Faculty of Resource Science & Technology

The Development of Ternary TiO_2/ZnS/g-C_3N_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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Signature

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ABSTRACT

The photocatalytic degradation efficiency of titanium, TiO_2-based photocatalysts is limited, especially under visible light. To enhance their efficiency, ternary composites can be created by combining TiO_2 with other photocatalysts which are graphitic nitride (g-C_3N_4) and zinc sulphide (ZnS). To investigate the photocatalytic efficiency for the degradation of single and mixed pollutants under visible light, a ternary TiO_2/ZnS/g-C_3N_4 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-C_3N_4 loading in the TiO_2/ZnS/g-C_3N_4 ratio was determined through several ratios (1:1:X), where X represents different quantities of g-C_3N_4 (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-C_3N_4 loading of 1 g, resulting in a TiO_2/ZnS/g-C_3N_4 ratio of 1:1:1. The synthesised ternary TiO_2/ZnS/g-C_3N_4 (1:1:1) photocatalyst exhibited enhanced absorption in the visible light region compared to the pristine TiO_2. 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 TiO_2/ZnS/g-C_3N_4 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 TiO_2/ZnS/g-C_3N_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, g-C_3N_4, photodegradation

Pembangunan Fotokatalis Ternari TiO_2/ZnS/g-C_3N_4 untuk Mempertingkatkan Fotodegradasi Pencemar Organik Menggunakan Cahaya Nampak

ABSTRAK

Prestasi fotokatalis titanium diokosida, TiO_2 dalam penguraian fotokatalisis pencemar adalah terhad, terutamanya di bawah cahaya nampak. Untuk meningkatkan kecekepannya, komposit ternari boleh disintesis dengan menggabungkan TiO_2 dengan fotokatalis lain seperti zink sulfida, ZnS dan grafitik karbon nitrida, g-C_3N_4. Untuk mengkaji kecekapan fotokatalis ternari iaitu TiO_2/ZnS/g-C_3N_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 g-C_3N_4 yang diperlukan untuk menghasilkan TiO_2/ZnS/g-C_3N_4 ditentukan melalui beberapa nisbah (1:1:X), di mana X mewakili kuantiti g-C_3N_4 yang berbeza (dalam g): X = 0.3, 0.5, 0.7, 1, dan 2. Kadar fotodegradasi RhB tertinggi dicapai pada jumlah g-C_3N_4 ialah 1 g, menghasilkan nisbah TiO_2/ZnS/g-C_3N_4 sebanyak 1:1:1. Fotokatalis ternari TiO_2/ZnS/g-C_3N_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 TiO_2/ZnS/g-C_3N_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 TiO_2/ZnS/g-C_3N_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, g-C_3N_4, fotodegradasi*

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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_3N_4	Graphitic carbon
G	Graphene
GO	Graphene oxide
Fe_2O_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_2O	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 (TiO_2) 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 TiO_2 that require attention. The large band gap of TiO_2 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 TiO_2 nanoparticles, resulting in the formation of suspension (Romanello & Fidalgo de Cortalezzi, 2013). This could block the active sites on the TiO_2 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 TiO_2/ZnS/g-C_3N_4 photocatalyst to overcome the limitations of TiO_2. 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 TiO_2 and ZnS enhanced the photocatalytic efficiency rate by increasing ROS production (Talebi et al., 2017; Sivaranjani et al., 2022).

Despite their advantages, TiO_2/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 TiO_2/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 TiO_2/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 TiO_2/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 TiO_2/ZnS binary photocatalysts with carbonaceous materials can be considered. Carbon can function as a sensitizer to sensitize TiO_2 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-C_3N_4), a visible-light-driven

photocatalyst with a narrow band gap. g-C_3N_4 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-C_3N_4 to TiO_2 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 TiO_2/ZnS/g-C_3N_4 photocatalyst for the degradation of OPs under visible light irradiation, providing valuable insights for environmental remediation applications.

1.2 Problem Statement

TiO_2 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 TiO_2 often leads to the aggregation of TiO_2 nanoparticles and the formation of suspensions. The aggregation of active sites on the TiO_2 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 TiO_2/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 TiO_2/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, g-C_3N_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 TiO_2/ZnS/g-C_3N_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 g-C_3N_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 TiO_2/ZnS/g-C_3N_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 TiO_2/ZnS/g-C_3N_4 photocatalyst in degrading single pollutant, RhB dye?,

iv. How does the ternary TiO_2/ZnS/g-C_3N_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 TiO_2/ZnS/g-C_3N_4 photocatalyst in the degradation of RhB dye?

1.4 Objectives

The objectives of this study are to:

i. investigate the modification of ternary TiO_2/ZnS/g-C_3N_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 TiO_2/ZnS/g-C_3N_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