Heterogeneous TiO$_2$ Photocatalysis
- Fundamental Chemical Aspects and Effects of Solid Phase Alterations

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Doctoral Thesis

AKADEMISK AVHANDLING

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Abstract

Heterogeneous photocatalysis on TiO$_2$ is an emerging green technology for water disinfection. The rationale for this technology is based on in-situ generation of highly reactive transitory species for degradation of organic and inorganic pollutants as well as microorganisms. Recent research has concentrated on improving the efficiency of the photocatalytic process, however, some fundamental information on the mechanistic aspects and rate limiting properties still remain elusive.

The focus of this thesis has been to identify the primary oxidant in heterogeneous TiO$_2$ photocatalysis and to create prerequisites for further evaluation of how selected internal (material specific) and external (system specific) alterations influence the photocatalytic activity. Furthermore, an attempt to induce visible light activity to a modified TiO$_2$ film was also made.

Production of H$_2$O$_2$ was used to probe the existence of the hydroxyl radical as the primary oxidizing species in aqueous TiO$_2$ photocatalysis. The only possible pathway to produce H$_2$O$_2$ in an oxygen free environment is through hydroxyl radical recombination. A significant amount of H$_2$O$_2$ could be detected in deoxygenated solutions confirming the existence of hydroxyl radicals. To further elucidate the origin of the H$_2$O$_2$, experiments with the hydroxyl radical scavenger Tris(hydroxymethyl)aminomethane (Tris) were performed. The results further support the hypothesis that the hydroxyl radical is the primary oxidant in TiO$_2$ photocatalysis.

Tris was evaluated as a probe in aqueous photocatalysis. Hydrogen abstracting species such as hydroxyl radicals are able to abstract hydrogen atoms from Tris, which leads to formation of formaldehyde. Formaldehyde was detected and quantified by a modified version of the Hantzsch reaction. This route to probe the photocatalytic efficiency allows for assessment of the maximum photocatalytic efficiency with high accuracy and sensitivity and was further used to study how selected solid phase alterations and dissolved electron acceptors affect the photocatalytic efficiency. The results showed that the surface area of immobilized photocatalysts affects the efficiency and a high surface area is advantageous for photocatalysis. It was also shown that TiO$_2$ enhanced with Ag nanoparticles significantly increases photocatalytic activity. This is explained partly by an increased O$_2$ adsorption and reduction process on the Ag enhanced TiO$_2$ compared to pure TiO$_2$ and partly as a Schottky barrier formation at the metal-semiconductor interface. These processes lead to a prolonged charge separation in the photocatalyst, which is advantageous for the efficiency. Moreover, the effect of the external, dissolved electron acceptors H$_2$O$_2$ and O$_2$ were also evaluated by Tris. The results showed an increased photocatalytic activity upon addition of the electron acceptors. It was also shown that the adsorption affinity of a reactant to the photocatalyst is rate controlling and governs the kinetics.

An attempt to induce visible light activity into a TiO$_2$ film was also made by a post-treatment in liquid NH$_3$. The slightly narrowed bandgap of the resulting film caused a red-shift in the absorption band and the film showed visible light activity under illumination by white light with a cut-off filter at 385 nm.
Sammanfattning

Heterogen fotokatalys på TiO$_2$ är en lovande, miljövänlig teknik för desinfektion av vatten. Denna teknik baseras på *in-situ* generering av mycket reaktiva, kortlivade specier som har förmåga att bryta ned organiska och oorganiska föroreningar samt mikroorganismer. Forskning inom området har på senare tid till stor del koncentrerats till att förbättra effektiviteten av den fotokatalytiska processen, dock är viss grundläggande information om de mekanistiska aspekterna och de hastighetsbegränsande egenskapherna fortfarande oklar.

Fokus för denna avhandling har varit att identifiera den primära oxidanten vid heterogen fotokatalys på TiO$_2$ och att skapa förutsättningar för att vidare kunna studera hur utvalda interna (*materialspezifika*) och externa (*systemspezifika*) förändringar påverkar den fotokatalytiska effektiviteten. Ett försök att modifiera TiO$_2$ för att få materialet aktivt i synligt ljus har också utförts.

Bildning av H$_2$O$_2$ användes för att påvisa förekomsten av hydroxylradikalen som den primära oxidanten vid fotokatalys på TiO$_2$ i vattenlösning. Den enda möjligheten för bildning av H$_2$O$_2$ i en syrefri miljö är via rekombination av hydroxylradikaler. En betydande del H$_2$O$_2$ kunde detekteras i syrefria vattenlösningar, vilket bekräftar förekomsten av hydroxylradikaler. För att ytterligare studera upphovet till H$_2$O$_2$ genomfördes experiment tillsammans med hydroxylradikal-infångaren Tris(hydroxymetyl)aminometan (Tris). De erhållna resultaten stödjer hypotesen att hydroxylradikalen är den primära oxidanten vid TiO$_2$ fotokatalys.


List of Papers

This thesis is based on the following papers:

I. “Tris(hydroxymethyl)aminomethane as a Probe in Heterogeneous TiO₂ Photocatalysis”  

II. “Effects of O₂ and H₂O₂ on TiO₂ Photocatalytic Efficiency Quantified by Formaldehyde Formation from Tris(hydroxymethyl)aminomethane”  

III. “Improved Texturing and Photocatalytic Efficiency in TiO₂ Films Grown Using Aerosol-Assisted CVD and Atmospheric Pressure CVD”  
Veronica Diesen, Mats Jonsson and Ivan P. Parkin, Chemical Vapor Deposition, Accepted, 2013, DOI: 10.1002/cvde.201307067

IV. "Silver Enhanced TiO₂ Thin Films: Photocatalytic Characterization using Aqueous Solutions of Tris(hydroxymethyl)aminomethane”  

V. "Comment on the Use of Phenols as Probes for the Kinetics of Heterogeneous Photocatalysis”  
Veronica Diesen and Mats Jonsson, Manuscript

VI. "Formation of H₂O₂ in TiO₂ Photocatalysis of Oxygenated and Deoxygenated Aqueous Systems: A Probe for Photocatalytically Produced Hydroxyl Radicals”  
Veronica Diesen and Mats Jonsson, Manuscript

VII. “Visible Light Photocatalytic Activity in AACVD Prepared N-modified TiO₂ Thin Films”  
Veronica Diesen, Charles W. Dunnill, Mats Jonsson and Ivan P. Parkin, Submitted to Chemical Vapor Deposition
My contribution to the papers

I. I planned and performed all experimental work and participated in evaluating the results. I wrote the first draft of the manuscript.

II. I planned and performed all experimental work and participated in evaluating the results. I wrote the first draft of the manuscript.

III. I planned and performed all experimental work and participated in evaluating the results. I wrote the first draft of the manuscript.

IV. I planned and performed some experimental work. I evaluated the results and wrote the first draft of the manuscript.

V. I contributed to the results and took part in the preparation of the paper.

VI. I planned and performed all experimental work. I participated in evaluating the results and wrote minor parts of the manuscript.

VII. I planned and performed some experimental work and evaluated the results. I wrote the first draft of the manuscript.
Abbreviations

XRD X-ray diffraction
SEM Scanning electron microscopy
XPS X-ray photoelectron spectroscopy
AFM Atomic force microscopy
TEM Transmission electron microscopy
SAED Selected area electron diffraction
HRTEM High resolution transmission electron microscopy
EDX Energy dispersive X-ray spectroscopy
UV-Vis Ultra-violet visible
CVD Chemical vapor deposition
AACVD Aerosol-assisted chemical vapor deposition
APCVD Atmospheric pressure chemical vapor deposition
SG Sol-gel
SP Screen-printed
Tris Tris(hydroxymethyl)aminomethane
Rz Resazurin
Rf Resorufin
Ti[OCH(CH₃)₂]₄ Titanium(IV)-isopropoxide
LaB₆ Lanthanum hexaboride
SHE Standard hydrogen electrode
AQY Apparent quantum yield
HOMO Highest occupied molecular orbital
LUMO Lowest unoccupied molecular orbital
SPR Surface plasmon resonance
CB Conduction band
VB Valence band
\( e^-_{CB} \) Conduction band electron
\( h^+_{VB} \) Valence band hole
\( E_g \) Bandgap
\( A \) Acceptor species
\( A^- \) Reduced acceptor species
\( D \) Donor species
\( D^{**} \) Oxidized donor species
\( k \) Rate constant
\( K_{LH} \) Adsorption equilibrium constant
\( E_F \) Fermi level
\( Gy \) Gray
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1. Introduction

1.1 Background

In recent years, there has been great concern over many serious environmental problems that we are facing on a global scale. One of them concerns water, our most important natural resource. A combination of a growing population and a rapid development of industry have resulted in a steady increase of water pollution in many parts of the World due to the accelerated release of harmful agents. This has positioned the water issue as one of the fastest growing social, political and economic challenges of today.\(^1\) As the need for clean water increases the demand for new purification technologies with low environmental impact grows. Recognizing these needs, development of efficient, sustainable and environmentally friendly water treatment technologies is crucial for our future.

Heterogeneous photocatalysis has appeared as an innovative and promising technology for water disinfection. Photocatalysis is a process in which highly reactive transitory species are formed on a semiconductor material, usually TiO\(_2\), under exposure to light of energies higher than or equal to the bandgap of the material. The high oxidizing power of these species can induce degradation and ultimately result in complete mineralization of many refractory organic and inorganic pollutants in water according to reaction (1).

\[
\text{Contaminant} + \text{Photocatalyst} \xrightarrow{h\nu \geq E_g} \text{CO}_2 + \text{H}_2\text{O} + \text{intermediates} \quad (1)
\]

The starting point of photocatalysis dates back to the early 20\(^{th}\) century, although it was not until 1972 when Fujishima and Honda published a paper in Nature\(^2\) where they reported that water splitting was possible upon illumination of TiO\(_2\) that the interest for the field attracted considerable attention from scientists in a broad area. Many promising environmental applications ranging from photo-electro-catalytic production of hydrogen and renewable energy to disinfection of water have since then been developed, Figure 1.
A few years after the breakthrough of photocatalysis, in 1977 Frank and Bard\(^3\) showed that cyanide in water could be decomposed on TiO\(_2\) in water upon illumination and this immensely increased the interest for using heterogeneous photocatalysis to purify water. Since then, intense research has been carried out on TiO\(_2\) and other photocatalytic materials in order to elucidate the mechanisms behind and to improve the efficiency of the process. Although the great interest in heterogeneous photocatalysis, a clear consensus about the reactions and processes involved is not yet available and some fundamental questions regarding the initial reactions and the rate limiting processes still remain to be clarified.

1.2 Principles of Heterogeneous Photocatalysis

When a semiconducting metal oxide absorbs a photon of energy equal to or higher than its bandgap \((h\nu \geq E_g)\), an electron is promoted from its valence band to its conduction band, within a femtosecond timescale.\(^4,5\) The photonic excitation leaves behind an exciton with an empty valence band hole and a filled conduction band (electron-hole pair). The fate of the separated electron and hole can follow different pathways.\(^6\) One possibility is migration of the electron and hole to the semiconductor surface. While at the surface, the photocatalyst is able to donate the electron to an electron acceptor \((A)\), usually molecular oxygen. In turn, a donor species \((D)\) can be oxidized by the valence band hole. These charge transfer processes are dependent on the position of the valence and the conduction band edges respectively and also on the redox potential of the adsorbed species.\(^6\) As this reaction path results in a prolonged lifetime of the electron-hole pair, a higher quantity of reactive oxidant species is produced resulting in more efficient degradation of pollutants in water. Electron-hole recombination is
reaction competing with hole-donor and electron acceptor electron-transfer reactions. Recombination can occur either in the semiconductor bulk or at the surface resulting in the release of heat (or light) and is detrimental for the photocatalytic activity as the redox properties of the semiconductor are quenched. The photocatalytic events are illustrated in Figure 2.

Figure 2: Photo-excitation of a semiconducting metal oxide particle (a) and the de-excitation events; (b) electron-hole recombination within the semiconductor bulk, (c) oxidation of surface adsorbed electron donors, (d) reduction of surface adsorbed electron acceptors and (e) electron-hole recombination at the semiconductor surface.

The primary photocatalytic events are given by reactions (2)-(5):

\[
\begin{align*}
\text{Semiconductor} \xrightarrow{h\nu \geq E_g} &\quad e_{CB}^- + h_{VB}^+ \quad (2) \\
h_{VB}^+ + D &\rightarrow D^+ \quad (3) \\
e_{CB}^- + A &\rightarrow A^- \quad (4) \\
e_{CB}^- + h_{VB}^+ &\rightarrow \Delta \text{ and/or } h\nu \quad (5)
\end{align*}
\]
1.3 Photocatalysis on TiO$_2$

Among many candidates for photocatalysis, TiO$_2$ has become the benchmark photocatalyst with the highest activity, chemical stability (resistance to photo-corrosion) and abundance.$^7$

1.3.1 The Lattice and Electronic Structure of TiO$_2$

TiO$_2$ exists mainly in three crystallographic phases: anatase, rutile and brookite. Particle size experiments has shown that the relative phase stability becomes size dependent when particle sizes decrease to sufficiently low values due to surface energy effects such as surface stress and surface free energy alterations.$^8-10$ For particle sizes below 11 nm, anatase is the most stable phase, while rutile is the most stable for particles above 35 nm.$^8$ Brookite has been found to be the most stable phase for particles between 11-35 nm, although contradictory results have been presented.$^{11-13}$

Anatase is indicated as the most photocatalytically active phase. Rutile also displays photocatalytic activity but to a lesser extent$^{14}$ and brookite generally does not show appreciable photocatalytic activity.$^{15}$ Although anatase is considered to be the single most photoactive phase, synergistic mixtures of anatase and rutile have been reported to possess even higher photo-activity. The difference in lattice and band structure between anatase and rutile ($E_g$,rutile $\sim$ 3.0 eV and $E_g$,anatase $\sim$ 3.2 eV) can to some extent explain the difference in photo-activity, but the lower capacity of rutile to adsorb O$_2$ can also be ascribed the poorer photocatalytic activity observed in aerated systems.$^{16}$

1.3.2 The Band Energy Positions

The band energy positions $i.e.$ the oxidation potential of the valence band and the reduction potential of the conduction band is crucial for the photocatalytic properties of the semiconductor. The energy band diagram for TiO$_2$ in an aqueous solution at pH 7 is shown in Figure 3. The oxidation potential for the photo-generated hole is $+2.53$ V vs. SHE, which is theoretically powerful enough to oxidize water and hydroxide ions to produce hydroxyl radicals ($OH^\cdot$). The reduction potential for the conduction band electrons is $-0.52$ V vs. SHE is sufficient to reduce O$_2$. $^7$
**Figure 3**: Schematic diagram showing the reduction potential of the photo-excited conduction band electron and the oxidation potential of the valence band hole along with the redox potentials for various processes occurring at the TiO$_2$ surface at pH 7.

