



Faculty of Resource Science & Technology

**The Development of Ternary $\text{TiO}_2/\text{ZnS}/\text{g-C}_3\text{N}_4$ Photocatalyst with
Enhanced Photodegradation of Organic Pollutants Under Visible Light**

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DECLARATION

I declare that the work in this thesis was carried out in accordance with the regulations of Universiti Malaysia Sarawak. Except where due acknowledgements have been made, the work is that of the author alone. The thesis has not been accepted for any degree and is not concurrently submitted in candidature of any other degree.



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ABSTRACT

The photocatalytic degradation efficiency of titanium, TiO₂-based photocatalysts is limited, especially under visible light. To enhance their efficiency, ternary composites can be created by combining TiO₂ with other photocatalysts which are graphitic nitride (g-C₃N₄) and zinc sulphide (ZnS). To investigate the photocatalytic efficiency for the degradation of single and mixed pollutants under visible light, a ternary TiO₂/ZnS/g-C₃N₄ photocatalyst was synthesised using a facile hydrothermal method. Various characterisation techniques were employed to evaluate the surface area, morphology, crystallinity, and optical and elemental properties via x-ray diffraction (XRD), fourier transform infrared spectroscopy (FTIR), field emission scanning electron microscopy with energy-dispersive x-ray spectroscopy (FESEM-EDX), transmission electron microscopy (TEM), Brunauer-Emmett-Teller (BET), and ultraviolet-visible diffuse reflectance spectroscopy (UV-DRS), respectively. The optimal g-C₃N₄ loading in the TiO₂/ZnS/g-C₃N₄ ratio was determined through several ratios (1:1:X), where X represents different quantities of g-C₃N₄ (in g): X = 0.3, 0.5, 0.7, 1, and 2. The highest removal rate of 89.9% of Rhodamine B, RhB was achieved using g-C₃N₄ loading of 1 g, resulting in a TiO₂/ZnS/g-C₃N₄ ratio of 1:1:1. The synthesised ternary TiO₂/ZnS/g-C₃N₄ (1:1:1) photocatalyst exhibited enhanced absorption in the visible light region compared to the pristine TiO₂. Under visible light exposure, the ternary photocatalyst efficiently removed approximately 90% of RhB (10 mg/L) within 180 minutes. Moreover, in the presence of mixed pollutants, the ternary photocatalyst simultaneously eliminated 82.7% of RhB, 78.2% of methyl orange (MeO), and 62.2% of 2-chlorophenol (2CP) within a similar treatment time. Further investigations determined an optimal dosage of 1 g/L for the 1:1:1 ratio ternary TiO₂/ZnS/g-C₃N₄ composite. Additionally, the optimal initial RhB concentration for achieving maximum efficiency was found to be 10 mg/L. In the case of the

effect of pH study, the highest RhB degradation efficiency (89.9%) was observed at an unadjusted pH of 7.2, followed by pH 10 (85.4%) and pH 7.0 (82.5%), while the lowest degradation was observed at pH 3 (72.4%). After four cycles of recycling, a slight decrease in RhB degradation from 89.9% to 86.6% was observed, indicating improved stability and recycling capabilities of the ternary photocatalyst. The successful synthesis and application of the ternary $\text{TiO}_2/\text{ZnS}/\text{g-C}_3\text{N}_4$ photocatalyst, along with its efficient degradation of both individual and mixed pollutants, demonstrate its significant potential for sustainable wastewater treatment.

Keywords: Photocatalytic activity, optical absorption, organic pollutants, charge separation, ternary composite, $\text{g-C}_3\text{N}_4$, photodegradation

**Pembangunan Fotokatalis Ternari $\text{TiO}_2/\text{ZnS}/\text{g-C}_3\text{N}_4$ untuk Mempertingkatkan
Fotodegradasi Pencemar Organik Menggunakan Cahaya Nampak**

ABSTRAK

Prestasi fotokatalis titanium dioksida, TiO_2 dalam penguraian fotokatalisis pencemar adalah terhad, terutamanya di bawah cahaya nampak. Untuk meningkatkan kecekapannya, komposit ternari boleh disintesis dengan menggabungkan TiO_2 dengan fotokatalis lain seperti zink sulfida, ZnS dan grafitik karbon nitrida, $\text{g-C}_3\text{N}_4$. Untuk mengkaji kecekapan fotokatalis ternari iaitu $\text{TiO}_2/\text{ZnS}/\text{g-C}_3\text{N}_4$ dalam penguraian pencemar tunggal dan campuran di bawah cahaya nampak, kaedah hidrotermal telah digunakan untuk mensintesis fotokatalis tersebut. Pelbagai teknik pencirian telah digunakan untuk menyokong aktiviti fotokatalisisnya, termasuk sifat permukaan dan optik seperti difraksi sinar-x (XRD), spektroskopi inframerah transformasi fourier (FTIR), mikroskopi elektron penyinaran medan dengan spektroskopi tenaga-difraksi sinar-x (FESEM-EDX), mikroskopi elektron transmisi (TEM), brunauer-emmett-teller (BET) dan spektroskopi ultraungu pantulan resapan (UV-DRS). Jumlah optimal $\text{g-C}_3\text{N}_4$ yang diperlukan untuk menghasilkan $\text{TiO}_2/\text{ZnS}/\text{g-C}_3\text{N}_4$ ditentukan melalui beberapa nisbah (1:1:X), di mana X mewakili kuantiti $\text{g-C}_3\text{N}_4$ yang berbeza (dalam g): $X = 0.3, 0.5, 0.7, 1$, dan 2 . Kadar fotodegradasi RhB tertinggi dicapai pada jumlah $\text{g-C}_3\text{N}_4$ ialah 1 g , menghasilkan nisbah $\text{TiO}_2/\text{ZnS}/\text{g-C}_3\text{N}_4$ sebanyak $1:1:1$. Fotokatalis ternari $\text{TiO}_2/\text{ZnS}/\text{g-C}_3\text{N}_4$ yang disintesis menunjukkan penyerapan yang lebih baik di bawah cahaya nampak berbanding dengan TiO_2 asli. Di bawah pendedahan cahaya nampak, fotokatalis ini menyingkirkan kira-kira 89.9% RhB pada kepekatan 10 mg/L dalam masa 180 minit. Apabila bahan pencemar wujud dalam bentuk campuran, fotokatalis ini secara serentak dapat menyingkirkan 82.7% RhB, 78.2% methyl jingga (MeO), dan 62.2% 2-klorofenol (2CP) dalam jangka masa rawatan yang

sama. Seterusnya, jumlah optimal untuk komposit ternari nisbah 1:1:1 $\text{TiO}_2/\text{ZnS}/\text{g-C}_3\text{N}_4$ adalah 1 g/L. Tambahan pula, kepekatan RhB awal yang optimal untuk mencapai kecekapan maksimum ialah 10 mg/L. Dalam kajian pH, kecekapan penguraian RhB tertinggi (89.9%) diperolehi pada pH tanpa penyesuaian iaitu pH 7.2, diikuti oleh pH 10 (85.4%) dan pH 7.0 (82.5%), manakala penguraian terendah diperolehi pada pH 3 (72.4%). Terdapat sedikit penurunan dalam degradasi RhB daripada 89.9% kepada 86.6% selepas empat kitaran kitar semula fotokatalis. Hasil ini menunjukkan bahawa fotokatalis ternari ini mempunyai kestabilan dan kebolehan mengitar semula yang lebih baik, menjadikannya calon yang sesuai untuk aplikasi praktikal. Kebolehan sintesis dan aplikasi fotokatalis ternari $\text{TiO}_2/\text{ZnS}/\text{g-C}_3\text{N}_4$, bersama dengan penguraian yang efisien terhadap pencemar individu dan campuran, menunjukkan kebolehan yang ketara untuk rawatan air sisa yang mampan.

Kata kunci: Aktiviti fotokatalisis, penyerapan optik, pencemar organik, pemisahan cas, komposit ternari, $\text{g-C}_3\text{N}_4$, fotodegradasi

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LIST OF ABBREVIATIONS

AOP	Advanced oxidation processes
BiVO ₄	Bismuth vanadate
BET	Brunauer–Emmett–Teller
COFs	Covalent organic frameworks
EDX	Energy-dispersive X-ray
FESEM	Field Emission Scanning Electron Microscope
FTIR	Fourier transform infrared spectroscopy
g	grams
g-C ₃ N ₄	Graphitic carbon
G	Graphene
GO	Graphene oxide
Fe ₂ O ₃	Iron oxide
MOFs	Metal-organic frameworks
MeO	Methyl orange
Mo	Molybdenum
OPs	Organic Pollutants
pzc	Point zero charge
rGO	Reduced graphene oxide
RhB	Rhodamine B
ROS	Reactive oxygen species
TEM	Transmission electron microscopy
TiO ₂	Titanium oxide
UV-DRS	UV–Vis diffuse reflectance spectroscopy

H ₂ O	Water
XRD	X-ray diffractometry analysis
ZnO	Zinc oxide
ZnS	Zinc sulphide
2CP	2-Chlorophenol

CHAPTER 1

INTRODUCTION

1.1 Study Background

As urban development and population growth continue to accelerate, the scarcity of clean water affects a staggering 7.7 billion people worldwide. This situation is now precarious, and projections suggest that over the next decade, it will only worsen (Boretti & Rosa, 2019). The United Nations World Water Development Report of 2018 estimates that by 2050, around 6 billion people will be facing water scarcity (WWAP, 2018). The discharge of harmful organic pollutants (OPs) by industries such as textiles, pharmaceuticals, pesticides, and herbicides significantly exacerbated the problem OPs, which include phenolic compounds and dye molecules, pose a threat to both the aquatic ecosystem and human health. While conventional treatment methods like adsorption using activated carbon, coagulation, and membrane filtration are often used to treat wastewater (Ahmed, 2016), the removal efficiency is up to 70-80% and produces secondary pollutants that require additional treatment, adding to the cost (Adnan et al., 2020). Therefore, it is critical to develop an effective, low-cost operation method to remove organic contaminants from wastewater.

Advanced oxidation processes (AOPs) offer a promising solution for the treatment of wastewater, and among the available AOPs, semiconductor photocatalysis is a particularly safe, eco-friendly, and cost-effective option (Ameta & Ameta, 2018). In contrast to conventional methods which produce secondary pollutants and necessitate additional post-treatment steps, thus escalating the economic burden and adding complexity to the wastewater treatment process, AOPs stand out as a superior solution for wastewater treatment. AOP treatment proves more effective in wastewater treatment when compared to

traditional methods. For example, this approach has been reported to effectively break down > 85% of OPs in wastewater into harmless substances like water and carbon dioxide via mineralization (Mittal et al., 2019; Kale et al., 2020). Photocatalysts, which can be made of metals, non-metals, or carbonaceous materials, play a crucial role in this process. An ideal photocatalyst should be non-toxic, chemically stable, have good photo carrier separation efficiency and utilise a broad light absorption spectrum (Zhu & Zhou, 2019).

Titanium dioxide (TiO₂) has emerged as a highly potential semiconductor due to its excellent photostability, high photocatalytic activity, non-toxicity, and cost-effectiveness (Guo et al., 2019). Nevertheless, there are limitations associated with pristine TiO₂ that require attention. The large band gap of TiO₂ nanoparticle (3.2 eV for anatase) restricts the photocatalytic activity only under UV light region (Yan et al., 2013). Furthermore, the high recombination rate of electron-hole pairs decreases its overall quantum efficiency (Qian et al., 2019). Another limitation is the inherent instability of the produced nanoparticles often leads to the aggregation of pristine TiO₂ nanoparticles, resulting in the formation of suspension (Romanello & Fidalgo de Cortalezzi, 2013). This could block the active sites on the TiO₂ surface from absorbing photon energy thus reducing the photodegradation rate. Hence, modifications become necessary to extend its application, enhance the photoefficiency and increase the production of reactive oxygen species (ROS).

This study attempted to prepare a new ternary TiO₂/ZnS/g-C₃N₄ photocatalyst to overcome the limitations of TiO₂. ZnS has been chosen due to various reasons. ZnS, a metal sulfide with a wide band gap of 3.6 eV, is a highly promising photocatalyst due to its remarkable attributes such as quantum confinement effect, efficient electron mobility, high thermal stability, low recombination rate of photon carriers, and non-toxicity (Zhang et al.,

2013; Ayodhya & Veerabhadram, 2018). Studies have reported that the coupling of TiO₂ and ZnS enhanced the photocatalytic efficiency rate by increasing ROS production (Talebi et al., 2017; Sivaranjani et al., 2022).

Despite their advantages, TiO₂/ZnS binary photocatalysts also have some limitations. These include difficulties in efficient charge transfer and their reliance on UV light activation for effective photodegradation of OPs. Consequently, researchers are currently directing their efforts towards the development of TiO₂/ZnS-based ternary photocatalysts (Danish et al., 2020; Liu et al., 2022). Ternary photocatalyst could demonstrate enhanced spectral responsiveness to utilize a larger wavelength region ($\lambda > 400$ nm) due to the synergistic effects of the narrow band gaps, which could simultaneously reduce the recombination of electron-hole pairs (Zheng et al., 2020). The ternary photocatalysts were fabricated by modifying TiO₂/ZnS binary composite and embedding co-catalysts like metals, metal oxides, and metal sulphides (Kanakaraju & Chandrasekaran, 2023). However, incorporating metals, metal oxides, and metal sulphides into TiO₂/ZnS photocatalysts can be costly, and the synthesis process demands sophisticated machinery, making such alterations impractical and uneconomical (Al Jitan et al., 2020).

As a result, the modification of TiO₂/ZnS binary photocatalysts with carbonaceous materials can be considered. Carbon can function as a sensitizer to sensitize TiO₂ under light irradiation, linking many thermal energies and facilitating charge transfer to create a large number of active species (Mittal et al., 2019). The advantages of carbon doping include its metallic conductivity, acting as a trapping center and transit channel for photogenerated electrons and boosting the dispersion of photogenerated charge carrier pairs (Khalid et al., 2017). This study introduces graphitic carbon nitride (g-C₃N₄), a visible-light-driven

photocatalyst with a narrow band gap. g-C₃N₄ is known as a metal-free conductor that has good chemical stability, high surface area, and an appealing electrical structure with a low band gap of 2.7 eV (Inagaki et al., 2019; Ismael, 2020). The addition of g-C₃N₄ to TiO₂ has been reported to reduce the band gap, improve charge separation, decrease electron-hole recombination, and enhance photocatalytic activity (Wu et al., 2017; Girish et al., 2022). Therefore, this study fills the existing knowledge gap by synthesising and characterising the TiO₂/ZnS/g-C₃N₄ photocatalyst for the degradation of OPs under visible light irradiation, providing valuable insights for environmental remediation applications.

1.2 Problem Statement

TiO₂ is a photocatalyst that possesses a large band gap, is inefficient in the exploitation of visible light, and is only limited to ultraviolet light. The inherent instability of TiO₂ often leads to the aggregation of TiO₂ nanoparticles and the formation of suspensions. The aggregation of active sites on the TiO₂ surface results in a hindrance to the absorption of photon energy, leading to a reduction in the photodegradation rate of pollutants in wastewater. Previous research has demonstrated that the combination of TiO₂/ZnS photocatalysts in a binary system has effectively enhanced the photoefficiency of the resulting materials. However, these binary photocatalysts encounter limitations, such as challenges in charge transfer and their dependence on UV light (400 nm) for the photodegradation of OPs (Velásquez-Torres et al., 2022). To address these limitations, great efforts are being devoted towards developing TiO₂/ZnS-based ternary photocatalysts. These ternary photocatalysts offer a lower band gap energy compared to their binary counterparts, enabling the photodegradation of OPs under longer-wavelength light sources ($\lambda > 400$ nm) and effectively preventing the recombination of electron-hole pairs. In previous studies, researchers explored various methods, such as doping these ternary photocatalysts with

metals, metal oxides, and metal sulphides, to enhance their photodegradation efficiency for individual pollutants (Mittal et al., 2019; Danish et al., 2020; Liu et al., 2022). Nevertheless, most TiO_2/ZnS -based ternary photocatalysts studies have been only tested on the degradation of single pollutants. Furthermore, modified TiO_2/ZnS with metal oxides and metal sulphides are not suitable for application in wastewater treatment plants due to the risk of photocorrosion, contamination, and metal leaching (Liu et al., 2015). Therefore, the modification of carbonaceous material on the binary TiO_2/ZnS photocatalyst should be considered. Among various carbonaceous materials, $\text{g-C}_3\text{N}_4$, a metal-free conductor, is highly preferred due to its narrow band gap (~ 2.7 eV), making it responsive to visible light (Inagaki et al., 2019). The addition of carbon material to the binary TiO_2/ZnS photocatalyst can serve as a trapping centre and transit channel for photogenerated electrons, enhancing the dispersion of photogenerated charge carrier pairs (Ismael, 2020). However, there are currently no established studies examining the application of ternary $\text{TiO}_2/\text{ZnS}/\text{g-C}_3\text{N}_4$ for the simultaneous degradation of both individual and mixed OPs under visible light.

1.3 Research questions

The research questions of this study are:

- i. How does the introduction of $\text{g-C}_3\text{N}_4$ as a carbonaceous material modify the photodegradation efficiency of TiO_2 and ZnS photocatalyst in the degradation of a single pollutant, RhB dye?
- ii. What is the influence of synthesis on the structural and morphological properties of the ternary $\text{TiO}_2/\text{ZnS}/\text{g-C}_3\text{N}_4$ photocatalyst, as determined by x-ray diffraction (XRD), fourier transform infrared spectroscopy (FTIR), field emission scanning electron microscopy with energy-dispersive x-ray spectroscopy (FESEM-EDX), transmission electron microscopy (TEM),

Brunauer-Emmett-Teller (BET), and ultraviolet-visible diffuse reflectance spectroscopy (UV-DRS) techniques?,

- iii. How do the operational parameters namely catalyst dosage (0.3-2.0 g/L), initial dye concentration (10-25 mg/L), and initial pHs (pH 3-10) and the presence of multipollutant, including RhB, methyl orange (MeO), and 2-chlorophenol (2CP) affect the photocatalytic performance of ternary $\text{TiO}_2/\text{ZnS}/\text{g-C}_3\text{N}_4$ photocatalyst in degrading single pollutant, RhB dye?,
- iv. How does the ternary $\text{TiO}_2/\text{ZnS}/\text{g-C}_3\text{N}_4$ photocatalyst perform in the presence of multiple pollutants, such as RhB, methyl orange (MeO), and 2-chlorophenol (2CP)? and
- v. What are the main driving active species and potential photocatalytic mechanisms of the ternary $\text{TiO}_2/\text{ZnS}/\text{g-C}_3\text{N}_4$ photocatalyst in the degradation of RhB dye?

1.4 Objectives

The objectives of this study are to:

- i. investigate the modification of ternary $\text{TiO}_2/\text{ZnS}/\text{g-C}_3\text{N}_4$ photocatalyst via a hydrothermal route in the degradation of a single pollutant, RhB dye,
- ii. to analyse crystallinity, functional groups, morphological, structural, specific surface area and band gap of the ternary $\text{TiO}_2/\text{ZnS}/\text{g-C}_3\text{N}_4$ photocatalyst using techniques such as XRD, FTIR, FESEM-EDX, TEM, BET, and UV-DRS, respectively,
- iii. to investigate the influence of catalyst dosage (0.3 g/L to 2.0 g/L), initial dye concentration (10 mg/L to 25 mg/L), initial pH levels (pH 3 to pH 10), and

the presence of multipollutant, including RhB, methyl orange (MeO), and 2-chlorophenol (2CP) on the photocatalytic degradation of RhB dye,

- iv. evaluate the performance of the ternary photocatalyst in the presence of multipollutant, including RhB, methyl orange (MeO), and 2-chlorophenol (2CP), and
- v. determine the main active species and elucidate the potential photocatalytic mechanisms involved in the degradation of RhB dye using the ternary $\text{TiO}_2/\text{ZnS}/\text{g-C}_3\text{N}_4$ photocatalyst through radical scavengers study.

CHAPTER 2

LITERATURE REVIEW

2.1 Photocatalysis

Photocatalysis is the acceleration of photoreaction in the presence of a catalyst and is an example of the advanced oxidation processes (AOP) (Som et al., 2020). Photocatalytic reactions are widely utilised in a variety of applications such as water splitting for hydrogen production (Tahir et al., 2020), dye degradation (Anwer et al., 2019), and CO₂ reduction (Nahar et al., 2017). It can be initiated by photocatalysts or semiconducting materials such as titanium dioxide (TiO₂), zinc oxide (ZnO), molybdenum (Mo), zinc sulfide (ZnS), bismuth vanadate (BiVO₄), iron oxide (Fe₂O₃) and graphitic carbon nitride (g-C₃N₄).

The photocatalytic process occurs when the band gap energy of a photocatalyst matches the energy of the incident light which would then generate electron-hole pairs which would subsequently participate in various chemical reactions, such as oxidation and reduction, to transform organic and inorganic compounds into non-harmful byproducts. Figure 2.1 shows the band gap energy of different photocatalysts. The band gap energy is crucial as it determines the wavelengths of light that a photocatalyst can effectively absorb (Abdullah et al., 2017). Photons with energy equal to or greater than the band gap energy can be absorbed by photocatalysts, promoting electrons from the valence band to the conduction band. This absorption of light energy is the initial step in generating electron-hole pairs that are essential for driving photocatalytic reactions.

