

# Artificial Photosynthesis for Sustainable and Environmental Friendly Construction: A Review

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*Abstract:* - Artificial photosynthesis processes using semiconductor as photocatalyst, has emerged as an important destructive technology leading to the formation of eco-friendly end products. Interesting part of this process is the ability to convert pollutants into harmless substances directly in the contaminant source. Recently, artificial photosynthesis is a modern technology, which has potential for the reduction of “global warming”. This paper reviews recent developments in this emerging technology and provides information on the parameters that control the process. The effects of the photosynthetic reaction on the cementations materials are discussed and future potential applications of this technology are also considered. Finally, it also provides the scope for the future research on this topic with adequate literature support.

*Key-Words:* - Artificial Photosynthesis, Carbon Dioxide, Physisorption, Photocatalyst

## 1 Introduction

The topic of global climate change is frequently seen in the news. The International Panel on Climate Change (IPCC) reports that the increase in the concentration of many compounds in the atmosphere will impact on global climate [1]. These compounds are commonly referred to as greenhouse gases that might be emitted from natural sources or manmade (anthropogenic) sources. Some of these greenhouse gases are long-lived [2], they are stable in the atmosphere and they may impact on climate for many years. The most notable of the long-lived greenhouse gas is carbon dioxide. The concentration of carbon dioxide in the atmosphere has risen from 280ppm to 370ppm over the last 150 years [3]. Therefore, it is necessary to reduce atmospheric carbon dioxide (CO<sub>2</sub>) for a sustainable environment.

The reduction of CO<sub>2</sub> by the process of artificial photosynthesis is believed to be one such alternative that emits oxygen using atmospheric CO<sub>2</sub> and water in presence of photocatalyst. It is a scientific challenge, and if this process is successful, it will help to reduce CO<sub>2</sub> emission. This innovative approach of the science also demonstrates the photocatalytic activity of photocatalyst such as LiNbO<sub>3</sub> with the cementitious construction materials and subsequently its role to reduce the emission of global warming gas. Therefore, this study is carried out thorough the review of the literature related to the importance of solar assisted reduction of

atmospheric carbon dioxide and the role of LiNbO<sub>3</sub> in cementitious construction to reduce CO<sub>2</sub> emission from the point of view of global warming.

## 2 Carbon Dioxide and Global Warming

Global Warming is defined as a gradual increase in planet-wide temperatures, which is now well documented and accepted by scientists as fact. A panel convened by the U.S National Research Council, the nation's premier science policy body, in June 2006 voiced a "high level of confidence" that Earth is the hottest it has been in at least 400 years, and possibly even the last 2,000 years. Studies indicate that the average global surface temperature has increased by approximately 0.5-1.0°F over the last century [4]. This is the largest increase in surface temperature in the last 1,000 years and scientists are predicting an even greater increase over this century [5]. This warming is largely attributed to the increase of greenhouse gases (primarily carbon dioxide) in the Earth's upper atmosphere caused by human burning of fossil fuels, industrial, farming, and deforestation activities and others.

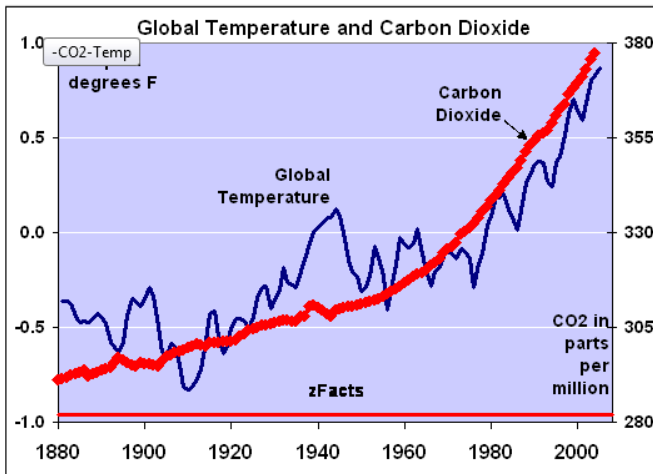


Fig.1 Yearly variation of global temperature and carbon dioxide (Graphics from <http://zfacts.com/p/226.html>)

Average global temperatures may increase by 2.5-10.4°F by the end of the 21st century [4]. Although the numbers sound small, they can trigger significant changes in climate. Besides resulting in more hot days, many scientists believe an increase in temperatures may lead to changes in precipitation and weather patterns [5]. Warmer ocean water may result in more intense and frequent tropical storms

and hurricanes. Sea levels are also expected to increase by 0.09 - 0.88 m. in the next century [5], mainly from melting glaciers and expanding sea water. Global warming may also affect wildlife and species that cannot survive in warmer environments and may become extinct. Finally, human health also gets stake as global climate change may result in the spreading of certain diseases such as malaria, the flooding of major cities, a greater risk of heat stroke for individuals, and poor air quality [6].