### 1.3.3 General Mechanisms of Heterogeneous Photocatalysis on TiO$_2$ and Characteristic Rates

The characteristic time intervals for the photo-reactions occurring on TiO$_2$ are given in Table 1.
Table 1: Primary events in heterogeneous TiO$_2$ photocatalysis and their characteristic times.$^{17}$

<table>
<thead>
<tr>
<th>Electronic step</th>
<th>Primary process</th>
<th>Characteristic times</th>
</tr>
</thead>
<tbody>
<tr>
<td>Charge-carrier generation</td>
<td>$TiO_2 + h\nu \rightarrow e^-<em>{CB} + h^+</em>{VB}$</td>
<td>fs ($10^{-15}$ s)</td>
</tr>
<tr>
<td>Charge-carrier trapping</td>
<td>$h^+_{VB} + &gt; Ti^{IV}OH \rightarrow &gt; Ti^{IV}OH^{*+}$</td>
<td>10 ns ($10^{-8}$ s)</td>
</tr>
<tr>
<td>Shallow trap</td>
<td>$e^-_{CB} + &gt; Ti^{IV}OH \Leftrightarrow &gt; Ti^{III}OH$</td>
<td>100 ps ($10^{-10}$ s)</td>
</tr>
<tr>
<td>Deep trap</td>
<td>$e^-_{CB} + &gt; Ti^{IV} \rightarrow &gt; Ti^{III}$</td>
<td>10 ns ($10^{-8}$ s)</td>
</tr>
<tr>
<td>Charge-carrier recombination</td>
<td>$h^+_{VB} + &gt; Ti^{III}OH \rightarrow &gt; Ti^{IV}OH$</td>
<td>100 ns ($10^{-7}$ s)</td>
</tr>
<tr>
<td></td>
<td>$e^-_{CB} + &gt; Ti^{IV}OH^{*+} \rightarrow &gt; Ti^{IV}OH$</td>
<td>10 ns ($10^{-8}$ s)</td>
</tr>
<tr>
<td>Interfacial charge transfer</td>
<td>$&gt; Ti^{IV}OH^{<em>+} + D \rightarrow &gt; Ti^{IV}OH + D^{</em>+}$</td>
<td>100 ns ($10^{-7}$ s)</td>
</tr>
<tr>
<td></td>
<td>$&gt; Ti^{III}OH + A \rightarrow &gt; Ti^{IV}OH + A^{*-}$</td>
<td>ms ($10^{-3}$ s)</td>
</tr>
</tbody>
</table>

1.3.4 Photo-Induced Superhydrophilicity

One interesting aspect with TiO$_2$ is that it gives rise to two simultaneous phenomena upon illumination namely photocatalysis and superhydrophilicity.$^7$ The photo-induced superhydrophilicity is an effect that causes water to fully wet the surface i.e. the water contact angle (the angle at which a liquid/vapor interface meets a solid) is $< 10^\circ$. This phenomenon has been related to structural changes on the surface although the mechanism is still controversial.$^7, 13, 18$-$20$ One explanation to this effect is that $Ti^{IV}$ is reduced to $Ti^{III}$ by photogenerated electrons which results in oxygen vacancies on the surface.$^7$ By dissociation of adsorbed water, hydroxyl groups are produced on the surface resulting in a hydroxylated surface which enables water droplets to fully wet the surface. An illustration of the process is shown in Figure 4.
Figure 4: Proposed mechanism of photo-induced hydrophilicity on TiO$_2$ and photographs showing the effect. By illumination of an hydrophobic surface oxygen vacancies are formed and replaced by dissociated water molecules resulting in a hydrophilic surface.  

The superhydrophilic property displayed by TiO$_2$ has attracted much attention due to applications such as self-cleaning, antifogging and antibacterial materials.\(^7,\,18,\,21\) The water contact angle (degree of wetting) of a TiO$_2$ surface is also highly relevant as it can be related to textural properties and there are two main models used for this; the Wenzel and the Cassie-Baxter models.\(^22,\,23\) In the Cassie-Baxter model the water does not completely penetrate the surface as air is trapped under the water droplet. In the Wenzel model the water droplet is able to fully penetrate the surface, which results in a lower contact angle. Generally, the rougher the surface, the more hydrophobic it is.

1.3.5 The Main Challenge: Second-Generation Photocatalysts

In several aspects, TiO$_2$ is close to being an ideal photocatalyst. However, being a wide-bandgap semiconductor with a large intrinsic bandgap, activation of TiO$_2$ is restricted to UV-photons which only make up less than 5 % of the solar energy spectrum. As the visible light accounts for the major part of the solar spectrum (~ 45 %),\(^24\) extensive investigations have been carried out to extend the photo-response of TiO$_2$ into the visible light region in order to more effectively utilize the solar energy.\(^25\)–\(^34\) The challenge has been to shift the absorption band towards the visible light region without sacrificing the photocatalytic activity. Approaches to achieve this have included metal-ion implanting,\(^35\)–\(^38\) noble metal loading,\(^26,\,39\) non-metal doping\(^33,\,40\)–\(^44\) and organic dye sensitizing.\(^45\) Among the attempts, non-metal doping in general and nitrogen-doping in particular are considered to be the most effective routes.\(^25,\)
Although heavily investigated, the reason for the increased visible light activity is not yet established and different explanations have been proposed in the literature. These include:

1. **Band gap narrowing**: Asahi *et al.*\(^{25}\) found that in N-doped anatase TiO\(_2\), the N 2p states hybrids with O 2p states as these energies are very close. This results in narrowing of the band gap and the material is able to absorb light in the visible light region.

2. **Oxygen vacancies**: Ihara *et al.*\(^{48}\) showed that visible light activity could be realized in polycrystalline TiO\(_2\) particles as oxygen deficient sites can be formed in grain-boundaries and nitrogen incorporation into these sites are important for re-oxidation prevention.

3. **Impurity energy levels**: Irie *et al.*\(^{49}\) stated that oxygen sites in TiO\(_2\) substituted by nitrogen atoms are able to form isolated impurity energy levels above the valence band which, upon visible-light irradiation, enable excitation of electrons from the impurity energy level to the conduction band.

4. **Interstitial nitrogen**: Dunnill *et al.*\(^{50}\) showed good visible light photocatalysis with samples containing only interstitial nitrogen, thus highlighting the importance of the interstitial doping for enhanced visible light photocatalytic activity.

Despite the disagreement of the reason for the photo-response in the visible region by nitrogen-modified TiO\(_2\), the development of visible light active photocatalysts or “second generation TiO\(_2\) photocatalysts” which efficiently harvest visible light from the solar energy and convert it into chemistry, is still a main challenge in the field.

### 1.4 Mechanistic Aspects of Heterogeneous TiO\(_2\) Photocatalysis

The mechanistic aspects of photocatalytic reactions are complex. In particular, the oxidation paths are of major interest and different oxidation routes have been proposed for the reactions occurring at the interface between the solid and the liquid. Information about the oxidant in photocatalysis is essential as not every reactant will necessarily be sensitive to all possible oxidation pathways (in all systems). The complexity arises as the species involved in photocatalysis are not only transitory, but also almost chemically equivalent which makes it even more difficult to distinguish between them. In this section the present mechanistic paths and subsequent kinetic models are presented.
1.4.1 Hydroxyl Radicals or Photo-Generated Surface Trapped Holes?

One heavily debated question in the field of heterogeneous photocatalysis of aqueous systems is the identity of the oxidant.\textsuperscript{51-64} Currently, there are two suggested main oxidation pathways. One involves oxidation through hydroxyl radicals, mainly formed upon oxidation of water or hydroxide ions, and the second alternative is that oxidation proceeds through the photo-generated surface-trapped holes. A lot of research has been devoted to bring clarity to this fundamental question. The hydroxyl radical is a very powerful oxidant with a redox potential of $+2.80 \text{ V vs. SHE}$ at pH 7, while the photo-generated valence band hole in TiO\textsubscript{2} has a redox potential of $+2.53 \text{ V vs. SHE}$ at pH 7.\textsuperscript{65} Experimental techniques such as combined spin trapping and electron spin resonance (ESR) have been used to verify the existence of the hydroxyl radical in photocatalysis and have often been regarded as a proof for the existence of hydroxyl radicals under illumination of TiO\textsubscript{2} in aqueous suspensions.\textsuperscript{63, 66-72} Detection of hydroxylated reaction intermediates\textsuperscript{73, 74} as well as final hydroxylation product distribution\textsuperscript{75, 76} also supports this mechanism. The debate of the initial reaction step often hinges on how the hydroxyl radicals are formed. One possibility is via direct hole-oxidation of adsorbed water or hydroxide ions\textsuperscript{72} another via electron scavenging reactions involving O\textsubscript{2}.\textsuperscript{57, 77} Recently Salvador\textsuperscript{57} reported that hydroxyl radicals cannot be photo-generated via hole trapping by water species. The presented analysis of the electronic structure of surface bound water, obtained from electron photoemission spectroscopy data reported in the literature, showed that the valence band holes formed on rutile TiO\textsubscript{2} do not have enough potential to oxidize adsorbed water species \textit{i.e.} valence band holes cannot be trapped by extrinsic states associated with adsorbed water species. Nakamura and Nakato\textsuperscript{78} had earlier claimed that the O 2p levels of the surface hydroxyl groups are below the top of the TiO\textsubscript{2} valence band which means that the these groups cannot be oxidized by valence band holes. Although these studies were conducted on rutile (because of the difficulty of obtaining big enough oriented single crystals of anatase) the authors expect similar behavior for anatase since both phases have the same density of fivefold coordinated terminal Ti sites where non-dissociative adsorption of water takes place and the adsorption energy of water on anatase is very close to that of rutile.

It is important to note that not every reactant will necessarily be sensitive to only one of the two suggested oxidants and numerous studies have assumed competing roles for the photo-generated hydroxyl radical and the trapped valence band hole. Factors such as reaction conditions can also play a role in deciding which oxidant is available and most useful. As an example, Yu and Chuang\textsuperscript{53} reported that the valence band holes are most important at high surface coverage of organic compounds (concentrated solutions) as the formation of hydroxyl radicals is hindered due to the limited access of water molecules or hydroxide ions for the surface. Thus, oxidation of the organic compounds is more likely to proceed through the valence band holes in concentrated solutions.\textsuperscript{79, 80}

Even though hole-oxidation and hydroxyl radical mediated reaction pathways are vastly different processes they generate similar product distributions in oxygenated aqueous solutions thus making distinction between the two pathways difficult.
1.4.1.1 Free or Surface Adsorbed Oxidants?

Another subject of controversy refers to the localization of the degradation process, which is dependent on the localization of the oxidant. The valence band hole can only be present at the surface while the hydroxyl radical can be present either at the surface or diffused into the surrounding media. Interesting observations that direct hole-mediated oxidation is not the only oxidation-pathway is found in observations of “remote” oxidation. In this phenomenon, oxidation events are detected at regions not exposed to light or at a distance away from the photocatalytic surface. Molecular fluorescence markers have also been used to verify the emission of hydroxyl radicals from a TiO₂ photocatalyst during UV illumination.

Further, Salvador claims that free hydroxyl radicals in the water layer close to the TiO₂ surface may be generated, but only via reduction of dissolved molecular oxygen by the photo-excited conduction band electrons since oxidation of non-adsorbed water molecules or solvated hydroxyl groups by the valence band hole is hindered both thermodynamically and kinetically. Although diffusion of hydroxyl radicals may be possible, adsorption of reactants on the photocatalytic surface is often reported as a prerequisite for an efficient photocatalytic process as the oxidant have been found to be adsorbed on the surface. A vast number of both experimental and theoretical studies based on density functional methods have been considered as proof for this hypothesis. The hydroxyl radical is a highly reactive species and even if diffusion is possible, reaction is expected in close proximity to photocatalytic surface due to the highly reactive and nonselective nature of this oxidant. Adsorption can therefore be considered critical for photocatalytic reactions.

1.4.2 Kinetics

As there is still disagreement on the fundamental mechanistic aspects of photocatalysis, models describing the kinetics are also a subject of controversy. The first and most widely applied kinetic model is the Langmuir-Hinshelwood model. This classical surface-adsorption model is based on the assumptions that the surface has a limited number of surface adsorption sites, only one single layer can be adsorbed and there are no interactions between the adsorbed molecules. It is also, implicitly, based on the assumption that the adsorption/desorption equilibrium is independent of the photochemistry. The model establishes that the reaction rate depends on the concentration of the reactants according to Eqns. 1-3:

\[ r = k \theta \]  
\[ \theta = \frac{K_{LH}C}{(1+K_{LH}C)} \]
\[ r = -\frac{dC}{dt} = \frac{kK_{LH}C}{(1+K_{LH}C)} \]  \hspace{1cm} \text{Eq. 3}

where \( \theta \) is the surface coverage of reactant(s), \( K_{LH} \) is the Langmuir equilibrium adsorption/desorption constant, \( C \) denotes the reactant concentration in the liquid phase, \( r \) is the rate of product formation and \( k \) represents the maximum rate. According to the L-H model the reaction rate is proportional to the surface area covered by the reactant and the rate increases with the concentration of the reactants until the catalyst surface becomes saturated.

The L-H model has been applied to TiO\(_2\) photocatalytic degradation of numerous compounds in aqueous and gas-phase media with good agreement.\(^{95-101}\) However, several limitations to this model have been observed which has initiated a debate regarding the accuracy of the L-H model when applying it to photocatalytic reactions. One of the concerns includes incapacity of the model to define a relationship between the photon flux and the reaction rate. The kinetic parameter \( k \) is obviously dependent on the light intensity, but some authors have reported that \( K_{LH} \) is also a function of the light intensity.\(^{102-104}\) This would consequently be attributed to adsorption/desorption equilibrium not being established under illumination, which is not in line with the L-H model. Ollis\(^{105}\) presented a pseudo-steady state analysis based upon the stationary state hypothesis for reaction intermediates, which he found consistent for the reported intensity dependence. In this approach it is assumed that the reactant adsorption/desorption equilibrium is not established due to the continued displacement of the adsorbed substrates from the photocatalytic surface caused by reactions with the hole (\( h^+ \)), electron (\( e^- \)) or the hydroxyl radical.

As previously stated, the very existence of the hydroxyl radical in photocatalysis is still discussed.\(^{51-64}\) If hydroxyl radicals are not the primary oxidants then oxidation must proceed through valence band holes. One model that is exclusively based on oxidation through valence band holes is the direct-indirect (D-I) model.\(^{106}\) In this alternative kinetic approach two interfacial charge transfer mechanisms are considered: the direct transfer (DT) mechanism based on the direct reaction of organic substrates and delocalized (free) valence band holes and the indirect transfer (IT) mechanism in which the photo-oxidation occurs through surface trapped holes. Both mechanisms are governed by the specific adsorption of the dissolved organic species and since the distribution of products between the DT and IT is similar, distinction between them is difficult. In a recently published paper, it was reported that for the special case of photo-degradation of phenol the D-I model did not fit the experimental data.\(^{107}\) This discrepancy was attributed to a back reaction not being considered \( i.e. \) the reduction of the organic radical by the conduction band electron back to the parent compound. In the work presented, a new kinetic expression that takes into account the back reaction and non-specific adsorption of substrates on the photocatalytic surface is proposed.

1.5 Immobilization Techniques and Properties: Liquid-Solid and Vapor-Solid Approaches

Powdered photocatalysts in nanometer-dimensions have a large surface area to volume ratio which is highly desirable for catalytic reactions, as a higher concentration of pollutants can be
adsorbed and decomposed on the photocatalyst. However, the usage of photocatalytic powders entails later separation from the liquid phase. In order to avoid a costly separation step, considerable efforts have been devoted to fixation of nano-particular photocatalysts on different substrates. A number of deposition techniques have been developed, both liquid-solid and vapor-solid transformations. The photocatalytic activity is directly dependent on the immobilization method and the subsequent sintering processes since they give decisive influence on the chemical and physical properties of the photocatalyst. Properties such as thickness, porosity and surface structure are crucial features to be considered in the immobilized system. The choice of substrate material is also of great significance as introduction of foreign impurities from this material can have a negative effect on the photocatalytic activity.  

Here, the immobilization techniques that have been used in the studies for this thesis are presented.

1.5.1 Liquid-Solid Transformations

1.5.1.1 Sol-gel

In the sol-gel process, metal oxides are prepared via hydrolysis of metal precursors, usually metal alkoxides and an alcoholic solution, followed by multiple condensation reactions. In the initial hydrolysis step, the metal alkoxide ("sol") is involved in nucleophilic reactions with water as follows (reaction (6)):

\[ M(OR)_y + xH_2O \leftrightarrow M(OR)_{y-x}(OH) + xROH \]  

(6)

The mechanism of this reaction includes addition of a negatively charged \( HO^- \) group to the positively charged metal center (\( M^+ \)). In the subsequent step the proton is transferred to an alkoxy group whereby \( ROH \) is removed and a metal hydroxide is formed. The hydroxide molecules polymerize by condensation upon release of water. This process leads to the formation of a metal hydroxide network and a dense, porous “gel” is obtained. By removal of the solvents and by appropriate drying and heat treatment processes, nano-scaled metal oxides can be obtained.

