A LITERATURE REVIEW ON THE APPLICATION OF TITANIUM DIOXIDE REACTIVE SURFACES ON URBAN INFRASTRUCTURE FOR DEPOLLUTING AND SELF-CLEANING APPLICATIONS

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ABSTRACT

Purpose of this paper – This study was performed in order to understand what work has been completed regarding the application of reactive surfaces primarily for pollution abatement in urban areas. The hope is that these surfaces could then be applied to South African infrastructure for the benefit of the people.

Methodology/Scope - Journal articles from peer reviewed journals were studied in order to understand the level of work that has so far been completed.

Findings - It was found that a great deal of research is currently underway in this topic globally and that titanium dioxide reactive surfaces show good potential for depolluting and self-cleaning applications.

Research limitations - There is a large amount of published work on this topic, consequently not all of the relevant articles and studies could be read for inclusion into the literature review. However it is thought that the important details and findings are included.

Practical implications - Titanium dioxide reactive surfaces have been shown to work under real life conditions and have real potential to be used in basic urban infrastructure. Utilisation of such surfaces could become a standard building practise within South Africa.

Value - This paper is a collection of the applicable results of studies that have been completed globally. It shows the potential of such surfaces and if utilised could provide real health benefits for people living in urban areas. Economic advantages can also be experienced by the owners of such surfaces due to lower maintenance requirements.

Keywords: Coatings, Titanium Dioxide, Depolluting, Self-Cleaning, Photocatalysis

1 INTRODUCTION

Photocatalysis has attracted extensive attention since the discovery of the Fujishima and Honda phenomenon in the early 1970's. (Fujishima & Honda, 1972) Fujishima and Honda discovered that photolysis of water could occur by using photocatalysts such as titanium dioxide. This discovery suggested a large number of potential applications, including photovoltaic cells, photoinduced superhydrophilicity, organic synthesis, degradation of pollutants and photolysis of water. Since that discovery, photocatalysis has been a subject of serious research and exploration.

2 FUNDAMENTALS OF PHOTOCATALYSIS

Although titanium dioxide (TiO_2) was the semi-conductor initially used by Fujishima and Honda, many other semi-conductors have been identified and used in experimentation, including CdS, SnO_2, WO_3, SiO_2, ZrO_2, ZnO, Nb_2O_3, Fe_2O_3, $SrTiO_3$ and TiO_2.

In catalysed photolysis, light is absorbed by the semi-conductor (catalyst) which causes an electron to become excited and forms an electron-hole pair. Each semi-conductor used as a photocatalyst corresponds to a range of light wavelengths with which electron hole-pairs may be induced. The size of the band gap of the electron hole-pairs, varies between the semi-conductors and the band gap is the amount of energy the semi-conductor requires to absorb in order produce an electron hole-pair.

Photocatalysts are characterised by their ability to absorb and undergo two different reactions simultaneously, one reaction involving the excited electron (e^-) and the other involving the electron hole. (h^+) (O. Carpe et al, 2004) Photo generated holes that are produced on TiO_2 surfaces have strong oxidising power (3.0 eV) and can oxidise almost all toxic organic compounds to CO_2. (Ohko & Fujishima, 1998)
The photocatalytic reaction is initiated by absorption of UV light, an electron-hole pair is then formed on the titanium dioxide, each of which are then able to react with nearby molecules. (Banerjee1,S et al, 2006) There are a number of reactions which can then lead to the production of hydroxyl radicals or reactive oxygen species. (ROS)

The hydroxyl radical or any of the ROS are capable of oxidising pollutants on or near the TiO_2. Desoiling agents, such as Rhodamine B or pollutants such as, NOx, VOC (Volatile Organic Carbons) and BTEX (benzene, toluene, ethylbenzene, o-xylene), have all been shown to be oxidised by these agents produced by the photocatalysts.

