

# Photo-catalytic Reduction of Carbon dioxide to Value Added Chemicals

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## Abstract

Among the various options for energy conversions, the reduction of water to produce hydrogen, reduction of carbon dioxide (to reduce the greenhouse effect) and the reduction of dinitrogen (for fertilizer production) assume great relevance in today's context. Among these three options, reduction of carbon dioxide has been focused in recent times due to the innumerable possible pathways. The objective of this presentation is to examine the prospects of these pathways and also to indicate how near these attempts are to commercial exploitation. It is true that commercial application of these processes are still a way ahead but many of the manufacturers are keenly watching the progress made in this sphere of activity.

## Introduction

Photo-catalysis is one of the emerging areas of research especially from the energy and environmental perspectives. In this direction three processes are important namely decomposition of water to generate hydrogen, reduction of dinitrogen to ammonia and reduction of carbon dioxide to produce hydrocarbon molecules. Among the various chemical species, carbon-dioxide is one of the atmospheric species which is receiving attention in recent times due to green house effect. The global average atmospheric carbon dioxide in 2019 was 409.8 parts per million (ppm for short), with a range of uncertainty of plus or minus 0.1 ppm. For centuries, the CO<sub>2</sub> level in the atmosphere was modulated by natural photosynthesis process involving the reduction of CO<sub>2</sub> by water. Since 1970, the CO<sub>2</sub> in the atmosphere has been increasing steeply (see Table.1.) due to excessive use of fossil based resources and due to the effects of large scale industrialisation.

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**Table 1. Concentration of carbon dioxide in the atmosphere**

Year	Amount (ppm)
1860	290 <sup>+</sup>
1970	320 <sup>+</sup>
1985	345 <sup>+</sup>
1987	348 <sup>+</sup>
1988	351 <sup>+</sup>
2000	400 <sup>+</sup>
2019	410 <sup>+</sup>
2020	415 <sup>+</sup>
2050	>600 <sup>*</sup>

<sup>+</sup> Estimated value.

<sup>\*</sup> Projected value

The common products of carbon dioxide photoreduction are CO, methanol, and methane, even though other products like formaldehyde, formic acid, and hydrocarbons are also reported. Theoretical calculations indicate that suitable semiconducting photocatalysts must exhibit low band-gaps (visible light spectrum absorption), increased charge transfer, and effective charge separations. While pristine catalysts like TiO<sub>2</sub> and g-C<sub>3</sub>N<sub>4</sub> have suitable properties, the semiconductor systems possess deficiencies like a high band gap and a high recombination rate which are not suitable for photocatalytic process. To overcome deficiencies of these systems, one can resort to defects integration (doping/oxygen vacancies), addition of cocatalysts (electron traps), or a synergistic system of combining two catalysts as in the so called Z-scheme catalyst configuration.

It is necessary that one carefully analyses the equations involved in the formation of these preferred products alone though, the whole picture of photo-reduction of carbon dioxide may involve many more chemical reactions. Before that, one must understand

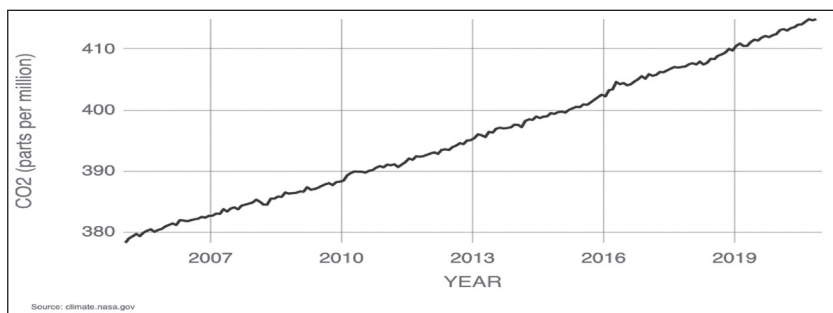


Fig.1. The rise in carbon dioxide in the atmosphere in the last 15 years reaching 415 ppm in November 2020.