The sol can be applied to the substrate by conventional coating techniques such as dip- or spin coating and the final chemical and physical properties of the product are primarily determined by the hydrolysis and drying steps. In general, slow hydrolysis and condensation rates favour generation of smaller particles, advantageous for photocatalysis. The kinetics of these reactions is influenced by the electronegativity of the metal ion, the structure of the alkoxy group, the solvent and the molecular structure of the metal alkoxide. Briefly, slow hydrolysis and condensation is favoured by high electronegativity of the metal ion. The coordination number of the metal in the metal alkoxide precursor is also an important factor.
and the rate of hydrolysis decreases with increasing coordination number. Other parameters, easier to control, are the size of the OR-group in the metal alkoxide and the solvent. These are linked since interchange reactions are possible between alcohols. In general, large -OR groups give slow hydrolysis. The sol-gel process has the advantage that it is relatively inexpensive and can accommodate industrial-scale production.

1.5.1.2 Screen-printing

Screen-printing is a film deposition method where a paste containing photocatalytic nanoparticles (when depositing photocatalytic films) is printed onto a substrate. A subsequent heating step removes the organic solvents comprised within the paste and sinters the particles. The process allows for control of film thickness and position as well as porosity, depending on the particle sizes of the paste used. Strongly adhesive, nanocrystalline TiO$_2$ layers of over 17 µm thicknesses have been obtained by screen-printing and the best performing TiO$_2$ electrodes for dye-sensitized solar cells (DSCs) have been fabricated by this technique.$^{112}$ Highly photocatalytically active films produced by screen-printing have also been reported in the literature.$^{113}$ The key-point of the screen-printing process is the quality and characteristics of the paste.$^{112}$ Synthesis of a TiO$_2$ paste generally involve hydrolysis of Ti(OC$_3$H$_7$)$_4$ in water, followed by conversion of water to ethanol by centrifugation and finally exchange of ethanol to α-terpineol by sonification and evaporation.$^{114}$ The entire paste preparation process usually takes several days, which also makes the commercially available pastes rather expensive. Currently, a lot of research is focusing on faster, alternative routes to TiO$_2$ paste fabrication.$^{112,115}$

1.5.2 Vapor-Solid Transformations

1.5.2.1 Chemical Vapor Deposition (CVD)$^{116}$

Chemical vapor deposition (CVD) is a chemical processes where a substrate is exposed to one or more volatile precursors which react and decompose to form a film. CVD is used to deposit a wide range of materials including several metals and metal oxides and is widely used in the microelectronics and glass industry. A typical CVD process involves the following steps (illustrated in Figure 5):

1. Transport of reagents (precursors) in the gas phase to the deposition zone. Usually, a carrier gas is used for this.

2. Diffusion of the reagents through a boundary layer (a hot gas layer adjacent to the substrate).
3. Adsorption of the reagents onto the substrate surface.

4. Deposition of the reagents and formation of a solid film. By-product is formed at the same time.


6. Transport of the gaseous by-products out of the reactor.

Figure 5: A schematic representation of the steps in a typical CVD process.

CVD is practiced in a variety of formats which generally differ in the means by which chemical reactions are initiated. Two commonly applied CVD techniques are atmospheric pressure CVD (APCVD) which is classified by operating pressure, and aerosol-assisted CVD (AACVD) process, classified by the physical characteristics of the vapor. The APCVD process is very fast with film growth rates in the range of 200 nm-4 µm min⁻¹. AACVD is similar to the APCVD but uses an aerosol, generated ultrasonically, to act as a transport vector. The growth rates are usually much lower compared to APCVD and the precursor often becomes involved in the chemistry as it can react differently with various solvents in the gas phase. This may lead to the formation of different intermediates and thus to a different crystallographic phase of TiO₂.¹¹⁷
1.6 Assessing the Photocatalytic Activity

Although not commonly accepted, numerous studies suggest that the hydroxyl radical is the key reactant responsible for oxidation of organic substrates in aqueous photocatalysis. Knowledge of the hydroxyl radical yield is therefore essential in order to determine the photocatalytic efficiency and for comparison of different photocatalytic materials. Several routes to assess the hydroxyl radical yield, both direct and indirect, have been reported in the literature including oxidation of organic dyes, hydroxylation of organic substances, and electron paramagnetic resonance detection by spin traps that scavenge the OH radical. However, few of the methods are hydroxyl radical selective, fast and convenient. Dye degradation is a popular method for assessing the efficiency since it is a rather fast and easy method. Dyes usually have relatively high extinction coefficients at the wavelengths used to activate the photocatalyst and will consequently absorb a significant amount of the incoming light, which makes it difficult to assess the full photocatalytic activity. Phenols are also popular probes in photocatalysis and numerous substituted probes have been employed for photocatalytic evaluation.

In this section, two photocatalytic assessment methods, one quantitative and one qualitative method, which have been used for the studies in this work, are presented.

1.6.1 Tris(hydroxymethyl)aminomethane

Tris(hydroxymethyl)aminomethane (Tris), has been evaluated as probe molecule for assessment of photocatalytic efficiencies. Hydrogen abstraction from Tris, by e.g. hydroxyl radicals, yield formaldehyde as one of the products, according to Scheme 1.

![Scheme 1: Hydrogen abstraction from Tris.](image)

Formaldehyde is a stable product that can be detected and quantified through a modified version of the Hantzsch reaction, Scheme 2.
Since it is the formation of a product, rather than the consumption of a reactant that is being measured, the method is quite sensitive even at low conversions of the scavenger. Even though formaldehyde is a compound known to undergo oxidation in photocatalysis, this is considered unlikely partly due to the low conversion (less than 0.1 %) of Tris during the test and partly as the adsorption affinity of formaldehyde for TiO$_2$ is low. Degradation of formaldehyde would also make it difficult to detect this product in the solution. The concentration of formaldehyde formed by a photocatalyst is proportional to the rate of formation of hydrogen abstracting species. Furthermore, as Tris has a low extinction coefficient at the wavelengths used to activate the photocatalyst, it is possible to perform a concentration variation without interfering with the incoming light. A concentration profile is necessary to ascertain that the full scavenging capacity of the probe has been reached which is crucial for comparison of different photocatalysts. One drawback with the method is that since it is an indirect probe, hydrogen abstraction by other species than hydroxyl radicals can take place.

1.6.2 Resazurin

Another method to study the photocatalytic activity is by the redox ink Resazurin ($R_z$). The resazurin dye test is a qualitative, fast and well-established method for evaluation of the photocatalytic efficiency. The method can be semi-qualitative using a RGB-extractor protocol to map the color changes and has been used for mapping of composition gradients. The ink comprises of two main constituents; Resazurin and glycerol, a sacrificial electron donor in excess within the ink. The Resazurin test operates via a photo-reductive mechanism in which the photo-generated valence band holes react irreversibly with glycerol. The photo-generated conduction band electrons (and/or other mediating reducing species) reduce the indicator ink.
to Resorufin (Rf), visually observed as a color change from blue to pink ($E^\circ (Rz/Rf) \approx -0.020 \, V$).\textsuperscript{130} This key initial stage is irreversible and is not affected by $O_2$, which is an advantage of Resazurin as many other redox dyes, including methylene blue, are reversible and react with $O_2$ in their reduced form to regenerate back to the original dye.\textsuperscript{128} A consequence of this is that bleaching can only take place under anaerobic conditions.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{Scheme_3}
\caption{Scheme 3: Photo-reduction of Resazurin to Resorufin and colourless intermediates.}
\end{figure}

### 1.6.3 Photochemical Quantum Yield

Quantum yields in photochemistry are defined as Eq. 4:\textsuperscript{131}

\[
\theta_{QY} = \frac{\text{Amount of molecules formed or consumed}}{\text{Amount of photons absorbed}} 
\]

\textbf{Eq. 4}

For a photocatalytic system it is difficult to determine an absolute quantum yield. One reason for this is the difficulty to determine the amount of photons absorbed by the photocatalyst.\textsuperscript{132} Often polychromatic light is used to activate the photocatalyst and light scattering effects on the surface makes it virtually impossible to quantify the exact amount of photons absorbed by the photocatalyst. Another reason is that the probe concentration used need to be above the concentration independent region to be able to assess the full (maximum) photocatalytic efficiency. This can be difficult for probes with a high extinction coefficient. For these reasons, it is more appropriate to use the term “apparent quantum yield” (AQY) as this will be a system specific entity.

The apparent quantum yields reported using Tris as a probe are the formaldehyde quantum yield in the system. In homogeneous solutions hydrogen abstraction by hydroxyl radicals has been determined to 35 \%,\textsuperscript{133} however in photocatalytic systems other hydrogen abstracting species may also be present and therefore it is more accurate to use the formaldehyde quantum yield. Further, the amount of absorbed photons by the photocatalyst was calculated using the \textit{Lambert-Beer law} assuming that monochromatic light was used. Due to light
scattering effects, the “operational” extinction coefficient determined in this way constitute an upper limit.

1.7 Enhancing the Photocatalytic Efficiency

A lot of research is directed towards improving the photocatalytic activity. To successfully enhance the oxidant yield, the rate limiting properties have to be recognized. A complete understanding of the processes involved in heterogeneous photocatalysis is not yet available, although factors such as particle size, structure and composition of the photocatalyst are known to influence the photocatalytic activity. Three ways to an enhanced photocatalytic activity are presented below.

1.7.1 Surface Area

The chemistry of nano-materials is strongly dependent on the size of the particles. When the particle size decrease, the surface to volume ratio increase and a larger surface area will be available for photochemical reactions. A decreased particle size does not only affect the surface area and number of active sites but also the optical properties. This is explained by energy levels becoming discrete as the particle size decreases, ultimately resulting in a larger spacing between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO). The material properties that have a major impact on the photocatalytic activity such as the textural properties i.e. the surface area and number of active sites can, to some extent, be tuned by the preparation conditions, heating processes and post-treatments. By immobilization of particles a significant amount of active surface area is lost, however adhesion of nanoparticles to a substrate have other advantages, as described above (section 1.5).

1.7.2 Metal Doping

One of the main drawbacks associated with photocatalysis is the fast, inherent recombination of the electron-hole pair, formed following light absorption. It is possible to annihilate/diminish this undesired process by using surface traps. Surface traps increase the performance of the photocatalyst by introducing alternative electron transfer paths which suppress the electron-hole recombination rate. This can be achieved by using a second semiconductor which can, if the material is adequate, act as an effective charge transfer between the coupled states of the semiconductors. Another approach is positioning or integration of metals or non-metal ions on the semiconductor surface. Noble metals often have an advantageous Fermi-level position for electron accumulation. By acting as an
electron sink for the photo-generated electrons, the lifetime of the electron and hole is extended. Metal doping in general and noble metal doping in specific is an interesting way to manipulate the photocatalytic surface. At the metal-semiconductor interface a Schottky barrier is created as a result of the different energy levels (Figure 6b) and band alignment occurs. Electrons can thus start to migrate from the semiconductor into the metal as the Fermi-levels are aligned due to the higher work function in the metal compared to the work function in the semiconductor. The surface of the metal acquires an excess negative charge while the semiconductor becomes excessively positively charged due to the electron transfer and a Schottky barrier forms at the interface which serve as an electron trap and facilitates the charge separation in the semiconductor.

**Figure 6:** (a) A schematic representation of the energy bands of an isolated metal and an isolated n-type semiconductor where $\Phi_m$ is the metal work function, $\Phi_{sc}$ is the semiconductor work function, $E_F$ is the Fermi-level, $\chi_{sc}$ is the electron affinity, $E_g$ is the bandgap and $E_{vb}$ and $E_{cb}$ is the valence- and conduction band levels. The vacuum level ($E_{vac}$) is used as a reference level. (b) After contacting between the metal and the semiconductor, electron migration from the semiconductor to the metal occurs until the two Fermi-levels are aligned. The surface of the metal acquires a negative charge, while the semiconductor obtains an excess positive charge and the bands of the semiconductor bends upward toward the surface creating a Schottky barrier, $\Phi_b$.

Furthermore, metal doped semiconductor photocatalysts will also alter the light absorption properties. When metal nanoparticles are exposed to light, a polarization of free electrons with respect to the much heavier ionic core of a spherical nanoparticle is induced. A net charge difference is only created at the nanoparticle surface and the surface charges generate a restoring force. In this way, dipolar oscillations of the electrons are initiated. The collective oscillations of the conduction band electrons are known as surface plasmon resonance effects (SPR). The process is displayed in Figure 7.
Figure 7: The surface-plasmon oscillations, induced by incoming photons, in a spherical metal nanoparticle. The oscillations cause displacement of the conduction electrons (light blue) relative to the nuclei (blue).

The localized surface plasmon has a significant impact on the light absorption properties of the material and is strongly dependent on parameters such as particle size and shape and the dielectric constant.\textsuperscript{144, 146, 147} About a century ago, Mie could theoretically model the plasmon absorption band by applying Maxwell equations to describe the interaction between a metal nanoparticle with a known dielectric function and an electromagnetic field.\textsuperscript{148} Mie’s theory can explain the size dependence of the surface plasmon absorption for metallic nanoparticles larger than 20 nm. For smaller particles, an enhanced electron-surface scattering leads to a broadening of the plasmon absorption due to the fact that the electron mean free path becomes longer than the dimensions of the particle. The strength with Mie’s theory is that it only requires knowledge of the metal dielectric constant in order to calculate the nanoparticle absorption spectrum. It has been shown in previous works that metals contacted to semiconductors are also able to induce surface plasmon effects in the absorption properties.\textsuperscript{149} For example, TiO$_2$ incorporated with Ag is known to red shift the absorption band due to the high dielectric constant of the TiO$_2$.\textsuperscript{144, 146, 147} Therefore, the surface plasmon absorption is a unique feature determined by the characteristics of both the metal and the semiconductor.

1.7.3 External Dissolved Electron Acceptors

Another route to an enhanced photocatalytic activity is through external electron acceptors. External, dissolved electron acceptors are species that has a tendency to adsorb on the photocatalyst surface and become reduced by conduction band electrons. The removal of the electron from the photocatalyst conduction band results in a suppressed electron-hole recombination rate. Several research groups have reported increased photocatalytic efficiency
upon addition of dissolved electron acceptors. A wide range of electrophilic molecules can act as electron acceptors in solution, although the simplest are molecular oxygen and hydrogen peroxide. Both compounds readily adsorb to the TiO$_2$ surface and thereby enable capture of the photo-excited conduction band electron. Molecular oxygen has two main functions in photocatalysis. Firstly, O$_2$ is considered to be the primary electron acceptor and is reduced to O$_2^-$, according to reaction (7).

$$O_2 + e_{CB}^- \rightarrow O_2^-$$  \hspace{1cm} (7)

Secondly, O$_2$ can combine with (C-centered) organic radicals formed upon oxidation of, or hydrogen abstraction from, organic solutes and form peroxyl radicals. Depending on the structure of the organic substance, the organic peroxyl radical may induce further oxidation. One-electron reduction of H$_2$O$_2$ yields a hydroxide ion and an additional hydroxyl radical, reaction (8). Hence, H$_2$O$_2$ is also a direct source of hydroxyl radicals and will thereby boost the photocatalytic activity more efficiently than O$_2$.

$$H_2O_2 + e_{CB}^- \rightarrow OH^- + OH^-$$  \hspace{1cm} (8)
1.8 Research Aim

The aim of the research presented is to bring more knowledge and understanding to the fundamental chemical processes occurring at the interface between the photocatalyst and the surrounding aqueous medium. This issue is of high relevance for the development of environmentally friendly processes based on photocatalysis. In this work, focus has been on the liquid-solid interface which is of great significance for application in water disinfection.

In order to achieve a clearer picture of the initial stages of heterogeneous photocatalysis, materials and methods have been developed and evaluated within the project and both kinetic and mechanistic studies have been performed. More specifically, these include:

I. Identification of the primary oxidant in TiO$_2$ photocatalysis

II. Identification of an appropriate probe molecule for quantitative assessment of the photocatalytic activity

III. Studies of the rate limiting properties such as the effect of:
   - The surface area of immobilized TiO$_2$ films
   - External dissolved electron acceptors \textit{i.e.} H$_2$O$_2$ and O$_2$
   - Metal dopants (Ag)

IV. Identification of an efficient route to induce visible light activity to TiO$_2$
2. Experimental

In this chapter, a description of the methods and procedures used in the studies for the thesis is provided.

