PREPARATION AND CHARACTERIZATION OF COPPER-DOPED AND SILVER-DOPED TITANIUM DIOXIDE NANO-CATALYSTS FOR PHOTO CATALYTIC APPLICATIONS

Haya Abdel Ra’ouf Ahmed Ra’ouf Ahmed

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United Arab Emirates University

College of Engineering

Department of Mechanical Engineering

PREPARATION AND CHARACTERIZATION OF COPPER-DOPED AND SILVER-DOPED TITANIUM DIOXIDE NANO-CATALYSTS FOR PHOTOCATALYTIC APPLICATIONS

Haya Abdel Ra’ouf Ahmed

This thesis is submitted in partial fulfilment of the requirements for the degree of Master of Science in Material Science and Engineering

Under the Supervision of Professor Samir I. Abu-Eishah

May 2015
Declaration of Original Work

I, Haya Abdel Ra’ouf Ahmed, the undersigned, a graduate student at the United Arab Emirates University (UAEU) and the author of the thesis titled “Preparation and Characterization of Cu-doped and Ag-doped TiO$_2$ Nano-catalysts for Photocatalytic Applications”, hereby solemnly declare that this thesis is an original work that has been done and prepared by me under the supervision of Prof. Samir I. Abu-Eishah, in the College of Engineering at UAEU. This work has not been previously formed as the basis for the award of any degree, diploma or similar title at this or any other university. The materials borrowed from other sources and included in my thesis have been properly cited and acknowledged.

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Copy of
Abstract

The goal of this work was to improve the performance of TiO$_2$ nanomaterials by increasing their optical activities by shifting the onset of the response from the UV to the visible-light region. Among the several ways to achieve this goal, doping TiO$_2$ nanomaterials with other elements (e.g. metals) was selected to narrow the band gap and enhance the optical properties of TiO$_2$ nanomaterials. In this work, we have prepared Cu-doped TiO$_2$ and Ag-doped TiO$_2$ nano-catalysts, characterized them and studied their properties, and the optical ones in particular. The Ag-doped TiO$_2$ catalyst was prepared by the sol-gel method while the Cu-doped TiO$_2$ catalyst was prepared by using two different techniques for comparison purposes: the sol-gel method and the inert gas condensation technique under ultra-high vacuum.

The Ag-doped TiO$_2$ nano-catalysts prepared by the sol-gel method were characterized by using Fourier transform infrared spectroscopy (FTIR), Field emission scanning electron microscopy (FESEM) and Electron Probe Micro-Analyser (EPMA) for surface morphology and chemical composition, Brunauer–Emmett–Teller (BET) analysis for surface area and porosity measurements, X-ray diffraction (XRD) to determine their crystal structure and UV-visible absorption spectrometry (UV-Vis) to measure the optical properties. The same characterization methods have been applied on the Cu-doped TiO$_2$ photocatalysts prepared by the sol-gel method, in addition to some rheological measurements to determine their flow behaviour.

Furthermore, X-ray diffraction (XRD), transmission electron microscopy (TEM), scanning electron microscopy (SEM) and UV-visible absorption spectrometry (UV-Vis) analyses have been conducted to characterize the Cu-doped TiO$_2$ catalysts prepared by the inert gas condensation technique.
The experimental work conducted here revealed promising results for improving the performance of the TiO$_2$ nanomaterial by doping it with Cu and Ag metals where the optical activity was enhanced and shifted to the visible region causing an appreciable increase in its effectiveness for photocatalytic applications.

**Keywords:** TiO$_2$ nanomaterials, Cu-doped TiO$_2$, Ag-doped TiO$_2$, optical properties, techniques, photocatalytic applications.
تحضير وتوصف عوامل مساعدة متناهية الصغر من النحاس المثبت على أوكسيد التيتانيوم والفضة المثبتة على أوكسيد التيتانيوم لاستخدامها في التطبيقات المحفزة ضوئياً.


وقد تم دراسة الفضة المثبتة على أوكسيد التيتانيوم والمحضرة بطريقة سول-جل باستخدام تحويل فورييه الطيفي لانعكاس تشتت الأشعة تحت الحمراء (DRIFTS)، المجهر الإلكتروني الماسح للانبعاثات الهندسية (EPMA)، الكترون المسيطر للتحليل الدقيق (FESEM) للسطح والدراسة التركيب الكيميائي، تحليل السطح ودراسة التركيب الكيميائي (BET) لإيجاد مساحة السطح والقياسات المسامية، حيود الأشعة السينية (XRD) لتحليل تردد التردد البصري، و有这样的 الامتصاص للأشعة فوق البنفسجية والمرئية (UV-Vis) لدراسة القياسات البصرية. وقد تم تطبيق طرق التحليل ذاتها على النحاس المثبت على TiO2 والمحضور بطريقة سول-جل، بالإضافة إلى عمل بعض القياسات الريولوجية (دراسة سلوك أنساب المنتج كمائع).

كما تم توصيف النحاس المثبت على TiO2 والمحضور بطريقة تكثيف الغاز الخامل عن طريق استخدام كيكيون الأشعة السينية (XRD)، المجهر الإلكتروني الدافئ للإلكترونات (TEM)، المجهر الإلكتروني الماسح ضوئياً (SEM)، ومطيافية الامتصاص للأشعة فوق البنفسجية والمرئية (UV-Vis).
ويكشف العمل التجريبي هنا نتائج واعدة لتحسين أداء $\text{TiO}_2$ المتناهي الصغر عن طريق تثبيت أو إضافة منشطات معدنية (النحاس أو الفضة) حيث تم تعزيز النشاط البصري وانتقال امتصاص الضوء إلى المنطقة المرنية بما يتوافق أن يزيد في فعاليتها الضوئية -التجهيزية لدى تطبيقها.

كلمات مفتاحية: مواد متناهية الصغر من أوكسيد التيتانيوم، النحاس المثبت على أوكسيد التيتانيوم، الفضة المثبتة على أوكسيد التيتانيوم، الخصائص البصرية، تقنيات، تطبيقات محفزة ضوئية.
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My special thanks are extended to the National Energy and Water Research Center (NEWRC) for analysing the Cu-doped and Ag-doped TiO₂ nanoparticles in powder form samples by using the XRD, FESEM, and EPMA. The X-Ray Center for Material Analysis in University of Sharjah, for performing the Ti-Cu thin films samples by using SEM-EDX and UV-Vis Spectrometer. The Gas Research Center in Petroleum Institute for conducting the BET analysis for Cu-doped and Ag-doped TiO₂ nanoparticles in powder form samples.
Dedication

This thesis is dedicated to:
My parents, Abdel Ra’ouf Ahmed and Basima Salameh,
My sisters, Hiba, Hana’a,
My brothers, Hani, Ahmed and Hisham,
And to all those who supported me during this journey.
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<tbody>
<tr>
<td>BET</td>
<td>Brunauer–Emmett–Teller</td>
</tr>
<tr>
<td>DRIFTS</td>
<td>Diffuse reflectance infrared Fourier transform spectroscopy</td>
</tr>
<tr>
<td>EDS</td>
<td>Energy dispersive spectrometer</td>
</tr>
<tr>
<td>FESEM</td>
<td>Field emission scanning electron microscopy</td>
</tr>
<tr>
<td>IGC</td>
<td>Inert gas condensation technique</td>
</tr>
<tr>
<td>QCM</td>
<td>Quartz crystal monitor</td>
</tr>
<tr>
<td>QMF</td>
<td>Quadrupole mass filter</td>
</tr>
<tr>
<td>$S_{\text{BET}}$</td>
<td>Surface area</td>
</tr>
<tr>
<td>SEM</td>
<td>Scanning electron microscopy</td>
</tr>
<tr>
<td>TEM</td>
<td>Transmission electron microscopy</td>
</tr>
<tr>
<td>UHV</td>
<td>Ultra-high vacuum</td>
</tr>
<tr>
<td>UV-Vis</td>
<td>UV-visible absorption spectrometry</td>
</tr>
<tr>
<td>XRD</td>
<td>X-ray diffraction</td>
</tr>
<tr>
<td>$C$</td>
<td>Speed of light</td>
</tr>
<tr>
<td>$E_g$</td>
<td>Energy band gap</td>
</tr>
<tr>
<td>$f_{\text{Ar}}$</td>
<td>Argon inert gas flow rate</td>
</tr>
<tr>
<td>$h$</td>
<td>Plank's constant</td>
</tr>
<tr>
<td>$I$</td>
<td>Current</td>
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<tr>
<td>$L$</td>
<td>Aggregation length</td>
</tr>
<tr>
<td>nm</td>
<td>Nanometer</td>
</tr>
<tr>
<td>$P$</td>
<td>Sputtering discharge power</td>
</tr>
<tr>
<td>Symbol</td>
<td>Description</td>
</tr>
<tr>
<td>--------</td>
<td>-------------</td>
</tr>
<tr>
<td>$P_c$</td>
<td>Chamber pressure</td>
</tr>
<tr>
<td>sccm</td>
<td>Flow unit (standard cubic centimeter per minute)</td>
</tr>
<tr>
<td>$U/V$ ratio</td>
<td>Resolution of the mass filter</td>
</tr>
<tr>
<td>$\lambda$</td>
<td>Lambda (represents the wavelength)</td>
</tr>
<tr>
<td>$\lambda_{cutoff}$</td>
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Chapter 1: Introduction

1.1 Overview

In 1972, titanium dioxide (TiO$_2$) was firstly discovered by Fujishima and Honda as an active photocatalyst$^1$. Since then, TiO$_2$ has become one of the most important semiconductor materials in daily life, moreover, it has been widely used in fuel cell, solar energy conversion, photocatalysts/catalyst for environmental remediation processes, white pigment in paints and paper, bone implant material, ultra-violet (UV) absorber in sunscreen cream and other cosmetic products, and additive in food products$^2$. Titanium dioxide, in comparison with other semiconductor catalysts, has many advantages such as suitable optical and electron properties, chemical stability, corrosion resistance, and non-toxicity$^3$, making it a perfect candidate for photocatalytic processes.

Titanium dioxide has been widely used as a catalyst under UV irradiation and was considered the best choice among several other metal oxides where it has relatively low band-gap values of ~3.0 for rutile phase and 3.2 eV for anatase phase$^4$. Rutile does absorb some visible light, while anatase only absorbs in the UV region of spectra. The optimal photocatalytic efficiency is obtained using anatase with a small admixture of rutile$^5$. Typically, anatase phase form at 300–600°C, while at higher temperatures, anatase to rutile phase transformation occurs. The generally accepted theory of phase transformation is that two Ti–O bonds break in the anatase structure, allowing rearrangement of the Ti–O octahedra, leading to the formation of a smaller volume, dense rutile phase. The removal of O ions, which generates lattice vacancies, accelerates this transformation. The breaking of these bonds can be affected by a number of factors, including the addition of dopants, synthesis method and thermal treatment$^6$. Various research studies were done recently on TiO$_2$ photocatalyst as pointed out below.

Bessekhouad et al.$^7$ prepared nanosized titanium oxide (TiO$_2$) powders by various techniques (emulsification-gelation technology, hydrolysis and reflux process) and studied the photocatalytic activity of the nanopowders obtained by using Benzamide photodecompositions in aqueous solution. It was concluded that the level of
crystallinity was a deciding factor for benzamide degradation and there was no evidence of relations between photocatalytic performance and surface area.

Choi et al.\cite{8} investigated the relationship between the size and structure of TiO$_2$ nanoparticles in which three samples of size selected TiO$_2$ nanoparticles were prepared. The results suggested that the sample with TiO$_2$(II) structure may become more favourable than the samples with anatase structure when the particle size decreased from 12 nm to 7 nm. Kočí et al.\cite{9} assessed the effect of the primary particle size on the photocatalytic reactivity of TiO$_2$ exemplified by the photoreduction of CO$_2$ by water. It was found that methane and methanol were the main reduction products in which the optimum particle size corresponding to the highest yields of both products was 14 nm. The observed optimum particle size is a result of competing effects of specific surface area, charge–carrier dynamics and light absorption efficiency.

Sayilkan, et al.\cite{10} investigated the effects of annealing temperature and hydrolysis catalyst on the crystalline form and crystallite size of TiO$_2$ prepared by the sol-gel process. The results showed that the acid catalyst and catalyst/alkoxide ratio have a large effect on the formation of anatase TiO$_2$ and the crystallite size of the nanocatalysts increased when the thermal treatment temperature was raised from 400 to 500°C. However, Viana et al.\cite{11} correlated the effect of heating on the structural, morphological, and textural properties of the synthesized TiO$_2$ nanoparticles and evaluated the photocatalytic activity and the UV absorption of the samples. Systematic decrease of the specific surface area and porosity resulted with the increase in heating temperature, evidencing the sample densification and the consequent increase in the average particle size. Viana et al.\cite{11} results also showed that the amorphous TiO$_2$ nanoparticles crystallized to anatase nanophase below 300°C and a diffuse phase transition from anatase to rutile occurred between 570°C and 800°C. The TiO$_2$ nanoparticle heated at 300°C showed the best results for potential application in solar protection. In contrast, Ba-Abbad\cite{12} studied the effect of calcination temperatures on the crystalline structure, surface area and the photocatalytic activity of TiO$_2$ nano-photocatalyst (prepared by the sol-gel method)
by the degradation of toxic compounds of poly-chlorinated phenol (PCPS) under solar irradiation.

Lin et al.\cite{13} investigated the sol-gel synthetic routes and property identification of the anatase-type TiO$_2$ nanoparticles. They studied the morphology, particle size distribution, crystallinity of the anatase-type TiO$_2$ nanoparticles and the oxidative state, bonding length, coordination number of a central Ti atom in the nanophase anatase-type TiO$_2$ photocatalysts. Further, metals such as Fe, Zn or Cu were doped into the nanophase TiO$_2$ photocatalysts by the impregnation method with a cation exchange process and selected acetic acid as a typical pollutant for photo-decomposition on nanophase TiO$_2$ photocatalyst film. Their results showed that the removal amounts of acetic acid were Cu-doped > Fe-doped > Zn-doped > anatase-type > P25 TiO$_2$ nanocatalysts.

Ganesan et al.\cite{14} analysed the effect of pH on the surface morphology, structural property and photocatalytic activity of TiO$_2$ nanocrystals, and compared that with commercial TiO$_2$ nanocrystals. Their results showed that the pH of the precursor solution affected the particle size of the TiO$_2$ nanocrystals. Further, the degradation of methylene blue by the synthesized TiO$_2$ nanocrystal was greater than that of the commercially available TiO$_2$ nanocrystals.

Tan et al.\cite{15} used TiO$_2$ pellet form to reduce carbon dioxide in the presence of saturated water vapour into gaseous hydrocarbons under room conditions by illuminating the catalyst under UV irradiation in a quartz tube reactor and compared it with the thin-film form catalyst. They found that the pellet-form TiO$_2$ catalyst was feasible and attractive for use in further investigation of CO$_2$ reduction. The yield of the product was fairly good as compared to those obtained from the process using thin-film technique and anchoring method, but not high enough to use them as fuels.

Hanaor et al.\cite{16} synthesized TiO$_2$ thin films by the sol-gel method. They examined the morphology, phase assemblage and photocatalytic activity of mixed phase thin-film TiO$_2$ photocatalysts. They used the metal dopants to investigate the consequent effects of dopants on the phase assemblage of biphasic TiO$_2$ thin films and the prospect of increased photon absorption through inter-valence charge transfer.
between dopants of different valences. They found that the sol-gel synthesis of TiO$_2$ thin films on single crystal quartz substrates yields highly oriented and thermally stable anatase. They found that the addition of Cu dopant enhanced the transformation of anatase to rutile through an increase in oxygen vacancies in the TiO$_2$ lattice while the undoped TiO$_2$ thin film showed the formation of rutile as oriented parallel bands in the anatase. Moreover, the transition metal dopants segregated in TiO$_2$ thin films and brought about a localised isotropic formation of the rutile phase. They also found that the presence of low levels of rutile was sufficient to alter the optical transmittance of TiO$_2$ thin films and transition metal doping and codoping was detrimental to the photocatalytic performance of TiO$_2$ thin films.

