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Photonics and optoelectronics with bacteria: making materials from photosynthetic microorganisms

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A critical selection of the recent literature reports on the use of photosynthetic and photo-responsive bacteria as a source of materials for optoelectronics and photonic devices is discussed, together with the applications foreseen in solar energy conversion and storage and light information technologies. The use of both photoactive cellular components and entire living cells is reviewed, aiming to highlight the great conceptual impact of these studies. They point out possible deep changes in the paradigm of design and synthesis of materials and devices for optoelectronics. Although the possible technological impact of this technology is still hard to be predicted, these studies advance understanding of photonics of living organisms and developing new intriguing concepts in biomaterials research.

1. Introduction

Development of functional materials has been at the hearth of the progresses of organic photonics and optoelectronics over the last decades. The efforts to optimize devices for energy conversion and storage, sensing, information transmission and elaboration have led to design materials with very high

level of molecular sophistication to be precisely tailored for specific functions. As a common limitation, the production of these materials often requires complex chemical routes which are difficult to be up-scaled for industrial production. Requirements of advanced performances and large scale availability are presently driving the studies on molecular and supramolecular materials for new generation optoelectronics and photonic devices. In this frame, functional photoactive structures found in photosynthetic organisms can be envisaged as the most perfected materials, which have been optimized over billions of years of evolution to use light for specific functions including light collection and conversion for energy storage, elaboration of light signals for metabolic purposes, but also for motion and self-organization. Thus, photosynthetic structures have been seen as a source of inspiration to design molecular and supramolecular architectures for photonics and optoelectronics. On a different perspective, living photosynthetic organisms can be envisaged directly as sources of materials for photonic and optoelectronic devices. This approach represents a full change of the paradigm, shifting the materials production routes from the classical chemical synthesis to biotechnological protocols for extraction, purification and derivatization. The challenges of this approach are also very different, being mainly relevant to addressing the materials and improving their stability in the devices' operating conditions rather than to reducing the synthetic complexity and production costs. Particularly photosynthetic microorganisms, rather than plants,^[1] are interesting in the development of totally biotechnological approaches to optoelectronics and photonic materials. The research performed has mainly explored bacteria and unicellular algae,^[2] together with a few other classes of microorganisms, and it is so far still in its infancy. However, the results described by many groups make clear that the use of components,^[3] or of entire microorganisms,^[4] as the materials for devices can open groundbreaking directions in the future technologies of energy storage and collection and light-based communications.

A critical overview of the new concepts in this rapidly progressing research field is, in our opinion, extremely worthy and timely, especially to highlight the new biological perspective that these studies

are introducing in materials science and engineering, together with the new language which results from the unprecedented hybridization of device engineering, chemistry and microbiology.

Starting from these considerations, our review is not meant to give a complete overview of the wide literature on this subject, but rather to highlight the logic emerging from the progress in this field, together with the new language, the major challenges and possible impact. We discuss the subject focusing on bacteria, and particularly photosynthetic bacteria, as a key class of microorganisms representative of the manifold results and opportunities.

The review is organized in three sections. The first two present the use of photosynthetic bacteria as a source of materials in optoelectronic devices for energy conversion. In particular, the first section focuses on the use of isolated bacterial photoenzymes, the Reaction Centers, as the unitary efficiency photoconverters of all the photosynthetic organisms. The emphasis is on the challenges and opportunities of having the bacterial RC embedded as the active material on electrodes, improving stability, and designing proper interfaces for the charge transfer. In the second section, the studies on the use of the living bacteria as the active optoelectronic units are overviewed. This is a thoroughly new approach which poses unprecedented challenges. In fact, in this case, the biological entities are fed with nutrients (ideally only light and inorganic substrates) and their energy producing apparatus remains efficient as long as the bacteria remain alive. The main difficulty, here, is how to efficiently extract the produced energy to an external circuit in addition to the metabolic needs of the organisms. Starting from the concept of having photosynthetic bacteria as the photoconverters in optoelectronic devices, the third section enlarges the overview to the use of photosynthetic and non-photosynthetic bacteria as microstructures for photonics, this showing how the concept of using bacteria as photoactive materials can be general for many applications.

Overall, making optoelectronics and photonics with photosynthetic microorganisms emerges from this analysis as an intriguing field of investigation which may impact on technology of completely new classes of materials while, at the same time, will progress fundamental research and insight into biological and artificial photonics.

2. Photosynthetic enzymes for energy conversion

The problem of fulfilling the energetic needs for the diverse metabolic processes of the cells was solved by Nature capturing the virtually inexhaustible energy associated to solar radiation and converting it in energy-rich compounds in the process named photosynthesis.^[5] The concept of assembly artificial devices able to mimic photosynthesis for the sustainable generation of electrical power is presently widely investigated.^[6] In principle, three steps must be performed by a photosynthesis-mimicking device: light harvesting, charge separation and feeding of the charges into an external electrical circuit. Supramolecular chemistry made big progresses in mimicking these functions, but the performances of the natural enzymes are yet largely unmatched. Along with a totally synthetic approach, in which the principles of photosynthesis serve only as inspiration, *e. g.* the Dye Sensitized Solar Cells (DSSCs)^[7] introduced by Graetzel, the last decade has witnessed an explosion of research aimed at directly exploiting the photosynthetic isolated enzymes, fragments or entire microorganisms for power generation. Several reviews have summarized the progresses in this field dealing with specific classes of enzymes^[8] or particular aspects of cell construction.^[9] In this section of the review we will present an overview of the different cell typologies that have been recently used, and focusing on the latest, more intriguing and unconventional directions that this research field has developed and may strengthen in the near future.

2.1. General working principles of biophotovoltaic cells

In its highest simplified form, a biophotovoltaic (BPE) cell is composed by a two- or three-electrode system (see **Figure 1**) in which a light-induced redox reaction is catalyzed by a photoactive enzyme, typically the photosynthetic reaction center (RC).

The photosynthetic RC is a membrane-spanning enzyme that represents the photochemical core of any photosynthetic organism. The structural motifs of this photochemical core are rather similar in all the classes of photosynthetic organisms, but the complexity of the entire enzyme increases moving from the anoxygenic photosynthetic bacteria, the most ancient photosynthetic species living on Earth, and the oxygenic organisms like cyanobacteria, algae, higher and lower plants.^[10] The purple non-

sulphur photosynthetic bacteria *Rhodobacter (R.) sphaeroides* possess one of the simplest RCs in Nature that has been widely used as a model for understanding the molecular mechanisms of photosynthesis. This photoenzyme, described in details elsewhere,^[11] converts the excitation energy associated to light into an intra-protein hole-electron couple in which the opposite charges, generated by the absorption of a photon and moved apart by a cascade of electron transfer reactions, sit on the oxidized electron donor (D^+ , with midpoint potential (E_m) \approx 450 mV) and on the reduced electron acceptor (Q^- , $E_m \approx$ 0 mV) located roughly 3 nm apart within the protein scaffold. In isolated enzymes, the lifetime of the hole-electron couple varies from 100 ns to 1 second, according to specific structural condition of the protein. The potential difference of \sim 0.5 V is the maximum open circuit voltage (OCV) achievable under illumination by a device based on this protein. In the more complex photosystem I (PSI) reaction center found in plants, algae and cyanobacteria,^[12] light absorption generates a charge separated state as well, between the primary donor P700 ($E_m \approx$ 500 mV) and an iron-sulfur center F_B ($E_m \approx$ -600 mV) with a lifetime of 60 ns. The PSI charge separated state achieves a potential difference of 1.1 V and can catalyze the reduction of NADP to NADPH and the reduction of protons to H_2 at pH 7.^[13] In photosystem II (PSII), also found in plants, algae and cyanobacteria^[14] and functioning cooperatively with PSI, light absorption generates a charge separated state between the primary donor P680 ($E_m \approx$ 1200 mV) and a quinone acceptor (Q^- , $E_m \approx$ 0 mV). The extremely high E_m of the PSII primary donor, arising from the unique property that this protein,^[15] triggers the process of water splitting taking place in the specialized PSII subunit called oxygen evolving complex (OEC). Such high performance, however, has the drawback of a marked protein instability,^[16] hence PSII utilization can be conceived only for application that do not require long term stability, like in biosensing.^[17] Alternative approaches require more stable forms of the enzyme such as those isolated from extremophile organisms^[18] or even those produced by genetic engineering.

The light-induced redox reaction catalyzed by the RC displaces the BPE cell from its dark open circuit voltage (V_{OC}) resulting in the production of a photocurrent. The performance of the BPE is measured by the value of the short-circuit current density (J_{SC}) and of the V_{OC} achievable under illumination. The RC can be either embedded in its intact organism (see the section **Optoelectronics with living photosynthetic bacteria**) or isolated in more or less pure form. The isolated RC can be dispersed in the solution together with electrochemical mediators,^[19] but in most cases is immobilized on the working electrode (WE) that acts as a biophotocathode or biophotoanode depending on the direction of electron flow under illumination. The electrochemical mediators can be still present to facilitate electron wiring between the RC and the electrode, but there are examples of direct electron transfer (DET) systems.^[20] Generally, a liquid electrolytic solution ensures the electric contact between the electrodes, but examples of solid-state devices are present as well.^[21]

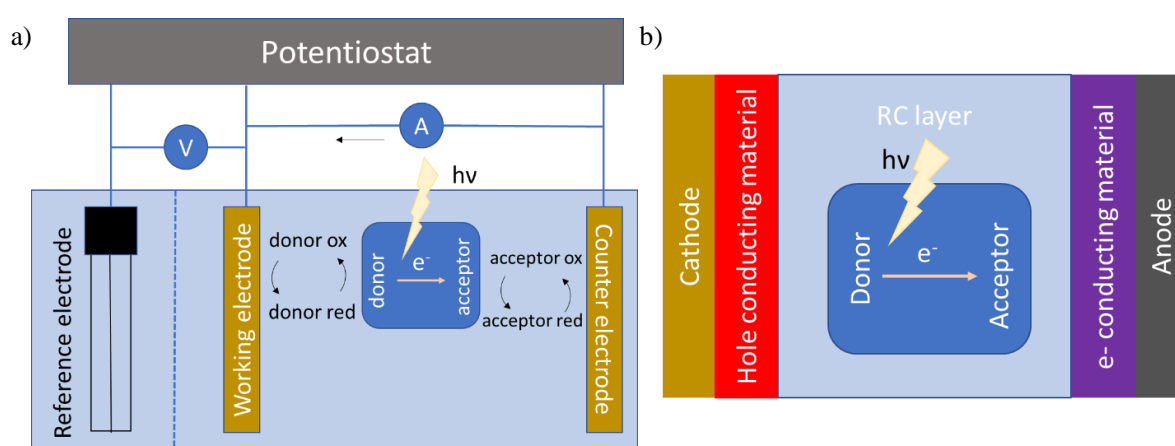


Figure 1. (a) Schematic representation of a three-electrode BPE cell in which RCs – represented as a cyan box formed by an electron donor and an electron acceptor – are solubilized in the electrolytic solution with redox mediator. In the specific case the WE acts as a cathode, but the opposite electron flow is possible. Very frequently the RC is immobilized on the WE. (b) Schematic representation of a solid state-two electrode BPE in which the electron flow is driven by the intrinsic material properties.