The photocatalytic process starts when photon energy (visible light or UV radiation) is absorbed by the surface of the photocatalyst till reaches or exceeds the band gap energy

(Eg) (Figure 2.2). It is driven by various reactive oxygen species (ROS) such as $\bullet\text{OH}$, (hydroxyl radical), h^+ (hole) and $\bullet\text{O}_2^-$ (superoxide radical). It has been well-documented that the superior performance of a photocatalytic process is driven by the high oxidation potential of ROS. Among various ROS, superoxide ($\bullet\text{O}_2^-$) possessed the highest oxidation potential value of 2.7 eV followed by hydroxyl ($\bullet\text{OH}$) radicals which is 2.3 eV. These ROS are recognised as strong radicals that could degrade pollutants from wastewater (Maarisetty et al., 2020)

The series of reaction mechanisms involved in the photocatalytic processes are summarized below. When the photocatalyst's surface is stimulated by light energy, electrons excite and move from the valence band to the empty conduction band (Kale et al., 2020; Liu et al., 2022). This would produce the electron-hole pair, electron (e^-) and hole (h^+) pair on the surface of the photocatalyst used. The positive hole on the valence band (h_{VB}^+) and electron on the conduction band (e_{CB}^-) molecules can subsequently travel to the photocatalyst semiconductor's surface and undergo a redox reaction (Eq. 1.1). Considering that electron-hole recombination could happen when the positive hole in the valence band reintegrates with the excited electron in the conduction band simultaneously could be evaporated as heat (Eq. 1.2). As a result, it will reduce the photocatalytic activity for the degradation of pollutants. So, the presence of oxygen as electron scavengers slows the recombination, while developing superoxide anion radicals ($\bullet\text{O}_2^-$). The photogenerated electrons may react with oxygen in the wastewater containing pollutants to produce superoxide anion radical ($\bullet\text{O}_2^-$) (Eq. 1.3). Simultaneously, the $\bullet\text{OH}$ radical is formed when the hole combines with the H_2O . Meanwhile, photogenerated holes (h^+) could react with the hydroxide ion to form strong oxidants ($\bullet\text{OH}$) (Eq. 1.4). These ROS ($\bullet\text{O}_2^-$ and $\bullet\text{OH}$) play a major role in oxidising the pollutants present on the surface. As a result, reduction-oxidation (redox reaction) could

work against recombination processes for efficient photodegradation, which is vital for treating wastewater containing pollutants (Eq. 1.5-1.7).

Photoexcitation:



Electron hole-recombination:



Production of superoxide anion radical:



Production of hydroxyl radical:



Degradation processes:



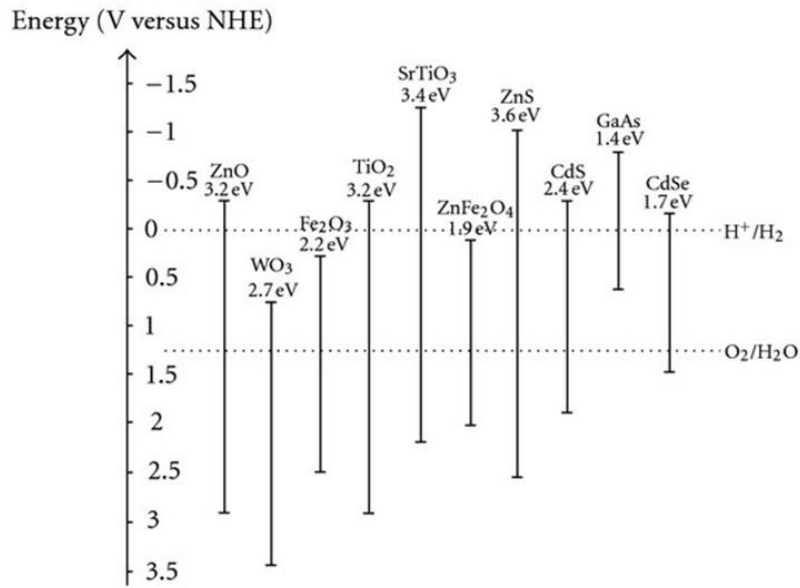


Figure 2.1: The bandgap energy of various photocatalysts. (Zhang et al., 2012)

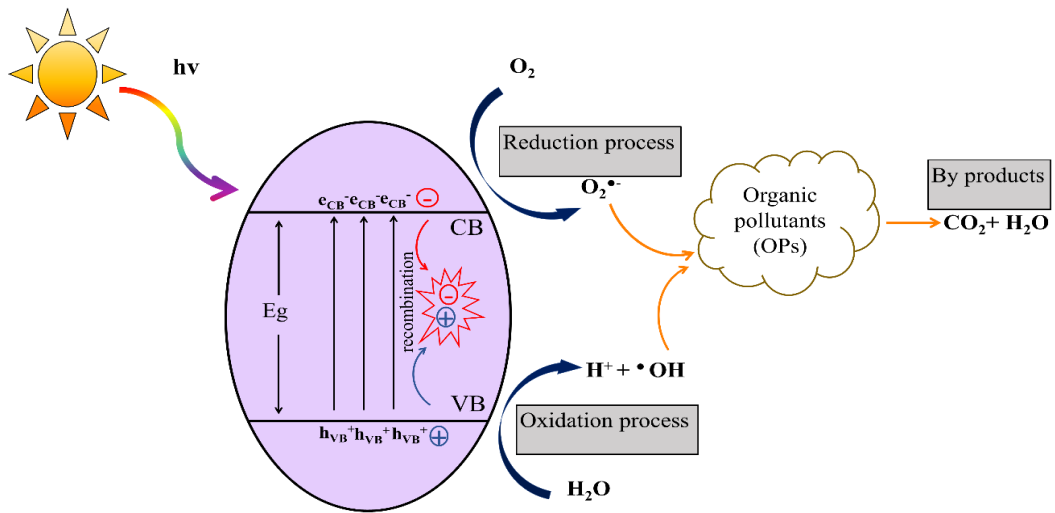


Figure 2.2. Mechanism of photocatalytic activity on degradation of pollutants (Kanakaraju & Chandrasekaran, 2023)

2.2 Titanium dioxide (TiO₂) photocatalyst crystalline structures

Generally, TiO₂ photocatalyst has three crystal structures which are anatase, rutile and brookite (Tay et al., 2013). Figure 2.3 shows the crystalline structures of TiO₂. The band

gap energy of anatase is 3.2 eV, while that of rutile is 3.02 eV and 2.96 eV for brookite (Wunderlich et al., 2004). The rutile structure of TiO_2 is highly stable, but anatase and brookite are both considered metastable. In addition, the lower band gap should theoretically allow rutile to harvest more energy from longer wave radiation.

It was discovered that different TiO_2 structures show different photocatalytic performances (Zhang et al., 2014). Although rutile TiO_2 is more stable, anatase has a stronger photocatalytic activity than other forms of TiO_2 due to its high surface area, wide band gap, and greater porosity (Praveen et al., 2014). Anatase TiO_2 shows superior performance of photocatalytic activity over rutile TiO_2 due to its energetic separation capacity between the valence and conduction band upon irradiation of UV (Allen et al., 2018). Additionally, the chemical properties of the anatase TiO_2 , including high electron mobility, low dielectric constant, and low density, further support its preference as a photocatalyst in photocatalytic activity (Yamakata & Vequizo, 2019).

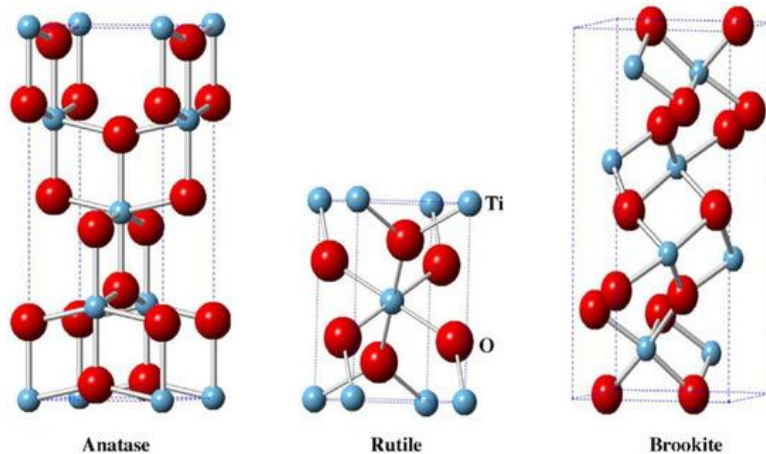


Figure 2.3: The crystalline structures of TiO_2 (Etacheri et al., 2015)

2.2.1 TiO_2 as a photocatalyst

Titanium dioxide (TiO_2) can be referred to as titanium (IV) or titania. TiO_2 has been considered one of the most promising photocatalysts due to its excellent photocatalytic efficiency, physiochemical stability and non-toxicity and its remarkable excitation state whereby the activation of photons with light energy is larger than the band gap energy (Adnan et al., 2020). It is popular in various applications such as water treatment (Mohadesi et al. (2022)), water splitting (Eidsvag et al., 2021), air purification (Mamaghani et al., 2020), and dye-sensitised solar cells for energy generation (Huang et al., 2020). Nevertheless, TiO_2 has a large band gap of 3.2 eV and it restricts the absorption to UV light, making it ineffective for the exploitation of visible light (Ozturk & Soylu, 2016). Other deficiencies of TiO_2 that need to be resolved include agglomeration because of its nanosized particles, quick recombination of electron-hole pairs, and the tendency to form suspension during treatment. Thus far, various attempts have been made to get beyond the constraints of pristine TiO_2 to improve their photocatalytic performances by surface defects, loading of cocatalysts and band gap engineering (Gupta & Chauhan, 2021; Li et al., 2022; Liu et al., 2022).

One of the approaches to overcome the limits of pristine TiO_2 is modifying the surface of the photocatalyst by introducing dopants or functional groups to enhance the photocatalytic activity (Al-Mamun et al., 2019). Various combinations of TiO_2 are available in the literature. For example, TiO_2/ZnS (Prasannalakshmi & Shanmugam, 2017), TiO_2/CdS (Zhao & Yang, 2016), TiO_2/ZnO (Qin et al., 2019) and TiO_2/WO_3 (Zhang et al., 2017). These studies have demonstrated that coupling TiO_2 with another semiconductor(s) suppresses electron-hole recombination and produces materials with a smaller band gap and increases the photoefficiency of the materials (Wu et al., 2017). Also, coupling of TiO_2 with more than one semiconductor such as TiO_2 -based heterojunctions has paved the way for the

growth of materials with unique chemical and physical properties and a wide range of photocatalytic applications (Khalid et al., 2020; Ferreira et al., 2021; Mousavi et al., 2021).

Another strategy is to fabricate composite photocatalysts by combining two or more materials to enhance their photocatalytic properties. For example, researchers have developed new materials such as metal-organic frameworks (MOFs) and covalent organic frameworks (COFs) as potential visible-light responsive photocatalysts (Lee et al., 2019). These materials have tuneable structures and band gap energies, allowing them to absorb visible light and initiate chemical reactions.

2.3 Zinc Sulfide semiconductor

Apart from TiO_2 photocatalyst, zinc sulphide (ZnS) is also considered as one of the promising semiconductors. ZnS is an II-VI group semiconductor material that has good properties such as non-toxic, high stability, high electron stability which exhibits rapid generation of photo-excited electron-hole pairs and highly negative potentials of excited electrons. It has recently been comprehensively studied for its high potential for applications such as optical coating (Nayak & Choudhary, 2019), dye decolorization (Rajabi & Farsi, 2015), removal of heavy metal (Qin et al., 2020), solar cell (Salih et al., 2017) and biosensor (Mostafa et al., 2021). ZnS also has a band gap energy of 3.72 eV (for cubic zinc blende) and 3.77 eV (for hexagonal wurtzite) (Fang et al., 2011; Sharifi et al., 2019) and can be used as a semiconductor photocatalyst to treat wastewater and degrade OPs under UV irradiation. However, the large band gap limits the photoactivity only under UV light and ZnS also suffers from rapid recombination of electron hole that reduces the photoactivity. Therefore, it is necessary to consider coupling ZnS with another semiconductor to overcome these limitations and enhance the resulting materials' photoefficiency. The coupling of ZnS with

other semiconductors for example, ZnS/SnO₂ (Hojamberdiev et al., 2020), ZnS/BiOBr (Yan et al., 2020), CuS/ZnS (Varghese, 2021) and ZnS/CdS (Guo et al., 2021) reduces the recombination rate of electron-hole pairs and enhances the photocatalytic activity.

The incorporation of ZnS on TiO₂ has also been reported as another modification that has been giving remarkable results. This binary material is superior compared to single photocatalysts because they can alter band bending at interfaces and offer a driving force for carrier separation, thus reducing the rate of charge carrier recombination (Zheng et al., 2020). Rahmawati et al. (2015) claimed that ZnS serve as electron sinks when electrons are excited in the conduction band of TiO₂. Other than that, ZnS reduces the likelihood of electron-hole recombination because of the charge transfer of electrons. Additionally, the quantum confinement properties of the binary TiO₂/ZnS composite can aid in the degradation of organic contaminants (Wang & Zhang, 2014) and increase the electron density in ZnS which will result in a wider range of light absorption (Sharma et al., 2021). To conclude, the coupling strategy of ZnS and other semiconductors reduces the band gap, enhances photogenerated electron-hole pair recombination, and allows photon absorption over a broad range of wavelengths (Lee & Wu, 2017).

2.4 Carbonaceous material as photocatalyst dopant

Carbonaceous materials have received significant attention for their potential as modifiers or dopants in photocatalysts due to their non-toxic nature, sustainability, exceptional photostability, and inherent photoluminescence capabilities (Mei et al., 2022). Graphene (G), graphene oxide (GO), reduced graphene oxide (rGO), graphitic carbon nitride (g-C₃N₄), carbon nanodots, carbon quantum dots, activated carbon and C60 fullerenes are a

few examples of the many carbonaceous materials that exist. These materials offer unique properties and functionalities that can enhance the performance of photocatalytic systems.

One notable advantage of incorporating carbonaceous materials as dopants is their metallic conductance. This feature enables them to serve as electron traps and transit channels, facilitating the efficient dispersion of charge carrier pairs generated by photons (Purabgola et al., 2022). This characteristic contributes to improved charge separation and promotes enhanced photocatalytic activity.

Moreover, carbonaceous materials can reduce the band gap of semiconductors, which is particularly advantageous in visible light photocatalysis. Table 2.1 shows the reduction of the band gap after the addition of carbonaceous materials to various semiconductors. By reducing the band gap, these materials extend the absorption range of photocatalysts into the visible light region, thereby enhancing their utilization of solar energy for catalytic reactions. For example, TiO₂ doped with rGO reduced the band gap from 3.08 eV to 2.62 eV and extends the photocatalytic activity under visible light irradiation (Ruidíaz-Martínez et al., 2020).

Table 2.1: Selected studies on the reduced band gap after the addition of carbonaceous material

Semiconductor	Carbonaceous material used	Band gap (before) (eV)	Band gap (after) (eV)	References
TiO ₂	g-C ₃ N ₄	3.08	2.62	(Li et al., 2016a)
	rGO	3.20	2.75	(Ruidíaz-Martínez et al., 2020)
ZnO	GO	2.92	2.71	(Puneetha et al., 2021)
	g-C ₃ N ₄	3.14	2.70	(Manimozhi et al., 2021)

WO ₃	G	2.58	2.23	(Gan et al., 2016)
Fe ₂ O ₃	rGO	1.98	1.85	(Mohan et al., 2019)

2.5 Graphitic carbon nitride

A polymeric graphitic carbon nitride (g-C₃N₄) is also known as a metal-free conductor (Mamba & Mishra, 2016). The heptazine ring structure and high condensation degree allows the metal-free g-C₃N₄ to have good chemical stability, high surface area, and an appealing electrical structure with a low band gap of 2.7 eV (Zhao et al., 2015). As a result, the properties of g-C₃N₄ lead to a visible light-driven photocatalyst for photocatalytic applications utilising longer wave radiation ($\lambda > 400$ nm) (Liao et al., 2019). g-C₃N₄, a carbon-based material has been extensively applied in many applications such as environmental (Hao et al., 2020), biomedical (Liao et al., 2020), optoelectronic (Bian et al., 2016) and energy storage (Zhao et al., 2020).

g-C₃N₄ is highly preferred compared to other carbonaceous materials due to its narrow band gap (~2.7 eV), which makes it highly responsive to visible light contrary to GO with a larger band gap of 3.0-3.5 eV. Other carbonaceous materials, for example, graphene and activated carbon, have low degradation rates due to their low charge mobility and inefficient electron transfer (Khalid et al., 2017; Ge et al., 2019; Zhang et al., 2022). On the other hand, g-C₃N₄ has high stability and can withstand high temperatures which makes it an excellent candidate for the use of photocatalytic degradation. It also possesses high charge mobility which exhibits high photocatalytic activity. This is due to its unique electronic structure, which enables it to efficiently generate electron-hole pairs and facilitate redox reactions.

Many precursors can be used to synthesize g-C₃N₄ by pyrolysis method such as cyanamide (Kim et al., 2018), melamine (Bellardita et al., 2018), thiourea (Hua et al., 2019), and urea (Kim et al., 2018). Figure 2.4 shows the illustration using different precursors to synthesize g-C₃N₄. Among all the precursors used to synthesize g-C₃N₄, urea is a low-cost and widely available precursor, making it a more economically viable option and having a higher nitrogen content (Mun & Park, 2019). Therefore, the use of urea as a precursor for synthesising g-C₃N₄ offers a cost-effective and efficient approach to producing high-quality carbon materials.

The temperature used to synthesize g-C₃N₄ plays a crucial role in determining the properties and quality of the resulting material (Paul et al., 2019). Typically, the synthesis process involves heating the precursor used at a high temperature in an inert atmosphere, which leads to its decomposition and subsequent carbonization. The temperature range used for the synthesis process ranges between 500°C and 800°C, with the optimum temperature depending on several factors such as the precursor type, reaction time, and heating rate (Qi et al., 2020). At lower temperatures, incomplete carbonization can result in the formation of amorphous carbon, while higher temperatures can lead to the formation of graphite. Therefore, the temperature used for synthesising graphitic carbon nitride from urea needs to be carefully optimised to achieve the desired properties and quality of the resulting material.

However, pristine g-C₃N₄ has poor electrical characteristics, including a high rate of electron and hole recombination, low product yield and low visible light utilization efficiency (Li et al., 2016b; Ye et al., 2015). Combination of g-C₃N₄ with other semiconductors, for example, ZnO/g-C₃N₄ (Bhosale et al., 2023), g-C₃N₄/TiO₂/GO (Lin et al., 2018) and Ag/g-C₃N₄ (Nagajyothi et al., 2017) could reduce the electron-hole

recombination, enhance the visible light efficiency and improve the photoactivity of g-C₃N₄ (Zhu et al., 2018).

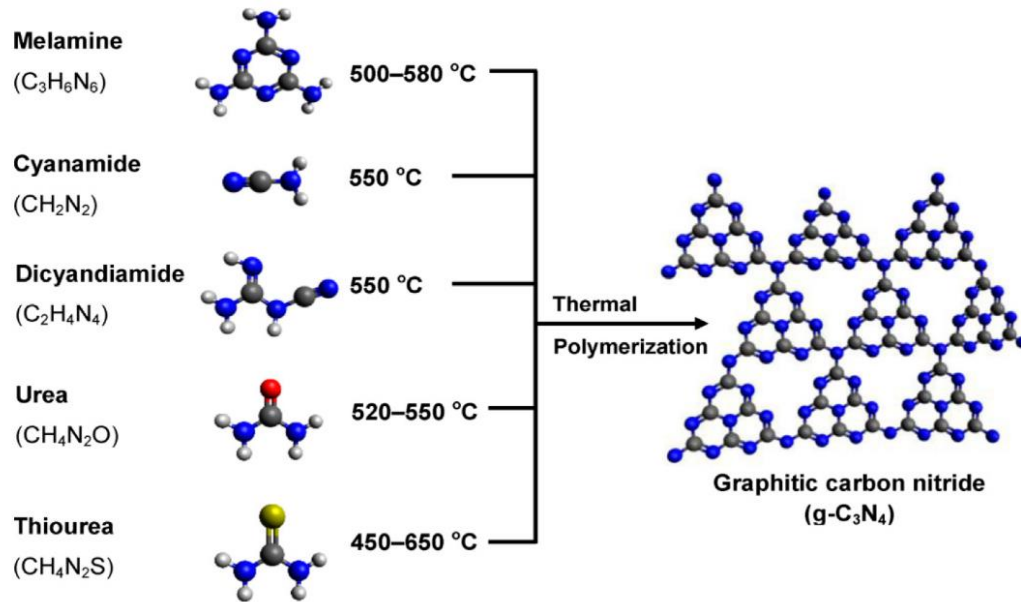


Figure 2.4: Illustration of the process of synthesising g-C₃N₄ from various precursors (Mun & Park, 2019)

2.6 Ternary photocatalyst nanocomposite

2.6.1 Ternary photocatalyst

Recently, the application of ternary photocatalyst systems has become popular in environmental applications as a result of the drawbacks displayed by both single and binary photocatalysts. Single and binary photocatalyst systems possess numerous limitations such as (1) high recombination rate of electron-hole, (2) low separated charge carriers, (3) less stability and (4) large band gap causing a poor response in the visible range (Kanakaraju & Chandrasekaran, 2023). A ternary photocatalyst refers to a type of photocatalyst that is composed of three different semiconductors (Kausar et al., 2022). The modification involving the design of a ternary nanocomposite system, achieved by incorporating

additional photocatalysts may offer a solution to the limitations of single and binary photocatalyst systems (Prasad et al., 2019). This is because ternary photocatalysts could reduce the rate of charge carrier recombination, ease the transfer of the separated charge to enhance photocatalytic activity, improve the stability of nanocomposite, lower the band gap which could extend its application under longer wavelengths and have great potential to be applied in environmental remediation and renewable energy production (Mittal et al., 2019; Qin et al., 2019; Liu et al., 2022).