Joshi et al.\cite{17} studied the photocatalytic degradation of dyes on TiO$_2$ and ZnO semiconductors. TiO$_2$ showed more photocatalytic efficiency than ZnO. Ozcan et al.\cite{18} utilized organic dyes with proven photo-dynamic therapy applications to generate electrons from visible light which can be transferred to TiO$_2$ in order to initiate CO$_2$ photo-reduction reactions with water in the gas phase. Pt was incorporated in the films either by adding the precursor salt in the sol, Pt(in), or by wet impregnation of calcined film with an aqueous solution of the precursor salt, Pt(on). It was indicated that under UV illumination, the methane yields of platinized TiO$_2$ thin films decreased in the following order: Pt(on).TiO$_2$ > Pt(in).TiO$_2$ > TiO$_2$. Han et al.\cite{19} synthesized TiO$_2$ nanopowder by using sol-gel combustion hybrid method using acetylene black as a fuel and studied its application in dye sensitized solar cells (DSCs). It was indicated that this process offered simple and effective route to the synthesis of uniform TiO$_2$ nanopowders, which can be used in dye-sensitized solar cells and photocatalysts and also for the large scale production of nanosized ceramic materials.

On the other hand, Costa et al.\cite{20} assessed the effects of photocatalytic TiO$_2$-painted walls on the air quality inside a swine weaning unit, on both the emissions of particulate matter (PM$_{10}$ and PM$_{2.5}$), NH$_3$ and greenhouse gases release into the environment, in relation to the parallel effects on the animal productive performance. As a conclusion, the photocatalytic treatment with TiO$_2$ coating had positive effects
not only on methane concentration, particulate matter concentration and emission, but also significantly improved the feed conversion ratio of growing piglets, very likely due to the increased quality of indoor air, with positive economic repercussions for the farmer. Internal photocatalytic treatment in swine husbandry could thus be considered as a potential Best Available Technology (BAT).

Further, Pan et al.\textsuperscript{[21]} used sol-gel method to synthesize TiO\textsubscript{2} nanoparticles, followed by in situ surface-modification with silane coupling reagent octadecyl tri-methoxy-silane (WD-11) and evaluated their anti-wear behavior as additive in liquid paraffin. It was indicated that the surface-capped TiO\textsubscript{2} nanoparticles can be well dispersed in various organic solvents of weak polarity, showing potential for fabrication of inorganic/organic nanocomposites used in optic field. Moreover, they were able to improve the anti-wear ability of liquid paraffin, showing promising application as a multifunctional lubricating oil additive.

Karimipour\textsuperscript{[22]} prepared TiO\textsubscript{2} nanoparticles by using sol-gel process with two different complex agents [acidic (citric acid) and organic complex agent (acetyl acetone)] at 400, 500, and 650°C sintering temperatures, in order to study the role of polymeric and non-polymeric agents in phase purity and size formation. It was found that acetyl acetone is a proper candidate to synthesize particles in pure anatase phase below 10 nm. Also, sintering at 650°C showed pure rutile phase with narrow size distribution of ~100 nm. In addition, at high sintering temperature, the particles obtained from polymeric agent tend to agglomerate larger in size than in the acidic product.

Šíma and Hasal\textsuperscript{[23]} tested two ways (what are they?) of TiO\textsubscript{2} immobilization for application in photocatalytic degradation of textile dyes. In conclusion, TiO\textsubscript{2} immobilized in the PVA proved to be more suitable for MB decolorization. Higher light intensity made the dye degradation substantially faster.

Lee\textsuperscript{[24]} modelled global eco-TiO\textsubscript{2} materials and monitored by-products of treated water in an in vitro cytotoxicity assay measuring the level of water purification after photocatalytic treatment. Further, studied the detailed eco-TiO\textsubscript{2} formation mechanism and its fundamental photochemical properties. It was indicated that eco-
TiO$_2$ shows an efficient water-treatment performance together with an economic dividend. While, da Motta et al.$^{[25]}$ applied photoreactor combining UV light and TiO$_2$, immobilized in cellulosic fabric, for the treatment of two industrial textile wastewaters. High colour and COD removal, and detoxification, were achieved for both wastewaters, at controlled pH of 5.5. Effluents showed very poor biodegradability due to their complex composition; thus, the proposed process was efficient alternative. During that time, Chang$^{[26]}$ studied the photocatalytic destruction of VOCs (volatile organic compounds) by using TiO$_2$ particles which were synthesized in a flame aerosol reactor. The results showed that the TiO$_2$ particle generation by the premixed flame aerosol reactor and the direct coating on the substrate was good combination to construct the UV-TiO$_2$ decomposition system for the destruction of VOCs. In the system, it was found that the decomposition rate of gaseous benzene was much higher than that of formaldehyde.

Finally, Erdogan et al.$^{[27]}$ used polystyrene cross-linked divinyl benzene (PS-co-DVB) microspheres as an organic template in order to synthesize photocatalytic TiO$_2$ microspheres and micro-bowls and studied the photocatalytic activity of the micro-bowl surfaces in the gas phase via photocatalytic NO$_{(g)}$ oxidation by O$_2{(g)}$ as well as in the liquid phase via Rhodamine B degradation. It was demonstrated that the polymer microsphere templated TiO$_2$ photocatalysts offered a promising and a versatile synthetic platform for photocatalytic DeNO$_x$ applications for air purification technologies.

1.2 Principle of Photocatalysis

The term photocatalysis will always be used to describe the process that semiconductor materials such as TiO$_2$ undergo when irradiated by light of a certain wavelength. It is a term that implies photon assisted generation of catalytically active species.$^{[6]}$
The principle of semiconductor photocatalytic reaction is straightforward. Upon absorption of photons with energy larger than the band gap of TiO$_2$, electrons are excited from the valence band to the conduction band, creating electron-hole pairs\cite{28}. Figure 1.1 depicts the mechanism of the electron-hole pair formation when the TiO$_2$ particle is irradiated with adequate light, $h\nu$. The light wavelength for such photon energy usually corresponds to $l < 400$ nm. The photonic excitation leaves behind an empty unfilled valence band, and thus creating the electron-hole pair ($e^-\cdot h^+$)\cite{29}. These charge carriers migrate to the surface and react with the chemicals adsorbed on the surface to decompose these chemicals. This photo-decomposition process usually involves one or more radicals or intermediate species such as $^\bullet$C, CO, H$^+$, $^\bullet$OH, H$_2$, O$_2$ and H$_2$O$_2$, which play important roles in the photocatalytic reaction mechanisms\cite{28}. If organic matter is present, reaction of the hydroxyl radical will result in mineralization of the matter. The series of reactions generated by irradiation of TiO$_2$ and the generation of various oxidants are shown below\cite{30}.

\begin{align*}
\text{TiO}_2 + h\nu & \rightarrow e^-_{cb} + h^+_{vb} \\
\text{O}_2 + e^-_{cb} & \rightarrow ^\circ\text{O}_2^- \\
h^+_{vb} + \text{H}_2\text{O} & \rightarrow ^\circ\text{OH} + \text{H}_3\text{O}_2^+ \\
^\circ\text{OH} + ^\circ\text{OH} & \rightarrow \text{H}_2\text{O}_2
\end{align*}
In order to enhance the absorption of light by the TiO$_2$ semiconductor, the largest possible surface area of this material is required. Larger surface area adsorbs more photo-energy, while a shift of the light frequency from UV irradiation to visible range of spectra is feasible. The extent of the TiO$_2$ surface area is indirectly proportional to the particle size. However, the particle size is directly proportional to the range of the bandgap$^5$. As an example, the most frequently used TiO$_2$ photocatalyst is the Degussa P25 material. Its particle size is about 25 nm and its surface area is small (50 m$^2$/g). Reducing the particle size, up to a few nanometres, has the benefit of increasing the external surface area. These small particles tend to agglomerate by strong inter-particle forces when the nano-metric size region is reached. Further decrease of the particle size to a few nano-meters reaches one point below which quantum size effects also start to operate and the band gap of the semiconductor increases, blue-shifting the light absorption$^{31}$. Recombination of photo-induced electron/hole pairs is also promoted with larger surface areas. This is usually because increased amounts of crystal defects are present with larger surface areas. The surface defects will act as recombination centres for the photo-induced electron/hole pair. Surface hydroxyl groups also affect the photocatalytic efficiency of the materials. Surface hydroxyl groups participate in the photocatalytic process in a number of ways. They trap photoexcited electrons and produce OH$^\cdot$ radicals and they can also act as active absorption sites for pollutants. The high temperature calcination of TiO$_2$ results in the removal of surface hydroxyl groups. Because rutile is produced from the high temperature calcination of anatase, rutile possesses fewer surface hydroxyl groups and as such this is considered as one of the reasons why rutile is a weaker photocatalyst than anatase$^6$.

1.3 Improving Photocatalytic Properties of TiO$_2$

TiO$_2$-based photocatalysis has been researched exhaustively for environmental clean-up applications. The single drawback is that it does not absorb visible light$^{32}$ due to its wide band gap, which limits its application under sunlight. To overcome this
problem, several approaches including sensitization, doping, coupling and capping of TiO₂ have been studied extensively [33], as shown in Figure 1.2. However, doping with metals is one of the most promising because it shifts the TiO₂ responses towards longer wavelengths and an enhanced photoactivity is obtained from incorporation of metallic dopants.

![Diagram of modification paths for TiO₂ nano-materials](image)

Figure 1.2: Illustration of the modification paths for TiO₂ nano-materials

1.3.1 Doping

Doping and/or deposition are effective strategies to increase spectral response of TiO₂ through narrowing electronic properties and by altering optical responses. The metal ions deposited on the TiO₂ surface usually act as a sink for the photo-induced charge carriers and thus can improve the interfacial charge transfer processes. The materials have been under investigation for TiO₂ doping/depositions are noble metals such as (Pt, Au, Pd, Rh, Ni, Cu, Sn, Ag), transition metals such as (Zn, Fe, Mn, Co, Pd, Ni, etc.), rare-earth metals such as (La, Ce, Pr, Nd, Sm, Eu, Dy, Gd), other metals and non-metal ions [35].

1.3.1.1 Doping with metals

To reduce the bandgap energy, doping of TiO₂ with appropriate metal atoms seems to be a promising method. Doping material can either add an energy level filled with electrons in the band-gap which can be easily excited into the conduction band (n-type) or a level of extra holes in the bandgap to allow the excitation of the valence
band electrons, to create mobile holes in the valence band ($p$-type). Hence, doping of TiO$_2$ causes sufficient reduction of the TiO$_2$ bandgap energy thus allowing the generation of $e^-/h^+$ pairs by irradiation with visible light and supplying enough energy to generate such pairs$^{[3]}$, see for example Figure 1.3. Researchers worked excessively on metal doping of TiO$_2$ nano-photocatalyst.

Figure 1.3: Positions of the redox potentials of various metallic couples related to the energy levels of the conduction and valence bands of TiO$_2$ Degussa P-25 at pH 0$^{[36]}$.

Moon et al.$^{[37]}$ mentioned that Sb was more photoactive for the degradation of methylene blue as compared to other dopants such as Cr, Fe, Nb, and Ta. So, synthesized nano-crystalline TiO$_2$ particles doped with antimony metal ion and studied the photocatalytic behaviour by the degradation of an organic dye, methylene blue, in the aqueous suspension. It was found that the Antimony doing significantly
improved photocatalytic performance as compared to the undoped TiO$_2$. While, Paola et al.$^{[38]}$ carried out two probe photocatalytic reactions, i.e. ethanoic acid and 4-nitrophenol photooxidation, in different experimental conditions by using suspensions of transition metal (Co, Cr, Cu, Fe, Mo, V and W) doped polycrystalline TiO$_2$ powders in aqueous systems. However, a beneficial influence of the presence of metal species was observed only with the samples containing copper and tungsten. In particular, the TiO$_2$/Cu powders showed to be more photoactive of bare TiO$_2$ for the ethanoic acid oxidation while the TiO$_2$/W samples were more efficient for 4-nitrophenol degradation.

Later, Wu and Chen$^{[39]}$ synthesized series of vanadium-doped TiO$_2$ catalysts by two modified sol–gel methods. The photocatalytic activity was evaluated by the degradation of crystal violet (CV) and methylene blue (MB) under visible light irradiation. It was shown that the degradation rate of CV and MB on V-doped TiO$_2$ were higher than those of pure TiO$_2$ which possessed better absorption ability of visible light. Furthermore, Ishibai et al.$^{[40]}$ developed novel Pt modified TiO$_2$ photocatalyst that showed significant activity in the degradation of acetaldehyde under visible-light irradiation. The synthesis procedure involved hydrolysis of TiCl$_4$, calcination and a Pt-modification process. The calcinations temperature before the Pt-modification process greatly affected absorbance in the visible region and photocatalytic activity. The optimum calcination temperature was around 300–450 °C, which was found to be related to the number of the hydroxyl groups per unit of surface area. Application of this Pt-modified TiO$_2$ photocatalyst shows promise in the fields of gas-phase reaction systems under visible-light irradiation.

A year later, Štengl et al.$^{[41]}$ used the rare earth (La, Ce, Pr, Nd, TiO$_2$TiO$_2$Sm, Eu, Dy, Gd) for doped titania to investigate their photocatalytic activity under UV and visible light. Orange II dye was selected as a model reactant for photodegradation. It was found that Nd$^{3+}$ doped TiO$_2$ (approx. 10 wt.%) had the highest activity among all rare earth doped. After that, Sun et al.$^{[42]}$ evaluated the photocatalytic performance for o-xylene degradation over 0.5 at.% M-TiO$_2$ (M = Ag, Fe, Cu, Co) in different humidity levels under visible light irradiation. M-TiO$_2$ (M = Ag, Fe, Cu, Co) photocatalysts were prepared by a sol-gel method with the doping concentration
ranging from 0.1 at.% to 1.0 at.% . Transition metal ions doping increased the surface area and extended the absorption of TiO$_2$ to visible light region. The Fe-doped TiO$_2$ shows the best activity among these M-TiO$_2$ (M = Ag, Fe, Cu, Co) photocatalysts. In addition, Loganathan et al.$^{[43]}$ prepared different weight percentages of Ag, Pt, and Au doped nano TiO$_2$ using the acetic acid hydrolyzed sol-gel method and evaluated the photocatalytic activity of doped nano TiO$_2$ by using 4-chlorophenol as the model pollutant. As a result, Au doped (0.5 wt %) nano TiO$_2$ exhibited higher photocatalytic activity than the other noble metal doped nano TiO$_2$, pure nano TiO$_2$ and commercial TiO$_2$ (Degussa P-25). This enhanced photocatalytic activity was due to the cathodic influence of gold in suppressing the electron-hole recombination during the reaction.

Pawar et al.$^{[44]}$ synthesized pure and Ce$^{3+}$ doped TiO$_2$ nanoparticles by sol-gel auto-combustion method and studied their photocatalytic activity in presence of UV light for photo-degradation of cango red dye at different Ce$^{3+}$ concentrations and heat treatment temperature. It was found that Ce$^{3+}$ ions doping significantly enhanced the photocatalytic efficiency of TiO$_2$ towards the degradation of dye and the photocatalytic activity of 0.5 mol% was the most suitable Ce$^{3+}$ ions concentration in TiO$_2$ at which catalyst exhibits a large surface area and higher efficiency of electron/hole separation.

Reszczynska et al.$^{[45]}$ used sol-gel method to synthesize Er and Yb modified TiO$_2$ nanoparticles. It was observed that the dopant amount affected photocatalytic activity of semiconductor. The presence of erbium was found more beneficial for visible light activation of TiO$_2$ doped photocatalysts than ytterbium. Moreover, they$^{[46]}$ used the same method to prepare various concentrations of Pr-TiO$_2$ nanoparticles to study the visible and ultraviolet light photocatalytic activity by using photodegradation of phenol. It was observed that the dopant affected the surface area and crystal size of TiO$_2$ powder samples, TiO$_2$ doped with 0.25 mol% of praseodymium had the highest photocatalytic activity under visible light and the absorption spectra of Pr-TiO$_2$ samples showed stronger absorption in the UV–Vis region than pure TiO$_2$.