The geometry of BPE cells can be divided in two main categories: three or two electrodes cell.^[22] In the three electrodes configuration, sketched in **Figure 1a**, a potentiostat imposes a constant potential difference between the working electrode and the reference electrode (RE) while recording the current between the WE and the counter electrode (CE). The potential difference between the WE and the

CE is neither controlled or monitored, so this configuration is very useful for the characterization of the biohybrid WE but gives little information about the BPE as a whole.^[23] Moreover, the direction of the current can be controlled by applying a bias potential to the WE. For example, using solution dispersed RC in the presence of cyt c and ubiquinone-0 (UQ₀) as electrochemical mediators and gold WE a cathodic photocurrent is obtained with a bias potential of -0.1 V vs Ag/AgCl and an anodic one is obtained at + 0.1 V.^[19a] In the two-electrode configuration, summarized in **Figure 1b**, the reference electrode is missing and the potential of the electrodes is not controlled. Since usually no potential difference is applied between the two electrodes, the voltage and the current flowing in the cell are intrinsic properties of the materials used, hence the optimization of the energy levels of the various components is a key step in the device fabrication.^[24]

2.2. Wiring electrons from the RC protein to the electrodes

One of the simplest ways to build a BPE is to bind the RC to the WE of a classical three electrode cell using a salt as the support electrolyte. The mechanism of electron injection from RC to the WE in this case is the so-called direct electron transfer (DET) involving either the reduction of D⁺ or oxidation of Q⁻ by the electrode without the use of mediators. Such approach, however, proved to be very limited. Binding engineered RC on a gold electrode and using UQ₀ as the sole mediator, small cathodic photocurrents could be observed in the nA range.^[25] However, upon addition of the redox protein cytochrome c, that mediates the ET between the RC and the WE, a 40-fold current increase was observed.^[26]

Efforts to attain higher photocurrents without the use of mediators have been demonstrated more useful for theoretical studies or biosensing applications than for power generation. For example, small photocurrents (0.5 $\mu\text{A}/\text{cm}^2$) but with sufficient signal to noise ratio were obtained in a mediatorless system in which RC are bound to the gold surface of a screen printed electrode through the laser induced forward transfer (LIFT).^[20a] This technique enables a tight contact between the deposited material and the target surface as demonstrated earlier for thylakoids.^[27] Thanks to the absence of any quinone electron carrier the sensitivity of the sensor device for the herbicide terbutryn was very high

with a detection limit of 8 nM.^[20a] DET was also observed with the photosystem II (PSII) of oxygenic microorganisms, a photoenzyme that functions on the same principle of the RC but has a more elaborated function and which is able to oxidize water to molecular oxygen. PSII physically adsorbed as a monolayer onto a gold electrode modified with a conductive layer of poly-mercapto-p-benzoquinone (polySBQ) produces anodic photocurrents in the nA range without the addition of any mediator, indicating that the polySBQ layer drains electrons directly from the photoenzyme; the electrode activity was inhibited by the herbicide DCMU detectable down to 0.7 nM.^[28] PSII has been also employed in a three electrode cell in which the PSII-modified electrode acted as a photoanode for the light-induced oxidation of H₂O to O₂, and a bilirubin oxidase/carbon nanotubes (BOD/CNTs)-functionalized electrode acted as a cathode for the reduction of O₂ to H₂O,^[29] with no need of a diffusional mediator to generate steady-state currents. In this device, a gold surface is modified with mercapto benzoquinone that both binds the PSII through quinone plugging into a specific pocket of the protein and acts as electron mediator. The photocurrent generated by the system remained constant for a time-interval of 3 h irradiation degrading by 15% after 10 h.

Also electrode surface covering with functional SAM for covalent and oriented deposition of RC was criticized in some works, pointing out that the low electron conductance of the organic layer separating the electrode and the protein is detrimental for overall device efficiency.^[30] In fact, the comparison of photocurrents obtained with RC adhered to bare gold surfaces versus SAM functionalized surfaces evidenced that the former configuration was more effective both for RC^[31] and for the complex formed by the RC and its associated light harvesting proteins, the so-called RC-LHI complexes.^[19a] The adhesion of RC to bare gold was shown to be very effective^[31] likely via the bonding with a surface exposed cysteine. Isolated RC-LHI supercomplexes were deposited onto bare gold surface using the Langmuir Blodgett (LB) technique, obtaining an oriented monolayer of RC-LHI via forward dipping. In the presence of cyt c and UQ₀, this electrode produces photocurrents of 40 $\mu\text{A}/\text{cm}^2$ upon 23 mW/cm^2 illumination at 880 nm.^[32]

2.3 Optimizing the intrinsic RC protein functioning

Optimization of the intrinsic functioning of the photoactive protein can improve the BPE performances. It is well-known that the charge separated state lifetime of detergent-solubilized RC is shorter than that of RC in their phospholipid based membrane environment,^[33] with an important role played by the negatively charged phosphatidylglycerol (PG). On these basis, RC-LHI complexes were incorporated in PG vesicles and the resulting solution was placed on a modified NH₂-ITO to form a planar membrane via spontaneous vesicle adsorption and fusion on the electrode.^[34] Photocurrents measured using ubiquinone-0 (UQ₀) and cyt c as mediators were higher in PG vesicles-reconstituted RC-LHI compared to both phosphatidylcholine (PC) (zwitterionic) vesicles and detergent. It is known that negatively charged phospholipids, as PG, significantly enhances the yield of charge separation by stabilizing the charge-separated state under a low level of irradiation.^[35] Moreover, like the membrane matrix, PG increases the fraction of functioning LHI-RC complexes resulting from their preferred orientation and electrical contact with the electrode.

2.4 Increasing the RCs loading on electrode surface

The use of protein monolayer films, even if properly oriented and connected to the electrode, limits the device performance due to the low absorbance cross section, and hence to the small amount of photons that can be collected. An obvious way to overcome this limitation is increasing the RC amount close to the electrode. To this aim, tailored wormlike mesoporous WO₃-TiO₂ films were developed, capable to entrap high amounts of RCs and at the same time to split the RC photoinduced electron hole pairs more efficiently than single TiO₂ or WO₃. In the presence of dithionite, the measured anodic photocurrents reached 25-30 $\mu\text{A}/\text{cm}^2$ illuminating with 5 mW/cm^2 white light.^[36] Electron transfer from RC to TiO₂ is possible since in the presence of dithionite both RC quinone acceptors are chemically reduced and illumination produces the triplet state ${}^1\text{P}^+\text{BPhe}^-$ with $E_m \approx -400$ mV, lower than the TiO₂ flat band potential of -340 mV.^[37]

Analogously, PSI-based devices were built by air drying surfactant stabilized PSI molecules on mesoscopic, high-surface area semiconducting electrodes (TiO₂ nanocrystals and ZnO nanowires) and completing the circuits by a Co(II)/Co(III) electrolyte and platinized glass as is common for conventional DSSCs.^[38] Without any further optimization, these devices achieved electrical power outputs of up to 81 $\mu\text{W}/\text{cm}^2$, V_{OC} up to 0.5 V and J_{SC} up to 362 $\mu\text{A}/\text{cm}^2$ when illuminated with a solar simulator. In this case, injection of electrons into the TiO₂ layer from the electron acceptor F_B is possible thanks to its redox potential -600 mV.

Another example of enhanced loading of RC onto the electrode has been studied more recently,^[39] using a diamond surface functionalized with polymer brushes composed of poly(tert-butyl methyl acrylate) (PtBuMA). This polymer offers carboxyl groups to bind aminomethyl-ferrocene (AMF) or cyt-c via amide bonds used as electron donors to the RC primary electron donor D. Finally, RC are bound to the modified electrode via simple physisorption. Cathodic photocurrents of 0.2 and 0.3 $\mu\text{A}/\text{cm}^2$ were detected in the case of AMF and cyt c respectively in a three-electrode cell containing also UQ₀ as electron carrier.

Further examples of enhanced protein loading are given also in the next section.

2.5. Two electrodes and solid-state devices

A two electrode liquid state cell was built using a simple procedure in which a mixture of protein and the redox mediator *N,N,N',N'*-tetramethyl-p-phenylenediamine (TMPD) was injected into a 10 μL cavity formed between a fluorine-doped tin oxide (FTO) glass front electrode and a Pt-coated rear electrode.^[40] The authors argued that the RC binds specifically to the FTO based on higher hydrophilicity on this surface and that TMPD acts as mobile electron carrier between the quinones and the Pt counter electrode. In this case the vacuum potentials of the two electrodes are -4.4 eV for FTO and -5.7 eV for Pt. The electrons are hence forced to travel from Pt to FTO in the external circuit thanks to the continuous feeding of electrons to the Pt by the photochemical reactions of RC. The vacuum potentials of the electrodes explain also the transient reverse currents observed upon

switching off the light: electrons are donated by the over-reduced RC cofactors to the FTO electrode, and the TMPD^+ pool is reduced by the Pt electrode.