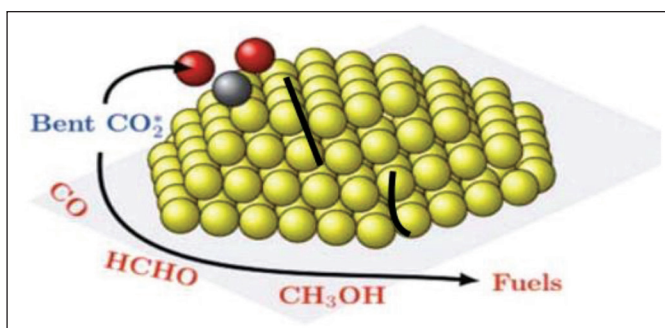
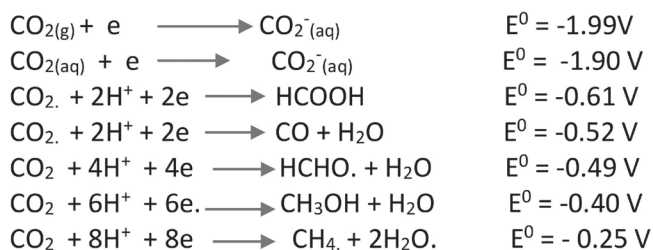


Fig.2. The possible configuration of carbon dioxide on catalyst surface to undergo reduction reaction.<sup>[2]</sup>

why direct reduction of carbon dioxide is so difficult. The free carbon dioxide molecule is linear and without any net dipole moment and hence non-reactive in this state. When the bond angle becomes less than  $180^\circ$  and the molecule will be bent and in this configuration the molecule becomes active to undergo reduction.

The required reduction potentials (versus SHE at 298K and pH=7) are:



It is seen that though carbon dioxide can be activated if it can be directly reduced though the barrier involved is huge ( $\sim -2.0\text{V}$ ). But the barrier towards reduction is considerably reduced in the presence of protons in the medium. Thus, there appears to be a way out for this process, but the hurdle is the identification of suitable catalyst system that will promote this process on an industrial scale in an economical way. Therefore, the purpose of this presentation is to address this aspect to the extent possible. There are other relevant features which should be addressed to make this process

Even though, conceptually, the photo-process appears to be simple, there can be many other side processes like recombination and preferential photoreaction of other impurity substrates (including the semiconductor itself involving in this photo-process termed photo-corrosion) can compete with the desired photoreaction. The essential thermodynamic criterion is that the conduction band minimum of the semiconductor should be more negative than the substrate reduction potential in electrochemical scale and in the same sense the oxidation potential of the substrate should be less positive relative to the valence band maximum.

commercially feasible. The design and execution of appropriate technology and economic analysis of the production are the other important aspects which are not taken up for discussion in this article.

## Harnessing Solar Radiation

Materials in a simple way can be classified into metals, semiconductors and insulators. Among these three classes of materials, semiconductors are most suitable for harnessing solar radiation. Conceptually, the photo-catalytic process can be visualized into three steps: namely photoexcitation, charge generation and charge transfer. All these three steps have their own limitations, for example photoexcitation can be effective only when the energy of the incident radiation is equal to or greater than the band gap of the semiconductor. Charge generation is energy alteration of the excited electron and the hole. Charge transfer has to overcome

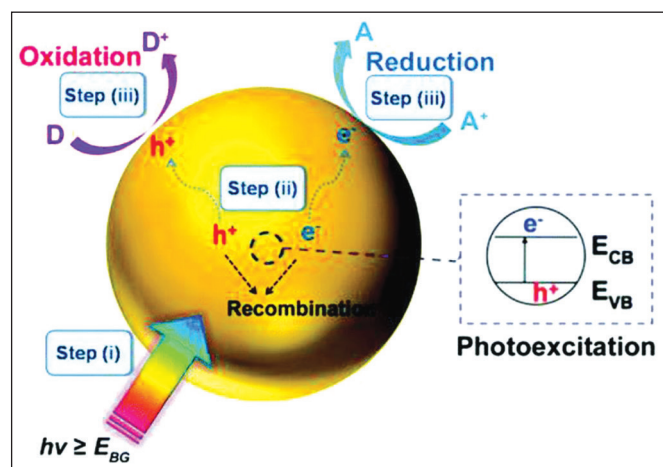


Fig.3. Pictorial representation on the photo-reduction/oxidation of substrates by the excited electrons and holes respectively [Figure reproduced from Ref.1].

the charge recombination and also depends on the reduction potential of the adsorbed substrate. Thus, it is clear that the net quantum efficiency of photo-process can ultimately be a small percentage of the absorbed radiation.

