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Rare Earth doped Titania/Carbon Nanomaterials Composite Photocatalysts for Water Treatment

by

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Thesis in fulfilment of the requirement for the degree

PHILOSOPHIAE DOCTOR

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UNIVERSITY OF JOHANNESBURG

Supervisor : Prof A.K. Mishra
Co-supervisor : Prof X.Y. Mbianda
DEDICATION

This work is dedicated to my wife Tsakasile H. Mamba, my daughter Yenzile “Nony” Mamba and my parents (Mr M.M. Mamba and Mrs L.N. Mamba).
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ABSTRACT

Pre-synthesised gadolinium oxide decorated multiwalled carbon nanotubes (MWCNT-Gd) were coupled with titania to form nanocomposite photocatalysts (MWCNT-Gd/TiO$_2$) using a sol-gel method. Rare earth metal ions (Eu, Nd and Gd), nitrogen and sulphur tridoped titania were decorated on MWCNT-Gd to yield composite photocatalysts (MWCNT-Gd/Eu/Nd/Gd/N,S-TiO$_2$) by a similar method, using thiourea as nitrogen and sulphur source. Different carbon nanomaterials were incorporated into tridoped titania to form various composite photocatalysts (MWCNT/Gd,N,S-TiO$_2$, MWCNT/Nd,N,S-TiO$_2$, SWCNT (single walled carbon nanotube)/Nd,N,S-TiO$_2$ and rGO (reduced graphene oxide)/Nd,N,S-TiO$_2$) via the sol-gel method. Likewise, gadolinium doped graphitic carbon nitride (g-C$_3$N$_4$-Gd$^{3+}$) was obtained by heating a mixture of gadolinium nitrate hexahydrate and cyanoguanidine and subsequently hybridised with MWCNT/TiO$_2$ using the sol-gel method to yield composite photocatalysts with varying g-C$_3$N$_4$-Gd$^{3+}$ loadings. All the prepared photocatalysts were characterised by microscopic tools (FE/FIB-SEM-EDX, TEM), crystallographic technique (XRD), spectroscopic tools (UV-Vis, Raman and FT-IR) and nitrogen sorption technique (BET).

The prepared photocatalysts were evaluated for the degradation of various aqueous dye solutions under simulated solar light irradiation. MWCNT-Gd/TiO$_2$ nanocomposites showed higher photocatalytic degradation efficiency for methylene blue (MB) (1MWCNT-Gd/TiO$_2$, 96.2% and 3MWCNT-Gd/TiO$_2$, 98.7%) compared to MWCNT/TiO$_2$ and commercial titania. MWCNT/Gd,N,S-TiO$_2$ nanocomposites displayed enhanced visible light absorption and photocatalytic degradation efficiency for naphthol blue black (NBB) (MWCNT/Gd,N,S-TiO$_2$ (0.6%), 95.7%) compared to Gd,N,S-TiO$_2$ and N,S-TiO$_2$. Further improvement in photocatalytic activity was observed upon coupling MWCNT-Gd with tridoped titania for the degradation of acid blue 74 (AB74) (MWCNT-Gd/Nd,N,S-TiO$_2$, 95.0%, MWCNT-Gd/Eu,N,S-TiO$_2$, 98.8% and MWCNT-Gd/Gd,N,S-TiO$_2$, 100%). Coupling Nd,N,S-TiO$_2$ with SWCNT, MWCNT and rGO significantly improved the photocatalytic performance of the resultant nanocomposites for eosin blue shade (EBS) and eriochrome black T (EBT) both from single (between 89% and 99.3%
removal) and mixed dye solutions (between 49.0% and 65.7% removal). Moreover, the photocatalytic degradation efficiency of the nanocomposites increased in the order MWCNT/Nd,N,S-TiO$_2$< SWCNT/Nd,N,S-TiO$_2$< rGO/Nd,N,S-TiO$_2$. Hybridising gadolinium doped graphitic carbon nitride with MWCNT/TiO$_2$ yielded composite photocatalysts with enhanced photocatalytic properties for trypan blue (TB) degradation compared to the individual materials (g-C$_3$N$_4$-Gd$^{3+}$ and MWCNT/TiO$_2$) and the sample containing 30% g-C$_3$N$_4$-Gd$^{3+}$ showed the highest activity (100% removal in 150 mins).

The degradation of the dye molecules by the prepared nanocomposite photocatalysts was based on synergy between the various components of the photocatalysts. Improvement of charge transfer between MWCNTs and TiO$_2$ was enhanced through decoration of Gd$_2$O$_3$ nanoparticles on MWCNTs prior to coupling with TiO$_2$ resulting to improved photoactivity. Tridoping titania with N, S and metal ions introduced sub-band gap states or defects within the TiO$_2$ band gap enabling the excitation of electrons by visible light from these sub-band gap states into the conduction band of TiO$_2$. This did not only improve visible light absorption but also charge separation. Furthermore, incorporation of the carbon nanomaterials improved visible light absorption and charge separation and transportation resulting to further improvements in the overall photocatalytic activity the nanocomposites.

The fabricated composite photocatalysts were evaluated for potential reuse by recycling the photocatalysts several times in order to determine their stability and all the evaluated nanocomposites showed more than 85% degradation efficiency after five cycles. Total organic carbon (TOC) analyses were performed in order to gain an insight into the extent to which the different dyes were being broken down during photocatalysis and the results obtained showed that more than 50% of the dye molecules were completely mineralised. Furthermore, radical scavenging experiments were performed using benzoquinone (superoxide radical scavenger) and 2-propanol (hydroxyl radical scavenger) to identify the active species responsible for dye degradation. The formation of hydroxyl radicals during
photocatalytic degradation of the dye molecules was also probed using terephthalic acid.
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MWCNT/TiO$_2$  Multiwalled carbon nanotube/titania

MWCNT-Gd/TiO$_2$  Gadolinium nanoparticle decorated multiwalled carbon nanotube/titania

N,S-TiO$_2$  Nitrogen and sulphur codoped titania

NBB  Naphthol blue black

Ppm  Parts per million

rGO  Reduced graphene oxide

rGO/Nd,N,S-TiO$_2$  Reduced graphene/neodymium, nitrogen, sulphur tridoped titania

SWCNT  Single walled carbon nanotube

SWCNT/Nd,N,S-TiO$_2$  Single walled carbon nanotube/neodymium, nitrogen, sulphur tridoped titania

TB  Trypan blue

TDS  Total dissolved solids

TEM  Transmission Electron Microscope

TOC  Total organic carbon

UV-Vis  Ultraviolet-Visible

VB  Valence band

XRD  X-ray Diffraction
CHAPTER 1:
INTRODUCTION

1.1 Problem statement

Water quality and supply remains a big challenge to developing countries which are either experiencing water stress (water supply between 1000 and 1500 m$^3$ per capita per year) or water scarcity (water supply of less than 1000 m$^3$ per capita per year).\(^1\) The situation is expected to worsen as it is projected that about 14 countries will face water scarcity while around 11 countries will experience water stress in Africa by 2025. Since water is life, according to the Africa Water Vision 2025 inadequate quality and quantity of water serve as a limiting factor in poverty alleviation and economic recovery. This results to poor health, low productivity, food insecurity and constrained development.\(^2\) Furthermore, it is reported that there is low access to adequate water and sanitation in Africa which result to high incidence of communicable diseases that reduce vitality and economic productivity of the continent.\(^2\) It is reported that a sizable portion of all patients occupying African hospital beds suffer from water-borne illnesses as a result of lack of access to clean water and sanitation.\(^1\)

Anthropogenic activities such as sewage disposal, agricultural activities, mining, manufacturing industries, pharmaceuticals, etc. directly or indirectly impact negatively on the environment and water quality through the release of foreign substances (organic and inorganic substances). This infringes on the basic human right to clean environment and water as stated in the Constitution of the Republic of South Africa, Act 108 of 1996. According to the Bill of Rights in the Constitution, Section 24 and 27, not only does everyone have a right to clean water and environment, everyone has the responsibility to protect the environment from pollution and ecological degradation for the benefit of the present and future generations.\(^3\)
In terms of the volume of effluent discharged and the complexity of its matrix, the textile industry is regarded as the leading polluter of the environment accounting for about 20% of all industrial water pollution. Thousands of tonnes of dyes are produced and utilised annually, mostly in the textile industry. However, inefficiencies in various stages of textile processing lead to large quantities of dyes being lost directly into the effluent where they impart bright colours due to their ability to absorb visible light. Other major consumers of dyestuffs include pulp and paper industry, Kraft bleaching industry, dye and dye intermediates industry and food industry, pharmaceutical industries. The bright colours of dyes can be detected at trace concentrations and lower the aesthetic merit of the water. Furthermore, the presence of dyes in water leads to the disruption of the aquatic ecosystem. Azo dyes, the most extensively used class of dyes (makes up about 70% of all dyestuff used) can be partially broken down under anaerobic conditions to yield aromatic amines which are known carcinogens and mutagens. The complex and stable structure of dyes offer resistance to biodegradation and results to bioaccumulation. Due to the aforementioned undesirable effects, treatment of dyestuff pollution is an area of concern.

Conventional treatment methods such as adsorption, biological methods, coagulation (chemical and electrocoagulation), membrane processes, oxidation using hydrogen peroxide, ozone and their combination, have been employed for treatment of dye pollution and some positive results obtained. However, secondary pollution due to sludge formation is a major set-back for adsorption and coagulation and the toxicity and stability of dyes render biological processes ineffective. Fouling and the short half-life of ozone are some of the drawbacks of membrane processes and ozonation, respectively. Semiconductor photocatalysis on titania has shown the potential as an environmental clean-up tool for dye pollution and eliminates the drawbacks associated with the aforementioned conventional methods. The biocompatibility, chemical inertness, high photocatalytic activity and cost-effectiveness, make titania the benchmark of semiconductor photocatalysis. However, the optical response of pure titania lies in the UV region which only accounts for about 4% of the solar spectrum, ruling out the possibility of exploiting sunlight as a source of energy. Moreover, pure
titania suffers from a high recombination rate of the photogenerated charge carriers which drastically lower its photocatalytic activity.\textsuperscript{11,12} Therefore, extending the optical response of titania into the visible light region and improving charge separation are critical areas of research. This would enable the use of sunlight (consist of about 40\% visible light) as a source of energy and make the process cost-effective and efficient for practical applications.

\subsection*{1.2 Justification}

Tailoring the TiO\textsubscript{2} crystal structure to improve charge separation and extend its light response into the visible light region is an active area of research. These modifications are aimed at narrowing the band gap of TiO\textsubscript{2} or introduce impurity states within the band gap which can facilitate visible light absorption. Moreover, modifications are also introduced to trap either electrons or holes and prolong the life time of the charge carriers. Doping titania with metal ions (transition metals, rare earth metals and noble metals), non-metals (N, S, B, C, P and halogens), codoping (metal+metal, metal+non-metal and non-metal+non-metal), multidoping, coupling titania with narrow band gap semiconductors and formation of titania/carbon nanomaterials nanocomposites are some of the strategies investigated to improve the photocatalytic properties of titania under visible light irradiation.

It has been reported that doping titania with anionic species results to band gap narrowing and visible light absorption.\textsuperscript{13} Similarly, doping titania with metals has also shown improvement in visible light absorption and charge separation.\textsuperscript{14} Rare earth metal ions have been reported as effective electron scavengers due to their unique electronic configuration of an incompletely filled 4\textit{f} orbital and an empty 5\textit{d} orbital. Moreover, the chelating properties of rare earth ions aid in improving titania/dye interactions.\textsuperscript{15,16} The collaborative effect of the dopants has been reported in codoped titania resulting in improved photocatalytic activity under visible light irradiation. Synergy has also been reported as the mode of action in multidoped titania resulting to better visible light absorption, charge separation and the overall photocatalytic activity compared to mono- and co-doped titania.\textsuperscript{17,18}
Coupling titania with narrow band gap semiconductors has also been reported as an alternative solution to improving visible light absorption and charge separation in titania. Graphitic carbon nitride (g-C\textsubscript{3}N\textsubscript{4}) has recently emerged as an attractive metal-free, narrow band gap semiconductor which can act as a good sensitisier to titania due to their well-matched band energies.\textsuperscript{19,20} Composite photocatalysts of titania and carbon nanomaterials such as MWCNTs, SWCNTs, GO and rGO have shown enhanced visible light absorption, charge separation and transportation, improved surface area and absorption properties due to the incorporation of the carbon nanomaterials.\textsuperscript{21–23} A strong and intimate interface between titania and the carbon nanomaterials is necessary in order to realise their co-operative effect during photocatalysis.\textsuperscript{24}

Carbon nanomaterials/titania nanocomposites are well reported in the literature, but to the best of our knowledge, gadolinium oxide nanoparticles has not been decorated on MWCNTs using a modified sol-gel method and subsequently coupled with titania for photocatalytic dye degradation. This is anticipated to improve the MWCNT/TiO\textsubscript{2} interface and the overall photocatalytic activity of the nanocomposite. Furthermore, MWCNT-Gd has not been coupled with rare earth (Gd, Eu and Nd), nitrogen and sulphur tridoped titania which is anticipated to enhance both visible light absorption and charge separation and transportation in the nanocomposite. Gadolinium, nitrogen and sulphur tridoped titania has been reported in the literature, however, tridoped titania decorated on MWCNTs has not been explored. Nd, N and S tridoped titania decorated on MWCNTs, SWCNTs and rGO for dye degradation has not been attempted. A comparison of the photocatalytic activity between MWCNT/tridoped titania and rGO/tridoped titania, and between SWCNT/tridoped titania and MWCNT/tridoped titania, is lacking in the literature. Moreover, evaluation of the photocatalytic activity of these nanocomposites towards dye degradation in single and mixed dye solutions is seldom attempted. Numerous reports are available on the preparation and photocatalytic application of g-C\textsubscript{3}N\textsubscript{4}/TiO\textsubscript{2} but the preparation and photocatalytic application of gadolinium doped graphitic carbon nitride coupled with MWCNT/TiO\textsubscript{2} is reported in this thesis for the first time.
1.3 Objectives of the study

The study seeks to formulate a combination of materials (composite photocatalysts) capable of overcoming the drawbacks of pure titania in photocatalytic degradation of organic pollutants under visible light irradiation. Therefore, the following objectives were formulated:

a) Decoration of MWCNTs with gadolinium oxide nanoparticles via a modified sol-gel technique followed by microscopic characterisation and qualitative elemental analysis using EDX.

b) Fabrication of gadolinium oxide decorated MWCNT/titania (MWCNT-Gd/TiO$_2$) nanocomposites and their characterisation using TEM, SEM-EDX, BET, FT-IR, UV-Vis and XRD.

c) Evaluate the photocatalytic activity of the MWCNT-Gd/TiO$_2$ nanocomposites towards dye degradation under simulated solar light.

d) Synthesis and characterisation of MWCNT/Gd,N,S-TiO$_2$ nanocomposites with varying Gd$^{3+}$ loadings for photocatalytic degradation of dye under simulated solar light.

e) Preparation and characterisation of MWCNT-Gd/rare earth (Gd$^{3+}$, Eu$^{3+}$, Nd$^{3+}$), nitrogen, sulphur tridoped titania composite photocatalysts for degradation of dye in solution under simulated solar light.

f) Coupling Nd, N, S-tridoped titania with MWCNTs, SWCNTs and rGO and subsequent characterisation by various microscopic and spectroscopic techniques.

g) Investigating the photocatalytic activity of MWCNT/SWCNT/rGO/Nd,N$_3$S$_2$TiO$_2$ towards dye degradation in single and mixed dye solutions under simulated solar light.
h) Compare the photocatalytic activity of rGO/Nd,N,S-TiO$_2$ and MWCNT/Nd,N,S-TiO$_2$ in order to establish the effect of the different carbon nanomaterials on the photocatalytic properties of the nanocomposites.

i) Investigate the effect of incorporating different forms of carbon nanotubes (MWCNTs and SWCNTs) into the Nd,N,S-TiO$_2$ matrix in terms of the overall photocatalytic activity of the resultant nanocomposites.

j) Preparation and characterisation of gadolinium ion doped graphitic carbon nitride/MWCNT/TiO$_2$ nanocomposites of varying g-C$_3$N$_4$-Gd$^{3+}$ contents for photocatalytic degradation of aqueous dye solution under simulated solar light.

### 1.4 Thesis outline

The following outline provides a brief overview of the contents of the thesis and a chapter summary has been given at the end of each chapter:

**Chapter 1** introduces the study undertaken in terms of the problem that it sought to address and the justification of undertaking this study. The objectives of the thesis are also presented in this chapter.

**Chapter 2** gives a review of the literature on water availability and the effect of industrial pollution with special emphasis on the textile industry (dye pollution). A brief discussion on the current conventional treatment tools for dye pollution mitigation and the various challenges associated with each one of them is presented herein. The fundamental principles of semiconductor photocatalysis and the positives of the technology are described. Semiconductor photocatalysis on titania for dye pollution remediation is also explored. Strategies for manipulating pure titania in order to improve its visible light photocatalytic activity are detailed in this chapter.
Chapter 3 presents a detailed account of the synthesis procedures employed to prepare the different photocatalysts discussed in Chapters 4-9. A brief description of each of the different characterisation tools utilised is presented in this chapter. Materials and reagents utilised for the preparation of the photocatalysts are also listed in this chapter. The procedure for evaluation of the photocatalytic properties of the prepared photocatalysts is presented in this chapter.

Chapter 4 explores the photocatalytic degradation of methylene blue (MB) using MWCNT-Gd/TiO$_2$ composite photocatalysts under simulated solar light irradiation. The improved photocatalytic activity of these materials is discussed in terms of improved interface between titania and MWCNTs as a result of the gadolinium oxide nanoparticles which function as charge transfer stations. A possible photocatalytic degradation mechanism is proposed in this chapter.

Chapter 5 delves into the use of tridoped titania (Gd,N,S-TiO$_2$) decorated on MWCNTs (MWCNT/Gd,N,S-TiO$_2$) for the degradation of the diazo dye naphthol blue black (NBB) under simulated solar light. The higher photocatalytic activity of the composite photocatalysts is explained in terms of synergy between tridoping and incorporation of the carbon nanotubes within the titania matrix. A proposed mechanism for the degradation of NBB is also presented.

Chapter 6 reports on the exploitation of MWCNT-Gd/RE,N,S-TiO$_2$ (RE: Gd, Eu and Nd) composite photocatalysts for the degradation of acid blue 74 (AB74) under simulated solar light irradiation. The improved photocatalytic activity of the composite photocatalysts is explained in terms of creation of a multi-channel electron conduction system, improved optical properties and efficient generation of the oxidising species. The effect of the rare earth ion on the photocatalytic property of the resulted material is explained in this chapter.
Chapter 7 investigates the photocatalytic activity of Nd, N and S tridoped titania decorated on reduced graphene oxide (rGO) (rGO/Nd,N,S-TiO$_2$) for the degradation of eriochrome black T (EBT) and eosin blue shade (EBS) under simulated solar light. A comparison is drawn between this composite photocatalyst and its MWCNT/Nd,N,S-TiO$_2$ analogue in order to establish the effect of changing the carbon nanomaterial incorporated. Photocatalytic degradation of EBT and EBS from mixed dye solutions is studied to establish the performance of the prepared composite photocatalysts under competitive conditions.

Chapter 8 is linked to Chapter 7 and presents another comparative study on the photocatalytic degradation of EBS and EBT using SWCNT/Nd,N,S-TiO$_2$ and MWCNT/Nd,N,S-TiO$_2$ as influenced by the type of carbon nanotube incorporated. The photocatalytic activity of these nanocomposites is also matched against MWCNT/TiO$_2$, SWCNT/TiO$_2$ in order to highlight the significance of tridoping titania with Nd, N and S.

Chapter 9 explores the photocatalytic degradation of trypan blue (TB) on g-C$_3$N$_4$-Gd/MWCNT/TiO$_2$ composite photocatalysts. The effect of g-C$_3$N$_4$-Gd loading on the photocatalytic activity of the composite material is investigated. Enhanced photocatalytic activity of the prepared composite photocatalysts is explained in terms of the combined contribution of the different components of the composite photocatalyst in a typical sensitisation mechanism.

Chapter 10 provides some general conclusions and highlights some recommendations on possible future studies on different aspects of this work.
1.5 References


CHAPTER 2:
LITERATURE REVIEW

2.1 Introduction

This chapter begins with a review of the current status of water availability, future projections and challenges related to water scarcity and water stress. Textile dye pollution and the effects of dyestuffs on living organisms are discussed in this chapter. A brief discussion on the current dye pollution remediation measures is presented. Subsequently, a detailed discussion of semiconductor photocatalysis with specific interest on titania as the semiconductor, is provided. Methods for modifying titania for improved visible light photocatalytic activity, are also presented in this chapter.

2.2 Water availability

Adequate, clean water is one of the fundamental catalysts of development, food security, human health and environmental sustainability. Approximately 70% of the earth’s surface is occupied by water but only a tiny portion (~0.3%) of this water is accessible for human use. Development coupled with rapid population growth put the available water sources under strain. According to the Pan African Chemistry Network report of 2010 Africa’s population exceeded a billion in 2009 and continued to grow at an annual rate of 2.4%. However, from this population about 341 million people lack access to clean drinking water while a further 589 million do not have access to proper sanitation.¹ A broader picture is painted in the United Nations Development Programme (UNDP) report of 2006 where it is reported that about 1.1 billion people mostly in the developing countries lack access to clean water and 2.6 billion people lack adequate sanitation. Furthermore, 1.8 million children die annually from poor sanitation and water related ailments.² This is negatively affecting development in the different countries and proves to be a serious challenge towards attaining the Millennium Development Goal of improving sanitation and access to clean water supply by 50% in 2015.³ The
unequal demand and distribution of the available water to agriculture, manufacturing industry, cities and communities and the pollution emanating from these sectors are the driving forces of water stress and scarcity. Climate change is also a contributing factor.\(^4\)

World-wide, an estimated 3.9 billion people will live in water scarce regions by 2030.\(^5\) Pollution of the available water sources by various human activities plays a significant role in the water crisis. Improved agricultural methods (use of herbicides, pesticides, fertilisers, etc.) and rapid industrialisation lead to the release of undesirable chemical substances into the environment including portable water sources. Therefore, it is important to monitor these industrial activities to ensure that the environment is protected while we continue to benefit from the industries.

### 2.3 Industrial pollution

Industries are essential for development in any country. However, industrial activities are also responsible for degrading the environment and the standard of living of people through the release of foreign and potentially toxic substances into the environment. These foreign substances come into contact with the soil, air, ground water, rivers, swamps, streams, dams, etc. where they interrupt the biotic environment.\(^6\) The kind and quantity of waste that could potentially be released to the environment depends on the type of industry in question. Generally, the textile industry is regarded as the major polluter of the environment, accounting for about 20% of industrial water pollution. This is in light of the quantity and complexity of the waste water generated by this industry.\(^7,8\) Water is a very important raw material in the textile industry, an estimated 200 to 500 L of water are utilised per kilogram of finished textile product. In the USA, an average dying facility may generate an estimated 1 to 2 million gallons of waste water per day.\(^9,10\)

In terms of composition, textile waste water consists of a very complex matrix made of surfactants, heavy metals, suspended solids, sulphides, detergents, solids, salts, dyestuffs, organic solvents, etc.\(^11\) Figure 2.1 shows a representation
of typical cotton processing stages and the different pollutants originating from each stage which are then released into waste water and may find their way into the receiving waters.

Textile waste water is further characterised by fluctuating pH (2-12), high total organic carbon (TOC), temperature, chemical oxygen demand (COD), total dissolve solids (TDS) and biological oxygen demand (BOD). A typical variation in these parameters and water usage at different stages of cotton wet processing are presented in Table 2.1.
Table 2.1: Variation in wastewater parameters and water usage at different cotton wet processing stages.\textsuperscript{11}

<table>
<thead>
<tr>
<th>Process</th>
<th>COD (g/L)</th>
<th>BOD (g/L)</th>
<th>TS (g/L)</th>
<th>TDS (g/L)</th>
<th>pH</th>
<th>Colour (ADMI)</th>
<th>Water (L/Kg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Desizing</td>
<td>4.6-5.9</td>
<td>1.7-5.2</td>
<td>16.0-32.0</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>3-9</td>
</tr>
<tr>
<td>Scouring</td>
<td>8.0</td>
<td>0.1-2.9</td>
<td>7.6-17.4</td>
<td>-</td>
<td>10-13</td>
<td>694</td>
<td>26-43</td>
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<td>6.7-13.5</td>
<td>0.1-1.7</td>
<td>2.3-14.4</td>
<td>4.8-19.5</td>
<td>8.5-9.6</td>
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<td>1.6</td>
<td>0.05-0.1</td>
<td>0.6-1.9</td>
<td>4.3-4.6</td>
<td>5.5-9.5</td>
<td>-</td>
<td>232-300</td>
</tr>
<tr>
<td>Dyeing</td>
<td>1.1-4.6</td>
<td>0.01-1.8</td>
<td>0.5-14.1</td>
<td>0.05-100</td>
<td>5-10</td>
<td>1450-4750</td>
<td>8-300</td>
</tr>
</tbody>
</table>

TS- Total solids; ADMI- American dye manufacturer institute

There are more than 10 000 dyes that are in common use in the textile industry but the amount of dyestuffs produced per annum is not known. Over 100 000 dyes are commercially available, accounting for an estimated annual production of around 7 x 10\textsuperscript{7} tons of which 60 to 70% are azo dyes.\textsuperscript{13,14} Inefficiencies in the dyeing processes result in a substantial amount (15-20%) of the dyestuff released directly into waste water. Worldwide, a massive 280 000 tons of dyes are released in textile effluent annually.\textsuperscript{15} Textile effluent pose a serious threat to the environment and requires special treatment before being released into receiving water bodies. Other consumers of dyestuffs are the tannery, paper and pulp, electroplating, petroleum products, food, pharmaceutical and cosmetic industries.\textsuperscript{16} All these industrial sectors contribute to the environmental concerns emanating from dye pollution.

2.4 Effects of dye pollution

There are different types of dyes with different structures but they all have one thing in common, absorption in the visible light region. Dye containing effluent is
characterised by rich colour and if this effluent reaches water bodies it impacts negatively on the aesthetic merit of the water. For some dyes, colour can be detected in water even at concentrations less than 1 ppm.\textsuperscript{17} This makes removal of colour often more important than other colourless organic compounds. The presence of colour in water affects light penetration which impedes on photosynthesis and the normal functioning of the biotic ecosystem at large. Moreover, the presence of dyes in water reduces gas solubility resulting to insufficient oxygen triggering anaerobic respiration and suppress aerobic organisms. Bacterial growth is affected by low levels of dissolved oxygen which lowers the breakdown of dead organic matter and the release of the corresponding nutrients.\textsuperscript{16} Azo dyes, the most utilised class of dyes is very stable towards microbial degradation under aerobic conditions. However, under anaerobic conditions these dyes are partially broken down into aromatic amines. These aromatic amines are known carcinogens, mutagens and hemotoxins.\textsuperscript{18}

Furthermore, the complex matrix of chemical substances found in textile effluent which include detergents, dyes, additives and surfactants may induce teratogenic, carcinogenic and mutagenic effects to living organisms. The presence of dyes or their degradation derivatives have been linked to a number of health effects such as damage of the kidneys, reproductive system, central nervous system, brain, liver and disorders such as nausea, haemorrhage and ulceration of the skin and mucous membranes.\textsuperscript{19} Metal containing dyes may release these metals into the receiving water bodies and they can accumulate to toxic levels and some of the metal ions such as Cr$^{6+}$ are known to be carcinogenic and mutagenic.\textsuperscript{20} Dyes are intentionally synthesised to be very stable towards photolysis, sweat, microbial degradation and detergents.\textsuperscript{21} This means that they can persist in the environment for a long time and cause negative environmental effects. For an example, hydrolysed Reactive Blue-19 has a half-life of about 46 years at pH 7 and 25°C.\textsuperscript{22}

In addition to the large volumes of dyestuffs, textile effluent contains dissolved solids which when discharged can lead to high levels of total dissolved solids (TDS) of the receiving ground and surface water.\textsuperscript{15} This bears harmful effects on vegetation and hinders the utilisation of such water for agricultural exploits.
Moreover, residual chlorine is also a common pollutant; it results in the depletion of dissolved oxygen and adversely affects aquatic life especially aerobic living organisms. Additionally, the residual chlorine may react with some aromatic compounds to yield the toxic chlorinated aromatics. There are other non-biodegradable organic additives which may be found in the textile effluent which may cause an increase in COD of the effluent and negatively impact on the balance of the aquatic ecosystem.

Dye pollution does not only affect the biotic environment but also puts the textile industry operations under strain. In water scarce localities there are restrictions in terms on the amount of portable water allocated to the various industrial sectors. Consequently, water has to be used sparingly which then affect the daily production. The textile industry is required to treat dye containing effluent to comply with national and international regulations. Furthermore, efficient treatment of textile effluent would enable recycling of the water which will ease the daily requirements of fresh water. However, high quality water is required during textile processing so treatment of textile effluent for reuse remains a daunting challenge. The search for sustainable and effective dye pollution remediation tools remain a subject of intense research.

2.5 Dye pollution remediation

Several technologies have been proposed for textile effluent treatment to remove among the many contaminants, colour, which is as a result of the presence of dyestuffs. There is no single method that has been developed and shown the potential to treat dye pollution efficiently to comply with the environmental protection regulations. Consequently, the available treatment tools are used in conjunction with others to achieve improved results. Nonetheless, the challenge to meet the stringent regulations regarding textile effluent quality remains unsolved. This compromise the environment’s integrity and self-sustainability, as these pollutants are released into the receiving waters.
The available treatment methods can be classified into biological, physical/physiochemical, chemical and advanced oxidation processes (AOPs). Biological processes entailing biodegradation, bioaccumulation and biosorption are largely exploited in the textile industry for removal of colour. These methods are considered as environmentally friendly and economical. However, these methods are often difficult to employ on large scale applications and the complexity and fluctuating effluent parameters (pH, temperature, complex chemical additives, etc.) makes biological processes less effective. These effluent parameters need to be controlled and kept at optimum for microbial growth, which is often difficult. The complex nature of dye structures and their stability towards biodegradation makes biological processes ineffective especially under aerobic conditions. Decolourisation of effluent may be achieved under anaerobic condition but the potential formation of aromatic amines which are known carcinogens and mutagens, makes this route undesirable.

Another important category of dye pollution treatment tools is the physical/physiochemical methods which include adsorption, chemical and electrocoagulation, membrane processes and ion-exchange. Adsorption is one of the most widely used physical method for removal of colour; however, this method transfers the pollutants from the aqueous phase to the solid phase. As a result, highly concentrated sludge is generated which pose a serious handling and disposal challenge. Chemical and electrocoagulation though yielding positive results, also generate large amounts of concentrated sludge which cause secondary pollution and treatment problems. Moreover, the large doses of chemical coagulates added to facilitate coagulation in chemical coagulation are not eco-friendly.

Ion exchange is one of the least exploited physical techniques due to lack of versatility in application since it can only work for a narrow range of ionic dyes. Membrane processes (microfiltration, ultrafiltration, nanofiltration, reverse osmosis and forward osmosis) have the potential to generate high quality water from effluent especially when coupled with other pre-treatment methods. High removal of colour, inorganic ions, microbes and other organic compounds may be
achieved. However, the need for high operating pressures and susceptibility to fouling which affects permeation and rejection properties of the membranes are the major drawbacks.\textsuperscript{30} This inflates the operation costs of the treatment process.

Chemical oxidation has been exploited for removal of colour, using oxidising agents such as chlorine, chlorine dioxide, hypochlorite, etc. but the results have not been uninspiring due to the stability of dye molecules towards these oxidising agents. The potential formation of toxic chlorinated organic compounds is another challenge when using chlorine.\textsuperscript{23} Failure of the conventional oxidation processes to decolourise textile effluent prompted the development of a new set of oxidation tools known as advanced oxidation processes (AOPs). AOPs are based on the \textit{in situ} generation of hydroxyl radicals (OH) which are extremely powerful and non-selective oxidising species.\textsuperscript{31} The hydroxyl radical is responsible for attacking and mineralising dye molecules into smaller colourless molecules (carbon dioxide and water) and ions. This new set of oxidising agents includes ozone (O\textsubscript{3}), hydrogen peroxide (H\textsubscript{2}O\textsubscript{2}) and Fenton’s reagent (Fe\textsuperscript{2+}/H\textsubscript{2}O\textsubscript{2}). Semiconductor photocatalysis is another addition to the list of AOPs. In order to activate and improve the generation of the hydroxyl radicals, these oxidising agents are coupled with others and also with UV irradiation.\textsuperscript{32,33} Examples of such combinations include O\textsubscript{3}/H\textsubscript{2}O\textsubscript{2}, O\textsubscript{3}/H\textsubscript{2}O\textsubscript{2}/UV, H\textsubscript{2}O\textsubscript{2}/UV/Fe\textsuperscript{2+}, H\textsubscript{2}O\textsubscript{2}/UV, O\textsubscript{3}/UV, etc.

The main advantage of AOPs over other conventional treatment innovations is their potential to completely mineralise dye molecules which eliminate the formation of sludge which would otherwise pose further treatment and disposal challenges.\textsuperscript{31,34} Furthermore, the non-selective nature of the hydroxyl radicals ensures versatility of AOPs in mineralising a wide spectrum of dyes and other organic additives.\textsuperscript{21} AOPs are immune to the toxicity of textile effluent and there is no fouling which are major problems for biodegradation and membrane processes, respectively.\textsuperscript{35,36} However, the use of UV light is not sustainable since UV only accounts for about 4\% of the solar spectrum and artificial UV sources are costly.\textsuperscript{37} The refractory nature of dyes towards some of these oxidising agents makes their application ineffective. In the case of ozonation, the success of the oxidation process depends on the rate of mass transfer of ozone from gas to liquid state.
This rate of mass transfer decreases in textile effluent due to the poor water quality.\textsuperscript{38} Moreover, ozone needs continuous regeneration owing to its short half-life (20 mins).\textsuperscript{39} The use of large doses of the ferrous ion (40-80 ppm) in the Fenton’s process is not environmentally friendly and may result in the formation of sludge.\textsuperscript{40}

\section*{2.6 Semiconductor photocatalysis}

Semiconductor photocatalysis is one of the most emerging advanced oxidation processes for organic pollution abatement, and possess several advantages over other oxidation tools. One of the merits of this process is the provision of a fixed reaction environment by the photocatalyst surface on which a wide range of adsorbed organic and inorganic species can be chemically altered via light induced redox reaction. Moreover, the semiconductor which catalyses these redox reactions is often stable towards photolysis which allows for multiple oxidative conversions per active site of the photocatalyst.\textsuperscript{41} Other advantages of semiconductor photocatalysis include its lack of limitations in mass transfer, applicability at ambient temperature and pressure and ability to completely mineralise many organic pollutants into carbon dioxide, water and inorganic ions.\textsuperscript{42} Unlike biological methods which often fail due to the toxicity of the textile effluent, semiconductor photocatalysis is immune to this toxicity. Furthermore, during degradation of azo dyes, the formed aromatic amines can be further degraded on the photocatalyst into carbon dioxide, water and inorganic ions.\textsuperscript{18,43}

Semiconductor photocatalysis is an energy driven process whereby the semiconductor absorbs energy (hv) equal or above its band gap energy (E_g). This is basically an activation step where the absorbed energy initiates the excitation of electrons from the valence band (VB) to the conduction band (CB) of the semiconductor. At absolute zero, the valence band is fully occupied with electrons and has lower energy while the conduction band is empty and possesses higher energy.\textsuperscript{41,44} The size of the band gap which is the energy gap (barrier) between the valence and the conduction bands of the semiconductor determines its optical properties and colour. For example, semiconductors with band gaps between
1.5 eV and below 3.0 eV absorb energy in the visible light region and have colours ranging from red to violet. Some selected common semiconductors and their corresponding band gaps are presented in Table 2.2.

Table 2.2: List of selected semiconductors and their band gaps.

<table>
<thead>
<tr>
<th>Semiconductor</th>
<th>Band gap (eV)</th>
<th>Semiconductor</th>
<th>Band gap (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe₂O₃</td>
<td>2.3</td>
<td>CdSe</td>
<td>1.7</td>
</tr>
<tr>
<td>CdS</td>
<td>2.5</td>
<td>C₃N₄</td>
<td>2.7</td>
</tr>
<tr>
<td>WO₃</td>
<td>2.8</td>
<td>Cu₂O</td>
<td>2.2</td>
</tr>
<tr>
<td>TiO₂ (rutile)</td>
<td>3.0</td>
<td>V₂O₅</td>
<td>2.4</td>
</tr>
<tr>
<td>TiO₂ (anatase)</td>
<td>3.2</td>
<td>CeO₂</td>
<td>2.94</td>
</tr>
<tr>
<td>ZnO</td>
<td>3.2</td>
<td>ZnS</td>
<td>3.6</td>
</tr>
<tr>
<td>SnO₂</td>
<td>3.5</td>
<td>SiC</td>
<td>3.0</td>
</tr>
</tbody>
</table>

Following photoexcitation of the electron, a vacant hole is created in the valance band and an electron occupies the conduction band. Subsequently, the valence band acquires a positive charge and it is oxidising while the conduction band attains a negative charge and it is reducing. The photoexcitation reaction is depicted in Equation 2.1.

\[
\text{Semiconductor (SC)} \xrightarrow{hv} e^-_{\text{CB}} + h^+_{\text{VB}} \quad [2.1]
\]

There are a number of scenarios that could occur following the generation of the electron-hole pairs. One of the most undesirable scenarios during photocatalysis is the recombination of the photogenerated species which occurs very fast (in nanoseconds) following photoexcitation. The hole and the electron may recombine releasing the absorbed energy as heat and light. As much as about 90% of the
photogenerated electron-hole pairs recombine in less than 10 nanoseconds resulting in fewer charge carriers available for the surface reactions.\textsuperscript{52} This leads to poor photoactivity of the semiconductor. Alternatively, the electron may be trapped in defect sites in the semiconductor particle or in surface states of slightly lower energy than the conduction band.\textsuperscript{53,54} This ensures separation of the electron-hole pairs which leads to the formation of the oxidising species responsible for attacking the organic pollutants. In an ideal scenario, the holes and electrons migrate to the surface of the semiconductor where they undergo redox reactions with electron acceptors and donors trapped on the surface of the semiconductor.\textsuperscript{52,55} Reduction and oxidation of organic molecules adsorbed on the surface of the semiconductor by electrons and holes proceed via interfacial charge transfer to yield the radical species.\textsuperscript{54} A simplified schematic showing the fate of the electron-hole pairs subsequent to excitation is illustrated in Figure 2.2.