3 SELECTION OF THE SEMI-CONDUCTOR

Of the available semi-conductors which can be used as photocatalysts, TiO_2 is generally considered to be the best semiconductor photocatalyst available at present. (Mills et al, 2002)

The overwhelming majority of the literature concerning photocatalysis is concerned with identifying the properties, applications and theory of the use of titanium dioxide as a semiconductor. There are indeed good reasons for favouring TiO_2 as the semi-conductor of choice, including:

- Strong oxidising power, at ambient temperature and pressure (3.0 eV)
- Photo-generated electrons are reducing enough to produce superoxide from dioxygen

- Anti-bacterial
- Self-cleaning
- Depolluting
- Chemical inertness
- Physical stability
- Non-toxic
- Superhydrophilic
- Stable in the presence of aqueous electrolyte solutions
- Cheap and readily available

Titanium dioxide is close to being an ideal photocatalyst, displaying all of the required properties, the only exception being that it does not react well with visible light. (Carp et al, 2004)

There are already a number of commercial photocatalytic TiO_2 products available on the market and notably, Degussa P25 TiO_2, which is in many respects considered a standard and is often used as a comparison in scientific experimentation for determining photocatalytic activity. (Mills et al, 1997)

4. REAL WORLD APPLICATIONS OF THE DEPOLLUTING EFFECT OF TITANIUM DIOXIDE SURFACES

4.1 Applications in Japan

It is known that Japan has applied titanium dioxide coatings in many of their cities, such as Osaka, Chiba, Chigasaki, Suitama and Shinatoshin. At least 50 000m^2 of surface area in Japan has been coated with such surfaces, and the claim is that the daily removal rate is 0.5 - 1.5 mmol per m^2 and that the photocatalytic material can maintain its effectiveness with very little performance deterioration.

A titanium dioxide coating was used to coat highway sound barriers Osaka, Japan, 1999, the purpose of which was to reduce NOx pollutants as well as providing a self-cleaning effect.

Figure 1. View of soundproof highway walls coated with titanium oxide photocatalysts for the elimination of NOx. These new walls were constructed in Osaka, April 1999. (Anpo, M, 2000)

4.1.1 Highway Case Study

Details regarding a specific case study in Tokyo were obtained. Photocatalytic panels were used, which were made of polyvinyl chloride resin. The panels were placed alongside a 6 lane highway running in an east/west direction. The traffic estimation for on highway was 113 000 vehicles a day.

Metrological measurements were taken and the UVA intensity at noon was over 0.1mW cm^{-2}, these measurements were taken during winter. Two types of panels were used, an open panel and a windowed panel.

The windowed panel had a glass covering and air was pumped into contact with the photocatalytic surface. The average percentage removal of NOx for the windowed panel was between 31-69%. SO_2 and non-methane hydrocarbons were removed, 67-79% and 17-20% respectively. The removal percentages for the windowed panels are dependant on the air flow over them. The rate estimated was 3 mmol (NOx) $m^{-2}d^{-1}$. (Kaneko & Okura, 2002)

4.2 Applications in Europe:

PICADA is a research group which is partially funded by the European Union and comprises of companies and universities from England, France, Italy, Denmark and Greece, including CTG Italcementi, GTM Construction, Millennium Chemicals and the Aristotle University of Thessaloniki.

They have produced numerous photocatalytically active materials with one in particular even entering into the commercial market, TxActive, produced by Ital Cementi, which is a photocatalytic cement. Some of the results of their work have been published.

They compared a 10mm thick mortar rendering (mixture of cement lime and sand) and a 1mm thick mineral paint (mixture of cement and fillers) which were compared with a standard concrete mix, CEN mortar. It is reported that both samples contained the same amount of titanium dioxide, in the anatase form, with an average crystallite size of 20nm. Some of their results are shown below.

