



UTHM

Universiti Tun Hussein Onn Malaysia

GARIS PANDUAN PENULISAN *WRITING GUIDELINE*

TESIS SECARA PENERBITAN *THESIS BY PUBLICATIONS*

PUSAT PENGAJIAN SISWAZAH
CENTRE FOR GRADUATE STUDIES

UNIVERSITI TUN HUSSEIN ONN MALAYSIA
UNIVERSITI TUN HUSSEIN ONN MALAYSIA

EDISI PERTAMA | APRIL 2023
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1.0 TUJUAN

PURPOSE

Garis panduan ini diwujudkan bertujuan untuk memberikan panduan yang jelas berkenaan format, susun atur dan tatacara penulisan tesis secara penerbitan kepada warga Universiti Tun Hussein Onn Malaysia (UTHM) umumnya dan para pelajar pascasiswazah khususnya. Penggunaan penulisan tesis secara penerbitan ini adalah terhad kepada para pelajar pascasiswazah yang berdaftar di dalam mod penyelidikan sahaja.

This guideline is established to provide a clear direction with regards to the format, arrangement, and procedure in writing the thesis by publication for Universiti Tun Hussein Onn Malaysia (UTHM) as a whole, and particularly for the postgraduate students. The employment of the thesis by publication is limited to postgraduate students enrolled in research mode only.

2.0 TAFSIRAN

DESCRIPTION

Tafsiran bagi suatu terma/perkataan yang digunakan dalam garis panduan ini adalah merujuk kepada tafsiran yang dinyatakan dalam **Buku Peraturan Akademik Pengajian Siswazah; Universiti Tun Hussein Onn Malaysia Edisi ke-5 tahun 2021** atau apa-apa pindaan yang berkaitan selepas ini. Tafsiran tambahan selain dari yang disenaraikan di Buku Peraturan Akademik Pengajian Siswazah Universiti Tun Hussein Onn Malaysia adalah:

The description for the terms/word use throughout this guideline are in accordance with the description reported in the Fifth Edition (5th Edition) of the Postgraduate Academic Regulation, year 2021 or any related amendments done onwards. Additional description apart from the one listed in the Postgraduate Academic Regulations; Universiti Tun Hussein Onn Malaysia are:

“penulisan tesis secara penerbitan” ertinya penulisan tesis yang disertakan bersama kompilasi artikel-artikel jurnal yang telah diterbitkan.

“thesis writing by publication” is defined as a thesis writing embedded with the compilation of published journal articles.

3.0 PENULISAN TESIS SECARA PENERBITAN

THESIS WRITING BY PUBLICATION

Penulisan tesis secara penerbitan merupakan salah satu pilihan format penulisan tesis yang diterima pakai oleh UTHM. Secara amnya, semua pelajar sarjana dan doktor falsafah UTHM yang berdaftar di dalam mod penyelidikan diberikan **TIGA (3)** pilihan format penulisan seperti yang tersenarai di bawah:

*Thesis writing by publication is one of the theses writing format accepted by UTHM. Generally, UTHM's postgraduate students enrolled in Master and Doctor of Philosophy programmes by research mode is given **THREE (3)** writing format options as listed below:*

- I : Penulisan Tesis secara Konvensional
Conventional based thesis writing
- II : Penulisan Tesis secara Penerbitan
Thesis writing by publications
- III : Penulisan Tesis secara Industri
Industrial based thesis writing

Penulisan tesis secara penerbitan ini adalah terhad kepada pelajar pascasiswazah yang telah berjaya menerbitkan artikel – artikel hasil dapatan dari penyelidikan yang dijalankan sepanjang pengajian di jurnal-jurnal tersohor dan berindeks *Web of Science (WOS)* dalam bidang yang diiktiraf oleh Senat.

Thesis writing by publication is limited to postgraduate students who had managed to publish articles related to the findings gained from the research work done throughout the study duration in prominent journal and Web of Science (WOS) indexed in the field recognized by the Senate.

Peraturan-peraturan yang terkandung di dalam garis panduan ini adalah tafsiran dari **Perkara 17**, yang dinyatakan di dalam **Buku Peraturan Akademik Pengajian Siswazah, Universiti Tun Hussein Onn Malaysia Edisi ke-5 tahun 2021** atau apa-apa pindaan yang berkaitan selepas ini.

*Regulations consist in this guideline is reflected from **Perkara 17**, stated in the **Fifth edition (5th Edition) of Postgraduate Academic Regulation, Universiti Tun Hussein Onn Malaysia, year 2021** or any related amendments done onwards.*

4.0 PROSEDUR OPERASI STANDARD (SOP) PERMOHONAN PENULISAN TESIS SECARA PENERBITAN

STANDARD OPERATING PROCEDURE (SOP) FOR THE APPLICATION OF THESIS WRITING BY PUBLICATION

Kelulusan permohonan penulisan tesis secara penerbitan adalah tertakluk kepada kriteria yang disenaraikan seperti berikut:

The approval for thesis writing by publication is subjected to the following criteria:

- a) Pelajar perlu membuat permohonan ke fakulti melalui penyelia untuk menulis tesis secara penerbitan.

The student needs to apply to the faculty via their respective supervisor to write the thesis by publication.

- b) Pihak Fakulti perlu melaksanakan proses semakan kualiti penerbitan artikel pelajar mengikut kriteria yang disenaraikan di bawah:

The respective faculty need to execute an evaluation process to determine the quality of students' published articles in accordance with the criteria as listed below:

- i) Pelajar yang memohon untuk menulis tesis secara penerbitan hendaklah telah menduduki dan lulus penilaian pertama (*proposal defence*) dan;
Student applying to write the thesis by publication should had undergoes and passed the first assessment (proposal defense) and;

- ii) Artikel jurnal yang diterbitkan selari dengan skop dan objektif penyelidikan yang sedang dijalankan dan;
The published journal articles should be in line with the ongoing research scope and objectives and;

- iii) Tarikh artikel diterbitkan adalah di dalam julat masa pelajar berdaftar di program pascasiswazah UTHM sebagai pelajar aktif dan;
The journal articles should be published within the range of time whereby the student is matriculated in UTHM's postgraduate programme as an active student and;

- iv) Pelajar mestilah merupakan samada penulis utama "*first author*" atau pengarang yang dirujuk "*corresponding author*" bagi setiap artikel jurnal dan;
The student should be either the first author or the corresponding author for each journal article.

- v) Setiap artikel jurnal perlu ditulis bersama sekurang-kurangnya penyelia utama dan;

Each journal article should at least be written alongside with the main supervisor and;

- vi) Sekiranya pelajar mempunyai **DUA (2)** atau lebih afiliasi, UTHM perlu diletakkan sebagai afiliasi pertama dan;

Should the student have TWO (2) or more affiliation, UTHM should be assigned as the first affiliation and;

- vi) Setiap artikel jurnal perlu berstatus diterbitkan “*published*” atau berstatus “*article in press*”.

Each journal article should hold the status of either “published” or “article in press”.

- c) Sekiranya permohonan pelajar di sokong oleh penyelia dan fakulti, pihak fakulti perlu mengemukakan surat rasmi serta bukti penerbitan kepada Dekan Pusat Pengajian Siswazah untuk proses semakan; dan kelulusan permohonan penulisan tesis secara penerbitan oleh Jawatankuasa Akademik Pascasiswazah (JAPS).

Should the student’s application be approved by the supervisor and faculty, the respective faculty should provide an official letter along with proof of publications to the Dean of Centre for Graduate Studies for review; and the approval of thesis writing by publication to be made by Jawatankuasa Akademik Pascasiswazah (JAPS)

Carta alir Prosedur Operasi Standard (SOP) bagi permohonan tesis secara penerbitan adalah seperti di **Lampiran 1**.

*The flowchart of the Standard Operating Procedure (SOP) for the application of thesis writing by publication are as in **Attachment 1**.*

5.0 KRITERIA PENERBITAN BAGI KELULUSAN PENULISAN TESIS SECARA PENERBITAN

PUBLICATION CRITERIA FOR THE APPROVAL OF THESIS WRITING BY PUBLICATION

Kelulusan permohonan penulisan tesis secara penerbitan adalah tertakluk kepada jumlah penerbitan dan kualiti penerbitan minimum seperti yang dinyatakan di bawah:

Approval towards the application of thesis writing by publication are subjected to the number of publication and the minimum quality of publication as tabulated below:

Kriteria <i>Criteria</i>	Sarjana <i>Master</i>	Doktor Falsafah <i>Doctor of Philosophy</i>
Bilangan Minimum Artikel Jurnal yang Diterbitkan <i>The minimum number of Published Journal Articles</i>	Tidak kurang dari DUA (2) artikel jurnal yang diterbitkan di jurnal berindeks <i>Web of Science (WOS)</i> dan; <i>No less than TWO (2) journal articles published in Web of Science (WOS) indexed journal and;</i>	Tidak kurang dari TIGA (3) artikel jurnal yang diterbitkan di jurnal berindeks <i>Web of Science (WOS)</i> dan; <i>No less than THREE (3) journal articles published in Web of Science (WOS) indexed journal and;</i>
Kriteria Jurnal dan Bilangan Minimum Artikel Jurnal <i>Journal Criteria and the Minimum Number of Journal Articles</i>	SATU (1) artikel jurnal diterbitkan dalam jurnal kuartil Q1 dan; <i>ONE (1) journal article published in the first quartile (Q1) journal and;</i> SATU (1) artikel jurnal diterbitkan dalam jurnal kuartil Q2 dan; <i>ONE (1) journal article published in the second quartile (Q2) journal and;</i>	DUA (2) artikel jurnal diterbitkan dalam jurnal kuartil Q1 dan; <i>TWO (2) journal article published in the first quartile (Q1) journal and;</i> SATU (1) artikel jurnal diterbitkan dalam jurnal kuartil Q2 dan; <i>ONE (1) journal article published in the second quartile (Q2) journal and;</i>
<p>Penentuan kuartil artikel jurnal adalah mengikut kriteria yang dinyatakan di bawah: <i>The determination of journal articles' quartile is in accordance with the criteria listed below:</i></p>		

	<p>1. Penentuan kuartil sesuatu artikel yang diterbitkan di jurnal adalah merujuk kepada Journal Citation Indicator (JCI) – Web of Science – Clarivate. <i>The determination of the published journal article's quartile is by referring to the Journal Citation Indicator (JCI) – Web of Science – Clarivate.</i></p> <p>2. Penentuan kuartil sesuatu artikel yang diterbitkan di jurnal adalah merujuk kepada tahun penerbitan artikel tersebut. <i>The determination of the published journal article's quartile is by refereeing to the year where the journal article was being published.</i></p>	
<p>Kriteria Tambahan <i>Additional Criteria</i></p>	<p>Artikel jurnal perlu berstatus diterbitkan "published" atau berstatus "article in press". <i>Each journal article should hold the status of either "published" or "article in press".</i></p>	<p>Artikel jurnal perlu berstatus diterbitkan "published" atau berstatus "article in press". <i>Each journal article should hold the status of either "published" or "article in press".</i></p>

6.0 KRITERIA TAMBAHAN BAGI KELULUSAN PENULISAN TESIS SECARA PENERBITAN

ADDITIONAL CRITERIA TOWARDS THE ENDORSEMENT OF THESIS WRITING BY PUBLICATION

Permohonan penulisan tesis secara penerbitan yang telah diluluskan di JAPS juga tertakluk kepada kriteria tambahan seperti yang dinyatakan di bawah:

The application of thesis writing by publication that had been endorsed by JAPS are subjected to the additional criteria as mentioned below:

- a) Bagi objektif penyelidikan yang telah tercapai tanpa penerbitan yang diterbitkan di jurnal berstatus kuartil Q1 dan Q2, dapatan dari objektif penyelidikan tersebut perlu di tulis merujuk kepada format **Penulisan Tesis secara Konvensional**.
For research objective(s) that had been fulfilled without any publication published in quartile 1 and quartile 2 journal, the findings gained from the respective objective need to be written by referring to the Conventional Based Thesis Writing format.

- b) Bagi calon warganegara Malaysia, tesis dan penerbitan mestilah ditulis dalam **SATU (1)** bahasa sahaja sama ada Bahasa Melayu atau Bahasa Inggeris.

