TERNARY LANTHANUM COBALTITE PEROVSKITE AND TITANIA BASED NANOCOMPOSITES FOR PHOTOCATALYTIC RENEWABLE HYDROGEN PRODUCTION

SEHAR TASLEEM

UNIVERSITI TEKNOLOGI MALAYSIA

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SEHAR TASLEEM

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School of Chemical and Energy Engineering
Faculty of Engineering
Universiti Teknologi Malaysia

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ABSTRACT

Photocatalytic hydrogen (H_2) production via water splitting is one of the favourable technologies to overcome concerns of exploitation of fossil fuels and issues of global warming. Thus, it is recognized as clean solar to energy conversion for replacing non-renewable fossil fuels. However, available semiconductors and photoreactors are less efficient for splitting water into renewable H_2 under solar energy. The objective of this study is to design and develop structured photocatalysts and photoreactors for stimulating photocatalytic H_2 production. Specifically, cocatalyst including titanium aluminium carbide (Ti_3AlC_2) and titanium carbide (Ti_3C_2) MXene multilayers heterojunctions with TiO_2 and graphitic carbon nitride nanosheets (PCN) were fabricated to promote conductive properties. Further modification of TiO_2 and PCN was carried out to form ternary nanocomposites involving lanthanum cobaltite ($LaCoO_3$) perovskite and nickel phosphide (Ni_2P) to maximize photoactivity under visible light irradiations. Initially, the hydrofluoric acid etching process was employed to get Ti_3C_2 multilayers, whereas, $LaCoO_3$ nanotextures were obtained through hydrothermal method. Good morphology, improved light absorption, and superior charge separation were observed in the $Ti_3AlC_2/TiO_2/Ni_2P$, and $LaCoO_3/g\text{-}C_3N_4/TiO_2@Ti_3C_2$ nanocomposites. The performance of nanocomposites was determined in a liquid phase slurry photoreactor under visible irradiation. The TiO_2 grown Ti_3C_2 modified $LaCoO_3/g\text{-}C_3N_4$ composite generated 125 µmol of H_2, significantly higher than pure components, attributing to the visible light activity, efficient mobility and charge separation, good interfacial contact and conductivity of Ti_3C_2. Comparatively, Ti_3AlC_2 modified TiO_2/Ni_2P generated 1300 µmol of H_2 based on the inhibited charge recombination, improved visible light response and good redox potential of TiO_2. The comparative performance of slurry, fixed bed, and monolith photoreactors over $Ti_3AlC_2/TiO_2/Ni_2P$ was conducted. The monolith photoreactor generated 2050 µmol of H_2 under ultraviolet light which was 136 times higher than H_2 generated from monolith photoreactor under visible light. This is attributed to the improved light penetration of ultraviolet light into monolith channels for maximum interaction with catalysts. The highest H_2 generating $Ti_3AlC_2/TiO_2/Ni_2P$ nanocomposite was involved in testing of operating parameters using response surface methodology for optimization with the amount of H_2 as the response. Optimization revealed 10.5 methanol concentration, 0.11 g catalyst loading and 3.59 h reaction time as optimum conditions for maximum H_2 generation. Finally, a modified Langmuir-Hinshelwood (L-H) mechanism-based kinetic model was developed for TiO_2 and PCN based nanocomposites and calculation of adsorption and rate constants were also carried out for investigating the adsorption behaviours. In conclusion, this study will contribute to the development of an efficient photo-technology for H_2 production towards sustainable solar fuels.

