SYNTHESIS AND CHARACTERIZATIONS OF COMPOSITE BASED ON Cu_2O-ZnO-POLYANILINE FOR REMOVAL OF CONGO RED DYE

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DEDICATION

This thesis is dedicated to my first daughter (Maimoona-Hidaya), who was born while I was away for this study. Although she does not know me yet, because I couldn't go back home to see her, due to the covid-19 pandemic, my love and prayers are always with her. It is also dedicated to my wife (Salma), who endured and encouraged me throughout our trying periods, her endless love and prayers have changed my life and turned me into a better person.

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ABSTRACT

In this study, ternary composite photocatalyst based on copper(I) oxide (Cu_2O), zinc oxide (ZnO) and polyaniline (PANI) was synthesized using a facile one-pot solvothermal method and *in-situ* polymerization of aniline. At the initial stage, binary composites of Cu_2O were prepared with titanium dioxide (TiO_2) and ZnO where the loadings of both TiO_2 and ZnO precursors were varied while keeping Cu_2O precursor constant (0.045 mol). Preliminary photocatalytic activity testing and further characterizations of the samples showed that the sample containing equal precursor amount of Cu_2O and ZnO (CZ(0.045-0.045)) has superior properties. This sample was then used to form a ternary nanocomposite with PANI by *in-situ* polymerization of aniline at room temperature (Cu_2O/ZnO-PANI), while studying the effects of different oxidants and aniline loading. The Cu_2O/ZnO-PANI (CZP) composite was first produced using ammonium persulfate (APS), and two composite oxidants comprising of a mixture of APS and potassium dichromate ($K_2Cr_2O_7$) as well as potassium permanganate ($KMnO_4$), under the same amount of aniline monomer to select the best one among the three oxidants. Composite oxidant comprising of APS and $KMnO_4$ (APS/$KMnO_4$) was found to be the best, therefore, the amount of aniline monomer was then varied (0.13, 0.1, 0.05, and 0.03 mL) while using APS/$KMnO_4$ as the oxidant to produce the rest of the CZP composites. The composite produced using 0.1 mL aniline (CZP (0.1)) was found to have the best photocatalytic activity, so it was subjected to full characterizations as well as a photocatalytic test. Meanwhile, the amount of PANI on the optimised composite was quantified using thermogravimetric analysis (TGA) and found to be about 28%. Furthermore, the photodegradation of Congo Red (CR) dye was studied as a model reaction with the optimized catalyst (CZP (0.1)). The CZP (0.1) composite demonstrated outstanding adsorption properties, increased photocatalytic activity with a percentage degradation of 100% in less than 30 minutes, enhanced stability, and reusability on CR dye under visible-light irradiation. The reusability and stability studies were conducted by repeating the CR photodegradation experiment for five cycles, in which the recovered sample after the fifth cycle was subjected to X-ray diffraction spectroscopy (XRD), Fourier transform infrared spectroscopy (FTIR), and X-ray photoelectron spectroscopy (XPS) analyses to see if there was a change in its structure and stability. The result revealed no significant change in all the analyses between the unused and five times reused samples. The photodegradation process of CR was further studied using *in-situ* capture, total organic carbon (TOC), and high performance liquid chromatography (HPLC) analyses. *In-situ* capture studies revealed that the holes (h^+) and superoxide radicals ($•O_2^-$) were the main active species responsible for the degradation of CR using CZP (0.1), while the hydroxyl radical (•OH) plays a secondary role in the reaction. Likewise, the TOC studies revealed a removal of 90% after 30 min. Meanwhile, HPLC analysis also confirmed the degradation of CR by CZP (0.1) and revealed the formation of some possible intermediates as evident in the TOC analysis. Finally, the electron transfer mechanism was discussed and a double Z-scheme electron transfer mechanism is proposed for the CZP (0.1) composite system according to the experimental data, sample characterization, and band theory.

