Structural and Functional Hierarchy in Photosynthetic Energy Conversion—from Molecules to Nanostructures

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Abstract

Basic principles of structural and functional requirements of photosynthetic energy conversion in hierarchically organized machineries are reviewed. Blueprints of photosynthesis, the energetic basis of virtually all life on Earth, can serve the basis for constructing artificial light energy-converting molecular devices. In photosynthetic organisms, the conversion of light energy into chemical energy takes places in highly organized fine-tunable systems with structural and functional hierarchy. The incident photons are absorbed by light-harvesting complexes, which funnel the excitation energy into reaction centre (RC) protein complexes containing redox-active chlorophyll molecules; the primary charge separations in the RCs are followed by vectorial transport of charges (electrons and protons) in the photosynthetic membrane. RCs possess properties that make their use in solar energy-converting and integrated optoelectronic systems feasible. Therefore, there is a large interest in many laboratories and in the industry toward their use in molecular devices. RCs have been bound to different carrier matrices, with their photophysical and photochemical activities largely retained in the nano-systems and with electronic connection to conducting surfaces. We show examples of RCs bound to carbon-based materials (functionalized and non-functionalized single- and multiwalled carbon nanotubes), transitional metal oxides (ITO) and conducting polymers and porous silicon and characterize their photochemical activities. Recently, we adapted several physical and chemical methods for binding RCs to different nanomaterials. It is generally found that the $P^+(Q_A Q_B)^-$ charge pair, which is formed after single saturating light excitation is stabilized after the attachment of the RCs to the nanostructures, which is followed by slow reorganization of the protein structure. Measuring the electric conductivity in a direct contact mode or in electrochemical cell indicates that there is an electronic interaction between the protein and the inorganic carrier matrices. This can be a basis of sensing element of bio-hybrid device for biosensor and/or optoelectronic applications.

Keywords: Photosynthesis, Bio-composites, Nano-composites, Bioelectronics

Review

Introduction

Photosynthesis, the conversion of light energy into chemical energy by living organisms, is the energetic basis of virtually all life on Earth; also, fossil fuels are energy deposits of photosynthesis of past million years. The photosynthetic utilization of light energy requires a machinery organized in a structural and functional hierarchy from molecules through protein complexes to entire organisms [1]. One of the major goals of photosynthesis research, conducted worldwide in academic laboratories and industrial institutes, is to find biomimetic and biotechnological applications and technologies of utilization of the environmentally safe and essentially inexhaustible solar energy. One interesting concept is green synthesis of nanoparticles for diverse application in almost all fields of medicine, agriculture and technology reviewed by Husen and Siddiqi [2]. In addition, new generations of light-harvesting and photoactive intelligent materials are also of high interest [3–10]. Bio-nano-composite materials are considered the
materials for the future [11, 12]. Biological systems offer inherently good examples for phenomena in nanotechnology, since the length scales of functional molecular assemblies, such as protein complexes and membrane fragments, fall in the 5–10-nm range. In the following sections, examples of nanotechnological applications of photosynthetic systems will be presented, with our attention focused mainly on systems containing purple bacterial reaction centres.

The Basic Molecules of the Photosynthetic Energy Conversion Are the Chlorophylls

The photosynthetic energy conversion begins with the absorption of light by the photosynthetic pigments, most notably by chlorophyll molecules. The special biological and chemical functions of chlorophylls are determined by their molecular structures, containing highly delocalized conjugated molecular orbitals (Figs. 1 and 2). The energy difference between the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) is reflected in the spectroscopically measurable $S_0 \rightarrow S_1$ transition which is about 660 nm for chlorophyll-a in organic solution (see Fig. 2). Chlorophyll-a is a redox-active pigment with a redox mid-potential of $E_m = 500$ mV in organic solution. When the chlorophylls are bound to proteins (e.g. in the photosynthetic reaction centre (RC) protein, the site of primary photochemistry), the $E_m$ is shifted to a more positive (oxidizing) value, $E_m = 1200$ mV. It is interesting to note that this is the most oxidizing redox system in living cells and fulfils the energetic requirements of water splitting; the $E_m$ of water/oxygen system is $E_m = 820$ mV.

The importance of the molecular structure in determining the biological function can be understood when the properties of the chlorophylls are compared with those of bacteriochlorophylls, found in un-oxygenic photosynthetic prokaryotes. In bacteriochlorophyll, the conjugation of the electron shells is disrupted (Fig. 1). The lower degree of delocalization increases the energy level of HOMO and decreases, in turn, that of LUMO. This change in the energy difference is reflected by spectroscopic features. The $S_0 \rightarrow S_1$ transition for bacteriochlorophyll-a corresponds to $\lambda = 760$ nm in organic solution (in contrast to $\lambda = 660$ nm for chlorophyll-a), and the oxidizing power is smaller, $E_m = 400$ mV (as opposed with 500 mV for chlorophyll-a) in organic solution. When bacteriochlorophylls form the special pair in the RC protein, $E_m$ is shifted only moderately (from 400 to 450 mV); this is far too low with respect to the energetic requirement of water oxidation.

