PHOTOCATALYTIC PROPERTIES OF ZINC OXIDE NANOSTRUCTURES SYNTHESIZED USING SYNERGISTIC PULSE LASER ABLATION AND HYDROTHERMAL METHODS

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Dedicated to my beloved family

To the most precious persons in my life, my parents, my wives, my brothers and sisters, and my sweetheart beautiful son and daughters.

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ABSTRACT

Mild growth conditions based novel techniques are essential for the controlled synthesis of zinc oxide (ZnO) nanostructure (ZNS) with desired properties. Most of the existing synthesis methods of ZNSs are limited by complicated growth conditions such as high vacuum, expensive devices, high temperature, long growth time and requirement of template. The freshwater pollution due to residual industrial organic dyes is presently being a major environmental concern that needs efficient photocatalytic materials to overcome it. To achieve these goals, this work synthesized good quality ZNS films using two different methods and evaluated the photodegradation of industrial methylene blue (MB) dye by these ZNS films under sunlight irradiation. Such films were grown on glass and silicon (Si) substrates via a simple hydrothermal method in the absence of any catalyst. Prepared samples were characterized using various techniques to determine their physical and optical properties. The effects of growth time and temperature, substrate type, nutrient pH and concentration on the morphology, size, crystallinity, and the emission properties of as-grown ZNS films were evaluated. Results showed that the morphology of these ZNSs was strongly influenced by the growth time, nutrient pH and concentration. A good quality ZNS was achieved within 5 min whereby nutrient solution with lower pH was appropriate for the growth of 1D ZNSs. However, higher pH values produced 3D flower-like ZNSs. Variation of growth temperature from 90-110 ^{o}C allowed good size-control of ZNSs. Growth conditions and substrate type dependent emission spectra were used to evaluate the optical band-gap energy. To get better control of the ZNS growth and evolving morphology, a novel catalyst-free and rapid preparation technique was adopted. In this method a mixture of precursor solution and ZnO nanoparticles (ZNPs) colloid/or only ZNPs colloid as a nutrient solution was used. Pulse laser ablation in liquid (PLAL) was combined with hydrothermal (H) method to develop PLAL-H growth technique. A Q-switched Nd:YAG laser with wavelength 532 nm, 8 ns pulse duration, and 10 Hz repetition rate was employed as the irradiation source. Metallic zinc target of 1 mm thick was used to produce colloidal ZNPs. The effects of varying growth time of 0.5, 5, 30 and 60 min and ablation energy of 200-400 mJ on the physical and optical properties of the grown ZNSs were examined. Four types of ZNSs with varying sizes and shapes were obtained on Si substrate at 110 ^{o}C for 5 min duration. Increasing ablation energy led to a substantial change of ZNS morphology and promoted the structure quality together with photoluminescence emission intensity. ZNSs synthesized under prolonged growth time of 60 min exhibited remarkable morphology alteration from rod/flower-like ZNSs to ZNPs with higher crystallinity and enlarged band-gap due to increase of nutrient pH of 10.5. Finally, the photocatalytic activities of the optimal ZNS films were assessed via sunlight driven photodegradation of MB dye. Experimental findings verified that the ZNPs prepared by PLAL-H technique possessed excellent photocatalytic efficiency (97.4%) towards degradation of MB dye. The observed boost in the photocatalytic activities was ascribed to the synergism of the improved surface area and band-gap modification. It was established that the proposed novel PLAL-H growth strategy is not only cost-effective but greatly useful for the rapid production of different quality of ZNSs at low temperature in a controlled way. This may overcome the shortcomings involving the effective exploitation of sunlight source towards practical photocatalytic applications of ZNSs.