ABSTRAK

Dalam kajian ini, fotomangkin komposit pertigaan berasaskan kuprum(I) oksida (Cu_2O), zink oksida (ZnO) dan polianilina (PANI) telah disintesis menggunakan kaedah solvoterma setempat yang mudah dan pempolimeran *in-situ* anilina. Pada peringkat awal, komposit dedua Cu_2O telah disediakan dengan titanium dioksida (TiO_2) dan ZnO di mana muatan pelopor TiO_2 dan ZnO diubah sementara mengekalkan pelopor Cu_2O malar (0.045 mol). Ujian awal aktiviti pemfotomangkin dan pencirian lanjut sampel telah menunjukkan bahawa sampel yang mengandungi amaun pelopor Cu_2O and ZnO yang sama, CZ(0.045-0.045) mempunyai sifat-sifat yang unggul. Sampel ini kemudiannya telah digunakan untuk membentuk nanokomposit pertigaan dengan PANI melalui teknik pempolimeran anilina *in situ* pada suhu bilik(Cu_2O/ZnO-PANI) sementara mengkaji kesan bahan pengoksidaan dan pemuatan anilina yang berbeza. Komposit Cu_2O/ZnO-PANI (CZP) dihasilkan terlebih dahulu menggunakan ammonium persulfate (APS) dan dua bahan pengoksidaan komposit yang terdiri daripada kalium dikromat ($K_2Cr_2O_7$) dan kalium permanganate ($KMnO_4$), di bawah jumlah monomer anilina yang sama untuk memilih bahan pengoksidaan yang terbaik di antara ketiga-tiga bahan pengoksidaan itu. Bahan pengoksidaan yang terdiri daripada APS dan KMnO4 (APS/$KMnO_4$) didapati adalah yang terbaik, oleh itu, jumlah monomer anilina telah diubah (0.13, 0.1, 0.05, dan 0.03 mL) sementara menggunakan APS/$KMnO_4$ sebagai bahan pengoksidaan untuk menghasilkan komposit CZP selebihnya. Komposit yang dihasilkan menggunakan 0.1 mL anilin (CZP (0.1)) didapati mempunyai aktiviti pemfotomangkin terbaik, oleh sebab itu ia menjalani pencirian penuh serta ujian pemfotomangkin. Sementara itu, jumlah PANI pada komposit optimum telah dikuantifikasi menggunakan analisis gravimetri terma (TGA) adalah sebanyak kira-kira 28%. Tambahan lagi, fotodegradasi Merah Congo (CR) dikaji sebagai model tindak balas dengan mangkin optimum (CZP (0.1)). Komposit CZP (0.1) menunjukkan sifat penjerapan yang cemerlang, peningkatan aktiviti pemfotomangkin dengan peratusan degradasi 100% dalam masa 30 minit, peningkatan kestabilan, dan penggunaan semula mewarna CR di bawah penyinaran cahaya nampak. Kajian kebolehgunaan semula dan kestabilan dilakukan dengan mengulangi eksperimen fotodegradasi CR bagi lima kitaran, di mana sampel yang dipulihkan selepas kitaran kelima telah menjalani analisis spektroskopi pembelauan sinar-X (XRD), spektroskopi inframerah transformasi Fourier (FTIR), dan spektroskopi fotoelektron sinar-X (XPS) untuk melihat sama ada terdapat perubahan struktur dan kestabilannya. Keputusan menunjukkan tiada perubahan ketara dalam semua analisis antara sampel yang belum diguna dan sampel yang telah diguna semula lima kali. Proses fotodegradasi CR dikaji lebih lanjut menggunakan analisis tangkapan *in situ*, karbon organik keseluruhan (TOC), dan kromatografi cecair berprestasi tinggi (HPLC). Kajian tangkapan *in situ* menunjukkan bahawa lubang (h^+) dan radikal superoksida ($\bullet O_2^-$) adalah spesies aktif utama yang bertanggungjawab untuk degradasi CR menggunakan CZP (0.1), sementara radikal hidroksil (•OH) memainkan peranan sekunder dalam tindak balas itu. Begitu juga, kajian TOC menunjukkan penyingkiran 90% selepas 30 min. Sementara itu, analisis HPLC juga mengesahkan degradasi CR oleh CZP (0.1) dan menunjukkan pembentukan beberapa produk perantara yang mungkin sebagai bukti dalam analisis TOC. Akhirnya, mekanisme perpindahan elektron telah dibincangkan, dan mekanisme perpindahan elektron skema-Z ganda dua telah dicadangkan untuk sistem komposit CZP (0.1) menurut data ujikaji, pencirian sampel, dan teori jalur.

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

LIST OF ABBREVIATIONS

AOP	-	Advanced Oxidation Process
APS	-	Ammonium persulfate
BET	-	Brunauer-Emmett-Teller
CB	-	Conduction Band
CR	-	Congo Red
CT	-	Cu_2O/TiO_2
CZ	-	Cu_2O/ZnO
CZP	-	Cu_2O/ZnO-PANI
EDS	-	Energy Dispersive Spectroscopy
EDX	-	Energy Dispersive X-ray
SEM	-	Scanning Electron Microscopy
FTIR	-	Fourier Transmission Infrared
GCMS	-	Gas Chromatography-Mass Spectroscopy
HPLC	-	High Performance Liquid Chromatography
HR-TEM	-	High-Resolution Transmission Electron Microscopy
MB	-	Methylene Blue
MO	-	Methyl Orange
NA	-	Nitrogen Absorption-desorption Analysis
NIR-UV	-	Near-Infrared Ultraviolet
NPs	-	Nanoparticles
PANI	-	Polyaniline
SAED	-	Scanning Atomic Electron Diffraction
SEM	-	Scanning Electron Microscopy
UV	-	Ultraviolet
UV-Vis	-	Ultraviolet/visible
VB	-	Valence Band
XPS	-	X-ray Photoelectron Spectroscopy
XRD	-	X-ray Diffraction