![Fig. 1](image-url) The molecular structures (left and right) and energy levels (ground state-binding and excited state-unbinding orbitals (labelled by asterisks), in the middle) of chlorophyll-a and bacteriochlorophyll-a molecules. Arrows indicate the electronic transitions between the highest occupied and lowest unoccupied molecular orbitals, HOMO and LUMO, respectively. The basic differences between the two molecular structures are indicated by red characters.
It is important to note that the difference in the $E_m$ values between the excited and ground state couples of the primary donors are $\Delta E_m = 1840$ mV (corresponding to a free energy difference, $\Delta G = 177.6$ kJ/mol) and $\Delta E_m = 1370$ mV ($\Delta G = 132.2$ kJ/mol) for chlorophyll-a and bacteriochlorophyll-a, respectively. These values coincide with the $S_0 \rightarrow S_1$ transitions in the red ($\lambda = 660$ nm ($\Delta G = 180$ kJ/mol)) and near infrared $\lambda = 800$ nm ($\Delta G = 148.5$ kJ/mol) for chlorophyll-a and bacteriochlorophyll-a, respectively. For summary, see Fig. 2.

**Organization of the RC Protein**

The photosynthetic pigments (chlorophylls and bacteriochlorophylls, together with other molecules) are arranged in special pigment-protein complexes (light-harvesting antenna complexes and RC proteins) in which efficient light absorption, energy transfer, charge separation and stabilization are warranted. Upon excitation by light primary charge, separation takes place in the photosynthetic RCs, which are the most efficient light energy converter systems in nature [6, 13]. Although different types of RCs have been evolved in nature (photosystem I (PS-I) and photosystem II (PS-II) in plants, algae and cyanobacteria and type I and II RCs in green and purple photosynthetic bacteria, respectively), they all perform very similar basic processes: pigment excitation upon the absorption of light, charge separation and stabilization, rearrangements of charges, and hydrogen bonding interactions within and around the RC proteins.

In purple bacteria, the absorption of light initiates a vectorial $e^-$ transport in the RC—electrons are transferred from the specially organized chlorophyll or bacteriochlorophyll type primary $e^-$ donor (P) through redox-active cofactor pigments to quinone (Q) acceptor molecules (for review, see, e.g., [14–16]). Finally, a pair of “+” and “−” centres ($P^\cdot Q_A$ or $P^\cdot Q_B$ for fully reconstituted RCs) is created after stabilization of the excited electron (Figs. 3 and 4). In vivo (or in artificial systems mimicking the in vivo conditions), the oxidized primary donor is reduced by an external electron donor, and the excited electron is funneled in the direction of the metabolic pathways of the cells, warranting the conditions for repeated turnover of the RCs. In isolated system in the absence of secondary electron...
donor and/or acceptors, the RC is reset by the recombination of the “+” and “−” charges. The constitution of the RC and the time constants of charge separation (forward) and recombination (backward) steps are summarized in Fig. 4.

The time constant of the redox cycle of the RC is determined by the redox components bound to it. By changing the appropriate redox component, a wide range of RC turnover rates can be designed (from $10^{12}$ to $10^{-1}$ s$^{-1}$). From a practical point of view, it is important to note that every redox cofactor component of the RC can be artificially changed (washed out from the RC and chemically or genetically modified; see e.g. [17, 18]). In general, proteins can be designed and constructed at will, in a broad range, to generate redox processes with different turnover times and conditions.

The Photosynthetic Membrane

The RC proteins, together with other pigment-protein complexes (light-harvesting complexes; cytochrome bc$_1$ or cytochrome bf$_6$ (in plants); and the ATP synthase), are embedded in the photosynthetic membrane, which plays central role in the energetics of the cell [19–21].

The energy of light stored in redox potential of the cofactors in the RC ($\Delta G = nF\Delta E_h$) is converted to proton motive force (p.m.f.; [22]), consisting of a transmembrane proton gradient and an electrical potential difference:

\[
\begin{align*}
\Delta G &= nF\Delta E_h \\
E_m &= -\frac{RT}{zF} \ln \frac{[H_+]_m}{[H^-]_m}
\end{align*}
\]

\(E_m\) is the membrane potential, \([H_+]_m\) and \([H^-]_m\) are the concentrations of protons inside and outside the membrane, respectively, \(R\) is the gas constant, \(T\) is the temperature, \(z\) is the valence of the redox component, and \(F\) is the Faraday constant.

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**Fig. 3** The structure of the RC protein of *Rhodobacter sphaeroides* R-26 (an anoxygenic purple bacterium). The secondary structures of the protein (H: green, L: brown, M: blue) subunits are shown by ribbons. The cofactors bound to the RC are also displayed; for further details, see Fig. 4. The molecular model of the reaction centre was calculated from the data of crystal structure downloaded from the Brookhaven Protein Data Bank (www.rcsb.org, code name: 1pst).