![Figure 2.2: Fate of the electron-hole pair following photoexcitation](image)

Figure 2.2: Fate of the electron-hole pair following photoexcitation

Basically, the valence band hole react with adsorbed hydroxide ions (OH\textsuperscript{−}) or water (H\textsubscript{2}O) to form the extremely powerful, non-selective, oxidising hydroxyl radical
(OH\(^+\)). Similarly, the conduction band electron may reduce any adsorbed oxygen (O\(_2\)) to form the superoxide radical (O\(_2^•\)), another oxidising species.\(^{56,57}\) The hydroxyl and superoxide radicals are responsible for attacking and degrading organic pollutants into carbon dioxide, water and inorganic ions. Scavenging of the conduction band electrons by oxygen to yield the superoxide radical is a very important step in semiconductor photocatalysis. It not only produces the oxidising species but also suppress electron-hole recombination and prolongs the life of the holes leading to the formation of the hydroxyl radicals.\(^{53,58,59}\) The formation of these oxidising species is summarised in Equations 2.2-2.8. Formation of these radical species is determined by the valence and conduction band potentials relative to the redox potential of the surface reaction. For example, if the oxidation potential of the surface reaction is more positive than the valence band potential, then oxidation cannot be accomplished. Likewise, if the reduction potential of the surface reaction is more negative than the conduction band, reduction will not be achieved.\(^{41}\) This implies that there will be no formation of the hydroxyl and superoxide radicals from the valence band and conduction band, respectively.

\[
\begin{align*}
\text{SC} (h^+\text{VB}) + \text{H}_2\text{O} & \rightarrow \text{SC} + \text{OH}^• + \text{H}^+ \quad [2.2] \\
\text{SC} (h^+\text{VB}) + \text{OH}^- & \rightarrow \text{SC} + \text{OH}^- \quad [2.3] \\
\text{SC} (e^-\text{CB}) + \text{O}_2 & \rightarrow \text{SC} + \text{O}_2^• \quad [2.4] \\
\text{OH}^- + \text{OH}^- & \rightarrow \text{H}_2\text{O}_2 \quad [2.5] \\
\text{H}_2\text{O}_2 & \xrightarrow{h\nu} 2\text{OH}^• \quad [2.6] \\
\text{H}_2\text{O}_2 + \text{O}_2^• & \rightarrow \text{OH}^- + \text{O}_2 + \text{OH}^- \quad [2.7] \\
\text{SC} (e^-\text{CB}) + \text{H}_2\text{O}_2 & \rightarrow \text{SC} + \text{OH}^- + \text{OH}^- \quad [2.8]
\end{align*}
\]
2.6.1 Mechanism of hydroxyl radical attack on organic pollutants

The hydroxyl radical is the second strongest oxidising species after fluorine. Its strong oxidation potential \( E_{\text{ox}} = +2.8 \ \text{V}_{\text{NHE}} \) and non-selective nature enables it to oxidise a wide range of organic compounds including dyes which have a complex and stable structure. Table 2.3 gives the oxidation potentials of some common oxidising agents including ozone, atomic oxygen, chlorine and hydrogen peroxide which all have lower oxidation potentials than the hydroxyl radical. During photocatalysis, both the superoxide and hydroxyl radicals are important and they complement each other.\textsuperscript{54,56} The superoxide radical can either oxidise the organic pollutants directly or undergo further reactions to form the hydroxyl radical as depicted in Equation 2.7.

Table 2.3: Oxidation potentials of some oxidising species.\textsuperscript{60}

<table>
<thead>
<tr>
<th>Oxidant</th>
<th>Oxidation potential ( (\text{V}_{\text{NHE}}) )</th>
<th>Oxidant</th>
<th>Oxidation potential ( (\text{V}_{\text{NHE}}) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fluorine</td>
<td>3.03</td>
<td>Hypobromous acid</td>
<td>1.59</td>
</tr>
<tr>
<td>Hydroxyl radical</td>
<td>2.80</td>
<td>Chlorine dioxide</td>
<td>1.57</td>
</tr>
<tr>
<td>Atomic oxygen</td>
<td>2.42</td>
<td>Hypochlorous acid</td>
<td>1.49</td>
</tr>
<tr>
<td>Ozone</td>
<td>2.07</td>
<td>Hypoiodous acid</td>
<td>1.45</td>
</tr>
<tr>
<td>Hydrogen peroxide</td>
<td>1.78</td>
<td>Chlorine</td>
<td>1.36</td>
</tr>
<tr>
<td>Perhydroxyl radical</td>
<td>1.70</td>
<td>Bromine</td>
<td>1.09</td>
</tr>
<tr>
<td>Permanganate</td>
<td>1.68</td>
<td>Iodine</td>
<td>0.54</td>
</tr>
</tbody>
</table>
The degradation of organic compounds by the hydroxyl radical can proceed either through hydrogen abstraction, electrophilic attack or electron transfer. However, hydrogen abstraction has been highlighted as the most common route for degradation of organic compounds. During hydrogen abstraction, hydrogen is removed from the organic compound to form an organic radical as shown in Equation 2.9. Subsequent reaction with oxygen, transforms the organic radical to peroxyl radical. These peroxyl radicals undergo a series of thermal reactions of oxidative degradation, leading to the complete mineralisation of the organic compound to carbon dioxide, water and inorganic salts (Equation 2.10). Electrophilic addition is another proposed mechanism whereby the hydroxyl radical is added to the organic compound’s π-system to form the organic radical (Equation 2.11). In cases where hydrogen abstraction or electrophilic addition is unfavourable due to multiple halogen substitution or steric hindrance, electron-transfer is a possible route for initiating degradation of the organic compound. The hydroxyl radical is reduced to hydroxide ions by the organic compound while forming the organic radical (Equation 2.12). Thereafter, the organic radical undergoes the transformations depicted in Equation 2.10. In addition to radical attack on organic compounds, direct reduction by the conduction band electrons (Equation 2.13) and oxidation by the valence band holes (Equation 2.14) have been reported as other possible routes through which degradation of organic pollutants such as dyes is initiated during semiconductor photocatalysis.

\[
\begin{align*}
\text{OH}^\cdot &+ \text{RH} &\rightarrow &\text{R}^\cdot + \text{H}_2\text{O} &\text{[2.9]} \\
\text{R}^\cdot + \text{O}_2 &\rightarrow \text{RO}_2^- &\rightarrow &\text{CO}_2 + \text{H}_2\text{O} + \text{Inorganic ions} &\text{[2.10]} \\
\text{PhX} &+ \text{OH}^\cdot &\rightarrow &\text{HOPhX}^- &\text{[2.11]} \\
\text{OH}^\cdot &+ \text{RX} &\rightarrow &\text{RX}^+ + \text{OH}^- &\text{[2.12]} \\
\text{Dye} + e^-_{\text{CB}} &\rightarrow \text{Dye}^- &\rightarrow &\text{Degradation products} &\text{[2.13]} \\
\text{Dye} + h^+_{\text{VB}} &\rightarrow \text{Dye}^+ &\rightarrow &\text{Degradation products} &\text{[2.14]}
\end{align*}
\]
The effectiveness of the photocatalytic degradation of the organic pollutants depends on the effective generation of the hydroxyl radicals and prevention of the electron-hole recombination. Electron-hole recombination is undesirable because it consumes the reacting species for the formation of the hydroxyl radical which in turn impacts negatively on the photocatalytic activity of the semiconductor. Since semiconductor photocatalysis is a surface process, the electron donor and acceptor have to be confined on the surface of the semiconductor.\(^{64,65}\) This is to ensure effective separation of the electron-hole pairs and improve the photocatalytic degradation of the pollutants. Several approaches have been proposed for controlling the interfacial electron transfer at the semiconductor-electrolyte interface. Strategies such as electrostatic incorporation of electron acceptors at the semiconductor surface, modifying the semiconductor surface with electron acceptors and immobilising semiconductor photocatalysts in redox functionalised polymers have been proposed.\(^{64}\)

### 2.6.2 Summary of key steps during semiconductor photocatalysis

Semiconductor photocatalysis is a very complex process which involves a lot of possible reaction pathways which are responsible for the eventual degradation of the organic pollutants. However, there is a general consensus that the process can be summarised into five key steps (Figure 2.3) leading to the degradation of the organic pollutants. The first step is mass transfer of the organic pollutants through diffusion from the bulk solution onto the surface of the semiconductor (step (i)). In the second step there is simultaneous adsorption of the organic pollutant to the semiconductor surface and excitation of the semiconductor (step (ii)). This is followed by the attack and degradation of the organic compound by the oxidising species (step (iii)). This is followed by desorption of the degradation products from the photocatalyst’s active surface (step (iv)). Lastly, the degradation products diffuse from the photocatalyst interface into the bulk solution (step (v)).\(^{66}\) It is important to note that the overall degradation rate depends on the slowest step in the process.\(^{66}\) For example, regardless how fast the adsorption of the organics on the semiconductor (ii) and their degradation (iii), if the desorption of
the degradation products (iv) and their diffusion into the bulk solution (v) is slow, the whole process will depend on these two steps (iv and v).

**Figure 2.3: Summary of semiconductor photocatalysis.**

### 2.7 Photocatalysis on titania for organic pollution mitigation

#### 2.7.1 Introduction

The use of titania powders in white pigments dates back in ancient times. However reports on the photocatalytic applications of titania emerged early in the 20th century. In 1938 *Goodeve* and *Kitchener*\(^67\) reported the bleaching of the azo dye Chlorazol Sky Blue FF by titania powder under UV light irradiation. The decolourisation of the dye was attributed to a phenomenon referred to as photosensitisation on TiO\(_2\) powder, whereby the powder absorbed the UV light and induced irreversible changes in the dye structure. These reactions involved in mutating the dye structure were proposed to occur on the surface of the TiO\(_2\) powder and involved either rearrangement of nuclei, electron loss or gain.\(^68\) Noteworthy, there were other reports before and after the ones by *Goodeve* and *Kitchener*. However, vast interests in titania for photocatalytic applications were
ignited by Fujishima and Honda in 1972 who demonstrated that photoexcitation of TiO$_2$ can be utilised to chemical water splitting$^{69}$

In 1977 the heterogeneous photocatalytic oxidation of cyanide ion in aqueous solutions$^{70}$, oxidation of cyanide and sulphite$^{71}$ and the photolysis of water and photoreduction of nitrogen$^{72}$ on TiO$_2$ were reported. Mineralisation of acetic acid to methane on platinised TiO$_2$ powder was reported in 1978.$^{73}$ Pruden and Ollis$^{74}$ demonstrated the complete mineralisation of trichloroethylene to hydrochloric acid and carbon dioxide on TiO$_2$ in 1983 while Hsiao et al.$^{75}$ studied the photocatalytic degradation of dichloromethane (CH$_2$Cl$_2$), chloroform (CHCl$_3$), and carbon tetrachloride (CCl$_4$) on photoexcited TiO$_2$, in the same year. From 1990s onwards, there has been an ever increasing interest in exploiting TiO$_2$ in various applications. Such applications include hydrogen production from water splitting, dye sensitized solar cells, environmental remediation by treatment of organic and inorganic pollutants, inactivation of killing of bacteria, organic synthesis, sensors, pigments, whitening products (for paints, paper or plastics), cosmetics, food colorants, air purification, antifogging and self-cleaning mirrors, construction industry, hospital equipments, etc.$^{46,76}$

### 2.7.2 Preparation of titania

Recent advancements in materials chemistry have been greatly enhanced by the emergence of nanotechnology which allows for control of materials properties by assembling these materials at the molecular or atomic scale (nanoscale). Nanotechnology entails the manipulation of nanomaterials which are basically materials with basic structural units smaller than 100 nm in at least one dimension.$^{77,78}$ Nanomaterials can be engineered into larger materials or incorporated into bulk materials to influence certain properties of the bulk material such as electrical and thermal properties. Decreasing the particle size of the material to the molecular scale offers new properties which are not realised in the bulk material. Such properties include large surface to volume ratio, increase in surface energy, electrical conductivity, optical properties, catalytic properties, magnetic properties, etc.$^{79,80}$ The smaller sizes of nanomaterials enables
decontamination at low concentrations and fewer amounts of the nanomaterials are required to facilitate decontamination compared to the bulk material. Moreover, the increase in surface energy in nanomaterials results in novel reactions which are not possible with the bulk material.\textsuperscript{81} Nanosemiconductors (e.g. nanotitania) provide better results than their bulk form owing to improved movement of electrons and holes which depend on the size of semiconductor particles. The transport properties related to photons and phonons are largely affected by size and geometry of the nanosemiconductor.\textsuperscript{82}

There are several methods that have been extensively exploited for preparation of titania nanoparticles and they have their own merits and drawbacks. These methods include coprecipitation, Solvothermal synthesis, sol-gel method, micro-emulsion, electrochemical synthesis, gas phase methods, chemical vapour deposition, physical vapour deposition, spray pyrolysis deposition, microwave synthesis, sonochemical method, etc.\textsuperscript{82,83} The different methods yield titania nanoparticles with different degrees of crystallinity, different phases, particle sizes and shapes. The sol-gel method is often preferred over the other methods due to a number of advantages that it offers. Such advantages include high purity of titania obtained, homogeneity (good mixing of multi-component systems), felicity and flexibility in introducing dopants in large concentrations, stoichiometry control, ease of processing, control over the titania composition and the ability to allow coating of titania on various substrates.\textsuperscript{77,84} Additionally, sol-gel method allows for effective control of particle size, shape and properties of the resultant titania, facilitate tailoring of special titania nanomaterials such as films, powders, etc., and selection of the sol-gel precursors and other building blocks enables the designing of the desired material structure and property.\textsuperscript{85,86}

Basically, the sol-gel method is a wet-chemical method which is popular in various fields of ceramic engineering, materials science and photocatalysis for preparation of various metal oxides. Titanium precursors such as titanium alkoxides (titanium (IV) isopropoxide, titanium (IV) butoxide) and titanium salts (titanium tetrachloride, titanium sulphate) are commonly used.\textsuperscript{87} Formation of titania involves a series of hydrolysis and polycondensation reactions. Titanium-oxo and titanium-hydroxo
polymers are formed in solution via connection of the titanium centres either with oxo (Ti-O-Ti) or hydroxo (Ti-OH-Ti) linkages. During this step, a diphasic system is formed (containing both liquid and solid phases) as the solution evolves into a gel-like structure whose morphology may range from discrete particles to continuous polymer networks. Acids such as hydrochloric acids, formic acid, acetic acid, sulphuric acid, etc. are often used to catalyse the hydrolysis of the alkoxides. The gel or precipitate formed is dried to yield amorphous titania. This is then subjected to calcination at temperatures between 350 to 500 °C to obtain anatase titania. Calcination at temperatures above 500 °C yield a mixture of anatase and rutile while further increasing the temperature gives exclusively rutile titania. Therefore, by choosing the right calcination temperature, the desired phase of nanotitania can be obtained.

2.7.3 Crystal structure and properties of TiO$_2$

Titanium is the fourth most abundant metal after aluminium, iron and magnesium and the ninth most abundant element constituting about 0.63% of the earth’s crust. TiO$_2$ is a transition metal oxide with an estimated annual world-wide production of over 4 million tons. There are four naturally occurring polymorphs of titania: anatase and rutile which have tetragonal structures, brookite with an orthorhombic structure and TiO$_2$ (B) which is monoclinic. Two synthetic forms of titania have also been reported resulting from high pressure synthesis using rutile TiO$_2$ as the starting material. These are TiO$_2$ (II) with a PbO$_2$ structure and TiO$_2$ (H) which has a hollandite structure. The structures of anatase, rutile and brookite can be explained in terms of (TiO$_6$) octahedrals linked together in different ways using the edges and vertices. Each of the Ti$^{4+}$ cations is surrounded by an octahedron of six O$^2-$anions. In anatase, the octahedrals are connected by their vertices forming an elongated structure while in rutile the octahedrals are connected by their edges. In brookite, connection of the octahedrals is by both the vertices and edges. Figure 2.4 shows the structures of anatase, rutile and brookite.
Figure 2.4: Crystal structures of (a) anatase, (b) rutile and (c) brookite.\textsuperscript{88}

Rutile is relatively more stable than anatase but the Gibbs free energy of formation between them is small (less than 15 KJmol\textsuperscript{-1}). As a result, changing the annealing temperature during synthesis leads to formation of a different TiO\textsubscript{2} phase. Anatase can be obtained by calcining the samples at temperatures around 400 °C while at temperatures between 500 and 600 °C, rutile start forming and becomes the predominant phase at higher temperatur.\textsuperscript{52} Titania is an n-type semiconductor, owing to the presence of small amounts of oxygen vacancies which are compensated by the presence of Ti\textsuperscript{3+} centers. The valence band of TiO\textsubscript{2} is formed by the overlapping of the oxygen 2\textit{p} orbitals while the lower part of the conduction band is mainly constituted by the 3\textit{d} orbitals of Ti\textsuperscript{4+} with t\textsubscript{2g} symmetry.\textsuperscript{52,93} Bad gap energies of 3.2, 3.0 and 2.96 eV have been calculated for anatase, rutile and brookite.\textsuperscript{92}

Titania is regarded as the benchmark of semiconductor photocatalysis owing to its fascinating properties making it an ideal photocatalyst for organic pollution remediation. Such merits include non-toxicity, biological and chemical stability, photoactivity, resistance towards photocorrosion, suitable flat band potential, insoluble in water under most environmental conditions, inexpensive and largely available.\textsuperscript{51,55} Anatase has been found to be the most photocatalytic active TiO\textsubscript{2} phase. This is attributed to its slightly higher Fermi level, lower capacity to adsorb
oxygen and high adsorption of hydroxyl group on its surface.\textsuperscript{88} Furthermore, anatase is the preferred choice in solar energy application due to its high electron mobility, low dielectric constant and low density compared to the other polymorphs.\textsuperscript{91} Rutile shows lower or no photoactivity while brookite and TiO\textsubscript{2} (B) show no photocatalytic activity. However, according to Sclafani et al. rutile may be active or inactive depending on the preparation conditions.\textsuperscript{94}

2.7.4 Mechanism for degradation of organic pollutants on TiO\textsubscript{2}

Photocatalytic degradation on titania is initiated by the adsorption of energy equal or above 3.2 eV for anatase and 3.0 eV for rutile which leads to the formation of electron-hole pairs, as previously explained in Section 2.6. This result to a series of possible redox reactions leading to the formation of the oxidising species and the eventual attack of the organic pollutants, as discussed in Section 2.6.1. However, since titania is a wide band gap semiconductor its absorption edge lies in the UV region and the photoexcitation mechanism discussed in Section 2.6 is applicable to titania under UV light irradiation (Figure 2.5a). However, photocatalytic degradation of dye molecules on titania have also been reported under visible light irradiation. Since TiO\textsubscript{2} does not absorb light in the visible region, but all dyes do, it was proposed that the photoexcitation step involved excitation of the dye molecules instead of TiO\textsubscript{2} upon visible light absorption (Figure 2.5b).\textsuperscript{95} This mechanism is referred to as photosensitisation where the dye acts as a visible light sensitizer. Prior to photosensitisation, the dye has to be adsorbed onto the surface of titania to ensure intimate contact and the co-operative effect.
Figure 2.5: Photocatalytic degradation of dye on TiO₂ under (a) UV and (b) visible light irradiation

The dye absorbs visible light and an excited state (dye*) is formed. In the presence of TiO₂, the dye’s excited state injects an electron into the conduction band of TiO₂ resulting in the free electron in the conduction band and a positive dye radical (dye⁺) as illustrated in Figure 2.5b. Subsequently, the conduction band electron is trapped by adsorbed molecular oxygen and reacts to form the
superoxide radical which can directly be involved in dye degradation or undergo transformations to form the hydroxyl radical. The cationic dye radical reacts with hydroxyl ions to form the hydroxyl radicals which then attack the dye molecules. Alternatively, the cationic dye radical interacts with the superoxide radical, hydroperoxyl radical (HO$_2^\cdot$) or hydroxyl radical to form intermediate organic species and eventually carbon dioxide, water and inorganic ions.$^{62,96}$ The photosensitisation mechanism and generation of the reactive species is summarised in Equations 2.15-2.24.$^{96,97}$

$$\text{Dye} + h\nu \rightarrow \text{Dye}^\ast \quad [2.15]$$

$$\text{Dye}^\ast + \text{TiO}_2 \rightarrow \text{Dye}^{\ast\ast} + \text{TiO}_2 (e^-_{\text{CB}}) \quad [2.16]$$

$$\text{TiO}_2 (e^-_{\text{CB}}) + O_2 \rightarrow O_2^{-\ast} + \text{TiO}_2 \quad [2.17]$$

$$\text{Dye}^{\ast\ast} + OH^- \rightarrow \text{Dye} + OH^\ast \quad [2.18]$$

$$\text{Dye} + OH^- \rightarrow H_2O + \text{Dye oxidation products} \quad [2.19]$$

$$O_2^{-\ast} + H^+ \rightarrow HO_2^\ast \quad [2.20]$$

$$\text{HO}_2^\ast + H^+ + \text{TiO}_2 (e^-_{\text{CB}}) \rightarrow H_2O_2 + \text{TiO}_2 \quad [2.21]$$

$$H_2O_2 + \text{TiO}_2 (e^-_{\text{CB}}) \rightarrow OH^- + OH^- + \text{TiO}_2 \quad [2.22]$$

$$\text{Dye}^{\ast\ast} + O_2^{-\ast} \rightarrow \text{Dye degradation products} \quad [2.23]$$

$$\text{Dye}^{\ast\ast} + OH^-/HO_2^\ast \rightarrow \text{Dye degradation products} \quad [2.24]$$

### 2.7.5 Drawbacks of TiO$_2$ as a photocatalyst

Titania is referred to as the “gold standard” of semiconductor photocatalysis with Degussa P25, a commercially available mixture 80% anatase and 20% rutile often used as a reference photocatalyst.$^{98}$ However, pure TiO$_2$ has some serious limitations which hinder its full exploitation as an environmental clean-up tool for
organic pollution especially dye-pollution. Titania has a wide band gap (3.2 eV, anatase and 3.0 eV, rutile) which only allows absorption in the UV region. This poses a serious energy problem because UV light only accounts for about 4% of the solar spectrum which rules out the possibility of using sunlight as a source of energy. Visible light absorption would enable titania to harness sunlight as a source of energy owing to its approximately 40% abundance in the solar spectrum.\textsuperscript{99,100} Solar energy which is a clean, natural energy would replace the artificial UV sources which consume a lot of electrical energy and require protection of the eyes and skin during application which ultimately lead to escalating treatment costs.\textsuperscript{51,101}

The other major shortfall of TiO\textsubscript{2} is the fast recombination rate of the photogenerated electron-hole pairs. This limits the formation of the hydroxyl and superoxide radicals which are responsible for the photocatalytic degradation of the organic pollutants. Consequently, the efficiency of the photocatalysis process is remarkably lowered.\textsuperscript{48,50,51} Scavenging either the electrons or the holes is key towards improving the photocatalytic activity of titania. Other problems associated with the use of titania powders relate to the requirement of separation and recycling of the photocatalyst from the treated water before being released. This can be a difficult, time consuming and expensive process.\textsuperscript{102} Furthermore, titania tends to aggregate in aquatic media which lowers its photoactivity.\textsuperscript{46} However, TiO\textsubscript{2} can be immobilised on inert substrates such as glass for ease of separation from the water but these systems have low surface areas, low mass transfer and often require occasional physical coating of TiO\textsubscript{2} on the inert substrate.\textsuperscript{103}
2.8 Strategies for modifying titania

In order to fully exploit the photocatalytic properties of titania, there is a need to overcome the drawbacks highlighted in Section 2.7.5. This means tailoring titania so as to extend its photoresponse into the visible light region and improve charge separation. This would enable utilisation of the abundant solar energy and improve the photocatalytic activity of titania which could pave way for effective environmental clean-up and protection.

2.8.1 Sensitisation

Visible light sensitisation of TiO$_2$ can be achieved through the use of dye molecules (dye sensitisation), polymers (polymer sensitisation) and surface complexes (surface complex sensitisation). Dye sensitisation of TiO$_2$ has already been discussed in Section 2.7.4. Briefly, the process involves adsorption of dye molecules onto the surface of TiO$_2$ which up visible light irradiation undergoes oxidation by injecting an electron into the conduction band of TiO$_2$. The dye molecule is reduced back to its original state either by accepting an electron from an electron donor or from other adsorbed pollutants. Good interaction between the sensitiser and TiO$_2$ is essential since, only the surface bound dye molecules take part in the photocatalytic process.

A good sensitiser must have strong adsorption capacity, high visible light absorption efficiency, long lifetime of excited states, high quantum yield and a matching band structure (to that of TiO$_2$) to reduce energy losses during electron transfer. Factors such as the dye concentration, nature of the dye, surface area of TiO$_2$ and the pH of the solution govern the adsorption of the sensitiser on titania. Degradation of the sensitiser is not favourable until the pollutant in the bulk solution is depleted. Thereafter, the sensitiser undergoes self-destruction once the pollutant in the bulk is finished which makes reusability of dye sensitised TiO$_2$ almost impossible. Besides undergoing self-destruction, the dye molecules may gradually leach out from the TiO$_2$ surface resulting to a decline in the photocatalytic activity.
Polymer sensitisation is another strategy to extend TiO$_2$ light response into the visible light region and it is similar to dye sensitisation. The polymer absorbs visible light and injects an electron into the conduction band of TiO$_2$ to initiate the photocatalytic process.$^{108}$ Polymers often offer better photocatalytic activities than dyes owing to their low solubility in water which minimise leaching out which is rife in dye sensitisation.$^{109}$ Polyaniline (PANI) which is a conductive polymer is an attractive choice for sensitisation because of its photo and thermal stability, extended π-conjugated structure which ensure efficient charge separation and also shows good photoabsorption from the visible to the near infrared region. This allows for the possible exploitation of solar light as a source of energy.$^{108,110}$ Another TiO$_2$ sensitisation strategy involves the formation of strong chemical bonds between an organic compound (complex) and TiO$_2$, where the organic complex is the visible light sensitiser. In surface complex sensitisation, there is no formation of an excited state in the complex; instead the electron is excited directly from the ground state to the conduction band of TiO$_2$.$^{111}$

2.8.2 Doping TiO$_2$ with non-metal ions

Incorporating non-metal ions within the TiO$_2$ lattice has been underlined as the most effective approach towards development of visible light responsive photocatalysts.$^{112}$ A good dopant should result in the formation of states within the TiO$_2$ band gap that absorb visible light and the conduction band maximum, including the impurity states, should be as high as that of TiO$_2$ or higher than the H$_2$/H$_2$O level to ensure its photoreactivity. Moreover, sufficient overlap between the new dopant states and TiO$_2$ states is a prerequisite in order to facilitate quick transfer of photoexcited carriers to reactive sites at the catalyst surface.$^{112}$ These conditions favour anionic doping over cationic doping for improving visible light absorption and photocatalytic activity of TiO$_2$ since anions are not involved in charge carriers’ transport so they are less likely to form recombination centres.$^{113}$
2.8.2.1 Nitrogen doping

There are currently three proposed mechanisms regarding nitrogen doping in TiO\textsubscript{2}. In the first line of thinking, Sato prepared NO\textsubscript{x}-TiO\textsubscript{2} via thermal treatment of Ti(OH)\textsubscript{4} incorporated with NH\textsubscript{4}Cl or NH\textsubscript{4}OH which showed visible light absorption. This visible light activity of NO\textsubscript{x}-TiO\textsubscript{2} was ascribed to the formation of an impurity level by NO\textsubscript{x} within the TiO\textsubscript{2} band gap similar to metal ion doping.\textsuperscript{114} In the second school of thought, Asahi et al. performed theoretical studies (density of states calculations) and experimental work on nitrogen doped TiO\textsubscript{2} and both correlated that substitutional doping of nitrogen in TiO\textsubscript{2} yields good results in terms of visible light absorption. This visible light response of substitutional nitrogen doped TiO\textsubscript{2} originated from the sufficient mixing of the N 2\textit{p} states with the oxygen 2\textit{p} states, resulting to band gap narrowing.\textsuperscript{112}

Similarly, Irie et al. prepared visible light active TiO\textsubscript{2-x}N\textsubscript{x} powders by annealing anatase TiO\textsubscript{2} in NH\textsubscript{3} flow and investigated their photocatalytic properties towards decomposition of gaseous propanol under the same adsorbed photon number of visible or UV light. The visible light activity of the prepared powders was attributed to the formation an isolated narrow band above the valence band of TiO\textsubscript{2} and higher quantum yields were obtained when using UV light than visible light. It was reasoned that irradiating with UV light excite electrons from both the valence band and the narrow band formed above it while visible light only excite electrons from the newly formed narrow band, hence the lower quantum than UV. The authors further argued that if substitution of oxygen for nitrogen narrowed the band gap, then the quantum yield would have been the comparable both under visible and UV light irradiation.\textsuperscript{115}

According to the third mechanism, the red shift observed in anion doped TiO\textsubscript{2} emanates from formation of oxygen vacancies and colour centres (e.g. F, F\textsuperscript{+}, F\textsuperscript{++} and Ti\textsuperscript{3+}) within the TiO\textsubscript{2} lattice during doping which absorb visible light. Therefore, it was concluded that band gap narrowing is not responsible for the visible light activity of doped TiO\textsubscript{2}.\textsuperscript{116} Despite the different ideologies regarding the mechanism of visible light activity of N doped TiO\textsubscript{2}, there seem to be a host of studies
supporting the idea of band gap narrowing proposed by Asahi et al.\textsuperscript{112,117,118} The formation of oxygen vacancies during doping is also an accepted ideology. Although there is a general consensus that N doping leads to visible light absorption of TiO\textsubscript{2}, debate exist about the nature of N doping within the TiO\textsubscript{2} lattice whether the nitrogen is interstitial or substitutional doped and which form of doping yield the best results.\textsuperscript{117,118}

Peng and co-workers prepared both substitutional and interstitial nitrogen doped TiO\textsubscript{2} by annealing P25 in NH\textsubscript{3} and by microwave method, respectively. X-ray photoelectron spectroscopy analysis revealed that the interstitial N is in a positive oxidation state ranging from hyponitrite species, to nitride and nitrate species. Most interestingly, a higher photocatalytic activity for phenol and MO was observed using interstitial N doped TiO\textsubscript{2}. This was explained in terms of the interstitial N states occupying higher positions in the TiO\textsubscript{2} band gap thereby favouring excitation of electrons by visible light from these states than from substitutional states (Figure 2.6).\textsuperscript{119} This explanation is based on experimental work and theoretical calculations (DFT calculations) by Valentin et al. who observed that there were two forms of N doping within the TiO\textsubscript{2} matrix: interstitial and substitutional doping. DFT calculations revealed that interstitial N states lie about 0.73 eV above the top of the valence band while substitutional N states lie about 0.14 eV above the top of the valence band (Figure 2.6).\textsuperscript{120}
The form and localization of the nitrogen atoms in the TiO$_2$ lattice depends largely on the experimental conditions and ingredients used during synthesis.Interstitial N doped TiO$_2$ is produced preferentially under relatively low temperatures (<500 °C) and in an oxygen rich environment which hinders the substitution of O$^{2-}$ for N in the TiO$_2$ lattice. Contrary, oxygen deficient conditions (reducing conditions) favour the preparation of substitutional N doped TiO$_2$.\textsuperscript{120-123} \textit{Zhao} and \textit{Liu} used the plane-wave ultrasoft pseudopotentials (PW-USP) methods based on DFT to investigate the mechanism of N doping in TiO$_2$.\textsuperscript{120} Theoretical calculations revealed that the most possible form of N doping was interstitial followed by substitutional N doping. Furthermore, it was shown that anatase TiO$_2$ doped with interstitial N can be easily fabricated and result in band gap narrowing. However, a combination of substitutional N doping and the presence of oxygen vacancies was the most effective way of improving the photocatalytic activity since it has both shallow acceptors and donors in the TiO$_2$ band gap. Finally, it was highlighted that there has to be an optimum nitrogen doping level that maintains a balance between attaining light absorption and retaining excellent photocatalytic properties.\textsuperscript{124}
2.8.2.2 Sulphur doping

Theoretical studies revealed that doping TiO$_2$ with sulphur results to a red shift in the absorption edge of TiO$_2$ in a similar manner to nitrogen doping. The red-shift in S doped TiO$_2$ was explained in terms of band gap narrowing emanating from the mixing of the S 3$p$ orbitals with the O 2$p$ orbitals.$^{112,125}$ Band gap values of 2.3 eV and 2.2 eV were theoretically calculated for S doped rutile and anatase TiO$_2$, respectively.$^{125}$ However, Asahi et al. argued that even though TiO$_2$ band gap narrowing could be achieved via S doping, the actual preparation of substitutional S doped TiO$_2$ would be difficult due to the large ionic radius of S$^{2-}$ (0.184 nm) compared to O$^{2-}$ (0.140 nm). This would require a large formation energy which may not be favourable.$^{112}$ However, several reports have emerged on the preparation and photocatalytic properties of substitutional S doped TiO$_2$.$^{126,127}$ However, in most cases S doped in TiO$_2$ exists as cationic sulphur (S$^{4+}$ or S$^{6+}$) which substitute Ti$^{4+}$ instead of O$^{2-}$ in the TiO$_2$ lattice and this is often favourable due to low energy requirements.$^{121,128}$

Wei and co-workers prepared N,S-TiO$_2$ from mixed aqueous solution of Ti(SO$_4$)$_2$ and thiourea using a hydrothermal method and XPS analysis of the photocatalyst revealed that sulphur existed in two states: cationic sulphur (S$^{6+}$) and anionic (S$^{2-}$). The presence of S$^{6+}$ was linked to SO$_4^{2-}$ ions adsorbed on the surface of TiO$_2$ while S$^{2-}$ was due to the existence of Ti-S bonds, suggesting the substitution of O$^{2-}$ for S$^{2-}$ in the TiO$_2$ lattice. Consequently, the size differences between the oxide and sulphide ion lead to lattice distortions upon incorporation of S$^{2-}$.$^{129}$ S-doped and sulphated nanosized TiO$_2$ was prepared via a low temperature solvothermal method using potassium persulphate as a sulphur source. The presence of S$^{4+}$ and S$^{6+}$ was reported from XPS corresponding to Ti-O-S bonds in TiO$_2$ lattice and surface bound SO$_4^{2-}$ ions, respectively. Improved photocatalytic activity of S-doped and sulphated TiO$_2$ was credited to the synergistic effect of S$^{4+}$ incorporated into the TiO$_2$ lattice and surface bound sulphate ions depicted in Figure 2.7.$^{130}$ It was proposed that the substitution of Ti$^{4+}$ for S$^{4+}$ creates an impurity level below the conduction band of TiO$_2$ enabling the excitation of electrons by visible light from the O 2$p$ level to the impurity level. These electrons are subsequently transferred
to the S$^{6+}$ states ($\text{SO}_4^{2-}$) on the surface of TiO$_2$ where they are trapped by oxygen to form the superoxide and hydroxyl radicals responsible for the degradation process.$^{130,131}$

![Figure 2.7: Synergistic effect between S-TiO$_2$ and sulphate ions$^{130}$](image)

As previously observed with N doping, the experimental conditions and starting materials determine the nature of S doping. Some methods and ingredients yield exclusively anionic sulphur, cationic sulphur or a mixture of cationic and anionic sulphur.$^{132}$

### 2.8.2.3 Doping TiO$_2$ with other non-metals

Theoretical studies on N, S and C doped TiO$_2$ highlighted that C doping is potentially the most plausible due to sufficient overlap between the O 2$p$ states and the C 2$p$ states near the valence band edge. It was concluded that C doping resulted in the largest red shift compared to N and S doping.$^{125}$ Experimental results have shown that incorporation of C into the TiO$_2$ lattice (Ti-C) results in a red shift and visible light photocatalytic activity of TiO$_2$.$^{133}$ Matos et al. prepared C-doped TiO$_2$ using a solvothermal method and the prepared photocatalyst displayed enhanced visible light response and photocatalytic activity compared to undoped TiO$_2$.$^{134}$ Similar experimental results have been reported in the literature.$^{135,136}$
Titania doped with phosphorous (P-TiO$_2$) has also been prepared and evaluated for its visible light photocatalytic activity. Incorporation of P into the TiO$_2$ lattice led to modification of the TiO$_2$ band gap and improved visible light absorption and photocatalytic activity of TiO$_2$.\textsuperscript{137,138} Doping boron into the TiO$_2$ framework has also yielded positive results in extending the photoresponse of TiO$_2$ into the visible light region and enhanced its visible light photocatalytic activity compared to undoped TiO$_2$.\textsuperscript{139} Titania doped with halogen ions such as I$^-\textsuperscript{140}$, F$^-\textsuperscript{141}$ and Cl$^-\textsuperscript{142}$ displayed improved optical and photocatalytic properties under visible light irradiation.