Meanwhile, Khairy and Zakaria$^{[47]}$ studied the effect of doping of some transition metals such as Cu, Fe, Ag, Zn on the photo catalytic activity and efficiency of nano-
sized TiO$_2$ and ZnO toward the degradation of organic matter in wasted water under visible irradiation light. All the doped samples were prepared by both precipitation and sol-gel methods. All samples exhibited a higher photocatalytic activity than that of pure oxides under both of UV and visible light irradiation. It is presumed that the incorporation of the doping lead to diminish the electron–hole recombination that improved the photocatalytic activity under light irradiation. One year later, they used the sol-gel method to investigate the photocatalytic activities of samples for methyl orange (MO) degradation and the chemical oxygen demand (COD). The results showed that doping ions led to increase in the absorption edge wavelength, and decrease in the band gap energy of TiO$_2$ nanoparticles, resulting in higher photocatalytic activities than the pure ones. Moreover, Cu doped TiO$_2$ nanoparticles showed the best photocatalytic activity based on the measured COD values.

1.3.2 Sensitization

Sensitization is classified into two methods: dye sensitization and composite semiconductor. Dye sensitization is widely applied to utilize visible light for energy conversion and textile wastewater having wavelength in the range from 442 nm to 665 nm. Some dyes which have redox property and visible light sensitivity are used in solar cells and photocatalytic reaction. When the dye absorbs visible light, the dye is excited. The dye in the excited state includes lower redox potential than the corresponding ground state. If the redox potential is lower than the CB of TiO$_2$, an electron is injected from the excited state into the CB; leading to initiation of photocatalytic reactions. Some dyes (safranine, O/EDTA and T/EDTA) absorb visible light and generate electrons as reducing agents to produce hydrogen.

Organic dyes have been widely employed as sensitizers for TiO$_2$ nanomaterials to improve their optical properties. Organic dyes are usually transition metal complexes with low lying excited states, such as polypyridine complexes, phthalocyanine, and metalloporphyrins. The metal centers for the dyes include Ru(II), Zn(II), Mg(II), Fe(II), and Al(III), while the ligands include nitrogen heterocyclics with a delocalized Π or aromatic ring system.

If the sensitizers are adsorbed (either chemisorbed or physisorbed) on the surface of TiO$_2$, they can be much more easily excited than TiO$_2$. Hence, the excitation process
can be efficiently improved. The sensitizers can extend the range of excitation energies of the TiO$_2$ into visible region. However, the sensitizers themselves can degrade. Thereby, there is a need to add more sensitizers in reaction systems. Because of this reason, the publication of this kind of modification method has diminished these years.$^{[50]}$

1.3.3 Coupling

It is possible to create coupled colloidal structures, in which illumination of one semiconductor produces a response in the other semiconductor at the interface between them. Coupled semiconductor photocatalysts exhibit very high photocatalytic activity for both gas and liquid phase reactions by increasing the charge separation and extending the energy range of photoexcitation. The geometry of particles, surface texture, and particle size play a significant role in interparticle electron transfer. Appropriate placement of the individual semiconductors and optimal thickness of the covering semiconductor are crucial for efficient charge separation. There has been much interest in coupling different semiconductor particles with TiO$_2$, with coupled samples such as CdS-TiO$_2$, Bi$_2$S$_3$-TiO$_2$, WO$_3$-TiO$_2$, SnO$_2$-TiO$_2$, MoO$_3$-TiO$_2$, and Fe$_2$O$_3$-TiO$_2$$^{[51]}$.

1.3.4 Capping

The coating of one semiconductor or metal nanomaterial on the surface of another semiconductor or metal nanoparticle core is called capping. Semiconductor nanoparticles are coated with another semiconductor with a different band gap in core-shell geometry to passivate the surface of the initial nanoparticle and enhance its emissive properties. The capped semiconductor system has similar mechanism of charge separation as in coupled semiconductor systems, while, the interfacial charge transfer and charge collection in this multicomponent semiconductor system is significantly different. In coupled semiconductor systems, the two particles are in contact with each other and both holes and electrons are accessible for selective oxidation and reduction processes on different particle surfaces. On the other hand, capped semiconductors have core-shell geometry. By depositing a relatively thick shell of the second semiconductor with a thickness is similar to the core radius it is possible to maintain the individual identities of the two semiconductors. Under these
circumstances, only one of the charge carriers is accessible at the surface, while opposite charge transfer to the inner semiconductor occurs, thus improving the selectivity of the interfacial transfer and enhancing the oxidation or reduction reaction. Core-shell geometry has an important consequence in terms of imparting enhanced photoelectrochemical stability to the system, taking into account that many of these semiconductors (especially group II–VI compounds) are prone to anodic photo-corrosion in aqueous media\textsuperscript{[51]}.

1.4 Synthesis

Many processes can be employed for the production of TiO\textsubscript{2} particles, such as gas-phase synthesis (deposition method), hydrothermal synthesis\textsuperscript{[52]}, and sol–gel synthesis \textsuperscript{[53]}. This section focuses mainly on sol-gel processing and gives a brief overview on the deposition method and hydrothermal synthesis. The deposition method (sputtering technique) will be explained more in depth in chapter 4.

1.4.1 Gas-Phase Methods (Deposition Method)

Gas phase methods are ideal for the production of thin films. It refers to any process in which materials in a vapor state are condensed to form a solid phase material. Vapor deposition processes usually take place within a vacuum chamber. If no chemical reaction occurs, this process is called physical vapor deposition (PVD), otherwise it is called chemical vapor deposition (CVD)\textsuperscript{[34,54]}. CVD is a widely used industrial technique that can coat large areas in a short space of time\textsuperscript{[6]}. In CVD processes, thermal energy heats the gases in the coating chamber and drives the deposition reaction. Other CVD approaches include electrostatic spray hydrolysis, diffusion flame pyrolysis, thermal plasma pyrolysis, ultrasonic spray pyrolysis, laser-induced pyrolysis, and ultrasonic-assisted hydrolysis. In PVD, materials are first evaporated and then condensed to form a solid material. The primary PVD methods include thermal deposition, ion plating, ion implantation, sputtering, laser vaporization and laser surface alloying\textsuperscript{[34,54]}. 
1.4.2 Hydrothermal Method

Hydrothermal synthesis is normally conducted in steel pressure vessels called autoclaves under controlled temperature and/or pressure with the reaction in aqueous solutions. The temperature can be elevated above the boiling point of the water, reaching the pressure of vapor saturation. The temperature and the amount of solution added to the autoclave largely determine the internal pressure produced\(^{[6,34]}\).

The hydrothermal synthesis is particularly interesting since it directly produces a crystalline powder, without the need of a final calcination step, which is necessary in the sol–gel process. However, the lack of knowledge of the chemical equilibria of the species in solution and of the kinetics of nucleation and growth of the different phases makes it difficult to control the overall process\(^{[55]}\).

1.4.3 Sol-Gel Method

Sol–gel process is at the moment the most common and promising one at a lab scale. Although the sol–gel process has been known almost for a century and some of the most important aspects have been cleared, there exists room for improvement of individuating synthesis conditions that result in a powder with improved properties, when compared with the commercial products available at the moment\(^{[55]}\). Furthermore, it is a common chemical approach to produce high purity materials shaped as powders, thin film coatings, fibres, monoliths and self-supported bulk structures. The sol-gel method has several advantages over other synthesis techniques such as low sintering temperature (which allows the preparation of TiO\(_2\)-anatase at low temperature), purity, homogeneity, stoichiometric control, ease of preparation (doesn’t require complicated instruments such as chemical vapor deposition) and ease of introducing dopants, composition and the ability to produce thin film coatings or porous powders\(^{[6,31,39]}\).

Recently, many experimental works have been conducted on sol-gel method, even compared between sol-gel technique and other techniques. Shahruz and Hossain\(^{[56]}\) used sol-gel technique to investigate how to control the size and morphology of TiO\(_2\) nanoparticles with changing the synthesis parameters. It was found that independent changes of calcinations temperatures and/or gelatinization time accompanied by
ultrasound waves and specific pH value could alter the diameter of the TiO$_2$ nanoparticles. Shahini et al.\textsuperscript{[57]} synthesized highly crystalline TiO$_2$ anatase nanoparticles via gel–sol method and studied the substantial reduction in the synthesis time together with a narrow size distribution and the effect of first and second aging treatments on nanoparticles size and crystal structure. It was concluded that the time and temperature of aging did not affect the crystallite structure, but increased the particulate size and decreased the specific pore volume of the powder. Hayle and Gonfa\textsuperscript{[58]} reported the effect of temperature on the properties of TiO$_2$ nanomaterials that were synthesized by sol-gel method. Generally, it has been observed that as the calcination temperature increases, the size of TiO$_2$ nanomaterial increases. Hema et al.\textsuperscript{[59]} and SharmilaDevi et al.\textsuperscript{[60]} focused on synthesizing high efficient nanosized titania particles having large surface area by using sol-gel method. Kavitha et al.\textsuperscript{[61]} presented a systematic study on the growth, physical and chemical characterization of TiO$_2$ nanostructures prepared by sol-gel and hydrothermal method. The structural, morphological and photocatalytic activity were analyzed. It was shown that the hydrothermally prepared TiO$_2$ particles had very fast degradation of methyl orange solution. Concluding that the nanoparticles prepared by hydrothermal method shows better structural, morphological and photocatalytic property. While, Vijayalakshmi and Rajendran\textsuperscript{[62]} studied the difference between sol-gel and hydrothermal methods by preparing TiO$_2$ nanoparticles with those two different methods in which both were done under the same ambient conditions. It was evident that the TiO$_2$ nanoparticles prepared via sol-gel route were highly crystalline and had smaller crystallite size (~ 7 nm) as compared to the one prepared by hydrothermal method (~ 17 nm).

![Figure 1.4](image)

Figure 1.4: Process flow chart for the preparation of TiO$_2$-based photocatalysts by sol–gel method.
1.4.3.1 Mechanism of Sol-Gel Synthesis

A sol-gel process for preparing TiO\textsubscript{2} photocatalyst is illustrated in Figure 1.4. There are two possible routes for carrying out sol-gel synthesis, the non-alkoxide route and the alkoxide route. The non-alkoxide route uses inorganic salts (TiCl\textsubscript{4}) as the starting material. This requires the removal of the inorganic anion to produce the required oxide (titanium dioxide). However, halides often remain in the final oxide material and are difficult to remove. The alkoxide route involves hydrolysis of a metal alkoxide, followed by condensation\textsuperscript{[6]}. This section will discuss a general mechanism of alkoxide route.

The sol-gel process involves hydrolysis and condensation of the metal alkoxide followed by heat treatment at elevated temperatures which induce polymerisation, producing a metal oxide network. In general, transition metals have low electronegativities and their oxidation state is frequently lower than their coordination number in an oxide network. Therefore, coordination expansion occurs spontaneously upon reaction with water or other nucleophilic reagents to achieve their preferred coordination. Metal alkoxides are in general very reactive due to the presence of highly electronegative OR groups (hard-\pi donors) that stabilise the metal in its highest oxidation state and render it very susceptible to nucleophilic attack. The lower electronegativity of transition metals causes them to be more electrophilic and thus less stable toward hydrolysis, condensation and other nucleophilic reactions. Controlling the conditions can be difficult but successful control of the reaction conditions has the potential to produce materials of consistent size, shape and structure\textsuperscript{[6]}.
Chapter 2: Characterization of Silver Doped Titanium Dioxide Produced by the Sol-Gel Method

2.1 Introduction

Noble metals are mainly used as electron traps. The low cost and easy preparation of silver (Ag) made it extremely suitable for industrial applications\cite{63,64}. Silver can trap the excited electrons from TiO$_2$ and leave the holes for the degradation reaction of organic species. It also results in the extension of their wavelength response towards the visible region\cite{65,66}. Moreover, silver particles can facilitate the electron excitation by creating a local electric field, and plasmon resonance effect in metallic silver particles shows a reasonable enhancement in this electric field\cite{66}. Due to silver properties, doping TiO$_2$ with Ag improves the photocatalytic reactions and anti-microbial activity which makes it a current interest. Many researchers have worked on Ag-doped TiO$_2$ for different photocatalytic applications.

In 2003, Tan et al.\cite{67} used Ag-modified TiO$_2$ to elucidate its effect on the photocatalytic reduction of selenate (Se) ions. They observed in terms of electron mediation from TiO$_2$ to elemental Se via the Ag metals, greatly enhancing the electron density in the Se particles and hence leading to the formation of H$_2$Se via the self-reduction of Se. Increasing the Ag-loading amount on TiO$_2$ resulted in greater H$_2$Se generation.

In 2004, Liu et al.\cite{68} prepared silver-loaded TiO$_2$ photocatalysts by photochemical impregnation method and photo-oxidation of phenol and photo-reduction of Cr(VI) to evaluate the photocatalytic Activity. They found that the better separation of electrons and holes on the modified TiO$_2$ surface allows more efficient reductions and oxidations. Moreover, in 2004, Sung-Suh et al.\cite{69} evaluated and distinguished different effects of Ag deposits on the TiO$_2$ photocatalytic activity by examining the photocatalytic degradation of the rhodamine B (RhB) dye in the aqueous suspensions of TiO$_2$ and Ag-deposited TiO$_2$ nanoparticles under visible and UV light irradiation. They also compared the activities of the synthesized TiO$_2$ and Ag-deposited TiO$_2$ to those of the commercial
Degussa P25 TiO$_2$ and Ag-deposited P25 in the same photocatalytic condition. The Ag–TiO$_2$ nano-sol showed a 30% increase in the RhB photodegradation under visible light irradiation, as compared to the pure TiO$_2$. While under UV irradiation, the Ag-TiO$_2$ sample revealed only 10% more RhB photodegradation as compared to the pure TiO$_2$. Under visible light irradiation, the significant enhancement in the Ag–TiO$_2$ photoactivity can be ascribed to simultaneous effects of Ag deposits by both acting as electron traps and enhancing the RhB adsorption on the Ag–TiO$_2$ surface. Under UV irradiation, however, Ag deposits may exhibit the effect only as electron traps, thus leading to the slight enhancement in the Ag–TiO$_2$ photocatalytic activity.

In 2005, Xin$^{[70]}$ synthesised Ag-TiO$_2$ catalysts with different Ag contents by a sol-gel method in the absence of light for the evaluation of the photocatalytic activity for degrading rhodamine B (RhB) solutions, it was found that the Ag dopant promoted the phase transformation as well as had an inhibition effect on the growth of anatase crystallite and could effectively inhibit the recombination of the photo-induced electrons and holes. Moreover, Lee et al.$^{[71]}$ prepared Ag-TiO$_2$ nanoparticles with sol–gel method using a reduction agent. The presence of Ag in TiO$_2$–Ag nanoparticle improved the photodegradation of $p$-nitrophenol and the photocatalytic activity of Ag-TiO$_2$ increased with the increase in the AgNO$_3$ content.

In 2006, Sobana et al.$^{[72]}$ worked on the preparation of Ag doped TiO$_2$ (anatase) by a photodeposition method to compare the activity of the photocatalyst before and after surface modification with metallic silver for the degradation of two azo dyes DB 53 and DR 23. Higher activity of silver doped TiO$_2$ was detected due to the enhancement of electron–hole separation by the electron trapping of silver particles.

In 2008, Bansal et al.$^{[73]}$ studied the photocatalytical degradation and mineralization of humic acid in presence of bare TiO$_2$ and silver loaded TiO$_2$ (0.5–5.0 at.% Ag). It was stated that silver loading over TiO$_2$ improved the rate of mineralization and degradation of humic acid with a maximum loading of 1.0 at.% Ag. In the same year, Anandan et
al.\textsuperscript{[74]} evaluated the efficiency of Ag–TiO\textsubscript{2} photocatalyst by following the kinetics and mechanism of the photocatalytic degradation of a textile dye (Acid Red 88, AR88) in the absence and presence of oxidants, such as peroxomonosulfate (PMS), peroxodisulfate (PDS) and hydrogen peroxide (H\textsubscript{2}O\textsubscript{2})) under visible light irradiation. This study shows that under illumination of visible light the prepared nano-meter sized Ag–TiO\textsubscript{2} nanomaterials is very active as a photocatalyst to effectively photo-degrade Acid Red 88 in the presence of electron acceptors such as PMS and PDS.