ABSTRAK

Penghasilan hidrogen (H_2) fotomangkin melalui pemisahan air ialah salah satu teknologi yang baik untuk mengatasi masalah eksploitasi bahan-bahan api fosil dan isu pemanasan global. Oleh itu, ia dikenali sebagai penukaran tenaga suria kepada tenaga yang bersih untuk menggantikan bahan api fosil yang tidak boleh diperbaharui. Walau bagaimanapun, semikonduktor dan fotoreaktor yang ada kurang cekap untuk menukar air menjadi H_2 yang boleh diperbaharui di bawah tenaga suria. Objektif kajian ini adalah untuk merekabentuk dan membangunkan fotomangkin berstruktur dan fotoreaktor untuk merangsang pengeluaran H_2 fotomangkin. Secara khusus, titanium aluminium karbida (Ti_3AlC_2) dan titanium karbida (Ti_3C_2) MXene berbilang lapisan digunakan sebagai sokongan membentuk heterosimpang dengan TiO_2 dan lembaran nano karbon nitrida bergrafit (PCN) telah difabrikasi untuk meningkatkan sifat konduktif. Modifikasi selanjutnya ke atas TiO_2 dan PCN telah dijalankan untuk membentuk nanokomposit ternari melibatkan lantanum kobaltit ($LaCoO_3$) perovskites dan nikel fosfida (Ni_2P) untuk memaksimumkan fotoaktiviti di bawah cahaya nampak. Pada awalnya, proses punaran asid hidrofluorik digunakan untuk mendapatkan berbilang lapisanTi_3C_2 berbilang lapisan, sementara, nanotekstur $LaCoO_3$ diperoleh melalui kaedah hidroterma. Morfologi yang baik, penyerapan cahaya yang lebih tinggi, dan pemisahan cas yang unggul diperhatikan dalam nanokomposit $Ti_3AlC_2/TiO_2/Ni_2P$, dan $LaCoO_3/g\text{-}C_3N_4/TiO_2@Ti_3C_2$. Prestasi nanokomposit ditentukan dalam fotoreaktor buburan fasa cecair di bawah pancaran radiasi tampak. Komposit $LaCoO_3/g\text{-}C_3N_4$ terubah suai TiO_2 cambahan Ti_3C_2 menghasilkan 125 μmol H_2, jauh lebih tinggi daripada komponen tulen, disebabkan oleh aktiviti cahaya nampak, mobiliti dan pemisahan cas yang cekap, hubungan antara muka dan kekonduksian Ti_3C_2 yang baik. Secara perbandingan, TiO_2/Ni_2P terubah suai Ti_3AlC_2 menghasilkan 1300 μmol H_2 berdasarkan penggabungan semula cas yang direncatkan dan tindak balas cahaya nampak yang lebih baik dengan potensi redoks TiO_2 yang baik. Perbandingan prestasi fotoreaktor buburan, lapisan tetap, dan monolit ke atas $Ti_3AlC_2/TiO_2/Ni_2P$ dijalankan. Reaktor monolit menghasilkan H_2 tertinggi 2050 μmol di bawah cahaya ultraungu, iaitu 136 kali ganda lebih tinggi daripada H_2 dihasilkan daripada fotoreaktor monolit di bawah cahaya nampak. Ini disebabkan peningkatan penembusan cahaya ultraungu ke dalam saluran monolit untuk interaksi maksimum dengan mangkin. Penjanaan H_2 tertinggi $Ti_3AlC_2/TiO_2/Ni_2P$ nanokomposit telah digunakan dalam mengkaji parameter operasi menggunakan kaedah sambutan permukaan untuk pengoptimuman penghasilan H_2 sebagai gerak balas. Pengoptimuman menunjukkan kepekatan metanol 10.5, pemuatan mangkin 0.11 g dan masa tindak balas 3.59 jam sebagai keadaan optimum untuk penjanaan H_2 maksimum. Akhirnya, model kinetik berasaskan mekanisme Langmuir-Hinshelwood (L-H) dibangunkan untuk komposit TiO_2 dan PCN, di mana pengiraan pemalar penjerapan dan pemalar kadar dijalankan untuk menyiasat tingkah laku penjerapan. Kesimpulannya, kajian ini akan menyumbang kepada pembangunan teknologi foto yang cekap untuk pengeluaran H_2 ke arah bahan api solar yang lestari.

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LIST OF ABBREVIATIONS

CO_2	-	Carbon dioxide
H_2	-	Hydrogen
O_2	-	Oxygen
TiO_2	-	Titanium dioxide
g-C_3N_4	-	Graphitic carbon nitride
RGO	-	Reduced graphene oxide
Ni_2P	-	Nickel phosphide
Ti_3AlC_2	-	Titanium aluminium carbide
Ti_3C_2	-	Titanium carbide
GE	-	Gibbs free energy
H^+	-	Protons
RSM	-	Response surface methodology
L-H	-	Langmuir-Hinshelwood
TiO_2@Ti_3C_2	-	TiO_2 grown Ti_3C_2
PCN	-	Graphitic carbon nitride nanosheets
$LaCoO_3$	-	Lanthanum cobaltite
UV	-	Ultraviolet
0D	-	Zero dimensional
2D	-	Two dimensional
3D	-	Three dimensional
N_2	-	Nitrogen
Hg lamp	-	Mercury lamp
AC	-	Alternating current
H_2O	-	Water
C_2H_5OH	-	Ethanol
CH_3OH	-	Methanol
(CH_2OH)	-	Ethylene glycol
$C_3H_8O_3$	-	Glycerol
TEA	-	Triethanolamine
CCD	-	Central composite design

DoE	-	Design of experiments
VB	-	Valance band
CB	-	Conduction band
GO	-	Graphene
CdS	-	Cadmium sulfide
$NiTiO_3$	-	Nickel titanate
$AgNbO_3$	-	Silver niobate
BiOBr	-	Bismuth oxybromide
MoS_2	-	Molybdenum disulfide
N-ZnO	-	Nitrogen doped zinc oxide
$Ni(OH)_2$	-	Nickel II hydroxide
Fe_2O_3	-	Hematite
Au	-	Silver
Ti	-	Titanium
Co		Cobalt
Fe	-	Iron
Ni	-	Nickel
Ce	-	Cerium
F		Fluorine
P		Phosphorus
SPR	-	Surface plasmon resonance effect
CoO_x	-	Cobalt oxide
Pt	-	Platinum
$BiVO_4$	-	Bismuth vanadate
$ATaO_3$	-	Tantalates
$AgTaO_3$	-	Silver tantalate
$NaTaO_3$	-	Sodium tantalate
$KTaO_3$	-	Potassium tantalate
$ANbO_3$	-	Niobates
$NaNbO_3$	-	Sodium niobate
$KNbO_3$	-	Potassium niobate
$ATiO_3$	-	Titanates
$SrTiO_3$	-	Strontium titanate