ABSTRAK

Teknik novel berdasarkan keadaan pertumbuhan lambut adalah perlu untuk sintesis terkawal struktur-nano (ZNS) zink oksida (ZnO) dengan sifat yang dikehendaki. Kebanyakan kaedah sintesis ZNS sedia ada adalah terhad oleh keperluan pertumbuhan yang rumit seperti keadaan vakum tinggi, peralatan yang mahal, suhu tinggi, tempoh pertumbuhan yang lama dan keperluan terhadap templet. Pencemaran air tawar oleh sisa pewarna organik industri kini merupakan masalah persekitaran utama yang memerlukan bahan foto pemangkin yang efisien untuk mengatasinya. Untuk mencapai matlamat ini, kajian ini mensintesis filem ZNS yang berkualiti dengan menggunakan dua kaedah yang berbeza dan menilai fotodigredasi pewarna biru metalin (MB) industri oleh filem ZNS di bawah sinaran cahaya matahari. Filem tersebut dihasilkan di atas substrat kaca dan wafer silikon (Si) melalui kaedah hidroterma mudah tanpa pemangkin. Sampel yang disediakan dicirikan bagi menentukan ciri fizikal dan optik dengan menggunakan pelbagai teknik. Kesan masa pertumbuhan dan suhu, jenis substrat, pH dan kepekatan nutrien, terhadap morfologi, saiz, penghabluran, dan sifat pancaran filem ZNS telah dinilai. Hasil kajian menunjukkan bahawa morfologi ZNS ini sangat dipengaruhi oleh masa pertumbuhan, pH dan kepekatan nutrien. Kualiti ZNS yang baik telah dicapai dalam masa 5 minit apabila cecair nutrien dengan pH lebih rendah adalah sesuai untuk pertumbuhan ZNS 1D. Walau bagaimanapun, nilai pH yang lebih tinggi menghasilkan ZNS berbentuk bunga 3D. Perubahan suhu pertumbuhan dalam lingkungan 90-110 ^{o}C membolehkan kawalan saiz ZNS yang baik. Spektrum pancaran yang bergantung kepada keadaan pertumbuhan dan jenis substrat telah digunakan untuk menilai jurang tenaga optik. Untuk mencapai kawalan yang lebih baik ke atas pertumbuhan ZNS dan perkembangan morfologi, teknik penyediaan yang novel dan bebas pemangkin serta pantas telah digunakan. Dalam kaedah ini, campuran cecair pelopor dan koloid nanopartikel ZnO (ZNP)/atau hanya koloid ZNP telah digunakan sebagai cecair nutrien. Ablasi laser denyut dalam cecair (PLAL) telah digabungkan dengan kaedah hidroterma (H) untuk menghasilkan teknik pertumbuhan PLAL-H. Laser Nd:YAG pensuisan-Q dengan panjang gelombang 532 nm, tempoh denyutan 8 ns, dan kadar ulangan 10 Hz telah digunakan sebagai sumber sinaran. Sasaran logam zink dengan ketebalan 1 mm digunakan untuk menghasilkan koloid ZNP. Kesan masa pertumbuhan yang berbeza-beza dari 0.5, 5, 30 dan 60 minit dan tenaga ablasi 200-400 mJ terhadap ciri fizikal dan optik ZNS telah diperiksa. Empat jenis ZNS dengan pelbagai saiz dan bentuk telah diperolehi pada substrat Si pada suhu 110 ^{o}C untuk tempoh 5 minit. Peningkatan tenaga ablasi membawa kepada perubahan ketara pada morfologi ZNS dan mempromosikan kualiti struktur bersama-sama dengan keamatan pancaran kefotopendarcahayaan. ZNS yang disintesis di bawah masa pertumbuhan selama 60 minit mempamerkan transformasi morfologi luar biasa dari ZNS berbentuk rod/bunga ke ZNP dengan penghabluran yang lebih tinggi dan nilai jurang yang lebih besar disebabkan oleh peningkatan pH nutrien kepada 10.5. Akhir sekali, aktiviti fotopemangkin filem ZNS optimum telah dinilai terhadap fotodigeradasi pewarna biru metalin (MB) berpacuan cahaya matahari. Hasil eksperimen mengesahkan bahawa ZNP yang disediakan oleh teknik PLAL-H memiliki kecekapan fotopemangkin yang sangat baik (97.4%) ke arah degradasi pewarna MB. Peningkatan yang diperhatikan dalam aktiviti fotopemangkin telah disifatkan sebagai sinergi peningkatan kawasan permukaan dan perubahan jurang jalur. Ternyata bahawa strategi pertumbuhan PLPAL-H novel yang dicadangkan ini bukan sahaja menjimatkan kos tetapi berguna untuk pengeluaran pantas secara terkawal ZNS dengan kualiti yang berbeza pada suhu rendah. Ini boleh mengatasi kelemahan yang melibatkan keberkesanan penggunaan sumber cahaya matahari untuk aplikasi praktikal fotopemangkin ZNS.

