UNIVERSITI PUTRA MALAYSIA

SYNTHESIS, CHARACTERIZATION, AND APPLICATION OF ZNO/SNSX (X=1 OR X=2) NANOCOMPOSITE PHOTOCATALYSTS FOR CIPROFLOXACIN DEGRADATION UNDER VISIBLE LIGHT

MAKAMA ABDULLAHI BABA

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By

MAKAMA ABDULLAHI BABA

Thesis Submitted to the School of Graduate Studies, Universiti Putra Malaysia, in Fulfillment of the Requirements for the Degree of Doctor of Philosophy.

November 2015

DEDICATION

This Thesis is dedicated to my late mother, Sa'adatu Umar who passed away on Sunday, 9^{th} September, 2001. May Allaah SWT forgive her and admit her to Aljannar Firdaus, Ameen.

Abstract of thesis presented to the Senate of Universiti Putra Malaysia in fulfillment of the requirement for the degree of Doctor of Philosophy

SYNTHESIS, CHARACTERIZATION, AND APPLICATION OF ZnO/SnS$_x$ (x = 1 or 2) NANOCOMPOSITE PHOTOCATALYSTS FOR CIPROFLOXACIN DEGRADATION UNDER VISIBLE LIGHT

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MAKAMA ABDULLAHI BABA

November 2015

Chair: Salmiaton Bt. Ali, Ph.D.
Faculty: Engineering

In this research work, the potentials and limitations of using ZnO/SnS and ZnO/SnS_2 nanocomposites as photocatalysts for the removal of ciprofloxacin from water were studied. The two sets of photocatalysts containing various quantities of the SnS and SnS_2 were prepared by calcination of their respective precursor zinc carbonate ($ZnCO_3$/SnS and $ZnCO_3$/SnS_2) nanocomposites at 633 K for 6h. The parent $ZnCO_3$ nanocomposites were synthesized in PVP-ethylene glycol solution by microwave-assisted synthesis. The as-synthesized ZnO/SnS_x (x = 1 or 2) were characterized by X-ray diffraction, electron microscopy, energy dispersive X-ray spectroscopy, ultraviolet-visible spectroscopy and Brunauer - Emmett - Teller techniques. The results confirmed the products to consist of hexagonal wurtzite ZnO phase /orthorhombic SnS phase (for ZnO/SnS) and hexagonal wurtzite ZnO/hexagonal SnS_2. They also show that the samples exist as mesoporous nanoparticles that are active in visible light.

The visible-light photocatalytic activities of the as-prepared samples were investigated using ciprofloxacin as a model pollutant in distilled deionized water. The tests results showed that ZnO/SnS samples were not as efficient as ZnO/SnS_2 samples. The most active ZnO/SnS sample exhibit kinetics that is about eleven times less than the activity of the most active ZnO/SnS_2. The low visible light activity exhibited by the ZnO/SnS sample was attributed to high densities of interfacial states due to lattice mismatch. In UV/ZnO/SnS system, ciprofloxacin degradation rate constant increased tenfold. However, much of the enhancement comes from direct UV photolysis of ciprofloxacin. The results of stability tests showed that the efficiency of ZnO/SnS to remove ciprofloxacin decreased by about 27 % under UV light in 5 repeat runs. In the case of ZnO/SnS_2 however, no significant activity loss was recorded after five repeat runs in visible light. The results of these tests established the superiority of ZnO/SnS_2 over ZnO/SnS as possible visible light active photocatalyst for the removal of aqueous ciprofloxacin.

Robustness tests on ZnO/SnS_2 revealed that the catalyst is also effective in removing methylene blue and Cr(VI) ions. Mechanistic test results showed that as expected pH plays a crucial role in the oxidation of ciprofloxacin. Oxidation of the antibiotic was more efficient in the pH range of 6-8 than in strongly acidic or basic media. Finally, results from scavenger inhibition tests revealed that the principal mechanism of ciprofloxacin oxidation over ZOSS-2 photocatalyst is driven by photogenerated holes and surface ad-

sorbed $^{\bullet}OH$ radicals. Based on the scavenger inhibition tests, a mechanism for the visible light-driven oxidation of ciprofloxacin in suspended ZnO/SnS_2 was proposed.