$ZnTiO_3$	-	Zinc titanates
$PbTiO_3$	-	Lead titanate
$CdTiO_3$	-	Cadmium titanate
$MgTiO_3$	-	Magnesium titanate
$CaTiO_3$	-	Calcium titanate
$LaFeO_3$	-	Lanthanum ferrite
$BiFeO_3$	-	Bismuth ferrite
$PrFeO_3$	-	Praseodymium ferrite
$GaFeO_3$	-	Gallium ferrite
$YFeO_3$	-	Yttrium ferrite
$AlFeO_3$	-	Aluminium ferrite
Sn	-	Tin
Sr	-	Strontium
$SrZrO_3$	-	Strontium zirconium oxide
$CaSnO_3$	-	Calcium tin oxide
$BaSnO_3$	-	Barium tin oxide
$SrSnO_3$	-	Strontium tin
PdO	-	Palladium (II) oxide
Sc	-	Scandium
V	-	Vanadium
Zr	-	Zirconium
Hf	-	Hafnium (Hf),
Mn	-	Manganese
Ta	-	Tantalum
Cr	-	Chromium
Mo	-	Molybdenum
Al	-	Aluminium
CH_3COOH	-	Acetic acid
NH_4OH	-	Ammonium hydroxide
La $(NO_3)_3$ $6H_2O)$	-	Lanthanum (III) nitrate hexahydrate
$Co(NO_3)_2.3H_2O$	-	Cobalt (II) nitrate hexahydrate
NaOH	-	Sodium hydroxide
$C_3H_6N_6$	-	Melamine

C_3H_8O	-	Isopropanol
$C_{12}H_{28}O_4Ti$	-	Titanium tetra Isopropoxide
HF	-	Hydrofluoric acid
$CuInS_2$	-	Copper indium sulphide
IO^{3-}/I^-	-	Iodate/iodine ion
NO^{3-}/NO^{2-}	-	Nitrate/nitrite ion
Fe^{3+}/Fe^{2+}	-	Ferric/ferrous ion
Co^{3+}/Co^{2+}	-	Cobaltic/cobaltous ion
XRD	-	X-ray diffraction
FE-SEM	-	Emission scanning electron microscopy
HR-TEM	-	High resolution electron microscopy
XPS	-	X-ray photoelectron spectroscopy
EDX	-	Energy dispersive X-ray spectroscopy
UV-Vis	-	UV-Visible spectroscopy
PL	-	Photoluminescence Spectroscopy
BE	-	Binding energy
Na_2S	-	Sodium sulphide
Na_2SO_3	-	Sodium sulphite
MMT	-	Montmorillonite
Fe_2P	-	Iron phosphide
In_2S_3	-	Indium (III) sulphide
CPSI	-	Cells per square inch
TN	-	TiO_2/Ni_2P
TTAC	-	TiO_2/Ti_3AlC_2
TNTAC	-	$TiO_2/Ni_2P/Ti_3AlC_2$
MOF	-	Metal organic framework
MFC	-	Mass flow controller
APE	-	Apparent photonic efficiency
SY	-	Space yield
DF	-	Degree of freedom
R^2	-	Coefficient of determination
MSSSR	-	Mean of square regression
SSR	-	Division of sum of squares

SSE	-	Division of sum of residual
E_g	-	Band gap
E_{CB}	-	CB edge potential
E_{VB}	-	VB edge potential
E^e	-	Free electron energy
X	-	Absolute electronegativity
Y_1	-	H_2 response
X_1	-	Catalyst loading
X_2	-	Methanol concentration
X_3	-	Reaction time

LIST OF SYMBOLS

W	-	Watt
$mWcm^{-2}$	-	Milliwatt per square centimetre
Wm^{-2}	-	Watt per square metre
wt. %	-	Weight percent
^{o}C	-	Degree centigrade
h	-	Hour
g	-	Gram
$\mu molg^{-1}h^{-1}$	-	Micromole per gram per hour
$\mu molh^{-1}\,cm^{-3}$	-	Micromole per hour per centimetre cube
eV	-	Electron volt
λ	-	Wavelength
nm	-	Nanometre
kV	-	Kilovolt
mA	-	Milliampere
β	-	Beta
<	-	Less than
kcal	-	Kilocalorie
K	-	Scherer constant
$mg\ mL^{-1}$	-	Milligrams per millilitre
$mg\ L^{-1}$	-	Milligrams per litre
k	-	Reaction rate
n	-	Reaction order
mm	-	Millimetre
m	-	Meter
m^2	-	Meter square
J	-	Joule
cm^{-1}	-	Per centimetre
cm^3	-	Centimetre cube
mL/min	-	Millilitre per minute
m	-	Minute