A further evolution of the two electrode cell was introduced using a so-called tandem cell.^[41] This configuration was used to take advantage of the complementary absorption spectra of two mutants of RC-LHI complexes, one incorporating the native red carotenoid ($\text{RC-LHI}_{\text{red}}$) and the other incorporating green carotenoids ($\text{RC-LHI}_{\text{green}}$). Each subcell was constructed by connecting front FTO glass and rear poly(3,4-ethylenedioxythiophene): polystyrene sulfonate (PEDOT:PSS) transparent electrodes with a 50 μm thick U-shaped thermoplastic spacer. The RC-LHI complexes were inserted inside the spacer together with the mediators TMPD and UQ_0 . Each subcell using the PEDOT:PSS rear electrode produced larger photocurrents than the corresponding one using Pt electrode, thanks to the smaller potential drop for the electron transfer from Q_0 , due to the smaller vacuum potential of PEDOT:PSS (5.0 eV) versus Pt (5.7 eV), as shown in **Figure 2a**. When the two subcell were connected in parallel (**Figure 2b**), photocurrent density of about 10 $\mu\text{A}/\text{cm}^2$ were detected using 100 mW/cm^2 illumination (1 sun).

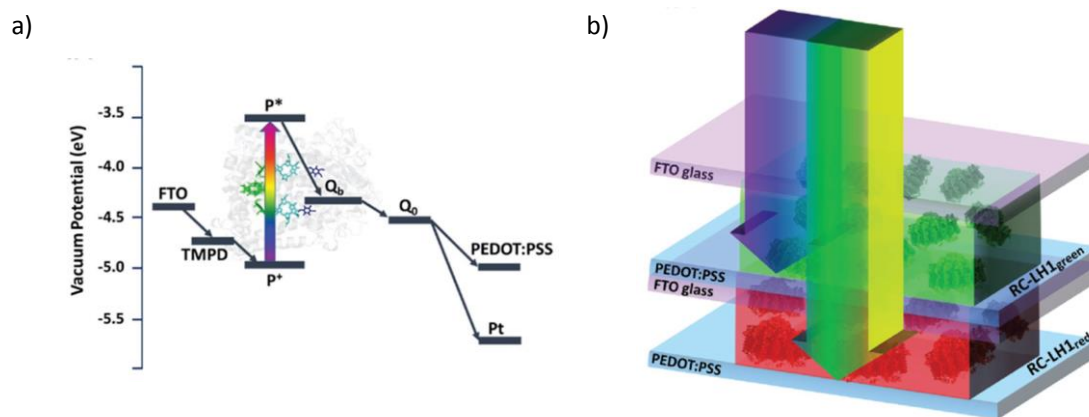


Figure 2. a) Energetic scheme of an RC based BPE cell in which RC-LHI is in close contact with the electrodes FTO and PEDOT:PSS in the presence of TMPD and UQ_0 mediators and b) its tandem configuration using native red and mutant green antennas. Reproduced with permission.^[41] Copyright 2017, Wiley.

A two electrode solid state cell featuring a series of technical improvements was built recently, using the spin coating technique and a mechanoresponsive phase-changing electrolyte.^[42] A layer of RC-LHI was deposited on a FTO electrode, followed by a series of LHI multilayers. The electrolyte was based on succinonitrile, a polar organic plastic crystalline material that can provide a nonconducting matrix for a conducting salt. This matrix was suffused by an equimolar mixture of 5-mercapto-1-methyltetrazole (T^-) and di-5-(1-methyltetrazole) disulfide (T_2) producing a plastic gel-phase material with a high ionic and molecular diffusivity. Remarkably, this material undergoes a reversible gel-to-liquid transition under mechanical vibration without the need of heating. This sonication-liquified electron carrier was applied to the protein multilayers letting it to permeate among them. After the subsequent solidification of the electrolyte, the Ti counter electrode was placed on the gel surface and the cell sealed with epoxy resin. Upon illumination, anodic photocurrents with intensity up to the record figure of $860 \mu\text{A}/\text{cm}^2$ were observed thanks to the optimal charge conduction enabled by a high concentration of permeating gel phase electrolyte, overcoming commonly observed diffusive restrictions. Last but not least, the RC-LHI complex showed enhanced long-term stability thanks to the conductive gel coating since after 28 d at room temperature and a continuous ambient illumination the photocurrent showed a 27% decrease.

Solid state examples of PSI-based biophotovoltaic devices are also present in literature. In one of the first reports, a monolayer of PSI was applied on titanium suboxide (modified with a dihydroxyacetone phosphate SAM) and then covered by a hole-conducting polytriarylamine polymer (PTAA) and MoO_3/Al as the top electrode. PSI was found mainly oriented with the acceptor side towards the metal oxide surface. Upon illumination with a solar simulator, the measured V_{OC} of 0.76 V was remarkably close to the maximum achievable with PSI, but the $J_{\text{sc}} = 0.29 \mu\text{A}\cdot\text{cm}^{-2}$ was low.^[43] Subsequently, a 3D PSI protein network was entrapped onto the TiO_2 anode by electropolymerization of aniline in the presence of solubilized PSI; an evaporated silver cathode completed the device. Enhanced J_{SC} up to $72 \mu\text{A}\cdot\text{cm}^{-2}$ were obtained, with a V_{OC} of 0.3 V.^[44] Further improvement has been recently obtained by optimization of the energetic band alignment between semiconductors and PSI for an efficient

charge transfer from protein to electrodes and using nearly 100 layers of PSI complexes. In particular, as depicted in **Figure 3**, LiF/Al was used as anode since its energy level lays below that of the F_B of PSI while PEDOT:PSS layered onto ITO was used as cathode since its energy level is relatively close to that of $P700^+$; therefore, holes transfer through the PEDOT:PSS layer to the ITO electrode. The resulting device produced J_{SC} close to $1 \text{ mA}\cdot\text{cm}^{-2}$ with a V_{OC} of 0.25 V under a solar simulator illumination.^[45]

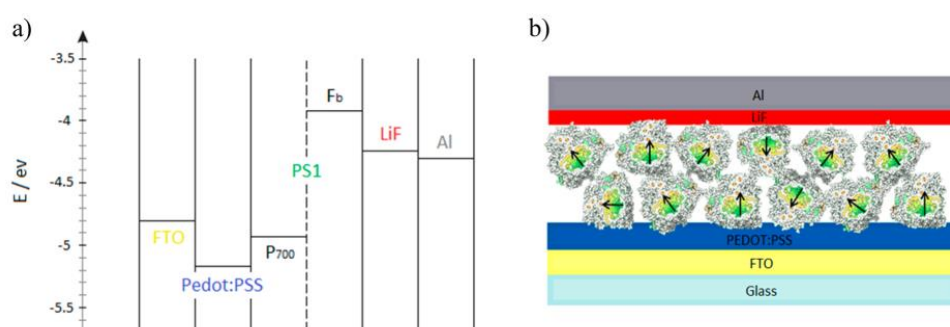


Figure 3. a) Energetic scheme of a PSI based BPE cell in which 100 layers of PSI are sandwiched between an FTO/PEDOT:PSS cathode and an LiF/Al anode and b) its schematic representation evidencing the random orientation of the PSI complexes. Reproduced with permission.^[45] Copyright 2017, American Chemical Society.

The concept of using multilayers of PSI to increase the absorption of light derives from the observation that in bulk heterojunction organic solar cells process, the performance improves increasing the interfacial area for the charge separation in spite of increasing recombination rate of free charge carriers. Very recently this concept has guided the fabrication of a biophotovoltaic device by attaching onto a gold electrode a series of oriented PSI multilayers obtained by cross-linking free amine residues located on the surface of PSI monolayer to thiols located at the oxidizing side of successive PSI cysteine mutants. The device was completed by topping the multilayers with a carboxyfullerene with very good electron accepting properties. With four layers of PSI, a V_{OC} of 0.43 V was obtained under nitrogen atmosphere and illuminating with a 40 mW laser emitting at 680 nm.^[46]

2.6 Plasmonic light collection enhancement

RC-based photovoltaic devices have been also built using the concept of plasmonic enhanced light absorption borrowed from the field of classical silicon-based photovoltaic panels. Photovoltaic absorbers must be 'optically thick' (180–300 μm) to allow near-complete light absorption but such high thickness is detrimental for device performance because the photocarriers collection is strongly diminished.^[47] Plasmonic materials (nanostructured noble metal systems in which incident electromagnetic radiation is coupled with collective oscillations of surface electrons) can help reducing the physical thickness of the photovoltaic absorber layers acting as sub-wavelength scattering elements trapping the freely propagating plane waves coming from the Sun into an absorbing semiconductor thin film. Additionally, metallic nanoparticles can be used as sub-wavelength antennas in which the plasmonic near-field is coupled to the semiconductor, increasing its effective absorption cross-section. These concepts have been adopted in the field of RC-based PEC by adsorption of RC-LHI complexes on nanostructured rough silver (RS), a large surface area material used for surface enhanced Raman spectroscopy (SERS). Such biohybrid photocathode was used in a three electrode cell using cyt c and UQ₀ as electrochemical mediators, yielding photocurrents of 166 $\mu\text{A cm}^{-2}$ under illumination with a solar simulator.^[48] Likewise, PSI was immobilized on plasmonic metal structures constituted by Fischer patterns of silver nanopramids (Ag-NP). The plasmonic peaks of Ag-NP were then tuned to match the PSI absorption peaks at ~ 450 and ~ 680 nm obtaining plasmon-enhanced photocurrents ~ 6.5 and ~ 5.8 fold higher as compared to PSI assembly on planar Ag substrates for nominal excitation wavelengths of 660 and 470 nm, respectively.^[49]

Plasmonic enhancement of fluorescence emission from light-harvesting complexes of bacteria^[50] and for PSI from chloroplasts^[51] via coupling between the plasmon band of a metal nanoparticle and a spectroscopic transition in the biomolecule have been observed as well. Symmetrically, changes in the extinction of metal nanostructures are measured after the attachment of LHC due to strong coupling to their excited states. In particular, surface plasmon resonances (LSPR) of gold nanostructures in macroscopically extended, periodic arrays are found strongly coupled to excitons

in the pigment molecules in LHC 1 and 2 from *R. sphaeroides*, leading to a substantial splitting of the plasmon band and the observation of significant changes in the nanostructure extinction spectrum.^[52]

2.7 Further RC applications

As already mentioned, the electron acceptor F_B of PSI has a redox potential low enough to drive the H_2 production at pH 7. This feature has been exploited by realizing a covalent link between F_B and an Au or Pt nanoparticle via a molecular wire that enables electron transfer and subsequent hydrogen production.^[53] This was possible thanks to a variant of the PsaC subunit that lacks a native cysteine ligand on the F_B cluster at a solvent exposed position. This enabled the use of a dithiolated molecules to bind the nanoparticle at one end and the F_B at the other end. The resulting bioconjugate was able to produce H_2 upon illumination at a rate of $50 \mu\text{mol } H_2 \text{ mg Chl}^{-1} \text{ h}^{-1}$, using reduced cyt c_6 as electron donor to $P700^+$.