**Fig. 4** The lifetimes of the forward (blue solid arrows) and the backward recombination (red dashed arrows) electron transfer steps between the cofactors of the RC. Insert shows the arrangement of the cofactors and the pathway of the electron transfer after saturating single-turnover flash excitation. P: primary electron donor; BChl: bacteriochlorophyll; BPhe: bacteriopheophytin; QA: primary quinone type electron acceptor; QB: secondary quinone type electron acceptor.
(p.m.f. =) $\Delta \mu_H = \frac{\Delta G}{F} = U - \frac{2.3RT}{F} \Delta pH$

Here $n$ is the number of moles, $\Delta E_h$ is the redox potential according to the Nernst equation, $F$ is the Faraday constant (=0.0965 kJ/mol mV), $R$ is the universal gas constant, $T$ is the absolute temperature, $U$ is the membrane potential. The p.m.f. serves the driving force of the ATP synthesis [19, 23].

**RCS in Nanostructures**

It is interesting to note that even though the RC proteins—called the "nature's solar power stations"—have changed the surface of our globe, these are "real nano-systems". Their size represents only nanometre scale in the cells (about 10 nm [24–26]), and their work is also only "nano" (one photon initiates one charge separation [13]). This protein possesses such technical properties that unique applications are possible, for example, its use in the nanostructures or in the optoelectronic systems [3, 4, 27–29]. These properties prompted huge efforts for creating bio-nanocomposite materials and using RCS attached to different carrier matrices and led to numerous publications. The physico-chemical properties (photochemical activity, electric conductivity) of the bio-nanocomposite materials containing RCS and different carrier matrices have been investigated. A couple of examples will be presented in the following paragraphs.

**Artificial Lipid Membranes (Proteo-liposomes)**

Biological materials are developed by nature for extremely efficient, sensitive and specific functions. When they are isolated from their natural environment, their activity is usually decreased. One obvious possibility is to combine them with nano-systems which mimic the in vivo conditions. For this purpose, artificial lipid membranes (liposomes) seem to be good and obvious choices [30, 31]. On the one hand, RC is a transmembrane protein, so that lipid membrane environment resembles the in vivo conditions [32–35]. In addition, the liposome/RC nanosystem can be a good model for the Mitchell chemiosmotic hypothesis (awarded by Nobel Prize in Chemistry in 1978 [19]), which is the basis of the cell bioenergetics. The radius of the specifically prepared liposome embedding the RCS is about 100 nm [32], which falls in the range of the systems usually called "nano". Note that this size is about one fourth of the wavelength of the visible light. When the liposome/RC system is illuminated by light, the electromagnetic field is inherently heterogeneous because of the commensurate sizes of the diameter of proteo-liposomes and the wavelength of the visible light.

By externally added donors (e.g. cytochrome $c_3$) and acceptors (ubiquinone, UQ), conditions for the continuous turnover of the photocycle and the possibility of building up p.m.f. can be warranted. The change in the pH can be monitored by pH-sensitive fluorescent dyes which are sensitive to specific ionophores, like gramicidin, which eliminates the transmembrane proton gradient (Fig. 5, [36]).

**Carbon-Based Materials**

Recently, we have shown that RC proteins can be attached to functionalized and non-functionalized, single-walled (SWCNT [37, 38]) and multiwalled (MWCNT [39]) carbon nanotubes (CNTs). In addition to the physical binding, different strategies have been elaborated for the chemical attachment of the RC protein to CNTs ([40]). The successful binding was visualized by EM and AFM measurements, and the functioning of the RC was checked by flash photolysis experiments. We found that (a) RCS can be attached to CNTs effectively, while they largely retain their activity; (b) this binding induces changes in the intra-protein electron transport (stabilization of the charge-separated state); and (c) there is an electronic communication between the SWCNTs and RCS. Circular dichroism (CD) measurements indicate that the binding of the protein to CNT does not alter the excitonic interactions, i.e. there is no substantial change in the RC structure after the binding [24].

The long-term stability of the system, which depends on many internal and external factors, is very important for potential applications. Figure 6 shows results of different structural (AFM) and functional (CD, LD, flash photolysis) experiments showing the successful binding of RCS. It is to be noted that after 3 months, the stability drops very suddenly in every sample under the experimental conditions we conducted up to now [38]. However, in the absence of CNTs the inactivation is much faster. There are indirect (via monitoring flash-induced absorption change at specific wavelength or monitoring the redox state of the secondary quinone acceptor by EPR [37]) or direct (measuring the change in the light-induced conductivity of MWCNT bundles/RC composites [40]) proofs of redox interaction between CNTs and the RCS.

**Transitional Metal Oxide/RC Complexes**

Transparent conducting oxides (TCOs) are made of indium oxide ($\text{In}_2\text{O}_3$), tin oxide (SnO$_2$) and ITO, and their combination has been widely used in semiconductor and electronic device industry [41–43]. ITO as a component of the composite electrode in bio-hybrid systems offers unique possibility for application due to its transparency in the visible range. Realization of protein-based bio-nanocomposite materials (among them RC protein-based ones) will lead to conceptual revolution in the development of integrated optical devices, e.g. optical switches, micro-imaging systems, sensors, telecommunications technologies or energy harvesting [44–46].
The spectroscopic properties and electric conductivity of ITO/RC composite provide direct evidence that the RC keeps its photochemical activity even if it is dried on ITO. A direct electric contact between the metal oxide layer and the protein is shown by the light-induced conductivity change of the composite. This bio-nanocomposite provides a model for new generations of applications, e.g. in integrated optoelectronic devices [43].