Mechanistically, the processes that are envisioned in the photoreduction/oxidation of the substrates are pictorially shown in Fig.3.

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It can be deduced that of all known semiconductors only a few chosen ones are capable of reducing  $\text{CO}_2$  to the desired products. The usually studied materials for the photoreduction of  $\text{CO}_2$  are metal oxides, particularly,  $\text{TiO}_2$ ,  $\text{MgO}$ ,  $\text{Ga}_2\text{O}_3$ ,  $\text{Bi}_2\text{MoO}_6$ ,  $\text{In}_2\text{O}_3$ ,  $\text{Ta}_2\text{O}_5$ , and systems based on  $\text{C}_3\text{N}_4$  and  $\text{B}_4\text{C}_3$ . Most often, these materials are also (surface or bulk-) doped with metals like Pt, Cu, Cr, Ru, Pd, Ag, Fe, Co, and Ni, which may decrease the charge recombination. This happens because of the metal acting as an electron sink, trapping the electrons and stabilizing charge separation, thus improving the photocatalytic properties of the material. In spite of these extensive studies on a variety of semiconductors, the reduction rate has yet to cross the micromoles per hour per gram of the catalyst. The exercise of band gap engineering has enabled the possibility of utilising visible region of the solar spectrum. Possibly, one can consider that the thermodynamic barrier is understood to an extent but the same cannot be said of the kinetic barriers. Most of the semiconductors shown in Fig.4 have the energy of the minimum of the conduction band edge at more negative potential with respect to the reduction potential of  $\text{CO}_2$  (these

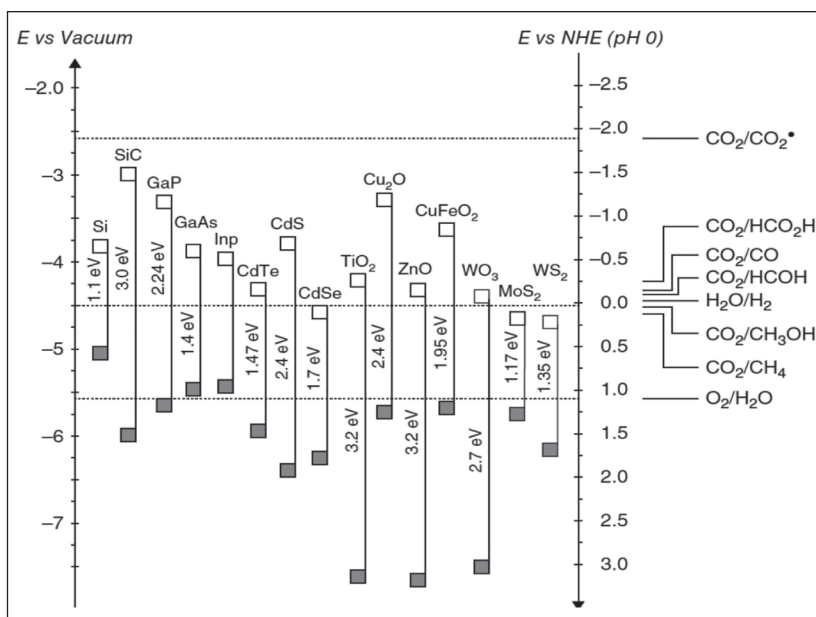


Fig.4. The relative reduction potentials of selected (one carbon atom molecule) reduction products of carbon dioxide relative to conduction band minimum and valence band maximum of chosen semiconductors. The values of reduction and oxidation potentials of water and direct one electron reduction potential of  $\text{CO}_2$  have also been indicated in this figure.

values are shown on the right side in this figure. Even though energetically these systems are favourable for photo-catalytic reduction of  $\text{CO}_2$  these systems still do not yield sufficient amount (still the values are only micromoles per unit time) of reduced products.