Abstrak tesis yang dikemukakan kepada Senat Universiti Putra Malaysia sebagai memenuhi keperluan untuk ijazah Doktor of Falsafah

SINTESIS, PENCIRIAN, DAN PEMAKAIAN ZnO/SnS$_x$ (x = 1 or 2) NANOKOMPOSIT PHOTOCATALYSTS UNTUK CIPROFLOXACIN BURUK DI BAWAH CAHAYA YANG BOLEH DILIHAT

Oleh

MAKAMA ABDULLAHI BABA

November 2015

Pengerusi: Salmiaton BT. Ali, Ph D
Fakulti: Kejuruteraan

Dalam kerja-kerja penyelidikan ini, pontials dan batasan menggunakan ZnO /SnS dan ZnO/SnS_2 nanokomposit sebagai photocatalysts untuk purfication air telah dikaji. Dua set photocatalysts mengandungi pelbagai kuantiti daripada SnS dan SnS_2 telah disediakan oleh pengkalsinan masing-pelopor zink karbonat mereka ($ZnCO_3$/SnS dan $ZnCO_3$/SnS_2) nanokomposit di 633 K untuk 6h. Parent $ZnCO_3$ nanokomposit telah disintesis dalam PVP-etilena glikol penyelesaian oleh sintesis microwave dibantu. Sampel yang disintesis telah disifatkan oleh x-ray pembelauan, mikroskop elektron, tenaga serakan X-ray spektroskopi, spektroskopi ultraungu boleh dilihat dan Brunauer-Emmett-Teller teknik. Keputusan itu mengesahkan produk terdiri daripada wurtzite heksagon ZnO fasa/otorombik SnS fasa (untuk ZnO/SnS) dan wurtzite heksagon ZnO/SnS_2 heksagon. Mereka juga menunjukkan bahawa sampel wujud nanopartikel sebagai mesoporous yang aktif dalam cahaya yang boleh dilihat.

Aktiviti photocatalytic kelihatan cahaya sampel as- bersedia disiasat menggunakan ciprofloxacin sebagai pencemar model dalam air ternyahion suling. Hasil ujian menunjukkan bahawa sampel ZnO/SnS tidak secekap ZnO/SnS_2 sampel. Aktif ZnO/SnS kinetik sampel pameran yang kira-kira 10 kali kurang daripada acitvity ZnO paling aktif /SnS_2. Aktiviti cahaya yang boleh dilihat rendah dipamerkan oleh sampel ZnO/SnS disebabkan kepadatan tinggi negeri antara muka yang tidak berpadanan kekisi. Dalam sistem UV/ZnO/SnS, ciprofloxacin Kadar kemerosotan berterusan meningkat sepuluh kali ganda. Walau bagaimanapun, banyak peningkatan itu datang dari fotolisis UV langsung ciprofloxacin. Keputusan ujian kestabilan menunjukkan bahawa kecekapan ZnO / SnS untuk membuang ciprofloxacin menurun sebanyak kira-kira 27 % di bawah cahaya UV dalam 5 berjalan berulang. Dalam kes ZnO/SnS_2 bagaimanapun, tiada kerugian kegiatan yang penting dicatatkan selepas lima berjalan berulang dalam cahaya yang boleh dilihat. Keputusan ujian ini ditubuhkan keunggulan ZnO/SnS_2 lebih ZnO/SnS yang mungkin cahaya yang boleh dilihat fotokatalis aktif untuk penyingkiran ciprofloxacin berair.

Ujian pelbagai aktiviti di ZnO/SnS_2 mendedahkan bahawa pemangkin juga berkesan dalam menghapuskan metilena biru dan Cr(VI) ion. Keputusan ujian mekanistik menunjukkan bahawa seperti yang diharapkan pH memainkan peranan yang amat penting dalam pengoksidaan ciprofloxacin. Pengoksidaan antibiotik adalah lebih berkesan dalam julat pH 6-8 berbanding media kuat berasid atau asas.

Akhir sekali, hasil dari ujian perencatan penyapu jalan telah mendedahkan bahawa mekanisme utama ciprofloxacin pengoksidaan lebih ZnO/SnS_2 fotokatalis didorong oleh lubang photogenerated dan permukaan terjerap $^{\bullet}$OH radikal. Berdasarkan ujian perencatan penyapu jalan, satu mekanisme untuk pengoksidaan cahaya yang didorong oleh yang boleh dilihat daripada ciprofloxacin dalam digantung ZnO/SnS_2 telah dicadangkan.