2.8.3 Metal ion doping

Transition metal, noble metal and rare earth metal ions are the most extensively exploited metal ions for modification of TiO$_2$ to extend its visible light response into the visible light region and improve charge separation. Incorporation of metal ions into the TiO$_2$ lattice structure induce new states within the band gap of TiO$_2$ making it possible to excite electrons by visible light from these new states into the conduction band of TiO$_2$. Visible light activity of metal ion doped TiO$_2$ may also originate from d-d transitions in transition metals or f-f transitions in the rare earth ions.$^{143,144}$ Alternatively, the newly formed states may facilitate electron trapping, leading to a prolonged life of the holes and improve formation of the superoxide and hydroxyl radicals responsible for pollutant degradation.$^{145,146}$ Electrons trapped by metal ions on the surface of TiO$_2$ are inhibited from recombining with the holes by the formation of a barrier known as the Schottky barrier at the TiO$_2$/metal ion interface (\textbf{Figure 2.8}). This barrier originates from the lower work function of TiO$_2$ relative to most metal ions.$^{13}$ This effectively leads to improved photocatalytic activity. However, the nature and extent to which metal ions influence the photocatalytic activity of TiO$_2$ may vary with different metal species and also depends on the experimental conditions.$^{147}$
Chapter 2: Literature review

Figure 2.8: Generalised schematic of metal ion doped TiO$_2$ ($M^{3+} =$ metal ion)

Noteworthy, the photocatalytic activity of doped TiO$_2$ is a complex function of the dopant concentration, energy level of the dopant within the TiO$_2$ lattice, the electronic configuration, the distribution of the dopants, electron donor concentration and the light intensity.\textsuperscript{148} Ideally, the concentration of the dopant has to be kept at an optimum level for best results. Beyond the optimum level, the dopants act as charge recombination centres as a result of the decrease in the average distance between trap sites with increasing concentration (number of dopants confined within a particle).\textsuperscript{149} At dopant concentrations below the optimum, the photocatalytic activity is lower, owing to insufficient charge separation due to fewer trap sites. In addition to modifying the optical and charge trapping properties of TiO$_2$, metal ion doping may also hinder or suppress the anatase to rutile phase transformation during calcination.\textsuperscript{150}

2.8.3.1 Rare earth metal ion doping

Rare earth metals also known as lanthanides or lanthanoids is a special group of metals consisting of 15 metals (from lanthanum 57 to Lutetium 71) but also include scandium and yttrium due to comparable chemical properties. The term “rare
earth” has nothing to do with these elements being rare (except promethium which is radioactive) or the elements being earth-like (forming refractive insoluble basic oxides) but it originates from their isolation from rare or uncommon minerals. Hence the term lanthanide which means lying hidden and came from lanthanum which was first discovered “hidden” in a cerium containing mineral.\textsuperscript{151}

Rare earth metals are characterised by their unique electronic configuration which consist of an incompletely filled $4f$ orbital and an empty $5d$ orbital enabling them to function as potential catalysts.\textsuperscript{152} The incompletely filled $4f$ orbital of rare earths is responsible for the unique complexing properties for Lewis bases such as organic acids, alcohols, amines, aldehydes and thiols. Consequently, incorporation of lanthanide ions into the TiO$_2$ framework aid in improving the catalyst-pollutant interaction by concentrating the organic pollutants onto the surface of the semiconductor.\textsuperscript{153} This is crucial during degradation of the organic pollutants since photocatalysis occurs on the surface of the semiconductor. Enhanced visible light photocatalytic activity for nitrite was observed upon doping TiO$_2$ with La$^{3+}$, Ce$^{3+}$, Er$^{3+}$, Pr$^{3+}$, Gd$^{3+}$, Nd$^{3+}$ and Sm$^{3+}$. The observed improvement was attributed to the contribution of the incorporated rare earth ions towards improving visible light response of TiO$_2$, adsorption of nitrite and the increase in the interfacial transfer rate.\textsuperscript{154}

Owing to the significantly larger ionic radii of rare earth ions compared to Ti$^{4+}$, they cannot replace Ti$^{4+}$ in the TiO$_2$ lattice instead the ions exist as rare earth oxides (RE$_2$O$_3$) bound on the surface of TiO$_2$ where they act as electron traps and facilitate charge separation.\textsuperscript{154,155} It has been reported that during preparation of lanthanide doped TiO$_2$, rare earth ions can bond with non-bridging oxygen ion at the surrounding of -Ti-O-Ti-network structure and facilitate electron scavenging.\textsuperscript{156} Xu and co-workers reported that Gd$^{3+}$-TiO$_2$ showed the best photocatalytic properties than the other rare earth doped titania samples and this observation was explained in terms of the half-filled ($4f^7$) electronic configuration of Gd$^{3+}$. This configuration is very stable and trapping electrons interrupt its stability as a result electrons are easily lost to oxygen on the surface of TiO$_2$ leading to the formation of the radical species. Subsequently, Gd$^{3+}$ returns to its stable half-filled electronic
configuration. Similar results have been reported for other metal ions with half-filled electronic configurations (Fe$^{3+}$, Ru$^{3+}$ and Os$^{3+}$) and their ability to trap and detraps electrons is an important factor in photocatalysis.

Titania doped with La$^{3+}$, Ce$^{3+}$, Ce$^{4+}$, Eu$^{3+}$, Gd$^{3+}$ and Sm$^{3+}$ showed red shift in their absorption edge and this was ascribed to electronic transitions between the lanthanide ions and the conduction or valence band of TiO$_2$. Moreover, visible light absorption due to f-f electronic transitions was observed in Nd$^{3+}$, Pr$^{3+}$ and Dy$^{3+}$ doped TiO$_2$. Band gap narrowing has been reported for Nd and Yb doped TiO$_2$ and was attributed to presence of new 4f states positioned within the TiO$_2$ band gap (Figure 2.9). These states occupy positions close to the lower edge of the conduction band forming a new lowest unoccupied molecular orbital. Consequently, electrons are excited by visible light from the valence band into these new states instead of the conduction band. In addition to controlling the optical, adsorption and charge carrier separation properties, rare earth doping may influence the grain size of TiO$_2$ and inhibit the anatase to rutile transformation during calcination.

![Figure 2.9: Modification of TiO$_2$ band gap by Nd$^{3+}$ doping](image)

**2.8.3.2 Titania doped with other metal ions**

Titania doped with metal ions such as the transition metals, alkaline earth metals and noble metals have been prepared by various methods and their photocatalytic
properties studied. Photoreactivities of titania doped with 21 metal ions was studied by Choi and co-workers and reported contrasting effects from some sets of different metal ions. Doping TiO$_2$ with Fe$^{3+}$, Mo$^{5+}$, Ru$^{3+}$, Os$^{3+}$, V$^{4+}$ and Rh$^{3+}$ significantly improved the oxidation and reduction of CHCl$_3$ and CCl$_4$, respectively, while doping with Co$^{3+}$ and Al$^{3+}$ suppressed the photocatalytic activity of TiO$_2$. There was a generally insignificant effect of doping TiO$_2$ with Li$^+$, Mg$^{2+}$, Zn$^{2+}$, Ga$^{3+}$, Zr$^{4+}$, Nb$^{5+}$, Sn$^{4+}$, Sb$^{5+}$ and Ta$^{5+}$ and this was ascribed to the closed-shell electronic configuration which is very stable and makes electron trapping unfavourable. Mn$^{3+}$ doped titania displayed low photocatalytic activity despite Mn$^{3+}$ having the ability to trap both hole and electron which is expected to enhance the activity of TiO$_2$. This observation was explained in terms of the poor electron detrapping from Mn$^{2+}$ due to the smaller energy driving force between Mn$^{2+}$ and Mn$^{3+}$. Devi et al. reported higher photocatalytic activity of Mn$^{2+}$ doped TiO$_2$ towards degradation of aniline blue compared to Ni$^{2+}$ and Zn$^{2+}$ doped titania. However, the higher activity of Mn$^{2+}$ doped TiO$_2$ was attributed to the synergy between rutile and anatase phases observed in this sample and not in the Ni$^{2+}$ and Zn$^{2+}$ doped TiO$_2$ samples. This reason is based on the potential influence of Mn$^{2+}$ in phase composition of TiO$_2$ not in its electronic scavenging properties.

In a recent study by Inturi and co-workers TiO$_2$ doped with V$^{4+}$, Cr$^{3+}$, Fe$^{3+}$, Mn$^{3+}$, Mo$^{5+}$, Ni$^{2+}$, Cu$^{2+}$, V$^{3+}$, Ce$^{3+}$ and Zr$^{4+}$ was fabricated using a one-step liquid flame aerosol synthesis technique and probed its visible light photocatalytic degradation efficiency for gaseous acetonitrile. Cr$^{3+}$, Fe$^{3+}$ and V$^{4+}$ doped TiO$_2$ showed significantly improved photocatalytic activity with Cr doped titania displaying the highest activity. As previously observed by Choi et al. Mn$^{3+}$ doped TiO$_2$ was inactive and this was linked to the low energy driving force for electrons to detraps from Mn$^{2+}$. Titania doped with Ca$^{2+}$ and Sr$^{2+}$ showed improved photocatalytic activity compared to P25 and undoped titania, owing to improved separation of charge carriers and large surface areas.

Similarly, noble metals such as Pt, Pd, Ag and Au have been incorporated in TiO$_2$ for photocatalytic applications. Improved photoactivity of the noble metal doped titania is attributed to the combined contribution of improved charge separation
and visible light absorption.\textsuperscript{163,166,167} Recent interest in metal ion doped titania has been on the synthesis and photocatalytic properties of self-doped titania (Ti\textsuperscript{3+}-TiO\textsubscript{2}). The presence of Ti\textsuperscript{3+} within the TiO\textsubscript{2} lattice leads to enhanced visible light absorption, charge separation and photocatalytic activity of TiO\textsubscript{2}. The extension of TiO\textsubscript{2} photoresponse into the visible light region by Ti\textsuperscript{3+} doping is ascribed to the formation of new states below the conduction band of TiO\textsubscript{2} which allows for visible light excitation of electrons from the valence band to these newly inserted states.\textsuperscript{168,169}

Despite the numerous successes achieved by modifying titania with either metal ions or non-metal ions, there are still some challenges that need to be addressed regarding the fabrication of doped titania. Some of the underlying challenges in metal and no-metal doping are outlined in Figure 2.10.

![Figure 2.10: Challenges of metal and non-metal ion doped TiO\textsubscript{2}.\textsuperscript{61}]

2.8.4 Co- and multi-doping TiO\textsubscript{2}

Co-doping titania entails the simultaneous incorporation of two heteroatoms into the TiO\textsubscript{2} lattice to tune its optical and photocatalytic properties, surface area and crystal structure. It is advancement from mono-doping where only one heteroatom is incorporated into the TiO\textsubscript{2} framework. Co-doping TiO\textsubscript{2} may be achieved by
introducing two non-metals\textsuperscript{170}, two metals\textsuperscript{171} or a metal and a non-metal\textsuperscript{172} and the mechanism of action is based on synergy between the two dopants and TiO\textsubscript{2}\textsuperscript{144,173}. Co-doping TiO\textsubscript{2} allows for tailoring of materials with the combined properties of the two dopants such as good visible light absorption (band gap narrowing) and efficient electron scavenging resulting in improved photocatalytic performance\textsuperscript{173}.

Titania co-doped with nitrogen and sulphur (N,S-TiO\textsubscript{2}) has been prepared by various methods and its photocatalytic properties studied. Incorporation of N and S improved its photocatalytic performance under visible light irradiation compared to N-TiO\textsubscript{2}, S-TiO\textsubscript{2} and P25. This improvement was credited to the formation of sub-band gap states by N and S states in the TiO\textsubscript{2} band gap (band gap narrowing) allowing for visible light excitation of electrons from these new states into the conduction band of TiO\textsubscript{2} (Figure 2.11). Simultaneous incorporation of the two dopants provided more routes through which the hydroxyl and superoxide radicals can be generated leading to enhanced photocatalytic activity. Moreover, co-doping TiO\textsubscript{2} with N and S has been found suppress TiO\textsubscript{2} grain size, improve surface area, and enhance the surface acidity of the photocatalyst\textsuperscript{129,131,140,174}. Hojamberdiev \textit{et al.} prepared N-F co-doped TiO\textsubscript{2} by thermal decomposition of ammonium oxofluorotitanate and the co-doped titania showed good photocatalytic activity for MO degradation compared to P25. This was explained in terms of the combined contribution of strong absorption in the visible light region, good crystallinity and porous structure\textsuperscript{175}. 
Figure 2.11: Schematic showing synergy in a typical N,S-TiO$_2$

Strong visible light absorption, band gap narrowing and enhanced photoactivity were reported as key modifications induced on titania by the combined contribution of N and C co-doping.$^{176}$ Similarly, codoping titania with other double non-metal combinations such as I-F$^{170}$, B-F$^{177}$, N-P$^{178}$, N-I$^{179}$ and C-F$^{180}$ displayed the synergistic effect of the dopants towards improvement of the overall photocatalytic activity of TiO$_2$.

Gadolinium and nitrogen co-doped TiO$_2$ (Gd,N-TiO$_2$) nanotubes were prepared by a hydrothermal method and ion exchange technique and investigated for visible light photocatalytic degradation of rhodamine B (RB). Higher photocatalytic degradation efficiency was observed and attributed to co-doping which inhibited the particle growth resulting to a large surface area of the photocatalyst. Moreover, co-doping improved charge separation, visible light absorption and crystallinity of the photocatalyst.$^{144}$ Similarly, Wu et al. prepared praseodymium and nitrogen co-doped TiO$_2$ (Pr,N-TiO$_2$) via sol-gel and microwave methods for the photocatalytic degradation of MB. Both Pr and N were incorporated into the TiO$_2$ lattice and restrained TiO$_2$ grain size growth, extended visible light response into the visible region and inhibited recombination of the charge carriers, leading to higher photocatalytic activity.$^{146}$ Europium and nitrogen co-doped titania
(Eu,N-TiO$_2$)$_{172}$, Ce,N-TiO$_2$$_{181}$, La,B-TiO$_2$$_{149}$ and Cr,S-TiO$_2$$_{128}$ prepared by different methods displayed improved visible light response, charge separation and photoactivity, owing to the cooperative effect of the co-dopants. Double metal doped titania such as Gd/La-TiO$_2$$^{171}$, Nd/Er, Nd/Eu, Eu/Ho-TiO$_2$$^{182}$, La,Eu-TiO$_2$$^{183}$ and Li-Y-TiO$_2$$^{184}$ displayed enhanced photocatalytic properties for degradation of various organic compounds compared to mono-doped TiO$_2$. This was attributed to efficient visible light harnessing and charge separation.

The quest to find an efficient visible light active photocatalyst has led to the modification of titania with more than two heteroatoms resulting in multi-doped titania. Carbon, nitrogen and sulphur tridoped titania (C,N,S-TiO$_2$) hollow spheres were synthesised using carbon spheres as templates and C,N,S-tridoped TiO$_2$ nanoparticles as building blocks. The prepared tri-doped hollow spheres showed strong absorption of light in the visible region owing to the narrow band gap. Band gap narrowing resulted from the mixing of the TiO$_2$ O 2$p$ and the C 2$p$, N 2$p$ and S 3$p$ states. Moreover, sufficient charge separation was realised upon tri-doping TiO$_2$ which led to higher photocatalytic activity over P25 and undoped TiO$_2$.$_{127}$ Similar results were reported for the degradation of MO, RB, Orange G and Reactive Red X using microwave synthesised N-B-F-tri-doped mesoporous titania under visible light irradiation.$^{185}$ Charanpahari et al prepared Gd,N,S-TiO$_2$$_{186}$ and Ce,N,S-TiO$_2$$_{187}$ and studied their photocatalytic properties towards degradation of MO under visible light irradiation. In both experiments, the tri-doped titania showed higher photocatalytic activity than P25, single and co-doped titania which was attributed to improved visible light absorption, narrow band gap, efficient charge separation and efficient generation of the hydroxyl and superoxide radicals responsible for dye degradation. The metal ions facilitate good charge separation as well as contributing towards visible light absorption while the non-metal species ensure band gap narrowing and good visible light absorption.$^{186,187}$ Umare and co-workers reported similar results for visible light degradation of MO using Ga,N,S-TiO$_2$.$_{188}$ The synergistic effect in multi-doped titania is illustrated in Figure 2.12.
The interesting results obtained from multi-doping have led to a sudden interest in exploring various dopants in order to achieve the desired results. Multi-doped titania based photocatalysts such as Sm,N,P-TiO$_2^{189}$, Gd,C,N,P-TiO$_2^{190}$, Pr,N,P-TiO$_2^{191}$, Yb,N,P-TiO$_2^{192}$, Bi,C,N-TiO$_2^{193}$ and Ta,N,F-TiO$_2^{194}$ have been exploited for the photocatalytic properties under visible light irradiation. There is a unifying conclusion that multi-doping improves the photocatalytic activity of TiO$_2$ and the improvement is based on the combined contribution of the multi-dopants.

### 2.8.5 Coupling titania with other semiconductors

Fabrication of heterojunctions (binary semiconductors) by combining TiO$_2$ with narrow band gap semiconductors is another attractive route towards extending TiO$_2$ photoresponse into the visible light region in a similar mechanism as sensitisation. The binary semiconductor photocatalyst exploit the efficient photogenerated charge transfer from the narrow band gap semiconductor (sensitiser) to the TiO$_2$ substrate, leading to higher photoactivity. The prepared heterojunction can be controlled in terms of morphology and grain size to yield materials with high surface area and good photoresponse. However, sufficient
contact between the coupled semiconductors is mandatory since their interface is the channel which transfers the charge carriers from the sensitiser to TiO$_2$.\textsuperscript{195,196}

Cadmium sulphide/titania (CdS/TiO$_2$) nanocomposites were prepared by a simple wet chemical method and investigated for the degradation of RB under visible light irradiation. A significant enhancement in the visible light activity was observed and nanocomposites of CdS:TiO$_2$ ratio of 4:1 showed the highest photocatalytic activity. Under visible light irradiation, CdS act as a sensitiser, absorbing visible light and injecting electrons into the conduction band of TiO$_2$. This prolonged the life of the photogenerated charge carriers and maximise the formation of the hydroxyl and superoxide radicals responsible for RB degradation.\textsuperscript{197} Similarly, enhanced photocatalytic degradation of 4-chlorophenol and RB over mesoporous CdS/TiO$_2$ was reported by Jiang and co-workers.\textsuperscript{198} Li et al. employed sol-gel method to prepare WO$_x$-TiO$_2$ composite photocatalyst for visible light photocatalytic degradation of MB. Introduction of WO$_x$ at a doping level of 3\% significantly improved the photocatalytic performance of TiO$_2$. This was linked to the role of WO$_x$ in shifting the photoresponse of TiO$_2$ into the visible light region and sufficient charge carrier separation by coupling the two semiconductors.\textsuperscript{199} Comparably, improved photocatalytic removal of NO was achieved by coupling TiO$_2$ and WO$_3$ via a co-precipitation method.\textsuperscript{200} Fe$_2$O$_3$/TiO$_2$ nanocomposites have been prepared by different methods and displayed good photocatalytic properties which are attributed to improved optical response and charge separation. Furthermore, coupling TiO$_2$ and Fe$_2$O$_3$ allows for easy separation (by a magnet) of the photocatalyst from the treated solutions due to the magnetic nature of Fe$_2$O$_3$.\textsuperscript{201}

\textbf{2.8.5.1 Graphitic carbon nitride/titania heterojunctions}

The recent discovery of graphitic carbon nitride (g-C$_3$N$_4$), a polymeric, metal-free semiconductor which can absorb visible light better than most metal oxide semiconductors sparked huge interests in photocatalytic applications of this material.\textsuperscript{202} The polymeric nature of g-C$_3$N$_4$ arise from heptazine units which are fused together to form a graphene-like structure (Figure 2.13). The heptazine
structure and high degree of condensation make g-C₃N₄ possess good chemical and thermal stability, visible light absorption due to moderate band gap (2.7 eV) and unique electronic structure.²⁰³,²⁰⁴ g-C₃N₄ can be prepared in large quantities from abundant, low-cost, nitrogen-rich precursors such as urea, melamine, cyanoguanidine, cyanimide, etc.²⁰⁵ Photocatalytic water splitting for generation of hydrogen and decontamination of the environment from organic pollutants are some of the many sectors exploring the possible use of g-C₃N₄. However, the small surface area, high recombination rate of photogenerated charge carriers and the low quantum efficiency of g-C₃N₄ hinder its practical exploitation.²⁰⁶

**Figure 2.13: Structure of g-C₃N₄²⁰⁷**

Coupling g-C₃N₄ and TiO₂ has the potential to yield useful materials with interesting optical and photocatalytic properties. Carbon nitride polymer sensitised TiO₂ arrays were prepared via an electrodeposition method and their photocatalytic properties probed for the degradation of acid orange II. The composite photocatalyst displayed higher visible light photoelectrochemical and photocatalytic activity. This was ascribed to the incorporation of g-C₃N₄ which allowed for multiple excitations from the absorption of a single photon. Furthermore, the crystalline nature of TiO₂ nanotubes allowed for sufficient interaction with g-C₃N₄ which led to efficient transfer of the photogenerated
electrons from g-C\textsubscript{3}N\textsubscript{4} to TiO\textsubscript{2} and this improved charge separation and photocatalytic performance.\textsuperscript{208} Catalyst films of g-C\textsubscript{3}N\textsubscript{4}/TiO\textsubscript{2} were prepared by directly heating a mixture of melamine and presynthesised TiO\textsubscript{2}. The prepared catalyst films with varying loadings of g-C\textsubscript{3}N\textsubscript{4} were employed for the visible light photocatalytic degradation of MB, with the 50\% g-C\textsubscript{3}N\textsubscript{4}/TiO\textsubscript{2} sample showing the highest activity. It was concluded that increased visible light absorption and retarded charge carrier's recombination were the key factors contributing towards the enhanced performance. Good contact at the g-C\textsubscript{3}N\textsubscript{4}/TiO\textsubscript{2} interface allowed for electron transfer from g-C\textsubscript{3}N\textsubscript{4} to TiO\textsubscript{2}. Furthermore, according to band potential calculations, only the excited electrons not holes took part in the formation of the oxidising species and the sensitisation and charge separation mechanism was proposed to proceed as illustrated in Figure 2.14.\textsuperscript{209}

\begin{figure}[h]
\centering
\includegraphics[width=0.8\textwidth]{image.png}
\caption{Proposed mechanism of excitation and charge separation in g-C\textsubscript{3}N\textsubscript{4}/TiO\textsubscript{2} heterojunction under visible light irradiation.\textsuperscript{209}}
\end{figure}

\textit{Gu and co-workers} synthesised g-C\textsubscript{3}N\textsubscript{4}-hybridized TiO\textsubscript{2} nanosheets with reactive (001) facets via a solvent evaporation method for UV and visible light photocatalytic degradation of MB, RB, acid orange (AO) and 2,4-dichlorophenol (2,4-DCP). Enhanced photoactivity was realised both under UV and visible light irradiation which was attributed to synergy between g-C\textsubscript{3}N\textsubscript{4} and TiO\textsubscript{2} resulting to good light absorption and charge separation. It was proposed that under UV light irradiation, photogenerated electrons g-C\textsubscript{3}N\textsubscript{4} were transferred to the conduction band of TiO\textsubscript{2} and the hole in the valence band of TiO\textsubscript{2} could migrate to the surface
of g-C$_3$N$_4$ through the interfacial interaction as a result of their well-matched energy levels. This prolongs the life of the electron/hole pairs (Figure 2.15a). Under visible light, g-C$_3$N$_4$ could absorb photons and generate the excited electron and hole in the valence band. The electron migrated through the π-conjugated systems of g-C$_3$N$_4$ and transfer to the intimately bound TiO$_2$ resulting in sufficient charge separation (Figure 2.15b).

Figure 2.15: Proposed mechanism for synergy between g-C$_3$N$_4$ and TiO$_2$ under (a) UV light irradiation and (b) visible light irradiation.
Other authors have reported on the synergistic effect from g-C$_3$N$_4$ coupled with TiO$_2$ towards improvement of visible light absorption, separation of charge carriers, efficient generation of radical species and the overall improved photocatalytic activity.$^{196,211,212}$ However, there is still a lot of ground to cover in terms of tailoring the right materials with the desired properties and photocatalytic efficiency in order to enable practical utilisation of solar light as a source of energy.

### 2.8.6 Titania hybridised with carbon nanomaterials

Graphite and diamond are the most well-known allotropes of carbon and have been in use for years. However, there are other $sp^2$ hybridised allotropes of carbon that have in recent years attracted tremendous research interest for their potential applications. These include graphene, carbon nanotubes and fullerenes.$^{213}$ Graphene is a single, one atom thick layer of $sp^2$ hybridised carbon atoms arranged in a flat honeycomb structure (Figure 2.16). It is the elemental structure of graphite.$^{213,214}$ Fullerenes on the other hand can simply be defined as $sp^2$ hybridised carbon atoms arranged in a spherical, closed-cage structure.$^{214}$

![Figure 2.16: Ball and stick model of (a) graphene$^{215}$ and (b) fullerene$^{216}$](image)

Carbon nanotubes (CNTs) can be viewed as either one or more graphene sheets rolled up to form a tubular structure with diameters less than 100 nm and large
length to diameter ratios.\textsuperscript{217} One graphene sheet may be rolled up to form a single walled carbon nanotube (SWCNT, Figure 2.17a and 2.17b), two graphene sheets rolled up for a double walled carbon nanotube (DWCNT, Figure 2.17a and 2.17c) or three or more graphene sheets concentrically stacked to form a multiwalled carbon nanotube (MWCNT, Figure 2.17a and 2.17d).\textsuperscript{214,218}

![Figure 2.17: Ball and stick models of SWCNT, DWCNT, MWCNT and TEM images of (b) SWCNT\textsuperscript{219}, (c) DWCNT\textsuperscript{220} and (d) MWCNTs](image)

Carbon nanotubes possess a unique set of interesting properties such as ultra-high Young’s modulus and tensile strength, thermal and chemical stability, high surface area, good adsorption properties for inorganics and organics, good electrical conductivity and ultra-light nature.\textsuperscript{218,221,222} Since their discovery, CNTs have been prepared by several methods such as chemical vapour deposition (CVD, arc discharge, laser ablation, molten salt, plasma-enhanced chemical
vapour deposition (PECVD), thermal chemical vapour deposition, vapour phase growth, electrochemical synthesis, use of supercritical fluids, solvothermal methods, etc.\textsuperscript{214} Carbon nanotubes have attracted interests from various scientific fields such as drug delivery, material science, electronics and devices, sensors, adsorption of pollutants, conductive films, hydrogen storage, photocatalysis, etc.\textsuperscript{223,224}

In photocatalytic applications for organic pollution remediation CNTs hybridised with titania (CNT-TiO\textsubscript{2}) showed significant improvement in activity both under visible and UV light irradiation. This improvement was explained in terms of the collective contribution of TiO\textsubscript{2} and CNTs.\textsuperscript{65,225} CNTs surface modification with functional groups such as carboxylic, carbonyl and hydroxyl groups is often necessary to improve their chemical properties and dispersibility in various solvents. This ensures good interaction with the TiO\textsubscript{2} nanoparticles during formation of the composite photocatalyst.\textsuperscript{224} CNTs incorporated within the TiO\textsubscript{2} matrix act as supports and dispersing agents, minimising aggregation of TiO\textsubscript{2} nanoparticles which would otherwise reduce the surface area of TiO\textsubscript{2} and lower its photocatalytic activity.\textsuperscript{226,227} An increase in the surface area of the CNT/TiO\textsubscript{2} nanocomposite ensures sufficient active sites for the degradation of the organic pollutants. In addition, incorporation of CNTs within TiO\textsubscript{2} affects the grain size and morphology of TiO\textsubscript{2}.\textsuperscript{228} However, there is an optimum dose of CNTs that allows for improved size control as well as photocatalytic activity beyond which the CNTs affect light absorption by TiO\textsubscript{2} and subsequently lower the photocatalytic activity.\textsuperscript{225,229}

Another contribution of CNTs towards the improved activity of CNT-TiO\textsubscript{2} nanocomposites emanates from their good adsorption capacity for organic pollutants. Prior to degradation, the pollutant has to be adsorbed on the surface of the photocatalyst, CNTs aid in concentrating the organic pollutants onto the surface of the photocatalyst.\textsuperscript{230} In addition to adsorption of pollutant molecules, oxygen is also adsorbed on the surface of CNTs and this oxygen is trapped by the photogenerated electrons to form the superoxide radicals which are responsible for pollutant degradation.\textsuperscript{231} Under visible light irradiation, CNTs act as a visible
light sensitisers, absorbing visible light and injecting electrons into the conduction band of TiO$_2$. These electrons are trapped by adsorbed oxygen to form the radical species. Subsequently, electrons can migrate from the valence band of TiO$_2$ into the positively charged CNT skeleton where they can be trapped by adsorbed oxygen while the holes created in the valence band may be trapped by water or hydroxide ions to form the hydroxyl radicals.$^{232,233}$ Figure 2.18 shows the visible light sensitisation role of CNTs.

![Diagram](image.png)

Figure 2.18: Visible light sensitisation of TiO$_2$ by CNTs

Another important role of CNTs relates to separation and transportation of the photogenerated charge carriers. CNTs function as electron sinks, trapping photogenerated electrons from the conduction band of TiO$_2$ (Figure 2.19). This prolongs the life of the electron/hole pairs ensuring sufficient time for the formation of the radical species responsible for the degradation of the organic pollutants.$^{226,234}$ The good electronic conductivity of CNTs makes them ideal for charge transfer and transportation in order to minimise charge accumulation and recombination. At room temperature, CNTs can potentially conduct electrons with almost no resistance, a phenomenon known as the Ballistic transport.$^{230}$
A number of reports have highlighted that CNTs may also function as a source of carbon doping in TiO$_2$. Formation of Ti-C and Ti-O-C bonds at the interface of CNT/TiO$_2$ nanocomposites had been observed in composite samples annealed at temperatures from around 350 °C and upwards. Formation of these bonds not only improve visible light absorption of the composite photocatalyst but also facilitate efficient electron movement between TiO$_2$ and CNTs. A strong and intimate contact between CNTs and TiO$_2$ is crucial in the quest to exploit the collaborative effect of the two materials during photocatalysis.

Yao and co-workers prepared photoreactive anataseTiO$_2$/carbon nanotube (SWCNTs and MWCNTs) composites via a simple hydration and dehydration method. Higher photocatalytic degradation of phenol was recorded when using the composites compared to when using P25 and pure titania. However, the authors not clearly account for the enhancement of the photocatalytic activity of the CNT/TiO$_2$ composite prepared by simple hydration and dehydration. Enhanced photocatalytic degradation of 2,6-dinitro-p-cresol (DNPC) over MWCNT/TiO$_2$ composite photocatalyst prepared by a sol-gel method was observed under visible light irradiation. This observation was attributed to the MWCNTs acting as visible light sensitisers. TiO$_2$/SWCNT nanocomposites prepared via a solvothermal
method showed improved degradation performance for RB and nitrobenzene (NB) and this was related to the large surface area, smaller crystalline size and ester bonds formed at the interface of TiO$_2$ and SWCNTs which facilitated good charge separation.$^{240}$ Hybrid nanostructures of MWCNT/TiO$_2$ were prepared by sol-gel and solvothermal method. The hybrid nanostructures showed good photocatalytic activity for MB degradation with the solvothermally prepared hybrid containing 20% MWCNTs showing the highest activity. Formation of Ti-C bonds at the TiO$_2$/MWCNT interface which led to improved optical and photocatalytic activity was highlighted as the key factor in the improved performance of the hybrids.$^{241}$

Kuvarega and co-workers employed a modified sol-gel method to decorate MWCNTs with nitrogen, palladium codoped titania (MWCNT/N,Pd codoped TiO$_2$) and the resultant nanocomposites were investigated for degradation of eosin yellow (EY) under simulated solar light irradiation. The nanocomposites containing 0.5% MWCNTs showed the highest photoactivity and the synergy between MWCNTs, Pd and N-TiO$_2$ was cited to explain the improvement.$^{242}$ Ma et al. recently reported on the photocatalytic properties of CNT/Fe-Ni/TiO$_2$ nanocomposites prepared by an in situ fluidized bed chemical vapour deposition (FBCVD) method. The Sample prepared at 500 °C displayed the highest photocatalytic activity for MB degradation both under UV and visible light irradiation. This was ascribed to the co-operative effect of the various components of the nanocomposites. CNTs and Ni were highlighted as responsible for charge separation and transfer and the CNTs further act as adsorbents for MB. The Fe ions induced mid-band gap states within the TiO$_2$ band gap which led to absorption in the visible light region.$^{243}$

Graphene is another carbon nanomaterial that has attracted huge interests from various scientific fields such as memory devices, energy generation and storage, solar cells, polarizers, photovoltaic devices, adsorption of organic and inorganic pollutants, photocatalysis, transistors, etc.$^{244,245}$ The wide interest in graphene stems from its unique and fascinating properties such as massless fermions, ballistic electronic transport and ultrahigh electron mobility (200 000 cm$^2$V$^{-1}$s$^{-1}$),
flexible structure, large surface area (2630 m\(^2\)/g), high transparency (optical transmittance is 97.7\%) and high thermal conductivity (~5000 Wm\(^{-1}\)K\(^{-1}\)).\(^{246,247}\)

Graphene or reduced graphene oxide (rGO) can be obtained in varying yields and purities using methods such as mechanical exfoliation of graphite, CVD, solvent exfoliation of graphite, pyrolysis, Hummers method, etc.\(^{248,249}\) In methods where graphene oxide (GO) is formed it is then subjected to reductive conditions to yield rGO. Composite photocatalysts obtained by combining graphene and TiO\(_2\) showed improved physical, optical and photocatalytic properties.\(^{250}\) Like CNTs, graphene incorporated within the TiO\(_2\) matrix had been found to act as a visible light sensitisier, induce formation of Ti-C and Ti-O-C at the graphene/TiO\(_2\) interface, improve charge separation and transportation and improve the surface area of the composite by minimising the aggregation of TiO\(_2\) nanoparticles.\(^{251–253}\)

Figure 2.20 shows the proposed interaction and collaborative effect between rGO and TiO\(_2\) for the degradation of organics under UV light irradiation.

![Proposed co-operative effect between rGO and TiO\(_2\) for phenol degradation under UV light irradiation.](image)

Figure 2.20: Proposed co-operative effect between rGO and TiO\(_2\) for phenol degradation under UV light irradiation.\(^{254}\)

Titania anchored on acid treated graphene oxide was prepared and investigated for the degradation of MB under UV and visible light irradiation. It was highlighted that the full and intimate coverage of GO by TiO\(_2\) was beneficial during
photocatalysis due to the presence of Ti-C and Ti-O-C bonds at the GO/TiO$_2$ interface. This enhanced visible light absorption and charge separation and transportation.$^{252}$ La/TiO$_2$-graphene nanocomposites fabricated by a two-step hydrothermal method were tested for the visible light photocatalytic degradation of MB. Improved photocatalytic efficiency was observed and attributed to synergy between graphene and La/TiO$_2$ resulting to improved photoresponse of TiO$_2$, efficient charge separation and improved interaction of the photocatalyst with MB due to π-π interaction of graphene.$^{255}$ Similar results were reported by Wang and co-workers for the degradation of MB on rGO/TiO$_2$ nanocomposites obtained via a dye-sensitisation-induced visible light reduction mechanism.$^{256}$

Huang et al. used a solvothermal method to prepare TiO$_2$/graphene nanocomposites with a chemically bonded (Ti-C) interface and observed a higher photocatalytic activity from the nanocomposites compared to pure titania, P25 and a mechanical mixture of TiO$_2$ and graphene, for degradation of formaldehyde in air. This observation highlighted the significance of strong interaction between graphene and TiO$_2$.$^{257}$ Likewise, Liang et al. recently demonstrated and supported the ideology that a strong and intimate interface between TiO$_2$ and rGO plays a key role in enhancing the photoactivity of the nanocomposite.$^{258}$ Furthermore, theoretical studies support the experimental observations about formation of a strong interface between TiO$_2$ and graphene and its role in charge separation and transportation.$^{259,260}$ Other carbon nanomaterials such as activated carbon and fullerenes also showed positive effects on the photocatalytic performance of titania for degradation of various organic pollutants.$^{261,262}$

2.9 Chapter summary

The global environmental and health challenges posed by pollution and the contribution of the textile industry towards environmental pollution are have been highlighted in this review. Progress has been made to design and fabricate various treatment tools for dye pollution mitigation but there has not been absolute success in this regard. Photocatalysis on nanotitania has proved to be an attractive prospect but its inability to utilise the solar spectrum and poor separation
of the photogenerated charge careers remain unresolved. Several strategies for modifying titania have been reviewed but the synthesis of a titania based semiconductor photocatalysis with good visible light absorption, charge separation and high photocatalytic activity and efficiency, remain elusive. Non-metal doping improves visible light absorption but not much improvement in terms charge separation and the overall photocatalytic activity. Similarly, metal ion doping may influence charge separation but has little influence on the overall photocatalytic efficiency. Alternative approaches such as co-doping, coupling titania with small band gap semiconductors and hybridising titania with carbon nanomaterials have all been extensively studied and promising results have been reported. However, more work needs to be done to develop efficient visible light photocatalytic active materials in the laboratory with the potential to be exploited at industrial level.

It is evident from the literature perused that there has not been any studies on the preparation and visible light photocatalytic activity of gadolinium oxide nanoparticles supported on MWCNTs and hybridised with titania. Moreover, the incorporation of various carbon nanomaterials into nitrogen, sulphur and rare earth doped titania matrix has not been exploited. These materials show the potential visible light absorption and good photocatalytic activity. The hybridisation of Gd\(^{3+}\) doped graphitic carbon nitride with MWCNT/TiO\(_2\) has been attempted and evaluated for the visible light photocatalytic degradation of dye solution for the first time in this work.
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Chapter 2: Literature review


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CHAPTER 3
EXPERIMENTAL METHODOLOGY

3.1 Introduction

This chapter gives a detailed account of the materials, photocatalyst synthesis methods and characterisation tools utilised in this study. The photocatalytic evaluation procedure for the prepared photocatalysts is also discussed in this chapter.