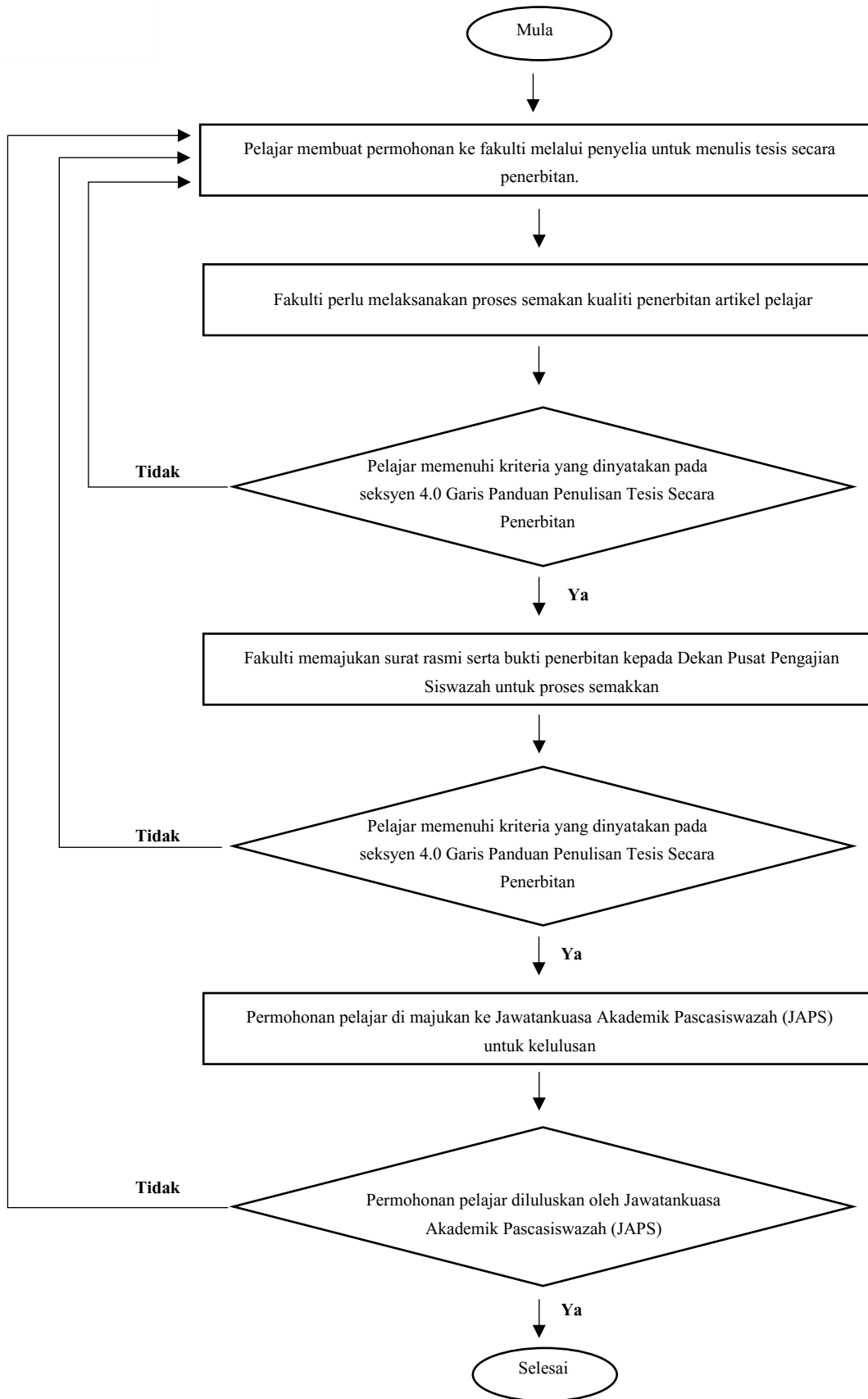
*For Malaysian citizen, both thesis and publications should be written in **ONE (1)** language only of either Bahasa Melayu or English.*

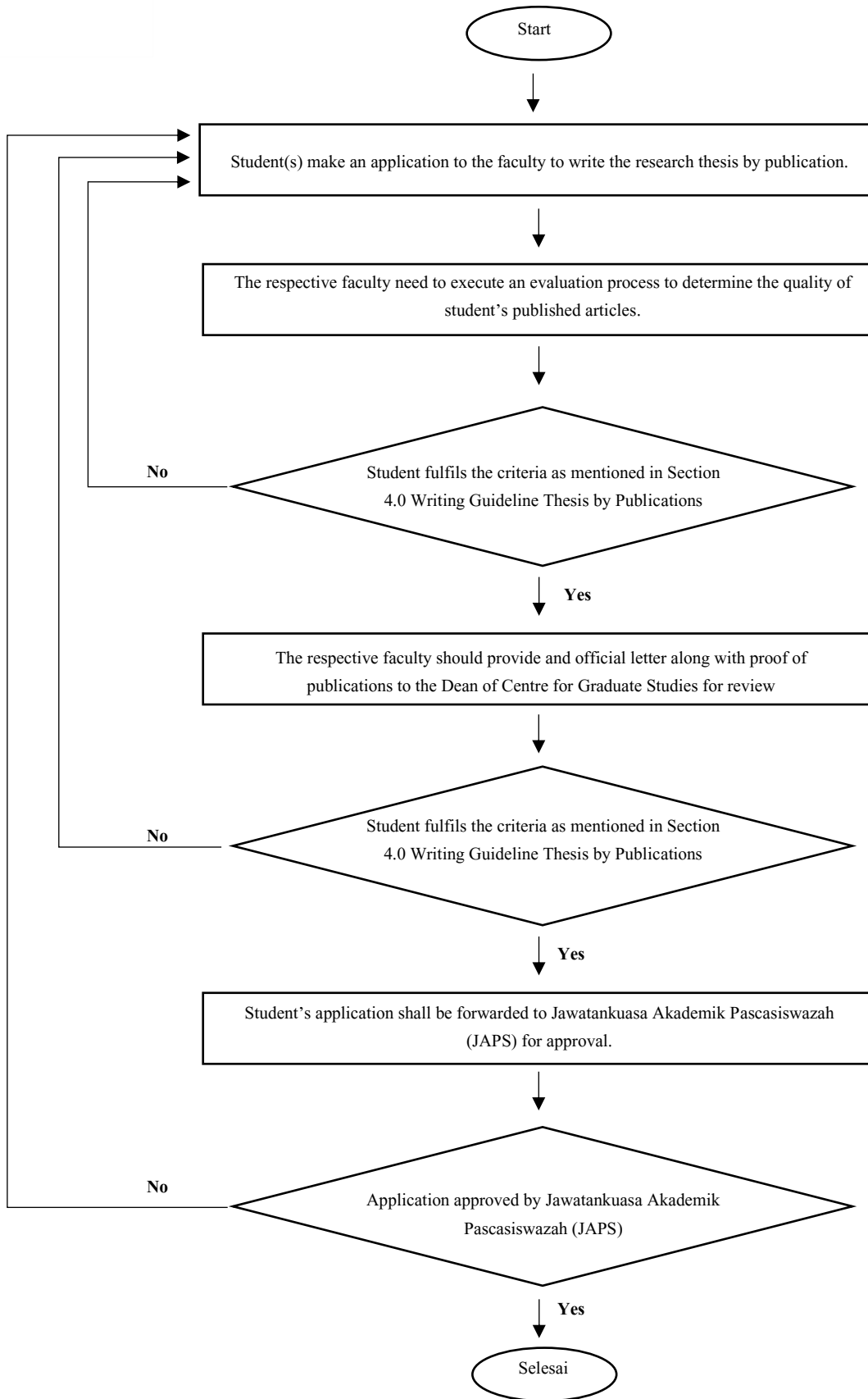
7.0 FORMAT DAN SUSUN ATUR TESIS SECARA PENERBITAN

FORMAT AND ARRANGEMENT OF THESIS BY PUBLICATION

Format dan susun atur tesis secara penerbitan adalah seperti di **Lampiran 2**.

The format and arrangement of thesis by publication are as in Attachment 2.





RESEARCH TITLE

(CAPITAL LETTER, TNR 12; 1.5 SPACING)

STUDENT'S NAME

(CAPITAL LETTER, TNR, 12)

UNIVERSITI TUN HUSSEIN ONN MALAYSIA

**UNIVERSITI TUN HUSSEIN ONN MALAYSIA
CONFIRMATION STATUS FOR ACADEMIC THESIS OF
MASTER'S / DOCTOR OF PHILOSOPHY DEGREE**

RESEARCH TITLE (TNR, 12, 1.5 SPACING)

ACADEMIC SESSION: 2022/2023

(ACADEMIC SESSION DURING THESIS SUBMISSION)

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FACULTY'S NAME (CAPITAL LETTER, TNR, 12, SINGLE SPACING)
UNIVERSITI TUN HUSSEIN ONN MALAYSIA

Examiners:

EXAMINER'S NAME (CAPITAL LETTER, TNR, 12, SINGLE SPACING)
FACULTY'S NAME (CAPITAL LETTER, TNR, 12, SINGLE SPACING)
UNIVERSITY'S NAME (CAPITAL LETTER, TNR, 12, SINGLE SPACING)

EXAMINER'S NAME (CAPITAL LETTER, TNR, 12, SINGLE SPACING)
FACULTY'S NAME (CAPITAL LETTER, TNR, 12, SINGLE SPACING)
UNIVERSITY'S NAME (CAPITAL LETTER, TNR, 12, SINGLE SPACING)

RESEARCH TITLE

(CAPITAL LETTER, TNR, 12; 1.5 SPACING)

STUDENT NAME

(CAPITAL LETTER, TNR, 12; 1.5 SPACING)

UNIVERSITI TUN HUSSEIN ONN MALAYSIA

I hereby declare that the work in this thesis is my own except for quotations and summaries which have been duly acknowledged.

Student :
STUDENT'S NAME (TNR, 12)

Date :

Supervisor :
SUPERVISOR'S NAME (TNR, 12)

ACKNOWLEDGEMENT

Kindly provide your acknowledgement here.

(TNR, 12, 1.5 SPACING)

ABSTRACT

Kindly provide your research abstract here (English Version).

(TNR, 12, 1.5 SPACING)

ABSTRAK

Kindly provide your research abstract here (Bahasa Melayu Version).

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- 5.6 Conclusion

CHAPTER 6 OBJECTIVE / THEME 4

- 6.1 Brief overview/ motivation of Objective 4/ Theme 4
- 6.2 List of Publications related to Objective 4 / Theme 4 (Limited to Q1 and Q2 only)
- 6.3 Major Findings related to Objective 4/ Theme 4
- 6.4 Attachments of Publications related to Objective 4/ Theme 4
- 6.5 Supplementary Information/ Findings from the research that is not reported in the Q1/Q2 Publications (May include other publications)
- 6.6 Conclusion

CHAPTER 7 CONCLUSION AND FUTURE WORK

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- A.1 CERTIFICATE 1
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- B.1 COPYWRITE CLEARANCE PAPER 1
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LIST OF SYMBOLS AND ABBREVIATIONS

A	- Absorbance
AS	- <i>Acacia senegal</i>
Au	- Gold
AV	- Aloe vera
BET	- Brunauer-Emmett-Teller
β	- Full Width at Half Maximum
C	- Concentration
CB	- Conduction Band
D, d	- Diameter
DR-UV	- Ultraviolet-Visible Diffuse Reflectance
E_{BG}	- Band gap energy
F	- Fluorine
FE-SEM	- Field Emission-Scanning Electron Microscopy
FTIR	- Fourier Transform Infrared
GNP	- Gold nanoparticle
HF	- Hydrogen fluoride
HOMO	- Highest occupied molecular orbital
k	- First-order-reaction rate
λ	- Wavelength
LUMO	- Lowest unoccupied molecular orbital
NBu.F	- Tetrabutylammonium fluoride
PTA	- Peroxotitanic acid
RB19	- Reactive Blue 19
SPR	- Surface plasmon resonance
STEM	- Scanning Transmission Electron Microscopy
TEM	- Transmission Electron Microscopy
TTIP	- Titanium isopropoxide
θ	- Angle of diffraction
t	- Time
TiO ₂	- Titanium dioxide

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CHAPTER 1

INTRODUCTION

1.1 OVERVIEW OF THE RESEARCH

The term photocatalysis is no longer unusual in the world of science and technology today. Dated back in 1910, the terms photocatalysis and photocatalyst made their first debut in a Germany textbook on photochemistry [1]. In general, photocatalysis can be defined as the alteration of chemical reaction in the presence of light, where a photocatalyst; a light-activated catalyst by absorbing light photon increases the rate of reaction without itself being altered or consumed at the end of reaction. This process is an excellent way to degrade organic pollutants [2,3]. Among the potential photocatalysts ever studied, titanium dioxide (TiO₂) has been more superior than the others and act as an ideal material for environmental remediation. TiO₂ has been widely applied in photocatalysis as coating agent, air purifier, water remediation agent, as well as for cancer treatment [4,5]. Being inexpensive, chemically stable, non-toxic, commercially available, easy to be prepared in the laboratory, and possessing high photocatalytic reactivity made TiO₂ being intensively studied for its photocatalytic properties [6–8].

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1.2 PROBLEM STATEMENT AND MOTIVATION

TiO₂ has emerged as a promising photocatalyst that can be applied in treating environmental pollution because of its photogenerated electron-hole pair that can transform to radical species which are highly oxidizing to mineralize organic pollutants adsorbed to its surface. However, large band gap that requires ultraviolet light activation and high photogenerated electron-hole recombination rate at the surface limit the versatility of TiO₂ as an efficient photocatalyst [29,32].

Therefore, the primary motivation of this research is to (TNR, 12, SINGLE SPACING)

1.3 OBJECTIVES OF STUDIES

To tackle the problems addressed in Section 1.1 and 1.2, this research has been designed with specific objectives as below:

1. To synthesize blank TiO₂, and modified TiO₂ (F-TiO₂, Au-TiO₂ and Au/F-TiO₂) by thermal degradation of PTA, and analyse the effect of foreign species on the characteristics of TiO₂

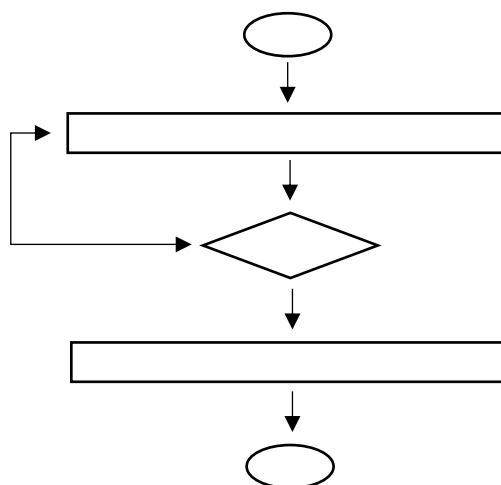
2. To quantify the effect of Acacia Senegal and aloe vera as stabilizers in the synthesis of Au-colloid
3. To quantify the effect of eucalyptus globulus honey, Zingiber officinale, MicroAlgae and Cyanobacteria in the synthesis of Au-colloid
4. To determine the photocatalytic efficiency and further evaluate the degradation kinetics of the synthesized TiO₂ in degrading reactive dye
5. (TNR, 12, SINGLE SPACING)

1.4 SCOPE OF STUDY

In order to achieve the above-mentioned objectives, the scope of study is limited as below:

1. TiO₂ is synthesized by thermal degradation of PTA using TTIP and H₂O₂
2. The synthesized TiO₂ is characterized using XRD, FTIR, FE-SEM, BET, and DR-UV
3. Fluorine modifiers are limited to NBu₄F, and HF
4. The deposition of GNP are limited to two method namely direct deposition and post deposition
5. Au-colloid stabilizers are limited to Arabic gum and aloe vera
6. Au-colloid shall be modified via the addition of eucalyptus globulus honey Zingiber officinale, MicroAlgae and Cyanobacteria
7. RB19 was used as the target effluent to assess the photocatalytic efficiency of synthesized TiO₂.
8. Photocatalytic reaction was done under the illumination of blue light (475 nm) to mimic the visible light in the environment.
9. (TNR, 12, SINGLE SPACING)