### 3 Approach to Artificial Photosynthesis

The goal of artificial photosynthesis is to mimic the green plants and other photosynthetic organisms that use sunlight to make valuable substances [7]. This is a challenging goal because success requires integration of multiple chemical functions in a stable chemical architecture. As a result, artificial photosynthesis has developed more slowly than other approaches to sustainable conversion of CO<sub>2</sub> [8].

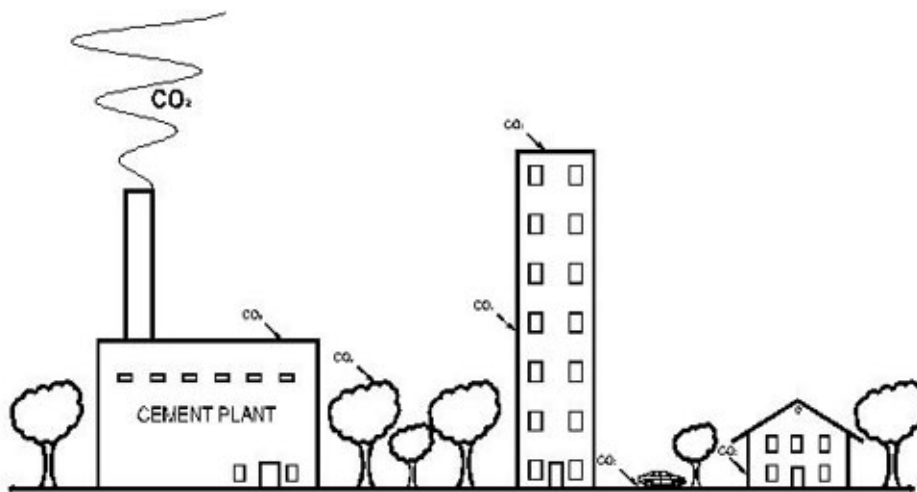


Fig.2 Carbonation of concrete materials and carbon cycle in the atmosphere.

Natural photosynthesis in the green plants occurs through a complex reaction scheme, where solar energy is used to convert H<sub>2</sub>O into O<sub>2</sub> [9]. In artificial photosynthesis, the goal is to harness the energy of the sun to drive high-energy small-

molecule reactions such as water splitting Fig.3. An ultimate goal is water splitting with the photochemically produced high value-added substances [10].

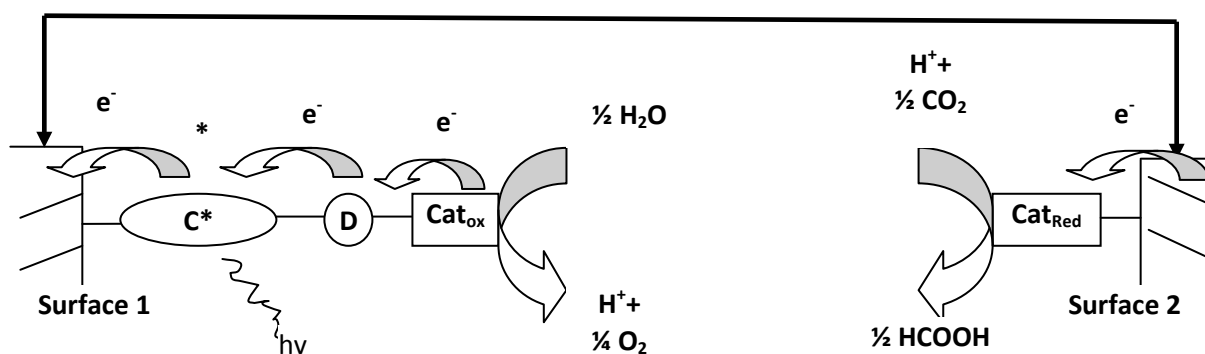


Fig.3 Schematic diagram illustrating the photo-electrochemical reaction between  $\text{CO}_2$  and  $\text{H}_2\text{O}$  to give  $\text{HCOOH}$  and  $\text{O}_2$  initiated by excitation and photoinjection in presence of photocatalyst. Adapted from [10]

The efficiency of the whole process is a complex function of several parameters, which are as follows:

### 3.1 Photocatalyst and its Characteristics

The greatest chemical challenge in the modular approach to artificial photosynthesis is identifying photocatalysts that have ability to carry out the necessary multiple electron transformations at energies and rates consistent with the solar irradiance [11]. Based on the accessibility of pathways such as atom transfer, hydride transfer, oxidative addition, reductive elimination, insertion, etc., catalysts must be identified with the reactivities required to carry out the small-molecule transformations of artificial photosynthesis [10]. From the literature review, some characteristics of photocatalyst are identified that must be fulfilled by the photocatalyst to create artificial photosynthesis. The required characteristics include: (1) strong remnant polarization, which resulted in high reaction efficiency; (2) activation by sequential  $1e^-$  transfers and, where needed energetically, the availability of Electron Proton Transfer (EPT) pathways; (3) redox potentials sufficient to drive the half-reactions; (4) sufficiently rapid reaction rates for catalyst turnover i.e., rate-limited solar irradiance and (5) strategies for incorporating modules and components into assemblies.

### 3.2 Interaction of Photocatalysts with Light

Semiconductor particles may be photoexcited to form sites for the donor of electron (reducing sites) and acceptor of electron (oxidising sites) and

provided great scope as redox reagent [12]. The molecular orbitals of semiconductors have a band structure. The bands of interest in photocatalysis are the occupied valence band and the unoccupied conduction band. They are separated by an energy distance referred to as the band gap ( $E_g$ ). When the semiconductor is illuminated with light of greater energy than that of the band gap, an electron is promoted from the valence band to the conduction band. This leaves a positive hole in the valence band as illustrated in Fig. 4.

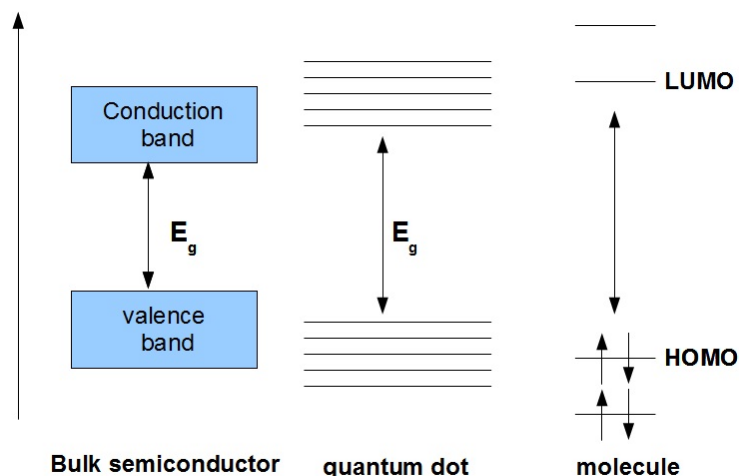
The electron ( $e^-$ ) and holes ( $h^+$ ) pair may be recombined with the generation of heat. If they are separated they can become involved in electron transfer reactions with other species in the solution, for example oxidation of species D or reduction of species A.

To occur oxidation (step 3), the valence band must have a higher oxidation potential than the material under consideration [10]. The redox potentials of the valence and conduction bands for different semiconductors vary between +4.0 eV and -1.5 eV v's Normal Hydrogen Electrode (NHE), respectively [12]. Therefore, a wide range of species can be converted via these processes by careful selection of the photocatalyst. Table 1 displays a list of materials which are used for photocatalytic reactions, together with the valence band and conduction band positions. The final column in the table indicates the wavelength of radiation required to activate the catalysts.

Till now, the majority of the work in this area has involved  $\text{TiO}_2$  in construction purpose [13]. This material has a band gap energy of 3.2 eV and therefore it absorbs light energy which is close to ultraviolet range ( $\sim 380\text{nm}$ ). In 2011, Matt Stock

and Steve Dunn found that  $\text{LiNbO}_3$  could be produced more products under UV and visible irradiation than  $\text{TiO}_2$  despite its wider band gap (3.78 eV). The surprisingly high yield product using  $\text{LiNbO}_3$  is explained by its strong remnant

polarization ( $70\mu\text{C}/\text{cm}^2$ ) [14], which is not found in  $\text{TiO}_2$  [11]. The remnant polarization facilitates improve carrier life times as well as allowing lower energy injection of charge carriers, which enhance the  $\text{LiNbO}_3$ 's efficiency [15].



