

## **HYBRID PHOTOCATALYST FOR CORROSION REDUCING AND SUSTAINABLE CONCRETE CONSTRUCTION**

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### **ABSTRACT**

Corrosion is the main problem in Reinforced concrete (RC). RC usually absorbs carbon dioxide from surrounding environment in operational period. This carbon dioxide reacts with the calcium oxide, which is already present in RC and forms a calcium carbonate an acidic compound that enhances corrosion on the surface of the reinforcement. Addition of photo catalytic materials to the RC structure during its construction phase could reduce the corrosion problem of RC materials. This material hinders calcium oxide to form acidic compound and creates a complex compound. In combination with light, this complex compound is oxidized, and residual compound will exist in or surface of RC material. In this study it is aimed to find out the proper photo catalytic material adjustable with RC material for reducing corrosion problem and enhancing oxidization process of volatile organic compounds.

**Keywords:** *Corrosion, Carbonation, Photocatalysis, Reinforced Concrete*

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### **1.0 INTRODUCTION**

Photocatalyst shows its activity in redox process. Redox reactions on the photocatalyst surface, are promoted by sunlight (or in general, weak U.V. light), and drive the oxidation of environmental pollutants [1]. The photo-induced surface hydrophilicity enhances this self-cleaning effect of the materials [2]. The addition of a photocatalyst to ordinary building materials such as concrete creates environmental friendly concrete material by which air pollution or pollution of the surface can be diminished itself [2]. For example, white concrete – whether used for precast concrete pavers or roofing – reflects much of the sun's heat and reduces the heat gain associated with dark construction materials like asphalt paving. This keeps cities cooler and reduces the need for air conditioning. It also reduces the formation of smog as chemical reactions of materials in presence of photocatalyst reduce the surface temperature of material that creates smog [1]. Photocatalyst in concrete keeps the concrete surface clean to optimize environmental benefit like degradation of organic pollutants, destruction of bacteria and viruses, decomposition of dyes or synthesis of some compounds.

When concrete or any other cement-based material in contact with the embedded reinforcing steel is carbonated, the steel surface is depassivated. Therefore, the reinforcing steel is no longer protected from corrosion. Corrosion may also commence when chloride, phosphate, moisture and oxygen gain access to the steel surface [3]-[6]. One of the means of protecting steel reinforcement in concrete from chloride induced corrosion is the addition of corrosion inhibiting additives[7]-[10]. Sodium nitrite, zinc oxide, titanium dioxide monoethanol amine, diethanolamine, and triethanol amine have been used as inhibitors in concrete in different percentages for reducing chloride induced corrosion [11]. Chloride induced corrosion depends mainly on concrete pH and oxygen content. In presence of photocatalyst the corrosion problem of RC materials can be reduced [12], [13]. In this study, a hybrid photocatalyst is made from

chemical mixture of ZnO and TiO<sub>2</sub> and its beneficial effects on concrete material are examined. It has also been discussed the principle and chemical combination process of hybrid photocatalyst in this study.

## 2.0 PRINCIPLES OF HETEROGENEOUS PHOTOCATALYSIS

Heterogeneous photocatalytic system consists of semiconductor particles (photocatalyst) which remain in close contact with a liquid or gaseous reaction medium. Exposing the catalyst to light, excited states are generated which are able to initiate subsequent processes like redox reactions and molecular transformations [14]-[16]. A simplified reaction scheme of photocatalysis is shown in Fig. 1. Due to the electronic structural behavior of photocatalyst, which is characterized by a filled valence band (VB) and an empty conduction band (CB), semiconductors (metal oxides or sulfides as ZnO, CdS, TiO<sub>2</sub>, Fe<sub>2</sub>O<sub>3</sub>, and ZnS) act as sensitizers for light-induced redox processes. The energy difference between the lowest energy level of the CB and the highest energy level of the VB is called band gap energy (E<sub>g</sub>). It corresponds to the minimum energy of light required to make the material electrically conductive.

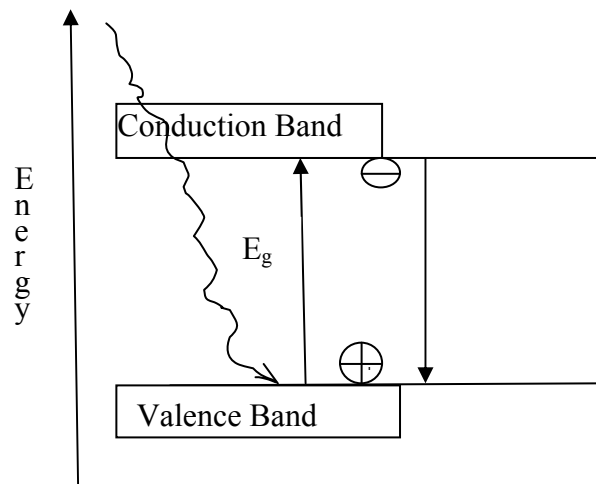
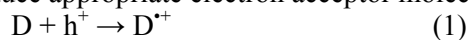