1.5 FLOW CHART OF THE STUDY



1.6 SIGNIFICANCE OF STUDY AND NOVELTY

This study is hoped to be able to contribute in broadening the spectrum of TiO₂ research and development by improvising an effective method in synthesizing visible light active TiO₂ for environmental purification. Based on literature (**TNR, 12, SINGLE SPACING**)

1.7 LIST OF PUBLICATIONS

- 1.7.1 Comparative on Study on the Performance of Au/F-TiO₂ Photocatalyst Synthesized from Zamzam Water and Distilled Water Under Blue Light Irradiation

Rabiatul Adawiyah Zayadi, Faridah Abu Bakar

Journal of Photochemistry and Photobiology A: Chemistry

DOI: 10.1016/j.jphotochem.2017.06.012

Rank by Journal Citation Indicator (JCI) – WOS – Clarivate: Q2

(TNR, 12, SINGLE SPACING)

- 1.7.2 Elucidation of Synergistic Effect of Eucalyptus Globulus Honey and Zingiber Officinale in the Synthesis of Colloid Biogenic Gold Nanoparticles with Antioxidant and Catalytic Properties

Rabiatul Adawiyah Zayadi, Faridah Abu Bakar, Mohd Khairul Ahmad

Sustainable Chemistry and Pharmacy

DOI: 10.1016/j.scp.2019.100156

Rank by Journal Citation Indicator (JCI) – WOS – Clarivate: Q2

(TNR, 12, SINGLE SPACING)

- 1.7.3 Comparative Study on Stability, Antioxidant and Catalytic Activities of Bio-Stabilized Colloid Gold Nanoparticles using MicroAlgae and Cyanobacteria

Rabiatul Adawiyah Zayadi, Faridah Abu Bakar

Journal of Environmental Chemical Engineering

DOI: 10.1016/j.jece.2020.103843

Rank by Journal Citation Indicator (JCI) – WOS – Clarivate: Q1

(TNR, 12, SINGLE SPACING)

CHAPTER 2

LITERATURE REVIEW

2.1 INTRODUCTION

To provide for a better understanding on the concepts employed in this study and the overall direction of this study, this chapter gathers the literature on photocatalysis, titanium dioxide (TiO₂), and textile dye. The synthetic method and the modification of TiO₂, particularly using fluorine as surface modifier and the deposition of gold nanoparticles (GNP) are also reviewed. There are also past works on utilizing TiO₂ to photocatalytically degrade textile dye in the literature. Previous works are presented in tables for easy visualization of what had been done and what more can be done to tackle the matter. (TNR, 12, SINGLE SPACING)

2.2 PHOTOCATALYSIS

In IUPAC Gold Book, photocatalysis is defined as change in the rate of chemical reaction or its initiation under the action of ultraviolet, visible or infrared radiation in the presence of photocatalyst – a substance that absorbs light and is involved in the chemical transformation of the reaction partners [51]. (TNR, 12, SINGLE SPACING)

2.2.1 PHOTOCATALYSIS FOR ENVIRONMENTAL REMEDIATION

Photocatalysis is considered as an Advanced Oxidation Process (AOP) because of the formation of reactive and short-lived oxygen-containing radicals, and the exploitation of such species to mineralize organic contaminant [53]. (TNR, 12, SINGLE SPACING)

2.2.2 MECHANISM OF SEMICONDUCTOR PHOTOCATALYSIS

The application of semiconductor materials in photocatalysis for the purpose of elimination of organic pollutants in the environment has grown exponentially [55]. Semiconductor such as titanium dioxide has been applied in heterogenous photocatalysis or AOP to aid complete mineralization of organic pollutants in water and air [61]. (TNR, 12, SINGLE SPACING)

2.3 TITANIUM DIOXIDE

Titanium dioxide (TiO_2), also known as titania, titanium oxide and titanium (IV) oxide with physical characteristics of white, odourless powder [9,10]. Remarkable optical and electrical properties of TiO_2 made it very useful in various industries including as white pigment for paints and cosmetics; food colouring; coating for welding rod, floor, and fabric; production of electronic components such as capacitor; used as raw material for glass; and also utilized for photocatalysis [11,68,71,72].

(TNR, 12, SINGLE SPACING)

2.3.1 CRYSTAL PHASE OF TITANIUM DIOXIDE

Commonly, TiO_2 exists in three different mineral forms (polymorphs) with the same chemical formula but different crystalline structures. Those three polymorphs of TiO_2 are anatase, rutile, and brookite [11,68,72,77–79]. (TNR, 12, SINGLE SPACING)

CHAPTER 3

SYNTHESIS AND MODIFICATION OF TITANIUM DIOXIDE

3.1 OVERVIEW OF THE STUDY

TiO₂ has emerged as a promising photocatalyst that can be applied in treating environmental pollution because of its photogenerated electron-hole pair that can transform to radical species which are highly oxidizing to mineralize organic pollutants adsorbed to its surface. However, large band gap that requires ultraviolet light activation and high photogenerated electron-hole recombination rate at the surface limit the versatility of TiO₂ as an efficient photocatalyst [29,32]. This chapter shall highlight the effect of different parameters in towards modifying the crystal structure, crystallinity, and optical properties of TiO₂.

(TNR, 12, SINGLE SPACING)

3.2 LIST OF PUBLICATIONS

One main publication had been published shed light upon this objective.

Comparative on Study on the Performance of Au/F-TiO₂ Photocatalyst Synthesized from Zamzam Water and Distilled Water Under Blue Light Irradiation

Rabiatul Adawiyah Zayadi, Faridah Abu Bakar
Journal of Photochemistry and Photobiology A: Chemistry
DOI: 10.1016/j.jphotochem.2017.06.012

This publication contributes to broaden the spectrum of TiO₂ research and development by improvising an effective method in synthesizing visible light active TiO₂ for environmental purification. Based on literature, Zamzam water is alkaline water (pH 8) with some levels of mineral contents [34]. Incorporation of Zamzam water in the synthesis will amplify the potential uses of this mineral water for scientific applications, especially the novel use of this water in photocatalysis.

The utilization of plant extracts to stabilize Au-colloid; Arabic gum and aloe vera promotes green synthesis of GNP. Interesting findings on the crystallinity, morphology, optical property, and photocatalytic reactivity revealed throughout this publication backed the justifications of selected methods and materials employed in this study, which therefore provide wider options for future researchers interested to venture in this field. Moreover, the successful application of TiO₂ in the degradation of RB19 suggested that TiO₂ has what it takes to be promoted as remediation agent for wastewater in textile industry.

3.3 MAJOR FINDINGS

The results from this study showed that synthesizing Peroxo and Zamzam TiO₂ using different solvents; distilled water and Zamzam water respectively brought a slight difference in the photocatalytic properties of TiO₂. Fluorine modifier utilized in the synthesis of F-TiO₂ managed to control the morphology from irregular to ovoid shape and improve the crystallinity from mixed anatase-rutile to single anatase phase compared to blank TiO₂.

GNP deposition caused a shift in band gap from 3.08 eV in blank TiO₂ to 2.78 eV and 2.90 eV in Peroxo and Zamzam Au-TiO₂ samples respectively. Peroxo Au/F-TiO₂ synthesized with the incorporation of arabic gum as GNP stabilizer and HF as fluorine modifier appeared to degrade RB19 dye more efficiently compared to other samples. The degradation result indicates that visible light activity of TiO₂ can be achieved through surface modification and deposition of GNP due to improved charge separation.

(TNR, 12, SINGLE SPACING)

3.4 FULL TEXT PUBLICATIONS

The full text publication which echoes this objective of study are as follows:



Invited paper

Comparative study on the performance of Au/F-TiO₂ photocatalyst synthesized from Zamzam water and distilled water under blue light irradiation

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ABSTRACT

Recurring problems of titanium dioxide (TiO₂) for needing UV light to be activated and high electron-hole recombination rate limit the application of TiO₂ as a prolific photocatalyst. By modifying the morphology and introducing electron trapping species into TiO₂, the photocatalytic activity of TiO₂ could be improved. Solvents of two different kinds; distilled water and Zamzam water were used in peroxotitanic acid synthesis of TiO₂ and the photocatalyst was utilized to degrade Reactive Blue 19 (RB19) dye under blue light irradiation (475 nm) to assess the visible light activity of synthesized TiO₂. Fluorine was incorporated to control the morphology while gold nanoparticles (GNP) stabilized by arabic gum were deposited to trap electrons. The morphology of F-TiO₂ which appeared to be in ovoid shape was confirmed by Field Emission-Scanning Electron Microscope (FE-SEM) and Transmission Electron Microscope (TEM). Brunauer-Emmett-Teller (BET) surface area and crystallite size estimated from X-ray Diffraction (XRD) data revealed that F-TiO₂ modified using HF was smaller in size and exhibited single anatase phase. The band gap of Au-TiO₂ synthesized by distilled and Zamzam water was 2.78 eV and 2.89 eV respectively; shifted from 3.08 eV in blank TiO₂. Peroxo Au/F-TiO₂ synthesized with the incorporation of arabic gum as GNP stabilizer and HF as fluorine modifier degraded up to 49.23% of RB19 within two hours of reaction. The addition of fluorine and gold demonstrated high ability to enhance visible light activity of TiO₂ with distilled water used as solvent displayed higher photocatalytic performance compared to Zamzam water.

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1. Introduction

Titanium dioxide, the most widely studied photocatalyst is also known as titania, titanium oxide and titanium (IV) oxide [1]. It appears as white, odourless powder and noncombustible solid [2]. TiO₂ exists in three different mineral forms (polymorphs) with the same chemical formula but different crystalline structures. The three polymorphs of TiO₂ are anatase, rutile, and brookite [3]. Photocatalysis can be defined as the alteration of chemical reaction by a catalyst in the presence of light. Photocatalyst; a light-activated catalyst absorbs light photon and increases the rate of reaction without itself being altered or consumed at the end of reaction. This process is considered to be an excellent way to degrade organic pollutants [4,5].

In literature, TiO₂ has been used successfully to photocatalytically degrade dyes [6–10]. Dyes in wastewater including reactive dyes consist of hardly biodegradable pollutants including persistent organic compounds, thus threatening the environment and our health [11,12]. Therefore, an effective and environmental friendly technology is very much needed to treat dye wastewater. Reactive Blue 19 (RB19) dye is a type of reactive dye used in textile industry with fixation efficiency of about 75–80% [13]. Dyes which are unfixed are washed out into the wastewater. In a study on photodegradation of reactive dyes by Lizama et al. RB19 was found to be the most recalcitrant [14]. RB19 is said to be highly resistant towards chemical oxidation due to its fused aromatic anthraquinone structure, and thus remains coloured for a long time in wastewater [15,16]. The chemical structure of RB19 is shown in Fig. 1.

Past researches proved the ability of TiO₂ in breaking down RB19 when ultraviolet (UV) lamps were utilized [15,17,18]. Despite its displayed potential in breaking down organic contaminants, particularly dyes in this case; there are few drawbacks of TiO₂ that

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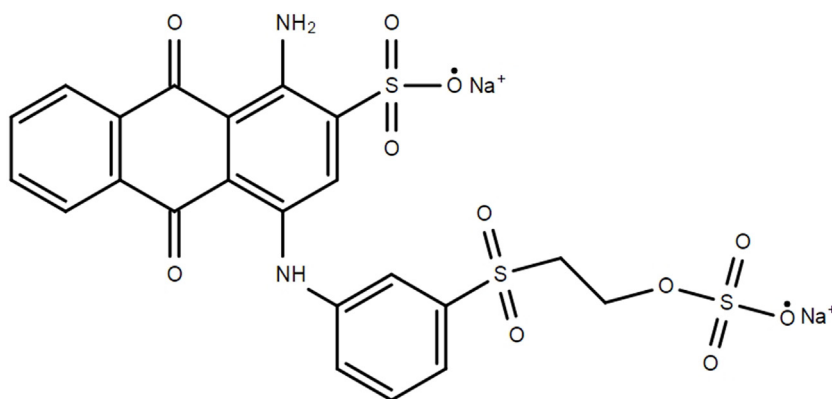


Fig. 1. Chemical structure of Reactive Blue 19 dye.

limit its photocatalytic properties. Firstly, TiO_2 is naturally activated by ultraviolet (UV) light because of its large band gap of 3.2 eV for anatase and 3.0 eV for rutile [19]. The dependency on UV light lowers the energy efficiency of TiO_2 because UV light only counters for 4–5% of the solar spectrum while visible light dominated by 40%. Therefore, attempts had been made to widen the absorption edge of TiO_2 from the UV region to the visible light region to increase its photocatalytic potential [20,21]. Secondly, the photogenerated electron-hole pair will recombine at the surface of TiO_2 . Their accumulation in bulk at the surface thus reduces the active sites for photocatalysis. This will result in low photocatalytic activity that lowers the potential degradation rate by TiO_2 on the target contaminant [22].

To counter for the drawbacks of TiO_2 , this study was aimed to produce visible light active TiO_2 photocatalyst by thermal degradation of peroxotitanic acid (PTA) method using two types of solvents, namely distilled water (Peroxo TiO_2) and Zamzam water (Zamzam TiO_2). Zamzam water was claimed to have the most beautiful crystal molecule than other water [23]. Thus, TiO_2 was synthesized using distilled water and Zamzam water to see if any variation in performance of TiO_2 as photocatalyst would occur when using different solvents. PTA method was chosen because it is simple, cheap and does not incorporate the usage of hazardous chemicals, and is therefore called as green synthesis [24].

Fluorine was incorporated as surface modifying agent to control the morphology, crystallinity and to improve absorbance of TiO_2 particles in visible region [25–27]. TiO_2 was also deposited with gold nanoparticles (GNP) to direct stronger absorption in the visible light region due to its plasmonic effect [28]. Further, the addition of fluorine and the deposition of GNP provided synergetic effect on promoting electron-hole recombination and thus improve the photodegradation performance of TiO_2 . The visible light activity of synthesized TiO_2 was then evaluated by photocatalytic degradation of RB19 dye under blue light illumination.