A similar biohybrid, in which a gold nanoparticle was anchored to the PSI through a molecular wire ending with a naphthoquinone plugging in the quinone pocket, has been employed to photo-activate a field effect transistor (FET) depicted in **Figure 4**.^[54] The light irradiation induced a marked change in the voltage between the gate and the source (V_{GS}) from -3.3 V to -5.4 V when the current between the drain and the source (I_{DS}) was below $1 \mu\text{A}$. Light intensity affected the magnitude of V_{GS} , thus indicating the potential use of this system for imaging applications

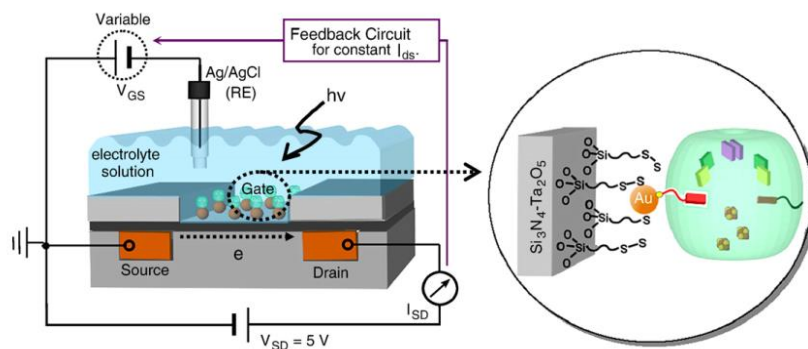


Figure 4. Schematic representation of a field effect transistor photo-activated by a PSI layer anchored onto the gate electrode. Reproduced with permission.^[54] Copyright 2007, Elsevier.

In a very recent publication,^[55] RC/LHI complexes were exploited in a device assembled from a flexible top electrode (indium tin oxide coated polyethylene terephthalate film (ITO-PET)) a blend of photosynthetic protein and UQ₀ in a gel matrix formed from succinonitrile (SCN) and water, and a flexible base electrode comprising a gold-coated PET film. This architecture conferred to the device a triple function under illumination (touch sensing, depicted in **Figure 5**, UV-detection, and nanopower generation) paving the way for possible applications like artificial skins and wearable sensors capable of remote data transmission.

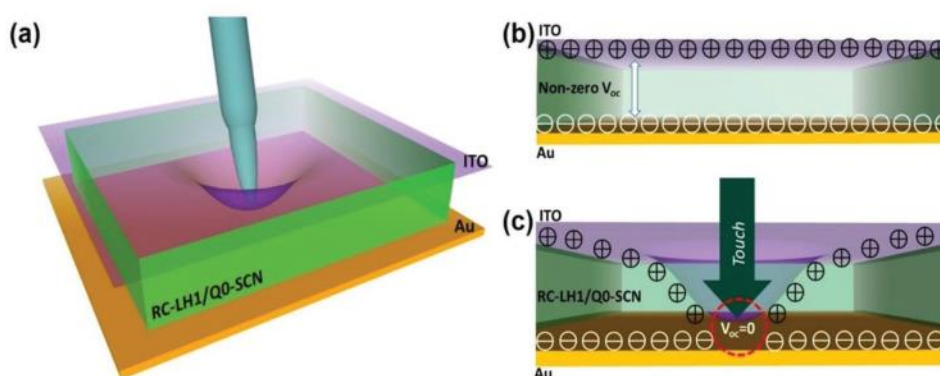


Figure 5. Schematic representation of a RC-based touch sensing device. a) deformation of the top electrode and the protein/Q0-SCN blend. b) Illumination of the blend gives rise to a V_{oc} between the PET-ITO and PET-Au electrodes. c) An applied pressure that brings the electrodes into contact suppresses the V_{oc} giving rise to a signal. Reproduced with permission.^[55] Copyright 2018, Wiley.

This literature survey shows that, from the first attempts of combining photoenzymes with electrodes, aimed to unveil the mechanisms of electron transfer between protein-buried redox centers and electrode surface, many progresses have been made in terms of device durability and photocurrent output. When continuously illuminated with intense light, RCs undergo denaturation mainly because of singlet oxygen sensitization and localized heating. The stability has been found to increase by removing oxygen from the environment and by accurately sealing the device,^[56] by using membrane-mimicking environments,^[34] or by adding specific detergent peptides. In this latter case a remarkable long-term PSI stability up to 280 days in dry state at room temperature have been achieved.^[57] Concerning the photocurrent output, the major breakthroughs have been obtained increasing the amount of active protein onto the electrode surface by using multilayers,^[46] using 3D protein

network^[44] or using high surface area electrodes.^[38] To date the obtainable photocurrents are in the mA/cm² range.^[45] Other factors can also contribute to the optimization of power output, like proper choice of electrode material and redox mediators, further enhancement of photon collection by exploiting the plasmonic effect and/or by decorating the proteins with synthetic antennas and genetic manipulations to modulate the E_m of protein redox centers.

3. Optoelectronics with living photosynthetic bacteria

3.1. General working principles of Microbial Fuel Cells

A great variety of living microorganisms has been investigated so far for their ability to generate bioelectricity through biocatalytic reactions in devices known as microbial fuel cells (MFCs, **Figure 6A**).^[4b] The class of devices converting the sunlight into electrical power by means of oxygenic and anoxygenic photosynthetic microorganisms are defined as photosynthetic MFCs (photo-MFCs, **Figure 6B-D**).^[4a, 58] According to a classification proposed by McCormick^[4c, 59] and used by other authors^[60] photo-MFCs can be further classified as photo-MFCs based on anoxygenic microorganisms (**Figure 6B**), complex photo-MFCs using a combination of photosynthetic and heterotrophic microorganisms (**Figure 6C**), biophotovoltaic systems using only oxygenic photosynthetic organisms or their components (BPVs, **Figure 6D**).^[4c]

With regard to the devices' working principle, in MFCs, heterotrophic microorganisms placed at the anode catalyze an oxidation process of organic substrates releasing both electrons and protons to the cathode, which are respectively conveyed to the external circuit and to an inner proton exchange membrane (PEM) placed between electrodes. Then, electrons and protons react with molecular oxygen at the cathode eventually producing water (**Figure 6A**). The potential difference between the anodic and cathodic reactions drives the current production. Photo-MFCs use phototrophic anoxygenic bacteria, typically Purple Non-Sulfur (PNS) bacteria, to generate electricity under anaerobic and light-dependent conditions. These bacteria require an exogenous supply of organic/inorganic reducing nutrients and can avail of a variety of carbon sources. The working

principle of complex photo-MFCs is similar to that of MFCs, with the exception that organic carbon is provided by photosynthetic microorganisms to heterotrophic microorganisms at the anode. Complex photo-MFCs typically require moderately limited maintenance but are challenging to be optimized and replicated experimentally. The progresses on photo-MFCs based on anoxygenic phototrophic bacteria^[60a] and on complex photo-MFCs^[4a, 4c, 61] have been recently reviewed and, for this reason, will be not reported herein.

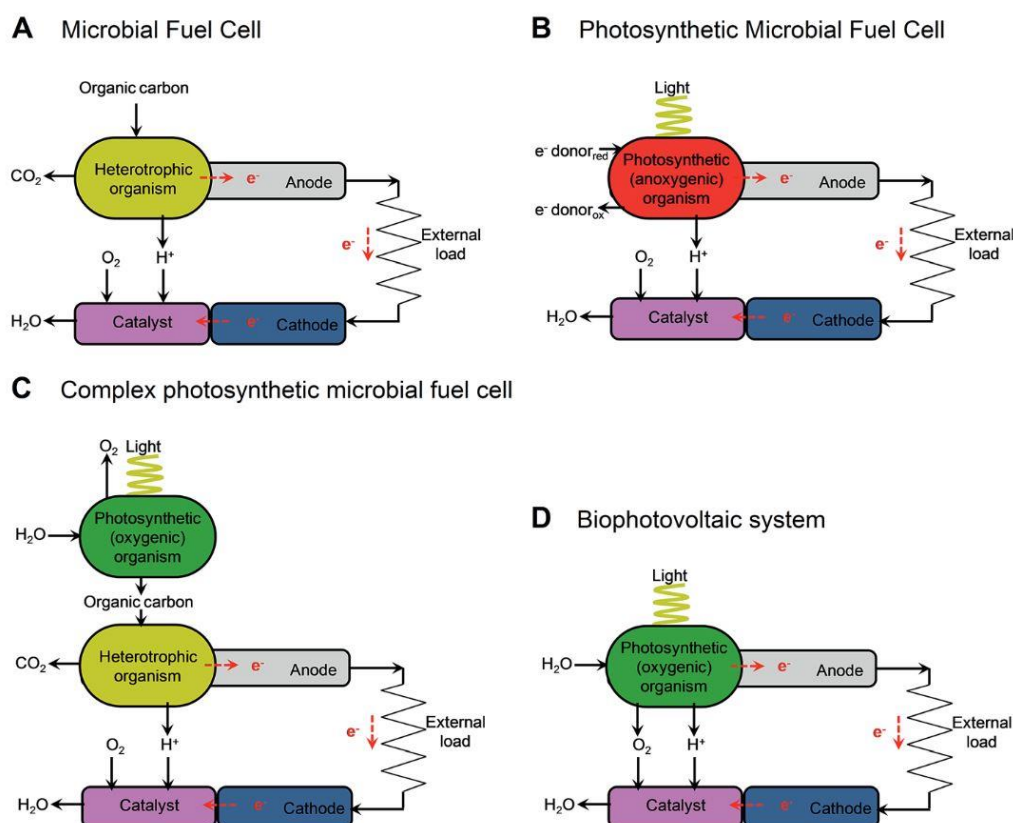


Figure 6. Working principle of (A) microbial fuel cells (MFCs), (B) photosynthetic microbial fuel cells (photo-MFCs), (C) complex photo-MFCs and (D) biophotovoltaic systems (BPVs). In all archetypes, a catalyst bound to the cathode facilitates the terminal electron acceptor reaction (e.g. $O_2 + 2H^+/H_2O$). Reproduced with permission.^[4c] Copyright 2015, the Royal Society of Chemistry.

