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Gathering Light: Artificial Photosynthesis

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1. Introduction

Life is dependent on photosynthesis, directly or indirectly. Photosynthesis is converting sunlight, water, and carbon dioxide into carbohydrates and oxygen (Govindjee et al., 2010). Artificial photosynthesis is a research field that attempts to replicate the natural process of photosynthesis. The goal of artificial photosynthesis is to use the energy of the sun to make different useful material or high - energy chemicals for energy production. In this regard, a good question is that why artificial photosynthesis is important and necessary?

There are some reasons for believing that artificial photosynthesis is necessary in future. Two reasons are very important: the first, oil will become scarcer and more expensive and we should find a better source of energy. The second is causing serious environmental problems by fossil fuels.

Artificial photosynthesis could be divided into a series of approaches:

2. Antenna systems

Absorbing photos by an antenna pigment is the first stage in photosynthesis. Pigments can be a chlorophyll, xanthophylls, phycocyanin, carotenes, xanthophylls, phycoerythrin and fucoxanthin depending on the type of organism and a wide variety of different antenna complexes are found in different photosynthetic systems. Each year, the energy of 10^{24} Joule reaches the planet's surface through solar radiation. It is interesting that this is three orders of magnitude more than what is projected for the future global anthropogenic energy demand of

10^{21} Joule (Moore, 2005). The development of artificial antenna for collecting and harvesting solar energy efficiently is an active and complex field as the distance between the pigments to be used, their respective angle, and electronic coupling, must be engineered carefully. Sakata et al. (2001) have designed and synthesized a well-defined, rigid-sheet-structured oligoporphyrin (Fig. 1) with 21 porphyrin chromophores. The compound is a model for light harvesting compounds in *Nature* and showed promising properties for collecting and harvesting solar energy.

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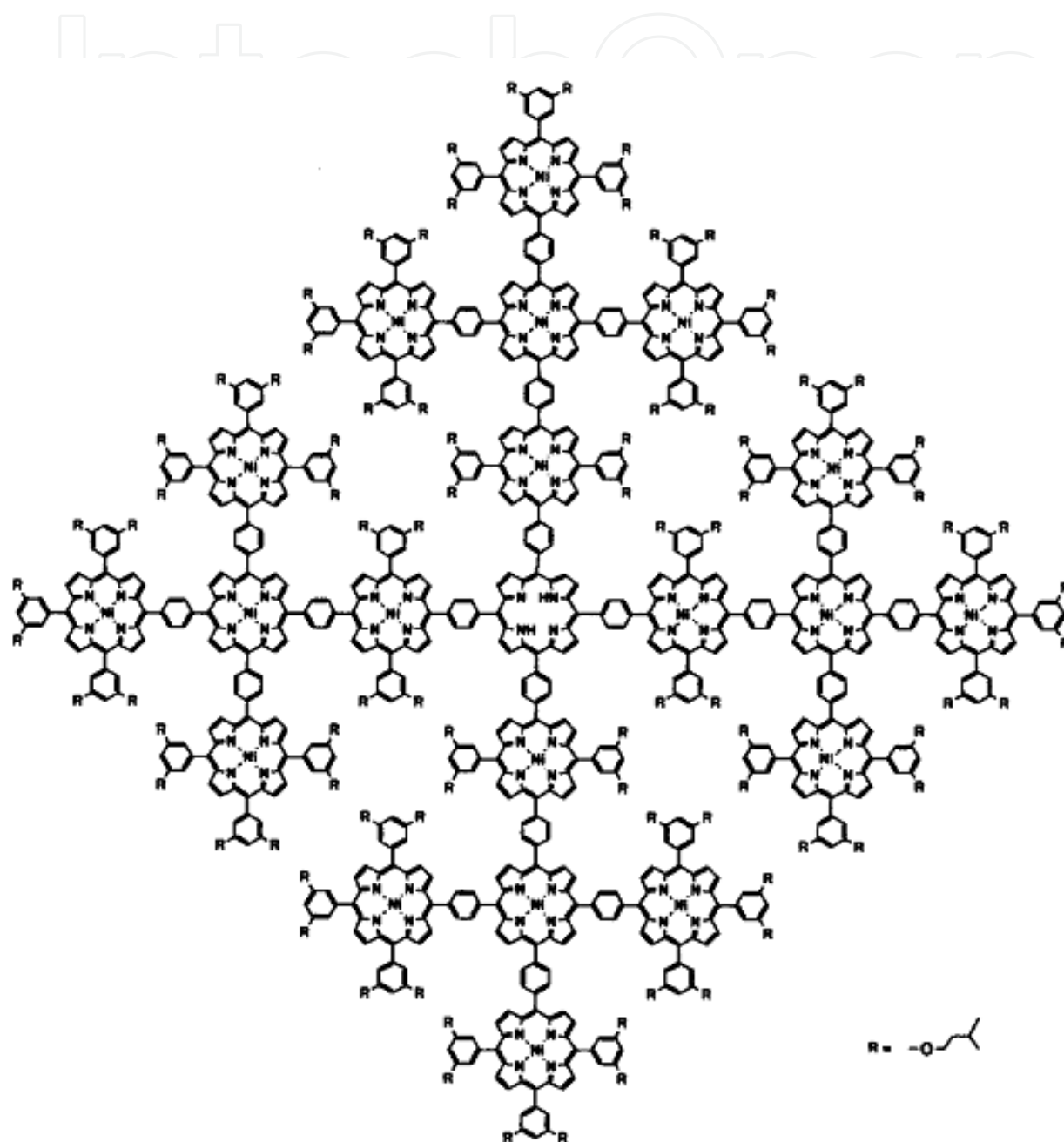