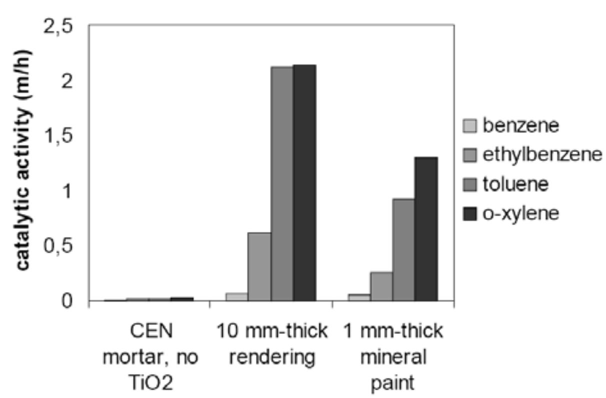

Figure 2. Photocatalytic activity of the cement-based materials at 300 ng/LBTEX nominal concentration, PICADA Results. (Vallee, F, et al ,2004)

Another report from the PICADA group also studied the photocatalytic effects of two different photocatalytic paints intended to be used on cementious materials. (Maggos, Th. et al., 2005) The two paints considered were designated, C1 and T1.

The first paint, C1 is a commercially available mineral paint (1mm thick) for aesthetic surfaces and contains about 3% wt of titanium dioxide. The second paint, T2 is a translucent paint obtained from

Millennium Chemicals Co. It's a water-based product using siloxanes as binders and contains 10% by volume of titanium dioxide.

They found that during their macro experiments, in a $30m^3$ chamber, at 30 C^o, 50% humidity and under 2.1 W/m^2 that the degradation rates for the mineral and translucent paints were, $0.21 g/m^2/s$ and $0.06 g/m^2/s$ respectively.

4.2.1 Car Park Case Study

A photocatalytic paint that was produced by Picada was tested in a real world scenario, in a closed off car park. A car was used to pollute the air and the ceiling was painted with a photocatalytic paint, which was illuminated by UV lamps.

The volume of the car park was $917m^3$ and the surface area that was covered with paint was $322m^2$. The paint used contained 10% titanium dioxide and was provided by Millennium Chemicals. The tests recorded the concentration of NO and NO_2 in the car park environment, also a blank test was performed, in which the UV lights were not turned on.

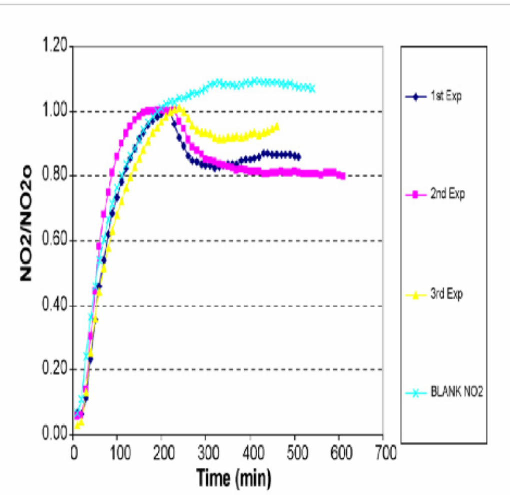

Figure 3. $NO_2/NO_{2}o$ **variation during the Car Park experiments (**$NO_{2}o$ **is the concentration in the steadystate condition). (Maggos et al, 2007)**

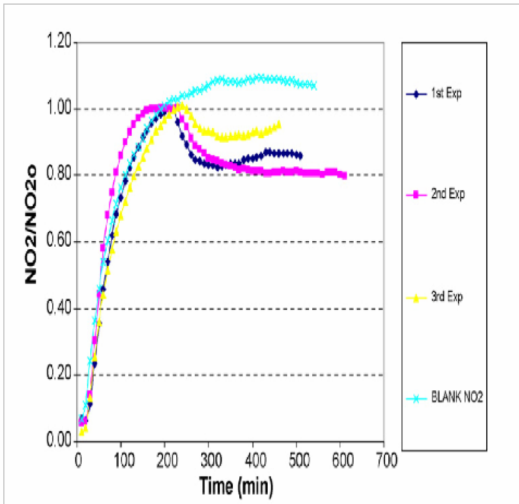

Figure 4. NO/NOo variation during the Car Park experiments (NOo is the concentration in the steadystate condition). (Maggos et al, 2007)

Lab scale tests using the same paint and the same irradiance showed complete destruction of NO, however the car park test did not perform as well. This is thought to be due to the fact that the car not only produces NO, but NO_2 and other VOC which could have an inhibition effect on the TiO_2 paint and the other pollutants will also be degraded by TiO_2 and occupy reaction sites which could otherwise be used for NO.