LIST OF SYMBOLS

e^-	-	Electron
h^+	-	Hole
hv	-	Energy (photon)
λ	-	Wavelength
$\boldsymbol{\beta}$	-	Peak broadness at full width of half maximum intensity
$2\boldsymbol{\theta}$	-	Bragg diffraction angle
$\boldsymbol{\theta}$	-	Theta angle
nm	-	Nanometers
R^2	-	Coefficient of determination
K	-	Rate constant

LIST OF APPENDICES

CHAPTER 1

INTRODUCTION

1.1 Research Background

The industrial revolution has brought about a wide range of problems including water pollution, leading to a significant impact on the environment and living things. Direct discharge of industrial effluents into waterways makes it unfit for consumption, as the water may receive non-biodegradable and undesirable chemicals from the effluents which proved to be hazardous, and death by pollution-related diseases is increasing day by day [1,2].

The textile and dye industries being one of the most chemically intensive industries in the world need much attention due to the large effluents they discharge into waterways which are highly toxic in nature [3]. This leads to the contamination of surface and groundwater as it contains a high concentration of heavy metals and other harmful organic compounds, these compounds are believed to be carcinogenic, mutagenic, and in some cases teratogenic to living things [3,4]. Surprisingly about 72 toxic chemicals were detected from textile effluents, out of which 30 could not be removed [3–5].

Textile and dyeing industries use a lot of water in dyeing and finishing fabrics, approximately about 60 liters of water is required in dyeing 1 kg of clothes, as such World Bank estimated that about 17-20% of Industrial water pollution comes from textile industries [6–8]. Therefore, the search for an alternative, efficient, and cost-effective method for the treatment of textile wastewater or dyes is imperative, to reserve this precious limited natural resource [2,4].

Regular water remediation methods used, like coagulation, flocculation, sedimentation, filtration, and disinfection are not fast and efficient. Some of these conventional methods, apart from being incompatible with the environment, also require large space that leads to wastage of chemicals and in some cases can't remove a lot of hazardous pollutants, but rather lead to the generation of secondary harmful products [4,9]. Advanced Oxidation Processes (AOPs) are among the new facile water treatment methods developed, it has become popular due to their effectiveness and capability to degrade contaminants through redox reaction in water [10,11].

The AOPs are based on the generation and use of hydroxyl radicals (•OH), due to their high reduction potential (2.80 V vs. Normal hydrogen electrode), they can degrade a wide range of organic pollutants including stable gaseous pollutants like carbon dioxide (CO_2) [12]. Ultraviolet (UV) photolysis, hydrogen peroxide photo-fenton, photo-ozonation, and heterogeneous photocatalysis are the main classes of AOPs. However, heterogeneous photocatalysis has gained more popularity due to the advantage of the usage of sunlight, which is an abundant and free source of energy [13,14].

Photocatalysis is a chemical reaction under photoabsorption of solid material, namely a photocatalyst, that is chemically unaffected during and after the reaction [15,16]. The beginning of research in the field of photocatalysis was started by Fujishima and Honda in 1972 when they used TiO_2 electrodes in the splitting of water [17]. Photocatalysis can mineralize toxic compounds completely at low temperature and pressure and therefore gains much popularity in the treatment of contaminated gaseous and liquid wastes [4,18].

Binary metal oxides ranging from titanium dioxide(TiO_2), tungsten trioxide(WO_3), zinc oxide(ZnO), tin dioxide(SnO_2), ferric oxide(Fe_2O_3), tantalum pentoxide(Ta_2O_5), cupric oxide(CuO), and perovskites metal oxides like bismuth ferrite ($BiFeO_3$) and lanthanum ferrite ($LaFeO_3$) are widely used as photocatalysts [19]. Others are heterojunction and composite photocatalysts formed using two or more metal oxides photocatalyst [20–26]. Conductive polymers such as polyaniline (PANI), polypyrrole (PPy), poly(3,4-ethylenedioxythiophene) (PEDOT)), and polythiophene (PTh) are also incorporated with other semiconductors or metal oxides to form stable photocatalysts [27].