ppm	-	Parts per million
M	-	Molar
µmol/s	-	Micromole per second
e^-	-	Electron
h^+	-	Hole
h	-	Plank's constant
v	-	Photon density
α	-	Significance level
θ	-	surface coverage
K_{CH_3OH}	-	Adsorption constant of CH_3OH
K_{H2O}	-	Adsorption constant of H_2O
C_{H2O}	-	Concentration of H_2O
C_{CH3OH}	-	Concentration of CH_3OH
$molL^{-1}$	-	Mol per liter
≥	-	Greater than equal to
≤	-	Less than equal to
I	-	Light flux
a	-	Reaction order of intensity

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CHAPTER 1

INTRODUCTION

1.1 Background of Study

Currently, most of the global energy consumption is achieved by utilization of non-renewable resources including fossil fuels [1]. However, excessive burning of these fuels produces greenhouse gases particularly carbon dioxide (CO_2) which causes global warming [2]. Therefore, the utmost challenge of the time is to develop environment-friendly and carbon-free renewable energy resources. In recent years, the hydrogen (H_2) economy is a prominent research area in which H_2 can replace fossil fuels and overcome environment associated problems. Moreover, H_2 energy is considered as a sustainable, long-lasting, clean and renewable energy with easy storage [3, 4].

Generally, solar energy is converted into electrical energy using photovoltaic cells. It is a commercialised technique, and its efficiency has risen dramatically in recent years, surpassing a considerable value of 20%. Despite significant advancements in smart grids and new batteries, large-scale energy storage remains a significant barrier. Converting solar energy into chemical energy, which produces renewable fuels known as "solar fuels," on the other hand, has obvious practical benefits [5]. Likewise, the use of wind energy as well as hydropower are green energy power sources of interest however, they face drawbacks related to their intrinsically dependence on day-night intervals, seasons and fluctuating environmental conditions that result in periods of deficit and surplus of energy output [6]. Thus, keeping in view the solar fuels, several methods have been used to produce H_2 such as steam reforming [7, 8] where H_2 is produced at industrial scale using hydrocarbon particularly methane, and renewable liquids like ethanol (C_2H_5OH) and methanol (CH_3OH) [9]. The steam reforming for hydrogen production is an endothermic, reversible, and high-temperature reaction. Also, it faces limited availability of fossil fuels and the

production of CO_2, a major GHG that contributes to the global warming [10]. Similarly, the gasification of coal or biomass to produce H_2 requires input energy, leading to emission of CO_2 and is an expensive process [11]. Furthermore, electrolysis of water (H_2O) needs electric current through H_2O while, redox reactions occur at electrodes. Thus, an alternative, eco-friendly, and carbon-free renewable energy system is necessary for sustainable development [12]. Therefore, the conversion of solar energy into chemical energy such as H_2 from H_2O is an interesting strategy to effectively utilize solar light irradiations [13, 14]. This method is a standalone process for harvesting and storing solar energy as chemical energy. Photo-reforming is a technique that uses oxygenated organic substrates and solar radiation as an alternative to pure water splitting. When bio-available oxygenates are used as sacrificial agents, the approach comes near to being carbon-neutral, because the CO_2 produced can be transformed back into biomass by plant photosynthesis. The origin of the organic substrate, i.e., non-sustainable first-generation biomasses or appealing second/next generation biomasses, has a significant impact on overall sustainability [15]. Photogenerated H_2 can easily be stored and used as a green fuel. Green technology like photocatalytic H_2 production from H_2O is a promising approach to fulfil the energy demands and is safe for the environment.

1.2 Photocatalytic H_2 Production

Green technology like photocatalytic H_2 production from H_2O is a promising approach to fulfil the energy demands and is safe for the environment [16, 17]. Motivation for photocatalysis comes from the natural photosynthesis process, where plants absorb solar light and produce chemical energy in the form of glucose with the help of chlorophyll. In addition, it is the most simple and proven technology to produce H_2 using renewable solar light irradiations [18]. In photocatalytic process, solar light irradiation directly provides energy to split H_2O, whereas utilization of this H_2 fuel produces only H_2O, which becomes part of the H_2 cycle [19, 20].

Several semiconductor materials as photocatalyst have been studied for H_2O splitting to achieve high efficiency [21]. Presently, there are limited suitable materials

with appropriate band gap positions for overall H_2O splitting and also lack high efficiency as well as require stability for photocatalytic processes [22, 23]. Semiconductor photocatalysts face limitations of lower efficiency, wide band gap, lower surface area, and faster charge recombination [24]. Among photocatalytic semiconductors, titanium dioxide (TiO_2) is an excellent metal oxide semiconductor photocatalyst having low cost, high photochemical stability, and non-toxic nature. However, it has a wide band gap (3.2 eV) and also faces charge recombination. Moreover, metal-free semiconductors like graphitic carbon nitride (g-C_3N_4) are also under consideration. It has a narrow band gap (2.7 eV), low cost and gives off less pollution [21], but it shows faster charges recombination [25]. To overcome these limitations, several approaches such as doping with metals, coupling with cocatalysts, and modification with other semiconductor materials have been employed [26-29].