Even so the photocatalytic removal of NO and NO_2 was about 19% and 20%, respectively, while the corresponding photocatalytic rate ($gm^{-2}s^{-1}$) ranged between 0.05 and 0.13 and between 0.09 and 0.16 respectively.

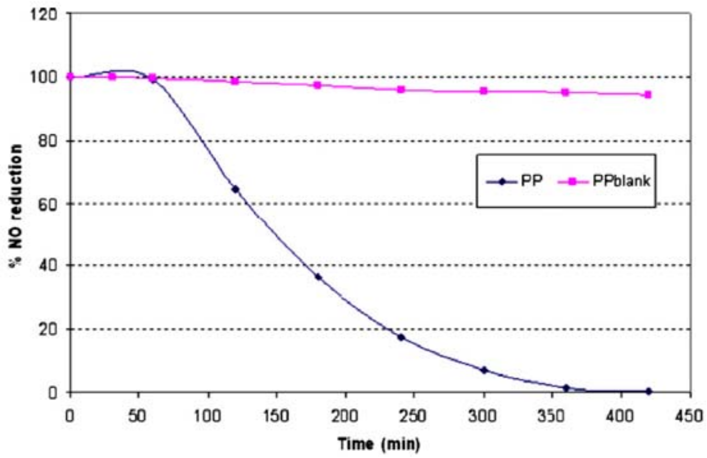

Figure 5. Percentage of NO removal during laboratory scale experiments. (Maggos et al, 2007)

4.3 Applications in America

The Houston Advanced Research Centre is also involved in the study of using titanium dioxide surfaces as a means of degrading NOx and VOC gases. Detailed instructions of how they manufactured the concrete slabs that they tested, the titanium powder that they used and their methodology is all included in their report. (Daniel H, 2007)

For the experiments that were run, a constant stream of NO gas was pumped through the reactive chamber and the outlet stream was measured for NO concentration. Consequently the photoreactive concrete only had a limited time in which to degrade the NO gas.

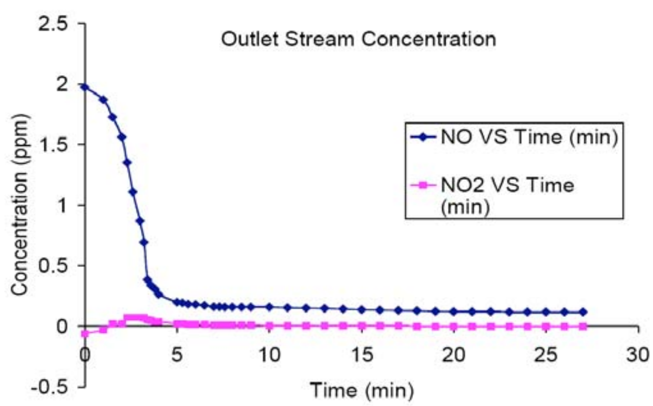

Figure 6. NO and NO_2 concentrations versus time, (Daniel H. Chen, 2007)

5 SELF-CLEANING EFFECT OF TITANIUM DIOXIDE SURFACES

Titanium dioxide surfaces have been shown to also display self-cleaning properties. It is the same hydroxyl radicals or reactive oxygen species which oxidise pollutants that are able to oxidise material which could dirty the surface, such as organic compounds and other soilants. Rhodamine B is a dye that is most commonly used for testing the self-cleaning properties of such surfaces, the reason being that it is a stubborn pollutant which has a strong a^* colourmetric value.

Several high profile buildings have been built by such products such as Dives in Misericordia Church, Rome, Italy, shown in the figure below and Cite de la musique, Chambery, France.