Copper(I) oxide, also known as cuprous oxide (Cu_2O), is among the most capable photocatalysts. This promising p-type semiconductor is abundant in nature, has low toxicity, and has high visible light absorptivity with ~2.20 eV direct bandgap [28]. Its ease of production as well as good environmental acceptability makes it one of the most investigated photocatalysts. However, photocorrosion and fast electron-hole pair recombination limit Cu_2O efficiency during the photocatalytic reaction [29,30]. Although Cu_2O is thermodynamically stable under the ambient condition, during photoexcitation its activity is greatly suppressed by photocorrosion. Generally, photocorrosion happened through the self-usage of the photoexcited electrons and holes [29].

As such, illumination causes photostability deterioration, which leads to a considerable detrimental effect on the photocatalytic and photoelectrochemical performances of Cu_2O. An efficient charge transfer that prevents light-induced self-reduction and oxidation of Cu_2O is a vital step in suppressing its photocorrosion. Similarly, the incorporation of secondary components can also enhance their photostability. The formation of composite materials would increase the catalyst's ability to transfer charges, thereby reducing excess photogenerated charges within the particles, thus improving its photocatalytic activity [29,31].

To further improve Cu_2O's photocatalytic properties, many strategies have been developed like, surface engineering to control the exposed facets [32], coupling with n-type semiconductors e.g. TiO_2 [33], ZnO [25], Ferric oxide [34], and Tantalum oxynitride [35], and binary system formation with noble metals such as aurum (Au) [36], argentum (Ag) [37], and copper (Cu) [38]. However, the long-term efficiency of Cu_2O photocatalyst is generally low due to the occurrence of self-photodecomposition that constrains its overall performance [24,29].

Recently the fabrication of ternary nanocomposites leading to the formation of a Z-scheme heterojunction especially with conducting polymers is gaining more attention in the improvement of properties of various photocatalysts [39]. The synergetic effect enhancement that occurs among all the three components is responsible for the enhanced activity. Various strategies like metal/semiconductor/polymer and semiconductor/semiconductor/polymer nanocomposites were developed given interesting results [40].

PANI is considered as one of the extremely suitable conductive polymers that can serve as a candidate for ternary nanocomposites with other semiconductors, because it serves as a p-type semiconductor, and has tremendous properties like unique electron-hole transporting ability, simple synthesis methods, high chemical stability, high absorption coefficients in the visible-light range, high mobility of charge carriers and suppression of photocorrosion [27,39]. Similarly, PANI in its undoped or partially doped states is an electron donor upon photoexcitation and is known as a good hole conductor. Likewise, PANI has shown promising results in the suppression of photocorrosion and enhancing stability in some of the photocatalysts having the problem of photocorrosion like silver phosphate (Ag_3PO_4) [41] and manganese ferrite ($MnFe_2O_4$) [42].

Recently, ternary nanocomposites containing PANI and other semiconductor photocatalysts like PANI/Ag_3PO_3/$NiFe_2O_4$ [40], RuO_2-TiO_2/PANI [43], TiO_2/$CoMoO_4$/PANI [44], Co_2TiO_4/$CoTiO_3$/PANI [45] have been synthesized and demonstrated higher photocatalytic activity, enhanced stability, and reusability for pollutants degradation.

As such, this study deals with the preparation of novel ternary nanocomposites of Cu_2O (Cu_2O/ZnO-PANI), with wide bandgap n-type semiconductor (ZnO) and PANI, by a simple solvothermal method and room temperature in-situ polymerization of aniline, for the treatment of textile dyes.

1.2 Problem Statement

Textile and dye industries use a large amount of water and also discharge a large number of toxic effluents into waterways, leading to contamination of surface and ground waters. This leads to so many environmental and health hazards. Regular and conventional water treatment methods are not fast, efficient, and cost-effective. Among the new facile water treatment methods, photocatalysis is seen as a panacea to the problem of wastewater, due to its effectiveness, the capability to degrade contaminants through a redox reaction, and most importantly, the usage of sunlight which is an abundant and free source of energy.

Wide bandgap semiconductors were the first investigated photocatalysts, they have been popular as an effective photocatalyst, and their photocatalytic behavior has been studied extensively. However, the photocatalytic activity of wide bandgap semiconductors is limited to irradiation wavelengths in the UV region. Thus, the optimal use of solar energy is limited to approximately 3-5% of all solar energy, whereas 43% of solar energy comprises visible light, therefore a significant amount of solar radiation is lost. Likewise, the use of UV photocatalysis on an industrial scale is very expensive and its prolonged exposure may cause serious health risks like skin aging, cancers, eye damage, and immune system suppression [46]. Owing to these factors growing interest was also focused on the visible light-driven narrow bandgap semiconductors like Cu_2O.