**Fig.4** Energy diagram of a semiconductor photocatalyst interface

The possible reactions that can occur when a semiconductor (SC) absorbs a photon ( $h\nu$ ) of a suitable wavelength are as follows [17]:

- |                      |  |
|----------------------|--|
| (1) Light Absorption | $\text{SC} + h\nu \rightarrow e^- + h^+$   |
| (2) Recombination    | $e^- + h^+ \rightarrow \text{Excitation} (\sim \text{Energy Transfer to other species})$ |
| (3) Oxidation        | $\text{D} + h^+ \rightarrow \text{D}^{*\cdot+}$ (Free radical cation)                    |
| (4) Reduction        | $\text{A} + e^- \rightarrow \text{A}^{*\cdot-}$ (Free radical anion)                     |

**Table 1.** The band positions of some common photocatalyst in aqueous solution

| Semiconductor    | Valence band<br>(V vs NHE) | Conductance band<br>(V vs NHE) | Band gap<br>(eV) | Band gap<br>wavelength<br>(nm) |
|------------------|----------------------------|--------------------------------|------------------|--------------------------------|
| $\text{LiNbO}_3$ | +0.48                      | -3.30                          | 3.78             | 333                            |
| $\text{TiO}_2$   | +2.70                      | -0.50                          | 3.20             | 380                            |
| $\text{SnO}_2$   | +4.10                      | +0.30                          | 3.90             | 318                            |
| $\text{ZnO}$     | +3.00                      | -0.20                          | 3.20             | 390                            |
| $\text{ZnS}$     | +1.40                      | -2.30                          | 3.70             | 336                            |
| $\text{WO}_3$    | +3.00                      | +0.20                          | 2.80             | 443                            |
| $\text{CdS}$     | +2.10                      | -0.40                          | 2.50             | 491                            |

### 3.3 Catalyst for CO<sub>2</sub> Reduction through Artificial Photosynthesis

To perform artificial photosynthesis, the photocatalyst must be able to drive the reduction of CO<sub>2</sub> and, ideally, the oxidation of water. To obtain this, the reaction potentials must be inside the band edges of the photocatalyst. Many tested semiconductors (ZnO, Fe<sub>2</sub>O<sub>3</sub>, CdS, ZnS, TiO<sub>2</sub>, LiNbO<sub>3</sub>) turn to be close to the perfection.

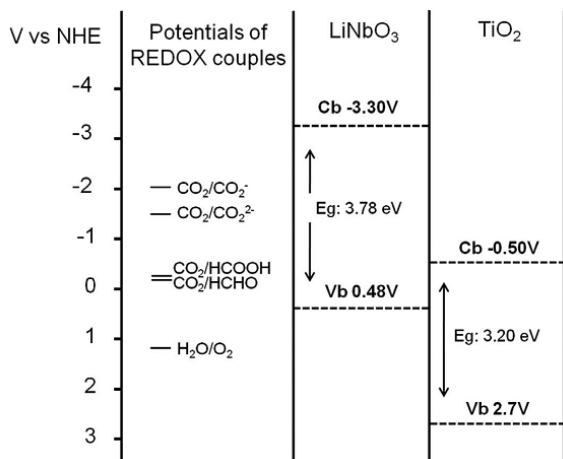


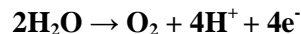
Fig.6 Band positions of LiNbO<sub>3</sub> and TiO<sub>2</sub> versus NHE in relation to the redox reactions of artificial photosynthesis [11]

Fig.6 compares the potential of the valence and conduction bands of LiNbO<sub>3</sub> and TiO<sub>2</sub> in relation to the cell potential of conversion of CO<sub>2</sub> and water to formic acid and formaldehyde as well as the half-equations for the reduction of CO<sub>2</sub> and the oxidation of water. It shows that TiO<sub>2</sub> drives the reaction of CO<sub>2</sub> and water to formic acid and formaldehyde, valence band holes oxidize water and conduction band electrons cannot reduce CO<sub>2</sub> to CO<sub>2</sub><sup>-</sup>. LiNbO<sub>3</sub> also drives the reaction of CO<sub>2</sub> and water to formic acid and formaldehyde, but the valence band holes don't oxidize water [14]. Conduction band electrons of LiNbO<sub>3</sub> are, however, highly reduced and subsequently reduce CO<sub>2</sub> to CO<sub>2</sub><sup>-</sup> (1.9V v's NHE) or CO<sub>2</sub><sup>2-</sup> (1.45V v's NHE) unlike TiO<sub>2</sub> [16]. The reaction step of LiNbO<sub>3</sub> allows a different reaction pathway because of its highly reducing conduction band electrons [11].