Colourimetric measurements have been taken of these buildings over a period of over 2 years and the conclusion is that the photocatalytic cement displays a desoiling effect and that the colour of the cement can be preserved.

Photocatalytic surfaces are also superhyrdophilic and have contact angles with water of nearly 0^o, which causes water to fully wet the surface and aids in the cleaning of the surface of dirt or compounds which cannot be degraded photocatalytically. (Yu et al, 2001)

Figure 7. Dives in Misericordia Church, Rome, Italy. (The active photocatalytic principle)

6 ENCHANING THE PHOTOCATALYTIC PROPERTIES OF TITANIUM DIOXIDE

While it has been shown that titanium dioxide surfaces perform while under direct sunlight, it is only a small portion of the visible light spectrum with which the surface reacts. Light of a wavelength of lower than 388nm is required to activate the surface, this corresponds to less than 5% of the visible light spectrum.

Considering the potential that such surfaces offer, a great deal of research has been done in order to firstly enhance the effectiveness of TiO_2 and secondly to expand the range of light with which it reacts into longer wavelengths.

Unfortunately the manner in which such surfaces were produced within the literature varies greatly as well as the pollutants against which they were tested. Consequently comparisons of performance of modifications are difficult to make and justify. (Zainal et al, 2004)

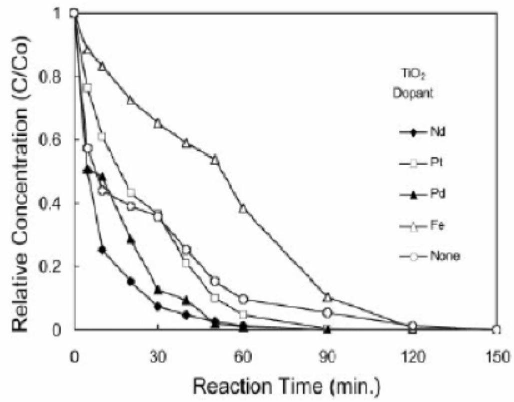

Figure 8. Photodegradation of 2-CP with undoped TiO_2 and transition metalion-(Nd3+, Pd2+, Pt4+, and Fe3+) doped TiO_2 under an UV light source. (Shah et al,2002)

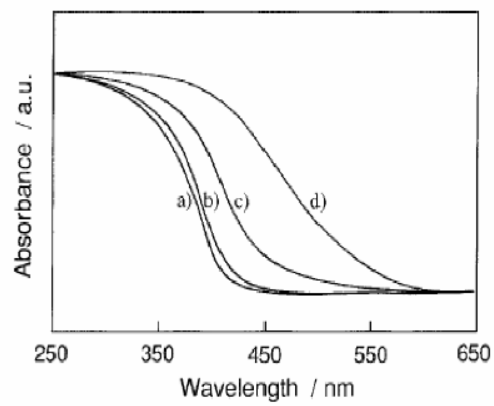

Figure 9. Effects of Cr ion-implantation on the UV-VIS diuse reectancespectra of the TiO2 catalyst (absorption spectrum).Number of implanted Crions (N/cm2): (a) 0.0 (original TiO2),(b) 11016, (c) 61016, (d) 121016. (Anpo, M, 1997)

Chromium and vanadium doping have been shown to significantly improve the photocatalytic properties of titanium dioxide, as well as many other ions.

Much research is currently being done on trying to improve the performance of titanium dioxide surfaces through doping. Recently co-doping, with more than one element has been tried and improvements have been recorded using bromine and chlorine.

7 POTENTIALLY HARMFULL BYPRODUCTS

There is significant evidence to suggest that several harmful by products may be formed by the general photocatalysis performed by titanium dioxide. Of considerable concern is the oxidation of NO to form NO_2 as well as the formation of ozone and carbon monoxide. (Daniel, H, et al, 2007) However, NO_2 can be further oxidized to form nitrate salts which are mostly harmless. Of more concern is the formation of ozone, O_3, which is a highly toxic gas. (Gurol, 2006)

It has been shown, through the research done by PICADA, that photocatalytic degradation of NO yields NO_2 and some ozone. Also, the photocatalytic degradation of NO_2 yields O_3 and small amounts of NO. (Maggos, 2005)

It should be noted that NOx and some VOC's are the main causes of tropospheric ozone and the degradation of such compounds will decrease the concentration of tropospheric ozone. Consequently, despite forming ozone, the net result could be a lower concentration of ozone due to the degradation of NO_2, which is a main cause of tropospheric ozone.