Table 2.2 shows the list of ternary photocatalysts which have been applied for the degradation of various pollutants. Based on Table 2.2, ternary nanocomposites that utilize a wavelength of ≤ 400 nm (UV light irradiation) demonstrated good photodegradation performance with $> 88\%$ removal efficiency. Comparatively, ternary nanocomposites also displayed good photocatalytic performance under visible light with $> 90\%$ removal efficiency (Mittal et al., 2019; Qin et al., 2019; Danish et al., 2020; Liu et al., 2022; Saeidapour et al., 2022). Despite almost similar performances, visible light-responsive ternary nanocomposites would offer a more practical solution compared to the UV light-responsive counterparts as solar energy and visible-type light sources could be applied in the treatment process. As such, the development of new ternary nanocomposites with new structural and optical properties could find ways for pollutant remediation, particularly in treating a wide spectrum of pollutants.

Table 2.2: Selected TiO₂-based ternary nanocomposites and their degradation efficiency of various pollutants

Ternary nanocomposite	Pollutants	Removal efficiency (%)	Light source, wavelength (nm)	References
TiO ₂ /ZnS-CdS	Methylene blue	88.0	UV light, < 365	(Mumin et al., 2015)
TiO ₂ /ZnS-Cu	Salicylic acid	90.0	UV light, 365	(Labiadh et al., 2014)
TiO ₂ /ZnO-g-C ₃ N ₄	Methylene blue	94.6	UV light, 300–400	(Saeidpour et al., 2022)
TiO ₂ /ZnS-Fe	Paracetamol	94.0	UV light, 300–400	(Danish et al., 2020)
TiO ₂ /ZnS@ZnO	Tetracycline hydrochloride	86.7	Visible light, 420	(Liu et al., 2022)
TiO ₂ /ZnS/rGO	Methylene blue	90.0	Visible light, > 420	(Qin et al., 2019)

2.6.2 TiO₂/ZnS-based ternary photocatalysts

TiO₂/ZnS-based ternary photocatalysts with modified intrinsic characteristics are being engineered with a great deal of scientific attention to overcome the drawbacks of their single and binary counterparts. With the aim to further improve the physio-chemical properties of the TiO₂/ZnS-based ternary photocatalysts, various modifications have been attempted. Such modifications include the inclusion of carbonaceous materials (non-metal) (Kale et al., 2020), metal oxides (Liu et al., 2022) and metal sulfides (Xu et al., 2021). Liu et al. (2015) reported the modification of binary TiO₂/ZnS using a metal sulphide, indium (III) sulfide (In₂S₃). The modification resulted in the enhanced photocatalytic degradation of

RhB azo dye from 27.2% for bare TiO₂ to 93.8% under the visible light region within 80 mins under visible irradiation (Figure 2.5a). This is due to the large specific surface area of 57.7 m²g⁻¹ in contrast to bare TiO₂, which has a specific surface area of 51.7 m²g⁻¹. The ternary TiO₂/ZnS/In₂S₃ photocatalyst also reduced the large band gap of TiO₂ (3.43 eV) to 2.76 eV (Figure 2.5b) hence extending the photocatalytic activity under visible light. Therefore, the modification of In₂S₃ on the binary TiO₂/ZnS resulted in a ternary TiO₂/ZnS/In₂S₃ photocatalyst which is highly responsive to visible light and possesses excellent charge carrier separation. Modification of binary TiO₂/ZnS with metal oxides like ZnO could result in materials with intriguing properties including exceptionally high specific surface area through relatively inexpensive synthesis pathways (Harish et al., 2017; Talebi et al., 2017). For instance, the addition of ZnO to TiO₂/ZnS greatly boosted the specific surface area of the ternary compound, TiO₂/ZnS@ZnO to 73.328 m²g⁻¹ compared to that of the pure TiO₂ with 39.540 m²g⁻¹ (Liu et al., 2022). Accordingly, the degradation of tetracycline hydrochloride using ternary TiO₂/ZnS@ZnO under visible irradiation resulted in 86.67% removal within an hour contrary to only 26.25% using pure TiO₂ due to the greater specific surface area and more reactive sites in the former (Figure 2.5c). Therefore, the modification of ZnO on the binary TiO₂/ZnS resulted in a ternary TiO₂/ZnS@ZnO photocatalyst which is highly responsive to visible light and possesses excellent charge carrier separation.

The addition of metals, metal oxides, and metal sulfides comes at a considerable expense, and the chemical synthesis process necessitates the use of more advanced machinery or equipment. As a result, implementing such modifications is neither practical nor cost-effective. (Al Jitan et al., 2020). In addition, it is not recommended to utilize the modified TiO₂/ZnS with metal oxides and metal sulfides in wastewater treatment plants for

producing clean water. The main reason for this caution is the possibility of encountering issues such as photocorrosion, contamination, and the leaching of metals (Liu et al., 2015). So, an alternative approach, modifications with carbonaceous materials should be considered. Currently, there is a lack of extensive research on incorporating carbonaceous material into TiO_2/ZnS binary photocatalysts for the degradation of various organic pollutants (OPs). Hence, this study aims to address this knowledge gap by synthesising and characterising the $\text{TiO}_2/\text{ZnS}/\text{g-C}_3\text{N}_4$ photocatalyst. The purpose is to assess its effectiveness in degrading OPs under visible light irradiation, thereby offering valuable insights for potential applications in environmental remediation.

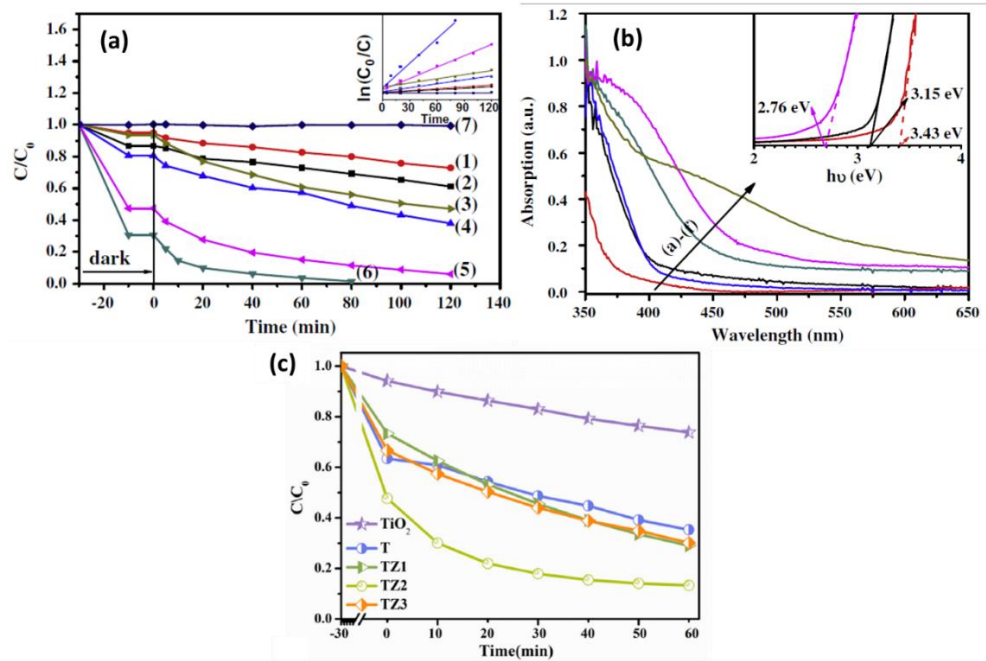


Figure 2.5: (a) photocatalytic degradation of ternary $\text{TiO}_2/\text{ZnS}/\text{In}_2\text{S}_3$ on Rhodamine B (b) UV-vis diffuse reflectance spectra of TiO_2 , binary TiO_2/ZnS and ternary $\text{TiO}_2/\text{ZnS}/\text{In}_2\text{S}_3$ and (c) photocatalytic degradation of ternary $\text{TiO}_2/\text{ZnS}@\text{ZnO}$ on tetracycline hydrochloride (Liu et al., 2015; Liu et al., 2022)

2.7 Synthesis methods of TiO₂/ZnS-based ternary photocatalysts

Numerous methods have been applied as strategies for the synthesis of many ternary nanocomposites including TiO₂/ZnS/g-C₃N₄ such as the hydrothermal method (Liu et al., 2015; Mittal et al., 2019), solvothermal method (Nuengmatcha et al., 2016; Maarisetty et al., 2020), sol-gel method (Dong et al., 2014; Park et al., 2014), chemical precipitation method (Danish et al., 2020), calcination method (Wang et al., 2019) and immobilization method (Du et al., 2014; Jbeli et al., 2018).

These approaches are frequently used to modify ternary nanocomposites for various reasons. The sol-gel method, for example, is environmentally friendly, requires neither complex and difficult synthesis conditions nor equipment, and therefore is generally regarded to be a cost-efficient technique. Aside from that, adopting this process allows for greater control over product consistency and purity, increased stability for the composite, and flexibility to add dopants in any quantity with either high or low concentrations (Ummartyotin & Infahsaeng, 2016). Many studies have reported the synthesis of ternary photocatalysts via the sol-gel method (Table 2.3). According to Kong et al. (2017), bare CuInS₂/ZnS-TiO₂ lost around 35% of its initial efficiency due to photocorrosion and weight loss, whereas CuInS₂/ZnS-TiO₂ fabricated via the sol-gel process maintained about 90% of its composite performance throughout the recyclability test. The sol-gel approach applied for the synthesis of ternary photocatalysts significantly improved the stability and photocatalyst recycling, making it a promising option for practical application.

Besides that, Maarisetty et al. (2020) synthesised TiO₂/ZnS/rGO using the one-pot solvothermal method in N, N-dimethylformamide (DMF) as a solvent. Graphene oxide (GO) undergoes reduction to produce rGO. However, the removal of oxygen molecules from the

surface causes vacancies and reduces charge transfer on the surface of the compound. As a result, DMF, a reducing agent, is often chosen as a solvent to provide excellent defect density control, as it outperforms conventional chemical reduction approaches (Jiang et al., 2011). In a manner similar to this, Qin et al. (2019) also produced $\text{TiO}_2/\text{ZnS}/\text{rGO}$ through a solvothermal method; however, their preferred solvent was ethylene glycol. Ethylene glycol helps in producing homogeneous and smooth graphene sheets which allow for the deposition of TiO_2 and ZnS. A 3.7-fold increase in methylene blue elimination over binary ZnS/rGO was achieved (Qin et al., 2019).

Apart from the solvent system, the solvothermal approach is nearly identical to the hydrothermal technique. The solvothermal technique utilises organic solvents, whereas the hydrothermal method uses water as a reaction system. Both solvothermal and hydrothermal methods influence the morphology, shape, crystalline size, and shape distribution of ternary photocatalysts nanocomposite. The hydrothermal approach used for the fabrication of $\text{ZnS}/\text{CdS}/\text{TiO}_2$ at 180°C produced nanoparticles that resulted in more active sites to expedite degradation (Mittal et al., 2019). Consequently, more than 99% of RhB dye removal was obtained. A bush-like $\text{ZnS}-\text{In}_2\text{S}_3$ solid that was deposited on the surface of TiO_2 nanofibers was synthesised via the hydrothermal method (Liu et al., 2015). A total of 98% removal efficiency of RhB was attained after three successive cycles. It was indicated that the photocatalysts had no residual RhB dye after the recycling procedure. The hydrothermal approach successfully produced a highly stable ternary $\text{TiO}_2/\text{ZnS}-\text{In}_2\text{S}_3$ photocatalyst that would make it feasible for practical applications.

Additionally, the chemical precipitation approach produces almost no impurities that could interfere with the treatment and affect the compound's crystallinity, making it one of

the best techniques to fabricate TiO₂/ZnS-based composite. Danish et al. (2020) synthesised Fe@ZnSQDs/TiO₂ via chemical precipitation which produced both anatase and rutile phase TiO₂. The presence of Fe@ZnSQDs did not affect the TiO₂ crystal structure which was confirmed by the X-ray diffractometry (XRD) analysis. In a separate study, TiO₂/ZnSQDs/CdS synthesised by Mumin et al. (2015) via the chemical precipitation method observed 90% removal of methylene blue under solar light after two consecutive cycles. The great recycling ability and high stability were attributed to the core-shell in ZnSQDs coupled with TiO₂. The core-shell in ZnSQDs was also implicated in a significantly reduced rate of electron-hole recombination. The photogenerated electrons are transmitted to the covalent band of TiO₂, which results in a larger concentration of electrons because its covalent band is more positive than this ideal covalent band of the core-shell ZnSQDs. Since the ideal valance band of ZnSQDs is more cathodic when compared to TiO₂, the holes created on this valence band would not move to the valence band of TiO₂ (Chang et al., 2014). Dissolved oxygen molecules were scavenged by the electrons deposited at the covalent band of TiO₂ to form ROS. As such, the band edge of the fabricated photocatalyst is important for ROS generation.

Each approach has its own merits and demerits. For instance, the hydrothermal approach, which commonly uses water in its reaction system is relatively inexpensive but time-consuming. This method is highly favoured as it produces photocatalysts with superior properties for the degradation of pollutants. Chemical precipitation appears to be one of the least preferred processes because it typically involves the use of harsh chemicals and can result in low purity and poor control over the composition and morphology of the resulting ternary photocatalysts. However, this procedure is relatively a simple and straightforward method to synthesize ternary photocatalysts. Hence, it can be concluded that the synthesis

method and conditions applied are critical in determining the physical and electronic characteristics of ternary photocatalyst nanocomposites.

Table 2.3: Commonly used methods for the synthesis of ternary TiO₂/ZnS-based composite

Type of photocatalyst	Characterization [BET, TEM, morphology (SEM/FESEM)]	Organic pollutant	Removal efficiency (%)	Recyclability efficiency (cycles)	Light source / wavelength	Reference(s)
Hydrothermal						
TiO ₂ /ZnS/In ₂ S ₃	BET: 57.7 m ² g ⁻¹ , TEM: 200 nm, Morphology: Bush-like ZnS–In ₂ S ₃ solid deposited on the surface of TiO ₂ nanofibers	Rhodamine B	~100	98% removal of RhB after 3 cycles	380 < λ < 700 nm	Liu et al., (2015)
TiO ₂ /ZnS/CdS	BET: 62.896 m ² g ⁻¹ , TEM: 10 nm, Morphology: CdS and ZnS particles deposited on uniform-size TiO ₂ nanoparticles	Methylene blue	88	N/A	380 < λ < 700 nm	Mittal et al., (2019)
Sol-gel						
TiO ₂ /ZnS-graphene	BET: 13.288 m ² g ⁻¹ , TEM: 20 nm, Morphology: Homogeneous and uniform distribution of TiO ₂ and ZnS on the graphene-like sheets	Methylene blue	90.1	N/A	380 < λ < 700 nm	Park et al., (2014)

Table 2.3 continued

Solvothermal						
TiO ₂ /ZnS/GO	BET: 440.67 m ² g ⁻¹ , TEM: 2 nm, Morphology: TiO ₂ and ZnS uniformly deposited graphene sheets	Methylene blue	100	>80% removal of methylene blue after 4 cycles	Solar sunlight	Maarisetty et al., (2020)
TiO ₂ /ZnS-rGO	Morphology: TiO ₂ and ZnS dispersed on smooth-like and homogeneous graphene	Methylene blue	90	N/A	380 < λ < 700 nm	Qin et al., (2019)
TiO ₂ /ZnO/GO	Morphology: Round-shaped TiO ₂ and triangle-shaped ZnO on flaky graphene sheets	Rhodamine B	92.52	82.70% removal after 4 cycles	380 < λ < 700 nm	Nuengmatcha et al., (2016)
Calcination						
TiO ₂ /ZnS@ZnO	BET: 73.328 m ² g ⁻¹ , Morphology: Hollow tube of PAN coated with TiO ₂ and ZnS	Tetracycline hydrochloride	86.67	77.24% removal of tetracycline hydrochloride after 5 cycles	380 < λ < 700 nm	Liu et al., (2022)
TiO ₂ /ZnS-chitosan	TEM: 20–30 nm, Morphology: TiO ₂ and ZnS entrapped in chitosan thin film	Methyl orange	93.5	85.2% removal MeO after 5 cycles	Solar sunlight	Du et al., (2014)

Table 2.3 continued

Immobilization						
TiO ₂ /ZnS-chitosan	Morphology: TiO ₂ and rod shaped ZnS in thin chitosan film	Toluidine	88	N/A	380 < λ < 700 nm	Jbeli et al., (2018)
TiO ₂ /ZnS/Fe	Morphology: Spherical-shaped ZnSQDS with non-uniform Fe and TiO ₂ distribution	Paracetamol	94	N/A	380 < λ < 700 nm	Danish et al., (2020)
Chemical precipitation						
TiO ₂ /ZnS-CdS	TEM: 50nm, Morphology: Rough surface wire-like shaped	Methylene blue	88	90% removal of methylene blue after 2 cycles under solar light	100 < λ < 400 nm	Mumin et al., (2015)
TiO ₂ /ZnS-bromothymol blue (BTB)	Morphology: Non-uniform and aggregated	para-nitrophenol	95	N/A	380 < λ < 700 nm	Pouretedal et al., (2016)

2.8 Organic Pollutants in Wastewater

Effluents contain both organic and inorganic pollutants in the form of suspensions, particulates, or dissolved materials. Examples of OPs are solvents, pesticides, dyes, and phenolic compounds. The biochemical oxygen demand and chemical oxygen demand are the two indicators that are most frequently used to estimate the number of organic contaminants in wastewater (Fernandes et al., 2020). Since OPs are hazardous to marine life, human beings and the environment when exposed at levels above the threshold, the degradation of the pollutants is very necessary. Additionally, the existence of organic contaminants is unavoidable because they are byproducts of daily used items, including plastics, insecticides, dyes, detergents, and pharmaceutical compounds. Wastewater can be treated using various methods such as the AOPs (Pandis et al., 2022), filtration (Porter & Porter, 1995), precipitation, and adsorption (Awad et al., 2019).

2.9 Dyes

Synthetic dyes have gained popularity in various manufacturing industries due to their versatility, vibrant colors, and cost-effectiveness. Annually, these industries collectively produce nearly 800,000 tons of synthetic dyes worldwide. The textile, paper production, agriculture, medicine, leather, and beauty product sectors all benefit from the use of synthetic dyes. In the textile industry alone, over 10,000 different types of dyes are employed, with azo dyes being particularly prevalent. Azo dyes are known for their complex chemical structure and account for approximately 70% of all synthetic dyes used in textiles (Carmen & Daniela, 2012). However, not all dyes used in the dyeing process become permanently adsorbed onto the textiles. While some dyes remain on the textiles, others may wash out during subsequent washings (Hassaan et al., 2017). During the manufacturing and processing of synthetic dyes, around 12% of these dyes find their way into the environment

through accidental spillage or outflow. Additionally, approximately 20% of synthetic dyes are discharged into the environment through industrial wastewater (Patwardhan, 2017).

The removal of dyes from wastewater is a complex task, especially using primary treatments such as filtration (Porter & Porter, 1995), chlorination (Yuan et al., 2012), coagulation (Lau et al., 2015) and absorption (Yan et al., 2016). These primary treatments convert the dyes from colored liquid to colorless liquid and merely transform the liquid phase to solid form, these activities may result in secondary harmful contamination (Chiu et al., 2019). Therefore, additional remedies are required to address the secondary pollution issue. The removal of dyes from wastewater is a complex task, especially using primary treatments such as filtration, primarily due to their high solubility in water. Consequently, it becomes necessary to limit the quantity of persistent dyes present in textile wastewater. Synthetic dyes have been found to have adverse effects on the environment, particularly when they enter surface waters. When synthetic dyes are released into the environment, they can pose a threat to aquatic ecosystems. These dyes can persist in water bodies and adversely affect water quality. Research has shown that surface waters often contain detectable concentrations of synthetic dyes due to their extensive use in various industries, including textiles (Yusuf, 2019).

In summary, synthetic dyes are widely used in manufacturing industries due to their versatility and cost-effectiveness. The textile industry, in particular, employs a vast array of synthetic dyes, with azo dyes being predominant. However, not all dyes become permanently absorbed into textiles, leading to potential environmental impacts. Synthetic dyes can contribute to the pollution of surface waters, and their presence in such environments has been documented through various studies. Depending on their charges when dissolved in an

aqueous medium, dyes comprise colored organic molecules that are commonly categorised as anionic (acidic dyes) and cationic (basic dyes) (Ahmed, 2016). To mitigate these effects, it is crucial to treat the wastewater containing synthetic dyes.

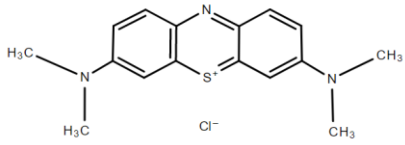
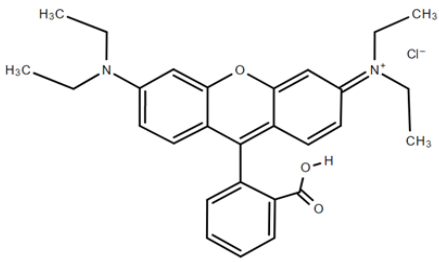
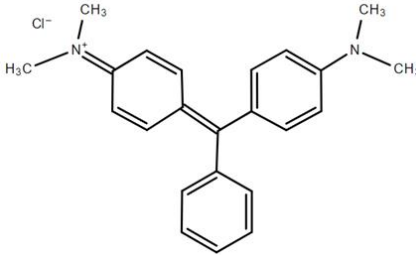
2.9.1 Cationic dyes

Cationic dyes are a class of highly soluble compounds that exhibit the ability to form positively charged ions when dissolved in water (Tripathi, 2013). These dyes are commonly used in the colouring of materials such as cotton, leather, and silk staining. Among the different types of soluble dyes, basic dyes stand out as the brightest and possess exceptionally strong tinctorial properties. Basic dyes are characterised by the presence of positively charged ammonium groups, contributing to their cationic nature (Leodopoulos et al., 2015).