Although various studies have been carried out on photocatalytic H_2 generation by utilizing photocatalyst material, however, still the efficiency of the photocatalytic system is low based on various limitations discussed above, leading to a need for photocatalyst with higher efficiency, narrow band gap, excellent morphology, efficient charge transfer and separation, good visible light absorption and a lower rate of recombination. In this context, the fabrication of semiconductors including TiO_2 and g-C_3N_4 by the formation of heterojunctions or Z-scheme is recognized to be an efficient approach for efficient H_2 generation photoactivity. Recently, perovskite oxides have been explored for the formation of efficient composites with TiO_2, g-C_3N_4 as well as reduced graphene oxide (RGO) as a promising approach for minimizing charge carrier's recombination and band gap tuning for improved photoactivity towards H_2 generation [30]. Incorporation of cocatalyst like nickel phosphide (Ni_2P) is been explored for visible light responsive photocatalyst composites and can be coupled with various wider band gap catalysts for their activation, thus leading to improved photocatalytic activity under solar energy [31]. Moreover, the utilization of 2D materials from MAX phase (M stands for the front metal element of the transition group; A represents the elements of the main group, mainly the elements of the third group and the fourth group; X is for carbon or nitrogen) including titanium aluminium carbide (Ti_3AlC_2) and MXene- titanium carbide (Ti_3C_2) are currently under exploration for their extraordinary electrical conductivity, metal like properties, and attractive morphology [32].

Efficient photocatalysis requires an appropriate photoreactor in which photocatalytic reaction takes place after contact between photocatalyst, sacrificial agent, and photons. The most commonly used photoreactor is the slurry reactor, involving three phase system in which the catalyst bed is in fluidized form and mass transfer between catalyst and reactants is increased by agitation which provides an increased surface area to be illuminated [33]. In a fixed bed photoreactor, photocatalyst is immobilized (fixed) on the bed of reactor while, in monolith the catalyst is dispersed onto a supporting material i.e., monolith, and placed inside the photoreactor [34, 35]. However, these photoreactors lack overall higher efficiency based on the inappropriate selection of operating parameters such as light to form an effective photocatalytic scheme for the enhancement of photoactivity. This can be addressed by considering the necessary engineering approach elements including proper distribution of photons in the reactor, efficient mass transfer, and effective interaction of catalyst with reactants.

The operating parameters have a significant effect on the efficiency of the photosystem towards photocatalytic H_2 generation. However, the common method of varying different operating parameters in a way that the parameter to be studied is varied and others are taken as constant lacks the identification of the relation between the parameters and also does not identify the optimum range of parameters for high efficiency. Response Surface Methodology (RSM) is a combination of mathematical and statistical analysis for the effect of parameters in the complex study of photoactivity, leading to a cost-effective and time-saving approach for improved efficiency [36]. Moreover, the reaction kinetics of reactants into products can be investigated by developing a rate equation. Generally, Langmuir– Hinshelwood (L-H) mechanism determines the rate of reaction.

Overall, work aims at exploring and studying an entire photocatalytic system involving the investigation for an efficient nanocomposite for photocatalytic H_2 generation along with the exploration for effect of the four components of photocatalytic process including light, sacrificial agent, photocatalyst, photoreactor for efficiency improvement. Specifically, the study focuses on the efficiency improvement of two widely researched and industrially applied semiconductor photocatalysts

including TiO_2 and g-C_3N_4 for photocatalytic H_2 generation by formation of heterojunctions and in cooperation of cocatalysts. The study also includes the study of the role of photoreactor and their parameters for maximizing the interaction of irradiation, photocatalyst and reactants for boosted H_2 generation. Else, the work also goals to carry out optimization study to identify the optimized conditions of various parameters including catalyst loading, sacrificial agent and irradiation time along with developing of kinetic model for studying the rate of reaction for studying the effect of reactant concentration governing the rate of H_2 producing reaction.

1.3 Problem Statement and Research Hypothesis

Currently, among the several alternatives for energy requirements and global warming, production of H_2 is the best strategy to replace fossil fuels and to mitigate global effects [37]. While, photocatalysis is a rapidly growing H_2 production method as well as is cost-effective and shows high efficiency with zero pollution [38, 39].

Among binary semiconductor photocatalyst, TiO_2 and g-C_3N_4 are the most widely employed photocatalysts as compared to all existing semiconductors. g-C_3N_4 has attracted great attention in photocatalytic applications of hydrogen production and pollutant degradation especially due to metal free nature and low price of raw materials. TiO_2 is also been researched widely for its environmental and energy applications due to the maximum quantum efficiency achieved from low cost TiO_2. However, both of these materials offer limitations of less efficiency towards photocatalytic processes. TiO_2 lacks the photocatalytic efficiency due to the charge recombination and wide band gap. Likewise, g-C_3N_4 in spite of visible light activity show low visible light activity, charge recombination, and fewer reaction sites for photoreaction make it less efficient [21]. Various modification approaches have been applied for the efficiency improvement of TiO_2 and g-C_3N_4 however, the efficiency still need to be improved under sunlight mimicking visible irradiation.