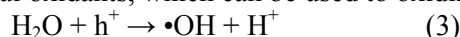
Figure 1: Operation of a photochemical excited TiO<sub>2</sub> particle

When a photon with energy of  $h\nu$  ( $h \rightarrow$  Plank's constant,  $\nu \rightarrow$  frequency of light) exceeds the energy of the band gap an electron ( $e^-$ ) is promoted from the valence band to the conduction band and subsequently a hole ( $h^+$ ) is created. In electrically conducting materials, i.e. metals, the produced charge carriers are immediately filled this hole by another electron. In semiconductors a portion of this photoexcited electron and hole together (electron-hole pairs) diffuse to the surface of the catalytic particle (electron-hole pairs are trapped at the surface) and take part in the chemical reaction with the adsorbed donor (D) or acceptor (A) molecules.

The holes can oxidize donor molecules (Equation1) whereas the conduction band electrons can reduce appropriate electron acceptor molecules (Equation2).



A characteristic feature of semiconducting metal oxides is the strong oxidation power of their holes  $h^+$ . They can react in an one-electron oxidation step with water (Equation3) to produce the highly reactive hydroxyl radical ( $\bullet OH$ ). Both the holes and the hydroxyl radicals are very powerful oxidants, which can be used to oxidize most organic contaminants.

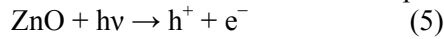


In general, air oxygen acts as electron acceptor (Equation4) and forms the super-oxide ion  $O_2^-$  which are also highly reactive particles and are able to oxidize organic materials.



### 3.0 COMBINATION OF ZnO AND TiO<sub>2</sub> AS HYBRID PHOTOCATALYST

The ZnO is found in the form of hexagonal crystal or as a white powder. It also occurs in nature as mineral zincates. The Wurtzite structure of ZnO is a wide band gap semiconductor with band gap energy of near about 3.2eV, which corresponds to electromagnetic radiation in the UV (ultraviolet) region. The top of valence band is composed of 2p orbital from the O<sup>2-</sup> atoms while the bottom of the conduction band is composed of 4s orbital from the Zn<sup>2+</sup> atom.



Therefore, the creation of electron hole pairs is through a ligand to metal charge transfer of an electron from the UV on oxygen to the conduction band on zinc.



Figure 2: Zinc oxide powder

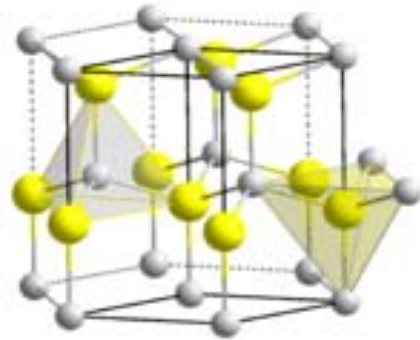


Figure 3: unit cell of ZnO

The reaction rate of the photocatalyst is surface area dependent, as its electron-hole transfer takes place on the surface. Therefore, the photocatalyst morphology is an important property in determining the effectiveness of the photocatalyst [17]. When the surface-to-volume ratio increases, the rate of electron-hole pairs transfer from the semiconductor to the absorbed molecule also increases due to the ability of the ZnO to absorb more molecules on the surface.

TiO<sub>2</sub> exists in three crystalline forms: rutile, anatase, and brookite (Fujishima et al.) [18]. Titanium dioxide, particularly in the anatase form, is a photocatalyst under ultraviolet (UV) light. Recently, it has been found that titanium dioxide, when spiked with nitrogen ions or doped with metal oxide like tungsten trioxide, works as a photocatalyst under either visible or UV light [19]. The strong oxidative potential of the positive holes oxidizes water and creates hydroxyl radicals. It can also oxidize oxygen or organic materials directly. Titanium dioxide is thus added to paints, cements, windows, tiles, or other products for its sterilizing, deodorizing and anti-fouling properties and is used as a hydrolysis catalyst.