In 2009, Amin et al.\textsuperscript{[75]} used sol-gel method to prepare Ag–TiO\textsubscript{2} composite in nano-range for a feasible maximum antibacterial activity. The antibacterial activity of calcined powder at 300 and 500 °C was studied in the presence and in the absence of UV irradiation against Escherichia coli as a model for Gram-negative bacteria. The antibacterial tests confirmed the powder calcined at 300 °C possessed more antibacterial activity than the pure TiO\textsubscript{2}. Furthermore, in 2009, Sun et al.\textsuperscript{[76]} presented novel approach for preparing TiO\textsubscript{2} nanotube array photocatalyst loaded with highly dispersed Ag nanoparticles through an ultrasound aided photochemical route. The effects of Ag content on the photoelectrochemical (PEC) property and photocatalytic activity of TiO\textsubscript{2} nanotube array electrode were studied. The results showed that Ag loading significantly enhanced the photocurrent and photocatalytic degradation rate of TiO\textsubscript{2} nanotube array under UV-light irradiation.

In 2010, Li et al.\textsuperscript{[77]} prepared Ag-modified TiO\textsubscript{2} powders with various Ag/Ti molar ratios by microwave-assisted method. The photocatalytic degradation of toluene was used to evaluate the photocatalytic activity of prepared photocatalysts. In conclusion, exhibited a better photostability in toluene degradation compared to TiO\textsubscript{2}. In contrast, Kočí et al.\textsuperscript{[78]} studied the photocatalytic reduction of carbon dioxide in the presence of silver-modified TiO\textsubscript{2} to investigate the influence of the Ag-doped TiO\textsubscript{2} on the yields in both phases (liquid and gas). The Ag-doped sol–gel TiO\textsubscript{2} powder possessed higher photocatalytic activity, however, the main factor which influenced the yields of CO\textsubscript{2} photocatalytic reduction is the Ag content. Later in 2011, Kočí et al.\textsuperscript{[79]}, assessed the
effect of wavelength (254, 365 and 400 nm) on the photocatalytic reactivity of Ag-TiO₂ exemplified by the photoreduction of CO₂ by water. CO₂ saturated liquid phase with suspended Ag-TiO₂ catalyst powder were used. As a result, the radiation with the shorter wavelength of 254 nm was significantly more effective for CO₂ photoreduction than the 365 nm radiation while 400 nm was not effective at all and the increased efficiency of electron-hole generation with the shorter wavelength of irradiation increased the efficiency of the catalyst.

In 2011, Zhao and Chen[80] prepared thin film of Ag-TiO₂ to study the photocatalytic activity of the photodegradation of methylene blue (MB) under UV light irradiation. Ag-TiO₂ film showed a significant increase in photocatalytic activity compared to the TiO₂ film. Ko et al.[81] investigated photochemical synthesis and visible light induced catalytic activity of nanosized silver (Ag) doped titania (TiO₂). Synthesis of the composite was achieved by photochemical reduction of a mixture of P25 Degussa TiO₂ and silver nitrate (AgNO₃) solution under ultraviolet (UV) irradiation. Photocatalytic activity was evaluated by decomposition of methylene blue (MB) dye solution under visible light irradiation. In comparison to pure TiO₂, the composite nanoparticles exhibited enhanced visible light-induced photocatalytic activity. Moreover, Xiong et al.[82] synthesized Ag-modified mesoporous anatase TiO₂ by a photoreduction method. They used Non-biodegradable dye, Rhodamine B (RhB), and a gram-negative bacterium, E. coli as probes to investigate the photocatalytic detoxification and disinfection properties of the composite materials under UV irradiation. The effect of Ag loadings on catalyst performance and the role of Ag nanoparticles in the photocatalytic degradations were also investigated. It was found that the deposited Ag nanoparticles slightly decreased the extent of adsorption of RhB, but increased the affinity of the surface to oxygen, which seemed to play a much more important role in enhancing the photocatalytic reactions. After four cycles of reuse, the composite catalyst still showed significant capacity for dye degradation.
In 2012, Ismail\textsuperscript{[83]} evaluated Ag-TiO\textsubscript{2} films by photocatalytic oxidation of 2-chlorophenol (2-CP) as a model reaction. Ag nanoparticles were incorporated into the mesoporous titania by in situ heat-induced reduction through the oxidation of template at 400°C. The photocatalytic oxidation of 2-CP results indicated that, the Ag-TiO\textsubscript{2} films show good performance due to their highly ordered mesopores, one crystal phase and small particle size. The photocatalytic activity of mesoporous TiO\textsubscript{2} and Ag-TiO\textsubscript{2} films for photo-oxidation of 2-CP is higher 4 and 8 times than nonporous Pilkington Active\textsuperscript{TM} glass respectively. The recycle tests of Ag-TiO\textsubscript{2} films confirm that the films are very stable and high photoactive. In 2012, Liu\textsuperscript{[84]} prepared TiO\textsubscript{2} and Ag-TiO\textsubscript{2} by the simple co-precipitation method. The photocatalytic inactivation and disinfection of \textit{E. coli}, by using the catalysts under irradiation of different light sources were studied and compared. The results showed that the visible light may effectively be applied for the disinfection unit of water and wastewater treatment system by using photocatalysts of Ag-TiO\textsubscript{2}. Suwanchawalit et al.\textsuperscript{[63]} studied the photocatalytic performance of Ag-modified TiO\textsubscript{2} photocatalyst under visible light and compared it with that of commercial Degussa P25-TiO\textsubscript{2} under visible irradiations. The photocatalyst was prepared by the sol-gel using hydrazine as a reducing agent. The Ag-modified TiO\textsubscript{2} catalyst has high photocatalytic efficiency than those of undoped TiO\textsubscript{2} and commercial P25-TiO\textsubscript{2} under visible light irradiation. Furthermore, the Ag-modified TiO\textsubscript{2} catalyst can be used several times without any treatment process. Peerakiatkhajorn et al.\textsuperscript{[85]} provided the photocatalytic approach for treatment of some hazard air pollutants such as benzene, toluene, ethylbenzene and xylene (BTEX) under visible light by using silver doped titanium dioxide (Ag-TiO\textsubscript{2}) thin films dipped on polyvinyl chloride (PVC) sheet. The results exhibited the best performance for gaseous BTEX degradation under visible light.

In 2013, Pugazhenthiran et al.\textsuperscript{[86]} synthesized a very high surface area TiO\textsubscript{2} nanotubes (TiO\textsubscript{2} NTs) through a simple hydrothermal method and their surface was modified with silver nanoparticles (Ag NPs). Their photocatalytic activity were studied toward the degradation of ceftriaxone sodium (CFS), a third-generation cephalosporin antibiotic. The
surface deposited Ag NPs significantly increased their photocatalytic degradation rate, owing to the plasmonic feature of Ag NPs as well as due to the effective charge separation (electron–hole separation) at the Ag-TiO₂ interface. Kong et al.⁸⁷ also used hydrothermal method to grow TiO₂ nanorods on transparent conductive fluorine-doped tin oxide (FTO) substrates where Ag nanoparticles were deposited on TiO₂ nanorods by double-potentiostatic methods under different nucleation potentials. The catalysts were evaluated by photo-reduction CO₂ under UV irradiation. It was proved that TiO₂ decorated with Ag nanoparticles improved photocatalytic activity, and Ag deposited TiO₂ under −1.0 V nucleation potential had better performance for the better size variation and uniform spatial distribution compared to other nucleation potentials.

In 2014, Suwarnkar et al.⁸⁸ described the doping of TiO₂ with Ag by an energy efficient microwave method. The photocatalytic activity of the catalyst was evaluated by using methyl orange as a model pollutant and studied the effect of catalyst (Ag doping) loading, and pH. It was found that the degradation efficiency of TiO₂ increased gradually with increase in Ag dopant. Ag doped TiO₂ photocatalyst significantly improved the photocatalytic activity. Lee and Chen⁸⁹, investigated the effect of silver content in Ag-TiO₂ catalyst for methylene blue destruction under UV light irradiation by synthesizing nano Ag-TiO₂ catalysts by chemical deposition method. The photocatalytic activity increased after loading with Ag. In addition, Aazam⁹⁰ used Ag-TiO₂ photocatalyst supported on multi-wall carbon nanotube (MWCNT) to degrade thiophene by photocatalysis under visible light irradiation in an aqueous solution. The results showed that the re-use of the photocatalyst remains effective and active after six cycles, which indicates the promising recyclability of a MWCNT/Ag–TiO₂ photocatalyst.

In this study, we are interested in Ag-doped TiO₂ because Ag-doping into TiO₂ prevents the recombination of electron-hole pairs and improves the photocatalytic reactions. All samples with various concentrations of Ag-TiO₂ were characterized using FTIR, XRD, FESEM/EPMA/ mapping, BET and UV-Vis spectrophotometer. We studied the effect of Ag-dopant on the optical response of the Ag-doped TiO₂.
2.2 Materials and Research Methods

2.2.1 Materials

Titanium IV butoxide, Butanol, 2-Propanol, Acetonitrile, Acetylacetone (Pentane-2,4-dione) were purchased from Sigma-Aldrich, Pure Silver nitrate from Applichem and freshly prepared distilled water was used throughout the experiment.

2.2.2 Preparation of Ag-TiO$_2$ photocatalysts

Ag-TiO$_2$ was prepared by using sol-gel method. A mixture of 2.55 ml Acetylacetone (pentane-2,4-dione) in 32 ml butanol was prepared to chelate 17.19 ml titanium n-butoxide. The mixture of Acetylacetone in butanol was used to stabilise the Ti centre. Titanium solution was covered with parafilm and kept on stirring for 1 h. Then, 3.6 ml of distilled water was dissolved in 11.5 ml of 2-propanol and added dropwise to hydrolyse the titanium solution which was left for 1 h stirring. Appropriate amount of AgNO$_3$ (for the preparation of 6, 8, 10, and 12 mol.% silver doped titanium) was dissolved in 2.09 ml acetonitrile. The acetonitrile was used as a coordinating solvent to stabilise the Ag. Ag solution was added to titanium solution dropwise which was stirred for an hour. A clear, yellow solution was produced, with no precipitation. Later, the obtained gel was dried to get rid of all volatiles using a hot water bath and calcined at 500°C for 4 h to obtain the final product in a powder form. The powder turned to greyish black color after calcination.

2.2.3 Characterization of Ag-TiO$_2$

2.2.3.1 Diffuse Reflectance Infrared Fourier Transform Spectroscopy (DRIFTS)

Diffuse reflectance infrared Fourier transform spectra was performed by using a Shimadzu IR-Affinity-1 spectrometer in the range of 4000–400 cm$^{-1}$ at 4 cm$^{-1}$ resolution. A background spectrum was recorded for KBr at 25 °C after pretreatment at 150 °C under nitrogen flow, 10 ml/min.
2.2.3.2 Brunauer–Emmett–Teller (BET)

N₂ adsorption-desorption studies for surface area and porosity measurements were conducted on a Quantochrome Autosorb-1 volumetric gas sorption instrument at 77 K. Samples were degassed at 150 °C for 8 h before measurements. The surface area was obtained by the Brunauer–Emmett–Teller (BET) method and the pore size distribution was determined by Barett–Joyner–Halenda (BJH) model from the desorption branch of the N₂ isotherms.

2.2.3.3 X-ray diffraction (XRD)

X-Ray Diffraction (Ultima IV-XRD) θ/2θ technique was used to study the crystal structure. The mortar grinder was used to prepare the various contents of Ag-TiO₂ powder samples for XRD analysis. The powder was mounted on the powder sample holder and examined for crystal structure identification. The XRD pattern for the powder samples was obtained by Rigaku Ultima IV X-Ray Diffractometer using a Cu Kα radiation source operating at 40kV and 50 mA. For the qualitative analysis (i.e., phase identification), the x-ray pattern was analysed using pattern processing software equipped with the International Center for Diffraction Data (ICDD) and powder diffraction file (PDF) database of the standard reference materials.

2.2.3.4 UV-visible absorption spectrometry (UV-vis)

High-Resolution Spectrometer (Ocean Optics Inc., HR-2000) used to study the optical properties of the various contents of Ag-TiO₂. Tungsten halogen lamp (LS-1) used as a light source which was adjusted at 4 mm from the surface of the samples. A polished mirror was used as a reference.

2.2.3.5 Field emission scanning electron microscopy (FESEM)

Field emission scanning electron microscope (JSM-7001F-SEM) was used to examine the surface morphology of the samples. The various contents of Ag-TiO₂ samples (in the
form of particles) were mounted on the SEM stub using a double-sided carbon adhesive tape and then the mounted samples were coated by carbon at thickness of ~15 nm using the vacuum evaporator in order to avoid the charging effect. The surface was observed at accelerating voltage = 2 kV to obtain high resolution images at 30 kx magnification range.

2.2.3.6 Electron Probe Micro-Analyser (EPMA)

Electron Probe Micro-Analyser (JXA-8230) was used to obtain the chemical analysis of the samples and to study the chemical variability over the surface of the specimens. Qualitative and quantitative measurements were done for these samples using energy dispersive spectrometer (EDS) detector to determine the chemical composition. Moreover, the same detector was used to obtain the distribution of elements over selected particles or areas on the samples.

The particles of each Ag-TiO$_2$ sample were mounted on the EPMA stub using double sided carbon tape and analysed for chemical composition and elemental distribution. All samples were coated by 15 nm thickness of carbon using vacuum evaporator to remove charging. The analysis was performed at accelerating voltage of 15 kV using the energy dispersive spectrometer (EDS). The Qualitative and quantitative analysis for all Ag-TiO$_2$ samples were obtained at 1kx magnification.

2.3 Results and Discussion

2.3.1 DRIFTS Analysis

The DRIFTS spectra of TiO$_2$ Figure 2.1 showed two peaks at 3443 and 1640 cm$^{-1}$ which are attributed to OH-stretching and bending vibrations, respectively. Another band due to Ti-O was observed between 500-900 cm$^{-1}$. In Ag-doped TiO$_2$ with different percentage of Ag, spectra bands were observed at 3400-3472 cm$^{-1}$ and 1612-1619 cm$^{-1}$, again due to OH-stretching and bending, respectively. A Ti-O band also appeared between 500 cm$^{-1}$ and 900 cm$^{-1}$. In Ag-TiO$_2$ composites, the absorption bands of OH (stretching and bending) and Ti-O bands were reduced. The presence of new peaks in
the region between 500-1000 cm\(^{-1}\) different from pure CuO and pure TiO\(_2\) indicate new metal-oxygen bonding. These results support the formation of mixed oxide (i.e., Ti-O-Cu) bonding.

![DRIFTS spectra of Ag-TiO\(_2\) for various contents of Ag (mol.%).](image)

**Figure 2.1:** DRIFTS spectra of Ag-TiO\(_2\) for various contents of Ag (mol.%).

**2.3.2 Surface Analysis by using BET**

The surface area of pure TiO\(_2\) and Ag-doped TiO\(_2\) was measured by the nitrogen gas adsorption technique employing the BET method. The results are summarized in Table 2.1. The photocatalytic activity of nanoparticles is highly related to their surface properties. As surface area (and porosity) increases, the number of active sites also increases\([88]\).
The BET surface area of the unmodified TiO\textsubscript{2} was found to be about 67 m\textsuperscript{2}/g, which is close to that reported by Kočí et al.\textsuperscript{[78]}. It was observed that when 6 mol.% Ag was introduced, the surface area decreased to 31.7 m\textsuperscript{2}/g. It seems that the agglomeration of the nanoparticles were formed when Ag particles were introduced into the TiO\textsubscript{2} matrix, resulting in the decrease of the surface area. This is evident in the SEM images (\textbf{Figure 2.4}) which shows that the morphologies of the Ag-doped TiO\textsubscript{2} nano-catalysts represent highly agglomerated nanoparticles. Furthermore, the surface area has slightly increased with increasing the mol.% of the Ag dopant. The pore volume of all samples is almost the same regardless of the Ag mol.%. The average pore size shows has significantly increased at 12 mol.% Ag.