A relevant advantage of BPVs, based on oxygenic photosynthetic microorganisms, versus other MFCs consists in the possibility to generate electrical power through photolysis of water, in the absence of exogenous supply of organic nutrients and with concomitant removal of CO_2 from the external environment.^[4c, 62] Besides working upon light illumination, BPVs can also generate current

in the dark since oxygenic photosynthetic microorganisms can oxidize their internal carbon storage produced by photosynthesis providing electrons to the external circuit, contrary to other photovoltaic systems (inorganic, organic and bio-hybrid based on isolated photoactive enzymes) which are driven solely by light. BPV technology is also promising since catalytic microbes, besides being self-sustainable and able to produce current in the whole circadian cycle, *i.e.* during both daylight and night, are relatively inexpensive to culture and able to assemble and self-repair in diverse environmental conditions.^[4c, 63] Due to the regenerative ability of living cells, BPVs are reported to be more durable compared to their counterparts based on isolated photoactive enzymes whose light-induced damage is irreversible.^[4c, 64] However, power outputs from BPVs remain considerably low due to intrinsic metabolic losses and intracellular competition for energy resources. Bombelli *et al.*^[65] reported, for instance, a maximum BPV power density of 105 mW m^{-2} , that is about three orders of magnitude lower than the power output of common silicon based photovoltaic devices.

Performances of BPVs are strictly dependent on several factors, among which a key role is played by *i)* the selection of photosynthetic microorganism, *ii)* the chemical composition and morphological features of the anode in deep contact with the microbial culture and *iii)* the design and miniaturization of devices. These factors will be discussed in the following sub-sections, highlighting the main related advantages and issues by means of examples selected from the recent literature.

3.2. Photosynthetic microorganisms for BPVs

Among oxygenic photosynthetic microorganisms available for BPVs, cyanobacteria have a primary relevance due to their relatively simple physiology and low basal energy requirements versus more complex eukaryotes photosynthetic organisms, such as algae or plants.^[62] Contrary to higher plants, cyanobacterial energy-transducing photosynthetic membranes are not located into chloroplasts but contained in a densely packed membrane systems, the thylakoids, in the cytoplasm.^[66] Cyanobacteria are the sole prokaryotes capable to perform oxygenic photosynthesis. Their photosynthetic, respiratory and extracellular electron transport (EET) pathways have been recently discussed in a

review,^[67] despite EET pathways are still object of investigation.^[60b, 68] These studies are beyond the scope of this section, which will be mainly focused on highlighting the recent research efforts to improve performances and architectures of cyanobacteria based BPVs. The main issue related to the use of living cyanobacteria in BPVs consists in the low exoelectrogenic bacterial activity, *i.e.* the low efficiency of bacteria to transfer electrons to the external electrode. This issue arises from *i)* the lack of specific features of the bacterial outer membrane promoting EET and *ii)* the dispersion of photo-generated electrons into competitive (*e.g.* respiratory) transport pathways rather than to the anode.^[68] A possible strategy to favor the electrical contact between the anode and bacteria consists in the use of exogenous redox mediators that shuttle electrons from the microorganisms to the electrode: however, despite increasing power generation, these mediators do not selectively accept electrons from bacterial photosynthesis and are believed to be partially responsible for cell toxicity. Due to the high costs and potential environmental impact of such artificial redox mediators, mediator-less BPV devices have recently gained much more attention in view of their possible large-scale and low-cost availability.^[4a, 4c]

BPVs rely on either suspending photosynthetic bacteria in solution or immobilizing them directly onto the anode, with some similarities to the approaches described in the section **Photosynthetic enzymes for energy conversion**. Immobilization is preferable since the formation of the biofilm is expected to optimize electron transport to the anode and reduce internal potential losses. Among cyanobacteria used in BPVs,^[4c, 63] specific strains such as *Synechocystis* sp. PCC 6803 and *Oscillatoria limnetica* have been reported to form biofilms onto conductive materials.^[69] Recent efforts to increase the bacterial exoelectrogenic activity and, in turn, the current generation in BPVs also include the creation of metabolic mutant strains with enhanced performances versus the wild-type cyanobacteria, by deactivation of respiratory terminal oxidase complexes^[68, 70] or by expression of a non-native redox protein.^[71] Indeed, a relevant advantage of using integer photosynthetic bacteria in BPVs lies in the possibility to avail of the genetic engineering approach to enhance their electrogenic activity and improve photocurrent generation.^[68, 70-71] A recent review article surveys the

synthetic biologic approaches to the engineering of membrane-electrode interfaces by means of the introduction of foreign EET pathways in bacterial host cells.^[63]

Further studies reported in 2018 also highlight the active role of some physical treatments and controlled environmental factors in modulating the exoelectrogenic activity of cyanobacteria strains. Saper *et al.* observed that a non-harmful gentle physical treatment with a microfluidizer of live *Synechocystis* sp. PCC 6803 cyanobacteria enables light-driven electron transfer by an endogenous water-soluble molecular mediator to a graphite electrode, without the addition of exogenous electron donors or mediators.^[72] Gonzalez-Aravena *et al.* demonstrated that higher exoelectrogenic activity can be achieved for *Synechococcus elongatus* PCC7942 by controlling the bacterial growth under limited iron concentration.^[73]

3.3. Microbial substrate anodes in BPVs

The optimization of electrodes' morphology and composition also represents a key parameter for photovoltaic devices performances since the electrical and surface characteristics of the anode play a critical role in the bacterial film formation and adhesion, as well as in the electrochemical reaction rates and electron transfer from bacteria to the electrode surface. A general review on anode and cathode materials for photo-MFCs has been recently published.^[74] Two main strategies can be adopted to develop electrodes with increased microbial interaction and enhanced power outputs: *i*) the electrode coating with artificial electron mediators or conductive polymers, such as polypyrrole and polyaniline that may also positively charge the surface and enhance the biofilm adhesion; *ii*) the surface area increase with consequent improvement of direct microbial attachment.^[75]

Among materials suitable for MFCs anodes, carbon-based materials are the most widely explored due to their relatively low cost, high biocompatibility, chemical stability and conductivity.^[76] Carbon-based anodes (*e.g.* carbon nanotubes,^[77] carbon fibers,^[78] graphite,^[79] carbon paint,^[80] reduced graphene oxide rGO^[81]) with or without conductive polymer coatings (polyaniline,^[80] polypyrrole,^[77b, 78, 80] osmium redox polymers,^[79] polymeric azines^[79b]) have been investigated in

cyanobacteria-based BPVs. However, despite being ideal materials for anodes, carbon-based electrodes have a significant drawback when used in photo-MFCs: they are dense black materials and light can only penetrate the first layer of a biofilm growing onto their surface. Hence, in this case, the benefits of using high surface area porous electrodes are wasted.

Bombelli *et al.* compared the performances, in a multichannel BPV device, of *Oscillatoria limnetica* photosynthetic biofilms grown onto various anode materials, including indium tin oxide-coated polyethylene terephthalate (ITO), stainless steel (SS), polyaniline coated glass and carbon paper (CP).^[82] The highest photo response values were recorded using ITO and SS rather than CP. ITO based anodes have been also used in biophotovoltaic platforms as substrates for the biofilm growth of other cyanobacteria strains, such as *Synechocystis* sp. PCC6803 and *Synechococcus* sp. WH5701,^[59] or *Synechococcus elongatus* (UMACC 105).^[81, 83] Nevertheless, although being one of the best performing transparent electrode materials, ITO lacks the high surface area typical of a porous material. In 2018, a comparative study was carried out by Wenzel *et al.* on performances in BPVs of three types of ITO-based electrodes with different porosity, namely (a) a non-porous ITO electrode, (b) a thick film of ITO nanoparticles with 10-100 nm pores size accessible only by the electrolyte, and (c) a ‘microporous’ inverse-opal structure with 10-40 μm pore size in length scale similar to that of cyanobacteria.^[84] Two cyanobacteria strains, the *Nostoc punctiforme* and *Synechocystis* sp. PCC 6803, were used and, in both cases, a two orders of magnitude increase in current generation was observed using the porous (b) and (c) electrodes versus the (a) non-porous ITO counterpart, with photocurrent values of 11.5, 8.4 and 0.04 mA m^{-2} recorded for the coated *Synechocystis* sp. PCC 6803 (a), (b) and (c) electrodes, respectively. Moreover, for both cyanobacteria strains, the photoresponse in porous anode-based devices was faster than in non-porous analogues, with current peaks reached in 1-6 minutes rather than in one hour of light exposure. The similarity of performances of bacterial films on (b) nanoporous and (c) microporous ITO electrodes suggests the occurrence of an endogenous redox shuttle mechanism over a direct conduction mechanism in the electron transfer from living cells to the anode.

Ng *et al.* found that in BPVs using *Synechococcus elongatus* (UMACC 105), an rGO based anode fabricated by Langmuir-Blodgett technique, is more efficient than an ITO based electrode:^[81] maximum power densities of 0.52 mW m^{-2} and 0.32 mW m^{-2} were recorded for rGO- and ITO-based devices in light conditions, respectively.

To improve power generation under low intensity light conditions and to efficiently capture electrons from *Synechococcus sp.* cyanobacteria an ingenious approach was also proposed by Kaushik.^[85] In this case, a new anode was prepared casting a nanocomposite matrix made of cadmium telluride (CdTe) quantum dots, graphene nanoplatelets and silk-fibroin on a graphite electrode. Each component had a specific task: i) the biocompatible silk-fibroin promotes the bacterial film formation; ii) CdTe quantum dots are responsible for FRET energy transfer to the cyanobacteria photosystems; iii) the highly conductive graphene nanoplatelets provide an electroactive surface funneling the cells electrons to the electrode across the semiconducting silk-fibroin film. Moreover, since no detrimental effect on bacterial growth was detected, silk-fibroin was thought to stabilize the quantum dots avoiding their cells' toxicity. The nanocomposite anode, besides acting as a substrate for the cyanobacteria film, is also photoactive and, upon broad visible photoexcitation (λ_{exc} : 350-644 nm), it absorbs light by the CdTe component and transfers *via* FRET the specific energy (λ : 650-750 nm) absorbed by the bacterial photosystems, thus facilitating the metabolic electron release to the anode. The maximum current and power density values under white light illumination were 1.89 A m^{-2} and 610 mW m^{-2} , respectively, these being ~ 5.7 and ~ 50.8 times higher than the values (0.33 A m^{-2} , 12 mW m^{-2}) recorded for a blank graphite reference bioanode. The positive effect of CdTe quantum dots was further confirmed by comparison of photocurrents produced in the circadian cycle: similar values of photocurrents were indeed measured under the daylight and the dark phases ($4.83 \cdot 10^{-4}$ and $4.43 \cdot 10^{-4} \text{ A}$, respectively), this meaning that quantum dots enable bacteria to harvest photons and to generate photocurrent even at the low intensity light conditions of the dark phase.