Examples of basic dyes that are common and have been extensively applied in many industries are methylene blue, RhB, malachite green. Table 2.4 provides examples of specific cationic dyes and their distinct characteristics. Even at small concentrations exceeding 1 mg/L, cationic dyes are vividly evident in water and can cause significant alterations in water conditions and quality (Rajagopal et al., 2020). These colours are categorised as poisonous compounds, posing potential harm to human health by causing allergic rashes and exhibiting mutagenic and carcinogenic effects (Eren, 2009).

Due to the tendency of cationic dyes to contaminate water, it becomes imperative to treat wastewater containing these pollutants using suitable methods. The presence of cationic dyes in wastewater necessitates effective treatment measures to mitigate their negative environmental and health impacts. Appropriate treatment processes can help remove or reduce the concentration of cationic dyes, thus minimising the potential contamination they pose to water resources and ecosystems.

Table 2.4: Examples of cationic dyes and their characteristics

Cationic Dye	Physical properties	Chemical structure	Molecular formula	Molecular weight (g/mol)	pKa value	Absorption, λ_{max} (nm)	Reference
Methylene Blue	Dark green crystalline powder or crystal		C ₁₆ H ₁₈ N ₃ SCl	319.85	8.33	646	(Kaur et al., 2022)
RhB	Reddish-violet powder		C ₂₈ H ₃₁ N ₂ O ₃ Cl	479.02	5.54	554	(Kareem et al., 2021)
Malachite green	Green crystalline powder		C ₂₃ H ₂₅ N ₂ Cl	364.91	10.3	618	(Hassan-Zadeh et al., 2021)

2.9.1.1 Rhodamine B

RhB is a typical azo dye that is soluble in several solvents like ethanol, butanol and especially in water. It has a molecular formula of $C_{28}H_{31}N_2O_3Cl$ and a molecular weight of 479.02 g/mol. Rhb is one of the fluorescent xanthene dyes produced by the modification of the xanthene compound which combines two molecules to create a glycosidic bond which includes amino and amino molecules (Singh et al., 2020). RhB dye has been extensively used on many materials like leather, wool, and paper.

Unfortunately, the RhB dye molecules could lead to significant biological and environmental issues, even known to have neurotoxin and mutagenic properties and have a significant potential to cause several disorders in humans (Sulistina & Martini, 2020). Previously, products containing paprika and chilies commonly utilised RhB as a food coloring (Mason & Edwards, 1989). RhB was found illegal to be applied in food according to the European Union (EU), and the European Food Safety Authority (EFSA) as RhB poses danger to humans and is reported to be carcinogenic (ESFA, 2005). As a result, the application of RhB as food coloring is prohibited in the EU and many other nations. According to the China Food and Drug Administration (CFDA) and Larsen (2008), China has also banned the application of RhB as a food additive.

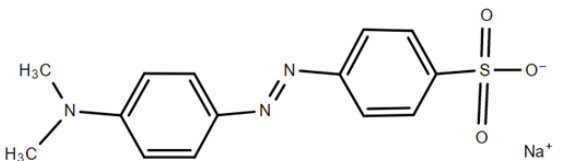
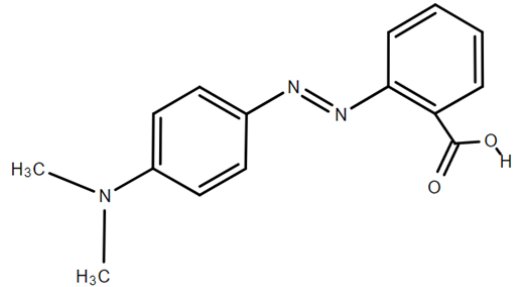
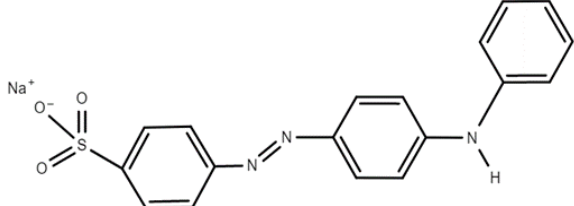
Besides that, water has been contaminated by RhB as it has been utilised as a tracing tool in water treatments and as a color indicator in pesticide sprays (Tatebe et al., 2014). Research has demonstrated that water contaminated with RhB dye (> 0.1 mg/L) has been medically proven to possess carcinogenic and mutagenic properties, leading to the development of subcutaneous tissue borne sarcoma, as well as causing irritation to the skin, eyes, and respiratory tract (Singh et al., 2020). Thus, addressing the issue of water contamination from RhB dyes is of paramount importance and effective wastewater

treatment methods must be implemented to mitigate the harmful impact of these pollutants on the environment and public health.

2.9.2 Anionic dyes

Anionic dyes are a class of dyes characterised by their negatively charged chromophores. The chemical properties of anionic dyes include the presence of sulfonic acid or carboxylic acid groups, which impart a negative charge to the dye molecules. Anionic dyes possess low pH numbers due to the presence of sulphate and carboxylic in the dye compound (Chiu et al., 2019). When mixed with water, anionic dyes like MeO undergo a process of splitting, resulting in the formation of negatively charged ions, or anions (Azam et al., 2022). By creating an ionic bonding with the acid group of the dye and the amine group of the fiber, these dyes could be used in the textile industry to dye materials like silk, cotton, and nylon. Examples of anionic dyes that have been extensively used in the textile industry are MeO, methyl red and acid yellow 36. Table 2.5 summarises the examples of anionic dyes and their characteristics. However, the extensive use of anionic dyes also raises concerns regarding their environmental impact. When released into the environment through wastewater, these dyes can cause water pollution, leading to adverse effects on aquatic organisms and ecosystems. The high solubility of anionic dyes in water contributes to their persistence in the environment. Therefore, appropriate treatment methods are crucial to minimizing the negative environmental consequences associated with anionic dye pollution.

Table 2.5: Examples of anionic dyes and their characteristics

Cationic Dye	Physical properties	Chemical structure	Molecular formula	Molecular weight (g/mol)	pKa	$\lambda_{\max}$ (nm)	Reference
MeO	Orange-yellow powder or crystals		$C_{14}H_{14}N_3NaO_3S$	327.33	3.47	464	(Mohammed et al., 2020)
Methyl red	Shiny purple crystalline or red-brown powder		$C_{15}H_{15}N_3O_2$	269.30	5.00	409	(Hadi et al., 2019)
Acid yellow 36	Yellow powder		$C_{18}H_{14}N_3NaO_3S$	375.38	3.74	200	(Sathya et al., 2015)

2.9.2.1 Methyl Orange

MeO is a commonly used anionic dye with the chemical formula $C_{14}H_{14}N_3NaO_3S$ and has a molecular weight of 327.33 g/mol. It is a bright orange solid that dissolves in water, making it suitable for a wide range of applications. For example, MeO is an azo dye that could be used as a pH indicator in many acid-base and redox titrations. Apart from that, MeO has been widely used in various sectors such as paper, food, and textile manufacturing. Despite its wide application, MeO poses significant environmental challenges. When MeO is released into water bodies, it can disrupt aquatic ecosystems by reducing sunlight penetration, which inhibits the growth of aquatic plants. Additionally, MeO can negatively impact water quality making it unsuitable for drinking and other uses. The global production of anionic dyes including MeO releases 5 – 20% of the dyes as textile effluents into the ecosystem (Selvaraj et al., 2021). Thus, proper treatment of wastewater containing MeO is crucial to prevent environmental pollution and protect aquatic life.

2.10 Phenolic compound

Phenolic compounds are extensively utilised in various sectors like pharmaceuticals, plastics, food, cosmetics, textile, oil, and gas (Raza et al., 2019; Albuquerque et al., 2021). For instance, phenols are applied in the food manufacturing industry, specifically packaging to increase product shelf life whilst preserving nutritional content for better food quality (Martillanes et al., 2017). An example of a phenolic compound that is used in food packaging is anthocyanins. When applied to the packaging composition, it had remarkable color characteristics and a high level of antioxidant properties which could stop the oxidation of olive oil lipids (Wang et al., 2019). Other than that, phenols are also used in the pharmaceutical sector as a disinfectant due to their ability to denaturize proteins and inhibit the oxidation of lipids and DNA (Albuquerque et al., 2021).

Fundamentally, phenols have an aromatic ring of one or several functional groups, thus the structures vary from basic phenolic compounds to other compounds that are strongly polymerised (Balasundram et al., 2006). Phenols can be classified into several types based on their carbon chain, with the most common being simple phenols, phenolic acids, flavonoids (flavanols, flavones, flavanones and anthocyanins), tannins, lignans and stilbenes (Hazafa et al., 2020). Through various chemical processes like oxidation, disinfection, and hydrazine processing, phenolic can transform into a wide range of derivatives in water. For instance, when phenol is combined with chloride or nitrate molecules, the derivatives of phenol which are chlorophenol and nitrophenol will be produced, respectively (Raza et al., 2019). Phenol and its derivatives are very poisonous, corrosive, weakly biodegradable, and could produce toxins in biological organisms. Phenol has been labelled as one of the 65 toxicants by the United States Environmental Protection Agency (USEPA). The USEPA has imposed a threshold of 0.1 mg/L of phenolic compound in processed waste to safeguard against any potentially harmful consequences from phenol exposure (Daffalla et al., 2013). In terms of phenol legislation, the World Health Organization (WHO) is more restrictive. The maximum allowed level of phenolic compounds in drinking water is fixed at 0.001 mg/L (Asgari & Salari, 2019).

Additionally, phenolic compounds are believed to threaten both aquatic habitats' life, especially human existence, and the ecosystem. Numerous research has been conducted to remove phenolic compounds in wastewater by employing adsorption (Bazrafshan et al., 2016), microbial fuel cell (Feng et al., 2015), membrane filtration and coagulation (Yu et al., 2021) techniques. However, these methods are not promising due to high capital costs, heavy power utilization, and production of secondary pollutants (Raza et al., 2019). Consequently, it is imperative to apply eco-friendly and economical ways to remove phenol and its

derivatives from wastewater systems. Photocatalytic-mediated treatment is known to be one of the best methods to degrade phenolic compounds (Bhattacharjee et al., 2022). Table 2.6 shows the application of photocatalysis using various photocatalysts for the treatment of different types of phenolic compounds.

Table 2.6: Photocatalytic treatment on various phenolic compounds using selected photocatalyst

No.	Selected photocatalyst	Phenol compound	Experiment Condition (initial concentration, light source, time irradiation)	Percentage removal (%)	Reference
1.	Ag/TiO ₂	2CP	8 mg/L, UV light, 150 min	74	(Onkani et al., 2020)
2.	g-C ₃ N ₄ /ZnO/C	4-chlorophenol	10 mg/L, Visible light, 5 h	72	(de Sousa et al., 2020)
3.	TiO ₂ /g-C ₃ N ₄	3-chlorophenol	25 mg/L, Visible light, 2 h	64	(Kobkeatthawin et al., 2022)
4.	TiO ₂ /ZnS	4-chlorophenol	55 mg/L, mercury lamp, 400 min	74	(Velásquez-Torres et al., 2022)

2.10.1 2-Chlorophenol

A class of compounds known as chlorophenols (CPs) is formed when phenol is electrophilically halogenated with chlorine. CPs are known as derivatives of phenol compounds. There are five basic types of chlorophenols: mono-, di-, tri-, tetra- and penta-chlorophenol. To sum up, there are 19 combinations of numerous CPs,

which correspond to the various ways that chlorine molecules could be linked to 5 carbons in the benzene ring of the phenolic compound, except the carbon atom that is attached to the hydroxyl group. In contrast, pentachlorophenol possesses a single isomer since all 5 of the phenol's possible ring atoms have been entirely occupied by chlorine atoms. CPs are common environmental pollutants that are mostly released through industrial and agricultural effluent (Igbiosa et al., 2013). Most of these CPs exist in solid form at room temperature, with the exception of 2CP, as it exists in liquid form. Photocatalysis treatment is one of the methods that could degrade phenolic compounds, especially 2CP. 2CP is one of many phenolic compounds that is colorless, and has a pungent, strong, and carbolic odor (Ashford, 1994; Lewis, 2016). Figure 2.5 shows the structure of 2CP. It is mainly used for disinfectants or biocides for houses, and hospitals, pesticides, and the textiles industry like for printing, dyeing, and finishing. Since 2CP has high toxicity, is poorly biodegradable, can cause skin irritation and is highly carcinogenic (Ahamd et al., 2017). Other than that, they cause complex issues for water sources, including a pungent scent and odor in the water supply, the mortality of aquatic life, and the disruption of healthy microbial population activity in water treatment facilities (Ge et al., 2017). Therefore, the removal of this 2CP via photocatalysis treatment to treat wastewater is very much needed.

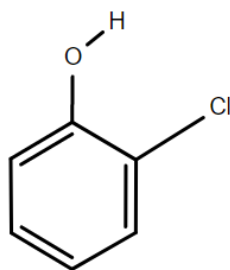


Figure 2.6: Chemical structure of 2-chlorophenol

2.11 Parameters that affect photodegradation

The photodegradation of nanocomposite towards pollutants is influenced by a variety of factors. The main variables that affect the efficiency of the photocatalytic treatment are the dosage of the catalyst, the initial concentration of pollutants and the pH level of solution. In this subtopic, the importance of every parameter will be discussed.

2.11.1 Dosage

The amount of catalyst loading plays a vital role in the removal efficiency of OPs. The photodegradation of OPs has been shown to considerably increase with an increase in catalyst loading. This is because more catalyst loadings promote an increase in the active sites in contact with the target pollutants. As reported by Kale et al., (2020), the photodegradation of methylene blue dye rises from 94.83% to 97.02% when the catalyst concentration $\text{TiO}_2/\text{ZnS-rGO}$ was increased from 0.3 g/L to 0.4 g/L. Interestingly, when the catalyst concentration was increased to 0.5 g/L, the photodegradation rate significantly decreased to 96.30%. This is because, in the photocatalytic treatment, the nanoparticles tend to agglomerate and reach the saturation limit. When the catalyst dosage approaches its saturation limit, the reaction rate will either decrease or remain constant with the subsequent increases in the catalyst dosage. Additionally, an excessive amount of catalyst dosage would prevent the maximum quantity of photons from being absorbed. Similarly, another paper reported that the removal efficiency of acetaminophen increased from 74.7% to 99.3% after 30 min of treatment when the $\text{TiO}_2/\text{g-C}_3\text{N}_4$ catalyst dosage was increased from 0.15 g/L to 0.50 g/L (Du et al., 2020). This is due to the increase of catalyst dosage enhanced the production of electron-hole which increases ROS generation and photodegradation efficiency. However, when the $\text{TiO}_2/\text{g-C}_3\text{N}_4$ catalyst dosage exceeds 0.50 g/L, the removal efficiency decreases. Water treatment with an excessive amount of catalyst loading will have

high turbidity hence hindering the photon penetration and reducing the photodegradation activity to degrade the pollutant. Thus, an optimal dosage for efficient removal of OPs mixture must be identified to efficient removal of OPs.

2.11.2 Initial concentration of pollutants

The initial concentration of OPs is another important variable that influences the rate of photodegradation. The amount of OPs that are adsorbed on the surface of the photocatalyst determines how fast they disintegrate. Typically, as the concentration of OPs increases while keeping the catalyst loading constant, the rate of degradation steadily decreases. The increase in initial concentration of OPs would cause a collision or blockage of the saturated adsorbed organic pollutant molecules and greater contact and irradiation time are needed for the photodegradation of these pollutants. For instance, 0.50 g/L of g-C₃N₄/TiO₂ photocatalyst shows a decrease in rate degradation of 0.49 min⁻¹, 0.19 min⁻¹ and 0.09 min⁻¹ on acid orange 7 (AO7) dye when the initial concentration of the dye increased from 5 mg/L, 10 mg/L and 20 mg/L, respectively (Liu et al., 2020). When the initial concentration of dye increases, more dye molecules would be adsorbed on the surface of the g-C₃N₄/TiO₂ photocatalyst. Therefore, a fewer number of photons would be in contact with the surface of the photocatalyst. Additionally, the lower production of ROS would result in a decrease in degradation efficiency (Rafiq et al., 2021). Another study reported a similar trend, the degradation rate of TiO₂/g-C₃N₄ decreases from 100% to 67 % when the initial brilliant green (BG) dye concentration increases from 15 to 30 mg/L dye (Sutar et al., 2020). With a higher initial concentration, the opacity of the solution is higher hence reducing the light scattering effect which decreases the ROS production throughout the photocatalytic treatment. Therefore, the initial concentration of OPs would influence the efficiency of photodegradation in the water system.

2.11.3 pH level

Wastewater that exists is expected to have various pH levels which makes the photocatalytic activity complex. Photocatalytic degradation starts with the adsorption of pollutants on the surface of the photocatalyst. Hence, the pH value of the wastewater is an important factor that appears to be related to the surface charge of the photocatalyst that might be either positively, negatively, or neutrally charged. Furthermore, ROS production is also influenced by the pH value of wastewater. For example, at low pH, positive holes (h^+) would be produced and are known to be an important oxidative species. Meanwhile, at neutral or high pH levels, hydroxyl radicals ($\bullet OH$) are responsible for the oxidation process. (Alaton et al., 2002).

The term “point of zero charge” (pzc) also known as the isoelectric point can determine the surface charge of the photocatalyst depending on the pH condition of wastewater. The catalyst surface ought to be positively charged when the pH value is less than pzc or is at acidic pHs. When the surface charge is positive, the photocatalyst is prone to attract anionic or negatively charged compounds. However, the catalyst surface ought to be negatively charged when the pH value is greater than pH_{pzc} or is at alkaline pH. So, when the surface charge is negative, the photocatalyst tends to attract cationic or positively charged compounds. Therefore, the surface charge of photocatalysts and OPs has a serious influence on the photodegradation process.

Labiadh et al. (2014) reported that the ternary $TiO_2/ZnS:Cu$ composite produced the best degradation of 90% of salicylic acid (SA) removal within 60 min at pH 4.35 under UV light radiation, However, under basic pH conditions the photodegradation efficiency decreases. As TiO_2 nanoparticles have a pH_{pzc} value of 6.8 (Alaton et al., 2002), the surface

charge of the photocatalyst becomes positive in an acidic medium or at a pH level below than pHpzc ($\text{pH} < 6.8$) and vice versa. As a result, at pH values below pHpzc, the affinity of the carboxylate or carboxylic acid groups for the neutral TiO_2 surface likely enhances adsorption and therefore improves photodegradation efficiency. In addition, a pH value above pzc causes the carboxylate group of SA and the negative surface charge of TiO_2 to repel one another hence in basic conditions, the photodegradation efficiency decreases.

2.11.4 Radical Scavengers

Several studies have investigated the effect of various radical scavengers on the photocatalytic degradation of OPs in the presence of TiO_2/ZnS -based photocatalysts to elucidate the photocatalytic mechanism and understand the role of active species. Commonly used scavengers include isopropyl alcohol (IPA) and methanol as $\bullet\text{OH}$ radical scavengers, EDTA and tert-butanol (t-BuOH) as h^+ scavengers, and benzoquinone (BQ) as $\bullet\text{O}_2^-$ radical scavengers (Chen et al., 2020; Du et al., 2014; Mittal et al., 2019). In a photocatalytic system of $\text{TiO}_2/\text{ZnS-In}_2\text{S}_3$, the addition of EDTA and t-BuOH was found to cause the degradation of RhB to decrease to 92.4% and 89.7%, respectively, compared to complete degradation in the absence of any scavengers, indicating that both $\bullet\text{O}_2^-$ and h^+ influenced the degradation rate of the dye (Liu et al., 2015). Mittal et al. (2019) reported that the addition of EDTA caused a minor effect on the photodegradation rate of RhB using $\text{TiO}_2/\text{ZnS/CdS}$ photocatalyst, compared to IPA and BQ as scavengers of $\bullet\text{OH}$ and $\bullet\text{O}_2^-$, which markedly decreased the degradation rates of RhB by 87% and 91%, respectively. These findings suggest that different scavengers can have varying effects on the photocatalytic degradation rate, highlighting the importance of understanding the specific roles of active species in the reaction (Mittal et al., 2019).

CHAPTER 3

MATERIALS AND METHODS

3.1 Materials

Titanium (IV) butoxide, zinc sulphide (ZnS), methanol ($\geq 99.6\%$), p-benzoquinone (BQ), 2CP, RhB and MeO were purchased from Sigma-Aldrich (USA) while urea was procured from Bendosen. 2-Propanol and sodium hydroxide were obtained from Merck (Germany). Perchloric acid (HClO_4) and 30% hydrogen peroxide (H_2O_2) were supplied by R&M Chemicals (UK) and HmbG Chemicals (Germany), respectively.