### Kinetic Barrier of the Photo-catalytic Reduction of Carbon dioxide

The ground state carbon dioxide molecule is linear configuration and  $\text{C}=\text{O}$  bond energy is approximately 750 kJ/mol. The reduction of this molecule depends on the energy of the Lowest Unoccupied Levels (LUMO) which can be reduced by changing the configuration from linearity to a bent state.  $\text{CO}_2$  is an inert and very stable compound with a formation energy of  $-393.5$  kJ/mol as stated in earlier sections. Because its geometry is linear ( $\text{O}=\text{C}=\text{O}$  angle is  $180^\circ$ ,  $\text{C}=\text{O}$  bond length is  $1.16 \text{ \AA}$ ), the molecule is not polar. While the reduction potential of  $\text{CO}_2/\text{CO}_2\cdot^-$  vs NHE is  $-2.22 \text{ V}$ , it can

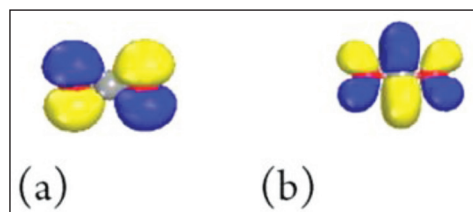


Fig.5. The orbital configuration of HOMO (a) and LUMO (b) levels of free carbon dioxide.



be changed by adsorption ( $-1.98$  V on anatase  $\text{TiO}_2(101)$ ). Suitable photocatalysts should activate the  $\text{CO}_2$  molecule, which is rather inert. Upon adsorption, the C-O bond is elongated, and the molecule is bent, as  $\text{CO}_2$ -is formed. Defects and cocatalysts possibly improve the activation of the inert molecule. Another important aspect of the catalyst is the exposed surface, as different surfaces exhibit different affinities for CO and consequently also the intermediates and products. The orbital configuration of the Highest Occupied Level (HOMO) and LUMO levels of free carbon dioxide is shown in Fig.5.

If the overlap of the LUMO level of free carbon dioxide were to overlap with the frontier orbitals of the surface, then the bond disposition of the carbon dioxide may be altered and the bond angle will decrease from  $180^\circ$ . Thus it will become amenable for reduction. If this kind of activation has to occur the adsorption mode has to be similar as shown in Fig.2. This defines the nature of the active sites necessary for activation of carbon dioxide to undergo reduction. This type of configuration of active sites can be of several configurations like adatom or ad-molecular species or vacancy site or other configurations whose frontier surface orbitals will be able to overlap with the LUMO level of carbon dioxide. This will result in a bent configuration and thus become amenable for reduction. It is known that carbon dioxide may adsorb on oxide surfaces in a configuration of carbonate like species that will facilitate easy reduction or facile thermal decomposition. A stepped surface (in other ways various different Miller Indices planes) may also function as the site for the activation of the molecule. As of now the essential feature of the surface should be such that the activation of carbon dioxide will occur with reduction in bond angle so that the band of C-O bond also is altered to facilitate the reduction. This means that the surface morphology or topology has to be modulated suitably for proper activation of carbon dioxide for facile reduction.

### Scope of Photo-catalytic Reduction of Carbon dioxide

The possible reactions of carbon dioxide to form various value added chemicals is almost infinity. A partial list of the possible reactions of carbon dioxide to yield value added products is assembled for information in Table 2.