2.1 Synthesis of Photocatalytic Films

2.1.1 Screen-printing

A commercial paste (Solaronix™) containing 13 nm TiO$_2$ colloidal anatase particles was used for screen-printing TiO$_2$ films. In this deposition method, a tape frame was used on the substrate to govern the thickness of the paste layer. The sample was then placed on a hotplate and the heat was gradually increased from room-temperature up to 500 °C. Once the final temperature was reached, sintering lasted for 1 h. The temperature was then slowly decreased until 25 °C before removing the sample from the hotplate.

2.1.2 Sol-gel

The precursor solution for the sol-gel deposition was prepared by dissolving acetylacetone (2.52 g, 0.03 mol, Sigma Aldrich, 99+ %) in butan-1-ol (32 cm$^3$, 0.35 mol, Sigma Aldrich, 99.4%). Titanium n-butoxide (17.50 g, 0.05 mol, Fluka, 97.0%) was then added and the solution was stirred vigorously for 60 min before addition of distilled water (3.64 ml, 0.20 mol) dissolved in isopropanol (9.05 g, 0.15 mol, Fisher Scientific, analytical grade). Stirring continued for another hour before acetonitrile (1.66 g, 0.04 mol, Fisher Scientific equipment 99%), was added to the solution. The precursor solution was then stirred for a final hour. Samples of TiO$_2$ were prepared on clean microscope slides by dipping into the sol and retracting at a steady rate of rate of 120 cm min$^{-1}$ using a custom made dip-coating apparatus. The slides were heated in a muffle furnace at 10 °C min$^{-1}$ up to 500 °C where the sintering lasted for 1 h. The films were then allowed to cool slowly.

2.1.2.1 Ag Enhanced TiO$_2$ Sol-gel Films

The sol-gel synthesized TiO$_2$ films were post treated in AgNO$_3$ to adhere islands of silver nanoparticles to the film surface. The films were dipped in a silver nitrate methanol solution ($5 \times 10^{-3}$ M made up from AgNO$_3$, Fisher Scientific) for 30 seconds and withdrawn at 120 cm min$^{-1}$ before being exposed to UVC radiation (254 nm) for 120 seconds. This step generates the Ag nanoparticles from the AgNO$_3$. 

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2.1.3 Chemical Vapor Deposition (CVD)

The substrates used for all chemical vapor depositions were supplied by Pilkington NSG Group. This material consists of a standard 3.2 mm thick float glass pre-coated with 50 nm SiO\textsubscript{2} barrier layer. Depositions were made on the barrier side of the glass to avoid contamination from impurities within the glass. The glass supports were washed with acetone and iso-propanol and were allowed to completely air-dry before coating.

2.1.3.1 Aerosol-Assisted CVD (AACVD)

Titanium(IV)-isopropoxide (Ti[O\textsubscript{3}(CH\textsubscript{3})\textsubscript{2}]\textsubscript{4}, 97%, Sigma-Aldrich) was used as precursor for deposition of TiO\textsubscript{2} films. The precursor solution was prepared by mixing 2 mmol of Ti[O\textsubscript{3}(CH\textsubscript{3})\textsubscript{2}]\textsubscript{4} with 50 ml EtOH (reagent grade, Sigma-Aldrich) acting as solvent. An aerosol was generated at room temperature using an ultrasonic humidifier. A nitrogen gas (BOC 99.99%) flow of 2.0 L min\textsuperscript{-1} was passed through the aerosol mist, directing the aerosol to a horizontal-bed cold-wall CVD reactor containing a heated graphite block onto which the glass support was placed. A glass top-plate was positioned 8 mm above and parallel to the glass support. The whole setup was contained in a quartz tube. The aerosol passed between the heated glass support and the top-plate and the gas flow was continued until all the precursor solution has passed the reactor chamber. At the end of the deposition, only N\textsubscript{2}-gas flowed through the reactor while the film was slowly cooled down to room-temperature.

2.1.3.1.1 Nitrogen Modification

TiO\textsubscript{2} films prepared by AACVD were surface modified by nitrogen via a post treatment process involving immersion in liquid NH\textsubscript{3}. The TiO\textsubscript{2} films were soaked for 2 hours in liquid NH\textsubscript{3} prepared by flowing NH\textsubscript{3} (BOC gas) through a dreshel bottle housed within a solid CO\textsubscript{2}/EtOH bath at -78 °C. The films were then transferred to a furnace and heated to 500 °C for 1 hour before cooling to room temperature.

2.1.3.2 Atmospheric Pressure CVD (APCVD)

Atmospheric pressure CVD were carried out in a horizontal, cold-walled, tubular APCVD quartz deposition chamber. Titanium tetrachloride, TiCl\textsubscript{4} (99.9 % Sigma-Aldrich) used as precursor and ethyl acetate, EtAc (reagent grade, Fischer Scientific) used as the oxygen source were contained in two separate, heated bubblers at a temperature of 70 °C and 40 °C, respectively. The glass supports were placed on a graphite reactor-bed containing three cartridge heaters (Whatman) inside the quartz reactor. The graphite reactor-bed was heated at 10 °C min\textsuperscript{-1} up to 500 °C were it allowed to equilibrate for 60 min before deposition started. N\textsubscript{2} was used as the carrier gas and all gas lines were pre-heated to 150 °C with a flow rate of
0.5 L min\(^{-1}\), prior to deposition. The two reactants were pre-mixed in a stainless steel chamber at 250 °C by which an additional N\(_2\) gas flow of 6.0 L min\(^{-1}\) passed and carried the reagents into the deposition chamber. The gases in the reaction passed between the heated glass support and a top plate positioned 4 mm above the substrate.

2.2 Surface Characterization Techniques

2.2.1 X-ray Diffraction (XRD)

X-ray diffraction is an effective method for determining crystal structures of materials. The basic principle of XRD is that diffraction effects occur when electromagnetic radiation impinges on periodic structures (crystalline solids). When an X-ray beam interacts with an atom, the electrons around the atom start to oscillate with the same frequency as the incoming beam. Since the atoms in a crystal are arranged in a regular pattern, constructive interference is formed when conditions satisfy Bragg’s Law \(n\lambda = 2d \sin \Theta\) and well defined X-ray beams leave the sample at various directions. The Bragg’s Law relates the wavelength \(\lambda\) of the electromagnetic radiation to the diffraction angle \(\Theta\) and the lattice spacing \(d\) in a crystalline material. By scanning the sample through a range of 2\(\Theta\) angles a diffractogram with all possible diffraction directions of the lattice is attained and by matching the pattern with reference samples from a database, the crystallographic structure can be determined.

XRD data for the screen-printed films were collected by a PANanalytical X’pert instrument using Cu K\(_\alpha\) irradiation. Data was collected over the range 5° < 2\(\Theta\) < 65°. The CVD films were characterized using a Bruker D8 diffractometer fitted with a GADDS area detector and a Cu K\(_\alpha\) source. The diffraction patterns were collected for 20 min per sample using a fixed incident angle of 5°.

2.2.2 X-ray Photoelectron Spectroscopy (XPS)

X-ray photoelectron spectroscopy was used to study the elemental composition of the surface and the penetration depth of dopants. In XPS, a material is irradiated by X-rays which causes electrons to emit from the surface. By measuring the binding energy and the quantity of the emitted electrons, information about the elemental identity, chemical state and quantity can be determined.

XPS was carried out using a Thermo Scientific K-Alpha spectrometer with Al K alpha radiation. A dual beam charge compensation system was used with constant pass energy of 50 eV to identify the chemical constituents and their state.
2.2.3 UV-Visible Spectroscopy

UV-Visible absorption spectroscopy is the measurement of the attenuation of a photon beam after it passes through a sample or after reflection from a sample surface. Absorption of visible or ultraviolet radiation corresponds to the excitation of outer electrons from their ground state to an excited state. The absorbance ($A$) of a sample is, according the Lambert Beer’s law which states that $A = e c l$, proportional to the concentration ($c$), path length ($l$) and extinction coefficient ($e$). UV-vis spectroscopy is useful not only for quantitative measurements but also for characterizing absorption, transmission and reflectivity of a variety of materials. Information extracted from UV-vis spectrum can further be used for estimation of the band onset (band gap), color and the thickness of photocatalytic films.

A Perkin Elmer Lambda λ950 UV-Visible spectrometer and a JASCO V-630 spectrophotometer were used for UV-vis spectroscopy.

2.2.4 Raman Spectroscopy

Raman spectroscopy is a powerful tool to analyze structural properties of solid oxides at a local level. TiO$_2$ is a strong Raman scatterer and identification of the crystallographic phases is usually very fast. Upon irradiation of a sample with a monochromatic laser beam, a scattering process occurs. The Raman scattering can be either elastic (Rayleigh) or inelastic (Stokes and anti-Stokes) depending on the energy difference between the absorbed and emitted photons. The interaction between the photons and the molecular vibrational energy states give rise to a spectrum of vibrational bands characterized by their frequency (energy), intensity (polarizability) and band shape (bond environment). As the frequency of the molecular vibrations is unique to each molecule, the Raman spectrum can be used as a “fingerprint” of a particular molecule and to explain molecular structures.

Raman spectra were obtained using a Renishaw Invia Raman Microscope System 1000 with a 50x microscope objective and a Helium-Neon laser (632.8 nm). The spectrometer was calibrated against the emission lines of Ne and Si as a standard reference.

2.2.5 Scanning Electron Microscopy (SEM)

SEM provides surface topography information with very high resolutions, often down to a nanometer. In this technique a focused high-energy electron beam is used to scan over the surface area of a specimen. The primary electrons interact with the surface atoms causing energy exchange between the electron beam and the sample which results in reflection of high-energy electrons by elastic scattering, emission of secondary electrons by inelastic scattering and emission of electromagnetic radiation. Specialized detectors and electronic amplifiers collect and amplify the signals to produce an image of the surface consisting of a
distribution map of the intensity variations of the signals being emitted from the scanned surface. An important feature of the SEM is the retained large depth of field which generates a three dimensional appearance of its images.

The images presented in this thesis were taken using a JEOL JSM-6301F field emission SEM at an accelerating voltage of 3 or 5 kV.

### 2.2.6 Transmission Electron Microscopy (TEM)\(^{165}\)

Transmission electron microscopy was used to image and analyze the microstructure of the photocatalytic materials with atomic scale resolution. The TEM uses accelerated high-energy electrons in vacuum to pass through a thin section specimen of a material. Depending on the density of the material present, some of the electrons are scattered and disappear from the beam, while the un-scattered electrons hit a fluorescent screen and a sophisticated system of electromagnetic lenses focuses the scattered electron into an image. Since the beam goes through the sample during TEM analysis, the interaction of the beam with the sample is much more complex than other electron microscopy techniques and this enable the TEM to generate various imaging modes. The high resolution transmission electron microscopy (HRTEM) mode is a phase-contrast imaging technique, which makes it possible to examine atomic planes and grain boundaries. Selected area electron diffraction (SAED) uses diffracted electrons to elucidate crystallographic information from selected regions of the sample. The spacings and orientation of the diffraction spots can be interpreted in terms of planar spacings and orientations in the sample. Energy dispersive x-ray analysis (EDX) is a technique used to identify the elemental composition of materials. When the electron beam hits the sample, X-rays are generated which have characteristic energies for each element. This provides a qualitative analysis of the elements present and with further analysis, a quantitative composition can be determined.

TEM, HRTEM, SAED and EDX were recorded on a JEOL JEM-2100 with a LaB\(_6\) filament at an acceleration voltage of 200 KeV. Images were recorded on a Gatan Orius charge-coupled device. Samples were prepared by delamination of a TiO\(_2\) film, followed by sonication of the material in hexane before drop-casting onto an Agar Scientific 400 mesh holey carbon grid.

### 2.2.7 Atomic Force Microscopy (AFM)\(^{166, 167}\)

Atomic force microscopy is used to obtain topographical surface profiles in three dimensions. In this technique, a cantilever with a sharp tip is used to scan the surface. When the tip is brought into proximity of a sample surface, an ionic repulsive force arise which leads to a deflection of the cantilever according to Hooke’s law which states that the force, \(F\), required to compress or expand a spring is equal to \(k\), a constant factor characteristic of the spring and the distance \(x\), according to \(F = kx\). A reflected laser beam is used to calculate the force of the bending mode. The vertical movement of the tip across the sample follows the surface profile...
and generate topographical image of the surface. Surface roughness factors at the nanoscale can also be extracted by this technique. The average surface roughness ($R_a$) is described as Eq. 5:

$$R_a = \frac{1}{L} \int_0^L |Z(x)| dx$$  \hspace{1cm} \text{Eq. 5}$$

Where $Z(x)$ is the function that describes the surface profile analyzed in terms of height ($Z$) and position ($x$) of the sample over the evaluation length “$L$”. In this work the root-mean square roughness (RMS) was used. RMS is similar to the roughness average with the only difference being the mean squared absolute values of the surface roughness profile. The function $R_q$ is defined as Eq. 6:

$$R_q = \sqrt{\frac{1}{L} \int_0^L |Z^2(x)| dx}$$  \hspace{1cm} \text{Eq. 6}$$

AFM was conducted on a Veeco Dimension 3100 in air using a tapping operating mode and a silicon tipped cantilever. Sample areas of 1×1 µm were used for analysis.

### 2.2.8 Film Thickness

The film thicknesses were determined by cross-section SEM images and by a Filmetrics F20 thin-film analyzer.

### 2.2.9 Contact Angle

The hydrophilic and hydrophobic properties of the photocatalytic materials were studied by water contact angle measurements. The contact angle is the angle of the interface at which a liquid meets a solid surface and is a result of the surface free energies between the liquid, solid and the surrounding vapor, as shown in Figure 8.
The contact angle ($\theta$) is quantified by Young’s equation, given as:

$$\gamma^{SV} = \gamma^{SL} + \gamma^{LV} \cos \theta$$  \hspace{1cm} \text{Eq. 7}

where $\gamma^{SV}$, $\gamma^{SL}$ and $\gamma^{LV}$ are the interfacial tensions between the solid and the vapor, the solid and the liquid, the liquid and the vapor, respectively.

Measurements of the water contact angles were performed at room temperature (295 K) using a commercial contact angle meter (FTA 1000 droplet analyzer). The experimental error was 2°. The values presented are an average of three measurements using a 3 µL deionized water droplet. A black light UV lamp (365 nm) was used to follow the wetting profile of the CVD surfaces.

### 2.3 Assessment of the Photocatalytic Activity

#### 2.3.1 Tris(hydroxymethyl)aminomethane

To probe photocatalytic efficiencies by formaldehyde formation upon oxidation or hydrogen abstraction of Tris(hydroxymethyl)aminomethane, aqueous Tris (CAS[77-86-1], BDH Chemicals 99 %) solutions of concentrations between 0.1-500 mM were prepared. The pH was adjusted to 7.5 by HCl and measured with a Metrohm 713 pH meter. The photocatalyst was placed on the bottom of a reaction beaker (56 cm$^2$) and placed below the light source. 20 ml of the Tris solution was used for each measurement. The solution was constantly stirred by a magnet during illumination to maintain a homogeneous solution and to facilitate mass transfer to the surface. A modified version of the Hantzsch method was used to determine the concentration of formaldehyde formed upon illumination. In this method 1.5 ml of the reactant solution was extracted after different time intervals of illumination and mixed with 1
ml of 0.2 M solution of acetoacetanilide (CAS [102-01-2], Alfa Aesar > 98 %) in 99.5 % ethanol and 2.5 ml of 4 M ammonium acetate (CAS [631-61-8], Lancaster 98 %). The mixture was left to react in a thermostatic bath for 15 min at a temperature of 313 K. Since the dihydropyridine derivative formed during the reaction, has a maximum absorption wavelength at 368 nm, the absorbance was measured at this wavelength using a JASCO V-630 spectrophotometer. The yield of formaldehyde upon reaction with hydroxyl radicals was determined by quantifying the amount of formaldehyde produced when a known amount of hydroxyl radicals are present in the system. The total incident photon flux was continuously monitored at the irradiation distance with a photometer (International light, Inc.) during the measurements.