3.2 Synthesis

3.2.1 Synthesis of TiO_2 and g- C_3N_4 precursors

TiO_2 was synthesised using the sol-gel method with titanium (IV) butoxide as the precursor (Kanakaraju et al., 2017). 30 mL of titanium (IV) butoxide and 15 mL of 2-propanol were mixed for 15 mins to achieve a homogeneous mixture. About 100 mL of distilled water was added drop by drop and the mixture was left to stir for two hours. The solution was filtered and washed three times with distilled water. The sol-gel was dried in the oven for 2 hours at $100\text{ }^\circ\text{C}$. Then, it was ground and calcinated in the furnace for 5 hours at $300\text{ }^\circ\text{C}$ to complete the synthesis. A yield of 5 g of white TiO_2 composite was obtained.

3.2.3 Synthesis of g- C_3N_4 precursors

g- C_3N_4 was synthesised via the pyrolysis method using a fixed amount of urea (Liu et al., 2011). About 6 g of urea was placed in a crucible and wrapped with aluminium foil. The pyrolysis of urea took place in a muffle furnace under $550\text{ }^\circ\text{C}$ for 3 hours. The g- C_3N_4

was then dispersed in water and washed with deionised water followed by air and oven drying. Approximately 1 g of pale yellow g-C₃N₄ composite was obtained.

3.2.4 Synthesis of ternary nanocomposite

The synthesised TiO₂ and g-C₃N₄ were mixed with commercially available ZnS at a ratio of 1:1:1 in 100 mL of distilled water under continuous magnetic stirring for 2 hours. Subsequently, the resulting mixture was transferred into a hydrothermal flask and subjected to a hydrothermal process at a temperature of 150 °C for 5 hours. The resulting ternary compound was filtered and subsequently dried at 100 °C for a period of 2 hours. Figure 3.1. demonstrates the steps involved in the synthesis of TiO₂/ZnS/g-C₃N₄ photocatalyst.

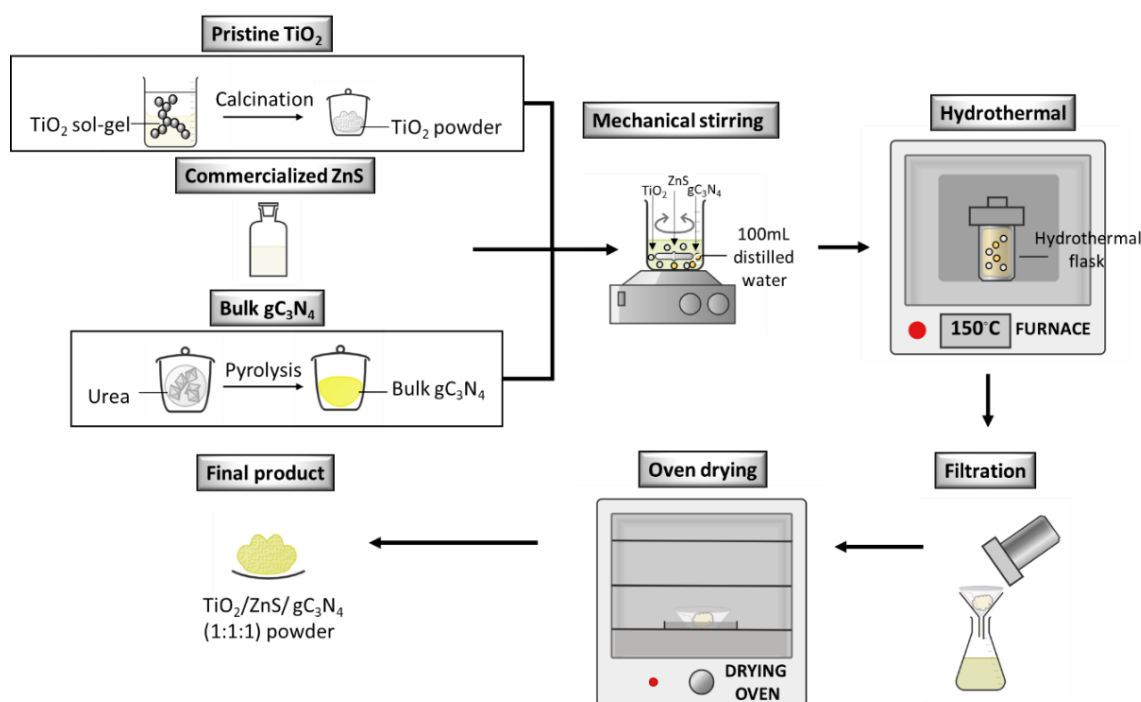


Figure 3.1: Schematic illustration synthesis of TiO₂/ZnS/g-C₃N₄ (1:1:1) photocatalyst

3.3 Characterisation of nanocomposites

In this study, a comprehensive characterization of the pristine TiO_2 , $\text{g-C}_3\text{N}_4$, ZnS and the ternary photocatalyst was undertaken using various advanced techniques. For FESEM and EDX analysis, photocatalyst samples were placed on a carbon tape and coated with a thin layer of conductive material which is platinum to enhance conductivity. The surface morphology was analysed using a field emission scanning electron microscope (FESEM Model JSM-6390LA), while the elemental composition of the ternary photocatalyst was determined using energy-dispersive x-ray (EDX). The specific surface area of the ternary sample was measured by the Brunauer–Emmett–Teller (BET) analyser (Quantachrome Autosorb iQ ASIQC0000-3) with N_2 adsorption at 77 K was applied. The analysis of microstructures was conducted by placing the photocatalyst sample on a copper grid for transmission electron microscopy (TEM), employing a JEM-2010 electron microscope (JEOL, Japan). The crystallinity and crystal structure of the ternary photocatalyst were examined using an x-ray diffraction spectrometer (XRD). The infrared absorption bands were analysed using thin pellets prepared by grinding the photocatalyst samples into a fine powder and mixing them with potassium bromide (KBr) for the fourier transform infrared spectroscopy (FTIR, Thermo Nicolet iS10) in the range of $4000\text{--}400\text{ cm}^{-1}$. UV–Vis diffuse reflectance spectroscopy (UV-DRS, Model Cary 5000) was used to determine the band gap of the ternary photocatalyst with the excitation wavelength scanned from 200 to 800 nm.

3.4 Photocatalytic activity assessment

The degradation efficiency of ternary $\text{TiO}_2/\text{ZnS}/\text{g-C}_3\text{N}_4$ photocatalysts was investigated based on the removal of RhB dye. Figure 3.2 illustrates the experimental setup. Firstly, a fixed amount of $\text{TiO}_2/\text{ZnS}/\text{g-C}_3\text{N}_4$ was added into 10 mg/L of RhB dye solution and mixed using a magnetic stirrer. The suspension was placed in the dark for 30 mins to

achieve adsorption and desorption equilibrium. After the first 30 mins, the suspension was irradiated under visible light (100 W). The photocatalytic experiment under visible light took place for 120 mins and a fixed amount of aliquot was collected every 30 mins. All samples were spun in a tabletop centrifuge (Hettich, EBA 200) using 6000 rpm for 10 mins prior to UV-Vis spectrophotometer analysis. The following formula (Eq. 3.1) was used to calculate the percentage removal of RhB.

$$\text{Percentage removal (\%)} = \frac{C_i - C_f}{C_i} \times 100\% \quad \text{Equation 3.1}$$

where C_i is the initial concentration of the dye and C_f is the final concentration of the dye. Preliminary studies were conducted by comparing unpurified g-C₃N₄ with purified g-C₃N₄ and determining the optimal ratio of g-C₃N₄ in a ternary photocatalyst composed of TiO₂/ZnS/g-C₃N₄ for the degradation of RhB. Next, photocatalytic treatments were conducted by applying different catalyst dosages (0.3-2.0 g/L), initial concentrations of RhB dye (10-25 mg/L), and initial pH of RhB dye solution (pH 3, 5, 7, and 10). For the pH effect study, HOCl and NaOH were used for pH adjustment. In the case of the scavengers study, MeOH (0.2 mmol/L), IPA (0.2 mmol/L), H₂O₂ (0.1 mmol/L) and BQ (0.2 mmol/L) were added to the prepared RhB dye solution (10 mg/L) to deduce the possible photocatalytic mechanism.

Experiments involving multi-pollutants were conducted to evaluate the degradation efficiency of mixed OP by simultaneously degrading 10 mg/L of RhB (554 nm), MeO (464 nm), and 2CP (274 nm) under visible light irradiation (>400 nm). Studies have shown that photocatalytic activity achieves optimal removal rates for RHB, MO, and 2CP at concentrations between 8 mg/L and 12 mg/L (Du et al., 2014; Liu et al., 2015; Onkani et al.,

2020). Therefore, a concentration of 10 mg/L which falls within this range was chosen in this study.

By setting the degradation limit at 10 mg/L, we are prioritizing water quality that significantly exceeds the established guidelines. This approach provides a substantial safety margin, ensuring the effective removal of these contaminants and guaranteeing the delivery of treated water well within the permissible levels outlined in drinking water regulations. This commitment to exceeding regulatory requirements underscores our dedication to public health and environmental protection, providing reassurance to consumers and regulatory bodies alike.

Evaluating the degradation efficiency under multiple pollutants is a more realistic approach as it closely mimics actual conditions and can provide a better understanding of the overall photocatalytic treatment efficiency.

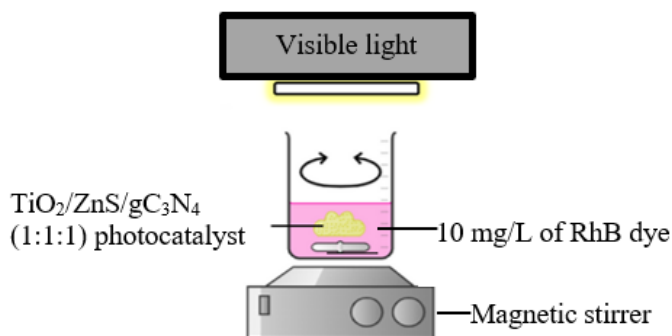


Figure 3.2: Schematic illustration of photocatalytic experimental setup of TiO₂/ZnS/g-C₃N₄ (1:1:1) photocatalyst under visible light.

CHAPTER 4

RESULTS AND DISCUSSION

4.1 Preliminary Study

4.1.1 Comparing unpurified g-C₃N₄ and purified g-C₃N₄

Figure 4.1a compares the XRD analysis between impure and pure g-C₃N₄. Unpurified g-C₃N₄ refers to a sample that has not undergone washing with deionised water, whereas purified g-C₃N₄ designates a sample that has been subjected to multiple washes with deionised water. Both unpurified and purified g-C₃N₄ exhibited peaks at $2\theta = 27.5^\circ$, which corresponds to the (011) lattice plane of hexagonal g-C₃N₄. Additionally, a distinct peak for g-C₃N₄ was observed at $2\theta = 13.0^\circ$, corresponding to the (001) plane (Figure 4.1a). However, unpurified g-C₃N₄ displayed three unknown peaks at $2\theta = 38.4, 44.2, 65.0, \text{ and } 78.1^\circ$. Upon washing the unpurified g-C₃N₄ sample ten times (100 mL of deionised water) to produce purified g-C₃N₄, all the unknown impurities peaks at $2\theta = 38.4, 44.2, 65.0, \text{ and } 78.1^\circ$ disappeared. This observation aligns with the findings reported by Zhang et al. (2012). Moreover, the purified g-C₃N₄ nanocomposite demonstrated higher photodegradation performance for RhB dye compared to unpurified g-C₃N₄ (Figure 4.1b). The purified g-C₃N₄ achieved a photodegradation efficiency of 70.3%, while the degradation efficiency of RhB by unpurified g-C₃N₄ was 58.7%. This performance improvement can be attributed to several factors. The washing process effectively removed impurities present in the impure g-C₃N₄, leading to a higher purity material. This increase in purity is crucial as it reduces the recombination of photogenerated charge carriers, allowing more efficient utilization of the generated electron-hole pairs in the catalytic reactions. By minimizing recombination, the photocatalytic activity of g-C₃N₄ is significantly enhanced, leading to improved degradation

efficiency (Hao et al., 2016). Furthermore, the removal of impurities not only enhances the purity but also increases the available surface area for catalytic reactions. A cleaner surface provides more active sites for RhB dye molecules to interact with, increasing the likelihood of successful degradation. This higher surface area, coupled with the improved purity, ensures a more effective catalytic process and, consequently, higher photodegradation efficiency.

Additionally, the washing process likely contributed to the improvement in the crystallinity and structural integrity of g-C₃N₄. Increased crystallinity means that the atoms or molecules in the material are arranged in a more ordered manner, which can enhance the material's stability and catalytic performance. A well-structured and crystalline g-C₃N₄ material can absorb light more effectively, promoting better light-harvesting capabilities. This improved light absorption, in turn, leads to enhanced photocatalytic activity, as a higher number of photons can initiate the photocatalytic reactions on the surface of the material (Li et al., 2020). In summary, the washing process not only removed impurities but also played a pivotal role in improving the purity, surface area, crystallinity, and structural integrity of g-C₃N₄. These enhancements collectively led to the elimination of unknown peaks in the XRD pattern and a substantial improvement in the photodegradation efficiency of RhB dye. The purified g-C₃N₄, with its optimized structural and compositional properties, exhibited superior photocatalytic performance, underscoring the importance of purification processes in tailoring photocatalysts for efficient pollutant degradation applications.

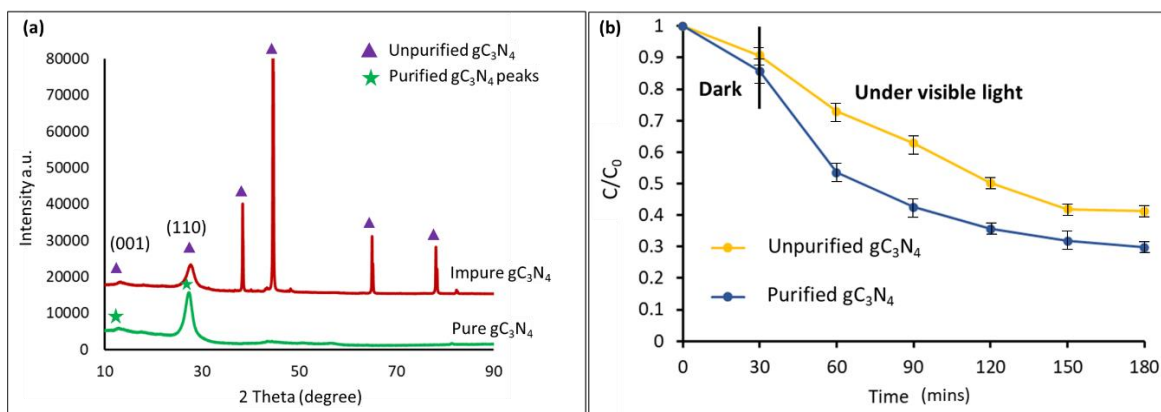


Figure 4.1: XRD patterns and the photocatalytic degradation of RhB using unpurified g-C₃N₄ and purified g-C₃N₄.

4.1.2 Different ratios of ternary TiO₂/ZnS/g-C₃N₄

This preliminary study aims to determine the optimal ratio of g-C₃N₄ in a ternary photocatalyst composed of TiO₂/ZnS/g-C₃N₄, to achieve enhanced photocatalytic performance and maximising overall efficiency. Previous research has reported a successful TiO₂/ZnS (1:1 w/w) (Kanakaraju et al., 2017), indicating an equal proportion of 1 gram each for TiO₂ and ZnS. However, the specific dosage of g-C₃N₄ remains unknown. It is important to determine the specific dosage of g-C₃N₄ to avoid the overloading of photocatalysts. The investigation focuses on identifying the ideal ratio of TiO₂/ZnS/g-C₃N₄ for efficient photocatalytic degradation of RhB under visible light conditions over 150 mins. Several ratios were considered, specifically 1:1:X, where X represents different quantities of g-C₃N₄ ranging from 0.3 g to 2.0 g. Figure 4.2 illustrates the photocatalytic degradation of RhB using various TiO₂/ZnS/g-C₃N₄ ratios. As the g-C₃N₄ loadings in the TiO₂/ZnS 1:1 ratio increased from 0.3 g to 1 g, the removal efficiency of RhB significantly improved, rising from 71.0% to 89.9%. The highest removal rate of 89.9% was achieved at g-C₃N₄ loading of 1 g in the TiO₂/ZnS 1:1 ratio resulting TiO₂/ZnS/g-C₃N₄ ratio of 1:1:1. However, with a g-C₃N₄ loading of 2 g in TiO₂/ZnS, the removal rate declined to 82.1%. This suggests that exceeding

the optimal ratio can saturate the adsorbent photocatalyst surface, limiting the available sites for RhB molecules and thus reducing overall removal efficiency. While increased catalyst loading provides more binding or sorption sites for RhB molecules on $\text{TiO}_2/\text{ZnS}/\text{g-C}_3\text{N}_4$, potentially enhancing the generation of (ROS, excessive usage of the ratio can lead to the aggregation of adsorption sites, diminishing the total surface area available for RhB adsorption (Liu et al., 2015; Nuengmatcha et al., 2016). Furthermore, excessive loadings of $\text{g-C}_3\text{N}_4$ in $\text{TiO}_2/\text{ZnS}/\text{g-C}_3\text{N}_4$ can cause heightened opacity, scattering, and a screening effect, ultimately resulting in decreased light penetration and reduced photocatalytic efficiency (Kale et al., 2020). Therefore, a ternary $\text{TiO}_2/\text{ZnS}/\text{g-C}_3\text{N}_4$ ratio of 1:1:1 was chosen as the optimal ratio for further characterisation and degradation studies.

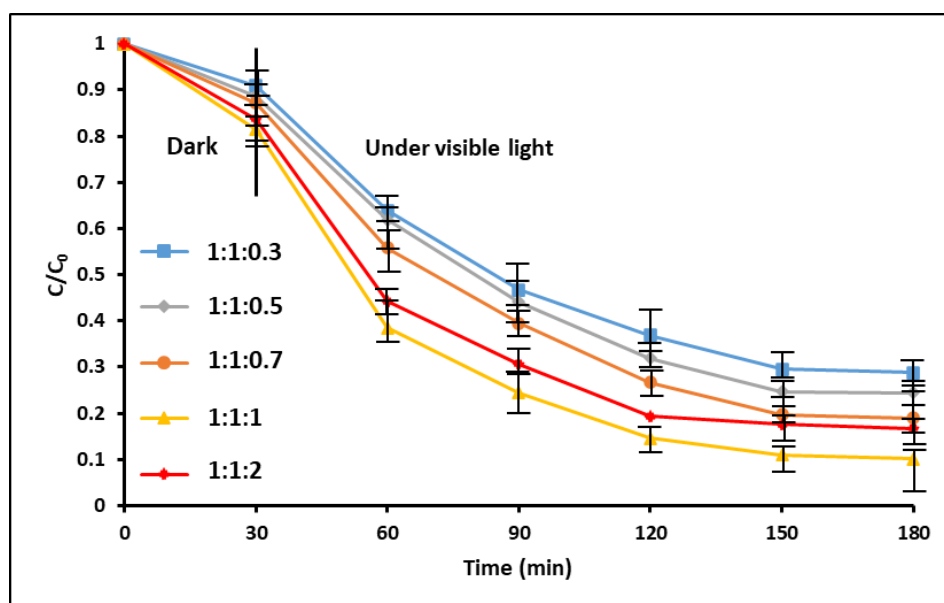


Figure 4.2: Photocatalytic degradation of RhB using different ratios of $\text{TiO}_2/\text{ZnS}/\text{g-C}_3\text{N}_4$

4.2 Characterisation of ternary TiO₂/ZnS/g-C₃N₄

4.2.1 Functional groups (FTIR)

Based on Figure 4.3a, the pure TiO₂ shows an absorption peak at 3403 cm⁻¹, corresponding to the stretching vibration absorption peak of -OH, whereas the strong absorption at 600 cm⁻¹ is ascribed to Ti-O-Ti bonds. In Figure 4.3b, the peak at 1080 cm⁻¹ shows the vibration peak of Zn-S. The characteristic peaks of g-C₃N₄ are generally located in the region of 800–1700 cm⁻¹ (Fagan et al., 2016) (Figure 4.3c). A sharp peak detected at 807 cm⁻¹ corresponds to the characteristic breathing mode of the tri-s-triazine ring. The peaks at 1249 cm⁻¹ and 1438 cm⁻¹ could be ascribed to the typical stretching vibration modes of the C=N bond and the band at 1635 cm⁻¹ is ascribed to the stretching vibration of the C=O bond. Meanwhile, the broad peak of 3441 cm⁻¹ is attributed to the N-H bond. In the case of TiO₂/ZnS/g-C₃N₄ spectra, the O-H bond for TiO₂ is broader compared to the O-H bond in pristine TiO₂ due to the N-H peaks being placed nearly at the same position. Similarly, around 600-800 cm⁻¹, two peaks could be observed at 600 cm⁻¹ and 807 cm⁻¹ which can be ascribed to the Ti-O-Ti bond and the triazine ring, respectively. In Figure 4.3d, the TiO₂/ZnS/g-C₃N₄ spectra demonstrate that the peak intensity at 807 cm⁻¹ is markedly reduced, while the peak shape of the absorption peak within the 1200–1650 cm⁻¹ range became more defined. This change in peak shape may be indicative of a tri-s-triazine ring order stacking (Hu et al., 2021). The presence of C=N and C=O is confirmed in the TiO₂/ZnS/g-C₃N₄ spectra at 1247 cm⁻¹, 1438 cm⁻¹ for C=N and 1635 cm⁻¹ for C=O. Thus, the spectra demonstrate the presence of TiO₂, ZnS, and g-C₃N₄ in the ternary TiO₂/ZnS/g-C₃N₄ photocatalyst.