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This thesis was submitted to the Senate of Universiti Putra Malaysia and has been accepted as fulfillment of the requirement for the degree of Doctor of Philosophy.

The members of the Supervisory Committee were as follows:

Salmiaton Bt. Ali, Ph D
Associate Professor
Faculty of Engineering
Universiti Putra Malaysia
(Chairperson)

Elias B. Saion, Ph D
Professor
Faculty of Science
Universiti Putra Malaysia
(Member)

Thomas S. Y. Choong, Ph D
Professor, Ir.
Faculty of Engineering
Universiti Putra Malaysia
(Member)

Norhafizah Abdullah, Ph D
Associate Professor
Faculty of Engineering
Universiti Putra Malaysia
(Member)

BUJANG BIN KIM HUAT, Ph D
Professor and Dean
School of Graduate Studies
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LIST OF ABBREVIATIONS

AOP	Advance Oxidation Process
AR	Antibiotic Resistance
ARB	Antibiotic Resistance Bacteria
ARG	Antibiotic Resistance Gene
CEC	Contaminant of Emerging Concern
CIP	Ciprofloxacin
CNT	Classical Nucleation Theory
CS	Core/Shell
DI	Deionized
DO	Dissolved Oxygen
EC	Emerging Contaminant
EDC	Endocrine Disrupting Chemicals
EDS	Energy-Dispersive X-ray Spectroscopy
FESEM	Field Emission Scanning Electron Microscopy
FETEM	Field Emission Transmission Electron Microscopy
GMO	Genetically Modified Food
ICDD	International Centre for Diffraction Data
LH	Langmuir – Hinshelwood
MB	Methylene Blue
MWTP	Municipal Wastewater Treatment Plant
MWW	Municipal Wastewater
nZVI	Nanoscale Zero Valent Iron
NC	Nanocrystal
PCD	Photocatalytic Decomposition
PhAC	Pharmaceutically Active Compound
PVP	Polyvinylpyrrolidone or Poly(N-vinylpyrrolidone)
PXRD	Powder X-ray Diffraction
QSE	Quantum Size effect
ROS	Reactive Oxidizing Species
RPM	Revolution per minute
SEM	Scanning Electron Microscopy
SC	Semiconductor
SCF	Supercritical Fluid
SCW	Supercritical Water
SnS	Tin(II) Sulfide
SnS_2	Tin(IV) Sulfide

TEM	Transmission Electron Microscopy
UV-Vis	Ultraviolet-Visible Spectroscopy
UV-vis DRS	Ultraviolet-Visible Diffuse Reflectance Spectroscopy
WCS	Wet Chemical Synthesis
XRD	X-Ray Diffraction
ZnO	Zinc Oxide
ZnO/SnS_x	A generic formular depicting the as-synthesized nanocomposite photocatalysts. x can take the value 1 for SnS or 2 for SnS_2
$\langle D \rangle$	Average crystallite sizes, nm
E^e	Energy of free electrons on the hydrogen scale ($\approx$ 4.5 eV)
E_{cb}	Conduction band potential, eV
E_{vb}	Valence band potential, eV
K_e	Monolayer Adsorption Equilibrium constant, mg/Lmin
e^-_{cb}	Photogenerated Electron
h^+_{vb}	Photogenerated Hole
k_a	Apparent first order rate constant (= $k_r K$), min^{-1}
k_r	Photocatalytic reaction rate constant, Lmg^{-1}
rGO	Reduced Graphene Oxide
Γ	Full-width at half-maximum (FWHM) in radians
β	Integral breadth = $(\pi/2)\Gamma$ or $(\pi/(4\ln 2))^{\frac{1}{2}}\Gamma$ for Lorentzian peak or a Guassian peak
λ	Wavelength, nm
ψ	Absolute electronegativity of a semiconductor, eV
θ	Diffraction angle, ^{o}

CHAPTER 1

INTRODUCTION

1.1 Background of Study

In many parts of the world, freshwater sources are becoming scarce. Factors contributing to this problem are growing population, rapid industrialization and urbanization in developing countries. Others include increased consumption in developed countries, contamination of surface water and groundwater sources, wasteful water distribution and utilization policies, and extreme global weather patterns (US National Research Council, 2012). The devastating effects of inadequate clean water supply and water quality deterioration represent serious contemporary issues of concern.