2.3.1.1 Experiments Involving Dissolved Electron Acceptors

To elucidate the electron scavenging capacity of O₂ and H₂O₂, a closed reaction cell was used to enable control of the atmospheres during the experiments. The experiments were carried out in N₂ (inert), air and in O₂ saturated atmospheres by purging the Tris solution with the respective gas and by flowing the gas through the reaction cell during illumination. Experiments involving H₂O₂ were conducted in an inert atmosphere to avoid competitive electron scavenging by O₂.

2.3.1.2 The Effect of O₂ on the Production of Formaldehyde Studied by γ-Radiolysis

Gamma radiolysis was employed to study the effect of O₂ on the production of formaldehyde. Gamma radiolysis of water produces OH radicals, H, eₐq⁻, H₂O₂ and H₂ of which OH radicals and eₐq⁻ are the major products (the radiation chemical yield is 0.28 µmol J⁻¹ for both products). Two reaction vessels containing 15 ml of 80 mM Tris solutions (pH 7.5) were saturated with O₂ and N₂ respectively and irradiated in parallel for 90 minutes using a MDS Nordion 1000 Elite Cs⁻¹³⁷ γ-source. The dose rate was determined to 0.15 Gy s⁻¹ by Fricke dosimetry.

The modified Hantzsch method was used to determine the amount of formaldehyde produced, as described above (section 2.3.1).

2.3.2 Resazurin

An ink based on the dye Resazurin was prepared as formulated by Mills et al.¹²⁸ The ink consisted of 3 g of a 1.5 wt.% aqueous solution of hydroxyl ethyl cellulose (HEC) polymer, 0.3 g of glycerol and 4 mg of the redox dye, Resazurin (Rz). The solution was loaded into an aerosol spray-gun (SIP Emerald Spray Gun/Halfords Plc.) and the films were spray-coated evenly at an air pressure feed of 3.5 bar. All surfaces had been irradiated for 1 h with UVC 254 nm light prior to spray-coating with ink. The films were subsequently illuminated by
UVA (365 nm) and the photocatalytic reduction of the dye was followed and monitored by an Epson Perfection 1200 Photo Scanner at 2 minute intervals.

### 2.4 H$_2$O$_2$ Detection by the Ghormley Method

The Ghormley triiodide method was used to detect and quantitatively measure H$_2$O$_2$. In presence of H$_2$O$_2$, I$^-$ is oxidized to I$_3^-$, which is measured spectrophotometrically at 360 nm (reactions (9) and (10)).

\[
H_2O_2 + 2I^- \rightarrow 2OH^- + I_2 \quad (9)
\]

\[
I_2 + I^- \rightleftharpoons I_3^- \quad (10)
\]

A sample volume was extracted at different time intervals and diluted in water along with 0.1 ml 1 M KI and 0.1 ml 1 M HAc/NaAc (including a few drops of ADM, acting as catalyst). The total volume was 2 ml. The solution was left to react for 2 minutes before measuring the absorbance at 360 nm. A linear correlation between the I$_3^-$ absorbance and H$_2$O$_2$ concentration was obtained by a calibration curve where the I$_3^-$ absorbance was plotted as a function of the H$_2$O$_2$ concentration.

H$_2$O$_2$ studies were performed to explore the rate controlling reactions in photocatalysis and to probe photocatalytically produced hydroxyl radicals.
3. Results and Discussion

3.1 Mechanistic Study of Photocatalysis

The mechanistic aspects of the photocatalytic reaction paths on TiO$_2$ in contact with an aqueous phase are complex. One of the major issues is the identification of the oxidant. In particular, there is a frequent debate in the context of oxidation reactions and the role of the valence band holes for direct oxidation versus indirect oxidation by hydroxyl radicals. The key issue is not which oxidant is the most important, it is rather how the valence band holes and the hydroxyl radicals can be adequately characterized.

To elucidate the mechanism of TiO$_2$ photocatalysis H$_2$O$_2$ was used to prove the existence of photocatalytically produced hydroxyl radicals. Heterogeneous photocatalysis of aerated aqueous solutions results in formation of hydrogen peroxide via reduction of molecular oxygen by the photo-excited electrons according to reactions (11)-(13).

$$O_2 + e_{CB}^- \rightarrow O_2^\cdot$$  \hspace{1cm} (11)

$$O_2^\cdot + H^+ \rightarrow HO_2^*$$  \hspace{1cm} (12)

$$HO_2^* + HO_2^* \rightarrow H_2O_2 + O_2$$  \hspace{1cm} (13)

Another potential path to hydrogen peroxide formation is through recombination of hydroxyl radicals at or in the vicinity of the surface of the photocatalyst. This process is the only possible route to hydrogen peroxide in an oxygen free system. The overall chemistry of an oxygen free aqueous system is described by reactions (14)-(18).

$$H_2O + h_{VB}^+ \rightarrow H^+ + OH^*$$  \hspace{1cm} (14)

$$OH^- + h_{VB}^+ \rightarrow OH^*$$  \hspace{1cm} (15)

$$OH^* + OH^* \rightarrow H_2O_2$$  \hspace{1cm} (16)

$$OH^* + H_2O_2 \rightarrow H_2O + HO_2^*$$  \hspace{1cm} (17)

$$e_{CB}^- + H_2O_2 \rightarrow OH^* + OH^-$$  \hspace{1cm} (18)
Detection of hydrogen peroxide in an oxygen free system can therefore serve as an indicator for formation of hydroxyl radicals in photocatalysis. In this study, the hydrogen peroxide concentration was measured as a function of illumination time for N₂ saturated, air and oxygen saturated aqueous solutions using an immobilized, screen-printed TiO₂ film activated by black light (365 nm). The morphology and crystallographic phase of the film is shown in Figure 9. As can be seen, the film consists of particles of sizes between 20-80 nm and is very rough. The XRD pattern show reflections at 25.3, 38.6, 48.1, 53.9, 55.1 and 62.7° 2Θ corresponding to the anatase crystallographic phase, which is usually identified as the predominant phase of TiO₂ when annealed at 500 °C.

![Figure 9](image)

**Figure 9:** (a) Scanning electron micrograph of the TiO₂ film prepared by screen-printing using a Solaronix™ commercial paste (b) X-ray diffraction pattern of the TiO₂ film annealed at 500 °C. The anatase peak positions are displayed in brackets.

### 3.1.1 Formation of H₂O₂ in Aqueous Photocatalysis

The concentration of hydrogen peroxide in oxygenated, air and deoxygenated aqueous solutions detected and quantified using the Ghormley triiodide method is shown in Figure 10.
As can be seen, the hydrogen peroxide concentration increases with illumination time until it reaches a constant level. This level corresponds to the steady state where the rate of H$_2$O$_2$ formation is equal to the consumption. The main path for formation of H$_2$O$_2$ in oxygenated systems is via the combination of hydroperoxyl radicals formed upon O$_2$ reduction by conduction band electrons, reactions (11)-(13). The steady-state concentration is thus dependent on the O$_2$ concentration in the solutions and increases with the O$_2$ content due to the more efficient trapping of the electron. No proportionality between the O$_2$ concentration and the steady-state is observed. An interesting observation from Figure 10 is that a significant amount of H$_2$O$_2$ was also produced in the N$_2$ saturated solutions. The steady-state concentrations of H$_2$O$_2$ in the N$_2$ saturated system and in the oxygen containing systems are given by Eqns. 8 and 9 based on the mechanism above.

\[
[H_2O_2] = \frac{k_{16}[OH]^2}{k_{17}[OH]^2+k_{18}[e^-]} \tag{Eq. 8}
\]

\[
[H_2O_2] = \frac{k_{16}[OH]^2+k_{13}[HO_2]^2}{k_{17}[OH]^2+k_{18}[e^-]} \tag{Eq. 9}
\]

As the concentrations of all the radical species in the steady-state expressions above depend on the rate of primary photolysis as well as on the concentrations of O$_2$ and H$_2$O$_2$, a direct quantitative comparison between the two equations is not straightforward. It should be noted that the effective rate of oxidant production increases with increasing electron scavenging capacity of the system, i.e., formation of species consuming hydrogen peroxide is enhanced if oxygen is present or if the hydrogen peroxide concentration is increased.
To determine whether the H₂O₂/TiO₂ system is in equilibrium during continuous illumination, the hydrogen peroxide concentration in solution and in the whole system (solution and TiO₂ surface) was measured under steady state conditions for the three systems. It was recently shown that H₂O₂ has a tendency to adsorb to TiO₂ surfaces.¹⁵³ The adsorption equilibrium constant was determined to (6 ± 1) × 10⁴ M⁻¹ based on the Langmuir isotherm.¹⁵³ In order to measure the total production of H₂O₂, the surface adsorbed H₂O₂ has also to be accounted for. The amount of surface adsorbed H₂O₂ and the amount of H₂O₂ in solution is presented in Figure 11.

Figure 11: Concentration H₂O₂ detected in solution and adsorbed on the TiO₂ surface after 60 min of black light illumination in 20 ml H₂O saturated with N₂, air, and O₂.

As can be seen, the fraction of H₂O₂ adsorbed to the TiO₂ surface is significant for all three systems. The fraction of adsorbed H₂O₂ increases with decreasing total amount of H₂O₂ as expected from the adsorption isotherm. The relative fractions are in good agreement with the equilibrium constant and the obvious conclusion is that the system is equilibrated throughout the illumination process.

To further test the hypothesis of the two processes behind the formation of H₂O₂, experiments were performed with and without Tris(hydroxymethyl)aminomethane (Tris). Tris is an efficient hydroxyl radical scavenger that has been used both to probe the efficiency of photocatalysis and to verify the existence of hydroxyl radicals in catalytic decomposition of H₂O₂ on metal oxide surfaces.¹³³,¹⁶⁸,¹⁶⁹ The purpose of performing these experiments here is to confirm the existence of the hydroxyl radical as the primary oxidizing species in aqueous TiO₂ photocatalysis. The anticipated effect of adding Tris to the system is a reduction in the H₂O₂ steady-state concentration in the deoxygenated system where all the H₂O₂ production can be attributed to hydroxyl radical recombination. For the oxygen containing systems, the opposite effect is expected since Tris will protect the hydrogen peroxide from attack by the hydroxyl radicals and thereby reduce the rate of H₂O₂ consumption. This can also be seen
from the steady-state expressions for the two cases (Eqns. (8) and (9)). The results are summarized in Table 2.

**Table 2:** Concentration H$_2$O$_2$ formed in pure H$_2$O and in aqueous Tris solutions under air and N$_2$-saturation.

<table>
<thead>
<tr>
<th>Atmosphere</th>
<th>H$_2$O</th>
<th>200 mM Tris</th>
</tr>
</thead>
<tbody>
<tr>
<td>Air</td>
<td>0.97 ± 0.06</td>
<td>1.99 ± 0.02</td>
</tr>
<tr>
<td>N$_2$ saturated</td>
<td>0.31 ± 0.01</td>
<td>0 ± 0.001</td>
</tr>
</tbody>
</table>

As can be seen in Table 2, the effect of adding the hydroxyl radical scavenger is very clear. In the deoxygenated system where Tris will scavenge hydroxyl radicals the steady-state hydrogen peroxide concentration is reduced to below the detection limit. For the air saturated system, addition of Tris has the opposite effect. These observations are in line with the hypothesis that the hydroxyl radical is the primary oxidant and that formation of hydrogen peroxide in deoxygenated systems can be attributed to recombination of hydroxyl radicals.

### 3.2 Probing the Photocatalytic Efficiency of Heterogeneous Photocatalysis

Probing the efficiency in photocatalysis is of key-importance in order to be able to compare photocatalysts and explore how certain modifications to a material and/or to a photocatalytic system will affect the overall efficiency. Here, Tris(hydroxymethyl)aminomethane is demonstrated as a probe molecule in photocatalysis. A correlation between Tris and the well-established photocatalytic assessment method based on the indicator ink Resazurin is also made followed by a discussion of the use of phenols as probe molecules.

#### 3.2.1 Tris(hydroxymethyl)aminomethane

Tris was evaluated as a probe in aqueous TiO$_2$ photocatalysis. Hydrogen abstracting species such as hydroxyl radicals react with Tris through hydrogen abstraction which leads to formation of formaldehyde. The rate of which formaldehyde is produced from a photocatalyst upon illumination is therefore proportional to the ability of the material to form hydrogen abstracting species and can be used to quantify the photocatalytic efficiency of the material. Formaldehyde is a stable product that can be detected and quantified by a modified version of the Hantzsch method. The Hantzsch method, introduced by Nash,$^{170}$ is a well-known method for detection of formaldehyde. In its original form, acetylacetone or 2,4-pentadione are used as reagents. These compounds are known to be able to interact with H$_2$O$_2$, which is formed upon photocatalysis, and therefore the reagent was replaced with acetoacetanilide, to increase the selectivity for hydrogen abstracting radicals in this work. The formaldehyde yield upon hydrogen abstraction by hydroxyl radicals in homogeneous solutions has been determined to
However, Tris is not selective towards hydroxyl radicals and other hydrogen abstracting species can potentially also induce decomposition of the probe.

The formaldehyde concentration as a function of illumination time is shown for a screen-printed TiO$_2$ photocatalyst in Figure 12. Under the present conditions i.e. at very low conversions of Tris, the formaldehyde formation rate is constant with illumination time.

![Figure 12](image)

**Figure 12**: Formaldehyde concentration, formed from a 200 mM aqueous Tris solution ($V = 20$ ml, pH 7.5) as a function of illumination time using a screen-printed TiO$_2$ photocatalyst illuminated by black light ($I = 0.10 \pm 0.01$ mW cm$^{-2}$).

As Tris has a very low extinction coefficient at the wavelengths used to activate the photocatalyst ($\varepsilon_{365\text{nm}} = 0.05$ M$^{-1}$ cm$^{-1}$)$^{113}$ it is possible to perform a concentration variation without interfering with the incident light. A concentration profile is necessary to ascertain that the full scavenging capacity of the probe has been reached and is especially important when comparing photocatalysts. The effect of the Tris concentration on the formaldehyde formation rate is presented in Figure 13. A strong concentration dependence of Tris is observed below 100 mM for this material, indicating that Tris does not fully cover the photocatalytic surface and therefore the full scavenging capacity of the probe has not yet been reached. Once, the Tris concentration rises beyond this critical limit the formaldehyde production rate becomes independent of the scavenger concentration, implying that the maximum scavenger capacity has been reached. The level at which the rate of formaldehyde production becomes independent of the scavenger concentration is determined by the adsorption properties of Tris towards the photocatalyst. A strong adsorption affinity of Tris towards the surface requires a lower concentration to saturate the surface and reach the maximum scavenger capacity. For comparative studies of different photocatalysts, it is important to use concentrations of the probe where it is independent of the Tris concentration.
Photocatalytic reactions have often been shown to follow Langmuir-Hinshelwood (L-H) kinetics. A good fit to this model is also seen in Figure 13. When applying L-H kinetics to photocatalytic decomposition of Tris using a TiO$_2$ photocatalyst, it is assumed that the formaldehyde formation rate ($r$) is proportional to the surface (TiO$_2$) coverage of the Tris according to Eqns. 10-12:

$$r = -\frac{dC}{dt} = k\theta$$  \hspace{1cm} \text{Eq. 10}$$

$$\theta = \frac{K_{LH}C}{1+K_{LH}C}$$  \hspace{1cm} \text{Eq. 11}$$

$$r = -\frac{dC}{dt} = \frac{kK_{LH}C}{1+K_{LH}C}$$  \hspace{1cm} \text{Eq. 12}$$

where $r$ is the rate of product (formaldehyde) formation, $C$ denotes the reactant (Tris) concentration in the liquid phase, $t$ is the illumination time, $k$ represents the maximum rate of product formation and $K_{LH}$ is the Langmuir equilibrium adsorption/desorption constant. The linear expression of the Langmuir-Hinshelwood model (Eq. 13) can be used to derive the kinetic parameter $k$ and the Langmuir constant $K_{LH}$. There are certain limitations with the L-H kinetic model when applying it to photocatalytic reactions, as has previously been discussed in section 1.4.2 and the $K_{LH}$ parameter might therefore not correspond to the thermodynamic equilibrium constant as the adsorption/desorption equilibrium might not be established during illumination.
\[ \frac{1}{r} = \frac{1}{k} + \frac{1}{kK_{LH}C} \]  

Eq. 13

The intercept and slope of Figure 14, where the reciprocal reaction rate has been plotted against the initial Tris concentration are used to determine \( k \) and \( K_{LH} \).