2. Materials and methods

2.1. Materials

Isopropanol (IPA, 99.75%; Riendemann Schmdt) was used to initiate the decomposition of titanium precursor towards the formation of PTA. Titanium (IV) isopropoxide (TTIP, 97%; Aldrich) was used as titanium precursor, tetrabutylammonium fluoride (NBu_4F , 1 M; Acros) and hydrogen fluoride (HF, 70%; Aldrich) were used as fluorine modifiers, and hydrogen peroxide (H_2O_2 , 50%; Emory) was used as oxidizing agent in the synthesis of TiO_2 photocatalyst. Gold (III) chloride (HAuCl_4 , 99.99%; Aldrich) was used as gold precursor, pharmaceutical grade collagen powder

(Emory) and pharmaceutical grade arabic gum powder (Emory) were used in the synthesis of gold colloid. Remazol Brilliant Blue (C.I: Reactive Blue 19; Sigma) was used as targeted pollutant in photocatalytic reaction. All of the materials were used as-received without any purification.

2.2. Synthesis of TiO_2 photocatalyst

TiO_2 was synthesized following peroxotitanic acid (PTA) method as employed by Abu Bakar (2014) [22]. Distilled water and Zamzam water were used as the solvents to produce blank Peroxo and Zamzam TiO_2 respectively. 5.34 g (0.0188 mol) of TTIP was added to 15 mL of IPA and stirred at 300 rpm 75 mL of water was added and the mixture was then stirred at 600 rpm for 10 min. The colorless solution turned milky instantly due to hydrolysis of TTIP. H_2O_2 was added dropwise in molar ratio 1:1 to TTIP, forming the PTA solution, and the solution turned bright yellow. The solution was refluxed at 100 °C for 24 h, washed several times with water, and centrifuged to collect the precipitate formed. The precipitate was aged in oven at 100° for 24 h, yielding powdered TiO_2 photocatalyst for characterization and photocatalytic reaction.

Fluorine-modified TiO_2 was produced following the same manner as blank TiO_2 , only with the addition of fluorine modifier in molar ratio of 1:1 to TTIP. GNP was deposited on TiO_2 by post deposition mechanism. Synthesized Au-colloid was deposited in the support (blank TiO_2 and F- TiO_2) followed by stirring at 800 rpm for 24 h. The collected precipitate was aged in oven at 50 °C for 16 h to avoid denaturation of collagen.

2.3. Synthesis of Au-colloid

8 mL of 2 mg/mL collagen solution was mixed and stirred at 800 rpm with 26.7 mg (0.0786 mol) HAuCl_4 giving 0.50% Au weight loading on TiO_2 . 16 mL of 0.01 M trisodium citrate was added followed by 9.6 mL of 0.01 M ascorbic acid. The solution turned ruby red and was stirred at 800 rpm for 6 h in the dark. To stabilize the GNP, *Acacia senegal* or Arabic gum (AS) and *Aloe vera* (AV) were incorporated as the stabilizing agent. The best stabilizer was chosen from optimization using different ratios of stabilizer to Au-precursor of 0:1, 1:1 and 2:1. The chosen stabilizer with the best ratio was added into the Au-colloid and deposited on TiO_2 via post deposition method.

2.4. Characterization of TiO_2 photocatalyst

Morphology of TiO_2 was observed by Field Emission-Scanning Electron Microscope (FE-SEM) using JEOL JSM-7600F. Brunauer-

Emmet-Teller (BET) surface area was determined by nitrogen adsorption using Quantachrome BET Autosorb-1. X-ray diffraction (XRD) analysis was performed using Bruker D8 Advance for determination of crystal phase and estimation of crystallite size. Band gap was calculated following Tauc's plot based on the data obtained from Perkin Elmer Lambda 900 Ultraviolet-Visible/Near Infrared Spectrometer (UV-vis/NIR). Ultraviolet-Visible Spectrophotometer (UV-vis) was employed for optical analysis and evaluation of photocatalytic reaction kinetics.

2.5. Photocatalytic reaction

0.04 g/L dye stock solution was prepared and 0.3 g/L of powdered TiO_2 photocatalyst was mixed with the solution. The dye-catalyst slurry was agitated in photocatalytic reactor equipped with two 475 nm blue LED lamps for a total reaction of 120 min. No light was irradiated at the first 15 min to ensure complete equilibrium of adsorption process. 3 mL of aliquot was withdrawn

every 15 min to be analyzed with UV-vis at 200–800 nm. Photocatalytic activity of the best sample for each category is conducted with the aid of green light irradiation (520 nm) at identical condition for comparative purposes.

3. Results and discussion

3.1. Morphology of TiO_2

The study of shape, distribution, and structure of TiO_2 particles were conducted using FE-SEM at magnification $\times 50,000$. FE-SEM images of blank TiO_2 and F- TiO_2 were shown in Fig. 2. Blank Peroxo- TiO_2 (P- TiO_2) and Zamzam- TiO_2 (Z- TiO_2) appeared in no specific shape and size. Various shapes of particles is caused by the lack of reactant after the complete breakdown of PTA occurred which impeded the growth of particles [22]. F- TiO_2 samples evolved to ovoid (egg-shaped) corresponding to studies by [29–31]. Images from Scanning Transmission Electron Microscope

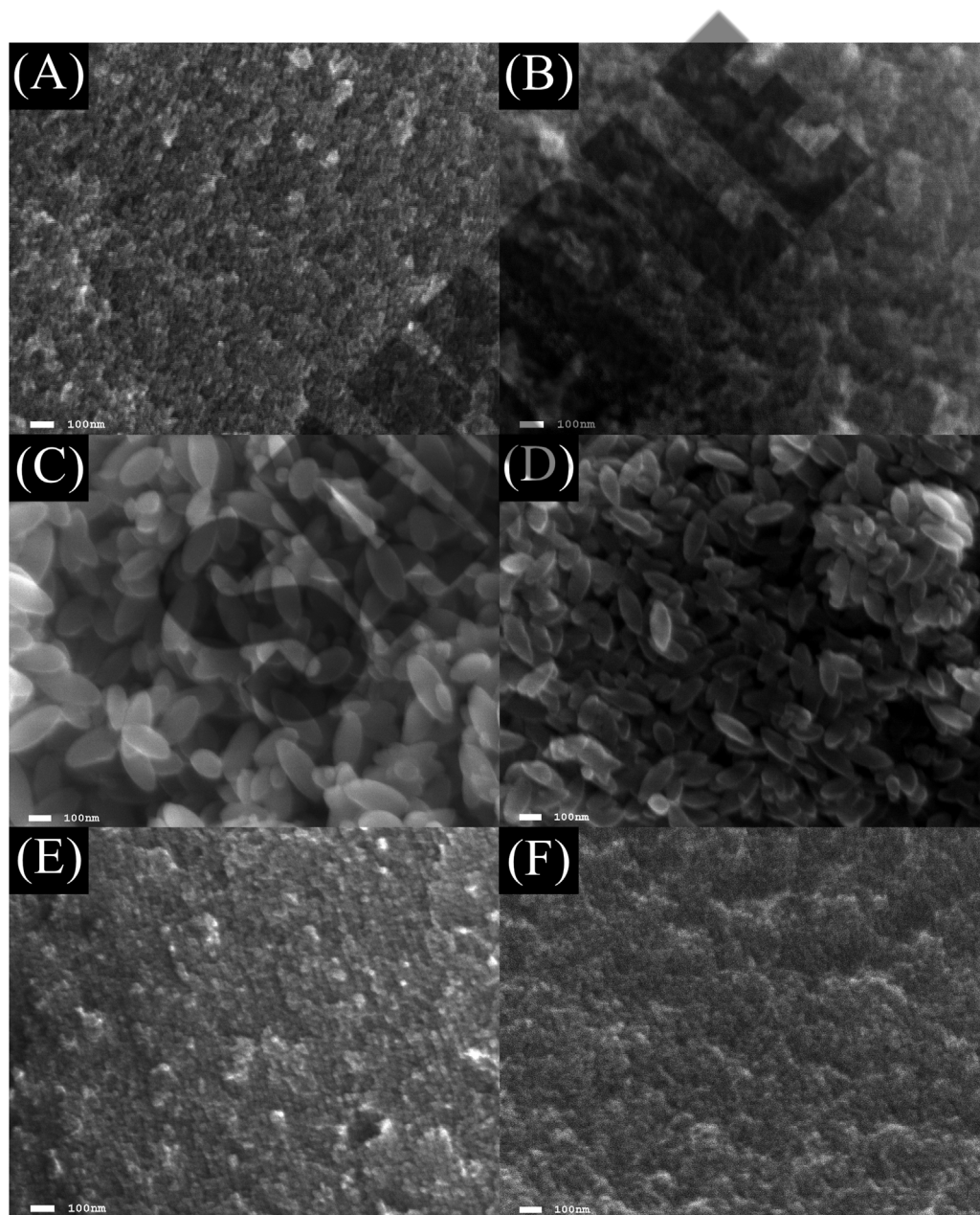


Fig. 2. FE-SEM images at $\times 50,000$ magnification of TiO_2 photocatalyst; (a) P- TiO_2 ; (b) Z- TiO_2 ; (c) F-P- TiO_2 (NBu₄F); (d) F-Z- TiO_2 (NBu₄F); (e) F-P- TiO_2 (HF); (f) F-Z- TiO_2 (HF).

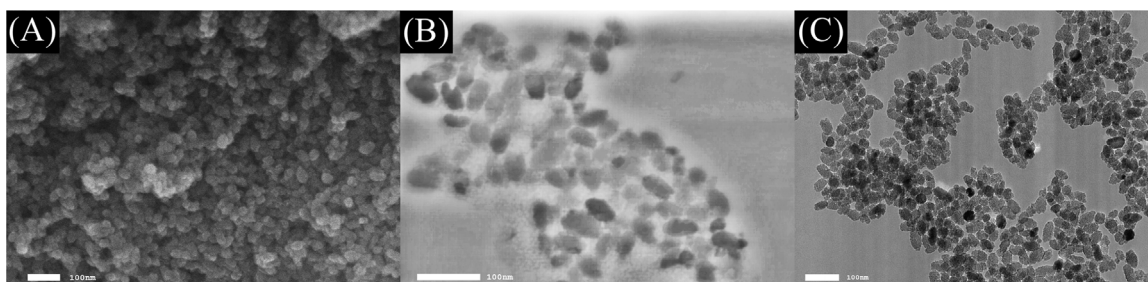


Fig. 3. FE-SEM STEM and TEM micrographs of Au(AS)/F-P-TiO₂ (HF): (a) FE-SEM; 100,000 magnification, (b) STEM; 200,000 magnification, (c) TEM; 25,000 magnification.

(STEM) and Transmission Electron Microscope (TEM) in Fig. 3 further confirm the morphology of F-modified TiO₂ using HF. Uniform ovoid shape was obtained in F-modified TiO₂ samples because F-modifier bind to one face of the crystal, stunting the growth on that specific face, leading to the control of crystal shape [32]. In this case, the dominating crystal face belongs to (101) anatase plane as proven by XRD analysis. The sizes of F-TiO₂ samples synthesized using NBu₄F was generally bigger than the one synthesized using HF, and the same trend can be seen in BET and XRD results. The same morphologies were observed in blank Au-TiO₂ and F-modified Au-TiO₂. Au/F-TiO₂ retained the ovoid shape while blank Au-TiO₂ appeared in irregular shapes regardless the types of solvents used. The Au loading used is 0.50% during the synthesis. This loading percentage is considered ideal since Kim et al. stressed that too much deposition of metal nanoparticles on TiO₂ will trigger a shadow effect that blocks the light photon absorption and therefore potentially reduce the photoactivity of TiO₂ [33]. Energy dispersive X-ray (EDX) analysis was conducted with FE-SEM to analyse the percentage of elements present in TiO₂ sample. It was found out that a sample of Au(AS)/F-P-TiO₂ consisted of 33.12% titanium (Ti), 49.02% oxygen (O) and 10.97% fluorine (F) as shown in the EDX spectrum in Fig. 4.

3.2. BET surface area

Surface area of TiO₂ samples were determined based on BET theory which proposed that gas molecules are adsorbed in multilayer pattern on surface of solid sample [34]. This theory is the extension of Langmuir theory which claimed that the gas molecules are arranged in monolayer only [35]. Adsorption of nitrogen gas on the surface of TiO₂ particles by physisorption gave an isotherm providing the necessary information to determine BET

Table 1

BET surface area and particle size of selected samples.

Sample	BET Surface Area (m ² /g)	Particle size (nm)
P-TiO ₂	113.8	12.55
Z-TiO ₂	110.7	12.90
F-P-TiO ₂ (NBu ₄ F)	18.38	77.72
F-Z-TiO ₂ (NBu ₄ F)	31.34	45.58
F-P-TiO ₂ (HF)	110.1	12.98
F-Z-TiO ₂ (HF)	113.2	12.62

surface area. Table 1 summarized the BET surface area of blank TiO₂ and F-TiO₂ analysed using multi-point BET. The surface area of both P-TiO₂ and Z-TiO₂ were greater, indicating smaller particle size than F-TiO₂ samples. Surface area for F-TiO₂ synthesized from NBu₄F was smaller than HF, proving that F-TiO₂ (NBu₄F) particles are bigger than F-TiO₂ (HF) as shown in FE-SEM images. The F-modifiers used provided acidic condition for the synthesis, and higher acidity leads to the formation of TiO₂ particles with smaller surface area [36,37]. NBu₄F poses more H than HF, making it more acidic and thus resulted in smaller surface area of F-TiO₂ (NBu₄F) compared to F-TiO₂ (HF).