Inadequate access to safe water and the use of polluted water are major causes of diseases and deaths. A global estimate puts the number of people who die annually as a result of lack of clean drinking water, poor water sanitation, and other hygiene-related causes at 3.4 million (Prüss-Üstün et al., 2008). About 783 million people mostly in the developing countries are presently at risk due to lack of access to potable water (UN-Water, 2013). Clean water is, therefore, essential for the continued existence of life and its importance to human development cannot be overemphasized.

Demand for water is projected to increase rapidly (Cai and Rosegrant, 2002). But because of the finite natures and limitations, it is unlikely that natural sources can meet the projected increased in demand (Pickering and Davis, 2012). Therefore, bridging the gap between demand and supply to ensure long-term sustainable access is one of the major human development challenges of the 21st century (World Economic Forum, 2015; United Nations Develpment Program, 2006). Averting the impending gap in supply is likely to come through a combination of paradigm shifts in water utilization and management. That is source water protection, identification and development of new and untapped water sources including the reuse of reclaimed water such as municipal wastewater. (US National Research Council, 2012; Asano, 2001).

Municipal wastewater (MWW) is a highly polluted water source. It consists of effluents from diverse sources including households, offices, hospitals, industrial wastes and storm runoffs. Thus, MWW is contaminated by all kinds of organic and inorganic chemical substances, microbes, and pathogens. Extensive purification is required before wastewater can augment existing water sources or discharge safely into the environment. Traditionally, treatment of MWW involves processing in physical, biological and chemical unit operation equipment assembled in a municipal wastewater treatment plants (WTP). However, advances (Bixler et al., 2014; Shi et al., 2012; Wu et al., 2010; Richardson, 2008) in the sensitivity and accuracy of analytical methods and detection equipments have shown (Luo et al., 2014; Liu and Wong, 2013; Zuccato et al., 2008; Nakada et al., 2007; Bendz et al., 2005) that "treated" sewage contains trace ($ng\,L^{-1}$ to $\mu g\,L^{-1}$) amounts of different types of micropollutants that were not effectively removed by conventional treatment. Consequently, many materials (see Section 2.1 on page 8) of unknown toxicity and effects are increasingly being detected in effluents of WTP, surface water, groundwater, and drinking water (Luo et al., 2014; Sauve and Desrosiers, 2014; Liu and Wong, 2013; Loos et al.,