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LIST OF ABBREVIATIONS

AOPs	-	Advanced Oxidation Processes
BSEs	-	Back-Scattered Electrons
CB	-	Conduction Band
CVD	-	Chemical Vapor Deposition
DW	-	Distilled Water
EDX	-	Energy Dispersive X-ray Diffraction
EDA	-	Ethylenediamine
FESEM	-	Field Emission Scanning Electron Microscopy
FTIR	-	Fourier-Transform Infrared
FTO	-	Fluorine-Doped Tin-Oxide-Coated Glass
IR	-	Infrared
ITO	-	Indium Tin Oxide
H	-	Hydrothermal
HRTEM	-	High Resolution Transmission Electron Microscopy
JCPDS	-	Joint Committee on Powder Diffraction Standards
MOCVD	-	Metal Organic Chemical Vapor Deposition
MBE	-	Molecular Beam Epitaxy
m-ZnO	-	Modified ZnO
NPs	-	Nanoparticles
NWs	-	Nanowires
NRs	-	Nanorods
NLs	-	Nanoleafs
NBs	-	Nanobelts
NCs	-	Nanocages
NFs	-	Nanoflowers
Nd:YAG	-	Neodymium-Doped Yttrium Aluminum Garnet

NIR	-	Near Infrared
NBE	-	Near Band Edge Emission
n-type	-	Donor Type
1D	-	One Dimension
O_i	-	Oxygen Interstitials
Vo	-	Oxygen Vacancies
O_{Zn}	-	Oxygen Antisites
PLD	-	Pulsed Laser Deposition
PLAL	-	Pulse Laser Ablation Under Liquid
PL	-	Photoluminescence
PVD	-	Physical Vapor Deposition
p-ZnO	-	Pure ZnO
PEs	-	Primary Electrons
QDs	-	Quantum Dots
QCEs	-	Quantum (Size) Confinement Effects
RT	-	Room Temperature
SEM	-	Scanning Electron Microscopy
SPR	-	Surface Plasmon Resonance
PLAL-H	-	Synergistic Effect of PLAL and Hydrothermal Methods
SEs	-	Secondary Electron
2D	-	Two Dimensions
3D	-	Three Dimensions
UV	-	Ultraviolet
Vis	-	Visible
VB	-	Valance Band
XRD	-	X-ray Diffraction
RF	-	Radio-Frequency
ZMNSs	-	ZnO Micro/Nanostructures
ZNSs	-	Zinc Oxide Nanostructures
ZNPs	-	Zinc Oxide Nanoparticles
ZNRs	-	Zinc Oxide Nanorods
ZNFs	-	Zinc Oxide Nanoflowers
0D	-	Zero Dimension

V_{Zn}	-	Zinc Vacancies
Zn_i	-	Zn Interstitials
Zn_o	-	Zn Antisites

LIST OF SYMBOLS

α	-	Absorption Coefficient
Å	-	Angstrom
D	-	Average Crystallite Size
Atm	-	Atmosphere
NH_3	-	Ammonia
I-V	-	Current-Voltage
^oC	-	Celsius (Degree Centigrade)
cm	-	Centimeter
k	-	Crystallite Shape-Dependent Scherrer's Constant
C_{mb}	-	Concentration of MB After Irradiation Time (t).
Co	-	Cobalt
Cu	-	Copper
C	-	Carbon
CO_2	-	Carbon Dioxide
CdS	-	Cadmium Sulfide
d	-	Distance Between Atomic Layers
θ	-	Diffraction Angle
δ	-	Dislocation Density
eV	-	Electron-Volt
e-h	-	Electron-Hole
E_g	-	Energy Band Gap
υ	-	Frequency
β (FWHM)	-	Full Width at Half-Maximum
6HCHO	-	Formaldehyde
F	-	Fluorine
Au	-	Gold