In conclusion, recent literature shows that biocompatibility and porosity of anodes used as bacterial substrates are crucial features for the optimization of device performances, since they affect the bio-

film formation and, in turn, the electron transfer from bacteria to the electrode surface. Moreover, the recent results show that the use of photoactive nanocomposite anodes^[85] can be envisaged as a very promising strategy to improve power generation under low intensity light conditions.

3.4. BPV device miniaturization

A further way to enhance BPVs' performances consists in reducing resistive losses by device miniaturization^[65, 86] and consequent reduction of charge carriers migration pathways. The use of micro-anodes would increase their active specific surface area leading to high power densities. Moreover, miniaturized devices have promising potential as portable power supplies and for scale-up by connection of multiple units in array configuration.

Choi *et al.* developed a series of micro-sized devices architectures (**Figure 7a-d**) based on the use of *Synechocystis* sp. PCC 6803 cyanobacteria, reaching an optimized self-sustaining and long-life micro-BPV device (**Figure 7d**) with maximum power density and current density of 438 mW m^{-2} and 2.27 A m^{-2} , respectively, and with a power production for 20 days of $\sim 186 \text{ mW m}^{-2}$ upon daylight and $\sim 114 \text{ mW m}^{-2}$ upon night.^[87] The overall evolution of device architectures, referred as microbio-solar cells (micro-BSCs), is depicted in **Figure 7**. In device (a), a conventional membrane-based two-chambered configuration is proposed, including a thin, transparent gold anode and a proton-exchange membrane (PEM) and requiring continuous introduction of potassium ferricyanide as an electron acceptor. In device (b), a single-chambered configuration allows to reduce the internal resistance, and an air-bubble trap is used to facilitate the gas exchange to the bacteria. Moreover, an air-cathode allows the introduction of freely available oxygen that acts as the electron acceptor. The device (c) contains a carbon cloth anode whose external surface is coated with a screen-printed graphite/polytetrafluoroethylene (PTFE) nano-composite which improves the cyanobacteria film formation and the electron transfer efficiency. Moreover, device (c) shows a sandwiched anode/PEM/cathode configuration to reduce the internal ohmic resistance and it is equipped with a superior gas permeable membrane which allows to store the carbon dioxide and oxygen produced

from bacteria and to favor the reverse gas exchange to the bacteria. Finally, the optimized device configuration (d) is based on a micro single-chamber comprising a 3-D conductive polymeric PEDOT:PSS coated carbon cloth anode. The anode is highly porous and allows the formation of densely packed biofilm. Moreover, a superior polydimethylsiloxane (PDMS) gas permeable membrane ensures the gas exchange to the bacteria.

Choi *et al.* also developed a scalable and stackable bio-solar panel with maximum power output of $5.59 \mu\text{W}$ by installing a series of nine micro-BPVs by a common microfluidic channel.^[86b]

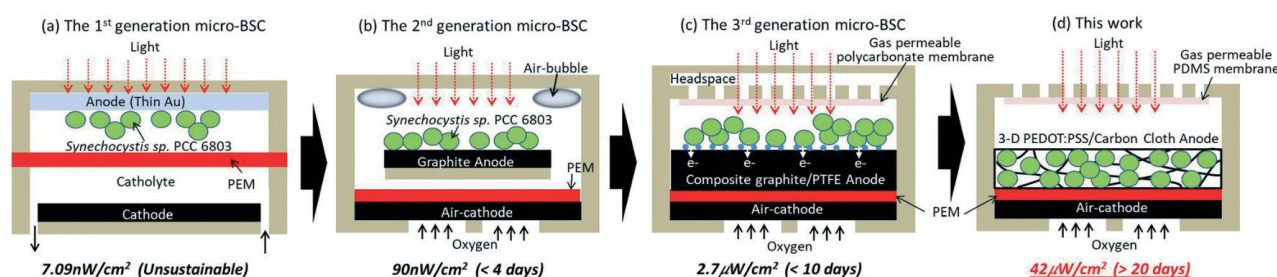


Figure 7. (a) 1st generation of micro-devices using a face-to-face electrode configuration with a thin gold anode and a liquid electron acceptor. (b) 2nd generation of micro-devices using a face-up electrode configuration with an air-bubble trap and a single-chambered air-cathode. (c) 3rd generation micro-devices using a sandwich electrode configuration with a nano-composite graphite/PTFE anode and a microfluidic head space through a gas permeable polycarbonate membrane. (d) Optimized micro-device with a 3-D PEDOT:PSS coated carbon cloth anode and a gas permeable PDMS membrane. Reproduced with permission.^[87] Copyright 2017, the Royal Society of Chemistry.

The advantages of device miniaturization, such as the short start-up time and the small internal resistance, were also demonstrated in the literature for micro-sized self-sustaining complex photo-MFC devices working with a co-culture of heterotrophic and photosynthetic bacteria.^[88]

In the frame of miniaturized BPVs, Bombelli *et al.* developed in 2015 a simple method of fabrication of microfluidic BPV (μBPV) devices that do not require an artificial redox mediator or a proton-exchange membrane.^[65] Soft lithography was used to fabricate microscopic channels equipped with a self-aligned electrode made of low-melting InSnBi alloy and platinum sealed inside the microfluidic tubing. μBPVs (400 nL) loaded with *Synechocystis sp.* PCC 6803 bacteria work without any

additional energy supply (*e.g.* gas purging or application of bias potential to the electrodes) and produces a biotic output power density of 105 mW m^{-2} under white LED illumination.

In 2018,^[86a] the same authors improved the power density using a μ BPV device based on *Synechocystis* mutant cells and designed with a configuration that spatially decouples the charging process (*i.e.* the reduction of carrier molecules by exoelectrogenic electrons) and the power delivery process (*i.e.* the electron transfer to the external circuit). The device working principle is described in **Figure 8**: upon sunlight illumination, cyanobacteria placed in the charging unit, release electrons and reduce molecular carriers (E: $[\text{Fe}(\text{CN})_6]^{3-}$) that migrate to the anode located in the power delivery unit, where they are re-oxidized and driven back to the charge unit by the anodic fluid flow. Inside the power delivery unit, the oxidation of molecular carriers allows migration, along an external circuit, of electrons to the cathode where oxygen is reduced to water in the presence of protons (**Figure 8b**). The device does not require use of a physical PEM because an effective diffusion-controlled barrier between the cathodic and anodic areas, which can be crossed only by protons, is generated by properly selecting the relative flow rates of cathodic and anodic fluids as well as the dimension of the power delivery unit. Such a μ BPV device configuration allows to reduce resistive losses at small length scales reaching an anodic power density peak of 540 mW m^{-2} for the mutant cells *vs* 270 mW m^{-2} for the wild-type cells. This is a further example of performances optimization by device miniaturization.

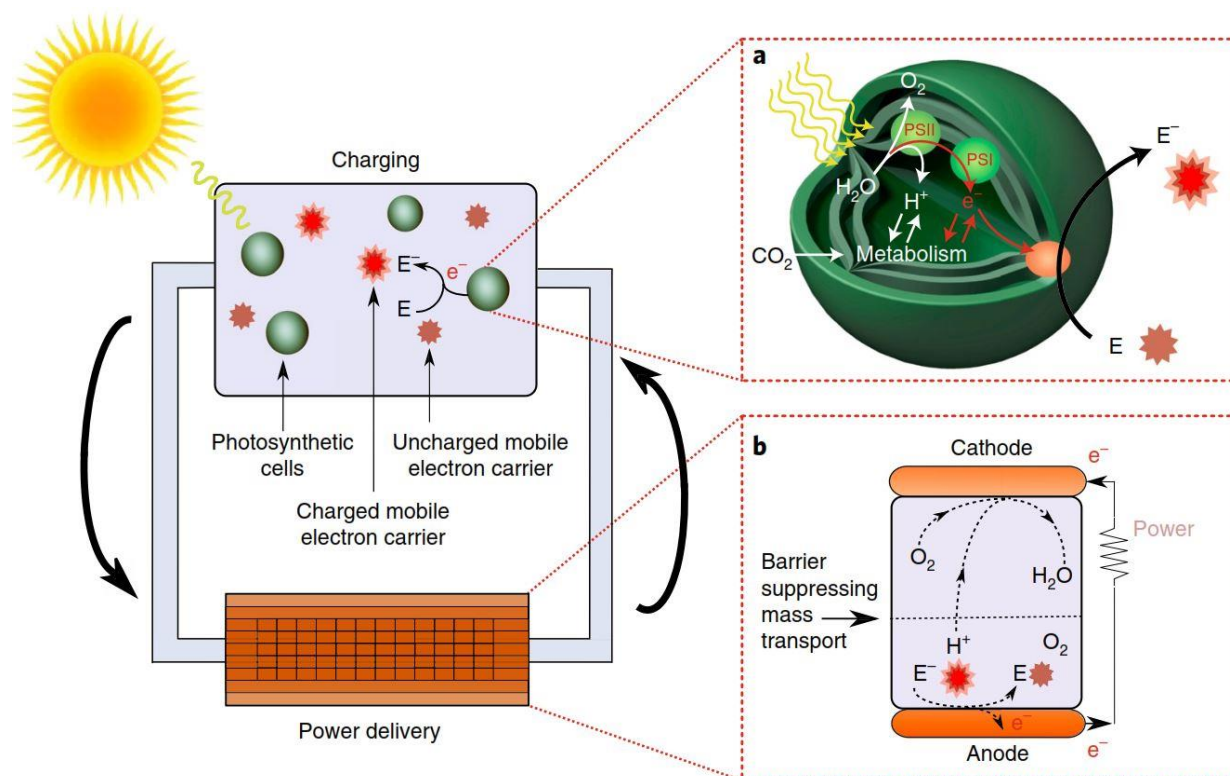


Figure 8. Charging and delivery processes spatially decoupled in a μ -BPV: a) In the charging unit, high-energy electrons (e^-) are generated by the photosynthetic cells and released to the external environment via electron molecular carriers (E: $[\text{Fe}(\text{CN})_6]^{3-}$); b) in the power delivery unit, the reduced charged carriers (E^-) provide electrons to the anode from where the electrons flow to the cathode, generating current. Protons (H^+) diffuse to the cathode where water is catalytically regenerated. Reproduced with permission.^[86a] Copyright 2018, Springer Nature.