Reaction	$E^0_{\text{redox}}$ (eV)
$\text{CO}_2 + 2\text{H}_2\text{O} + 2e^- \longrightarrow \text{HCOOH} + 2\text{OH}^-$	-1.491
$\text{CO}_2 + 2\text{H}^+ + 2e^- \longrightarrow \text{CO} + \text{H}_2\text{O}$	-0.53
$\text{CO}_2 + \text{H}_2\text{O} + 2e^- \longrightarrow \text{CO} + 2\text{OH}^-$	-1.347
$2\text{CO}_2 + 2\text{H}^+ + 2e^- \longrightarrow \text{H}_2\text{C}_2\text{O}_4$	-0.913
$2\text{CO}_2 + 2e^- \longrightarrow \text{C}_2\text{O}_4^{2-}$	-1.003
$\text{CO}_2 + 4\text{H}^+ + 4e^- \longrightarrow \text{C} + 2\text{H}_2\text{O}$	-0.20
$\text{CO}_2 + 4\text{H}^+ + 4e^- \longrightarrow \text{HCHO} + \text{H}_2\text{O}$	-0.48
$\text{CO}_2 + 3\text{H}_2\text{O} + 4e^- \longrightarrow \text{HCHO} + 4\text{OH}^-$	-1.311
$\text{CO}_2 + 2\text{H}_2\text{O} + 4e^- \longrightarrow \text{C} + 4\text{OH}^-$	-1.040
$\text{CO}_2 + 6\text{H}^+ + 6e^- \longrightarrow \text{CH}_3\text{OH} + \text{H}_2\text{O}$	--0.38
$\text{CO}_2 + 5\text{H}_2\text{O} + 4e^- \longrightarrow \text{CH}_3\text{OH} + 6\text{H}_2\text{O}$	-1.225
$\text{CO}_2 + 8\text{H}^+ + 8e^- \longrightarrow \text{CH}_4 + 2\text{H}_2\text{O}$	-0.24
$\text{CO}_2 + 6\text{H}_2\text{O} + 8e^- \longrightarrow \text{CH}_4 + 8\text{OH}^-$	-1.072
$2\text{CO}_2 + 12\text{H}^+ + 12e^- \longrightarrow \text{C}_2\text{H}_4 + 4\text{H}_2\text{O}$	-0.349
$2\text{CO}_2 + 8\text{H}_2\text{O} + 12e^- \longrightarrow \text{C}_2\text{H}_4 + 12\text{OH}^-$	-1.177
$2\text{CO}_2 + 12\text{H}^+ + 12e^- \longrightarrow \text{C}_2\text{H}_5\text{OH} + 3\text{H}_2\text{O}$	-0.329
$2\text{CO}_2 + 9\text{H}_2\text{O} + 12e^- \longrightarrow \text{C}_2\text{H}_5\text{OH} + 12\text{OH}^-$	-1.157
$2\text{CO}_2 + 14\text{H}^+ + 14e^- \longrightarrow \text{C}_2\text{H}_6 + 4\text{H}_2\text{O}$	-0.270
$2\text{CO}_2 + 18\text{H}^+ + 18e^- \longrightarrow \text{C}_3\text{H}_7\text{OH} + 5\text{H}_2\text{O}$	-0.310
$2\text{CO}_2 + 18\text{H}^+ + 18e^- \longrightarrow \text{CH}_3\text{CHOHCH}_3 + 5\text{H}_2\text{O}$	-0.300
$2\text{CO}_2 + 10\text{H}^+ + 10e^- \longrightarrow \text{CH}_3\text{CHO} + 3\text{H}_2\text{O}$	-0.360
$3\text{CO}_2 + 16\text{H}^+ + 16e^- \longrightarrow \text{CH}_3\text{CH}_2\text{CHO} + 5\text{H}_2\text{O}$	-0.320
$3\text{CO}_2 + 16\text{H}^+ + 16e^- \longrightarrow \text{CH}_3\text{COCH}_3 + 5\text{H}_2\text{O}$	-0.310
$2\text{CO}_2 + 8\text{H}^+ + 8e^- \longrightarrow \text{CH}_3\text{COOH} + 2\text{H}_2\text{O}$	-0.310
$2\text{H}^+ + 2e^- \longrightarrow \text{H}_2$	-0.420

**Table 2. Values of reduction potentials for some of the possible reactions of carbon dioxide to yield value added products. The corresponding value for hydrogen production from water is included for reference and also for its relevance in carbon dioxide reduction.**

The list of 25 reactions in Table 2 is only indicative and it shows the scope of studies on the conversion of carbon dioxide and therefore the possibility of developing technologies for the selective production of chemicals from carbon dioxide appears to be bright.

Various modifications and configurations in order to generate active sites (like doping) or coupling semiconductors (to make them active in visible region) have been tried, Even then the carbon dioxide conversion levels to fuel type molecules were found to be in the range of micromoles per gram per hour. Another exercise of employing Nafion™ (almost bare proton) instead of water as a source for hydrogen has also been tried. Another aspect that has been attempted is to increase the concentration of the substrate concentration in the reaction medium (like employing alkaline solutions), but still the conversion levels were low.

Turning to natural photosynthesis, where plant leaves harness solar energy and effectively reduce carbon dioxide with water as shown in the figure 6.

