatalytic bioelectrochemical systems (BESs) that convert hydrogen from photosynthesis and sediment-based BESs that can convert excreted organics from cyanobacteria or plants. In addition, illumination on the cathode may provide either oxygen for an electrocatalytic reduction reaction or a promising anoxygenic biocathode.

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Introduction
Microbial fuel cells (MFCs) are bioelectrochemical systems (BESs) for electric power generation based on the exploitation of biocatalytic reactions with active microbial cells. In power-generating MFCs, electrons are liberated from substrates through biocatalysts at an anode, pass through an external load as electric current, and combine with a cathodic electron acceptor through electrocatalytic or biocatalytic reductions. When sunlight is converted into electricity within the metabolic reaction scheme of a MFC, we describe this system as a photosynthetic MFC (photoMFC). Here, we review the latest development in photoMFCs in five separate sections. Each section represents a description of one or three system diagram(s) (visualized in Figure 1a–g) in which a MFC is coupled to photosynthetic reactions. Each section heading or subsection heading indicates which system diagram will be discussed (a–g). Additional variations of system diagrams that include photosynthesis and MFCs are possible, but for this review these five sections are inclusive for the targeted recent literature survey.

PhotoMFCs were originally tested in the 1960s with metal electrocatalysts (‘Hydrogen-generating photosynthetic bacteria with an electrocatalytic anode (b)’ section) and in the 1980s with artificial electron mediators in the anode chambers (‘Photosynthetic bacteria at the anode with artificial mediators (a)’ section) [1,2]. With increasing concerns about sustainable energy supplies, solar-energy technologies are gaining increasing attention again. In the last decade (i.e. 2000–2010), new approaches to convert sunlight into bioelectricity evolved with BESs. Many of these new developments are based on the temporal or spatial separation of photosynthetic energy conservation and dark (heterotrophic) electricity generation without the use of artificial mediators (‘Hydrogen-generating photosynthetic bacteria with an electrocatalytic anode (b)’ to ‘Photosynthesis at the cathode to provide oxygen (g)’ sections). Besides bioelectricity generation, an additional benefit of photoMFCs is that carbon dioxide is removed from the atmosphere by the integrated photosynthetic process [3**–4†]. Many of the results in the recent literature were achieved with small systems under laboratory-controlled environmental conditions. The reader must, therefore, be aware and critical that scale up may not be feasible or economical. Recently, however, Dekker et al. [5] have provided some hope for a successful MFC scale up. They achieved a power output of 144 W/m³ with a 20-L dark MFC, albeit at a great financial cost. Delivering light into the system with, for instance, photobioreactors, would further increase complexity and costs. On the other hand, much scale up may not be necessary if we are interested in generating enough electric power with photoMFCs to operate environmental sensors in remote areas.

Photosynthetic bacteria at the anode with artificial mediators (a)
During a previous period of intensified photoMFC research (i.e. 1985–2000), mainly cyanobacterial species of Anabaena and Synechocystis were investigated as biocatalysts with HNQ (i.e. 2-hydroxy-1,4-naphtoquinone) as an artificial redox mediator to shuttle electrons from the microorganisms to the anode (mediated photoMFC — Figure 1a) [2,6–9]. Most of these studies observed increasing power generation during the dark phases when...
Seven different configurations of photosynthetic microbial fuel cells (MFCs). (a)-(g) corresponds to separate sections of the review. The sun represents biochemical reactions in the light and the moon represents reactions in the dark. The sun/moon symbol represents reactions that are dependent on the day/night cycle, respectively.
in intracellular carbon storages (glycogen) were oxidized and electrons were recovered with BES; while oxygen production limited power production during light phases when the intracellular carbon storages were refueled [2,8]. The use of unsustainable and environmentally problematic artificial redox mediators prevented these early photoMFCs from practical realization. It is, therefore, not a surprise that this type of photoMFC is no longer very popular to work on.

**Hydrogen-generating photosynthetic bacteria with an electrocatalytic anode (b)**
A ubiquitous feature of photosynthetic microbial metabolisms is the production of molecular hydrogen [10–12]. Photosynthetic biohydrogen production is of vast interest for renewable hydrogen generation and intensive research programs have been established (see other reviews in this special bioenergy issue). It may be advantageous to convert hydrogen rapidly to electric power to overcome hydrogen inhibition effects and problems with hydrogen gas recovery. To reap the advantages of maintaining very low hydrogen partial pressures, coupling the photosynthetic hydrogen production with *in situ* hydrogen oxidation through an electrocatalytic-conversion step presents a promising technology (electrocatalytic photoMFC — Figure 1b). Hereby, H$_2$/H$^+$ serves as a natural electron mediator between the microbial metabolism and the anode. This idea was already successfully tested in 1964 [1]. More recently, a study with the green alga *Chlamydomonas reinhardtii* indicated that *in situ* hydrogen removal (keeping the hydrogen partial pressure very low) enhanced hydrogen production [13**]. Also, anoxygenic photosynthetic purple bacteria, which produce hydrogen in a photofermentation process from organic material, have been studied in combination with electrocatalytic electrodes for immediate hydrogen removal [14,15]. It is, therefore, not a surprise that Cho *et al.* [14] showed the direct relation of photosynthetic activity and power production with *Rhodobacter sphaeroides* (3 W/m$^3$ in the light versus 0.008 W/m$^3$ in the dark). The crucial point for electrocatalytic photoMFCs is a stable, cost-efficient electrocatalyst. Typical hydrogen proton-exchange membrane fuel cell catalysts are prone to inactivation under dirty microbial conditions. Although the protection of the platinum catalyst by conductive polymers has been effective [16,17], cheaper non-noble-metal electrocatalysts, such as tungsten carbide [WC], seem more promising for this low-rate technology [18]. However, also with those non-noble-metal catalysts, stability issues must be overcome before real applications become possible [19,20].