hr	-	Hour
Hz	-	Hertz
H_2O_2	-	Hydrogen Peroxide
H^+	-	Hydrogen (Cationic)
OH^-	-	Hydroxide Ion
$HO^{\bullet}_2$	-	Hydroperoxyl Radical
$(CH_2)6N_4$ or HMT	-	Hexamethylenetetramine
H_2O	-	Water
n	-	Order of Diffraction
Fe_2O_3	-	Iron Oxide
C_o	-	Initial Concentration of MB
J	-	Joule
mJ	-	Milli-Joule
kV	-	Kilo-Volt
K	-	Kelvin
k_B	-	Boltzmann Constant
a and *c*	-	Lattice Constant
m	-	Meter
mm	-	Millimeter
µm	-	Micrometer
nm	-	Nanometer
min	-	Minute
hkl	-	Miller Indices
M	-	Molarity
$C_{16}H_{18}N_3SCl$ /MB	-	Methylene Blue
ε	-	Microstrain
N	-	Nitrogen
NiO	-	Nickel Oxide
O	-	Oxygen
pH	-	Potential of Hydrogen
Pa	-	Pascal
kPa	-	Kilopascal
GPa	-	Gigapascal

ps	-	Picosecond
ns	-	Nanosecond
h	-	Planck's Constant
Pt	-	Platinum
$\eta\%$	-	Percentage Photodegradation Efficiency
N1	-	Precursor Solution
m_o	-	Rest Mass of the Electron (9.110×10^{-31} kg)
SiO_2	-	Silicon Dioxide (Silica)
Si	-	Silicon
Ag	-	Silver
t	-	Time
T	-	Temperature
SnO_2	-	Tin Dioxide
TiO_2	-	Titanium Dioxide
WO_3	-	Tungsten Oxide
λ	-	Wavelength
W	-	Watt
ZnO	-	Zinc Oxide
Zn	-	Zinc
N2	-	ZNPs Colloid
$Zn(OH)_2$	-	Zinc Hydroxide
$Zn(NO_3)_2.6H_2O$	-	Zinc Nitrate Hexahydrate
$Zn(NO_3)_2$	-	Zinc Nitrate
ZrO_2	-	Zirconium Dioxide

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CHAPTER 1

INTRODUCTION

1.1 Overview

Richard Feynman (1959) first introduced the concept of "nanotechnology" in a seminar presentation entitled "*There's Plenty of Room at the Bottom*" [1]. This notion was further extended by E. Drexler in a celebrated book titled "engines of creation: the coming era of nanotechnology" [1, 2]. Since then, several discoveries and inventions related to nanoscience and nantechnology have made a significant impact in terms of potential applications. Presently, nanoscience is the frontier research topic in every frontier of science, technology and engineering. Intense efforts are made to achieve new functional nanomaterials for efficient, economic and environmental friendly applications. Nanotechnology involves materials or structures at length scales ranged between sub-nanometer to few hundreds of nanometer. Over the years, it is realized that properties of materials can be fine-tuned by changing the dimension (size and shape) without altering the chemical composition.

It is proven that the properties materials at nanoscale are very different from their bulk counterpart. The large surface area to volume ratio and the quantum confinement or quantum size effects make low dimensional distinct compared to bulk materials. For example, metals (e.g. Au and Ag) at nanoscale possess an enhanced absorption and scattering properties for visible light due to the influence of surface plasmon resonance (SPR) [3]. Whereas, semiconductors materials (e.g. ZnO

and TiO_2) at lower dimensions (nanometer size) show emerging optical and electronic structure properties due to quantum size effects. Several studies revealed that the effect of quantum confinement in semiconductor nanostructures appears more prominent at length scale comparable to exciton Bohr radius, where energy levels become quantized [4-6].

Nanotechnology offers diverse prospective applications in the field of optics, energy system, electronics, biomedicine, biology, environment, security, gas sensing etc. to cite a few [7]. Depending on the dimension of nanostructures, materials are categorized as zero dimensional (0D) called nanoparticle (NP), one dimensional (1D) called nanowire (NW) and nanorod (NR); two dimensional (2D) known as quantum well (QW) and three dimensional (3D) flower- and multipod- like nanostructures as shown in Figure 1.1 [8-10].