Table 2.1: BET specifications for various concentrations of Ag-TiO\textsubscript{2}.

<table>
<thead>
<tr>
<th>Ag-TiO\textsubscript{2} (mol. % Ag)</th>
<th>S\textsubscript{BET} (m\textsuperscript{2}/g)</th>
<th>Pore volume (cc/g)*</th>
<th>Average Pore size (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>67</td>
<td>0.06</td>
<td>32.4</td>
</tr>
<tr>
<td>6</td>
<td>32</td>
<td>0.07</td>
<td>42.3</td>
</tr>
<tr>
<td>8</td>
<td>34</td>
<td>0.05</td>
<td>46.7</td>
</tr>
<tr>
<td>10</td>
<td>35</td>
<td>0.06</td>
<td>48.2</td>
</tr>
<tr>
<td>12</td>
<td>36</td>
<td>0.06</td>
<td>120.1</td>
</tr>
</tbody>
</table>

* Pore volume at P/P\textsubscript{0} = 0.1

\textbf{2.3.3. Optical Analysis by UV/Vis.}

The yield of photo-generated electron-hole pair first depends on the intensity of incident photons with energy exceeding or equalling to the TiO\textsubscript{2} bandgap energy \textsuperscript{[68]}. The effect of silver loading on the band energy of TiO\textsubscript{2} was investigated with high-resolution Spectrometer. \textbf{Figure 2.2} shows the UV–Vis spectra of Ag–TiO\textsubscript{2} catalysts. It is seen that the maximum absorption wavelength increased with increasing Ag content, i.e. the absorption was shifted into the visible region for Ag–TiO\textsubscript{2} catalysts and the shift increased with the increasing amount of silver.
The bandgap can be calculated by the following formula,

\[ E_g = h \frac{C}{\lambda} = \frac{1240}{\lambda_{\text{cutoff}}} \]  

(1)

where \( h \) (Planks constant) = \( 6.63 \times 10^{-34} \) J.s; \( C \) (speed of light) = \( 3.0 \times 10^8 \) m/s; \( \lambda_{\text{cutoff}} \) (cut off wave length) = \( 4.11 \times 10^{-7} \) m. Note: 1 eV = \( 1.6 \times 10^{-19} \) J (conversion factor).

The calculated band gap energy for pure TiO\(_2\) and various contents of Ag-TiO\(_2\) are listed in **Table 2.2.** In this work, the pure TiO\(_2\) has a band gap energy, \( E_g = 2.95 \) eV, respectively, while the band gap energies of the Ag-TiO\(_2\) samples decreased from 2.95 eV (0 mol. % Ag) to 2.55 eV (12 mol. % Ag), i.e., the band gap energy is inversely proportional to Ag content.

![Absorption spectra for pure TiO\(_2\) and Ag-TiO\(_2\) at various Ag contents (mol.%)](image)

**Figure 2.2:** Absorption spectra for pure TiO\(_2\) and Ag-TiO\(_2\) at various Ag contents (mol.%).
Table 2.2: $\lambda_{\text{cutoff}}$ and bandgap of prepared TiO$_2$ and various contents of Ag-doped TiO$_2$.

<table>
<thead>
<tr>
<th>Sample (mol.% Ag)</th>
<th>$\lambda_{\text{cutoff}}$ (nm)</th>
<th>Bandgap (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pure TiO$_2$</td>
<td>420.91</td>
<td>2.95</td>
</tr>
<tr>
<td>6% Ag-TiO$_2$</td>
<td>467.84</td>
<td>2.65</td>
</tr>
<tr>
<td>8% Ag-TiO$_2$</td>
<td>472.01</td>
<td>2.63</td>
</tr>
<tr>
<td>10% Ag-TiO$_2$</td>
<td>478.49</td>
<td>2.59</td>
</tr>
<tr>
<td>12% Ag-TiO$_2$</td>
<td>486.81</td>
<td>2.55</td>
</tr>
</tbody>
</table>

2.3.4. Phase Structural Analysis by using XRD

XRD test has been done to investigate the effect of Ag content (mol.%) on the crystal structure of the Ag-doped TiO$_2$ nanocatalyst. The analysis was carried out in the range of $2\theta = 10$–90° for different concentrations of Ag. The diffraction patterns are shown Figure 2.3 a-e for pure and Ag-doped TiO$_2$. For the pure TiO$_2$ (Figure 2.3 a), two phases of tetragonal TiO$_2$ are observed; one is anatase TiO$_2$ (highest peak) and the other phase is rutile TiO$_2$ (the short peak adjacent to anatase peak, which represents a very small amount of rutile TiO$_2$). The small amount of the rutile phase acts as a structural defect or impurity in the anatase phase and causes high photocatalytic activity$^{[91]}$. The strong diffraction peaks at 25.29°, 27.51°, 37.95°, 48.09°, 54.18°, 62.68°, 68.78°, 74.80° and 82.75° correspond to the crystal planes [101], [110], [103], [200], [105], [213], [116], [107], and [303] respectively. This is attributed to reflections of anatase TiO$_2$ which is compared with JCPD Card No (2-0494) for rutile phase and JCPD Card No (21-1272) for anatase phase.

After the addition of Ag, only anatase diffraction peaks were detected in different Ag contents (Figure 2.3 b-e). It can also be seen that most of the $2\theta$ peak positions of major diffraction pattern in all samples show no shifting, having similar values of pure TiO$_2$, except the changes in the intensities of these peaks (i.e., intensity increases as Ag increases). No Ag phases were identified in any of the samples due to their well dispersion. This shows the good homogeneity of the nanoparticles. In addition, Ag loading did not cause significant changes in crystallinity since, Ag$^+$ ion radii is too large.
to replace Ti$^{4+}$ ions in the TiO$_2$ matrix. As seen in Figure 2.3 b-e, the addition of Ag didn’t change the phase structure of the TiO$_2$; this may indicate that Ag is formed on the crystal borders and on the surface of the TiO$_2$; which promotes visible light absorption as shown in Figure 2.2.

Figure 2.3: XRD patterns of (a) TiO$_2$, (b) 6 mol.% Ag-TiO$_2$, (c) 8 mol.% Ag-TiO$_2$, (d) 10 mol.% Ag-TiO$_2$, and (e) 12 mol.% Ag-TiO$_2$. 
2.3.5. Surface Morphology and Chemical Composition Analysis by Using FESEM and EPMA

Figure 2.4 shows the FESEM images of pure TiO$_2$ and different concentrations of Ag-TiO$_2$. This study was performed to investigate the surface morphology of the synthesized Ag doped TiO$_2$ nanoparticles. Relatively uniform spherical shaped nanoparticles were indicated, which are the aggregation of tiny crystals. FESEM images of prepared Ag-doped TiO$_2$ compared with those of pure TiO$_2$ confirm that Ag-doped TiO$_2$ has a slightly smaller particle size than that of pure TiO$_2$ as mentioned in Table 2.3. Moreover, the calcination temperature plays a role in affecting the crystallite size of TiO$_2$ and Ag-TiO$_2$. The crystallinity increases with increasing calcinations temperature because higher ordering in the structure of titania particles makes X-ray peaks sharper and narrower \cite{64}.

The presence of Ag and Ti in the prepared pure and Ag-TiO$_2$ powders was determined using the EDS mapping illustrated in Figure 2.5. The results indicate that the constitutive elements are O, Ti and Ag nanoparticles, which were prepared by the sol–gel method with different AgNO$_3$ contents. It was observed from the elemental mapping analysis that Ag nanoparticles are uniformly dispersed in the TiO$_2$ nanoparticles.
Figure 2.4: FESEM images of (a) TiO$_2$, (b) 6 mol.\% Ag-TiO$_2$, (c) 8 mol.\% Ag-TiO$_2$, (d) 10 mol.\% Ag-TiO$_2$, and (e) 12 mol.\% Ag-TiO$_2$.

Table 2.3: Crystallite size of various contents of Ag (mol\%) by FESEM analysis.

<table>
<thead>
<tr>
<th>Ag (mol.%)</th>
<th>Crystallite size (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>58.7</td>
</tr>
<tr>
<td>6</td>
<td>55.4</td>
</tr>
<tr>
<td>8</td>
<td>55.2</td>
</tr>
<tr>
<td>10</td>
<td>48.1</td>
</tr>
<tr>
<td>12</td>
<td>47.2</td>
</tr>
</tbody>
</table>
Figure 2.5: EDS mapping and elemental analysis and distribution of O, Ag & Ti for (a) TiO$_2$, (b) 6 mol.% Ag-TiO$_2$, (c) 8 mol.% Ag-TiO$_2$, (d) 10 mol.% Ag-TiO$_2$, and (e) 12 mol.% Ag-TiO$_2$ samples.
2.4 Conclusion

TiO$_2$ and Ag-doped TiO$_2$ (with various Ag mol. %) nanoparticles were prepared by the sol-gel method and characterized using FTIR, XRD, FESEM/EPMA/mapping, BET and UV-Vis spectrophotometer. XRD results showed that the Ag-doped TiO$_2$ samples were in pure anatase phase and the presence of Ag prevented the formation of the rutile phase which is less reactive than the anatase phase. FESEM images showed that both TiO$_2$ and Ag-TiO$_2$ have spherical morphology. EDS showed uniform dispersion of Ag in the TiO$_2$ nanoparticles. The UV/Vis analysis showed that the light absorption for the Ag–TiO$_2$ nanoparticles was shifted to the visible region and the shift increases with the increase of Ag molar concentration. Our results showed that doping TiO$_2$ with silver has enhanced the optical properties of TiO$_2$ and is expected to be a good potential candidate for photocatalytic applications.
Chapter 3: Characterization of Copper Doped Titanium Dioxide Produced by the Sol-Gel Process

3.1 Introduction

Recently, copper has been increasingly investigated as a dopant for titania. It is one of the best candidate metal dopant for TiO$_2$ surfaces, because of its relative abundance, high electronic conductivity and low cost as compared to noble metals$^{[92,93]}$ such as Ag. Cu is also a metallic element essential to human health and is considered a low toxicity metal to humans and is used in intrauterine devices$^{[94]}$.

Several works on the applications of Cu-TiO$_2$ have been reported in the areas of solar energy, environmental remediation for chemical contaminants removal, and microbial treatment. In solar energy, the existence of Cu element significantly shifts the light response of TiO$_2$ into the visible region, resulting in the enhancement of the photoelectrochemical properties of the TiO$_2$, and increasing the activity of the TiO$_2$ as catalyst for hydrogen generation. Cu dopant was also effective in increasing the properties of TiO$_2$ for converting carbon dioxide to higher carbon compounds and for generating hydrogen from water. In microbial treatment area, the Cu species can be used as an impurity material to enhance the TiO$_2$ activity for the treatment of water containing harmful biological contaminants. It is noticeable that the activity is affected by the presence of Cu species in TiO$_2$ matrix, because Cu could influence the particle size, and optical or electronic properties of TiO$_2$, as well as the number of oxygen or intermediate species on the surface of the TiO$_2$$^{[95]}$. A large number of studies on Cu doped TiO$_2$ nanomaterials have been reported.

In 2004, Tseng et al.$^{[96]}$ extended the fundamental understanding of the relationships among the sol–gel procedure, the properties of catalysts and photocatalytic activity. Copper-loaded titania (Cu-TiO$_2$) photocatalysts was used to evaluate the photocatalytic performance and was synthesized via an improved sol–gel process; the results of which demonstrated a promising technique for preparing such photocatalysts.

In 2005, Slamet et al.$^{[97]}$ investigated the photocatalytic reduction of CO$_2$ with H$_2$O at the liquid/solid interface of copper-doped titania photocatalysts. The photocatalysts with
various copper species $\text{Cu}^0\text{-TiO}_2$, $\text{Cu}^1\text{-TiO}_2$ and $\text{Cu}^{\text{II}}\text{-TiO}_2$ (0.5, 1.0, 3.0, 5.0, 10.0% $\text{CuO}\text{-TiO}_2$, 3.0% $\text{Cu}\text{-TiO}_2$, 3.0% $\text{Cu}_2\text{O}\text{-TiO}_2$) were prepared by an improved impregnation method via the reduction–oxidation steps. It was concluded that copper was an effective electron trapper and able to prohibit the recombination of electron–hole pairs, hence significantly promoting the photo-efficiency.

In 2006, Colón et al.$^{[98]}$ tried to improve the photocatalytic activity of TiO$\text{2}$ by different Cu doping procedures (prepared by sol-gel method) and combined the structural and surface effect of different acids used in the preparation procedure, and the presence of Cu doping species. In summary, the different behaviour between $\text{CuTiO}_2$, $\text{CuTiO}_2\text{N}$ and $\text{CuTiO}_2\text{S}$ series could be related to the different structural and electronic stability that surface sulphate (and subsequent O vacancies formed) could produce in the TiO$\text{2}$ doped systems. In the same year, H.S. Park et al.$^{[99]}$ prepared 2.5 wt.% of Cu-doped TiO$\text{2}$ powder by mechanical alloying (MA) and homogeneous precipitation process at low temperature (HPPLT) then investigated the effect of Cu doping on the photocatalytic activity, crystal size and structure. The Cu-doped powder had higher reaction ability than that of P-25 and HPPLT because the energy level was induced in the TiO$\text{2}$ band gap by the doped Cu.

In 2007, Choi and Kang$^{[100]}$ investigated the production of hydrogen from the methanol/water photodecomposition over Cu (1, 5, 10, and 15 mol%)/TiO$\text{2}$ photocatalysts loaded with CuO with an anatase structure. It was prepared by the conventional impregnation method. As a result, CuO component present on the external surface of the TiO$\text{2}$ anatase structure was confirmed to improve the H$_2$ production via methanol/water photodecomposition.

In 2008, Xin et al.$^{[101]}$ prepared Cu-TiO$\text{2}$ nanoparticles with different Cu dopant content (0, 0.02, 0.04, 0.06, 0.08, 0.10, 0.15, 0.20, 0.40, 0.60, 0.80, 1 and 3 mol%) were prepared by sol–gel method and the effects of the surface species on the photocatalytic activity were investigated. It was found that Cu (about 0.06 mol%) possess abundant electronic trap, such as the O vacancies and Cu (II) ions and the content of surface hydroxyl on the surface of the 0.06 mol% Cu-TiO$\text{2}$ is increased remarkably in contrast to that of pure TiO$\text{2}$. These factors can improve the photocatalytic activity of TiO$\text{2}$. 
In 2009, Yoong et al.\textsuperscript{[102]} investigated the advantage of copper doping onto TiO\textsubscript{2} semiconductor photocatalyst for enhanced hydrogen generation under irradiation in the visible range of the electromagnetic spectrum. Two methods of preparation for the copper-doped catalyst were selected, complex precipitation and wet impregnation methods. The dopant loading varied from 2 to 15 wt.%. Finally, it was noted that the synthesis of titania by the sol–gel method rather than using the Degussa P25 variety may be a better option since this material can be obtained in essentially anatase form by suitably selecting the sintering temperature. Also, the copper salt may be incorporated during the sol–gel preparation step for uniform dispersion of the dopant in the final product.

In 2010, Wu and Huang\textsuperscript{[103]} studied the photocatalytic CO\textsubscript{2} reduction on the TiO\textsubscript{2} and Cu-TiO\textsubscript{2} photocatalysts. The photocatalysts were prepared by sol-gel method. It was observed that, copper acted as electron trapper and enhanced the rate of CO\textsubscript{2} photoreduction.

In 2011, Wei et al.\textsuperscript{[104]} evaluated the photocatalytic activity by using the products measurement of CO\textsubscript{2} photoconversion under UV light irradiation. Various copper-modified TiO\textsubscript{2} NPs contents (0.1, 0.6, 2, 7, 20, 30 wt.% Cu-TiO\textsubscript{2}) was used and synthesized via sol-gel method. It was found that 0.6 and 20 wt.% Cu-TiO\textsubscript{2} NPs possessed the higher photoconversion efficiency of CO\textsubscript{2}.