To improve BPVs miniaturization and overcome issues related to devices large-scale production, a new approach to bioanodes' fabrication based on the use of thin paper as the anode support material has been recently proposed by Sawa *et al.*^[64] Paper has gained considerable interest in the last years due to a large number of advantages related to its use as material for biosensors and bioelectronics, such as low cost, widespread availability, flexibility, biocompatibility and biodegradability.^[81, 86b, 89] Contrary to the conventional fabrication via gravity-induced deposition of liquid bacteria culture onto the electrode surface, new bioanodes have been produced by inkjet printing, on top of thin paper, a carbon nanotube conducting layer and a film of *Synechocystis* sp. PCC 6803 cyanobacteria that survive after the print process and grow on the conductive electrode surface forming a solid culture. A hybrid BPV was obtained using the new printed bioanode and a platinized carbon cathode exposed

to the air. The device maximum current density and power output were of 4 mA m^{-2} and 0.38 mWm^{-2} upon daylight, 3 mA m^{-2} and 0.22 mWm^{-2} in the dark, respectively. Arrays of nine hybrid BPVs were also proven to be suitable to power a digital clock or a LED.

Furthermore, a BPV device was designed and developed by inkjet-printing both the anode and the cathode on paper and using a hydrogel as a salt bridge for the electrodes' connection and as a supply of minimal growth medium and water to the printed cells (see **Figure 9**). The so-formed device was also defined as a 'thin-film semidry' BPV in which the hydrogel replaces the bulky liquid reservoir typically required in conventional BPVs. This feature allows device miniaturization and portability, disclosing possible development of portable paper-based low-cost devices for low-power applications. Indeed, despite having power output values lower than those of hybrid BPV, the 'thin-film semidry' BPVs were found to be sustained in light/dark cycles for over 100 h.

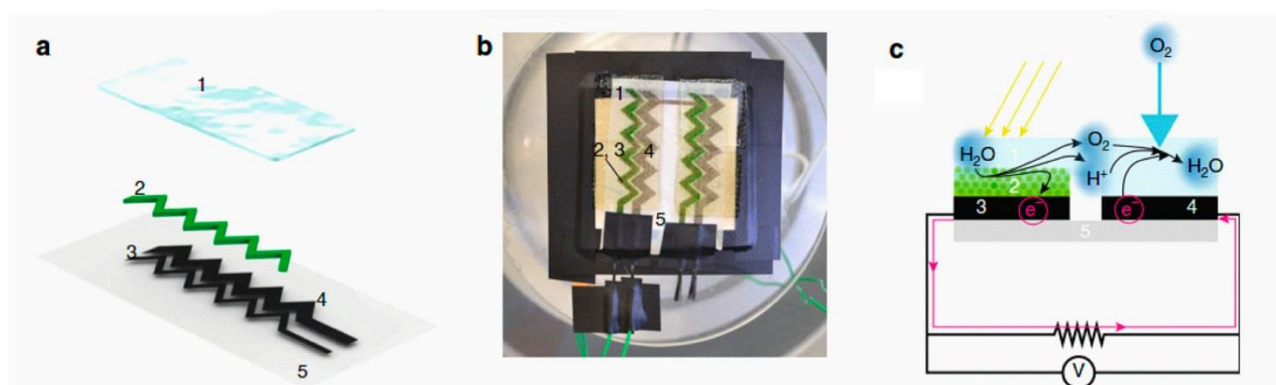


Figure 9. a) Schematic components (semi-exploded view) of the printed paper-based BPV cell: paper support in grey (5); printed anode (3) and cathode (4) in black; printed *Synechocystis* in green (2); bridging hydrogel in pale blue (1). b) Photograph of the experimental setup (excluding the potentiostat), showing a pair of BPV modules printed in series. c) Schematic representation of the BPV cross-section showing electron, proton and oxygen flows. Adapted with permission under Creative Commons Attribution.^[64] Copyright 2017, Springer Nature. To view a copy of this license, visit <http://creativecommons.org/licenses/by/4.0/>

In summary, the examples discussed in this paragraph show that miniaturization represents a profitable approach for the development of portable environmentally friendly power supplies for low-energy devices off-grid. Moreover, the bacteria self-sustainability and self-repair in diverse

environmental conditions can represent, in principle, further advantageous features promoting fabrication of device power supplies working in world's remote areas.

4. Photonics based on photoactive bacteria

The photonics research community has recently started viewing living microorganisms interacting with the electromagnetic radiation either for metabolic needs or for adventitious happenings as promising bio-optical components for fabrication of photonic devices. The research field is still in its infancy and, to the best of our knowledge, only a limited number of studies have been reported in the literature so far, as discussed in this paragraph. Although still largely being curiosity-driven, understanding light-matter interactions in microbial suspensions can be actually of great interest both to elucidate the mechanisms evolved by Nature to optimize light harvesting, reflection or refraction in living microorganisms and to pave the way to a new generation of bio-optical devices for photonics, medicine, bioimaging and sensing. On this ground, bacteria can interact with incident light by metabolizing, adsorbing, reflecting or refracting photons and very interesting studies have been recently carried out on light propagation and scattering effects induced by the motion, orientation or static behavior of such microorganisms when they are subjected to illumination.

For instance, *Escherichia coli* cells in aqueous solution were found to avail of their self-propelling features to respond to illumination with linear and branched optical fibers.^[90] In particular, when irradiated with the branched light-beam output from a four segment tapered optical fiber (4-STF), *E. coli* cells were orderly oriented along the direction of the branched beam and, due to the higher refractive index ($n = 1.39$) of cells versus water ($n = 1.33$), a light guiding effect was observed over several tens of μm through the aligned cells by total internal reflection at the interface of the cell membrane and the water (**Figure 10**).^[90b]

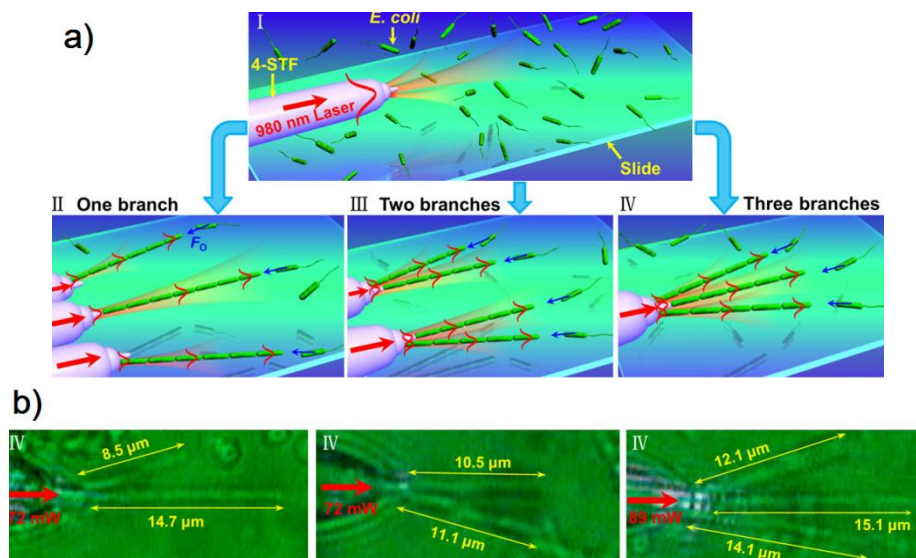


Figure 10. a) Experimental scheme: (I) a 980-nm laser beam is launched into a 4-STF placed in an *E. coli* suspension, three light beams are output from the 4-STF and irradiate on randomly suspended *E. coli*. (II–IV) *E. coli* cells are assembled into structures with (I) one branch, (II) two branches, and (IV) three branches. Red arrows and blue arrows indicate input laser beams and the optical force (F_O) exerted on the cells, respectively. b) Optical microscope images of the assembled branches. Reproduced with permission.^[90b] Copyright 2015, Wiley.

This observation might disclose the development of bacteria-based multidirectional biophotonic waveguides and beam splitters with potential sensing applications in biological living systems, avoiding the use of exogenous inorganic nanowire-based nanophotonic devices which might damage the biological environment.^[91] *E. coli* bacterial cultures were also found to act as optical speckle decorrelation devices able to lower the coherence of imaging systems and to enhance the quality of images in terms of signal-to-noise ratio (**Figure 11**).^[92] In fact, irradiating hidden objects placed behind the *E. coli* culture by a coherent laser source, the bacteria use their self-propelling ability to compensate the optical wavelength distortion caused by themselves. Hence, starting from out of focus images of the hidden objects, a spontaneous refocusing induced by the bacteria movement can be observed with no need of mechanical z-scanning.