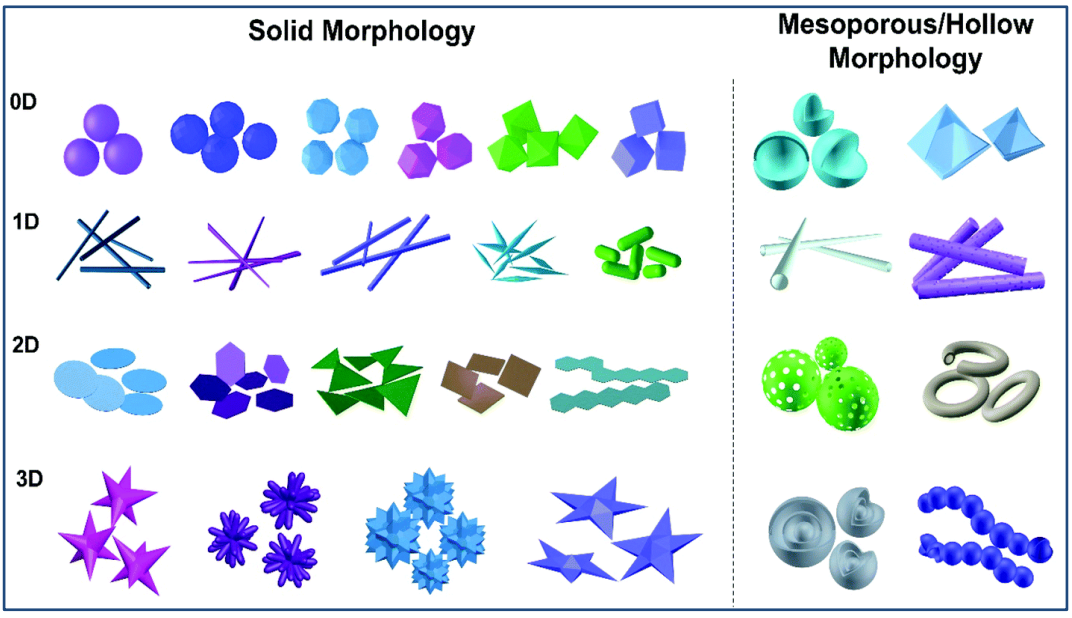

Figure 1.1 Overview of different structures and geometries at nanoscale [11]

Amongst various wide band-gap semiconductor nanomaterials, zinc oxide (ZnO) nanostructures (ZNSs) are very prospective in broad array of technological applications owing to their excellent electronic structure properties. Diverse

nanostructures of ZnO with unique features can easily be achieved using different synthesis methods. These nanostructures possess outstanding optical properties which are advantageous for the advancement of photovoltaic and optoelectronic nanodevices. Furthermore, control of ZnO epitaxial layer quality together with native and dopant point defects remains a vital issue for direct nanodevice production [12].

In the past, numerous techniques are developed for the production of diverse ZNSs under specific controlled growth conditions [12-17]. These methods include pulsed laser deposition (PLD), sol-gel processing, spray pyrolysis, electrochemical deposition, pulse laser ablation in liquid (PLAL), metal organic chemical vapour deposition (MOCVD), molecular beam epitaxy (MBE), radio-frequency (RF) sputtering, hydrothermal etc. Different techniques produce different kinds of ZNSs morphology such as ZNPs, ZNWs, ZNRs, ZnO nanoleafs (ZNLs), ZnO nanobelts (ZNBs), ZnO nanocages (ZNCs), ZnO nanoflowers (ZNFs) etc. Figure 1.2 shows the scanning electron microscope (SEM) images of different types of ZNSs grown via hydrothermal method.

