

Review and Critical Analysis of the Research Papers published till date on Artificial Photosynthesis

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ABSTRACT

Artificial photosynthesis is a very important necessity in the world to full fill our requirement of energy consumption. And also, resolve the Environmental issues like global warming. Every year a number of publications appear in various journals and conferences claiming to offer Different technique and method developed of artificial photosynthesis for resolve environment issues and fulfil energy requirement of the world. In year no.of publication in various journal, research etc. offer different method to resolve this problem. This review paper provides a concise yet comprehensive critical analysis of these techniques with an in depth review of their advantage and application. . This review is unique as there has been no other research paper so far that offers such a complete and up-to-date investigation of artificial photosynthesis techniques in the world. Therefore this research paper can serve as a precise reference for the future research on artificial photosynthesis.

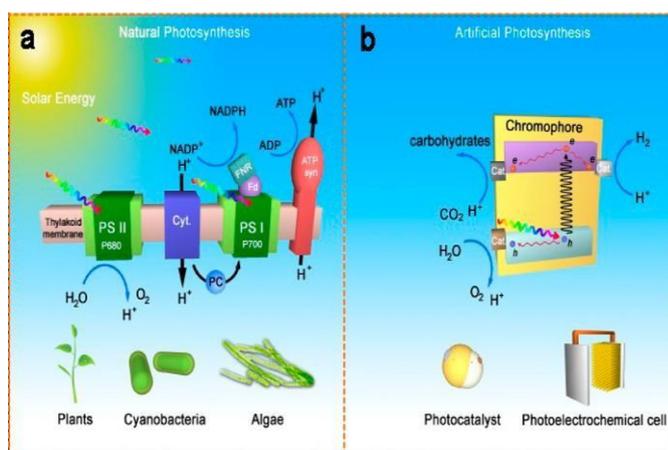
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INTRODUCTION

In my opinion, this decade is witnessing the widest consequences of man-made activities on our planet. The environmental risk for public health is now at a record high and does represent an even greater challenge than global warming and climate change. Indeed, staggering air and water pollution worldwide-now chronic in certain major cities in Asia and in the Western world-due to toxic gases, chemicals, and ultrafine particles from industry, agriculture, and transportation sectors has become one of the most, if not The most, important problem that humanity is facing. Consequently, it is now crucial to transition to new societies where environmental, energy, and economic policies are no longer based on endless-growth financial models and fossil fuel technologies to substantially decrease our ecological footprint and environmental and health impact. As a matter of fact, everyone is at risk of inflammatory reactions and lung infections to cancer and death. It affects millions every year and not only in emerging countries but in rich nations; furthermore, air and water pollution knows no borders, easily crossing countries and continents, via naturally occurring atmospheric and oceanographic current patterns. The origin of this strong imbalance between human activities and the environment can be found in the endless-growth

economic system in place in major countries worldwide. Indeed, this model inherently requires the use of endless cheap energy to be sustained, hence the massive use of coal and fossil fuels as energy sources for a more profitable energy return on energy invested, which might be good for the economy but clearly is not for our environment, health, and sustainable future. Energy conservation has rightfully been pushed forward upon people but turned out not to be as effective as originally thought given the fact that when fuel/energy demand decreases so does its price, which in turn leads to more consumption (of cheaper energy). Technology, through innovations, has always helped boost the economy and has done it numerous times throughout civilizations, even recently with solid-state lighting technology for instance. However, technological innovation enabling large-scale implementation of a renewable, sustainable, and environmentally friendly substitute energy source into our societies is clearly in itself an entirely different problem and daunting task. Moreover, the transition period time must be contained, ideally within a decade, to avoid devastating environmental pollution and health impacts as well as energy shortages, resources depletion, and world economic crisis. Technological advancements must also involve large-scale, clean, and cost-effective fabrication techniques at moderate to low temperature and be based on highly efficient materials that mostly contain earth-abundant elements, easily extractable and fully recyclable rather than expensive, scarce, and toxic metals, and rare earths. In addition, given that conventional technologies that attempt to improve the efficiency and performance of existing materials and devices by further development along the same incremental approaches are reaching their limits, it is also crucial to develop novel (multi)functional materials where bulk limitations are overcome by changing the fundamental underlying physics and chemistry, by, for example, Nano scale design and quantum confinement effects. And Despite mixed response from the public and scientific communities on climate change, recent reports [1,2] reiterated the grim links among persistent anthropogenic CO₂ emission, rise in global temperature and the increased occurrence of extreme seasonal weather. Together with concerns about energy supply and energy efficiency, artificial photosynthesis process has been emerging as one of the most promising solutions. Artificial photosynthesis is capable of not just generating alternative source of energy but also reducing and/or recycling waste products such as CO₂. Furthermore, with 120 000 TW worth of practically free solar radiation received by the earth each year, development of artificial photosynthesis systems (APS) using CO₂ as feedstock makes an excellent economical affordable and environmentally friendly source of renewable energy. Solar Energy Conversion to Chemical Fuels. Solar energy is indeed the largest exploitable renewable energy resource, providing more energy to our blue planet per hour than the total energy consumed by human activities in 1 year. Direct conversion of solar energy into chemical fuels does represent an optimal approach to address the globally growing energy demand in a sustainable way. Photosynthesis is a massive production activity by nature when sunshine is shed on earth. The product is food for life.