### 3.4. Water Oxidation Catalyst for Artificial Photosynthesis

Water oxidation is a more complex chemical reaction than proton reduction. In natural photosynthesis, the oxygen-evolving complex

performs this reaction by accumulating reducing equivalents (electrons) in a manganese-calcium cluster within photosystem II (PS II), then delivers them to water molecules [17], with the resulting production of molecular oxygen and protons:



Without a catalyst (natural or artificial), this reaction is very endothermic and it requires high temperatures (at least 2500 K) [18]. Many metal oxides have been found to have water oxidation catalytic activity, especially those from relatively abundant transitional metals, but suffer from low turnover frequency and slow electron transfer properties, and their mechanism of action is hard to decipher and, therefore, to adjust [19].

On the other hand, LiNbO<sub>3</sub> allow this process at different reaction pathway. Remnant polarization of LiNbO<sub>3</sub> leads to a charge experienced at the interface. This charge interacts with species in contact with the surface, producing a tightly bound layer [20] which changes the nature of bonding in physisorbed materials. In case of water, LiNbO<sub>3</sub> will physisorb a tight layer of molecules. The valence band location of LiNbO<sub>3</sub> (0.48V v's HNE) is unable to oxidize water directly, it seems likely that the physisorbed water prevents any further reactions on the surface [11]. In the gas-solid reaction, there is significantly more CO<sub>2</sub> available and bound on the surface of the LiNbO<sub>3</sub> [11]. This bound CO<sub>2</sub> reacts with photoexcited holes and electrons in the LiNbO<sub>3</sub> and so produces reactive species that react with H<sub>2</sub>O to form end products [21]. One such species is CO<sub>2</sub><sup>-</sup> (H<sub>2</sub>O + CO<sub>2</sub><sup>-</sup> → HCOOH + ½ O<sub>2</sub> + e<sup>-</sup>). It has been shown that the physisorption of molecules on ferroelectric surfaces [25] affects the localization of electrons in the molecule as well as the bond angles. This allow easier injection or removal of electrons than in less chemically strained systems.

## 4 Role of Photocatalyst in Construction Material

A new and innovative approach to the material science has demonstrated that photocatalytic activity may be applied to cement-based construction materials, such as concrete, mortars, etc. Photocatalyst is needed for a cleaner environment and a better quality of life that leads to thoughts of a more eco-compatible use of sunlight. In this context photochemistry could be applied to construction materials that could provide a very interesting solution [10]. It could become an integral part of the

strategies adopted for reducing environmental pollution through the use of construction materials containing photocatalysts. Photocatalysts induce the formation of strongly oxidizing reagents which can decompose some organic and inorganic substances present in the atmosphere [22]. Photocatalysis is, therefore, an accelerator for oxidization processes that already exist in nature. Indeed, it promotes faster decomposition of pollutants and prevents them from accumulating on the surfaces [23]. The worsening of the level of pollution in urban areas has recently driven research towards the application of the capability of removing harmful substances present in the atmosphere.

In brief, the use of photocatalytic construction materials in building environment has the following benefits:

- Contributes to air pollution reduction
- Improves indoor and outdoor air quality
- Decrease organic smells and bacteria loads in critical areas such as hospitals
- Helps to keep the aesthetic option of the exterior walls

Usually  $\text{TiO}_2$  is used as photocatalyst in construction purpose. However, it is found from the literature review that photocatalytic property of  $\text{LiNbO}_3$  is better than  $\text{TiO}_2$  [11]. In the carbonation process carbon dioxide from the atmosphere penetrates into the concrete and reacts with calcium hydroxide to form calcium carbonates [24], which is a slow process. In presence of  $\text{LiNbO}_3$  and using energy from sunlight it can create artificial photosynthesis. As a result cementitious materials would absorb more  $\text{CO}_2$  from atmosphere. Therefore it could be proposed that the use of  $\text{LiNbO}_3$  as photocatalyst in construction purpose could make an effective contribution to improve air quality by reducing global warming gas ( $\text{CO}_2$ ) through artificial photosynthesis process.

## 5 Conclusion

The importance of artificial photosynthesis should not be overlooked. Reduction of the problem of 'global warming' using photocatalyst  $\text{LiNbO}_3$  as a constructing material to emit oxygen using atmospheric  $\text{CO}_2$  and water reliably and inexpensively would have a remarkable positive impact on our environment in near future. Indeed, a new class of functional cement-based material ( $\text{LiNbO}_3$ ) would have been presented, which would

allow a breakthrough in building industry, from the environmental point of view.

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