3.2 Reagents and Materials

Most of the reagents and materials used were of analytical reagent grade, sourced from Sigma Aldrich, South Africa (unless specified otherwise) and were used as received. The following materials and reagents were utilised in this study: Multiwalled carbon nanotubes (purity > 95.0%), titanium (IV) oxide nanopowder, mixture of rutile and anatase (purity > 99.5%, particle size <100 nm), citric acid (99.0%), methylene blue (95.0%), titanium (IV) butoxide (97.0%), butanol (99.4%), formic acid (99.9%), nitric acid (70.0%), thiourea (>99.0%), gadolinium nitrate hexahydrate (99.99%), neodymium nitrate hexahydrate (99.99%), europium nitrate hydrate (99.9%), acid blue 74 (85%), graphite flakes (+100 mesh (>75%)), KMnO₄ (>99.0%), Vitamin C, H₂SO₄ (98.0%), phosphoric acid solution (85% in water (v/v)), hydrogen peroxide solution (30% in water (v/v)), ammonia solution (25%), eriochrome black T (55.0%), single walled carbon nanotubes (purity >90.0%), cyanoguanidine (99.0%), terephthalic acid (98.0%) and trypan blue (60.0%).

3.3 Preparation of the photocatalysts

3.3.1 Decoration of oxidised MWCNTs with Gd nanoparticles

MWCNTs (2.0 g) were refluxed in nitric acid for 16 hrs to introduce carboxylic and hydroxyl groups on their surface and improve their chemical properties. The
MWCNTs/acid mixture was then diluted with deionised water before being filtered through a membrane filter (PTFE, 0.45 μm). The residue was washed with deionised water several times until the pH of the filtrate was around 7. It was then dried in an oven at 80 °C for 12 hrs. A similar procedure was used for oxidation of SWCNTs except that the SWCNT/acid mixture was refluxed for 6 hrs instead of 16 hrs as was the case with MWCNTs.

Decoration of MWCNTs with gadolinium oxide nanoparticles (Equation 3.1) was adapted from the literature\(^2\) and modified to suit our experimental goal. Oxidised MWCNTs (0.5 g) was sonicated in deionised water (50 mL), for 30 mins to form a uniform suspension. Gadolinium nitrate hexahydrate (0.19 g, 4.21 x 10\(^{-4}\) mol) was mixed with citric acid in a 1:1 mole ratio and dissolved in distilled water (50 mL) with stirring in a beaker. This mass represented 3% Gd\(^{3+}\) (m/m) relative to the oxidised MWCNTs. The solution was heated to boiling while adjusting the pH to around 8 or 9 using ammonia solution (25%). This was followed by addition of the MWCNT suspension. Stirring and heating was continued until the solvent was near complete evaporation, then the sample was dried in an oven overnight at 80 °C. The dried sample was transferred into a quartz boat and calcined under argon at a ramp rate of 10 °C/min to a maximum temperature of 400 °C and maintained for 5 hrs to yield 3% MWCNT-Gd denoted as 3MWCNT-Gd. A similar procedure was used to prepare the 1% MWCNT-Gd, denoted as 1MWCNT-Gd.

\[
\text{MWCNT} + \text{Gd(NO}_3\text{)}_3\cdot6\text{H}_2\text{O} \rightarrow x\text{MWCNT-Gd (x= 1 and 3%)} \ [3.1]
\]

3.3.2 Preparation of rGO

Preparation of reduced graphene proceeded through subjecting natural graphite to a strongly oxidizing environment to produce graphite oxide using a modified Hummers method.\(^3\) The obtained graphite oxide was transformed into graphene oxide via ultrasonication and then subjected to reduction to yield reduced graphene oxide. In a typical oxidation, a 9:1 mixture (v/v) of H\(_2\)SO\(_4\)/H\(_3\)PO\(_4\) was added to a mixture of graphite flakes (3.0 g) and KMnO\(_4\) (18.0 g) (1:6, m/m). The reaction temperature was raised to 50 °C and maintained for 12 hrs with
continuous stirring. The mixture was cooled to room temperature, deionised water (400 mL) and 30% H₂O₂ (3 mL) was added slowly. The solution was centrifuged (7500 rpm for 20 mins at 4 °C), and the supernatant was decanted. The residual solid material was washed several times with deionised water and 30% HCl. This was followed by dispersion of the solid material in deionised water (1000 mL), centrifugation and decanting. The remaining material was coagulated with petroleum ether (200 mL) and filtered through a 1 µm pore size Teflon membrane filter. The solid material obtained (graphite oxide) was vacuum-dried overnight at room temperature.

Reduction of graphite oxide was adapted from a literature procedure. Basically, graphite oxide was dispersed in deionised water at a concentration of 0.1 mg mL⁻¹. Ammonia solution (25%) was used to adjust the pH of the mixture to about 10 to promote the colloidal stability of the graphite oxide sheets through electrostatic repulsion. This was followed by sonication of the mixture for about 1 hr. Vitamin C (2 mmol) was added as a reducing agent. The reaction temperature was elevated to 95 °C under continuous stirring and maintained for 12 hrs. After about 15 mins of heating and stirring, the brown mixture started to turn dark. The reduced graphene oxide was filtered with 1 µm pore size teflon membrane filter and washed repeatedly with warm deionised water. Finally, the reduced graphene oxide was dried under vacuum at room temperature for 24 hrs but most of it was dispersed in butanol and stored in tightly closed sample vials.

3.3.3 Fabrication of MWCNT-Gd/TiO₂ nanocomposites

Preparation of the nanocomposite photocatalysts (Equation 3.2) was adapted from the literature with modifications to fulfil the purpose of our experiment. Titanium (IV) butoxide (10 mL, 0.0294 mol) was dissolved in butanol (30 mL) with sonication for 30 mins. In another beaker, 3MWCNT-Gd (0.00852 g) was dispersed in butanol (50 mL) with sonication for 30 mins. The two solutions were mixed and stirred using a magnetic stirrer for 2 hrs at room temperature. This was followed by drop wise addition of formic acid (15 mL) and stirring was continued for a further 1 hr. The formed precipitate was aged for 24 hrs, and then dried in an
oven at 100 °C for 12 hrs. The dried precipitate was ground into a fine powder using a pestle and mortar and the powder was loaded into quartz boats and calcined at 400 °C in a tube furnace for 3 hrs to yield 0.36% (m/m) 3MWCNT-Gd relative to TiO$_2$ denoted as 3MWCNT-Gd/TiO$_2$. A similar procedure was used to prepare 0.36% (m/m) 1MWCNT-Gd and neat MWCNTs relative to TiO$_2$ and denoted as 1MWCNT-Gd/TiO$_2$ and MWCNT/TiO$_2$, respectively.

\[
x\text{MWCNT-Gd} + \text{Ti(OC}_4\text{H}_9)_4 \rightarrow x\text{MWCNT-Gd/TiO}_2
\]  

[3.2]

### 3.3.4 Preparation of carbon nanomaterial/rare earth ion,N,S-TiO$_2$ nanocomposites

Preparation of the tridoped titania decorated MWCNTs (Equation 3.3) was adapted from a literature procedure with some modifications.$^8$ In a typical synthesis experiment, titanium (IV) butoxide (10 mL, 0.0294 mol) was dissolved in butanol (20 mL) with sonication for 30 mins. In another beaker, oxidised MWCNTs (0.0117 g) was dispersed in butanol (30 mL) with sonication for 30 mins. The two solutions were mixed and stirred using a magnetic stirrer for 30 mins at room temperature. This was followed by addition of gadolinium nitrate hexahydrate solution (0.1093 g, $2.42 \times 10^{-4}$ mol in 10 mL butanol). A solution of thiourea (N and S source) (1.0 g, 0.0131 mol in 15 mL formic acid) was added drop wise with vigorous stirring and stirring was continued for a further 2 hrs. The formed precipitate was dried in an oven at 100 °C for 12 hrs. The dried precipitate was ground into fine powder using a pestle and mortar and the powder was loaded into quartz boats and calcined at 400 °C in a furnace for 3 hrs to yield 0.6% (m/m) Gd relative to TiO$_2$ denoted as MWCNT/Gd,N,S-TiO$_2$ (0.6% Gd). The amount of MWCNT was kept at 0.5% for all the nanocomposites fabricated. A similar procedure was used to prepare 0.2, 1.0 and 3.0% Gd containing nanocomposites. Nitrogen and sulphur codoped titania (N,S-TiO$_2$) and gadolinium, nitrogen and sulphur tridoped titania (Gd,N,S-TiO$_2$) were prepared in a similar manner and used as controls.
Chapter 3: Experimental methodology

MWCNT + Gd(NO$_3$)$_3$ .6H$_2$O + Ti(OC$_4$H$_9$)$_4$ + SC(NH$_2$)$_2$  \[\rightarrow\]

MWCNT/Gd,N,S-TiO$_2$ (x Gd) (x = 0.2, 0.6, 1.0 and 3.0%)  \[3.3\]

The same procedure was employed to prepare SWCNT/Nd,N,S-TiO$_2$, MWCNT/Nd,N,S-TiO$_2$ and rGO/Nd,N,S-TiO$_2$ nanocomposites (Equation 3.4) from the appropriate precursors. Controls such as MWCNT/TiO$_2$, SWCNT/TiO$_2$ were also prepared using the same procedure without the addition of the rare earth ion source and nitrogen and sulphur source. The amount of Nd was kept at 0.6% relative to TiO$_2$ while the amount of all the carbon nanomaterials was kept at 0.5% in all the nanocomposites.

SWCNT/MWCNT/rGO + Nd(NO$_3$)$_3$ .6H$_2$O + Ti(OC$_4$H$_9$)$_4$ + SC(NH$_2$)$_2$  \[\rightarrow\]

SWCNT/MWCNT/rGO/Nd,N,S-TiO$_2$  \[3.4\]

Likewise, MWCNT-Gd/Nd,N,S-TiO$_2$, MWCNT-Gd/Eu,N,S-TiO$_2$ and MWCNT-Gd/Gd,N,S-TiO$_2$ (Equation 3.5) were prepared using a similar procedure to MWCNT/Gd,N,S-TiO$_2$ substituting MWCNT for MWCNT-Gd.

MWCNT-Gd + Gd/Eu/Nd(NO$_3$)$_3$ .6H$_2$O + Ti(OC$_4$H$_9$)$_4$ + SC(NH$_2$)$_2$  \[\rightarrow\]

MWCNT-Gd/Gd/Eu/Nd,N,S-TiO$_2$  \[3.5\]

3.3.5 Preparation of g-C$_3$N$_4$-Gd/MWCNT/TiO$_2$ composite photocatalysts

A modified literature procedure was adopted for the preparation of the gadolinium doped graphitic carbon nitride (g-C$_3$N$_4$-Gd$^{3+}$) (Equation 3.6). Cyanoguanidine (20.0 g, 0.238 mol) was added in an aqueous solution of gadolinium nitrate hexahydrate (0.344 g, 7.62 x 10$^{-4}$ mol in 80 mL H$_2$O) in a beaker and the mixture was stirred using a magnetic stirrer. The temperature was raised to about 70 °C and the mixture turned from cloudy white to clear indicating that the cyanoguanidine had completely dissolved. Stirring and heating was maintained and the water slowly evaporated until a white solid remained in the beaker and the
white solid was further dried in an oven at 80 °C overnight. The dried white solid was milled into a fine powder, transferred into a porcelain crucible and introduced into a muffle furnace which was heated up to 500 °C at 10 °C/min and maintained for 2 hrs. Subsequently, the temperature was increased to 550 °C and maintained for another 2 hrs after which the furnace was switched off and allowed to cool overnight. Yellow crumbs of the product (gadolinium doped graphitic carbon nitride), were obtained and milled into a fine yellow powder which was kept in air-tight sample vials for further use.

\[
\text{C}_2\text{H}_4\text{N}_4 + \text{Gd(NO}_3)_3 \cdot \text{H}_2\text{O} \rightarrow \text{g-C}_3\text{N}_4\cdot\text{Gd}^{3+} \quad [3.6]
\]

Preparation of the g-C\textsubscript{3}N\textsubscript{4}-Gd/MWCNT/TiO\textsubscript{2} composite photocatalysts proceeded as illustrated in Equation 3.7. Oxidised MWCNTs (0.0117 g) in butanol (50 mL) were sonicated for 30 mins followed by addition of titanium (IV) butoxide (10 mL, 0.0294 mol) and sonication continued for another 30 mins to ensure a homogeneous suspension. Appropriate amounts of g-C\textsubscript{3}N\textsubscript{4}-Gd\textsuperscript{3+} were weighed and added to the suspension and sonicated for 10 mins. Weighed amounts of g-C\textsubscript{3}N\textsubscript{4}-Gd\textsuperscript{3+} ranged from 10 to 40% (m/m) in relation to TiO\textsubscript{2}. The mixture was then stirred vigorously using a magnetic stirrer followed by drop wise addition of formic acid (15 mL). Stirring was continued for 2 hrs and the precipitate formed was dried in an oven at 80 °C for 16 hrs and subsequently milled into a fine powder. The fine powder was transferred into quartz boats and calcined in a horizontal tube furnace at 400 °C for 3 hrs. Greyish powders were obtained and stored in air-tight sample vials for further use. The samples were denoted as g-C\textsubscript{3}N\textsubscript{4}-Gd/MWCNT/TiO\textsubscript{2} (x%) where x is the percentage g-C\textsubscript{3}N\textsubscript{4}-Gd\textsuperscript{3+} in the sample. MWCNT/TiO\textsubscript{2} was prepared under the same conditions without addition of the graphitic carbon nitride and used as a control.

\[
g\textsubscript{C3N4-Gd}^{3+} + \text{Ti(OC}_4\text{H}_9)_4 + \text{MWCNTs} \rightarrow g\textsubscript{C3N4-Gd/MWCNT/TiO2} \text{(x%)} \\
(x= 10, 20, 30 and 40\% \text{g-C}_3\text{N}_4\cdot\text{Gd}^{3+}) \quad [3.7]
\]
3.4 Materials characterisation

3.4.1.1 Microscopy analyses

The surface morphology of the prepared photocatalysts was investigated using microscopy techniques. Transmission electron microscopy (TEM) analysis was done on a Jeol JEM 2100 transmission electron microscope (Japan) under a bright field at 120 kV. A small amount of sample was sonicated for a few minutes in methanol and a small drop of the suspension was put on a copper grid. The grid was allowed to dry in air before being mounted on the sample holder for analyses. Scanning electron microscopy (SEM) images were obtained from a Jeol JSM-7500F field emission scanning electron microscope (FE-SEM) (Japan) (working distance 3.9-6.5 mm, acceleration voltage 2.00 kV, secondary electron imaging mode (SEI)) coupled with an INCA energy dispersive x-ray analyzer (EDX) (acceleration voltage 15 kV) for qualitative elemental analysis. Sample powders were mounted on glass slides using a double-sided carbon tape and coated with carbon before being loaded in the FE-SEM for analysis.

3.4.1.2 Infrared spectroscopy

Fourier transform infrared spectroscopy (FT-IR) was employed to probe the presence of different functional groups in the fabricated photocatalysts. FT-IR analysis was done on a PerkinElmer Spectrum 100 FT-IR spectrophotometer (USA). Samples were analysed as KBr pellets. The sample was mixed with KBr in a ratio 1:20, ground and pressed to form the pellet which was then mounted on the FT-IR sample holder and analysed.
3.4.1.3 UV-Vis spectroscopy

The optical properties of the samples were studied using UV-Visible spectroscopy. UV-Vis absorption spectra of the photocatalysts were collected on a Shimadzu UV-2450 UV-Vis spectrophotometer (Japan) fitted with an IRS 240A integrating sphere and barium sulphate was used as a reference. Small amounts of powdered samples were mixed with barium sulphate and ground using a pestle and mortar to ensure adequate mixing of the sample and the reference. The mixture was then mounted in the UV-Vis solid sample holder and introduced into the instrument for analysis.

3.4.1.4 Raman spectroscopy

Raman spectroscopy was employed to investigate the formation of the nanocomposite photocatalysts and the phase composition of titania. Raman spectra were collected from a PerkinElmer RamanMicro 200 Raman microscope (UK), excited by a red diode laser at 785 nm and equipped with a cooled charged device detector which was set at -50 °C and an Olympus BX51M microscope which was operated at a beam path magnification of 50X. The laser power, exposure time and number of exposures were varied to get the best Raman spectra.

3.4.1.5 Thermal analysis

Investigation of the thermal stability and decomposition behavior of the photocatalyst was carried out using a PerkinElmer TGA 4000 thermogravimetric analyser (USA). Samples (about 10 mg) were heated under nitrogen in a temperature range of 30 °C to 900 °C, at a ramping rate of 10 °C/min and the weight loss as a function of temperature was monitored.

3.4.1.6 Surface area analysis

The Brunauer-Emmett-Teller (BET) surface area analysis was employed to determine the surface areas of the prepared nanocomposites. A larger surface
area is desirable in a photocatalyst as it presents a larger number of active sites for the degradation of the organic pollutants. BET analyses were done on a Micromeritics ASAP 2020 surface and porosity analyser (USA). Prior to analysis, the photocatalyst samples were degassed at 200 °C under vacuum to remove moisture and other solvents.

3.4.1.7 X-ray diffraction measurements

X-ray diffraction (XRD) gave an insight into the mineral phases of titania, degree of crystallinity and the average crystallite size of the particles of titania. A Rigaku UltimaIV x-ray diffractometer (Japan) was used to obtain the diffraction patterns of the prepared nanocomposites from a 2θ range of 20-80° at a scanning rate of 5 °min\(^{-1}\). The diffractometer was operated at 40 kV and 40 mA. A Cu\(\alpha\) radiation beam with an excitation wavelength of 0.15406 nm was used as an x-ray source. The average crystallite size of anatase TiO\(_2\) (\(D\)) was computed from Scherrer equation (Equation 3.8) for a specific angle (\(\theta\)), FWHM (full width at half maximum for the (101) anatase peak, \(\beta\)) and a shape factor (\(k\)) of 0.9:

\[
D = \frac{k\lambda}{\beta\cos \theta}
\]

3.5 Photocatalytic activity evaluation

The prepared photocatalytic materials were evaluated for the degradation various aqueous dye solutions under simulated solar light. Methylene blue (MB) (Figure 3.1a), naphthol blue black (NBB) (Figure 3.1b), eriochrome black T (EBT) (Figure 3.1c), eosin blue shade (EBS) (Figure 3.1d), acid blue 74 (AB74) (Figure 3.1e) and trypan blue (TB) (Figure 3.1f). In all the experiments the photocatalysts (0.10 g) was mixed with the dye solution (30 ppm in the case of MB and 20 ppm in all other experiments, 150 mL) and the mixture was stirred in the dark for a specific period to establish adsorption equilibrium. A sample was drawn from the solution using a syringe fitted with a PTFE, 0.45 μm syringe membrane filter and that was taken as the initial concentration (\(C_0\)). The solar simulator Oriel Newport (USA)
was equipped with an Oriel 500 W xenon lamp and set at an input power of 400 W. The solar simulator was fitted with a dichroic UV filter ($\lambda > 420$ nm). Samples were drawn from the solution at 30 or 40 mins intervals, filtered and analysed using a Shimadzu UV-2450 UV-Vis spectrophotometer (Japan) at the wavelength of maximum absorption ($\lambda_{\text{max}}$) of the dye under investigation. A calibration curve was prepared from which the percentage dye degraded was calculated using Equation 3.9:

\[
\% \text{ Dye degraded} = \frac{C_0 - C_t}{C_0} \times 100
\]  

[3.9]

where $C_0$ is the initial dye concentration and $C_t$ is dye concentration after time, $t$. UV-Vis absorption spectra of the dyes were also recorded to monitor any changes in the absorption spectra with increasing irradiation time.
3.5.1 Total organic carbon analysis

Total organic carbon (TOC) analysis which basically measures the amount of organic carbon in the samples was done in a Teledyne Tekmar TOC fusion (USA). Standard solutions of 1 ppm, 5 ppm, 10 ppm, 20 ppm and 30 ppm carbon were prepared using potassium hydrogen phthalate (KHP) and de-ionised water. The standard solutions were run prior to sample analysis for instrument calibration. TOC was measured as the difference between total carbon (TC) and total inorganic carbon (TIC).
3.6 References


CHAPTER 4:
GADOLINIUM NANOPARTICLE DECORATED MULTIWALLED CARBON NANOTUBE/TITANIA NANOCOMPOSITES FOR DEGRADATION OF METHYLENE BLUE IN WATER UNDER SIMULATED SOLAR LIGHT

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This chapter reports on the preparation, characterisation and photocatalytic properties of gadolinium oxide nanoparticle decorated multiwalled carbon nanotube/titania nanocomposites (MWCNT-Gd/TiO$_2$) for methylene blue degradation under simulated solar light irradiation. Decoration of Gd$_2$O$_3$ nanoparticles on MWCNTs prior to incorporation into TiO$_2$ matrix aimed at creating an electron transfer channel between TiO$_2$ and MWCNTs in order to improve charge separation and transportation. A proposed MB degradation mechanism and catalyst recycling experiment is discussed in this chapter. Moreover, total organic carbon analysis is also reported.

4.1 Introduction

Dye pollution presents a daunting challenge to the environment as well as to the daily operations of the textile industry due to difficulties related to its treatment and the undesirable environmental and health effects.$^{1,2}$ On a daily basis, textile industries utilize large volumes of water for processing which puts a strain on the water sources especially in water scarce locations. This compels the industries to consider recycling their water after each processing cycle to ease on their consumption of fresh water. However, this could only be possible if the effluent has been efficiently treated.$^3$

Combining titania and carbon nanotubes (CNTs) to form nanocomposites has been highlighted as an attractive approach towards photocatalytic degradation of organic pollutants such as dyes in water. This approach improves the
photocatalytic activity of titania both under visible and UV light irradiation, resulting in higher degradation efficiencies of the pollutants.\textsuperscript{4–6} Furthermore, this approach allows for the exploitation of the properties of both titania and CNTs. The resultant nanocomposite is a new material with new and improved properties. CNTs have been found to act as visible light sensitisers, adsorbents, electron traps and transport systems. Moreover, CNTs act as TiO\textsubscript{2} dispersing agents and also improve the surface area of the nanocomposites.\textsuperscript{4,7} However, in order to exploit the benefits of both the CNTs and TiO\textsubscript{2} a strong and efficient interaction between the CNTs and TiO\textsubscript{2} nanoparticles is essential. This ensures efficient electron transfer between the CNTs and TiO\textsubscript{2} and minimise electron/hole recombination which would otherwise lower the photocatalytic activity of the photocatalyst.\textsuperscript{4,5}

4.2 Experimental

4.2.1 Materials

Materials and reagents used in this work are described in Chapter 3, Section 3.2

4.2.2 Preparation of photocatalysts

Detailed procedures for the preparation of the nanocomposite photocatalysts are given in Chapter 3, Sections 3.3.1 and 3.3.3.

4.2.3 Materials characterisation

In order to ascertain formation of the desired materials, several characterisation techniques described in Chapter 3, Section 3.4 were employed.

4.2.4 Photocatalytic activity evaluation

The prepared nanocomposites were exploited for the degradation of MB under simulated solar light as detailed in Chapter 3, Section 3.5. UV-Vis photometric measurements were done at 668 nm. TOC analysis was performed according to the procedure outlined in Chapter 3, Section 3.5.1.
4.3 Results and discussion

4.3.1 TEM and SEM-EDX analysis

TEM was employed to get an insight into the surface morphology of the Gd decorated MWCNTs and the prepared nanocomposites. Figure 4.1 shows TEM images of oxidised MWCNTs, 1MWCNT-Gd and 3MWCNT-Gd which show the clean oxidised MWCNTs (Figure 4.1a) and Gd nanoparticles decorated on the surfaces of 1% and 3% MWCNT-Gd (Figure 4.1b and 4.1c). Gd nanoparticles have a relatively uniform distribution on the surfaces of the MWCNTs. TEM measurements gave a Gd$^{3+}$ nanoparticle diameter range of 2 to 5 nm. This shows that the use of citric acid as a capping agent yielded positive results in controlling the size of the Gd nanoparticles and there was no major nanoparticle aggregations observed. Furthermore, the Gd nanoparticles are nearly spherical in shape. The sol-gel method resulted in uniformly decorated Gd nanoparticles on the CNTs as well as relatively uniform shape and particle size.
Chapter 4: Gadolinium nanoparticle decorated multiwalled carbon nanotube/titania nanocomposites for
degradation of methylene blue in water under simulated solar light

FE-SEM images of pure TiO$_2$, 1MWCNT-Gd/TiO$_2$ and 3MWCNT-Gd/TiO$_2$ are presented in Figure 4.2 and the pure TiO$_2$ nanoparticles appear as aggregates of relatively uniform shape and sizes. The FE-SEM images of the MWCNT-Gd/TiO$_2$ nanocomposites (Figure 4.2b and 4.2c) show that the MWCNT-Gd are interwoven between TiO$_2$ nanoparticles and are largely covered by the TiO$_2$ nanoparticles which indicate good interaction between the two materials. This is essential for exploiting the intrinsic properties of the different components of the nanocomposite. Furthermore, the strong interaction between TiO$_2$ and the MWCNT-Gd enhances electron transfer between the two materials and improve the photocatalytic activity of the nanocomposites.

Figure 4.1: TEM images of (a) oxidised MWCNTs, (b) 1MWCNT-Gd and (c) 3MWCNT-Gd.
Figure 4.2: FE-SEM images of (a) TiO$_2$ nanopowder, (b) 1MWCNT-Gd/TiO$_2$ and 3MWCNT-Gd/TiO$_2$.

Elemental analysis of the Gd decorated MWCNTs (Figure 4.3a) show the presence of C, O and Gd which is an indication of the decoration of the MWCNTs with Gd$_2$O$_3$ species. The presence of C, O, Gd and Ti (Figure 4.3b) in the EDX spectrum analysis of the MWCNT-Gd/TiO$_2$ nanocomposites suggests the formation of the nanocomposite. As a result of the small amount of the Gd nanoparticles in relation to TiO$_2$, very small amount of Gd could be detected from the EDX analysis. Another reason for the low Gd intensities in the nanocomposites could be the complete coverage of the Gd$_2$O$_3$ decorated MWCNTs by the titania nanoparticles reducing x-ray penetration.
4.3.2 FTIR analysis

FTIR was employed to probe the functional groups present in the photocatalysts and the peaks observed around 3410 cm⁻¹ and 1630 cm⁻¹ (Figure 4.4), may be assigned to the OH stretching and bending vibrations, respectively. These may be due to the adsorption of moisture on the surfaces of the photocatalysts. The presence of hydroxyl groups on the photocatalysts surface is essential for the formation of the oxidising hydroxyl radicals during photocatalytic degradation of the organic pollutants. The intense, broad band centred around 600 cm⁻¹ may be assigned to the mixed contribution of Ti-O and O-Ti-O stretching vibrations and bending modes which confirms the presence of TiO₂. A similar absorption band is observed in the MWCNT/TiO₂ nanocomposite. However, in the 1MWCNT-Gd/TiO₂ and 3MWCNT-Gd/TiO₂ the absorption band is less broad and it is shifted to higher wavenumbers (720 cm⁻¹). This may be ascribed to the possible presence of Ti-O-Gd and Gd-O bonds. These would have originated from the interaction of the Gd₂O₃ decorated on the surfaces of the MWCNT and TiO₂. Notably, no peaks due to the MWCNTs were observed probably due to their small amounts (0.36%) relative to TiO₂ and their complete coating by TiO₂ nanoparticles made them undetectable by FTIR. Similarly, Kuvarega et al. reported no peaks due to MWCNTs even at a loading of 10% MWCNTs which may suggest that their coating with TiO₂ is the main reason for not being detected. Similar results have been reported by Wang et al. and Aryal et al.
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**Figure 4.4:** FTIR spectra of TiO$_2$, MWCNT/TiO$_2$, 1MWCNT-Gd/TiO$_2$ and
3MWCNT-Gd/TiO$_2$.

### 4.3.3 Raman spectroscopy

**Figure 4.5** shows the Raman spectra of the different photocatalysts and all show
peaks at 146, 207, 399, 515 and 638 cm$^{-1}$ which are characteristic of the anatase
phase of TiO$_2$, implying that the anatase phase is the predominant phase in the
photocatalysts. These peaks represent Raman active modes with symmetries $E_g$, $E_g$, $B_{1g}$, $A_{1g}$ and $E_g$, respectively.$^{5,14}$ The presence of these peaks in the
nanocomposites reveals that neither the MWCNTs nor the MWCNT-Gd caused
any phase changes in TiO$_2$ during synthesis. In addition to the anatase peaks, the
MWCNT/TiO$_2$ and MWCNT-Gd/TiO$_2$ nanocomposites display peaks at 1313 and
1598 cm$^{-1}$ which are ascribed to the D band and G band of the MWCNTs, further
supporting the possible formation of the nanocomposite.$^{14}$ The D band arises from
defects in the sp$^2$ hybridised framework of MWCNTs while the G band signifies the
presence of ordered sp$^2$ hybridisation of the MWCNT skeleton.$^{15}$ The intensities of
these peaks are low which may be attributed to the coating of the MWCNTs by
TiO$_2$ nanoparticles as evidenced by the FE-SEM images (**Figure 4.2b** and **4.2c**).
**Figure 4.5:** Raman spectra of TiO$_2$, MWCNT/TiO$_2$, 1MWCNT-Gd/TiO$_2$ and 3MWCNT-Gd/TiO$_2$.

### 4.3.4 Thermogravimetric analysis

TGA was utilised to probe the thermal stability of the photocatalysts (Figure 4.6) and they all exhibit high thermal stability. The commercial TiO$_2$ nanoparticles showed no significant weight loss which indicates its purity. In the nanocomposites, weight losses from 50 °C to 100 °C may be attributed to the loss of moisture absorbed by the photocatalysts and weight losses from 100 °C to around 300 °C may be linked to the loss of other carbon based compounds incorporated in the nanocomposites. Further weight loss above 500 °C may be linked to the decomposition of the MWCNT skeleton.\textsuperscript{16} Furthermore, Kuvarega et al.\textsuperscript{12} noted that for the MWCNT/TiO$_2$ nanocomposites, decomposition of the MWCNT skeleton occurs at much higher temperatures than neat MWCNTs and happens over a wider temperature range. Consequently, the decomposition of the MWCNT skeleton could not be clearly established from the thermograms mainly due to the smaller MWCNTs loading (0.36%). The 1MWCNT-Gd/TiO$_2$ nanocomposite showed better thermal stability than the 3MWCNT-Gd/TiO$_2$.
nanocomposite and the MWCNT/TiO$_2$ nanocomposite. This difference in thermal stabilities could be due to differences in the degree of coating of the CNTs by the TiO$_2$ nanoparticles as evidenced by FE-SEM image (Figure 4.2b and 4.2c) which show some MWCNTs incompletely coated by TiO$_2$ which may decompose faster than the completely coated MWCNTs.

![TGA plots of the different photocatalysts](image)

**Figure 4.6:** TGA plots of the different photocatalysts.

### 4.3.5 UV-Vis analysis

**Figure 4.7** shows the UV-Vis absorption spectra of the different photocatalysts from which it could be established that the TiO$_2$ nanopowder show strong absorption only in the UV region. This is due to its wide band gap which is 3.2 eV for the anatase phase and 3.0 eV for the rutile phase of TiO$_2$. Contrary, the MWCNTs incorporating nanocomposites all showed a slight red shift into the visible region, which could mainly be ascribed to the MWCNTs skeleton which may act as a visible light sensitisier, absorbing visible light and injecting electrons into the conduction band of TiO$_2$. Moreover, CNTs may function as a source of carbon doping resulting in the formation of the Ti-C and Ti-O-C bonds during
calcination which introduces defects in the band gap of TiO$_2$, resulting in band gap narrowing and visible light absorption.$^{5,18,19}$ This red shift allows for the photocatalytic degradation of pollutants by these nanocomposites under visible light irradiation. Furthermore, the 3MWCNT-Gd/TiO$_2$ showed a larger red shift than the MWCNT/TiO$_2$ and 1MWCNT-Gd/TiO$_2$ nanocomposites which may be explained in terms of the higher Gd$^{3+}$ loading on the MWCNT surface which are known to contribute towards visible light absorption due to their 4$f$ electron transitions.$^{20,21}$ A synergetic effect between the MWCNT and Gd nanoparticles for visible light absorption may be responsible for the better red shift of the 3MWCNT-Gd/TiO$_2$ nanocomposite.

![UV-Vis absorption spectra of TiO$_2$, MWCNT/TiO$_2$, 1MWCNT-Gd/TiO$_2$ and 3MWCNT-Gd/TiO$_2$.](image)

**Figure 4.7:** UV-Vis absorption spectra of TiO$_2$, MWCNT/TiO$_2$, 1MWCNT-Gd/TiO$_2$ and 3MWCNT-Gd/TiO$_2$.

### 4.3.6 X-ray diffraction

XRD was employed to investigate the crystalline phases of the nanocomposites and the results are displayed in **Figure 4.8**. It could be established that nanocomposites and the TiO$_2$ nanopowder were fairly crystalline as depicted by the sharp XRD peaks. The commercial TiO$_2$ nanopowder (mixture of rutile and anatase) clearly showed XRD peaks characteristic of the two TiO$_2$ phases while
the prepared nanocomposites displayed only the anatase TiO$_2$ phase. The peaks at 2θ 27.5, 36.1, 39.4, 41.3, 44.1, 56.7 and 64.2° are attributed to the (110), (101), (200), (111), (210), (211) and (200) crystal planes, respectively, which are characteristic of the rutile phase of TiO$_2$.\textsuperscript{22} These peaks were clearly visible in the commercial TiO$_2$ nanopowder. In the prepared nanocomposites, peaks at 2θ 25.3, 37.8°, 47.9, 53.9, 55.1, 62.7 and 75.1° which correspond to the (101), (004), (200), (105), (211), (204) and (215) crystal planes, respectively, are characteristic of the anatase phase of TiO$_2$.\textsuperscript{11} Notably, no XRD peaks observed due to the MWCNTs probably due to their small amounts relative to TiO$_2$ or due to overlap between the (101) peak of MWCNTs and the prominent anatase (101) peak of TiO$_2$.\textsuperscript{23} The incorporation of the Gd nanoparticles on the MWCNTs did not have any significant influence on the crystallinity of the nanocomposites probably due to their small amounts. Crystallite size calculations of the anatase phase of TiO$_2$ gave an average value of 13 nm from Scherrer equation.

![Figure 4.8: XRD patterns of the different photocatalysts.](image-url)
4.3.7 BET surface area measurements

BET surface area analysis was employed to get an insight into the surface areas of the photocatalysts. Surface area is important during photocatalysis as it provides more active sites at which the oxidation of the pollutants can take place. The surface areas of all the nanocomposites (110.77, 125.18 and 123.79 m²/g for MWCNT/TiO₂, 1MWCNT-Gd/TiO₂ and 3MWCNT-Gd/TiO₂, respectively) were larger than the surface area of TiO₂ nanopowder (56 m²/g)²⁴ which may be ascribed to the incorporation of the MWCNTs or the MWCNT-Gd. Similarly, both the MWCNT-Gd/TiO₂ nanocomposites show larger surface areas than the neat MWCNT/TiO₂ nanocomposite which may be ascribed to the incorporation of the Gd₂O₃ nanoparticles on the surface of the MWCNTs. This may minimise any possible aggregation of the MWCNTs which could otherwise lower the surface area of the resultant nanocomposites.

4.4 Photocatalytic degradation studies

The photodegradation results of MB under simulated solar light are displayed in Figure 4.9. TiO₂ nanopowder showed the lowest photocatalytic activity compared to the prepared nanocomposites which may be attributed to its poor absorption of visible light due to its wide band gap (3.2 eV, anatase and 3.0 eV, rutile). This is in agreement with the diffuse reflectance UV-Vis results (Figure 4.7) which showed that the TiO₂ nanopowder mainly absorb in the UV region. The fabricated nanocomposites displayed improved photocatalytic activity compared to the TiO₂ nanopowder which is credited to the incorporation of the MWCNTs which extended light absorption into the visible region.²⁵ Moreover, incorporation of the MWCNTs improved the surface area of the nanocomposites which is essential for a higher photocatalytic activity. Gd₂O₃ decorated MWCNTs based nanocomposites showed higher photocatalytic activity compared to the neat MWCNT/TiO₂ nanocomposite which may be linked to improved charge separation as a result of the strong interface between TiO₂ and the MWCNTs. The Gd₂O₃ nanoparticles located at the TiO₂/MWCNT interface act as electron transfer channels which ensure efficient charge separation and higher photocatalytic
activity. Furthermore, the 3MWCNT-Gd/TiO\textsubscript{2} nanocomposites showed slightly higher photocatalytic activity than the 1MWCNT-Gd/TiO\textsubscript{2} nanocomposite probably due to more uniform coverage of the MWCNTs surface with Gd nanoparticles ensuring adequate charge transfer between TiO\textsubscript{2} and the MWCNT.

The photocatalytic degradation results correlate well with the UV-Vis absorption spectra where the 3MWCNT-Gd/TiO\textsubscript{2} showed better visible light absorption compared to the other photocatalysts. Therefore, its higher photocatalytic activity may be ascribed to the combined effect of higher visible light absorption capability and more improved electron transfer between TiO\textsubscript{2} and the MWCNTs.

![Photodegradation of MB using TiO\textsubscript{2}, MWCNT/TiO\textsubscript{2}, 1MWCNT-Gd/TiO\textsubscript{2} and 3MWCNT-Gd/TiO\textsubscript{2}.](image)

In terms of photocatalytic degradation efficiency a maximum of 53.6%, 85.8%, 96.2% and 98.7% was recorded for TiO\textsubscript{2}, MWCNT/TiO\textsubscript{2}, 1MWCNT-Gd/TiO\textsubscript{2} and 3MWCNT-Gd/TiO\textsubscript{2}. Cong et al.\textsuperscript{4} evaluated the photocatalytic activity of carbon doped TiO\textsubscript{2} supported on MWCNTs for degradation of MB under visible light
irradiation and a maximum photocatalytic degradation of about 70% was recorded. This is lower than the obtained results, suggesting superior performance of the prepared nanocomposites for photocatalytic degradation of MB. Jiang et al. evaluated MWCNT/TiO nanocomposites for photocatalytic degradation of MB both under visible and UV irradiation. The percentage MB degraded under visible light irradiation was lower than the values recorded in this work.