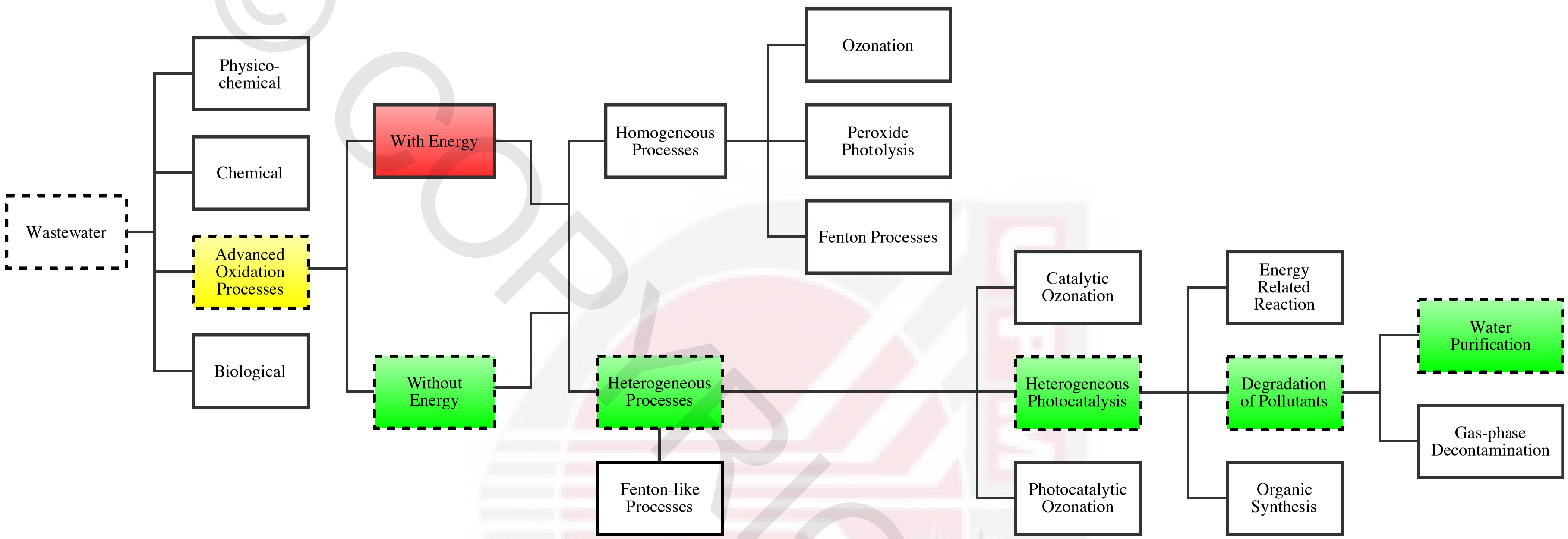

Figure 1.1: Treatment methods being developed for the degradation of emerging contaminants, including conventional tertiary techniques and advanced oxidation processes.

2013; Jia et al., 2012; Lapworth et al., 2012; Kasprzyk-Hordern et al., 2009; Stuart et al., 2012; Zuccato et al., 2008; Nakada et al., 2007; Bendz et al., 2005).

Several laboratory studies aimed at assessing the effectiveness of existing wastewater treatment technologies in removing antibiotics from wastewater have shown that they are not effective (Adams et al., 2002; Ingerslev and Halling-Sørensen, 2000; Ternes, 1998). Because of this, there is the need to develop alternative cleaning measures —that are effective, sustainable, and environmentally friendly— to guard against the unforeseen impacts of antibiotic pollution on life. Among the many technologies being proposed and developed for this purpose are the conventional tertiary treatment processes and the advanced oxidation processes (Fig. 1.1). The conventional tertiary processes use electric energy, expensive chemicals as inputs and generate secondary wastes. The high-pressure membrane processes — nanofiltration (NF), and reverse osmosis (RO) — and biodegradation (biological activated carbon (BAC)) are capable of producing high-quality water. Unfortunately, the membrane processes are prohibitively expensive for large-scale (municipal) water purification. Microbial degradation is not ideal for micropollutants because many are toxic and refractory materials. Furthermore, the carbon effluents and membrane concentrates from these processes usually contain recalcitrant ECs and waste treatment residuals necessitating the need for further treatment (Luo et al., 2014; Sauve and Desrosiers, 2014; Liu and Wong, 2013; Loos et al., 2013; Dolar et al., 2009; Westerhoff et al., 2009; Snyder et al., 2007). In contrast, advanced oxidation processes (AOPs) hold much promise in complete removal of ECs because of their ability to produce highly reactive oxidative species (ROS) such as photogenerated hole (h^{+}_{vb}), $^{\bullet}OH$, H_2O_2, and $O_2^{\bullet -}$. The ROS react with and degraded recalcitrant (organic, inorganic, and biological) pollutants (Kim et al., 2011; Comninellis et al., 2008). In some instance, the pollutants are completely mineralized to primary molecules H_2O, CO_2 and inorganic salts. Equation (1.1) shows the generic reaction of a pollutant with ROS.

$$\text{Pollutant} + \text{ROS} \longrightarrow \text{Intermediates} \longrightarrow CO_2 + H_2O + \text{Salts} \tag{1.1}$$

Many types of AOPs are being considered for removal of ciprofloxacin from contaminated water (Feng et al., 2013; Rivera-Utrilla et al., 2013). These include electrochemical, photochemical, photocatalytic processes or their combinations. The photochemical and electrochemical processes such as ozonation (Liu et al., 2012a; Vasconcelos et al., 2009), photo/electro-Fenton (Miralles-Cuevas et al., 2013; Yahya et al., 2014), persulfate (Mahdi-Ahmed and Chiron, 2014; Ji et al., 2014), and others. Also, they use expensive precursors chemicals (O_3, H_2O_2, Fe^{2+}) and expensive energy sources (UV photons or electricity) to generate ROS. On the other hand, the photocatalytic decomposition (PCD) produces ROS without the need of any chemical and can be operated at ambient conditions. Furthermore, PCD has the inherent potential to be simple, reusable, efficient, clean, and can be designed to utilize a significant portion of the infinitely free energy from the sun. For these reasons, PCD is widely regarded as a potentially viable AOP for water purification (Liu et al., 2014b; Ryu and Choi, 2007; Zhao et al., 2014). In heterogeneous photocatalytic decontamination (PCD) process, a semiconductor (SC) material harnesses energy from photons that posse energies equal to or greater than its band gap. The absorbed energy is utilized to excite electrons from the valence band to the conduction band of the semiconductor. The photogenerated electrons and holes then react with adsorbates such as O_2, H_2O to initiate the production of ROS radicals that directly degrade pollutants (Gaya and

Abdullah, 2008; Herrmann et al., 1993; Houas et al., 2001). A more detailed discussion on some of the major AOPs is given in Section 2.3.2 on page 14.

