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# Photocatalysis: Implications in Zero carbon society

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## Abstract

**I**n this gen-Z world of rapidly increasing technology and rapidly increasing pollution, it is important to reduce carbon emission so that global warming is reduced which has already started affecting the weather pattern on the earth detrimentally. From a global perspective, it is necessary to instill sustainability in research nowadays which will cause impact on the society. Sustainability is the new key to pollution free earth. This study has been done to contribute to the understanding of certain chemical compounds called perovskites that will be of great use in the making of next generation solar cells. This report elucidates the painstaking process of building a photocatalysis setup in the lab. In addition to this the procedure of

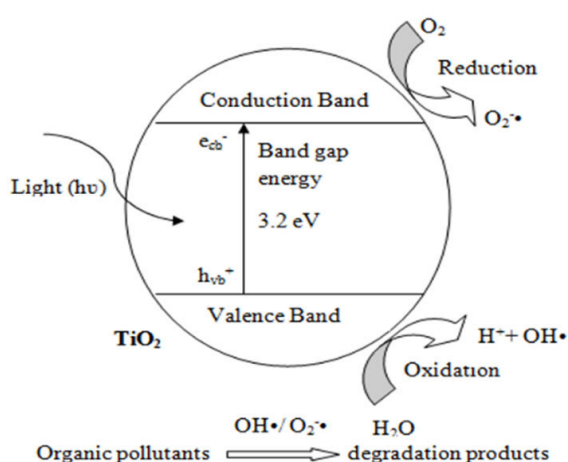
synthesis of perovskites and their unique features have also been discussed after a detailed study. Our aim in this paper is to make a setup of photocatalysis and to test the working of perovskites, synthesised in the lab by that device.

## Introduction

Ferroelectricity is a characteristic of certain materials that have a spontaneous electric polarization that can be reversed by the application of an external electric field. The ability of some materials to generate an electric charge in response to applied mechanical stress is called piezoelectric effect. All ferroelectrics are pyroelectric, with the additional property that their natural electrical polarization is

reversible. Since times immemorial, human beings have been in an attempt to mimic natural processes to lead life and enhance the way of living. And now, looking at global crisis we all are facing, research and sustainability come hand in hand. The development of green, sustainable, and economical chemical processes represents a cornerstone challenge within chemistry today.

Just like aeroplanes were made by being inspired by birds, similarly in this era of deforestation, scientists are searching new ways of  $CO_2$  reduction. By analysing how photosynthesis takes place in plants, the process of photocatalysis, aka, artificial photosynthesis has been developed. Though they are thermodynamically quite different from each other, but the main aim is to reduce  $CO_2$  and reduce global warming. Semiconductor heterogeneous photocatalysis is currently utilized within a wide variety of societally impactful processes, spanning reactions such as hydrogen production and  $CO_2$  conversion, to the organic transformation of raw materials for value-added chemicals. Metal halide perovskites (MHPs) have recently emerged as a new promising class of cheap and easy to make photocatalytic semiconductors, though their unstable ionically bound crystal structure has thus far restricted widespread application.



**Figure 1:** Photocatalysis

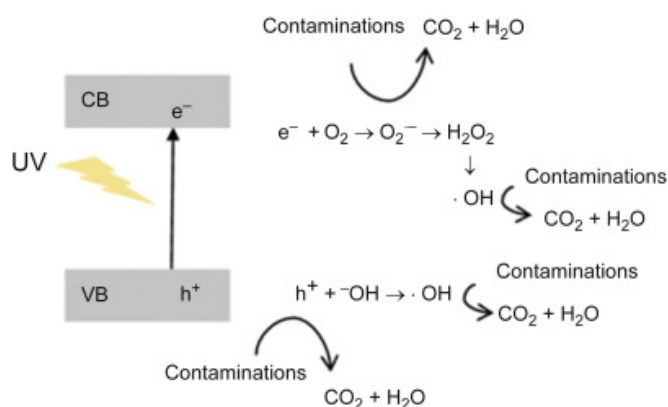
First, let us start with semiconductors. It is evident from the word itself that these materials