Fig. 1. An artificial antenna for collecting and harvesting solar energy

3. Photoactive chromophore

Synthetic porphyrin derivatives have been widely used to mimic the natural chlorophyll pigments to convert light energy into chemical energy. $[\text{Ru}(\text{bpy})_3]^{2+}$ presents an absorption band in the region around 450 nm corresponding to a metal to ligand charge transfer (MLCT) band with an extinction coefficient of about $13,000\text{M}^{-1}\text{cm}^{-1}$. Upon irradiation in the MLCT band, the input light energy is converted into a $(d^6) \rightarrow (d^5\pi^*)$ excited state, which in turn relaxes to form the lowest triplet state ($^3\text{MLCT}$) in less than a picosecond. The oxidation potential of $[\text{Ru}(\text{bpy})_3]^{3+}$ is similar to oxidized photosystem II primary donor in natural photosynthesis, therefore making it a suitable candidate to reproduce the oxidation reactions performed by the natural system.

4. Water oxidizing complex

The hydrogen production from water splitting is an appealing solution for the future energy as discussed by Bockris (Bockris, 1977). A strategy is to employ solar, wind, ocean currents, tides or waves energy to water splitting. However, to evolve hydrogen efficiently in a sustainable manner, it is necessary first to synthesize a stable, low cost, and efficient, environmentally friendly and easy to use, synthesis, manufacture catalyst for water oxidation, which is the more challenging half reaction of water splitting. In past few years, there has been a tremendous surge in research on the synthesis of various metal compounds aimed at simulating water oxidizing complex (WOC) of photosystem II. Particular attention has been given to the manganese compounds aimed at simulating the water oxidizing complex of photosystem II (Umena et al., 2011) not only because it has been used by *Nature* to oxidize water but also because manganese is cheap and environmentally friendly.

5. The dye-sensitized solar cell approach

Photovoltaic is a method of generating electricity by converting light into electricity. Photovoltaic devices work base on the concept of charge separation. A new family of devices, the dye-sensitized solar cell, is shown in Fig. 2. In the system, there is an oxide layer (for example TiO_2) which to allow for electronic conduction to take place. The material oxide layer is attached to a monolayer of the charge transfer dye. Photo excitation of the dye results in the injection of an electron into the conduction band of the oxide. Usually the iodide/triiodide couple restores the original state of the dye. The dye-sensitized solar cell made of low-cost materials, robust, does not require elaborate apparatus to manufacture, can be engineered into flexible sheets, requiring no protection from minor events like hail or tree strikes. Thus, there are technically attractive. In this devise, light is absorbed by a dye, the sensitizer is grafted onto the TiO_2 surface and then light induced electron injection from the adsorbed dye into the TiO_2 conductive (Grätzel, 2003).