In 2012, Khodadadi et al.\textsuperscript{[92]} synthesised Cu-doped TiO\textsubscript{2} nanocomposite by the sol-gel method with and without three additives; Poly(ethylene glycol) (PEG), Carboxy Methyl Cellulose (CMC), and Pectin. Finally, the influence of these additives on the properties, structure and photocatalytic activity under UV-irradiation was investigated for the removal of organic pollutant. The results showed that the photocatalytic activity of the nanocomposites increased in the presence of additives and pectin was more effective than others.

In 2013, Choudhury et al.\textsuperscript{[93]} discussed the doping effect of Cu on the crystallinity of pure TiO\textsubscript{2} nanoparticles and examined how Cu extends the absorption edge of TiO\textsubscript{2} to the visible region and reduces the effective band gap of TiO\textsubscript{2}. The photocatalysts were prepared by sol-gel method. In the same year, Heciak et al.\textsuperscript{[105]} investigated influence of
the modification procedure and copper precursor on the physico-chemical properties and photoactivity of the photocatalysts towards formation of useful hydrocarbons from acetic acid. The Cu-modified photocatalysts were prepared by three methods: impregnation, photodeposition or mechanical alloying. In conclusion, most of the Cu-TiO$_2$ photocatalysts revealed significantly improved activity in the photocatalytic generation of useful aliphatic hydrocarbons and hydrogen compared to the crude TiO$_2$ or commercial TiO$_2$ P25.

In 2014, Pham and Lee$^{[94]}$ reported the chemical mechanism of Cu in enhancing the photocatalytic activity of TiO$_2$ in the Cu-TiO$_2$/GF photocatalyst system for the disinfection of E. coli in aerosols under visible light irradiation and also investigated the effect of humidity on bio-aerosol disinfection using the Cu-TiO$_2$/GF photocatalytic system. In conclusion, Cu doped in the TiO$_2$ lattice enhanced electron-hole separation efficiency and electron-hole separation capacity of the photocatalyst and the photocatalytic disinfection of E. coli was dependent on Cu content in the Cu-TiO$_2$/GF photocatalysts. Ganesh et al.$^{[106]}$ prepared different amounts of Cu-doped TiO$_2$ powders and thin films were prepared by following a homogeneous co-precipitation method and sol-gel dip-coating technique for the evaluation of: (1) electrochemical reduction of CO$_2$ in a two-compartment electrochemical cell, (2) photocurrent generation in PEC cells, and (3) photocatalytic methylene blue (MB) degradation reactions under the irradiation of a simulated solar light having different wavelength regions. As a result of this work, UV-light-induced TiO$_2$ was found to be responsible for photocatalytic methylene blue (MB) degradation, and TiO$_2$ was not sensitized by MB. The in-situ formed compounds of TiO$_2$ and CuO/Cu$_2$O were found to absorb visible light, but showed little visible-light-induced photocatalytic activity.

In this work, a series of copper doped TiO$_2$ NPs were synthesized via the sol-gel method. All samples with various concentrations of Cu in Cu-TiO$_2$ were characterized using FTIR, XRD, FESEM / EPMA/ mapping, BET and UV-Vis spectrophotometer. Rheological analysis was also conducted on Cu-doped TiO$_2$ where no similar research work have been done yet. The different effects of copper species were studied with respect to the characteristics of Cu-TiO$_2$ NPs.
3.2 Materials and Research Methods

3.2.1 Materials

Titanium IV butoxide and Ethanol were purchased from Sigma-Aldrich, Cu(NO$_3$)$_2$.3H$_2$O and nitric acid from Riedel-de Haën, and freshly prepared distilled water was used throughout the experiments.

3.2.2 Preparation of Cu-TiO$_2$ photocatalysts

Cu-TiO$_2$ was prepared by using sol–gel method. 52.5 mL of Ti(OBu)$_4$ was dissolved in 100 mL ethanol and solution was stirred for 10 min. Then 7.5 mL of concentrated HNO$_3$ was added dropwise to this solution and kept on stirring for further 30 min. Appropriate amount of Cu(NO$_3$)$_2$.3H$_2$O (for the preparation of 1.6, 2, 3.2, 4.8, 5, 6.4, 8, 10, and 15 mol.% Copper-doped Titanium) was dissolved in 100 mL of ethanol and 15 mL of H$_2$O. Copper nitrate solution was added dropwise to titanium solution and was stir for 1 h. A clear, light blue solution was produced, with no precipitation. After 69 h of aging, the solvents in the obtained gel were evaporated using a hot water bath, and then calcined at 500°C for 4 h to obtain the final product powder, which had turned to greyish black color after calcination.

For rheological measurements, the preparation of the sol-gel was the same as discussed lately, but it was tested before and after aging as a gel form. Neither evaporation nor calcinations was applied.

3.2.3 Characterization of Cu-TiO$_2$ photocatalysts

3.2.3.1 Rheological Measurements

The rheological properties performed to determine the sol–gel flow behavior were carried out using a Rheolab QC viscometer from Anton Paar, Germany. The system has an inner cylinder rotating in a stationary outer cylinder. A bob with a radius of 13.329 mm and a cup with a radius of 14.460 mm and 120° cone angle were used to form a gap of width 1.132 mm. The temperature was controlled by using thermo-stated-circulating
bath. All rheological tests were carried out at 25°C. The pH of the sol-gel was measured by pH meter at 25 °C using pH meter (691 pH meter, Metrohm Herisau Switzerland).

3.2.3.2 Diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS)

Diffuse reflectance infrared Fourier transform spectra were performed by using a Shimadzu IR-Affinity-1 spectrometer in the range of 4000–400 cm⁻¹ at 4 cm⁻¹ resolution. A background spectrum was recorded for KBr at 25 °C after pretreatment at 150 °C under nitrogen flow, 10 ml/min.

3.2.3.3 BET

N₂ adsorption-desorption studies for surface area and porosity measurements were conducted on a Quantochrome Autosorb-1 volumetric gas sorption instrument at 77 K. Samples were degassed at 150 °C for 8 h before measurements. The surface area was obtained by the Brunauer–Emmett–Teller (BET) method and the pore size distributions were determined by Barett–Joyner–Halenda (BJH) model from the desorption branch of the N₂ isotherms.

3.2.3.4 X-ray diffraction (XRD)

X-Ray Diffraction (Ultima IV-XRD) θ/2θ technique was used to study the crystal structure. The mortar grinder was used to prepare the various contents of Ag-TiO₂ powder samples for XRD analysis. The powder was mounted on the powder sample holder and examined for crystal structure identification. The XRD pattern for the powder samples was obtained by Rigaku Ultima IV X-Ray Diffractometer using a Cu Kα radiation source operating at 40 kV and 50 mA. For the qualitative analysis (i.e., phase identification), the x-ray pattern was analysed using pattern processing software equipped with the International Center for Diffraction Data (ICDD) and powder diffraction file (PDF) database of the standard reference materials.
3.2.3.5 UV-visible absorption spectrometry (UV-vis)

High-Resolution Spectrometer (Ocean Optics Inc., HR-2000) was to study the optical measurements of the various contents of Ag-TiO₂. Tungsten halogen lamp (LS-1) used as a light source which was adjusted 4mm from the surface of the samples. A polished mirror was used as a reference.

3.2.3.6 Field emission scanning electron microscopy (FESEM)

Field Emission Scanning Electron Microscope (JSM-7001F-SEM) was used to examine the surface morphology of the samples. The various contents of Ag-TiO₂ samples (in the form of particles) were mounted on the SEM stub using a double-sided carbon adhesive tape and then the mounted samples were coated by carbon at thickness ~ 15 nm using the vacuum evaporator in order to avoid the charging effect. The surface was observed at accelerating voltage = 2 kV to obtain high resolution images and at 100x, 200x, 1kx, 5kx, 30kx and 50kx magnification range.

3.2.3.7 Electron Probe Micro-Analyser (EPMA)

Electron Probe Micro-Analyser (JXA-8230) was used to obtain the chemical analysis of the samples and to study the chemical variability over the surface of the specimens. Qualitative and quantitative measurements were done for these samples using energy dispersive spectrometer (EDS) detector to determine the chemical composition. Moreover, the same detector was used to obtain the distribution of elements over selected particles or areas on the samples.

The particles of each Ag-TiO₂ sample were mounted on the EPMA stub using double sided carbon tape and analysed for chemical composition and elemental distribution. All samples were coated by 15 nm thickness of carbon using vacuum evaporator to remove charging. The analysis was performed at accelerating voltage 15 kV using the energy dispersive spectrometer (EDS). The Qualitative and quantitative analysis for all Ag-TiO₂ samples were obtained at 1kx magnification.
3.3 Results and Discussion

3.3.1 Rheological Analysis

This study examines the rheological characteristics of the Cu-TiO$_2$ prepared by the sol-gel method. In the flow curve measurements, the shear stress ($\tau$) of the samples was measured as a function of shear rate ($\dot{\gamma}$) at constant temperature. In the time-dependent measurements, the apparent viscosity of the samples was measured as a function of time at constant shear rate. At constant time, the viscosity versus shear rate was measured for different Cu concentrations in the Cu-TiO$_2$ nano-material.

Figure 3.1 shows the viscosity dependence on shearing time measured at constant shear rate of (10 s$^{-1}$) for different Cu concentrations in the Cu-TiO$_2$ sol-gel. Cu concentrations of (0, 2, 5, 10 and 15) mol.% reached the gelation point smoothly. Gradual increase in the viscosity reached in 6000s with uniform slope. The gelation occurred very slowly due to the slow and continuous increase in the viscosity with time this due to the protonation of the Ti surface resulted from the reaction with the acid where a continuous network formed from the linking of the charged colloidal particles. The results indicated that the gelation process for the Cu-doped TiO$_2$ catalyst could be completed in several hours or even days.
Figure 3.1: Viscosity versus shear time for different Cu contents at 0 h, (a) TiO₂, (b) 2 mol.% Cu-TiO₂, (c) 5 mol.% Cu-TiO₂, (d) 10 mol.% Cu-TiO₂, (e) 15 mol.% Cu-TiO₂.

The sol-gel was left under ambient conditions for 69 h to make sure that the catalyst had reached complete gelation. The physical appearance of the gel did not change. Figure 3.2 shows the viscosity versus time at constant shear rate measurements. The viscosity of 10% and 15% Cu was constant and no change was observed, which implies that the viscosity is homogeneous in time, and even if any settlement of the particles occurs the gel can be shaken to be re-homogenized. While the viscosity of 2% and 5% Cu slightly increased in the shearing process, which might be due to some kind of particle arrangement as a result of shearing to reach more stable condition.
Figure 3.2: Viscosity versus shear time for different Cu contents at 69 h, (a) TiO$_2$, (b) 2 mol.% Cu-TiO$_2$, (c) 5 mol.% Cu-TiO$_2$, (d) 10 mol.% Cu-TiO$_2$, (e) 15 mol.% Cu-TiO$_2$.

The difference in concentration and pH can play a role in shear rate dependency of the viscosity. **Figure 3.3** shows a shear thinning (pseudoplastic) behavior where the viscosity decreases with increasing shear rate. This behavior can be due to the deformed and/or rearranged particles, resulting in lower flow resistance and consequently lower viscosity. At low shear rates the viscosity is very high, which is evidence of a strong, cohesive structure. On the other hand, there is a very little increase in the pH of the gel with the increase of the Cu content, as shown in **Table 3.1**. This slight increase in pH with increasing the concentration of Cu has lower viscosity than the viscosity of low pH. Moreover, the flow properties of Cu-TiO$_2$ under acidic conditions show shear thinning/non-Newtonian pseudo-plastic behavior that might be function of particle-particle aggregation formed just after lowering the pH due to weak forces of attraction$^{[107,108]}$. 
Gel strength is also one aspect that may affect the viscosity of the dispersion. The increase of the gel strength and the formation of the flocks could be the reason behind the maximum increase of viscosity. In this case, the decrease of gel strength and the re-dispersion of the flocks results in the decrease of viscosity[^108]. However, in dip coating applications, the increase of viscosity increases the layer thickness[^109].

Table 3.1: pH values for different Cu contents.

<table>
<thead>
<tr>
<th>Cu content (mol.%)</th>
<th>2</th>
<th>5</th>
<th>10</th>
<th>15</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH</td>
<td>1.02</td>
<td>1.05</td>
<td>1.15</td>
<td>1.27</td>
</tr>
</tbody>
</table>

![Figure 3.3: Viscosity versus shear rate for different Cu contents.](image)

The shear stress–shear rate relationship for various Cu contents in the gel is shown in **Figure 3.4**. The linearity of the curves indicates a Newtonian fluid behavior that increases with the increase of the Cu concentration.
Figure 3.4: Shear stress versus shear rate for different Cu contents: (a) TiO$_2$, (b) 2 mol.% Cu-TiO$_2$, (c) 5 mol.% Cu-TiO$_2$, (d) 10 mol.% Cu-TiO$_2$, and (e) 15 mol.% Cu-TiO$_2$.

3.3.2 DRIFTS Analysis

The absorption bands in TiO$_2$ spectra were observed at 3296 and 1629 cm$^{-1}$ which are due to OH-stretching and bending vibrations, as shown in Figure 3.5. A broad band was observed between 500-900 cm$^{-1}$ which is attributed to Ti-O. Similarly, in Cu-TiO$_2$ spectra’s bands were observed at 3450 and 1623 cm$^{-1}$ which are due to OH-stretching and bending respectively. A band of Ti-O was also observed between 500-900 cm$^{-1}$. The intensities of OH (stretching and bending) and Ti-O bands were decreased in Cu-TiO$_2$ nanoparticles. The nitrate band of starting material which appeared at 1384 cm$^{-1}$ was not found in Cu-TiO$_2$ spectra which show that calcinations process was good enough to remove the nitrate. The peaks in the 500-1000 cm$^{-1}$ region are different from pure CuO and pure TiO$_2$ indicate new metal-oxygen bonding. These results support the formation of mixed oxide (Ti-O-Cu) bonding.
Figure 3.5: DRIFTS spectra for of Cu-TiO₂ catalyst at various Cu contents (mol.%)

3.3.3 Surface Analysis by using BET

The surface area, pore size and pore volume of TiO₂ and Cu-TiO₂ nanoparticles are shown in Table 3.2. It can be seen that with increasing percentage of Cu in TiO₂ the total pore volume slightly increases indicating of more porosity that leads to the enhancement of the diffusion of molecules.

Pure TiO₂ nanocatalyst showed the same specific surface area as have been determined in the previous chapter which was 66.9 m²/g, which agrees with that reported by Karunakaran et al. In comparison to the reported commercial TiO₂ (Degussa P25), the specific surface area of the prepared TiO₂ in this work is larger indicating that the prepared TiO₂ could be more effective in photocatalytic activity than the
Degussa P25. In addition, a significant increase in the surface area of Cu-TiO$_2$ samples ranging from 30.1 to 75.3 m$^2$/g, 15 mol.% Cu-TiO$_2$ had the highest surface area. It can be inferred that Cu-TiO$_2$ nano-catalyst did not show significant change in specific surface area. A small decrease in some nano-catalysts surface area could be caused due to thermal treatment during the preparation. The average pore size shows a slight increase with increasing of the Cu dopant content.

Table 3.2: BET results for Cu-TiO$_2$ nanocatalyst at various Cu contents.