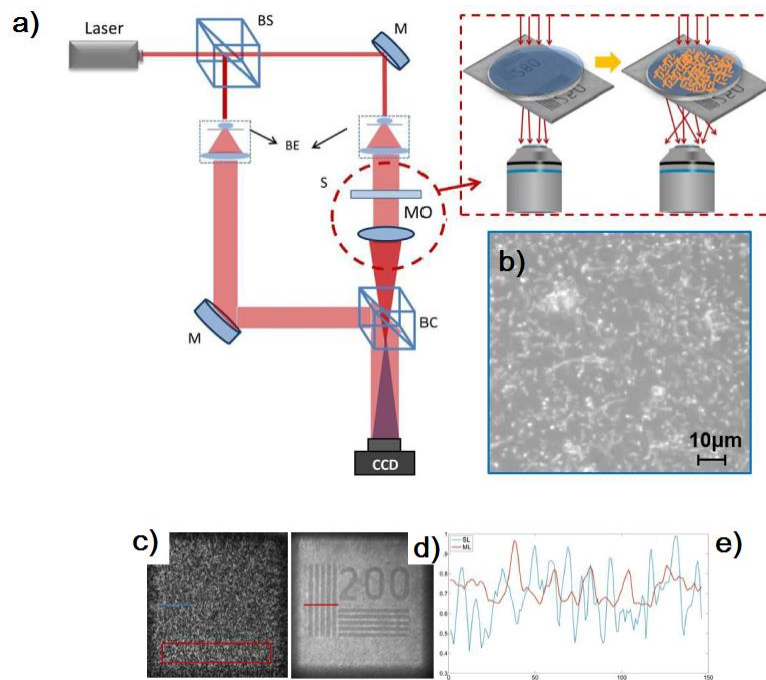


Figure 11. a) Digital Holography set-up employed to image a test target through a severely scattering bacteria volume. BS: Beam Splitter. M: Mirror. BE: Beam Expander. BC: Beam Combiner. MO: Microscope Objective. S: Sample. b) 20x Microscope image of the bacteria suspension. c,d) Amplitude reconstructions of a test target (200 lines/mm) through a bacteria suspension at 2×10^5 cell/mL concentration: (c) Single Look image. (d) Multiple Look image. e) Image contrast over the lines indicated with the horizontal bars. Blue: Single Look. Red: Multiple Look image. Reproduced with permission.^[92] Copyright 2015, OSA Publishing.

Another interesting study was recently reported by Bennet *et al.*, who demonstrated the possibility to fabricate a remotely tunable photonic device based on a dense suspension of live helicoid magnetotactic bacteria acting as a tunable optical attenuator.^[93] Magnetotactic bacteria metabolically assemble magnetite nanoparticles lined up inside lipid vesicles along an actin-like filament that extends from pole to pole of the cells. These microorganisms use this nanostructure to sense and align their cells with the magnetic field of Earth. The fabricated photonic device is similar to a liquid crystal display in which the bacteria suspension, similarly to liquid crystal molecules, can be used to control the amplitude and phase of transmitted light.^[93] In particular, in the absence of an applied magnetic field, magnetotactic bacteria are randomly oriented and are responsible for maximum light scattering and minimum projection area on the plane perpendicular to the light propagation direction. Conversely, applying a weak magnetic field, the bacteria are oriented and, due to their shape

anisotropy, they can exhibit birefringence and induce variation of the intensity of light transmitted through the photonic device.

Contrary to the common belief that a nonlinear optical response cannot be exhibited by cells suspensions, because light deep penetration through cells is strongly prevented by scattering, in 2017 the first evidence of nonlinear wave guiding effects was observed for seawater suspensions of *Synechococcus* sp. photosynthetic cyanobacteria illuminated by a continuous wave 532 nm laser source.^[94] In particular, the light guiding efficiency of cyanobacteria was found to be dependent on both the laser power and the environment hosting the marine cyanobacteria. As shown in **Figure 12** (a, e), upon illumination of the sole seawater in the absence of bacteria and regardless of the laser power, the beam diffracts normally to about 650 μm . Conversely, in the presence of cyanobacteria and when the laser power is low (0.1 W), the light beam significantly expands to about 1.25 mm due to light scattering (**Figure 12b, f**). Increasing the laser power to 3 W, a light guiding effect of bacteria was observed (**Figure 12c, g**) due to an optical trapping of bacteria along the beam path, as confirmed by the detection along the beam of the red autofluorescence of chlorophyll *a* arising from the viable trapped bacteria (**Figure 12d, h**). Such a deep light propagation could be explained considering that the refractive index of bacteria is slightly higher than that of seawater (1.38 vs 1.33). Hence, bacteria could be attracted to the center of the high power laser beam due to an optical gradient force that inhibits the cells diffusion in seawater. The consequent increase of the cell density along the beam path induces a waveguide effect. Conversely, suspending cyanobacteria in glycerol-rich environments, cells aggregate in clusters and act as light diffusers rather than waveguides.

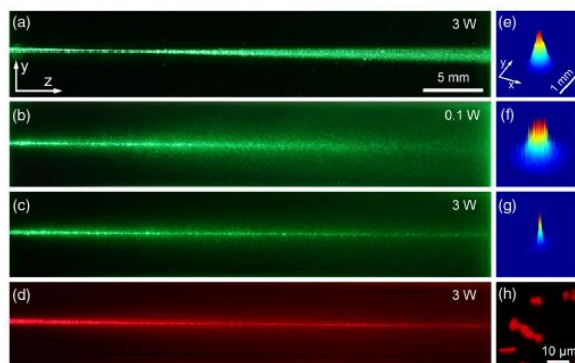


Figure 12. (a) Side view of normal diffraction of an intense laser beam in seawater. (b) Linear diffraction and scattering of the beam at low power when *Synechococcus* cells are suspended in seawater. (c) Deep light propagation due to self-trapping of cells at high laser power. (d) Red autofluorescence of chlorophyll a (indicating survival of the trapped cells under high power laser illumination). (e)-(g) Corresponding 3D plots of the beam's normalized intensity profiles after 4 cm of propagation, captured by a CCD camera. Reproduced with permission.^[94] Copyright 2017, American Physical Society.

In 2017, Coles *et al.* also reported the first evidence of the possibility to modulate, by optical engineering, the electronic energy states of components involved in light harvesting and exciton transport inside living photosynthetic *Chlorobaculum tepidum* green sulfur bacteria (GSB).^[95] This study was carried out after a preliminary demonstration that a strong exciton-photon coupling can occur between the light-harvesting chlorosome complexes extracted from GSBs and a confined optical mode within a metallic optical microcavity.^[96] On this basis, the GSB living bacteria were then placed within a photonic microcavity and, operating in strong coupling regime, a coherent exchange of energy was observed between excitons of the living bacteria and photons of the microcavity, with consequent formation of polariton states whose energy could be tuned changing the energy of optical modes of the microcavity. Such optical approach of tuning the energy states of light harvesting components inside living photosynthetic bacteria may pave the way to new methods of noninvasive control of photosynthetic processes *in vivo* and of the enhancement of light harvesting ability and photosynthesis in living bacteria.

Besides the living photoactive bacteria, some biomolecules extracted from these organisms have gained interest for their photonic properties. In particular, the bacteriochlorophyll *a* contained in light-harvesting (LH) pigment-protein complexes of the purple *R. sphaeroides* photosynthetic

bacterium, was found to exhibit up-converted fluorescence under continuous-wave infrared laser excitation at 1064 nm.^[97] This photonic feature was observed to increase linearly with the excitation power and a delayed fluorescence involving intermediate long-lived energy levels was proposed as the most viable mechanism to explain the observed up-converted fluorescence.

In summary, although photonics based on living microorganisms or their components still represents a under-explored research field, the pioneering studies on wave guiding, light scattering and beam splitting effects, as well as on non-linear optical properties of living bacteria are extremely interesting and can inspire the photonic research community for future potential applications in biocompatible devices for sensing in biological living systems.

5. Conclusions

Although constructing optoelectronic and photonic devices out of either photosynthetic bacteria or their isolated enzymes is probably far from becoming any time soon an actual technology, still this intriguing possibility is driving basic and applied research efforts in many laboratories around the world. Turning attention from photoactive materials obtained via the chemical routes to those obtained via biotechnological processes can potentially reduce costs and mitigate the environmental impact of large scale chemical production. On the other hand, relying on living organisms, biology poses limitation in the structural flexibility of materials and changes the paradigm from tailoring the molecules for the device to adapting the device architecture to the needs of the delicate biological structures, and even more to the living organisms. Further efforts in designing the device architectures require a long-range time duration and chemical stability of the biological components. The achievement of these requirements will eventually tell if these biohybrid systems will impact future technologies and to which extent.

What is already clear is that these original research efforts are deeply impacting the detailed understanding of the photonic properties of photoactive living bacterial systems, suggesting and inspiring new architectures for optoelectronic devices.

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Massimo Trotta graduated in Chemistry in Bari in 1988. As Early stage researcher he spent two years at the Department of Biology the University of Bologna and two years at the Department of Physics at the University of California in San Diego. He is officer of the Executive Committee of the European Society for Photobiology (since 2014) and editor of the Comprehensive Series in Photochemistry and Photobiology (since 2011). Since 2005 he is heavily involved in public understanding of science for non-specialized audience. Since 1990 his research topic is bacterial photosynthesis and environmental applications of the bacterial reaction center.



Dr. Francesco Milano graduated in Chemistry in 1997, received his PhD in Chemical Sciences in 2001 and is researcher at the Italian National Research Council, Institute for Physical and Chemical Processes. His research interests are in bacterial photosynthesis with special focus on the functioning of the reaction center both for basic science and for applications like energy conversion and biosensing. He is involved also in research dealing with liposomes preparation as membrane mimicking and drug delivery systems.



Dr. Angela Punzi graduated in Chemistry at the University of Bari in 1990. Currently, she is Assistant Professor at the Chemistry Department of the same University. Her research interests focus on the synthesis of π -conjugated compounds, such as stereodefined polyenes, aromatic heterocycles and molecular or polymeric materials for both biological and optoelectronic applications, by organometallic-based and/or direct arylation protocols.



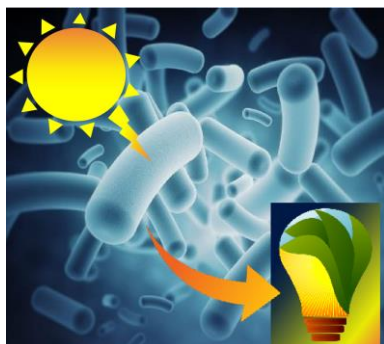
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Photosynthetic and photo-responsive bacteria can be used as a source of materials for optoelectronics and photonics. A review of applications of either photoactive cellular components or metabolically active photosynthetic bacterial cells in devices for solar energy conversion and storage and in light information technologies is presented. Emphasis on new concepts in materials design and device architectures emerging from recent research is given.

Keywords: photosynthetic bacteria, biophotonics, biophotovoltaics, reaction center, bioelectronics

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Photonics and optoelectronics with bacteria: making materials from photosynthetic microorganisms



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