From BET data, the particle size, *D* (nm) was estimated using Eq. (1) where *S*_{BET} refers to BET surface area (m²/g) and ρ refers to density of TiO₂ (g/cm³) [38–40]. The equation gives inversely proportional relationship between particle size and surface area where greater surface area owing to smaller particle size as tabulated in Table 1. The values correspond with crystallite size estimated from XRD analysis.

$$D = 6000 / (S_{BET} \times \rho) \quad (1)$$

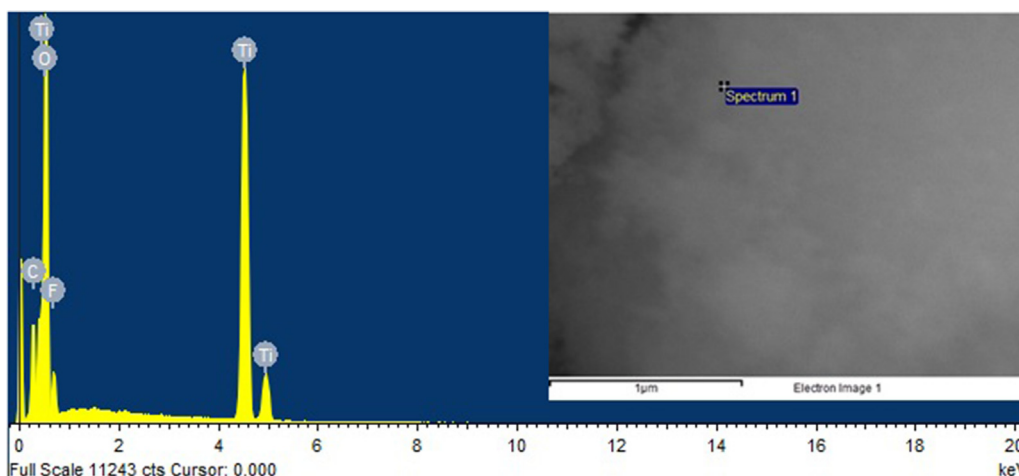


Fig. 4. EDX spectrum of Au(AS)/F-P-TiO₂ (HF).

3.3. Crystal phase and crystallite size

X-ray diffraction (XRD) analysis was conducted on all samples using Cu K α radiation as the primary X-ray source ($\lambda = 1.54060 \text{ \AA}$) with respect to angle of 2θ in the range of 20° to 80° . The XRD patterns showing the peaks of respective crystal phases were compared with International Centre Diffraction Data (ICDD) database. Anatase and rutile peaks were denoted with letter A and R respectively in the XRD patterns, and the miller indices were shown to indicate the planes attributed to each peaks.

As displayed on Fig. 5, P-TiO₂ and Z-TiO₂ depict a mixed-phase of anatase and rutile. For both samples, the XRD pattern show a dominant peak at 2θ 27° attributed for rutile phase. Au-deposited TiO₂ either with or without the addition of arabic gum as stabilizer, also showed mixed phase with rutile dominant. The percentage of anatase to rutile as summarized in Table 2 also suggested that rutile phase is more dominant for these samples. This result complies with the finding from Seok et al. (2006) for blank TiO₂ synthesized via PTA method [41]. From the XRD pattern, different solvents (distilled water and Zamzam water) used in the synthesis of TiO₂ gave a relatively similar crystal pattern.

All F-TiO₂ samples showed single anatase phase where all diffraction peaks matched with anatase pattern 00-021-1272 from ICDD as in Figs. 6 and 7. This suggest that the addition of fluorine in TiO₂ favors the formation of anatase phase [29,42]. Ti-F bond is formed as fluoride will bind strongly to titanium during the synthesis, encouraging the growth of anatase rather than rutile [43]. According to Thamaphat et al., when particle size increases, the diffraction peak intensity of TiO₂ also increases [44]. The main anatase peak belongs at 2θ 25° (101) became more intense and narrower from HF to NBu₄F implying smaller particle size for F-TiO₂ (HF) as agreed by morphology and surface area analyses.

Raman spectroscopy also confirms the phase of the samples where F-modified samples are anatase and blank or Au-deposited samples are mixed of anatase and rutile based on the Raman spectra shown in Fig. 8. The Raman spectra for F-modified samples

Table 2

Estimated crystallite size, D from Scherrer's formula and the crystal phase corresponds to each TiO₂ photocatalyst.

Sample	2θ ($^\circ$)	β , FWHM ($^\circ$)	D (nm)	F _A (%)	Phase
P-TiO ₂	27.4	0.6298	12.47	30	R
Z-TiO ₂	27.4	0.3936	19.96	40	R
F-P-TiO ₂ (NBu ₄ F)	25.2	0.1378	57.01	100	A
F-Z-TiO ₂ (NBu ₄ F)	25.2	0.1968	39.92	100	A
F-P-TiO ₂ (HF)	25.2	0.4330	18.14	100	A
F-Z-TiO ₂ (HF)	25.3	0.4330	18.14	100	A
Au-P-TiO ₂	27.4	0.6298	12.47	35	R
Au-Z-TiO ₂	27.3	0.3149	24.95	35	R
Au(AS)-P-TiO ₂	27.4	0.7085	11.21	27	R
Au(AS)-Z-TiO ₂	27.4	0.4330	18.35	36	R
Au/F-P-TiO ₂ (NBu ₄ F)	25.2	0.1378	57.01	100	A
Au/F-Z-TiO ₂ (NBu ₄ F)	25.2	0.1968	39.92	100	A
Au/F-P-TiO ₂ (HF)	25.2	0.2362	33.26	100	A
Au/F-Z-TiO ₂ (HF)	25.2	0.2362	33.26	100	A
Au(AS)/F-P-TiO ₂ (NBu ₄ F)	25.2	0.1378	57.65	100	A
Au(AS)/F-Z-TiO ₂ (NBu ₄ F)	25.2	0.1968	40.37	100	A
Au(AS)/F-P-TiO ₂ (HF)	25.2	0.3149	25.23	100	A
Au(AS)/F-Z-TiO ₂ (HF)	25.2	0.2558	30.71	100	A

and commercial anatase (Sigma Aldrich) showed peaks at 155 cm^{-1} , 398 cm^{-1} , 516 cm^{-1} , and 639 cm^{-1} correspond to E_g, B_{1g}, A_{1g} (superimposed with B_{1g}), and E_g modes of anatase phase respectively. The shift of peak position of the prepared samples from commercial anatase may be attributed to the size difference of the samples [45]. Rutile peaks are observed at 445 cm^{-1} (E_g) and 617 cm^{-1} (A_{1g}) indicating the presence of rutile phase in blank TiO₂ and Au-deposited TiO₂ samples. A_{1g} mode is representing the pure O vibration, B_{1g} mode is the pure Ti vibration, and E_g mode belongs to the vibration of mix of O-atom and Ti-atom motions [46].

The [101] facet obviously dominated the crystal structure as seen in the XRD patterns. Zhao et al. explained that fluorine preferentially adsorbed to the [001] facet at first due to its higher surface energy. Then, as the growth along [001] direction is retarded, the crystal starts growing on [101] direction of lower

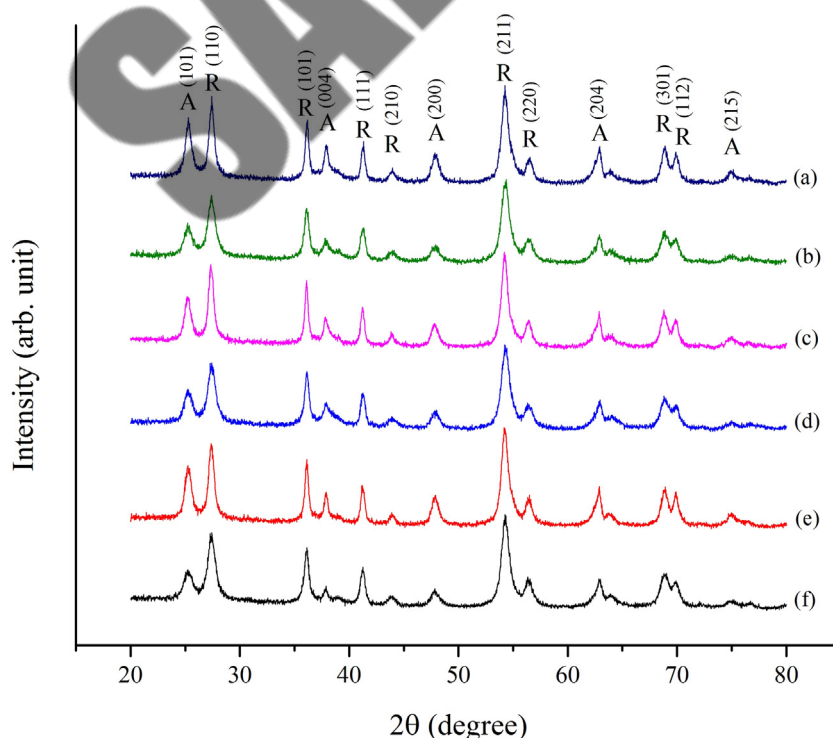


Fig. 5. XRD patterns of blank and Au-deposited TiO₂ photocatalyst; (a) Au(AS)-Z-TiO₂; (b) Au(AS)-P-TiO₂; (c) Au-Z-TiO₂; (d) Au-P-TiO₂; (e) Z-TiO₂; (f) P-TiO₂.

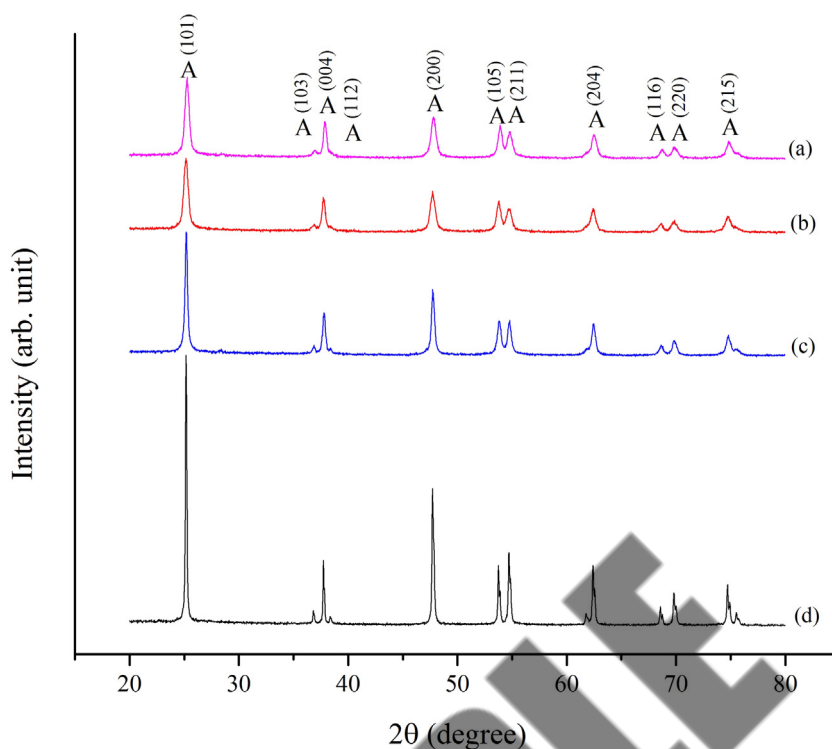


Fig. 6. XRD patterns of F-modified TiO₂ photocatalyst; (a) F-Z-TiO₂ (HF); (b) F-P-TiO₂ (HF); (c) F-Z-TiO₂ (NBu₄F); (d) F-P-TiO₂ (NBu₄F).

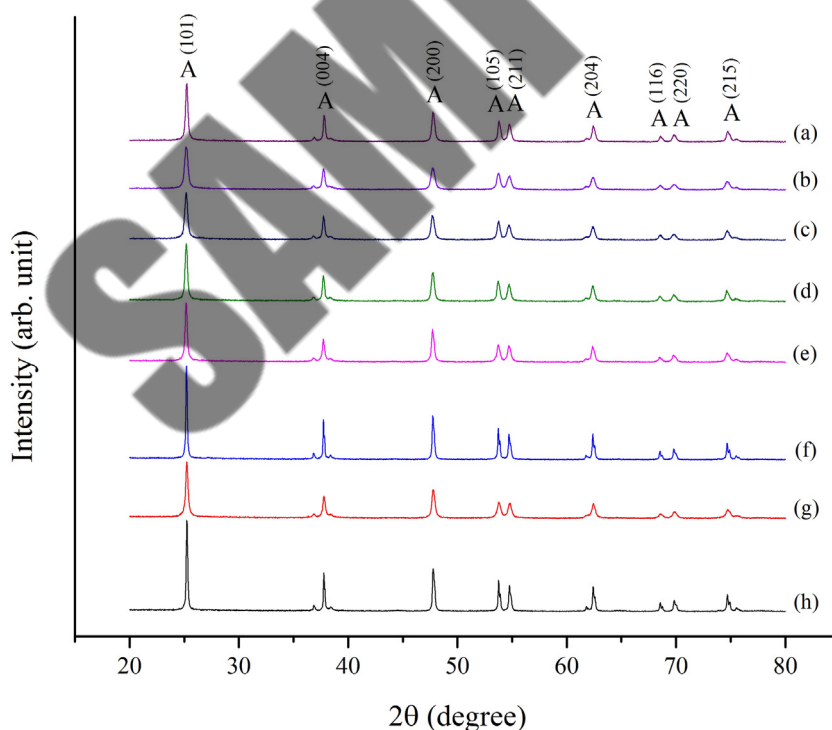


Fig. 7. XRD patterns of Au/F-TiO₂ photocatalyst; (a) Au(AS)/F-Z-TiO₂ (HF); (b) Au(AS)/F-P-TiO₂ (HF); (c) Au/F-Z-TiO₂ (HF); (d) Au/F-P-TiO₂ (HF); (e) Au(AS)/F-Z-TiO₂ (NBu₄F); (f) Au(AS)/F-P-TiO₂ (NBu₄F); (g) Au/F-Z-TiO₂ (NBu₄F); (h) Au/P-Z-TiO₂ (NBu₄F).

surface energy [47]. Moreover, the enhanced growth of [004] and [101] peak indicated well-developed high-energy [001] facet [47,48]. The development of [004] facet is befitting because it said to enhance the photocatalytic activity of TiO₂ photocatalyst [49–51].