**Photosynthesis coupled with mixed heterotrophic bacteria at the anode (c–e)**
Organic matter can be accumulated via photosynthetic processes, and subsequently oxidized by heterotrophic MFC biocatalysts to produce electricity. Synergistic relationships between photosynthetic producers and heterotrophic consumers are widely established in various eco-systems, which often also contain diverse populations of anode-respiring bacteria. Over the last two years (i.e. 2008–2009) researchers have investigated photosynthetic carbon dioxide fixation coupled to heterotrophic electricity generation with three types of systems.

**Synergism between phototrophic microorganisms and mixed heterotrophic bacteria in sediments (c)**
In marine or freshwater sediments, algae and some bacterial groups, such as cyanobacteria, can supply organic matter (e.g. excreted polysaccharides) to heterotrophic bacteria via photosynthesis, and thus maintain synergistic communities in, for instance, microbial mats. This relationship was examined in a freshwater sediment-type photoMFC for electricity generation (heterotrophic *in situ* photoMFC — Figure 1c) [21*]. It was found that the MFC with a well-adapted microbial community produced electric current repeatedly in response to illumination. Similar to the early photoMFC studies, electricity generation exhibited an inverse relationship with illumination: the current increased during darkness and decreased upon illumination. Continuous illumination inhibited current production, possibly because of accumulation of oxygen evolved during photosynthesis, which is confirmed by the findings in other studies [22,23]. Marine microbiota were also tested in a sediment-type photoMFC with a microbial anode and cathode [24]. Here, photosynthetic microorganisms in the overlying water layers produced oxygen for the cathodic oxygen reduction and organic matter, which could be utilized as carbon source at the anode in the anaerobic sediment, resulting in a self-maintained synergistic BES with light input and electricity output. Other than in the previous studies, light-dependent current generation was observed in this work, because the system was depending on photosynthetic oxygen production at the cathode.

**Synergism between plants and mixed heterotrophic bacteria in sediments (d)**
Plants are known to release organics into soil or aquatic sediments as rhizodeposits, which comprise of carbohydrates, fatty acids, amino acids, hormones, and other organic compounds. Rhizodeposits can account for up to 40% of the plants’ photosynthetic productivity [25*] and can be a significant fuel source for electricity generation in sediment-type photoMFCs (heterotrophic-plant *in situ* photoMFC — Figure 1d). Researchers adopted reed mannagrass (*Glyceria maxima*) as a model plant in photoMFCs and achieved a maximum power output of 67 mW/m$^2$ [25*]. Two independent research groups have studied rice plants in photoMFCs with the idea to reap energy from ubiquitous rice paddy fields [26*,27*]. Both studies operated their phototrophic MFCs for thousands of hours and showed a direct correlation between photosynthetic activity and power output (increased rhizodeposit = fuel production during photosynthetic phases).
During the first study, the excretion of organic compounds by roots was stimulated by subsequent rapid removal of these compounds through anodic oxidation. These workers also found that the presence of actively growing rice plants increased the power output sevenfold (compared to a MFC without plants) [26*]. Therefore, the addition of plants is an elegant way to increase the organic substrate in the anoxic sediment, which is often limiting the power output of sediment-type MFCs [23]. A maximum power generation of 33 mW/m² was obtained from this photoMFC. During the second study, organic exudates from roots in the light and dark were analyzed and compared to show that plant photosynthesis was coupled to microbial conversion of rhizodeposits into electricity [27*]. One of the key factors to improve power output from these in situ photoMFCs is to understand the detailed role of plants in electricity generation and their interaction with microbes. The European Union currently funds an international research initiative entitled ‘PlantPower’ (www.plantpower.eu) with the hope that full-scale systems can provide green energy one day.