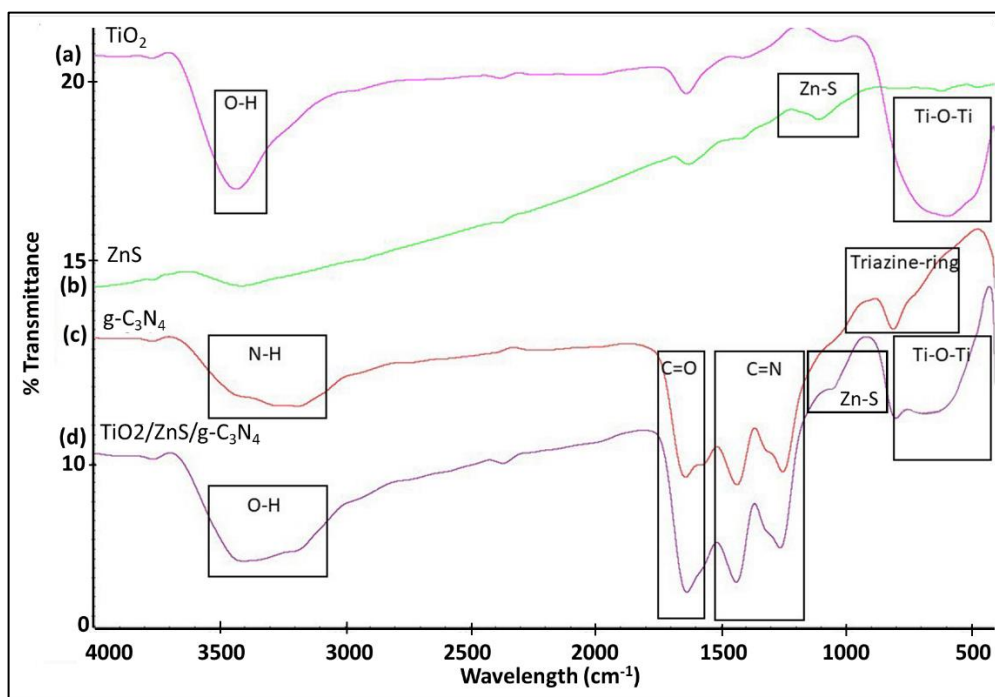


Figure 4.3: FTIR spectra of (a) TiO₂ (b) ZnS (c) g-C₃N₄ and (d) TiO₂/ZnS/g-C₃N₄

4.2.2 Crystallinity phase (XRD)

The crystal structures of as-synthesised materials were characterised by XRD (Figure 4.4). For pristine TiO₂, the XRD pattern shows the characteristics peaks around $2\theta = 25.4, 38.5, 48.1, 55.1, 63.0^\circ$ which correspond to (101), (112), (200), (201) and (204) anatase planes (JCPDS 21-1272) (Bayan et al., 2020; Muñoz-Batista et al., 2015). Whereas cubic ZnS is highly crystalline with diffraction peaks at $2\theta = 28.6, 33.5, 47.6, 56.4, 59.3, 69.5$ and 76.8° corresponding to (111), (200), (220), (311), (222), (400) and (331) plane, respectively (JCPDS No. 03-065-0309) (Karpuraranjith et al., 2022). g-C₃N₄ has a hexagonal crystal system (space group P31c) with diffraction peaks at $2\theta = 13.0$ and 27.5° corresponding to (001) and (110) respectively. The XRD for ternary TiO₂/ZnS/g-C₃N₄ indicates a significant reduction in the intensity of diffraction peaks corresponding to g-C₃N₄ and ZnS after being combined with TiO₂. This reduction in intensity can be attributed to the fact that the peaks

representing TiO_2 are more prominent compared to those of $\text{g-C}_3\text{N}_4$ and ZnS , as observed in the study by Jiang et al. (2018).

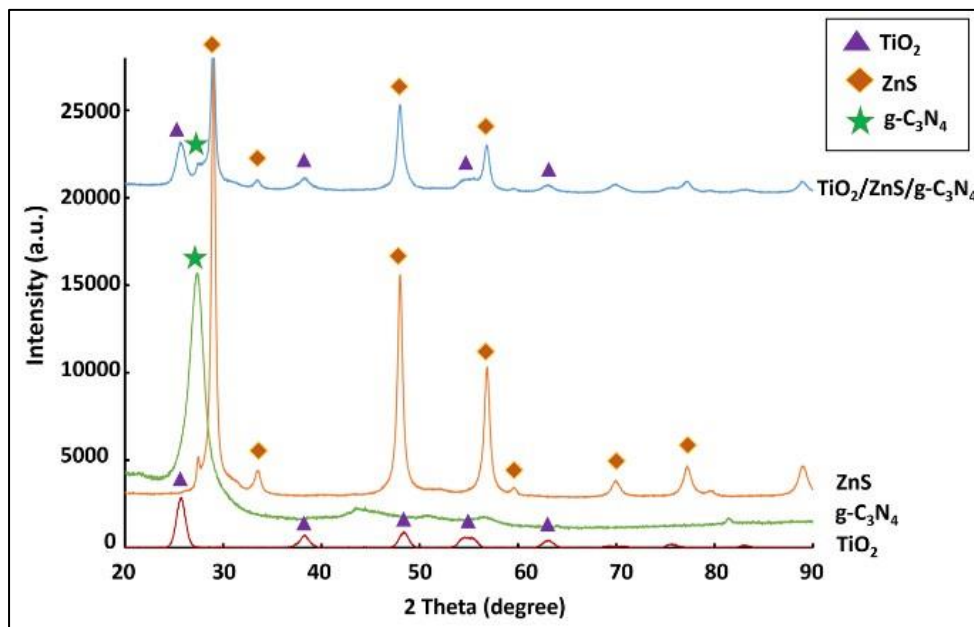


Figure 4.4: XRD patterns for TiO_2 , ZnS , $\text{g-C}_3\text{N}_4$ and $\text{TiO}_2/\text{ZnS}/\text{g-C}_3\text{N}_4$

4.2.3 Morphology (FESEM-EDX)

The photocatalytic performance of the catalysts is greatly influenced by the surface and shape of the catalysts synthesised (Velempini et al., 2021). Figure 4.5a displays the SEM image of unmodified TiO_2 , which exhibits spherical shapes that have aggregated together, consistent with the findings reported by Liu et al. (2022). In contrast, Figure 4.5b illustrates the spherical flower-like shape of ZnS (Talebi et al., 2017), while the sheets in Figure 4.5c depict the pristine $\text{g-C}_3\text{N}_4$ which aligns with the findings by Paul et al. (2019). Figure 4.5d shows that all three compounds are present in the ternary $\text{TiO}_2/\text{ZnS}/\text{g-C}_3\text{N}_4$. It can be seen that all main components of the prepared catalysts are easily differentiated and identified in the ternary $\text{TiO}_2/\text{ZnS}/\text{g-C}_3\text{N}_4$ whereby the $\text{g-C}_3\text{N}_4$ sheet-like and circular TiO_2 was observed to be wrapped around the flower-like ZnS . Figure 4.5e and 4.5f. shows the elemental

composition and elemental map of ternary $\text{TiO}_2/\text{ZnS}/\text{g-C}_3\text{N}_4$. The elemental images confirmed the presence of C, N, O, Zn, S and Ti in the $\text{TiO}_2/\text{ZnS}/\text{g-C}_3\text{N}_4$ photocatalyst.

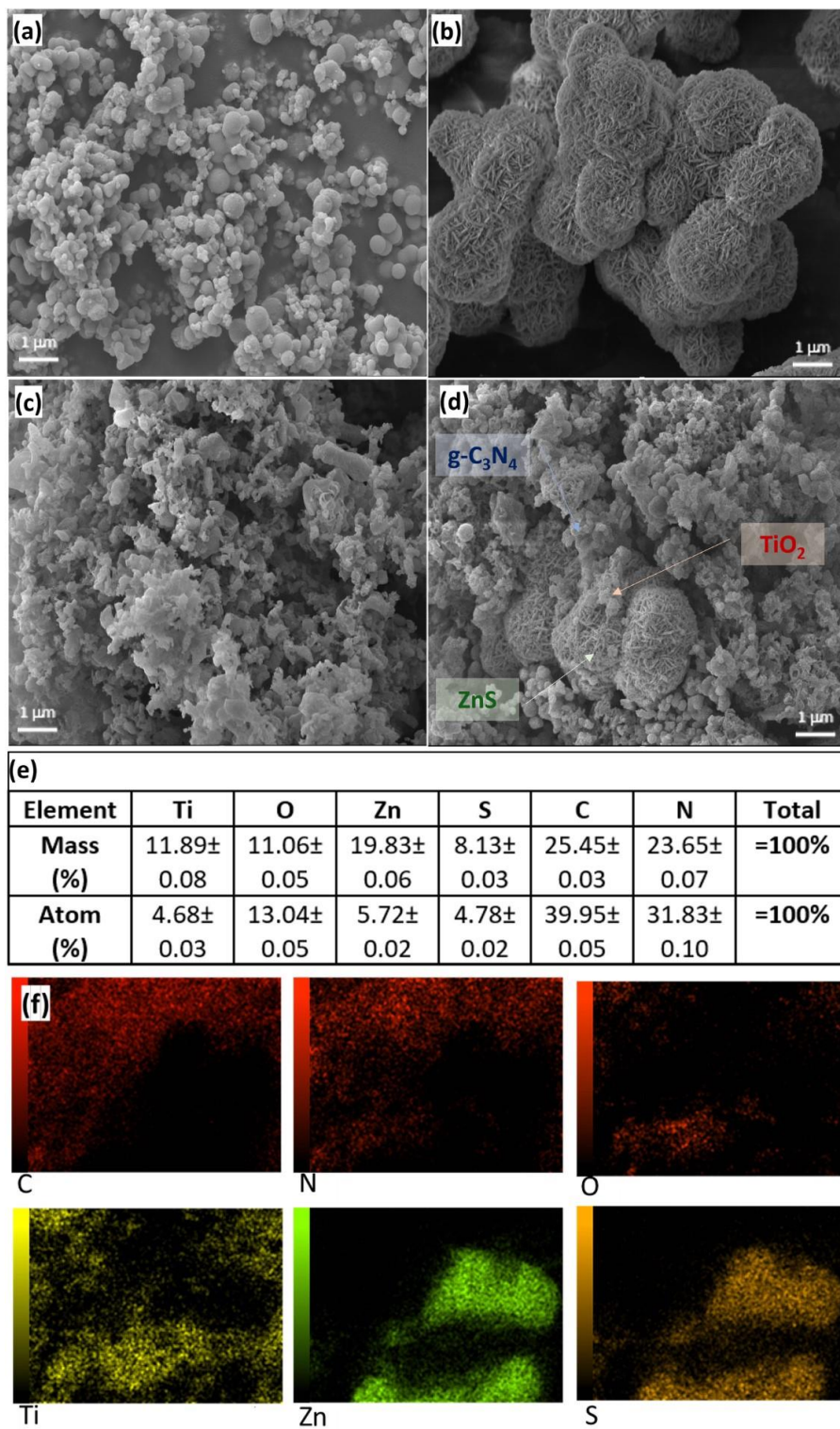


Figure 4.5: SEM images of **(a)** TiO₂ **(b)** ZnS **(c)** g-C₃N₄ **(d)** TiO₂/ZnS/g-C₃N₄ **(e)** EDX elemental composition and **(f)** elemental mapping of TiO₂/ZnS/g-C₃N₄ photocatalyst

4.2.4 Specific surface area (BET)

The specific surface area of ternary TiO₂/ZnS/g-C₃N₄ was further characterised by plotting the N₂ adsorption-desorption isotherm using the BET performance analysis (Figure 4.6). The individual components exhibit distinct adsorption isotherm types: pristine TiO₂ displays an adsorption type IV isotherm, while ZnS and g-C₃N₄ both exhibit adsorption type III isotherms. Interestingly, the TiO₂/ZnS/g-C₃N₄ composite demonstrates an adsorption type IV isotherm, highlighting the unique characteristics of this ternary photocatalyst. The specific surface area and mean pore diameter of as prepared TiO₂, ZnS, g-C₃N₄ and TiO₂/ZnS/g-C₃N₄ are given in Table 4.1. The specific surface area values further support the superior performance of the composite, with TiO₂ having a specific surface area of 151.3 m²/g, ZnS with 13.5 m²/g, g-C₃N₄ with 83.5 m²/g, and TiO₂/ZnS/g-C₃N₄ with 70.74 m²/g. Although the specific surface area decreases in the composite, the composite material still maintains a substantial surface area for efficient adsorption. Moreover, the pore size distribution analysis reveals that the TiO₂/ZnS/g-C₃N₄ composite possesses a pore size of 10.4 nm, indicating the presence of hierarchical porosity and providing additional evidence of its enhanced photocatalytic performance.

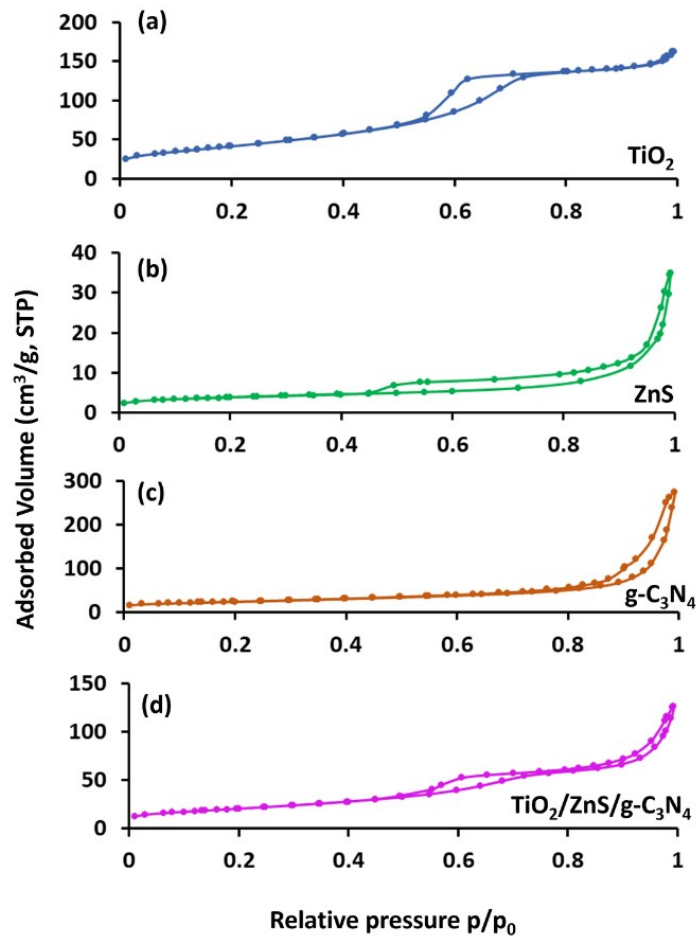


Figure 4.6: BET adsorption-desorption isotherm (a) TiO_2 (b) ZnS (c) $\text{g-C}_3\text{N}_4$ and (d) $\text{TiO}_2/\text{ZnS}/\text{g-C}_3\text{N}_4$

Table 4.1: Specific surface area, mean pore diameter and pore volume of TiO_2 , ZnS , $\text{g-C}_3\text{N}_4$ and $\text{TiO}_2/\text{ZnS}/\text{g-C}_3\text{N}_4$

No.		TiO_2	ZnS	$\text{g-C}_3\text{N}_4$	$\text{TiO}_2/\text{ZnS}/\text{g-C}_3\text{N}_4$
1.	Specific surface area (m^2/g)	151.3	13.5	83.5	70.74
2.	Mean pore diameter (nm)	6.6	16.0	19.1	10.4

4.2.5 Microstructure (TEM)

To investigate the microstructures, TEM images of the materials were recorded (Figure 4.7). TiO_2 shows prominent particle aggregation, consistent with the findings reported by Qin et al., (2018) (Figure 4.7a). In contrast, ZnS did not display any agglomeration and exhibited a rough surface, aligning with the results reported by Liu et al. (2017) (Figure 4.7b). A dispersed sheet like $\text{g-C}_3\text{N}_4$ can be seen in Figure 4.7c. As reported by Xue et al. (2016), the addition of ZnS to $\text{g-C}_3\text{N}_4$ produces crushing and thinner sheet-like structures compared with bulk $\text{g-C}_3\text{N}_4$. The addition of ZnS onto the structures of $\text{g-C}_3\text{N}_4$ would be more exfoliated and could provide more adsorption sites for pollutants hence enhancing the photo activity (Xue et al., 2016). Based on the observations from Figure 4.7d, it can be inferred that the presence of $\text{g-C}_3\text{N}_4$ on TiO_2 resulted in reduced aggregation of TiO_2 particles. Additionally, the co-existence of ZnS led to a smoother appearance in the composite material.

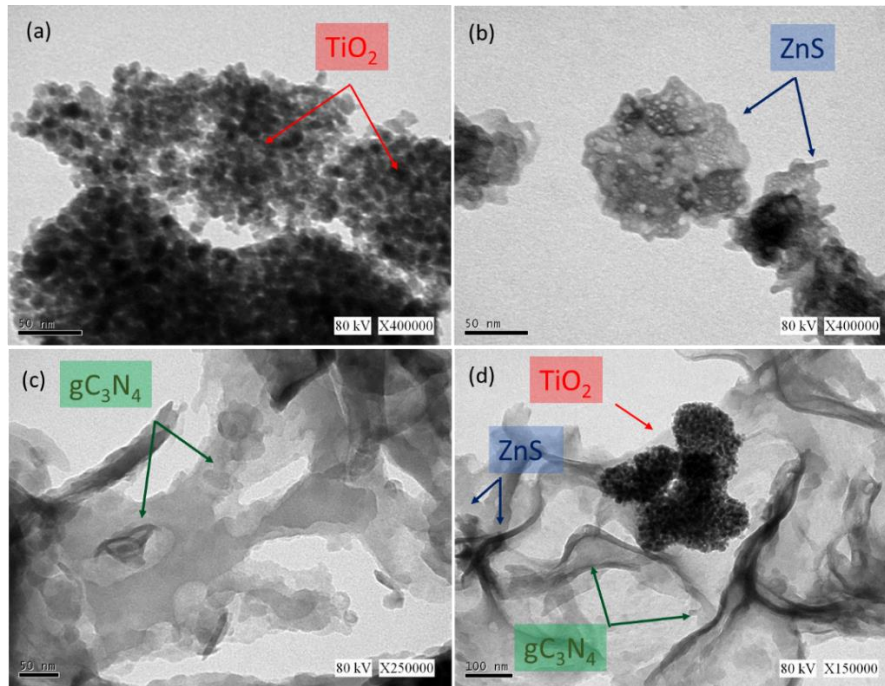


Figure 4.7: TEM images (a) TiO_2 (b) ZnS (c) $\text{g-C}_3\text{N}_4$ and (d) $\text{TiO}_2/\text{ZnS}/\text{g-C}_3\text{N}_4$

4.2.6 Band gap (UV-DRS)

UV-DRS analysis was used to determine the optical properties of TiO_2 , ZnS , $\text{g-C}_3\text{N}_4$ and $\text{TiO}_2/\text{ZnS}/\text{g-C}_3\text{N}_4$ (Figure 4.8). Both TiO_2 and ZnS exhibit weak ultraviolet absorption intensity and cannot effectively absorb visible light due to their relatively large band gaps of 3.35 eV and 3.49 eV, respectively. As a result, TiO_2 and ZnS are constrained to utilising only the UV light component from sunlight, as their absorption edges are shorter than 360 nm (Guo et al., 2021; Sarangi et al., 2022). On the other hand, bulk $\text{g-C}_3\text{N}_4$ exhibits its potential to utilize the visible light region due to its lower band gap energy of 2.88 eV compared to TiO_2 and ZnS and absorption edge of 460 nm. The synthesised ternary $\text{TiO}_2/\text{ZnS}/\text{g-C}_3\text{N}_4$ has a reduced band gap of 2.81 eV, the absorption edge was extended to 440 nm, could efficiently utilize visible light irradiation and a red shift was observed upon the modification with $\text{g-C}_3\text{N}_4$. Consequently, by constructing a ternary photocatalyst of $\text{TiO}_2/\text{ZnS}/\text{g-C}_3\text{N}_4$, it becomes possible to significantly decrease the band gap energy of pure TiO_2 and ZnS , resulting in the development of a material that is responsive to visible light.