For all TiO₂ samples deposited with gold nanoparticles (GNP), indistinct peaks at 2θ 38° and 44° were observed, assigned to Au [52–54]. The Au peaks are corresponding to ICDD pattern (00-004-0784) but are not labelled in the figures. Dai et al. suggested that low loading of Au on TiO₂ caused insignificant peak of Au in XRD

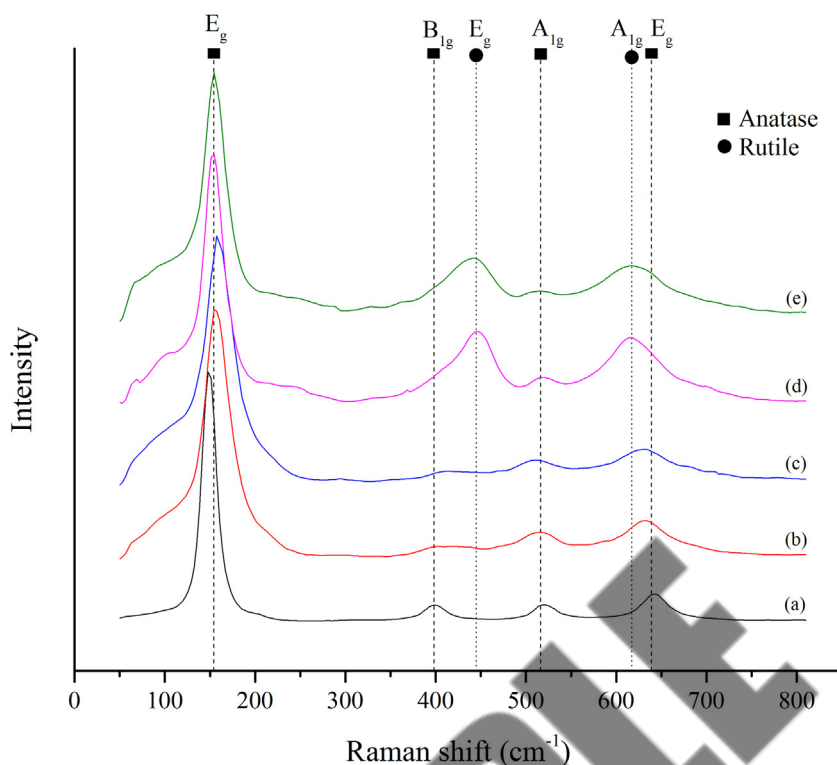


Fig. 8. Raman spectrum of (a) Commercial Anatase, (b) F-P-TiO₂ (HF), (c) Au(AS)/F-P-TiO₂ (HF), (d) P-TiO₂, (e) Au(AS)-P-TiO₂.

whereas Rahulan *et al.* (2011) mentioned that low Au loading made the gold nanoparticles (GNP) uniformly dispersed and did not have adequate dimensions to produce their characteristic patterns [55,56].

Scherrer's formula (Eq. (2)) was used to estimate the crystallite size where D is the crystal size in the direction of d spacing, k is a constant of 0.9, λ (nm) is the wavelength of X-ray radiation, β (rad) is the full width at half maximum (FWHM) of the selected peak, and θ (rad) is the angle of diffraction for the peak [57]. The crystal size was calculated with reference to the corresponding values of (101) plane for anatase or (110) plane for rutile [58,59]. The weight fraction of anatase in anatase-rutile mixture, F_A , was calculated following Spurr-Myers' equation adapted from Spurr and Myers (1957) to indicate the amount of anatase present (Eq. (3)) where I_R

and I_A are the strongest intensities of rutile (110) and anatase (101) respectively [60]. The crystallite size and phase of TiO₂ samples are as summarized in Table 2.

$$D = k\lambda / \beta \cos \theta \quad (2)$$

$$F_A = 100 \times I_A / (I_A + 1.26I_R) \quad (3)$$

3.4. Effect of GNP

GNP was deposited into TiO₂ in order to enhance absorption in the visible light region as well as to act as electron trap to further improve charge separation on the surface of TiO₂. The addition of

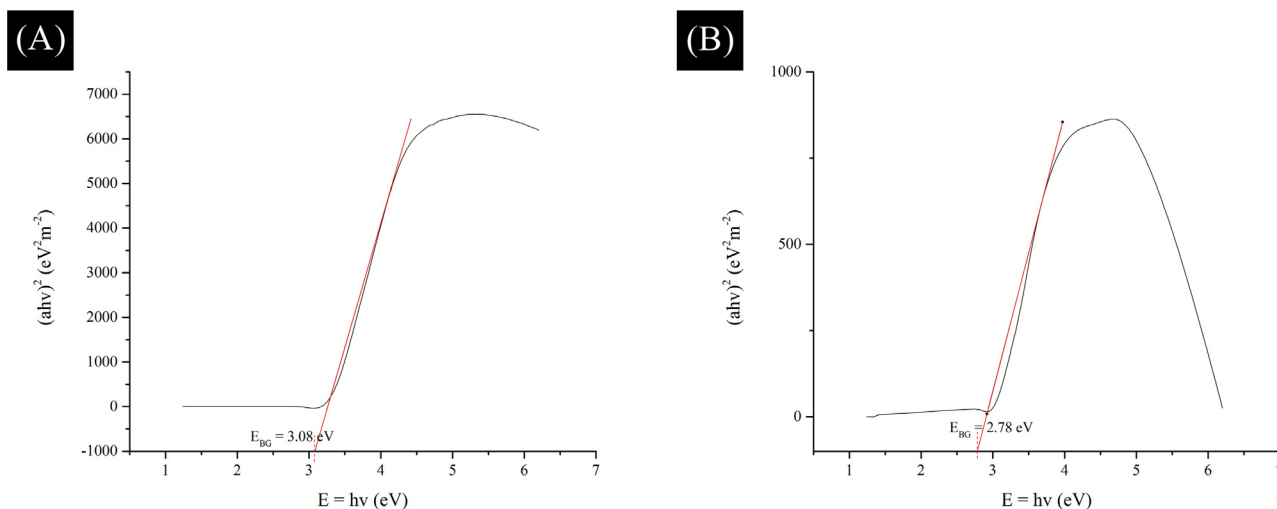


Fig. 9. E_{BG} estimation of TiO₂ photocatalyst from Tauc's plot; (a) P-TiO₂; (b) Au-P-TiO₂.

GNP managed to shift the bandgap of TiO_2 with the lowest E_{BG} reported by Au-P- TiO_2 was 2.78 eV compared to 3.08 eV of P- TiO_2 without the addition of GNP as shown in Fig. 9 and Table 3. This is possible due to the surface plasmon resonance (SPR) effect by noble metals such as Au that induces strong absorption in the visible region which is caused by collective excitation of free electrons [28,61]. The electric field of incoming light wave will cause the free electrons in the conduction band to oscillate, so when the frequency of light is in resonance with the motion of electrons, strong absorption occurs; resulting in SPR effect. The absorption occurs at the region where the original colour of the Au-colloid is observed, which is in the visible light region [28]. In a study by Padikkaparambil et al., enhanced photocatalytic activity on dye degradation was achieved because GNP act as electron traps [62]. This is indeed possible because of Schottky barrier; an electronic potential barrier which influences the capture of photogenerated electrons, thus increases the charge separation of electron-hole pairs [63].

It is important to ensure the stability of GNP for its practical application because stable dispersion of GNP on nanoparticles in aqueous solution is not easily obtained since the GNP tend to agglomerate and form clusters [64,65]. Therefore, stabilizer is needed when GNP is synthesized. *Acacia Senegal* (AS) or arabic gum and *Aloe vera* (AV) were chosen as the candidates for stabilizing agent. Plant extract has been used as stabilizer for GNP as a mean of green synthesis to produce non-toxic, biocompatible GNP [66,67]. This plant-based synthesis or phyto-synthesis is beneficial in producing controlled size, morphology and stability of GNP by optimizing the experimental conditions [68]. Optimization of GNP stabilized by AS and AV was done using 0:1, 1:1 and 2:1 wt ratio of stabilizer to Au precursor. The reduction of gold ions produces ruby red gold colloid due to the SPR effect [28,68–70]. In this study, the Au-colloid stabilized by AS and AV produced dark violet and ruby pink colloids respectively as shown in Fig. 10. In SPR phenomenon, a strong absorption will occur at the colour of the Au-colloid itself which is in the visible light region [28,71]. Fig. 11 demonstrated the absorbance spectra for 2:1 ratio where GNP synthesized using AS showed better stability with the absorbance did not deviated further from 0 h to 6 h.

The size of GNP was estimated using the formula proposed by Haiss et al. where the size of GNP can be determined from UV–vis spectra following Eq. (4). Eq. (4) is useful to determine the size of GNP in the range of 5 to 80 nm where d is the diameter of GNP, A_{SPR} is the absorbance at SPR peak, A_{450} is absorbance at 450 nm, B_1 is 3.00, while B_2 is 2.20 [72]. GNP diameter were determined for Au-

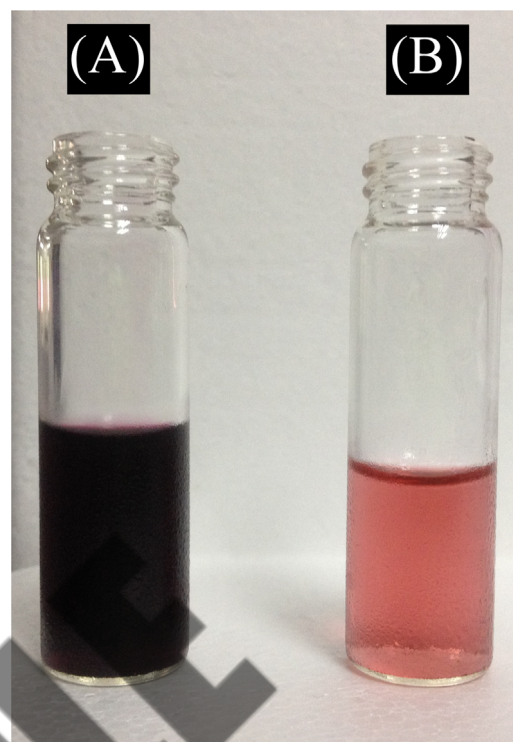


Fig. 10. Variation of stabilized Au-colloid colour; (a) Au-colloid stabilized by *Aloe vera*, (b) Au-colloid stabilized by *Acacia Senegal*.

colloid stabilized with AS and AV for all three ratios of stabilizing agent to Au-precursor (0: 1, 1: 1, 2: 1) using the UV–vis spectrum obtained from their 6-hourly UV–vis analysis as presented in Table 4.

$$d = \exp [B_1 (A_{\text{SPR}}/A_{450}) - B_2] \quad (4)$$

With the smallest GNP diameter obtained of 9.01 nm, and the illustrious stability shown by AS with ratio 2:1, hence, this preference was chosen as the stabilizer for GNP. The maximum peak absorbance of GNP or λ_{SPR} is also shown in Fig. 11. According to Kattumuri et al., AS has complex polysaccharides and protein structure, making it an ideal material to produce stable GNP [73]. By using AS, the GNP synthesized was non-toxic too because AS is extracted from acacia trees and the use of AS as the stabilizer also lessen the GNP agglomeration in the aqueous solution [68,74,75].

Table 3

Band gap energy and the percentage of adsorption, decolourization and degradation of RB19 by TiO_2 photocatalyst.

Sample	E_{BG} (eV)	% Adsorption	% Decolourization	% Degradation
P- TiO_2	3.08	7.61	28.47	28.66
Z- TiO_2	3.08	1.11	2.33	2.37
F-P- TiO_2 (NBu ₄ F)	3.25	2.54	4.59	4.62
F-Z- TiO_2 (NBu ₄ F)	3.25	3.69	4.05	4.08
F-P- TiO_2 (HF)	3.16	20.19	37.49	37.65
F-Z- TiO_2 (HF)	3.13	12.80	25.11	25.25
Au-P- TiO_2	2.78	2.55	4.59	4.61
Au-Z- TiO_2	2.90	1.47	2.33	2.35
Au/F-P- TiO_2 (NBu ₄ F)	3.27	9.47	17.36	17.45
Au/F-Z- TiO_2 (NBu ₄ F)	3.20	6.74	9.90	9.96
Au/F-P- TiO_2 (HF)	3.18	17.02	23.58	23.80
Au/F-Z- TiO_2 (HF)	3.15	13.49	21.88	21.98
Au(AS)-P- TiO_2	2.89	4.26	9.21	9.26
Au(AS)-Z- TiO_2	2.90	2.31	4.09	4.11
Au(AS)/F-P- TiO_2 (NBu ₄ F)	3.19	4.01	12.22	12.27
Au(AS)/F-Z- TiO_2 (NBu ₄ F)	3.12	2.95	7.34	7.37
Au(AS)/F-P- TiO_2 (HF)	3.22	28.01	49.00	49.23
Au(AS)/F-Z- TiO_2 (HF)	3.19	23.34	32.70	32.85

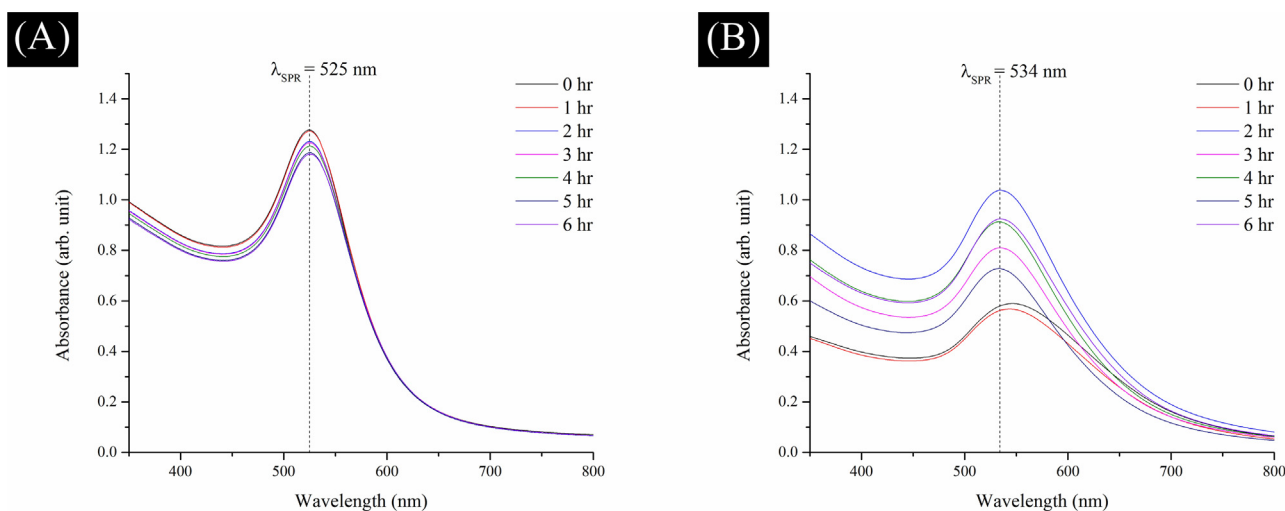


Fig. 11. Optical absorption of stabilized Au-colloid at 2:1 wt ratio of stabilizer to Au-precursor; (a) Au-colloid stabilized by *Acacia Senegal*, (b) Au-colloid stabilized by *Aloe vera*.