**Ex situ photosynthesis coupled with mixed heterotrophic bacteria at a dark anode (e)**

Alternatively, externally generated biomass formed through photosynthetic growth can be fed to a heterotrophic MFC to generate electricity (heterotrophic ex situ photoMFC — Figure 1e). Algae have been successfully used as the anodic fuel in MFCs for electricity production [28,29]. These ex situ photoMFC systems require separated photobioreactors for optimal algal growth (no shading by electrode material) and less-complicated dark MFC systems for optimal electricity generation. During the first study, dried algae powder was successfully fed to a MFC [28]. During the second study, the separated photobioreactor and MFC were connected in series. It is important to note the limitations of feeding a complex organic matter (i.e. algae cells) to a mixed heterotrophic bacterial community in a MFCs because coulombic efficiencies are very low (2.8% [29]). A more attractive system may be a photobioreactor with immobilized cyanobacteria to generate easy-to-degrade metabolic products in series with a dark MFC to increase the coulombic efficiency of the BES because, for instance, carboxylic acids achieve much higher efficiencies than complex materials [30].

**Direct electron transfer between photosynthetic bacteria and electrodes (f)**

It remains to be shown if direct electron transfer (DET) between a photosynthetic microorganism and the electrode is possible (DET photoMFC — Figure 1f; without artificial redox mediators, electrocatalytic electrode, or heterotrophic bacteria). Thus far, publications in which DET was identified at the anode also included electrocatalysts [31,32], such as platinum or polyaniline, which are catalytically active toward hydrogen that is produced by these photosynthetic microorganisms. On the other hand, independent from a BES, potentially conductive microbial nanowires have been described for the cyanobacterium *Synechocystis* sp. PCC 6803 [33], suggesting that direct electronic interaction of this organism with an electrode is feasible. Even more excitingly, Cao *et al*. [4*] have shown bicarbonate reduction with light in a photo-biocathode as a DET process because these autotrophic microbes (no organic material was present) did not generate oxygen, electrocatalysts were absent, and flushing the cathode to wash away soluble redox mediators did not disrupt a satisfying electric current. This anoxygenic photosynthetic process would use carbon dioxide as the electron acceptor with the cathode as the electron donor, which may be mimicking iron(II)-mineral oxidation as described for photoautotrophic bacteria [34]. Cao *et al*. did, however, use an undefined mixed culture as inoculum, which guaranteed the presence of other autotrophic bacteria that may have played a role. Further research is therefore, required to verify DET with a photosynthetic bacterial pure culture.

We anticipate to read future research reports that observe small current peaks that coincide with the dark/light cycle; however, the effect of small environmental changes, such as oxygen absence/presence, pH changes, microbial community dynamics [35], and conductivity changes [36], on electric current generation in MFCs will be hard to differentiate from DET. Another possible signal, which may be interpreted as DET, originates from light-sensitive and electrochemically active mediators, such as certain quinones, which will show an increased electrochemical signal upon illumination with sunlight [37,38]. Thus, all these confounding possibilities must be taken into consideration and eliminated before a general acceptance will emerge that photosynthetic bacteria could transfer electrons directly to or from the anode and cathode.

**Photosynthesis at the cathode to provide oxygen (g)**

Photosynthetic oxygen generation can be performed *in situ* [1,39] or *ex situ* by recirculating the solution from the photobioreactor into the cathode of the photoMFC [3**] with the goal to provide the terminal electron acceptor oxygen without aeration. This concept has been considered very early on in the development of BESs [1] (oxygen-providing photoMFC — Figure 1g). These authors operated a photoMFC that provided the oxygen at the cathode by marine algae. In more recent work, Powell *et al*. [39] grew the algal species *Chlorella vulgaris* at the cathode and claimed mediated electron transfer with the electrode because an artificial mediator was added. We believe, however, that it cannot be ruled out that oxygen played a more important role; the artificial redox mediator may have transferred electrons directly from the noncatalytic cathode to the photosynthetically produced oxygen (without a biocatalytic reaction step). In a very
recent study, the in situ oxygen generation in a photoMFC with an undefined mixed culture was used to reverse the anode and cathode during dark and light cycles, respectively [40]. Small amounts of photosynthetic oxygen at the anode may even be beneficial for heterotrophic current generation because of advantageous energetic profiles under micro-aerobic conditions [41]. Finally, we already mentioned (in ‘Synergism between phototrophic microorganisms and mixed heterotrophic bacteria in sediments (c) section) that oxygen generation by photosynthetic bacteria during the light cycle may be advantageous at the cathode on top of anaerobic sediment in regards to electric current generation in sediment-type MFCs.

Outlook
Over the last two or three years, we have seen a real renaissance in integrating photosynthesis with MFCs. The work was built on previous photoMFC research with either electrocatalytic or artificial mediator anodes. Recently, however, excreted organic matter or photosynthetic biomass were used as a feedstock for heterotrophic electrode-respiring bacteria at the anodes of MFCs. Notably, the sediment-based BESSs that can provide electric current in remote places from excreted organic matter or photosynthesis from cyanobacteria or plants seem promising because not much scale up is necessary to provide enough current to power environmental sensors. In addition, really exciting is a recent finding of possible DET in a photo-biocathode. If this is further verified to be correct, then a full photoMFC with, for example, the promising in situ hydrogen oxidation in the photo-anode and anoxic photosynthesis in the photo-biocathode becomes a real possibility.

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References and recommended reading
Papers of particular interest, published within the period of review, have been highlighted as:

- of special interest
- of outstanding interest

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