work as conductors only under certain conditions. The energy gap between the valence band and conduction band plays a very important role in the working of semiconductors. The merging of the physics of semiconductors and the chemistry of photocatalysts indeed make a good potential for being used in energy science. In the semiconductor photocatalysts, the electron in valence band is excited and jumps to its conduction band with light assistance. Substantially, the excited electrons and holes are transferred to the catalyst surface.  $TiO_2$  is one of the best semiconductor photocatalysts. The substrate that absorbs light and acts as a catalyst for chemical reactions is a photocatalyst. The electron hole pair is generated on exposure of a semiconductor material to light.

The meaning of photocatalysis is self explanatory. Photo means light and catalysis means breaking down. So photocatalysis is the process of breaking down of chemical components in the presence of light.

## History of ferroelectric materials and photocatalysis

The first ever work on photocatalysis was done by scientists Honda and Fujishima.



**Figure 2:** Honda Fujishima Effect

The method is called Honda-Fujishima effect, where photochemical  $H_2O$  splitting occurs using single-crystal Titanium electrode. The photocatalytic activity depends on the ability of catalyst to create electron-hole pairs that generate free hydroxide radical.

1. Band edges of electrode was not overlapping with acceptor and donor states(minimum band gap is to be 1.23eV).
2. Charge transfer from the surface of semiconductors were slow due to which photocorrosion took place.
3. Shift of band edges occurred due to which photon energy decreased.

*More about ferroelectricity:* The first ferroelectric material was prepared by scientist Pierre Signette in La Rochelle . The compound was potassium sodium tartarate tetrahydrate( $KNaC_4H_4O_6 \cdot 4H_2O$ ), commonly known as Rochelle Salt. Ferroelectric materials came to the market with commercial production of lead zirconate tartarate and other aurivillius oxides.

Ferroelectricity is observed only in crystal structures with space inversion symmetry breaking, where there is an asymmetric distance of positive and negative charges within crystal unit cell, which generates a dipole moment. And talking about piezoelectricity, there are 32 point symmetry groups and 21 non centrosymmetry groups that lack presence of inversion center in unit cell. Applying pressure to those crystals generate positive and negative charges which become the reason for generation of potential difference, thus leading to piezoelectricity. While, 10 noncentrosymmetric groups show a spontaneous electric polarization along a preferential direction and those materials exhibiting this property are called pyroelectrics.

With pyroelectrics whose polarization can be reversed by an external electric field are called ferroelectrics.

*Photocatalysis and photosynthesis:* First of all let us discuss about natural photosynthesis.

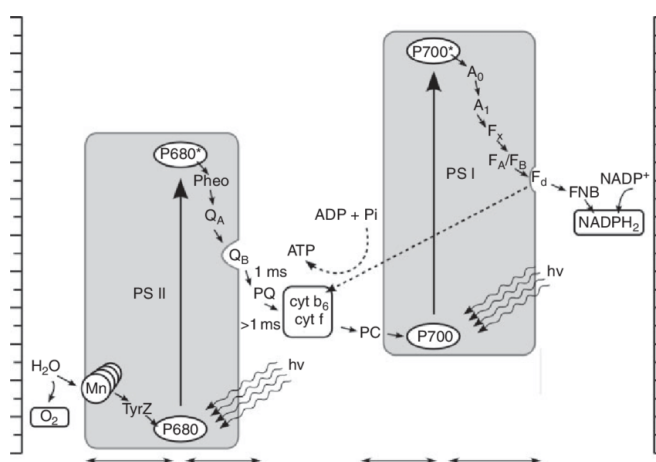
As we have discussed earlier that photocatalysis is a thermodynamically uphill reaction. Now we will discuss about the various schemes of photosynthesis.