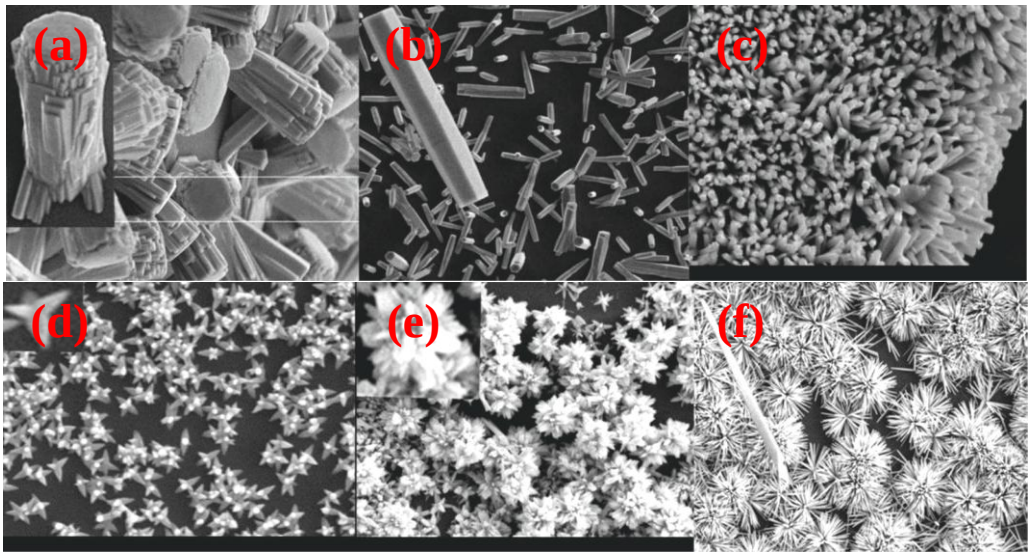

Figure 1.2 SEM images of various ZNSs synthesized on Si substrates using hydrothermal method: (a, b and c) rod-like, (d) star-like, and (e and f) flower-like [18]

Despite much progress in the preparation methods, controllable growth of ZNSs with desired properties are still demanding for several applications including electronics, optoelectronics, gas sensing, energy conversion/storage devices and photocatalysis [19-24]. Research revealed that the characteristics of produced ZNSs and their subsequent applications are critically decided by the nature of growth technique and the inter-play of different growth parameters (temperature, time, precursor type and concentration, seed layer, nutrient pH value etc.). All these parameters associated with the conventional growth techniques revealed their strong influence on the quality of ZNSs (morphology, structure quality, size, density, alignment, electrical and optical properties etc.) [25-27]. Earlier, many attempts are made to control the physical, structural, electrical and optical properties of ZNSs under mild growth conditions. The main aim was to determine the significant behaviors of ZNSs towards the advancement of novel and efficient nanodevices [13, 24, 28-30].

Among various methods of synthesis, both PLAL and hydrothermal (H) techniques have added advantages for the production of good quality ZNSs (undoped and doped) under mild growth conditions. Considering these notable merits, present thesis made a synergistic combination of the PLAL and hydrothermal methods (hereafter called PLAL-H technique) for the controlled growth of ZNSs with evolving morphologies. Using this novel method, varieties of ZNSs-based films are grown, which depended on the growth conditions including ablation energy mediated production of ZNPs colloids, substrate nature, growth temperature and time, precursor type and concentration, and nutrient pH values. Such growth conditions dependent ZNSs morphology, size, density and crystallinity, and optical properties are determined. Propose and understanding growth mechanisms processes are investigated. Furthermore, these as-synthesized ZNSs morphology driven improvement in the photocatalytic activity under sunlight irradiation is evaluated.

1.2 Photocatalytic Application

In recent time, freshwater pollution due to residual organic dyes emanating from the industries such as textile, pharmaceutical, pesticides, tannery, craft bleaching, cosmetic, food processing and agriculture is a major environmental concern (Figure 1.3). In fact, about 7×10^5 tonnes of organic dyes are annually produced worldwide in which more than 10-15% is leached into the wastewater during manufacturing and processing [31]. These chemicals are not only highly toxic and hazardous to the living organism but their intermediates can undergo reductive processes and result in the formation of potentially carcinogenic or mutagenic compounds unless inhibited. Thus, considering the toxicity potential of these dyes in the environment their immediate remediation before being discharging into the surroundings is mandatory.

Figure 1.3 Pictures showing the freshwater pollution (a and b) due to chemicals fallout and (c and d) its influence on the living organism [32]

In the past, diverse methods are developed to diminish the impact of such toxic chemical pollutants on the non-human environment, aquatic systems, and human life. Methods including adsorption, membrane separation and biological treatments are limited due to their high operating cost and inefficient in removing these pollutants. Currently, photocatalytic reactions based photodegradation processes have been introduced as an effective and economic strategy to eliminate such pollutants. In this regard, semiconductor nanomaterials (ZnO, SiO_2 and TiO_2) revealed great prospects for photocatalytic applications to treat the environmental pollutants. Categorically, heterogeneous photocatalysis-based ZNSs owing to their unusual attributes such as diverse morphologies, ability to absorb a wide solar spectrum, high chemical stabilizations, nontoxicity, abundance in nature and low cost became attractive. Thus, this material is chosen for the effective remediation of toxic environmental pollutants [19, 33, 34]. Many literature findings showed that the optimization of physical properties of as-synthesized ZNSs in terms of large surface area and modified bandgap can be useful for the increase of the number of active sites and subsequent charge transfer useful for enhanced photocatalytic activity. This in turn enhances the electron–hole pairs' separation efficiency in the photocatalytic reactions, resulting in the enhancement of the photocatalytic efficiency [19, 31, 34-36].