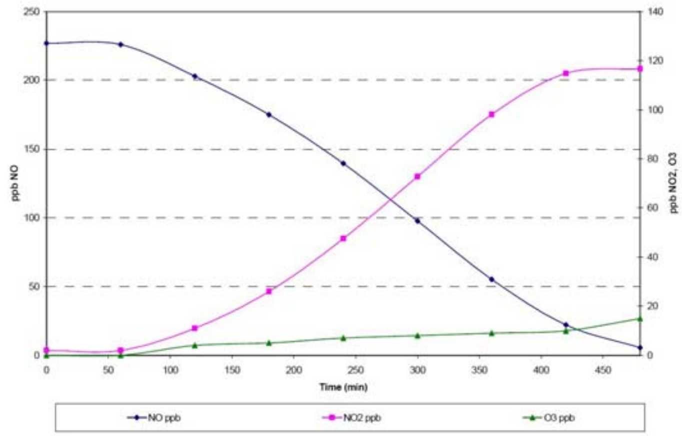

Figure 10. NO_2, O_3 production through the degradation of NO. (Maggos, 2005)

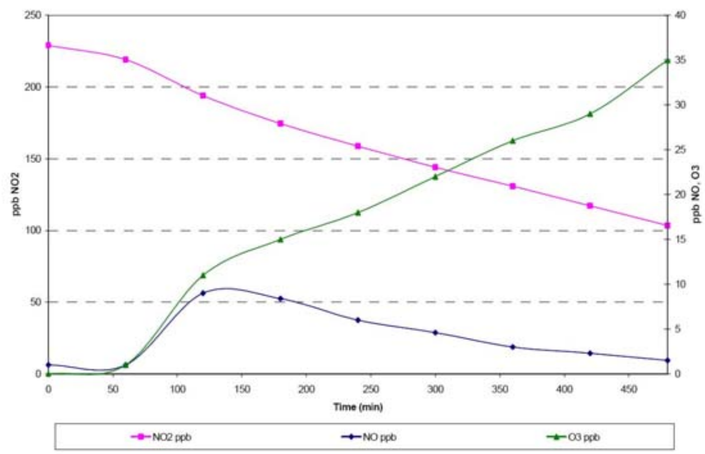

Figure 11. O_3 production through the degradation of NO_2 . (Maggos, 2005)

8 CONCLUSIONS

Titanium Dioxide has by far shown itself to be the most practical semi-conductor available for photocatalysis. The amount of literature available on this single semi-conductor is astounding with most authors in the field regarding titanium dioxide as the semi-conductor best suited for commercial applications. Indeed there are already a large number of commercial photocatalytic TiO_2 products available.

There is a great deal of research currently trying to improve the photocatalytic potential of titanium dioxide, both in effectiveness and in trying to expand the light spectrum with which it reacts into the visible range. The most common technique currently tried is to dope titanium dioxide with another element and more recently two elements, co-doping has been tried.

However, many factors, within the preparation process of photocatalytic surfaces can have an impact on its photocatalytic ability. Also, the experiments conducted, often measure the effectiveness of such surfaces against different pollutants or even bacteria, such as, e-coli or to decompose methylene blue, rhodamine, acetaldehyde, NOx, or any number of a multitude of other organic pollutants. Consequently, comparing results from such experiments can be difficult and speculative.

However, virtually all studies confirm its photocatalytic potential for pollution abatement, self-cleaning, and anti-bacterial effects, leaving many well known authors very excited about the potential of this semi-conductor. It is expected that research in this field will grow as will the availability of commercial products.

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