### Z -SCHEME IN PHOTOSYNTHESIS:

This PS-I and PS-II are used in this scheme of photosynthesis. Upon illumination of the leaf by light, the chlorophylls in PS-II absorb photons with maximum wavelength , in this case which

is 680nm. So it is also called P680 due to this reason. Then the transfer of energy to PS-II occurs. This energy is used to extract electrons from  $H_2O$  and then produce oxygen by  $H_2O$  oxidation catalysis.

The electrons separation occurs and then they get transferred to PS-I. Chlorophylls of PS-I absorb photons, a reason due to which they are also called P700 since they absorb photons of 700nm. The photon energy excite electrons from PS-II. The electrons reduce  $NADP^+$  to NADP (Nicotinamide Adenine Dinucleotide Phosphate).



**Figure 3:** Photocatalysis setup

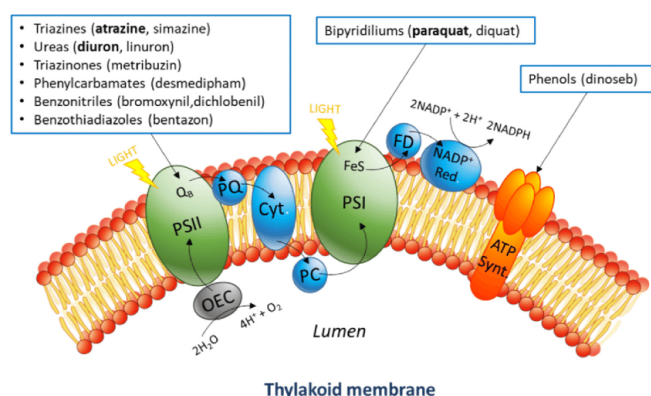
The proton gradient and the NADPH together involve in downstream reaction. For example, conversion of  $CO_2$  to H.C by Calvin Cycle. When a material uses light energy to drive thermodynamically uphill reactions( $(\Delta G > 0)$ ), then it is called photosynthesis. The material is called photocatalyst if the photon is a reactant, for example, water splitting, carbon dioxide reduction , which are essentially thermodynamically essential reactions.

The material, photocatalyst does not change thermodynamics of the reaction, rather, it changes the chemical kinetics and establishes new routes for chemical reactions. For example, oxidation of phenol to hydroquinone by oxygen.



**Figure 4:** Photocatalysis setup

The figure above shows the setup of photocatalysis apparatus that was setup in the lab of RGIPT.



**Figure 5:** Photosynthesis

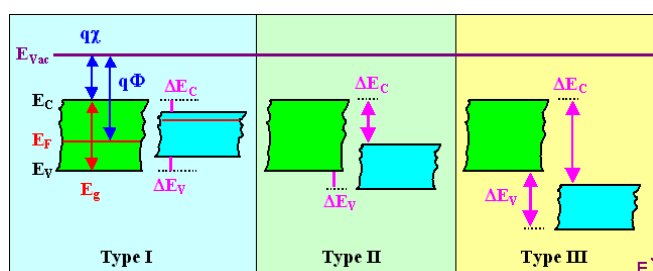
## Heterojunctions

Heterojunctions involve stopping of recombination, which otherwise would have hindered photocatalysis. The analogous material of heterojunctions that we use for the case of photocatalysis is, heterocatalysts.

Heterocatalysts are the coupling of two semiconductor photocatalysts. The driving force of a reaction depends upon the potential between the conduction band and valence band. If strong redox ability is the goal of a monocomponent photocatalyst, it showed to have a high conduction band and a deep valence band.

## Type II Mechanism:

The interparticle electron transfer to interparticle hole transfer occurs, when two coupled semiconductors display staggered band structures. After the electron and hole pairs are generated by both photocatalysts under irradiation, photogenerated electrons are transferred from photocatalyst I to photocatalyst II, while photogenerated holes are transferred from photocatalyst II to photocatalyst I. The electrons and holes are accumulated on photocatalyst II for reduction and on photocatalyst I for oxidation, so photogenerated holes and electrons are spatially separable.