1.3 Problem Statement

Despite the development of various syntheses methods of ZNSs a controlled growth technique with mild conditions that produce evolving morphologies and desirable properties is far from being achieved. Controlled growths of ZNSs are significant for determining the overall properties as well as potential applications. Most of the existing synthesis methods have complicated conditions such as high vacuum, expensive devices, specialized laboratory, complex growth procedures, high temperature, requirement of catalyst or template, and longer growth time. It is necessary to develop a simple, fast, scalable, cost-effective and catalyst-free new growth approach such as PLAL-H (combination of PLAL and hydrothermal

methods). This novel technique is expected to achieve better control on the growth of ZNSs-based film, which is still lacking. A better understanding of the PLAL-H growth mechanism that produces ZNSs with evolving morphologies in addition to improved photocatalytic efficiency toward MB dye under sunlight irradiation is prerequisite.

Modifications in the photocatalytic activity of ZNSs for practical applications remain a major issue due to their wide band-gap nature and subsequent absorption in the UV region only. On top, the wide band-gap nature of ZNSs allows only ~ 4-5% of the solar spectrum in the UV-range for effective use as a renewable energy source, which is the main limitation for photocatalytic application. Furthermore, studies on superior photo-degradation ability of MB by un-doped ZNSs-based film under sunlight irradiation are rarely performed. Earlier studies mainly focused on ZNSs-based powder to achieve photodegradation of MB dye. These are not only expensive, but required complex processing tools such as centrifugation. Consequently, it is necessary to overcome the limitations associated with weak photocatalytic activities of ZNSs where an enhancement in the harvesting (absorption) efficiency of the solar spectra in the broad region (UV and visible (Vis) regions) and reduction of processing cost is necessary. In this view, present thesis took a fair attempt to develop a new PLAL-H growth technique for overcoming all the above mentioned limitations associated with the synthesis of ZNSs using conventional methods as well as the photocatalytic application of ZNSs driven by sunlight irradiation.

1.4 Research Objectives

Based on the aforementioned problem statement and research background on ZNSs the following objectives are set:

1. To develop a new PLAL-H technique with mild growth conditions for the controlled synthesis of ZNSs-based film having evolving morphologies.
2. To determine the influence of growth parameters on the morphology, size, density, structure, composition, optical properties and photocatalytic activities of the synthesized ZNSs-based film.
3. To evaluate the photocatalytic activity of the as-grown ZNSs-based films in terms of photo-degradation ability of MB under sunlight irradiation.

1.5 Scope of the Study

Present study includes the synthesis, characterization and determination of photocatalytic properties of ZNSs-based films. Amongst all the metal oxides semiconductors ZnO is preferred for various applications because of their distinct physical and chemical attributes including wide direct band gap, large exciton binding energy, excellent stability, environmental friendliness, low cost and easy availability. These fascinating properties are supported by ability of ZnO to easy formation of different nanostructures (ZNSs) gained high surface area to volume ratio and effective quantum confinement compared to bulk structure. Intense researches revealed the possibility of tuning the electronic band structure of ZnO via controlled synthesis of ZNSs useful for light-emitting diodes, sensors, catalysts, field emitters, biosensors, solar cell and photocatalytic application. Preparation of ZNSs-based films with controlled morphologies will be achieved via newly proposed PLAL-H growth technique as well as using conventional hydrothermal route to authenticate its ability for producing high quality ZNSs with diverse morphologies. The growth conditions optimization by varying different growth parameters would

be the major focus. The impact of various processing parameters including laser energy, nutrient type, nutrient pH, nutrient concentration, growth temperature and time on the ZNSs growth mechanism will be determined. Such NSs properties such as morphology, density, orientation, aspect ratio, crystal size and crystallinity are found to be strongly depended on the synthesis technique and processing conditions.