Cu_2O is a p-type semiconductor with a direct bandgap of 2–2.20 eV. It is seen as an interesting photocatalytic material due to its abundance in nature, low toxicity, and ability to absorb visible light [24,30]. However, despite all its interesting properties and capabilities, Cu_2O particularly those with nanoscale structure has less activity due to easy photocorrosion and loss of light activity in the case of long-term illumination [29]. Apart from that, Cu_2O application is restricted by the fast recombination of electron-hole pairs [47].

It is understood that if two semiconductors are properly integrated into one system, namely composite or heterojunction, this system can be expected to achieve high photocatalytic activity even if none of the semiconductors has high activity, by increasing the efficiency of load separation or visible light absorption [48]. The p-n heterojunction is produced by combining p-type and n-type semiconductors and is seen as one of the effective ways of improving photocatalytic performance [49,50].

Cu_2O p-n heterojunctions have been produced by some researchers and improvement was noticed, however, the Cu_2O p-n type heterojunctions still have some problems of recombination at the heterojunction interface due to an excessive formation of cupric oxide (CuO) on the Cu_2O surface as the illumination of light continues, as well as self-photodecomposition, this limits its efficiency [48]. Apart from that, most of the Cu_2O p-n heterojunctions could not be reused for many times without obvious loss in the photocatalytic activity [51,52]. Likewise, the general issue of most p-n heterojunctions in reducing the redox potential of photogenerated charges all constitute a great drawback to the use of p-n heterojunctions of Cu_2O [53,54].

Sequel to the limitations of p-n heterojunction, ternary Z-scheme heterojunction was constructed to overcome the said problems. It is well known that the Z-scheme photocatalytic mechanism is another important class of composite with excellent photocatalytic activities [39]. Generally, Z-scheme heterojunction comprises semiconductors, with or sometimes without electron acceptor-donor component. Subsequent to the illumination of light, the generated electrons and holes with lower reduction and oxidation ability will move from one semiconductor to the other through the electron acceptor-donor component or directly recombine with each other, thereby leaving behind electrons and holes with higher reduction and oxidation ability. This generates electrons and holes with higher oxidation-reduction ability on the semiconductor, thus achieving effective separation of the charge carriers. Therefore strong redox potential is retained for a large period of time [55,56].

With the formation of ternary Z-scheme heterojunction, the effect of heterojunctions promotes the separation of photogenerated electrons and holes, also the oxidation and reduction ability of photogenerated holes and electrons can be retained for a long period of time [48]. Looking at the problems of Cu_2O and its p-n heterojunctions, a novel technique is needed to effectively form a stable Cu_2O based photocatalyst that can be reused several times in the treatment of textile dyes and wastewater in general. Thus, instead of getting stuck in binary composites, more efforts should be devoted to preparing multicomponent nanocomposites of Cu_2O based photocatalyst, that can be reused several times in the treatment of textile dyes and wastewater, for better functional performance and wider applications. As such, a ternary nanocomposite with Z-scheme heterojunction properties can serve as an alternative and efficient way of improving the photocatalytic properties of Cu_2O.

By virtue of the capabilities of PANI in the suppression of photocorrosion and enhancing photocatalytic activity and reusability in ternary nanocomposites like PANI/Ag_3PO_4/$NiFe_2O_4$ [40], and other binary composites. PANI can be a suitable candidate to address the problems of Cu_2O, thereby producing very stable Cu_2O ternary nanocomposite photocatalysts, for the degradation of organic pollutants and other photocatalytic applications.

PANI supports photocatalytic activity by acting as a good photosensitizer. It is one of the p-type conjugated polymers with π conjugated electrons present at the major backbone of the molecule with an absorption range lying in the visible light wavelength region. PANI, therefore, exhibits good semiconducting behavior by offering electrons and accepting holes under the excitation of a light source, thereby reducing electron-hole recombination and improving photocatalytic activity [46]. Likewise, due to its amine, imine and π conjugated electrons; PANI can easily bind with other inorganic molecules thereby forming a hybrid composite that can easily adsorb organic pollutants with better visible light absorption property [39]. Thus, in this study ternary nanocomposite of Cu_2O (Cu_2O/ZnO-PANI) was prepared with ZnO and PANI.

Initially, a one-pot solvothermal method was used to prepare Cu_2O/ZnO and Cu_2O/TiO_2 with one solvent acting as both reducing agent and solvent respectively, Cu_2O/ZnO was found to have superior properties than Cu_2O/TiO_2. Cu_2O/ZnO was then modified with PANI through room temperature in-situ polymerization of aniline with different oxidants to systematically investigate its effects on the physicochemical properties of the ternary nanocomposite. To the best of my knowledge, there is no systematic study on the ternary nanocomposite of Cu_2O with PANI and ZnO (Cu_2O/ZnO-PANI), and the effects of different oxidants on the in-situ polymerization of aniline to form PANI-based Cu_2O composite.