**Figure 6:** Types of heterojunctions

**How the construction of Type II heterojunctions is done:**

1. Spatial separation is done at the cost of redox potential.
2. Photogenerated electrons accumulate on conduction band of pc II and holes on valence band of pc I.
3. Repulsion from existing electrons in pc II hinder continuous transfer of electrons from pc I.
4. Electrostatic attraction between electrons in pc I and holes inhibits electron transfer from pc I to pc II. Similar is the case for holes transfer from pc II to pc I.
5. Transfer mode weakens overall redox ability of heterojunctions. This phenomenon is similar to that of attraction between magnets and iron.



## Z scheme:

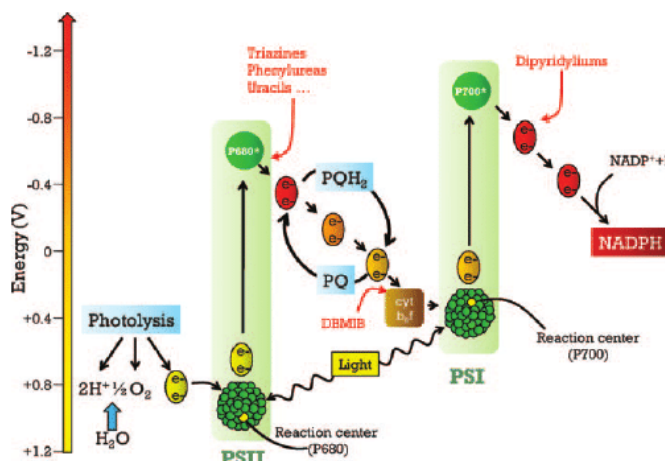


Figure 7: Z scheme mechanism-light reaction

Now we will discuss about the heterojunction that is generally used in Z-scheme light reactions, commonly referred to as Z-scheme heterojunctions.

### Construction:

The Z-scheme heterojunction is made up of two semiconductors with suitable intermediate couples ( $Fe^{3+}/Fe^{2+}$ ,  $IO_3^-/I^-$ ). It has staggered band configuration. The photogenic holes in valence band of photocatalyst I react with electron donors (to be denoted by D). As a result, the corresponding electron acceptors (to be denoted by A) form. The photogenerated electrons in the conduction band of the photocatalyst II react with A and it engenders D. The reserved photogenerated electrons in conduction band of photocatalyst I and holes in valence band of photocatalyst II involve in redox reactions.

This scheme has been found to have numerous advantages including strong redox capacity and spatially separable redox reaction sites.

However, some of the shortcomings are:

- It is confined to the solution phase and hence, has narrow scope of application.
- Shuttle redox ion pairs can achieve migration in solution only.
- Electrons have higher potential different than acceptors.

Now let us consider four reactions:



It is obvious that reaction III is much more favourable than I because the latter is against the mechanism.

- Light shielding occurs which leads to low utilisation of light.
- pH sensitivity turns up as an issue.

## Z-Scheme types:

### (I) All solid-state z scheme:

It is a three component nanojunction made up of  $Cd - Au - TiO_2$ . A solid conductor is used in place of shuttle redox pairs. They can also be used in gases. **However its disadvantages are:**

- Charge transfer problem
- prevention of Schottky barrier, suppresses electron flow from  $CdS$  and  $TiO_2$  to  $Au$ .
- low utilisation of light
- hard to control synthesis process, as conductors lie randomly on photocatalyst surface.

Due to these shortcomings, another kind of z-scheme heterojunction was developed, which has been discussed in the following part.