The UV-Vis absorption spectra of MB were recorded after photocatalytic degradation by the different photocatalysts (Figure 4.10) and two important peaks were observed at 610 and 664 nm. These are attributed to the benzene ring and the heteropolyaromatic linkage of MB. Figure 4.10 shows that both peaks gradually decrease with time and eventually became smooth. Similarly, the deep blue colour of MB was fading with time which indicates that both the aromatic ring and chromophore were degraded during photocatalysis. Notably, there were no new absorption peaks observed in the spectra. Complete degradation of MB is proposed to yield simple inorganic species such as CO$_2$, H$_2$O, NH$_4^+$/NO$_3^-$, SO$_4^{2-}$ and Cl$^-$.  

![Figure 4.10: UV-vis absorption spectra of MB during photocatalysis using 3MWCNT-Gd/TiO$_2$.](image)
4.4.1 Total organic carbon analysis

TOC analysis (Figure 4.11) were done to establish the extent of mineralization of MB by the 3MWCNT-Gd/TiO₂ and a gradual increase in TOC removal was observed, reaching a maximum of 80.0% after 5 hours. The higher TOC removal indicates that not only does the photocatalyst decolourise MB but also break the MB molecules into inorganic species. This is desirable since it ensures that there is minimum formation of toxic by-products during the photocatalytic degradation of MB.

![Figure 4.11: TOC removal using 3MWCNT-Gd/TiO₂ nanocomposite.](image)

4.4.2 Degradation kinetics

In order to determine the photocatalytic degradation rates of MB using the different photocatalysts under simulated solar light, first-order kinetics (Equation 4.1) were employed to fit the obtained data. Figure 4.12 shows that the photocatalytic degradation of MB by the different photocatalysts obeys the first-order kinetics. The highest photodegradation rate for MB was realized with 3MWCNT-Gd/TiO₂.
which could be linked to the synergistic effect of the MWCNTs, TiO$_2$ and Gd$_2$O$_3$ nanoparticles.

\[ \ln \frac{C_0}{C} = k(t) \]  \[4.1\]

Table 4.1 presents the calculated photodegradation rate constant for MB using the different photocatalysts. All the values are higher than that of MB degradation by commercial TiO$_2$ nanopowder ($2.5 \times 10^{-3}$ min$^{-1}$). The Gd-MWCNTs/TiO$_2$ nanocomposites show higher photocatalytic degradation rates ($1.1 \times 10^{-2}$, $1.3 \times 10^{-2}$ min$^{-1}$ for 1MWCNT-Gd/TiO$_2$ and 3MWCNT-Gd/TiO$_2$, respectively) than neat MWCNT/TiO$_2$ ($6.9 \times 10^{-3}$ min$^{-1}$). This could be attributed to the improved interface between TiO$_2$ and MWCNTs by incorporation of the Gd$_2$O$_3$ nanoparticles. Tian et al.$^{23}$ recorded a rate constant of $1.0 \times 10^{-3}$ min$^{-1}$ for degradation of MB using 20% MWCNT/TiO$_2$ hybrid nanostructures under visible light, this value is substantially lower than the recorded values in this study. In another work, Min et al.$^{28}$ prepared oxidised graphene/TiO$_2$ nanocomposites for degradation of MB both under UV and visible light irradiation and the degradation rate under visible light is $7.15 \times 10^{-3}$ min$^{-1}$ which is lower than the values obtained for the Gd-MWCNTs containing nanocomposites suggesting improvement of the photocatalytic activity of the prepared nanocomposites by incorporating the Gd nanoparticles.
Figure 4.12: Kinetics for photocatalytic degradation of MB under simulated solar light.
Table 4.1: Photocatalytic degradation rate constants of MB by the different photocatalysts.

<table>
<thead>
<tr>
<th>Sample name</th>
<th>Rate constant (min^{-1})</th>
<th>$R^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>TiO$_2$</td>
<td>$2.5 \times 10^{-3}$</td>
<td>0.978</td>
</tr>
<tr>
<td>MWCNT/TiO$_2$</td>
<td>$6.9 \times 10^{-3}$</td>
<td>0.983</td>
</tr>
<tr>
<td>1MWCNT-Gd/TiO$_2$</td>
<td>$1.1 \times 10^{-2}$</td>
<td>0.998</td>
</tr>
<tr>
<td>3MWCNT-Gd/TiO$_2$</td>
<td>$1.3 \times 10^{-2}$</td>
<td>0.973</td>
</tr>
</tbody>
</table>

4.5 Proposed photocatalytic degradation mechanism

The enhanced photocatalytic activity of the MWCNT-Gd containing nanocomposites may be ascribed to the strong interaction between the Gd$_2$O$_3$ nanoparticles, MWCNTs and TiO$_2$, as evidenced by the FE-SEM and TEM images. This allows for the synergistic effect of the different components of the nanocomposite, resulting in improved performance. Two possible mechanisms can be put forward for the degradation of MB by the prepared nanocomposites under visible light irradiation which may proceed through dye sensitisation and CNT sensitisation. During dye sensitisation (Figure 4.13, mechanism 1), MB must be adsorbed onto the surface of the photocatalyst. The adsorbed MB will absorb visible light and get excited from its ground state (MB) to its excited state (MB$^*$) which can then inject an electron into the conduction band of TiO$_2$. The electron may be captured by the Gd$^{3+}$ at the interface of TiO$_2$ and MWCNT, where it can react with adsorbed oxygen to form the oxidising superoxide radical (O$_2^-$) and eventually the hydroxyl radical (OH$^-$) which then oxidise the aromatic rings and chromophore of MB. The incompletely filled 4f orbitals of lanthanide ions is believed to lie slightly below the lower band gap edge of the conduction band of
TiO$_2$, making it possible to capture electrons from the conduction band of TiO$_2$.\textsuperscript{29} Alternatively, the electron in the conduction band of TiO$_2$ may react with adsorbed oxygen to form the oxidising species. On the Gd$_2$O$_3$ nanoparticle surface, electrons may accumulate and migrate into the MWCNT skeleton where they will react with oxygen to form the superoxide radical. This ensures generation of sufficient oxidising species and improves the photocatalytic activity of the nanocomposites. In this proposed mechanism, MB acts as a visible light sensitisier and a substrate.

In the second mechanism (Figure 4.13, mechanism 2), the MWCNTs absorb visible light, resulting to an excited state which can inject an electron into the conduction band of TiO$_2$. This electron may be trapped by the sub-band gap states created by the Gd$^{3+}$ where it reacts with oxygen adsorbed on the surface of the nanoparticles to form the superoxide radical and eventually the hydroxyl radical, which then attack MB.\textsuperscript{23} The positively charged MWCNT skeleton may trap electrons from the valence band of TiO$_2$, leaving positively charged holes (h$^+$). These holes may react with water or hydroxide ions to form the extremely oxidising hydroxyl radicals which then degrade MB. The Gd nanoparticles act as electron scavengers and facilitate charge separation which improves the photocatalytic activity of the nanocomposites. Furthermore, at the MWCNT-Gd/TiO$_2$ interface, the Gd species may also help in concentrating the degradation intermediates onto the surface of the photocatalyst for further degradation into the simpler products such as CO$_2$, H$_2$O, NO$_3^-$ and SO$_4^{2-}$. This is facilitated by the ability of the lanthanide ions to form complexes with various Lewis bases such as alcohols, aldehydes, thiols, amines, etc., when these groups interact with the 4$f$ orbitals of the lanthanide ion.\textsuperscript{30}
4.6 Recycling of the Photocatalyst

The stability of the photocatalyst (3MWCNT-Gd/TiO$_2$) was evaluated by using the same catalyst for five photodegradation experiments of the same initial MB concentration. After each experiment, the catalyst was washed with deionised water and ethanol to remove any MB which may be adsorbed on the surface and then dried in the oven. The photocatalyst showed substantial stability after the five cycles, reaching a maximum of 85.9% MB degradation (Figure 4.14). The decrease in the degradation efficiency could mainly be attributed to loss of the photocatalyst during the washing in between the cycles. The stability of the photocatalyst allows for its re-use several times which cut on the effluent treatment costs.

Figure 4.13: Proposed photocatalytic degradation mechanism of methylene blue.
Chapter 4: Gadolinium nanoparticle decorated multiwalled carbon nanotube/titania nanocomposites for degradation of methylene blue in water under simulated solar light

4.7 Chapter summary

Gadolinium oxide nanoparticles of relatively uniform size (<5 nm) were successfully anchored on MWCNTs which was then used as a precursor to fabricate MWCNT-Gd/TiO$_2$ nanocomposites via a sol-gel method. The MWCNT-Gd/TiO$_2$ nanocomposites showed higher photocatalytic activity over neat MWCNT/TiO$_2$ and commercial TiO$_2$ nanopowder MB degradation under simulated solar light irradiation. This is attributed to the synergistic effect of the three components of the nanocomposites. Supporting the Gd$_2$O$_3$ nanoparticles at the MWCNT/TiO$_2$ interface improved charge separation and minimise electron/hole recombination which would otherwise lower the photocatalytic activity of the nanocomposites. Probing the photocatalytic degradation of MB by UV-Vis revealed that both the aromatic rings and chromophore of MB were degraded during photocatalysis as seen from the gradual disappearance of the peaks due to the aromatic rings and chromophore. TOC analysis revealed a higher degree of complete mineralisation of MB by the 3MWCNT-Gd/TiO$_2$ nanocomposite. The
photocatalytic degradation of MB by the MWCNT-Gd/TiO₂ nanocomposites was inferred to proceed via self-sensitisation and MWCNT sensitisation routes. The prepared nanocomposite photocatalyst displayed sufficient stability for reuse, with minimum loss of efficiency.
4.8 References


CHAPTER 5:
PHOTOCATALYTIC DEGRADATION OF THE DIAZO DYE NAPHTHOL BLUE BLACK IN WATER USING MWCNT/Gd,N,S-TiO$_2$ NANOCOMPOSITES UNDER SIMULATED SOLAR LIGHT

This work has been accepted for publication in Mamba G, Mbianda XY, Mishra AK. J. Environ. Sci. 2015

In this chapter, tridoped titania (Gd,N,S-TiO$_2$) was decorated on oxidised multiwalled carbon nanotubes via a simple sol-gel method to yield multiwalled carbon nanotubes/gadolinium, nitrogen, sulphur tridoped titania nanocomposite (MWCNT/Gd,N,S-TiO$_2$) with varying Gd$^{3+}$ contents (0.2, 0.6, 1.0 and 3.0%). Combining the tridoped titania and the MWCNTs is aimed at improving both visible light absorption and charge separation which result in enhanced photocatalytic activity of the nanocomposite. The prepared nanocomposites were evaluated for the degradation of naphthol blue black (NBB) under simulated solar light and the stability of the photocatalyst as well as the degree of complete mineralisation of the dye were evaluated.

5.1 Introduction

Azo dyes, characterised by the presence of at least one --N=N-- group (azo group) are the most widely exploited dyes in the textile industry accounting for about 70% of all dyestuffs used.$^{1,2}$ However, these dyes or their partial degradation products have been linked to various adverse health effects such as being toxic, carcinogenic, mutagenic and genotoxic.$^{3,4}$ Therefore, efficient treatment of textile effluent laden with azo dyes remains high priority to protect the living environment.

Recent research has highlighted that tridoped titania: Ga, N, S-TiO$_2$$^5$, Ce, N, S-TiO$_2$$^6$, Gd, N, S-TiO$_2$$^7$ and Sm, N, P-TiO$_2$$^8$ displayed improved photocatalytic activity than co-doped and single doped titania. This has been attributed to the combined effect of band gap narrowing by N, S doping and
charge separation by the metal species. Rare earth metal ions are an ideal addition in the nanocomposite due to their excellent electron scavenging property, contribution towards visible light absorption of titania and the ability to facilitate concentration of various organic pollutants on the surface of the photocatalyst. The remarkable properties of carbon nanotubes and their contribution towards improvement of the photocatalytic activity of titania have been discussed in details in Chapter 2. This prompted the formulation of the tridoped titania/multiwalled carbon nanotube nanocomposites (MWCNT/Gd,N,S-TiO$_2$) in order to exploit the combined properties of tridoped titania and the MWCNTs for improved photocatalytic properties.

5.2 Experimental

5.2.1 Materials

All the materials and reagents used in this work were described in Chapter 3, Section 3.2.

5.2.2 Fabrication of MWCNT/Gd,N,S-TiO$_2$ nanocomposites

The nanocomposite photocatalysts were prepared according to the procedures described in Chapter 3, Section 3.3.1 and 3.3.4.

5.2.3 Materials characterisation

Subsequent to the preparation, MWCNT/Gd,N,S-TiO$_2$ nanocomposites were characterised by various tools described in Chapter 3, Section 3.4.

5.2.4 Photocatalytic activity evaluation

The fabricated nanocomposites were exploited for the degradation of NBB under simulated solar light as detailed in Chapter 3, Section 3.5. UV-Vis photometric measurements were obtained at 618 nm. Moreover, UV-Vis absorption spectra of NBB were also recorded to monitor the degradation of NBB with increasing
irradiation time. TOC analysis was performed according to the procedure outlined in Chapter 3, Section 3.5.1.

5.3 Results and discussion

5.3.1 TEM and FE-SEM-EDX analysis

The surface morphology of the prepared photocatalyst was investigated by FE-SEM which shows that the TiO$_2$ nanoparticles were of relatively uniform sizes and shape (Figure 5.1a). This was further confirmed by TEM (Figure 5.1c) and the titania nanoparticles were found to have diameters around 20 nm. Figure 5.1b and 5.1d show that the MWCNTs are embedded within clusters of the Gd,N,S-doped titania matrix and that is essential for attaining the synergistic effect of the CNTs and TiO$_2$ during photocatalysis. Figure 5.1d (insert) shows that the titania is decorated on the outer surface of the CNTs. However, the coating of the Gd,N,S-TiO$_2$ on the CNTs surface is not continuous or uniform which may be caused by the loss of some of the thiourea derivatives and moisture during calcination, leaving behind the gaps in between the titania matrix.
Figure 5.1: FE-SEM image (a) Gd,N,S-TiO$_2$ (0.6% Gd) (b) MWCNT/Gd,N,S-TiO$_2$ (0.6% Gd) and TEM images of (c) Gd,N,S-TiO$_2$ (0.6% Gd) (d) MWCNT/Gd,N,S-TiO$_2$ (0.6% Gd).

Qualitative elemental analysis (Figure 5.2) of the MWCNT/Gd,N,S-TiO$_2$ (0.6% Gd) nanocomposite confirmed the presence of Ti, O, C, S and Gd. The presence of S and Gd is evidence of the possible incorporation of these elements into the titania matrix while the carbon mainly emanates from the MWCNTs, suggesting the formation of the nanocomposite.
Chapter 5: Photocatalytic degradation of the diazo dye naphthol blue black in water using MWCNT/Gd, N, S-TiO$_2$ nanocomposites under simulated solar light

Figure 5.2: EDX spectrum of MWCNT/Gd,N,S-TiO$_2$ (0.6% Gd).

5.3.2 Infrared spectroscopy

The functional groups present in the prepared photocatalysts were probed using FTIR (Figure 5.3) which show two peaks at 1633 cm$^{-1}$ and 3426 cm$^{-1}$ which are assigned to OH bending and stretching vibration due to adsorbed water.$^{11}$ The ability of the photocatalyst to adsorb moisture is essential for the generation of the hydroxyl radicals during photocatalysis. Peaks were also observed at 1404 cm$^{-1}$, 1385 cm$^{-1}$ and 2356 cm$^{-1}$, emanating from the deformation mode of ammonium ions, hyponitrite ion and N-H stretching vibrations, respectively.$^{12,13}$ The presence of these peaks suggests the incorporation of nitrogen species in the nanocomposites. Moreover, the nitrite/nitrate (NO-like species) peak appeared at 1550 cm$^{-1}$ which further support the incorporation of nitrogen.$^{12}$ The peaks appearing at 1130 cm$^{-1}$ and 1065 cm$^{-1}$ may be assigned to bidentate SO$_4^{2-}$ coordinated to metals such as Ti$^{4+}$.$^{14}$ These peaks suggest the incorporation of sulphur in the nanocomposites. The broad peak observed between 400 cm$^{-1}$ and 800 cm$^{-1}$ may be related to the combined contribution of Ti-O, Ti-O-Ti, O-Ti-N, Gd-O-Ti and S-O-Ti.$^{15}$
Chapter 5: Photocatalytic degradation of the diazo dye naphthol blue black in water using MWCNT/Gd, N, S-TiO$_2$ nanocomposites under simulated solar light

5.3.3 Optical properties of the photocatalysts

The photoresponse of the prepared photocatalysts was investigated using UV-Vis spectroscopy and the recorded absorption spectra are presented in Figure 5.4. All the prepared photocatalysts show a red shift which may be attributed to N and S doping of titania. Doping narrow the band gap of titania resulting in excitation of electron by visible light from N and S states into the conduction band of titania. The Gd,N,S-TiO$_2$ (0.6% Gd) photocatalyst showed improved visible light response compared to N,S-TiO$_2$. This phenomenon is attributed to the incorporation of Gd nanoparticles which result in the formation of sub-band gap states within the TiO$_2$ band gap. Consequently, electrons can be excited by visible light from the valence band of titania into the newly formed intermediate states. Furthermore, it was observed that the incorporation of the MWCNTs improved visible light absorption on the nanocomposites compared to N,S-TiO$_2$ and Gd,N,S-TiO$_2$. 

Figure 5.3: FTIR spectra of the different photocatalysts.
This could be linked to two possible effects of the MWCNTs: firstly, MWCNTs function as a source of carbon doping which introduces mid-band gap within the TiO\textsubscript{2} band gap, allowing electrons to be excited by visible light from these intermediate states into the conduction band of titania\textsuperscript{20,21}. Secondly, the MWCNTs act as visible light sensitisers, absorbing visible light and transferring electrons into the conduction band of titania\textsuperscript{22}. Therefore, the improved visible light absorption displayed by the nanocomposites emanates from the synergistic effect of Gd, N and S doping and the incorporation of the MWCNTs.

![UV-Vis absorption spectra of the different photocatalysts.](image)

**Figure 5.4: UV-Vis absorption spectra of the different photocatalysts.**

The absorption edge wavelengths of the different materials were obtained by extrapolating the absorption graphs in **Figure 5.4** and the results obtained are tabulated in **Table 5.1**. The wavelengths obtained were used to estimate the band gap energy of the different photocatalysts using the following equation:
where \( E_g \) is the band gap energy, \( h \) is Planck’s constant, \( c \) is the speed of light and \( \lambda \) is the absorption edge wavelength (Figure 5.4). The estimated band-gap energies are presented in Table 5.1. Notably, N,S-TiO\(_2\) showed the largest band gap energy of 2.96 eV which is however less than 3.2 eV for anatase TiO\(_2\), indicating a certain degree of narrowing due to N and S doping. The smallest band gap energy (2.50 eV) was recorded for the MWCNT/Gd,N,S-TiO\(_2\) (3.0% Gd) nanocomposite. Incorporation of Gd nanoparticles resulted in a slight decrease in the band gap energy of Gd,N,S-TiO\(_2\) (0.6% Gd) compared to N,S-TiO\(_2\), signaling a positive effect of Gd in band gap narrowing. Furthermore the band gap narrowed further upon incorporation of MWCNTs and it then showed a slight decrease with increasing Gd content in the nanocomposites. This is probably due to the formation of more sub-band gap states within the TiO\(_2\) band gap as the amount of Gd\(^{3+}\) increases.

**Table 5.1: Estimated band gap energies of the prepared photocatalysts.**

<table>
<thead>
<tr>
<th>Sample</th>
<th>Absorption edge wavelength (nm)</th>
<th>Estimated band gap energy (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>N,S-TiO(_2)</td>
<td>419.81</td>
<td>2.96</td>
</tr>
<tr>
<td>Gd,N,S-TiO(_2) (0.6% Gd)</td>
<td>433.50</td>
<td>2.86</td>
</tr>
<tr>
<td>MWCNT/Gd,N,S-TiO(_2) (0.2% Gd)</td>
<td>461.35</td>
<td>2.69</td>
</tr>
<tr>
<td>MWCNT/Gd,N,S-TiO(_2) (0.6% Gd)</td>
<td>475.03</td>
<td>2.61</td>
</tr>
<tr>
<td>MWCNT/Gd,N,S-TiO(_2) (1.0% Gd)</td>
<td>480.68</td>
<td>2.58</td>
</tr>
<tr>
<td>MWCNT/Gd,N,S-TiO(_2) (3.0% Gd)</td>
<td>496.78</td>
<td>2.50</td>
</tr>
</tbody>
</table>
5.3.4 X-ray diffraction

X-ray diffraction was employed to study the crystal structure of the prepared photocatalysts. Generally, a more crystalline TiO$_2$ structure is preferred over an amorphous structure for better photocatalytic activity. Figure 5.5 shows the XRD patterns of the prepared materials from which it can be inferred that all the photocatalyst were highly crystalline. The XRD peaks observed at 2θ 25.4, 38.1, 48.3, 54.2, 55.3, 62.9 and 75.4° are characteristic of the anatase phase of titania. These peaks correspond to the (101), (004), (200), (105), (211), (204) and (215) crystal planes, respectively.$^{17,23}$ There were no peaks observed due to Gd$_2$O$_3$ and it had no observable effect on the crystal structure of titania, probably due to its low loading relative to titania. The TiO$_2$ particle size range as calculated from Scherrer equation was between 15 and 22 nm which is in agreement with the TEM measurements (20 nm).

![Figure 5.5: XRD patterns of the prepared photocatalysts.](image_url)
5.3.5 Raman spectroscopy

Raman spectra of the fabricated photocatalysts are shown on Figure 5.6. Notably, the Raman spectrum of N,S-TiO$_2$ is identical to that of Gd,N,S-TiO$_2$, showing peaks around 144, 233, 447, 516 and 613 cm$^{-1}$. These peaks arise from the $E_g$, $E_g$, $B_{1g}$, $A_{1g}$ and $E_g$ modes which are characteristic of the anatase phase of TiO$_2$. This suggests that the anatase phase is the predominant phase which correlates well with the XRD results. In addition to the anatase peaks, the Raman spectra of the composite photocatalysts showed peaks around 1314 cm$^{-1}$ and 1603 cm$^{-1}$, corresponding to the D-band and G-band of the MWCNTs. The appearance of these peaks suggests the formation of the composite photocatalyst. Furthermore, the anatase peaks in the composite photocatalyst are shifted which may be attributed to close interaction between titania and the MWCNTs.

Figure 5.6: Raman spectra of the fabricated photocatalysts.
5.4 Photocatalytic degradation studies

The prepared nanocomposites were evaluated for the photocatalytic degradation of the Diazo dye naphthol blue black (NBB) under simulated solar light. Moreover, N,S-TiO$_2$ and Gd,N,S-TiO$_2$ (0.6% Gd) were evaluated for the degradation of NBB and were used as controls. First order kinetics was employed to determine the photocatalytic degradation rates of the different photocatalysts according to Equation 4.1.

Generally the photocatalytic activity of the photocatalysts increased from N,S-TiO$_2$, Gd,N,S-TiO$_2$ (0.6% Gd), MWCNT/Gd,N,S-TiO$_2$ (0.2% Gd), MWCNT/Gd,N,S-TiO$_2$ (0.6% Gd) and then decreased for MWCNT/Gd,N,S-TiO$_2$ (1.0% Gd) and MWCNT/Gd,N,S-TiO$_2$ (3.0% Gd) (Figure 5.7a), reaching maximum degradation of 62.3%, 77.5%, 83.8%, 95.7%, 75.2% and 69.6%, respectively. From first order kinetics (Figure 5.7b) the photodegradation rate constants were found to be 4.5 x 10$^{-3}$ min$^{-1}$, 6.6 x 10$^{-3}$ min$^{-1}$, 8.8 x 10$^{-3}$ min$^{-1}$, 1.5 x 10$^{-2}$ min$^{-1}$, 6.1 x 10$^{-3}$ min$^{-1}$ and 5.5 x 10$^{-3}$ min$^{-1}$ for N,S-TiO$_2$, Gd,N,S-TiO$_2$ (0.6% Gd), MWCNT/Gd,N,S-TiO$_2$ (0.2% Gd), MWCNT/Gd,N,S-TiO$_2$ (0.6% Gd), MWCNT/Gd,N,S-TiO$_2$ (1.0% Gd) and MWCNT/Gd,N,S-TiO$_2$ (3.0% Gd), respectively.

The superior performance of Gd,N,S-TiO$_2$ (0.6% Gd) compared to N,S-TiO$_2$ may be explained in terms of the combined effect of the improved solar light harvesting and charge separation.$^{17,25}$ In N,S-TiO$_2$, band gap narrowing (2.96 eV) was achieved through co-doping with N and S leading to absorption in the visible light region, however, insufficient charge separation, results in recombination of the electron/hole pairs. This lowers the quantum yield of the photocatalyst. Therefore, the incorporation of Gd into the N,S-TiO$_2$ matrix did not only contribute to band gap narrowing (2.86 eV) but also improve charge separation due to the remarkable electron scavenging properties of Gd.$^9$ Moreover, Gd may also aid in concentrating the dye species on to the surface of the photocatalyst.$^{26}$ The pollutant-photocatalyst interaction is essential since photocatalysis is a surface process which requires the pollutant to be on the surface of the photocatalyst for effective degradation.
Incorporation of the MWCNTs improved the photocatalytic activity of the nanocomposites which is attributed to the synergistic effect of the MWCNTs and the tridoped titania. The MWCNTs improved visible light absorption of the photocatalyst (Figure 5.4) which increases the generation of the oxidising species and results in higher degradation of NBB. Moreover, the MWCNTs aid in charge separation and transportation which lowers the rate of charge recombination and improved the degradation of the dye molecules.\textsuperscript{27,28} Furthermore, the inclusion of the MWCNTs improved the interaction between the nanocomposites and the dye molecules which ensure contact between the dye and the photocatalyst for degradation. Notably, the photocatalytic activity of the samples containing 1.0% Gd and 3.0% Gd declined and this decline may be explained in terms of the role of the Gd nanoparticles as electron scavengers. Generally an increase in the amount of Gd\textsuperscript{3+} will increase charge separation and the photocatalytic activity of the nanocomposite; however, this is only applicable until an optimum doping level is reached. Beyond the optimum doping level, the Gd nanoparticles may act as charge recombination centers thereby lowering the photocatalytic activity of the nanocomposite.\textsuperscript{9} According to the obtained results the optimum Gd doping level is around 0.6% but less than 1.0%. This observation emphasised the importance of the collective contribution of efficient visible light absorption and charge separation and transportation for better degradation results.
Figure 5.7: (a) Photocatalytic degradation of NBB under simulated solar light and (b) kinetics for NBB degradation under simulated solar light.
The UV-Vis spectra of NBB (Figure 5.8a) were recorded to monitor the changes during photocatalysis. Two major peaks are observed at 320 nm and 618 nm which are characteristic of the aromatic structure and the azo groups of NBB, respectively. During the photodegradation experiments, both peaks decreased gradually with increasing irradiation time. This was coupled with a gradual decolourisation of the blue NBB solution as shown in Figure 5.8b. The gradual smoothing of both peaks indicates that both the aromatic rings and the azo groups of NBB are cleaved during photocatalysis. From the UV-Vis absorption spectra, NBB was completely decolourised or degraded after 270 minutes which is evident from the disappearance of both peaks (Figure 5.8a).

Figure 5.8: (a) UV-vis absorption spectra of NBB during photocatalysis and (b) Fading of the blue colour of NBB with increasing irradiation time.
5.4.1 Radical scavenging experiments

Addition of benzoquinone (10 mL, $5 \times 10^{-2}$ M) (superoxide radical scavenger) and 2-propanol (10 mL, $5 \times 10^{-2}$ M) (hydroxyl radical scavenger) in the NBB solution during photocatalysis resulted in the decrease in the photocatalytic activity of MWCNT/Gd,N,S-TiO$_2$ (0.6% Gd). In the presence of benzoquinone (Figure 5.9) the rate of NBB degradation dropped to $7 \times 10^{-3}$ min$^{-1}$ which is about 1.8 times slower than in the absence of benzoquinone ($1.33 \times 10^{-2}$ min$^{-1}$). This corresponds to a maximum degradation of 77.8% which equals a 16.5% decrease (Table 5.2) compared to when benzoquinone is not added (94.3%). Similarly, the addition of 2-propanol slowed the degradation rate to $4.9 \times 10^{-3}$ min$^{-1}$ which is about 2.7 times slower compared to when 2-propanol was not added. This accounts for a maximum percentage degradation of 66.8% which shows a 27.5% decrease. The obtained results confirm that both the superoxide and hydroxyl radicals are the active species during dye degradation. This means that the degradation of the dye molecules is dependent on the availability of these active species. Addition of the radical scavenger consumes some of the active species and less will be available for the degradation of the dye molecules, hence the lower degradation efficiency.

![Figure 5.9: Kinetics for NBB degradation in the presence of radical scavengers.](image-url)
Table 5.2: Degradation rates and percentage degradation of NBB in the presence of radical scavengers.

<table>
<thead>
<tr>
<th>Sample</th>
<th>k (min⁻¹)</th>
<th>R²</th>
<th>Degradation (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MWCNT/Gd,N,S-TiO₂ (0.6 % Gd)</td>
<td>1.33 x 10⁻²</td>
<td>0.963</td>
<td>94.3</td>
</tr>
<tr>
<td>MWCNT/Gd,N,S-TiO₂ (0.6 % Gd) + 2-propanol</td>
<td>4.9 x 10⁻³</td>
<td>0.945</td>
<td>66.8</td>
</tr>
<tr>
<td>MWCNT/Gd,N,S-TiO₂ (0.6 % Gd) + Benzoquinone</td>
<td>7.3 x 10⁻³</td>
<td>0.992</td>
<td>77.8</td>
</tr>
</tbody>
</table>

5.4.2 Total organic carbon analysis

Complete mineralisation of the dye molecules is always a major concern in photocatalysis because partial degradation may result in the formation of even more toxic intermediates. Therefore, it is always desirable to degrade the dye molecules into smaller, simple and less toxic species such as carbon dioxide, water and ionic species. Total organic carbon (TOC) analysis which measures the amount of carbon chemically bound in organic species was employed to examine the extent of complete mineralisation of NBB by MWCNT/Gd,N,S-TiO₂ (0.6% Gd). The results obtained are presented in Figure 5.10, from which it can be established that a maximum TOC removal of 78.0% was attained. This signifies a fairly high degree of complete mineralisation of NBB which is essential for efficient dye pollution treatment.
Figure 5.10: TOC removal by MWCNT/Gd,N,S-TiO$_2$ (0.6% Gd).

5.4.3 Photocatalyst recycling

The photocatalyst was then evaluated for its stability towards recycling where it was reused five times during which it was washed with deionised water and ethanol after each experiment and dried before re-use. The nanocomposite displayed sufficient stability attaining a maximum NBB removal of 91.8% after five cycles (Figure 5.11). The decline in the degradation efficiency could be attributed to, amongst other things, the loss of the photocatalyst during the recovery and washing steps.
Chapter 5: Photocatalytic degradation of the diazo dye naphthol blue black in water using MWCNT/Gd, N, S-TiO$_2$ nanocomposites under simulated solar light

5.5 Proposed photocatalytic degradation mechanism

Several possible photocatalytic degradation routes may be put forward to account for the degradation of NBB under visible light irradiation. However, the actual degradation is a combination of improved adsorption of dye molecules onto the catalyst surface, charge separation and transportation, visible light absorption, generation of sufficient amounts of the oxidising species and improved surface area of the photocatalyst. This results from the synergistic effect of the various components of the nanocomposite. Figure 5.12 outlines some of the possible mechanisms through which the oxidising species (hydroxyl and superoxide radicals) may be formed to oxidise the NBB molecules. In mechanism 1, the doping of TiO$_2$ with nitrogen introduces sub-band gap states within the TiO$_2$ band gap, resulting in band gap narrowing. This allows for the absorption of visible light. Electrons may be excited by visible light from these newly formed sub-band gap states into the conduction band of TiO$_2$ where they are captured by adsorbed oxygen to form the superoxide radical ($\text{O}_2^{-}$). The superoxide radical may then oxidise NBB molecules adsorbed on the surface of the photocatalyst to form

**Figure 5.11**: Recyclability studies of MWCNT/Gd,N,S-TiO$_2$ (0.6% Gd).

**Figure 5.12**: Outlines some of the possible mechanisms through which the oxidising species (hydroxyl and superoxide radicals) may be formed to oxidise the NBB molecules. In mechanism 1, the doping of TiO$_2$ with nitrogen introduces sub-band gap states within the TiO$_2$ band gap, resulting in band gap narrowing. This allows for the absorption of visible light. Electrons may be excited by visible light from these newly formed sub-band gap states into the conduction band of TiO$_2$ where they are captured by adsorbed oxygen to form the superoxide radical ($\text{O}_2^{-}$). The superoxide radical may then oxidise NBB molecules adsorbed on the surface of the photocatalyst to form...
smaller and simpler molecules. Moreover, the incorporated MWCNTs may act as a source of carbon doping which also introduces new sub-band gap states within the TiO$_2$ band gap.$^{31}$ This allows for excitation of electrons by visible light from the new sub-band gap states into the conduction band of TiO$_2$ where they can be captured by adsorbed oxygen to form the superoxide radical (mechanism 1). Alternatively, the electrons in the conduction band may be captured by Gd$^{3+}$ on the surface of TiO$_2$ where they can accumulate and react with adsorbed oxygen to form the oxidising species. The half-filled 4$f$ electronic configuration gives Gd excellent electron trapping and detrapping properties which are essential for charge separation and superoxide radical formation.$^9$

The substitution of oxygen by sulphur during doping of TiO$_2$ is less likely due to the differences in ionic radius of O$^{2-}$ (1.22 Å) and S$^{2-}$ (1.7 Å) and due to bond energies of the Ti-S and Ti-O bonds.$^{32}$ However, cationic sulphur (S$^{4+}$ and S$^{6+}$) may substitute Ti$^{4+}$ in the TiO$_2$ framework resulting in the introduction of a new sub-band gap level below the TiO$_2$ conduction band.$^{32}$ Consequently, under visible light irradiation electrons are excited from the nitrogen and carbon sub-band gap states into the upper sulphur level where they can be captured by adsorbed oxygen (mechanism 2). Similarly, electrons can also be excited by visible light from the valence band of TiO$_2$ into the new sulphur levels (mechanism 3). This would leave positive holes in the valence band which may react with water or hydroxide ions to form the hydroxyl radical. The hydroxyl radical is an extremely powerful oxidising species which together with the superoxide radical are responsible for the degradation of NBB molecules.

Incorporation of Gd$^{3+}$ within the TiO$_2$ framework leads to the introduction of additional electron trap levels within the TiO$_2$ band gap created by the empty 4$f$ orbitals of Gd. These sub-band gap levels lie below the band gap edge of the conduction band of TiO$_2$. As a result, electrons are excited by visible light the nitrogen and carbon levels into the empty 4$f$ orbitals of Gd$^{3+}$ (mechanism 4). Moreover, electrons can also be promoted from the valence band of TiO$_2$ into the 4$f$ levels, leaving positive holes in the valence band (mechanism 5). This would lead to the formation hydroxyl radicals upon reaction with adsorbed water or
hydroxide ions. In another possible mechanism, the MWCNTs can act as a visible light sensitisier.\textsuperscript{20} The MWCNTs may absorb visible light resulting in the excitation of electrons and these electrons may be injected into the conduction band of TiO\textsubscript{2} (mechanism 6). These electrons may be trapped by adsorbed oxygen to form the oxidising species. The positive MWCNTs skeleton may trap electrons from the valence band of TiO\textsubscript{2}, leaving positive holes which may trap water or hydroxide ions to form the hydroxyl radicals. Another possible degradation mechanism (not shown in Figure 5.12) would be dye sensitisation. The NBB molecules would be adsorbed onto the surface of the photocatalyst. Upon visible light irradiation, the dye absorbs visible light and electrons are excited and can be transferred into the conduction band of TiO\textsubscript{2}. The oxidising species would then be generated upon reaction with water.

![Figure 5.12: Proposed mechanism for the photocatalytic degradation of NBB.](image)

Figure 5.12: Proposed mechanism for the photocatalytic degradation of NBB.
5.6 Chapter summary

Tri-doped titania was successfully decorated on MWCNTs to fabricate a visible light driven nanocomposite photocatalyst via a simple sol-gel method. The prepared nanocomposites displayed superior photocatalytic activity towards NBB compared to codoped TiO$_2$ and tridoped TiO$_2$ without the MWCNTs. This could be accounted for in terms of the synergistic effects of the various components of the nanocomposites which result to improved visible light absorption, charge separation and transportation, dye adsorption and the improved generation of the oxidising species. The photocatalytic degradation of NBB significantly dropped in the presence of radical scavengers, highlighting the role of the superoxide and hydroxyl radicals as the active species. Total organic carbon analysis revealed a higher degree of complete mineralisation of NBB which minimise the possibility of forming toxic degradation products.
5.7 References


CHAPTER 6:
GADOLINIUM OXIDE DECORATED MULTIWALLED CARBON
NANOTUBE/TRIDOPED TITANIA NANOCOMPOSITES FOR IMPROVED DYE
DEGRADATION

*Contents of this chapter have been prepared for submission in Mamba G, Mbianda XY, Mishra AK. J Rare Earth. 2015.

This chapter is an extension of Chapters 4 and 5, it sought to exploit the good charge separation observed in MWCNT-Gd/TiO$_2$ nanocomposites and the improved visible light absorption shown by the MWCNT/Gd,N,S-TiO$_2$ nanocomposites. In this chapter Gd,N,S-TiO$_2$, Nd,N,S-TiO$_2$ and Eu,N,S-TiO$_2$ were coupled with gadolinium oxide nanoparticle decorated MWCNTs to form MWCNT-Gd/Gd,N,S-TiO$_2$, MWCNT-Gd/Nd,N,S-TiO$_2$ and MWCNT-Gd/Eu,N,S-TiO$_2$, respectively. Photocatalytic properties of the prepared materials were evaluated for the degradation of acid blue 74 (AB74) in aqueous solutions under simulated solar irradiation. The effect of the different rare earth metal ions incorporated in the tridoped titania was investigated in terms of the overall photocatalytic activity of the nanocomposites.