3.5. Energy band gap

Band gap energy (E_{BG}) is the range of energy between the top of valence band and the bottom of conduction band in a semiconductor where no electron states exist [76]. The E_{BG} of TiO_2 is most commonly obtained through optical measurements, and in this study diffuse reflectance technique was employed using UV-vis/NIR at wavelength of 200–1000 nm. The E_{BG} was approximated using Tauc's plot in Eq. (5) [22,77] where α is absorption coefficient, $h\nu$ (eV) is the energy of incident light, A is a constant, and r is a constant value of 1 for direct transition. $(\alpha h\nu)^2$ was plotted against $h\nu$, and the value of E_{BG} (eV) was obtained by extrapolating the straight line portion of the graph to $(\alpha h\nu)^2 = 0$ for when $\alpha = 0$, $h\nu = E_{BG}$ (refer to Fig. 10). $h\nu$ (eV) was calculated from Planck's theory in Eq. (6) where h is Planck's constant of 4.136×10^{-15} eVs, c is speed of light (3×10^8 ms $^{-1}$), and λ is wavelength (nm) of incident light [78].

$$\alpha \cdot h\nu = A (h\nu - E_{BG})^r \quad (5)$$

$$h\nu = hc/\lambda \quad (6)$$

The values of calculated E_{BG} for all samples are as presented in Table 3. The value of E_{BG} for Blank P- TiO_2 and Z- TiO_2 which appeared to be rutile-dominant is about 3.08 eV while the values for F- TiO_2 (HF) for Peroxo and Zamzam are 3.16 eV and 3.13 eV respectively, while the band gap energy of F- TiO_2 (NBu₄F) for both Peroxo and Zamzam are 3.25 eV. These values tally with the reported band gap values of rutile and anatase TiO_2 of 3.0 eV and 3.2 eV respectively [79,80]. The slight increase in the E_{BG} of synthesized samples may be due to quantum confinement effect [81]. As for Au- TiO_2 , reduction of band gap was observed either with or without AS as the stabilizing agent. It can be seen that the

Table 4
Diameter, d , of GNP stabilized using different stabilizers at different ratios.

Sample	Stabilizer ratio to Au-precursor	λ_{SPR} (nm)	D (nm)
Blank	0: 1	526	18.03
Acacia senegal	1: 1	527	12.92
	2: 1	525	9.01
Aloe vera	1: 1	533	11.22
	2: 1	534	11.89

E_{BG} for Peroxo Au- TiO_2 is slightly lower than Zamzam Au- TiO_2 for both circumstances.

3.6. Photocatalytic degradation of RB19 under blue light

To evaluate the efficiency of synthesized TiO_2 samples, the percentage of adsorption, percentage of decolourization and percentage of degradation of RB19 within 2 h of radiation under blue light was calculated following Eqs. (7)–(9) where C_0 is the initial concentration, C_{15} is the concentration at 15 min, C_f is the final concentration, A_0 is the initial absorbance, and A_f is the absorbance measured at 120 min [22,82,83]. The concentration values were calculated from calibration curve of RB19 (Fig. 12) obtained at λ_{max} , the wavelength of maximum absorbance of RB19 which is found to be 592 nm (Fig. 13) as also reported by [13,83–87]. The corresponding values for each TiO_2 photocatalyst are as summarized in Table 3. A controlled reaction was conducted using commercial anatase TiO_2 powder in the dark under the same conditions, and the percentage of degradation is negligible which is below than 0.01%.

$$\% \text{ adsorption} = [(C_0 - C_{15}) / (C_0)] \times 100 \quad (7)$$

$$\% \text{ decolourization} = [1 - (A_f / A_0)] \times 100 \quad (8)$$

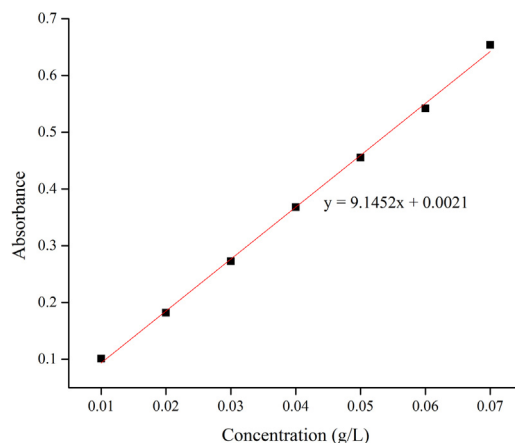


Fig. 12. Calibration curve of RB19 at 592 nm.

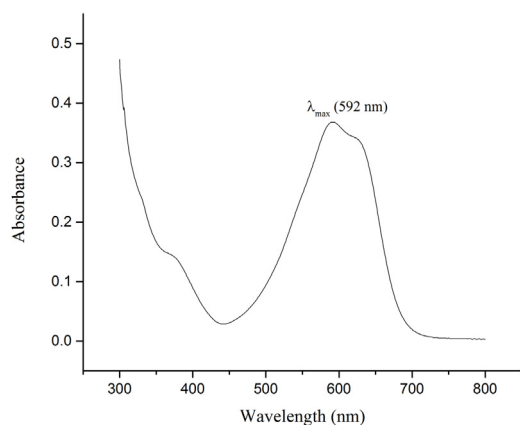


Fig. 13. Maximum absorption, λ_{\max} of RB19.

$$\% \text{ degradation} = [(C_0 - C_f)/(C_0)] \times 100 \quad (9)$$

The summarized data served as an indicator that it is possible to utilize TiO_2 for degradation of complex dyes like RB19 even under the irradiation of light with photon energy lower than UV light. Previous studies on the degradation of RB19 using TiO_2 photocatalyst were focused on the application of UV lamps as the photon energy source. A study by Lizama et al. using 1 g/L TiO_2 managed to degrade 90% of 0.05 g/L RB19 within 20 min under UV light illumination [15]. 86.2% of 0.002 g/L RB19 was degraded by 1 g/L TiO_2 after 60 min of photoreaction under UV light as published by Rezaee et al. [17]. In 2014, Siddique et al. reported 35% degradation of 0.1 g/L RB19 using 0.3 g/L of TiO_2 within 120 min irradiation of UV light [18]. In this study, 28.66% degradation of 0.04 g/L RB19 was achieved by 0.3 g/L blank P- TiO_2 after 120 min reaction under blue light.

Peroxo samples of Blank TiO_2 and Au- TiO_2 showcased a more astounding percentage of degradation compared to Zamzam samples of the kind. It is seen that percentage of RB19 adsorbed affect the photocatalytic activity. Z- TiO_2 with only 1.11% of adsorption only resulted in 2.37% of degradation of RB19 while P- TiO_2 with 7.61% of adsorption had degraded 28.66% RB19 under the same condition. The relationship between pH and adsorption percentage may explain this. The adsorption of dye molecules on the surface of TiO_2 was said to be increased in lower pH opposed to higher or more alkaline pH as reported by Barka et al. [88]. It was reported that the pH of Zamzam water is higher than distilled water and is alkaline [89,90]. This therefore resulted in a lower adsorption capacity of RB19 molecules on the surface of TiO_2 and affect the overall performance because the reactive radicals that are generated at the surface of TiO_2 will have to travel in a longer distance to attack the farther dye molecules, and may not even be able to attack due to short lifetime of hydroxyl radicals [82,88,91].

It is observed that TiO_2 modified by NBu_4F showed lower trend in degrading the target contaminant than TiO_2 modified by HF. Although F- TiO_2 synthesized from both NBu_4F and HF displayed ovoid shape, it is however revealed that F- TiO_2 (NBu_4F) possessed smaller surface area as shown in BET result. Dai et al. mentioned

that higher surface area will improve photocatalytic activity by providing more surface active sites, which suggest why F- TiO_2 (HF) samples performed better [92]. As noticed, the degradation of RB19 is more pronounced with fluorine modifier; indicating that ovoid morphology dictated by F-modifier also plays a role for photocatalytic activity contribution. Jiwei Ma et al. regarded fluoride anion as a structure-directing agent which inclined to non-linear arrangement as found in anatase and accentuated the ability of F^- to bind with Ti^{4+} which influences the geometry of polymeric building units that reflects the final arrangement of F- TiO_2 structure [93]. The adsorption of fluorine on TiO_2 also stabilizes the highly energetic [001] facet [94,50,51]. This is proven by the work of Ma et al. which revealed that fluorine adsorption weakens the Ti-O bond in [101] yet strengthens them in [001], making it more stable [95]. With the formation of stabilized, high-energy [001] facet, the photocatalytic activity of TiO_2 is expected to rise [96].

Ruzicka et al. concluded that there is an apparent correlation between the anion and cation groups of fluorine modifier with the abundance of Ti^{3+} in TiO_2 photocatalyst where $\text{F}^- > \text{NBu}_4^+$ indicating that Ti^{3+} present more abundantly in F- TiO_2 (HF) and enhance the visible light activity [30]. The presence of the Ti^{3+} centres improved visible light activity by creating localized mid-gap states of electrons needed for charge compensation [97,98]. Recap that all TiO_2 samples modified with fluorine are composed of single anatase phase, thus the data presented in Table 3 therefore reveals that single anatase TiO_2 phase act as a better photocatalyst than mix of anatase-rutile. As reported by previous researchers, it is generally accepted that anatase TiO_2 exhibit a better photocatalytic properties despite its higher band gap compared to rutile [19,31,99,100]. Such phenomenon is said to be due to the difference in the lattice structure that increases the band gap of anatase TiO_2 [99]. The higher band gap allowed the valance band maximum to rise to higher energy level and shift to larger redox potential which then increases the oxidation power of electron and increases the photocatalytic activity [19].

TiO_2 synthesized with AS-stabilized-GNP and modified with HF; Au(AS)/F-P- TiO_2 (HF) degraded about 49.23% of 0.04 g/L RB19 which is the highest among other samples as summarized in Table 3. The sample prepared using Zamzam water [Au(AS)/F-Z- TiO_2] degraded 32.85% of the dye within 120 min. Such pronounced degradation achieved due to the effect of fluorination and GNP deposition. Charge separation was promoted by the formation of Ti^{3+} centers by fluorine modifier to localize extra electron, and Schottky barrier that induces electron capture by gold. GNP deposited on TiO_2 is regarded as an electron-sink where the electron excited from valance band to the conduction band (CB) can be migrated to the GNP [62]. Noble metal like Au will form Schottky barrier when in contact with TiO_2 , which facilitate the electron capture and prevent electron-hole recombination [62,63,101,102]. It is also theorized that when more electrons is accumulated on Au- TiO_2 , the Fermi level (E_F) is shifted nearer to the CB, therefore electron is transferred from TiO_2 to the GNP, and subsequently reduced by O_2 molecules adsorbed on the surface to produce superoxide radical [103]. These in turn enhances the

Table 5
Percentage of adsorption, decolorization and degradation of RB19 at different photocatalyst and light sources.

Sample	% Adsorption		% Decolorization		% Degradation	
	Blue Light	Green Light	Blue Light	Green Light	Blue Light	Green Light
P- TiO_2	7.61	0.19	28.47	6.99	28.66	7.03
F-P- TiO_2 (HF)	20.19	0.64	37.49	5.98	37.65	6.01
Au(AS)-P- TiO_2	4.26	0.89	9.21	2.84	9.26	2.85
Au(AS)/F-P- TiO_2 (HF)	28.01	0.27	49.00	7.05	49.23	7.08

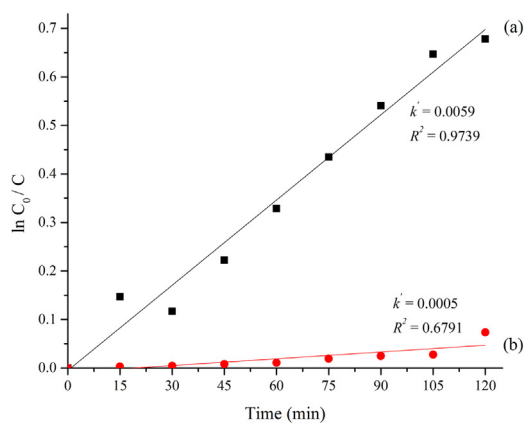


Fig. 14. Linear plot of $\ln C_0/C$ of Au(AS)/F-P-TiO₂ (HF) against time at different light irradiation; (a) blue light; 475 nm, (b) green light; 520 nm.

photocatalytic activity of Au/F-TiO₂ (HF) samples under blue light, and more dye was able to be degraded. The formation of large intermediates during degradation of RB19 which remained in the solution even after 2 h might slow down the photodegradation process by TiO₂ photocatalyst [104]. Hence, longer photoreaction time should be conducted in future to observe the true potential of the synthesized photocatalyst in breaking down RB19.

3.7. Photocatalytic degradation of RB19 under green light

To observe the performance of synthesized TiO₂ in a different light source within the visible light spectrum, the photocatalytic degradation of RB19 was repeated using green light (520 nm) for best samples of each category. The comparative result of adsorption, decolorization and degradation of the selected samples under both light illumination is tabulated in Table 5. Clearly, the photodegradation is more enhanced using blue light as the photon source. Using blue light, Au(AS)/F-P-TiO₂ (HF) decolorized 49.00% of RB19, but using green light, only 7.05% of RB19 was decolorized. The photon energy of green light falls under the range of 490–580 nm that provides photon energy lower than the blue light of range 450–490 nm in the visible light spectrum [105]. Longer wavelength results in lower frequency, and subsequently lower photon energy; therefore the photon energy provided by blue light is stronger to activate the photocatalyst.