It can be inferred that one has to find in situ hydrogen or proton source other than from the decom-

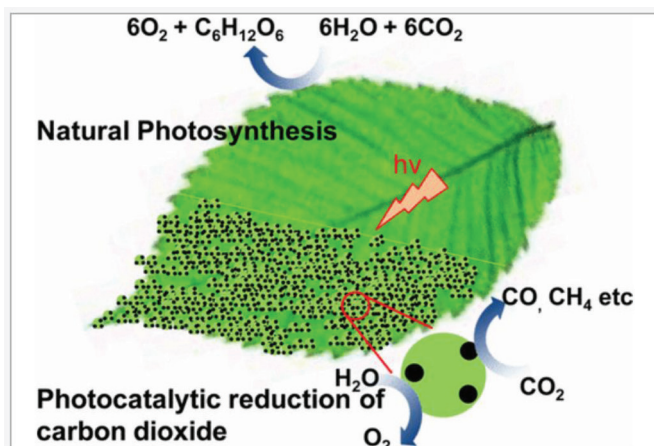
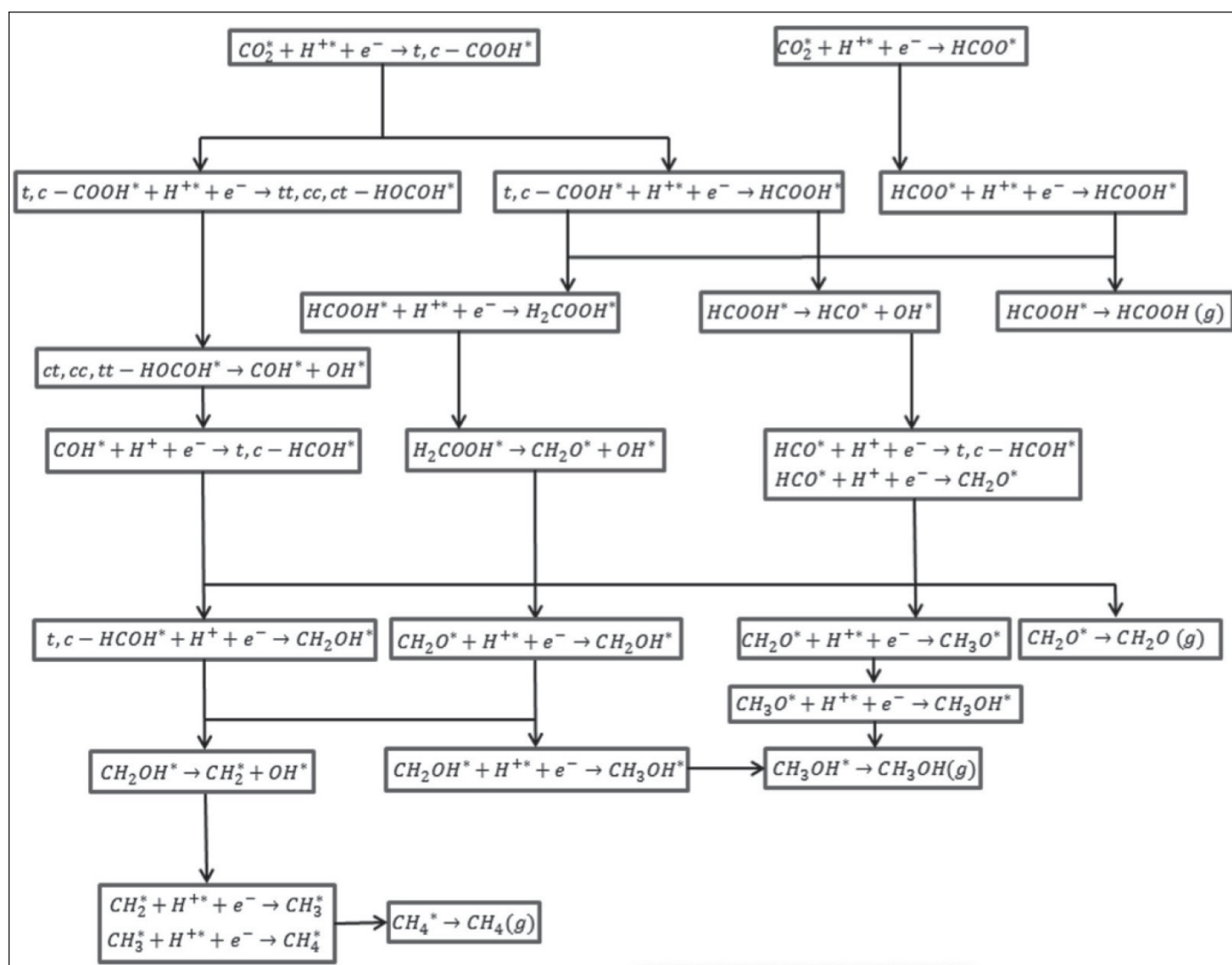