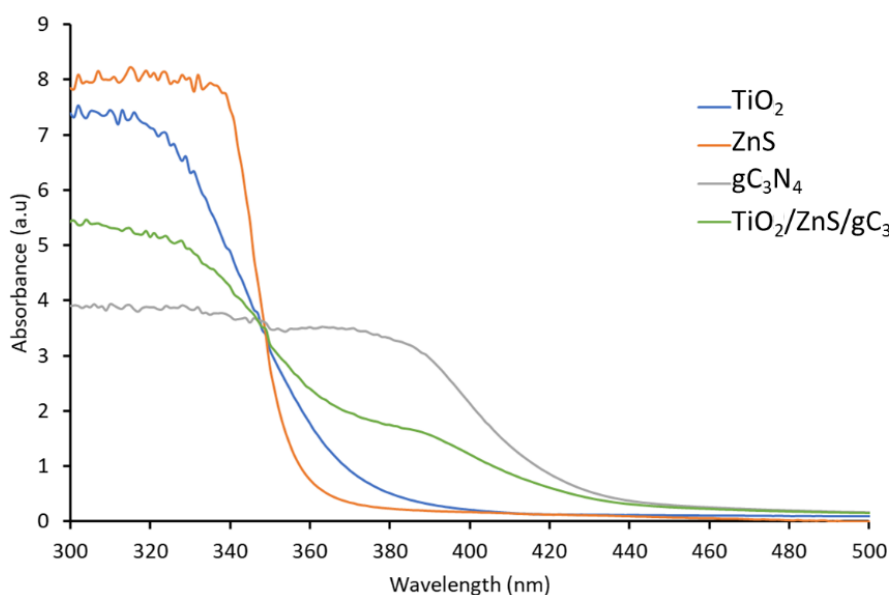


Figure 4.8: UV-Vis DRS spectra of TiO_2 , ZnS , $\text{g-C}_3\text{N}_4$ and $\text{TiO}_2/\text{ZnS}/\text{g-C}_3\text{N}_4$

4.3 Photocatalytic performance: Single RhB dye

RhB dye was used as a model dye pollutant to assess the photocatalytic performance of TiO₂, ZnS, g-C₃N₄, and ternary TiO₂/ZnS/g-C₃N₄ under visible light irradiation. The photocatalytic experiments were performed using a fixed dosage of 1 g/L for TiO₂, ZnS, g-C₃N₄, and the ternary TiO₂/ZnS/g-C₃N₄ and 10 mg/L of RhB dye solution. The results indicated that the ternary TiO₂/ZnS/g-C₃N₄ nanocomposite exhibited the highest adsorption compared with pristine TiO₂, ZnS and g-C₃N₄ (Figure 4.9a), which was attributed to its large BET surface area, after a dark reaction for 30 mins. Moreover, the ternary TiO₂/ZnS/g-C₃N₄ nanocomposite demonstrated the highest photodegradation performance of RhB dye among all the photocatalysts tested, with a photodegradation efficiency of 89.9%, compared to 21.6%, 17.2%, and 70.3% for pristine TiO₂, ZnS, and g-C₃N₄, respectively (Figure 4.9b). The presence of ZnS and g-C₃N₄ significantly reduces the recombination rate of charge carriers of TiO₂ and enhances the production of ROS (Xue et al., 2016; Saeidpour et al., 2022). Hence, this confirmed that the addition of ZnS and g-C₃N₄ can improve the photocatalytic performance of TiO₂ under visible light irradiation.

All photocatalytic degradation reactions followed the pseudo-first-order kinetic model (Figure 4.9c). In Figure 4.9d, the ternary TiO₂/ZnS/g-C₃N₄ composite exhibited a higher photodegradation rate constant (k) of 0.0141 min⁻¹, surpassing pristine TiO₂ (0.0015 min⁻¹), ZnS (0.0011 min⁻¹), and g-C₃N₄ (0.0072 min⁻¹). Ternary TiO₂/ZnS/g-C₃N₄ has the highest photodegradation rate due to several factors, including the increased surface area of the ternary composite, a red shift in the light absorption boundary, and enhanced light absorption capabilities. Hence, the ternary heterojunction can significantly improve the photocatalytic performance of pristine TiO₂ and ZnS.

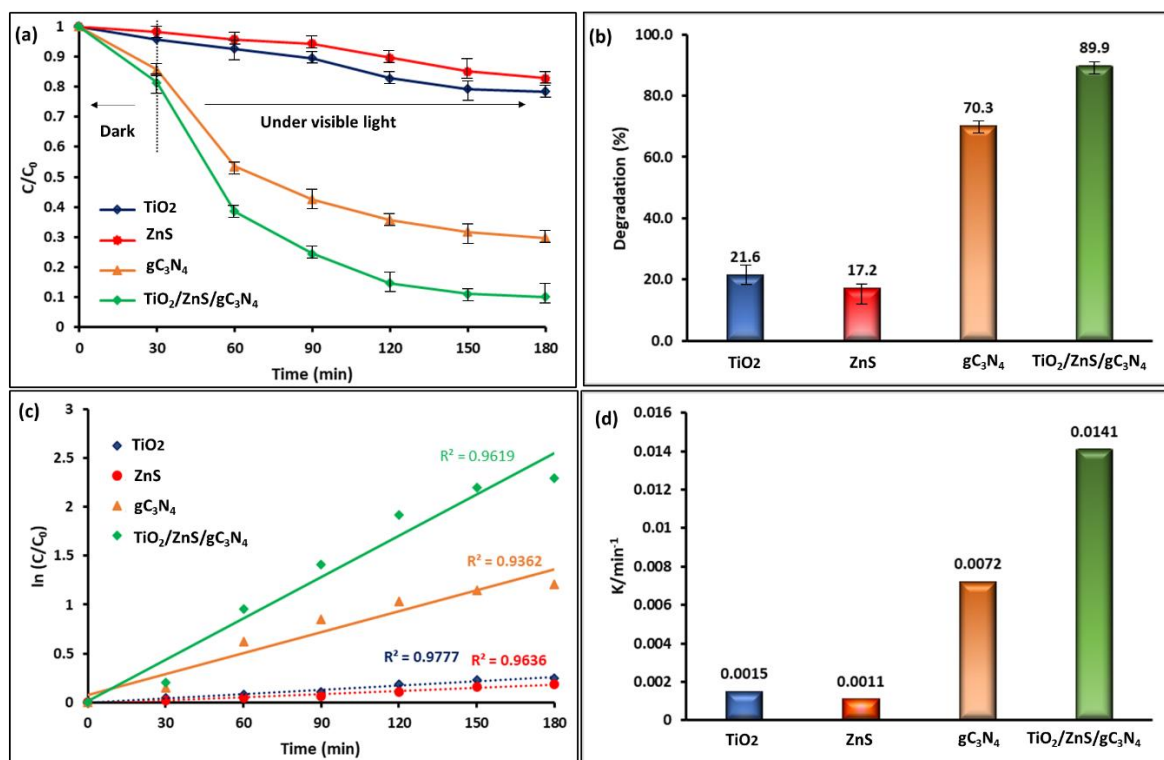


Figure 4.9: (a) Photocatalytic degradation of RhB, (b) pseudo-first-order kinetics, (c) comparison of degradation percentages of RhB and (d) the apparent rate constants of RhB dye degradation using different photocatalysts.

4.3.1 Effect of catalyst dosage on the photocatalytic degradation of RhB

The investigation focused on determining the optimal quantity of $\text{TiO}_2/\text{ZnS}/\text{g-C}_3\text{N}_4$ for efficient photocatalytic degradation of RhB under visible light conditions over 150 mins. Various catalyst loadings ranging from 0.3 g/L to 2 g/L were tested to evaluate their impact on the degradation process (Figure 4.10a). As the catalyst loading increased from 0.3 g/L to 1 g/L, the removal efficiency of RhB showed a significant improvement, rising from 71.2% to 89.9%. The highest removal rate of 89.9% was achieved at a catalyst loading of 1 g/L. However, further increasing the catalyst loading to 2 g/L resulted in a reduction in the removal rate to 83.3%. This indicates that exceeding the optimal catalyst loading can lead to saturation of the adsorbent photocatalyst surface, limiting the number of available sites for

RhB molecules and thus reducing the overall removal efficiency. An increased catalyst loading offers a greater number of binding or sorption sites for RhB molecules on $\text{TiO}_2/\text{ZnS}/\text{g-C}_3\text{N}_4$, thereby potentially enhancing the generation of ROS. Therefore, when the production of ROS increases, the degradation efficiency of RhB also experiences a corresponding increase. However, excessive catalyst loading can lead to the aggregation of adsorption sites, diminishing the total surface area available for RhB adsorption (Talebi et al., 2017). Moreover, an excessive quantity of $\text{TiO}_2/\text{ZnS}/\text{g-C}_3\text{N}_4$ caused heightened opacity, scattering, and a screening effect, which subsequently led to decreased light penetration, low ROS production and eventually reduced photocatalytic efficiency (Pouretedal & Sohrabi, 2016; Kale et al., 2020). Hence, an optimal dosage of 1 g/L of 1:1:1 ratio ternary $\text{TiO}_2/\text{ZnS}/\text{g-C}_3\text{N}_4$ was chosen for further studies.

4.3.2 Effect of initial concentration on the photocatalytic degradation of RhB

The study of the initial concentration of an aqueous solution that influences the photodegradation rate is necessary for the successful use of photocatalytic activity. According to the Beer-Lambert law, an increase in the initial OPs concentration would result in a decrease of photons penetrating the wastewater system, hence reducing the photon adsorption on the photocatalyst surface (Hassena, 2016). Therefore, the production of ROS would also decrease and reduce the degradation efficiency.

The degradation of RhB declined with the increasing amount of RhB concentration from 10 mg/L to 25 mg/L (Figure 4.10b). At a lower initial concentration of RhB, a higher rate of adsorption and removal under visible irradiation was observed. This phenomenon is attributed to the ability of visible light to easily penetrate the solution at lower RhB concentrations, thereby enhancing the photonic efficiency as the initial dye concentration

increases (Kanakaraju & Chandrasekaran, 2023). On the contrary, as the initial RhB concentration rises, the collision frequency between the dye molecules and photons also increases (Kanakaraju et al., 2022) resulting in a reduced degradation rate of RhB. Moreover, the increased number of RhB molecules absorbing a significant portion of the incoming photons leads to less efficient degradation of RhB. The optimal initial RhB concentration for achieving maximum efficiency of the 1:1:1 ratio ternary $\text{TiO}_2/\text{ZnS}/\text{g-C}_3\text{N}_4$ composite was determined to be 10 mg/L.

4.3.3 Effect of initial solution pH level on the photocatalytic degradation of RhB

The photocatalytic degradation of RhB demonstrates variation under different pH levels of the solution, which, in turn, affects the surface charge of the catalyst. The pH level at which the photocatalyst's surface has a net zero charge is referred to as pH_{pzc} (point of zero charge). Determination of pH_{pzc} provides insights into how functional groups ionize at the adsorbent surface and their interactions with the adsorbate in the solution. The pH_{pzc} of ternary $\text{TiO}_2/\text{ZnS}/\text{g-C}_3\text{N}_4$ heterostructure which was determined using the drift method (Kosmulski, 2020) was found to be at pH 6 which can be assumed almost near to neutral pH (Figure 4.11) (da Costa et al., 2015; Kanakaraju et al., 2018). The value represents the potential of attraction and repulsion between the catalyst and RhB dye in the treatment system. Figure 4.10c shows that the removal efficiency of RhB dye increases when the pH of the solution increases from acidic to basic (pH 3 to pH 10). When the pH is more than pH 6, the $\text{TiO}_2/\text{ZnS}/\text{g-C}_3\text{N}_4$ is expected to carry a negative charge and would attract a higher amount of RhB compound enhancing the adsorption and photocatalytic effects. Contrarily, when the operating $\text{pH} < \text{pH}_{\text{pzc}}$, $\text{TiO}_2/\text{ZnS}/\text{g-C}_3\text{N}_4$ is positively charged producing an electrostatic force that repels the RhB compound (cationic dye) from the surface of $\text{TiO}_2/\text{ZnS}/\text{g-C}_3\text{N}_4$. Therefore, reducing the degradation efficiency towards RhB dyes. The

correlation between pH_{pzc} and the enhanced degradation efficiency highlights the significance of surface charge interactions in the photocatalytic process, emphasizing the role of electrostatic forces in governing the effectiveness of the treatment system (Kumar & Pandey, 2017; Mittal et al., 2019). Thus, the RhB degradation efficiency using the ternary TiO₂/ZnS/g-C₃N₄ heterostructure exhibited the highest at the unadjusted pH of 7.2 (89.9%), followed by pH 10 (85.4%) and pH 7.0 (82.5%). The lowest degradation was attained at pH 3 (72.4%).

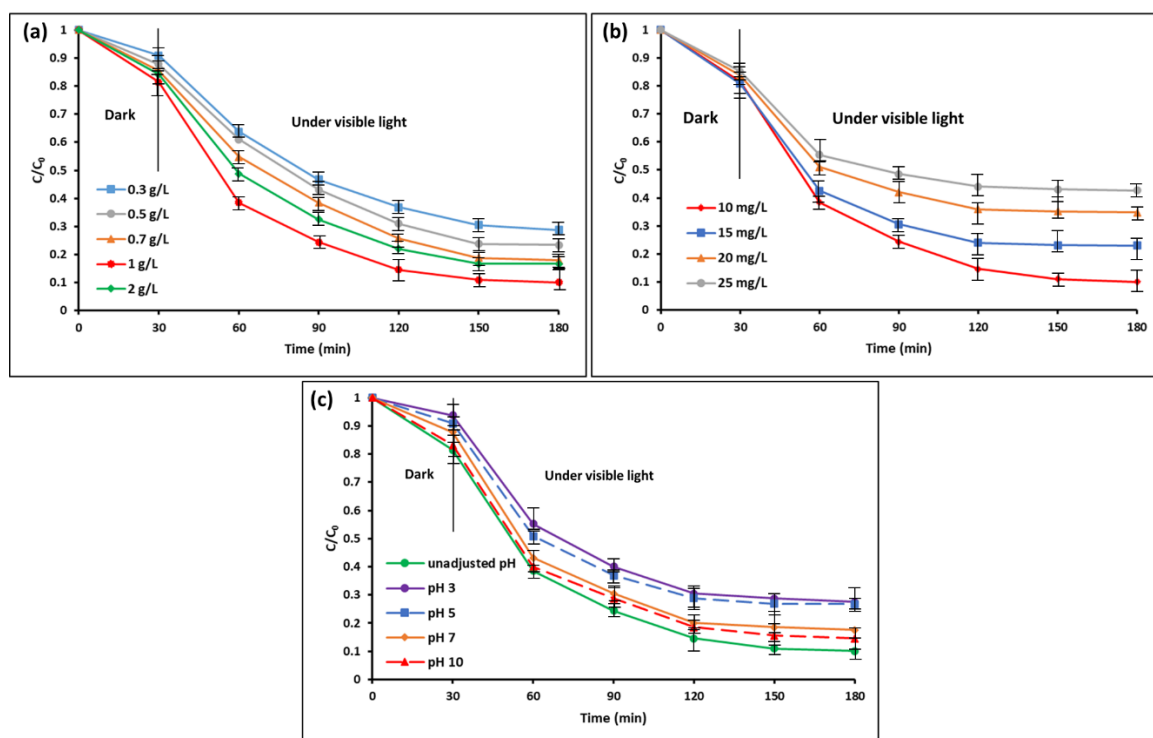


Figure 4.10: RhB degradation performance efficiency of TiO₂/ZnS/g-C₃N₄ under different conditions (a) dosage, (b) initial concentration and (c) solution pHs

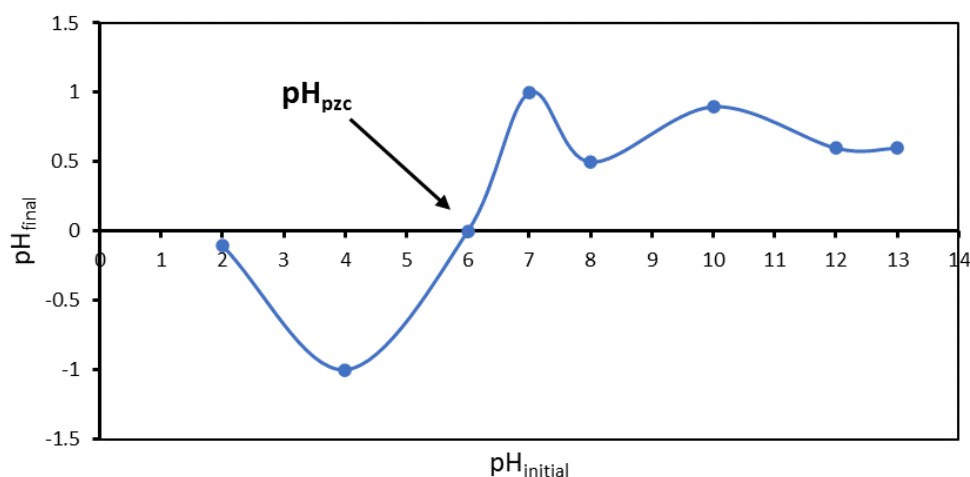


Figure 4.11: The point zero charge plot of TiO₂/ZnS/g-C₃N₄

4.4 Photocatalytic performance: Mixed organic pollutants

To further investigate the universality of the ternary TiO₂/ZnS/g-C₃N₄ nanocomposite, the photocatalytic degradation of hard-to-degrade OPs, such as a basic dye, anionic dye, and a phenolic compound (RhB, MeO, and 2CP) was assessed. The experimental findings demonstrated that the ternary TiO₂/ZnS/g-C₃N₄ nanocomposite exhibited superior degradation efficiency towards RhB compared to MeO but displayed the lowest degradation capability when exposed to 2CP (Figure 4.12a). Similar trends are exhibited in the kinetics study, whereby RhB shows the highest photodegradation rate constant (k) at 0.0105 min⁻¹ to compare with MeO and 2CP which are 0.0095 min⁻¹ and 0.0061 min⁻¹, respectively (Figure 4.12b). The absorbance spectra of different dyes over ternary TiO₂/ZnS/g-C₃N₄ could be observed at 554 nm (RhB), 454 nm (MeO) and 274 nm (2CP), when RhB was present alongside other pollutants (MeO and 2CP), a slight decrease in the degradation efficiency of RhB was observed (82.7%) compared to its degradation when treated alone (89.9%) (Figure 4.12c and 4.12d).

RhB is a fluorescent dye that belongs to the class of xanthene dyes (Shabir et al., 2018). On the other hand, MeO is an azo dye that belongs to the class of sulfonated aromatic compounds (Ren & Yang, 2017), which are relatively stable and difficult to degrade. The faster degradation of RhB compared to MeO can be attributed to several factors. First, the structure of RhB is more susceptible to ROS attack compared to MeO due to the presence of an electron-rich triarylmethane structure and a quaternary nitrogen atom (Nguyen et al., 2020). Second, RhB has a higher adsorption affinity to TiO_2 compared to MeO, which can enhance its photocatalytic degradation efficiency (Waghchaure et al., 2022). Finally, the degradation rate of MeO can be limited by its low solubility in water, which can reduce its availability for photocatalytic reactions (Boughelout et al., 2020).

Meanwhile, 2-chlorophenol (2CP) is a chlorinated phenolic compound commonly found in industrial wastewater and can have adverse effects on human health and the environment. Various studies have shown that 2CP has a slower degradation rate compared to other pollutants like RhB and MeO. A study by Jaafar et al. (2016) reported that photocatalytic degradation of 2CP (~20%) using TiO_2 -based nanoparticles resulted in a relatively low degradation rate compared to MO (~55%) under UV light. Similarly, as reported by Jiang et al., (2021) the degradation rate of 2CP (49%) using $\text{In}_2\text{O}_3/\text{TiO}_2$ is also lower than RhB (71%) under visible light irradiation. The chemical structure of 2CP, characterised by a chlorinated aromatic ring, is a contributing factor to its slow degradation rate. This specific ring configuration exhibits notable stability and resistance to degradation, making it less susceptible to common chemical and biological processes. In addition, the presence of the chlorine atom in the molecule makes it less reactive towards hydroxyl radicals, the powerful oxidising agents commonly used for the degradation of OPs.

The coexistence of other pollutants (MeO and 2CP) could interfere with the degradation of RhB because of the competition for oxidising agents and the competition for the ROS, hence, reducing the degradation efficiency of the RhB dye. Another reason is the adsorption of the dye molecule onto the surface of other pollutants or particles. The coexistence of other pollutants can shield the dye molecule from degrading agents, making it less accessible for degradation. Since the surface charge of ternary $\text{TiO}_2/\text{ZnS}/\text{g-C}_3\text{N}_4$ is negative, RhB dye molecules tend to adsorb significantly to the catalyst surface. The adsorption of RhB can decrease the degradation of other OPs in the solution because RhB molecules would have occupied some of the available reactive sites on the catalyst surface.

In addition, the real-world scenario of wastewater often involves the presence of various other contaminants that can interfere with the efficiency of photocatalytic treatment. Suspended solids, dissolved solids, and other particulate matter present in wastewater can adsorb onto the surface of the ternary $\text{TiO}_2/\text{ZnS}/\text{g-C}_3\text{N}_4$ photocatalyst, forming a barrier that hinders the contact between the catalyst and the target pollutants. These solid particles may shield the OPs from the active sites on the catalyst, reducing the availability of reactive species for degradation (Fernandes et al., 2020). Hence, the coexistence of other pollutants in the solution can interfere with the degradation of RhB dye.

