Applications of Photosynthetic Systems

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In biological and life science applications photosynthesis is an important process that involves the absorption and transformation of sunlight into chemical energy. During the photosynthesis process, the light photons are captured by the green chlorophyll pigments in their photosynthetic antennae and further funneled to the reaction center. One of the most important light harvesting complexes that are highly important in the study of photosynthesis is the membrane-attached Fenna-Matthews-Olson (FMO) complex found in the green sulfur bacteria. In this review, we discuss the mathematical formulations and computational modeling of some of the light harvesting complexes including FMO. The most recent research developments in the photosynthetic light harvesting complexes are thoroughly discussed. The theoretical background related to the spectral density, quantum coherence and density functional theory (DFT) has been elaborated. Further, details about the transfer and excitation of energy in different sites of the FMO complex along with other vital photosynthetic light harvesting complexes have also been provided. In particular, we will review recent results on spectral density, quantum coherence, quantum entanglement and excitonic energies of different pigments in the light harvesting complexes. We will also discuss the issues pertinent to the highest occupied orbital (HOMO) and lowest unoccupied orbital (LUMO) energies for all the bacteriochlorophyll utilizing the time-dependent DFT. These results would be helpful in studying the excitonic dynamics of the light harvesting complexes among different applications. Finally, we conclude this review by providing the current and potential applications in environmental science, energy, health and medicine, where such mathematical and computational studies of the photosynthesis and the light harvesting complexes can be readily integrated.

Keywords: photosynthetic systems ; light harvesting complexes ; Fenna-Matthews-Olson (FMO) ; bacteriochlorophyll (BChl) ; density functional theory (DFT) ; molecular dynamics ; artificial photosynthesis ; biomimetic and synthetic biology ; sustainability ; quantum biology

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1. Environmental Science Applications

Over the past years, significant research efforts have been devoted for the production of energy from biomass to meet the increasing energy demands worldwide and keeping a check on the environmental issues. Microorganisms such as cyanobacteria and microalgae possess a significant potential in the production of biofuels, chemicals, and bio-based products for meeting the global energy crisis [1][2][3][4][5][6][7][8]. Such renewable alternatives would not only limit the reliance on fossil fuel resources but could also serve as a stepping stone for effective transition from a petroleum-based economy to a bio-based economy [3][6]. Notably, the microbial fuel cell represents a promising alternative of electricity generation from the catalysis of microorganisms found in lakes, lagoons, ponds, or even waste water reserves [9][10][11]. Microalgae is one of the examples of the photosynthetic bioorganisms that is used for the production of green bioelectricity utilizing microbial fuel cells. Furthermore, owing to the natural abundance of such living microorganisms, the bioelectricity produced is a highly cost-effective and sustainable alternative for meeting the energy demands of the growing population. However, the large-scale industrial translation of this technology is currently limited owing to several biotechnological, economic and environmental issues. Some of the associated bottlenecks, mainly related to its low stability and efficiency, can be effectively tackled by the synergetic combination of synthetic biology and nanotechnology. For example, the native electrogenic capacity and the working lifetimes of microbiological cells can be augmented utilizing the tunability of nanomaterials. More recently, an overview of the different nanomaterials used to enhance bioelectricity generation through improved photosynthesis, extracellular electron transfer and anode performance have been reviewed in [11]. More details about the photosynthetic microbial fuel cells and their integration with the conventional technology of the microbial fuel cell can be found in [12][13][14][15][16][17]. The photosynthesis can also be used for energy storage, as described in [18][19][20][21][22][23].

The effects of different kinds of light sources on the production of biomass and pigments have been studied in the photosynthetic bacteria waste water treatment in [24]. The applications, opportunities and challenges of using microalgae group Chlorophyta for various energy and environmental applications have been reviewed in [25], highlighting some critical aspects such as the applicability of Chlorophyta in industrial and domestic waste water treatment, and removal of contaminating nutrients. Recent research advances in the waste water treatment utilizing the freshwater monocultures of filamentous algae have been reviewed and critically analyzed in [26], mainly focusing on microalgae and polyculture systems. Research gaps in translating this technology to large-scale system design, including species selection criteria, the effect of nutrient type and loading conditions, inorganic carbon supply, algae–bacteria interactions and parameters, viz., pond depth, mixing and harvesting regimes were identified along with providing a future road map for maximizing productivity and waste water treatment efficiency [27]. Furthermore, the green algae (Chlorella Kessleri) is one of the most common light harvesting complexes found in the water which can be used to measure the purity of water utilizing rigorous study of photosynthesis phenomena in them. This can be done by measuring the concentration of oxygen produced by photosynthesis in water containing green algae [28][29][30].

The detailed understanding and analysis of quantum coherence and spectral density in the light harvesting complexes would also be helpful in the understanding of processes pertinent to the solar and photovoltaic cells [31][32][33][34][35][36][37]. Recently, different theoretical models used for describing energy absorption and transmission in solar cells and photosynthetic systems, including the FMO complex, have been critically analyzed in [38]. This study highlights that the use of sinks, traps or any artificial relaxation process in the standard theoretical models of solar energy conversion, which is developed for studying the energy transfer to the reaction center in photosynthetic systems may contradict to the second law of thermodynamics. These findings could invalidate several existing models used for studying solar energy conversion and raise significant concerns regarding some of the earlier drawn conclusions. A possible solution to address this issue has been put forward in [38] by providing a thermodynamically-consistent version of the model that explicitly describes parts of the reaction center and employs a Hamiltonian transfer to describe the energy absorption and transmission instead of a decay rate or sink term. Owing to the difficulties to probe molecular self-assembling and packing structures at the atomic level by experimental techniques, theoretical simulations are becoming a useful tool in our better understanding of the structure–property relationship of the electronic processes for organic solar cells [39][40][41][42][43][44]. Recent advances in the theoretical simulations for organic solar cells ranging from the molecular dynamics simulated packing structures to the electronic processes computed by quantum-chemical, in combination with kinetic Monte Carlo, simulations have been reviewed in [39]. The future perspective and challenges associated with the prediction of electrical characteristics and photoelectric conversion efficiencies of organic solar cells from molecular structures utilizing theoretical simulations have also been highlighted in [39].