Current newly proposed simple PLAL-H technique is capable of controlling the morphology, aspect ratio, density, structure, optical and photocatalytic properties of ZNSs. This technique is cost-effective and can produce good quality ZNSs at short growth time and low temperature (under mild growth conditions) without requiring any catalysts. Moreover, more than three ZNSs can be grown simultaneously. Such ZNSs with diverse morphologies, sizes and crystallinity are essential for the development of ZNSs based optoelectronic devices which are cheap and efficient. Using the proposed systematic characterization method it is possible to determine the purity, size, emission and absorption properties, band gap, photocatalytic activity and morphology of ZNSs as well as other nanomaterials required for broad array of applications. The photocatalytic performance of the optimal ZNSs samples under sunlight irradiation will be measured in terms of photo-degradation of MB dye.

As-prepared samples are thoroughly characterized using various imaging and spectroscopic techniques. The experimental results on as-synthesized ZNSs are compared with similar existing findings for better understanding of the growth mechanisms. Samples structures and morphology (surface morphology, size, density, crystallinity, and elemental traces) are determined using field emission scanning electron microscopy (FESEM), X-ray diffraction (XRD) measurement, high resolution transmission electron microscopy (HRTEM), Energy dispersive X-ray diffraction (EDX) and Fourier-transform infrared (FTIR) spectroscopy. The optical properties of ZNSs samples are determined via photoluminescence (PL) spectroscopy and UV-Vis absorption spectroscopy.

1.6 Significance of the Study

Nowadays the pollution of freshwater due to the residual organic contaminants (dyes) in the form of chemical waste being the major environmental concern needs remediation. These chemical pollutants are highly toxic and harmful for the entire eco-system. Therefore, degradation of these organic contaminants is essential to circumvent the human health risks. In this view, ZNSs-based films grown via innovative PLAL-H route can be superior in terms of photocatalytic efficiency toward pollutant MB dye under sunlight irradiation. This study is expected to contribute towards the development of high performing ZNSs with excellent photocatalytic activity under sunlight irradiation which is a free, clean, and inexhaustible irradiation source. The capacity to use ZNSs-based films for useful exploitation of sunlight source to achieve enhanced photocatalytic action would certainly be beneficial in terms of economy and environment. Furthermore, PLAL-H technique can be extended for producing other semiconductor NSs morphologies. Present PLAL-H technique may constitute a basis for controlled manipulation of nanomaterials desirable for high performance nanodevices.

1.7 Thesis Organization

This thesis is composed into five chapters as follows:

Chapter 1 presents a brief background of the research to justify the importance of ZNSs and need for further studies. It clearly shows the research gap to set out the precise objectives to be accomplished. It includes the problem statement, research objectives, scope, and significance.

Chapter 2 describes the comprehensive literature survey to show the existing research gaps and the relevant findings on the cited topic made so far. It describes the

electrical, optical and structural properties of ZnO nanostructure. It explains the growth mechanism of ZNSs associated with the hydrothermal and PLAL synthesis techniques. Influence of growth technique and growth conditions on the morphology of ZNSs films are discussed. The mechanism of photocatalytic activity of ZNSs is underscored. The major parameters of different growth techniques that can achieve enhanced photocatalytic efficiency of ZNSs film are explained in depth.

Chapter 3 highlights the detailed research methodology in terms of synthesis techniques used and the adopted steps towards photocatalytic applications. The background information of major experimental techniques for collecting the data and analysis related to as-grown ZNSs samples are emphasized.

Chapter 4 presents detailed results, analysis and discussion. Findings from two different synthesis methods such as hydrothermal and PLAL-H are evaluated in terms of optimization of growth conditions to produce various catalyst-free ZNSs films at low temperature and growth time compared with previous studies. The remarkable features of the synergistic PLAL-H technique for controlled preparation of ZNSs-based film are explained. Photocatalytic performance of obtained optimal ZNSs samples under sunlight irradiation is assessed using photodegradation of MB dye. Dependence of photodegradation efficiency of MB dyes on morphology and structure evolution of as-grown ZNSs films as well as ability of these ZNSs film as photocatalysis to overcome the shortcomings for beneficial exploiting of sunlight source is attributed.

Chapter 5 concludes the thesis and provides some future outlook in terms of recommendations. The successful accomplishments of the proposed research objectives are demonstrated.

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