In Fig. 3 comparing between the spectral response of the photocurrent observed with the two sensitizers and TiO_2 is shown (Grätzel, 2003). The incident photon to current conversion efficiency of the dye-sensitized solar cell is plotted as a function of excitation wavelength. Both chromophores show very high incident photon to current conversion efficiency values in the visible range. Some companies work to develop dye-sensitized solar cells for applications in cars and homes.

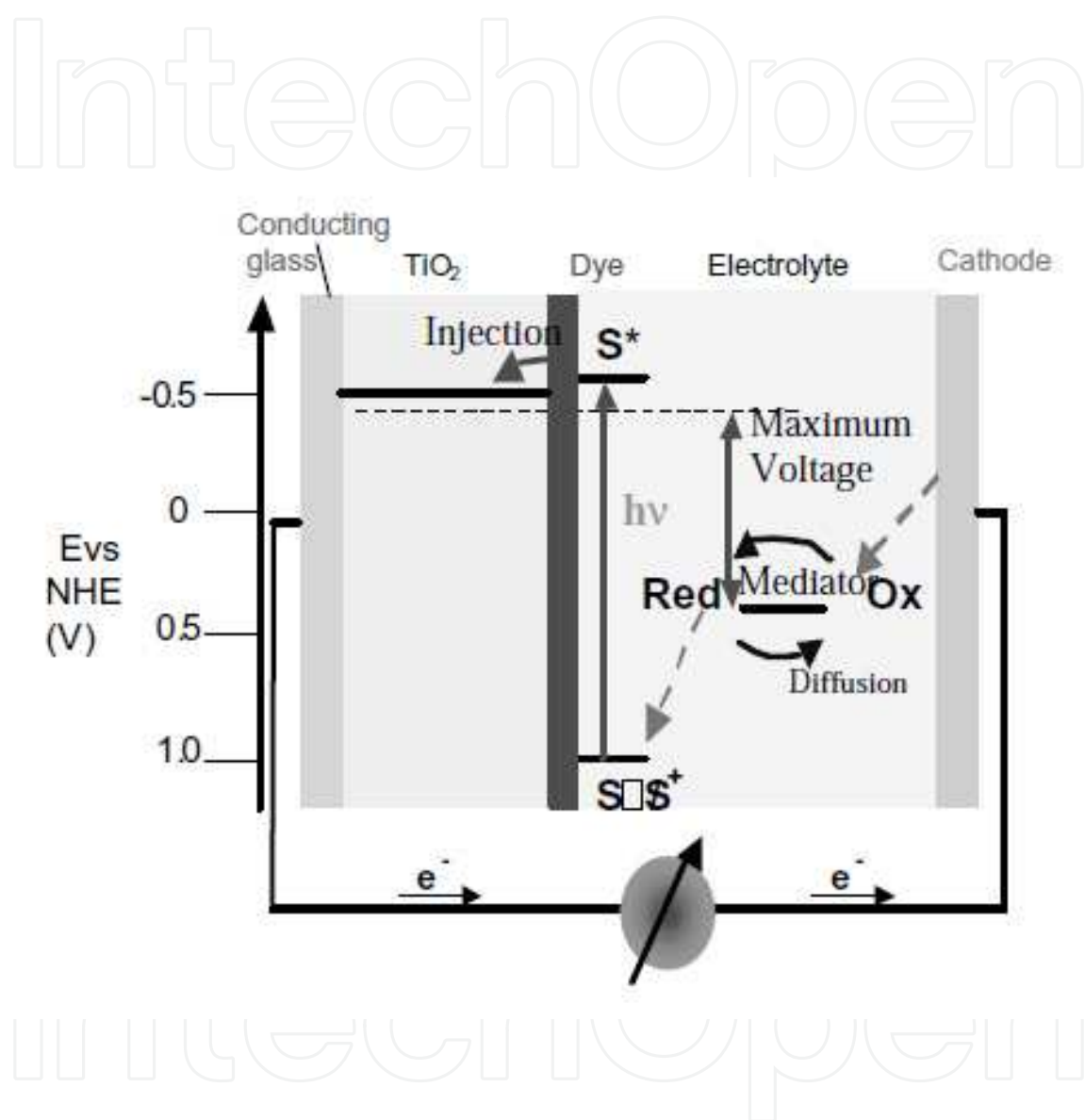
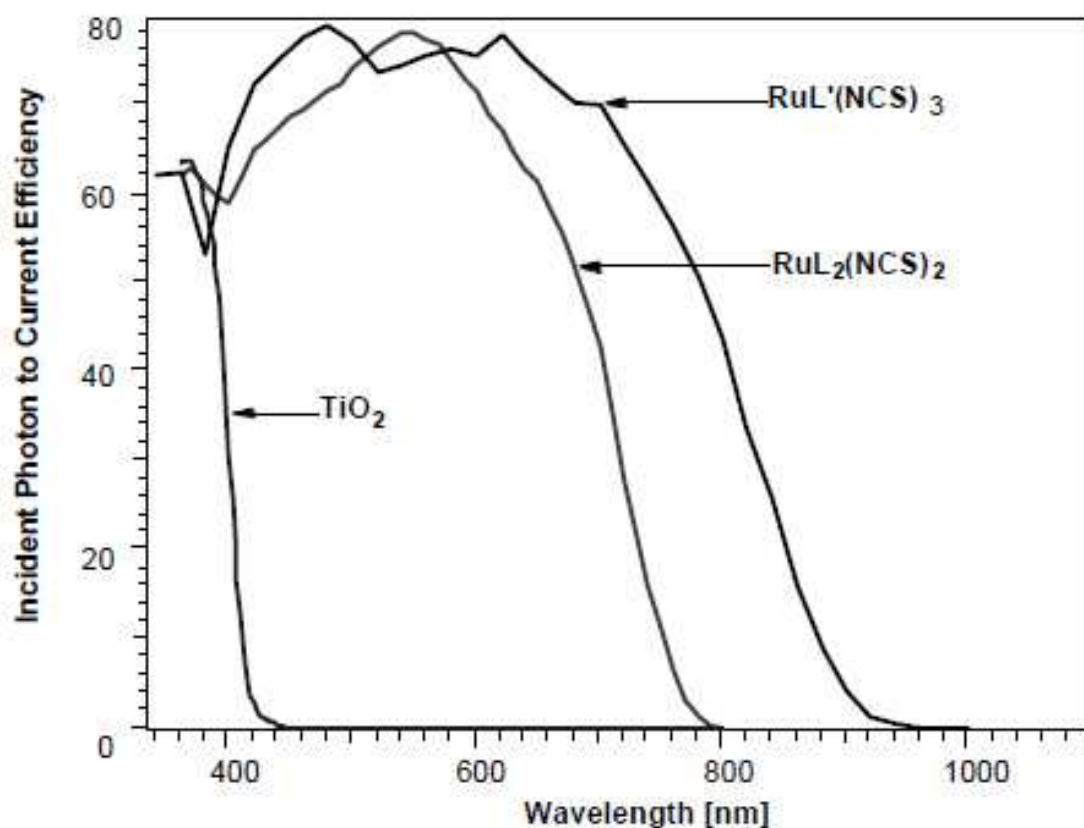