Moreover, perovskites are also considered good materials employed for photoactivity and in heterojunction formation for activity improvement, but the

photocatalytic efficiency of perovskites is been explored under UV light, making it less desirable for photocatalytic H_2 generation. Also, pristine perovskites show charge recombination and less surface area.

Apart from this, most of the studies focus on utilizing noble metals cocatalysts for activity enhancement however, their low abundance, availability, toxicity and cost factor makes them undesirable. Thus, there is a need for alternate cost-effective and efficient photocatalytic materials to replace utilization of noble metal.

Furthermore, the effective catalyst development for photocatalytic H_2 production, the design of a photocatalytic scheme effective for enhancement of photoactivity by proper distribution of photons in the reactor, efficient mass transfer, and effective interaction of catalyst with reactants are considered necessary engineering approaches. There is insignificant work been carried out for addressing the limitations and the parameter study of various photoreactors to address and enhance the efficiency towards photocatalytic H_2 generation. Currently, structured photocatalytic frameworks including monolith photoreactors are getting considerable attention for photocatalytic H_2 production with photocatalyst immobilized on the walls of the monolith. Monoliths have attained much consideration as compared to the slurry and fixed bed because of their flexible geometry and design of catalyst as well as more exposed catalyst surface [40]. However, the drawbacks of limited photon penetration to the surface of catalyst and reaction sites causing less interaction of light photons with catalyst and reactants are not considerably studied [41]. In this regard, based on the discussed problems following hypothesis is formulated:

(a) The photoactivity of binary semiconductors including TiO_2 and g-C_3N_4 nanosheets (PCN) can be effectively improved through the formation of binary or ternary nanocomposites with other semiconductors and by the introduction of cocatalysts. Perovskite can form heterojunction with binary semiconductors to improve charge separation and also provide band gap tunability. In terms of visible light driven photocatalysts, $LaCoO_3$ as a visible light active photocatalyst has been explored for photocatalytic H_2 generation. The cocatalyst activity of $LaCoO_3$ based on the narrow band gap for visible light

activity, charge trapping stability and efficiency enhancement has been explored.

(b) MAX/MXene 2D layered materials show electronic conductivity for electron trapping. Improvement in activity can be achieved by enhanced reaction area of MAX phase 2D Ti_3AlC_2 which will provide significant enhancement towards redox reaction. Also, 2D Ti_3C_2 MXene will contribute towards improved efficiency by building a strong interfacial connection with binary semiconductors for improved charge transportation and electron connectivity to promote charge separation. Ni_2P is visible light active with high conductivity.

(c) The efficiency of photoreactors can be enhanced towards photocatalytic H_2 generation activity through engineering approaches based on the type of light irradiations, the operational mode of reactors, the geometry of monolith for maximum photon utilization, and interaction of photons with catalyst and reactants. Also, the photocatalytic H_2 producing system involving study on nanocomposite as well as for all the four components of photocatalytic process towards efficiency enhancement; light, sacrificial agent, photocatalyst, photoreactor will improve the overall efficiency of system.

(d) The optimization of parameters like catalyst loading, reactant concentration, and reaction time along with their interactive relationship will be helpful in further maximizing the H_2 production. Moreover, the kinetic modelling will help to develop a reaction rate equation for determining the rate of H_2 generation.

1.4 Research Objectives

Following are the objective of this study:

(a) To fabricate and characterize MAX-Ti_3AlC_2/Ni_2P modified TiO_2 and MXene-Ti_3C_2/$LaCoO_3$ modified g-C_3N_4 based ternary nanocomposites for higher light utilization;

(b) To investigate the performance of synthesized nanocomposites and to calculate the photocatalytic H_2 generation under UV and visible light irradiations;

(c) To explore the performance of slurry, fixed bed, and monolith photoreactors towards photocatalytic H_2 generation over different ternary composites;

(d) To optimize reaction parameters and to identify the interactive relationship between parameters using RSM;

(e) To develop a kinetic model for determining reaction rate for photocatalytic H_2 generation and to propose reaction mechanism.