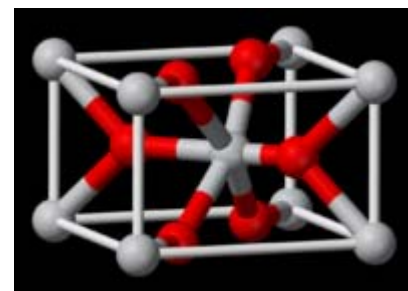
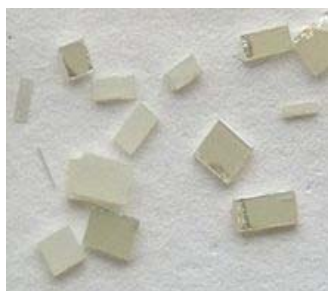
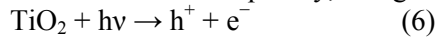


Figure 4: Crystals of TiO<sub>2</sub>    Figure 5: Titanium dioxide powder    Figure 6: unit cell of TiO<sub>2</sub>

Generally, titanium dioxide is a semiconducting material which can be chemically activated by light. Under the influence of light the material tends to decompose organic materials in presence of photocatalyst. This effect leads to the well-known phenomenon of "paint chalking", where the organic components of the paint are decomposed as result of photocatalytic processes [20]. Fujishima and Honda discovered the photocatalytic splitting of water on TiO<sub>2</sub> electrodes

[21]. This event marked the beginning of a new era in heterogeneous photocatalysis. Although  $\text{TiO}_2$  absorbs only approx. 5 % of the solar light reaching the surface of the earth, it is the best investigated semiconductor in the field of chemical conversion and storage of solar energy [21].

The conduction band of  $\text{TiO}_2$  is composed of 3d, 4s and 4p orbitals from  $\text{Ti}^{4+}$  atoms, with the 3d orbitals being the majority of the lower portion of the conduction band. Band gap energy of this material is  $E_g = 3.2\text{eV}$ . If this material is irradiated with photons of the energy  $> 3.2\text{eV}$  (wavelength  $\lambda < 388\text{ nm}$ ), the band gap increases and an electron is promoted from the valence to the conduction band. Consequently, charge-carrier is formed in its primary process (Equation 6).



The ability of a semiconductor to undergo photo induced electron transfer to adsorbed particles is governed by the band energy positions of the semiconductor and the redox potentials of the adsorbents [22], [23]. The relevant potential level of the acceptor species is thermodynamically required to be below the conduction band of the semiconductor. Otherwise, the potential level of the donor is required to be above the valence band position of the semiconductor in order to donate an electron to the empty hole.

From the theoretical description of the localized atomic-like Ti 3d state is induced by  $\text{Zn}^{2+}$  ions. It is seen that hybrid photocatalyst provides satisfactory results in increasing surface area, thermal stability and surface acidity.

#### 4.0 EXPERIMENTAL DETERMINATION OF $\text{p}^{\text{H}}$ OF HYBRID PHOTOCATALYST AND CEMENTATIONS MATERIALS

##### 4.1 DETERMINATION OF APPROPRIATE PROPORTION OF $\text{ZnO}$ AND $\text{TiO}_2$ AS HYBRID PHOTOCATALYST

Highly pure  $\text{TiO}_2$  and  $\text{ZnO}$  were used for measuring the appropriate proportion of the mixture for hybrid photocatalyst. At first 16mg cement was mixed with 100ml distilled water for maintaining 1N catalyst to cement ratio 1:100. Then 1N solution of  $\text{TiO}_2$  and 1N solution of  $\text{ZnO}$  were prepared separately. Thereafter, pH of individual solution was measured using BUTECH-810 pH meter. Solution of both photocatalystes was mixed at different ratios (As indicated in graph) and pH of the mixture was measured using the same pH meter. pH value for different mixing proportion of  $\text{TiO}_2$  and  $\text{ZnO}$  are shown in Fig.-7.

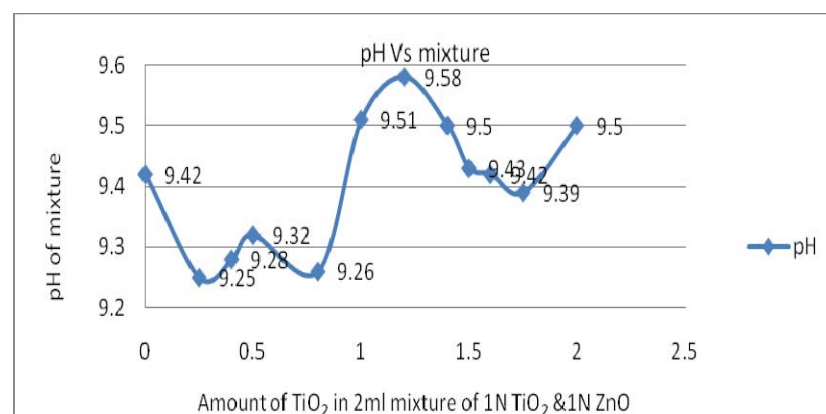


Figure 7:  $\text{p}^{\text{H}}$  for different mixing proportion of 1N  $\text{TiO}_2$  and 1N  $\text{ZnO}$  in mixture (2ml)

From this figure, it is seen that pH value is maximum at a mix proportion of  $\text{TiO}_2$  and  $\text{ZnO}$  of 1.2: 0.8. This pH value is also found to be greater than the pH value of individual photocatalyst.