Fig. 2. A schematic presentation of the operating principles of the dye-sensitized solar cell (The figure was reproduced from Grätzel, 2003).



L = 4, 4'-COOH-2,2'-bipyridine

L = 4,4',4''-COOH-2,2':6',2''-terpyridine

Fig. 3. The incident photon to current conversion efficiency of the dye-sensitized solar cell is plotted as a function of excitation wavelength. (The figure was reproduced from (Grätzel, 2003)).

6. Algal systems for hydrogen

Biological hydrogen production is a method of photobiological water splitting which done based on the production of hydrogen by algae. In 1939, it was observed that a green - algae would sometimes switch from the production of oxygen to the production of hydrogen. In the late 1990s, professor Anastasios Melis discovered that if the algae culture medium is deprived of sulfur it will switch from the production of oxygen (normal photosynthesis), to the production of hydrogen. However, under normal conditions where oxygen is a by-product of photosynthesis, sustained algal hydrogen photoproduction cannot be maintained for more than a few minutes. Many research groups are currently trying to find a way to take the part of the hydrogenase enzyme that creates the hydrogen and introduce it into the photosynthesis process. These include molecular engineering of the hydrogenase to remove the oxygen sensitivity and development of physiological means to separate oxygen and hydrogen production. The result would be a large amount of hydrogen, possibly on par with the amount of oxygen created (Federico Rossi & Mirko Filippini, 2011).