Heterogeneous photocatalytic decomposition (PCD) is one of the promising advanced oxidation processes (AOP) being developed for the removal of ECs especially antibiotics from contaminated water bodies (Van Doorslaer et al., 2015; Zhu et al., 2013). Photocatalysis on single phase semiconductor (TiO_2 (Kwiecien et al., 2014), ZnO (El-Kemary et al., 2010), CdS (Li et al., 2009)), doped/sensitized catalysts (N-$CsTaWO_6$ (Mukherji et al., 2011), C/N-TiO_2 (Wang et al., 2011), $ZnIn_2S_4$ (Shen et al., 2012)), or composite photocatalysts (CuO/$BiVO_4$ (Wang et al., 2014b), TiO_2/SiO_2 (Seo et al., 2012), CdS/g-C_3N_4 (Xu and Zhang, 2015)) has demonstrated potential in degrading a wide range of pollutants into biodegradable or less toxic organic compounds, as well as inorganic CO_2, H_2O, NO^{3-}, PO_4^{3-}, and halide ions according to the generic reaction Eq. (1.2).

$$\text{Pollutant} \xrightarrow[\text{Photocatalyst}]{\lambda \geq E_g} CO_2 + H_2O + \text{Intermediates} \tag{1.2}$$

The major appeal of PCD over other AOPs is that it can generate the transient reactive oxidizing species (ROS) from renewable resources: water and sunlight. Therefore, PCD has the potential of being economical and environmentally friendly (Kim et al., 2011). However, PCD has some challenges to overcome before commercial application in the water industry. A key challenge is in the development of a stable and effective photocatalyst(s) that can utilize a substantial portion of the solar spectrum for the generation of charge carriers. Therefore, it is necessary to continue the search for new photocatalyst(s) with improved performance (Wang et al., 2014a).

1.2 Statement of Research Problem

The sources, occurrence, fate, effects and risks of ECs especially pharmaceutically active compounds (PhACs) in the environment are issues of increasing importance (Schaider et al., 2014). Pharmaceutical compounds cover a wide range of compounds with substantial variability in structure, function, behavior and activity, and are used in both humans and animals to cure disease and fight infection. Among the different types of PhACs, the antibiotics are perhaps the most likely source of trepidation because they are linked to the evolution and prevalence of antibiotic resistance genes (ARGs) and bacteria (ARB) (Birošová et al., 2014; Marti et al., 2014; Xu et al., 2015; Sidrach-Cardona et al., 2014; Rizzo et al., 2013; Rodriguez-Mozaz et al., 2015). The fluoroquinolone group of antibiotics is one of the most important class of medication used worldwide to treat a broad variety of Gram (+) and Gram (-) bacterial infections (Oliphant and Green, 2002). Several studies have reported the environmental presence of fluoroquinolones especially ciprofloxacin (CIP) in many countries, such as China (Bu et al., 2013), Germany (Heberer, 2002), Canada (Nakata et al., 2005), and others (Heberer, 2002). The presence of CIP in the aquatic environments, albeit at low concentrations, may pose serious threats to the ecosystem and human health and thus should be removed from polluted water through PCD.

The application of heterogeneous photocatalytic degradation as a viable technology for the purification of contaminated water is contingent on the development of photocatalyst(s) that can meet intrinsic, operational, economic, and environmental requirements. For this purpose, many different types of materials have been developed and tested including metal oxides semiconductors (Kwiecien et al., 2014), chalcogenides (Tang et al., 2015), metal/nonmetal doped oxides (Xue et al., 2015b), semiconductor based nanocomposites (Liu et al., 2014d) and others.