**Porous Silicon/RC Complexes**

Among the different carrier matrices (carbon-based materials, conductive polymers, different metal oxides like ITO), silicon-based materials have special interest during the engineering of bio-inspired materials [47–56]. Due to its environmental, optical and electronic properties, porous silicon (PSi) is one of the most promising materials not only for biosensors and novel drug delivery systems but also for energy conversion and integrated optoelectronic devices [57–59]. Combination of RC and PSi can offer new possibilities in the field of bio-hybrid systems in nano-bionics.

In an earlier publication, we have shown that the donor and acceptor sites of the RC remained active and accessible for externally added donor (horse heart cytochrome c) and acceptor (UQ-0) agents after binding to PSi. We also predicted a possible redox interaction between the protein and the PSi to be proven directly by an independent experiment [60, 61].

**Conducting Polymer/RC Complexes**

The major goal of the current research is to find the most efficient systems and conditions for photoelectric energy conversion and for the stability of the RC bio-nanocomposite. We immobilized the RC protein to MWCNTs through specific chemical binding to amine functional groups and through conducting polymer (poly(3)-thiophene acetic acid, PTAA; Fig. 7). An efficient vectorial charge transfer can be driven in the composites by combining the three systems [62].

The photochemical or photophysical activity of the RC/PTAA/MWCNT complex can be characterized by the absorption change at 860 nm. At this wavelength, the redox state of the primary electron donor bacteriochlorophyll dimer (P\(^+\)/P) can be monitored. The decay curves could be analysed by a multi-exponential fit of sum of first-order reactions: 

\[
A(t) = \sum A_{(0,i)} \exp(-t/\tau(i)),
\]

where \(A(t)\) is the fluorescence intensity at time \(t\), \(A_{(0,i)}\) is the initial amplitude, and \(\tau(i)\) is the decay time constant for the \(i\)-th component.
where $A_{(i,j)}$ and $\tau_{(i)}$ are the contribution and the lifetime of the $i$th component, respectively. However, the monophasic decay, with the lifetime of $\tau = 480$ ms, indicates the homogenous functional binding of the RC to the complex. It is expected that the presence of the PTAA increases the electronic coupling between the RC and the MWCNT. In addition, the absorption cross section, which is a determining factor for the power of the energy converter system, is enhanced by the larger local concentration of the RC (i.e. by the larger chromophore density).

**Photocurrent, Optoelectronics**

Different biological organizations are used to create new-generation light-harvesting systems. In these composites, the advantages of the biological organizations and the carrier matrices are combined so that these composites can be a state-of-the-art, really smart, modern and innovative device. Photosynthetic RC proteins offer unique applications, for example, their use in the nanostructures or in the optoelectronic systems. In these systems, the electron—arising from charge separation—is trapped in the redox components of the RC or its molecular environment and, among other things, can participate in electric circuits. The fabrication of systems for efficient light energy conversion (e.g. photovoltaics), integrated optoelectronic systems or biosensors (e.g. for specific detection of pesticides) can be visualized for the near future.

Measuring light-induced change in the current in an electrochemical cell (called photocurrent) is an elegant demonstration of the suitability of the photosynthetic systems for photovoltaics, or other practical applications in optoelectronics (e.g. for sensing elements for specific compounds, like pesticides). Two of our RC-based

![AFM image of the SWCNT/RC complex.](image1)

*Fig. 6 a* AFM image of the SWCNT/RC complex. RCs are bound to amine-functionalized SWCNTs. *b* Circular dichroism (CD) spectra of RC in detergent solution and bound to SWCNTs as indicated. *c* Absorption change of the SWCNT/RC complex at 450 nm after a single-turnover saturating Xe flash excitation at different incubation times, as indicated. *d* The amplitude of the absorption change of different RC samples as a function of the incubation time. Filled and empty circles and triangles represent RCs and SWCNT/RC complexes at room temperature and at 4 °C, respectively.

![CD spectra](image2)
Fig. 7 (See legend on next page.)
composites were successfully tested and found to be active in electrochemical cells. It has been demonstrated that continuous redox turnover of nanocomposite prepared from PTAA/MWCNT and RCs bound to ITO can be driven by light if quinone is added to the solution for mediating the electron transport between the working and the counter electrode (Fig. 8).

Porous silicon/RC complex also shows photocurrent in electrochemical cell indicating that PSi is not only a material for hosting the RC protein in a large surface area but might be an active element in redox transitions as a working electrode (Fig. 9).

**Nano-bionics in Photosynthesis**

Nanotechnology offers new and potential direction for using interface between biological (as well as photosynthetic) structures and non-biological nanostructures with enhanced functions for harvesting

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**Fig. 7** a Schematic representation of the MWCNT/PTAA/RC complex. RC: photosynthetic reaction centre; PTAA: poly(3)-thiophene acetic acid conducting polymer; MWCNT: multiwalled carbon nanotube. b TEM image and c photochemical activity (monitored by the absorption change at 860 nm). The in the absorption at 860 nm monitors the redox state of the primary electron donor \( P^-/P \). Solid line is calculated by a first-order single-exponential decay with the lifetime of \( \tau = 480 \text{ ms} \).