<table>
<thead>
<tr>
<th>Cu-TiO$_2$ (mol. %)</th>
<th>$S_{\text{BET}}$ (m$^2$/g)</th>
<th>Pore volume (cc/g)</th>
<th>Average Pore Size (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0</td>
<td>66.92</td>
<td>0.06</td>
<td>32.42</td>
</tr>
<tr>
<td>1.6</td>
<td>45.96</td>
<td>0.05</td>
<td>21.04</td>
</tr>
<tr>
<td>2.0</td>
<td>36.86</td>
<td>0.06</td>
<td>32.42</td>
</tr>
<tr>
<td>3.2</td>
<td>36.02</td>
<td>0.06</td>
<td>31.90</td>
</tr>
<tr>
<td>4.8</td>
<td>36.01</td>
<td>0.06</td>
<td>33.11</td>
</tr>
<tr>
<td>6.4</td>
<td>42.40</td>
<td>0.07</td>
<td>32.91</td>
</tr>
<tr>
<td>8.0</td>
<td>50.68</td>
<td>0.11</td>
<td>42.08</td>
</tr>
<tr>
<td>10.0</td>
<td>49.41</td>
<td>0.11</td>
<td>45.17</td>
</tr>
<tr>
<td>15.0</td>
<td>75.36</td>
<td>0.17</td>
<td>43.83</td>
</tr>
</tbody>
</table>

3.3.4 Optical Analysis by UV/Vis.

Figure 3.6 displays the UV–vis spectra that show the influence of various prepared copper dopant concentrations on the UV–vis absorption. It can be observed that increasing Cu concentration, shifts the absorbance to the light-visible region. TiO$_2$ showed an absorbance at 420.9 nm, as presented in Table 3.3, corresponding to $E_g = 2.95$ eV (~3.0 eV), which is calculated by using formula (1) in Chapter 2. This $E_g$ value is consistent with the reported value for anatase TiO$_2$[111]. At 15 mol.% Cu content the $E_g = 2.62$ eV which indicates that as Cu concentration increases, the band gap energy decreases. This change in the band gap can be likely due to the fusion of Cu ions into TiO$_2$ crystal structure, and the defect centers formed by the substitution of Ti$^{4+}$ by Cu ions in the TiO$_2$ crystal lattice resulting in changes in the optical absorption.
In Cu-doped TiO$_2$, when Cu ions are either located inside the bulk TiO$_2$ or on the surface sites, a rearrangement of the neighbour atoms takes place to compensate the charge deficiency, resulting in lattice deformation. The lattice deformation affects the electronic structure causing the band gap shift$^{[112]}$. Furthermore, small amounts of Cu dopant in the lattice sites of TiO$_2$ introduce O vacancies due to the charge compensation effect. Increasing the copper doping concentration increases the O vacancies and probably forms a newly doubly occupied O vacancy as illustrated by Sahu and Biswas$^{[112]}$. In this case, it can be noted that the surface effects, doping-induced vacancies, and lattice strain may affect absorption and band gap shift of the doped nanoparticles. Therefore, copper-doped TiO$_2$ can be applied for different visible-light photocatalytic applications.

As a comparative work, Choi and Kang$^{[100]}$ did an equivalent work on Cu-doped TiO$_2$. They prepared Cu-doped TiO$_2$ photocatalysts with Cu contents of 1, 5, 10 and 15 mol%. Their results showed that the loading of the Cu didn’t affect the band gap energy of TiO$_2$ where no shifting was observed. This contradicts with our results, where the shifting from the UV region to the visible region was very clear in which a significant decrease in the band gap was detected, as illustrated in Table 3.3. Our work possessed better results, where TiO$_2$ optical response was improved by increasing the Cu dopant content. According to our results, Ag-doped TiO$_2$ that was studied in Chapter 2 showed better shifting of the optical response from the UV to the visible region. As can be seen, at 8 mol.% and 10 mol.% Ag, the band gap reached to 2.63 eV and 2.59 eV, respectively. While, Cu-doped TiO$_2$ shifted the band gap down to 2.66 eV at 15 mol.% Cu. This concludes that the Ag dopant enhanced the optical response of TiO$_2$ more than Cu dopant, but as mentioned earlier, Cu is much cheaper than Ag.
Figure 3.6: UV/Visible Absorption Spectra of TiO$_2$ and different contents of Cu-TiO$_2$.

Table 3.3: $\lambda_{\text{cutoff}}$ and band gap of prepared TiO$_2$ and various contents of Cu-doped TiO$_2$.

<table>
<thead>
<tr>
<th>Sample (mol.%)</th>
<th>$\lambda_{\text{cutoff}}$ (nm)</th>
<th>Band gap (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pure TiO$_2$</td>
<td>420.9</td>
<td>2.95</td>
</tr>
<tr>
<td>1.6% Cu-TiO$_2$</td>
<td>432.1</td>
<td>2.87</td>
</tr>
<tr>
<td>2.0% Cu-TiO$_2$</td>
<td>438.1</td>
<td>2.83</td>
</tr>
<tr>
<td>3.2% Cu-TiO$_2$</td>
<td>462.7</td>
<td>2.68</td>
</tr>
<tr>
<td>4.8% Cu-TiO$_2$</td>
<td>462.3</td>
<td>2.68</td>
</tr>
<tr>
<td>6.4% Cu-TiO$_2$</td>
<td>463.7</td>
<td>2.67</td>
</tr>
<tr>
<td>8.0% Cu-TiO$_2$</td>
<td>466.9</td>
<td>2.66</td>
</tr>
<tr>
<td>10% Cu-TiO$_2$</td>
<td>466.9</td>
<td>2.66</td>
</tr>
<tr>
<td>15% Cu-TiO$_2$</td>
<td>473.4</td>
<td>2.62</td>
</tr>
</tbody>
</table>
3.3.5 Phase Structural Analysis using XRD

Figure 3.7 shows the XRD patterns of the sol-gel prepared Cu-TiO$_2$ samples with different Cu contents (0 to 15 mol.%). The lattice planes (101), (103), (004), (200), (105), (211), (213), (116), (220), (107) and (303) correspond to 2θ values of 25.29°, 37.95°, 37.78°, 48.09°, 54.18°, 54.97°, 62.68°, 68.78°, 70.31°, 74.80°, and 82.75°, respectively. One rutile peak was observed in the prepared TiO$_2$ sample at 2θ = 27.51° corresponding to plane (110). All patterns were assigned to the tetragonal crystalline anatase phase structure of TiO$_2$ according to (JCPDS-21-1272) and tetragonal rutile phase structure of TiO$_2$ (JCPDS-02-0494). The presence of Cu prevented the formation of the rutile phase leading to a more reactive anatase phase. Most commercial titania powder catalysts are a mixture of rutile and anatase. For example, Degussa P25 contains approximately 80-90% anatase and the rest rutile. This makes the prepared TiO$_2$ more effective for photocatalytic applications.

In all Cu-doped samples, no significant diffraction peaks for Cu species were detected. This indicates that Cu is highly dispersed in the titania matrix. It also shows that the presence of Cu did not affect the crystalline structure of TiO$_2$. Also, the thermal pre-treatment procedure did not cause significant changes in the crystalline phase.

(a)
Figure 3.7: XRD patterns of (a) TiO$_2$, (b) 1.6 mol.% Cu-TiO$_2$, (c) 2 mol.% Cu-TiO$_2$, (d) 3.2 mol.% Cu-TiO$_2$, (e) 4.8 mol.% Cu-TiO$_2$, (f) 5 mol.% Cu-TiO$_2$, (g) 6.4 mol.% Cu-TiO$_2$, (h) 8 mol.% Cu-TiO$_2$, (i) 10 mol.% Cu-TiO$_2$ and (j) 15 mol.% Cu-TiO$_2$. 
3.3.6 Surface Morphology and Chemical Composition Analysis Using FESEM and EPMA

FESEM analysis of the photocatalysts shown in Figure 3.8 indicated that incorporation of Cu in TiO$_2$ can affect the surface morphology of the catalyst; however there is no significant effect on the aggregate sizes. The aggregate sizes of the catalysts were relatively uniform, ranging approximately from 40 nm to 52 nm. Highly agglomerated nanoparticles are detected with relatively uniform spherical aggregates shape. The EDS mapping demonstrates the presence of O, Ti and Cu in all Cu-TiO$_2$ nanoparticle samples. Also it shows that Cu is uniformly dispersed on the TiO$_2$ surface and further increase of Cu leads to the increase of the peak intensities of Cu, as illustrated in Figure 3.9. The Zn detected in Figure 3.9 (b) is mainly coming from the stub used, which can be neglected.
Figure 3.8: FESEM images of (a) TiO$_2$, (b) 4.8 mol.% Cu-TiO$_2$, (c) 5 mol.% Cu-TiO$_2$, (d) 6.4 mol.% Cu-TiO$_2$, (e) 8 mol.% Cu-TiO$_2$, (f) 10 mol.% Cu-TiO$_2$, and (g) 15 mol.% Cu-TiO$_2$. 
(b)
Figure 3.9: EDS mapping, spectra and elemental analysis showing the distribution of O, Cu & Ti on (a) TiO$_2$, (b) 4.8 mol.% Cu-TiO$_2$, (c) 5 mol.% Cu-TiO$_2$, (d) 6.4 mol.% Cu-TiO$_2$, (e) 8 mol.% Cu-TiO$_2$, (f) 10 mol.% Cu-TiO$_2$ and (g) 15 mol.% Cu-TiO$_2$. 

3.4 Conclusion

Ten samples of various Cu contents in Cu-TiO$_2$ nanoparticles have been prepared by the sol–gel method. Rheological analysis has been studied after the gelation process has been completed and a stable gel is obtained. The flow properties measurements were applied on sol–gel samples aged for 69 h. The sol–gel dispersion showed Newtonian behavior for all Cu content and non-Newtonian with time-dependent behavior for Cu content range of (0, 2, 5, 10, 15) mol.% The increase in the viscosity of sol–gel samples is due to the Cu concentration, reaching the maximum viscosity at 15 mol.% Cu content. Also, the increase of Cu content in the mixture results in a transition behavior from Newtonian to shear thinning behavior. High content of Cu contributed to significant yield stress. Further characterization was conducted after drying and calcining various contents of Cu-TiO$_2$ sol-gel. XRD analysis showed that most reactive phase of TiO$_2$ which is anatase TiO$_2$ phase existed in all samples with no rutile phase which is a less reactive phase except in pure TiO$_2$. This confirms that the presence of Cu prevented the formation of rutile which leads to more reactive nanoparticle. Moreover, the calcination temperature at 500°C was suitable for the samples because it did not cause significant changes or transformation in crystalline phase. The FESEM imaging for Cu-TiO$_2$ nanoparticles were relatively uniform spherical aggregates shape with a uniform size of approximately 40 - 52 nm and the presence of O, Ti and Cu were demonstrated by elemental analysis EDS/Mapping. The increase in Cu concentration showed a significant shifting from UV region to the visible region which makes it a promising material for different visible-light photocatalytic applications.
Chapter 4: Synthesis and Characterization of Cu-doped TiO$_2$ Thin Films Produced by the Inert Gas Condensation Technique

4.1 Introduction

Inert gas condensation (IGC) is one of the most widely used methods for synthesizing variety of materials in nanostructured form such as metals, alloys, compounds, semiconductors and ceramic materials. In this process, a metallic or inorganic material is vaporized using thermal evaporation sources, electron beam evaporation devices or sputtering sources in an inert atmosphere of argon or helium gas to synthesize nanoparticles with better control over size, distribution and purity$^{[113]}$. IGC has been the most popular since it can produce particles of well-defined grain size and with narrow size distribution.

Inert-gas condensation is a bottom-up approach to synthesizing nanostructured materials, which contains two basic steps. The first step is the evaporation of the material and the second step involves a rapid controlled condensation to produce the required particle size. The major technical difficulties to overcome in developing a successful bottom-up approach are (i) controlling the growth of the particles to retain the nanostructures and (ii) then stopping the newly formed particles from being agglomerated$^{[114]}$.

4.1.2 Thin Film Properties

The properties of the film in non-reactive sputter deposition depend greatly on the gas pressure, which identifies the thermalization of the reflected high energy neutrals and the sputtered species. The development of the columnar morphology, density, and residual film stress are affected by the energy of the species striking the surface of the growing film$^{[115]}$. 
4.1.3 Sputtering System

4.1.3.1 Vacuum

Vacuum deposition environment controls and monitors the contamination level and gaseous particle fluxes incident on a surface. The plasma deposition environment mainly composed of uncharged gaseous species providing ions that can be accelerated to high energies to allow concurrent energetic particle bombardment of the growing film to allow modification of the film properties\textsuperscript{[116]}.

4.1.3.2 Pressure

As discussed in section 4.1.2, the gas pressure may affect the sputter-deposited films properties. For example, the film stress can vary greatly with pressure. If the pressure is low, the deposited film can have a high compressive stress while, if the pressure is higher, the stress can be tensile. A systematic cycling of the pressure from a high to a low value during the deposition, controls the film stress. The thermalization of energetic particles in the system is determined by the pressure. Therefore, it is very important to have precise pressure measurements from run to run. Vacuum gauges depending on ionization are not useful in sputtering since many stray ions are present in the system\textsuperscript{[115]}.

4.1.3.3 Current and Voltage

Direct current power supplies should have an arc suppression circuit that reacts to a current surge or voltage drop. Arc suppression can be managed by shutting off the power or by providing a positive potential to counteract the arc\textsuperscript{[115]}.

4.1.4 Comparison between sol-gel and sputtering techniques

In comparison with the conventional wet processes (or liquid phase methods), sputter deposition have few advantages making it one of the most promising techniques for large-area uniform coatings (better film uniformity) with high packing density, strong
adhesion, higher deposition rate and better control of the film thickness\textsuperscript{[117,118]}. Many publications have reported the sputter deposition of TiO\textsubscript{2} and metal doped TiO\textsubscript{2} films. However, very few researches focused on studying the optical response of the sputter-deposited metal-doped TiO\textsubscript{2} thin films.

Liu et. al.\textsuperscript{[118]} fabricated TiO\textsubscript{2} films by direct current (DC) reactive magnetron sputtering on quartz glass substrates were annealed in several different ways. Then studied the effect of annealing on the ultraviolet–visible–near infrared (UV–vis–NIR) transmittance and correlate the spectroscopic phenomena with surface atomic character. The results were explained in terms of linear combination of atomic orbital-molecular orbital (LCAO-MO) and crystal-field (CF) model. It was concluded that the spectroscopic features result from the molecular orbital energy level ($t_{2g}^{-}-e_g^*$) electronic transition in the TiO\textsubscript{2} films. Further, Sheppard et al.\textsuperscript{[119]} reported the effect of niobium (Nb) on the structure of TiO\textsubscript{2} thin films deposited on glass substrates using the DC magnetron sputtering. It was indicated that in Nb concentration range between 0 and 40 at.%, Nb is incorporated into the TiO\textsubscript{2} lattice according to a substitution mechanism, entering Ti sites in the cation sub-lattice.

Eufinger et al.\textsuperscript{[120]} deposited TiO\textsubscript{2} thin films by the same technique\textsuperscript{[119]}. The sub-stoichiometric TiO\textsubscript{2-x} target was sputtered in pure argon (Ar) at different pressures to investigate the influence of the Ar pressure during deposition on the structural development during heat treatment. Moreover, the effect of the deposition conditions on the structural and photocatalytic properties of the thin films before and after heat treatment at different temperatures and the photocatalytic activity of the films was tested by measuring the decomposition rate of ethanol. It was concluded that a more open structure is beneficial for the photocatalytic activity of anatase TiO\textsubscript{2}. As a continuation to their work\textsuperscript{[121]}, Eufinger et al. used the same technique and target to study the effect of thickness as well as deposition conditions on the structural, optical and photocatalytic properties of the thin films. It was found that the photocatalytic activity was strongly dependent on the film thickness up to about 300–350 nm. For thicker films, only a very weak dependence was detected.
Furthermore, Yamagishi et al.\textsuperscript{[117]} deposited polycrystalline TiO$_2$ films by radio frequency (RF) magnetron sputtering under various total gas pressures to find the optimum conditions to deposit films with high photocatalytic activities. The photocatalytic activity showed a clear tendency to decrease with the decrease in total pressure during the deposition process.

Moreover, Pradhan et al.\textsuperscript{[122]} investigated the effects of total pressure and O$_2$/Ar flow ratio on the growth of rutile phase TiO$_2$ films crystallinity that have been prepared at low temperature ($\leq$100 °C) by a reactive RF magnetron sputtering method. They discussed the change in surface morphology and optical properties at different O$_2$/Ar flow ratios. It was found that the rutile phase crystallinity increased with decrease in total pressure and increase in O$_2$ flow and showed interesting optical characteristics such as high transmittance ($\sim$85%) and high refractive index ($\sim$2.7) with a band gap about 3.2 eV.