![Figure 14](image.png)

**Figure 14**: Reciprocal formaldehyde formation rate as a function of reciprocal Tris concentration.

For this system, where a screen-printed TiO\(_2\) photocatalyst was used, \( k \) and \( K_{LH} \) were determined to \( 5.1 \pm 0.2 \times 10^{-8} \text{ M s}^{-1} \) and \( 94 \pm 5 \text{ M}^{-1} \), respectively. \( K_{LH} \) for a few commonly used probes are presented in Table 3.

<table>
<thead>
<tr>
<th>Scavenger</th>
<th>( K_{LH} ) [M(^{-1})]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tris</td>
<td>94 ± 5</td>
</tr>
<tr>
<td>Methanol</td>
<td>61</td>
</tr>
<tr>
<td>Ethanol</td>
<td>175</td>
</tr>
<tr>
<td>Phenol</td>
<td>3 140</td>
</tr>
<tr>
<td>Methylene Blue</td>
<td>17 900</td>
</tr>
</tbody>
</table>

**Table 3**: \( K_{LH} \) values for a few commonly used probes in photocatalysis.\(^{104,172,173}\)

Probes with high adsorption affinity towards the photocatalyst such as the dye methylene blue will reach surface saturation earlier, *i.e.* at lower concentrations than Tris. For the specific case of methylene blue and other dyes with similar adsorption affinities, this means that 1 mM
is required to cover 95 % of the surface (using the Langmuir isotherm). However, with an extinction coefficient of 1128 M⁻¹ at 365 nm, most incident photons will be absorbed by the dye at concentrations in the mM-range. To avoid this, much lower dye concentrations are used, typically in the µM-range, which results in incomplete surface coverage and consequently only a fraction of the maximum photocatalytic activity can be assessed. Another important observation when probing the efficiency using the consumption of a probe rather than the formation of a product is that a higher conversion is necessary to establish a significant change in concentration. To achieve this, very long illumination times are required which will not only increase the risk of product degradation but also change the experimental conditions. A detailed knowledge of the adsorption isotherm is therefore of major importance when analysing the photocatalytic activity.

3.2.1.1 Effect of O₂ on the Production of Formaldehyde from Tris

Molecular oxygen is known to have a significant impact on the photocatalytic efficiency and it is therefore of relevance to study if O₂ affects the formaldehyde yield formed upon hydrogen abstraction from Tris. C-centered radicals, such as the radical formed upon hydrogen abstraction from Tris, are able to react with O₂ to form peroxyl radicals. Molecular oxygen may therefore potentially increase the formation of formaldehyde. To elucidate the effect of O₂ on the formaldehyde yield in the reaction between Tris and hydroxyl radicals, a gamma radiolysis study was performed, where the Tris solutions were saturated by O₂ and N₂ and exposed to gamma radiation. The experiments were repeated twice and it was found that the formaldehyde yield was not affected by the O₂ (Table 4). This ascertains that Tris can be used to probe the photocatalytic efficiency when comparing systems of different oxygen content.

<table>
<thead>
<tr>
<th>O₂ saturated</th>
<th>N₂ saturated</th>
</tr>
</thead>
<tbody>
<tr>
<td>[CH₂O] µM</td>
<td>[CH₂O] µM</td>
</tr>
<tr>
<td>9.4</td>
<td>10.5</td>
</tr>
<tr>
<td>10.3</td>
<td>11.0</td>
</tr>
</tbody>
</table>

3.2.2 Resazurin

A rapid qualitative assessment of the photocatalytic activity can be achieved by the redox ink Resazurin. Resazurin (blue) is reduced to Resorufin (pink) in a one electron process and further reduced to colorless intermediates. A characteristic absorption spectrum of Resazurin is shown in Figure 15. In Figure 16 the reduction of Resazurin is seen for four different TiO₂ films of the same thickness (between 200-300 nm) prepared by AACVD, A\_AACVD followed by APCVD, A\_PCVD and by APCVD followed by A\_ACVD. A color change was noticed after
only a few minutes of black light illumination and after 20 min of illumination the AACVD sample and the sample coated by APCVD followed by AACVD had almost completely reduced Resazurin.

Figure 15: A characteristic absorption spectrum of Resazurin. The arrows indicate the direction of change upon reduction. (Reused with permission from Elsevier)

Figure 16: Photographs of the color change of the Resazurin ink sprayed onto the TiO₂ films after 0, 5 and 20 min of black light illumination.

The rate of the dye reduction can be related to the rate of formaldehyde formation upon hydrogen abstraction from Tris. A 200 mM Tris solution was used to assess the formaldehyde formation rate of the four films. Control measurements using 400 mM Tris were also
performed to ascertain that the maximum scavenging capacity of Tris had been reached. The results presented in Figure 17 show that the samples reducing Resazurin with the fastest rate also show the highest apparent quantum yields, indicating that the two methods are in good qualitative agreement.

![Figure 17](image)

**Figure 17**: Apparent quantum yields for each TiO$_2$ CVD film using Tris as a probe ([Tris] = 200 mM, V= 20 ml, pH 7.5).

### 3.2.3 Phenols

Phenols are often used to probe the efficiency of heterogeneous photocatalysts. Substituted phenols are commonly employed for this purpose and the efficiency is quantified by measuring the consumption of the probe as a function of illumination time.\textsuperscript{122, 123, 125} It has been observed that for phenolic probes the rate of consumption is dependent on the nature \textit{i.e.} substituent pattern of the phenol.\textsuperscript{174-176} Oxidation of all phenols, in photocatalysis by the valence band hole or by photo-produced hydroxyl radicals, is a highly exothermic process.\textsuperscript{177, 178} Hence, the kinetics of the reaction can be assumed to be independent of the redox properties of the phenols and no substituent dependence would be expected from a thermodynamic point of view. Numerous kinetic models have been developed to describe photocatalytic processes and some of the models in the literature are based on data on phenols.\textsuperscript{107, 179-182} Kinetic models can be very useful for the understanding of a process itself; however, it is essential that the chemistry of the probe is accurately accounted for. One-electron oxidation of phenol leads to the formation of phenoxy radical (Reaction 1).
Reaction 1

Phenoxyl radicals undergo radical-radical combination reactions in oxygen-free aqueous solutions according to Reaction 2, which leads to consumption of phenol.

Reaction 2

Oxygen present in aqueous solutions will not interact with the phenoxyl radical and therefore not influence the consumption of the phenol. However, oxygen present in heterogeneous photocatalysis will be reduced to superoxide by the photo-excited conduction band electron. This process is particularly advantageous for the photocatalytic efficiency as the removal of the electrons from the photocatalyst suppresses hole-electron recombination. Superoxide is known to be able to react with phenoxyl radicals by either electron transfer or by radical-radical combination according to Reaction 3.
The electron transfer process yields phenol/phenolate and molecular oxygen. Hence, this process counteracts the consumption of phenol in the system. To the best of our knowledge, the competition between the electron transfer and the radical-radical combination reaction is not accounted for in the benchmarking of kinetic models for heterogeneous photocatalysis. In fact, none of the reactions leading to irreversible consumption of phenol are included. Not including the well-known chemistry of phenoxy radicals in aqueous solution containing superoxide renders the inclusion of new and unverified processes to fit experimental results meaningless.
Interestingly, the competition between the electron transfer and the radical-radical combination reaction has been systematically studied using pulse radiolysis about two decades ago.\textsuperscript{177} It turned out that the fraction of electron-transfer (i.e. back reaction) is strongly dependent on the redox properties of the phenoxy radical.\textsuperscript{177} For phenoxy radicals with high reduction potential (corresponding to phenols that are more difficult to oxidize), the fraction of electron transfer is higher than for phenoxy radicals with low reduction potentials (corresponding to phenols that are more easily oxidized). This can roughly be described to follow a linear free energy relationship. In general, the properties and reactivity of phenoxy radicals have been shown to follow Hammett type linear free energy relationships using Brown $\sigma^+$ substituent constants.\textsuperscript{184} Both the standard reduction potentials of substituted phenoxy radicals and the homolytic O-H bond dissociation enthalpies of substituted phenols are linearly correlated to the Brown $\sigma^+$ substituent constant.\textsuperscript{184} The correlations are valid also for multi-substituted phenols and phenoxy radicals. This enables us to analyze some of the results reported for photocatalytic systems where substituted phenols have been used as probes.

Serpone \textit{et al.}\textsuperscript{126} used a series of substituted phenols to determine the photocatalytic efficiency of TiO$_2$. The results presented clearly show that the photocatalytic efficiency of a given system varies by a factor of three depending on the structure of the phenol. By applying the linear free energy relationships described above, we can plot the relative photocatalytic efficiency against the sum of the Brown substituent constants (for multi-substituted phenols). This is comparable to plotting the relative photocatalytic efficiency against the standard reduction potential of the phenoxy radicals. The resulting plot is given in Figure 18.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure18.png}
\caption{Relative photonic efficiencies for different phenolic substances plotted against the sum of the Brown substituent constants. Phenol is the standard reference. The initial scavenger concentration is approximately 200 $\mu$mol L$^{-1}$, [TiO$_2$] = 2 g L$^{-1}$ and pH= 3.0.}
\end{figure}

As can be seen, there is a significant substituent effect on the relative photocatalytic efficiency and there is also a fairly good correlation between the relative photocatalytic efficiency and
the sum of the Brown substituent constants for each phenol. The relative photocatalytic efficiency decreases linearly with increasing standard reduction potential (more positive Brown substituent constant) of the phenoxyl radical. This is exactly what we would expect from the trend observed for the reaction between phenoxyl radicals and superoxide. Hence, it is obvious that the inclusion of the complete reaction scheme for phenoxy radical chemistry is required for kinetic models for heterogeneous photocatalysis when benchmarking against experimental results where phenols have been used as probes. A complete reaction scheme is not only required for the phenoxy radical chemistry but is necessary for all chemical probes. Knowledge of the process that gives rise to the signal i.e. the consumption of the reactant or the formation of product and any potential risks for re-formation of the probe is crucial when determining photocatalytic efficiencies.

3.3 Enhancing the Photocatalytic Activity

A prerequisite for exploring the rate limiting properties of a photocatalytic material or system, is a sensitive and quantitative assessment method for determination of the photocatalytic activity. In this section the rate of formaldehyde formation upon oxidation of Tris has been used to study how different internal (surface specific) and external (system specific) alterations affect the photocatalytic performance.

3.3.1 Immobilized TiO$_2$ films: Surface Properties and Effects on the Photocatalytic Activity

Immobilized TiO$_2$ films prepared by screen-printing (SP), sol-gel (SG), AACVD and APCVD were structurally and functionally characterized and compared. The chemical composition of the films was studied by XPS in order to confirm the purity of the material, Figure 19. The recorded data show that all films consist of titanium and oxygen.

![Figure 19: XPS survey scans of the screen-printed (SP), sol-gel (SG), aerosol-assisted CVD (AACVD) and atmospheric-pressure CVD (APCVD) TiO$_2$ films.](image-url)
The surface morphology, displayed in Figure 20, show that the microstructure of the films are very different.

**Figure 20:** Scanning electron micrographs of TiO₂ films immobilized by (a) SP (b) SG (c) AACVD (d) APCVD.

The surface morphology of an immobilized film is partly attributed to the specific precursor and the deposition technique. The precursor for screen-printed films is a paste containing nanoparticles. This method generally yields very porous films with large surface area. In the sol-gel process, the hydrolysis and condensation rates, governed by the properties of the constituents of the precursor, affect the resulting morphology. The APCVD and AACVD are similar processes but the film growth rates are very different, and produce films with completely different microstructures. The APCVD process is typically very fast with growth rates in the range of 200 nm-4 μm min⁻¹, while in AACVD an aerosol act as transport vector and growth rates are much lower, often 10 nm min⁻¹. The needle-like film produced by AACVD consists of thin plates of approximately 20 nm widths, grown mostly perpendicular to the glass support, while the APCVD surface is denser and consists of larger, granular fragments. The resulting surface area of the AACVD is very high compared to the less porous APCVD derived film. The reason for the difference in morphology between the different coating methods might be explained by the deposition processes and deposition rates. In AACVD an aerosol with small vapor droplets are slowly deposited onto the substrate while the deposition in the APCVD process occurs much faster. Apparently in this case, a slower and longer deposition time generate a more porous structure.

Water contact angles can be used as a confirmation of photo-induced superhydrophilicity. Figure 21 shows the measured water contact angles for each of the films studied. In general, rougher surfaces have a larger water contact angle as the water droplets are not able to penetrate the surface due to air pockets within the surface. By measuring the water contact angles during illumination it was shown that the screen-printed film reached the superhydrophilic state (< 10°) quickest of all films studied, after approximately 10 min of black light illumination.
Figure 21: Measured water contact angles as a function of irradiation time (black light, \( I = 0.15 \text{ mW cm}^{-2} \)) for the TiO\(_2\) films prepared by SP, SG, AACVD and APCVD.

The photocatalytic properties of the films were assessed by the rate of formaldehyde formation upon oxidation of Tris under the same conditions as above. The apparent quantum yields (AQY) are presented in Figure 22. The formaldehyde formation rates were determined using 200 mM Tris. To ensure that this concentration is above the surface saturation point, the rate of formaldehyde formation was determined as a function of Tris concentration for the screen-printed and the sol-gel film, while the formaldehyde formation rate from the CVD films were measured at 200 mM and at 400 mM and as the values obtained agreed well it was assumed that the maximum efficiency was measured.

Quantum yields were used for comparison between the films as the samples were of different thicknesses and geometries. For heterogeneous photocatalytic systems it is difficult to determine absolute quantum yields as the light scattering on the surface makes it virtually impossible to determine the exact amount of photons absorbed and it is therefore more appropriate to use the term “apparent quantum yield” as this will be a system specific entity.

Figure 22: Apparent quantum yield of the SP, SG, AACVD and APCVD TiO\(_2\) films using Tris as a probe.
The screen-printed film possesses the highest photocatalytic activity of the films included in this study. Visually, this film appears to have a very large surface area, however for a more accurate determination of the surface area adsorption studies could be performed or alternatively extraction of surface roughness factors by AFM. An interesting observation is that the water contact angles for non-illuminated TiO$_2$ films seem to follow the measured AQY’s and the film with the highest initial contact angle is also the film with the highest AQY. Possibly, rough films with a high surface area might be more difficult for water to penetrate as air can be trapped under the water droplet which would consequently increase the water contact angle. Films with a high surface area have more available reaction sites which can explain the higher AQY’s. Surface morphology and roughness are properties mainly determined by the precursor and deposition technique and the results presented here indicate that these influence the functional properties of the film.

### 3.3.2 Effects of Metal Dopants: Ag-Enhanced TiO$_2$

The effect on the photocatalytic properties of a TiO$_2$ film enhanced with Ag was studied by Tris and compared to a pure TiO$_2$ film. Islands of Ag nanoparticles were deposited onto a sol-gel prepared TiO$_2$ thin film by dip-coating in AgNO$_3$ followed by exposure of 254 nm radiation for 120 seconds. The Ag enhanced film was observed to be photochromic and shifted color from pink to orange upon illumination. This effect is likely attributed the reduction properties displayed by Ag. In a dark and oxygen containing environment, Ag is able to oxidize to Ag$_2$O, while upon illumination the Ag$_2$O is reduced back to pure silver. AFM characterization of the Ag enhanced film show that the deposited Ag nanoparticles are between 50-150 nm and covers 64 % of the surface (Figure 23). Surface roughness values ($Rq$-values) were calculated to 1.97 nm for the TiO$_2$ film and 10.2 nm for the Ag enhanced film, indicating that the surface area is decreased upon Ag deposition. It is important to note that this estimation may not necessarily be representative for the entire film as analysis is only performed on a small section of the film.