As those products were converted, stored, and transformed with time, fossil fuel was generated and contained beneath the earth's crust. Natural photosynthesis, which is conducted by cyanobacteria, algae, and plants, uses solar energy to reduce CO₂ to carbohydrates. Cyanobacteria and plants have evolved into highly organized photosynthetic systems. In this system1(Figure 1a), solar-to-chemical energy conversion was



conducted with interconnected light-harvesting systems, highly efficient charge separation functions, and the reaction center Photosystem I and II (PSI and PSII), followed by a dark reaction of the electron transport chain of the cytochrome with coenzyme NADPH as a redox carrier and the Calvin cycle for CO₂ reduction. In PSII, a central pair of chlorophylls, P680, is excited with an electron for CO₂ reduction, and then, its oxidized form, P680 is recovered by the electron from a Mn₄Ca-oxo cluster, which carries out the biological oxidation of water. Artificial Photosynthesis, which aims to emulate natural processes using man-made devices, is the best way to convert and store solar energy using chemical fuels as feedstock. For an artificial system (Figure 1b), a more practical approach is a direct and efficient way to convert abundant materials in nature like (sea)water and CO₂ to useful chemicals, for example, H₂, CO, and hydrocarbons. Compared to photovoltaic (PV) solar energy conversion, artificial photosynthesis converts sunlight into chemical products. While different from electricity energy storage, chemical fuel storage is more viable for massive energy storage, a requirement for future alternative renewable and sustainable energy sources. The challenges to achieve efficient artificial photosynthesis are now the focus of many worldwide ongoing scientific efforts and will have to be solved in the near future by concomitant multidisciplinary efforts from scientists from all basic sciences as well as engineers from various fields. it uses H₂O as both the electron donor and the proton source.

Pioneering work on photocatalytic CO₂ reduction was reported by Halmann in 1978, who bubbled CO₂ over a p-type GaP cathode illuminated with a Hg lamp yielding formic acid, formaldehyde, and methanol. Most of the commonly reported photosynthetic systems mimic the natural photosynthetic process yet incorporate only the most essential steps, that is, CO₂ reduction and H₂O oxidation. Significant developments in a variety of photo catalytic systems for photochemical CO₂ reduction have been achieved and reviewed. The reported systems are hybrids of semiconductors or molecular metal complex catalysts or are coupled with co catalysts and plasmonic photo catalysts working under sunlight irradiation.