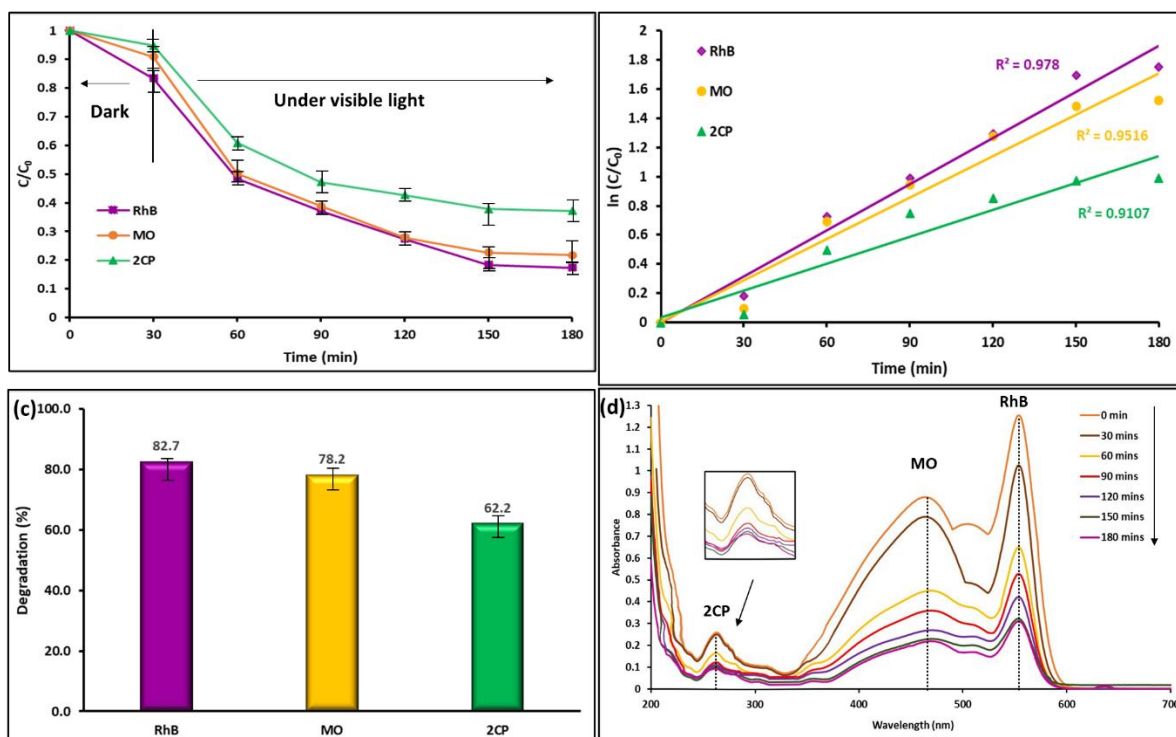


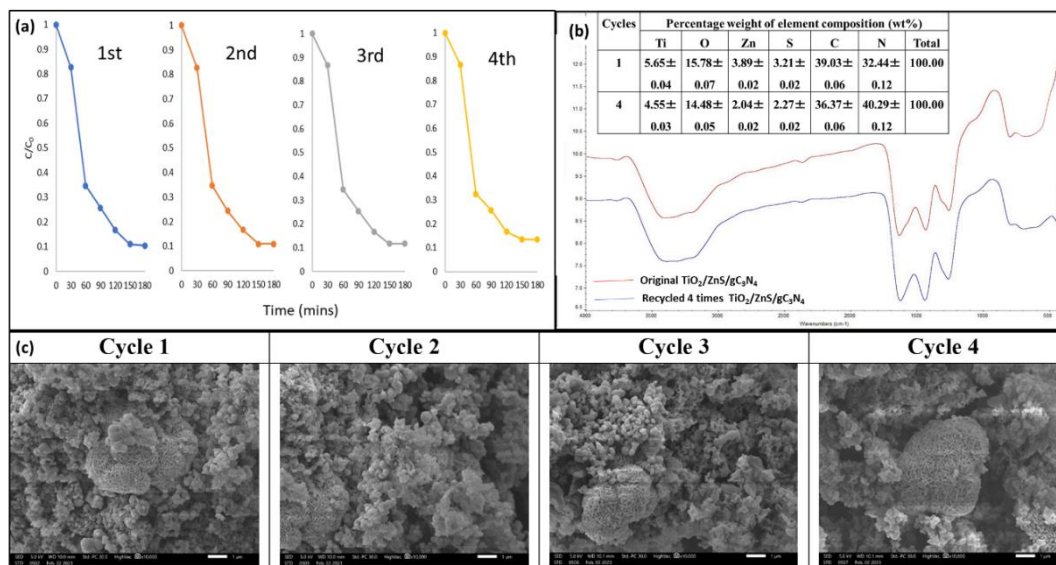
Figure 4.12 (a) Photocatalytic degradation of multi-pollutants, (b) pseudo first-order kinetic, (c) comparison of degradation percentages of multi-pollutants and (d) the UV spectra evolution versus time of different pollutants over ternary $\text{TiO}_2/\text{ZnS}/\text{g-C}_3\text{N}_4$

4.5 The recyclability studies

Stability is an important factor for industrial production and the large-scale application of catalysts (Ahmadpour et al., 2020). To assess the recyclability of the ternary $\text{TiO}_2/\text{ZnS}/\text{g-C}_3\text{N}_4$ nanocomposite, four cycles of degradation experiments were conducted under the same conditions (Figure 4.13). The results showed that the photocatalytic degradation rate of RhB dye and the percentage removal decreased from 89.9% to 86.6% after the ternary $\text{TiO}_2/\text{ZnS}/\text{g-C}_3\text{N}_4$ photocatalysts were cycled four times. This shows that the degradation rate of RhB dye by ternary $\text{TiO}_2/\text{ZnS}/\text{g-C}_3\text{N}_4$ photocatalysts only declined slightly after four consecutive cycles (Figure 4.13a).

Upon analysing the FTIR spectra, distinct changes, such as shifts in peaks and significant alterations in peak intensities, would likely be evident in cases of poor recyclability degradation of the photocatalyst. However, in the case of the original and recycled ternary $\text{TiO}_2/\text{ZnS}/\text{g-C}_3\text{N}_4$ samples, both showed similar FTIR pattern (Figure 4.13b) and FESEM images (Figure 4.13c), indicating the excellent stability of the as-prepared $\text{TiO}_2/\text{ZnS}/\text{g-C}_3\text{N}_4$. Nonetheless, a slight reduction could be observed from the comparison of the percentage weight of elemental compositions between cycle 1 and cycle 4. This reduction pertains to Ti (from $5.65 \pm 0.04\%$ to $4.55 \pm 0.03\%$), O (from $15.78 \pm 0.07\%$ to $14.48 \pm 0.05\%$), Zn (from $3.89 \pm 0.02\%$ to $2.04 \pm 0.02\%$), and S (from $3.21 \pm 0.02\%$ to $2.27 \pm 0.02\%$) as illustrated in Figure 4.11b..

The regeneration method of the $\text{TiO}_2/\text{ZnS}/\text{g-C}_3\text{N}_4$ photocatalyst involves straightforward filtration and washing of the photocatalyst with distilled water. This regeneration method offers advantages such as being cost-effective, minimising operational expenses and ensuring financial viability for large-scale industrial use (Liu et al., 2015; Liu et al., 2022). Secondly, the operational simplicity of this approach simplifies the regeneration process, making it advantageous for industrial settings where complex methods might be impractical.



4.13 (a) RhB removal of all four recycle treatments **(b)** FTIR spectra of $\text{TiO}_2/\text{ZnS}/\text{g-C}_3\text{N}_4$ photocatalyst before and after recycle study with their EDX elemental compositions **(c)** SEM images of recycled $\text{TiO}_2/\text{ZnS}/\text{g-C}_3\text{N}_4$ photocatalyst

4.6 Photocatalytic mechanism

When exposed to visible light irradiation, the composite catalysts become excited and generate various free radical species, such as holes (h^+), superoxide radical ($\bullet\text{O}_2^-$) and hydroxyl radical ($\bullet\text{OH}$), which possess strong redox reaction ability and are effective in degrading pollutants. To determine the primary role of active free radicals in the photocatalytic system, experiments were conducted using scavengers, including methanol (0.2 mmol/L), p-Benzoquinone (BQ) (0.2 mmol/L) and isopropyl alcohol (IPA) (0.2 mmol/L) for holes (h^+), superoxide radical ($\bullet\text{O}_2^-$), hydroxyl radical ($\bullet\text{OH}$), respectively. Additionally, hydrogen peroxide (H_2O_2) (0.1 mmol/L) was added as a stronger scavenger of the hydroxyl radical ($\bullet\text{OH}$). Figure 4.14 shows that methanol has a relatively weak inhibitory effect on degradation, indicating that h^+ is not significantly involved in the photocatalytic degradation process. Conversely, the presence of IPA and H_2O_2 especially BQ significantly

impairs the degradation performance of the 1:1:1 ratio ternary $\text{TiO}_2/\text{ZnS}/\text{g-C}_3\text{N}_4$, suggesting that $\bullet\text{O}_2^-$ and $\bullet\text{OH}$ free radicals are significantly important in the photocatalytic degradation of RhB dye. Based on the scavenger study, $\bullet\text{O}_2^-$ and $\bullet\text{OH}$ free radicals are significantly involved in the degradation of pollutants.

Figure 4.15 shows the schematic illustration of the proposed photocatalytic activity mechanism of ternary $\text{TiO}_2/\text{ZnS}/\text{g-C}_3\text{N}_4$ (1:1:1 ratio). The photocatalytic activity starts when photon energy is equal to or exceeds the band gap of the photocatalyst. The valence band (VB) electron will be at its highest occupied energy state, which increases the potential energy of the electron. The electrons would get excited and migrate to one of the highest energy levels in the conduction band (CB). The photocatalysis process leads to the generation of electron-hole pairs (e^-/h^+) on the surface of the photocatalyst. These pairs are composed of a positive hole on the valence band (h_{VB}^+) and an electron on the conduction band (e_{CB}^-) molecules. After formation, they can migrate to the surface of the photocatalyst semiconductor, where they undergo a redox reaction (as shown in Equation 4.1). The presence of oxygen as an electron scavenger can slow down the recombination rate of the electron-hole pairs. This allows the photogenerated electrons to react with oxygen in wastewater containing OPs, producing superoxide anion radicals ($\bullet\text{O}_2^-$) (Equation 4.2). At the same time, hydroxyl radicals ($\bullet\text{OH}$) are formed when $\bullet\text{O}_2^-$ combine with H_2O (Equation 4.3). Since the valence band potential is greater than that of the standard potential of $\bullet\text{OH}/\text{H}_2\text{O}$ and $\bullet\text{OH}/\text{OH}^-$, thus facilitating the oxidation of OH^- and H_2O to produce $\bullet\text{OH}$ radical. Additionally, the hydroxyl radical can react with hydrogen peroxide (H_2O_2) to form hydroperoxyl radical ($\bullet\text{OH}_2$) and water (Equation 4.4). These ROS, $\bullet\text{O}_2^-$ and $\bullet\text{OH}$, are critical for oxidising OPs on the surface of a 1:1:1 ratio ternary $\text{TiO}_2/\text{ZnS}/\text{g-C}_3\text{N}_4$ photocatalyst. This process ultimately results in the production of non-toxic by-products such as carbon dioxide

(CO₂) and water (H₂O) (Eq. 4.5). The photocatalytic reactions involved in this process are summarised as follows:

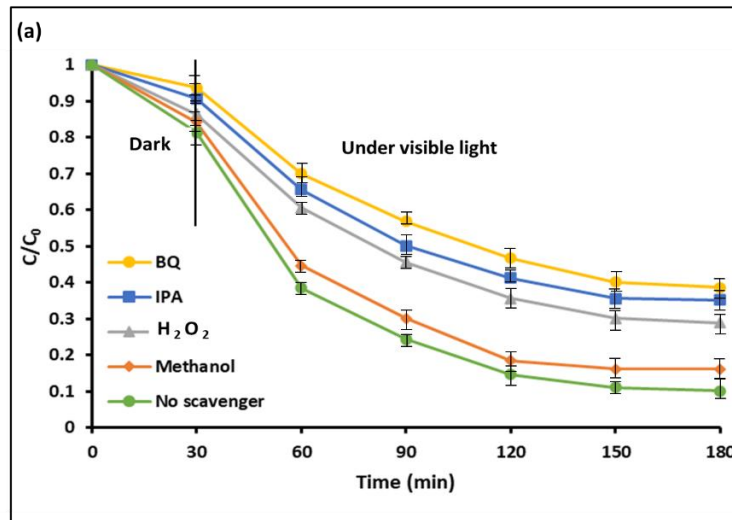
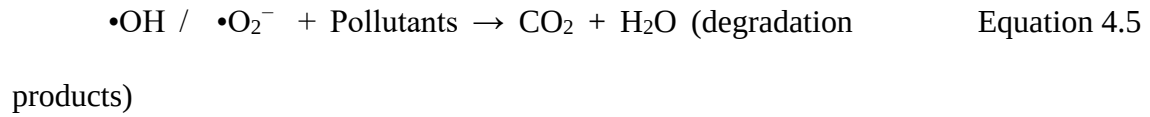
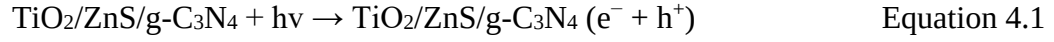


Figure 4.14: The determination of active species in the degradation of RhB using TiO₂/ZnS/g-C₃N₄

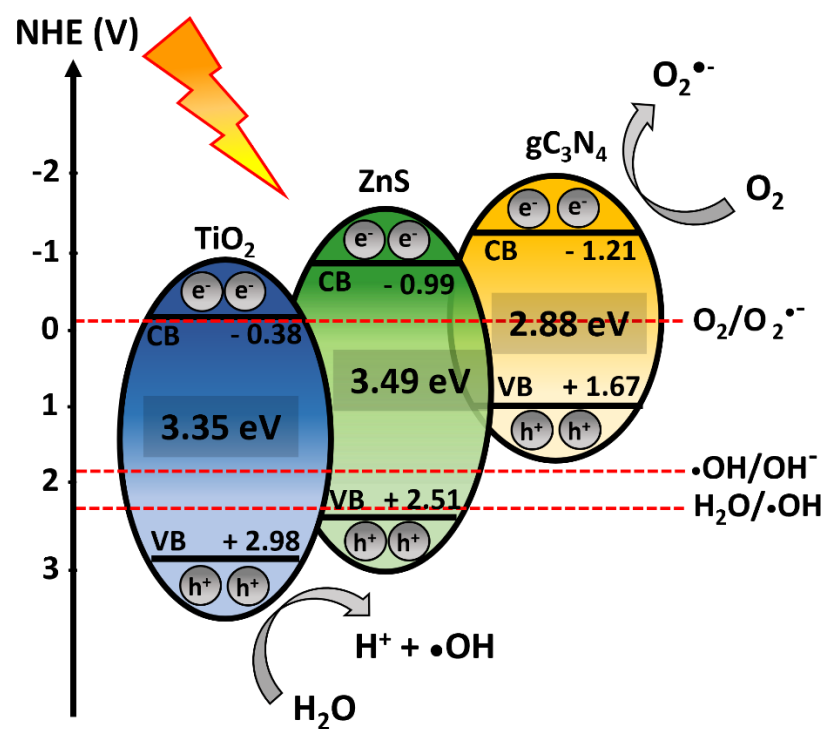


Figure 4.15 : The schematic illustration of the proposed photocatalytic activity mechanism of ternary TiO₂/ZnS/g-C₃N₄

CHAPTER 5

CONCLUSION AND RECOMMENDATIONS

5.0 Conclusion

In conclusion, this study underscores the significant potential of the ternary $\text{TiO}_2/\text{ZnS}/\text{g-C}_3\text{N}_4$ photocatalyst in efficiently breaking down pollutants in wastewater using visible light. The combination of TiO_2 with ZnS and $\text{g-C}_3\text{N}_4$ in a 1:1:1 ratio leads to exceptional photocatalytic performance and stability. Compared to pure TiO_2 , the synthesised ternary $\text{TiO}_2/\text{ZnS}/\text{g-C}_3\text{N}_4$ photocatalyst exhibits superior light absorption in the visible region due to its reduced band gap energy. When exposed to visible light, the photocatalyst demonstrates outstanding efficiency in degrading both individual and mixed pollutants. It achieves a remarkable removal rate of approximately 90% for RhB within a duration of 180 mins, while also significantly reducing the concentrations of RhB, MO, and 2CP when present together. The study also emphasises the crucial role played by superoxide radicals ($\cdot\text{O}_2^-$) and hydroxyl radicals ($\cdot\text{OH}$) as significant contributors to the photocatalytic degradation of RhB. The recycling experiments confirm the recyclability of the ternary $\text{TiO}_2/\text{ZnS}/\text{g-C}_3\text{N}_4$ photocatalysts, as it maintains its photocatalytic activity even after undergoing four cycles, albeit with a slight decline in the degradation rate of RhB dye. The stability of ternary $\text{TiO}_2/\text{ZnS}/\text{g-C}_3\text{N}_4$ photocatalysts, as demonstrated in the recycling tests, offers significant cost efficiency, productivity, and maintenance benefits. Their consistent photocatalytic performance ensures reliable operation, optimizing resource utilization and enhancing overall productivity. Moreover, lower maintenance requirements result in decreased downtime, reducing labour and equipment costs. This stability not only saves expenses but also lessens the environmental impact by minimizing the need for frequent

photocatalyst replacements, promoting sustainable practices. Overall, the ternary $\text{TiO}_2/\text{ZnS}/\text{g-C}_3\text{N}_4$ photocatalyst holds great promise for sustainable wastewater treatment, offering enhanced efficiency, stability, and recyclability in the degradation of OPs.

5.1 Recommendations

Alternative approaches are worth exploring for utilising the $\text{TiO}_2/\text{ZnS}/\text{g-C}_3\text{N}_4$ photocatalyst that deviates from its conventional powdered form, as the latter poses challenges in terms of retrieval after treatment. Instead, consideration can be given to the design of immobilised forms such as films or membranes, which would be more practical for pilot-scale applications in water treatment. Flat sheet or hollow fibre configurations, in particular, hold promise for such membrane-based designs. Additionally, future research could focus on investigating the use of natural polymers, specifically alginate, as a matrix for immobilising TiO_2/ZnS materials in the form of beads or hydrogels.

It is also recommended to employ analytical techniques such as liquid chromatography-mass spectrometry (LC-MS), liquid chromatography-tandem mass spectrometry (LC-MS/MS) and gas chromatography-mass spectrometry (GC-MS) for the identification of degradation products during the photodegradation of RhB using the $\text{TiO}_2/\text{ZnS}/\text{g-C}_3\text{N}_4$ photocatalyst. The extent of mineralisation can be monitored using total organic carbon (TOC) or dissolved organic carbon (DOC) indicators.

To advance the field, it is important to explore innovative designs for photocatalytic reactors that incorporate immobilised $\text{TiO}_2/\text{ZnS}/\text{g-C}_3\text{N}_4$ photocatalysts responsive to visible light, with a particular emphasis on utilising sunlight instead of artificial light sources, which have been predominantly used in laboratory settings. Significant effort should be directed towards addressing challenges related to material adhesion to the membrane, ensuring

functionality within the photoreactor (including configurations, types, mass transport, and radiative transfer), and minimising issues such as material leaching and fouling.

While the use of ternary TiO_2 -based photocatalysts for wastewater treatment is gaining popularity, there are concerns regarding their potential toxicity to plants, aquatic life, and human health. The toxicity of these catalysts, as well as the toxicity of the treated water, remains uncertain and requires further investigation. It is crucial to closely examine the relationship between toxicity and TiO_2 -based photocatalysts in future research. The assessment of catalyst toxicity should consider factors such as chemical composition and the presence of fine particles.

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APPENDICES

Appendix A: Journal Publications

1. Kanakaraju, D., & **Chandrasekaran, A.** (2023). Recent advances in TiO₂/ZnS-based binary and ternary photocatalysts for the degradation of organic pollutants. *Science of The Total Environment*, 868, 161525. <https://doi.org/10.1016/j.scitotenv.2023.161525>.

Appendix B: Photocatalytic degradation of RhB using unpurified g-C₃N₄ and purified g-C₃N₄.

g-C ₃ N ₄	Degradation of RhB ±SD (%)
Unpurified	58.529±0.001
Purified	70.278±0.001

Appendix C: Photocatalytic degradation of RhB using different ratios of TiO₂/ZnS/g-C₃N₄

TiO ₂ /ZnS/g-C ₃ N ₄ ratio	Degradation of RhB ±SD (%)
1:1:0.3	71.613±0.002
1:1:0.5	75.755±0.001
1:1:0.7	81.356±0.001
1:1:1	89.896±0.003
1:1:2	83.289±0.001

Appendix D: Photocatalytic degradation of RhB using different photocatalysts

Different photocatalyst	Degradation of RhB ±SD (%)
TiO ₂	21.600±0.0001
ZnS	17.215±0.0002

g-C ₃ N ₄	70.278±0.0002
TiO ₂ /ZnS/g-C ₃ N ₄	89.896±0.003

Appendix E: Photocatalytic degradation of RhB using different photocatalysts under different conditions (a) dosage (0.3 g/L -2.0 g/L), (b) initial concentration (10 mg/L -25 mg/L) and (c) solution pHs (pH 3- pH10)

Photocatalyst Dosage (g/L)	Degradation of RhB ± SD (%)
0.3	71.243±0.001
0.5	76.555±0.001
0.7	82.031±0.001
1.0	89.896±0.003
2.0	83.291±0.001
MB Concentration (mg/L)	Degradation of RhB ± SD (%)
10	89.896±0.003
15	76.930±0.003
20	65.124±0.002
25	57.333±0.001
pH	Degradation of RhB ± SD (%)
3	72.424±0.002
5	73.275±0.001
7	82.474±0.003
10	85.357±0.005

Appendix F: Photocatalytic degradation of multi-pollutants over ternary TiO₂/ZnS/g-C₃N₄

Pollutant	Degradation of pollutants ±SD (%)
RhB	82.670±0.002
MeO	78.236±0.004
2CP	62.192±0.004

Appendix G: RhB removal at different number of cycles using TiO₂/ZnS/g-C₃N₄ photocatalyst

Cycle	Degradation of RhB (%)
1	89.529±0.002
2	89.023±0.004
3	88.259±0.004
4	86.576±0.004

Appendix H: The determination of active species in the degradation of RhB using TiO₂/ZnS/g-C₃N₄

Scavengers	Degradation of RhB ±SD (%)
BQ	61.415±0.002
IPA	64.782±0.002
H ₂ O ₂	71.077±0.002
Methanol	83.901±0.001