**Fig. 8** Electrochemical cell (upper) and the photocurrent measured by illuminating the ITO/MWCNT/PTAA/RC electrode (down). The working electrode is ITO covered by MWCNT/PTAA/RC layer, the counter electrode is Pt, and the reference electrode is Ag/AgCl. The graph shows the light-induced photocurrent of the electrochemical cell without a mediator (blue curve) and with UQ-0 (2,3-dimethoxy-5-methyl-1,4-p-benzoquinone) (red curve).
solar energy or functioning as sensitive photonic chemical sensors [63]. Biological materials and photosynthetic RCs are structured for extremely efficient, sensitive and specific functions. The RC proteins own such technical properties that many unique applications are envisaged, for example, their use in nanostructures or in optoelectronic systems [3, 60]. Different types of RCs found in nature are investigated in different photoconverter applications, and their photoconversion power efficiency is far from the performance in vivo up to now. $\eta \approx 10^{-4}$ and $10^{-7}$ are found for bacterial reaction centres in electrochemical cell and dried in semiconductor layer structures, respectively [64]. These values are comparable with the one found for photosystem one (PS-I) in Z-scheme-inspired biophotovoltaics in redox hydrogels ($\eta \approx 10^{-5}$ [65]).

Although the photoconversion efficiency is very small in these systems up to now, the use of the RCs in bio-nano-systems is a real challenge. This protein assures the energy supply for the whole earthly life (including the fossil fuels as well), and we have this protein in our hand. It can be purified, fully engineered and can be designed to our wish. The function of the RC can be mimicked in many photo-sensibilization and photocatalytic processes in which the charge separation capacity of the protein is substituted by an inorganic analogue.

There is a versatile possibility to construct 2D or even 3D hybrid materials based on graphene and some organic materials in which electron–hole pairs are created upon light irradiation with oxidation and reduction power capability. The special hierarchical semiconductor-based heterogeneous organizations of these organic semiconductor catalysts can mimic the energetic schemes of the photosynthetic RCs which fulfil the conditions of separation and stabilization of light-driven charges by chain of redox reactions [66–68].

Due to its remarkable mechanical, thermal, optical and excellent electron conductivity, high transparency and unique two-dimensional (2D) morphology graphene became a promising material as a component of many optoelectronic assemblies. Coupling with proper semiconductor materials, the exceptional properties of graphene provide the possibility of designing new-generation high performance hierarchically structured artificial photosynthetic systems. The enhanced photochemical activity of these highly structured composites can be utilized in many fields of optoelectronics like environmental remediation, water splitting, CO$_2$ photoreduction and selective organic transformation, reviewed, e.g. in [69].

**Conclusion**

In this review we have shown that the vectorial charge transfer within the photosynthetic organisms initiated by light is assured in a system organized hierarchically from molecules to molecular complexes. The energy of light which is captured in the form of redox free energy of cofactors can be used for useful work either wiring out the electron in electric circuits or reducing chemical equivalents. This can be a basis of constructing artificial light-
energy converting molecular devices like sensing element of bio-hybrid device for biosensor and/or for optoelectronic applications. Future research should aim to find the most efficient energy converter system (the biological and the inorganic parts), the highest reproducibility and stability of the function.

Competing Interests
The authors declare that they have no competing interests.

Authors’ Contributions
Tsz. Eny and TT made the experimental work of photocurrent generation. MM completed the CNT experiments. HK made the experimental work of CNT and PSI. ML carried out the experiments with CNT bundle composites. MD carried out the CD experiments. GyG and HK supervised the CD and CNT experiments, respectively. LN supervised the whole work. All authors read and approved the final manuscript.