1.5 Scope of Study

The study focuses on maximizing the low efficiency of TiO_2 and PCN binary semiconductor photocatalysts towards visible light induced photocatalytic H_2 production. The modification by semiconductor incorporation and cocatalyst loading for the development of ternary nanocomposite is investigated. In this outlook, the nanocomposites were synthesized, characterized and tested for determining the efficiency towards H_2 generation. Comparative analysis of slurry, fixed bed, and monolith have been studied in detail for effective enhancement of H_2 production. Also, the optimization of reaction parameters was carried out. The study includes an in-depth discussion of the reaction mechanism for the nanocomposite catalysts with the deliberation of kinetic study. The detailed scope of the study is as under which aims at maximizing the amount of H_2 production:

(a) The synthesis of Ti_3AlC_2 modified TiO_2/Ni_2P and Ti_3C_2 modified $LaCoO_3$/PCN is carried out for photoactivity enhancement. The modification of TiO_2 is carried out by single sol-gel method. The Ni_2P loading onto TiO_2 is

varied as 1, 3, and 5 wt.% for the synthesis. A coprecipitation followed by hydrothermal method is used to synthesize $LaCoO_3$ while, for the synthesis Ti_3C_2, HF exfoliation of Ti_3AlC_2 is carried out and the calcination temperature is varied as 300°C and 500°C for growth of TiO_2 on Ti_3C_2. Modification of PCN is carried out by wet impregnation method. The loading of $LaCoO_3$ onto PCN is also varied as 10, 15 and 20 wt.% while, the loading of TiO_2 grown 300°C, 500°C calcined Ti_3C_2 and 300°C calcined TiO_2@Ti_3C_2 loading onto $LaCoO_3$/PCN was varied as 5, 10, 15 and 20 wt.%. The crystallinity, internal surface, and surface morphology, elemental distribution, elemental valance, extend of charge recombination, optical property, vibrational mode of components, and extend of charge recombination is analyzed by characterization of catalysts including XRD, HR-TEM, FE-SEM, EDX, XPS, Raman, PL, and UV-Visible spectroscopy.

(b) The performance test of pure catalyst, binary and ternary nanocomposites for testing the performance efficiency is conducted by photocatalytic experiments using liquid phase slurry photoreactor. The catalyst is in form of powder mixed with distilled H_2O and CH_3OH as sacrificial agent for reduction reaction under continuous stirring. A continuous flow of nitrogen (N_2) is supplied as well as a Xenon lamp of 35 W with 20 $mWcm^{-2}$ light intensity is used as a visible light source. The photocatalytic H_2 generated is analysed by an intelligent H_2 analyser in ppm and calculation were carried out for conversion into µmol.

(c) The comparative study of photocatalytic H_2 producing ability from slurry, fixed bed, and monolith photoreactors is carried out to maximize the efficiency of photosystem. Photocatalyst is dispersed in the H_2O/CH_3OH mixture under continuous stirring in slurry photoreactor whereas, the photocatalyst is immobilized on the bottom of the fixed bed photoreactor, and photocatalyst is coated onto the monolith in monolith photoreactor. For a comparative analysis to study the parameter of light source, slurry photoreactor is operated in continuous mode under visible light from 35 W Xenon lamp while, fixed bed and monolith is operated in continuous and batch mode under visible light as well as UV light from 35 W Xenon lamp and 200 W Hg lamp, respectively. The efficiency of 5 mm and 10 mm thick monolith for light utilization is also

explored under visible and UV irradiation along with the study of their efficiencies at 25 and 80°C temperatures from H_2O-CH_3OH mixture.

(d) Optimization by RSM with central composite design (CCD) is carried out for TiO2 and PCN based ternary nanocomposites to optimize reaction parameters including catalyst loading, CH_3OH concentration, and reaction time having DoE with minimum and maximum range of 0.05-0.15 g, 5-15 %, and to 1-4 h, respectively. The interactive relationship between parameters is also identified.

(e) The kinetic models for both TiO_2 and PCN based ternary nanocomposites are developed using a modified L-H mechanism-based equation to determine the rate constant (k), adsorption constant (K), and reaction rate (r) using Polymath software.

1.6 Significance of Study

The study addresses the concerns of excessive fossil fuel usage and related environmental issues by providing an alternate clean energy source in the form of H_2. The photocatalytic H_2 generation photosystem comprising of efficient photocatalytic nanocomposites and photoreactors for solar to energy conversion offers a vital and significant contribution towards sustainable development. Moreover, the study also opens up more effective approaches for boosting the efficiency of widely used binary semiconductors i.e., TiO_2 and g-C_3N_4. Following is the significance of the study:

(a) The Ti_3AlC_2 modified TiO_2/Ni_2P and Ti_3C_2 modified $LaCoO_3$/PCN lead to the development of highly efficient nanocomposites workable under visible light.

(b) Development of narrow band gap $LaCoO_3$ perovskite and ternary nanocomposites with effective charge separation heterojunction and Z-scheme for efficient photoactivity.

(c) Investigation of photoreactors under varying parameters to get more insight into overcoming the inefficiencies for large-scale production.

(d) Exploration for efficient nanocomposite as well as for all the four components of photocatalytic process towards efficiency enhancement.

(e) A major contribution towards sustainable, and environmentally friendly energy production, applicable on an industrial scale.