One of the semiconductors under investigation as a promising photocatalyst for ciprofloxacin removal is ZnO (El-Kemary et al., 2010). Zinc oxide is a promising photocatalyst, owing to its abundance in nature, low cost, non-toxicity, and high photocatalytic activity (El-Kemary et al., 2010; Zhang et al., 2011; Liu et al., 2013a). However, a fundamental drawback of ZnO is that it is only active in UV-light because of its wide band gap of 3.3 eV. The wide band gap constraint limits the utilization of terrestrial solar radiation by ZnO to about 3 %–5 %. Therefore, to utilize a substantial portion of terrestrial solar energy and improve the usefulness of ZnO as a photocatalyst. It is imperative to extend the photoactivity of ZnO to the visible light region. One possible scheme of doing this is to compound a wide band gap semiconductor such as ZnO with a narrow band gap semiconductor whose band edge(s) is strategically located to enhance interfacial charge carrier transfer between the two semiconductors (Wang et al., 2014b; Yang et al., 2009).

Among the narrow band gap materials under consideration as visible light harvesters for wide band gap semiconductors are tin (II) sulphide (SnS) (Ghosh et al., 2009; Ichimura and Takagi, 2009; Sohila et al., 2013; Yang et al., 2009) and tin (IV) sulphide (SnS_2) Yang et al. (2009, 2013a); Yuan et al. (2015); Zhang et al. (2014b). ZnO/SnS_x (x = 1 or 2) have matched conduction band potentials with ZnO (Xu and Schoonen, 2000). Compounding ZnO with nanosized SnS_x whose band gap is widen due to quantum size effect (QSE) could cause its conduction band to be more negative than that of ZnO and thus, allow the photogenerated electron on SnS_x to easily transfer to the conduction band of ZnO under visible light ($\lambda > 420$ nm) irradiation. Hence, enhancing the separation of photogenerated electrons and holes in SnS_x and bringing about the sensitization of ZnO. For this reason, the ZnO/SnS_x composites with appropriate compositions should have higher visible light-driven photocatalytic activity than individual SnS_x and ZnO. To the best of the author's knowledge, to date, no studies have reported the systematic evaluation of the potentials and limitations of using ZnO/SnS or ZnOSnS_2 nanocomposites as visible light responsive photocatalysts for water purification. This study, therefore, proposes to fill the identified gap

1.3 Research Goal and Objectives

Accordingly, it is, therefore, the goal of this research work to synthesize a series of ZnO/SnS and ZnO/SnS_2 nanocomposites and systematically evaluate their potentials and limitations as visible light active photocatalysts for water purification. The study will include investigations of their crystal and surface structures, optical properties, band gap alignments and the mechanistic studies of their visible light induced photocatalytic oxidation of a model emerging contaminant, ciprofloxacin. Towards this goal, the following research objectives were formulated based on analysis of existing body of knowledge on the subject of study.

1. To synthesize and characterize visible light active porous ZnO/SnS and ZnO/SnS_2 nanocomposites with different SnS and SnS_2 contents

2. To study their photocatalytic activities for the removal of ciprofloxacin from deionized water and determine the most effective photocatalyst formulation between the ZnO/SnS and ZnO/SnS_2 groups of nanocomposites.

3. To investigate the effects of charge carrier inhibitors and operating conditions (initial pH, catalyst dosage and initial ciprofloxacin concentration) on the visible light photocatalytic activity of the most effective catalysts identified in (2).

1.4 Scope and Organization of the Thesis

The research work is limited to the synthesis of a series of ZnO/SnS and ZnO/SnS_2 nanocomposites containing different ratios of SnS_x (x = 1 or 2) from non-toxic materials in a three step process. The as-produced samples where characterized using X-Ray, SEM and TEM, EDX, UV-Visible Spectroscopy, BET and BJH techniques. The photocatalytic performance of the as-synthesized photocatalysts (ZnO/SnS_x (x = 1 or 2)) to degrade ciprofloxacin in model contaminated water was systematically investigated to determine the most active formulation. Finally, the individual effects of operating parameters (pH, mass of catalyst, and initial ciprofloxacin concentration) and radical scavengers (potassium iodide, potassium bromate, isopropanol, dissolved oxygen, and 1,4-benzoquinone) were investigated in a series of batch experiments in order to propose the ciprofloxacin degradation mechanism over the most photoactive catalyst under visible light. The scope of the thesis is summarized in the flow diagram shown in Figure 1.2 on the facing page.