The kinetics of photocatalytic degradation of RB19 by TiO₂ photocatalyst is studied using Langmuir-Hinshelwood (L-H) kinetics which is the generally accepted model for heterogeneous photocatalysis [106,107]. The reaction rate constant was determined using first-order kinetics equation as in Eq. (10) where C_0 is the initial concentration of dye, C is the concentration of dye at time, t , and k' is the apparent first-order rate constant [6,17,81,106–108]. When $\ln C_0/C$ is plotted, a straight line is produced and the slope generated from the linear equation is equal to the k' . The value of k' is listed in Table 5 and the plot of $\ln C_0/C$ for Au(AS)/F-P-TiO₂ (HF) under blue and green light illumination is shown in Fig. 14. The rate constant accounted for the sample irradiated with blue light is higher as compared to green radiation which indicates faster degradation of RB19.

4. Conclusion

The results from this study showed that synthesizing Peroxo and Zamzam TiO₂ using different solvents; distilled water and Zamzam water respectively brought a slight difference in the photocatalytic properties of TiO₂. Fluorine modifier utilized in the synthesis of F-TiO₂ managed to control the morphology from

irregular to ovoid shape and improve the crystallinity from mixed anatase-rutile to single anatase phase compared to blank TiO₂. GNP deposition caused a shift in band gap from 3.08 eV in blank TiO₂ to 2.78 eV and 2.90 eV in Peroxo and Zamzam Au-TiO₂ samples respectively. Peroxo Au/F-TiO₂ synthesized with the incorporation of arabic gum as GNP stabilizer and HF as fluorine modifier appeared to degrade RB19 dye more efficiently compared to other samples. The degradation result indicates that visible light activity of TiO₂ can be achieved through surface modification and deposition of GNP due to improved charge separation.

Acknowledgments

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3.5 SUPPLEMENTARY INFORMATIONS AND FINDINGS

To ensure that the objective of the study is met, additional analysis was carried out in addition to the one that had been submitted, peer reviewed and published. The findings from this analysis shall be further explained in detail in this section. (TNR, 12, SINGLE SPACING)

3.5.1 DEGRADATION PATHWAY OF REACTIVE BLUE DYE

The degradation pathway of RB19 through photocatalytic degradation by TiO₂ is represented in Figure 3.39. RB19 is a type of anthraquinone reactive dye with the anthraquinone serve as the chromophore group [167,168,170,265]. The chromophore is responsible for colouring properties and is usually consisted of aromatic and heteroaromatic rings where it contains oxygen, nitrogen, or sulphur [20]. Typically, RB19 will form an anthraquinone intermediate; Uniblue-A (Figure 3.39b) when hydrolysed in water [32,266]. Uniblue-A also known as RB19-vinyl sulfone is said to be reduced in concentration steadily with illumination time and the formation of this intermediate gives out sulphuric acid [32,168].

According to Siddique et al., (2014), the most fragile bond in the structure of RB19 (marked red in Figure 3.39b) breaks and produce anthraquinone derivative (sodium; 1-amino-9,10-dioxoanthracene-2-sulfonate) and a product (Figure 4.39c). The derivative further decompose to anthraquinone (anthracene-9,10-dione) as shown in **Figure 3.39**. (TNR, 12, SINGLE SPACING)

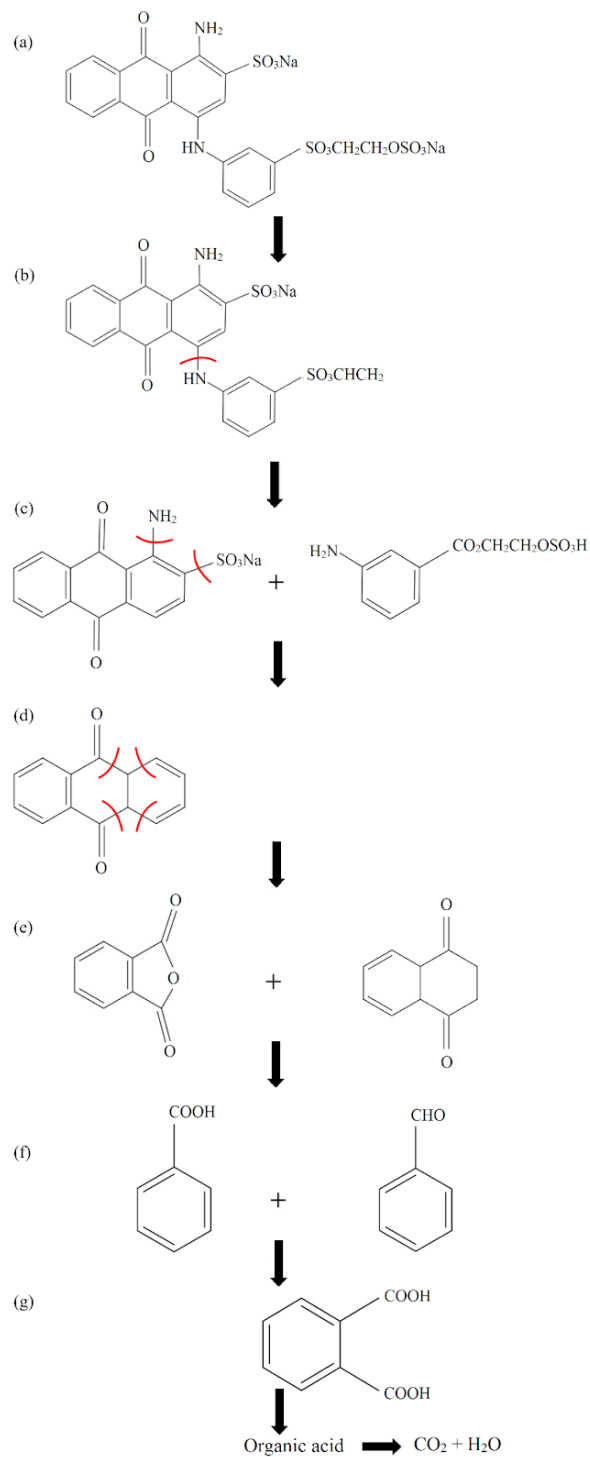


Figure 3.39: Proposed degradation pathway of Reactive Blue 19

3.5.2 ADDITIONAL PUBLICATIONS / PROCEEDING/ CONFERENCE/ AWARD

This study has also been presented in the following events:

1. “Synthesis of Visible Light Active Au/F-TiO₂ Photocatalyst for Degradation of Reactive Dye”, 3-Minute Thesis, Faculty of Science, Technology and Human Development, Universiti Tun Hussein Onn Malaysia, First Runner Up (February 2nd, 2017).
2. “Synthesis of Visible Light Active Au/F-TiO₂ Photocatalyst for Degradation of Reactive Dye”, 3-Minute Thesis, Centre for Graduate Studies, Universiti Tun Hussein Onn Malaysia, First Place (March 14th, 2017).

From this research, an honorary diploma in Water and Environment was granted by Mustafa Science and Technology Foundation (MSTF) for the participation in KANS Scientific Competition.

This research had been selected to be the Top 20 (Materials Science), in Merck Young Scientist Award (2018)

3.6 CONCLUSION

Looking back at the primary objective of this study which is to synthesize size and shape controlled TiO₂ with enhanced photocatalytic activity in the visible light region; it can be concluded that this objective had been fairly achieved based on the results discussed in Chapter 3 of this thesis. The study started with synthesizing blank TiO₂ (TNR, 12, SINGLE SPACING)

Note:

Should there be no publications published (Q1 and Q2) for the Theme or Objective of studies, the chapter should be written the same style as a conventional thesis.

CHAPTER 4

**Example of chapters without any Q1 or Q2 Publications*

EFFECT OF GOLD NANOPARTICLE DEPOSITION ON THE PHOTOCATALYTIC ACTIVITY OF F-MODIFIED TiO₂

4.1 OVERVIEW OF THE STUDY

The synthesis of chemically modified semiconductors from the molecular and atomic level to the nanoscale is reported to significantly enhance their functioning. In this respect, titania (TiO₂) has been widely studied for applications in the field of solar fuel production, environmental remediation, water splitting, air purification. It is still regarded as a benchmark photocatalyst under UV-irradiation. Although use of mixed phases would efficiently enhance the photocatalytic activity, the major setback of TiO₂ is the size of its band gap which requires UV light excitation and hence limits efficiency of TiO₂ photocatalysts under sunlight as an energy source.

In view of efficient utilization of visible light, it is necessary to develop TiO₂-based photocatalysts which could work efficiently under a wide range of visible-light irradiation. Great efforts have been made to narrow the band gap of TiO₂ to realize visible light photoexcitation as well as to reduce the recombination of photogenerated electron-hole pairs under such irradiation.

(TNR, 12, SINGLE SPACING)

4.1.1 DEPOSITION OF NOBLE METALS ON TiO₂

Sunlight is a unique natural resource. It is free, non-polluting, abundant and an endlessly renewable source of clean energy. The traditional TiO₂ photocatalyst requires UV light ($\lambda < 400$ nm) to operate, because its band gap is greater than 3 eV (3.2 eV for anatase TiO₂). Hence, it can utilize only about 4% of the total sunlight irradiation reaching Earth surface. It has been challenging to fabricate photocatalysts that are able to work under visible light, which covers 43% of sunlight. Among the various approaches that have been utilized to enhance the photoactivity of TiO₂, (TNR, 12, SINGLE SPACING)

4.1.2 GOLD NANOPARTICLES

Gold is the quintessential noble element. Gold nanoparticles can exhibit properties which are significantly different from these of the bulk gold. For example, unlike bulk gold, nanoscale gold exhibits various vivid colours which depend on the particle size and shape. The absorption of the visible light around 550 nm (or more) is explained by the surface plasmon

resonance which is due to the collective oscillations of electrons at the surface of the nanoparticles. (TNR, 12, SINGLE SPACING)

4.1.3 Au/TiO₂

Recently, gold nanoparticles have attracted significant interest, especially as catalysts in the degradation of contaminants in air and wastewater. Initially, bulk gold was known to be unreactive towards the dissociative adsorption of both molecular hydrogen and oxygen. In 1973, Bond et al. reported that gold in the nanoparticle state showed unique catalytic activity in selective hydrogenation of 1,3-butadiene to butane in the gas phase.

(TNR, 12, SINGLE SPACING)

4.2 EXPERIMENTAL PROCEDURE

4.2.1 SYNTHESIS OF GOLD COLLOID

For a 0.25 wt% Au loading on TiO₂, 8.9 mg of chloroauric acid (HAuCl₄·3H₂O) was dissolved in 4 mL of deionized water forming (TNR, 12, SINGLE SPACING)

4.2.2 SYNTHESIS OF Au/TiO₂

The gold loading was set constant (0.25 wt%) for each synthesis unless stated otherwise. The synthesis of unmodified or F-modified TiO₂ (TNR, 12, SINGLE SPACING)

4.2.3 SYNTHESIS OF UNMODIFIED AND F-MODIFIED TiO₂

Titanium isopropoxide (TTIP) precursor (1.780 g, 6.27 mmol) was dissolved in (TNR, 12, SINGLE SPACING)

4.2.4 PRE AND POST TREATMENT OF THE SYNTHESIZED TiO₂

1.000g of P-TiO₂ or F-modified TiO₂ support was added to (TNR, 12, SINGLE SPACING)

4.2.5 CHARACTERIZATION

The synthesized TiO₂ was characterized by powder X-ray diffraction using an Agilent SuperNova diffractometer with a molybdenum (Mo) K α source. The samples were further characterized by field-emission scanning electron microscopy (SEM) using an SEM JEOL 7000F FE-SEM, and transmission electron microscopy (TEM) images were obtained using a Philips CM-200 TEM operated at 200 kV. UV-visible diffuse reflectance spectroscopy (UV-vis DRS) was performed using an Agilent Cary 4000

UV-vis spectrometer with a diffuse reflectance integrating sphere. Band gaps were calculated from a modified (TNR, 12, SINGLE SPACING)

4.3 RESULTS AND DISCUSSION

4.3.1 OPTICAL PROPERTIES OF Au-TiO₂

Gold (Au) nanoparticles possess unique properties such as absorption of visible light and large enhancement in scattering. The enhancement of the optical and photothermal properties of Au nanoparticles also arises from the SPR of their free electrons in the presence of light. The DRS spectra for the unmodified TiO₂ (P-TiO₂) and P-TiO₂ modified with Au colloid with different weight percentages of gold are shown in **Figure 4.1**. The broad SPR band located around 500–620 nm confirms the presence of (TNR, 12, SINGLE SPACING)

4.3.2 MORPHOLOGICAL PROPERTIES AND CRYSTAL STRUCTURE OF Au-TiO₂

Figure 4.2 shows PXRD pattern of the as-synthesized P-TiO₂ and P-TiO₂-Au colloid samples with different weight percentages (wt%) of Au. All major peaks can be easily indexed to a mixture of anatase and rutile phases according to (TNR, 12, SINGLE SPACING)

4.3.3 EFFECT OF PRE AND POST TREATMENT ON THE MORPHOLOGICAL PROPERTIES AND CRYSTAL STRUCTURE OF Au-TiO₂

TiO₂ particles can directly or indirectly influence the reaction. The direct effect is due to TiO₂ properties, such as shape, size, formation aggregates in the reaction media, presence of specific types of surface defects (and their density) and conduction band (CB) position. On the other hand, (TNR, 12, SINGLE SPACING)

4.4 CONCLUSION

Kindly report the conclusion for this chapter. (TNR, 12, SINGLE SPACING)

4.5 REFERENCES

1. List of references should be written consistently in accordance to either APA, MLA, Chicago, Turabian or IEEE (TNR, 12, SINGLE SPACING)
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4. List of references should be written consistently in accordance to either APA, MLA, Chicago, Turabian or IEEE (**TNR, 12, SINGLE SPACING**)

CHAPTER 7

CONCLUSION AND FUTURE WORK

7.1 CONCLUSION

Kindly report the conclusion for this project. (TNR, 12, SINGLE SPACING)

7.2 FUTURE WORK

Kindly report the future work for this project. (TNR, 12, SINGLE SPACING)

APPENDIX A

AWARDS AND RECOGNITIONS

KINDLY ATTACH THE OFFICIAL LETTER OF AWARDS/ CERTIFICATES

APPENDIX B

COPYWRITE CLEARANCE DOCUMENTS

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