6.1 Introduction

Photocatalysis has been identified as a potential solution towards treatment of industrial effluents laden with organic compounds and the general decontamination of the environment. The release of industrial compounds such as dyestuffs into the environment leads to undesirable health, aesthetic and environmental effects.$^1$ Semiconductor photocatalysis presents a number of advantages over the conventional tools for organic pollution remediation. Such merits include its versatility in terms of application i.e. photocatalysis can be used for inactivation of micro-organisms such as bacteria$^2$, oxidation/reduction of inorganic species$^{3,4}$, organic compounds$^5$ and can be utilised in the treatment of the pollutants both in aqueous and gaseous form.$^6,7$ Moreover, photocatalysis has
the potential to completely mineralize organic pollutants into carbon dioxide, water and inorganic ions, thereby minimizing sludge formation which often poses further disposal challenges in processes such as adsorption and coagulation. The immunity of photocatalysis towards the toxic nature of some of the organic compounds and the absence of fouling are other advantages of the process over biological and membrane processes.

However, the search for an energy efficient photocatalyst with high photocatalytic activity remains a research challenge. Titania, which is regarded as the benchmark for semiconductor photocatalysis suffer from the inability to absorb visible light which rules out the possibility of utilizing sunlight as a source of energy and curb on the expensive energy requirements of the process. In addition to the energy problems, pure titania suffer from a high recombination rate of the photogenerated electron/hole pairs which significantly lower its photocatalytic activity. Coupling titania with carbon nanomaterials such as CNTs, GO and rGO has been highlighted as a promising method to improve the photocatalytic activity of titania through enhancing visible light absorption, surface area and charge separation and transportation. Strong and intimate interface between the carbon nanomaterial and titania is a prerequisite to ensure the exploitation of the combined properties of the materials. Previous work by Mamba et al. showed that decorating MWCNTs with gadolinium oxide nanoparticles prior to incorporation into titania matrix significantly improved the photocatalytic activity of the nanocomposite compared to MWCNT/TiO$_2$ nanocomposite. This was mainly credited to improved charge separation by the gadolinium oxide nanoparticles at the interface of the two materials which function as a charge transfer channel. Furthermore, it was shown that incorporating MWCNTs, SWCNTs and rGO in lanthanide, nitrogen and sulphur tridoped titania significantly enhance the photocatalytic activity of the nanocomposite compared to MWCNT/TiO$_2$, commercial TiO$_2$ and the tridoped titania. This enhancement was credited to improved visible light absorption as observed from UV-Vis, charge separation and transportation.
6.2 Experimental section

6.2.1 Materials

The materials and reagents used in this work are listed in Chapter 3, Section 3.2.

6.2.2 Preparation of MWCNT-Gd

Decoration of MWCNTs with gadolinium oxide nanoparticles proceeded as outlined in Chapter 3, Section 3.3.1.1. The loading of gadolinium ion nanoparticles was about 3.0% in relation to the MWCNTs.

6.2.3 Preparation of MWCNT-Gd/Rare earth, N,S-TiO₂ nanocomposites

The procedure employed during preparation of the nanocomposite photocatalyst was adopted from Chapter 3, Section 3.3.4. MWCNT/TiO₂, MWCNT/Gd,N,S-TiO₂ and MWCNT-Gd/TiO₂ were prepared from the corresponding starting materials following the same procedure.

6.2.4 Characterisation techniques

A series of characterisation tools were employed ascertain formation of the intended nanocomposite photocatalysts as outlined in Chapter 3, Section 3.4. Scanning electron microscopy studies were done on a ZEISS AURIGA Focussed Ion Beam-Scanning Electron Microscope (FIB-SEM) (Germany) coupled with an energy dispersive x-ray analyser (EDS). The samples were mounted on the sample holder using a double sided carbon tape and coated with carbon before analysis. X-ray diffraction patterns of the photocatalysts were obtained from a Philips PANanalytical X’pert diffractometer (Netherlands) operated at 40 KV and 40 mA. A Cuα radiation beam with an excitation wavelength of 0.15406 nm was used as an x-ray source. A nickel filter (0.02 mm) was fitted on the diffracted beam optics to filter off x-rays from tungsten. A beam knife, beam musk (20 mm), solar slits (0.04 rad), anti-scatter slit (4°) were used. Powdered samples were loaded
into the XRD sample holders and measurements were done from 5° to 90° (2θ values). Crystallite size calculations were performed using Equation 3.1.

### 6.2.5 Evaluation of the photocatalytic properties of the nanocomposites

Evaluation of the photocatalytic activity of the prepared materials is detailed in Chapter 3, Section 3.5. UV-Vis photometric measurements were recorded at 608 nm which is the wavelength of maximum absorption for AB74. TOC analysis was carried out according to the procedure outlined in Chapter 3, Section 3.5.1.

#### 6.2.5.1 Hydroxyl radical detection

Terephthalic acid solution (6 mM) was used as a diagnostic tool to probe the production of the hydroxyl radicals during photocatalytic degradation of AB74. The terephthalic acid solution (instead of AB74 solution) was mixed with MWCNT-Gd/Gd,N,S-TiO$_2$ (0.10 g) and treated in a similar manner as the dye solution. Aliquots were drawn at 30 mins intervals and the reaction was run for 2 hrs. Samples were analysed in a quartz cuvette using a PerkinElmer LS 45 fluorescence spectrometer with a xenon flash lamp. The samples were excited at 315 nm and the emission was measured from 200 to 600 nm.

### 6.3 Results and discussion

#### 6.3.1 Morphological properties

TEM images of the MWCNT-Gd (Figure 6.1a-6.1d) show that the MWCNTs were indeed decorated with Gd$^{3+}$ nanoparticles of relatively similar shape (nearly spherical) and size (less than 5 nm from TEM measurements, Figure 6.1d). The gadolinium nanoparticles show a relatively uniform distribution on the MWCNTs surfaces with fewer aggregations observed (Figure 6.1a-6.1c). This is desirable for fabrication of a photocatalyst to ensure a nearly uniform structural integrity. The thermal decomposition of the gadolinium nitrate most likely formed gadolinium oxide nanoparticles on the surfaces of the MWCNTs.
Figure 6.1: TEM images of MWCNT-Gd showing relatively uniform distribution (a-c) and sizes (d).

EDS (Figure 6.2) was employed to provide information about the qualitative elemental composition of the prepared material and the elements carbon, oxygen and gadolinium were revealed as present. The intense carbon peak originates from the MWCNTs which form the bulk of the sample while the presence of gadolinium and oxygen suggest that Gd nanoparticles are in the form of gadolinium oxide nanoparticles.
Chapter 6: Gadolinium oxide decorated multiwalled carbon nanotube/tridoped titania nanocomposites for improved dye degradation

Figure 6.2: EDS spectrum of MWCNT-Gd.

Formation of the tridoped titania/MWCNT-Gd nanocomposites was confirmed by SEM images which show the MWCNT-Gd covered with the titania (red arrows, Figure 6.3a and 6.3b). The MWCNT-Gd were embedded within the tridoped titania matrix and does not show any aggregation. TEM images (Figure 6.3c and 6.3d) further confirm the presence of the MWCNT-Gd (red circles showing rare earth nanoparticles on MWCNTs) within the titania matrix and further show that the coverage of MWCNT-Gd by the titania was not uniform. All three nanocomposite photocatalyst showed similar surface morphology with titania nanoparticle sizes of around 25 nm.
The presence of the elements carbon, sulphur, oxygen, gadolinium and titanium was revealed by EDX analysis of the MWCNT-Gd/Gd,N,S-TiO$_2$ nanocomposite (Figure 6.4) suggesting the incorporation of these elements in the nanocomposite photocatalyst. Similar EDX spectra were observed for MWCNT-Gd/Nd,N,S-TiO$_2$ and MWCNT-Gd/Eu,N,S-TiO$_2$, the difference being the additional presence of Nd.
and Eu, respectively, confirming the incorporation of these species in the nanocomposites.

Figure 6.4: EDS spectrum of MWCNT-Gd/Gd,N,S-TiO$_2$.

6.3.2 FT-IR analysis

The FT-IR spectra of MWCNT/TiO$_2$ and MWCNT-Gd/TiO$_2$ (Figure 6.5) are similar, both showing a broad peak around 3400 cm$^{-1}$ and another peak around 1600 cm$^{-1}$ corresponding to the OH stretching vibration and bending vibration of adsorbed water molecules, respectively. Another broad peak appeared between 608 cm$^{-1}$ and 828 cm$^{-1}$ which could be linked to the Ti-O, O-Ti-O bonds. The presence of Ti-O-C and Ti-C bonds could be another possible contribution to the appearance of this broad peak. Similarly, the MWCNT/Gd,N,S-TiO$_2$ and all the MWCNT-Gd/tridoped titania nanocomposites spectra showed these peaks but the OH peaks are much broader and intense which may suggest an improvement in adsorption of water which is a desirable property. Furthermore, the Ti-O peak observed in MWCNT/TiO$_2$ and MWCNT-Gd/TiO$_2$ appeared broader in the other nanocomposites, possibly due to the combined contribution of Ti-O, O-Ti-O, Ti-N, N-Ti-N, Ti-O-N, Ti-O-S, Ti-C, Ti-O-C and Ti-O-Gd/Ti-O-Nd/Ti-O-Eu. Two peaks located at 1402 cm$^{-1}$ and 3208 cm$^{-1}$ were also observed in MWCNT/Gd,N,S-TiO$_2$ and all the MWCNT-Gd/tridoped titania nanocomposites, corresponding to deformation and stretching mode of ammonium ions,
respectively.\textsuperscript{21} The presence of these peaks confirmed the incorporation of nitrogenous species in the nanocomposite. Sulphur species were also detected by FT-IR as indicated by the peaks at 1132 cm\textsuperscript{-1} and 1068 cm\textsuperscript{-1} corresponding to bidentate SO\textsubscript{4}\textsuperscript{2-} co-ordinated to metals such as Ti\textsuperscript{4+}.\textsuperscript{22}

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure6.5.png}
\caption{FT-IR spectra of the prepared photocatalysts.}
\end{figure}

6.3.3 Optical properties

UV-Vis was used to probe the optical properties of the prepared nanocomposite photocatalysts and the results obtained are presented in Figure 6.6. MWCNT/TiO\textsubscript{2} did not show much improvement in the visible light absorption behaviour probably due to the small amount of the MWCNT incorporated (0.5%). Decoration of the Gd\textsuperscript{3+} nanoparticles on the surface of the MWCNT prior to incorporation into titania resulted in a slight red shift in the absorption edge of titania into the visible light region due to the possible contribution of Gd\textsuperscript{3+} towards visible light absorption. A significant improvement in visible light absorption was observed after coupling the
tridoped titania and MWCNT-Gd. This phenomenon can be explained in terms of the collaborative effect of tridoping and incorporation of the MWCNT-Gd in titania. Tridoping titania with rare earth ions, nitrogen and sulphur introduces sub-band gap states or impurity states within the band gap of TiO$_2$. Subsequently, electrons may be excited by visible light from the sub-band gap states and the valence band of TiO$_2$ into the impurity states and conduction band of TiO$_2$, respectively.$^{23}$ Incorporation of the MWCNT-Gd also contributes towards visible light absorption in a sensitisation mechanism.

![Figure 6.6: UV-Vis diffuse reflectance spectra of the different photocatalysts.](image)

**Table 6.1** shows the calculated band gap energies of the various photocatalysts from which the effect of coupling MWCNT/MWCNT-Gd and tridoped titania was evident from the smaller band gap values compared to MWCNT/TiO$_2$ and MWCNT-Gd/TiO$_2$. A smaller band gap is desirable for photocatalytic applications under visible light irradiation. MWCNT/TiO$_2$ showed the largest band gap of
3.14 eV while MWCNT-Gd/Nd,N,S-TiO₂ showed the smallest band gap of 2.86 eV. There was no significant difference in band gap energies between the three MWCNT-Gd/tridoped titania nanocomposites.

**Table 6.1: Calculated band gap energies of the prepared photocatalysts.**

<table>
<thead>
<tr>
<th>Sample</th>
<th>Absorption edge wavelength (nm)</th>
<th>Calculated band gap energy (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MWCNT/TiO₂</td>
<td>395</td>
<td>3.14</td>
</tr>
<tr>
<td>MWCNT-Gd/TiO₂</td>
<td>406</td>
<td>3.05</td>
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<tr>
<td>MWCNT/Gd,N,S-TiO₂</td>
<td>422</td>
<td>2.94</td>
</tr>
<tr>
<td>MWCNT-Gd/Nd,N,S-TiO₂</td>
<td>433</td>
<td>2.86</td>
</tr>
<tr>
<td>MWCNT-Gd/Eu,N,S-TiO₂</td>
<td>429</td>
<td>2.89</td>
</tr>
<tr>
<td>MWCNT-Gd/Gd,N,S-TiO₂</td>
<td>415</td>
<td>2.99</td>
</tr>
</tbody>
</table>

**6.3.4 X-ray diffraction analysis**

X-ray diffraction was employed to determine the phase composition of TiO₂ in the nanocomposites, determine the crystallite size and the crystallinity of the prepared photocatalysts. The XRD patterns (Figure 6.7) revealed that all the prepared photocatalysts were crystalline in nature. Crystallite size calculations (Table 6.2) using Scherrer equation showed that the titania nanoparticles were of varying sizes, ranging from 12.11 nm to 23.12 nm and these values are comparable to the TEM measurements (25 nm). The MWCNT-Gd/rare earth nanocomposite had similar crystallite sizes of about 23.12 nm which could suggest that the nature of the rare earth ion had very little or no influence on the crystallite size. All the XRD patterns of the prepared materials showed peaks around 25.3°, 37.9°, 48.0°, 54.0°, 54.9°, 62.7, 68.8°, 70.2° and 75.1° (2 theta values) which can be matched with the (101), (004), (200), (105), (211), (204), (110), (220) and (215) crystal planes of anatase TiO₂. These were the only peaks observed in the XRD patterns which mean that titania was exclusively anatase or predominantly anatase. Neither the tridoping nor the incorporation of the MWCNT/MWCNT-Gd
had a significant influence on the crystalline nature as well as the phase composition of titania in the prepared photocatalysts.

Figure 6.7: XRD patterns of the different photocatalysts prepared.

Table 6.2: Crystallite size values from Scherrer equation.

<table>
<thead>
<tr>
<th>Samples</th>
<th>Crystallite size (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MWCNT/TiO₂</td>
<td>14.96</td>
</tr>
<tr>
<td>MWCNT-Gd/TiO₂</td>
<td>15.89</td>
</tr>
<tr>
<td>MWCNT/Gd,N,S-TiO₂</td>
<td>12.11</td>
</tr>
<tr>
<td>MWCNT-Gd/Nd,N,S-TiO₂</td>
<td>23.12</td>
</tr>
<tr>
<td>MWCNT-Gd/Eu,N,S-TiO₂</td>
<td>23.12</td>
</tr>
<tr>
<td>MWCNT-Gd/Gd,N,S-TiO₂</td>
<td>23.12</td>
</tr>
</tbody>
</table>
6.4 Photocatalytic degradation studies

The prepared photocatalysts were evaluated for the degradation of AB74 under simulated solar light irradiation and the results obtained are presented in Figure 6.8. MWCNT-Gd/Gd,N,S-TiO₂ showed the highest photocatalytic activity, reaching a degradation efficiency of 100% after 150 mins (Table 6.3) while MWCNT/TiO₂ reached 83.7% after the same amount of irradiation time. MWCNT/Gd,N,S-TiO₂, MWCNT-Gd/Nd,N,S-TiO₂ and MWCNT-Gd/Eu,N,S-TiO₂ reached 100% degradation after 180 mins of irradiation while MWCNT/TiO₂ and MWCNT-Gd/TiO₂ recorded degradation efficiencies of 90.5% and 95.1%, respectively, for the same irradiation time. The MWCNT-Gd/tridoped titania nanocomposites displayed significantly superior photocatalytic activity compared to the MWCNT/TiO₂, MWCNT-Gd/TiO₂ and MWCNT/Gd,N,S-TiO₂. This improvement in performance can be credited to the collective contribution of the various components of the nanocomposites which resulted in good visible light absorption, numerous routes for production of oxidising species (hydroxyl and superoxide radicals), charge separation and transportation.

Figure 6.8: Degradation of AB74 by the prepared photocatalysts.
Tridoping titania with nitrogen, sulphur and the rare earth ions improved visible light absorption and charge separation through the formation of sub-band gap states or impurity levels within the band gap of TiO$_2$ as shown in the proposed synergy mechanism in Figure 6.9. This led to band gap narrowing and visible light absorption as evident from the UV-Vis diffuse reflectance spectra (Figure 6.6) and band gap calculations (Table 6.1). These sub-band gap states can either receive electrons excited by visible light from the valence band of TiO$_2$ (act as electron sinks) or electrons can be excited from these states by visible light into the conduction band of TiO$_2$ (Figure 6.9).\textsuperscript{25,26} Incorporation of the MWCNT-Gd into the tridoped titania matrix aid in improving visible light absorption as well as charge separation and transportation. The Gd$^{3+}$ ions on the surface of the MWCNTs functioned as charge transfer channel between MWCNTs and TiO$_2$, thereby improving their interface and the Gd$^{3+}$ ions on the surface of TiO$_2$ facilitate another route through which electrons can be scavenged and suppress charge recombination. Furthermore, hybridising the MWCNT-Gd and tridoped titania provided numerous routes through which electrons could be excited by visible light and improved the formation of the radical species responsible for dye degradation (Figure 6.9)
Among the three MWCNT-Gd/tridoped titania composite photocatalyst, MWCNT-Gd/Gd,N,S-TiO$_2$ displayed the highest activity towards AB74 possibly due to the good electron trapping and detrapping properties of Gd$^{3+}$. The half-filled electronic configuration Gd$^{3+}$ ($4f^7$) is very stable and gets destabilised when electrons are trapped resulting to a quick loss of the electrons and the stable configuration restored. This phenomenon leads to efficient electron scavenging and improved charge separation.
Chapter 6: Gadolinium oxide decorated multiwalled carbon nanotube/tridoped titania nanocomposites for improved dye degradation

Figure 6.10: Kinetics for the degradation of AB74.

Table 6.3: Degradation efficiency after 150 mins and AB74 degradation rate constants by the photocatalysts.

<table>
<thead>
<tr>
<th>Samples</th>
<th>Degradation after 150 mins (%)</th>
<th>Degradation rate (k x 10^{-2}) (min^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>MWCNT/TiO₂</td>
<td>83.7</td>
<td>1.34</td>
</tr>
<tr>
<td>MWCNT-Gd/TiO₂</td>
<td>95.1</td>
<td>1.60</td>
</tr>
<tr>
<td>MWCNT/Gd,N,S-TiO₂</td>
<td>93.9</td>
<td>1.71</td>
</tr>
<tr>
<td>MWCNT-Gd/Nd,N,S-TiO₂</td>
<td>95.0</td>
<td>1.88</td>
</tr>
<tr>
<td>MWCNT-Gd/Eu,N,S-TiO₂</td>
<td>98.8</td>
<td>2.79</td>
</tr>
<tr>
<td>MWCNT-Gd/Gd,N,S-TiO₂</td>
<td>100</td>
<td>4.59</td>
</tr>
</tbody>
</table>
First order kinetics was employed to investigate the rate of degradation of AB74 by the different photocatalysts and the results are presented in Figure 6.10. MWCNT-Gd/Gd,N,S-TiO$_2$ showed the highest degradation rate and reached a maximum of $4.59 \times 10^{-2}$ min$^{-1}$ while the degradation of AB74 was the slowest with a rate constant of $1.34 \times 10^{-2}$ min$^{-1}$ (Table 6.3). All the MWCNT-Gd/tridoped titania showed higher degradation rates than MWCNT/TiO$_2$, MWCNT-Gd/TiO$_2$ and MWCNT/Gd,N,S-TiO$_2$ which signifies the importance of the combination of good charge separation and transportation and visible light absorption. UV-Vis spectra of AB74 (Figure 6.11a) was recorded to monitor changes in the absorption spectra of AB74 with increasing irradiation time. The major peak positioned around 600 nm decreased gradually with increasing irradiation time until it eventually disappears after 180 mins when using MWCNT-Gd/Eu,N,S-TiO$_2$ as the photocatalyst. This was coupled with the simultaneous decolourisation of the blue colour of AB74 until a clear solution was formed (Figure 6.11b).
6.4.1 Detection of the hydroxyl radicals

In the presence of hydroxyl radicals, terephthalic acid reacts almost exclusively to form 2-hydroxyterephthalic acid which is highly fluorescent and can be easily detected by PL. The intensity of the 2-hydroxyterephthalic peak around 420 nm is proportional to the amount of 2-hydroxyterephthalic acid present in solution.
which depends on the amount of hydroxyl radicals available in solution. Figure 6.12 shows the changes in the PL spectra with increasing irradiation time. At the beginning of the reaction (after the dark experiment but before irradiation) at time 0 mins, there was no PL peak observed which means that there was no hydroxyl radical produced hence no 2-hydroxyterephthalic acid formed. After 30 mins of irradiation, an emission peak appeared at 420 nm which is due to the presence of 2-hydroxyterephthalic acid and this peak increased in intensity with increasing irradiation time due to the increasing concentration of 2-hydroxyterephthalic acid. This observation proves that there was production of hydroxyl radicals on the surface of the photocatalyst upon irradiation with simulated solar light.

Figure 6.12: Changes in the PL spectra of terephthalic acid solution with increasing irradiation time using MWCNT-Gd/Gd,N,S-TiO$_2$ as the catalyst.
6.4.2 Total organic carbon analysis

One of the major challenges of photocatalysis is ensuring complete mineralisation of organic pollutants into carbon dioxide, water and inorganic ions. Partial degradation of organic pollutants such as azo dyes could lead to aromatic amines which are more toxic than the dyes itself. Consequently, TOC was employed to gain an insight into the degree of degradation of AB74 by MWCNT-Gd/Gd,N,S-TiO$_2$. A maximum TOC removal of 67.7% (Figure 6.13) was recorded which suggest that most of AB74 was completely mineralized but there was still some organic species remaining in solution. These could possibly require extended degradation time in order to reach complete mineralisation.

![Figure 6.13: Total organic carbon removal by MWCNT-Gd/Gd,N,S-TiO$_2$.](image-url)
6.5 Chapter summary

Gadolinium oxide nanoparticles were uniformly decorated on MWCNTs prior to incorporation into rare earth ion, nitrogen and sulphur tridoped titania via a sol-gel method. Coupling MWCNT-Gd and the tridoped titania resulted in nanocomposite photocatalysts with better visible light absorption and photocatalytic activity than MWCNT/TiO$_2$ and MWCNT-Gd/TiO$_2$. The different rare earth ions doped in TiO$_2$ show varying effects in the photocatalytic activity, with the Gd$^{3+}$ doped sample showing the highest photocatalytic activity due to the half-filled electronic configuration of Gd$^{3+}$ rendering it a good electron scavenger. Using PL, the production of hydroxyl radicals was confirmed through the use of terephthalic acid as a probing molecule. TOC analysis revealed that a larger portion of AB74 was completely mineralised during degradation, although some still remained in solution.
6.6 References


Chapter 6: Gadolinium oxide decorated multiwalled carbon nanotube/tridoped titania nanocomposites for improved dye degradation


CHAPTER 7:
Nd,N,S-TiO\textsubscript{2} DECORATED ON REDUCED GRAPHENE OXIDE FOR A VISIBLE LIGHT ACTIVE PHOTOCATALYST FOR DYE DEGRADATION: A COMPARISON TO ITS MWCNT/Nd,N,S-TiO\textsubscript{2} ANALOGUE

This work has been published in Mamba G, Mamo MA, Mbianda XY, Mishra AK. Ind. Eng. Chem. Res. 2014;53:14329-14338.

In this chapter we report on the preparation of neodymium, nitrogen and sulphur tridoped titania supported on rGO to yield a composite photocatalyst (rGO/Nd,N,S-TiO\textsubscript{2}). The prepared photocatalyst is anticipated to display improved visible light absorption, improved charge separation and transportation and higher photocatalytic activity. For comparison, Nd,N,S-TiO\textsubscript{2} was decorated on MWCNTs to yield the corresponding composite photocatalyst (MWCNT/Nd,N,S-TiO\textsubscript{2}). Eriochrome black T (EBT) and eosin blue shade (EBS) were utilised to compare the photocatalytic performance of the prepared nanocomposites, both in single and mixed dye solutions. The role of rGO in influencing the photocatalytic activity of the rGO/Nd,N,S-TiO\textsubscript{2} nanocomposite is compared to its MWCNTs analogue.

7.1 Introduction

Incorporation of various carbon nanomaterials such as MWCNTs, SWCNTS, rGO and carbon nanospheres (CNS) into the titania matrix has been found to yield composite materials with improved optical and photocatalytic properties compared to pure titania.\textsuperscript{1,2} The strong and intimate interaction between titania and the carbon nanomaterial enables the exploitation of the combined properties of the carbon nanomaterials and titania.\textsuperscript{3} Therefore, coupling rGO and tridoped titania is anticipated to yield a composite material with improved visible light absorption due to Nd, N and S doping as well as incorporation of rGO, improved charge separation and transportation as a result of rGO and subsequently higher photocatalytic activity. Details on the mechanisms of visible light absorption by multidoped titania and titania/rGO nanocomposites were discussed in Chapter 2.
7.2 Experimental

7.2.1 Materials

Details of the materials and reagents utilised are given in Chapter 3, Section 3.2.

7.2.2 Preparation of the photocatalysts

7.2.2.1 Preparation of rGO

Reduced graphene oxide was prepared following the procedure outlined in Chapter 3, Section 3.3.2.

7.2.2.2 Preparation of MWCNT/Nd,N,S-TiO$_2$ and rGO/Nd,N,S-TiO$_2$

Preparation of the nanocomposite photocatalysts followed the procedure described in Chapter 3, Section 3.3.4. Neodymium, nitrogen and sulphur tridoped titania (Nd,N,S-TiO$_2$) was prepared using the same method without the addition of the carbon nanomaterials and used as a control. Commercial titania (commercial TiO$_2$) (mixture of rutile and anatase) was also used as another control.

7.3 Materials characterisation

A number of microscopic, spectroscopic, crystallographic and surface area analysis tools were used to characterise the prepared photocatalysts following the procedures presented in Chapter 3, Section 3.4.

7.4 Photocatalytic application of the prepared materials

Evaluation of the photocatalytic properties of the prepared samples was adapted from Chapter 3, Section 3.5. The photocatalytic degradation experiments were carried out for 4 hrs. Aliquots were drawn from the solution at 30 mins intervals in the case of EBS and 40 mins in the case of EBT, filtered and analysed (EBT 503 nm and EBS 518 nm). During degradation of the dye mixture, equal volumes of
EBS solution (20 ppm) and EBT solution (20 ppm) were mixed before adding the photocatalyst. UV-Vis absorption spectra of EBS/EBT were also recorded to monitor the degradation of the dyes with increasing irradiation time. The experimental data was analysed using first order kinetics to establish the photocatalytic degradation rate constants according to Equation 4.1. TOC measurements were performed as described in Chapter 3, Section 3.5.1.

7.5 Results and discussion

7.5.1 TEM and SEM analysis

The surface morphology of the photocatalysts was investigated using FE-SEM and TEM. The FE-SEM images (Figure 7.1a) show that the MWCNTs are embedded within the titania matrix (about 22 nm in diameters) and the coverage was not complete. Figure 7.1b and 7.1c show the FE-SEM images of rGO/Nd,N,S-TiO$_2$ from which there are no observable graphene sheets probably due to their complete coverage by titania nanoparticles. Moreover, the rGO/Nd,N,S-TiO$_2$ appears to be a more compact unit which may suggest a strong and intimate interaction of rGO with the titania nanoparticles. The non-uniform and incomplete decoration of the titania nanoparticles on the MWCNTs was further confirmed by TEM (Figure 7.1d). There is improved coverage of the rGO by titania (Figure 7.1e and 7.1f, arrows) compared to MWCNTs probably due to its planar structure which allow for better interaction with the tridoped titania. This intimate interaction between rGO and tridoped titania is beneficial for realisation of their collaborative effect during photocatalysis. Moreover, there is no observable aggregation of the carbon nanomaterials which may suggest sufficient dispersion within the titania matrix.
Figure 7.1: FE-SEM images of (a) MWCNT/Nd,N,S-TiO$_2$, (b) and (c) rGO/Nd,N,S-TiO$_2$ and TEM images of (d) MWCNT/Nd,N,S-TiO$_2$, (e) and (f) rGO/Nd,N,S-TiO$_2$.

Energy dispersive x-ray analysis provided a qualitative elemental composition of the photocatalysts. Figure 7.2 shows the EDX spectrum of rGO/Nd,N,S-TiO$_2$ which indicates the presence of the elements C, S, O, Nd and Ti. The C largely originates from the incorporation of rGO and to a lesser extent, from the thiourea which is used as a source of nitrogen and sulphur. The EDX spectrum of the MWCNT/Nd,N,S-TiO$_2$ is identical to that of rGO/Nd,N,S-TiO$_2$. 
7.5.2 FT-IR analysis

FT-IR was employed to probe the different functional groups present in the prepared materials and the results are presented in Figure 7.3. For commercial titania, two prominent peaks are observed around 3428 cm\(^{-1}\), 1630 cm\(^{-1}\) related to the OH stretching and OH bending of adsorbed water molecules. Moreover, a broad peak between 500 cm\(^{-1}\) and 800 cm\(^{-1}\) also appears and is due to the Ti-O, O-Ti-O stretching vibration.\(^4\) Notably, these peaks are also present in the tridoped titania and the composite photocatalysts. However, the OH peaks are more intense compared to commercial titania which may be due to the presence of more moisture adsorbed on the surface of the photocatalyst. This may suggest improvement in the adsorption of moisture as a result of tridoping and incorporation of rGO/MWCNTs. Furthermore, the Ti-O peak is broader in the nanocomposites and tridoped titania compared to commercial titania. This may be due to the combined contribution of Ti-O, O-Ti-O, O-Ti-N, N-Ti-N, Ti-O-Nd and Nd-O.\(^5,6\) In addition to these three peaks observed in commercial titania, the tridoped titania and nanocomposites show peaks around 3200 cm\(^{-1}\) and 1398 cm\(^{-1}\) corresponding to deformation vibration of ammonium ions.\(^7\) Moreover, the peak at 2348 cm\(^{-1}\) may be attributed to N-H stretching vibration, further suggesting the incorporation of nitrogenous species in the photocatalysts.\(^8\) The presence of sulphur species may be responsible for the peaks appearing at 1134 cm\(^{-1}\), 1050
and 984 cm\(^{-1}\). These peaks are linked to the presence of bidentate SO\(_4^{2-}\) coordinated to Ti\(^{4+}\).\(^{4,9}\)

**Figure 7.3: FT-IR spectra of the prepared photocatalysts and commercial titania.**

### 7.5.3 UV-Vis spectroscopy

The optical properties of the photocatalysts were investigated using UV-Vis absorption spectroscopy. This is to determine the extent to which tridoping improves the visible light absorption of pure titania and the extent to which the incorporation of rGO/MWCNT contribute towards visible light absorption of the photocatalysts. **Figure 7.4** shows the UV-Vis absorption spectra of the different photocatalysts. Commercial titania shows intense absorption in the UV region and no absorption in the visible light region. This is characteristic of pure titania and emanates from the wide band gap of titania, 3.2 eV for anatase titania and 3.0 eV for rutile titania.\(^{10}\) The tridoped titania shows absorption both in the UV and visible
light region. Visible light absorption of tridoped titania is attributed to the incorporation of the three dopants (Nd, N and S) resulting in the formation of sub-band gap states within the titania band gap. Consequently, electrons are excited by visible light from the valence band of titania to some of the new sub-band gap states (Nd and S states).\textsuperscript{11,12} Alternatively, electrons may be excited by visible light from the N sub-band gap states into the conduction band of titania or the S and Nd sub-band gap states.\textsuperscript{11} The incorporation of rGO/MWCNTs significantly enhanced visible light absorption of the composite photocatalysts compared to tridoped titania. This may be credited to the rGO/MWCNTs acting as visible light sensitisers and sources of carbon doping which improves visible light absorption of titania.\textsuperscript{13} Notably, the rGO incorporating photocatalyst showed better visible light absorption probably due to better interaction between rGO and tridoped titania. This may result in the formation of numerous Ti-C bonds which are essential for electron transfer between rGO and titania during visible light irradiation.\textsuperscript{14}

Figure 7.4: UV-Vis absorption spectra of the different photocatalysts prepared.
7.5.4  Raman spectroscopy analysis

7.5.4.1 Raman analysis of rGO

Raman analysis (Figure 7.5a) and 7.5b) was used to gain an insight into the effectiveness of the reduction of graphene oxide (GO) to reduced graphene oxide (rGO). Two important peaks were observed in both spectra around 1350 cm\(^{-1}\) and 1580 cm\(^{-1}\), emanating from the D-band and G-band of graphene. The D-band originates from defects in the ordered sp\(^2\) structure of graphene. Such defects may result from oxidation of graphene which introduces a lot of oxygen containing functionalities and transform the structure from sp\(^2\) to sp\(^3\) hybridization. The G-band corresponds to ordered sp\(^2\) graphitic framework. A remarkably high intensity of the D-band compared to the G-band is observed for GO (Figure 7.5a) suggesting that the graphitic structure is largely defective (sp\(^3\) hybridized) due to the presence of oxygen containing functionalities. The intensity ratio of the D-band to the G-band (I\(_D\)/I\(_G\)) is 3.84 which is consistent with highly disordered graphene. However, upon reduction (Figure 7.5b) the D-band intensity decreased significantly while the G-band gained intensity, suggesting the removal of the oxygen containing functionalities. This transforms the carbon atoms from sp\(^3\) to sp\(^2\) which is characteristic of the ordered graphene framework. The I\(_D\)/I\(_G\) ratio is 0.441 which is considered low and signifies that the graphene framework is largely ordered with fewer defects.
Figure 7.5: Raman spectrum of (a) graphene oxide and (b) reduced graphene oxide.

7.5.4.2 Raman analysis of the photocatalysts

Figure 7.6 shows the Raman spectra of the prepared photocatalysts and commercial titania. Commercial titania and tridoped titania showed similar Raman spectra with peaks appearing at 149, 217, 391, 510 and 637 cm\(^{-1}\). These peaks can be linked to the anatase phase of titania and originate from the Raman active modes with symmetries \(E_g\), \(E_g\), \(B_{1g}\), \(A_{1g}\) and \(E_g\), respectively.\(^{16}\) The prepared nanocomposites also show these anatase peaks, suggesting the anatase phase as the predominant phase. In addition to the anatase peaks, the Raman spectra of the nanocomposites show peaks at 1308 and 1598 cm\(^{-1}\) which may be ascribed to the D-band and G-band of rGO/MWCNT.\(^{16}\) The appearance of these peaks in the spectra of the composite photocatalysts suggests the incorporation of rGO/MWCNTs within the titania matrix. Furthermore, the titania peaks are shifted in the composite photocatalysts compared to the tridoped and codoped titania which could be as result of the interaction of the titania and MWCNTs/rGO.
7.5.5 X-ray diffraction

Examining the XRD patterns of the photocatalysts (Figure 7.7) reveal that they are fairly crystalline and their crystallinity is not compromised by the incorporation of rGO/MWCNTs. The average crystallite size of titania estimated from Scherrer equation was found to range from 15 to 17 nm which correlate well with the value of about 20 nm estimated from TEM measurements. The mixed phases of commercial titania were confirmed by XRD analysis (Figure 7.7). The peaks observed at 2θ 27.4, 36.2, 39.3, 41.3, 44.0, 56.7, and 64.1° are characteristic of the rutile phase of titania. These peaks emanate from the (110), (101), (200), (111), (210), (220), and (110) crystal planes. In addition to these rutile peaks, there are peaks appearing at 2θ 25.4, 37.7, 48.1, 54.4, 55.1, 62.6, 69.0, 69.8 and 75.1° which are characteristic of the anatase phase of titania. These peaks correspond to the (101), (004), (200), (105), (211), (204), (116), (220) and (215) crystal planes. The same anatase peaks observed in commercial titania, are
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observed in the prepared photocatalysts and there are no rutile peaks, suggesting the preparation of single phase titania. Notably, there are no peaks due to Nd$_2$O$_3$ probably due to its low content relative to titania and also probably due to its well dispersion within the titania matrix. Moreover, there is no significant difference in the XRD patterns of rGO/Nd,N,S-TiO$_2$ and MWCNT/Nd,N,S-TiO$_2$. In both XRD patterns there is no peak due to the MWCNT/rGO possibly due to the smaller amounts of rGO/MWCNTs (0.5%) and the overlap with the (101) peak of anatase titania.$^{19}$

![Figure 7.7: XRD patterns of the different photocatalysts.](image)

**Figure 7.7: XRD patterns of the different photocatalysts.**

7.5.6 BET surface area

A large surface area is a desirable property for a photocatalyst to ensure adequate interaction with the pollutant species. Pollutant/photocatalyst interaction is essential since photocatalysis occurs on the surface of the photocatalyst, therefore, the pollutant species must be in contact with the surface of the
photocatalyst. The inclusion of rGO/MWCNT tremendously improved the surface area of the resultant photocatalysts reaching surface areas of 128.21 m$^2$/g and 144.87 m$^2$/g for MWCNT/Nd,N,S-TiO$_2$ and rGO/Nd,N,S-TiO$_2$, respectively, compared to 78.21 m$^2$/g for tridoped titania. The increase in surface area may be due to the incorporation of rGO/MWCNTs with large surface areas and their possible role in minimising aggregation of the titania nanoparticles.