In addition, Hajjaji et al.\textsuperscript{[123]} investigated the effect of doping Cr$^{n+}$ at different contents on the photocatalytic activity of TiO$_2$ thin films deposited on quartz and intrinsic silicon substrates by using the RF magnetron co-sputtering process. The photocatalytic efficiency was studied using the amido black dye. The results indicated that films doped with 2% Cr exhibited the highest UV and visible light photocatalytic activity.

In this work, the inert gas condensation (IGC) was used to study the optical performance of Cu-doped TiO$_2$ thin films at various contents of Cu, where no similar research has been done before. All Cu-TiO$_2$ samples with various Cu contents were characterized using XRD, TEM, SEM/EDS, and UV-Vis spectrophotometer.

\subsection*{4.2 Materials and Research Methods}

\subsubsection*{4.2.1 Materials}

Argon gas (99.999\% purity) with a mass flow controller (MKS Instruments, Andover, MA1810, USA) in the range of 0.0–100.0 sccm has been used. Ti (99.9\% purity), and Cu-Ti alloys (with Cu contents of 1.6, 3.2, 4.8, 6.4, and 8 wt.\%) supplied by Testbourne
Ltd. (USA) with 50.8 mm diameter x 6.35 mm thickness have been used as sputtering targets.

4.2.2 Preparation of the Cu-TiO$_2$ thin films

An ultra-high vacuum (UHV) compatible system with a nanocluster source of magnetron plasma sputtering and inert gas aggregation condensation (Nanogen-50, Mantis Deposition Ltd., Oxfordshire, UK) was used to produce Cu-Ti nanoclusters with various Cu contents (1.6, 3.2, 4.8, 6.4, and 8 wt.%). A schematic diagram of the ultra-high vacuum compatible nanocluster system used in this work along with the nanocluster source is shown in Figure 4.1.

The sputtering procedure was prepared according to previous work$^{[124]}$, with some variation in parameters. The target was fixed on a magnetron a water-cooled sputter head located inside the nanocluster source, which uses a DC magnetron discharge. The system was initially pumped down to a base pressure of $\sim 10^{-7}$ mbar. The produced nanoclusters travel from the source chamber through a quadrupole mass filter (QMF) where the nanocluster size distribution is measured in situ inside the vacuum system. The resolution of the mass filter adjusted for mass scan by setting the U/V ratio at 0.1-0.12.

Finally, the nanoclusters form a nanocluster beam inside the main chamber are deposited on a quartz glass substrate mounted on a sample holder facing the nanocluster beam. The nanocluster deposition rate was detected by using quartz crystal monitor (QCM), where the QCM is fixed on a motorized linear translator that enables driving the QCM facing the nanocluster beam, and then driving it back away from the beam path.

Argon inert gas has been used to generate the plasma, sputter Ti and Ti-Cu, and to establish the inert gas condensation inside the source chamber. The aggregation length ($L$), which is the distance from the surface of the sputtering target to the source exit nozzle, was controlled by a motorized linear translator that drives the sputter head by up to 100 mm without venting the source chamber. The current ($I$) was fixed to values that enhances the nanoclusters production and deposition rate.
4.2.3 Characterization of the Cu-TiO₂ Thin Films

4.2.3.1 X-ray diffraction (XRD)

The X-ray diffraction patterns of the nanocluster-based thin film samples have been obtained using Shimadzu 6100 X-ray Diffractometer with Ni and Cu-Kα radiation ($\lambda = 0.15406$ nm).

4.2.3.2 Transmission electron microscopy (TEM)

The TEM images have been obtained using a Philips CM10 transmission electron microscope. These images were used to measure the nanocluster size distribution and compared them with the nanocluster size distribution produced by the QMF.
4.2.3.3 Scanning electron microscopy (SEM)

A scanning electron microscope (variable pressure Tescan VEGA XM SEM) has been used to examine the surface morphology of the samples. Substrates with thin films of nanoclusters at various Cu contents were mounted on the SEM stub using a double-sided carbon adhesive tape. The mounted samples were then coated by gold /palladium (80% & 20%) at a thickness of ~ 10 nm using a sputter coating system (Quorum Technology Mini Sputter Coater, SC7620) in order to avoid the charging effect. Thin film surface was imaged at the maximum accelerating voltage = 25 kV and 30 kV to obtain high resolution images at (29.1, 45, 47, 60, 84, and 88.6) kx magnifications.

4.2.3.4 Energy Dispersive Spectrometer (EDS)

Qualitative and quantitative chemical composition measurements for the thin film samples have been made using energy dispersive spectrometer (Oxford Instruments X-Max 50 EDS detector (LN2 free system)) with 125 eV resolution. Moreover, the same detector was used to obtain the distribution of elements over selected areas on the samples.

4.2.3.5 UV-visible absorption spectrometry (UV-vis)

The UV–visible absorption spectra for the Cu-TiO₂ thin films have been obtained using UV-Vis/NIR spectrophotometer (JASCO 670) in the wavelength range of 200 to 3200 nm (0.39 to 6.2 eV photon energy).

4.3 Results and Discussion

4.3.1 Crystalline structure using XRD

XRD analysis showed that the as-deposited films are amorphous, where no diffraction peaks were observed. Thin films were then annealed at a temperature of 400°C for 1 h. Crystallinity also has a relation with peak intensity. Higher crystallinity result in higher peak intensity. It is expected that the TiO₂ films with a thickness of 100 nm and below
have a larger structural disorder than the thicker TiO$_2$ films because they grow directly on amorphous glass substrates.

**Figure 4.2** illustrates the XRD patterns of the annealed Cu-doped TiO$_2$ and undoped TiO$_2$ nanoparticles based thin films. The patterns clearly show peaks of anatase and rutile TiO$_2$ for the prepared TiO$_2$ and all Cu-doped TiO$_2$ thin films, the lattice planes of rutile phase (110), (111), (201), (211), (220) at 2θ values 27.4°, 41.1°, 44°, 54.3° and 56.5°. While the lattice planes of anatase phase (101), (200), (204), (116), (301), (206) at 2θ values 25.3°, 48.0°, 51.8°, 62.7°, 68.8°, 76.0°, 78.7°, respectively. For different contents of Cu-doped samples, no Cu, Cu$_2$O or CuO were observed. The formation of rutile phase could be due to higher concentration of the ionized or excited species resulting from the higher electron temperature in the plasma, or due to higher energy of the particles impinging on the growing film surface$^{[117]}$. Also on the XRD spectra, the strange peak at 2θ = 22° is not related to anatase phase nor rutile phase of the TiO$_2$ thin films. It could be due to instrument error. However, anatase mainly appears at 2θ = 25.3° and rutile at 2θ = 27.4°.
Figure 4.2: XRD patterns of (a) TiO$_2$, (b) 1.6 wt.% Cu-TiO$_2$, (c) 3.2 wt.% Cu-TiO$_2$, (d) 4.8 wt.% Cu-TiO$_2$, (e) 6.4 wt.% Cu-TiO$_2$, and (f) 8 wt.% Cu-TiO$_2$. 
4.3.2 Nanocluster size distribution, surface morphology, chemical composition and elemental analysis

Figure 4.3 illustrates the TEM image and QMF of pure Ti nanoclusters produced using Ar flow rate, \( f_{\text{Ar}} \) = 50 sccm, aggregation length, \( L \) = 70 mm, and sputtering discharge power, \( P \) = 49 W. This analysis is conducted to check the performance of the QMF used to measure the nanocluster size distribution. In order to get a reasonable comparison, the TEM image and the QMF were analysed by controlling the same source parameters. The TEM image in Figure 4.3(a) demonstrates the presence of individual clusters, aggregates and islands of TiO\(_2\) with irregular shapes. The nanocluster size distributions produced by QMF and TEM image are shown in Figure 4.3 (b), which indicate that the nanocluster size distribution trends are very close in range and at the same time demonstrates the effectiveness of using QMF source in studying the size of nanoclusters.

On Figure 4.3 (b), “I (nA)” and “Number” represent the frequency (nA = nano Ampere) and the number of the produced nanoclusters, respectively.

Figure 4.3: (a) TEM image of pure Ti nanoclusters, and (b) nanocluster size distribution as measured by QMF (solid line) and TEM image (open symbols)\(^{[124]}\).
Size distribution of Ti-Cu nanoclusters with different Cu contents (1.6, 3.2, 4.8, 6.4, and 8) wt.% measured using the quadrupole mass filter is shown in Figure 4.4. The nanoclusters were produced using Ar flow rate, $f_{\text{Ar}} = 35$ sccm, chamber pressure, $P_c = 3.37 \times 10^{-4}$ mbar, $U/V = 0.12$, $L = 90$ mm and $I = 200$ mA. The nanoclusters have a size distribution within the range of 5.4 to 7.1 nm. As observed in Figure 4.4, the intensity of the size distributions at various Cu contents is very low due to the small production yield of nanoclusters.

The parameters that have great influence on nanocluster size are the inert gas flow, $f_{\text{Ar}}$, and the aggregation length, $L$. In a previous work on pure Ti \cite{124}, we found that the changes in the inert gas flow and aggregation length affect the nanocluster size and yield (area under the nanocluster size distribution curve). The average nanoclusters size and yield were found mainly to decrease with the increase of the inert gas flow rate. Moreover, the nanoclusters average size is directly proportional to the aggregation length. On the other hand, the yield is inversely proportional to the aggregation length \cite{124}.

Furthermore, the collision probability plays an important role in controlling the clusters nucleation and growth. The collision probability is detected by the pressure inside the aggregation chamber and by the clusters’ residence time inside the cluster source, as reported by Manninen, et. al. \cite{126}. Therefore, as the inert gas (Ar) flow rate increases, the clusters will be removed faster, thus their residence time in the aggregation chamber will be reduced. Thus when the interaction between the inert gas and the clusters and metal atoms is reduced, it promotes a decrease in the clusters size \cite{126}. Moreover, the amount of clusters and aggregates increase with the increase of the deposition time of the Cu-Ti target alloy.
Figure 4.4: The size distribution of Ti-Cu nanoclusters with different Cu contents produced using $I = 200 \text{ mA}$, $f_{Ar} = 35 \text{sccm}$, $L = 70 \text{ mm}$ and $U/V = 0.12$.

SEM analyses have been conducted to observe the morphology of the Cu-TiO$_2$ thin films samples of various Cu contents. As seen in Figure 4.5, the shape of nanoparticles is almost spherical and, thin films are porous with some agglomeration. Figure 4.6 illustrates the EDS analyses for pure TiO$_2$ and 8 wt.% Cu-TiO$_2$ samples. For both samples, Ti, O, Si, and C were detected. Si shows the highest peak which is referred to the substrate (quartz glass). The appearance of C peak is due to the stub used. Both Si and C peaks were ignored in analysis.

However, the presence of O reveals that the samples are completely oxidized as soon as they are exposed to air (at room temperature). The samples have dark brown colour when prepared. However, after exposing them to air for ~24 h, they start to become transparent with a pale yellow reflection, which insures that the nanoparticles have been
oxidised. Thin films have very strong cohesive and adhesive strength, thus they cannot be wiped out even during sample handling. This makes the prepared films very useful in photocatalytic applications in which they can be used repeatedly for several times compared to the coated samples in the sol-gel method, which can be used only once. In Figure 4.6(b), only a very small amount of Cu has been detected; this could be due to its low concentration in the sample (1.6 wt.% Cu-Ti).

(a)
Figure 4.5: SEM images of (a) pure TiO$_2$, (b) 1.6 wt.% Cu-TiO$_2$, (c) 3.2 wt.% Cu-TiO$_2$, (d) 4.8 wt.% Cu-TiO$_2$, (e) 6.4 wt.% Cu-TiO$_2$, (f) 8 wt.% Cu-TiO$_2$. 
Figure 4.6: EDS analyses for (a) pure TiO$_2$ and (b) 8 wt.% Cu-TiO$_2$. 
4.3.3 Optical Analysis by UV-Vis Spectrophotometer

Figure 4.7 shows the optical absorption measurements of the Cu-TiO$_2$ nanoparticles based thin films of various Cu contents (wt.%). Pure TiO$_2$ reveals absorption at 389 nm, which lies in the range of the UV region. Introducing Cu dopant with (1.6, 3.2, 4.8, 6.0, and 8.0 wt.) resulted in shifting the absorption to the visible region. Absorption spectrum shifts up to 485 nm for the 8 wt.% Cu content, which indicates the improvement of the optical activity of the Cu-TiO$_2$ nanoparticles based thin films. The calculated band gap energy for pure TiO$_2$ and various Cu contents in Cu-TiO$_2$ thin films are presented in Table 4.1. The band gap energy varies between 3.19 eV (0.0 wt.% Cu or pure TiO$_2$) and 2.56 eV (8.0 wt.% Cu), as shown in Figure 4.8. This evolution could be linked to the presence of acceptor states in the band gap$^{[123]}$. As discussed earlier, transition metals narrow the electronic properties and alter the optical responses of TiO$_2$, causing a decrease in the band gap energy and resulting in a wide range absorber of visible light, which can be more effectively used in photocatalytic applications.
Figure 4.7: UV-Vis absorption spectra of Cu-TiO$_2$ thin films at various Cu contents (wt.%).

Table 4.1: Wavelength and band-gap of TiO$_2$ and various contents of Cu-doped TiO$_2$.

<table>
<thead>
<tr>
<th>Cu-TiO$_2$ (wt.%)</th>
<th>Wavelength (nm)</th>
<th>Band gap (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0</td>
<td>389</td>
<td>3.19</td>
</tr>
<tr>
<td>1.6</td>
<td>400</td>
<td>3.10</td>
</tr>
<tr>
<td>3.2</td>
<td>415</td>
<td>2.99</td>
</tr>
<tr>
<td>4.8</td>
<td>431</td>
<td>2.88</td>
</tr>
<tr>
<td>6.4</td>
<td>460</td>
<td>2.70</td>
</tr>
<tr>
<td>8.0</td>
<td>485</td>
<td>2.56</td>
</tr>
</tbody>
</table>
Figure 4.8: Effect of Cu wt.% on the band gap energy.

4.4 Conclusions

The inert gas condensation (IGC) technique was used in this work to prepare thin films of Cu-TiO$_2$ nanoparticles with various Cu contents (1.6, 3.2, 4.8, 6.0, and 8.0 wt.%). XRD analysis showed mixed phases of rutile and anatase TiO$_2$. SEM analysis showed homogeneous nanocluster films with almost spherical nanoclusters. EDS analysis insured the presence of Ti, O and Cu in the Cu-TiO$_2$ thin film samples. UV-Visible absorption spectra indicated that the presence of Cu in the Cu-TiO$_2$ thin film samples had shifted the light absorbance to the visible region. Increasing Cu content decreased the band gap energy form 3.19 eV (0.0 wt.% Cu or pureTiO$_2$) to 2.56 eV (8.0 wt.% Cu). The Cu-doped TiO$_2$ thin films produced by sputtering are expected to have high activities when used in photocatalytic applications.
**Recommendations**

- Test the photocatalytic activity of the prepared samples on some photocatalytic application.

- Make a comparative study between Cu-doped and Ag-doped TiO$_2$ by preparing them under the same conditions and applying both to the same photocatalytic application.

- Investigate the performance of the thin film catalyst prepared by the IGC sputtering technique in photocatalytic applications.

- Characterize the textural of the thin films catalyst prepared by the IGC sputtering technique, which could not be performed here due to the unavailability of the instrument.

- Analyze the photocatalyst samples by using X-ray photoelectron spectroscopy (XPS) to study the valence state of the metal dopant.
Chapter 1:


[42] Song, S., Jun, B., Chen, G., Jianjun, D., Photocatalytic degradation of gaseous o-xylene over M-TiO$_2$ (M=Ag, Fe, Cu, Co) in different humidity levels under visible-light irradiation: Activity and kinetic study, RARE METALS 30 (2011) 147.


Chapter 2:


**Chapter 3:**


Chapter 4:


List of Publications