![AFM images](image)

**Figure 23:** AFM images of the (a) TiO$_2$ film and (b) the TiO$_2$ film enhanced with Ag nanoparticles.
Raman spectra were also recorded for the TiO$_2$ and the Ag enhanced TiO$_2$ film and peaks were observed at 143, 396, 516 and 639 cm$^{-1}$ (Figure 24) which all correspond to the anatase phase.

**Figure 24:** Raman spectra of the TiO$_2$ and the Ag-TiO$_2$ film, indicating the presence of the anatase phase on both films.

Valence band XPS spectra were employed to show the difference in energy between the Fermi level and the valence band of the TiO$_2$.

**Figure 25:** XPS valence spectra showing the difference in energy between the valence band and the Fermi-level. Inset shows a band diagram for the interstate silver contributions.

The presence of electronic states up to the zero point $E_F$ is indicative of the metallic properties of the silver atoms. Extrapolation of the approach to the valence band of TiO$_2$ can then yield the difference in energy between the valence band and the Fermi level indicating that the effect of the silver on the bandgap is to generate interstate levels in just below the conduction band of the TiO$_2$. This indicates that the silver states are just below the conduction band of the TiO$_2$ ~ 0.3 eV as opposed to just above the valance band (Figure 25).
The rate of formaldehyde production upon oxidation of Tris was used to probe the efficiency of the TiO$_2$ and the Ag enhanced TiO$_2$ film and the formaldehyde formation rates from the films are shown in Figure 26.

![Figure 26: Measured formaldehyde concentrations formed from the TiO$_2$ and the Ag-TiO$_2$ films under black light irradiation (100 µW cm$^{-2}$). Initial Tris concentration was 100 mM ($V$= 20 ml, pH 7.5).]

As can be seen, the formaldehyde formation rate is constant with illumination time and a slightly increased rate is observed upon Ag addition to the TiO$_2$ surface ($k_{\text{TiO}_2} = (6.92 \pm 0.1) \times 10^{-9}$ M s$^{-1}$ and $k_{\text{Ag-TiO}_2} = (8.89 \pm 0.1) \times 10^{-9}$ M s$^{-1}$). To determine apparent quantum yields for the films the amount of light absorbed by each film must be known. The main absorption onset (Figure 27) is seen to be at about 365 nm for TiO$_2$ and 375 nm for the Ag enhanced TiO$_2$ film. This corresponds to a red shift of 10 nm. The Ag enhanced TiO$_2$ film has a broad absorption band in the visible light region, approximately between 430-470 nm which could be due to surface plasmon resonance effects of the Ag particles on the TiO$_2$ film. When metal nanoparticles, such as Ag or Au, are irradiated by light, scattering and absorption on the metal surface occurs, which generate an evanescent wave with a strong electromagnetic field. This wave is localized on the surface of the nanoparticle and remains at a distance of less than the particle diameter. The localized surface plasmon effect has a significant impact on the absorption properties of the material and is strongly dependent on parameters such as particle size and shape, the dielectric constant and the light wavelength. It has been shown in previous works that the plasmon absorption is also dependent on the type of oxide connected to the metal particle.$^{144, 146, 147, 149}$ When TiO$_2$ is incorporated with Ag nanoparticles, the surface plasmon band becomes red shifted, due to the high dielectric constant of the TiO$_2$.$^{146, 148, 149, 151}$
Figure 27: Recorded absorption spectra of the TiO$_2$ and Ag-TiO$_2$ films deposited on thin, transparent microscope slides.

All photocatalytic activity measurements in this work were carried out under UVA (365 nm) light. The average light absorption at this wavelength by the films was measured to 0.33 absorption units and 0.16 absorption units for the TiO$_2$ and the Ag-TiO$_2$ film, respectively. The apparent quantum yield based on each film’s production of formaldehyde from aqueous Tris-solutions of concentrations between 1-400 mM is presented in Figure 28.

Figure 28: Apparent quantum yields for the TiO$_2$ and Ag-TiO$_2$ films as a function of Tris concentration. 20 ml Tris solutions (pH 7.5) were used for each experiment.

Two interesting conclusions can be drawn from these results. Firstly, the adsorption of Tris was clearly altered upon addition of silver to the TiO$_2$ surface. This is shown by the difference in concentration dependence in the graph at lower Tris concentrations. Pure TiO$_2$ reached its plateau at ~10 mM, while Ag-TiO$_2$ required a Tris concentration of ~50 mM. Pure TiO$_2$ has a higher affinity for Tris than Ag-TiO$_2$ and therefore the plateau is reached at a lower concentration. Secondly, there is a significant difference in maximum apparent quantum yield
between the films, which may be attributed to the difference in oxygen adsorption as will be
discussed later.

The strong concentration dependence of Tris at low concentrations when used to probe the
efficiency of immobilized TiO$_2$ has been demonstrated previously.$^{113}$ Once the Tris
concentration is above a critical value, the rate of formaldehyde production becomes
concentration independent as the surface is fully covered with Tris.

The adsorption equilibrium constants were calculated from the data shown in Figure 29
using $L$-$H$ kinetics.

\[
\begin{align*}
K_{LH(TiO_2)} & = 615 \, M^{-1} \\
K_{LH(Ag-TiO_2)} & = 320 \, M^{-1}
\end{align*}
\]

Since, in general, the adsorption to noble metals with a filled d-band is
weak (due to the lack of available d-orbitals for bonding), the Ag enhanced TiO$_2$ film is
expected to have a lower affinity for Tris than the pure TiO$_2$ film. Inevitably, Ag will block
some adsorption sites for Tris and with a surface coverage at 64% a good agreement with the
difference in adsorption equilibrium constants is obtained. Similarly, the same trend has been
observed for adsorption of Rhodamine B on pure TiO$_2$ and on Ag-TiO$_2$ particles.$^{185}$ It was
found that the Rhodamine B molecule, which adsorbs to the TiO$_2$ surface with the
diethylamino- or the carboxyl group, displayed lower affinity for the photocatalyst if Ag
particles were present on the surface as these decrease the free TiO$_2$ surface area.

The adsorption property is obviously affected by the semiconductor composition. It is
therefore of major importance to be able to assess the full photocatalytic efficiency when
comparing different photocatalysts.

The Ag enhanced TiO$_2$ film increases the photocatalytic activity significantly compared to
the pure TiO$_2$ film. The apparent quantum yield of the TiO$_2$ film was found to be around 7% 
while the Ag enhanced film show an apparent quantum yield of 12%, similar to that observed
in a highly porous screen-printed TiO$_2$ film, at the same lighting conditions and setup as was

\[
\begin{align*}
y & = 0.0035x + 1.122 \\
R^2 & = 0.9762 \\
y & = 0.0018x + 1.1072 \\
R^2 & = 0.9931
\end{align*}
\]

Figure 29: Reciprocal formaldehyde formation rate as a function of the reciprocal Tris concentration. A slightly
increased slope due to the Ag nanoparticle islands is observed.
used for this study. The increased yield for the Ag enhanced TiO$_2$ film can partly be explained by a Schottky barrier formation at the Ag-TiO$_2$ junction. Since TiO$_2$ undergoes charge separation under UV-irradiation, the photo generated electrons can migrate from the semiconductor into the metal due to the different Fermi level positions of the Ag and the TiO$_2$. The Ag surface acquires an excess negative charge while TiO$_2$ exhibit an excess positive charge as a result of the electron transfer from the barrier region which leads to the formation of a Schottky barrier at the interface between Ag and TiO$_2$. Since the Schottky barrier acts as an efficient electron trap, electron-hole recombination is retarded, which may enable the Ag enhanced film to more efficiently produce hydroxyl radicals, hence the improved activity. Likewise Ag nanoparticles also act as sensitizers as electrons can be injected from TiO$_2$ and thus expand the wavelength range of excitation. The inserted electrons should in turn be able to be transferred to reduce surface adsorbed acceptor species.

### 3.3.2.1 Adsorption of O$_2$ to TiO$_2$ and Ag-TiO$_2$

The adsorption and reduction of O$_2$ on the semiconductor surface is recognized as a rate limiting step for formation of hydroxyl radicals and other reactive oxygen species as this process is known to prolong the charge separation. Thus, the adsorption of O$_2$ onto the photocatalytic surface plays an important role for the efficiency of the material. In order to quantitatively evaluate and compare the adsorption effect of O$_2$ between the TiO$_2$ and Ag-TiO$_2$ surface, measurements of the formaldehyde formation from the films were performed in N$_2$ and air saturated aqueous solutions. The results are presented in Figure 30.

![Figure 30: Apparent quantum yields of the TiO$_2$ and the Ag-TiO$_2$ films determined from 200 mM Tris solutions (V= 20 ml, pH 7.5) saturated with N$_2$ and air.](image)

The formaldehyde yield is to a large extent dependent on the electron scavenging effect by O$_2$ and increases for both films in air saturated solutions. The formaldehyde yields in the N$_2$ saturated solutions are 2.0 % and 2.6 % for TiO$_2$ and Ag-TiO$_2$, respectively. In air the values are 8.0 % and 12.7 %, respectively. The effect of Ag becomes even more prominent in air
saturated solution than in N₂ saturated solution. Xin et al.\textsuperscript{186} studied O₂ adsorption on TiO₂ and Ag-TiO₂ particles by XPS and found that O₂ has a stronger tendency to adsorb onto Ag than onto TiO₂. A stronger adsorption of O₂ to the surface favors the photocatalytic efficiency. Apparently, as the O₂ adsorption is more efficient on Ag-TiO₂ than on pure TiO₂, the removal of the conduction band electrons upon O₂ reduction results in increased photocatalytic efficiency.

To summarize the results presented in this section, three main factors contributing to the increased photocatalytic efficiency of the Ag enhanced TiO₂ film has been identified: (1) the Schottky barrier formed at the interface between Ag and TiO₂, which can act as an efficient electron trap and prolong the electron-hole lifetime (2) the sensitizing effect by the Ag nanoparticles which enhance visible light absorption resulting in an increased electron-hole pair formation through electron transfer processes (3) the increased adsorption of O₂ to Ag nanoparticles, compared to TiO₂.

### 3.3.3 Effects of External Dissolved Electron Acceptors: H₂O₂ and O₂

Electron acceptors are known to enhance the photocatalytic efficiency by prolonging the electron-hole lifetime.\textsuperscript{120, 150-152} Here, the effect on the photocatalytic activity of two dissolved, external electron acceptors, O₂ and H₂O₂, was studied by the rate of formaldehyde production upon oxidation of Tris. The formaldehyde formation rate was measured as a function of Tris concentration in N₂, air and O₂ (1 bar) saturated aqueous solutions using a screen-printed TiO₂ photocatalyst. Additionally, N₂ saturated solutions containing 1.32 mM H₂O₂ were used to study the effect of H₂O₂ in photocatalysis. The H₂O₂ containing solutions were deoxygenated in order to avoid any interference from O₂. The concentration of H₂O₂ in these solutions correspond to the O₂ concentration in the O₂ saturated (1 bar) solutions. The formaldehyde production rate as a function of the Tris concentration is presented in Figure 31.
Figure 31: Formaldehyde formation rates as a function of Tris concentration for solutions containing no O$_2$ (N$_2$ saturated), 0.27 mM O$_2$ (air saturated), 1.32 mM O$_2$ (O$_2$ saturated) and 1.32 mM H$_2$O$_2$. Experiments were performed using a screen-printed TiO$_2$ photocatalyst immersed in 20 ml Tris solutions illuminated by black light ($100 \pm 4$ $\mu$W cm$^{-2}$).

It is seen that the formaldehyde production rate increases with increasing Tris concentration until the maximum scavenging capacity is reached, at approximately 100 mM in this system. The concentration dependence is attributed to the incomplete scavenging capacity of the hydrogen abstracting species below the surface saturation point. The results are in good agreement with the Langmuir-Hinshelwood kinetic model.

A significant enhancement of the formaldehyde formation rate in the presence of an electron scavenger is also observed. H$_2$O$_2$ is an electron acceptor and also a direct source of hydroxyl radicals due to the reductive cleavage of the molecule upon reduction by the photo-excited electron. Apart from the additional hydroxyl radical formed upon H$_2$O$_2$ reduction, O$_2$ and H$_2$O$_2$ appear to be equally efficient as electron scavengers. Since H$_2$O$_2$ and O$_2$ have different electron affinities, the adsorption of the scavengers to the TiO$_2$ surface seem to be governing the efficiency. The adsorption equilibrium constant of O$_2$ has been reported to $K_{O_2\text{-TiO}_2} = (13 \pm 6) \times 10^4$ M$^{-1}$ $^{187}$ while our experimental results for H$_2$O$_2$ was $K_{H_2O_2\text{-TiO}_2} = (6 \pm 1) \times 10^4$ M$^{-1}$. It is interesting to note that while the O$_2$ concentration was increased by a factor of five between the air and the O$_2$ saturated systems, the rate of formaldehyde formation was only doubled. This discrepancy is likely attributed to the fact that the electron capture is dependent on the amount of adsorbed O$_2$ rather than the O$_2$ content in the solution. The considerably suppressed formaldehyde formation rate measured in the N$_2$-saturated system is due to an increased recombination rate of the electron-hole pair. The formaldehyde formed in this system likely originates from hydroxyl radicals formed by oxidation of H$_2$O and hydroxide ions by the valence band hole.
3.3.3.1 Discussion of the H$_2$O$_2$ Concentration Dependence

The presence of H$_2$O$_2$ can significantly enhance the formaldehyde formation rate; however H$_2$O$_2$ is also capable of scavenging hydroxyl radicals according to reaction (19). This reaction has a detrimental effect on the observed photocatalytic activity.

\[
H_2O_2 + OH^* \rightarrow HO_2^* + H_2O \quad (19)
\]

To investigate the effect of the H$_2$O$_2$ concentration on the formaldehyde formation rate, a series of experiments where the H$_2$O$_2$ concentration was varied at constant Tris concentrations were performed. The resulting formaldehyde production rates are presented in Figure 32.