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References
1. Govindjee, Beatty JT, Gest H, Allen JF (2006) Discoveries in photosynthesis. Advances in photosynthesis and respiration. Springer, Berlin
2. Husen A, Khwaja Sahaluddin Siddiq K (2014) Photosynthesis of nanoparticles: concept, controversy and application. Nanoscale Res Lett 9:229
3. Nagy L, Hajdu K, Fischer B, Hernádi K, Nagy K, Vincze J (2010) Photosynthetic reaction centres—from basic research to application possibilities. Notulae Scientiae Biologica 2:7–13
4. Nagy L, Hajdu K, Torma S, Cáskós S, Szabó T, Magyar M, Fejés D, Hernádi K, Kellermayer M,Honváth E, Mágez A, Forrò L (2014) Photosynthetic reaction center/carbon nanotube bundle composites. Phys Status Solidi B 251:2366–2371
5. Scholes GD, Flemming GR, Olaya-Castro A, van Grondelle R (2011) Lessons from nature about solar light harvesting. Nature Chem 3:763
6. Jones MR (2009) The petite purple photosynthetic powerpack. Biochem Soc Trans 37:400–407
7. Cogdell RJ, Gardiner AT, Molina PI, Cronin L (2013) The use and misuse of photosynthesis in the quest for novel methods to harness solar energy to make fuel. Phil Trans R Soc A 371:20110603
8. Cogdell RJ, Lindsay JG (1998) Can photosynthesis provide a ‘biological blueprint’ for the design of novel solar cells? Trends Biotechnol 16:521–527
9. Mongwaketse NP, Kotsedi L, Nuru ZY, Sparrow R, Garab G, Mzaou M (2014) Porphyrin nanorod-polymer composites for solar radiation harvesting applications. J Porphyr Phthaloc 18:1146–1156
10. Chappaz-Gillot C, Marek PL, Blaive BJ, Canard G, Bürck J, Garab G, Hahn H, Jávorfi T, Kelemen L, Krupke R, Mössinger D, Ormos P, Reddy CM, Roussel C, Steinbach G, Szabó M, Ulrich AS, Vanthuyne N, Vilayangarhavan A, Zupanovac A, Balaban TS (2012) Anisotropic organization and microscopic manipulation of self-assembling synthetic porphyrin micro-rods that mimic chlorosomes: bacterial light-harvesting systems. J Am Chem Soc 134:944–954
11. Darder M, Aranda P, Ruiz-Hitzky E (2007) Bionanocomposites: a new concept of ecological, biospirdred and functional hybrid materials. Adv Mater 19:1309–1319
12. Shooshey O, Levy I (2008) Nanobiotechnology: biospirdred devices and materials of the future. Humana Press Inc, Totowa
13. Wright CA, Clayton R (1974) The absolute quantum efficiency of bacteriochlorophyll photooxidation in reaction centres of Rhodopseudomonas sphaeroides. Biochim Biophys Acta 333:246–260
14. Wright CA (2004) Proton and electron in the acceptor quinone complex of photosynthetic reaction centers from Rhodobacter Sphaeroides. Front Biosci 9:309–337
15. Allen JP, Williams JC (1998) Photosynthetic reaction centers. FEBs Lett 4385–9
16. Paddock ML, Feher G, Okamura MY (2003) Proton transfer pathways and mechanism in bacterial reaction centers. FEBs Lett 555:445–50
17. Okamura MY, Isaacson RA, Feher G (1975) Primary acceptor in bacterial photosynthesis: obligatory role of ubiquinone in photoactive reaction centers of Rhodopseudomonas sphaeroides. Proc Natl Acad Sci U S A 72:3491–3495
18. Maróti P, Kimaien C, Wright CA, Holten D, Pearstein R (1985) Photochemistry and electron transfer on borohydride-treated photosynthetic reaction centers. Biochem Biophys Acta 810:132–139
19. Mitchell P (1961) Coupling of phosphorylation to electron and hydrogen transfer by a chemi-osmotic type of mechanism. Nature 191:144–148
20. Zuber H, Cogdell RJ (1995) Structure and organization of purple bacterial reaction antennae complexes. In: Blankenship RE, Madigan TM, Bauer CE (eds) Anoxygenic Photosynthetic Bacteria. Kluwer Academic Publisher, Dordrecht, pp. 315–348
21. Vernoniggio A, Joliot P, Joliot A (1995) Organization of electron transfer components and supercomplexes. In: Blankenship RE, Madigan TM, Bauer CE (eds) Anoxygenic Photosynthetic Bacteria: Kluwer Academic Publisher, Dordrecht, pp. 279–295
22. Blankenship RE, Madigan TM, Bauer CE (1995) Anoxygenic photosynthetic bacteria. In: Advances in photosynthesis. Kluwer Academic Publishers, Dordrecht
23. Gromet-Elhanan Z (1995) The proton-translocating F0F1 ATP synthase—ATPase complex. In: Blankenship RE, Madigan TM, Bauer CE (eds) Anoxygenic Photosynthetic Bacteria. Kluwer Academic Publisher, Dordrecht, pp. 807–820
24. Dorogi M, Lambrev PL, Magyar M, Hernádi K, Honváth E, Mágez A, Forró L, Nagy L, Garab GY, Photosynthetic reaction center structures in nanocomposite systems—what you can see with polarization spectroscopy. Cost Phototech, Training School Advanced Laser Spectroscopy in Green Phototecnology, October 18–23, 2014 Szeged, Hungary, P13