7.6 Photocatalytic degradation of eriochrome black T and eosin blue shade

7.6.1 Single dye degradation

The rGO/Nd,N,S-TiO$_2$ composite photocatalyst was evaluated for the degradation of EBS and EBT from single dye solutions under simulated solar light irradiation and its performance compared to the MWCNT/Nd,N,S-TiO$_2$ nanocomposite. Moreover, the photocatalytic activity of the nanocomposites is compared to that of tridoped titania and commercial titania in order to understand the influence of incorporating the carbon nanomaterials. The photocatalytic degradation of EBS and EBT is shown in Figure 7.8a and 7.8b, respectively. Notably, the prepared nanocomposites displayed superior photocatalytic activity for both EBS and EBT compared to tridoped titania and commercial titania. Degradation efficiencies of 95.7% and 99.3% for EBS and 85.8% and 94.6% for EBT, were attained using MWCNT/Nd,N,S-TiO$_2$ and rGO/Nd,N,S-TiO$_2$, respectively (Table 7.1a and 7.1b). These values are all higher than the degradation efficiency values obtained using the tridoped titania and commercial titania (Table 7.1a and 7.1b). The superiority of the nanocomposites may be explained in terms of improved visible light absorption compared to tridoped titania and commercial titania as observed in the UV-Vis absorption spectra of the photocatalysts (Figure 7.4). This improvement in visible light absorption emanates from the cooperative effect of carbon nanomaterials and tridoped titania resulting in enhanced formation of the superoxide and hydroxyl radicals responsible for dye degradation.$^{20,21}$ Furthermore, incorporation of the carbon nanomaterials may result to improved charge separation and transportation which minimise electron/hole recombination.
and leads to efficient formation of the oxidising species and degradation of the dye molecules.\textsuperscript{22} The presence of Nd\textsuperscript{3+} further improves charge separation in the nanocomposites due to its electron scavenging properties.\textsuperscript{23}

In addition to better visible light absorption and superior charge separation, the composite photocatalysts have large surface areas compared to tridoped titania and commercial titania, owing to the inclusion of rGO/MWCNTs. This provides adequate sites for the degradation of the dye species. Moreover, rGO/MWCNTs may aid in minimising aggregation of the tridoped titania nanoparticles which would otherwise lower the photocatalytic activity of the material.\textsuperscript{24} Commercial titania displayed the lowest photocatalytic due to its poor visible light absorption and high electron/hole recombination rate. The introduction of Nd, N and S improved visible light absorption, charge separation and photocatalytic activity of the tridoped titania relative to commercial titania.\textsuperscript{25}
Figure 7.8: Photocatalytic degradation of (a) EBS, (b) EBT under simulated solar light.
7.6.1.1 Photocatalytic degradation kinetics

Photocatalytic degradation kinetics of both EBS and EBT were studied using first order kinetics (Figure 7.9a and 7.9b) in order to determine the rate at which the dye molecules are degraded by the photocatalysts. Degradation rate constants of $1.4 \times 10^{-2}$ min$^{-1}$ and $1.9 \times 10^{-2}$ min$^{-1}$ for EBS and $8.0 \times 10^{-3}$ min$^{-1}$ and $1.1 \times 10^{-2}$ min$^{-1}$ for EBT were observed using MWCNT/Nd,N,S-TiO$_2$ and rGO/Nd,N,S-TiO$_2$, respectively. The degradation rate constants for the composite photocatalysts are higher than those obtained for tridoped and commercial titania for the same dyes (Table 7.1a and 7.1b). This is an indication of the superior performance of MWCNT/Nd,N,S-TiO$_2$ and rGO/Nd,N,S-TiO$_2$ for the degradation of both dyes compared to both controls and further support the proposed synergy between rGO/MWCNTs and tridoped titania. Moreover, it can be observed that EBS is degraded faster than EBT, probably due to their structural differences which can offer varying degrees of stability and interaction with the photocatalysts.

Photocatalytic degradation of methylene blue (MB) by rGO/TiO$_2$ has been studied by Min et al.$^{20}$ and recorded maximum degradation rates of $2.76 \times 10^{-2}$ min$^{-1}$ and $7.15 \times 10^{-3}$ min$^{-1}$, under UV and visible light irradiation, respectively. In another work, Wang et al.$^{26}$ reported the visible light photocatalytic degradation of methyl orange (MO) using rGO/TiO$_2$ composite photocatalyst prepared from dye-sensitization induced reduction of GO and observed a maximum degradation rate of $9.5 \times 10^{-3}$ min$^{-1}$. In both studies,$^{20,26}$ the rGO/TiO$_2$ composite photocatalysts displayed lower degradation rates compared to the values obtained in this study for the rGO/Nd,N,S-TiO$_2$ composite photocatalysts (Table 7.1a and 7.1b). Moreover, Lei et al.$^{27}$ reported the photocatalytic degradation of MB on Cds/MWCNT-TiO$_2$ and recorded degradation rates of $2.4 \times 10^{-3}$ min$^{-1}$ and $3.3 \times 10^{-3}$ min$^{-1}$ under visible and UV light irradiation. Tian et al.$^3$ prepared and evaluated TiO$_2$/MWCNT hybrid nanostructures for the photocatalytic degradation of MB under visible light irradiation and reported a maximum degradation rate of $1.0 \times 10^{-3}$ min$^{-1}$. Notably, our carbon nanotube based composite photocatalyst displayed superior photocatalytic activity compared to the highlighted reports. These observations suggest the crucial role played by the incorporation of Nd, S
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and N in improving the photocatalytic activity of both composite photocatalysts (rGO/Nd,N,S-TiO₂ and MWCNT/Nd,N,S-TiO₂).

**Table 7.1: Percentage degradation and degradation rate constants of (a) EBS and (b) EBT.**

(a)

<table>
<thead>
<tr>
<th>Sample</th>
<th>EBS degraded (%)</th>
<th>Rate constant, min⁻¹</th>
<th>R²</th>
</tr>
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<tr>
<td>Commercial TiO₂</td>
<td>58.8</td>
<td>4.1 x 10⁻³</td>
<td>0.986</td>
</tr>
<tr>
<td>Nd,N,S-TiO₂</td>
<td>68.0</td>
<td>5.2 x 10⁻³</td>
<td>0.973</td>
</tr>
<tr>
<td>MWCNT/Nd,N,S-TiO₂</td>
<td>95.7</td>
<td>1.4 x 10⁻²</td>
<td>0.986</td>
</tr>
<tr>
<td>rGO/Nd,N,S-TiO₂</td>
<td>99.3</td>
<td>1.9 x 10⁻²</td>
<td>0.989</td>
</tr>
</tbody>
</table>

(b)

<table>
<thead>
<tr>
<th>Sample</th>
<th>EBT degraded (%)</th>
<th>Rate constant, min⁻¹</th>
<th>R²</th>
</tr>
</thead>
<tbody>
<tr>
<td>Commercial TiO₂</td>
<td>50.0</td>
<td>3.1 x 10⁻³</td>
<td>0.977</td>
</tr>
<tr>
<td>Nd,N,S-TiO₂</td>
<td>58.8</td>
<td>3.8 x 10⁻³</td>
<td>0.987</td>
</tr>
<tr>
<td>MWCNT/Nd,N,S-TiO₂</td>
<td>85.8</td>
<td>8.0 x 10⁻³</td>
<td>0.977</td>
</tr>
<tr>
<td>rGO/Nd,N,S-TiO₂</td>
<td>94.6</td>
<td>1.1 x 10⁻²</td>
<td>0.966</td>
</tr>
</tbody>
</table>

UV-Vis spectra were also recorded to monitor the changes in the absorption spectra of both dyes with increasing irradiation time (Figure 7.10). Notably, the absorption peaks observed in both dyes (Figure 7.10a and 7.10b) decreased gradually and become smooth with increasing irradiation time. Moreover, there are no new peaks observed in both spectra suggesting that there were no derivatives of the two dyes formed as a result of photocatalytic degradation. This indicates that the dyes are degraded into inorganic species or smaller molecules such as CO₂, SO₃, NO₂, H₂O, etc.²⁸
Figure 7.9: Kinetics for degradation of (a) EBS and (b) EBT under simulated solar light.
Figure 7.10: UV-Vis absorption spectra of (a) EBS and (b) EBT during photocatalysis using rGO/Nd,N,S-TiO$_2$. 
A positive effect on the photocatalytic activity of the composite photocatalysts is observed upon incorporation of rGO/MWCNTs. However, the inclusion of rGO yield better results compared to MWCNTs. This observation highlights the significant role played by rGO/MWCNT in enhancing the photocatalytic activity of tridoped titania and the magnitude to which they differ in performing that function. Most often, these carbon nanomaterials are seldom compared in terms of their capacity to enhance the photocatalytic activity of semiconductors. Consequently, each carbon material is overly praised as superior in positively influencing the photocatalytic activity titania.\textsuperscript{1,20} The incorporation of rGO in the nanocomposite resulted to improved visible light absorption compared to MWCNTs (Figure 7.4) which is essential for generation of the oxidising species and degradation of the dye molecules. This superior visible light absorption may be due to better interaction of rGO and tridoped titania leading to a strong and intimate interfacial contact which is essential for harnessing the cooperative effect of the two components of the photocatalyst. Moreover, the strong interfacial contact between tridoped titania and rGO may be linked to adequate formation of the Ti-C, Ti-O-C bonds which play a pivotal role during visible light absorption.\textsuperscript{14} The influence of rGO on the surface area of the resultant composite photocatalyst is superior to that of MWCNTs, probably due to better interaction with the tridoped titania nanoparticles yielding sufficient dispersion and less aggregation. A large surface area provides adequate contact between the photocatalyst and dye molecules and improves degradation. Moreover, rGO has higher electronic conductivity compared to MWCNTs. Therefore its incorporation in the nanocomposite may account for superior charge separation and transportation which is crucial in lowering the recombination of the charge carriers.\textsuperscript{29} This would give rGO/Nd,N,S-TiO\textsubscript{2} a higher photocatalytic activity compared to its MWCNT/Nd,N,S-TiO\textsubscript{2} counterpart.

In order to ensure efficient exploitation of the combined properties of both tridoped titania and rGO, the method of preparation of the composite photocatalyst and method of preparation of rGO are important factors. There has to be sufficient intimate contact between the rGO and the tridoped titania. This ensures adequate formation of the Ti-C/Ti-O-C bonds which promote visible light activity of the photocatalyst and improves electron mobility between titania and rGO.\textsuperscript{22} Huang et
al.\textsuperscript{29} and Zhang et al.\textsuperscript{19} noted that complete and intimate coating of rGO/MWCNT with titania nanoparticles yielded better results than poorly coated carbon nanomaterials and a physical mixture of titania and rGO/MWCNTs. This probably explains the higher photocatalytic activity of rGO/Nd,N,S-TiO\textsubscript{2} compared to the MWCNT/Nd,N,S-TiO\textsubscript{2} nanocomposite which display sufficient intimate contact between rGO and the tridoped titania. This is evident from the FE-SEM and TEM images. Furthermore, the structural differences between rGO/MWCNTs render different interactions with the titania nanoparticles, resulting in varying interfacial contact and different photocatalytic activity of the resultant photocatalyst.\textsuperscript{19}

The method of preparation of rGO is also of paramount importance because it determines its structure which in turn influences its properties. For example, rGO is expected to show extremely high influence in the photocatalytic activity of tridoped titania but experimental results show a moderate difference compared to MWCNTs. Similar results have been reported elsewhere.\textsuperscript{30} An explanation for this phenomenon may lie with the method of preparation of the rGO. If the preparatory method introduced a lot of defects on the graphene framework, this will affect the electron conductivity of rGO and lowers its contribution towards charge separation and transportation in the composite photocatalyst.\textsuperscript{30} Therefore, it is imperative to produce rGO of minimum defects in order to harness its intrinsic electronic conductivity. Moreover, a sufficient degree of reduction needs to be attained in order to transform graphene oxide (GO) from the sp\textsuperscript{3} hybridised state to rGO which is largely sp\textsuperscript{2} hybridised. This is a very critical step necessary to transform the material from being an insulator to a conducting material.\textsuperscript{31,32} The degree of reduction will have implications in the role of the rGO in electron capturing and transportation.

7.6.2 Competitive photocatalytic degradation of EBS and EBT

The complex nature of textile effluent is one of the major challenges during treatment. In order to evaluate the performance of the prepared composite photocatalysts for the degradation of the dye molecules under competitive conditions, degradation was performed from mixed dye solutions. Photocatalytic
degradation of the mixture of EBS and EBT is shown in Figure 7.11a. The rGO/Nd,N,S-TiO$_2$ displayed superior photocatalytic activity compared to the MWCNT/Nd,N,S-TiO$_2$ for both dyes reaching maximum degradation efficiencies of 65.7% and 54.1% for EBS and EBT, respectively. These values are higher than the 58.9% and 49.0% obtained for EBS and EBT, respectively, when using the MWCNT/Nd,N,S-TiO$_2$ as the catalyst. There is a significant decline in the degradation efficiency for both dyes from the mixed dye solution compared to single dye solution. This may be due to competition between EBS EBT for the photocatalyst surface where degradation takes place. First order kinetics (Figure 7.11b) shows that EBS is degraded faster than EBT as observed in single dye solutions. The degradation rate constants are lower than those from single dye solutions, owing to the competitive conditions. The rGO/Nd,N,S-TiO$_2$ reached degradation rates of $5.2 \times 10^{-3}$ min$^{-1}$ and $3.7 \times 10^{-3}$ min$^{-1}$ for EBS and EBT, respectively. The obtained results suggest the application of the prepared photocatalysts as versatile dye pollution remediation tools.
Figure 7.11: (a) Competitive photocatalytic degradation of EBS and EBT and (b) kinetics studies for the competitive degradation of EBS and EBT.
7.6.3 Effect of radical scavengers on the degradation of EBS and EBT

The photocatalytic degradation of EBS and EBT by rGO/Nd,N,S-TiO$_2$ was evaluated in the presence of radical scavengers to ascertain the role of these radicals in the degradation of the dye molecules. Benzoquinone (10 mL, 0.1 M) and 2-propanol (10 mL, 0.1 M) were used as superoxide radical scavenger and hydroxyl radical scavenger, respectively. Photocatalytic degradation of EBS in the presence of benzoquinone and 2-propanol reached maximum efficiencies of 59.8% and 74.0%, respectively. For EBT, maximum degradation efficiencies of 39.1% and 55.5% were observed in the presence of benzoquinone and 2-propanol, respectively. A significant decrease in the photocatalytic activity of the nanocomposite for both dyes is observed and suggests that both the superoxide and hydroxyl radicals are the active species during EBS and EBT degradation. First order kinetics (Figure 7.12) gave degradation rates of $4.2 \times 10^{-3}$ min$^{-1}$ and $3.5 \times 10^{-3}$ min$^{-1}$ for EBS degradation in the presence of benzoquinone and 2-propanol, respectively. Similarly, degradation rates of $3.7 \times 10^{-3}$ min$^{-1}$ and $2.3 \times 10^{-3}$ min$^{-1}$ for EBT were observed in the presence of benzoquinone and 2-propanol, respectively. The lower degradation rates in the presence of the radical scavengers further emphasise the role of the radicals in dye degradation.
Figure 7.12: Kinetics for EBS and EBT degradation in the presence of radical scavengers using rGO/Nd,N,S-TiO$_2$. 

7.6.4 Total organic carbon analysis

Total organic carbon analyses provide an insight into the amount of carbon bound to organic compounds. This may be used to determine the extent to which the dye molecules are broken down during photocatalysis. Higher TOC values suggest a higher degree of complete mineralisation of the dye molecules which is desirable during photocatalysis to minimise formation of potentially toxic by-products. Maximum TOC values of 82.0% (Figure 7.13a) and 75.6% (Figure 7.13b) were obtained from the degradation of EBS and EBT, respectively, suggesting a fairly high degree of complete mineralisation of both dyes by rGO/Nd,N,S-TiO$_2$. It is evident from the TOC removal values that a small amount of organic degradation by-products remain in solution after the 4 hrs of irradiation. The higher decolourisation/degradation efficiency compared to the TOC removal values suggest that the dye molecules are broken down into smaller colourless products.
first before being mineralised to inorganic species. The residual organic materials may require extended irradiation times to ensure their complete mineralisation.

Figure 7.13: Total organic carbon removal by rGO/Nd,N,S-TiO$_2$ from (a) EBS and (b) EBT degradation.
7.7 Chapter summary

Tridoped titania was decorated on rGO and the resultant photocatalyst displayed improved optical and photocatalytic properties compared to its MWCNT/Nd,N,S-TiO$_2$ counterpart, tridoped titania and commercial titania. These improvements are credited to the co-operative effect of the tridoped titania and the rGO. This synergistic effect emanates from the intimate contact between the tridoped titania and rGO as evident from the FE-SEM and TEM images. Moreover, the superior electron conductivity of rGO over MWCNT is crucial in ensuring efficient electron trapping and transportation. The prepared composite photocatalysts displayed the capacity to degrade both dyes under competitive conditions which highlights the versatility of the photocatalysts and their potential application as environmental clean-up tools for dye pollution. Addition of radical scavengers in the dye solutions significantly lowers the photocatalytic degradation rates of both dyes, suggesting that the superoxide and hydroxyl radical are the active species responsible for dye degradation. A fairly high degree of complete mineralisation of both dyes was evident from TOC analyses which indicate that most of the dye molecules are broken down into simpler molecules and inorganic ions. This reduces the risk of forming toxic photocatalysis by-products.
Chapter 7: Nd,N,S-TiO\textsubscript{2} decorated on reduced graphene oxide for a visible light active photocatalyst for dye degradation: a comparison to its MWCNT/Nd,N,S-TiO\textsubscript{2} analogue

7.8 References


CHAPTER 8:
ENHANCED VISIBLE LIGHT PHOTOCATALYTIC DEGRADATION OF
ERIOCHROME BLACK T AND EOSIN BLUE SHADE IN WATER USING
TRIDOPED TITANIA DECORATED ON SWCNTS AND MWCNTS: EFFECT OF
THE TYPE OF CARBON NANOTUBE INCORPORATED

*Contents of this chapter have been published in Mamba G, Mbianda XY, Mishra AK. Mat Chem Phys. 2015;149-150:734-742.

This chapter is similar to Chapter 7 and reports on another comparative study on neodymium, nitrogen and sulphur tridoped TiO₂ is decorated on MWCNTs and SWCNTs to yield composite photocatalysts: MWCNT/Nd,N,S-TiO₂ and SWCNT/Nd,N,S-TiO₂. The effect of coupling the CNTs and Nd,N,S-TiO₂ is evaluated against MWCNT/TiO₂, SWCNT/TiO₂, Nd,N,S-TiO₂ and commercial TiO₂ for the degradation of EBT and EBS. Moreover, a comparison is drawn between the photocatalytic activities of the two nanocomposite photocatalysts (MWCNT/Nd,N,S-TiO₂ and SWCNT/Nd,N,S-TiO₂) to evaluate the effect of the different forms of CNTs utilised. Photodegradation experiments were performed from single and mixed dye solutions to evaluate the performance of the photocatalysts in a slightly complex dye matrix.

8.1 Introduction

There is a general consensus regarding the positive effect of incorporating carbon nanomaterials such as SWCNTs, MWCNTs, GO, rGO, EG, DWCNTS, etc. into titania matrix, however, their differences in structure, electron conductivity, surface area and adsorption properties instigate varying effects on the resultant carbon nanomaterial/titania nanocomposite. Liu et al. reported on the improved photocatalytic degradation of sulfathiazole on double-walled carbon nanotube-titania (DWCNT-TiO₂) hybrids prepared via a hydrothermal method. DWCNT-TiO₂ hybrids displayed superior photocatalytic performance over MWCNT/TiO₂ and SWCNT/TiO₂ which was attributed to the unique electronic structure of DWCNT
that facilitate visible light absorption and electron conduction.\textsuperscript{1} The merits of multidoping titania and the mechanism responsible for its improved visible light absorption and photocatalytic activity has been elucidated in Chapter 2. This led to the formulation of SWCNT/Nd,N,S-TiO\textsubscript{2} and MWCNT/Nd,N,S-TiO\textsubscript{2} nanocomposites for dye degradation and these nanocomposite are anticipated to benefit from synergistic effect of tridoping titania and incorporation of the carbon nanomaterials. Moreover, the different forms of carbon nanotubes are anticipated to cause varying effects on the overall photocatalytic activity of the nanocomposites.

8.2 Experimental

8.2.1 Materials

Reagents and materials utilised in this work are presented in Chapter 3, Section 3.2.

8.2.2 Preparation of photocatalysts

The nanocomposite photocatalysts were prepared according to the procedure described in Chapter 3, Section 3.3.4. MWCNT/TiO\textsubscript{2} and SWCT/TiO\textsubscript{2} composite photocatalysts were prepared using the same procedure without the addition of thiourea and Nd source and utilised as controls in addition to commercial titania and the tridoped titania (Nd,N,S-TiO\textsubscript{2})

8.3 Materials characterisation

For verification of the successful preparation of the desired nanocomposites, a number of characterisation tools were employed as described in Chapter 3, Section 3.4.
Chapter 8: Enhanced visible light photocatalytic degradation of eriochrome black T and eosin blue shade in water using tridoped titania decorated on SWCNTs and MWCNTs: Effect of the type of carbon nanotube incorporated

8.4 Photocatalytic activity evaluation

The fabricated nanocomposites were exploited for the degradation of EBS and EBT as described in Chapter 3, Section 3.5 with some modifications outlined in Chapter 7, Section 7.4. Total organic carbon was determined according to the procedure given in Chapter 3, Section 3.5.1.

8.5 Results and discussion

8.5.1 Electron microscopy analysis

FE-SEM and TEM were employed to probe the surface morphology of the prepared materials in order to establish how the incorporated CNTs physically interact with the tridoped TiO$_2$. Figure 8.1a shows the FE-SEM image of the MWCNT/Nd,N,S-TiO$_2$ nanocomposite which shows that the MWCNTs (red arrow) are well incorporated within the titania matrix. Similarly, the SWCNTs (red arrows) (Figure 8.1b and 8.1c) are also embedded within the titania matrix with no observable aggregation. This suggests that the CNTs are well dispersed within the tridoped TiO$_2$ which is desirable for a uniform photocatalyst structure and composition. The decoration of the tridoped TiO$_2$ (diameters of about 22 nm) on the surfaces of the SWCNTs and MWCNTs (red arrows) is evident from the TEM images (Figure 8.1d, 8.1e and 8.1f). However, the decoration is not uniform which may be as a result of calcination which removed some of the carbonaceous material from the thiourea, leaving the gaps behind. However, the intimate interaction between the tridoped titania and the CNTs is evident and it will benefit the photocatalytic performance of the nanocomposites.
Chapter 8: Enhanced visible light photocatalytic degradation of eriochrome black T and eosin blue shade in water using tridoped titania decorated on SWCNTs and MWCNTs: Effect of the type of carbon nanotube incorporated

Figure 8.1: FE-SEM images of (a) MWCNT/Nd,N,S-TiO$_2$, (b) and (c) SWCNT/Nd,N,S-TiO$_2$, and TEM images of (d) MWCNT/Nd,N,S-TiO$_2$, (e) and (f) SWCNT/Nd,N,S-TiO$_2$.

Qualitative elemental analyses (Figure 8.2) of the CNT/tridoped TiO$_2$ composites show the presence of the elements: carbon, neodymium, sulphur, oxygen and titanium, suggesting the incorporation of these elements in the nanocomposites. Nitrogen could not be detected by EDX due to the possible overlap of its x-ray lines with the Ti lines. Moreover, nitrogen may be incorporated into the photocatalysts at levels below the detection limit of this technique, resulting to insufficient intensity.$^2$
Figure 8.2: EDX spectra of SWCNT/Nd,N,S-TiO$_2$.

8.5.2 Infrared spectroscopy analysis

Figure 8.3 shows the FT-IR spectra of the prepared photocatalyst which display similarities in certain regions of the spectrum. The FT-IR spectrum of the tridoped TiO$_2$ resembles that of the MWCNT/Nd,N,S-TiO$_2$ and SWCNT/Nd,N,S-TiO$_2$. The broad and intense peak located between 400 cm$^{-1}$ and 800 cm$^{-1}$ is linked to the mixed contributions of Ti-O, O-Ti-O, N-Ti-N, O-Ti-N, Ti-C, Ti-O-C, Ti-O-Nd and Nd-O.$^3$$^4$ Hence the broadness of this peak in the tridoped TiO$_2$ and composite photocatalysts compared to commercial TiO$_2$ where only Ti-O and O-Ti-O are responsible for the appearance of the peak. Both the MWCNT/TiO$_2$ and SWCNT/TiO$_2$ also show a broad peak in this region but it is not as broad as in the tridoped titania/carbon nanotube composite photocatalysts. The presence of nitrogenous species is responsible for the appearance of the peaks around 3200 cm$^{-1}$ and 1398 cm$^{-1}$. These peaks relate to the deformation vibration of ammonium ions.$^5$ Another peak appears at 2348 cm$^{-1}$ which is due to the N-H stretching vibration.$^6$ The presence of bidentate SO$_4^{2-}$ coordinated to Ti$^{4+}$ is responsible for the peaks at 1134 cm$^{-1}$, 1050 cm$^{-1}$ and 984 cm$^{-1}$. These peaks suggest the incorporation of the sulphur species into the titania matrix. Furthermore, the OH peaks around 3400 cm$^{-1}$ and 1630 cm$^{-1}$ are more intense in the tridoped TiO$_2$ and the composite photocatalysts compared to commercial TiO$_2$. This may be an indication of better absorption of moisture which plays a pivotal
role during the formation of the oxidising species. The OH peaks were the second and only peaks observed in the spectra of the MWCNT/TiO$_2$ and SWCNT/TiO$_2$ indicating the absence of the sulphur and nitrogenous species.

Figure 8.3: FT-IR spectra of the different photocatalysts.

8.5.3 Raman spectroscopy measurements

The Raman spectra of the composite photocatalysts (Figure 8.4) show seven peaks located around 149, 217, 391, 510, 637, 1308 and 1598 cm$^{-1}$. The first five peaks are characteristic of the anatase phase of titania and emanates from Raman active modes with symmetries E$_g$, E$_g$, B$_{1g}$, A$_{1g}$ and E$_g$, respectively. The last two peaks are associated with the D-band (linked to defects in the carbon skeleton) and G-band (linked to ordered graphitic skeleton) of the CNTs, respectively. Anatase peaks are also present in the Raman spectrum of tridoped TiO$_2$ and commercial TiO$_2$ suggesting that it is the predominant phase of titania. Moreover, the emergence of the D-band and G-band in the Raman spectra of
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MWCNT/Nd,N,S-TiO$_2$, SWCNT/Nd,N,S-TiO$_2$, MWCNT/TiO$_2$ and SWCNT/TiO$_2$ suggests the possible formation of the composite material. There are no detectable phase transformations due to tridoping and incorporation of the CNTs.

![Figure 8.4: Raman spectra of the prepared photocatalysts and commercial titania.](image)

8.5.4 Optical properties of the photocatalysts

Improving visible light absorption is one of the challenges associated with the possible exploitation of titania for pollutant degradation using sunlight as the source of energy. Figure 8.5 shows the UV-Vis spectra of the tridoped TiO$_2$/carbon nanotube composite photocatalysts matched against MWCNT/TiO$_2$, SWCNT/TiO$_2$, tridoped TiO$_2$ and commercial TiO$_2$. A significantly higher visible light absorption is displayed by the tridoped TiO$_2$/carbon nanotube nanocomposites compared to all the other photocatalysts. This is ascribed to the cooperative effect of tridoping and incorporation of the CNTs. The CNTs may act as visible light sensitisers, absorbing visible light and injecting electrons into the conduction band of titania.$^{11}$ Moreover, the CNTs may function as sources of
carbon doping which results in the formation of sub-band gap states within the titania band gap leading to band gap narrowing (Table 8.1) and visible light absorption.\textsuperscript{11} Similarly, tridoping titania with Nd, N and S introduces new energy states within the band gap of titania, resulting to band gap narrowing and visible light absorption.\textsuperscript{12,13} Consequently, the tridoped TiO\textsubscript{2}/carbon nanotube composite materials display the combined properties of tridoped TiO\textsubscript{2} and the CNTs. Similarly, incorporation of the carbon nanotube resulted in a red shift in the absorption edge of MWCNT/TiO\textsubscript{2} and SWCNT/TiO\textsubscript{2}. Commercial titania shows no absorption in the visible region, owing to its wide band gap which allows photoresponse in the near UV region.\textsuperscript{14} SWCNT/Nd,N,S-TiO\textsubscript{2} nanocomposite displays better visible light absorption than its MWCNT incorporating counterpart. This is linked to their differences in sizes which may result to different interaction with the tridoped TiO\textsubscript{2}. Effective interaction with tridoped TiO\textsubscript{2} results in better exploitation of the combined properties of titania and the CNTs.

![UV-Vis absorption spectra of the different photocatalysts prepared.](image-url)
The band gaps of the different photocatalysts were estimated from the UV-Vis absorption spectra as described in Chapter 5, Section 5.3.3. The calculated band gaps are presented in Table 8.1. Slight band gap narrowing is observed in the MWCNT/TiO$_2$ and SWCNT/TiO$_2$ which can be attributed to carbon doping and the incorporation of Nd, N and S significantly narrowed the band gap of TiO$_2$ in the tridoped titania/carbon nanotube composites.

**Table 8.1: Calculated band gap energies of the different photocatalysts.**

<table>
<thead>
<tr>
<th>Sample</th>
<th>Absorption edge wavelength (nm)</th>
<th>Calculated band gap (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Commercial TiO$_2$</td>
<td>385.3</td>
<td>3.22</td>
</tr>
<tr>
<td>Nd,N,S-TiO$_2$</td>
<td>443.0</td>
<td>2.80</td>
</tr>
<tr>
<td>MWCNT/TiO$_2$</td>
<td>411.3</td>
<td>3.01</td>
</tr>
<tr>
<td>SWCNT/TiO$_2$</td>
<td>405.7</td>
<td>3.06</td>
</tr>
<tr>
<td>MWCNT/Nd,N,S-TiO$_2$</td>
<td>440.8</td>
<td>2.81</td>
</tr>
<tr>
<td>SWCNT/Nd,N,S-TiO$_2$</td>
<td>448.6</td>
<td>2.76</td>
</tr>
</tbody>
</table>

**8.5.5 XRD analysis**

X-ray diffraction was employed to examine the crystalline phase of titania in the tridoped TiO$_2$ and composite photocatalysts and to establish if the incorporation of the CNTs had any influence on the crystallinity of the materials. The XRD patterns of the prepared photocatalysts (Figure 8.6) reveal that they are all fairly crystalline and there is no observable change in the crystallinity upon incorporation of the CNTs. TiO$_2$ average crystallite size estimated from Scherrer equation, ranged between 15 and 17 nm and these values are in agreement with the TEM measurements (22 nm). The anatase phase is the predominant phase in all the prepared photocatalysts while commercial TiO$_2$ was confirmed to be a mixture of rutile and anatase phases. XRD peaks characteristic of the anatase phase of titania appear at 2θ 25.4, 37.7, 48.1, 54.4, 55.1, 62.6, 69.0, 69.8 and 75.1° which
are characteristic of the anatase phase of titania. These peaks emanate from the (101), (004), (200), (105), (211), (204), (110), (220) and (215) crystal planes. The XRD results are consistent with the Raman results where the anatase phase was observed as the predominant phase. There were no peaks due to Nd$_2$O$_3$ probably due to its low content relative to titania and also probably due to its well dispersion within the titania matrix.

![XRD patterns of the different photocatalysts.](image)

**Figure 8.6: XRD patterns of the different photocatalysts.**

### 8.5.6 Surface area measurements

BET surface area analyses gave surface area values of 78.21, 128.07 and 133.12 m$^2$/g for Nd,N,S-TiO$_2$, MWCNT/Nd,N,S-TiO$_2$ and SWCNT/Nd,N,S-TiO$_2$, respectively. Incorporation of the CNTs significantly improved the surface area of the resultant composite photocatalysts compared to tridoped TiO$_2$. This may be due to the large surface area of the CNTs and their potential role as dispersing agents for the titania nanoparticles which minimise aggregation that would
otherwise lower the surface area. The SWCNT incorporating composite displayed a larger surface area than its MWCNT based counterpart, owing to their differences in size, surface area and interaction with the tridoped TiO$_2$. A large surface area is but not the only critical requirement for a high photocatalytic activity. Therefore, a high surface area does not guarantee a high photocatalytic activity.

8.5.7 Photocatalytic degradation of eriochrome black T and eosin blue shade

8.5.7.1 Single dye degradation

Photocatalytic degradation of EBS and EBT were performed separately and in mixed dye solutions to evaluate the performance of the photocatalysts under competitive conditions. The results obtained from single dye degradation studies are presented in Figure 8.7a (EBS degradation) and 8.7b (EBT degradation). The experimental data was analysed using first order kinetics to establish the photocatalytic degradation rate constants and the results are presented in Figure 8.7c (EBS degradation) and 8.7d (EBT degradation).
Chapter 8: Enhanced visible light photocatalytic degradation of eriochrome black T and eosin blue shade in water using tridoped titania decorated on SWCNTs and MWCNTs: Effect of the type of carbon nanotube incorporated

(a)

(b)
Figure 8.7: Photocatalytic degradation of (a) EBS, (b) EBT under simulated solar light and kinetics for degradation of (c) EBS and (d) EBT under simulated solar light.
For the degradation of both EBS and EBT, the photocatalytic activity of the photocatalysts increased in the order commercial TiO$_2$<Nd,N,S-TiO$_2$<MWCNT/TiO$_2$<MWCNT/Nd,N,S-TiO$_2$<SWCNT/TiO$_2$<SWCNT/Nd,N,S-TiO$_2$. The photocatalytic degradation of EBS yielded maximum degradation percentages of 58.8%, 68.0%, 80.4%, 87.6%, 95.7% and 96.9% for commercial TiO$_2$, Nd,N,S-TiO$_2$, MWCNT/TiO$_2$, SWCNT/TiO$_2$, MWCNT/Nd,N,S-TiO$_2$, SWCNT/Nd,N,S-TiO$_2$, respectively. First order kinetic studies gave degradation rate constants of $4.1 \times 10^{-3}$ min$^{-1}$, $5.2 \times 10^{-3}$ min$^{-1}$, $6.8 \times 10^{-3}$ min$^{-1}$, $8.5 \times 10^{-3}$ min$^{-1}$, $1.4 \times 10^{-2}$ min$^{-1}$ and $1.5 \times 10^{-2}$ min$^{-1}$ for the degradation of EBS by commercial TiO$_2$, Nd,N,S-TiO$_2$, MWCNT/TiO$_2$, SWCNT/TiO$_2$, MWCNT/Nd,N,S-TiO$_2$ and SWCNT/Nd,N,S-TiO$_2$, respectively. Similarly, maximum degradation values of 50.0%, 58.8%, 72.9%, 74.1%, 85.8% and 89.2% were recorded for the degradation of EBT by commercial TiO$_2$, Nd,N,S-TiO$_2$, MWCNT/TiO$_2$, SWCNT/TiO$_2$, MWCNT/Nd,N,S-TiO$_2$ and SWCNT/Nd,N,S-TiO$_2$, respectively. The degradation rate constants observed from first order kinetics were $3.1 \times 10^{-3}$ min$^{-1}$, $3.8 \times 10^{-3}$ min$^{-1}$, $5.1 \times 10^{-3}$ min$^{-1}$, $5.7 \times 10^{-3}$ min$^{-1}$, $8.0 \times 10^{-3}$ min$^{-1}$ and $9.3 \times 10^{-3}$ min$^{-1}$ for commercial TiO$_2$, Nd,N,S-TiO$_2$, MWCNT/TiO$_2$, SWCNT/TiO$_2$, MWCNT/Nd,N,S-TiO$_2$ and SWCNT/Nd,N,S-TiO$_2$, respectively. The first order kinetics revealed that the photocatalysts degraded EBS faster than EBT, probably due to their structural differences which offer varying degrees of stability and their different interactions with the photocatalyst.

UV-Vis spectra were also recorded to monitor the changes in the absorption spectra of both dyes with increasing irradiation time during degradation by SWCNT/Nd,N,S-TiO$_2$ (Figure 8.8). The absorption spectra of both dyes (Figure 8.8a and 8.8b) decreased gradually and become smooth with increasing irradiation time. The gradual smoothening of the UV-Vis absorption peaks was accompanied by the fading away of the colours of the two dyes suggesting the breaking down of the chromophore. Moreover, there were no new peaks observed in both spectra suggesting that there were no derivatives of the two dyes formed as a result of photocatalytic degradation. This suggests that the dyes are largely degraded into inorganic species or smaller molecules such as CO$_2$, SO$_3$, NO$_2$, H$_2$O, etc.
Figure 8.8: UV-Vis absorption spectra of (a) EBS and (b) EBT during photocatalysis.
Commercial TiO$_2$ displayed the lowest photocatalytic activity for both EBS and EBT due to its wide band gap (Table 8.1) which results in poor visible light absorption. This means that there is insufficient formation of the hydroxyl and superoxide radicals which are responsible for dye degradation. The observed activity of commercial TiO$_2$ results from dye sensitisation and the possible presence of small amounts of UV light in the simulated solar light which can be absorbed by TiO$_2$.\textsuperscript{18,19} Moreover, undoped titania suffers from a high recombination rate of the photogenerated electron/hole pairs and this significantly lowers its photocatalytic activity.\textsuperscript{20} Tridoping titania significantly improved its photocatalytic activity and this improvement is ascribed to the combined contribution of N, S and Nd incorporation in the titania matrix. All three dopants have been found to enhance visible light absorption of titania through formation of sub-band gap states which result to band gap narrowing (Table 8.1).\textsuperscript{21,22} This ensures efficient visible light absorption and production of the oxidising species. The presence of Nd$^{3+}$ in the titania matrix also facilitate charge separation and improve the activity of tridoped TiO$_2$. Furthermore, Nd$^{3+}$ species may facilitate better interaction of the pollutant and catalyst due to its ability to form complexes with some Lewis bases such as carboxylic acids, alcohols, amines, etc., when these compounds interact with the 4$d$ orbitals of Nd.\textsuperscript{22} The intimate interaction of the pollutant and the photocatalyst is essential for harvesting the oxidising species on the surface of the photocatalyst.\textsuperscript{23} Enhanced photocatalytic activity was observed for the MWCNT/TiO$_2$ and SWCNT/TiO$_2$ compared to commercial TiO$_2$ and tridoped TiO$_2$ which is credited to the incorporation of the CNTs which improve visible light absorption, charge separation and transportation and act as sources of carbon doping.