1.3 Research Objectives

The objectives of the research are :

1) To synthesize Cu_2O, Cu_2O/TiO_2, and Cu_2O/ZnO using the solvothermal method and identify the effects of different n-type semiconductors (TiO_2 and ZnO) and loadings on the Cu_2O/TiO_2 and Cu_2O/ZnO heterojunction's physicochemical properties and performance.

2) To modify the best binary Cu_2O composite with PANI using in-situ polymerization of aniline and investigate the effects of oxidants on the physicochemical properties of the synthesized PANI-based ternary Cu_2O composite

3) To evaluate the photocatalytic performance of the synthesized pure and modified Cu_2O on the degradation of textile dyes in aqueous solution under visible light irradiation, its reusability, as well as the impacts of operating parameters such as pH, photocatalysts loading and initial dyes concentrations on the photocatalytic degradation efficiency.

4) To study the photodegradation process of the dyes over the best synthesized ternary nanocomposites of Cu_2O via in-situ capture study, total organic carbon (TOC), and High-Performance Liquid Chromatography (HPLC).

1.4 Scope of the study

This research is focused on addressing some major setbacks affecting Cu_2O-based photocatalysts for textile dyes and wastewater applications. The development of the ternary nanocomposite of Cu_2O was done with n-type semiconductors (ZnO) and conductive polymer (PANI) using a solvothermal method and in-situ polymerization of aniline for the photocatalytic degradation of Congo Red (CR) and Methylene Blue (MB) dyes in aqueous solution under visible light irradiation. The scopes of the study are:

1. Synthesis of Cu_2O, Cu_2O/TiO_2, and Cu_2O/ZnO using a solvothermal method and identification of the effects of different n-type semiconductors (TiO_2 and ZnO) on the Cu_2O/TiO_2 and Cu_2O/ZnO composites' properties and performance:

The pristine Cu_2O was synthesized by a solvothermal method using absolute ethanol which acts as both solvent and reducing agents, the physicochemical properties of the photocatalyst were determined using various characterization techniques as well as the photocatalytic activity. X-ray diffraction (XRD) analysis was done to study the structure and the crystallite size of the catalyst via Debye-Scherrer's equation. UV-Vis-NIR scanning spectrophotometer was employed for studying the optical properties. Scanning Electron Microscopy (SEM) and Transmission Electron Microscopy (TEM) were used to observe the morphology and lattice distance. Nitrogen adsorption-desorption was done to study the surface area and Fourier Transformed Infrared (FTIR) and Raman spectroscopy were employed to show the type of chemical bonds present in the sample. Energy Dispersive X-ray (EDX) and X-ray photoelectron spectroscopy (XPS) analyses were also done to examine the elemental composition and chemical state of the sample.

Likewise, the Cu_2O/TiO_2 and Cu_2O/ZnO composite were all synthesized using a solvothermal process with absolute ethanol. The loadings of both TiO_2 and

ZnO precursors were varied in the preparation while keeping Cu_2O constant to determine the best loading suitable for further treatment. Their photocatalytic activity, as well as the physicochemical properties, were determined using various characterization techniques such as XRD to study the structure and the crystallite size via Debye-Scherrer's equation, UV-Vis-NIR scanning spectrophotometer for studying optical properties, SEM and TEM to observe the morphology and lattice distance, Nitrogen adsorption-desorption to study the surface area while FTIR and Raman spectroscopy were employed to show the type of chemical bonds present in the samples. Photoluminescence (PL) spectroscopy was used to check the charge carrier recombination, while EDX and XPS were employed to examine the elemental composition as well as the chemical state of the composites. From the result obtained the best composite among Cu_2O/TiO_2 and Cu_2O/ZnO was selected for further modification with PANI to form the ternary nanocomposite of Cu_2O.

2. Modification of the best Cu_2O composite with PANI using in-situ polymerization of aniline and investigation of the effects of oxidants on the physicochemical properties of the synthesized PANI-based ternary Cu_2O nanocomposite

The modification of the best composite among Cu_2O/TiO_2 and Cu_2O/ZnO to form a PANI-based ternary Cu_2O nanocomposite was done by in-situ polymerization of aniline. The effect of oxidants on the in-situ polymerization of aniline to form PANI was identified by using three different types of oxidants; one single oxidant and two composite oxidants. Ammonium peroxydisulfate (APS) ($(NH_4)_2S_2O_8$) as the single oxidant, while a mixture of APS and potassium dichromate($K_2Cr_2O_7$) (APS/$K_2Cr_2O_7$) acts as the first composite oxidant, whereas a mixture of APS and potassium permanganate ($KMnO_4$) serves as the second composite oxidant (APS/$KMnO_4$) respectively. The loadings of aniline monomer were varied (0.13, 0.1, 0.05, and 0.03 mL) while using the best oxidant to produce the Cu_2O ternary nanocomposite of PANI.