1.7 Outline of Thesis

The thesis is dissected into six individual chapters eliminating the table of content, list of figures, list of tables, list of abbreviation, symbols, and abstract. Chapter 1 includes the background of the study, problem statement, and hypothesis, research objectives, the scope of study, significance, and outline of this study. Chapter 2 covers the literature review for the research conducted, including fundamentals of photocatalytic, study of previous work carried for various photocatalysts and photoreactor setups, characterization techniques, and development of kinetic models. The details for the methodology adopted for the work is been elaborated in Chapter 3 including synthesis technique for photocatalysts and nanocomposites, photoreactor setups, photoactivity test, regression model, and DoE for RSM as well as kinetic model development. Chapter 4 includes the results and discussion of all conduced characterizations while, Chapter 5 discusses the experimental results for photoactivity and reactors, reaction mechanism, statistical analysis using RSM, and kinetic model development with model fitting. Chapter 6 summarizes the conclusion of the entire research work along with the detailed recommendations.

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LIST OF PUBLICATIONS, PATENTS AND AWARDS

The current research on photocatalytic H_2 generation was conducted after synthesizing and modifying $LaCoO_3/PCN/TiO_2@Ti_3C_2$, and $TiO_2/Ni_2P/Ti_3AlC_2$ nanocomposites. They were tested for photocatalytic H_2 generation and $TiO_2/Ni_2P/Ti_3AlC_2$ nanocomposite was also tested for efficiency analysis of slurry fixed bed and monolith photoreactors. During the research work, the following literature reviewed and experimental data has been published and the remaining is under process:

Publications

a) Tasleem **S**, Tahir M. Recent progress in structural development and band engineering of perovskites materials for photocatalytic solar hydrogen production: A review. *International Journal of Hydrogen Energy.* 2020;45(38):19078-19111 **(I.F 5.8)**

b) Tasleem S, Tahir M. Current trends in strategies to improve photocatalytic performance of perovskites materials for solar to hydrogen production. *Renewable and Sustainable Energy Reviews.* 2020;132:110073. **(I.F 14.9)**

c) Tahir M, **Tasleem S**, Tahir B. Recent development in band engineering of binary semiconductor materials for solar driven photocatalytic hydrogen production. *International Journal of Hydrogen Energy*. 2020;45(32):15985-6038. **(I.F 5.8)**

d) Tasleem S, Tahir M, Zakaria ZY. Fabricating structured 2D Ti_3AlC_2 MAX dispersed TiO_2 heterostructure with Ni_2P as a cocatalyst for efficient photocatalytic H_2 production**.** *Journal of Alloys and Compounds.* 2020;842:155752 **(I.F 5.3)**

e) Tasleem S, Tahir M. Investigating the performance of liquid and gas phase photoreactors for dynamic H_2 production over bimetallic TiO_2 and Ni_2P dispersed MAX Ti_3AlC_2 monolithic nanocomposite under UV and visible light. *Journal of Environmental Chemical Engineering.* 2021;9(4):105351. **(I.F 5.9)**

f) Tasleem S, Tahir M. Constructing $La_xCo_yO_3$ Perovskite Anchored 3D g-C_3N_4 Hollow Tube Heterojunction with Proficient Interface Charge Separation for Stimulating Photocatalytic H_2 Production. *Energy & Fuels*. 2021; 35(11):9727-9746 **(I.F 3.6)**

g) Tasleem S, Tahir M. Synergistically improved charge separation in bimetallic Co–La modified 3D g-C_3N_4 for enhanced photocatalytic H_2 production under UV–visible light. *International Journal of Hydrogen Energy*. 2021;46(40):20995-1012. **(I.F 5.8)**

Patent Filing

(a) Sehar Tasleem, Dr. Muhammad Tahir, Dr. Zaki Yamani Bin Zakaria (2021). A MAX-Phase Nanocomposite Catalyst and a Method or Producing and Using Thereof for the Production of Clean Fuel, National Patent Filling **(PI2021002431),** Malaysia.

Awards

(a) 1st place in 21st Industrial Art & Technology Exhibition at State level, Universiti Teknologi Malaysia, September 2019, Green 2D MXene photocatalyst for CO_2 Conversion to Solar Methanol, (Gold Award).

(b) 2nd place in 21st Industrial Art & Technology Exhibition at State level, Universiti Teknologi Malaysia, September 2019, Hybrid Solar System for Water Treatment and Hydrogen Production, (Silver Award).

(c) 3rd place in 22nd Industrial Art & Technology Exhibition at State level, Universiti Teknologi Malaysia, December 2020, Perovskite Based Hybrid Scheme for Hydrogen Production and Wastewater Degradation, (Bronze Award).

(d) 2nd place in 22nd Industrial Art & Technology Exhibition at State level, Universiti Teknologi Malaysia, December 2020, Smart 2D Nano-catalysts for Carbon Dioxide Conversion to Green Methanol, (Silver Award).

(e) 3rd place in 22nd Industrial Art & Technology Exhibition at State level, Universiti Teknologi Malaysia, December 2020, Hybrid Nanoclay Photoreactor Solar System for CO_2 Conversion to Methane, (Bronze Award).