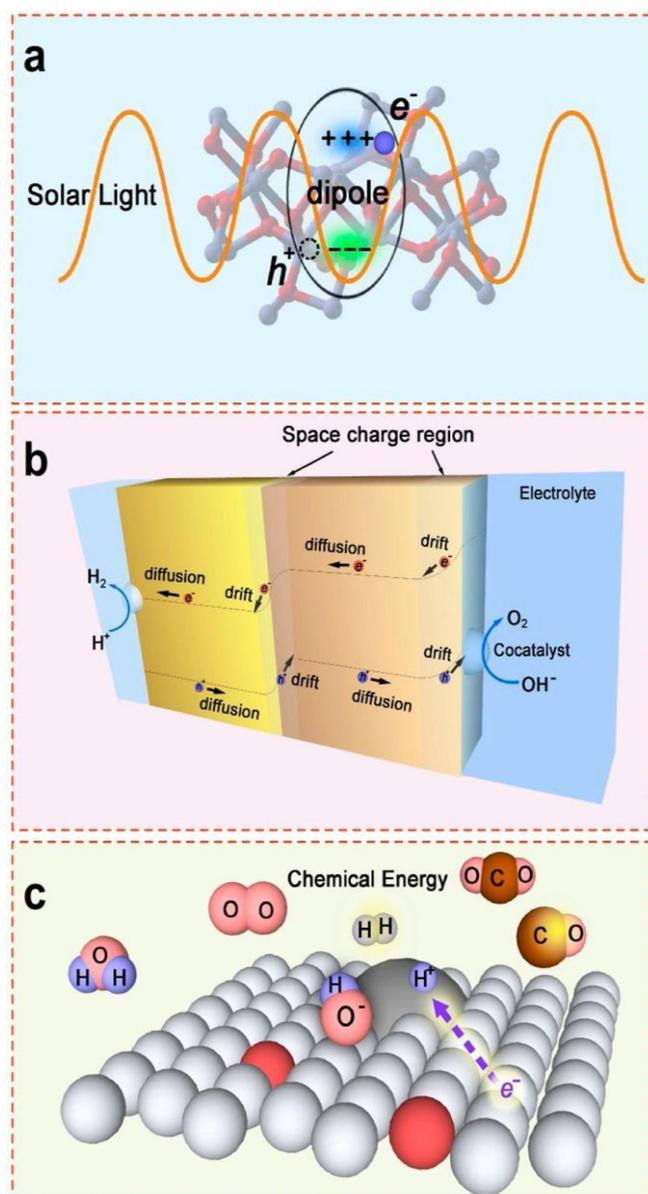


Figure 2. Schematic elementary steps from light energy to chemical bond energy. (a) Light absorption: the oscillating electric field of the incoming light induces an oscillating dipole within the chromophore associated with the photosynthetic system, leading to electron transition to a higher electronic energy state. (b) Charge carrier transportation/separation: photo excited electrons and holes are separated by the space charge regions established at the interfaces, the energy being carried by the electrons and holes. (c) Surface reaction: The electrons and holes reduce and oxidize the water to produce hydrogen and oxygen, respectively, with energy stored in the chemical bonds. As depicted in Figure 2, converting light energy to chemical bond energy requires three main steps, which are light absorption, charge carrier transportation/separation, and surface reaction. All three steps should be efficient enough to achieve substantial overall conversion efficiencies. Nano structural Design. Researchers turned back to earth abundant oxides such as TiO_2 , WO_3 , and $\alpha-Fe_2O_3$. This return was promoted by the emergence of low-cost nanostructure synthetic procedures such as hydrothermal and template assisted methods. These fabrication

techniques are simple and easily accessible to researchers in various fields and draw intense attention to novel nanostructure material development for artificial photosynthesis. In this context, earth-abundant transition-metal oxides became model photo electrodes intensively investigated for their PEC water-splitting properties. For most of them, charge recombination still remains a major barrier for efficient photochemical conversion. The competition between charge transfer (separation) and recombination determines the internal quantum efficiency of the water-splitting reaction.

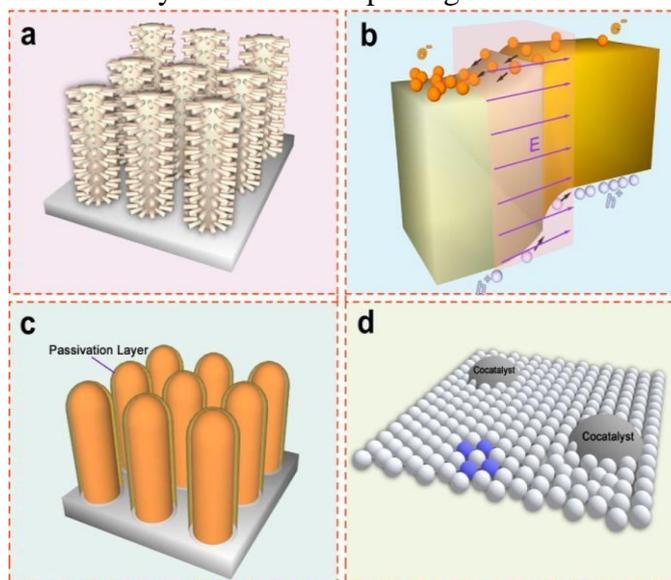


Figure 3. Common new strategies to improve overall efficiency. (a) Smart nanostructures: ordered hierarchical structures improve the surface area while keeping grain boundaries at a minimum. (b) Hetero junctions: promote the electron-hole separation by driving them toward opposite directions due to inherent built-in electric field. (c) Surface protection: a passivation layer is conformally deposited to prevent corrosion and eliminate surface state recombination centers. (d) Surface modification: co catalyst deposition and surface engineering facilitate the water reduction and oxidation reactions. Surface Passivation. A passivation layer is applied to improve the (photo) chemical stability of the semiconductor when operating in an electrolyte. The most effective material, so far, for passivation is TiO_2 , which has been tested on Si, GaAs, and InP. Other materials such as TiO_2 or an ultrathin carbon sheath were deposited on Cu_2O -based hetero junctions as a surface protection layer against photo corrosion to form buried semiconductor junctions for improved performance in photocurrent density and onset potential. Dual-layer thin TiO_2/Ni coatings were also utilized to stabilize polycrystalline BiVO_4 photo anodes against photo corrosion in an aqueous alkaline ($\text{pH} = 13$) electrolyte