The physicochemical properties of the optimized ternary composite were then determined using various characterization techniques such as XRD to study the structure and the crystallite size via Debye-Scherrer's equation, SEM, and TEM for imaging the morphology of the surface as well as the lattice distance. EDX and XPS were used to determine the elemental composition and chemical state of the composite. UV-Vis-NIR scanning spectrophotometer was employed to study its optical properties. Nitrogen adsorption-desorption was used to study the surface area, FTIR and Raman spectroscopy were employed to show the type of chemical bonds present in the sample, and PL spectroscopy was done to check the charge carrier recombination.

3. Evaluation of the photocatalytic performance of the synthesized pure Cu_2O and modified Cu_2O on the degradation of Congo red (CR) and methylene blue (MB) dyes in aqueous solution under visible light irradiation, its reusability, as well as the impacts of operating parameters such as pH, photocatalysts loading and initial dyes concentrations on the photocatalytic degradation efficiency.

The photocatalytic activity, photolysis, and adsorption studies were monitored using ultraviolet-visible (UV-Vis) spectrophotometry. Moreover, the operating parameters such as initial dyes concentration (i.e., 30 mg/L, 50 mg/L, and 80 mg/L), photocatalyst loading (i.e., 0.5 g/L, 1 g/L, and 1.5 g/L), and solution pH on the photocatalytic degradation of CR dye were all studied. While for MB, the preliminary result done at 30 mg/L concentration revealed no degradation, so the pH of the solution was varied to pH 3, pH 7, and pH 10, but still, the activity was very low. The reusability was tested by running five times repetitions of the experiment under similar conditions using CR dye over the optimum catalyst. XRD, FTIR, and XPS analyses were finally done to the sample after the reuse to determine whether there are changes in the structure and chemical state of the composite.

4. Study of the photodegradation process of the dyes over the best synthesized ternary nanocomposites of Cu_2O via in-situ capture study, total organic carbon (TOC), and HPLC.

An in-situ capture experiment was conducted to investigate the active species generated during the photocatalytic process. Ammonium oxalate (AO) was used as a hole (h^+) scavenger while benzoquinone (BQ) and isopropyl alcohol (IPA) were used as scavengers introduced into the photocatalytic process to capture superoxide radical ($\bullet O_2^-$) and hydroxyl radical (•OH), respectively. Finally, TOC and HPLC analyses were done to ascertain the degradation of the dyes over the optimized ternary nanocomposites of Cu_2O.

1.5 Significance of the study

A newly improved ternary nanocomposite of Cu_2O photocatalyst was developed by incorporating PANI and ZnO, to overcome the issues of photocorrosion and fast charged carrier (electrons and holes) recombination of Cu_2O, as well as improving its stability. Photodegradation of CR dye serves as a model reaction because it is one of the prominent hazardous anionic azo dyes resistant to many treatment methods, which is widely used in textile industries. The effective removal of such dye is sorely needed for the purification of wastewater. This study will provide insights into the development of efficient and stable nanocomposite for the treatment of textile effluents and subsequently combat the problem of water pollution.

Last but not least, this research will give insight into the functions of PANI and other conducting polymers, in enhancing the properties of nanocomposites photocatalysts, for degradation of various contaminants and to enhance the feasibility of AOP technologies in wastewater treatment.

1.6 Thesis outline

The research is targeted at the development of efficient ternary Cu_2O-PANI based photocatalyst, by one-pot solvothermal method and room temperature in-situ polymerization of aniline, for efficient degradation of textile dyes. The modification with ZnO and PANI was done to improve the electrons and holes separation ability and prevent the occurrence of photocorrosion of the catalyst, for increased activity and reusability. This thesis consists of seven chapters. The research background of the study area, problem statement, objectives, scope, and significance of this research was elaborately discussed in Chapter 1.

Chapter 2 presents a literature review on textile industries as well as dyes and their methods of removal. Potentials and challenges in the usage of Cu_2O photocatalyst were also discussed in the chapter, methods of synthesis and strategies used in improving the properties of Cu_2O were all discussed. Chapter 3 comprises the overall description of materials, methodology, characterizations, and experimental procedures applied during the course of the research. Chapter 4 covers the entire result of the binary composites (Cu_2O/ZnO and Cu_2O/TiO_2), as well as the discussions, and the analysis conducted to compare the two composites, leading to the selection of the best one suitable for further modification with PANI.