Fig.6. A pictorial representation of natural photosynthesis (the reaction is  $6CO_2 + 6H_2O \rightarrow C_6H_{12}O_6 + 6O_2$ ). [Figure reproduced from ref 3]

position of water which can add some kinetic control and other factors. The direct use of molecular hydrogen probably may be useful in overcoming the overpotential barrier but the dissociation and addition reactions may have kinetic limitation.

Even though there appears to be multiple paths for the reduction of carbon dioxide, most of these reactions are multielectron reduction reactions and hence photocatalytic reduction to these products will not become possible so easily and hence one has to concentrate on reduction to one carbon molecule possibly involving two electron reduction process. Even in these cases the ultimate yield of the product has limitations. In addition, the activation on the catalyst surface may require multiple chemisorption band. But such active sites on the catalyst surface may be rare.



Scheme.1. The representation of one of the mechanistic networks for the photo-catalytic reduction of carbon dioxide [Reproduced from ref.4.]

## Prospects of the Photo-catalytic Reduction of Carbon dioxide

First few projections [5,6] on the prospects of this process:

1. Even though there are multiple opportunities for the photocatalytic reduction of carbon dioxide, it is possible and desirable to concentrate on two electron reduction process more extensively.
2. It may be desirable to resort to direct proton or hydrogen source rather than the proton coming from the decomposition of water so that the photocatalytic reduction of carbon dioxide is more facile.
3. In case if proton has to be obtained from other sources, then one must ensure that the source undergoes electrochemical reaction within the potential range employed for the reduction of carbon dioxide.
4. The reactivity of proton source should be high as that obtainable in Nafion™ (almost bare proton). This is so since the proton in Nafion™ is present in the highly electro negative environment of fluorine atoms.
5. It may be possible that the photocatalyst employed may be designed to contain this electronegative environment by suitable modification with electro-negative elements.
6. It appears that the natural photosynthesis is still difficult to unravel and it may be possible if the photocatalyst systems employed can be designed similar to the situation existing in chlorophyll.

The key to make this process commercially viable appears to depend on finding alternate proton or hydrogen source and also appropriate photocatalyst which can activate carbon dioxide in multimode adsorption.

Even though, there are a numerous possibilities for photo-catalytic reduction of carbon dioxide, many or even most of these reactions have to face enormous barriers to become a successful process. One of them is the competing and simultaneous processes which have to be made selective process. This will be an uphill process since the reduction potential values for these reactions are very close and hence these processes will compete with each other in photo-catalytic reduction.

Another aspect which is relevant for photo-catalytic reduction of carbon dioxide is the activation of CO<sub>2</sub> molecule on the catalytic surfaces. As stated elsewhere, the activation can be caused by chemisorption (adsorption) through carbon or the two oxygen atoms of the

molecule. The highest occupied levels (HOMO) is non-bonding in character while the lowest unoccupied levels (LUMO) have pi\* character. The surface orbitals may have such symmetry so as to overlap the Pi\* orbital of CO<sub>2</sub>. This means that the surface frontier orbital may have specific symmetry and this may have to be taken as governing principle for selection of catalytic material. This may be considered as one of the possible ways for selection of catalytic material.

There can be alternate options which can also be attempted for successful reduction of CO<sub>2</sub> to the desired level, probably deserving separate consideration.

It is also necessary at this stage that suitable commercially suitable design of photo-reactor and of pilot plant has to be formulated and their feasibility has also to be established. These new designs or the designs already available should be capable of harnessing energy from solar radiation without much further investment.

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