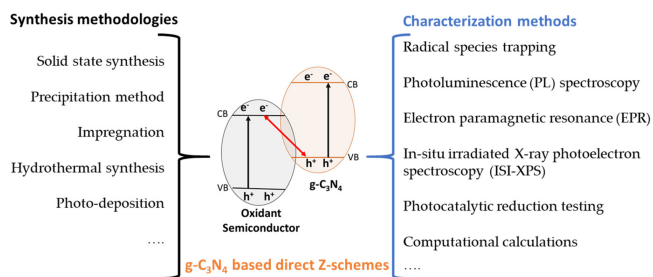
### (II) Direct Z-scheme:

Either redox couples or conductors are used as direct Z-scheme heterojunctions. It was first produced by scientist Gatzel. he prepared a tandem cell by coupling a nanocrystalline ( $Fe_2O_3$ ) on the top surface with  $TiO_2$  at the bottom.

It has various advantages that have catalysed its function as a heterojunction. **Some of them are:**

- Improved  $H_2$  performance
- Strong redox activity

- Charge carrier transfer scrutinized by density function theory.



**Figure 8:** Z scheme types

## S-Scheme heterojunctions:

The photocatalysts essentially involve in redox reactions, and the kind of reactions they are going to perform, as to whether it's oxidation or reduction depends upon the band structure of the photocatalysts. In the reducing photocatalysts, the conduction band is higher and they are generally used in constructing solar cells. In these types of photocatalysts, the photogenerated electrons are effective while the photogenerated holes are of no use. On the other hand, the oxidizing photocatalysts, it is vice versa and they are usually used for environmental degradation purposes.

In the S-scheme heterojunctions, both types of photocatalysts are used, and they exhibit staggered band structures. The charge transfer routes are different, similar to that of the type II heterojunctions. The photogenerated electrons and holes accumulate in the conduction band of reducing photocatalysts and valence band of oxidizing photocatalysts. The photogenerated charge carriers recombine which gives rise to a strong redox potential.

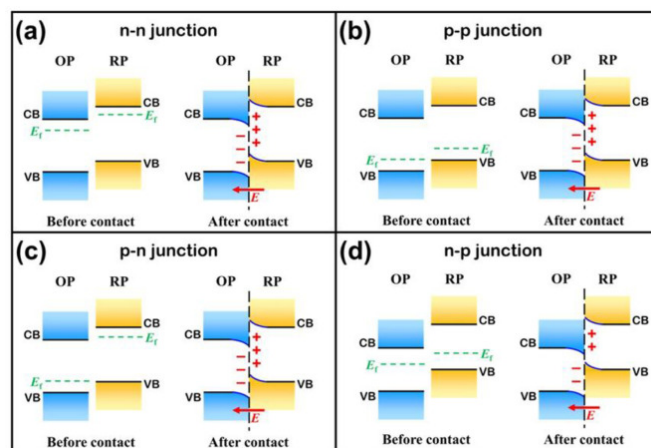
**The mechanism by which it occurs is:** The reducing photocatalyst has a higher conduction band, while the valence band has a smaller work-function. They come to close contact as a result of which electrons diffuse from the reducing photocatalyst (RP) to oxidizing photocatalyst (OP). The OP is negatively charged and the RP is positively charged, which generates an electric field, which accelerated the

transfer of photogenerated electrons from OP to RP. The Fermi energies of the OP increase while that of the RP decrease until they reach the same level. The band bending urges the photogenerated electrons in the conduction band of OP to and holes in valence band of RP at their interface to be recombined. This mechanism is an analogy to the fact that water always flows downhill. The photogenerated electrons in the conduction band of OP and the photogenerated holes in the valence band of RP recombine.

The factors that influence and affect the formation of S-scheme heterojunctions are the internal electric field between the photocatalysts, coulomb force and band bending. These kinds of photocatalysts are generally used in  $H_2$  production,  $CO_2$  reduction, bacteria disinfectant and pollution degradation.