The thesis consists of 5 Chapters which are organization as follows: Chapter 1 sets the context for embarking on this research work. It gives background of study, expresses the statement of research problem and highlights the research goal, objectives and scope. Chapter 2 presents a systematic review of relevant literature on important concepts, definitions and methods used throughout the thesis. It also includes the main trends and challenges which are useful to draw the objectives of this thesis. In Chapter 3, the materials, methods followed throughout the study and principles of the different characterization techniques are briefly presented. The main contributions of this work are essentially included in Chapters 4. In this Chapter, experimental results are presented, analyzed and discussed in detail. Finally, Chapter 5 summarizes and concludes the thesis contribution(s) and suggests future research directions.

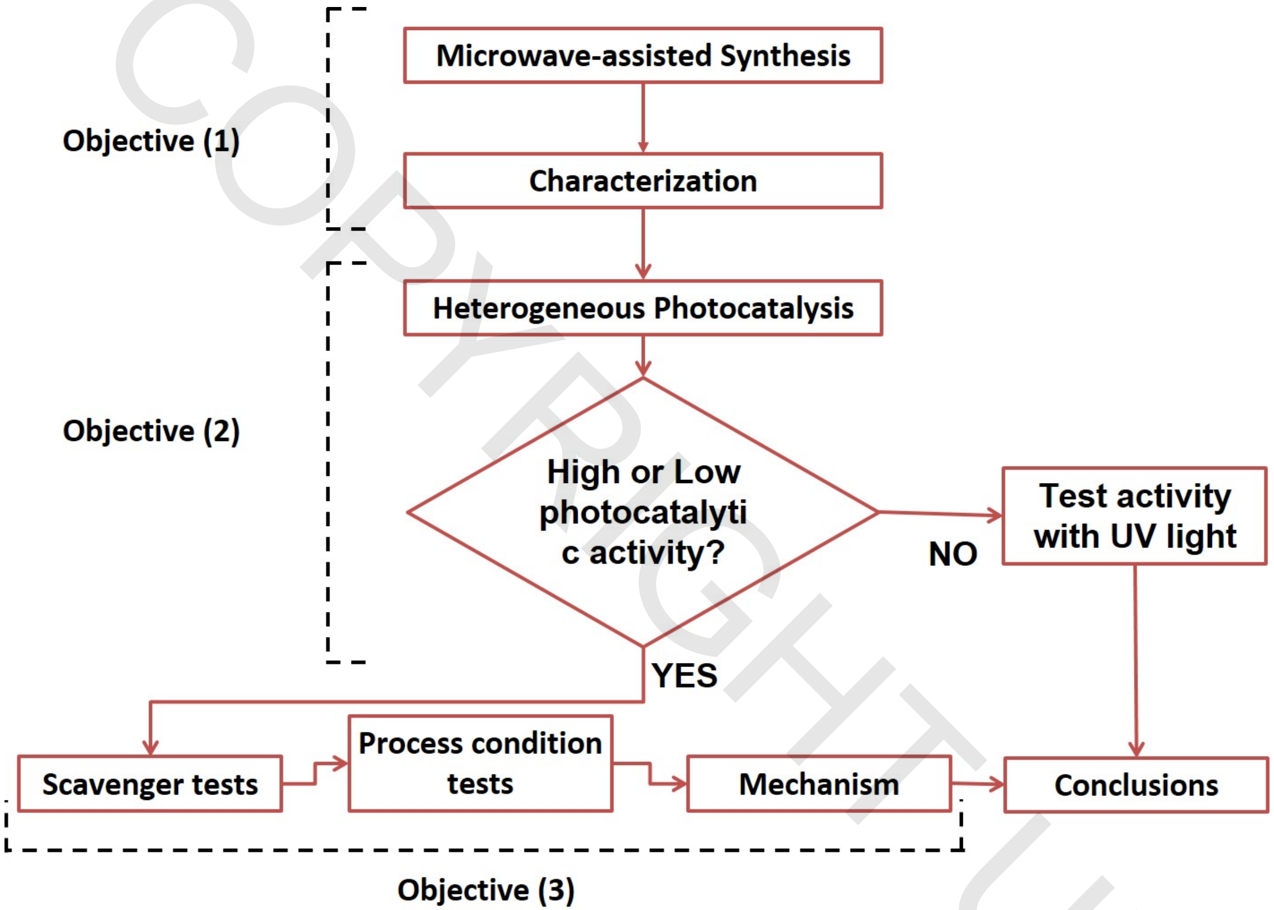

Figure 1.2: A flow diagram showing the scope of work for the thesis.

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