25. Palazzo G, Mallardi A, Francia F, Dezi M, Venturioli G, Piemo M, Vignatid E, Piazzad R (2004) Spontaneous emulsification of detergent solubilized reaction center: protein conformational changes precede droplet growth. Phys Chem Chem Phys 6:1439–1445
26. Nagy L, Maroti P, Teraízma M (2008) Spectrally silent light induced conformation change in photosynthetic reaction centers. FEBs Lett 582:3637–3662
27. Gardi MT, Pace E (2006) Biotechnological applications of photosynthetic. In: Gardi MT, Polescu EV (eds) Proteins: Biochips, Biosensors and Biodetectors. Springer, New York, pp. 47–154
28. Hollander MJ, Magis JG, Fuchsenberger P, Aartma TJ, Jones MR, Frese RN (2011) Enhanced photocurrent generation by photosynthetic bacterial reaction centers through molecular relays light-harvesting complexes and direct protein gold interactions. Langmuir 27:10282
29. Karmam M, Delgado JD, Frieve B, Aartma TJ, Jones MR, Frese RN (2014) Photosynthetic protein complexes as bio-photovoltaic building blocks retaining a high internal quantum efficiency. Biomacromolecules 15:2833–2838
30. Hellingweff KJ (1987) Reaction centers from Rhodopseudomonas sphaeroides in reconstituted phospholipid vesicles. I. Structural studies. J Bioenerg Biomembr 19(3):203–222
31. Ollivon M, Lesieur S, Gabrielle-Madelmont C, Patenostre M (2000) Vesicle reconstitution from lipid-detergent mixed micelles. Biochim Biophys Acta 1508:34–50
32. Milano F, Agostano A, Mavelli F, Troita M (2003) Kinetics of the quinone binding reaction at the QB site of reaction centers from the purple bacteria Rhodobacter sphaeroides reconstituted in liposomes. Eur J Biochem 270:4595–4605
33. Milano F, Italiano F, Agostano F, Troita M (2009) Characterisation of RC-proteoliposomes at different RC/lipid ratios. Photosynth Res 100:107
34. Milano F, Italiano F, Agostano F, Troita M (2009) Characterisation of RC-proteoliposomes at different RC/lipid ratios. Photosynth Res 100:107–112
35. Maróti P, Fodor E, Tandori J, Brinu L, Farkas T (1999) Lipids affect the charge stabilization in wild type and mutant reaction centers of Rhodobacter sphaeroides. Austr J of Plant Physiol 25:465–473
36. Nagy L, Milano F, Dorogi M, Troita M, Laczkó G, Szébenyi K, Váró G, Agostiano A, Maróti P (2004) Protein/lipid interaction in bacterial photosynthetic reaction center: the role of phosphatidylcholine and phosphatidylglycerol in charge stabilization. Biochemistry 43:12913–12923
36. Milano F, Trotta M, Dorogi M, Fischer B, Giotta L, Agostiano A, Marotti P, Kálmán L, Nagy L (2012) Light induced transmembrane proton gradient in artificial lipid vesicles reconstituted with photosynthetic reaction centers. J. Bioenerg. Biomembr. 44:373–384
37. Dorogi M, Bálint Z, Miko C, Vileno B, Milas M, Hernádi K, Forró L, Váró G, Nagy L (2006) Stabilization effect of single-walled carbon nanotubes on the functioning of photosynthetic reaction centers. J. Phys. Chem. B 110:21475–21479
38. Magyar M, Hajdu K, Szabo T, Hernadi K, Dombi A, Horvath E, Magrez A, Forró L, Nagy L (2011) Large temporal stability and charge separation of reaction center protein photochemistry by carbon nanotubes. Phys. Status Solidi B 248:2454–2457
39. Hajdu K, Szabó T, Magyar M, Benczik G, Németh Z, Nagy K, Magrez A, Forró L, Váró G, Hernádi K, Nagy L (2011) Photosynthetic reaction center protein in nanostructures. Phys. Status Solidi B 248:2700–2703
40. Nagy L, Magyar M, Szabo T, Hajdu K, Giotta L, Dorogi M, Milano F (2014) Photosynthetic machineries in nano systems. Curr. Protein Pept. Sci. 15:363
41. Granqvist CG, Hultaker A (2002) Transparent and conducting ITO films: new developments and applications. Thin Solid Films 411:1–5
42. Lany S, Zunger A (2007) Dopability, intrinsic conductivity, and nonstoichiometry of transparent conducting oxides. Phys. Rev. Lett. 98:046501
43. Szabó T, Benczik G, Magyar M, Vsey C, Gngl Z, Nagy K, Váró G, Hajdu K, Kozák G, Nagy L (2013) Photosynthetic reaction center/PtO hybrid nanostructure. Mater. Sci. Eng. C 33:679–773
44. Fábians L, Heiner Z, Mero M, Kiss M, Wolff EK, Ormos P, Osay K, Dé R (2011) Protein-based ultrafast photonic switching. Opt. Express 19:18861
45. Der A, Valkai S, Fabian L, Ormos P, Ramsden JJ, Wolff EK (2007) Integrated optical switching based on the protein bacteriorhodopsin. Photochem. Photobiol. 83:393–396
46. Vsevolodov N (1998) Biomolecular electronics. Birkhauser, Boston
47. Agarwal V, del Río JA (2003) Tailoring the photonic band gap of a porous silicon material: adsorption of photosystem II reaction center complex into 23 nm nanopores in SBA. Langmuir 27:713–719
48. Estevez JO, Arriaga J, Méndez Blas A, Agarwal V (2009) Enlargement of omnidirectional photonic bandgap in porous silicon dielectric mirrors with a Gaussian profile refractive index. Appl. Phys. Lett. 94:061914