**however, there are a few disadvantages of this scheme that are listed as follows:**

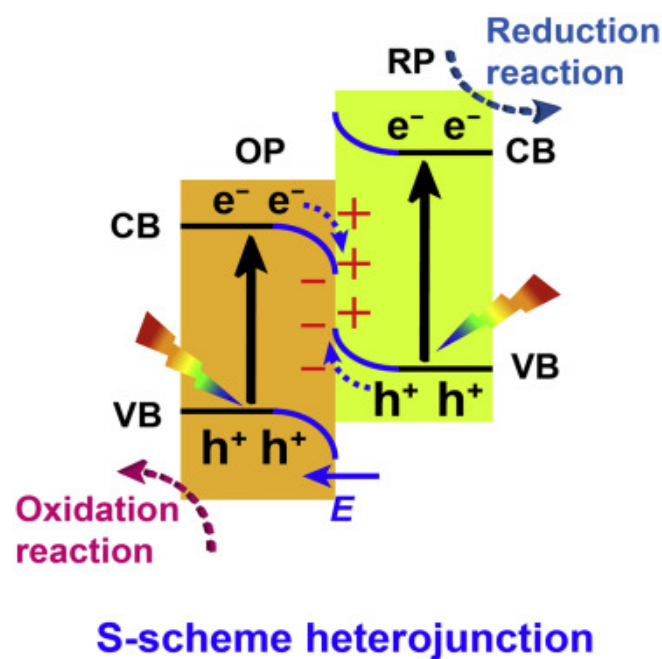
- They are limited to powder photocatalysts.
- They do not apply to photoelectrochemistry and solar cells with external circuit.
- Their construction is mostly limited to the use to two selected semiconductors, mostly n-type, with suitable band structures and Fermi levels.



**Figure 9:** Types of interfaces in S-scheme heterojunctions

Due to these shortcomings, various modifications can be brought to these s-scheme heterojunctions, like adjustments of the Fermi levels

of OP and RP by doping, modification by using co-catalysts that can benefit the charge separation. The oxidizing co-catalyst on the surface of oxidizing photocatalyst, and reducing co-catalyst below the surface of reducing photocatalyst can be done. And lastly, morphology engineering and interface regulation can largely help in the improvement in the performances of the S-scheme heterojunctions.



**Figure 10:** S-scheme heterojunction

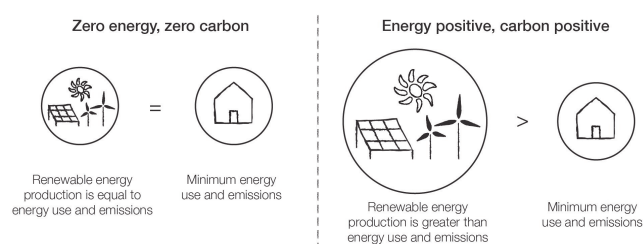
## Conclusion

In this article, we have discussed the basic idea of photosynthesis, how it has been mimicked by scientists to bring about the concept of photocatalysis. We have also thrown light upon the types of photocatalysis and how it is different from natural photosynthesis.

While elaborating on the mechanism, we have seen why there are chances of recombination taking place and how they can be eliminated using heterojunctions. So now, after getting a fairly good idea about the mechanism, we can move on to say that chemical compounds called perovskites have utmost potential to be used as photocatalysts due to their band structures, bandgaps, chemical characteristics and behavioral properties. Halide perovskites

are commonly used nowadays.

Cutting edge research is being conducted at various labs to modify the engineering and structure of these perovskites, modify them as carbon nanodots and study their properties by taking the help of sophisticated instruments like SEM and TEM. It is evident that if their use can be implemented in a easy way within day-to-day devices, a "greener society" will evolve. Pollution causing vehicles and machines can be vanquished and these perovskites can be implemented on Integrated circuits and achieve zero carbon society within a few years.



**Figure 11:** Zero Carbon

## Acknowledgements

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