7. Carbon capture and storage

The concentration of carbon dioxide in the atmosphere has risen from 280 to 370 PPM from 1860 to recent years. Industrial emission of CO₂ into the earth's atmosphere presently exceeds 10¹⁰ tons per year. Storage of the CO₂ either in deep geological formations, in deep ocean masses, or in the form of mineral carbonates is a way to decrease of CO₂ in atmosphere. In the case of deep ocean storage, there is a risk of decreasing pH an issue that also stems from the excess of carbon dioxide already in the atmosphere and oceans. In this regard, several concepts have been proposed. Injection CO₂ by ship or pipeline into the ocean water column at depths of 1000 - 3000 m, forming an upward-plume, and the CO₂ subsequently dissolves in seawater, injecting CO₂ directly into the sea at depths greater than 3000 m, where high-pressure liquefies CO₂, making it denser than water, and is expected to delay dissolution of CO₂ into the ocean and atmosphere, storing CO₂ in solid clathrate hydrates already existing on the ocean floor or using a chemical reaction to combine CO₂ with a carbonate mineral. Geological formations are currently considered the most promising sequestration sites. Geological storage involves injecting carbon dioxide, generally in supercritical form, directly into underground geological formations. Various physical and geochemical trapping mechanisms would prevent the CO₂ from escaping to the atmosphere. Recycling CO₂ is likely to offer the most environmentally and financially sustainable response to the global challenge of significantly reducing greenhouse gas emissions. Using artificial photosynthesis, scientists try to find a way to produce useful organic compounds from CO₂. For example, CO₂ and other captured greenhouse gases could be injected into the membranes containing waste water and select strains of organisms causing an oil rich biomass that doubles in mass every 24 hours or to convert CO₂ into hydrocarbons where it can be stored or reused as fuel or to make plastics (Cook, 2005).

8. Ribulose-1,5-bisphosphate carboxylase oxygenase

Ribulose-1,5-bisphosphate carboxylase oxygenase (RuBisCO) is an enzyme involved in the Calvin cycle that catalyzes a process by which CO₂ are made available to organisms in the

form of energy-rich molecules such as glucose. RuBisCO catalyzes either the carboxylation or the oxygenation of ribulose-1,5-bisphosphate.

It is believed that RuBisCO is rate-limiting for photosynthesis in plants and it is proposed that may be possible to improve photosynthetic efficiency by modifying RuBisCO genes in plants to increase its catalytic activity (Spreitzer & Salvucci, 2002). Engineered changes in Rubisco's properties Unpredictable expression of plastid transgenes and assembly requirements of some foreign Rubiscos that are not satisfied in higher-plant plastids provide challenges for future research.

There are the most important titles in artificial photosynthesis but we could increase our list as important titles in artificial photosynthesis and as it is considered by Pace, artificial photosynthesis is an umbrella term. As you see in each title, inspired by natural photosynthesis, in artificial photosynthesis novel approaches used to develop technologies for non-polluting electricity generation, fuel production and carbon sequestration using solar energy. (Pace, 2005). Researchers and scientists are trying to learn a great about the detail of natural photosynthetic systems and have been able to understand at least parts of this process. Therefore, artificial photosynthetic goal and capable of converting sunlight into chemically-bound energy seem to be a realistic scenario in near future.

9. Acknowledgment

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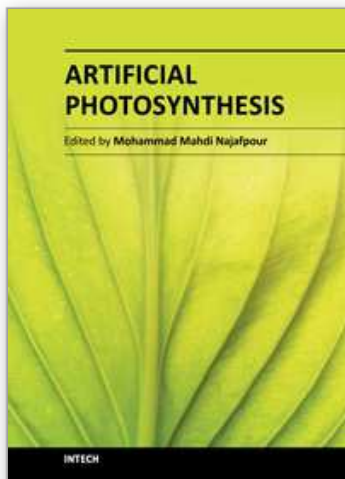
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Photosynthesis is one of the most important reactions on Earth, and it is a scientific field that is intrinsically interdisciplinary, with many research groups examining it. We could learn many strategies from photosynthesis and can apply these strategies in artificial photosynthesis. Artificial photosynthesis is a research field that attempts to replicate the natural process of photosynthesis. The goal of artificial photosynthesis is to use the energy of the sun to make different useful material or high-energy chemicals for energy production. This book is aimed at providing fundamental and applied aspects of artificial photosynthesis. In each section, important topics in the subject are discussed and reviewed by experts.

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