49. Martin M, Palestino G, Cloître T, Agarwal V, Zimányi L, Gergely C (2009) Three-dimensional spatial resolution of the nonlinear photoemission from biofunctionalized porous silicon microcavity. Appl. Phys. Lett. 94:223313
50. Thompson CM, Neuwoudt M, Ruminski AM, Sailor MJ, Miskelly GM (2010) Electrochemical preparation of pore wall modification gradients across thin porous silicon layers. Langmuir 26:7598–7603
51. Estephan E, Sabo MB, Agarwal V, Csuzsner FJG, Laroque C, Gergely C (2011) Peptides for the biofunctionalization of silicon for use in optical sensing with porous silicon microcavities. Adv. Funct. Mater. 21:2003–2011
52. Palestino G, Legros R, Agarwal V, Pérez E, Gergely C (2008) Functionalization of nanostructured porous silicon microcavities for glucose oxidase detection. Sens. Actuators B 134:6–10
53. Xiao L, Gu L, Howell SB, Sailor MJ (2011) Porous silicon nanoparticle photosensitizers for singlet oxygen and their photocytotoxicity against cancer cells. ACS Nano 5:3651–3659
54. Wu EC, Andrew JS, Buyanin A, Kinsella JM, Sailor MJ (2011) Suitability of porous silicon microparticles for the long-term delivery of redox-active therapeutics. Chem. Commun. 47:5699–5701
55. Kilan KA, Böcking T, Ilyas S, Gaus K, Jessup W, Gal M, Gooding JJ (2007) Forming antifouling organic multilayers on porous silicon by photolithography. Adv. Funct. Mater. 17:2884–2890
56. Orosco MM, Pacholski C, Miskelly GM, Sailor J (2006) Protein-coated porous-silicon photon crystals for amplified optical detection of prostate cancer. Adv. Mater. 18:1393–1396
57. Noji T, Kamedaki K, Kawakami K, Shen JR, Kajino T, Fukushima Y, Sekitoh T, Itoh S (2011) Photosynthetic oxygen evolution in mesoporous silica material: adsorption of photosystem II reaction center complex into 23 nm nanopores in SBA. Langmuir 27:705–713
58. Oda I, Hirata K, Watanabe S, Shibata Y, Kajino T, Fukushima Y, Iwai S, Itoh S (2006) Function of membrane protein in silica nanoparticles: incorporation of photosynthetic light-harvesting protein LH2 into F5M. J. Phys. Chem. B 110:11114–11120
59. Oda I, Iwaki M, Fujita D, Tsutsumi Y, Ishizaka S, Dewa M, Nango M, Kajino T, Fukushima Y, Itoh S (2010) Photosynthetic electron transfer from reaction center pigment-protein complex in silica nanoparticles. Langmuir 26:13399–13406
60. Hajdu K, Gergely C, Martin M, Cloître T, Zimányi L, Tenger K, Khoroshyy P, Palestono G, Agarwal V, Hernádi K, Németh Z, Nagy L (2012) Porous silicon/ photosynthetic reaction center hybrid nanostructure. Langmuir 28:11866–11873
61. Hajdu K, Gergely C, Martin M, Zimányi L, Agarval V, Palestono G, Hernádi K, Németh Z, Nagy L (2012) Light harvesting bio-nanomaterial using porous silicon and photosynthetic reaction center. Nano Res. Lett. 7:400
62. Szabó T, Magyar M, Németh Z, Hernádi K, Endrödö B, Benczik G, Vsey C, Horváth E, Magrez A, Forró L, Nagy L (2011) Charge stabilization by reaction center protein immobilized to carbon nanotubes functionalized by amine groups and poly(3-thiophene acetic acid) conducting polymer. Phys. Status Solidi B 248:2386–2389
63. Graido JP, Landy MP, Fabermeier SM, Nicholas TP, Ivenson NM, Boghossian AA, Reuel NF, Hilmer AJ, Sen F, Brew JA, Stranno M (2014) Plant nanobiobics approach to augment photosynthesis and biochemical sensing. Nat Mater 13:400–408
64. Szabó T, Nyerki E, Tóth C, Csekö R, Magyar M, Horváth E, Hernádi K, Endrödö B, Cs V, Forró L, Nagy L (2015) Generating photocatalyst by nanocomposites based on photosynthetic reaction center protein. Phys. Status Solidi B 252: 2614–2619
65. Hartmann V, Kothe VT, Poller S, El-Mohsna E, Novaczyk MM, Plumer N, Schuhmann W, Rogner M (2014) Redox hydrogels with adjusted redox potential for improved efficiency in Z-scheme inspired biophotovoltaic cells. Chem. Phys. 16:11936–11941
66. Zhang N, Yang MQ, Liu S, Sun Y, Xu YJ (2015) Watzling with the versatile platform of graphene to synthesize composite photocatalysts. Chem Rev. 115:10307–10377
67. Han C, Yang MQ, Wengab B, Xu YJ (2014) Improving the photocatalytic activity and anti-photocorrosion of semiconductor ZnO by coupling with versatile carbon. Phys. Chem. Chem. Phys. 16:16891–16903
68. Han C, Chen Z, Zhang N, Colmenero JC, Xu YJ (2014) Hierarchical hybrids: hierarchically CdS decorated 10D ZnO nanorods-2D graphene hybrids: low temperature synthesis and enhanced photocatalytic performance. Adv. Funct. Mater. doi:10.1002/adfm.201507001
69. Yang MQ, Zhang N, Paplaro M, and Xu YJ (2014) Artificial photosynthesis over graphene–semiconductor composites. Are we getting better? Chem. Soc. Rev. doi:10.1039/c4cs00213j