Geometrical consideration

One of the ways of improving photo catalyst performance is by applying nanostructured morphology. This provides both increased available surface for catalytic reaction and improved light absorption by acting as a non-reflective surface or light traps. There are two things that we can learn from the already established solar cell technology, improved surface area from nanotube arrays [4] and light sensitisation by means of dye absorption [5]. Nanotubes with large porosity can benefit the photo conversion efficiency from two

aspects. First, the large surface areas ensure the stronger light absorption and simultaneously a much shorter path towards wall surface than the hole diffusion length. Second, a larger inner space of nanotube is important to accelerate the ion migration in the tube and overcome the kinetic bottleneck [6]. Significant improvements in photo electrochemical performance have also been reported when highly porous branched TiO₂ was used

[7]. These branches not only increase the effective surface area, but also improve light absorption. The other example is ZnO rods. Recent findings show significant photocurrent improvement by ZnO grown on grooved substrate compared to planar nanotube arrays, linked to improved light trapping performance. The novel grooved Si design doubles light absorption as back-reflecting mirror, improving the photo electrochemical efficiency by a factor of 5 [8].

ADVANTAGES

- H₂ can be then be stored and either burned or run through a fuel cell to generate electricity.
- Resolve the global warming issue.
- Full fill the energy requirement.
- Fossil fuels are in short supply, and they're contributing to pollution and global warming. Artificial photosynthesis could offer a new, possibly ideal way out of our energy predicament.
- It has benefits over photovoltaic cells, found in today's solar panels. The direct conversion of sunlight to electricity in photovoltaic cells makes solar power a weather- and time-dependent energy, which decreases its utility and increases its price. Artificial photosynthesis, on the other hand, could produce a storable fuel.
- Unlike most methods of generating alternative energy, Artificial photosynthesis has the potential to produce more than one type of fuel.
- Artificial Photosynthesis produces a clean fuel without generating any harmful by-products, like greenhouse gasses and makes it an ideal energy source for the environment

DISADVANTAGES

- Safe storing of hydrogen gas.
- Freezing in sub zero temperatures.
- The efficiency needs to be improved.
- For high performance, the cost due to huge silicon solar cell increases.
- One of the major disadvantages of the artificial photosynthesis today is the fact that materials used often corrode in water, as most hydrogen catalysts are very sensitive to oxygen, being inactivated or degraded in its presence.
- The manganese that acts as a catalyst in plants doesn't work as well in a man-made setup, mostly because manganese is somewhat unstable.
- The other big obstacle is that the molecular geometry in plants is extraordinarily complex and exact -- most man-made setups can't replicate that level of intricacy.

Concluding remarks

Despite significant progress in the recent years, photo catalytic solar fuel generation from CO₂ is still far behind its counterpart water splitting. Furthermore one commonly reported problem is the diversity of reaction products, ranging from CO, CH₄, methanol, format /formic acid which are multi-electron process thus kinetically very challenging. It is also increasingly difficult to switch the reaction preference to favour carbonaceous product rather than highly competitive H₂ generation. The crux of the problem is lack of appropriate co-catalyst, like the widely used Pt for H₂ evolution catalyst. And

Despite great academic advances within the past decade, artificial photosynthesis for solar water splitting remains in its infancy and is frankly in critical need of efficiency standardization and certification (similar to the PV industry). This could easily be achieved through intensive industry-driven academic research (or academic-driven industrial research, whichever is the easiest and fastest) to unfold as a viable and striving technology. As important are new global energy and environmental policies, not necessarily in agreement with existing techno economic analysis and highest-profit/ endless growth driven financial systems, from governments worldwide to help implement solar water splitting (along with all other renewable energy sources for that matter) as the cleanest sustainable energy technology for our societies. Moreover, substantial financial support to scientists, engineers, and entrepreneurs should become available to actively spin-off academic research studies and develop businesses and companies for large-scale implementation of solar hydrogen generation. and Achieving the stoichiometric chemistry is another challenge.

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