2. Biomimetic Applications

Artificial photosynthesis is envisioned as a promising technique for harvesting solar energy through water splitting and CO_2 reduction to generate high-energy chemical fuels [45][46][47][48][49]. Although the field of artificial photosynthesis is still in its infancy phase of research, recent advances in synthetic biology have provided a significant boost to this interdisciplinary research field. The main goal of artificial photosynthesis is to assemble molecular systems into larger-scale constructs for replicating the natural processes of photosynthesis which is a quite challenging and complex task in itself [49]. Today, artificial photosynthesis is largely focused on understanding and mimicking the ultimate functionality of the natural photosynthetic phenomena for producing energy-rich fuel using cheap and environmentally friendly biomimetic compounds [47][49]. Thus, the essential components of an artificial photosynthetic device would be: (i) a light harvester (e.g., semiconductor) for converting solar photons to excited states, generation of charge-separation and regulation of the flow of collected excitation energy to the reaction sites, (ii) a reduction active reaction site and an oxidation active reaction site, where conversion of excited states to redox potential occurs, (iii) molecular catalysts (i.e., transition metal complexes) to assist water splitting and CO_2 reduction system, and (iv) linkages of different molecular and nano- and macro-scale components of artificial photosynthetic elements [47][48][50].

The artificial photosynthesis is a good source of production of chemical energy that can be used to reduce the amount of carbon dioxide present in the environment [51][52][53][54][55][56][57][58][59][60][61]. The use of artificial fertilizers has been increased in the past few decades for boosting food productivity for satisfying the needs of the growing population [62][63]. The increased consumption also brings production of the byproducts of the natural processes occurring on a daily basis that can be utilized in the production of sustainable and green energy utilizing artificial photosynthesis. Several computational techniques are also available in the literature for studying artificial photosynthesis [64][65][66][67]. In addition, the use of the small molecules to trigger the photosynthesis reaction has been recently studied in [68][69][70][71][72][73].

3. Health and Applications in Medicine

An exciting application of nano-sized self-assemblies of the chlorosomes found in the green sulfur as a contrast agent for medical imaging for visualizing different structures and pathologies within the human body has been demonstrated in [74][75][76][77]. The feasibility and potential of such studies can be attributed to the fact that light harvesting antennas like chlorosomes have a special structure through which they can absorb light even from the region with very low intensity of light source. The previtamin D3 from 7-dehydrochlorostel level can also be determined in human skin by studying photosynthesis in them through exposure to sunlight [78][79]. The photosynthetic bacteria are also a good source of vitamin B12 and have been used in some of the important medical applications, including the treatment of anemia, neuritis and eye problems [80]. Other applications of photosynthetic bacteria include the production of coenzyme Q10 that is used for treating heart disease, brain vascular injury and anemia [80]. These bacteria can also be used to produce the porphyrin and ribonucleic acids (RNA) that again can potentially be used in treating several diseases and deficiencies in the human body [80].

4. Enhancing the Quantum Efficiency of Excitonic Energy Transfer and Ultrafast Processes in Light Harvesting Complexes

Valuable lessons can be learned from the operating principle of photosynthesis that is a highly optimized process whose primary steps involve transport of energy while operating near theoretical quantum limits of efficiency [81]. In recent years, there have been significant research efforts that have been motivated by the hypothesis that nature may use quantum coherences to direct energy transfer [81]. There has been a resurgence of interest in quantum biology owing to the advances in experimental and computational techniques to accurately capture the quantum phenomena in biological systems at smaller length and timescales [82]. Notably, quantum effects in biology have been extensively studied in the FMO complex and small photosynthetic light harvesting antennas of bacteria and plants. Apart from our better understanding of quantum effects in these biological systems, these studies also pave the way for the rational design of optimal molecular photonic structures to achieve efficient transport of excitons [83]. Such analysis would be quite useful in designing organic semiconductors that provide an attractive alternative for the sustainable production of materials and devices in some of the emerging applications, such as consumer electronics, solar energy capture, photocatalysis, quantum computing, communication and sensing [83][84]. Clearly, a lot of work has to be done in this direction to test the proposed hypothesis, address raised controversies and discover many more functional quantum behavior [81]. Recall, e.g., earlier reported results claiming that the dynamic long-lived electronic quantum coherence in the FMO BChl complex explain its extreme efficiency that allows them to sample vast areas of phase space for finding the most efficient path. However, more recent evidence indicates that the observed long-lived coherences originate from impulsively excited vibrations and are too fast for electronic coherences to play a significant role in the exciton transfer between pigments [85]. Even more recently, the effect of underdamped intramolecular vibrational modes on enhancing excitation energy transfer has been investigated in [86], using the approach based on the numerically exact hierarchy equation of motion. This study reported that the weakly coupled underdamped vibrational mode fuels a faster excitation energy transfer, elucidating that long-lived vibrations can, in principle, enhance energy transfer, without involving long-lived electronic coherence [86]. Thus, more studies are needed in this intrinsically interdisciplinary research field, not only to improve our understanding of the mechanisms behind the fundamental photosynthetic process of nature, but also to transfer these ideas into the next-generation artificial light-harvesting materials.

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