Chapter 5 covers the result of the ternary composite (Cu_2O/ZnO-PANI) formed with Cu_2O/ZnO and PANI, through in-situ polymerization of aniline. Discussions of the analysis conducted were made with reference and comparison between Cu_2O and Cu_2O/ZnO throughout the chapter. Chapter 6 comprises the results of in-situ capture studies, TOC, HPLC as well as the study of the stability of the optimized ternary composite. The possible charge transfer mechanism over the optimized catalyst was also discussed in the chapter. Finally, Chapter 7 provides the conclusions drawn from this study and some recommendations proposed for future work.

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LIST OF PUBLICATIONS AND CONFERENCE PROCEEDINGS

List of publications:

1. **Abdussamad Mukhtar Mohammed,** Safia Syazana Mohtar, Farhana Aziz, Shakhawan Ahmad Mhamad, Madzlan Aziz, *Review of various strategies to boost the photocatalytic activity of the cuprous oxide-based photocatalyst,* JOURNAL OF ENVIRONMENTAL CHEMICAL ENGINEERING, 9(2), 105138, 2021, Q1 (IF 4.300) – Published
2. **Abdussamad Mukhtar Mohammed,** Safia Syazana Mohtar, Farhana Aziz, Madzlan Aziz, Anwar Ul-Hamid, *Cu_2O/ZnO-PANI ternary nanocomposite as an efficient photocatalyst for the photodegradation of Congo Red dye***,** JOURNAL OF ENVIRONMENTAL CHEMICAL ENGINEERING, 9(2), 105065, 2021, Q1 (IF 4.300) – Published
3. **Abdussamad Mukhtar Mohammed**, Safia Syazana Mohtar, Farhana Aziz, Madzlan Aziz, Anwar Ul-Hamid, Wan Norharyati Wan Salleh, Norhaniza Yusof, Juhana Jaafar, Ahmad Fauzi Ismail, *Ultrafast degradation of Congo Red dye using a facile one-pot solvothermal synthesis of cuprous oxide/titanium dioxide and cuprous oxide/zinc oxide pn heterojunction photocatalyst,* MATERIALS SCIENCE IN SEMICONDUCTOR PROCESSING, 122 (105481), 2020, Q2 (IF 3.085) – Published
4. **Abdussamad Mukhtar Mohammed**, Safia Syazana Mohtar, Farhana Aziz, Madzlan Aziz, Mustapha Usman Nasir, *Effects of oxidants on the in-situ polymerization of aniline to form Cu_2O/ZnO/PANI composite photocatalyst,* MATERIALS TODAY: PROCEEDINGS, (2021) Scopus (CiteScore 1.3) – Published
5. **Abdussamad Mukhtar Mohammed**, Rohul Hayat Adnan, Farhana Aziz, Madzlan Aziz, *A Novel Gold doped Cu_2O photocatalyst for efficient degradation of anionic dyes,* MALAYSIAN JOURNAL OF CATALYSIS, 4 (2), 2020, (Non-index) – Published
6. Shakhawan Ahmad Mhamad, **Abdussamad Mukhtar Mohammed**, Madzlan Aziz, Farhana Aziz, *Impact of Electron Transport Layers (ETLs) and Hole Transport Layers (HTLs) on Perovskite Solar Cells Performance,* NANOSTRUCTURED MATERIALS FOR NEXT-GENERATION ENERGY AND STORAGE CONVERSION, (227-246), 2019, (Scopus) – Published.

Conference proceedings:

1. **Abdussamad Mukhtar Mohammed**, Safia Syazana Mohtar, Farhana Aziz, Madzlan Aziz, Mustapha Usman Nasir, (2021). Effects of oxidants on the in-situ polymerization of aniline to form Cu_2O/ZnO/PANI composite photocatalyst. *Regional Congress on Membrane Technology 2020 (RCOM 2020) and Regional Conference Environmental Engineering (RCEnvE 2020).*Universiti Teknologi Malaysia (UTM), Skudai, Johor Bahru
2. **Abdussamad Mukhtar Mohammed**, Shakhawan Ahmad Mhamad, Safia Syazana Mohtar, Farhana Aziz, Khuzaifa Yahuza Muhammad, Madzlan Aziz, (2021). Study of the stability of Cu_2O photocatalyst against photocorrosion by the formation of ternary composite. *International Symposium of Reaction Engineering, Catalysis and Sustainable Energy (RECaSE 2020).* Universiti Malaysia Pahang (UMP), Kuantan, Pahang, Malaysia