## 4.2 DETERMINATION OF $p^H$ OF CEMENTATIONS MATERIALS IN PRESENCE OF HYBRID PHOTOCATALYST

In order to determine the pH of cementations materials in presence of hybrid photocatalyst cement solution was made first by mixing 16mg cement into 100ml distilled water for maintaining 1N catalyst to cement ratio 1:100. Thereafter, 1.2 ml 1N  $TiO_2$  and 0.8ml 1N ZnO were added to the 4ml cement solution (taken from the instant mixture of cement solution) for obtaining solution of cementations material in presence of photocatalyst. pH of this solution was measured instantly using the same pH meter used to measure pH of photocatalyst pH value of cementations material in presence of individual photocatalyst was also measured using the same pH meter in this study. The pH values obtained from this study are given in Table 1.

**Table 1:**  $p^H$  of photocatalyst in presence of cement

Component	$p^H$
Cement+ Hybrid photocatalyst	10.44
Cement+ ZnO	10.39
Cement+ $TiO_2$	10.26

From Table 1 it is seen that the mixture of 1N  $TiO_2$  and 1N ZnO at a ratio of 1.2:0.8 with cement solution gives the higher pH (10.44) value than that of the individual mixture of 1N  $TiO_2$  (pH 10.39) and 1N ZnO (pH 10.26) with cement solution. Higher pH value of cementations materials in presence of hybrid photocatalyst reduces the corrosion problem of RC materials.

## 5.0 ADVANTAGES OF HYBRID PHOTOCATALYST

The heterogeneous photocatalytic oxidation with ZnO and  $TiO_2$  could make it competitive with respect to other processes oxidizing contaminants. It has the following advantages:

- Low-cost material is used as photocatalyst.
- The reaction is quite fast at mild operating conditions (room temperature and atmospheric pressure).
- No chemical reactants are used and no side reactions are produced..

## 6.0 APPLICATION OF ZnO AND $TiO_2$ AS HYBRID PHOTOCATALYST

Photocatalyst is needed for a cleaner environment and a better quality of life that leads to thoughts of a more eco-compatible use of light. In this context photochemistry applied to construction materials that could provide a very interesting solution [24]. It could become an integral part of the strategies adopted for reducing environmental pollution through the use of construction materials containing photocatalysts [25].

Hybrid photocatalyst of ZnO and  $TiO_2$ , which creates local energy levels within the band gap of the photocatalyst, with corresponding absorption bands lying in the visible spectral range [26]. It is assumed that the photoexcitation of such hybrid photocatalyst to the generation of free charge carriers to initiate surface chemical processes. However, the efficiency of such systems under visible light strongly depended on the preparation method used and ratio of photocatalysts.

In figure 8, the main areas of activity in hybrid photocatalysis are shown. As already mentioned, in the last 10 years photocatalysis has become more and more attractive for the industry regarding the development of technologies for purification of water and air

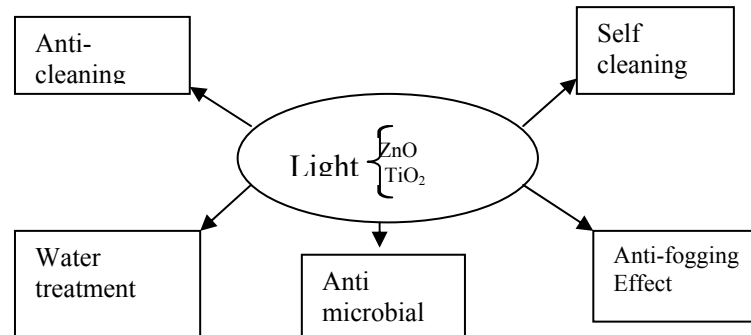


Figure 8: Major areas of activity in mixed photocatalysis

## 7.0 CONCLUSIONS

From the experimental study of  $p^H$  measurement of cementitious material in the presence of hybrid photocatalyst (made by ZnO and  $TiO_2$ ) it could be concluded that hybrid photocatalyst could help to reduce corrosion effect of R.C. concrete as its pH value are found to be higher than the pH value of cementation material with individual photocatalyst. Since hybrid photocatalyst (ZnO and  $TiO_2$ ) has large surface area, therefore, it exhibits a good photo degradation property. Hybrid photocatalyst could also help to absorb more carbon dioxide into the concrete from atmosphere due to creation of lower activation energy in their process. This phenomenon produces sustainable environment for human being. Though this study is in developing stage it needs to consider employing many of the options that might improve the sustainability of this material, and continue to gain knowledge and expertise in this area.

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