![Figure 32: H$_2$O$_2$ concentration dependence on the formaldehyde formation rate using 0.2, 0.5 and 1.0 M Tris.](image)

The formaldehyde formation rate reaches a maximum at a H$_2$O$_2$ concentration of approximately 2 mM, virtually independent of the Tris concentration. A continued increase of the H$_2$O$_2$ concentration dramatically reduces the formaldehyde formation rate, presumably as a result of the oxidant scavenging effect (reaction (19)) becoming more dominant. This behavior is not indicative of a straightforward competition between H$_2$O$_2$ and Tris for oxidants. To elucidate the inhibition by H$_2$O$_2$, a kinetic analysis was performed where the rate of photocatalytic oxidant formation is assumed to be proportional to the fraction of adsorbed H$_2$O$_2$ on the photocatalyst surface. The rate of formaldehyde will then be given by Eq. 14 if the oxidant formation in absence of electron acceptors is considered to be negligible.
\[ r = k \theta_A \theta_B \]  
\text{Eq. 14}

\[ \theta_A = \frac{K_A C_A}{1 + K_A C_A + K_B C_B} \]  
\text{Eq. 15}

\[ \theta_B = \frac{K_B C_B}{1 + K_A C_A + K_B C_B} \]  
\text{Eq. 16}

where \( r \) is the reaction rate (\textit{i.e.} formaldehyde formation rate), \( k \) is the maximum formaldehyde formation rate for oxidant formation when the surface is completely covered by \( \text{H}_2\text{O}_2 \), \( \theta \) is the surface coverage (adsorption) of compound \( A \) (Tris) and \( B \) (\( \text{H}_2\text{O}_2 \)), respectively, \( K \) is the adsorption constant and \( C \) is the concentration. A simulation using this model is shown in Figure 33.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure33.png}
\caption{Simulation of the formaldehyde formation rate in case of competition for adsorption between Tris and \( \text{H}_2\text{O}_2 \) for oxidants.}
\end{figure}

The impact of \( \text{H}_2\text{O}_2 \) in photocatalysis has previously been reported in several studies.\textsuperscript{120, 153, 154, 189, 190} Most of the work deals with photocatalytic degradation of dyes upon addition of \( \text{H}_2\text{O}_2 \). Dyes with low TiO\textsubscript{2} affinity, such as the safira dye, an anionic azo dye with \( K_{\text{LH}} = 2.0 \times 10^3 \text{ M}^{-1} \), display similar trends as in Figure 33, with an early maximum followed by a sharp decrease in the degradation rate.\textsuperscript{151} Substances with higher TiO\textsubscript{2} affinity, such as Triclopyr (\( K_{\text{LH}} =1.56 \times 10^4 \text{ M}^{-1} \)), a pyridine analogue of phenoxy herbicides, show a different pattern.\textsuperscript{152} In this case, a clear competition for adsorption to the photocatalyst between the substrate molecule and \( \text{H}_2\text{O}_2 \) was observed. This ultimately results in an extended \( \text{H}_2\text{O}_2 \) concentration range in which a maximum degradation rate can be observed.
Since the rate of formaldehyde formation mainly seems to be governed by the H$_2$O$_2$ concentration (at low H$_2$O$_2$ concentrations), we also performed an experimental series where we quantitatively determined the TiO$_2$ affinity of H$_2$O$_2$. The Ghormley triiodide method was used to quantify the H$_2$O$_2$ in the aqueous solutions. The fraction of adsorbed H$_2$O$_2$ as a function of initial H$_2$O$_2$ concentration is shown in Figure 34a.

**Figure 34:** (a) Fraction of adsorbed H$_2$O$_2$ onto the TiO$_2$ film as a function of initial H$_2$O$_2$ concentration. (b) Adsorbed H$_2$O$_2$ as a function of the equilibrium concentration ($C_{eq}$).

The value of the adsorption equilibrium constant for H$_2$O$_2$ onto TiO$_2$ was derived from Figure 34b using the Langmuir isotherm and as mentioned above was found to be $K_{H2O2} = (6 \pm 1) \times 10^4$ M$^{-1}$. As can be seen in Figure 34b, the plot is linear below approximately 0.2 mM H$_2$O$_2$. Above this concentration, a deviation from linearity is observed. The maximum, observed around 2 mM, indicates that a complete monolayer is obtained.

A combined Tris and H$_2$O$_2$ adsorption experiment was also performed. In this experiment a solution containing 50 µM H$_2$O$_2$ and a solution containing 50 µM H$_2$O$_2$ and 200 mM Tris were compared. Based on the respective adsorption equilibrium constants, the Tris concentration should be sufficiently high to compete with H$_2$O$_2$ adsorption. However, the resulting H$_2$O$_2$ equilibrium concentrations are 32 ± 3 µM and 29 ± 3 µM, respectively. Consequently, no influence of Tris on the adsorption of H$_2$O$_2$ is observed. This clearly shows that H$_2$O$_2$ and Tris adsorption do not compete for the same sites.

In case of pure competition between Tris and H$_2$O$_2$ for the same adsorption sites on the TiO$_2$ surface a good fit would be expected to the rate expression Eq. 14, but the results differs significantly from the experimental results presented in Figure 32 which indicates that there is no straightforward competition between H$_2$O$_2$ and Tris at concentrations below the maximum formaldehyde formation rate. However, at H$_2$O$_2$ concentrations above the maximum formaldehyde formation rate, additional H$_2$O$_2$ is adsorbed to the surface and a multi-layered structure is built up. This means that the H$_2$O$_2$ will adsorb weaker to the TiO$_2$ surface as the thickness of the H$_2$O$_2$ layer increases which enables competition between Tris and H$_2$O$_2$. 

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3.4 Inducing Visible Light Photo-Activity into TiO₂

There is a strong scientific incentive for efficiently converting solar energy into useful chemical energy. Visible light active photocatalysts are an interesting way of utilizing sunlight to activate the material. Achieving visible light activity without sacrificing the photocatalytic activity can be difficult. An efficient way of inducing visible light activity to a TiO₂ film is through nitrogen doping or modification. Most nitrogen-doped TiO₂ films are prepared in a one step-process where nitrogen atoms are incorporated into the film. However, some deposition techniques are more suitable for this approach than others.

TiO₂ films synthesized by AACVD have been shown to display high photocatalytic efficiencies due to the high surface area of films deposited by this technique. In the AACVD process, an aerosol is generated and small vapor droplets of the precursor solutions are deposited onto the substrate to give a highly porous film. Doping through the AACVD process have been shown difficult due to the complex chemistry that occurs as the droplets evaporates.

In this study a new route to surface modify a highly photoactive TiO₂ film prepared by AACVD with nitrogen is presented. In this method pure TiO₂ films were immersed in liquid NH₃ for 2 h prior to a 1 h heat treatment at 500 °C. The nitrogen modified films (N-TiO₂) were characterized and compared to pure TiO₂ films. SEM images, Figure 35 ab, show that the film morphology is left unchanged after the doping process and the rough, needle-like structure is retained. Cross-section SEM (Figure 35c) showed that the films were approximately 200 nm thick.

![Figure 35: SEM images of the (a) TiO₂ film and (b) N-modified TiO₂ AACVD film (c) cross-section SEM of the N-modified TiO₂ film (tilt angle ~ 40°).](image)

TEM analysis (Figure 36) of a delaminated film confirms the structure of the film observed in the SEM micrographs. HRTEM analysis reveal a highly crystalline material with crystal d-spacings of 0.311 nm, which corresponds to the <101> plane of anatase TiO₂. Grain sizes within the crystals are estimated to be in the region 6-10 nm.
Figure 36: TEM micrographs of the films showing (a) the plate-like morphology of the TiO$_2$ films (b) a selected area electron diffraction pattern for the plates. The apparent rings in the electron diffraction pattern appear to match the d spacing for the 010, 200 and the 221 miller indices that are present in the XRD pattern shown in Figure 38. (c) an HRTEM micrograph with the <101> crystal plane outlined with a corresponding d-spacing of 0.301 nm.

The X-ray diffraction patterns of the TiO$_2$ and the N-TiO$_2$ films show prominent peaks at 25.3, 48.1 and 55.0 2θ indexed to the expected peak positions for the anatase crystallographic phase of TiO$_2$ (Figure 37).

Figure 37: XRD pattern of the N-modified and pure TiO$_2$ thin films. The peaks shown at 25.3, 48.1 and 55.0 2θ are indexed to the anatase structure of TiO$_2$.

The UV-Vis absorption profiles of the TiO$_2$ and the N-TiO$_2$ films are shown in Figure 38. As can be seen the N-modified film has red shifted the band onset, which is likely due to the nitrogen content on the surface. The absorption band is directly related to the band gap of the material and a red shifted absorption band is an evidence of a narrowed band gap in the material.
Figure 38: UV-Vis absorption spectra for the N-modified and pure TiO$_2$ thin films.

To estimate the bandgap of the materials Tauc plots were used. Tauc plots are commonly employed for bandgap estimations of thin films. By plotting the square root of the absorption coefficient and photon energy versus the photon energy, a distinct linear regime is obtained which denotes the absorption onset. By extrapolating this linear region an estimation of the energy of the optical band gap of the material can be obtained.

Figure 39: Estimation of the bandgap of the TiO$_2$ and N-TiO$_2$ film using a Tauc plot where $a$ is the absorption coefficient and $h\nu$ is the photon energy.
A bandgap narrowing of approximately 0.1 eV was observed for the N-modified film compared to the pure TiO$_2$ film using the Tauc plot presented in Figure 39.

Nitrogen 1s core levels as determined by XPS for each film and across the whole film are shown in Figure 40.

![Figure 40: N1s XPS depth profiles for the (a) TiO$_2$ film and (b) N-modified TiO$_2$ film.](image)

The N-TiO$_2$ samples show a considerably enhanced nitrogen 1s signal at 399 eV. This peak has been attributed to interstitial nitrogen, indicating that the nitrogen resides within the lattice and not as a result of substitution of species.Interstitial nitrogen has previously been shown to have a positive impact on the visible-light response compared to substitutional nitrogen. A small quantity of the nitrogen could also be detected on the TiO$_2$ film, which is possibly due to residual physisorbed nitrogen. Several studies have reported that low concentrations of nitrogen favor the visible-light photocatalytic properties.

The photocatalytic properties of the films were quantified by formaldehyde formation from Tris. A white light lamp was used for the experiments with a filter cut-off at 385 nm to avoid any higher energy photons from entering the system. 200 mM Tris solutions were used for the experiments as this concentration is above the critical limit for assessing the maximum photocatalytic activity. The formation rates of formaldehyde from the two films are presented in Figure 41.
Addition of dopants to the TiO\textsubscript{2} surface has previously been shown to alter the adsorption affinity of the probe to the photocatalyst. The concentration of nitrogen on the N-modified TiO\textsubscript{2} film surface is very small and is not expected to change the adsorption properties to a larger extent. To confirm this, tests were also performed using 400 mM Tris solutions and the results are in line with the formaldehyde formation rates obtained at 200 mM Tris (Figure 41). The results show that the N-TiO\textsubscript{2} film exhibits a significantly higher formaldehyde formation rate than the pure TiO\textsubscript{2} film. The increased formation rate is likely due to the narrowed band gap and thus higher absorption in the visible light region. An apparent quantum yield (AQY) can be determined in order to compare the results to other reported visible-light active photocatalysts reported in the literature. A few assumptions are required for this. Firstly, the most intensive emission peak from the polychromatic light was chosen for the calculation and secondly, the maximum absorption peak was chosen for the calculation. The AQY determined using these assumptions will therefore constitute the minimum yield. The ratio between the amount of formaldehyde formed per time unit and the amount of photons absorbed by the photocatalyst per time unit was determined to 8 ± 1 % for the N-modified TiO\textsubscript{2} sample and 1 ± 0.3 % for the TiO\textsubscript{2} sample. Previously reported quantum yields in solutions are much lower. Kowalska et al.\textsuperscript{188} studied visible light-induced oxidation by 2-propanol by aerated gold-modified TiO\textsubscript{2} suspensions using wavelengths > 450 nm and reported a maximum yield of 2 × 10\textsuperscript{-4} while Tang et al.\textsuperscript{189} estimated a quantum yield of 0.15 % for a CaIn\textsubscript{2}O\textsubscript{4} photocatalyst when degrading methylene blue using a 300 W Xe arc lamp with an interference filter (cut-off at $\lambda = 400$ nm). While the probe concentration used in the former study was not reported, the methylene blue concentration used in the latter study was 47.8 μmol/L. In order to be able to compare different photocatalysts accurately, it is crucial that the full photocatalytic efficiency is assessed which require a complete surface coverage of the probe molecules i.e. probe...
concentration independence. The probe concentration required to saturate a surface is
governed by the adsorption affinity of the probe molecule to the photocatalyst. If surface
saturation has not been achieved the apparent quantum yield will be much lower than the
actual value and if this was the case for the study with methylene blue it is a possible
explanation for the very low quantum yield obtained.
4. Conclusions and Summary

The aim of this work was to bring further understanding of the processes and reactions occurring at the initial stages of heterogeneous photocatalysis. From the studies conducted within the project, the following conclusions can be drawn:

1. The hydroxyl radical is the primary oxidant in TiO$_2$ photocatalysis. Experimental studies using H$_2$O$_2$ production as a probe showed that a significant amount of H$_2$O$_2$ was formed in deoxygenated aqueous solutions upon photocatalysis. The only possible pathway to H$_2$O$_2$ under these conditions is through hydroxyl radical recombination. Additional experiments to elucidate the origin of the H$_2$O$_2$ were also made using the hydroxyl radical scavenger Tris. Those results showed that, in absence of O$_2$, the formation of H$_2$O$_2$ was significantly suppressed in presence of Tris due to the hydroxyl radical scavenging effect of Tris. In oxygen containing systems, increased H$_2$O$_2$ concentration was observed as Tris protects H$_2$O$_2$ from attack by hydroxyl radicals which reduces the rate of H$_2$O$_2$ consumption. These results support the hypothesis that the hydroxyl radical is the primary oxidant in TiO$_2$ photocatalysis.

2. Tris can be used as a probe in heterogeneous photocatalysis. Tris has several advantages compared to other commonly used probes such as a low extinction coefficient at the wavelength used for photocatalysis which makes it possible to use high concentrations without interfering with incoming light and since it is the formation of a product rather than consumption of a reactant that is being measured, the sensitivity is very high. It was found that there is a critical concentration limit of Tris indicating that when the surface of the photocatalyst is not fully saturated by the probe, the maximum scavenging capacity has not been reached. To be able to assess the full photocatalytic efficiency, the concentration of Tris needs to rise beyond the critical value to become concentration independent. Where this limit appears is a direct function of the adsorption affinity of the probe to the photocatalytic surface.

3. O$_2$ does not affect the formaldehyde yield formed upon hydrogen abstraction from Tris, which makes it possible to assess the photocatalytic efficiency by Tris also when different O$_2$ contents are used.

4. A good correlation between the quantitative method based on Tris and the qualitative method based on the redox ink Resazurin was observed when probing the photocatalytic efficiency.

5. A complete reaction scheme for phenoxy radical chemistry is required for kinetic models for heterogeneous photocatalysis when benchmarking against experimental results where phenols have been used as probes. This is due to an electron-transfer reaction between the phenoxy radical and superoxide, produced when dissolved oxygen scavenges the electron of the hole-electron pair. The reaction counteracts the degradation of phenol and is substituent dependent.

6. Functional properties such as photo-induced superhydrophilicity and photocatalytic activity of immobilized TiO$_2$ films are dependent on the surface morphology and can be tuned by the deposition technique and the precursor.
7. TiO₂ enhanced with Ag nanoparticles increase the photocatalytic efficiency under black light illumination. This is partly due to an increased adsorption affinity of O₂ to Ag enhanced TiO₂ which make the reduction of O₂ (recognized as a rate limiting step for photocatalysis) more efficient as it leads to a prolonged lifetime for the electron-hole pair. Another explanation is that a Schottky barrier is formed at the metal-semiconductor interface which acts as an efficient electron trap and also extends the electron-hole lifetime.

8. A surface plasmon resonance effect appears as TiO₂ is interconnected with Ag nanoparticles which shift the absorption peak towards the visible light region.

9. Tris has a poorer, while O₂ has a stronger, adsorption affinity for Ag enhanced TiO₂ compared to pure TiO₂, which shows that the adsorption properties of the photocatalyst change as the material composition is modified.

10. The photocatalytic activity is significantly enhanced in the presence of the dissolved electron acceptors H₂O₂ and O₂. This is due to an efficient electron capturing process extending the lifetime of the electron-hole pair. Molecular oxygen and hydrogen peroxide are equally effective in scavenging the photo-excited electron, which is attributed to similar adsorption properties.

11. Hydrogen peroxide concentrations in a photocatalytic system exceeding monolayer coverage of the photocatalyst will result in suppressed photocatalytic efficiency as hydrogen peroxide will start to scavenge hydroxyl radicals.

12. The adsorption affinity of reactants towards the photocatalyst governs both the photocatalytic efficiency and the selectivity.

13. Visible light photo-activity can be induced into a TiO₂ film by a post treatment in liquid NH₃. The post treatment of the film caused a red-shift in the absorption band and a band gap narrowing of ~ 0.1 eV. The photocatalytic efficiency, probed by formaldehyde formation from Tris using white light with a cut-off filter at 385 nm, showed that the apparent quantum yield had increased from 1 ± 0.3 % (for a non-modified TiO₂ photocatalyst) to 8 ± 1 % upon the N-modification.
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