Both MWCNT/Nd,N,S-TiO$_2$ and SWCNT/Nd,N,S-TiO$_2$ displayed superior photocatalytic activity compared to commercial TiO$_2$, tridoped TiO$_2$, MWCNT/TiO$_2$ and SWCNT/TiO$_2$ for both EBS and EBT (Figure 8.7). This could be due to the incorporation of the CNTs which resulted in a new material exhibiting the combined properties of tridoped TiO$_2$ and CNTs. Incorporation of CNTs significantly enhanced visible light absorption of the photocatalysts as evidenced in the UV-Vis absorption spectra (Figure 8.5). The enhanced visible light
absorption in the presence of the CNTs may be attributed to their possible role as visible light sensitisers. The CNTs absorb visible light and inject electrons into the conduction band of titania and these electrons may be trapped by adsorbed oxygen to form the oxidising species.\textsuperscript{14} Furthermore, CNTs may act as a source of carbon doping. This creates sub-band gap states which narrow the band gap of titania and further improve visible light absorption and the generation of the oxidising species.\textsuperscript{24} In addition to enhancing visible light absorption, the CNTs function as electron sinks and transport systems, thereby prolonging the life of the electron/hole pairs. The formation of the Ti-C and Ti-O-C bonds between titania and the CNTs facilitate effective electron mobility. This allows for the formation of the hydroxyl and superoxide radicals responsible for dye degradation.\textsuperscript{11} Moreover, incorporation of the carbon nanomaterials improves the interaction of the dye molecules and the photocatalyst, improves the surface area and also minimise aggregation of the titania nanoparticles.\textsuperscript{25} All these factors contribute to the enhanced photocatalytic activity of the tridoped TiO$_2$/carbon nanotube composites.

SWCNT/Nd,N,S-TiO$_2$ displayed a slightly superior photocatalytic activity over MWCNT/Nd,N,S-TiO$_2$. This is due to its better absorption of visible light (Figure 8.5) owing to its narrower band gap which results to more efficient generation of the superoxide and hydroxyl radicals responsible for the degradation of the dye species. Moreover, SWCNTs have better electrical conductivity than MWCNTs which may account for superior charge separation and transportation in the composite photocatalyst.\textsuperscript{26,27} This prolongs the life of the electron/hole pairs and improves the formation of the oxidising species.

Another contributing factor to the superiority of the SWCNT based photocatalyst may lie in structural differences, resulting in different interactions with the tridoped TiO$_2$. Strong and intimate interaction between the CNT and tridoped TiO$_2$ is crucial for efficient exploitation of the combined properties of the two materials.\textsuperscript{11} Good interaction between the tridoped TiO$_2$ and CNT results to sufficient formation of the Ti-C and Ti-O-C bonds which facilitate efficient electron transfer between CNTs and titania. Furthermore, the large surface area of the SWCNT/Nd,N,S-TiO$_2$ relative to its MWCNTs counterpart contribute to its superior photocatalytic activity.
Chapter 8: Enhanced visible light photocatalytic degradation of eriochrome black T and eosin blue shade in water using tridoped titania decorated on SWCNTs and MWCNTs: Effect of the type of carbon nanotube incorporated

### 8.5.7.2 Competitive photocatalytic degradation of EBS and EBT

MWCNT/Nd,N,S-TiO$_2$ and SWCNT/Nd,N,S-TiO$_2$ were evaluated for the degradation of a mixture of EBS and EBT and the results obtained are presented in Figure 8.9a. Notably, the photocatalytic activity of the composite photocatalysts for both dyes has dropped significantly compared to degradation of single dye solutions. This is attributed to competition between EBS and EBT for active sites in the photocatalysts, resulting to lower degradation efficiency. EBS is degraded faster than EBT which is consistent with the observation in single dye degradation experiments. Visible light photocatalytic degradation efficiencies of 58.9% and 61.4% were recorded for EBS degradation by MWCNT/Nd,N,S-TiO$_2$ and SWCNT/Nd,N,S-TiO$_2$, respectively. Similarly, degradation efficiencies of 49.0% and 54.1% were observed for the competitive degradation of EBT by MWCNT/Nd,N,S-TiO$_2$ and SWCNT/Nd,N,S-TiO$_2$, respectively. In order to gain an insight into rate at which the two dyes were being broken down, first order kinetics (Figure 8.9b) were utilised. For EBS, degradation rates of $3.6 \times 10^{-3}$ min$^{-1}$ and $3.9 \times 10^{-3}$ min$^{-1}$ were obtained for MWCNT/Nd,N,S-TiO$_2$ and SWCNT/Nd,N,S-TiO$_2$, respectively. Moreover, degradation rates of $2.9 \times 10^{-3}$ min$^{-1}$ and $3.1 \times 10^{-3}$ min$^{-1}$ were observed for the degradation of EBT by MWCNT/Nd,N,S-TiO$_2$ and SWCNT/Nd,N,S-TiO$_2$, respectively. Although the degradation rates dropped significantly under competitive conditions, the both photocatalysts displayed the potential as environmental clean-up tools for dye pollution.
Figure 8.9: (a) Competitive photocatalytic degradation of EBS and EBT and (b) kinetics studies for the competitive degradation of EBS and EBT.
8.5.8 Total organic carbon analysis

Total organic carbon measurements provide valuable information during photocatalysis. Ideally, complete mineralisation of the dye molecules is the main target during photocatalysis to minimise the formation of potentially toxic photocatalysis by-products. Therefore, TOC provides an insight into the extent to which the organic compounds are completely mineralised. TOC removal for both dyes (Figure 8.10) increased with increasing irradiation time, suggesting that complete mineralisation occurs over time. Maximum TOC removal values of 73.6% (Figure 8.10a) and 66.2% (Figure 8.10b) were observed for the degradation of EBS and EBT, respectively. These values indicate fairly high degree of complete mineralisation which suggests that the major end products of degradation are smaller inorganic molecules or ions.
Figure 8.10: Total organic carbon removal by SWCNT/Nd,N,S-TiO$_2$ from (a) EBS and (b) EBT degradation.
8.5.9 Recycling experiments

The stability of SWCNT/Nd,N,S-TiO$_2$ was evaluated by reusing the photocatalyst for five times for the degradation of EBS. After each use, the photocatalyst was washed with ethanol and then acetone and dried in an oven at 80 °C for 1 hr. The photocatalyst displayed sufficient stability, reaching a maximum degradation efficiency of 88.8% after five cycles (Figure 8.11). This means that the photocatalyst has the potential application over a prolonged period while maintaining good photocatalytic activity. Most of the decline in the photocatalytic activity with increasing number of cycles may be linked to the loss of the photocatalyst during the washing and recovery stage.

![Graph showing EBS degradation efficiency over cycles](image)

**Figure 8.11:** Recyclability studies of the SWCNT/Nd,N,S-TiO$_2$ composite for EBS degradation.
8.6 Chapter summary

Tridoped TiO$_2$ was decorated on MWCNTs and SWCNTs and the resultant photocatalysts displayed improved optical and photocatalytic properties compared to tridoped TiO$_2$, MWCNT/TiO$_2$ and SWCNT/TiO$_2$. These improvements are credited to the co-operative effect of the tridoped TiO$_2$ and the CNTs. This synergistic effect emanates from the intimate contact between the tridoped TiO$_2$ and the CNTs. The SWCNT/Nd,N,S-TiO$_2$ displayed superior photocatalytic activity over its MWCNTs counterpart. This could be attributed to among other factors, the good electrical conductivity of SWCNTs, large surface area and better interaction with the tridoped TiO$_2$ resulting in a much stronger interfacial contact and bond formation. The prepared composite photocatalysts displayed the capacity to degrade both dyes under competitive conditions which highlights the versatility of the materials and their potential application as environmental clean-up tools for dye pollution. A reasonably high degree of complete mineralisation of both dyes was evident from TOC analyses which indicate that most of the dye molecules are broken down into simpler molecules and inorganic ions. The SWCNT/Nd,N,S-TiO$_2$ is fairly stable and could be recycled for five times with high degradation efficiency.
8.7 References


Chapter 8: Enhanced visible light photocatalytic degradation of eriochrome black T and eosin blue shade in water using tridoped titania decorated on SWCNTs and MWCNTs: Effect of the type of carbon nanotube incorporated


In this chapter, gadolinium ion doped graphitic carbon nitride (g-C$_3$N$_4$-Gd$^{3+}$) was incorporated in a multiwalled carbon nanotube/titania (MWCNT/TiO$_2$) matrix to form gadolinium ion doped graphitic carbon nitride/multiwalled carbon nanotube/titania (g-C$_3$N$_4$-Gd/MWCNT/TiO$_2$) nanocomposite photocatalysts with varying graphitic carbon nitride contents. The photocatalytic properties of the prepared nanocomposites were evaluated for the degradation of the diazo dye trypan blue (TB) under simulated solar light. MWCNT/TiO$_2$ and g-C$_3$N$_4$-Gd$^{3+}$ were also prepared and used as controls to evaluate the effectiveness of coupling the two materials.

9.1 Introduction

Coupling titania with narrow band gap semiconductors is one of the strategies employed to extend its optical response into the visible light region, enhance charge separation and improve its photocatalytic activity. Narrow band gap semiconductors such as CdS$^1$, CuInS$_2$$^2$, CdSe$^3$, WO$_3$$^4$, Fe$_2$O$_3$$^5$, etc., have been used to modify titania and facilitate its visible light activity which is otherwise poor due to the wide band gap (3.2 eV, anatase and 3.0 eV, rutile). In the narrow band gap semiconductor/titania hybrid photocatalyst, visible light is absorbed by the narrow band gap semiconductor in a visible light sensitisation mechanism.$^1$. Noteworthy, visible light sensitisation and charge separation are achieved simultaneously, leading to better photocatalytic properties of the hybrid material than the two individual semiconductors. However, in order to exploit the combined...
properties of the semiconductors, their band energies must sufficiently match and there has to be a strong and intimate contact to ensure easy and efficient electron migration.\textsuperscript{6,7}

Graphitic carbon nitride (g-C\textsubscript{3}N\textsubscript{4}), a metal-free, polymeric, mild-band gap semiconductor (2.7 eV) has emerged as an attractive sensitisier for TiO\textsubscript{2}. Graphitic carbon nitride is based on heptazine units linked together to form a graphene-like structure with good chemical and thermal stability, visible light absorption properties and unique electronic structure.\textsuperscript{8,9} Despite good visible light absorption, pristine graphitic carbon nitride shows low photocatalytic activity due to high recombination rate of the photogenerated charge carriers and the smaller surface area.\textsuperscript{10} Reports on the fabrication and photocatalytic evaluation of g-C\textsubscript{3}N\textsubscript{4}/TiO\textsubscript{2} nanocomposites have revealed that coupling the two semiconductors results to improved optical properties, charge separation and photocatalytic properties of the nanocomposite. The well-matched band energies of TiO\textsubscript{2} and g-C\textsubscript{3}N\textsubscript{4} allows for efficient and easy electron movement between the two semiconductors.\textsuperscript{6,11,12}

Hybridising gadolinium ion doped g-C\textsubscript{3}N\textsubscript{4} and MWCNT/TiO\textsubscript{2} was envisioned as an effective route to exploit the combined properties of the individual materials making up the nanocomposite material. Doping graphitic carbon nitride with gadolinium ions sought to ensure charge separation and improved interaction of g-C\textsubscript{3}N\textsubscript{4} with the organic pollutant molecules. Incorporation of the doped graphitic carbon nitride in the MWCNT/TiO\textsubscript{2} matrix aimed at improving visible light activity, charge separation and transportation, adsorption properties and the photocatalytic activity of the nanocomposite.

9.2 Experimental section

9.2.1 Materials

All the materials and reagents used in this work are described in Chapter 3, Section 3.2.
9.2.2 Preparation of g-C$_3$N$_4$-Gd/MWCNT/TiO$_2$ nanocomposites

Synthesis of g-C$_3$N$_4$-Gd/MWCNT/TiO$_2$ nanocomposites proceeded according to the procedure outlined in Chapter 3, Section 3.3.5.

9.2.3 Characterisation techniques

The synthesised photocatalysts were characterised using various tools as outlined in Chapter 3, Section 3.4.

9.2.4 Evaluation of the photocatalytic properties of the nanocomposites

Aqueous solutions of TB were used to investigate the photocatalytic properties of the fabricated nanocomposites under simulated solar light irradiation as detailed in Chapter 3, Section 3.3. UV-Vis photometric measurements were obtained at 607 nm. TOC analysis was performed according to the procedure outlined in Chapter 3, Section 3.5.1.

9.2.4.1 Detection of hydroxyl radicals

The procedure for detection of the hydroxyl radical during photocatalysis and PL measurements are presented in Chapter 6, Section 6.2.4.2.

9.3 Results and discussion

9.3.1 Surface morphology studies

SEM images of the nanocomposites photocatalysts (Figure 9.1a and 9.1b) show that both the MWCNT and the g-C$_3$N$_4$-Gd (red arrows) were embedded within the titania matrix which is the ideal architecture for the nanocomposite. Good contact between the MWCNT, TiO$_2$ and g-C$_3$N$_4$-Gd$^{3+}$ is necessary for their collaborative effect during photocatalysis. The incorporation of the doped graphitic carbon nitride into the MWCNT/titania matrix was further confirmed by TEM (Figure 9.1c) and show that the TiO$_2$ particles (about 20 nm in diameters) were nearly spherical.
in shape. High resolution TEM (Figure 9.1d) further shows that there is sufficient contact between the doped graphitic carbon nitride and TiO$_2$. Measurement of the interplanar spacing (Figure 9.1d) gave a value of 0.352 nm which is characteristic of the (101) crystal plane of TiO$_2$.\textsuperscript{13}

![Figure 9.1: SEM images of (a) g-C$_3$N$_4$-Gd/MWCNT/TiO$_2$ (30%), (b) g-C$_3$N$_4$-Gd/MWCNT/TiO$_2$ (10%) and (b) and (c) TEM images of g-C$_3$N$_4$-Gd/MWCNT/TiO$_2$ (30%).]
9.3.2 FT-IR analysis

FT-IR spectra of the nanocomposites (Figure 9.2) showed the characteristic peaks of both titania and g-C$_3$N$_4$ suggesting the possible formation of the composite material. The broad peak centred around 3426 cm$^{-1}$ could be attributed to adsorbed moisture and the N-H vibration.$^{14}$ Absorption bands observed around 1243 cm$^{-1}$ and 1325 cm$^{-1}$ correspond to the stretching vibrations of connected units of N-(C)$_3$ (in case of full condensation during formation of g-C$_3$N$_4$) and C-N-C (for partial condensation in g-C$_3$N$_4$). Furthermore, peaks appeared at 1414 cm$^{-1}$, 1570 cm$^{-1}$ and 1641 cm$^{-1}$ which relate to the stretching vibration modes of heptazine-derived repeating units.$^{15,16}$ A weak, broad band also appeared between 2020 cm$^{-1}$ and 2215 cm$^{-1}$ which emanates from the C≡N bonds.$^9$ The small sharp peak observed in g-C$_3$N$_4$-Gd$^{3+}$ at 809 cm$^{-1}$ originates from the breathing mode of the heptazine arrangement (synphase and antiphase vibrations of N=N of the tetrazine ring).$^6$ This peak was not visible in the samples containing less than 30% g-C$_3$N$_4$-Gd$^{3+}$ and was clearly visible at 40% g-C$_3$N$_4$-Gd$^{3+}$. The broad Ti-O and O-Ti-O peak characteristic of TiO$_2$ was observed around 600 cm$^{-1}$ in the nanocomposite photocatalysts.
9.3.3 Optical properties of the photocatalysts

Gadolinium ion doped graphitic carbon nitride showed the typical UV-Vis absorption characteristics of g-C$_3$N$_4$ which extended from the UV into the visible light region (Figure 9.3) due to the narrow band gap of g-C$_3$N$_4$ (2.7 eV). There was no significant enhancement in visible light absorption by MWCNT/TiO$_2$ nanocomposite which could be due to the small amount of MWCNTs incorporated (0.5%). It is evident from the UV-Vis absorption spectra that coupling g-C$_3$N$_4$-Gd$^{3+}$ and MWCNT/TiO$_2$ significantly improved visible light absorption of the resultant nanocomposites. The synergy between MWCNT and g-C$_3$N$_4$-Gd$^{3+}$ in sensitizing TiO$_2$ contributed towards the visible light activity of the nanocomposites. MWCNTs and g-C$_3$N$_4$-Gd$^{3+}$ absorb visible light and inject electrons into the conduction band of TiO$_2$ resulting to a series of redox reactions to produce the radical species responsible for dye degradation. Sensitisation of TiO$_2$ by g-C$_3$N$_4$-Gd$^{3+}$ is favored
by their well-matched band energies and the intimate interface as observed in TEM images (Figure 9.1c and 9.1d).

Figure 9.3: UV-Vis diffuse reflectance spectra of the prepared photocatalysts.

Band gap modifications were observed in all the prepared photocatalysts with $\text{g-C}_3\text{N}_4$-$\text{Gd}^{3+}$ a typically smaller band gap of 2.64 eV (Table 9.1) which is smaller than for pure $\text{g-C}_3\text{N}_4$ due to the incorporation of Gd$^{3+}$ ions. Among the $\text{g-C}_3\text{N}_4$-$\text{Gd}/\text{MWCNT}/\text{TiO}_2$ nanocomposites, the sample containing 10% had the largest bandgap of 2.99 eV and the 40% sample had the smallest band gap of 2.83 eV. These modified band gaps of the nanocomposites are responsible for their absorption in the visible light region.
Table 9.1: Calculated band gap energies of the composite photocatalysts.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Absorption edge wavelength (nm)</th>
<th>Calculated band gap energy (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MWCNT/TiO₂</td>
<td>401.2</td>
<td>3.09</td>
</tr>
<tr>
<td>g-C₃N₄-Gd³⁺</td>
<td>469.5</td>
<td>2.64</td>
</tr>
<tr>
<td>g-C₃N₄-Gd/MWCNT/TiO₂ (10%)</td>
<td>414.8</td>
<td>2.99</td>
</tr>
<tr>
<td>g-C₃N₄-Gd/MWCNT/TiO₂ (20%)</td>
<td>424.0</td>
<td>2.92</td>
</tr>
<tr>
<td>g-C₃N₄-Gd/MWCNT/TiO₂ (30%)</td>
<td>424.0</td>
<td>2.92</td>
</tr>
<tr>
<td>g-C₃N₄-Gd/MWCNT/TiO₂ (40%)</td>
<td>437.6</td>
<td>2.83</td>
</tr>
</tbody>
</table>

9.3.4 XRD analysis

X-ray diffraction patterns of the prepared composite photocatalysts are shown in Figure 9.4. The diffraction pattern of g-C₃N₄-Gd³⁺ showed two peaks at 13.1° and 27.7° which can be indexed to the (100) and (002) crystal planes of g-C₃N₄ and correspond to the in-plane structural packing arrangement parallel to the c-axis and long–range interplanar stacking of aromatic rings, respectively. The (100) peak is much weaker than the (002) peak and did not appear in the composite photocatalysts. Contrary, the (002) started appearing in the sample containing 20% g-C₃N₄-Gd³⁺ and increased in intensity with increasing g-C₃N₄-Gd³⁺ content. In addition to the peaks characteristic of g-C₃N₄, the MWCNT/TiO₂ and g-C₃N₄-Gd/MWCNT/TiO₂ nanocomposites showed peaks characteristic of the anatase phase of TiO₂. Peaks were observed at 25.3°, 27.3°, 37.8°, 48.0°, 54.0°, 55.0°, 62.6°, 70.2° and 75.1° which can be indexed to the (101), (004), (200), (105), (211), (204), (110), (220) and (215) crystal planes of anatase TiO₂, respectively. Crystallite size calculations from Scherrer equation gave a size range of 12.11 to 14.96 nm (Table 9.2) which was smaller but comparable to the 20 nm obtained from TEM measurements.
**Figure 9.4:** XRD patterns of the prepared nanocomposites.

**Table 9.2:** Calculated crystallite sizes of the photocatalysts.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Crystallite size (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MWCNT/TiO&lt;sub&gt;2&lt;/sub&gt;</td>
<td>14.96</td>
</tr>
<tr>
<td>g-C&lt;sub&gt;3&lt;/sub&gt;N&lt;sub&gt;4&lt;/sub&gt;-Gd/MWCNT/TiO&lt;sub&gt;2&lt;/sub&gt; (10%)</td>
<td>12.72</td>
</tr>
<tr>
<td>g-C&lt;sub&gt;3&lt;/sub&gt;N&lt;sub&gt;4&lt;/sub&gt;-Gd/MWCNT/TiO&lt;sub&gt;2&lt;/sub&gt; (20%)</td>
<td>14.13</td>
</tr>
<tr>
<td>g-C&lt;sub&gt;3&lt;/sub&gt;N&lt;sub&gt;4&lt;/sub&gt;-Gd/MWCNT/TiO&lt;sub&gt;2&lt;/sub&gt; (30%)</td>
<td>12.11</td>
</tr>
<tr>
<td>g-C&lt;sub&gt;3&lt;/sub&gt;N&lt;sub&gt;4&lt;/sub&gt;-Gd/MWCNT/TiO&lt;sub&gt;2&lt;/sub&gt; (40%)</td>
<td>12.11</td>
</tr>
</tbody>
</table>
9.4 Photocatalytic evaluation of the nanocomposites

**Figure 9.5** shows the degradation of TB by the different composite photocatalysts prepared. Coupling g-C$_3$N$_4$-Gd and MWCNT/TiO$_2$ resulted in better photocatalytic activity of the resultant nanocomposites compared to g-C$_3$N$_4$-Gd$^{3+}$ and MWCNT/TiO$_2$. The g-C$_3$N$_4$-Gd/MWCNT/TiO$_2$ (30%) nanocomposite showed the highest photocatalytic activity and reached 100% TB degradation in 150 mins while g-C$_3$N$_4$-Gd$^{3+}$ showed the lowest photocatalytic activity and reached 32.2% TB degradation in the same irradiation time (**Table 9.3**). The photocatalytic activity of the prepared materials increased in the order g-C$_3$N$_4$-Gd$^{3+}$<MWCNT/TiO$_2$<g-C$_3$N$_4$-Gd/MWCNT/TiO$_2$ (40%)<g-C$_3$N$_4$-Gd/MWCNT/TiO$_2$ (20%)<g-C$_3$N$_4$-Gd/MWCNT/TiO$_2$ (10%)<g-C$_3$N$_4$-Gd/MWCNT/TiO$_2$ (30%). g-C$_3$N$_4$-Gd/MWCNT/TiO$_2$ (20%) and g-C$_3$N$_4$-Gd/MWCNT/TiO$_2$ (40%) reached 100% TB degradation after 180 minutes while g-C$_3$N$_4$-Gd/MWCNT/TiO$_2$ (10%), g-C$_3$N$_4$-Gd$^{3+}$ and MWCNT/TiO$_2$ reached degradation efficiencies of 99.5, 36.8 and 90.1%, respectively, in the same irradiation time.

Despite good visible light absorption (narrow band gap), g-C$_3$N$_4$-Gd$^{3+}$ displayed poor photocatalytic activity towards TB degradation probably due to insufficient charge separation as a result of the small amount of Gd$^{3+}$ ions incorporated (<0.5%). Another possible cause of the poor photocatalytic activity could be poor interaction between the dye molecules and the photocatalyst and the possibly smaller surface area of the photocatalyst. MWCNT/TiO$_2$ displayed lower photocatalytic activity compared to the g-C$_3$N$_4$-Gd/MWCNT/TiO$_2$ nanocomposites owing to its low visible light absorption as depicted in the UV-Vis spectrum in **Figure 9.3**. However, MWCNT/TiO$_2$ showed better photocatalytic activity than g-C$_3$N$_4$-Gd$^{3+}$ due to the presence of MWCNTs which improved separation and transportation of charge carriers. All the g-C$_3$N$_4$-Gd/MWCNT/TiO$_2$ nanocomposites benefitted from the combined contribution of g-C$_3$N$_4$-Gd$^{3+}$, MWCNT and TiO$_2$ resulting to enhanced activity. Doping g-C$_3$N$_4$ with Gd$^{3+}$ ions (**as illustrated in Figure 9.6**) minimised charge recombination due to the excellent electron scavenging properties of Gd$^{3+}$. Charge separation was further improved by...
coupling $\text{g-C}_3\text{N}_4$-$\text{Gd}^{3+}$ with MWCNT/TiO$_2$ due to the good electron conductivity and transportation properties of MWCNTs.$^{18,19}$

![Figure 9.5: Degradation of TB by the different photocatalysts.](image)

Electrons excited by visible light from the valence band of $\text{g-C}_3\text{N}_4$ are eventually transferred to the conduction band of TiO$_2$ due to their well-matched band energies. These electrons then migrate to the MWCNT skeleton attached to TiO$_2$ where they are trapped by adsorbed oxygen to form the superoxide and hydroxyl radicals as shown in the schematic of the proposed synergy between $\text{g-C}_3\text{N}_4$-$\text{Gd}^{3+}$ and MWCNT/TiO$_2$ (Figure 9.6). Moreover, some of the excited electrons were trapped by the Gd$^{3+}$ ions on the surface of $\text{g-C}_3\text{N}_4$ where formation of the oxidising species occurred upon reaction with adsorbed oxygen. Consequently, charge carrier recombination was sufficiently suppressed resulting to improved photoactivity. The holes left in the valence band of $\text{g-C}_3\text{N}_4$ could be involved in direct degradation of dye molecules or react with adsorbed water to form the
hydroxyl radicals which are responsible for dye degradation (Figure 9.6). Incorporation of the MWCNTs ensured good electron scavenging and transportation and good interaction between the dye molecules and the photocatalyst owing to the good adsorption properties of MWCNTs. Furthermore, the presence of Gd$^{3+}$ could also aid in concentrating the dye molecules onto the surface of the photocatalyst due to their chelating properties. This is an important step in ensuring the effectiveness of the photocatalytic process since it is a surface phenomenon, therefore, the pollutant must be in contact with the catalyst surface before degradation could occur.

Figure 9.6: Proposed synergy between g-C$_3$N$_4$-Gd$^{3+}$ and MWCNT/TiO$_2$.

In photocatalysis, the rate at which decolourisation or degradation of organic pollutants occurs, gives an insight into the efficiency and effectiveness of the photocatalyst. First order kinetics was used to study the degradation of TB by the prepared photocatalysts and the results obtained are given in Figure 9.7. Photocatalytic degradation of TB by the composite photocatalysts proceeded at
higher rates compared to g-C₃N₄-Gd³⁺. g-C₃N₄-Gd/MWCNT/TiO₂ (30%) showed the highest degradation rate of 3.3 x 10⁻² min⁻¹ while g-C₃N₄-Gd³⁺ showed the slowest degradation rate of 2.5 x 10⁻³ min⁻¹ (Table 9.3). The higher degradation rates observed when using the composite photocatalysts suggest the possibility of employing these materials for environmental clean-up.

Figure 9.7: Kinetics for the degradation of TB.
Table 9.3: Percentage TB degraded after 150 mins and degradation rates of TB by the different photocatalysts.

<table>
<thead>
<tr>
<th>Samples</th>
<th>Degradation after 150 mins (%)</th>
<th>Degradation rate $(k \times 10^{-2})$ (min$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MWCNT/TiO$_2$</td>
<td>83.8</td>
<td>1.3</td>
</tr>
<tr>
<td>$g$-C$_3$N$_4$-Gd$^{3+}$</td>
<td>32.2</td>
<td>0.25</td>
</tr>
<tr>
<td>$g$-C$_3$N$_4$-Gd/MWCNT/TiO$_2$ (10%)</td>
<td>97.2</td>
<td>2.8</td>
</tr>
<tr>
<td>$g$-C$_3$N$_4$-Gd/MWCNT/TiO$_2$ (20%)</td>
<td>96.6</td>
<td>2.4</td>
</tr>
<tr>
<td>$g$-C$_3$N$_4$-Gd/MWCNT/TiO$_2$ (30%)</td>
<td>100</td>
<td>3.3</td>
</tr>
<tr>
<td>$g$-C$_3$N$_4$-Gd/MWCNT/TiO$_2$ (40%)</td>
<td>96.8</td>
<td>2.1</td>
</tr>
</tbody>
</table>

The degradation of TB was further monitored by recording the absorption spectra with increasing irradiation time. Figure 9.8a show that the TB peak centred on 600 nm decreased gradually with increasing irradiation time until it disappeared completely after 150 mins, when $g$-C$_3$N$_4$-Gd/MWCNT/TiO$_2$ (30%) was used as a catalyst. This was also coupled with a slight blue shift in the TB peak which may be ascribed to the alteration of TB structure during degradation. The gradual fading of the deep blue colour of TB solution was further evidence of the degradation of TB (Figure 9.8b).
Figure 9.8: (a) UV-Vis absorption spectra of TB during degradation by \( \text{g-C}_3\text{N}_4\text{-Gd}^{3+}/\text{MWCNT/TiO}_2 \) (30\%) and (b) fading of the deep blue colour of TB with increasing irradiation time.

9.4.1 Detection of the hydroxyl radicals

2-Hydroxyterephthalic acid is formed exclusively when terephthalic acid reacts with hydroxyl radicals on the surface of the photocatalysts.\(^{2}\) There was no PL emission peak observed at time zero (Figure 9.9) suggesting the absence of 2-hydroxyterephthalic acid which is formed when hydroxyl radicals are present. Upon irradiation, the emission peak appeared at 420 nm due to the presence of 2-hydroxyterephthalic acid. Irradiating the terephthalic acid/photocatalyst mixture
resulted in the formation of hydroxyl radicals on the surface of the photocatalyst which reacted with the terephthalic acid in solution to form 2-hydroxyterephthalic acid which is responsible for the emission peak at 420 nm. The emission peak increased in intensity with increasing irradiation time due to an increase in the concentration of hydroxyterephthalic acid as more hydroxyl radicals were being produced.

![Fluorescence spectra of 2-hydroxyterephthalic acid different intervals using C$_3$N$_4$-Gd$^{3+}$/MWCNT/TiO$_2$ (30%).](image)

**Figure 9.9: Fluorescence spectra of 2-hydroxyterephthalic acid different intervals using C$_3$N$_4$-Gd$^{3+}$/MWCNT/TiO$_2$ (30%).**

### 9.4.2 Total organic carbon measurements

Total organic carbon analysis provides valuable information about the extent to which the dye molecules are degraded during photocatalysis. A higher TOC removal is desirable as an indication of a higher degree of complete mineralisation of the dye molecules. **Figure 9.10** shows the results obtained when measuring the TOC removal with increasing irradiation time. A maximum TOC removal of 69.2% was recorded after 3 hrs of irradiation. This value suggest that most of the TB structure was completely mineralised which could lower the possible formation of
toxic degradation products. However, there was still a lot of organic matter bound in solution which may require longer degradation times to fully mineralise.

![Figure 9.10: TOC removal by C₃N₄-Gd³⁺/MWCNT/TiO₂ (30%) at different time intervals.](image_url)
9.5 Chapter summary

Graphitic carbon nitride doped with gadolinium ions was coupled with MWCNT/TiO₂ via a simple sol-gel method. Combining g-C₃N₄·Gd³⁺ and MWCNT/TiO₂ resulted in improved optical and photocatalytic properties of the resulted nanocomposites compared to MWCNT/TiO₂ and g-C₃N₄·Gd³⁺ alone. The prepared nanocomposites showed good photocatalytic activity towards TB under simulated solar light irradiation which suggests their potential practical exploitation in treatment of dye pollution. Among the prepared nanocomposites, g-C₃N₄·Gd/MWCNT/TiO₂ (30%) displayed the highest photocatalytic activity suggesting existence of an optimum amount of g-C₃N₄·Gd³⁺ relative to TiO₂ that ensures good balance between visible light absorption, charge separation and photocatalytic activity. The hydroxyl radicals were confirmed as the active species during degradation of the dye molecules. Total organic carbon measurements revealed that most of the TB structure was completely mineralised but there was still organic bound carbon present in solution which may require longer irradiation times to degrade.
9.6 References


10. Jiang D, Chen L, Xie J, Chen M. Ag\textsubscript{2}S/g-C\textsubscript{3}N\textsubscript{4} composite photocatalysts for efficient Pt-free hydrogen production. The co-catalyst function of Ag/Ag\textsubscript{2}S formed by simultaneous photodeposition. *Dalt Trans.* 2014;43:4878-4885.


CHAPTER 10:
CONCLUSIONS AND RECOMMENDATIONS

10.1 Conclusions

The following general conclusions can be drawn from the work carried out:

- Microscopic, spectroscopic and crystallographic techniques revealed the successful preparation of the different composite photocatalysts (MWCNT-Gd/TiO$_2$, MWCNT/Gd,N,S-TiO$_2$, MWCNT-Gd/Nd/Gd/Eu, N,S-TiO$_2$, MWCNT/Nd,N,S-TiO$_2$, SWCNT/Nd,N,S-TiO$_2$, rGO/Nd,N,S-TiO$_2$ and g-C$_3$N$_4$-Gd/MWCNT/TiO$_2$) using the sol-gel method. Anatase titania was the predominant TiO$_2$ phase in all the prepared nanocomposites with crystallite sizes of less than 25 nm.

- Tridoping titania with rare earth metal ions, nitrogen and sulphur led to enhanced visible light absorption as a result of band gap narrowing. Further improvement in the optical properties was observed when the tridoped titania was coupled with different carbon nanomaterials (MWCNT-Gd, MWCNT, SWCNT and rGO) which showed that the carbon nanomaterials played a significant role in visible light absorption either as visible sensitisers or sources of carbon doping. Similarly, improved optical properties and band gap modification was observed when MWCNT/TiO$_2$ was hybridised with g-C$_3$N$_4$-Gd$^{3+}$ which mainly acted as the visible light sensitisier.

- This study showed that decorating gadolinium oxide nanoparticles on MWCNTs and subsequent incorporation into titania enhanced the photocatalytic dye degradation which was mainly attributed to improved charge separation and transportation as a result of the Gd$^{3+}$ ions at the MWCNT/TiO$_2$ interface. Furthermore, this study revealed for the first time that coupling tridoped titania with carbon nanomaterials not only improved...
its visible light absorption but also the photocatalytic degradation of dye molecules in solution. This improvement was explained in terms of the synergy between the tridoping and incorporation of the carbon nanomaterials resulting to enhanced visible light absorption and charge separation and transportation. Likewise, coupling g-C₃N₄-Gd³⁺ with MWCNT/TiO₂ resulted in enhanced photocatalytic activity, with the highest activity observed from the nanocomposite containing 30% g-C₃N₄-Gd³⁺.

- Another important finding of this study relates to the carbon nanomaterials/tridoped titania nanocomposites (SWCNT/Nd,N,S-TiO₂, MWCNT/Nd,N,S-TiO₂ and rGO/Nd,N,S-TiO₂) which showed the potential to degrade dye molecules both from single and mixed dye solutions. This suggests the potential application of these materials in complex dye matrices. However, the photocatalytic degradation efficiencies were lower in the mixed dye solutions than in the single dye solutions owing to competition among the dye molecules for the catalyst surface. Comparative studies showed that the rGO/Nd,N,S-TiO₂ nanocomposite was the most photocatalytically active followed by the SWCNT/Nd,N,S-TiO₂ and lastly MWCNT/Nd,N,S-TiO₂. This observation was explained in terms of the structural differences of the carbon nanomaterials which affect their interaction with the tridoped titania, differences in interaction with the dye molecules, electrical conductivity and surface area.

- Addition of radical scavengers (benzoquinone and 2-propanol) during photocatalytic dye degradation resulted in a significant decline in the photocatalytic degradation efficiency which confirmed that the hydroxyl and superoxide radicals were the active oxidising species during dye degradation. Furthermore, formation of the hydroxyl radicals during photocatalyst irradiation was confirmed by fluorescence spectroscopy using terephthalic acid as the probe compound.

- Finally, examination of the extent to which the dye molecules were broken down showed that most of the dye molecules were completely mineralised
into inorganic species, as evidence from the over 50% TOC removal. However, some organic components of the dye molecules remained in solution after the photocatalysis experiments which may require extended periods of irradiation to fully degrade. The prepared photocatalysts were found to be stable and reached dye degradation efficiencies of over 85% after 5 cycles. This is an important feature of the photocatalysts as this can reduce operational costs during dye pollution remediation.

10.2 Recommendations

Subsequent to the success of this work in improving the MWCNT/TiO$_2$ interface, extending the optical response of TiO$_2$ into the visible light region and improving charge separation and the overall photocatalytic activity of titania, future work can explore the following:

- Decorate MWCNTs with other rare earth metal nanoparticles such as cerium, europium and samarium
- Explore the possibility of using a combination of the rare earth metal nanoparticles.
- Since only Gd, Nd and Eu were used in the tridoped titania, other rare earth metal ions such as Sm, La and Ce can be explored.
- The prepared photocatalysts were successfully employed in synthetic dye solutions, real industrial dye effluent may be used to evaluate the performance of the different photocatalysts.
- Other combinations of non-metal ions such as P+S, P+N, halogens+N, halogens+S, etc. with the rare earth ions can be evaluated when preparing the tridoped titania.
- Instead of simulating sunlight, studies can be done using real sunlight in summer to determine the real applicability of the nanocomposites.
• Evaluation of the prepared photocatalysts for reduction/oxidation of inorganic compounds such as NO, CO, Cr (IV), etc. and also for the degradation of other organic compounds apart from dyes.